

Solvent Extraction of Gold from Hydrochloric Acid-Leached Nigerian Gold Ore by Tributylphosphate

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Abstract: This paper presents an experimental study on the dissolution kinetics and solvent extraction of total gold from Ijero-ekiti (Nigeria) gold ore deposit by hydrochloric acid leaching followed by extraction with Tributylphosphate (TBP) in kerosene. The leaching investigation showed that the gold ore dissolution in HCl solution increases with increasing acid concentration, temperature and with decrease in particle diameter at a stirring rate of 300rpm. The kinetics data has been analyzed and was found to follow diffusion control mechanism with surface chemical reaction as the rate limiting step. About 81.27% of the initial 10g/L of the ore concentrate was dissolved within 120 minutes by 2M HCl solution at 80°C using $0.09 < \Phi < 0.12$ mm particle diameter. The analysis of the residual product (18.73% of the initial gold ore) shows that it consists primary of α -quartz. Furthermore, the solvent extraction studies revealed the extraction efficiency of about 85.28% by TBP in kerosene. This was determined by analyzing the orange-red complex of gold with 4-(2-pyridylazo) resorcinol (PAR) spectrophotometrically at 450 nm from the ore leach liquor at optimal conditions. Finally, the calculated enthalpy and entropy change of 3.56kJ/mol and -21.83J/mol/K were obtained for the extraction system, respectively.

Keywords: Gold ore, Nigeria, dissolution kinetics, solvent extraction, gold, hydrochloric acid, tributylphosphate.

1. Introduction

Gold is widely distributed throughout the world, normally in very low concentration and generally in native form as metal. It is usually alloyed with silver and often contains small amount of copper. The only compound of gold found in nature are tellurides, typically calaverite (AuTe_2), petzite [$(\text{AuAg})_2\text{Te}$], sylvanite [$(\text{AuAg})\text{Te}_2$], among others

Gold in Nigeria is found in alluvial and eluvial placers and primary veins from several parts of supracrustal (schist) belts in the northwest and southwest of Nigeria. The most important occurrences are found in Maru, Anka, Malele, Tsohon Birnin Gwari-Kwaga, Gurmana, Bin Yauri, Okolom-Dongodaji and Iperido areas, all in the northwest and southwest Nigeria. The Nigeria Mining Corporation started exploration for Gold in Nigeria in the early 1980s, but failed to be sustained due to lack of funds. The discovery of petroleum and its subsequent domination of the Nigerian economy also contributed to the lack of attention to gold exploration despite the widespread potentials [2].

The enrichment and recovery of gold from the solution is an important stage of production. Gold is usually associated with other noble metals, such as silver and other base metals, such as copper and iron. These metals will enter the leaching solution with gold during leaching, so the separation of gold and these other metals has to be considered during the recovery of gold from the leaching solution [3].

The intrinsic nature of chloride leach liquors resulting from the hydrometallurgical treatment of ores is rather

complex; these solutions usually contain relatively high concentration of basic metals, as well as small contents of other rare metals, frequently precious metals [4].

With gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply the conventional pyrometallurgical methods for metal extraction. Hydrometallurgical processes are suited for lean and complex ores. If there is too much gangue in an ore, then, processing of the ores at high temperature causes waste of energy as well as disposal of slag and also evolution of gaseous pollutant to the environment [5].

Consequently, solvent extraction used in gold recovery offers high capacity, better selectivity and faster kinetics. With the increased popularity of heap leaching of lower grade gold ores, there is scope for the development of solvents to treat these relatively clean, clarified liquors [6]. To the best of our knowledge, there is limited data on the hydrometallurgical processing of gold ore deposit from Nigeria origin as reported by Mesubi et al [7]. Therefore, this work is aimed at presenting a dissolution kinetics and solvent extraction data on total gold recovery from Ijero-ekiti (Nigeria) gold ore deposit by hydrochloric acid leaching followed by extraction with Tributylphosphate in kerosene. Gold analysis was carried out by measuring spectrophotometrically its complex with 4-(2-pyridylazo) resorcinol.

2. Experimental

The gold ore concentrate used for this study was sourced from Ijero-ekiti origin, Ekiti State of Nigeria. The elemental analysis of the gold ore concentrate was carried

out by Inductively Coupled Plasma-Mass Spectrometry (Yokogawa model HP-4500) and the test for the mineralogical purity was examined by X-ray diffractometer (Philips PW 1800).

All chemicals and reagents used were of analytical grade. The doubly distilled water and distilled kerosene were used in the preparation of all aqueous and extractant solutions, respectively.

2.1. Concentrate processing

The gold ore concentrate was grinded with the aid of mortar and pestle in order to decrease the particle size. The powdered concentrate was then sieved into three different sizes: $0.09 < \Phi < 0.12\text{mm}$, $0.12 < \Phi < 0.212\text{mm}$ and $0.212 < \Phi < 0.345\text{mm}$ and the fraction with diameter $0.09 < \Phi < 0.12\text{mm}$ was retained for subsequent investigations by ICP-MS and XRD [8]. Dissolution studies by acid leaching were also examined using this sized fraction unless otherwise stated. All measurements were carried out in triplicate.

2.2. Leaching procedure

A 1.0g of the gold ore concentrate of particle diameter $0.09 < \Phi < 0.12\text{mm}$ was put into a glass reactor containing 0.1M HCl solution and the magnetic stirrer was introduced into the reactor containing the sample mixture on the Bibby stuart hotplate. The sample mixture was then heated at a temperature of $55\text{ }^{\circ}\text{C}$ and stirred at the rate of 300rpm. The same procedure was repeated for other concentration of HCl: 0.5M – 4.0M. Each HCl sample was contacted with 1.0g of the powdered concentrate for 10, 30, 60, and 120 minutes, respectively. At the end of the leaching process and for a given contact time, the mixture was allowed to cool and filtered using a Whatmann filter paper and then oven-dried at $60\text{ }^{\circ}\text{C}$ for about 12 hours and was then reweighed. The percentage of sample dissolved, α , was calculated from the initial mass (m_i) and from the undissolved amounts at various time intervals dissolved (m_f), by using the relation: $\alpha(\%) = (m_i - m_f)/m_i \times 100$ [9]. This calculation was done for all concentrations of HCl investigated. The concentration which gave the highest percentage of dissolution (2M) was used for the optimization of other parameters including temperature and particle size. The activation energy and Arrhenius constants were obtained from the Arrhenius relation [10]. The residue at the optimal condition was also analyzed for the presence of chloride and other metal ions after thorough washing by de-ionized water [11, 12].

2.3. Solvent Extraction Procedure

Batch experiments were carried out at ambient temperature ($25 \pm 2\text{ }^{\circ}\text{C}$) by equilibrating equal volume of 1M TBP in kerosene and 25mL of metallic gold dissolved in aqua regia with Gallenkamp orbital shaker (AMPS) for 30 minutes. The equilibrium distribution of metals between the aqueous and organic phase was determined by mixing the two phases using a magnetic stirrer. The solution pH was 2.5 and was adjusted by addition of a very small

volume of dilute H_2SO_4 or NaOH solution under agitation to prevent precipitation of elemental sulphur. An equal amount of the organic phase was added to maintain a fixed phase ratio of 1:1. When equilibrium was reached, stirring was stopped. The gold content in the aqueous phase was determined using AQUAMATE Thermo-electron Corporation UV-visible spectrophotometer [13, 14].

The same procedure was repeated for the analysis of the total gold from the leached liquor from section 2.2.2 at optimal condition.

2.4. Total gold analysis

The total gold analysis in the metallic gold solution and the leachate was determined spectrophotometrically by measuring the change in absorption of the reaction at 450nm. For each determination, 5ml of the gold solution or leachate was measured into 10ml volumetric flask and 2mL PAR (4-pyridyl 2-azo resorcinol), 0.6mL buffer of pH 9.25 were added and then make up to mark with doubly distilled water. This chromogenic mixture was left for 10 minutes for complexation after which a portion of the solution was transferred into 1.0cm quartz cell and the absorbance was measured and recorded at 450nm. The standard calibration curve of the change of absorbance of the different total gold concentration was constructed. This procedure was also used in determining the concentration of total Gold in the leach liquors.

3. Results and Discussion

3.1. Results of the gold ore concentrate elemental and phase studies by ICP-MS and XRD

The elemental analysis of the gold concentrate showed that Au(14.42%), Ta(1.65%), Fe(2.42%), Te(1.23%), S(0.14%), Si(12.09%) and Ag(0.97%) form the major elements. Other minor elements include Ti(0.049%), Zn(0.027%), Cu(0.051%), Sb(0.034%) and Pb(0.021%). However, elements such as W(0.0014%), Mg(0.0007%), Ni(0.00016%) and V(0.00025%) are recorded at trace levels. The remaining 66.89%, obtained by difference is attributed to the presence of oxygen and other components in the concentrate.

Also, the result of the mineralogical purity by X-ray diffraction is shown in Fig. 1.

It is important to note that the predominant compounds identified from Fig. 1 include sylvanite $[(\text{AuAg})\text{Te}_2]$ and silica ($\alpha\text{-SiO}_2$). Other minerals present in the concentrate are pyrrhotite (Fe_7S_8), ilmenite (FeTiO_3), tantalum oxide (Ta_2O_5) and chalcocite (Cu_2S). The results obtained from the XRD analysis supported the elemental composition by ICP-MS.

3.2. Leaching test

3.2.1. Effects of HCl concentration

The results obtained as seen in Fig. 2 showed that the rate of gold ore concentrate dissolution is affected directly by the hydrogen ion $[\text{H}^+]$ concentration. This is true up to

HCl, 2M concentration, after which there was a decline in the amount of the gold ore dissolved. Thus, 4M HCl concentrations gave a relatively lower value when

compared to 2M HCl dissolution. The reason for this decline could be probably due to the precipitation phenomenon [10].

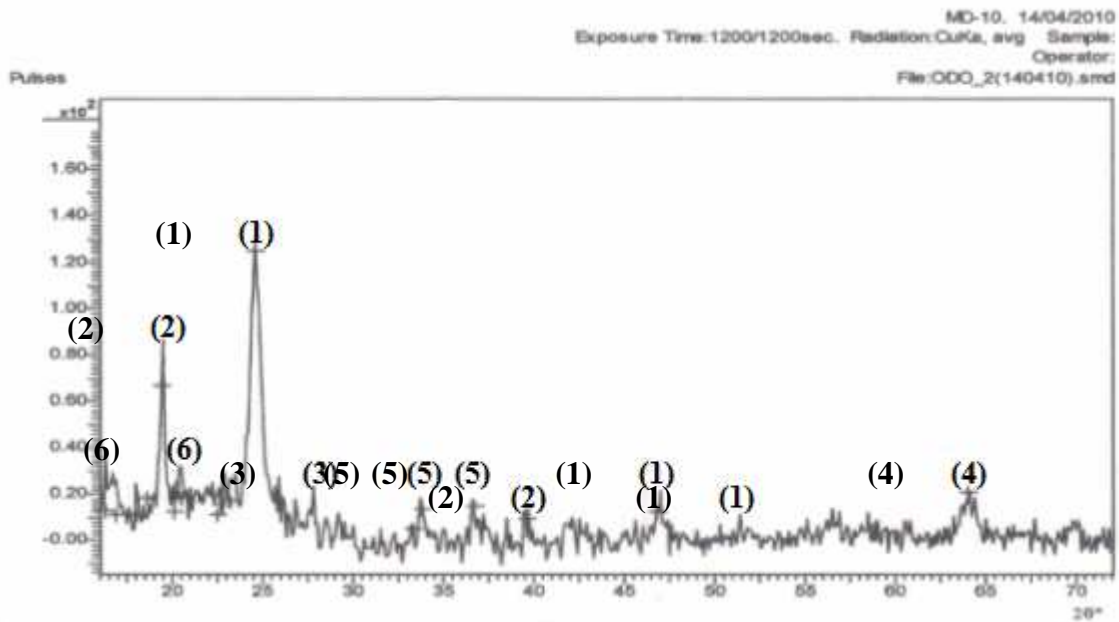


Figure 1. The X-ray spectra of Ijero-ekiti gold ore concentrate showing the most important compounds identified. The Joint Committee on Powdered Diffraction Standards (JCPDS) file numbers is in curl bracket. (1) (AuAg)Te₂ {29 - 1427}, (2) α-SiO₂ [46 - 1045], (3) Fe₇S₈{24-0079}, (4)FeTiO₃ {29-1360}, (5) Ta₂O₅ {13-4025}, (6) Cu₃S {33-0490}

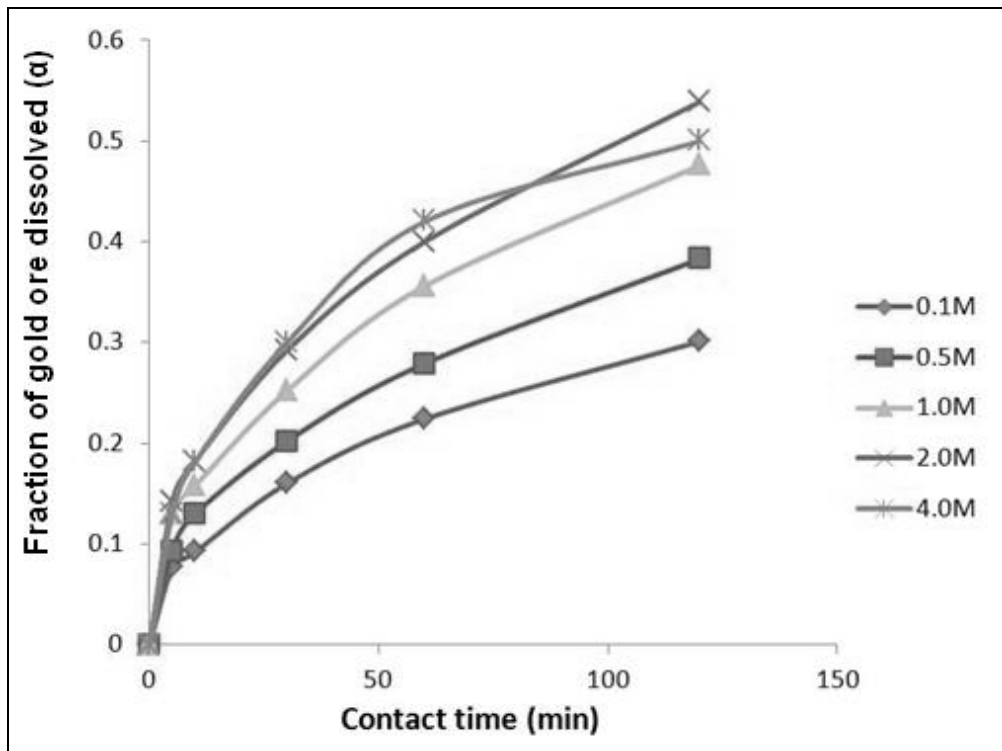


Figure 2. Fraction of gold ore concentrate dissolved versus contact time at different HCl concentration
 Experimental conditions: Mass of concentrate used = 10g/L, HCl concentration = 0.1M – 4.0M, System temperature = 55°C, Stirring rate = 300rpm, Particle diameter = 0.09 Φ <math>< 0.12\text{mm}</math>

3.2.2. Effect of system temperature

The rate of gold ore concentrate dissolution was studied over the system temperature ranges of 27 °C to 80 °C. The result are shown in Figure 3. As expected, increasing the system temperature greatly accelerates the dissolution rate.

3.2.3. Effect of particle diameter

The influence of particle diameter on the rate of gold ore concentrate dissolution was examined by 2M HCl solution at a system temperature of 80 °C over three sized fractions: $0.09 < \Phi < 0.12$, $0.12 < \Phi < 0.212$ and $0.212 < \Phi < 0.345$ mm.

As seen from Table 1, the rate of the ore dissolution in HCl media is inversely proportional to the average initial diameter of the ore particles.

TABLE 1. Results of the influence of particle diameter on gold ore dissolution

| Particle diameter (mm) | Fraction of gold ore dissolved |
|------------------------|--------------------------------|
| $0.09 < \Phi < 0.12$ | 0.827 |
| $0.12 < \Phi < 0.212$ | 0.534 |
| $0.212 < \Phi < 0.345$ | 0.261 |

3.3. Dissolution rates analysis

Understanding the dissolution kinetics of the gold ore concentrate is one of the aims of this study. Therefore, the rate of the ore dissolution was analyzed with the shrinking core models based on the assumption that the concentrate is

a homogenous spherical solid phase [15].

Since the rate of a heterogeneous process is directly proportional to the surface area of the reaction solid, then the kinetic model of such reaction must account for the diminishing surface area of the solid. Hence, two shrinking core models defined by equations (1) and (2) were used to interpret the dissolution rates in this study:

$$1 - (1 - \alpha)^{1/3} = k_1 t \quad (1) \quad [9, 12, 16]$$

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = k_2 t \quad (2) \quad [10, 17, 18]$$

From equations (1) and (2), α is the fraction of gold ore concentrate reacted at contact time, t and k_1 , k_2 are the apparent reaction rate constants. Model equation (1) is based on the assumption that the rate controlling step occurs by surface chemical reaction, and the model equation (2) is on the assumption that the rate controlling step is by diffusion through a semi-permeable product layer.

It is worthy to note that out of the two kinetic models tested in this study, only equation (2) has been found to give a perfect straight line with average correlation of 0.989. Consequently, the kinetic data in Fig. 2 was linearized by means of model equation (2) as seen in Fig. 4.

The resulting slopes of each line in Fig. 4 were calculated and these represent the apparent reaction rate constants k_1 . The plot of this relation, $\ln k$ as a function of $\ln[\text{HCl}]$ was obtained (Fig. 5), from which the reaction order of 0.47 was derived. This value suggests that the order of reaction with respect to HCl concentration is half (1/2) order for the ore dissolution process.

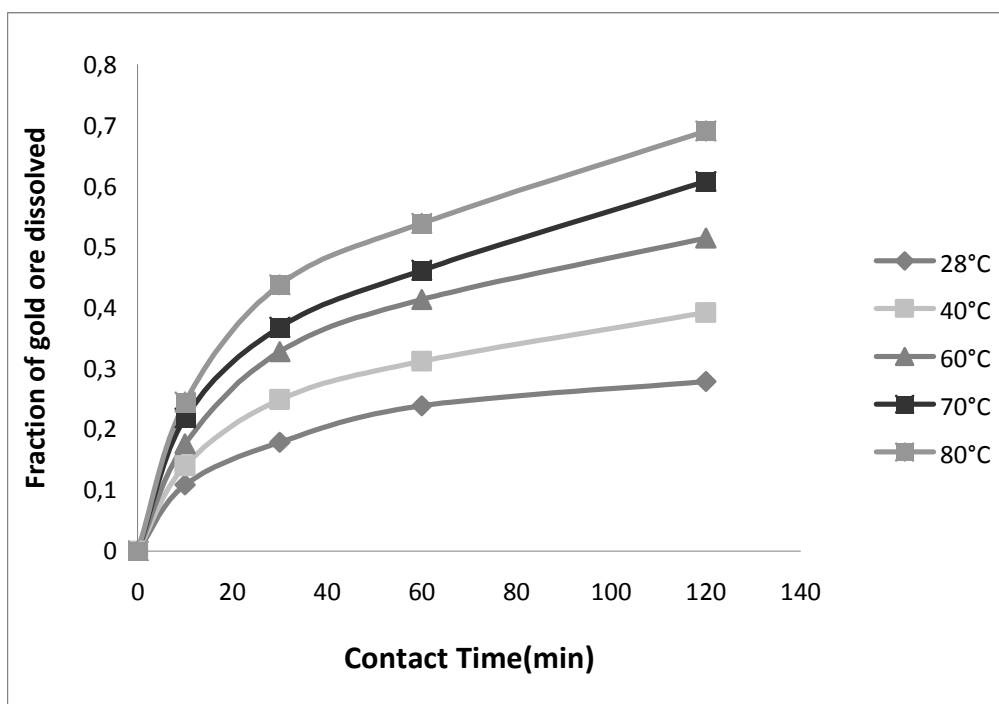


Figure 3. Fraction of gold ore concentrate dissolved versus contact time at different temperatures. Experimental conditions: Mass of concentrate used = 10g/L, HCl concentration = 0.1M – 4.0M, System temperature = 55°C, Stirring rate = 300rpm, Particle diameter = $0.09 < \Phi < 0.12$ mm

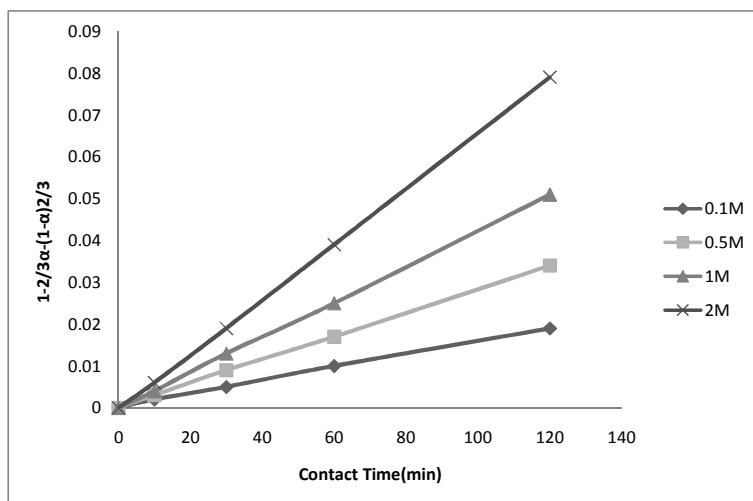


Figure 4. Plot of $1 - 2/3\alpha - (1 - \alpha)^2/3$ versus contact time at different HCl concentration for the data extracted from Fig. 2.

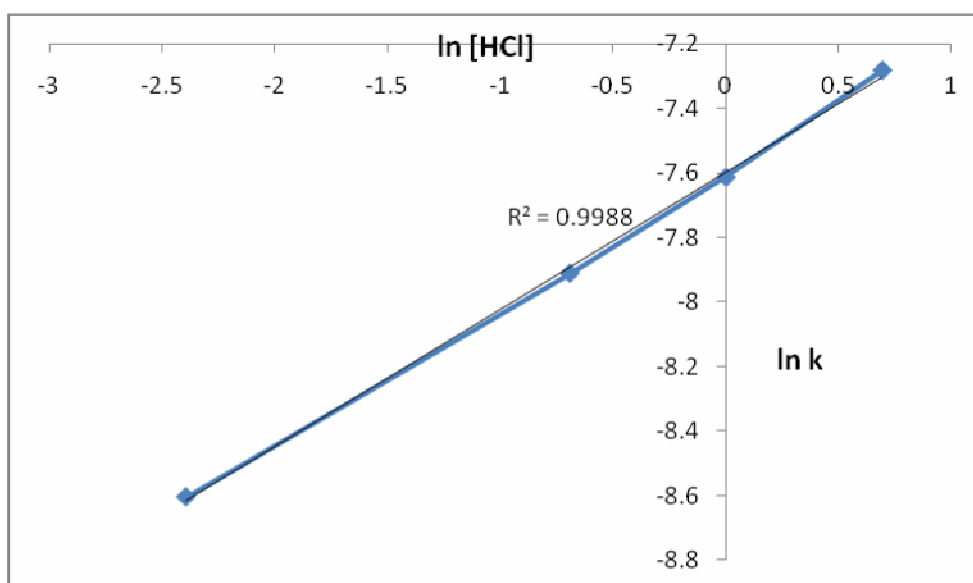


Figure 5. $\ln k$ versus $\ln [HCl]$

Also, the linearization of dissolution data in Fig. 3 was done using equation (2) to obtain the kinetic relation shown in Fig. 6.

The apparent rate constants, k_r derived from the slope of the linear plots in Fig. 6 were used to determine the activation energy, E_a as shown in Fig. 7. The Fig. 7 clearly shows that the kinetic data fitted relatively well into the surface diffusion model as proposed by several authors including Zuo-mei, et al [16]. Hence, the E_a determined using this surface diffusion kinetic model was 18.23kJ/mol.

This value falls within the range expected for the rate of surface diffusion reaction [17].

The Arrhenius constant for the dissolution process was found to be $12.43s^{-1}$. This was obtained from the re-plot of Fig. 7 from the origin [10, 18]. Finally, the linearization of the kinetic data in Table 1 was also carried out by means of equation (2). Consequently, the value of the rate constant k were then plotted against the reciprocal of the particle radii ($1/r_0$), yielding a linear relation (Fig. 8).

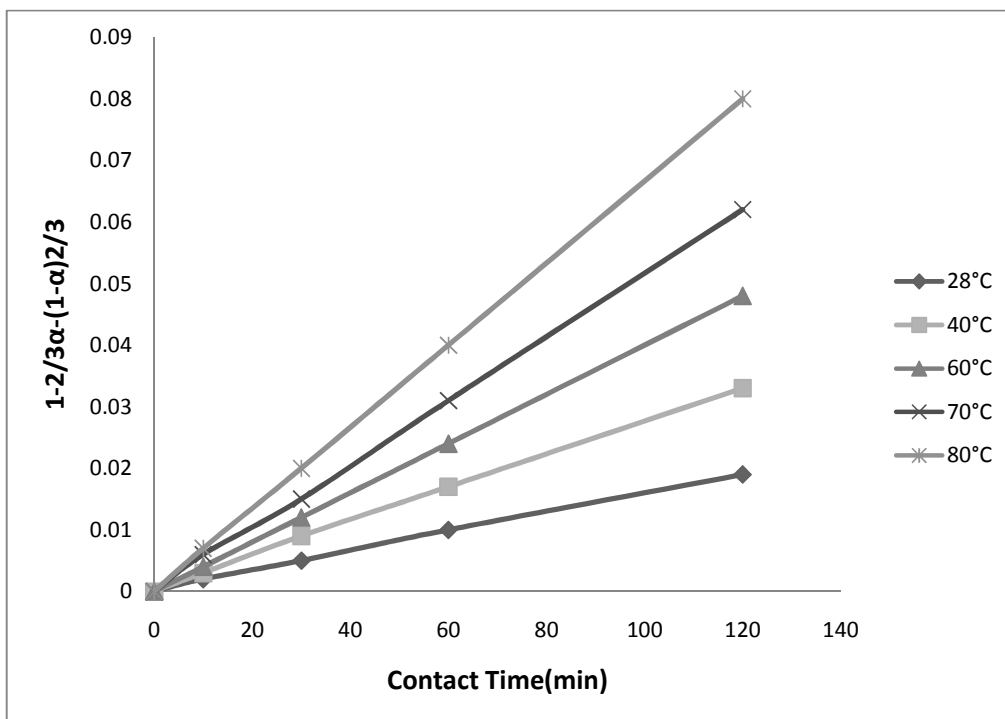


Figure 6. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus contact time at various temperatures

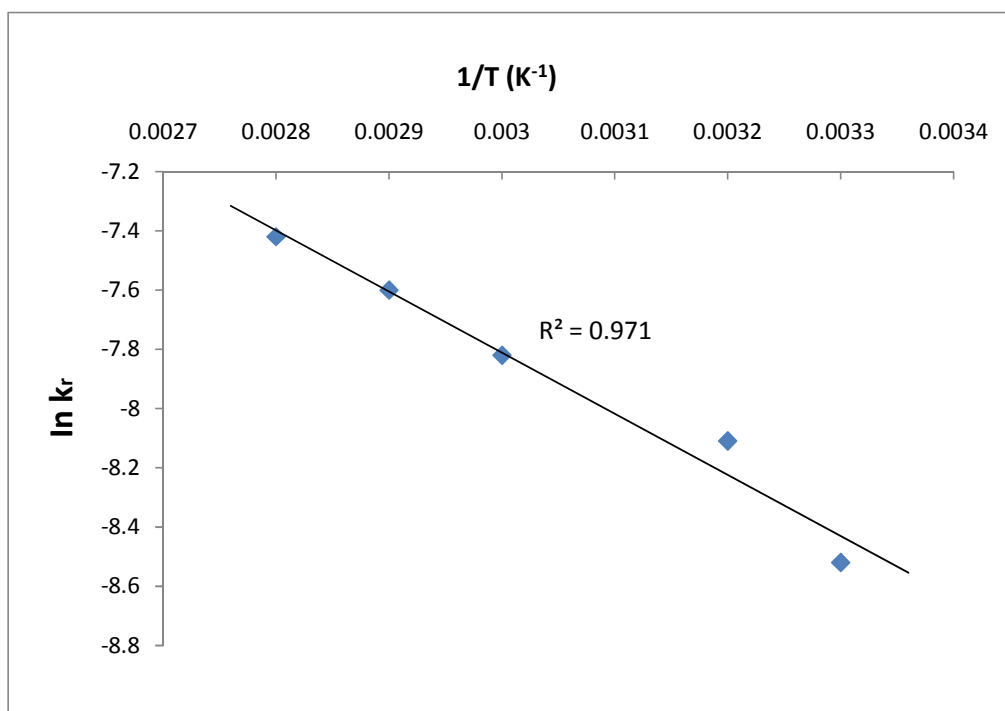


Figure 7. Arrhenius plot of $\ln k_r$ versus $1/T(K^{-1})$

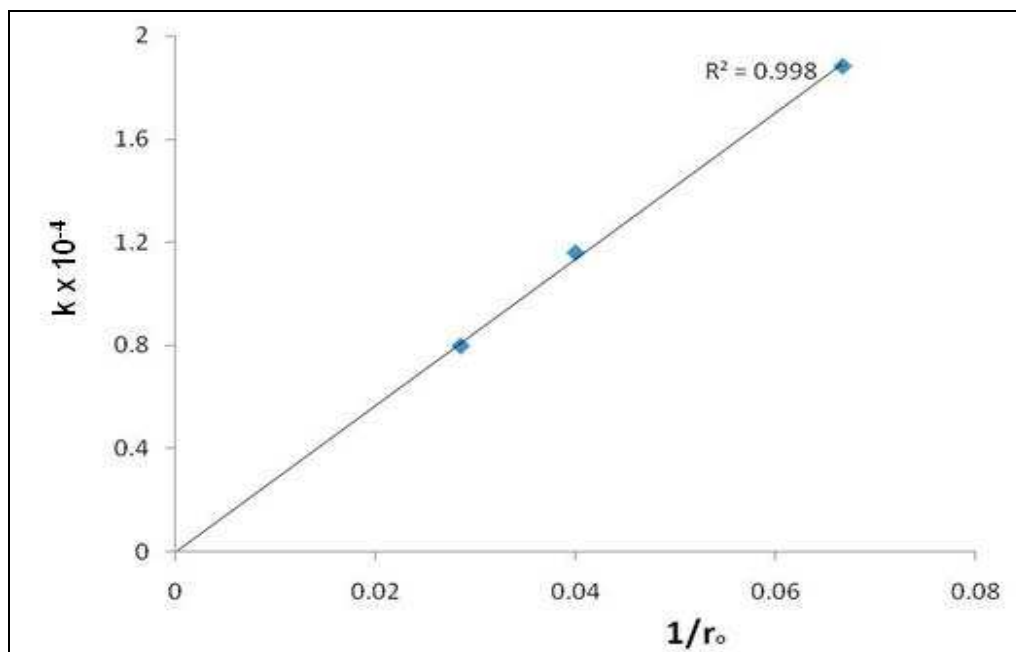


Figure 8. Plot of rate constant, k on inverse of particle radii

However, the plot of the rate constant k versus the square of the particle radii ($1/r_0^2$) did not result to a linear relation. Thus, the linear dependence of rate constants, k on the inverse of initial particle diameter indicates that a surface chemical reaction is the rate limiting step for the ore dissolution process [18]. Hence, the mechanism of the dissolution therefore follows the diffusion model via the influence of H^+ ion diffusing from the bulk of the solution into the gold ore concentrate.

The analysis of the post-leached residue obtained by leaching gold ore concentrate at $80^\circ C$ by 2M HCl solution for 120 minutes showed that the unreacted product consist primarily of silica (α -quartz). Its purity level was analyzed for the presence of chloride or other metal ions after thorough washing with de-ionized water following the standard procedure [19]. The results of these findings

showed the absence of both chloride and other metal ions in the post-leached residue [12].

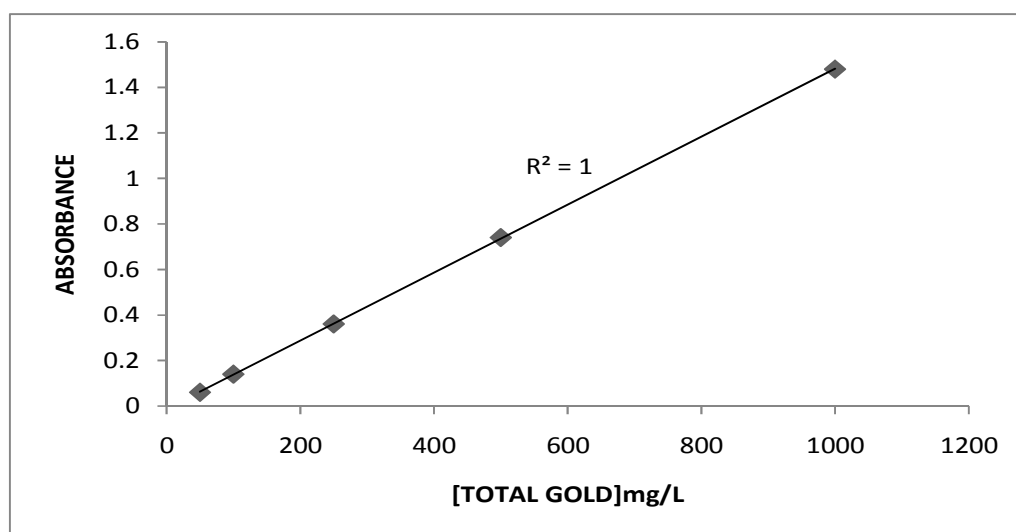
3.4. Solvent extraction studies

3.4.1. Working curve for total gold analysis

The calibration curve for total gold analysis by spectrophotometric technique used in this study is represented in Fig. 9.

3.4.2. Influence of extractant concentration on total gold extraction

The result of the influence of extractant concentration on the rate of total Gold extracted from the leached gold ore concentrate is shown in Fig. 10.

Figure 9. Calibration curve for the total gold analysis ($\lambda_{max} = 450nm$)

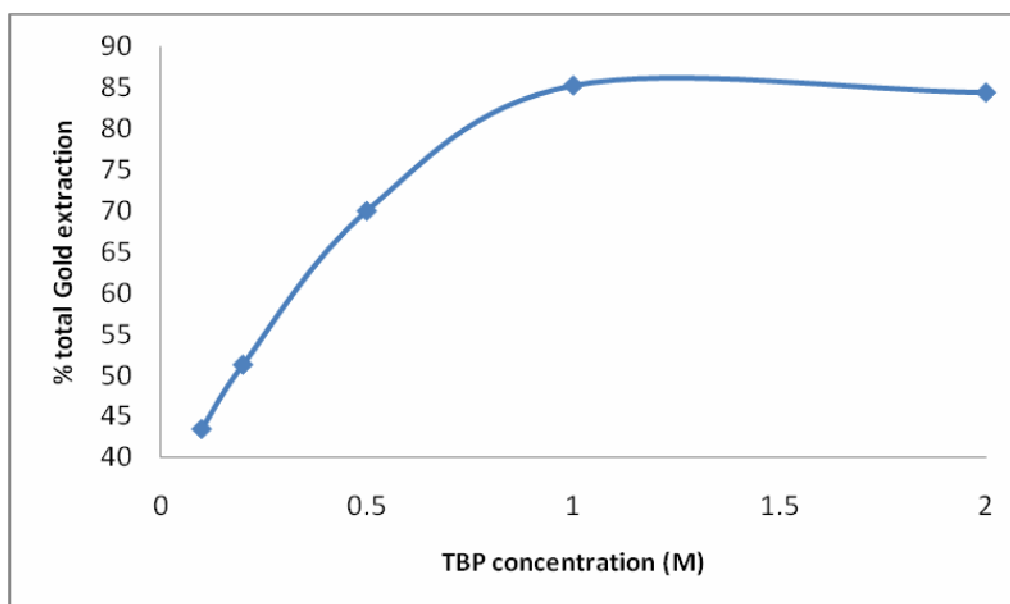


Figure 10. Result of the extractant concentration on total Gold extraction.
 Experimental conditions: Temperature = $25 \pm 2^\circ\text{C}$, TBP concentration = 0.05M – 2.0M

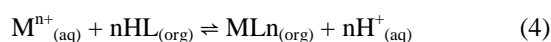
From Fig. 10, it results that an increase in the extractant concentration (0.05M – 1.0M TBP in kerosene) leads to a simultaneous increase of total gold extraction, since the ratio of the TBP concentration to total gold increases. Hence, increase in the initial TBP concentration in the organic phase considerably improve the extraction efficiency and thus reaches a maximum at 1.0mol/L TBP when about 85.28% total gold has been extracted.

3.4.3. Influence of temperature on the total Gold extraction

The effect of temperature on the total Gold extraction by TBP in kerosene was examined. As seen from Table 2, the temperature increase led to the decrease of both total efficiency of gold extraction and equilibrium constant [19]. The reaction is endothermic pathway. The evolution of the free energy change as a function of system temperature (Table 2) was drawn using the relation:

$$\Delta G = -RT \ln K \quad (3)$$

The equilibrium constant, K in equation (3) is proportional to temperature coefficient extractability expressed in terms of reacting species according to the following equation:



The reagent HL = TBP, initially dissolved in kerosene reacts with a metal ion, M^{n+} (leachate) in aqueous solution to form a product, MLn [20].

TABLE 2. Values of equilibrium constant, K and the free energy, ΔG for total Gold extraction versus system temperature

| | temperature, t ($^\circ\text{C}$) | | | |
|---------------------------|---------------------------------------|--------|--------|--------|
| | 27 | 32 | 37 | 42 |
| Total Gold extraction (%) | 85.28 | 78.14 | 72.59 | 64.11 |
| K (mol/L) $\times 10^3$ | 868.15 | 641.33 | 503.49 | 387.27 |
| ΔG (kJ/mol) | 23.33 | 24.48 | 25.09 | 26.61 |

The free energy, ΔG , for the ore dissolution is related to the entropy and enthalpy by the relation:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The plot of the relation between ΔG and the system temperature is shown in fig. 11.

From Fig.11, the slope of the resulting line is positive ($\Delta G > 0$). From this positive slope, it results: $\Delta G = -\Delta S$ and entropy change for the system is -21.83J/mol/K . Therefore, the system enthalpy was calculated from equation (5) to obtain 3.56kJ/mol and thus suggesting the endothermic pathway for the ore dissolution process. This positive value is amenable to some reported literature works which proposed that most extraction processes are endothermic [19].

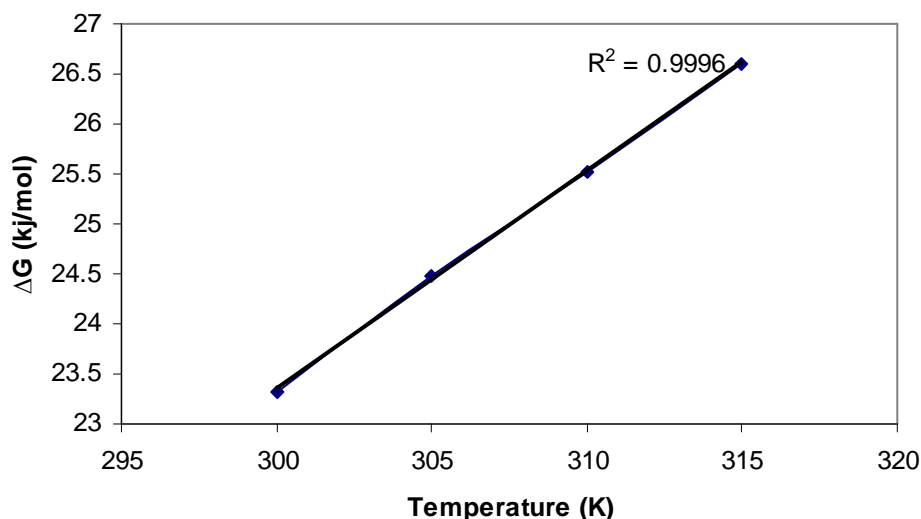


Figure 11. Dependence of free energy as a function of temperature

4. Conclusions

On the basis of experimental results, this study has shown that Ijero-ekiti (Nigeria) gold ore concentrate is amenable to hydrometallurgical treatment by hydrochloric acid leaching prior solvent extraction by TBP in kerosene. The leaching studies showed that the gold ore dissolution in HCl solution increases with increasing acid concentration and temperature and with a decrease in particle diameter at a stirring rate of 300rpm. With 2M HCl solution, about 81.27% of gold ore concentrate was dissolved within 120 minutes at temperature of 80°C by 0.09Φ<math><0.12\text{mm}</math> particle diameter. The calculated order, activation energy and Arrhenius constant of 0.47, 18.23kJ/mol and 12.43s⁻¹ were obtained for the dissolution process, respectively. The results of the dissolution studies showed that the kinetic data fitted diffusion control mechanism with surface chemical reaction as the rate limiting step. Finally, the results of the solvent extraction studies revealed the possibility of extracting the total gold from the gold concentrate leach liquor at optimal condition of about 85.28% by TBP in kerosene. The estimated enthalpy and entropy change of 3.56kJ/mol and -21.83J/mol/K were obtained for the system at 25±2°C, respectively.

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