Leaching Characteristics of Magnesium from Mine Residues by H_2SO_4 and HNO_3

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Abstract -The leaching characteristics of magnesium and iron were investigated by H_2SO_4 and HNO_3 in this study. Particle size of mine residue, reaction temperature, acid concentration, liquid/solid ratio and reaction time were discussed as parameters to raise leaching amount of magnesium. The leaching rate was increased with increasing temperature, acid concentration and reaction time. Maximum leaching amount of Mg was obtained at the condition of reaction temperature 80° C, 6M H_2SO_4 , 10/1 L/S ratio and 6hrs of reaction time. The best condition for HNO_3 was reaction temperature 80° C, acid concentration 6M, 15/1 L/S ratio and 6hrs of reaction time.

Keywords: Magnesium, Iron, Mine residue, Acid leaching, Sulfuric acid, Nitric acid

1. Introduction

The demand and importance for rare metal have been rapidly increased in recent with the development of IT industry. Rare metals are produced only in few countries such as China, South Africa, Australia and so on. Therefore the ministry of trade, industry and energy in Korea adopted 11 strategies to secure 35 rare metals(The Ministry of Knowledge Economy in Korea, 2011). Magnesium among them is used to produce car, cell phone, lap top and other electronics because of its light weight, a quarter of steel weight. Hence its consumption has been increased. Therefore the method to secure it is urgently needed, because most of it imported.

Mine residues are discharged as waste from a mine. They are not properly and safely treated and only piled up. Heavy metal leached from them is probably to contaminate the environment. But heavy metal can be recycled as electrical material if it is separated from them(Choi, 2004). Therefore there are several researches to recover magnesium from ferronickel in Korea(Chu et al., 2010; Kim et al., 2011; Park et al., 2013). But a study to recover magnesium from mine residue was not acted yet.

In our study, we discussed the leaching condition of magnesium and its affecting factors from mine residue. Other metal such as Fe was leached simultaneously in the acid leaching process of mine residue. It lowers the recovering rate of magnesium. Particle size of mine residue, reaction time and temperature, acid concentration and liquid/solid ratio were discussed as affecting parameters. And also the condition to lower leaching amount of iron was discussed.

2. Experimental

2. 1. Materials

The mine residue used in this study was sampled from S mine in Korea. The chemical composition of it was analysed by using X-Ray Fluorescence Spectroscopy(XRF) and given in Table. 1. It was composed of Fe_2O_3 41.1%, SiO_2 28.5%, MgO 14.7% and et.

Table. 1	۱.	Chemical	ana	lysis	of	mine	residue.	

Constant	Fe ₂ O ₃	SiO ₂	MgO	CaO	Al_2O_3	MnO	K ₂ O	F	SO ₃	TiO ₂
Wt(%)	41.1	28.5	14.7	8.14	4.38	1.19	1.14	0.214	0.159	0.125

2. 2. Experimental Method and Condition

 H_2SO_4 and HNO_3 were used to leach magnesium from mine residue. Particle size of mine residue, acid concentration, liquid/solid ratio, reaction time and temperature were discussed to elucidate leaching characteristics of magnesium and iron. The experimental condition was given in Table 2. Leached amount of magnesium and iron was analysed by Atomic Absorption Spectrometer(blow AAS).

Factor	Condition				
Particle size(mesh)	Above 30				
Temperature(°C)	40~80				
Acid concentration(M)	2 ~ 10				
Liquid/Solid ratio(ml/g)	5/1 ~ 20/1				
Reaction time(hour)	1 ~ 8				
Shaking speed(rpm)	180				

Table. 2. Experimental condition for acid leaching.

3. Results and Discussion

3. 1. Particle Size of Mine Residue

Leaching amount of magnesium is maybe affected by the particle size of mine residue. Particle size distribution was analysed by sieving method. The cumulative particle size distribution of mine residue was described in Fig 1. According to the result, 98.7% of mine residue was below 80mesh. The smaller particle size is, the more amount leached. However to choose too small size of particle as raw material lowers the recycling amount, because it is only small part of total amount of residue. Therefore we selected below 80mesh of particle size as raw material to recover magnesium in our study.



3. 2. Leaching Characteristics of Mg And Fe

3. 2. 1. Leaching Amount of Mg

Leaching amount of Mg was affected by reaction time, temperature and acid concentration. According to our previous result, we fixed upon the acid concentration of H_2SO_4 and HNO_3 as 6M. Leaching amount of Mg was given with reaction time and temperature in Fig. 2. It was discussed at the temperature range of 40° C to 80° C. The amount of Mg leached was increased from 6,315mg/L to 9,436mg/L with the increment of reaction time and temperature by using H_2SO_4 . In case of using HNO₃, it was increased from 5,640mg/L to 7,920mg/L. Consequently it seemed that H_2SO_4 was more suitable as leaching agent than HNO₃. Considering leaching amount of Mg, the best condition for reaction time and temperature was 80° C and 6hrs.



Fig. 2. Effect of temperature on the leaching amount of Mg from mine residue

3. 2. 2. Leaching Amount of Fe

Leaching amount of Fe by H_2SO_4 and HNO_3 was compared in Fig. 3. According to Fig. 3, leaching amount of Fe was increased from 23,250mg/L to 39,440mg/L by using 6M of H_2SO_4 . But it was increased from 3,024mg/L to 24,560mg/L by using 6M of HNO_3 . Namely Fe concentration leached was low in case of using HNO_3 . Because divalent iron was dissolved and existed as ferrous sulfate which did not precipitate in case of using H_2SO_4 . But HNO_3 acts as a lixiviant as well as oxidant(Ma et al., 2013). Fe leached precipitates as hematite particle in nitric acid solution as following stages.

The first stage is the dissolution of magnetite.

$$Fe_3O_4(s) + 8H^+(aq) \rightarrow 2Fe^{3+}(aq) + Fe^{2+}(aq) + 4H_2O(l)$$
 (1)

The second stage is the oxidization of divalent iron.

$$3Fe^{2+}(aq) + NO_3(aq) + 4H^+(aq) \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(1); \Delta G^0_{25\,\degree} = -54.2KJ$$
 (2)

The third stage is the precipitation of trivalent iron.

$$2Fe^{3+}(aq) + 3H_2O(1) \to Fe_2O_3(s) \downarrow + 6H^+(aq)$$
(3)

The high concentration of Fe in leachate lowers the recovering rate of Mg. Therefore it is need to reduce leaching amount of Fe. The use of HNO_3 was better than that of H_2SO_4 for lowering Fe concentration in leachate.

3. 3. Acid Concentration

From 2M to 10M concentration of H_2SO_4 and HNO_3 were used to evaluate the effect of acid concentration on the leaching characteristics of Mg and Fe. The results are described in Fig. 4. Leaching

amount of Mg was not small affected by the concentration of HNO_3 . However it was sharply decreased over 6M of H_2SO_4 . 9,241mg/L of Mg was leached at this condition. Leaching amount of Fe was quickly decreased similarly over 6M of H_2SO_4 . Considering leaching amount of Mg, 6M of acid concentration was suitable to leach Mg from mine residue.



Fig. 4. Effect of temperature on the leaching amount of Mg and Fe from mine residue

3. 4. Liquid/Solid Ratio

The effect of L/S ratio on leaching characteristics were discussed at the condition of reaction temperature 80° C, 6M of H₂SO₄ and HNO₃ and reaction time 6hrs. According to Fig. 5, the largest leaching amount of Mg was obtained at L/S ratio 10/1 of H₂SO₄. Mg was more leached by using H₂SO₄. The difference of leaching amount by H₂SO₄ and HNO₃ were due to the solubility of MgSO₄ and Mg(NO₃)₂ in acid solution. Leaching amount of Mg and Fe was increased with the increment of L/S ratio. The reason was that the pulp density was decreased at high L/S ratio, and mass transfer resistance was decreased on liquid-solid interface. Therefore the leaching reaction was accelerated by this phenomenon(Mu et al., 2010). The decrease of leaching amount was due to the precipitation of metal leached.

4. Conclusion

Particle size of mine residue, reaction time and temperature, acid concentration and L/S ratio were discussed to investigate the leaching characteristics of Mg in this study. The results are as follow;

- Leaching amount of Mg was largest at H_2SO_4 6M, reaction time 6hr and L/S ratio 10/1. But Fe was also more leached at this condition.
- 8,580mg/L of Mg and 24,653mg/L of Fe were leached at L/S ratio 15/1.
- It is important to maintain the low leaching level of Fe to raise the recovering rate of Mg.

Considering leaching amount of Mg and Fe, HNO₃ was effective leaching agent for recovering Mg from mine residue. But it is need to find the condition to raise the leaching amount of Mg from mine residue by using HNO₃.



Fig. 5. Effect of L/S ratio on the extraction of Mg and Fe from mine residue

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