Reductive Leaching Kinetics of Low Grade Manganese Deposits in H₂SO₄ Solution Using Malonic Acid as Reducing Agent

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Abstract

A leaching process was developed to extract manganese and metal values from Alloga manganese concentrate. The preferential leaching process was achieved through reductive leaching in dilute sulfuric acid medium with malonic acid as the reducing agent. Leaching parameters were optimized as 1.0 M H₂SO₄, 10% malonic acid in solid/liquid ratio 1:10 for 90 min at 80°C and using ore ground to – 74 µm. Under these conditions, the leaching efficiency of manganese reaches 97%, whilst iron dissolution did not exceed 14%. The leaching efficiencies of the interesting associated metal values (Cu, Co, Zn, Ni and U) have also been investigated.

The leaching kinetics results showed that, the leaching process is controlled by diffusion through a "product" layer and follows a shrinking core kinetic model $1-2/3(X)-(1-X)^{2/3} = k_d t$ with an apparent activation 29.86 kJ/mol.

Keywords: manganese metal values, reductive leaching, kinetics

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1. Introduction

For the vigorous growing demand of steel industry, carbon-zinc battery, dietary additives, fertilizers, and dyes industries, high grade manganese ores are exhausted step by step in the world, thus, much attention have been drawn to extract and recover manganese from low-grade manganese dioxide ores in recent years [1-3].

Manganese can be extracted from acidic reduced ore materials, coal roasting reduction followed by acid leaching technology is extensively applied to produce electrolytic manganese, but unfortunately, it causes serious problems including high consumption of energy, emission of smoke dust and gaseous pollutants [4-6]. Thus, many direct reductive acid leaching technologies have been developed to treat low-grade manganese oxide ore by using a variety of reducing agents, such as SO_2 [7-8], hydrogen peroxide [9], oxalic acid [10], thiosulfate [11] and iron [12]. However, complicated downstream purification process and serious water pollution makes these leaching processes difficult for industrial application [13]. Nowadays, biomass wastes, such as sawdust, molasses, straw, wheat straw, cornstalk and bamboo, have been considered as environment-friend and low-cost reducing agents for roasting reduction of manganese dioxide ores [14-15]. Sawdust, cornstalk and straw as reducing agents have been investigated by Cheng [16], Song [17] and Zhao [18] respectively, and the results showed that over 90% leaching recovery of manganese was achieved under the optimal experimental conditions. In particular, Su et al. [19-20] investigated cane molasses as a reducing agent in dilute sulfuric acid medium for leaching manganese(IV) minerals and found that the optimum leach conditions were 1.9 M H_2SO_4 and 60.0 g/L cane molasses at 90 °C for 120 min which extracted >93% manganese as Mn(II). Likewise, Lasheen et al. [21-22] recently reported the reductive leaching of manganese and other metals ions from the low grade Um Bogma manganese ore using 20% molasses (with respect to sample weight), a solid:liquid ratio of 1:12 in 2.7 M HNO_3 at 95 °C for 2 h. The kinetics results showed that, the rate of manganese(IV) oxide leaching using dilute HNO_3 in presence of molasses is controlled by diffusion through a "product" layer and follows a shrinking core kinetic model with an apparent activation energy of 25.7 kJ/mole. The kinetics study also showed strong dependence on acid and reductant concentration.

As a leachant, sulfuric acid in this work is preferred to other acids because of its low price. The object of the present investigation is to obtain essential information on the kinetics of the dissolution behavior of manganese and other associated metal values in sulfuric acid solutions with respect to the leaching mechanism. Also, the kinetic dissolution of manganese at optimal conditions was studied.

2. Experimental materials

The raw material, used in this study was from Alloga area, Sinai, Egypt; its chemical composition is demonstrated in Table 1-2. The XRD result of the studied sample, Diffraction data from ASTM Card Nos. 19-0389, 4-0775, and 13-0534 Fig. 1, shows that the main metallic minerals in the studied concentrate are cryptomelane (KMn_8O_{16}), paratacamite $Cu_2(OH)_3Cl$, hematite (Fe_2O_3), quartz (SiO_2)

and albite ($NaAlSi_3O_8$). The chemicals used in this study were malonic acid and sulfuric acid all of analytical grade.
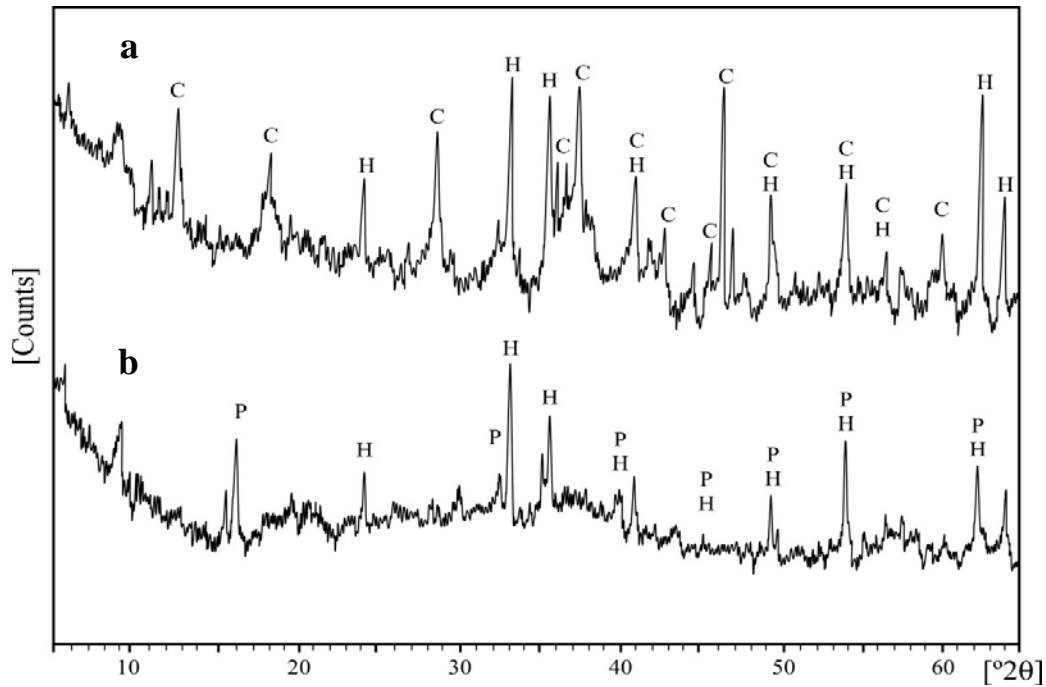

Fig. (1): (a) X-ray diffraction of the sample deposit separated of by liquid

bromoform and (b) after scratched of copper mineral. (P = Paratacamite ,

C = Cryptomelane, and H = Hematite).

Table (1): Chemical composition of the sample deposit.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	P_2O_5	LOI*	Total
Oxide, %	7.40	1.54	20.50	9.40	8.20	0.18	0.24	32.60	0.21	0.17	16.35	96.79

* Total loss in ignition at 1000°C.

Table (2): Assay of the associated metal values of the sample deposit.

Constituent	Conc., %
Cu	1.700
Zn	1.400
Co	0.057
Cd	0.0018
Ni	0.0546
U	0.0071

2.1 Leaching procedure

In the experiments, the primary ore was first crushed into −2mm particles, and then ground to the required size in a laboratory-scale ball mill. Agitation leaching tests were carried out in a 250 mL round bottom flask at the required temperature. Ten grams of manganese sample was used for each test. In the reductive leaching process, the ground ore, sulfuric acid and malonic acid were added to the reactor in sequence. After the reaction, the slurry was filtered and the residue was washed with distilled water. The contents of manganese and other associated metal values in filtrate were quantitively analyzed by Atomic Absorption Spectrometry. Laser fluorometry "UA-3" Uranium Analyzer (Scintrex, Canada) was used, in the present work, for uranium analysis.

3. Results and discussion

3.1 Effect of H_2SO_4 concentration

The effect of H_2SO_4 concentration on the leaching efficiency of Mn, Cu, Zn, Co, Ni, and U from the studied ore sample was investigated. The sulfuric acid concentrations were varied from 0.5 M to 1.5 M, temperature of solution was maintained upon the level of 80°C. The obtained results presented in Fig. 2 showed complete dissolution of Mn ions 99.9% at 1.5 M H_2SO_4. However, increasing acid concentration from 0.5 M to 1 M H_2SO_4 the following associated valuable metal ions (Cu, Zn, and Co) showed a relatively increase in their leaching efficiency as the concentration of acid increase from 0.5 M to 1 M, it reached 92, 75, and 60% respectively.

On the other hand, dissolution of Ni ions not exceed than 27%. Decreasing in leaching efficiency of some concomitants metal values may be related their presence in a refractory mineral phase which needs more vigorous conditions. In addition, the possible reduction of these metallic species in this mixture into their less soluble reduced species might occur. Therefore, 1 M H_2SO_4 would be sufficient for almost complete leaching of Mn, U, and nearly Cu cations while keeping minimum iron dissolution.

3.2 Effect of malonic acid concentration

In order to study the effect of malonic acid concentration upon reduction of Mn, Cu, Zn, Co, Ni, and U ions, a series of leaching experiments were carried out using 1.0 M H_2SO_4. These experiments were performed in the absence and the presence of different amounts of malonic acid varying from 1% to 20% of the input sample weight. The other leaching conditions were fixed at a solid/liquid ratio of 1:10 at 80°C for 90 min and using −74 μm for ore grain size. From the obtained data as shown in Fig. 3, it is evident that, in the absence of malonic acid 9.4% of input Mn has been dissolved and the leaching efficiencies of the associated valuable metals were lowered to 37% Zn, 52.5% Cu, 19% Co, and 12% Ni. These results indicated that, the latter elements may be partially incorporated in the Mn deposit.
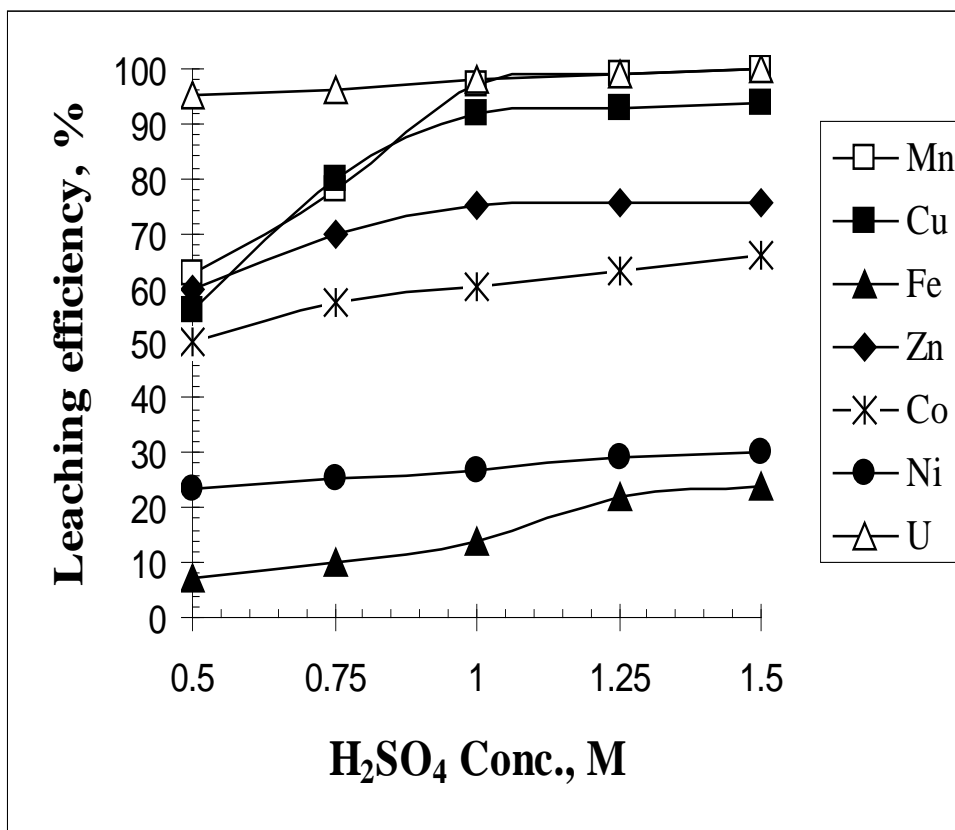
Fig. (2): Effect of H_2SO_4 acid concentration upon the leaching efficiencies of Mn, U, Cu,

Fe, Co, Ni, and Zn from studied sample (10% malonic acid, 1:10 S/L ratio, 80ºC,

90 min).

The greater the malonic acid concentration the higher the leaching efficiency of Mn and other studied metal values. Thus the reduction of manganese in its minerals to its bivalent state is a pre-requisite for its dissolution as mentioned above. The reduction of tetravalent manganese by malonic acid follows the reaction:

$$Mn^{4+} + CH_2 (COOH)_2 + 2H^+ \rightarrow Mn^{2+} + CH_2 (COO)^{2-} + H_2O \qquad (1)$$

Increasing the malonic acid amount beyond 10% has a pronounced effect upon iron dissolution since the percentage of iron dissolution increased from 14% to 31% on raising the amount of malonic acid from 10% to 20% respectively. So, 10% malonic acid would be optimum.

It is interesting to mention here that uranium doesn't affected by the presence of the reductant. This behavior is related to complex nature of mixture solution. The presence of Mn and Fe in the acidic medium maintains uranium in dissolved hexavalent state. Moreover, the oxidation/reduction potential of leach liquor is below 400-430 mv which confirm the presence of uranium in hexavalent state.
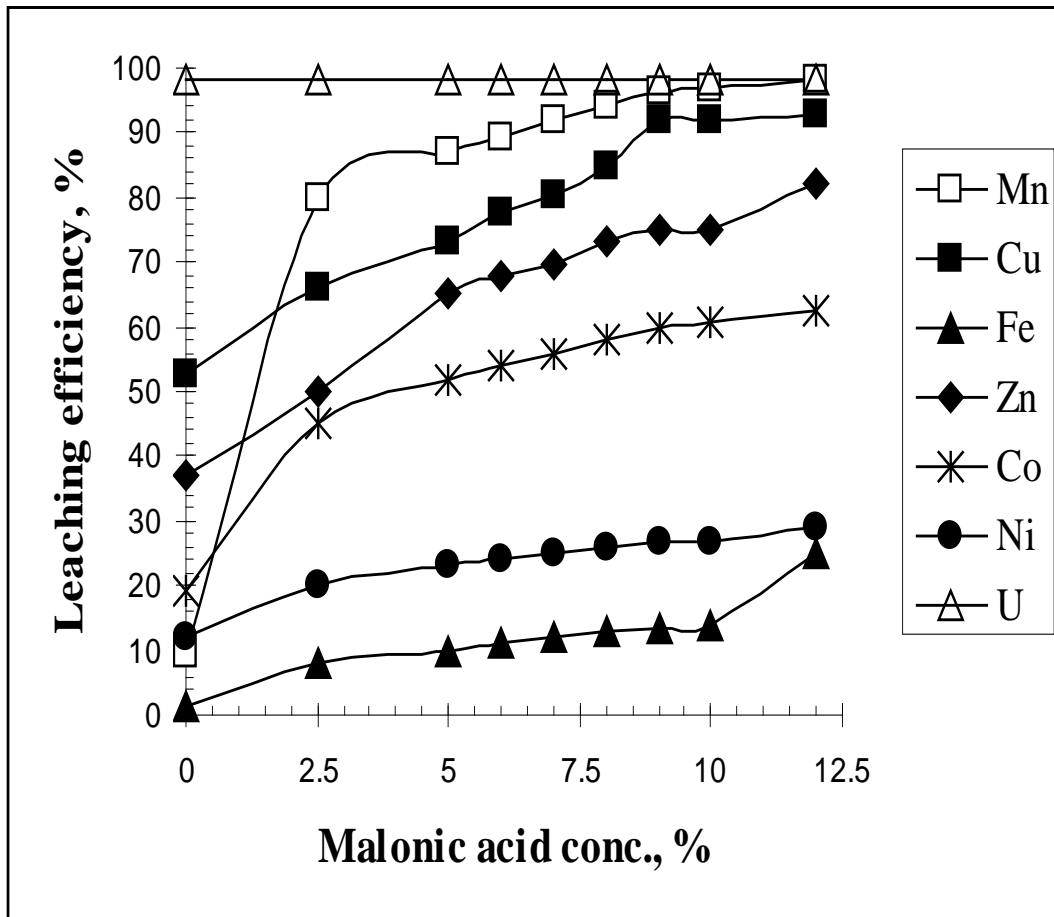
Fig. (3): Effect of malonic acid addition upon the leaching efficiencies of Mn, U, Cu, Fe,

Co, Ni, and Zn from studied sample (1M H_2SO_4, 1:10 S/L ratio, 80ºC, 90 min).

3.3 Effect of solid/liquid ratio

The effect of solid/liquid ratio on the leaching efficiency of Mn and associated metal values was investigated in the range 1:8 to 1:15, the results are presented in Fig. 4. it was noticed that; using 1:8 solid/liquid ratio, the leaching efficiencies of all the studied metals have been lowered for Mn, U, Cu, Co, Ni, and Fe to only 86%, 92%, 74%, 55%, 22% and 11% as compared to 97%, 98%, 92%, 60%, 27% and 14% at a solid/liquid ratio 1:10 respectively. Increasing the acid amount by applying the pulp ratio of 1:15 did not impart any perceptible improvement in the leaching efficiency of Cu, Zn, Co but increase the iron dissolution to 31%. On the contrary, the increase of solid/liquid ratio leads to a dilute leach liquor and the formation of ferric hydroxide, which is unfavorable to the separation of leaching liquor and residue. Therefore, 1:10 is used in the following experiments.
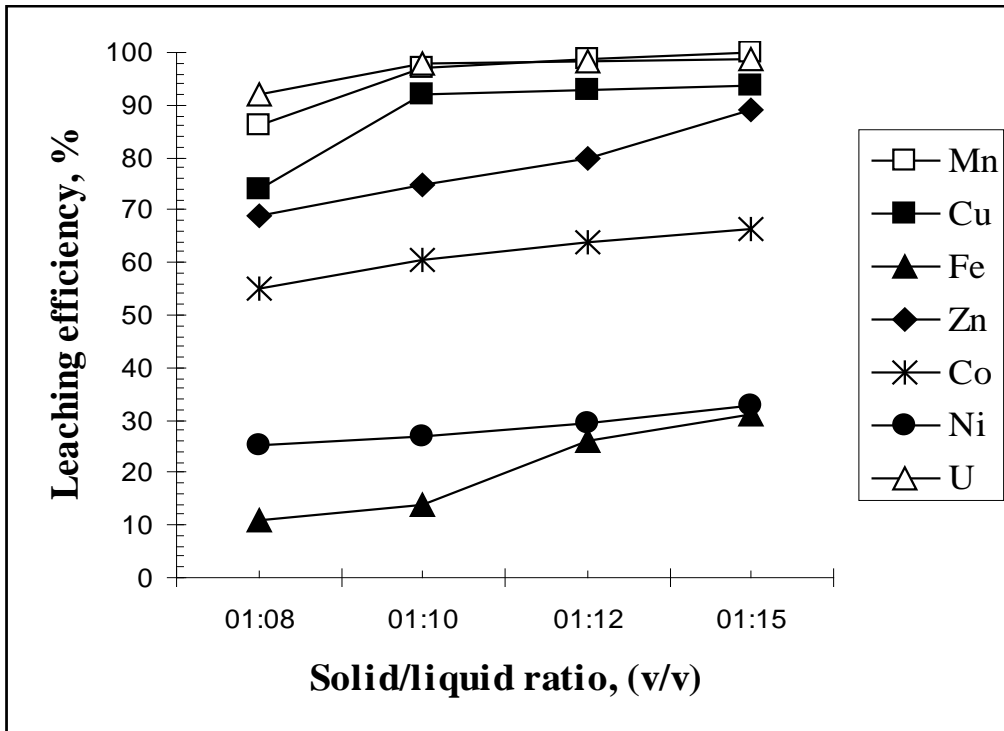
Fig. (4): Effect of solid/liquid ratio upon the leaching efficiencies of Mn, U, Cu, Fe, Co,

Ni, and Zn from studied sample at (1M H_2SO_4, 10% malonic acid, 90 min, 80ºC).
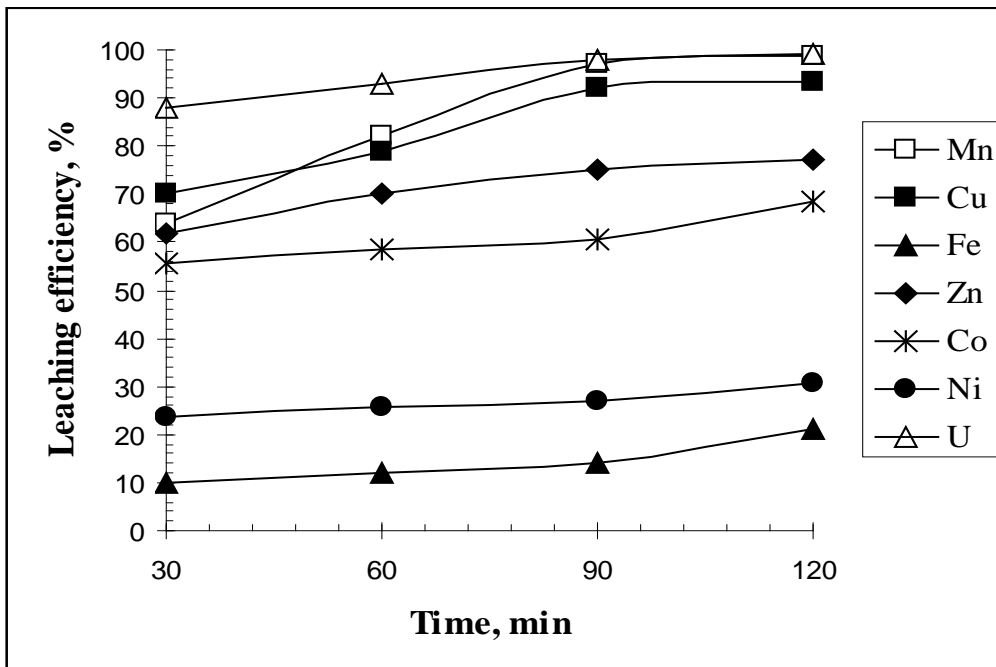

Fig. (5): Effect of time upon the leaching efficiencies of of Mn, U, Cu, Fe, Co, Ni, and Zn

from studied sample (1M H_2SO_4, 10% malonic acid, 1:10 S/L ratio, 80ºC).

3.4 Effect of time

The effect of leaching time on the extraction of manganese and associated metal values is shown in Fig. 5. The data reveal that Mn, Cu and Zn dissolution increases rapidly at the time range of 0 to 90 min and reaches 97%, 92% and 75% respectively in 90 min. A further increase in the leaching time has little influence on the leaching of Mn and other associated metal values. Therefore 90 min would be considered optimum.

3.5 Effect of temperature

The effect of temperature on the dissolution of Mn, Cu, Zn, Co, Ni, and U was investigated in 1.0 M H_2SO_4 solution using ore ground to –74 µm at temperatures of 25–95 °C. The leaching curves are shown in Fig. 6, which indicate that the leaching efficiency of the studied metal ions increased with an increase in reaction temperature up to 80°C. The leaching efficiencies of Mn and Cu reach 97% and 92% respectively at 80 °C, whilst, iron dissolution don't exceed 14%. Therefore, would be adequate and consider optimum.
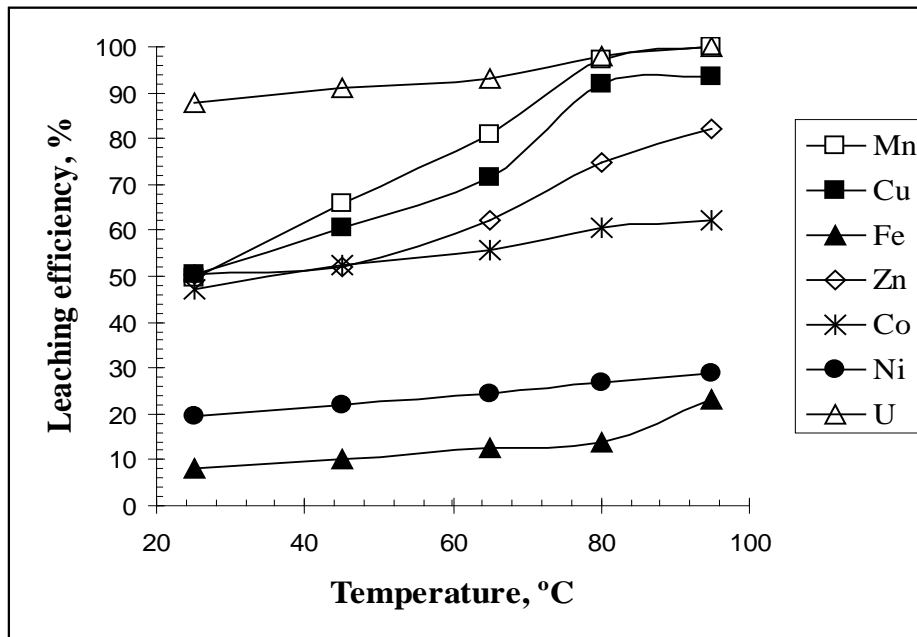

Fig. (6): Effect of temperature upon the leaching efficiencies of Mn, U, Cu, Fe, Co, Ni,

and Zn from studied sample at (1M H_2SO_4, 10% malonic acid, 90 min, 1:10 ratio).

3.6 Kinetic analysis

The dissolution rates of manganese were analyzed with the shrinking core model for reaction control under the assumption that the ore is a homogeneous spherical solid phase [23]. For the manganese dissolution kinetics, two established kinetic models were used, expressed by the following equations:

$$1-(1-X)^{1/3} = M.K_C.C_A.t/d.r = k_1t \qquad\qquad (2)$$

$$1-2/3(X)-(1-X)^{2/3} = 6u.M.D.\ C_A.t/\ d.r^2 = k_2t \qquad\qquad (3)$$

where k_c is the first-order rate constant (m s^{1-}), M is the molecular weight of the solid reactant (kg mol^{1-}), C_A is the acid concentration (mol m^{3-}), D is the diffusion coefficient (m^2.s^{1-}), d is the density of the particle (kg m^{3-}), r is the initial radius of the particle (m), a is the fraction reacted at time t (s), k_1 (m s^{1-}) and k_2 (m^2 s^{1-}) are the overall rate constants, u is the stoichiometric coefficient. Equation 2 is applicable to chemically controlled processes and Eq. 3 to diffusion controlled processes through the porous product layer [24]. Examination of plots of the above kinetic equations a function of time showed that Eq. 3 gives perfectly straight lines (from 0 to 90 min) with temperatures varying from 25 to 80°C.

3.7 Effect of temperature

The experiments were carried out at leaching temperature from 323 K to 363 K to evaluate the effects of this parameter which plays an important role in the reductive leaching of manganese. The results shown in Fig. 7 indicate that temperature has significant effect on the rate of leaching, and the leaching recovery of manganese increased with the increase of the leaching temperature. The experimental results (in Fig. 7) fit the reaction model of Eq. (3), as shown in Fig. 8 which demonstrated that the leaching kinetics of manganese could be described as diffusion through the solid layer consisted of an insoluble part of the ore around the unreacted core under the experimental conditions.
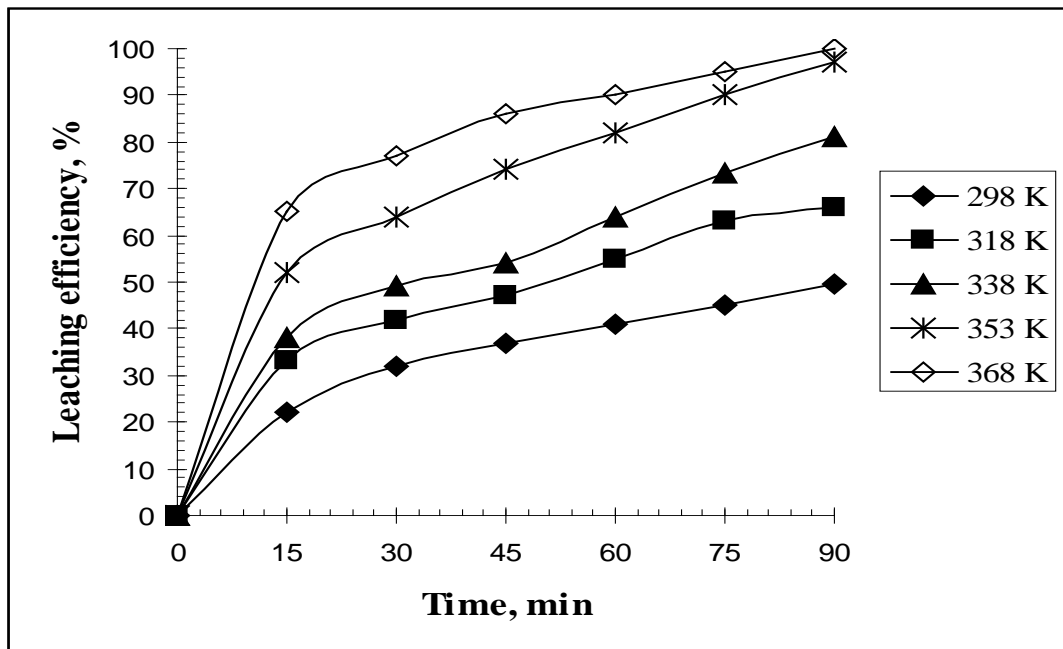

Fig. (7): Effect of temperature on leaching rate of manganese at 1M H_2SO_4, 10% malonic acid and 1:10 solid/liquid ratio from 0 to 90 min.
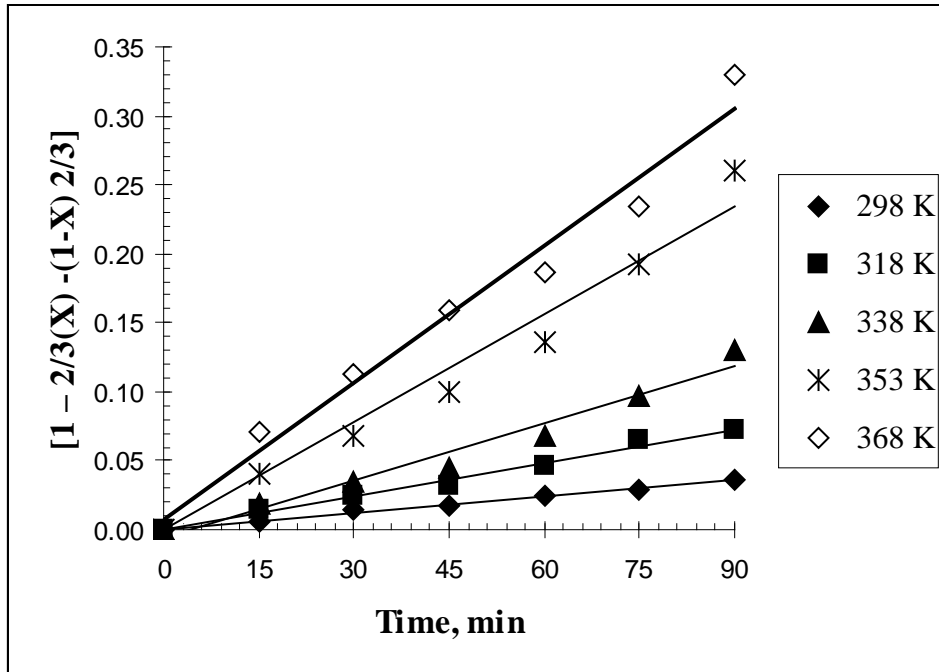
Fig. (8): Relationship between [1 – 2/3(X) -(1-X) $^{2/3}$] and leaching time for manganese leaching at various temperature at 1M H_2SO_4, 10% malonic acid and 1:10 solid/liquid ratio.
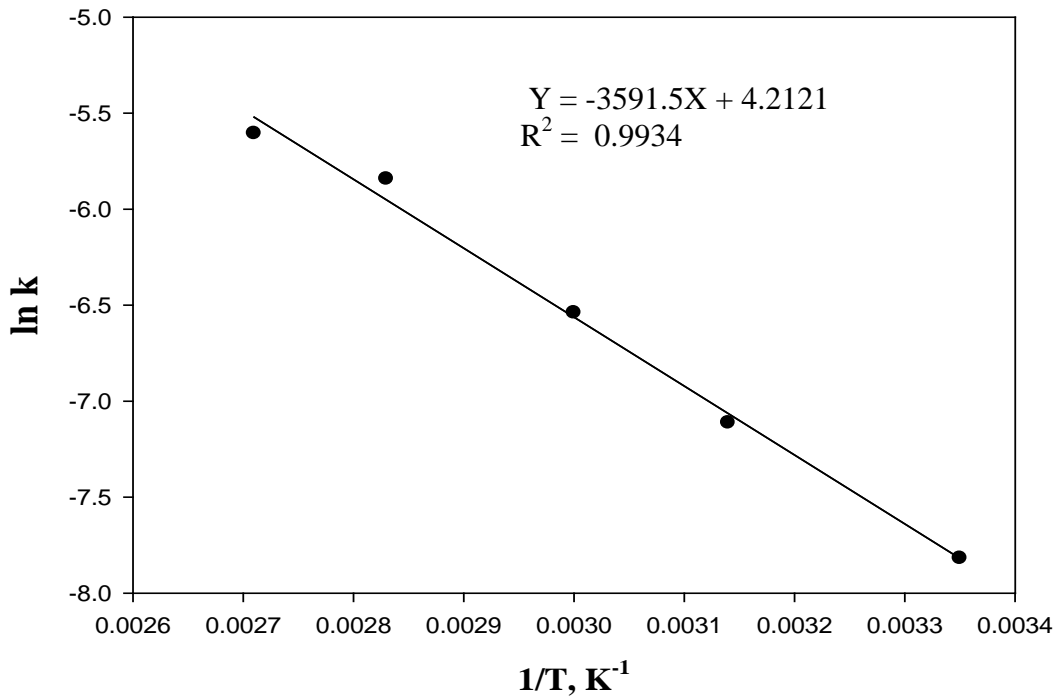

Fig. (9): Arrhenius plot for manganese leaching at 1 M H_2SO_4, 10% malonic acid and -74µm.

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The apparent activation energy was determined based on the Arrhenius equation, the lnk versus 1/T data for the five temperatures as graphed in Fig. (9). The regression analysis showed that the linear relationship is also significant. The apparent activation energy (Ea) was, hence, determined to be 29.86 kJ/mol.

4. Conclusions

A reductive leaching process for a low -grade manganese deposit has been successfully demonstrated using a mixture of sulfuric acid and malonic acid as reductant. The results indicate that the leaching efficiencies of metal values increase as the H_2SO_4 concentration, reductant concentration and reaction time increase. Metal leaching from the manganese deposit strongly depends on the reaction temperature. The optimum leach conditions were 1 M H_2SO_4 using 10% malonic acid at 80 °C for 90 minutes in a solid/liquid ratio of 1:10 and using deposit ground to − 75 μm grain size. Using this relatively low leaching time is justified by decreased energy consumption. Under these conditions the leaching efficiencies of manganese attained about 97% together with 92 % for Cu, 98% U, 75% for Zn, 60.5% for Co besides relatively low results of 27% for Ni. On the other hand, the iron dissolution was as low as 14%.

The leaching kinetics results showed that, the leaching process is controlled by diffusion through a "product" layer and follows a shrinking core kinetic model $1 – 2/3(X) -(1-X)^{2/3} = K_d t$ with an apparent activation energy of 29.86 kJ/mole.

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