Comparison of the Chemical Reactivity between Sulfuric and Methanesulfonic Acids as a Leaching Agent

Thanh Tuan Tran, Hyun Seung Moon and Man Seung Lee

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 58554, Korea

Abstract

Methanesulfonic acid (MSA) can be considered effective in the leaching of metals because of its advantageous physical and chemical properties. The chemical reactivities of MSA and sulfuric acid were compared based on their structures and the dissolution data of Co and Ni metal. The inductive and resonance effects play a vital role in the chemical reactivities of these two acids. The dissolution percentages of Co and Ni in the sulfuric acid solution were higher than those in the MSA solution under the same experimental conditions. Considering the strong acidity of MSA and the high solubility of its metal salts, MSA can be employed as a leaching agent for the recovery of metals.

Key words : methanesulfonic acid, sulfuric acid, chemical reactivity, leaching agent

1. Introduction

In hydrometallurgical processes, aqueous lixiviants play a critical role for dissolving metals from ores or concentrates into aqueous solutions. Mineral acid solutions such as H₂SO₄, HCl, and HNO₃ are the most widely used as lixiviants due to their advantages such as aggressiveness, low price and availability. However, there are

Received : April 6, 2021 · Revised : April 28, 2021 · Accepted : May 3, 2021

Corresponding Author : Man Seung Lee (E-mail : mslee@mokpo.ac.kr)
Department of Advanced Materials Science & Engineering, Mokpo National University, 1666 Yeongsan-ro, Cheonggye-myeon, Muan-gun, Chonnam 58554, Korea

The Korean Institute of Resources Recycling. All rights reserved. This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/), which permits unrestricted non-commercial use, distribution and reproduction in any medium, provided the original work is properly cited.
some drawbacks in the use of these acidic lixiviants for the leaching of metals from various resources. For instance, the leaching kinetics of copper from sulfidic ore minerals such as chalcopyrite, bornite, chalcocite, and digenite by H$_2$SO$_4$ solution is slow and the formation of passive film on the surface of chalcopyrite like solid sulfur hinders the progress of leaching in the absence of pitting agents like chloride ions$^{2-4}$. Although the leaching rate in chloride media is faster than that of sulfate media due to the high solubility of chloride salts, HCl solution has some disadvantages like the corrosion of the reactors and difficulty of electrowinning of high grade metal$^5$. Due to its highly oxidizing characteristics, nitric acid solutions can oxidize both metals and nonmetal elements like sulfide to sulfur or sulfate$^6$ and produce noxious and corrosive gas products like NO$_x$ in the leaching process, resulting in an increase in reagent consumption$^7,8$.

Methanesulfonic acid (CH$_3$SO$_3$H, MSA) has been widely used as an electrolyte for electrochemical processes (especially for tin and lead)$^9$ and can be applied in the synthesis of catalysis$^{10}$ and polymer$^{11}$. In recent years, the use of MSA for the leaching of metals in hydrometallurgical processes has attracted many interests due to its excellent chemical and physical properties such as high acidity, solubility of metal salts, high conductivity, high boiling point and less corrosiveness compared to commercially available inorganic acids$^{12}$. Some studies have pointed out that some metals such as Cu, Ni, Pb, Zn, and rare earth elements can be effectively leached by employing either dilute or concentrated MSA solutions in the presence and absence of oxidizing agents such as H$_2$O$_2$ and ferric chlorides (see Table 1). The leaching efficiency of Cu by the mixture of MSA and H$_2$O$_2$ from chalcopyrite is better than that of sulfuric acid$^{13}$. Besides, MSA is also known as a green acid owing to no production of dangerous volatile compounds, low toxicity, readily biodegradable$^{14,15}$. With its characteristics, MSA can be considered as a potential lixiviant for the recovery of valuable metals from the primary and secondary resources.

In this study, the chemical reactivity of MSA was compared with that of sulfuric acid on the basis of analysis of their structure and the dissolution behavior of Co and Ni metal. The dissolution data was obtained from our previously published data$^{16}$. These obtained results can contribute to provide further information on the application of MSA in hydrometallurgical processes.

| Resources | Condition | Leaching percentage of metals, % |
|-----------|-----------|----------------------------------|
| Chalcopyrite | 30 g/L MSA and 5 g/L ferric at 75°C for 96h | 47% Cu |
| Synthetic alloy containing Co, Ni, and Cu | 2.0 mol/L MSA + 10% (v/v) H$_2$O$_2$ solution at liquid/solid ratio: ~22.2 g/L at 20°C for 30 min with 300 rpm stirring speed | ~100% Co and below 5.0% Cu |
| Malachite | 0.36 mol/L MSA with liquid/solid ratio: 10 g/L 218K (~45°C), 60 min, and 500 rpm stirring speed. | 92.41 % Cu |
| Smithsonite | 0.4 mol/L MSA with liquid/solid ratio: 10 g/L at 323K (~50°C), 60 min, and 450 rpm stirring speed. | 92.58% Zn |
| Chalcopyrite | 0.05 mol/L MSA + 1.5 mol/L FeCl$_3$ with liquid/solid ratio: 100 g/L for 24h at 90°C | ~100% Cu |
| Zinc ore mineral hemimorphite | 0.15 mol/L MSA with liquid/solid ratio: 10 g/L at 25°C, 750 rpm stirring speed for 5 min. | 89.78% Zn |
| Residue of the Hydro WEEE process for lamp phosphor waste | Concentrated MSA with liquid/solid ratio: ~66.7 g/L at 473K (~200°C) 60 min | 74.3% Tb, 78.3% Ce, 82.7% Y, 58.2% Eu, 51.8% Gd and 94.7% La |

Table 1. Some reported literatures for using MSA in the leaching of metals$^{13,16,20-24}$.
2. Results and discussion

2.1. Chemical reactivity of acids

MSA is a strong organic (CH$_3$SO$_3$H, pK$_a$ = -1.19) and non-oxidizing acid. The acidity of MSA is close to some inorganic acids such as nitric acid (HNO$_3$, pK$_a$ = -1.3) and sulfuric acid (H$_2$SO$_4$, pK$_{a1}$ = -3) and higher than others such as phosphoric acid (H$_3$PO$_4$, pK$_{a1}$ = 2.12), acetic acid (CH$_3$COOH, pK$_a$ = 4.76) and maleic acid (C$_2$H$_2$(COOH)$_2$, pK$_{a1}$ = 1.83). MSA can be completely ionized into proton and methanesulfonate anions (CH$_3$SO$_3^-$) at 0.1 M in aqueous solution as represented in Eq. (1)\(^{17}\). Meanwhile, sulfuric acid is a strong inorganic acid with two protons and strong oxidizing agent at concentrated solutions and SO$_2$ gas can be produced at high temperature, which can act as a reducing agent\(^{18}\). The dissociation of sulfuric acid in water depends on solution acidity. When solution acidity is high, the first dissociation of sulfuric acid occurs completely, while the second dissociation can occur in dilute acid solution. The first and second dissociation of sulfuric acid is represented as Eqs. (2) and (3).

\[
\text{CH}_3\text{SO}_3\text{H} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CH}_3\text{SO}_3^- \quad \text{pK}_a = -1.19 \quad (1)
\]

\[
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HSO}_4^- \quad \text{pK}_{a1} = -3 \quad (2)
\]

\[
\text{HSO}_4^- + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \quad \text{pK}_{a2} = 2.0 \quad (3)
\]

Fig. 1 shows the similarity (-SO$_2$OH group) and difference (CH$_3$- and -OH groups) in the chemical structure of MSA and sulfuric acid, which relates to their chemical reactivity. In their structure, HOSO$_2^-$ and CH$_3$SO$_2^-$ groups attached to -OH groups are quite strong electron withdrawing groups owing to the presence of highly electronegative oxygen atoms and the moderately sulfur atom (see Fig. 2. A1&B1). The inductive effect increases the polarity of O-H bonds, resulting in the easy liberation of protons. Besides, resonance effects (see Fig. 2. A2&B2) also contribute to an increase in these polarity. The strong polarity of O-H bonds can explain for the strong

---

Fig. 1. Structure of MSA and sulfuric acid.

H$_2$SO$_4$ + H$_2$O = H$_3$O$^+$ + HSO$_4^-$ \quad pK$_{a1}$ = -3 \quad (2)

HSO$_4^-$ + H$_2$O = H$_3$O$^+$ + SO$_4^{2-}$ \quad pK$_{a2}$ = 2.0 \quad (3)

Fig. 2. Inductive and resonance effects of sulfuric acid (A1&A2) and MSA (B1&B2).
The higher acidity of sulfuric acid compared to MSA was ascribed to the positive inductive effect due to the electron donating group of methyl group (CH$_3$-) in MSA. Moreover, these inductive and resonance effects lead to the stability of hydrogen sulfate (HSO$_4^-$) and methane sulfonate (CH$_3$SO$_3^-$) ions due to the stabilization of the negative charge on the oxygen atom after being deprotonated$^{19}$. This can be shown in the solubility of their metal salts (see Table 2). Most metal methanesulfonates and hydrogen sulfates are highly soluble in aqueous solutions. Only some metal sulfates such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ag$^+$, and Pb$^{2+}$ are sparingly soluble in water. On the other hand, some studies have pointed out that MSA aqueous solutions can suppress the oxidation of metal ions to their high valence states$^{13,14}$. For instance, Sn(II) in the aqueous MSA solution can exist at the lower valence state and the oxidation to Sn(IV) would not occur. The oxidative stability of metal ions in MSA solution is ascribed to the formation of highly stable metal complexes$^{12,24}$. Thus, MSA will bring many advantages to extractive metallurgy as well as electrochemical processes in the production of metals from their solutions.

### 2.2. Dissolution behavior of individual metals by acid solutions

To compare the reactivity of MSA and sulfuric acid in aqueous solutions, the dissolution of Co and Ni metal is compared under the same experimental conditions. The data was obtained from our previous published data$^{16}$. Concentration of the two acids in the aqueous solutions was fixed at 2.0 mol/L. The experimental leaching conditions were as follows: 60°C temperature, 300 rpm stirring speed, 120 min reaction time, and 50 g/L pulp density. In Fig. 3, the dissolution percentage of Co and Ni by MSA solution were 70.8 and 42.1% and that by H$_2$SO$_4$ solution were 87.1 and 55.0%, respectively. These results showed that the dissolution of metals in sulfuric acid solution was more effective than that of MSA, which can be attributed to the stronger activity of hydrogen ions in sulfuric acid compared to MSA solution. The difference in the effect of the respective anions, CH$_3$SO$_3^-$ and HSO$_4^-$ on the dissolution of metals is negligible. This could be due to the insignificant

---

**Table 2.** The equivalent conductance (S cm$^2$/mol) of aqueous solutions of sulfuric acid and MSA$^{14}$

| Acid          | 2 N  | 1 N  | 0.5 N | 0.1 N | 0.05 N | 0.01 N |
|--------------|------|------|-------|-------|--------|--------|
| Sulfuric     | 413.84 | 444.88 | 464.12 | 529.08 | 572.76 | 699.40 |
| Methanesulfonic | 232.97 | 299.60 | 336.47 | 372.74 | 381.76 | 391.78 |

**Table 3.** The aqueous saturation solubility of metal salts at 22°C$^{14}$

| Metal ions | Methanesulfonate | Sulfate |
|------------|------------------|---------|
| Li$^+$     | 7.06             | 8.17    |
| Mg$^{2+}$  | 1.40             | 2.63    |
| Ca$^{2+}$  | 2.92             | 0.02    |
| Sr$^{2+}$  | 2.55             | 0.00    |
| Ba$^{2+}$  | 1.59             | 0.00    |
| Mn$^{2+}$  | 2.90             | 3.52    |
| Co$^{2+}$  | 2.53             | 2.16    |
| Ni$^{2+}$  | 2.13             | 2.44    |
| Cu$^{2+}$  | 2.00             | 1.35    |
| Ag$^+$     | 3.72             | 0.06    |
| Pb$^{2+}$  | 2.60             | 0.00    |
difference in the affinity of two anions to Co(II) and Ni(II) ions, which might be recognized in the solubility of their salts in water (see Table 3). Besides, the dissolution percentage of Co was higher than that of Ni in these acids, which was ascribed to the difference in their nature such as crystalline structure, reduction potentials of metals (= -0.28V and = -0.25V) and stable complexes in the solution. Dissolution reactions of metals can be written as

\[ \text{M}_\text{(s)} + 2\text{H}_2\text{SO}_4(\text{aq}) = \text{M}^{2+}(\text{aq}) + 2\text{HSO}_4^-(\text{aq}) + \text{H}_2(\text{g}) \]  

(4)

\[ \text{M}_\text{(s)} + 2\text{CH}_3\text{SO}_3\text{H}(\text{aq}) = \text{M}^{2+}(\text{aq}) + 2\text{CH}_3\text{SO}_3^-(\text{aq}) + \text{H}_2(\text{g}) \]  

(5)

where M denotes Co or Ni.

Thus, the dissolution efficiency of Co and Ni metal in the MSA and sulfuric acid solutions mainly depends on the redox potentials of the metals and the activity of hydrogen ions in the solutions.

3. Conclusions

Chemical reactivity between MSA and sulfuric acid was compared on the basis of their structure and dissolution data of metals in their aqueous acidic solutions investigated. The electronic effects such as inductive and resonance have significant contribution for the difference in the chemical properties of these acids such as acidity, solubility of metal salts and affinity to metal ions. The dissolution efficiency of Co and Ni mainly depends on the activity of hydrogen ions in the acid solution, resulting in more effective dissolution by sulfuric acid solution than MSA solution in the same experimental condition. Thus, these data showed MSA can be used as a lixiviant in the recovery of metals from the primary and secondary resources. And, further studies are necessary for the application of MSA in the real operation.

Acknowledgements

This work was supported by the Technology Innovation Program (Development of Material Component Technology) (Project number: 2011183) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

References

1. Wang, S., 2007 : Aqueous lixiviants: principle, types, and applications, JOM, 59, pp.37-42.
2. Li, Y., Kawashima, N., Li, J., et al., 2013 : A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite, Advances in Colloid and Interface Science, 197-198, pp.1-32.
3. Hackl, R., Dreisinger, D., Peters, L., et al., 1995 : Passivation of chalcopyrite during oxidative leaching in sulfate media, Hydrometallurgy, 39, pp.25-48.
4. Klauber, C., 2008 : A critical review of the surface chemistry of acidic ferric sulphate dissolution of chalcopyrite with regards to hindered dissolution, Int. J. Miner. Process., 86, pp.1-17.
5. Watling, H.R., 2014 : Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options, Hydrometallurgy, 146, pp.96-110.
6. Zarate-Gutierrez, R., Lapidus, G., Morales, R., 2012 : Aqueous oxidation of galena and pyrite with nitric acid at moderate temperatures, Hydrometallurgy, 115, pp.57-63.
7. Aydogan, S., Erdemoglu, M., Uçar, G., et al., 2007 : Kinetics of galena dissolution in nitric acid solutions with hydrogen peroxide, Hydrometallurgy, 88, pp.52-57.
8. Cho, K., Kim, H., Myung, E., et al., 2020 : Recovery of gold from the refractory gold concentrate using microwave assisted leaching, Metals, 10, pp.571.
9. Florence, F., Nisha, S.R., Srinivasan, K.N., et al., 2011 : Studies on electrodeposition of copper from methanesulfonic acid bath, International Journal of ChemTech Research, 3, pp.1318-1325.
10. Kulkarni, P., 2015 : Methanesulfonic acid is green catalyst in organic synthesis, Oriental Journal of Chemistry, 31, pp.447-451.
11. Gora, M., Kozik, B., Jamrozy, K., et al., 2009 : Solvent-free condensations of ketones with malononitrile catalyzed by methanesulfonic acid/morpholine system, Green Chemistr, 11, 863-867.
12. Palden, T., Ongheena, B., Regadio, M., et al., 2019 : Methanesulfonic acid: a sustainable acidic solvent for recovering metals from jarosite residue of the zinc
13. Ahn, J., Wu, J., and Lee, J., 2019: Investigation on chalcopyrite leaching with methanesulfonic acid (MSA) and hydrogen peroxide, Hydrometallurgy, 187, 54-62.
14. Gernon, M. D., Wu, M., Buszta, T., et al., 1999: Environmental benefits of methanesulfonic acid, Green Chemistry, 1, pp.127-140.
15. Finsgar, M., and Milosev, I., 2010: Corrosion behaviour of stainless steels in aqueous solutions of methanesulfonic acid, Corros. Sci. 52, pp.2430-2438.
16. Tran, T.T., Moon, H.S., and Lee, M.S., 2020: Separation of cobalt, nickel, and copper from synthetic metallic alloys by selective dissolution with acid solutions containing oxidizing agent, Mineral Processing and Extractive Metallurgy Review (online).
17. Patai, S., and Rappoport, Z., 1991: The Chemistry of Sulphonic Acids, Esters and their Derivatives, John Wiley and Sons, New York, p.251.
18. Sippola, H., and Taskinen, P., 2014: Thermodynamic Properties of Aqueous Sulfuric Acid, Journal of Chemical & Engineering Data, 59, pp.2389-2407.
19. Lynch, K., Maloney, A., Sowell, A., et al., 2015: Why is sulfuric acid a much stronger acid than ethanol? Determination of the contributions by inductive/field effects and electron-delocalization effects, Physical Chemistry Chemical Physics, 17, pp.138-144.
20. Feng, Q., Wen, S., Zhao, W., et al., 2015: Dissolution regularities of smithsonite in methane sulfonic acid, Russian Journal of Non-Ferrous Metals, 56, pp.365-371.
21. Feng, Q., Wen, S., Zhao, W., et al., 2015: Leaching of copper from malachite with methane sulfonic acid, Solvent Extraction Research and Development, Japan, 22, pp.159-168.
22. Hidalgo, T., Kuhar, L., Beinlich, A., et al., 2018: Kinetic study of chalcopyrite dissolution with iron(III) chloride in methanesulfonic acid, Minerals Engineering, 125, pp.66-74.
23. Zhang Q., Wen S., Feng Q., et al., 2019: Dissolution kinetics of hemimorphite in methane sulfonic acid, Physicochem. Probl. Miner. Process., 55, pp.1-9.
24. Gijsemans, L., Forte, F., Onghena, B., et al., 2018: Recovery of rare earths from the green lamp phosphor LaPO$_4$·Ce$^{3+}$, Tb$^{3+}$ (LAP) by dissolution in concentrated methanesulphonic acid, RSC Advances, 8, pp.26349-26355.

---

**Thanh Tuan Tran**

- Can Tho University Chemistry 학사
- Can Tho University Organic Chemistry 석사
- 현재 목포대학교 신소재공학과 박사과정

**문현승**

- 목포대학교 신소재공학과 학사
- 현재 목포대학교 신소재공학과 석사과정

**이만승**

- 현재 목포대학교 신소재공학과 교수
- 당 학회지 제11권1호 참조