

Recovery of Lead from Lead Laden Cupels by a Simultaneous Leaching and Electrowinning Process in a Methanesulphonic acid bath

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Abstract: Cupels are generated by mines during the fire assaying of precious group metals. The cupels contain lead which is a known environmental hazard hence the need to recover it. This work illustrates how leaching and electrowinning processes can be combined to produce a hybrid lead recovery process. Bench scale tests were conducted for the hybrid leaching and electro winning process using Methane Sulfonic Acid (MSA) as a leaching solvent at a concentration of 200g MSA per litre of water. A glass electrowinning cell fitted with a 9cm × 4cm pure lead cathode and 9cm × 4cm graphite anode with inter electrode gap of 15cm and a magnetic stirrer bar was used. Lead laden cupels (containing 30g lead) were subjected to simultaneous leaching and electrowinning and lead recovery after a period of 80 minutes was found to be 98%. The hybrid process was found to require about 20% less solvent than that required for the convectional leaching process which requires multiple stages to reduce the concentration of the solute in the raffinate to the same extent.

Keywords: Leaching, electrowinning, lead laden cupels, methane sulfonic acid.

Introduction

Platinum and gold mining firms in Zimbabwe which use a fire assaying technique known as cupellation are currently faced with a challenge of disposing the lead laden cupels. During the cupellation process lead is used as a flux to lower the melting point of the samples but the lead diffuses into the cupels hence these used cupels cannot be disposed into the environment^{1,2}. Analyses of the lead laden cupels show that they contain between 50w/w percent and 60w/w percent lead. Zimbabwean laws do not allow disposal of lead into the environment as it is a poisonous heavy metal. The problem has also delayed platinum mining companies from attaining ISO 14000 certification as disposal of the lead laden cupels is often an issue of concern.

Leaching

In the chemical processing industry, leaching has a variety of commercial applications, including separation of metal from ore using acid, and sugar from beets using hot water. In conventional leaching, the solid is generally a stationary heap or pile of ore and solution percolates through the solid³. Solvent and solid are mixed and allowed to attain equilibrium, and two phases are separated.

Depending on the rate controlling step leaching may be; reaction controlled, diffusion controlled or intermediate controlled. In the latter case both diffusion and reaction rate are controlling.

When optimizing the leaching process it is important to know if the process is reaction controlled or diffusion controlled. If the process is reaction controlled then it will be prudent to give priority to the parameters that affect reaction rate during the process optimization stage and if it is diffusion controlled then optimization must be such that priority is given to parameters that affect rate of mass transfer.

In reaction controlled leaching the limiting or slowest step is the chemical reaction occurring on the solid liquid interface. The best model for such a process is the shrinking particle model. The shrinking particle model states that the radius of the reacting particle decreases as the reaction progresses.

In reaction controlled leaching chemical reaction at the surface is much slower than the diffusion of reagents through the diffusion layer; this also implies that the concentration of reagents at the surface becomes equal to the concentration in the bulk, i.e. $C_i = C$.

The assumptions made are that the particles to be leached are spherical and of equal size and that the concentration of the reagent is constant during leaching. This leads to the following derivation⁴:

$$1 - (1 - \alpha)^{\frac{1}{3}} = \frac{k \times C \times t}{r_0 \times \rho}$$

Where:

α = fraction leached

k = rate constant

C = concentration of reagent

t = time of leaching

r_0 = initial radius of particle

ρ = density of particle

The equation shows that the leaching rate is inversely proportional to the radius of the particle. The rate constant may be determined by plotting the left hand side against time on a diagram. In the case where the chemical reaction on the surface is much faster than the diffusion, leaching becomes diffusion-controlled. The reagent concentration at the surface becomes zero, i.e. $C_i = 0$. The leaching mechanism might become diffusion-controlled when, during leaching, a porous product layer forms on the surface of the particle to be leached⁴. This can for example happen in the case of leaching of sulphides where a layer of elemental sulphur can be deposited on the sulphide surface. The mechanism of diffusion-controlled leaching of a spherical particle is often called the shrinking core model.

With the same assumptions as for the shrinking particle model i.e. that the reagent concentration is constant and that spherical and equal sized particles are leached, an expression for diffusion controlled leaching can be arrived at by applying Fick's law⁴.

$$1 - \frac{2}{3\alpha} - (1 - \alpha)^{\frac{2}{3}} = \frac{2 \times M \times D \times C}{\beta \times \rho \times r_0^2} \times t$$

Where:

α = fraction leached

β = stoichiometric factor

M = molecular weight of leached mineral

ρ = density of particle

t = time of leaching

C = concentration of reagent

D = diffusion constant (gram/cm² or mole/cm²)

r_0 = initial radius of particle at time zero

As is evident from the equation, the leach rate is inversely proportional to the square of the radius of the particle. The diffusion constant can be determined by plotting the left hand side against time in a diagram. Given the assumptions that C is constant and that volume changes has not been taken into account, this model is accurate until 80-90% has been leached out.

The major aspects for the leaching operation are the selection of process and operating conditions and the sizing of the extraction equipment. The main parameters that must be identified for process and operating conditions are the solvent to be used, the temperature, the terminal stream compositions and quantities, leaching cycle (batch or continuous), contact method, and specific extractor choice.

The desirable characteristics of a good solvent are; high saturation limit and selectivity for the solute to be extracted, capability to produce extracted material of quality that is unimpaired by the solvent, chemical stability under process conditions, low viscosity, low vapour pressure, low toxicity and flammability, low density, low surface tension, ease and economy of recovery from the extract stream and price. The specifics of each process determine the interaction and relative significance of these characteristics.

The temperature of the leaching process is chosen in a manner that balances solute solubility, solvent-vapour pressure, solute diffusivity, solvent selectivity, and sensitivity of product to thermal degradation. In some cases, temperature sensitivity of materials of construction to corrosion or erosion attack may be significant. The terminal stream compositions and quantities are linked to the production capacity of the leaching plant (rate of extract production or rate of raw-material purification by extraction). When options are permitted, the degree of solute removal and the concentration of the extract stream chosen are those that maximize process economy while sustaining conformance to regulatory standards.

The choice between continuous and intermittent operation is largely a matter of the size and nature of the process of which the extraction is a part. The choice of a percolation or solids-dispersion technique depends principally on the amenability of the extraction to effective, sufficiently rapid percolation. As is always true, the ultimate criteria are reliability and profitability.

Depending on whether leaching is diffusion or reaction controlled; parameters such as particle size, temperature, concentration gradient and agitation speed will influence leaching kinetics differently. Parameters such as particle size can necessitate size reduction/grinding which has a bearing on the economics of the process.

In this work, Methane Sulfonic Acid (MSA), was chosen as the leaching solvent because of its superior leaching and handling characteristics as reported in the literature^{5,6,7,8,9,10}. The very high solubility of lead methane sulfonate in aqueous solutions (approximately 500 g/l as lead) is of particular advantage in leaching operations that target lead as the solute of interest.

Electrowinning

Electrowinning is the recovery of solute on a suitable electrode surface when a direct electric current is passed through an ionic substance that is either molten or dissolved in a suitable solvent. An advantage of this method is that certain components of the system can be removed without introducing new contaminants. The standard potential of the electrode reaction gives an indication of whether a metal can be removed by electrowinning. The metals with positive standard potentials (noble metals) are easiest to recover. Metals whose standard potentials are negative are more difficult to recover because gaseous hydrogen may evolve simultaneously with metal deposition. Manganese, whose standard potential is $-1.18V$, is the least noble metal that can be deposited by electrowinning in aqueous solutions. The most widely applied electrowinning processes are the electro-refining of copper, nickel, silver and zinc. Approximately 53% of the zinc produced worldwide is obtained through electrolysis¹¹.

The main components required to achieve electrowinning are an electrolyte, direct current supply and two electrodes. An electrolyte is a substance containing free ions which is capable of conducting an electric current. A direct current (DC) supply provides the energy that is necessary to create or discharge the ions during the electrowinning process. Electric current is carried by electrons in an external circuit. The two electrodes provide the physical interface between the electrolyte and the electrical circuit that provides the energy¹². Metal, graphite and semiconductor material are widely used as electrodes. The choice of suitable electrode material depends on the chemical reactivity between the electrode and electrolyte and the cost of manufacturing it¹³.

Experimental

Experiments were carried out in order to characterize the simultaneous leaching and electrowinning process. All experiments were carried out at a temperature of 25 °C. All solutions were mixed with a Teflon coated magnetic stirrer (4 cm stir bar, 120 rpm). Methane Sulfonic Acid Solution (70% wt in H₂O) and lead methane sulfonate solution (50% wt in H₂O) from Sigma-Aldrich was used.

Determination of the leaching time for a given mass of lead laden cupel

A 70 wt. % MSA solution of methane sulfonic acid was diluted to 200 g MSA/L in a glass beaker and a magnetic stirrer (4 cm stir bar, 120 rpm) used to mix the solution. One lead laden cupel (96 g in mass containing an average lead content of 30g lead each) was added in the acid solution in the leaching cell and the stop watch started simultaneously. A pipette was used to extract 5 ml of the solution at 4 minutes intervals. Lead concentration analysis using the Atomic absorption spectrometer was carried out until a constant lead concentration was reached in the solution. The process was repeated three times and results recorded in each case.

Effect of particle size on rate of reaction.

The aim of this range of experiments was to determine whether the lead leaching kinetics are reaction controlled or mass transfer controlled. Lead laden cupels were crushed and classified using sieves of different aperture sizes (25mm, 19mm, 12mm, 10mm, 8mm and 6mm). 30 g of each particle size class were measured and mixed with 500ml of 200g MSA/L in separate beakers. Samples were taken at 4 minute intervals from each beaker and analysed for lead concentration using an Atomic Absorption Spectrometer and results were recorded.

Effect of initial leachant concentration on the amount of lead leached

Five separate 500ml solutions containing 207.3g MSA/L, 345.3g MSA/L, 518.0g MSA/L, 690.7g MSA/L and 828.8g MSA/L respectively, were prepared by diluting appropriate volumes of 70 wt. % MSA solutions, with distilled water. 30g of 19mm particle size were then added to each 500ml solution. 5ml of sample were withdrawn from each container after 4 minute intervals and analysed for lead concentration using an Atomic Absorption (AA) Spectrometer and results were recorded.

The rate of electrowinning (deposition of lead on the cathode) at a given initial Pb concentration, current and voltage.

A glass electrowinning cell fitted with a 9cm×4cm pure lead cathode and 9cm×4cm graphite electrode with inter electrode gap of 15cm was connected to a DC power pack. A one litre electrolyte solution was prepared using 500ml of 100 g/l lead methane sulfonate and 500ml of 200g MSA/L solution. The electrolyte mixture was placed in a glass electrowinning cell and the power pack connected before the magnetic stirrer was turned on. The power pack was switched on and maintained at a current of 7 amps and a voltage of 7 volts. The mass accumulated on the cathode was measured after every 5 minutes and the results recorded.

The rate of deposition of lead on the cathode for a simultaneous leaching and electrowinning operation.

A glass electrowinning cell fitted with a 9cm×4cm pure lead cathode and 9cm×4cm graphite electrode with inter electrode gap of 15cm was connected to a DC power pack. A 1 litre electrolyte solution was prepared using 200 g/l (18 wt/wt % MSA in water) Methane Sulfonic Acid. 30g of 19mm particle size lead laden cupel powder was added to the electrolyte. The magnetic stirrer was turned on. The power pack was switched on and maintained at a current of 7 amps. The mass accumulated on the cathode was measured at 5 minute intervals by subtracting the final mass from the initial mass. A pipette was used to extract 5ml from the electrolyte for lead concentration analysis using an Atomic Absorption spectrometer and the results were recorded.

Results

The results, analysis and deductions that were made after conducting the experiments are detailed below.

Determination of Leaching Rate and Leaching Time

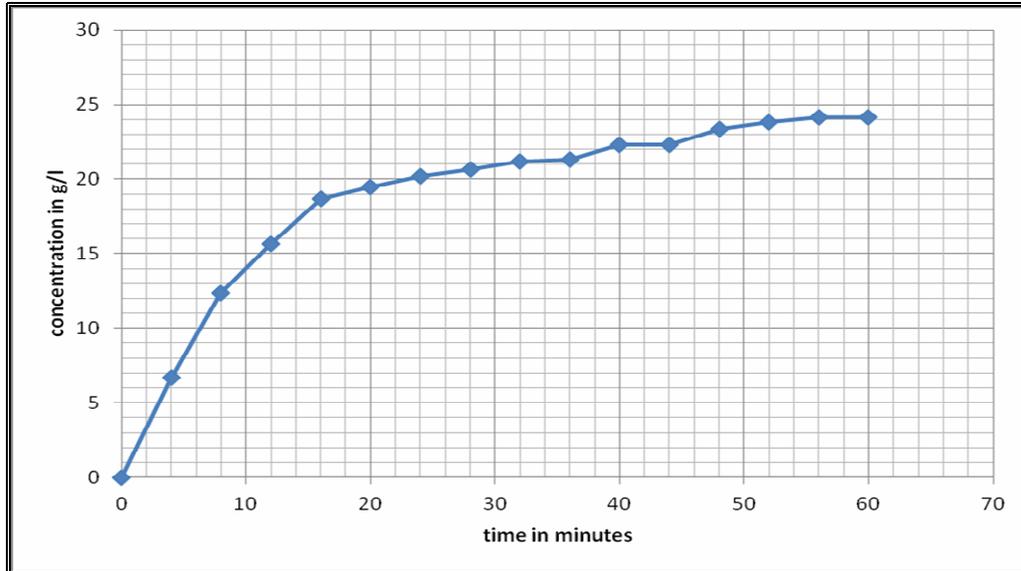


Figure 1. Graphical representation results of experiment for determination of leaching rate and leaching time

The time required to complete batch leaching of one cupel containing 30g lead using one litre M.S.A of a concentration of 200g/l at a temperature of 25 °C was found to be 52 minutes. 24g of lead were leached out of the cupel within a period of 50min and there was no further leaching taking place after the 52 minutes. A yield of (24g/30g) 80% lead was obtained from the leaching solution in 52 minutes.

Table 1: Results of calculated leaching rate

average concentration in g/l $\frac{C_x + C_{x+1}}{2}$	change in concentration in g/l $(C_x - C_{x+1})$	change in time in minutes $t_x - t_{x+1}$	rate of reaction (change in concentration/change in time) $\frac{\partial C}{\partial t}$	average time in minutes $\frac{t_x + t_{x+1}}{2}$
0	6.7	4.0	1.67	2.0
6.6	5.7	4.0	1.42	6.0
12.3	3.3	4.0	0.83	10.0
15.6	3.0	4.0	0.75	14.0
18.6	0.8	4.0	0.20	18.0
19.5	0.7	4.0	0.16	22.0
20.2	0.5	4.0	0.12	26.0
20.7	0.5	4.0	0.12	30.0
21.2	0.1	4.0	0.041	34.0
21.3	1.0	4.0	0.25	38.0
22.3	0.0	4.0	0.00	42.0
22.3	1.0	4.0	0.25	46.0
23.3	0.5	4.0	0.12	50.0
23.8	0.3	4.0	0.08	54.0
24.2	0.0	4.0	0.00	58.0

The initial rate of leaching was about 1.7 (g/l)/min. The rate of leaching rapidly decreased until it reached 0.2 (g/l)/min in about 20 minutes and finally reaches zero in 58 minutes as shown in figure 2 below and table 1 above.

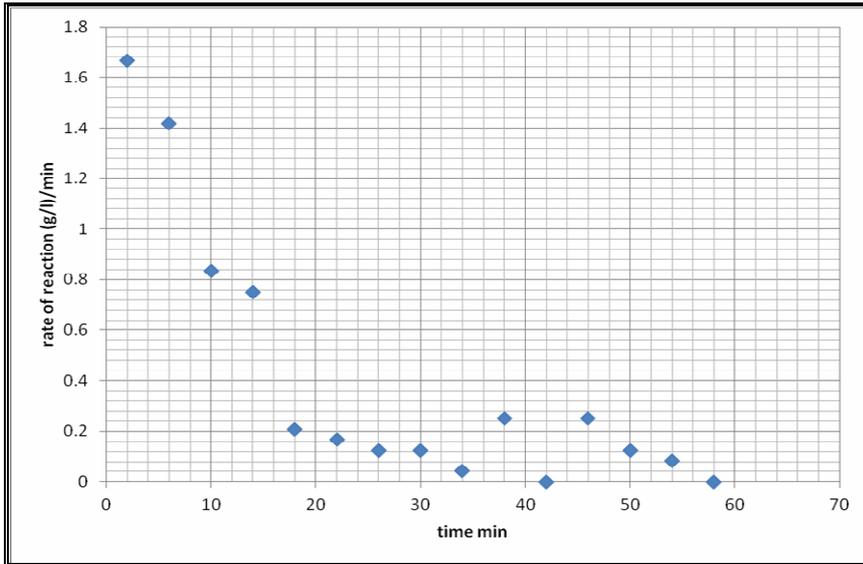


Figure 2. Graph of the rate of leaching versus time

Determination of Leaching Kinetics By Investigating The Effect of Particle Size on Rate of Reaction

The Shrinking Core Model Analysis

The shrinking core model equation.

$$1 - \frac{2}{3\alpha} - (1 - \alpha)^{\frac{2}{3}} = \frac{2 \times M \times D \times C}{\beta \times \rho \times r_0^2} \times t$$

Where:

α = fraction leached

β = stoichiometric factor

M = molecular weight of leached mineral

ρ = density of particle

t = time of leaching

C = concentration of reagent

D = diffusion constant (gram/cm² or mole/cm²)

r₀ = initial radius of particle at time zero

Taking $(2.M.D.C.t)/Bp$ as constant with a value of 2 and plotting the calculated value of α (fraction leached) in g/l versus r (initial radius of the particle).

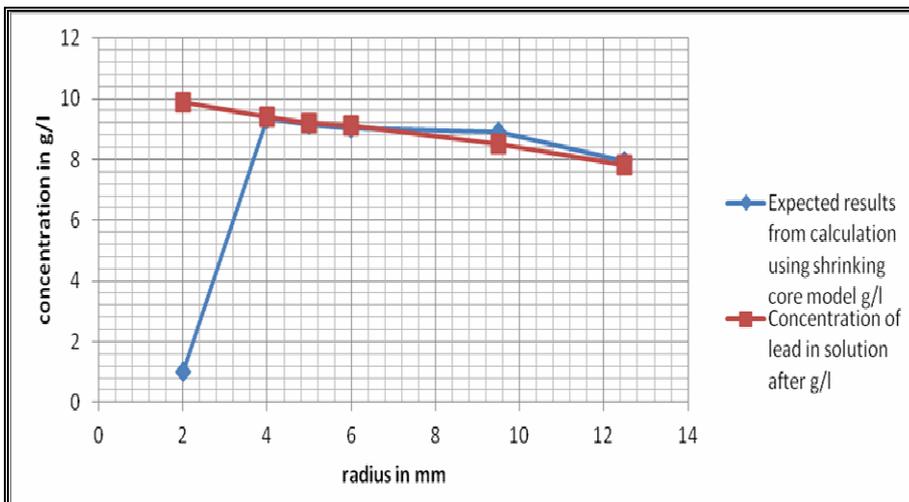


Figure 3. Graph of concentration versus radius, t=4mins

Figure 3 above shows that the graph labelled expected results compares very well with the graph obtained from experimental results labelled concentration of lead. It can be noted that the kinetics of the leaching of lead using MSA can be modelled after the shrinking core model with reasonable accuracy.

Effect of initial leachant concentration on the amount of lead leached

Calculation using the shrinking core model and taking the constant $(2.M.D.t)/B \rho$ as 2 results in the graph labelled ‘expected results’ which compares well with the graph obtained by experiment as shown in figure 4 below.

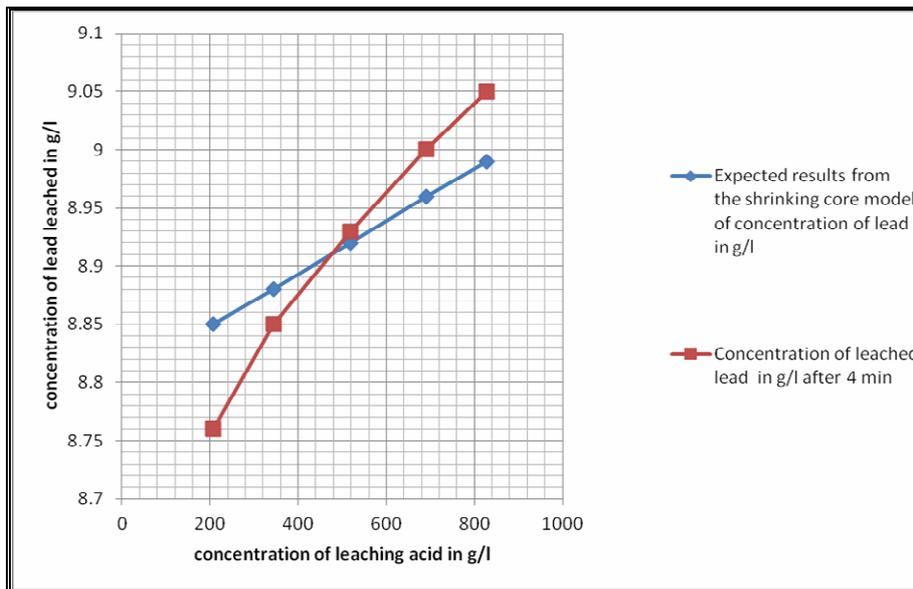


Figure 4. Graph of concentration of lead leached versus initial leachate concentration

Within experimental errors the leaching of lead using MSA can be reasonably modelled after the shrinking core model. Since the leaching of lead using MSA can be modelled by the shrinking core model it is reasonable to take the leaching process to be diffusion controlled.

According to the law of electrolysis

$$m = \frac{ItAr}{Fxe}$$

- Where :m = mass deposited (g)
- I = current (amps)
- t= time (s)
- Ar = atomic mass of atom
- F= faraday constant (96 500C)
- e= metal valance

This equation shows that the electrowinning rate is constant if all other variables are maintained reasonably constant, that is, mass or time is kept constant in the case for lead assuming a cell resistance of 1 ohm and using a voltage of 7 volts and a current of 7 amps and time in minutes, the ratio mass accumulated /time is 0.44. It can be noted that approximately the same theoretical ratio of 0.44g/min was obtained from experiment. Figure 5 below shows that for a solute pregnant solution containing 24g lead, the approximate amount that can be obtained from leaching one cupel, it would take 54 minutes to extract all the 24g from solution assuming that the conditions specified above are maintained.

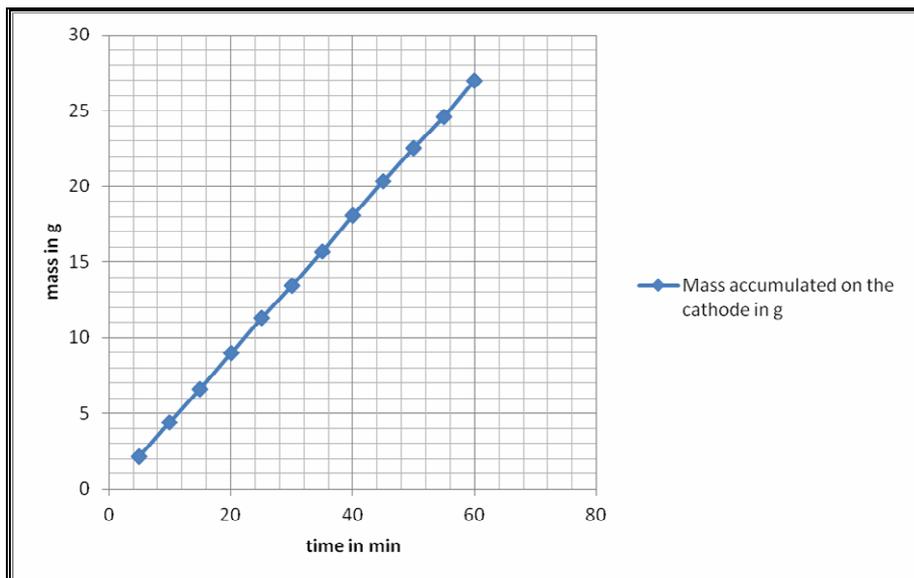


Figure 5. Graph of mass accumulated versus time

The Simultaneous Leaching and Electrowinning Process

The products of the simultaneous leaching and electrowinning process are shown in pictorial view in figure 6 below.



Figure 6. Photo showing the lead recovered from the solution (dark grey) and the part of the cathode (light grey)

For the simultaneous leaching and electrowinning process the amount of lead deposited on the cathode was observed to be constant until after 38 minutes after which it increased but at a much slower rate compared with the first 38 minutes as shown in figure 7 below.

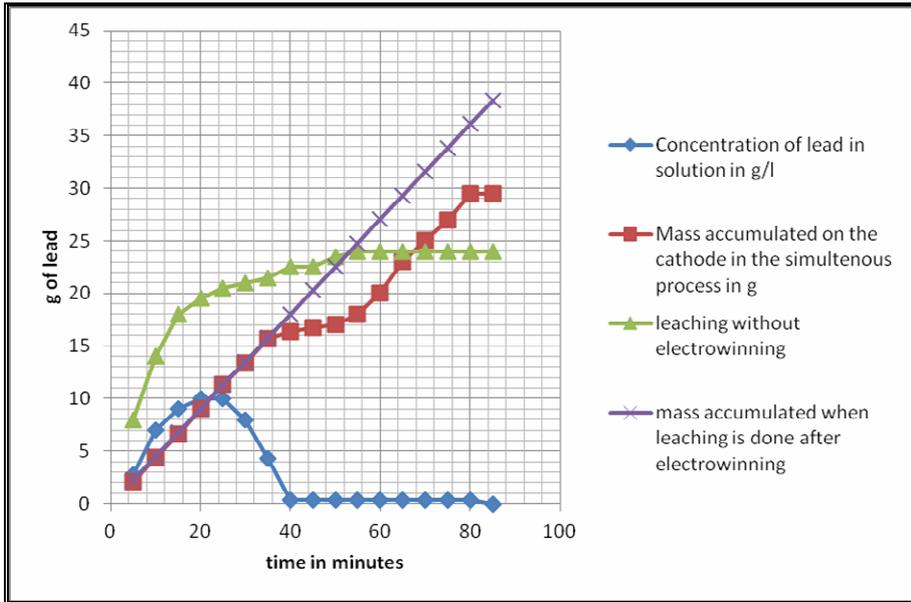


Figure 7. Concentration of lead in g/l versus time

Concentration of lead in the solution increased for the first 25 minutes and reached a highest value of 10g after which it decreased in 16 minutes to 0.3 g and remained constant for 40 more minutes. The maximum recovered amount of lead out of the total 30g lead was 29.5g = 98% recovery.

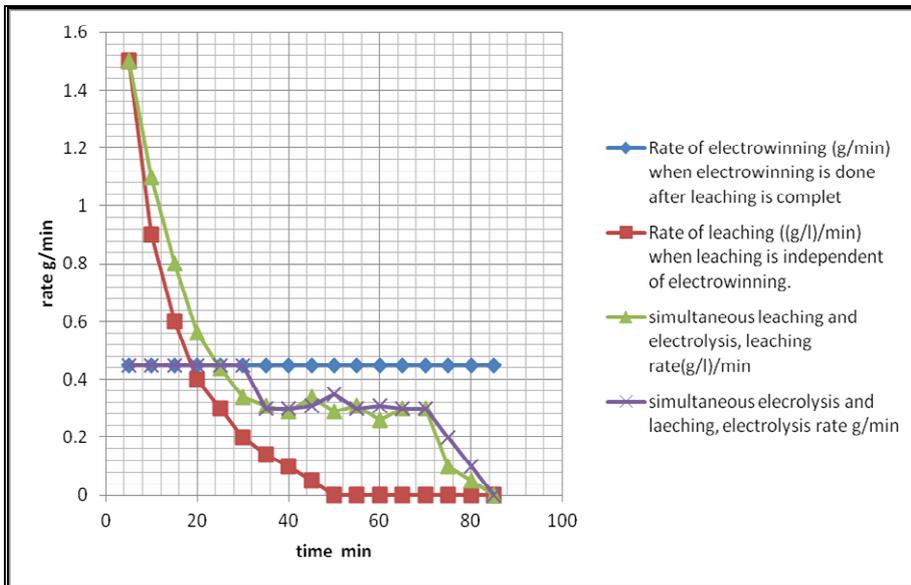


Figure 8. Graph of leaching rate versus time

In the first 18 minutes the leaching rate was greater than the electrowinning rate as shown in figure 8 above. During the first 18 minutes the electrowinning rate was constant at 0.44g/min but the leaching rate was decreasing until it reached a value of 0.44g/l/min. Soon after the first 18 minutes the electrowinning rate became higher than the leaching rate. After 30 minutes in the simultaneous process the leaching and electrowinning rate was found to be constant at a value of 0.3 g/min for about 40 minutes and finally dropped to zero. Generally, for the simultaneous leaching and electrowinning process, the rate of leaching was found to be faster than that of normal leaching. Overall electrowinning time for the simultaneous process increased to about 70 minutes for recovery of 24g lead, compared with 104 minutes required for the sequential leaching and electrowinning process. The yield of lead was higher for the simultaneous process (98%) after a period of 80 minutes.

Discussions

The higher leaching rate in the simultaneous process can be attributed to the concentration gradient being maintained by continuous removal of lead from the solution by the electrowinning process that is occurring simultaneously with the leaching. The fact that the leaching rate increased in the simultaneous process further strengthens the fact that the lead leaching process is diffusion controlled as indicated in previous deductions. High recovery of lead from the cupels is possible using the simultaneous process due to the high concentration gradients created by electrowinning which allow complete leaching to take place.

Conclusions

Methane sulphonic acid can be used as an environmentally friendly solvent for the leaching of lead from lead laden cupels in the mining industry. Higher recovery of lead over a shorter period of time can be realised by the simultaneous leaching of lead with methane sulphonic acid and electrowinning onto a pure lead cathode.

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