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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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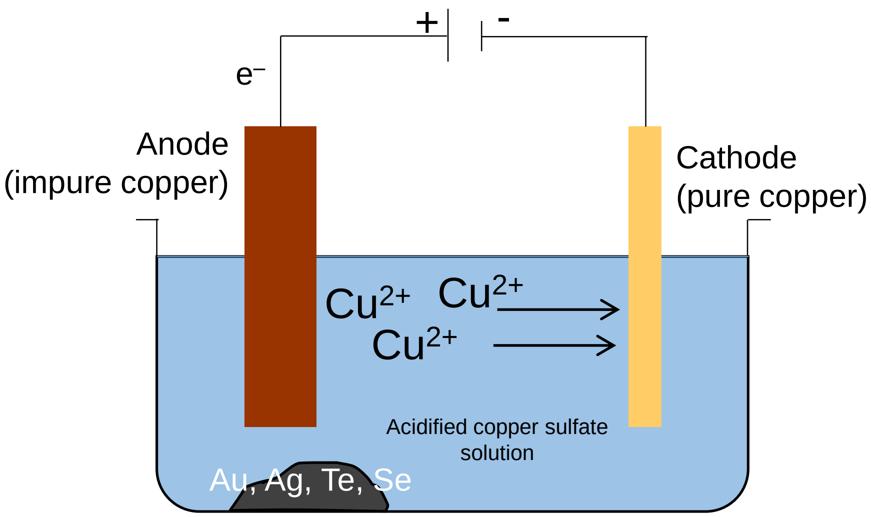
Outline

- Introduction
- Objective
- Experimental
- Results and discussion
- Conclusions

Introduction

Generation of copper anode slime

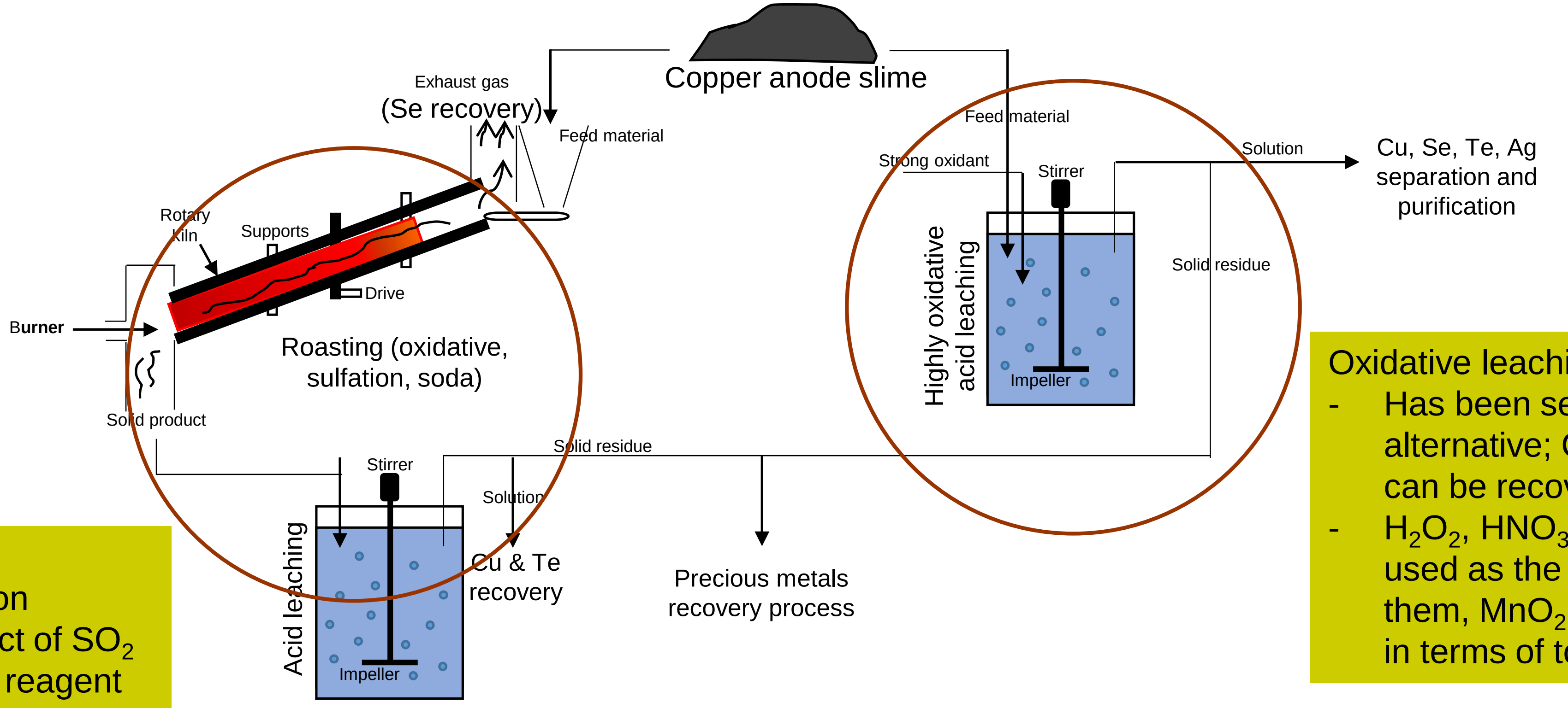


Copper electrorefining process

- Copper in the anode is oxidized, then reduced back to the cathode
- Impurities are left and settle down to the bottom of the cell as slime

Introduction

Metallurgical process of anode slime



Problems:
- Loss of Se fraction
- Harmful byproduct of SO_2
- High energy and reagent consumption

Oxidative leaching
- Has been seen as a promising alternative; Cu, Se, Te and even Ag can be recovered together
- H_2O_2, HNO_3 and MnO_2 have been used as the oxidants, which among them, MnO_2 is more advantageous in terms of toxicity and recyclability

Objective

- Reporting an efficient metal recovery process from CAS through sulfuric acid leaching in the presence of MnO_2
- Investigating the catalytic effect of graphite
- Investigating the leaching kinetics of constituent metals (Se, Te, Ag) from CAS

Experimental

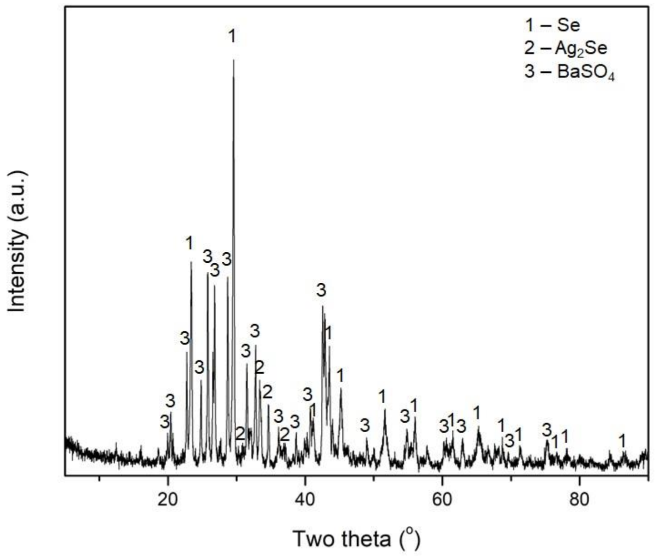
Material

CAS obtained from a copper smelter in South Korea

Chemical composition

Element	Se	Ba	Te	Ag	Au	Pt*	Pd*
Content (%)	22.23	12.13	1.53	9.66	0.046	37.93	2.94

*in ppm

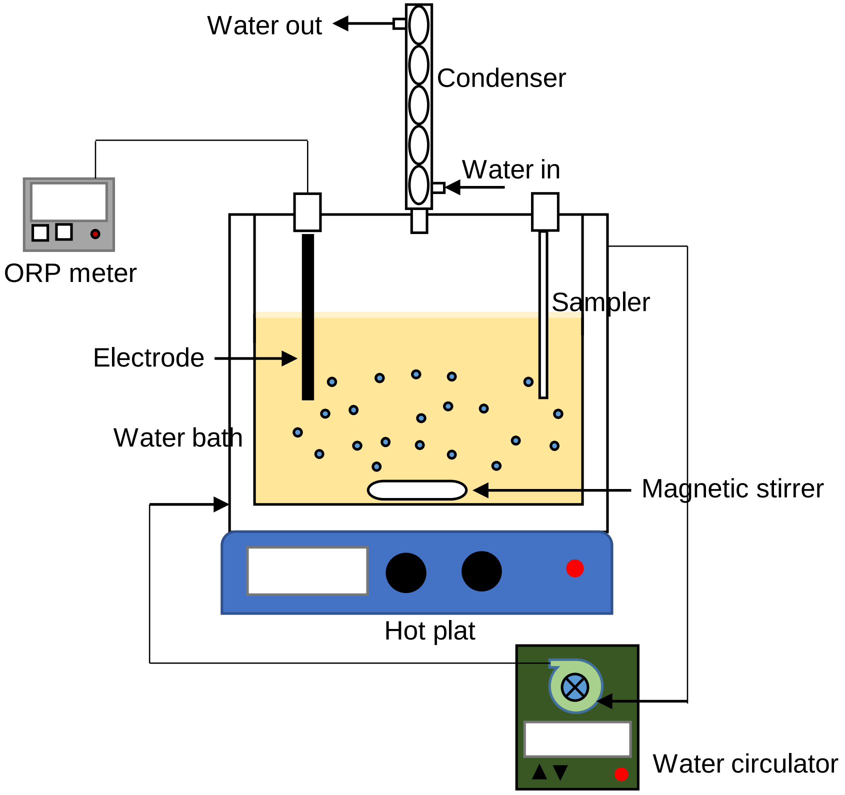


XRD Pattern

- Sample is rich of Se and Ag
- Major phases: Se^0, Ag_2Se, $BaSO_4$

Experimental

Leaching



Leaching set-up

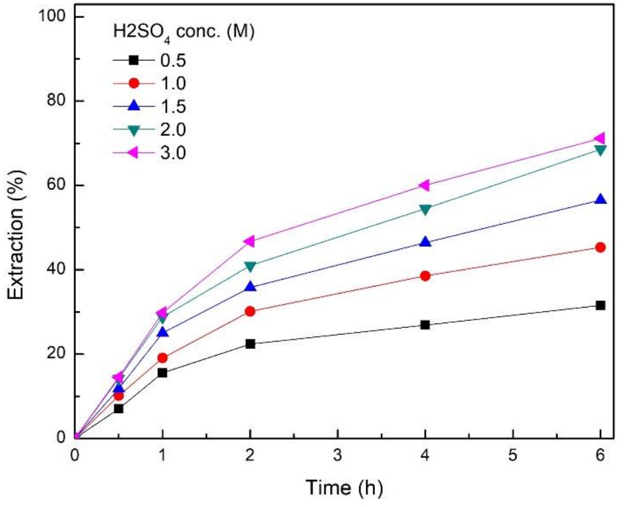
Table 2. Parameters investigated

Parameters	Variations
H_2SO_4 conc. (M)	0.5, 1.0, 1.5, 2.0, 3.0
MnO_2 dosage (MnO_2/CAS mass ratio)	0, 0.2, 0.4, 0.6, 0.8, 1.1
Graphite dosage (graphite/CAS mass ratio)	0, 0.2, 0.4, 0.6, 0.8, 1.0
Temperature (°C)	25, 50, 60, 70, 80, 90

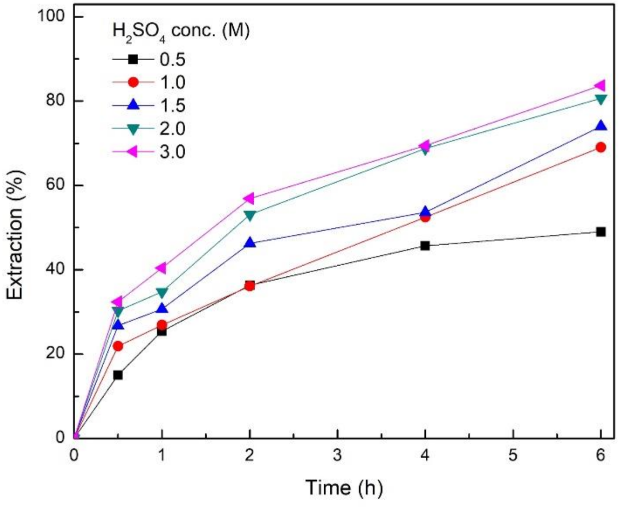
Fixed conditions: Stirring speed 500 rpm; leaching time 6 h; solid/liquid ratio 2.5 g/250 ml

Results and discussion

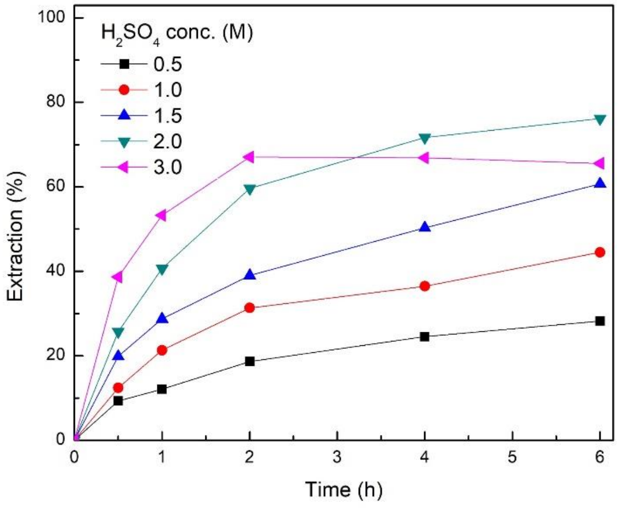
Effect of H_2SO_4 concentration



(a)



(b)



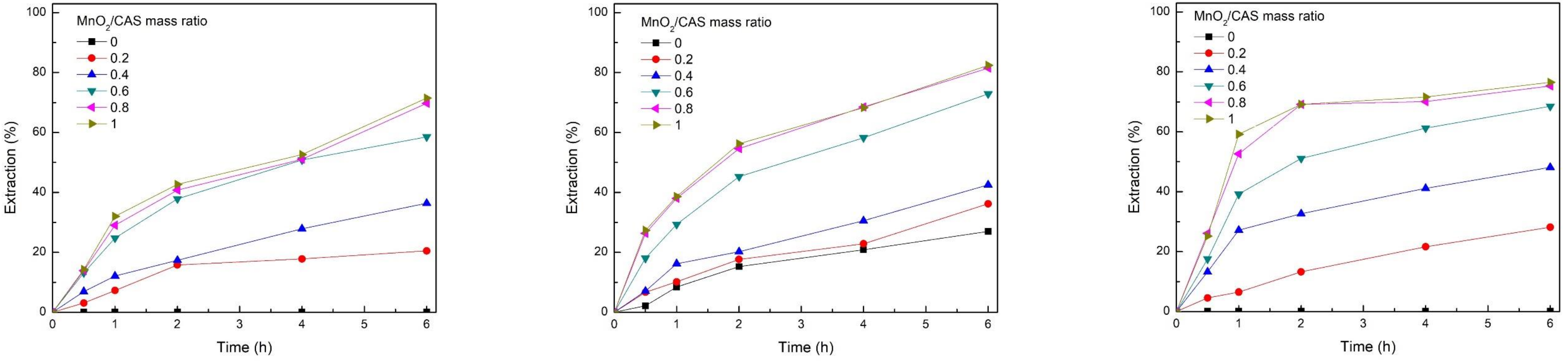
(c)

Leaching behavior of (a) Se, (b) Te, (c) Ag in H_2SO_4 solution as a function of time (Variation of H_2SO_4 conc., 0.5–3.0 M; MnO_2/graphite/CAS mass ratio 0.8/0.8/1; temperature 70 °C; stirring speed 500 rpm; time 6 h)

- Formation of Ag_2S at high H_2SO_4 concentration

Results and discussion

Effect of MnO_2 dosage



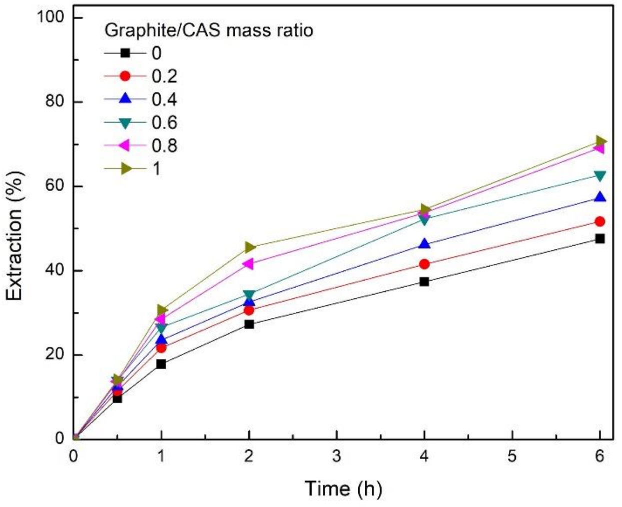
(a) (b) (c)

Leaching behavior of (a) Se, (b) Te, (c) Ag in H_2SO_4 solution as a function of time (Variation of MnO_2/CAS mass ratio, 0–1; H_2SO_4 conc. 2.0 M; graphite/CAS mass ratio 0.8/1; temperature 70 °C; stirring speed 500 rpm; time 6 h)

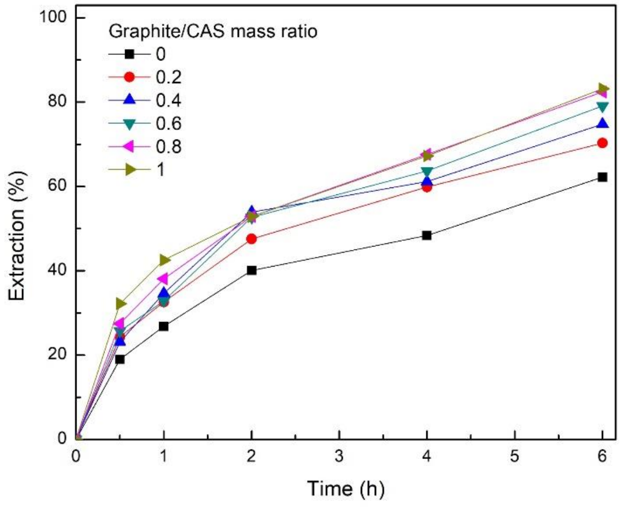
- Metallic ions become very crowded at high MnO_2 dosage

Results and discussion

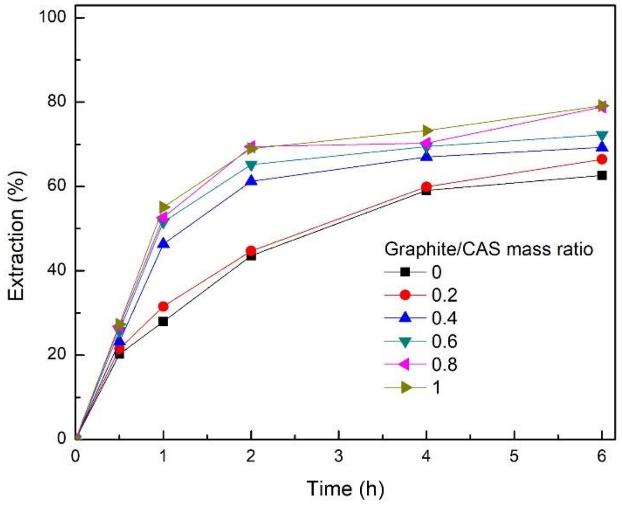
Effect of graphite dosage



(a)



(b)



(c)

Leaching behavior of (a) Se, (b) Te, (c) Ag in H_2SO_4 solution as a function of time (Variation of graphite/CAS mass ratio, 0–1; H_2SO_4 conc. 2.0 M; MnO_2/CAS mass ratio 0.8/1; temperature 70 °C; stirring speed 500 rpm; time 6 h)

- High dosage of graphite hindered the contact between CAS and lixiviant

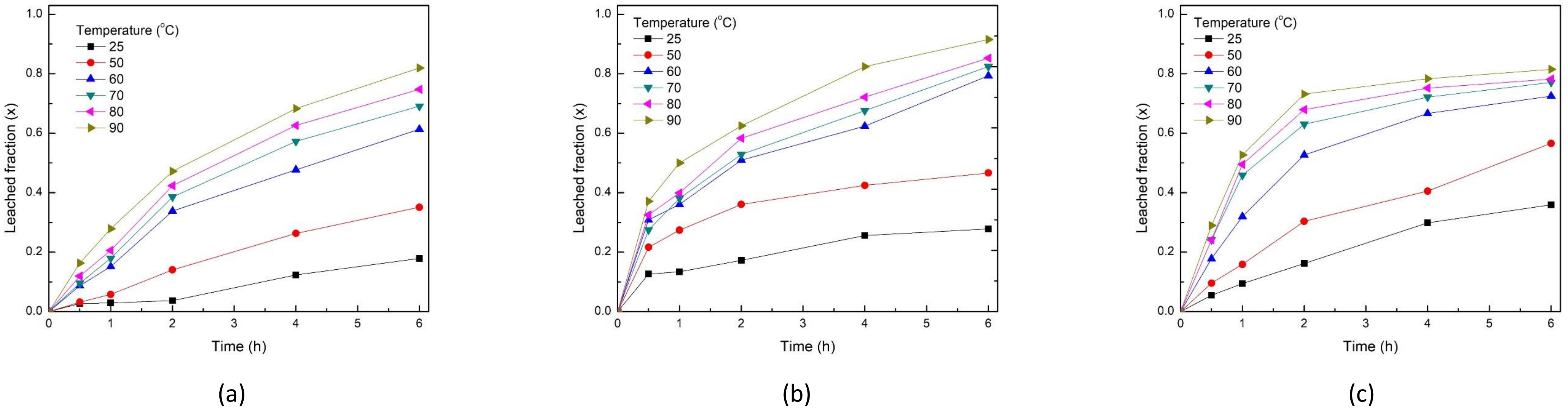
Results and discussion

Kinetics study

Shrinking core models are used:

- Diffusion through a product layer: $1 - \frac{2}{3}(1-x) + (1-x)^{\frac{2}{3}} = k_d t$
- Surface chemical reaction: $1 - (1-x)^{\frac{1}{3}} = k_r t$
- Empirical mixed kinetic model: $[1 - (1-x)^{\frac{1}{3}}]^2 = k_m t$

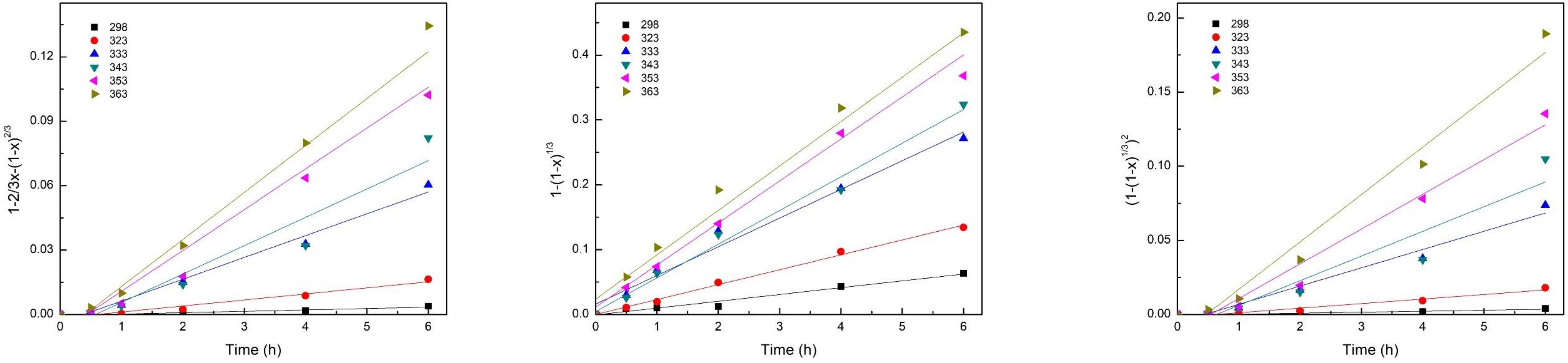
Leached fractions of Se, Te and Ag at different temperatures



Leached fraction of (a) Se, (b) Te, (c) Ag in H_2SO_4 solution as a function of time (Variation of temperature, 25–90 °C; H_2SO_4 conc. 2.0 M; MnO_2/graphite/CAS mass ratio 0.8/0.8/1; stirring speed 500 rpm; time 6 h)

Results and discussion

Kinetic study: Se



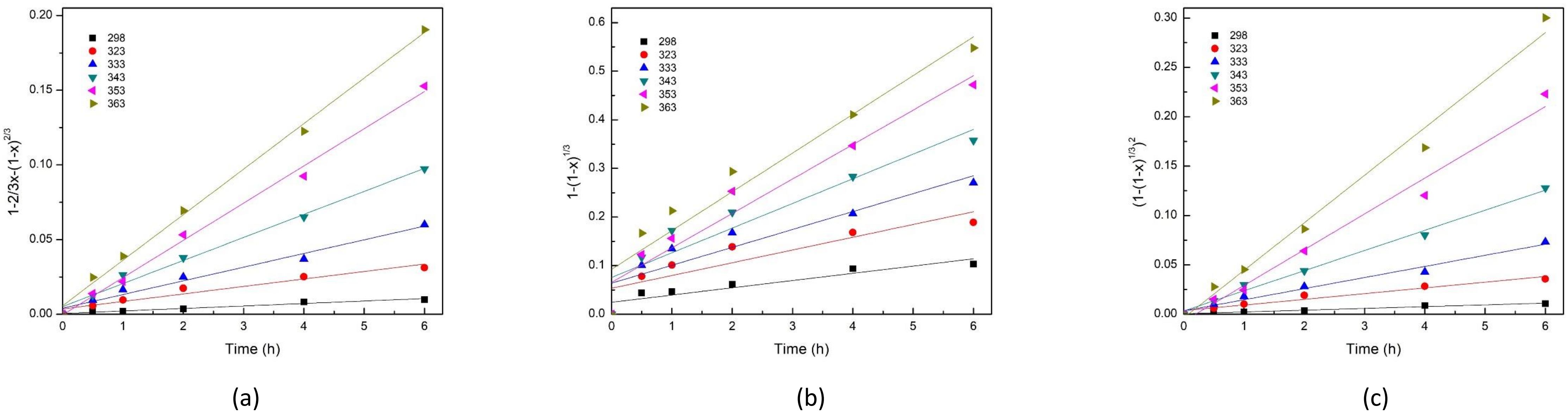
(a) (b) (c)

Plot of Se leaching using the kinetic models of (a) diffusion control, (b) surface chemical reaction, and (c) mixed control as a function of time at different temperatures

Se leaching rate at all investigated temperatures followed the surface chemical reaction with $R^2 > 0.97$

Results and discussion

Kinetic study: Te

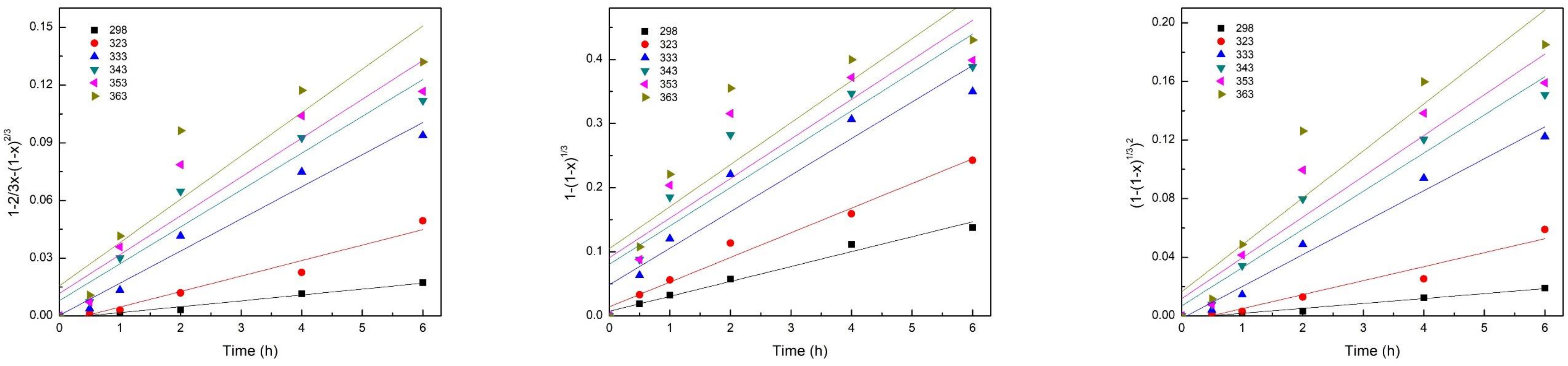


Plot of Te leaching using the kinetic models of (a) diffusion control, (b) surface chemical reaction, and (c) mixed control as a function of time at different temperatures

Change of rate-controlling step from mixed model (25–50 °C) to diffusion control model (60–90 °C)

Results and discussion

Kinetic study: Ag



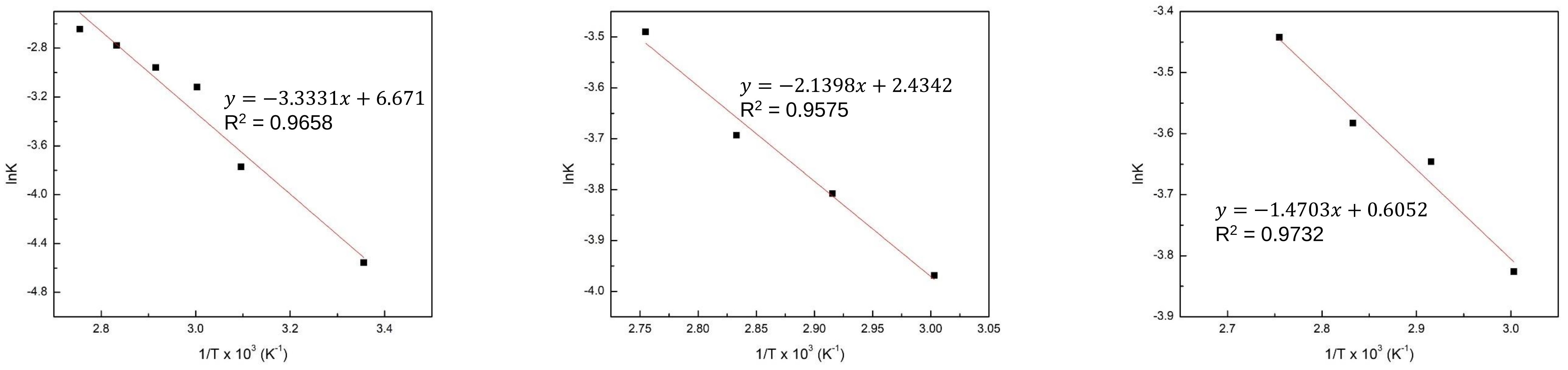
(a) (b) (c)

Plot of Ag leaching using the kinetic models of (a) diffusion control, (b) surface chemical reaction, and (c) mixed control as a function of time at different temperatures

Change of rate-controlling step from surface chemical reaction (25–50 °C) to mixed control (60–90 °C)

Results and discussion

Kinetic study: Arrhenius plot



(a) (b) (c)

Arrhenius plot of (a) Se, (b) Te, and (c) Ag

- Activation energies of Se = **27.7** kJ/mol (25–90 °C); Te = **17.8** kJ/mol (60–90 °C); and Ag = **12.2** kJ/mol (60–90 °C)
- Graphite lowered the activation energies

Conclusions

- An efficient process of sulfuric acid leaching of CAS with MnO_2 and graphite
- Graphite acted as the catalyst
- Increasing H_2SO_4 conc., MnO_2 and graphite dosage, and temperatura increased the leaching yields
- Kinetic data for Se, Te and Ag fitted well to shrinking core models