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Comparative analysis of the dissolution kinetics of galena in binary solutions of HCl/$FeCl_3$ and HCl/H_2O_2

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Abstract: A comparative study of the dissolution kinetics of galena ore in binary solutions of $FeCl_3$/HCl and H_2O_2/HCl has been undertaken. The dissolution kinetics of the galena was found to depend on leachant concentration, reaction temperature, stirring speed, solid-to-liquid ratio, and particle diameter. The dissolution rate of galena ore increases with the increase of leachant concentration, reaction temperature, and stirring speed, while it decreases with the increase of solid-to-liquid ratio and particle diameter. The activation energy (E_a) of 26.5 kJ/mol was obtained for galena ore dissolution in 0.3 M $FeCl_3$/8.06 M HCl, and it suggests the surface diffusion model for the leaching reaction, while the E_a value of 40.6 kJ/mol was obtained for its dissolution in 8.06 M H_2O_2/8.06 M HCl, which suggests the surface chemical reaction model for the leaching reaction. Furthermore, the linear relationship between rate constants and the reciprocal of particle radius supports the fact that dissolution is controlled by the surface reaction in the two cases. Finally, the rate of reaction based on the reaction-controlled process has been described by a semiempirical mathematical model. The Arrhenius and reaction constants of 11.023 s^{-1}, 1.25×10^4 and 3.65×10^2 s^{-1}, 8.02×10^6 were calculated for the 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl binary solutions, respectively.

Keywords: galena; hydrochloric acid; chloride compounds; hydrogen peroxide; dissolution; leaching

1. Introduction

Galena (PbS), a natural mineral form of lead sulphide, is the most important lead ore [1]. Pyrometallurgical processes are commonly used for the extraction of lead from galena concentrates. However, hydrometallurgical processes have recently been proposed as a good substitute based on environmental considerations [2]. The hydrometallurgical route comprises leaching of the ore and solvent extraction as important operational units.

A good number of authors have carried out leaching studies on galena using oxidative and nonoxidative reagents [3-5, 6-7]. The oxidative reagents used included ferric salts and hydrogen peroxide [3-5].

Ferric chloride leaching in the presence of hydrochloric acid and/or sodium chloride has been proven to be a possible means of extracting lead [8-9]. Hydrogen peroxide is another strong oxidant that has been found to be environmentally safe for use as a leachant [3].

Surface species found on galena during oxidation and dissolution has been characterized using many techniques [14]. It was assumed that complexation takes place at the surface of hydrous galena sulphides. The adsorption of H^+ ions onto the surface of S atoms in the aqueous phase was found to be favorable, while the adsorption onto the surface of Pb atoms was not favorable [14]. Hence, the present study is necessary for the understanding of the synergistic effect of 8.06 M HCl in 0.3 M $FeCl_3$ and 8.06 M H_2O_2 solutions on galena ore. The present study is therefore devoted to the comparison of the oxidizing effect of hydrogen peroxide and that of ferric chloride in hydrochloric acid medium *viz*-a-*viz* the dissolution of galena ore. To the best of our knowledge, no previous study of this nature has been documented on Nigeria galena ore except the work reported by Olanipekun [11] on the quantitative leaching of the ore in HCl. This author, however, did not investigate the dissolution mechanism of the ore.

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2. Materials and methods

The galena ore used for this study was from Abakaliki-Enyigba deposit in the Ebonyi State of Nigeria. The sample was finely pulverized and sieved into four fractions: −112+63, −250+112, −500+250, and >500 mm. All experiments were performed with −112+63 mm fraction except otherwise stated. Doubly distilled water and reagent grade (BDH) chemicals were used to prepare all the solutions. Chemical analysis of the ore by X-ray fluorescence (XRF) had earlier been reported [12-13]: Pb (58.66wt%), S (13.31wt%), Sn (2.65wt%), Fe (0.50wt%), and Zn (0.16wt%) occurred as major elements; while Sr (0.087wt%), Te (0.0043wt%), and Li (0.00012wt%) occurred in traces. The percent of oxygen (O) obtained by difference was 24.6wt%. The X-ray diffractogram of the ore showed characteristics as galena diffraction peaks at 0.293, 0.191, and 0.182 nm, respectively; other associated minerals include α-SiO_2, ZnS, FeS_2, and SnO_2.

The dissolution experiments were investigated in a 250-mL glass reactor equipped with a mechanical stirrer. The reactor was filled with 100 mL HCl solutions (0-12 M) at constant 0.3 M $FeCl_3$ and then heated to the desired temperature [3-4, 12-14]. After adding 100 mL HCl and $FeCl_3$ at the desired concentrations into the reactor and heating to 55°C, 10 g/L of galena ore was added. The concentration that gave the maximum dissolution (8.06 M HCl in 0.3 M $FeCl_3$) was subsequently used for the optimization of other leaching parameters including temperature and particle size. The energy of activation (E_a) and rate constants were calculated from the Arrhenius plots. For all the experiments, the fraction of the galena ore dissolved were evaluated from the difference in weight of the amount dissolved or undissolved at various constant time up to 120 min, after oven drying at about 60°C. The post-leached residue at 80°C after galena dissolution in 0.3 M $FeCl_3$/8.06 M HCl was also subjected to XRD examination.

The same procedure discussed above was adopted for dissolution investigations in H_2O_2/8.06 M HCl binary medium. Each experiment was repeated at least three times, and the results were averaged for the evaluation of the experimental results [3-4, 12-14].

3. Results and discussion

3.1. Dissolution of galena

3.1.1. Effect of the solid-to-liquid ratio

The effects of the solid-to-liquid ratio on the percent dissolution are summarized in Table 1.

Table 1. Influence of solid-to-liquid ratio on galena dissolution in 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl solutions within 120 min at different temperatures

Ratio of solid to liquid / ($g{\cdot}mL^{-1}$)	Dissolved galena in 0.3 M $FeCl_3$/8.06 M HCl / wt%		Dissolved galena in 8.06 M H_2O_2/8.06 M HCl / wt%	
	55°C	80°C	55°C	80°C
1:100	71.44	97.09	72.19	98.11
1:20	46.95	71.92	49.24	73.33
1:10	28.33	50.03	30.40	53.96
1:5	15.06	39.48	18.35	41.55

As expected, higher dissolution was achieved with the solid-to-liquid ratio of 1:100, corresponding to 10 g/L. For this, about 97wt% and 98wt% of galena were dissolved within 120 min at 80°C in 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl, respectively. The results further show an increase in the amount of the galena ore dissolved with temperature. The solid-to-liquid ratio of 1:100 was kept for subsequent experiments.

3.1.2. Effect of stirring rate

The effects of stirring speed on the rate of galena dissolution in 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl solutions are shown in Table 2.

Table 2. Effect of stirring rate on galena dissolution in 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl solutions

Stirring rate / min^{-1}	Galena dissolved / wt%	
	0.3 M $FeCl_3$ in 8.06 M HCl	8.06 M H_2O_2 in 8.06 M HCl
0	56.9	58.2
90	67.8	69.8
180	78.7	81.4
270	85.7	92.6
360	94.3	98.1
450	97.1	98.1
540	97.0	98.0
630	97.0	98.0
720	97.0	98.0

Experimental conditions: temperature, 80°C; particle size, −112+63 mm; ratio of solid to liquid, 10 g/L; contact time, 120 min.

It is evident in Table 2 that the amount of galena dissolved depends greatly on the stirring rate over the range 0-450 and 0-360 r/min for dissolution action with the solution of 0.3 M $FeCl_3$ in 8.06 M HCl and the solution of 0.3 M $FeCl_3$ in 8.06 M H_2O_2, respectively. A slightly higher percentage (98wt%) was obtained for H_2O_2/HCl compared to 97wt% dissolution obtained for $FeCl_3$/HCl at 450 r/min.

3.1.3. Effect of leachant concentration

(1) Effect of ferric chloride concentration on galena dissolution

In order to determine the effect of ferric ion concentration on galena dissolution, experiments were performed by varying the initial FeCl$_3$ concentration. HCl was kept constant at 0.1 M [17]. The results are illustrated in Fig. 1.

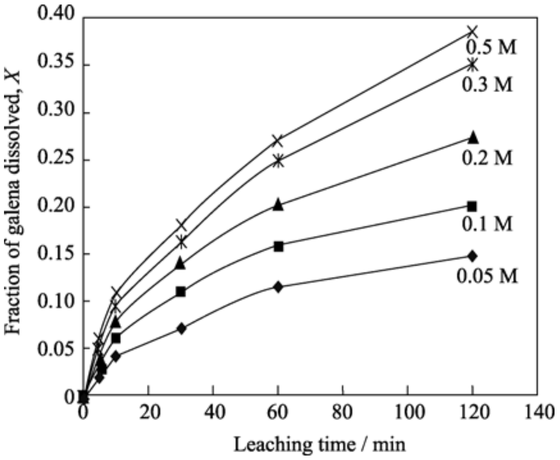

Fig. 1. Effect of ferric chloride concentration on galena dissolution (experimental conditions: particle size, −112+63 mm; ratio of solid to liquid, 10 g/L; stirring rate, 360 r/min; temperature, 55°C).

In Fig. 1, it is evident that the fraction of galena dissolved increases with the increase of ferric chloride concentration. This is particularly true when the Fe^{3+} ion concentration is increased from 0.1 to 0.3 M, after which no further increase in galena dissolution is recorded. This could be due to the formation of sparingly soluble lead chloride accelerated by the presence of Fe(III) ions. Therefore, lower dissolution occurs as a result of the low solubility of lead chloride at low chloride concentrations [18]. Hence, 0.3 M FeCl$_3$ in 0.1 M HCl solution was chosen as the optimum concentration [14] and was used for further investigations.

(2) Effect of FeCl$_3$ and H$_2$O$_2$ concentrations in the presence of various HCl concentrations

The dependence of hydrogen ion (H$^+$) concentration in the presence of 0.3 M FeCl$_3$ on the fraction of galena dissolved was investigated at various HCl concentrations in the range of 0.1-12 M at 55°C. The results are shown in Fig. 2. The highest dissolution of the ore was obtained in a mixture of 8.06 M HCl and 0.3 M FeCl$_3$. The results obtained with 12 M HCl is lower, and this could be attributed to the probable precipitation of PbCl$_2$ [18].

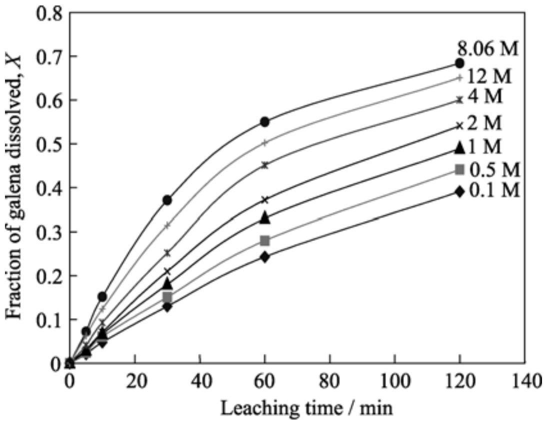

Fig. 2. Effect of varied HCl concentrations in 0.3 M FeCl$_3$ on galena dissociation.

Fig. 2 shows that about 68.4wt% of galena is dissolved within 120 min in 0.3 M FeCl$_3$/8.06 M HCl. In this case, the dissolution rate is higher, compared to the medium 0.3 M FeCl$_3$ in 0.1 M HCl, where about 38.45wt% is dissolved at the same contact time (Fig. 1). These results support the proposition of Feurstenau *et al.* [8] that the dissolution of galena ore is accelerated in the presence of an oxidizing agent like ferric ion.

Furthermore, in order to examine the effects of the concentration of hydrogen peroxide on the rate of galena dissolution, experiments were carried out by varying the initial concentration of H$_2$O$_2$ in the range of 0.1-12 M at 55°C in 8.06 M HCl solution using particle size −112+63 mm. These results are shown in Fig. 3.

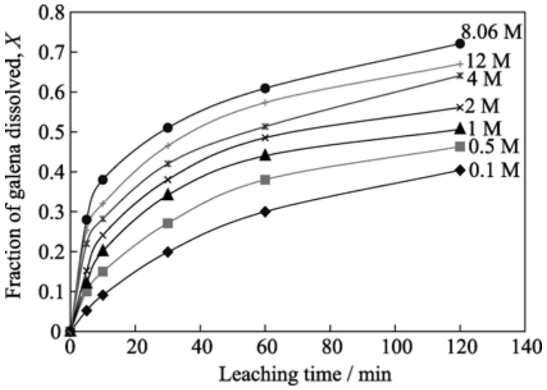

Fig. 3. Effect of H$_2$O$_2$ concentration in 8.06 M HCl on galena dissolution (experimental conditions: temperature, 55°C; ratio of solid to liquid, 10 g/L; stirring rate, 360 r/min).

It is apparent that the percent of galena dissolved increases with the increase in H$_2$O$_2$ concentration. This observation is true up to the H$_2$O$_2$ concentration of 8.06 M where about 73wt% dissolution is attained, after which the percentage dissolved moderately decreases with 12 M H$_2$O$_2$

in 8.06 M HCl. This could be attributed probably to the rapid precipitation of lead chloride [15]. The change in rate determining step at a higher reagent concentration due to the significant quantity of elemental sulphur produced [16] is another possible reason.

3.1.4. Effect of temperature on galena dissolution

The results showing the effect of temperature on the rate of galena dissolution by 0.3 M Fe(III) in the presence of 8.06 M HCl using the particle with a diameter of −112+63 mm are shown in Fig. 4. It shows that the fraction of galena dissolved increases with the increase of temperature.

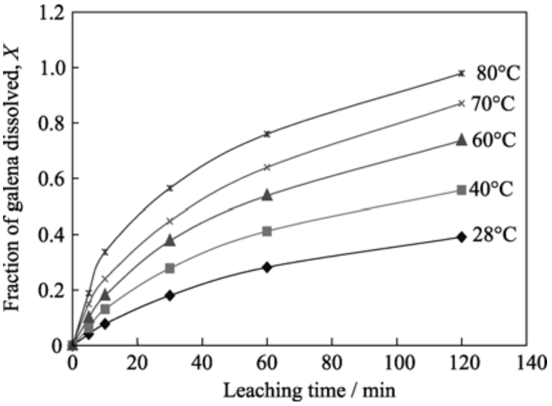

Fig. 4. Effect of temperature on galena dissolution with 0.3 M Fe(III) in the presence of 8.06 M HCl using the solid-to-liquid ratio of 10 g/L.

Interestingly, with 0.3 M Fe(III) in 8.06 M HCl, about 97wt% of the galena ore is dissolved within 120 min at 80°C. This value is slightly higher compared to when only 8.06 M HCl was used as the leachant under the same conditions, and for which 94.8wt% has been reported [12, 14]. Therefore, higher dissolution obtained with 8.06 M HCl in the presence of 0.3 M $FeCl_3$ could be attributed to the synergistic action of Fe(III) and HCl.

Similarly, the results of the effect of temperature on galena dissolution with 8.06 M H_2O_2/8.06 M HCl are illustrated in Fig. 5.

The results follow a similar trend as in Fig. 4, increasing the temperature is accompanied with an increase in the dissolution rate. The percent of galena dissolved is 98.1wt% at 80°C after exactly 120 min.

3.2. Kinetics of dissolution

In order to elucidate the reaction mechanism for comparative analysis of the dissolution kinetics of galena by HCl/$FeCl_3$ and HCl/H_2O_2 binary media, the shrinking core model as suggested by many authors [11, 15, 19-20] was used. According to the shrinking core model, if the reaction of galena can be represented as

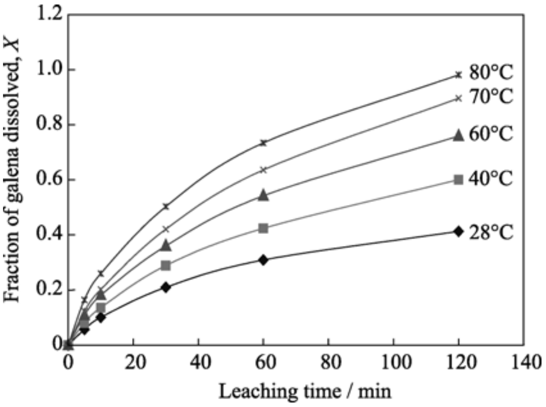

Fig. 5. Effect of temperature on galena dissolution with 8.06 M H_2O_2 in 8.06 M HCl solution.

$$A_{\text{fluid}}+B_{\text{solid}}\rightarrow\text{Fluid product}+\text{Solid product} \quad (1)$$

and the rate is controlled by surface chemical reaction, then the integral rate equation is constituted as follows [16]:

$$1-(1-X)^{1/3}=k_c M_B C_A/\rho_B a r_o t=k_1 t \quad (2)$$

where X is the fraction of galena dissolved at time t, k_c the kinetic constant, M_B the molecular mass of the solid, C_A the concentration of lixiviant A ($FeCl_3$, HCl, or H_2O_2), a the stoichiometric coefficient of the reagent in the leaching reaction, ρ_B the density of the solid, r_o the initial radius of the solid, and k_1 the rate constant from Eq. (2).

The shrinking core models for the diffusion controlled process through the product layer (Eq. (3)) and the mixed controlled process (Eq. (4)) have been investigated:

$$1-2/3X-(1-X)^{2/3}=2M_B D C_A/\rho_B a r_o^2\, t=k_2 t \quad (3)$$

$$1-(1-X)^{1/3}-y/6[(1-X)^{1/3}+1-2(1-X)^{2/3}]=k_3 t \quad (4)$$

where D is the diffusion coefficient, y is generally taken to be 1 for the mixed control process [20], and k_2 and k_3 are the rate constants calculated from Eqs. (3)-(4).

Only Eq. (2) is applied to the data presented in this study, since it is the only one that gives a perfect straight line with a good correlation coefficient of about 0.99. The analysis of the plots of other kinetics equations does not give a straight line. Consequently, all the data shown in Figs. 2 and 3 are found to fit the model equation $1-(1-X)^{1/3}=k_1 t$ with the average correlation coefficient of 0.996 and 0.992, respectively, and these are illustrated in Figs. 6 and 7.

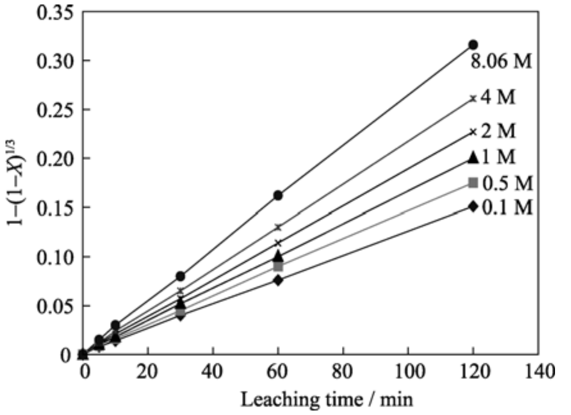

Fig. 6. Plot of 1−(1−X)$^{1/3}$=k_1t *versus* leaching time at different HCl concentrations in the presence of 0.3 M Fe^{3+} (experimental conditions: the same as Fig. 2).

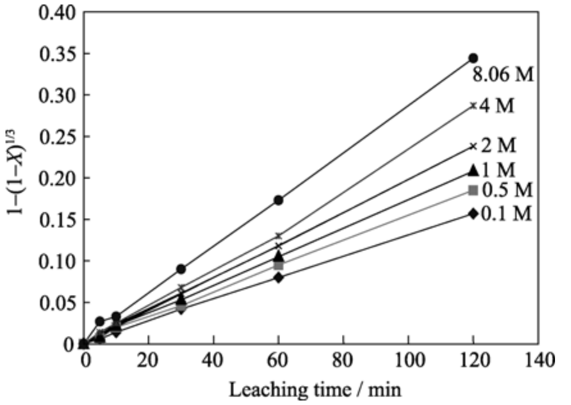

Fig. 7. Variation of 1−(1−X)$^{1/3}$=k_1t with leaching time for different H$_2$O$_2$ concentrations in 8.06 M HCl (experimental conditions: the same as Fig. 3).

From Fig. 6, the Arrehenius plots of lnk_1 *versus* ln[HCl]$_{0.3\text{ M Fe}^{3+}}$ and ln[H$_2$O$_2$]$_{8.06\text{ M HCl}}$ were made (Figs. 8 and 9), from which the slopes of the straight lines were calculated, respectively.

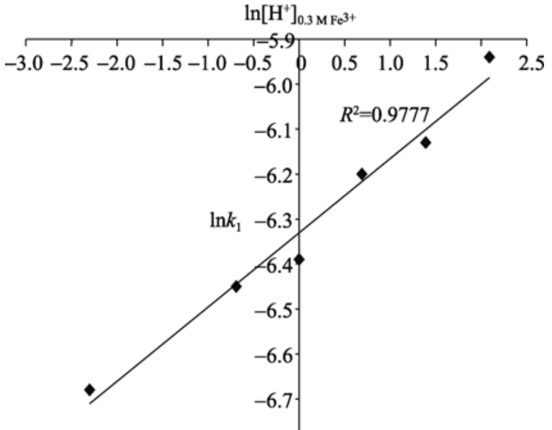

Fig. 8. lnk_1 *versus* ln[HCl]$_{0.3\text{ M Fe}^{3+}}$ for the data shown in Fig. 6.

In Figs. 8 and 9, the order of reaction with respect to [H$^+$]$_{0.3\text{ M Fe}^{3+}}$ and [H$_2$O$_2$]$_{8.06\text{ M HCl}}$ are proportional to 0.23 and 0.56 with the correlation coefficients of 0.9777 and 0.9999, respectively, for ferric chloride and hydrogen peroxide oxidizing media. Warren *et al.* [16] had earlier reported a reaction order of 0.21, on the effect of chloride ion in ferric chloride leaching of galena concentrate. The slight difference in reaction order may be due to the interactions between Fe^{3+} and H$^+$ ions on one hand and to the complexation effect of Cl$^-$ ions on the other hand. Furthermore, as for the hydrogen peroxide oxidizing medium, the reaction order of 0.56 obtained in this work is very close to the value of 0.61 reported by Aydogan *et al.* [3]. Most recently, a reaction order of 0.79 with respect to H$_2$O$_2$ concentration in acetic solution has been reported [17]. These varied values might be due to the mass transfer of H$_2$O$_2$ through the solution and surface layer.

Furthermore, the linearization of data in Figs. 4 and 5 at different temperatures is found to perfectly fit only the relation in Eq. (2). These are shown in Figs. 10 and 11.

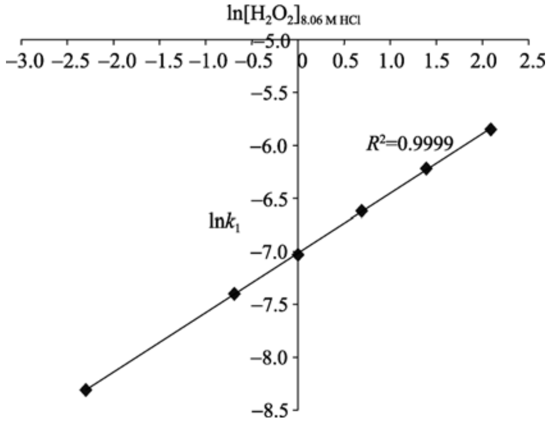

Fig. 9. lnk_1 *versus* ln[H$_2$O$_2$]$_{8.06\text{ M HCl}}$ for the data shown in Fig. 7.

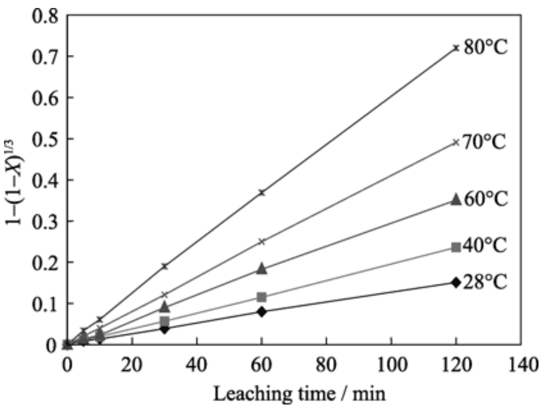

Fig. 10. Plot of 1−(1−X)$^{1/3}$ *versus* time at different temperatures from the experimental data presented in Fig. 4.

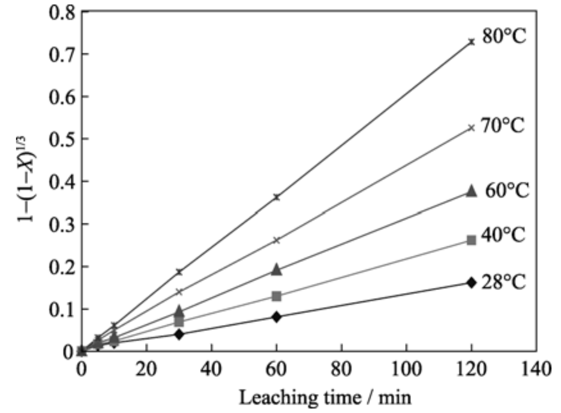

Fig. 11. Variation of $1-(1-X)^{1/3}$ *versus* time at different temperatures from the data shown in Fig. 5.

The rate constants, k_1, k_2 and k_3, obtained from the slopes of the lines in Eqs. (2)-(4), respectively for each temperature are shown in Table 3.

Apparent rate constants k_1 and k_2 were determined from the slopes of Figs. 10 and 11, respectively, and these values were used in the construction of the Arrhenius plots (Figs. 12 and 13), from which the activation energies, E_a, of 26.47 and 40.55 kJ/mol were calculated, respectively.

The E_a value of 26.47 kJ/mol with the correlation coefficient of 0.9995 obtained for the 0.3 M $FeCl_3$ in 8.06 M HCl medium indicated the surface diffusion mechanism due to the active participation of both H^+ and Fe^{3+} ions. Conversely, the E_a value of 40.55 kJ/mol obtained for H_2O_2/HCl suggested the surface chemical reaction mechanism for this binary medium. These results have been compared with other literature results reported for other galena, and these are summarized in Table 4. It is clear that Nigerian galena exhibits the lowest activation energy, and thus, making it more thermodynamically favorable.

Finally, the Arrhenius or frequency factor for the process was determined by the Arrhenius plots. The values of 11.0 and 3.65×10^2 s^{-1} were subsequently obtained for HCl/$FeCl_3$ and HCl/H_2O_2 media, respectively [23].

Table 3. Values of rate constants and their correlation coefficients at different temperatures for galena dissolution in 0.3 M $FeCl_3$/8.06 M HCl and 8.06 M H_2O_2/8.06 M HCl

Temperature / °C	0.3 M $FeCl_3$/8.06 M HCl						8.06 M H_2O_2/8.06 M HCl					
	Apparent rate constant / (10^{-3} min^{-1})			Correlation coefficient (R^2)			Apparent rate constant / (10^{-3} min^{-1})			Correlation coefficient (R^2)		
	k_1	k_2	k_3	k_1	k_2	k_3	k_1	k_2	k_3	k_1	k_2	k_3
28	1.258	0.175	1.834	0.983	0.950	0.953	0.559	0.200	1.962	0.973	0.934	0.893
40	1.967	0.392	2.811	0.986	0.967	0.948	1.613	0.475	3.100	0.961	0.945	0.905
60	3.520	0.808	4.118	0.991	0.974	0.971	2.851	0.883	4.313	0.979	0.899	0.942
70	4.520	1.350	5.483	0.989	0.969	0.963	4.087	1.500	5.825	0.985	0.897	0.913
80	6.000	2.242	7.571	0.992	0.981	0.977	6.080	2.275	7.946	0.993	0.934	0.895

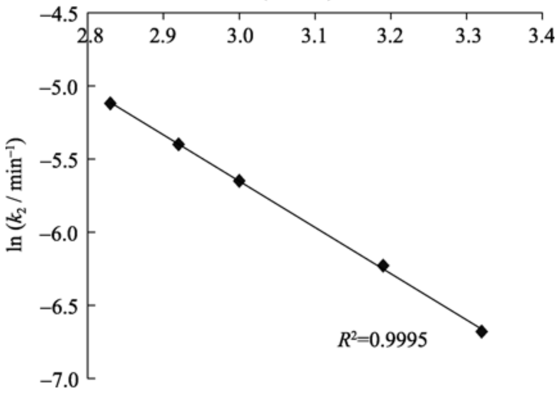

Fig. 12. Arrhenius plot for galena dissolution with 0.3 M $FeCl_3$ in 8.06 M HCl solution.

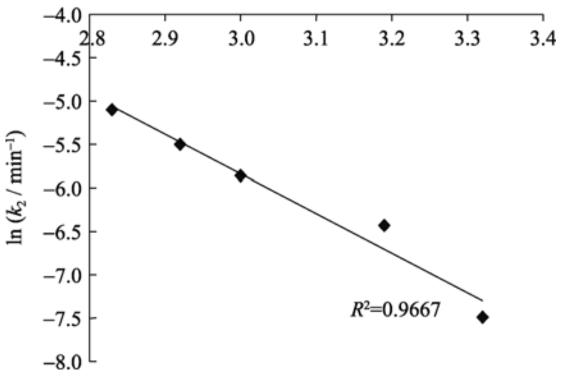

Fig. 13. lnk_2 *versus* 1000/*T* for the data presented in Fig. 11.

Table 4. Some reported activation energies for galena leaching by different leaching systems

Leaching in ferric chloride medium			Leaching in H_2O_2 medium		
Galena origin	Leachant	E_a / (kJ·mol^{-1})	Galena origin	Leachant	E_a / (kJ·mol^{-1})
Ottawa, Canada	0.3 M $FeCl_3$-0.3 M HCl in 4 M LiCl	40-45 [17]	Sivas, Turkey	0.5 M HNO_3 in 1.0 M H_2O_2	42.26 [3]
Rapid city, South Dakota	1 M HCl, 0.1 M $FeCl_3$/3.0 M NaCl	33.70 [21]	Sivas, Turkey	3 M CH_3COOH, 0.5 M H_2O_2	65.60 [17]
Alabama, Tuscaloosa	0.2 M $FeCl_3$-4 M NaCl, 0.1 M HCl	72.10 [16]	Bor,Yugo-slavia	2 M H_2O_2, 2 M H_2SO_4	60.00 [22]
Abakaliki, Nigeria	8.06 M HCl, 0.3 M $FeCl_3$	26.47 [This study]	Abakaliki, Nigeria	8.06 M H_2O_2, 8.06 M HCl	40.55 [This study]

The effect of particle diameter on galena dissolution by 0.3 M $FeCl_3$ in 8.06 M HCl and 8.06 M H_2O_2 in 8.06 M HCl solutions at 80°C are summarized in Table 5. The results of these investigations show that the smaller the galena particle, the higher the fraction of galena dissolved.

Table 5. Effect of particle diameter on galena dissolution by 0.3 M $FeCl_3$ in 8.06 M HCl for 120 min at 80°C

Particle diameter / mm	Fraction of galena dissolved	
	0.3 M$FeCl_3$ in 8.06 M HCl	8.06 M H_2O_2 in 8.06 M HCl
−112+63	0.976	0.981
−250+112	0.642	0.712
−500+250	0.507	0.539
>−500	0.407	0.411

The rate constants obtained from the linearization of the kinetic data in Table 5 are determined from the surface chemical reaction model of Eq. (2) and are plotted against the reciprocal of particle radius, yielding a linear relationship with the correlation coefficients of 0.9997 and 0.9999, respectively (Fig. 14).

Therefore, the linear dependence of rate constant k on the reciprocal of the particle radii passing through the origin confirms that the surface chemical reaction is the rate controlling step during the dissolution process. On the contrary, the plot of rate constant k *versus* the square of particle radii (r_o^2) does not give a linear relationship.

From the effects of solid-to-liquid ratios (Table 1) and particle diameters on galena dissolution (Table 5) for the leaching systems, 0.3 M $FeCl_3$ in 8.06 M HCl and 8.06 M H_2O_2 in 8.06 M HCl, respectively, the apparent rate constants for the two leaching systems were evaluated. Hence, the reaction orders with respect to the solid-to-liquid ratio and the initial particle size (r_o) for 0.3 M $FeCl_3$ in 8.06 M HCl and 8.06 M H_2O_2 in 8.06 M HCl leaching systems were determined to be inversely proportional to 0.23 power ($(S/L)^{-0.23}$), 0.49 power ($(S/L)^{-0.49}$); and 0.68 power ($r_o^{-0.68}$), 0.91 power ($r_o^{-0.91}$), respectively.

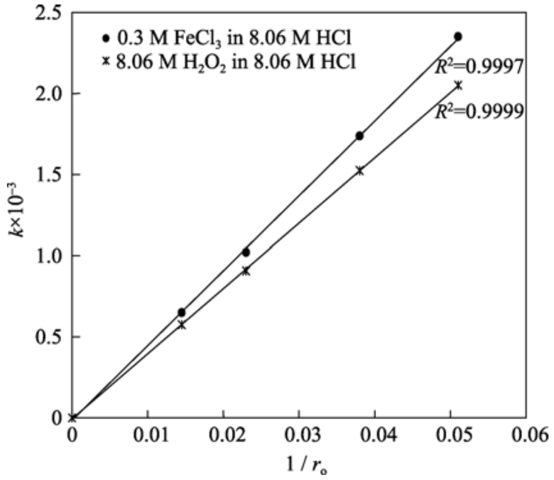

Fig. 14. Dependence of rate constant k on $1/r_o$ for different leaching systems.

Thus, the proposed dissolution model with 0.3 M $FeCl_3$ in 8.06 M HCl at 80°C can be described as

$$1-(1-X)^{1/3}=k_o(\mathrm{HCl})^{0.23}_{8.06\,\mathrm{M\,H^+}}(\rho\ \mathrm{S/L})^{-0.23}r_o^{-0.68}\exp^{(-26470/RT)}t \tag{5}$$

and the surface chemical control mechanism for galena dissolution by 8.06 M H_2O_2 in 8.06 M HCl is consistent with the following expression:

$$1-(1-X)^{1/3}=k_o(\mathrm{H_2O_2})^{0.56}_{8.06\,\mathrm{M\,H^+}}(\rho\ \mathrm{S/L})^{-0.49}r_o^{-0.91}\exp^{(-40550/RT)}t \tag{6}$$

where ρ is the ore density. In Eqs. (5) and (6), the reaction constant, k_o, is experimentally determined. At 80°C, the fraction of galena dissolved, X, in Eqs. (5) and (6) is 0.978 and 0.981, respectively, and the experimental values of k_o

are 1.25×10^4 and 8.02×10^6, respectively. The value of k_o, however, is found to vary depending on the leaching systems/conditions [3, 21].

3.3. Composition of the product layer of the leaching systems

The X-ray diffraction analysis of galena postleached residues after leaching for 2 h at 80°C by 0.3 M $FeCl_3$ in 8.06 M HCl and 8.06 M H_2O_2 in 8.06 M HCl, respectively, is shown in Figs. 15 and 16.

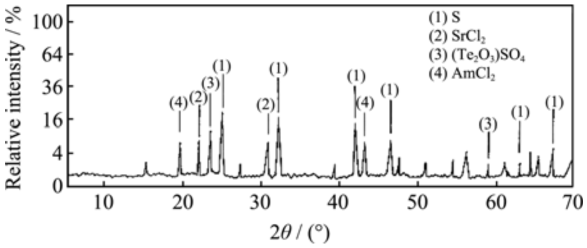

Fig. 15. X-ray diffraction pattern of the postleached residue after leaching for 2 h at 80°C by 0.3 M $FeCl_3$ in 8.06 M HCl.

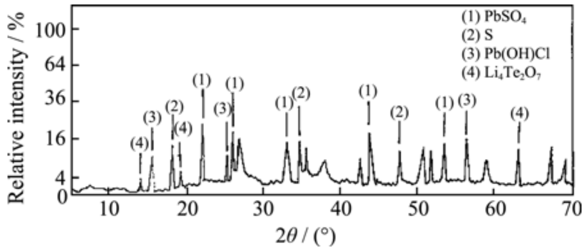

Fig. 16. X-ray difraction pattern of the postleached residue after leaching for 2 h at 80°C by 8.06 M H_2O_2 in 8.06 M HCl.

As seen in Fig. 15, sulphur and traces of strontium chloride ($SrCl_2$) and tellurium oxide sulphate $(Te_2O_3)SO_4$ are detected. As suggested by Feurstenau *et al.* [8], the mass transport of ferric chloro-complex through the product sulphur layer appears to be responsible for establishing the overall leaching reaction, which is consistent with the following stoichiometry:

$$PbS+2Fe^{2+}_{(aq)} \rightarrow S^o+Pb(II)+2Fe^{2+}_{(aq)} \tag{7}$$

A number of studies have also been performed on the ferric leaching of galena in chloride media, where $PbCl_2$ is only somewhat soluble. There exists conflicting reports as to whether this process is chemical or diffusion control, due to the formation of a lead chloride product layer [25].

Furthermore, the X-ray diffraction analysis shows that the postleached residue in 8.06 M H_2O_2/8.06 M HCl is composed of $PbSO_4$, traces of sulphur, lead hydroxyl chloride Pb(HO)Cl, and lithium tellurate $Li_4Te_2O_7$ (Fig. 16). Similar results of this nature have previous been reported [3], where the main reaction products were found to be dissolved sulphate and chloroplumbate, $(PbCl_4)^{2-}$ ions, elemental sulphur, and water.

4. Conclusions

(1) The activation energy (E_a) of 26.47 kJ/mol obtained for galena ore dissolution in 0.3 M $FeCl_3$/8.06 M HCl medium shows that the leaching reaction proceeds by the surface diffusion mechanism; while E_a of 40.55 kJ/mol obtained for galena dissolution in 8.06 M H_2O_2/8.06 M HCl suggests the surface chemical reaction mechanism for the leaching process. The present study has thus revealed Nigerian galena is more economically viable in the leaching process due to the low value of E_a obtained from the dissolution process.

(2) A semiempirical mathematical model has been proposed for the two binary solutions.

(3) The postleaching residue analysed by an X-ray diffractometer reveals that S is a major component for the two binary leachants.

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