Slag-metal interfacial reactions in pyrometallurgical processing of industrial wastes for recovery of valuable metals

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ABSTRACT

This study focuses on the recovery of valuable metals, specifically silver (Ag) and palladium (Pd), from copper-containing sludge (with copper content less than 20%) generated during PCB processing and from spent petrochemical catalysts used in vapor decomposition during oil refining processes. The present results indicate that an increase in the mixing ratio of alumina-based spent catalyst leads to a decrease in the recovery rate of Ag and Pd. The recovery rates for Ag and Pd range from 84% to 96% and 80% to 98%, respectively. This trend is attributed to the increased emulsification of copper droplets containing Ag and Pd in the slag. The emulsification is caused by the decrease in the settling velocity of the copper droplets due to the increased viscosity of the slag as well as by the decrease in the slag-metal interfacial tension due to an increase in sulfur content at higher mixing ratio of spent catalyst.

INTRODUCTION

Wasted printed circuit boards (WPCBs) are components of electronic waste that contain high concentrations of precious metals, such as gold (Au) and silver (Ag), exceeding average ore concentrations by 20 to 30 times (Ebin et al., 2016). Similarly, in the petrochemical industry, catalysts rich in precious metals like platinum group metals (PGMs) such as Pt, Pd, and Rh exhibit concentrations approximately five times higher than those found in natural resources (Ghalehkhondabi et al., 2021). The rise in industrial waste has a negative impact on the environment, but it also presents opportunities for extracting valuable metals and raw materials.

Several studies have been conducted on the recovery of metals from industrial wastes. Kim et al. (2004) developed smelting processes that extract precious metals, such as Au, Pd, and Pt, through mixing PCBs and auto catalysts. Up to 90% of Au, Pd and Pt in the raw materials were concentrated in a Cu-Sn alloy phase. Kwon et al. (2005) and Shin et al. (2008) conducted similar experiments and reported that for the efficient recovery of valuable metals, it is advantageous to use fluxes that can lower the melting point and viscosity of the slag.

Therefore, in the present study, we aim to determine the optimal slag conditions for the recovery of valuable metals through the $CaO-Al_2O_3$ based slag system, which is generated when the spent petrochemical catalyst and copper sludge were employed as raw materials. Several factors (e.g. basicity, viscosity, and interfacial tension) influencing the recovery efficiency of valuable metals were discussed.

EXPERIMENTAL PROCEDURE

The compositions of the raw materials for valuable metal extraction, i.e., copper sludge and spent petrochemical catalysts, were analyzed using an XRD, ICP-AES (ACROS, Spectro) and combustion analyser (CS800, ELTRA). The results are presented in TABLE 1.

TABLE 1 – Composition of copper sludge and spent petrochemical catalysts (wt %).

	Al_2O_3	$CaCO_3$	Cu_2O	Fe_2O_3	SnO_2	P_2O_5	SiO_2	MgO	C	S	Ag	Pd
Copper sludge	0.7	29.9	24.7	22.3	6.7	3.5	2.6	1.7	5.6	2.4	0.01	-
Spent catalyst	99.7	-	-	-	-	-	-	-	-	-	-	0.3

When blending the Al_2O_3-based spent catalyst and copper sludge, the mixing ratio of the spent catalyst was varied from 10% to 30%. Here, the mixing condition aims to limit the Al_2O_3 content not more than 30 wt% to prevent an abrupt increase in melting point of the slag. Three experiments were carried out using a high frequency induction furnace (FIG 1). A mixture of 100g raw materials (copper sludge and spent petrochemical catalyst) and 60g copper powder (to form collecting melt pool) were loaded in a fused magnesia crucible with a graphite heater for efficient heating. The furnace was filled with purified Ar gas controlled by a mass flow controller at a flow rate 500 ml/min. After the equilibration for 60 min at 1773 K, the samples were cooled under an Ar gas atmosphere.

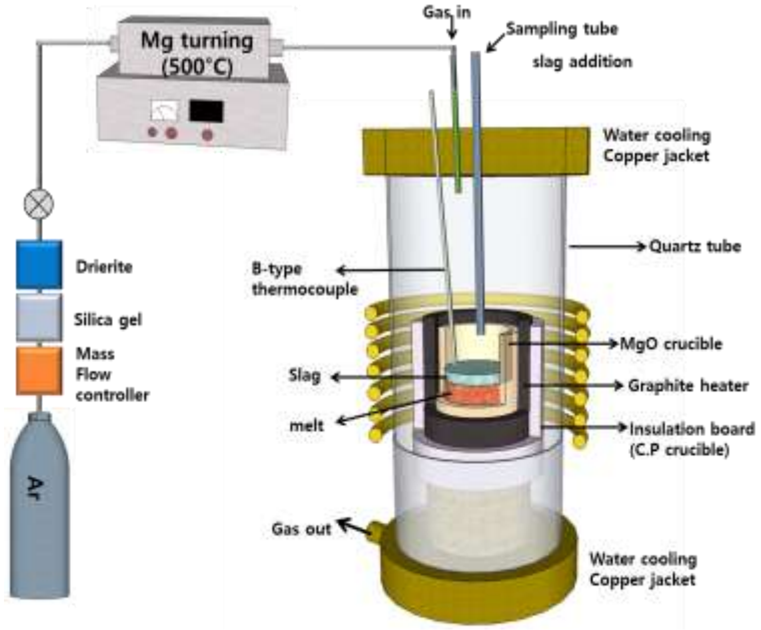


FIG 1 – Schematic diagram of the experimental apparatus.

RESULTS AND DISCUSSION

After experiments, the slag and metal were carefully separated from the crucible. the interface between the metal and slag was clearly defined and allowed a complete separation.

The slag was ground to a fine powder for chemical analysis. The equilibrium composition of the slag was analysed by ICP-OES (OPTIMA 8300; PerkinElmer, Waltham, MA) and combustion analyzer (TC-300, LECO). The results of all experiments are represented in FIG 2. Metal droplets and oxides in the slag were observed by using FE-SEM and EDS (Nova Nano SEM 450, FEI).

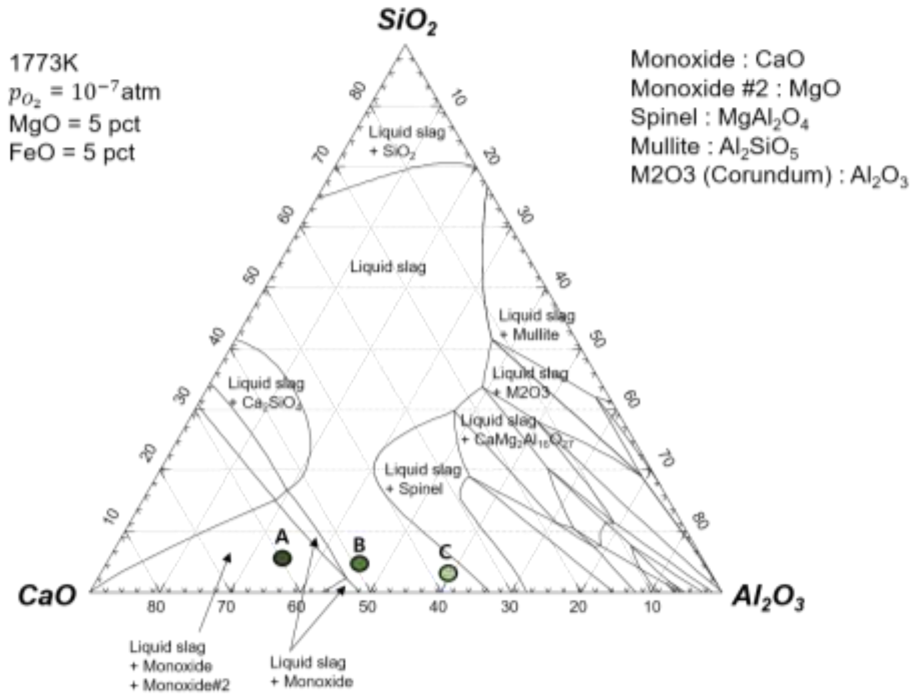


FIG 2 – The 1773K isotherm in the CaO-SiO_2-Al_2O_3 slag system (wt%). (A, B and C represent the final slag compositions with spent catalyst ratios of 10%, 20% and 30%)

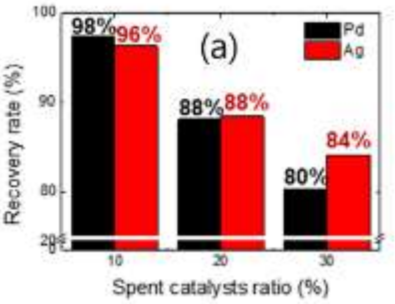
As shown in TABLE 2, the vertical section of metal ingots obtained from the experiments with 20% and 30% spent catalyst, both Cu-rich (yellow) and Fe-rich (grey) phases are present, while the only Cu-rich ingot is produced from the 10% catalyst experiment. However, Ag and Pd have a high solubility in copper phase, representing that they exist in the Cu-rich phase. The recovery rate was calculated using the following formula (Lee et al., 2010).

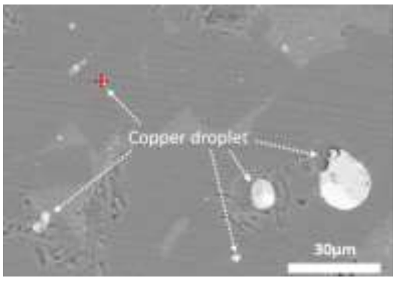
$$\text{Recovery rate of M}(=\text{Ag, Pd})\ (\%) = \frac{Recovered\ amount\ of\ M\ in\ metal\ ingot\ (g)}{Total\ content\ of\ M\ in\ raw\ materials\ (g)} \times 100 \qquad [1]$$

TABLE 2 – Morphology of metal and slag separated after smelting experiments.

	10% spent catalyst	20% spent catalyst	30% spent catalyst
Metal ingot			
Cross section of ingot			
Slag			

As the alumina content increases, which indicates an increase in the spent catalyst mixing ratio, the rate of recovery of Ag and Pd significantly decreases, as shown in FIG 3(a). FIG 3(b) and 3(c) illustrate the presence of copper droplets confined to the slag formed during 30% spent catalyst experiment, indicating the incomplete metal separation. Therefore, physical entrainment of copper droplets is the primary cause of copper loss as well as lower recovery rate of Ag and Pd.





(b)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]
Al	13	2.35	2.75	6.94
Ca	20	0.91	1.06	1.80
Fe	26	0.71	0.83	1.01
Pd	46	4.90	5.74	3.67
Sn	50	15.75	18.46	10.57
Cu	29	60.46	70.88	75.84
Ag	47	0.23	0.27	0.17
		85.31	100.00	100.00

(c)

FIG 3 – (a) Recovery rate of valuable metals as a function of spent catalysts ratio, (b) SEM image and (c) EDS result of copper droplets confined to the slag (30% catalyst experiment).

In the present study, the terminal velocity of copper droplets in the slag was calculated. It was assumed that copper droplets in the slag were spherical in shape. The force balance among gravity, buoyancy, and frictional forces on particles was taken into account. Assuming a Stokes regime due to no intentional stirring in the slag, the terminal velocity of metal droplet can be described by Eq. [2] (Poirier, 1994).

$$v_t = \frac{2}{9}\frac{r^2(\rho_m - \rho_s)g}{\eta}\ \text{(m/s)} \qquad [2]$$

From FIG 4, a decrease in the C/A ratio of the slag increases the viscosity, which reduces the settling velocity of copper droplets in the slag. As a result, the recovery rate of Ag and Pd decreases. Therefore, it is crucial to precisely control the settling velocity of copper droplets to maximize the recovery of valuable metals.

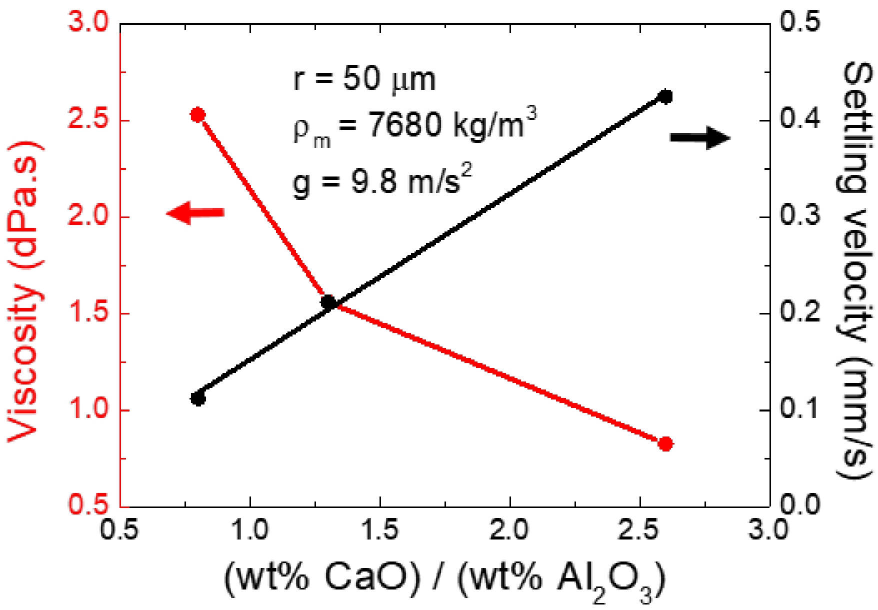


FIG 4 – Relationship between viscosity and settling velocity as a function of the CaO/Al_2O_3 ratio.

CONCLUSIONS

Loss of valuable metals due to physical entrainment means that copper droplets were not settled down completely but rather dispersed in the slag layer during smelting process. To quantitatively evaluate the physicochemical behavior of slag-metal interfacial phenomena, the interfacial tension of the slag-metal system and settling velocity of copper droplets was estimated. As the interfacial tension and settling velocity decrease with higher mixing ratio of spent catalyst, the higher the probability of copper droplets in the slag, resulting in a decrease of the recovery rate of valuable metals.

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