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A STUDY ON THE LEACHING KINETICS OF ISHIAGU GALENA IN H_2SO_4 SOLUTION

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ABSTRACT

An investigation of the important factors involved in the extraction of lead from galena ore has been carried out. The effective parameters studied were particle size, stirring speed, acid concentration and solid/liquid ratio. The dissolution rate increased with increase in temperature, stirring speed, acid concentration and solid/liquid ratio and with decrease in particle size. All the experimental parameters were found to have influence on the leaching rate. The results showed that the optimum leaching conditions were observed to be 400 rpm stirring speed, 2.15M H_2SO_4 acid concentration, 70°C reaction temperature, 20:100 solid/liquid ratio and 63µm particle size. The result showed that correlation coefficients (R^2) for surface chemical reaction and diffusion through product layer had large values of 0.97340 and 0.9954 respectively. This justifies the basis for combination of the two models involved in the leaching process. The mixed kinetic model also has a large value of 0.9928, and is the controlling step for the process.

Keywords: dissolution rate, controlling step, correlation coefficient, parameter and optimum

1.0 INTRODUCTION

Ishiagu is endowed with a rich reserve of galena (PbS) mineral deposit, which serves as the major source of lead and sulfides in the area. It is estimated to have proven reserves of about 711,237 tonnes (Ukpong and Olade, 1979, mineral and industry in Nigeria, 1987). Other associated minerals include Sphalerite (ZnS), Chalcopyrite ($CuFeS_2$), Siderite ($FeCO_3$), Argentite (AgS), Limestone ($CaCO_3$), and Calcium sulphide (CaS), (Ezepue, 1984, Duruibe *et al.*, 2007).

The photoelectric effect of galena is sometimes positive and sometimes negative (Mortazavi *et al*., 2007). Electrically, galena has an excellent intrinsic semi conductivity and is optimally photoconductive between 10,000A and 30,000A. Optically, it has a reflection coefficient of 32.2% of white light (Mortazavi *et al*., 2007).

The conventional route of processing complex ores is associated with the generation of solid, liquid and gaseous waste. The effect of complex and hazardous waste on the ecology and the environment is alarming to the environmentalist (Agrawal and Sohu, 2009). Over 80% of the worldwide primary lead is produced through a combined roast-leach-purification-electrowinning process. Pyrometallurgical oxidation has been practised around the world for decades and has been proven to be effective. However, these processes result in huge amounts of waste, such as the gas and solid residues which pose a serious environmental pollution problem.

As a result of the foregoing, many researchers have carried out studies on lead extraction by hydrometallurgical technique. In the past few decades, much attention has been focused on the processes of recovering lead from oxidized resources and other lead bearing renewable resources such as complex ores, lean over and solid materials from waste using the hydrometallurgical routes.

Studies on the dissolution kinetics of lead bearing minerals in acid lixiviant are few. The dissolution kinetics of Enyimgba galena ore in ferric chloride solution has been studied by Mbah, 2008. The result described the effect of ferric chloride ($FeCl_3$) solution concentration, temperature and particle size on the dissolution extent. The dissolution kinetic studies showed that when 0.05-0.1M$FeCl_3$) was added as oxidant, surface chemical reaction was the controlling

mechanism. When 0.15-0.25M $FeCl_3$ was added as oxidant, product layer diffusion became the controlling mechanism. The activation energy (E_a) obtained was 33.49kJ/mol while the reaction order was 0.73 (Mbah, 2008).

2.0 MATERIALS AND METHODS

2.1 Materials

Ishiagu galena samples obtained in lumps were crushed, ground and passed through standard test sieves to obtain the desired size fractions, using Denver Jaw crusher model BH53A, Denver cone crusher England, Deco rolling machine model B7141A, standard sieves, Jones Riffle splitter, laboratory flotation machine, weighing balance and spatula. The experimental reagents used include tetraoxosulphate (vi) acid, (H_2SO_4).

2.2 Experimental Procedure

Leaching experiment was carried out in a 250ml reactor, using a thermostat to maintain the contents at a constant temperature during the reaction. The reactor was equipped with a mechanical stirrer for stirring. In all the experiments, 50ml of the leaching solution was introduced into the reactor and heated to the desired temperature. When the desired temperature was reached, 0.5g of the groundmass of the bulk ore was added and the mixture stirred.

3.0 RESULTS AND DISCUSSION

The mineralogical analysis of Ishiagu Ore samples obtained by X-ray diffraction (XRD) is presented in Fig 1.

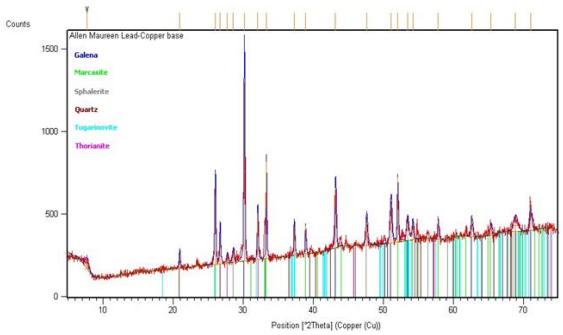

Figure 1: *XRD analysis of Ishiagu ore*

Table 1: Mineralogical analysis of Ishiagu ore

Mineral	Chemical Formula	Compound Name
Galena	PbS	Lead sulfide
Marcasite	FeS_2	Iron sulfide
Quartz	SiO_2	Silicon Oxide
Sphalerite	ZnS	Zinc sulfide
Thorianite	ThO_2	Thorium Oxide
Tugarinorite	MoO_2	Molybdenum Oxide

The results from the mineralogical sample indicate the presence of galena, quartz, marcasite, Sphalerite, Thorianite and Tugarinorite. The results of the mineralogical analysis on the galena are presented in Table 1. Based on the atomic absorption spectrometer (AAS), the sample consists of 31.75%Pb, 0.93%Zn, 0.5250%Fe, 0.0202%Ca and 0.0056%Ni.

Effect of particle size

The effect of particle size on the leaching of lead from the galena samples was studied under the following conditions; stirring speed 400 rpm, temperature $70°C$, acid concentration 2.15 M and solid liquid ratio 20:100 as shown in fig 2. It was observed that the percentage of lead leached in all the experiments increased gradually with decrease in particle size, which indicates that smaller particle sizes result in increase of the leaching rate as suggested by many authors (Ayodan *et al.*, 2005; Merwe, 2003; Habashi, 2005).

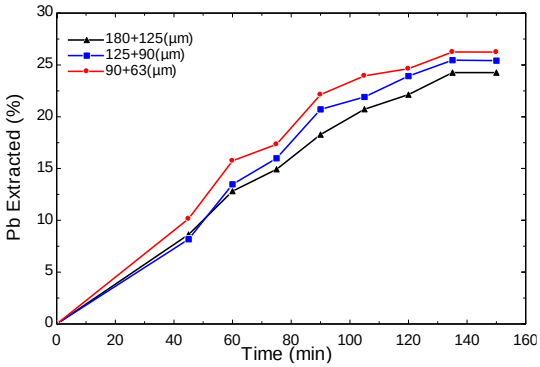

Figure 2: *Effect of particle size on % of Pb extracted with* H_2SO_4 *solution at 400rpm, 2.15 M,* 70^0C, $20:100$ *galena concentrates.*

Effect of temperature

The effect of the temperature on the leaching rate of lead from galena was investigated using a temperature range of 40 - $70°C$, under the following conditions; H_2SO_4 concentration (2.15M), particle size (63µm), stirring speed (400rpm) and solid/liquid ratio (20:100).The results presented in Fig.3 showed that temperature plays a vital role on the leaching rate. Leaching of lead increases with increasing temperature. After 150 min of leaching, the percentage of lead leached showed an increase with increase in temperature being 15.1% and 29.84%Pb, at 40 and $70°C$ respectively.

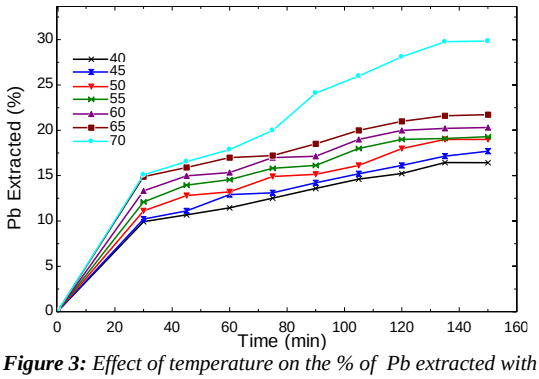

Figure 3: *Effect of temperature on the % of Pb extracted with* H_2SO_4 *at 63 µm, 400 rpm, 2.15M,* $20:100$ *galena concentrates*

Effect of Stirring Speed

The effect of stirring speed (100-500 rpm) on the rate of leaching of lead from galena was studied while other parameters were fixed and the results are shown in Fig 4. It was observed from the figure that increase in stirring speed increased dissolution of lead from galena. Within 150 min, the percentage of lead leached increased from 17.96% at 100 rpm to 23.98% at 400 rpm.

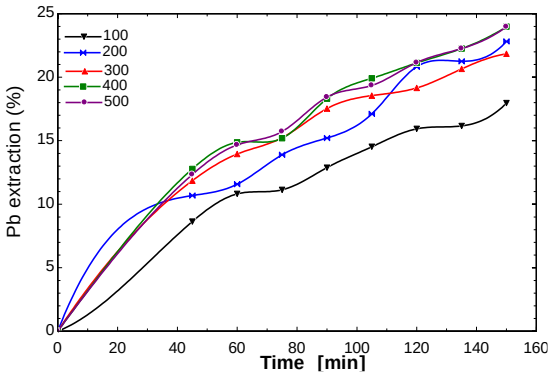

Fig 4: *Effect of stirring speed on the % of Pb extracted with* H_2SO_4 *at 63 µm, 2.15 M,* 70^0C, $20:100$ *from galena concentrates.*

Effect of Solid/Liquid Ratio

Figure 5 presents the effect of solid/liquid ratio on the leaching rate of lead from galena as a function of time under the following conditions: particle size of 63 µm, temperature of $70°C$, concentration of 2.15 M H_2SO_4 and stirring speed of 400 rpm. The result showed that the percentage of lead leached from galena increased with increase in solid/liquid ratio. Over the reaction time of 150min, about 18.25 % Pb at 5:100 and 24.98 % Pb at 20:100 respectively were leached.

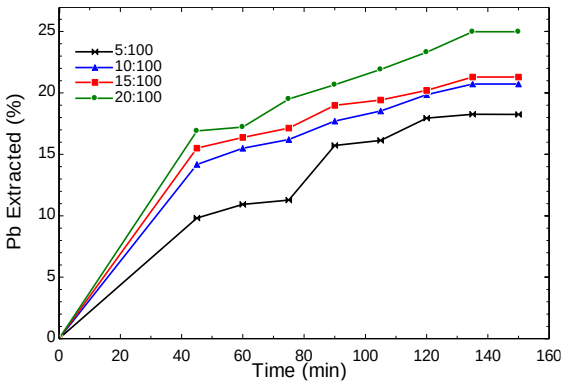

Figure 5: Effect of solid/liquid ratio on the % of Pb extracted with H_2SO_4, at 63 µm, 400 rpm, 2.15M, 70^0C, from galena concentrates

Effect of H_2SO_4 concentration

The effect of H_2SO_4 concentration on the leaching of lead from galena is shown in fig 6. The acid concentration varied from 0.05 to 2.15M while other parameters were kept constant. It was observed that the percentage of lead increased gradually with increase in acid concentration and time in all the experiments. The percentage of lead leached after 150min at $70°C$, with 0.05 and 2.15 M H_2SO_4 were 17.25 % and 26.24 % Pb respectively. This is attributed to H_2SO_4 behaving as a strong oxidizing agent.

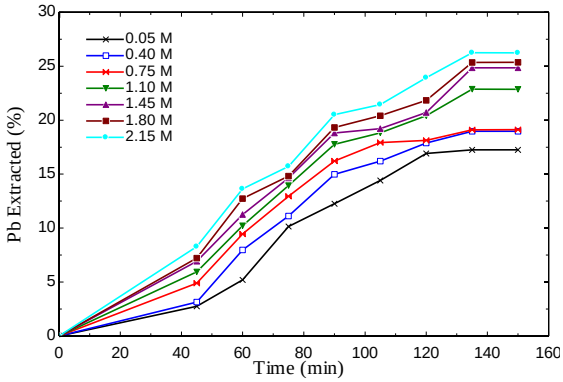

Figure 6: *Effect of* H_2SO_4 *on the % of Pb extracted at 63 µm, 400 rpm,* 70^0C, $20:100$ *from galena concentrates*

4.0 KINETIC INVESTIGATION

The leaching reaction of mineral particles involves the mass transfer of the reactant and product ions. The leaching of lead from galena was studied using different models. As the leaching proceeds, the particle sizes shrink with time until total surface area of the particles diminishes.

Whether or not a product layer is formed around the particles, the leaching process can be analyzed by the shrinking core model (SCM). The leaching of the H_2SO_4 system is a heterogeneous process. Most of the sulphide mineral leaching processes follow the shrinking core model (Ucar, 2009). Based on this model, the reaction of the galena ore may be expressed as;

$$A_{Fluid} + B_{Solid} \rightarrow P_{products} \quad (1)$$

The kinetic relationships in this study are expressed in terms of percentage of particle extracted with time.

The dissolution mechanism of galena ore may be based on different kinetic models. These include the surface chemical reaction (equation 2), diffusion through product layer (equation 3) and mixed kinetic models (equation 4). If either of the equations 2 and 3 holds then equation 4 holds. Equation 4 is the combination of equation 2 and 3 (Aydogan *et al*., 2005)

To determine the reaction rate controlling process the experimental parameters were tested in the three different kinetic models.

When surface chemical reaction mechanism is the controlling mechanism, equation 2 holds

$$1 - (1 - X)^{1/3} = K_s t \quad (2)$$

If the diffusion through the product layer is the controlling mechanism, equation 3 is applicable.

$$1 - 2/3X - (1 - X)^{1/3} = K_d t \quad (3)$$

If either of the equations 2 and 3 holds, the mixed kinetic model is applied.

$$\left\{1 - (1 - X)^{1/3}\right\}^2 = K_m t \quad (4)$$

Where:

K_s, K_d and K_m are linear rate constants

X = the leaching rate of lead

t = the reaction time

From the results presented in Figures 7-11, using all the experimental parameters, it is concluded that equation (4), which refers to the mixed kinetic model, is the rate controlling mechanism.

Determination of Activation Energy

Fig 12 shows the Arrhenius plot of *InK* against the reciprocal of the reaction temperature, from this the activation

energy was determined to be 29.68KJ/mol. The value indicates that the mechanism of lead dissolution from galena throughH_2SO_4 was through mixed kinetic controlled route.

$$K = Ae^{-Ea/RT} \quad \text{Or}$$

$$In\ K = -\frac{Ea}{R}\left(\frac{1}{T}\right) + In\ A$$

Where:

where k is the reaction rate constants at different temperatures; A is the pre-exponential factor; R is the mole gas constant; T is the thermodynamic temperature; *E*a is the apparent activation energy.

A plot of ln k versus 1/T (Fig. 12) yields a straight line from which the apparent activation energy (Ea) is determined.

Saxena and Mandre, (1992) and Feng *et al*., (2013) in their separate studies, reported that *E*a in the range of 12-39kJ/mol could be said to be related to a mixed kinetic control mechanism. This shows that the leaching of Ishiagu ore results from the combination of surface chemical reaction and diffusion through product layer. To further validate this, Table 2 presents the calculated values of k and correlation coefficient R^2 for the various experimental parameters studied. The result shows that correlation coefficient (R^2) for surface chemical reaction and diffusion through product layer had large values of 0.97340 and 0.9954 respectively. The mixed kinetic model also has large values of 0.9928 and is seen as the controlling step for the reaction.

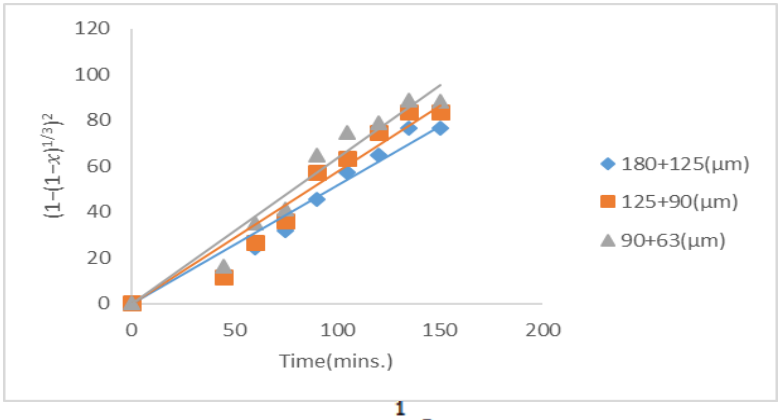

Fig 7: *Plot of* $(1-(1-x)^{\frac{1}{3}})^2$ *vs t at various particle sizes*

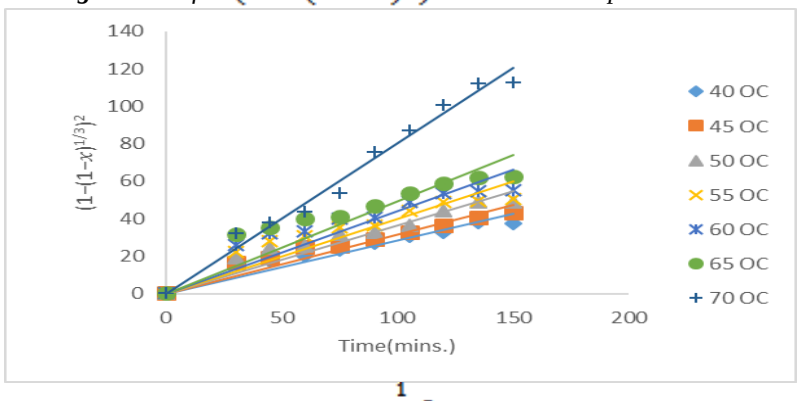

Fig 8: *Plot of* $(1-(1-x)^{\frac{1}{3}})^2$ *vs. t at various temperatures*

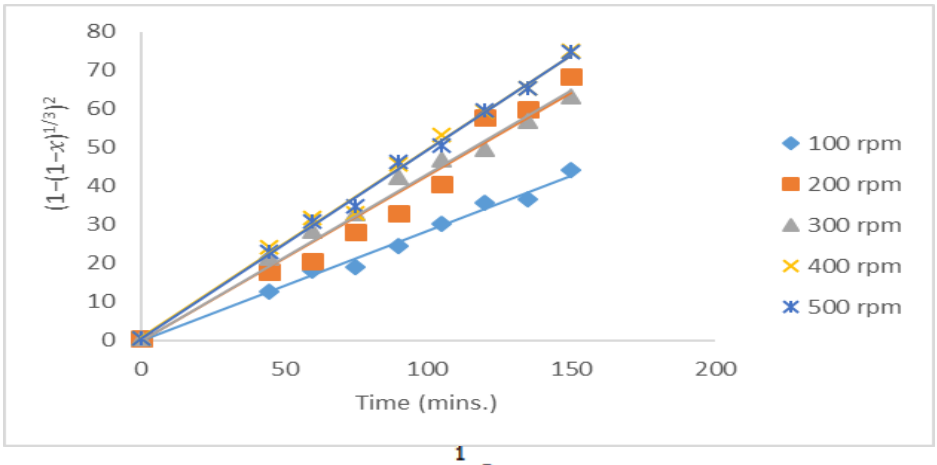

Fig 9: *Plot of* $(1-(1-x)^{\frac{1}{3}})^2$ *vs. t at various stirring speeds*

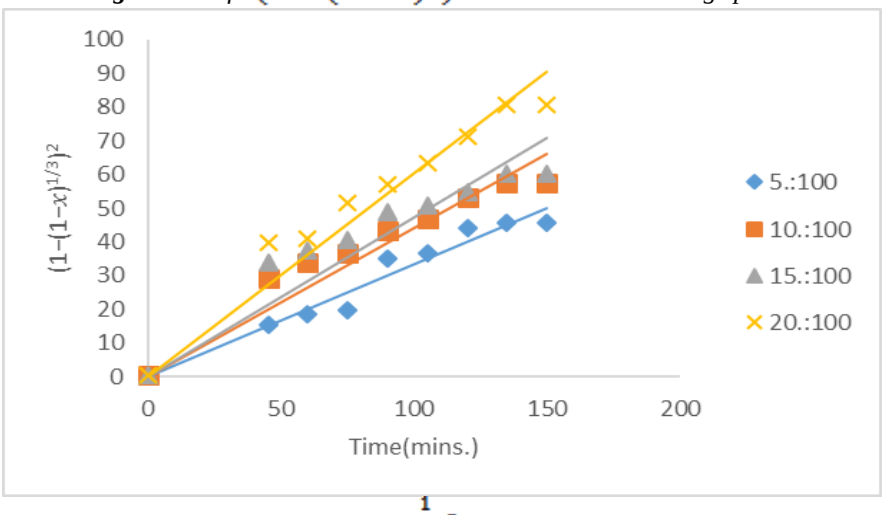

Fig 10: *Plot of* $(1-(1-x)^{\frac{1}{3}})^2$ *vs. t at various solid-liquid ratio*

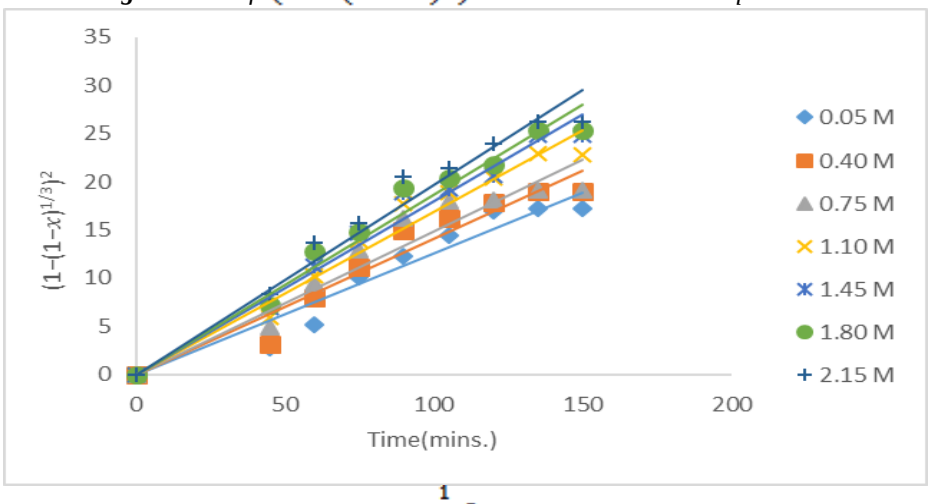

Fig 11: *Plot of* $(1-(1-x)^{\frac{1}{3}})^2$ *vs. t at various acid concentrations*

Arrhenius plots

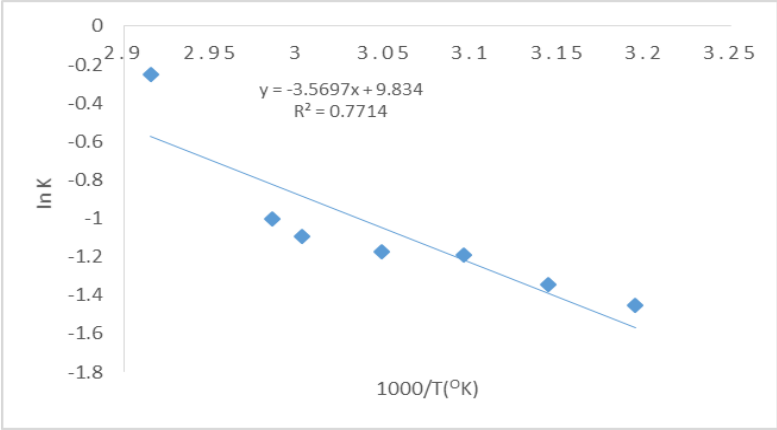

Fig 12: Arrhenius plot $\ln l$ *against* $\left(\frac{1}{T}\right)$

Table 2: The apparent rate constants, k_s, k_d and k_m) for the kinetic models and correlation coefficients, H_2SO_4

	Surface chemical reaction $1-(1-x)^{1/3}$		Diffusion through the product layer $1-\frac{2}{3}x-(1-x)^{2/3}$		Mixed kinetic model $(1-(1-x)^{\frac{1}{3}})^2$	
Parameter T(°K)	**k_s (min^{-1})**	**R^2**	**K_d (min^{-1})**	**R^2**	**K_m (min^{-1})**	**R^2**
313	0.0302	0.8129	-0.5807	0.9753	0.2338	0.9582
318	0.032	0.8163	-0.6522	0.979	0.2601	0.9628
323	0.0347	0.8097	-0.7707	0.9682	0.3032	0.9541
328	0.0346	0.7574	-0.7875	0.9392	0.3087	0.919
333	0.0359	0.7375	-0.8598	0.927	0.3345	0.9057
338	0.0375	0.7213	-0.9521	0.9214	0.3674	0.899
343	0.06	0.9032	-2.0987	0.9813	0.7796	0.982
C (mol^{-1})						
0.05	0.0451	0.9405	-0.835	0.8953	0.1354	0.9405
0.40	0.0482	0.9412	-0.9846	0.9186	0.1446	0.9412
0.75	0.0468	0.9223	-0.9906	0.9161	0.1405	0.9223
1.10	0.055	0.9647	-1.3646	0.9393	0.1651	0.9647
1.45	0.0581	0.9734	-1.5516	0.9319	0.1743	0.9734
1.80	0.0593	0.9706	-1.6296	0.9441	0.1779	0.9706
2.15	0.0614	0.9674	-1.7716	0.951	0.1842	0.9674
SS(rpm)						
100	0.0369	0.9412	-0.7125	0.9824	0.2867	0.9895
200	0.0487	0.9674	-1.2071	0.9547	0.4673	0.9682
300	0.0442	0.9015	-1.0546	0.9954	0.4105	0.9928
400	0.0488	0.921	-1.2711	0.9946	0.4884	0.9927
500	0.0489	0.9265	-1.2071	0.9908	0.4889	0.9967
r_o (μm)						
180+125	0.0561	0.9697	-1.5883	0.9594	0.5773	0.9695
125+90	0.06	0.9538	-1.7395	0.9485	0.6444	0.9566
90+63	0.06	0.9319	-1.8067	0.9526	0.6688	0.9578
S/L						
5:100	0.0401	0.9146	-0.8354	0.9476	0.3319	0.9537
10:100	0.0406	0.81	-0.9424	0.9638	0.3683	0.9482
15:100	0.0407	0.7688	-0.9635	0.9334	0.3755	0.9142
20:100	0.0493	0.8321	-1.3734	0.9749	0.5235	0.9644

5.0 CONCLUSION

The results indicate that the leaching rate increased with an increase in acid concentration, stirring speed, temperature, Solid/Liquid ratio and with a decrease in particle size. The best leaching condition was observed to be 400 rpm stirring speed, 2.15M H_2SO_4 acid concentration, 70^oC reaction temperature, 20:100 solid/liquid ratio and 63µm particle size. The time for extraction of over 95%Pb was found to be 15 minutes.

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