

Leaching Kinetics of Selenium, Tellurium and Silver from Copper Anode Slime by Sulfuric Acid Leaching in the Presence of Manganese(IV) Oxide and Graphite [†]

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Abstract: Sulfuric acid leaching of copper anode slime (CAS) in the presence of manganese(IV) oxide (MnO₂) and graphite was investigated for Se, Te and Ag recovery. The study reveals that the leaching of Se, Te and Ag was facilitated by the galvanic interaction with MnO₂, and graphite played the role of a catalyst. The leaching process could yield 81.9% Se, 90.8% Te, and 80.7% Ag leaching efficiency when the conditions were maintained as 500 rpm, 2.0 M H₂SO₄, 0.8/0.8/1 MnO₂/graphite/CAS, and 90 °C temperature. The kinetic study showed that Se leaching followed the surface chemical reaction at all the tested temperature range (25–90 °C) with the activation energy of 27.7 kJ/mol. Te and Ag leaching at temperature 25–50 °C followed the mixed and surface chemical reaction models, respectively, and changed to fit the diffusion and mixed control models, respectively, in the temperature range 60–90 °C with the corresponding activation energy of 17.8 and 12.2 kJ/mol.

Keywords: copper anode slime; tellurium; selenium; silver; galvanic leaching; kinetics

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1. Introduction

Copper anode slime (CAS), a byproduct of the copper electrorefining process, has long been used as a secondary resource for various critical metals, such as Au, Ag, Pt, Pd, Se, Te, Cu, etc. Metallurgical treatments of CAS for recovering these valuable metals include the stepwise thermal–aqueous, aqueous–thermal, aqueous–aqueous processes, consisting of roasting to recover Se and oxidative leaching to Te and Cu, prior to the recovery of precious metals [1]. Despite the extensive investigation on the aforesaid processes, problematic facts remain. For instance, roasting of CAS either through oxidative or sulfation roasting results in loss of Se fraction. Another option of soda roasting is unfavorable in practice because of the subsequent acid leaching process, which increases the reagent consumption for acidification/neutralization and produces low-cost byproducts. A similar problem appears when approaching alkaline pressure leaching for recovering selenium.

Recently, research on the treatment of CAS has focused on shortening the number of treatment stages to a single step. Sulfuric acid leaching in the presence of strong oxidant has shown the capability of simultaneous recovery of Se, Te, and even Ag. HNO₃ was used as the oxidant for the leaching of Se from de-copperized CAS, which achieved 97.8% of Se recovery [2]; however, the process faces the issue of the release of harmful NO_x gas, which required a complicated sealed-leaching system. H₂O₂ is a less toxic oxidant, but its

stability is sensitive to the higher temperature (it starts to decompose at temperature ≥ 70 °C) and is unrecyclable as well [3–5]. MnO_2 provides low environmental impact, high metal recovery, and recyclability; according to Xiao et al. [4], sulfuric acid leaching with MnO_2 can ensure a profit of \$82 per 1 t of CAS treated. With this potential, the leaching using MnO_2 critically depends on the constituent phases of the CAS, particularly selenides/tellurides.

In this study, leaching of constituent metals from CAS (Se, Te, Ag) was investigated using H_2SO_4 as the lixiviant, MnO_2 as the oxidant and graphite as the catalyst. The leaching conditions were optimized, and the leaching kinetics of the targeted metals were studied while adopting the shrinking core models.

2. Materials and Methods

The CAS sample used was supplied by a copper smelter in South Korea. The wet-chemical analysis of the sample revealed that the CAS contained 22.23% Se, 12.13% Ba, 9.66% Ag, 1.53% Te, and precious metals of 0.046% Au, 37.93 ppm Pd and 2.94 ppm Pt. The X-ray diffraction analysis (pattern given in Figure 1) shows the presence of Se^0 , Ag_2Se and BaSO_4 phases. For the leaching studies, a known concentration of H_2SO_4 solution was put into a glass reactor fitted over a water bath. Once the desired temperature was achieved, a weighed amount of CAS was added to the lixiviant while maintaining the solid/liquid ratio of 2.5 g/250 mL of H_2SO_4 solution. The leaching was performed at the stirring speed of 500 rpm for 6 h (after preliminary studies), and slurry liquid samples were withdrawn at regular times, filtered and diluted appropriately into 5% nitric acid for analyzing metal contents using inductively coupled plasma spectroscopy (ICP). Chemicals, such as H_2SO_4 (98%, Junsei Chemical, Japan), MnO_2 (87%, Wako Chemical, Japan) and graphite (Kanto Chemical, Japan) were used as received.

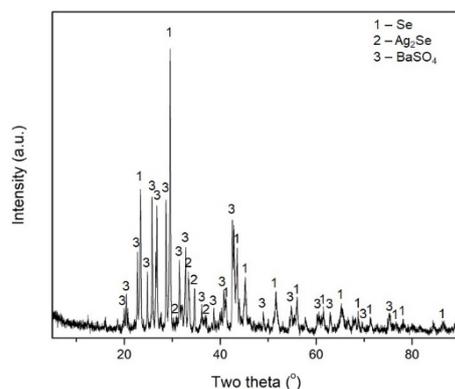


Figure 1. XRD pattern of raw copper anode slime.

3. Results

3.1. Effect of H_2SO_4 Concentration

The effect of H_2SO_4 in the range 0.5–3.0 M on the extraction percentage was investigated. For this, leaching conditions were maintained as stirring speed 500 rpm; MnO_2 /graphite/CAS mass ratio 0.8/0.8/1, and temperature 70 °C. The extraction behavior of Se, Te and Ag as a function of time at the investigated H_2SO_4 concentrations is given in Figure 2. As can be seen, the leaching of Se, Te and Ag increased significantly by increasing H_2SO_4 from 0.5 to 2.0 M; at 2.0 M H_2SO_4 , the leaching percentages of the metals are 80.7%, 68.6% and 76.8%, respectively. At still higher H_2SO_4 concentration, the leaching trends of Se and Te could show marginal improvements, but that of Ag decreased, which is attributed to the formation of Ag_2S [6–8] to limit the leaching of Ag-related phases [3–5]. Therefore, further leaching experiments were performed using 2.0 M H_2SO_4 .

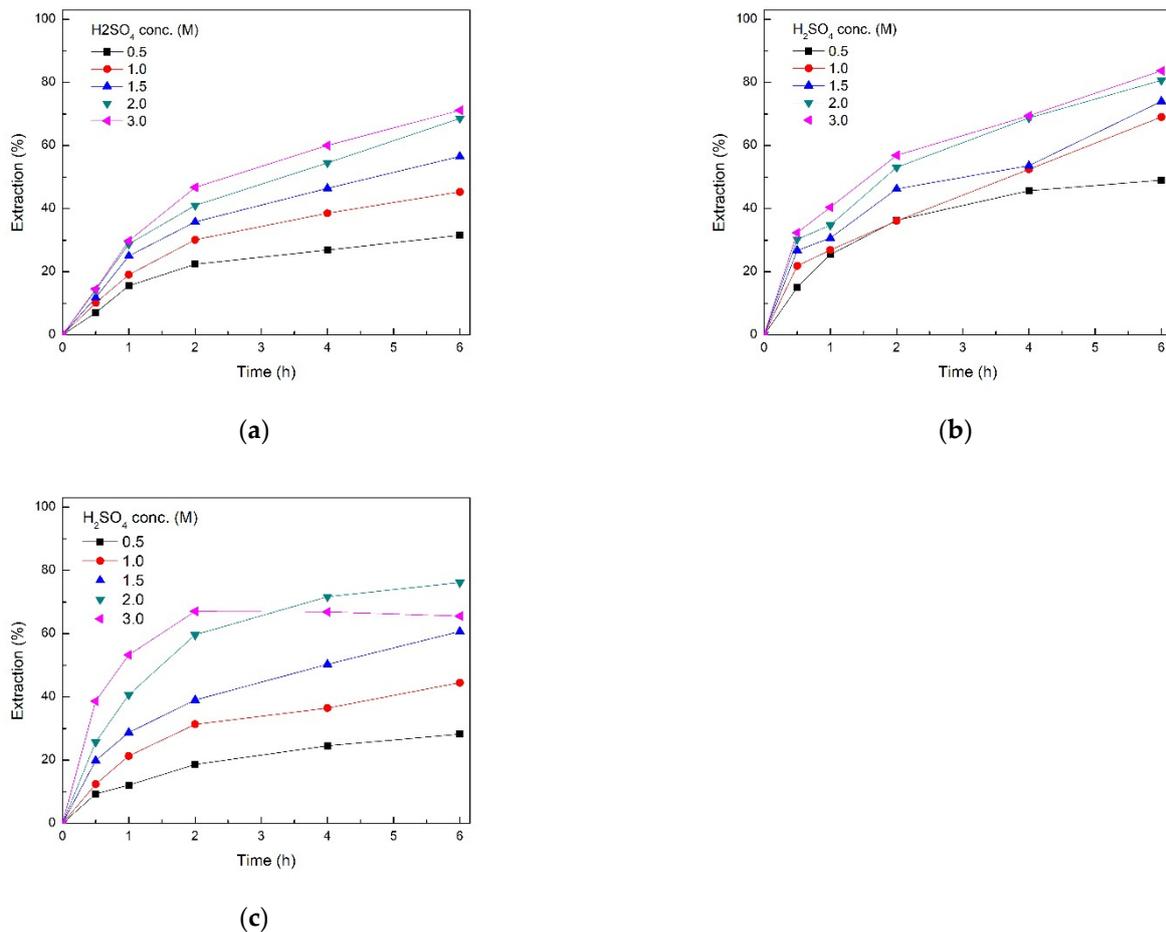


Figure 2. Dissolution behavior of (a) selenium, (b) tellurium and (c) silver in H₂SO₄ solution as a function of time (variation of H₂SO₄ conc., 0.5–3.0 M; stirring speed 500 rpm; MnO₂/graphite/copper anode slime (CAS) mass ratio 0.8/0.8/1; and temperature 70 °C).

3.2. Effect of MnO₂ Dosage

Here, MnO₂ dosage was expressed as the mass ratio of MnO₂ to CAS. Experiments were conducted under the conditions mentioned in Figure 3. It can be seen that MnO₂ has a pronounced effect on the leaching of Se, Te and Ag. In the absence of MnO₂, the leaching yield of Te was 32.8%, and those of Se and Ag were negligible. Increasing MnO₂/CAS mass ratio increased the leaching of the three metals; at MnO₂/CAS mass ratio 0.8/1, the leaching of Se, Te and Ag was 81.5%, 69.8% and 75.3%, respectively. Further increase in MnO₂/CAS mass ratio resulted in limited improvement, which could be ascribed to the high crowding of metallic ions in the solution [9–12]. Thus, the MnO₂/CAS mass ratio of 0.8/1 was chosen for the next experiments.

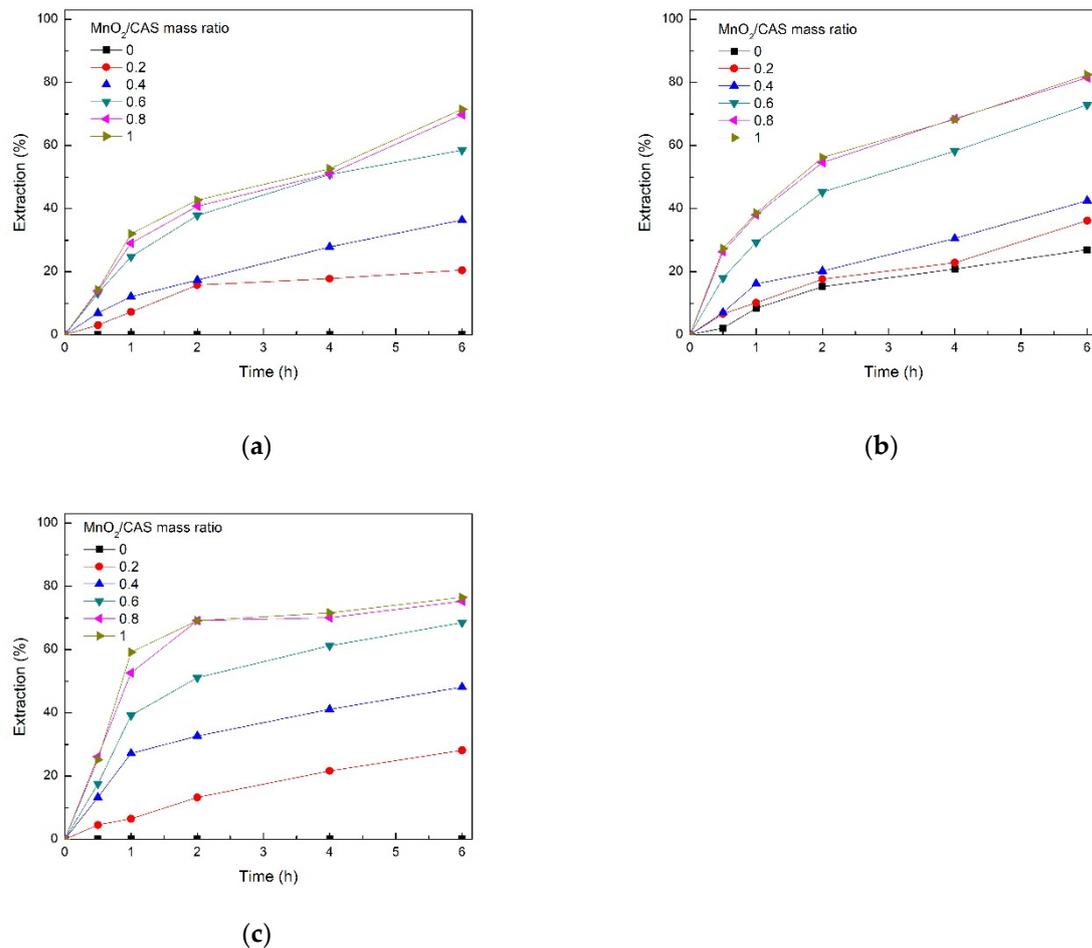


Figure 3. Dissolution behavior of (a) Se, (b) Te and (c) Ag in 2.0 M H_2SO_4 solution as a function of time (variation of MnO_2/CAS mass ratio, 0–1; stirring speed 500 rpm; graphite/CAS mass ratio 0.8/1; and temperature 70 °C).

3.3. Effect of Graphite Dosage

Figure 4 shows the results of leaching experiments while varying the graphite/CAS mass ratio (ranging from 0 to 1). Experiments were performed under the conditions: stirring speed 500 rpm; H_2SO_4 conc. 2.0 M; MnO_2/CAS mass ratio 0.8/1, and temperature 70 °C. It can be seen that the leaching yields of Se, Te and Ag have increased from 40.2% to 69.2%, 54.5% to 82.4% and 56.6% to 78.9%, respectively when the graphite/CAS mass ratio was increased from 0 to 0.8/1. More increasingly, the graphite dosage did not improve the leaching yields because the graphite particles hindered the contact between the CAS particles and lixiviant [10,11]. Thus, a graphite/CAS mass ratio of 0.8/1 was chosen for the subsequent experiments.

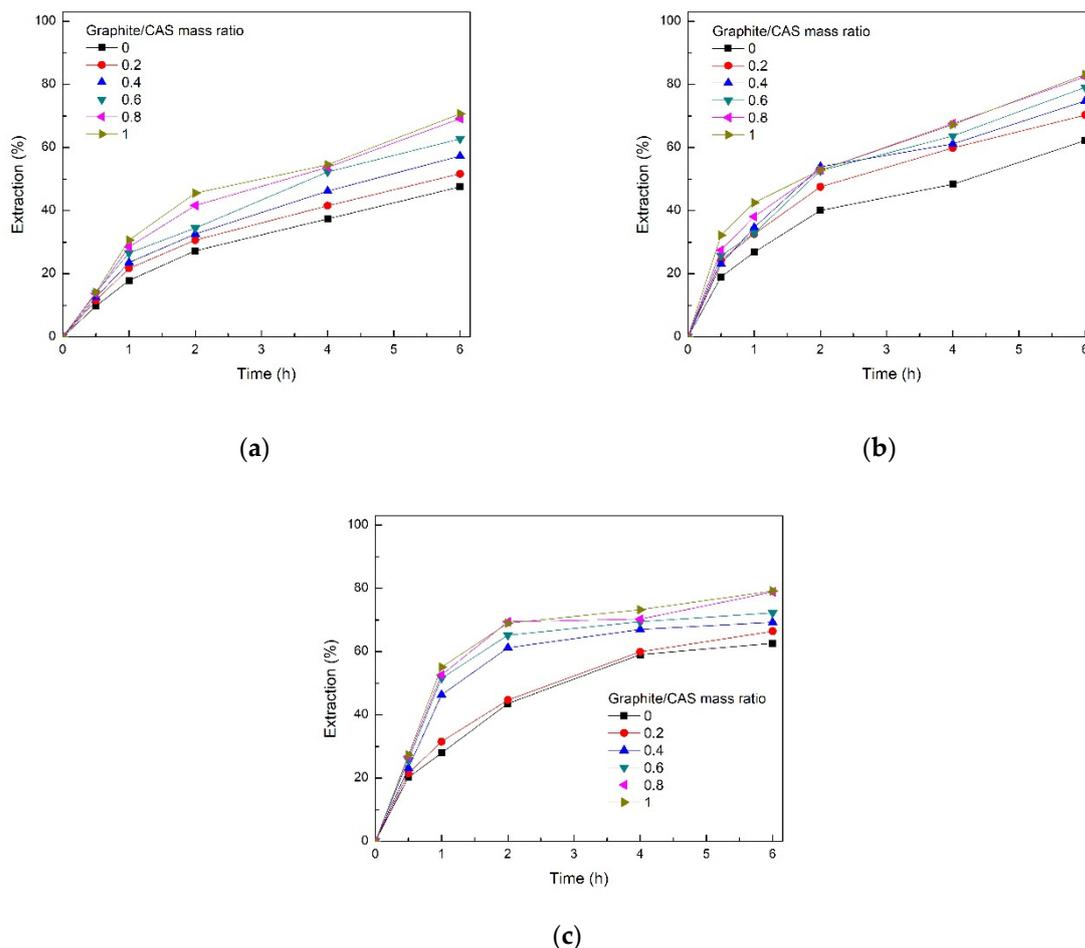


Figure 4. Dissolution behavior of (a) Se, (b) Te and (c) Ag in 2.0 M H₂SO₄ solution as a function of time (variation of MnO₂/CAS mass ratio, 0–1; stirring speed 500 rpm; MnO₂/CAS mass ratio 0.8/1; and temperature 70 °C).

3.4. Kinetic Study

The kinetics of leaching reactions of Se, Te and Ag is described by the shrinking core model, wherein the reaction involves the reaction between solid particles and the fluid extractants. Two common equations of shrinking core model, such as diffusion through a product layer (Equation (1)) and surface chemical reaction (Equation (2)) [3,13,14], and an empirical mixed kinetic model (Equation (3)) [15] were used to study the kinetics of leaching reactions.

$$1 - \frac{2}{3}(1-x) + (1-x)^{\frac{2}{3}} = k_d t \quad (1)$$

$$1 - (1-x)^{\frac{1}{3}} = k_r t \quad (2)$$

$$[1 - (1-x)^{\frac{1}{3}}]^2 = k_m t \quad (3)$$

where x is the fraction of metal leached in time t and k is the apparent rate constant with the corresponding subscript denoting the model type.

For the kinetic study, the temperature of leaching was varied from 25 to 90 °C. Figure 5 presents the leaching fraction of Se, Te and Ag as a function of time at the investigated temperatures, showing that increasing the temperature could increase the leached fraction of metals. At 90 °C, the leaching of Se, Te and Ag was 81.9%, 90.8% and 80.7%, respectively. These data are thus used for determining the rate constants and correlation coefficients based on the Equations (1)–(3), and details, of which are provided in Table 1.

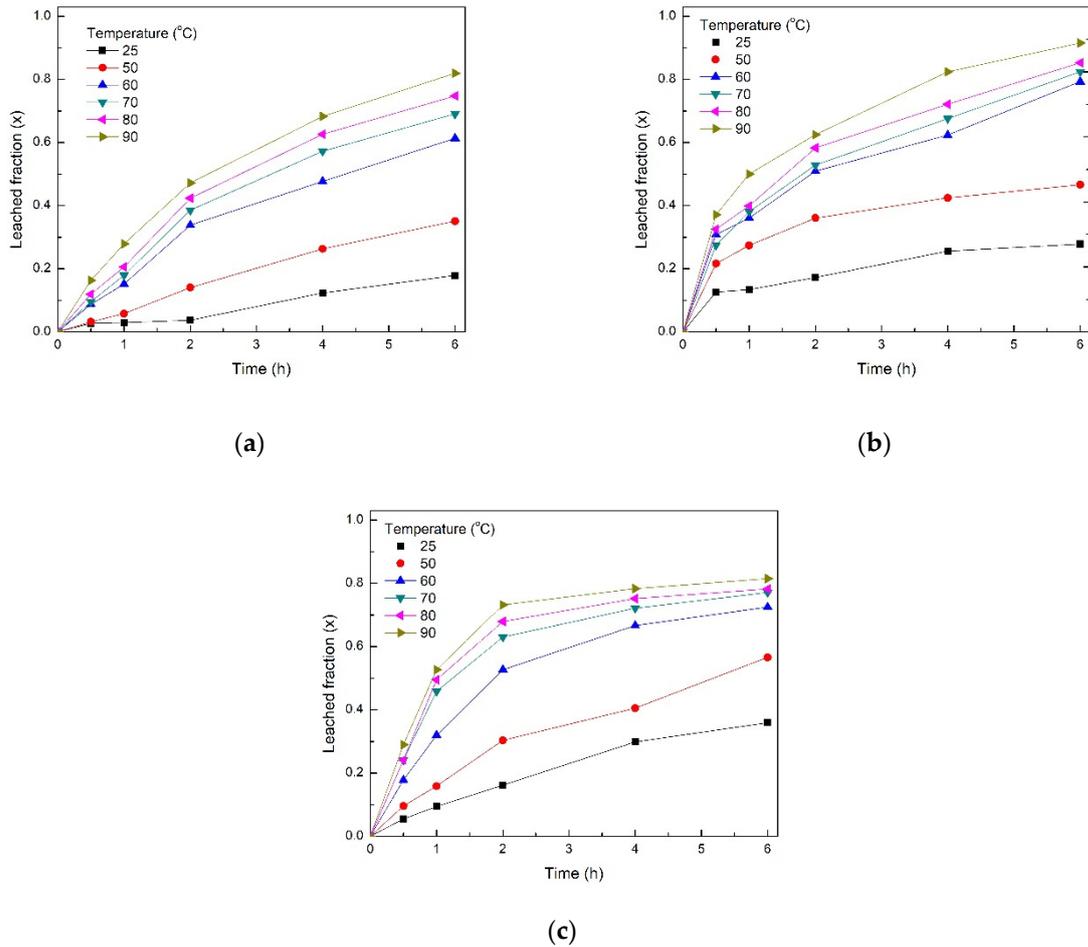


Figure 5. Leached fraction of (a) Se, (b) Te, and (c) Ag in 2.0 M H₂SO₄ solution as a function of time (variation of temperature, 25–90 °C; stirring speed 500 rpm; MnO₂/CAS mass ratio 0.8/1).

Table 1. Apparent rate constants k_d , k_r and k_m for the kinetic models and correlation coefficients.

Temperature (°C)	$1 - \frac{2}{3}(1-x) + (1-x)^{\frac{2}{3}} = k_d t$		$1 - (1-x)^{\frac{1}{3}} = k_r t$		$[1 - (1-x)^{\frac{1}{3}}]^2 = k_m t$	
	k_d	R ²	k_r	R ²	k_m	R ²
Se						
25	0.0006	0.92	0.0105	0.97	0.0007	0.91
50	0.0028	0.96	0.023	0.99	0.0031	0.96
60	0.0102	0.98	0.0442	0.98	0.0123	0.97
70	0.0132	0.93	0.0519	0.99	0.0167	0.90
80	0.0179	0.98	0.0621	0.99	0.0234	0.97
90	0.023	0.99	0.0711	0.99	0.032	0.97
Te						
25	0.0017	0.97	0.0149	0.85	0.0018	0.98
50	0.005	0.95	0.0262	0.78	0.0058	0.96
60	0.0189	0.97	0.0584	0.92	0.0259	0.96
70	0.0222	0.99	0.0662	0.96	0.0312	0.96
80	0.0249	0.99	0.0708	0.95	0.0362	0.98
90	0.03	0.99	0.0797	0.93	0.0481	0.98
Ag						
25	0.0031	0.98	0.0232	0.98	0.0034	0.98

50	0.08	0.96	0.0384	0.99	0.0095	0.95
60	0.0167	0.97	0.057	0.91	0.0218	0.98
70	0.0192	0.93	0.0617	0.79	0.0261	0.95
80	0.0202	0.88	0.0655	0.77	0.0278	0.91
90	0.0225	0.86	0.0598	0.83	0.032	0.89

For Se, the leaching rate at all investigated temperatures followed the surface chemical reaction with $R^2 > 0.97$. The apparent activation energy, calculated by the Arrhenius equation ($k = A \cdot \exp(-\frac{E_a}{RT})$) and the plot of $\ln(k)$ vs. the reciprocal of the absolute temperature ($1/T$) (Figure 6) was found to be 27.7 kJ/mol, which was lower than the typical range of chemically controlled reaction (>41.8 kJ/mol, [16]); this could be attributed to the catalytic effect of graphite to lower the activation energy [17–19].

For Te, a change of rate-controlling step from the mixed model (temperature 25–50 °C) to the diffusion control model (60–90 °C) was observed. This could be explained by the poor rate of chemical reaction at low temperatures [16], while at high temperatures, the reaction becomes faster. Diffusion of leached Te species could happen through the Ag_2S phase formed during the leaching as Te showed a paragenetic relationship with Se in the Ag_2Se phase. The calculated activation energy acquired during the diffusion-controlled step (Figure 6) was found to be 17.8 kJ/mol in the temperature range mentioned (60–90 °C).

Such a change in the leaching mechanism was also found in the case of Ag. The leaching was controlled by a chemical reaction at temperatures 25–50 °C and turned to be controlled by the mixed controlled mechanism at the higher temperatures, which could be attributed to a similar reason as that of Te. Moreover, the activation energy acquired in the latter case (mixed control) from the slope analysis of Figure 6 was 12.2 kJ/mol (60–90 °C); the low activation energy recorded was because of the catalytic effect of graphite [17–19].

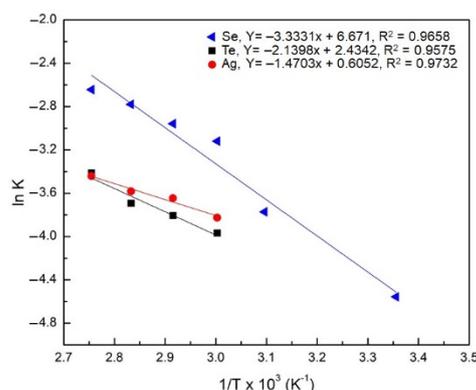


Figure 6. Arrhenius plot of Se, Te and Ag.

4. Conclusions

Se, Te and Ag from copper anode slime (CAS) were recovered by sulfuric acid leaching in the presence of MnO_2 . Graphite acted as the catalyst for the leaching reaction. Increasing leaching parameters, such as H_2SO_4 concentration, MnO_2 and graphite dosage, and temperature, resulted in significant improvements in the leaching of the three metals. With a stirring speed of 500 rpm, 81.9% Se, 90.8% Te and 80.7% Ag were leached out at H_2SO_4 conc. 2.0 M, MnO_2 /graphite/CAS mass ratio 0.8/0.8/1 and temperature 90 °C after 6 h time. Kinetic investigation showed that the leaching of the three metals followed the shrinking core model. Se leaching proceeded through the surface chemical reaction with the apparent energy activation of 27.7 kJ/mol (25–90 °C). For Te and Ag, change in the rate-controlling steps from mixed control to the diffusion control and chemical control to

mixed control were observed after increasing the temperature to ≥ 60 °C; the activation energy calculated being 17.8 and 12.2 kJ/mol (60–90 °C), respectively.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Lee, J.-c.; Kurniawan; Chung, K.W.; Kim, S. Metallurgical process for total recovery of all constituent metals from copper anode slimes: A review of established technologies and current progress. *Met. Mater. Int.* **2020**, *5*, 1–28. doi:10.1007/s12540-020-00716-7.
2. Li, X.J.; Yang, H.Y.; Jin, Z.N.; Tong, L.L.; Xiao, F.X. Selenium leaching from copper anode slimes using a nitric acid-sulfuric acid mixture. *Metallurgist* **2017**, *61*, 348–356. doi:10.1007/s11015-017-0500-2.
3. Dong, Z.; Jiang, T.; Xu, B.; Yang, J.; Chen, Y.; Li, Q.; Yang, Y. Comprehensive recoveries of selenium, copper, gold, silver and lead from a copper anode slime with a clean and economical hydrometallurgical process. *Chem. Eng. J.* **2020**, *393*, 124762. doi:10.1016/j.cej.2020.124762.
4. Xiao, L.; Wang, Y.; Yu, Y.; Fu, G.; Liu, Y.; Sun, Z.; Ye, S. Enhanced selective recovery of selenium from anode slime using MnO₂ in dilute H₂SO₄ solution as oxidant. *J. Clean. Prod.* **2019**, *209*, 494–504. doi:10.1016/j.jclepro.2018.10.144.
5. Kilic, Y.; Kartal, G.; Timur, S. An investigation of copper and selenium recovery from copper anode slimes. *Int. J. Miner. Process.* **2013**, *124*, 75–82. doi:10.1016/j.minpro.2013.04.006.
6. Hiroyoshi, N.; Arai, M.; Miki, H.; Tsunekawa, M.; Hirajima, T. A new reaction model for the catalytic effect of silver ions on chalcopyrite leaching in sulfuric acid solution. *Hydrometallurgy* **2002**, *63*, 257–267. doi:10.1016/S0304-386X(01)00228-6.
7. Nazari, G.; Dixon, D.G.; Dreisinger, D.B. The role of silver-enhanced pyrite in sulfuric acid media at 50 °C. *Hydrometallurgy* **2012**, *113*, 177–184. doi:10.1016/j.hydromet.2011.12.024.
8. Nazari, G.; Dixon, D.G.; Dreisinger, D.B. The mechanism of chalcopyrite leaching in the presence of silver-enhanced pyrite in the Galvanox™ process. *Hydrometallurgy* **2012**, *113*, 122–130. doi:10.1016/j.hydromet.2011.12.011.
9. Kowalczyk, P.B.; Manaig, D.O.; Drivenes, K.; Snook, B.; Aasly, K.; Kleiv, R.A. Galvanic leaching of seafloor massive sulphides using MnO₂ in H₂SO₄-NaCl media. *Minerals* **2018**, *8*, 235. doi:10.3390/min8060235.
10. Nakazawa, H.; Nakamura, S.; Odashima, S.; Hareyama, W. Effect of carbon black to facilitate galvanic leaching of copper from chalcopyrite in the presence of manganese(IV) oxide. *Hydrometallurgy* **2016**, *163*, 69–76. doi:10.1016/j.hydromet.2016.03.003.
11. Nakazawa, H. Effect of carbon black on chalcopyrite leaching in sulfuric acid media at 50 °C. *Hydrometallurgy* **2018**, *113*, 100–108. doi:10.1016/j.hydromet.2018.03.001.
12. Peng, H.; Yang, L.; Chen, Y.; Guo, J. Oxidative leaching of vanadium from vanadium-chromium reducing residue with MnO₂. *IOP Conf. Ser. Mater. Sci. Eng.* **2020**, *730*, 012041. doi:10.1088/1757-899X/730/1/01204.
13. Hait, J.; Jana, R.K.; Kumar, V.; Sanyal, S.K. Some studies on sulfuric acid leaching of anode slime with additives. *Ind. Eng. Chem. Res.* **2002**, *41*, 6593–6599. doi:10.1021/ie020239j.
14. Yang, H.Y.; Li, X.J.; Tong, L.L.; Jin, Z.N.; Lu, Y.I.N.; Chen, G.B. Leaching kinetics of selenium from copper anode slimes by nitric acid-sulfuric acid mixture. *Trans. Nonferrous Met. Soc.* **2018**, *28*, 186–192. doi:10.1016/S1003-6326(18)64652-7.
15. Wu, D.; Wen, S.; Deng, J. Leaching kinetics of cerussite using a new complexation reaction reagent. *New J. Chem.* **2015**, *39*, 1922–1929. doi:10.1039/C4NJ01549E.
16. Habashi, F. *Principles of Extractive Metallurgy: Hydrometallurgy*; Gordon & Breach: Paris, France, 1969.
17. Cordoba, E.M.; Munoz, J.A.; Blazquez, M.L.; Gonzalez, F.; Ballester, A. Leaching of chalcopyrite with ferric ion. Part III: Effect of redox potential on the silver-catalyzed process. *Hydrometallurgy* **2008**, *93*, 97–105. doi:10.1016/j.hydromet.2007.11.006.
18. Ghosh, M.K.; Das, R.P.; Biswas, A.K. Oxidative ammonia leaching of sphalerite Part II: Cu(II)-catalyzed kinetics. *Int. J. Miner. Process* **2003**, *70*, 221–234. doi:10.1016/S0301-7516(03)00024-3.
19. Xu, B.; Li, K.; Li, Q.; Yang, Y.; Liu, X.; Jiang, T. Kinetic studies of gold leaching from a gold concentrate calcine by thiosulfate with cobalt-ammonia catalysis and gold recovery by resin adsorption from its pregnant solution. *Sep. Purif. Technol.* **2019**, *213*, 368–377. doi:10.1016/j.seppur.2018.12.064.