

LEACHING KINETICS OF CU, CO, ZN, PB AND FE FROM COPPER SMELTING SLAGS COOLED IN DIFFERENT WAYS AFTER TAPPING

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Abstract

Slag samples from a copper smelting operation in a water jacket furnace from a DRC plant was used in the study. The study intends to determine the effect of cooling on the extraction of base metals. The cooling methods investigated were water quenching, air cooling and furnace cooling. The latter was compared to the original 'as received' slag. It was observed that the cooling rate of the slag affected the leaching of base metals as it changed the phase distribution in the slag and the base metals' distribution within the phases. It was also found that fast cooling of slag prevented crystallization and produced an amorphous phase that encloses the base metals. The amorphous slags from the slag dumps were more leachable in acidic medium (HNO₃), which leached 46% Cu, 95% Co, 85% Zn, 92% Pb and 79% Fe with no selectivity at pH 0, than in basic medium (NH₄OH). The modified slags by quenching in water had leached 89% Cu with a high selectivity as base metal extractions are less than 1% for Co, Zn, Pb and Fe at ambient temperature and pH 12. The total amount of base metals that were leached in slow cooled slags was very low compared to the quenched slag samples. For the furnace cooled slag, the leached base metals were 0.6% Cu and less than 0.03% for the other metals. The kinetic studies were done by using the leaching data to plot curves that yielded the rate constants. From the rate constants and the assumption of first order reactions, the activation energies for Cu, Co, Zn, Pb and Fe were determined for all cooling rates.

1. Introduction

Smelting is a very important stage in metal recovery, where the molten metal and slag are separated during tapping. Although most of the base metals are transferred to the molten metal during smelting of Cu, there are other quantities of base metals that are taken up in the slag. This will result in more toxic slag that causes danger to the environment where the slags are dumped. When there are acid rains, the rain water leaches out the base metals from the dumped slags to the ground, therefore; contaminating the surrounding environment and the underground water systems. (Piatak and Seal Ii 2010).

Slags are mostly formed from the elements that were not reduced during the reduction process or that were not oxidized during the oxidation process (Yen et al. 2006). Saffarzadeh et al (2009) studied the characterization of base metals containing phases and their localization in the glassy matrix. Gboh et al (2000) discussed how a thorough understanding of how these metals behave during leaching would make a huge impact and contribution in the design of a valuable metal

recovery process from the slag. Converter slags produced in copper productions contains high amounts of valuable metals like Cu, Co, Ni and Zn (Altundogan et al. 2004), however, the composition of the slag will depend on the origin of the raw material/ore being processed and the employed processing techniques.

Numerous publications have studied the leaching of base metals from different slag samples, these include leaching of slags (Altundogan et al. 2004) (Herreros et al. 1998) and cleaning slags by direct reduction (Maweja et al. 2009). Other research focused on investigating the factors affecting leachability of base metals from slag (Baghalha et al. 2007). It was found that the rate of which the slag was cooled from the liquid molten state to the cool solidus state has an effect on the slag sample's ability to be leached.

Slow cooling of the slag may result in significant contribution to crystallization of the slag components forming large number of mineral phases, whereas rapid cooling by quenching with water would enhance the formation of the glassy amorphous structure (Kuo et al. 2008a). The formation of the glassy amorphous phase will also depend on the chemical composition and the quenching type, e.g. high flow rate water jets that are presently used in slag cooling (Tossavainen et al. 2007). The amorphous phases are more resistant to chemical decompositions of slag by acid during the leaching process than the crystalline structures formed by slow cooling (Loncar et al. 2009). Li et al. (2009) found that a slag that was slowly cooled with a crystalline structure could be leached more easily than the quenched slag with an amorphous structure (Kuo et al. 2008b).

The previous work done in this research by Tshiongo et al. (2010) investigated the effect of cooling rate on the base metals recovery from copper matte smelting slags, and it was found that annealing of slag changes the phase arrangement in the slag, where the amorphous phase decreased with increase in the cooling rate and the crystallized phases increase with the increasing cooling rate. It was also shown that the extraction of base metals was higher in the slag containing larger amounts of amorphous phases and lower in crystallized phases (Tshiongo et al. 2010). The focus of the current work is on investigating the leaching kinetics of Cu, Co, Zn, Pb and Fe from the copper smelting slags cooled in different ways after tapping. The main objective of this research is to establish the effect of copper matter slag cooling rate on the recovery of base metals.

2. Materials and Procedures

2.1 Preparation

A copper smelting slag produced in a water jacket furnace was obtained from a mine in the Democratic Republic of Congo called GCM and it was used for this investigation. Bench top leaching experiments were conducted at atmospheric conditions using 500ml and 250ml beakers for leaching, volumetric flasks for solution preparation, magnetic stirrers for agitation, poly tops for sample collections and a hot plate for heating the solutions to the required temperature.

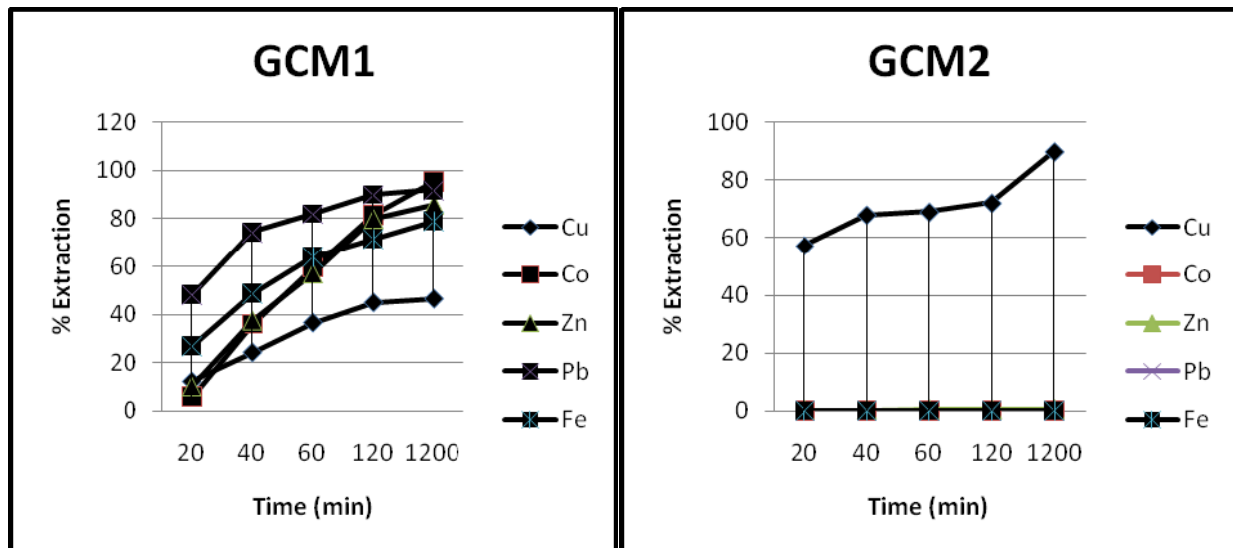
The sample were divided into four sub-samples of which one was left as received (GCM1), the remaining three samples were heated in crucibles in a furnace to the melting point of this slag between 1200°C to 1300°C, after which they were cooled from a liquidus temperature to solidus temperature by: water quenching (GCM2), air cooling (GCM3) and furnace cooling (GCM4). The samples were then leached to identify the leaching kinetics of base metals from each slag.

2.2 Leaching

All four samples were leached at four different temperatures in a 500ml beaker for 1200 minutes, taking samples at specific time intervals. The samples taken during leaching were diluted accordingly and were analyzed using Atomic Absorption Spectrometry for Cu, Co, Zn, Pb and Fe. Extraction percentages of all the metals were plotted against the 1200 minutes taken to complete the experiment.

3. Results

The results shown in Figure 1 were obtained from the leaching experimental data of Cu, Co, Zn, Pb and Fe. Using the extraction plots for all metals, a trend line was plotted and the slope was obtained. The slope indicates the rate constant at which the leaching took place at each temperature. The rate constants are plotted against all temperatures in one plot (k versus T). The activation energy is calculated from the slope obtained in a $\ln(k)$ versus $1/T$ plot assuming that the reactions are of first order reaction.



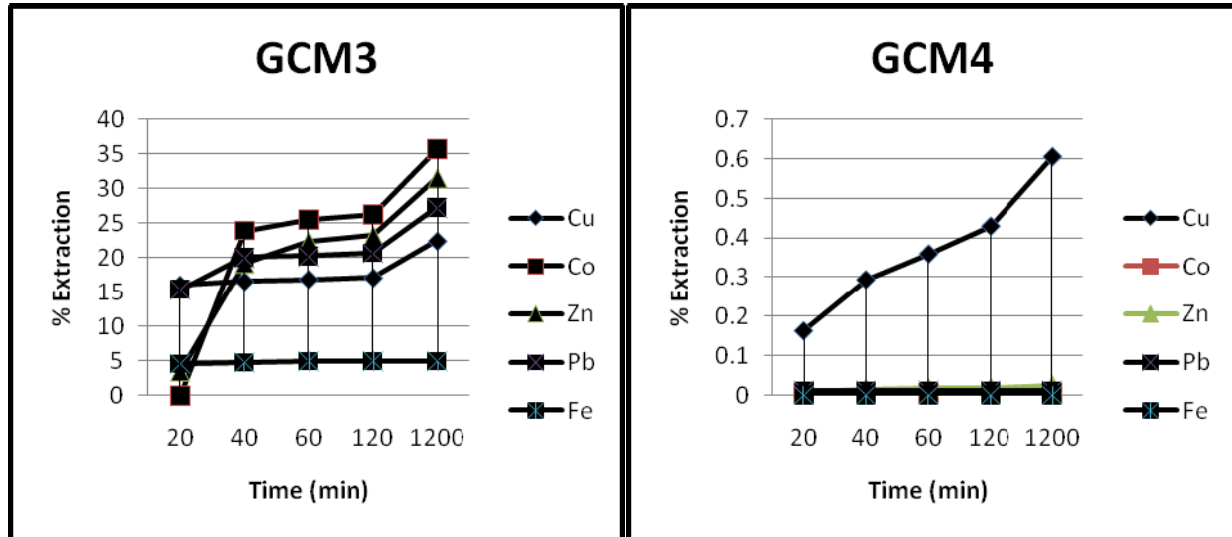


Figure 1: Leaching percentages of base metals at 25degC for slag sample GCM1 (as received) at pH 0 and GCM2 (water Quenched), GCM3(air cooled) and GCM4 (furnace cooled) at pH 12 for 1200 minutes of leaching.

The figure above shows the different recoveries of base metals that were achieved and how they are affected by the different cooling methods employed. Slag GCM1 contained a higher content of amorphous phase (96%) than any other slag sample. The overall extraction was 46.4% Cu, 78.96% Fe, 85.66% Zn, 91.94%Pb and 95.29% Co, but there was no selectivity in the leaching process of this slag. Slag sample GCM2 had an amorphous phase content of 22%. Leaching of this type of slag produced results with a higher selectivity of Cu in comparison to all the other base metals. The percentage leached was 89.88% Cu and <0.2% for all the other base metals.

The sample GCM3 had an amorphous phase content of 21%. Iron is present in the slag as an impurity, and can create difficulties in the next purification process like solvent extraction and electrowinning after leaching. Therefore: the lesser Fe extraction, the better. Leaching of slag GCM3 results in more extraction of the other elements at higher than 20% extraction, but Fe extraction is low at less than 5%. GCM4 slag had an amorphous phase content of 20% and the highest fayalite phase content of 21%. The extraction was selective for Cu in comparison to all other base metals present in the slag, and the recovery was 0.6% Cu and <0.03% for the other base metals. The overall amount of base metals was very low (less than 1%), meaning that this kind of cooling is safe to use with regards to slag disposal.

3.1 Leaching kinetics of Cu

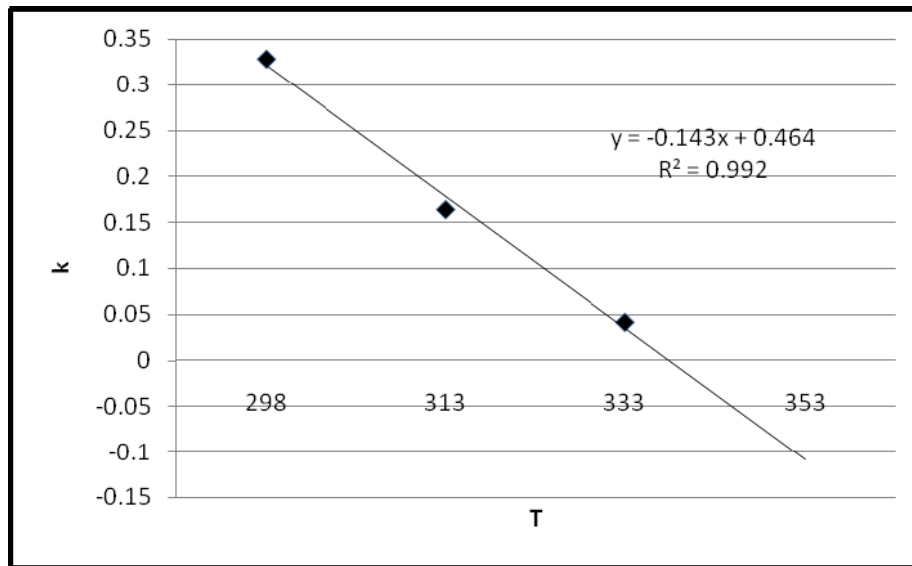


Figure 2: Plots of 1st order reaction rate constants of Cu versus temperature.

Figure 2 is an example of Cu kinetics which was achieved by leaching the ‘as received’ slag. The plot of k versus temperature in Figure 2 shows that there is a decrease in reaction rate with an increase in temperature. The correlation coefficient (R^2) for this plot is 0.992 and it shows that the points fit well in the 1st order plot. By considering that the reaction is a 1st order reaction, the plot of $\ln(k)$ versus $1/T$ will yield the activation energy that can be calculated from the slope of that plot.

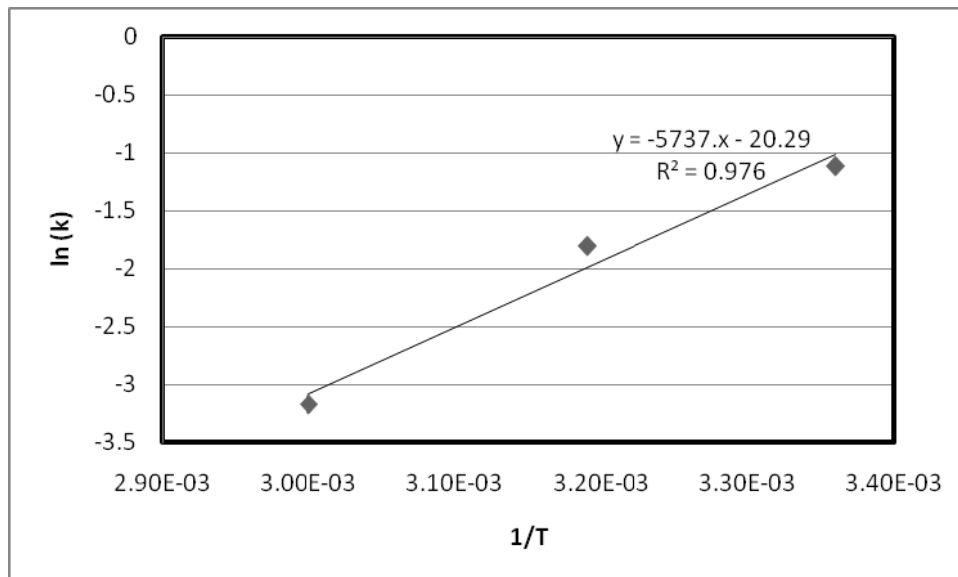


Figure 3: Plots of $\ln(k)$ vs $1/T$ for Cu recovery

Figure 3 shows the plot of $-E_a/R$ and this can be used to calculate the activation energy. The plot has an acceptable correlation coefficient (R^2) of 0.976 for this first order reaction and the calculated activation energy is 47.7 kJ/mol. The value of the activation energy shows that the leaching of Cu from GCM1 slag is chemically controlled, i.e. increasing the acid concentration will increase the reaction rate for Cu leaching. Activation energy for the other slag samples was 18.89kJ/mol, 10.72kJ/mol and 13.24kJ/mol for GCM2, GCM3 and GCM4 respectively.

3.2 Leaching kinetics of Co

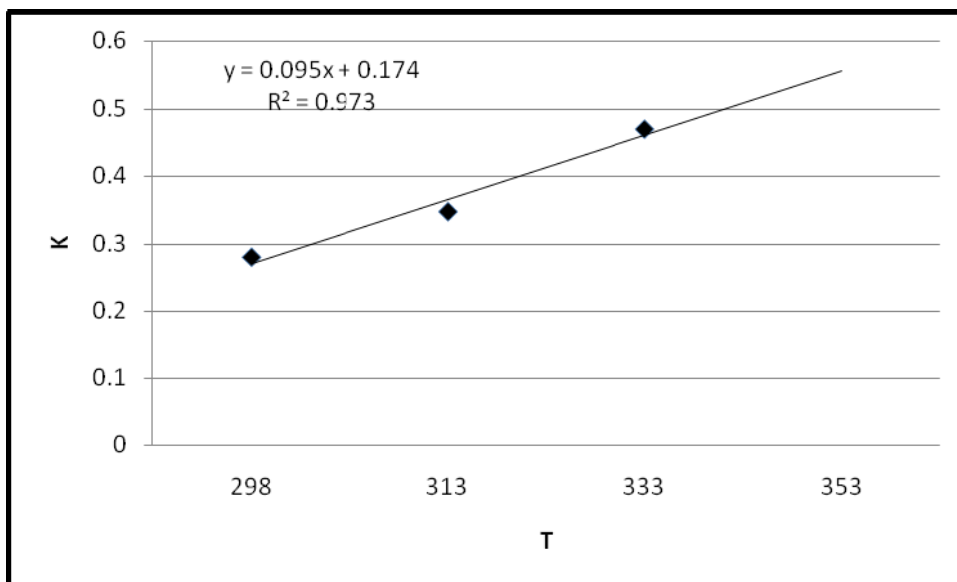


Figure 4: Plots of 1st order reaction rate constants of Co versus temperature.

Figure 4 above shows the 1st order plot of leaching Co from GCM2 slag. This plot shows that there is an increase in the reaction rate constant with the increase in temperature; the minimum operating temperature is 295K. The correlation coefficient (R^2) is found to be 0.973 which is a very good agreement with the Arrhenius plot.

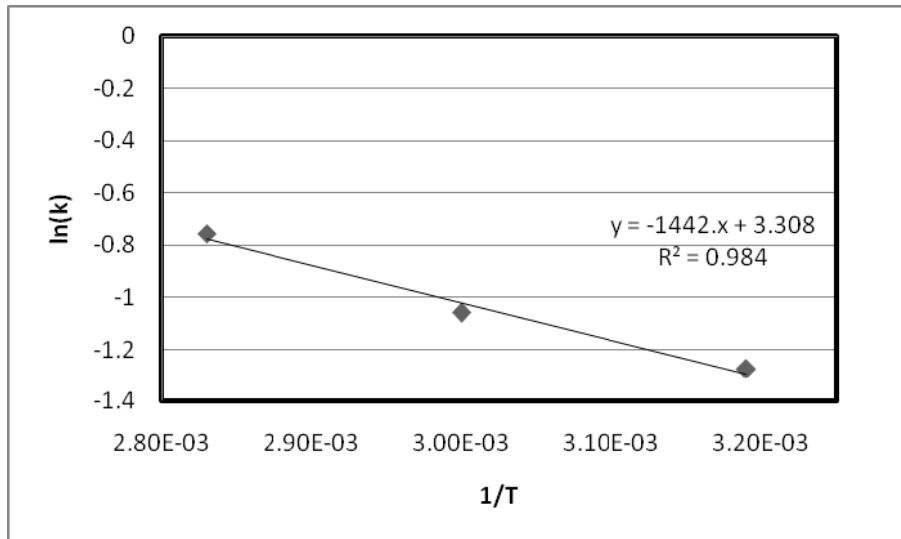


Figure 5: Plots of ln(k) vs 1/T for Co recovery

Figure 5 above shows the 1st order plot with a slope that can be used to calculate activation energy. The activation energy was calculated to be 11.99 kJ/mol, indicating this to be a reaction controlled by diffusion; meaning that if the agitation of the leaching process increases, the leaching of Co will also be increased. The correlation coefficient (R^2) for this plot is 0.984, which indicates the correctness of the experimental results achieved. For slag samples GCM1, GCM3 and GCM4, the activation energy was respectively calculated to be 30.72kJ/mol, 7.25kJ/mol and 13.56kJ/mol.

3.3 Leaching kinetics of Zn

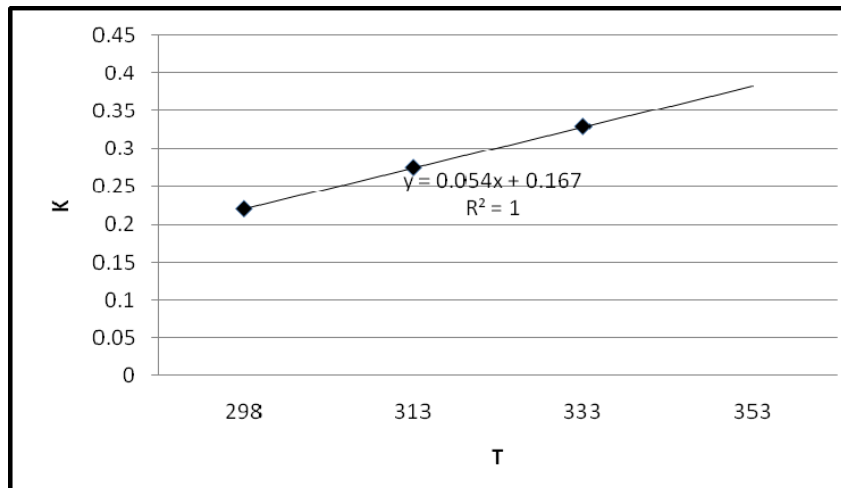


Figure 6: Plots of 1st order reaction rate constants of Zn versus temperature.

Figure 6 shows the 1st order plot of leaching Zn from slag sample GCM2, where the reaction rate constant is shown to be directly proportional to the temperature. This plot has a correlation coefficient (R^2) of 1 which means that this is a perfect Arrhenius behavior, with all the points lying on the linear plot.

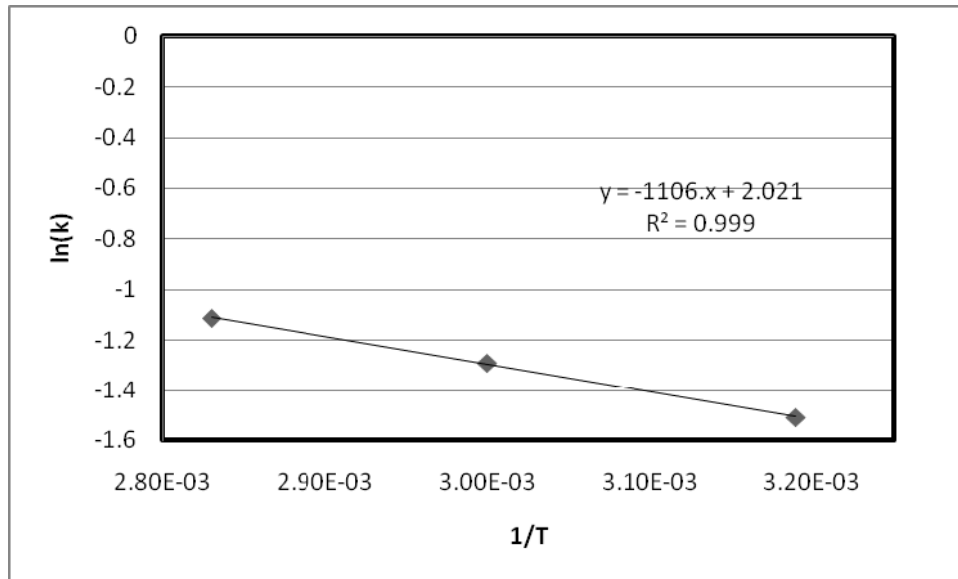


Figure 7: Plots of $\ln(k)$ vs $1/T$ for Zn recovery

Figure 7 above shows a 1st order plot for Zn recovery, the slope of the plot is used to calculate the activation energy which was found to be 9.2kJ/mol. The value of the activation energy being less than 21kJ/mol indicates that the reaction is controlled by diffusion through the interface into the bulk of solution. Therefore; the Zn recovery can be increased by increasing the agitation speed and reducing the particle size of the slag. The correlation coefficient for the plot is 0.999 for the first order reaction. Activation energy calculated for GCM1, GCM3 and GCM4 was 56.75kJ/mol, 17.69kJ/mol and 20.56kJ/mol respectively.

3.4 Leaching kinetics of Pb

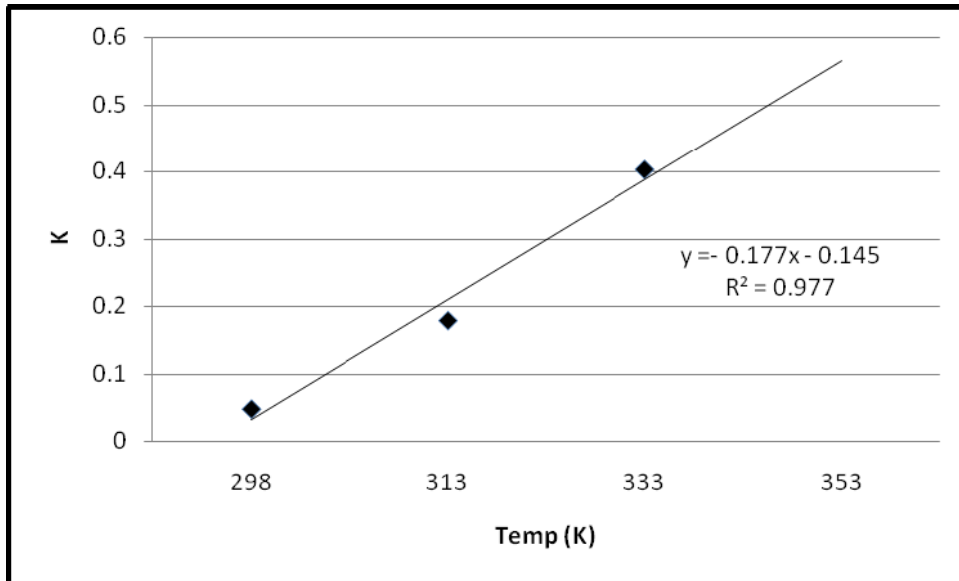


Figure 8: Plots of 1st order reaction rate constants of Pb versus temperature.

The above figure shows the first order reaction rate constants for Pb leaching versus the temperature for the slag sample GCM2. The figure shows that there is an increase in reaction rate constant with an increase in temperature. The correlation coefficient is 0.977 for the first order reaction, indicating a good fit to the Arrhenius plot. And the values from this figure are used to calculate the activation energy.

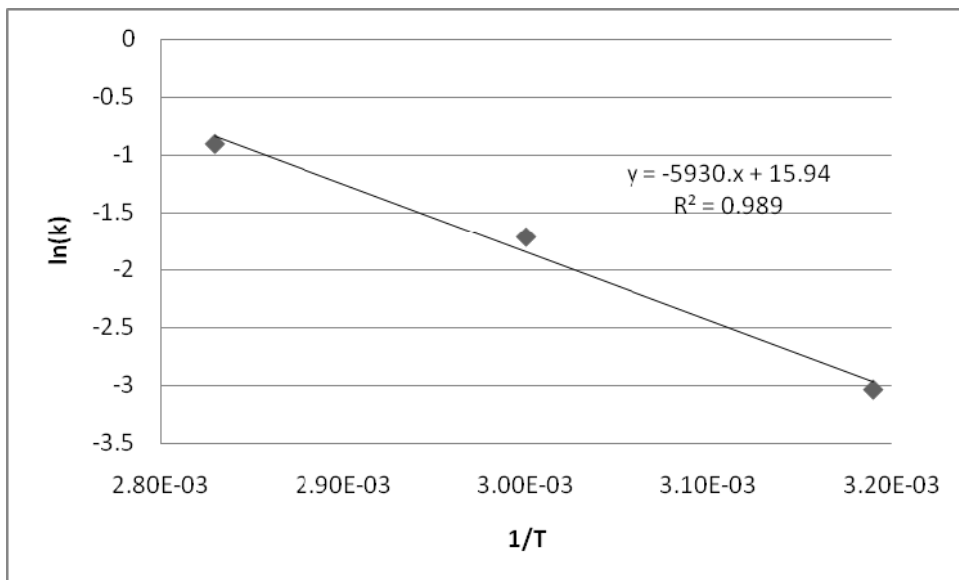


Figure 9: Plots of ln(k) vs 1/T for Pb recovery

The results from leaching Pb from copper smelting slag yielded a correlation coefficient of 0.989 and this shows that the data fits well on the Arrhenius plot for a first order reaction. The activation energy was calculated to be 49.30kJ/mol, and this value proves the reaction to be controlled by chemical reaction of the slag. Activation energy was 8.86kJ/mol, 12.79kJ/mol and 4.76kJ/mol for GCM1, GCM3 and GCM4 respectively.

3.5 Leaching kinetics of Fe

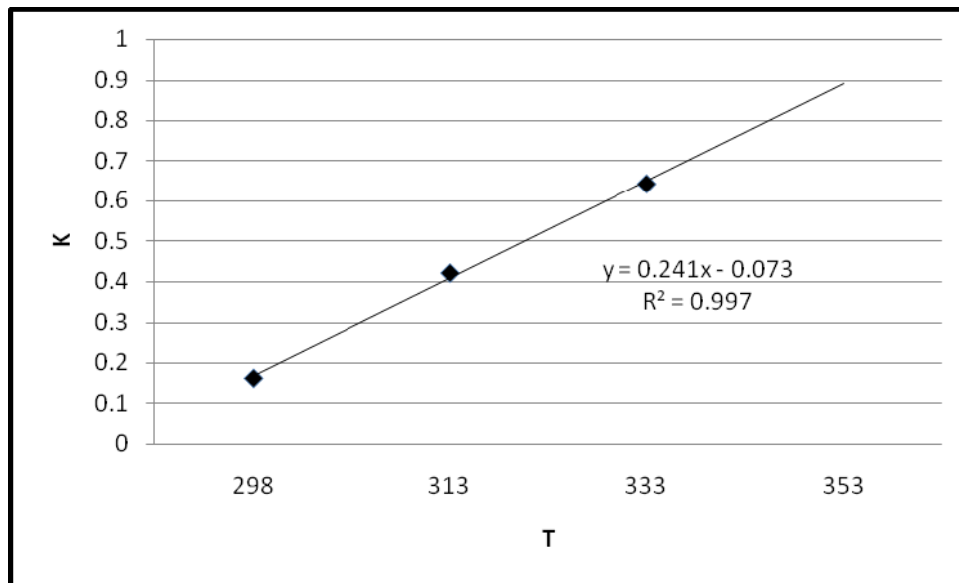


Figure 10: Plots of 1st order reaction rate constants of Fe versus temperature.

Figure 10 shows the first order reaction plot for Fe leaching from the slag sample GCM4. The first order reaction rate increases with an increase in temperature. The correlation coefficient for this slope is 0.997 which indicates a good fit to the Arrhenius plot.

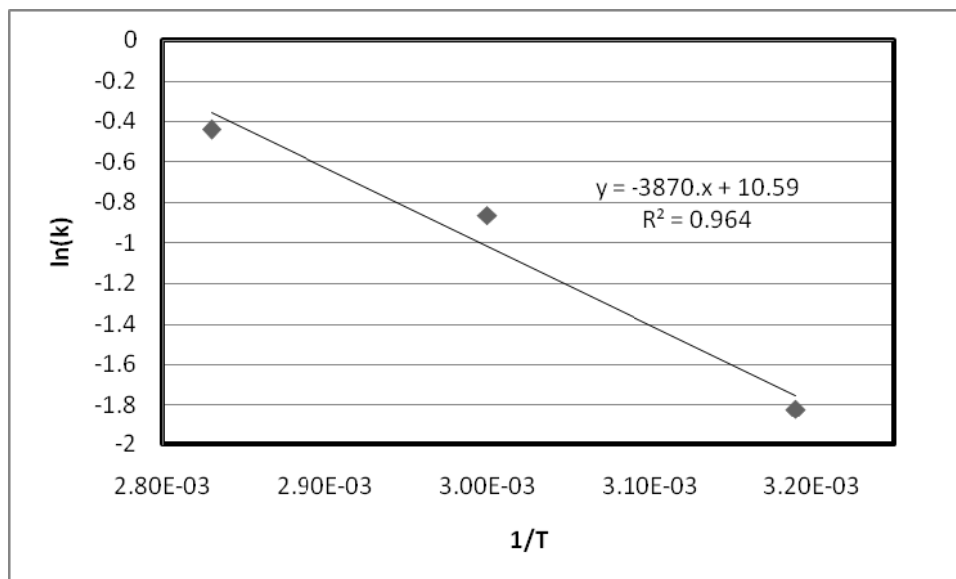


Figure 11: Plots of ln(k) vs 1/T for Fe recovery

Figure 11 above shows the 1st order plot of Fe with a slope equal to $-E_a/R$. The activation energy was calculated to be 32.18kJ/mol. The value of activation energy symbolizes that the reaction has a mixed control mechanism, i.e. there may be a change in mechanism from surface reaction to the diffusion controlling mechanism. The activation energies for the slag sample GCM1, GCM2 and GCM3 were calculated to be 19.5kJ/mol, 1.75kJ/mol and 21.34kJ/mol respectively.

3.6 Comparison of results

Table 1: Comparison of base metals kinetics and conditions for the leaching process.

ELEMENTS	TEMP (°C)	PH	MAX RECOVERY (%)	SLAG	Ea	TYPE REACTION CONTROL	OF
Cu	80	12	99.66	GCM2	18.89	Diffusion reaction mechanism.	
Co	25	0	95.29	GCM1	30.72	Surface intermediate mechanism.	
Zn	25	0	85.66	GCM1	56.75	Chemical reaction mechanism	
Pb	25	0	91.94	GCM1	8.86	Diffusion reaction mechanism	
Fe	25	0	78.96	GCM1	19.50	Diffusion reaction mechanism	

Table 1 shows the leaching conditions that resulted in the high recovery rate for base metals. From the table it can be seen that all base metals are leached effectively using the same

conditions (temperature=25°C, pH=0,slag sample GCM1) except for Cu (temperature of 80°C, pH =12, slag sample GCM2). But the slag samples that were showing high base metal extractions were all cooled by water quenching - one during tapping and the other after melting in the lab. But activation energies from all base metals were different and therefore contributed to the different kinds of reaction controlling mechanisms as listed in the table.

4. Conclusions

The cooling rate for the copper smelting slags affects its behavior when it comes into contact with leaching acids. When the slag is quenched by water after tapping, the amorphous phase forms in the slag and this slag can be easily leached to extract base metals. This causes environmental problems related to the presence of toxic metals. But as the cooling rate increases, the amorphous phases are decreased, making the slag difficult to leach. However, the selectivity of the leach process is improved. When the slag is slowly cooled in the furnace, leaching of this slag becomes very difficult and this slag is therefore suitable for dumping as simple acid rain cannot leach out the base metals in the slag. The kinetics of base metals, after the calculations of activation energy, shows that the reaction is controlled differently according to the base metal and the cooling rate of the specific slag sample involved. It is therefore recommended that the copper matte smelting slags are cooled slowly before dumping in disposal sites, and if any interest in base metals recovery arises, the slag can be re-melted and quenched in water.

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M-tech Metallurgy student in Tshwane University of Technology (TUT). I have been working at TUT, department of Chemical and Metallurgical Engineering doing various jobs including lab coordinating and lecturing as part time staff. Have been currently involved in research on base metals recovery from copper slags and the effect of slag cooling rate after tapping.