

QUANTITATIVE LEACHING OF A SPENT CELL PHONE PRINTED CIRCUIT BOARD BY HYDROCHLORIC ACID

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Abstract

This paper presents a kinetic data on the hydrometallurgical recovery of some metal ions from a printed circuit board (PCB) of a spent cell phone by hydrochloric acid leaching. The effects of acid concentration, temperature and particle diameter on the dissolution efficiency at various leaching time intervals were examined. The results of the leaching investigations showed that the powdered cell phone dissolution increases with increasing acid concentration, system temperature with decreasing particle diameter at 360 rpm. With 2M HCl solution, about 88.49% of the sample was dissolved within 120 minutes using 0.075-0.112 mm particle diameter at 80⁰C. The results of the study indicated that the dissolution reaction could be represented by a shrinking core model with surface chemical reaction. A value of 0.61, 60.67 kJ/mol and 12.9s⁻¹ were calculated as reaction order, activation energy and frequency factor, respectively for the dissolution process.

Keywords: Metals Recycling; Cell phone; Printed circuit board: dissolution kinetic; hydrochloric acid.

Introduction

Fast development in the telecommunications industry has brought the great benefits in everyday life, but its consequences are usually ignored or even unknown. Mobile phones are considered to be the fastest selling electronic equipment in the world. They are also considered to be the fastest growing waste streams in the world and thus,

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bringing about significant risks to human health [1]. Consequently, recycling, a significant factor in the supply of many metals used in our society provides environmental benefits such as energy savings, reduced volumes of waste and reduced emissions associated with energy savings. In addition, it reduces the amount of raw materials that must be mined to support our lifestyle [2].

In a study, the US environmental protection agency estimated that by 2005, as many as 130 million cell phones would be retired annually in the United State. By 2005, a total of 500 million obsolete cell phones had accumulated as predicted by INFORM Inc. Typically, cell phones are used for only 1½ years before being replaced. The obsolete mobile phones and accessories contain concentration of toxic heavy metals including cadmium, lead, mercury, manganese, lithium, zinc, arsenic, antimony and beryllium [3].

For instance, Karg and Shenung [1] showed that the average weight of compounds in mobile phones are estimated to be 113g, exclusive of batteries and chargers, metal contents are weighed in metric tons(t), unless otherwise noted. As seen in Table 1, values in US dollars are calculated by using the average prices for 2002-2004 for USGS mineral commodity, summaries in 2005. The gross values do not include costs of recycling. Data may not add to totals shown because of independent rounding.

Table 1: Weight and gross value of selected metals in cell phones [1].

Metal	Metal content and value estimated for a typical cell phone in 2002		Metal content and value for 180 million cell phones in use in 2004		Metal content and value for 130 million cell phones in use in 2005		Metal content and value for 500 million obsolete cell phones in storage in 2005	
	Weight (t)	Value (\$) million	Weight (t)	Value (\$) million	Weight (t)	Value (\$) million	Weight (t)	Value (\$) million
Copper	16	0.03	2900	6.2	2100	4.6	1900	17
Silver	0.35	0.06	64.1	1.1	46	7.9	178	31
Gold	0.034	0.40	6.2	72	3.9	52	17	199
Palladium	0.015	0.13	2.7	22.7	2.0	16	7.4	63
Platinum	0.00034	0.01	0.06	1.4	0.04	1	0.18	3.9
Total	16.34	0.63	2973	113	2152	82	8102	314

It is worthy to note that metals play an important part in modern society and historical been linked with industrial development and improved living standards. Society can draw on metal resources from earth's crust as well as from metal discarded including spent mobile phones after use in the economy. Insufficient recovery of metals from the economy increases reliance on primary resources and can impact nature by increasing the dispersions of metals in ecosystems [4]. Spent catalysts from industry and automotive catalytic converters, printed circuit boards of wastes computers, ash resulting from coal combustion, etc. represents another part of solid wastes with high content in valuable metals [5,6]. Metals can be recycled nearly indefinitely.

Nevertheless, the ability to recover metals economically after use is largely a function of how they are used initially in the economy and their chemical reactivity [4].

A good number of processing techniques to treat and recycle metals through chloride leaching have been achieved by hydrometallurgical methods, due to higher dissolution rate, low price of leaching reagents and non-pollution character [7,8]. Further, the use of hydrometallurgical techniques is becoming more attractive, since the need of high energy requirements or eventual gas collectors and cleaning systems, always necessary in the pyrometallurgical processes are avoided [9,10]. Therefore, this work constituting the first part of activities within the context of beneficiation of valuable metal ions from spent mobile phone by acid leaching in laboratory scale is aimed at establishing the dissolution kinetic parameters for the subsequent operational recovery conditions in acid medium. It is worthy to note that this work is promoted by the fact that metals extraction and processing from secondary sources are gaining more attention as cost of safe disposal of hazardous components are quite high with limited storage capacity, and hence the need for this investigation.

Materials and Methods

Materials

A typical spent mobile cell phone used for this study was collected from a cell phone repairer's workshop, situated beside Challenge Bookshop, Ilorin South Local Government Area, Ilorin, Kwara State – Nigeria. The reagent used for this research work is mainly hydrochloric acid (AnalaR product) and doubly distilled water was used in preparation of all aqueous solutions.

Methods

The sample (spent cell phone) was manually dismantled by loosening the plastic casing and the display screen with the aid of screw-driver after which the keypads and other parts were disassembled. The electronic circuitry, consisting of the printed board (panel) was then filed to about 0.1 mm particle diameter, which gives a larger surface area needed for further chemical processing via leaching operation [11]. This size was also retained for elemental analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using Yakogawa model HP-4500 as well as its purity assessment by Philips PW 1800 X-ray diffractometer (XRD) with CuK_α (1.54Å) radiation, generated at 40kV and 55mA.

The dissolution experiment was carried out in a 250 ml glass reactor equipped with a mechanical stirrer. For each leaching experiment, a 10 g/L of the sample was reacted with appropriate HCl solution and then transferred into 250 ml Pyrex glass reactor. The sample mixture was then heated to a required temperature and stirred at a rate of 360 rpm. For each run, samples were withdrawn at selected time intervals, and at various HCl concentrations (0.1M – 4.0M). After the completion of leaching tests, leach residues were filtered, water-washed, oven-dried and weighed [10-13]. The percentage of the sample dissolved was calculated from the initial difference in weights of the precipitate before and after leaching up to 120 minutes. This calculation was done for all concentrations of HCl investigated. The concentration which gave the highest percentage of dissolution (2 M) was used in optimizing other parameters such as temperature and particle size. The activation energy, E_a and Arrhenius constant were

evaluated from the appropriate plots [14]. The residue at the optimal conditions was also subjected to X-ray diffraction analysis for material purity assessment [15].

Results and Discussion

Characterization of powdered sample by ICP-MS and X-ray diffraction (XRD)

The elemental analysis of the spent cell phones Printed circuit board by ICP-MS revealed the following results: Cd(14.32%), Pb(15.29%), Ni(13.63%), Si(12.23%), Cu(10.28%), Ag(5.33%), Fe(3.72%), Sn(1.83%), Ti(0.041%), Mn(0.011%), Sb(0.0025%), U(<0.0005%), La(<0.0002%). It is evident that the sample is dominated by cadmium, lead, nickel, silver and iron. The minor elements in the sample are tin and copper, while elements such as titanium, molybdenum, antimony, uranium and lanthanum were recorded at trace levels. Oxygen and other components accounted to be 23.31% was obtained by difference.

The X-ray spectrum (Fig. 1) revealed the presence of the following intense compounds: Cadmium calcium, antimony [Cd_2CaSb_2], Itolite ($\text{Pb}(\text{S},\text{Ge})(\text{O},\text{OH})_4$), Copper antimony sulphide [Cu_3SbS_4], Nickel vanadium oxide [$\text{Ni}_2\text{V}_2\text{O}_7$], Silver-tin-sulphide [$\text{Ag}_4\text{Sn}_3\text{S}_8$] hydrated ferrous sulphate [$\text{FeSO}_4\cdot\text{H}_2\text{O}$] and α -quartz (SiO_2). The XRD data also revealed the presence of the following associated compounds occurring from low to trace levels are Titanium oxide fluoride [TiOF_2] and Titanium-manganese silicate [TiMnSiO_2]. All these supported the results of the elemental composition by ICP-MS.

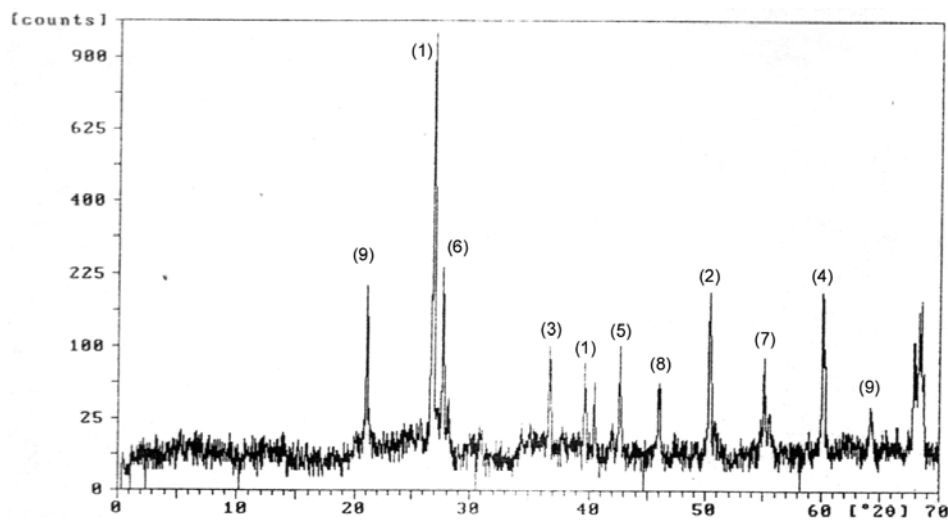


Fig. 1. The XRD Spectra of of a spent cell phone Printed Circuit Board with important compounds detected. The Joint Committee on Powder Diffraction Standard, JCPDS File Numbers are put in curl brackets:

- (1) Cd_2CaSb_2 {31-0087}, (2) $\text{Pb}(\text{S},\text{Ge})(\text{O},\text{OH})_4$ {12-0641}, (3) $\text{Ni}_2\text{V}_2\text{O}_7$ {38-0285},
 (4) $\text{Ag}_4\text{Sn}_3\text{S}_8$ {33-0245}, (5) $\text{FeSO}_4\cdot\text{H}_2\text{O}$ {45-1365}, (6) Cu_3SbS_4 {35-0581},
 (7) TiOF_2 {01-0490}, (8) TiMnSiO_2 {34-0431}, (9) SiO_2 {03-0444}.

Leaching tests

Effect of HCl concentration

The effect of HCl concentration on the rate of the powdered PCB dissolved is shown in Fig. 2. Fig. 2 shows that the powdered PCB dissolution in HCl solution increases gradually at various contact time, up till 2.0 M concentration. It is worthy to note that HCl concentrations above 2.0 M gave rise to the decrease in the amount of Printed circuit board dissolved. The reason for this may be attributed to possible precipitation of metal chloride [16].

Effect of temperature

The rate of powdered Printed circuit board was studied over the temperature range 27-80°C as shown in Fig. 3.

From Fig. 3, it is seen that increasing temperature greatly accelerates the dissolution rate. At 80°C, about 88.49% of the powdered cell phone was dissolved within 120 minutes.

Effect of particle diameter

The effect of particle diameter on the dissolution rate of powdered printed circuit board of spent cell phone was studied by measuring the reaction rates for three size fractions: 0.075-0.116, 0.116-0.212, and 0.212-0.325 mm at 80°C by 2 M HCl solution. The result is presented in Fig. 4.

From Fig. 4, it is observed that particle size with smallest size (0.075-0.116 mm) having the large surface area gave the highest dissolution rate. With 2M HCl solution at 80°C temperature using a stirring rate of 360 rpm, about 88.46% was dissolved within 120 minutes.

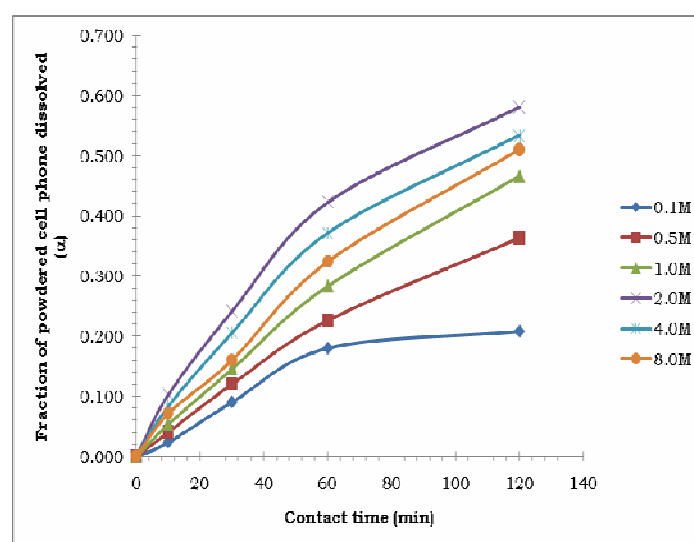


Fig. 2. Fraction of powdered cell phone (PCB) dissolved vs. contact time at various HCl concentrations. Experimental conditions: HCl concentration (0.1 M – 8.0 M), Temperature = 55°C; Solid/liquid ratio = 10 g/L; Particle diameter = 0.075-0.112 mm; Stirring rate = 360 rpm.

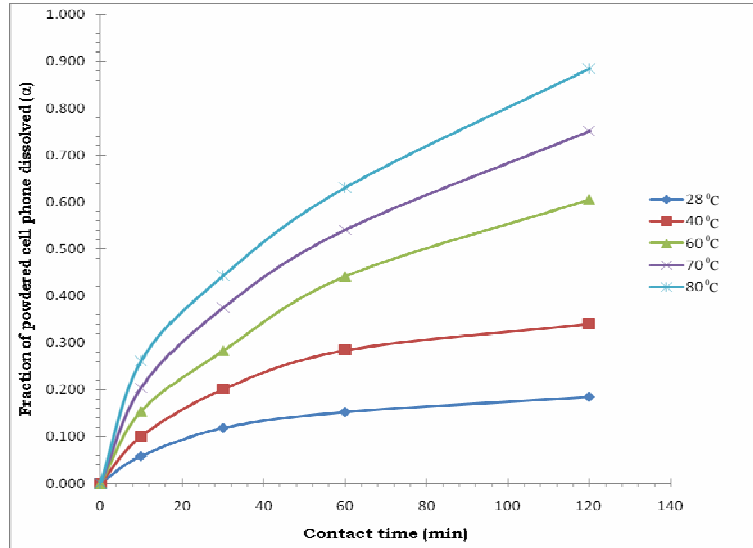


Fig. 3: Influence of temperature on powdered cell dissolved by 2.0 M HCl. Experimental conditions: 2.0 M HCl solution, Temperature (28 – 80°C); Solid/liquid ratio = 10 g/L. Particle diameter = 0.075-0.112 mm; Stirring rate = 360 rpm.

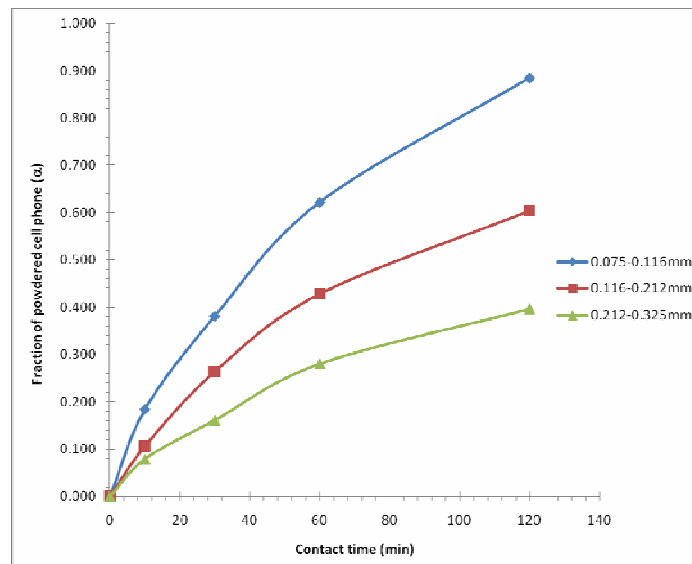


Fig. 4: Fraction of powdered cell phone (PCB) dissolution using different particle diameter.

Experimental conditions: 2.0 M HCl solution, Temperature = 80°C; Solid/liquid ratio = 10 g/L. Particle diameter = 0.075-0.325 mm; Stirring rate = 360 rpm.

Discussions

Evaluation of dissolution kinetics model

Basic understanding of the dissolution kinetics mechanism is the main objectives of this study. Consequently, the dissolution rates of the powdered cell phone were analyzed by two shrinking core models, under the assumption that the sample is a homogeneous spherical solid phase [17-20], according to the following relations:

$$1-(1-\alpha)^{1/3}=k_1t \quad (1)$$

$$1-2/3\alpha-(1-\alpha)^{2/3}=k_2t \quad (2)$$

The relation in equation (1) is applied to chemically controlled processes and equation (2) to diffusion controlled processes through the porous product layer [21]; α is the fraction of powdered spent printed circuit board dissolved at a particular leaching time and k_1 , k_2 are the apparent rate constants for the dissolution process.

It is important to note that, of the two tested model equations, only the relation in equation (1) gave good straight line correlation of about 0.995 and was used for the construction of the following kinetic plots.

In order to decide the order of reaction with respect to the reagent concentration, the results of the effect of HCl concentrations, obtained from Fig. 2 was applied to the kinetic model in equation (1). The apparent rate constants, k_1 values for each HCl concentration was evaluated [22]. From the corresponding k_1 and HCl concentration values, the plot of $\ln k_1$ versus $\ln[\text{HCl}]$ was made (Fig. 5).

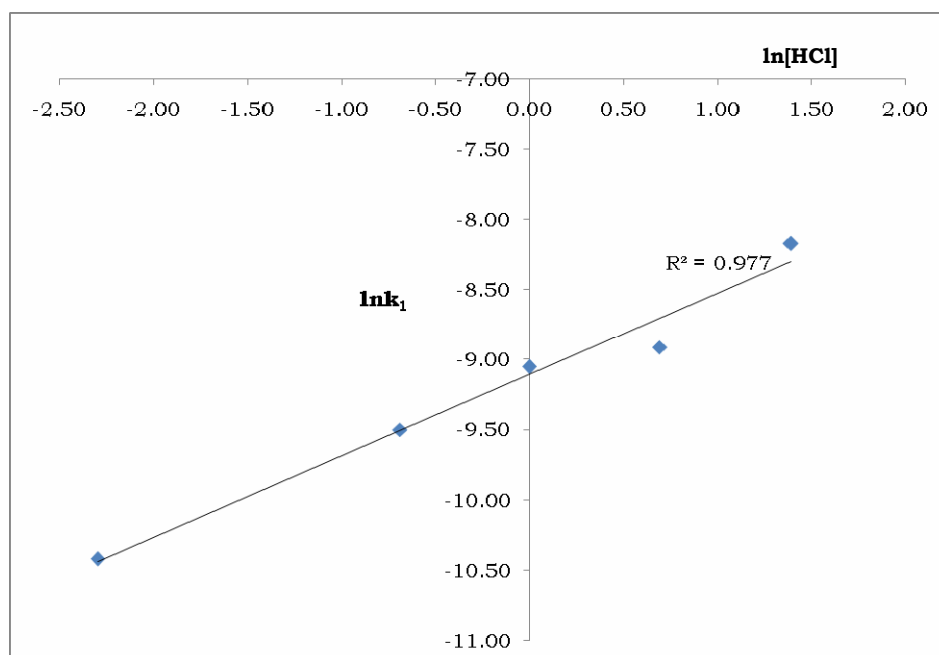


Fig. 5. $\ln k_1$ versus $\ln[\text{HCl}]$ for order of reaction determination.

From the resulting plot in Fig. 5, the order of reaction with respect to HCl concentration was found to be proportional to 0.61, with a correlation coefficient of 0.977.

Also, equation (1) was applied to the data obtained for each temperature (Fig. 3) which gives a straight line (Fig. 6).

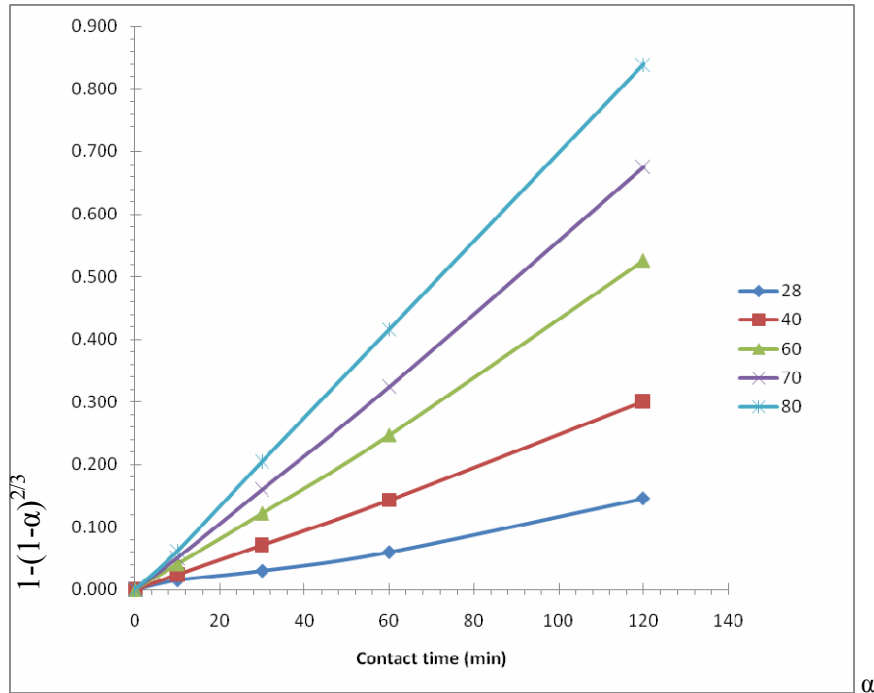


Fig. 6. Plot of $1-(1-\alpha)^{1/3}$ versus leaching time at different temperatures for the data shown in Fig. 3.

From Fig. 6, the apparent rate constants, k_2 , obtained from the slopes of each line were evaluated and was used for the Arrhenius plot of Fig. 7. It is generally accepted that a chemically controlled process is strongly dependent on temperature. The rate constant, k_2 is therefore exponentially dependent on temperature according to the following relation (equation 3) [22]:

$$k_2 = A e^{-E_a/RT} \quad (3)$$

where A is the frequency factor, E_a is the activation energy of the reaction, R is the Boltzmann constant and T is the absolute temperature. Therefore, the activation energy, E_a for the dissolution process was calculated as 60.67 kJ/mol. This value thus indicates a surface chemical reaction control mechanism.

The re-plot of the kinetic curves in Fig. 7 from the origin (Fig. 8) was used to determine the frequency factor, A of 12.9 s^{-1} for the dissolution process [20].

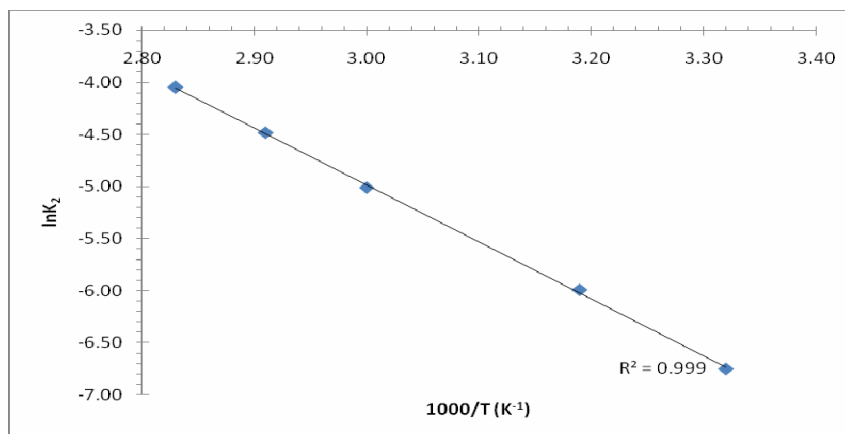


Fig. 7. Arrhenius relation of the data presented in Fig. 6.

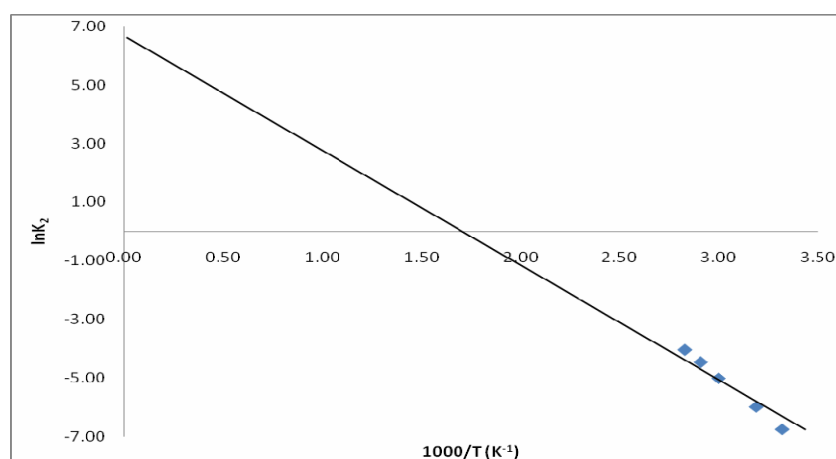


Fig. 8. A re-plot of Fig. 7 from the origin [23].

Finally, the linearization of the kinetic data in Fig. 4 was also carried out using model equation (1). The value of its rate constants, k_3 , determined from the surface chemical reaction model were plotted against the reciprocal of the particle radii ($1/r_0$), giving a perfect straight line with correlation coefficient of 0.987 (Fig. 9). However, the plot of the rate constants against the square of particle radii ($1/r_0^2$) did not give a linear relation. Hence, linearity from Fig. 9 affirmed that a surface chemical reaction is the rate controlling step for the dissolution process [22].

Characterization of reaction products

The residual analysis obtained after optimal leaching of the powdered cell phone by 2 M HCl solution at 80°C showed that the chemical composition consists principally of silicates. This was confirmed by testing for its purity level by analysis of the presence of chloride and other metal ions after thorough washing with de-ionized water by

titrimetric methods. Hence the results affirmed the absence of both chloride and other metal ions in the residue [24].

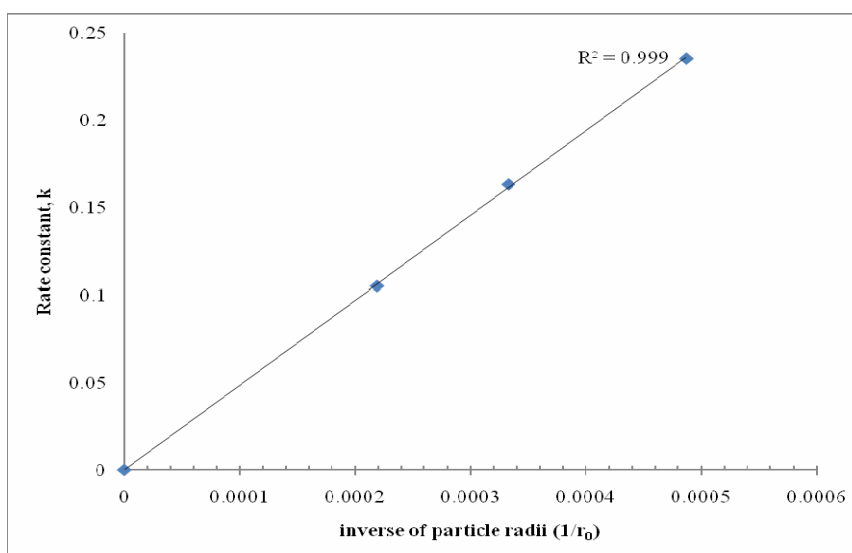


Fig. 9. Variation of Rate constant, k , on inverse of particle radii, ($1/r_0$)

Conclusions

On the basis of the results of dissolution investigations, the following conclusions can be drawn:

- (i) The dissolution kinetics of powdered cell phone (PCB) increases with increasing hydrochloric acid solution and system temperature with decreasing particle diameter at 360rpm stirring rate.
- (ii) The optimum leaching conditions were determined as 2 M HCl solution, 80°C temperature, stirring rate 360 rpm with a particle diameter of 0.075-0.112 mm. Under these conditions, about 88.49% of the powdered spent cell phone was dissolved within 120 minutes. The unleached products, about 11.51% comprised principally of silicates as detected by X-ray diffraction.
- (iii) The dissolution data were analyzed by shrinking core models to follow chemical reaction control with surface diffusion as the rate determining step
- (iv) The estimated order of reaction, activation energy, and frequency factor for the dissolution process were 0.61, 60.67 kJ/mol and 12.9 s⁻¹, respectively.
- (v) Work on the recovery of the metal ions in the leach liquor at the optimal condition is in progress in our laboratory.

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