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Oxidative Leaching Kinetics of Vanadium from Egyptian Boiler Ash under Acidic Oxidizing Conditions

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Abstract

Processing of Egyptian boiler ash in sulphuric acid solution using hydrogen peroxide as oxidant has been investigated. The results showed that leaching temperature, hydrogen peroxide, sulphuric acid concentration, leaching time, liquid-to-solid ratio and agitation speed, have significant effect; optimum process operating parameters were established as follows: temperature: 95 °C; concentration of H_2O_2: 0.5 M; sulphuric acid concentration: 1.5 M; time: 2 h; liquid-to-solid ratio: 5:1; agitation speed: 600 rpm. Under these experimental conditions, the extraction efficiency of vanadium attained about 98.5%, whilst iron and nickel dissolution reach 31% and 61% respectively. Leaching kinetics of vanadium showed that, the reaction rate of leaching process is controlled by chemical reaction at the particle surface. The leaching process follows the kinetic model $1-(1-X)^{1/3}=kt$ with an apparent activation energy of 34.35 kJ/mole.

Key words: oxidative leaching, vanadium, boiler ash, kinetics

1. Introduction

Vanadium is an important rare metal which has been widely used in ferrous and non-ferrous alloys to improve its hardness, tensile strength, and fatigue resistance [1]. Due to the increasing demand of vanadium and rapid depletion of its land based ores, there is a growing need to find alternate sources to meet the future demands and boiler ash is one of the vital sources. For this reason, the recovery of vanadium from fly and boiler ashes has received attention in recent years.

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Another reason for interest in this extraction process is that the disposal of this industrial waste may lead to environmental problems such as dusting and pollution of water with heavy metals. Several processes have been proposed to recover vanadium from fly and boiler ashes using hydrometallurgical processes. The recovery may be carried out directly by acid [2-5] alkaline [6, 7] or water [8] leaching; this may be followed by an oxidation of vanadium using air [8], $NaClO_3$ [9], NaClO [10], or oxygen [11]. Vanadium may be separated from the obtained leaching solution using by precipitation [2], ion exchange [12], or solvent extraction [13-15].

Kinetic study of any chemical reaction is an essential part in designing a chemical process and this is true for leaching. Most of the leaching processes are reactions between liquid and solid phases. The major models that have been developed for kinetics of non-catalytic liquid–solid reactions are the shrinking (including shrinking particle and shrinking core), homogeneous, grain, uniform pore and random pore models [16,17]. The shrinking core and shrinking particle models are suitable to the reaction between an initially non-porous particle and a reagent, during which the unreacted core gradually shrinks [18,19].

The aim of this work is to investigate a simple leaching process of the Egyptian boiler ash from El-Korimat thermal power station by H_2SO_4 solution in the presence of H_2O_2 as oxidizing agent. The effects of the main system variables on the leaching rate are examined. This paper also considers the kinetic aspects of leaching vanadium which provided a theoretical basis for the industrial application in the future.

2. Experimental

2.1 Characterization of the Egyptian boiler ash

Boiler ash used in this study was from El-Korimat thermal power station, Egypt; its chemical composition is 6.77 % SiO_2, 2.93% Al_2O_3, 12.49% Fe_2O_3, 5.81% CaO, 9.65% MgO, 3.51% K_2O, 2.85% Na_2O Beside the presence of 10.51% vanadium and 8.01% nickel. All the chemicals used in this study were of analytical grade.

2.2 Analytical procedures

The ore was analysed for its major and minor elements using the proper analytical methods [20-21].

2.3 Leaching procedures

All leaching experiments were carried out in a glass reactor equipped with a Teflon stirrer, condenser, thermometer, glass funnel for adding the solid sample and a sampling device. This set-up provides stable hermetic conditions and allows heating at constant temperature. The calculated volumes of H_2SO_4 and H_2O_2 solutions were added to the glass reactor and heated-up to the selected temperature. When the temperature was reached, the solid concentrate was added and the reaction commenced. After selected time intervals, the solution samples were taken for chemical analysis.

3. Results and discussion

3.1 Leaching results

3.1.1 Effect of stirring speed

Figure (1) presents the effect of stirring speed under the conditions of 1.5 M H_2SO_4, 0.5 M H_2O_2 and 1:5 solid/ liquid ratio at 95°C for 2h. The results indicated that, the leaching rate of V(IV), Ni(II), and Fe(II) increases quickly below 400 rpm and remains almost constant after 600 rpm. Clearly, stirring speed improves leaching efficiency of V(IV), Ni(II), and Fe(II), increase stirring speed usually increases the rate of leaching due to the suspension of the minerals particles and decreases the thickness of the mass transfer boundary layer on the surface of the particles. Therefore, the stirring speed is kept constant at 600 rpm in the following tests.

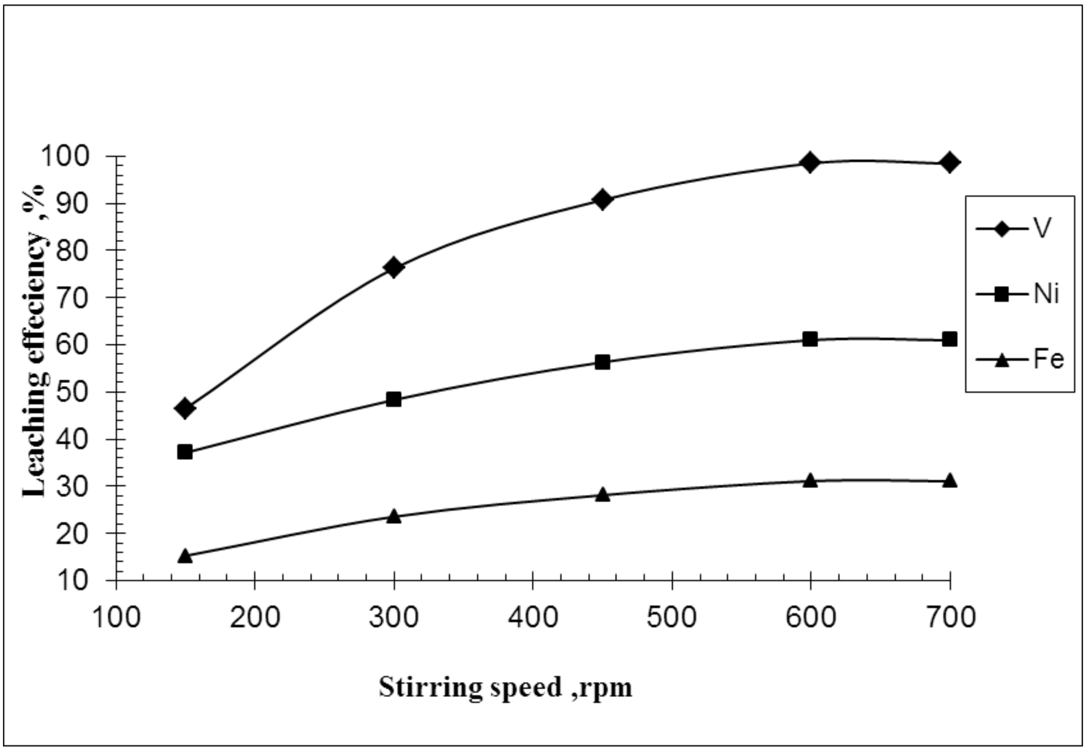

Fig. (1): Effect of stirring speed upon the leaching efficiencies of V(IV), Ni(II), and

Fe(II) (1.5M H_2SO_4, 0.5 M H_2O_2, 95°C, 1:5 solid/liquid ratio, 2 h).

3.1.2 Effect of H_2SO_4 concentration

Extraction of V(IV), Ni(II), and Fe(II) is strongly affected by H_2SO_4 concentration. A concentration range from 0.25 to 2.0 M was tested under the conditions of 0.5 M H_2O_2 and 1:5 solid/ liquid ratio at 95°C for 2 h. From the obtained leaching efficiencies shown in Fig. (2) it was observed that, V(IV), Ni(II), and Fe(II) extraction efficiencies increases from 65.17%, 41.50% and 17.2% to 98.5%, 61% and 31% respectively, when the H_2SO_4 concentration is increased from 0.25 to 1.5 M. A further increase in H_2SO_4 concentration to 2.0 M resulted in very little increase in the extraction efficiency of V(IV) and Ni(II). Therefore, the optimum H_2SO_4 concentration appears to be 1.5 M and all further experiments were carried out at this H_2SO_4 concentration.

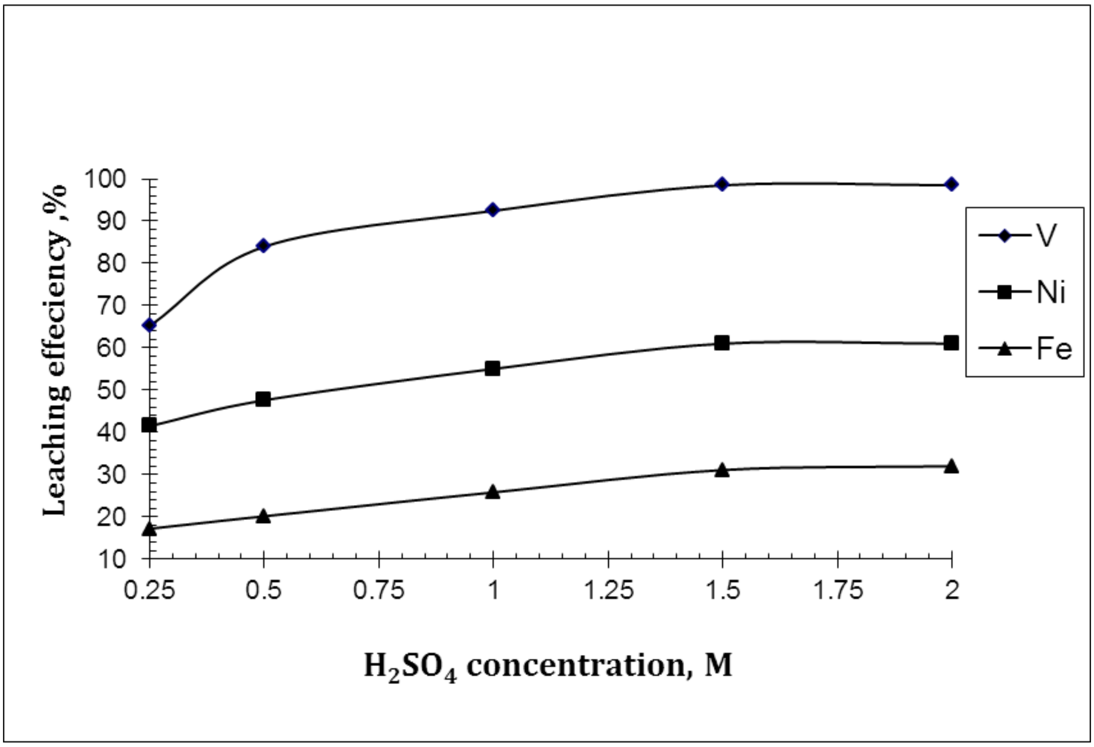

Fig. (2): Effect of H_2SO_4 concentration upon the leaching efficiencies of

V(IV), Ni(II), and Fe(II) at (0.5 M H_2O_2, 95°C, 1:5 solid/liquid ratio, 2h)

3.1.3 Effect of H_2O_2 concentration

The effect of H_2O_2 concentration was examined in the absence and presence of different concentrations of H_2O_2 varying from 0.1 to 0.6 M. The other leaching conditions were fixed at 1.5 M H_2SO_4, and 1:5 solid/ liquid ratio at 95°C for 2 h. From the obtained leaching efficiencies as plotted in Figure (3) it can be seen that, H_2O_2 concentration play a critical role in dissolution of V(IV). Hence the dissolution of V(IV) increase from 85.81% to 98.5% when the H_2O_2 concentration is increased from 0 to 0.5 M. With increase in H_2O_2 concentration to 0.6 M the extraction efficiency of V(IV) sharply decreased to 90.30%. Therefore, the optimum H_2O_2 concentration appears to be 0.5 M.

3.1.4 Effect of time

To improve the leaching conditions, another experimental leaching series was performed using < 120 min leaching time. In these experiments, the other leaching conditions were kept fixed; namely, 1.5 M H_2SO_4 and 0.5 M H_2O_2 at 95ºC in a solid/ liquid ratio of 1:5. From the results it is evident that at only 30 min leaching time, the leaching efficiencies of vanadium and nickel have been decreased to 46.66% and 29.86% respectively. With increasing leaching time, the extraction efficiency of vanadium and nickel sharply increased.

Therefore, it can be concluded that, 120 min leaching time would be adequate and could be considered as optimum for vanadium and nickel extraction.

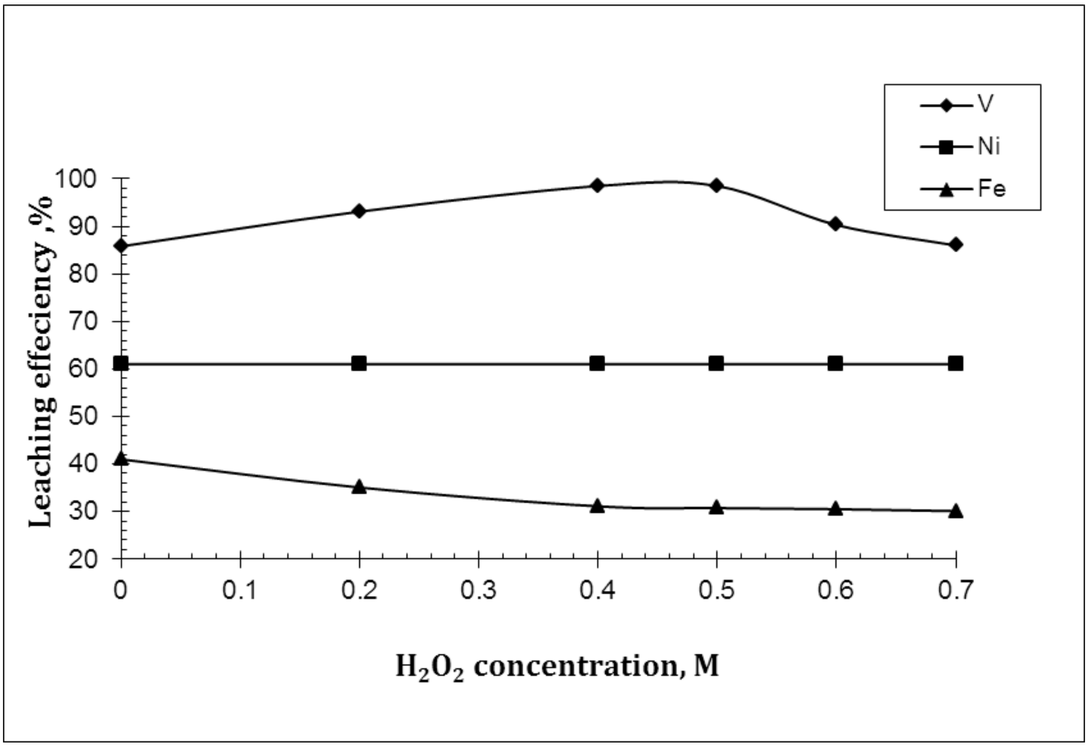

Fig. (3): Effect of H_2O_2 concentration upon the leaching efficiencies of V(IV), Ni(II), and Fe(II) at (1.5M H_2SO_4, 95°C, 1:5 solid/liquid ratio, 2 h).

3. 1. 5. Effect of temperature

In order to reduce the heat energy and leaching costs, four leaching experiments were carried out at room temperature, 50, 75, and 85ºC under the same conditions previously used at 95ºC. The resultant extraction efficiencies as shown in Fig. (4), indicate that the temperature plays a critical role in leaching vanadium and nickel. For example, working at room temperature, the obtained extraction efficiency for vanadium and nickel was decreased down to only 17.00% and 46.00% respectively and by increasing temperature to reach 75ºC the extraction efficiency of vanadium and nickel will reach 85.19% and 55% respectively, a further increase in temperature to reach 95ºC the extraction efficiency of vanadium and nickel become 98.5% and 61% respectively. Therefore, it can be concluded that 95ºC leaching temperature would be adequate and considered optimum.

3.1.6 Effect of solid/liquid ratio

Working with the fixed concentration of 1.5 M H_2SO_4 and 0.5 M H_2O_2 solution, another four leaching experiments were performed at solid/liquid ratios 1:2, 1:3, and 1:7 under the same leaching conditions used for the solid/liquid ratio 1:5. From the obtained results schemed in Fig (5), it was found that the extraction efficiencies of V(IV), Ni(II), and Fe(II) were decreased at 1:2 and 1:3 solid/liquid ratios. Increasing the acid amount by applying a solid/liquid ratio of 1:7, slightly increase the extraction efficiency. Therefore, it can be concluded that, solid/liquid ratio 1:5 is optimum.

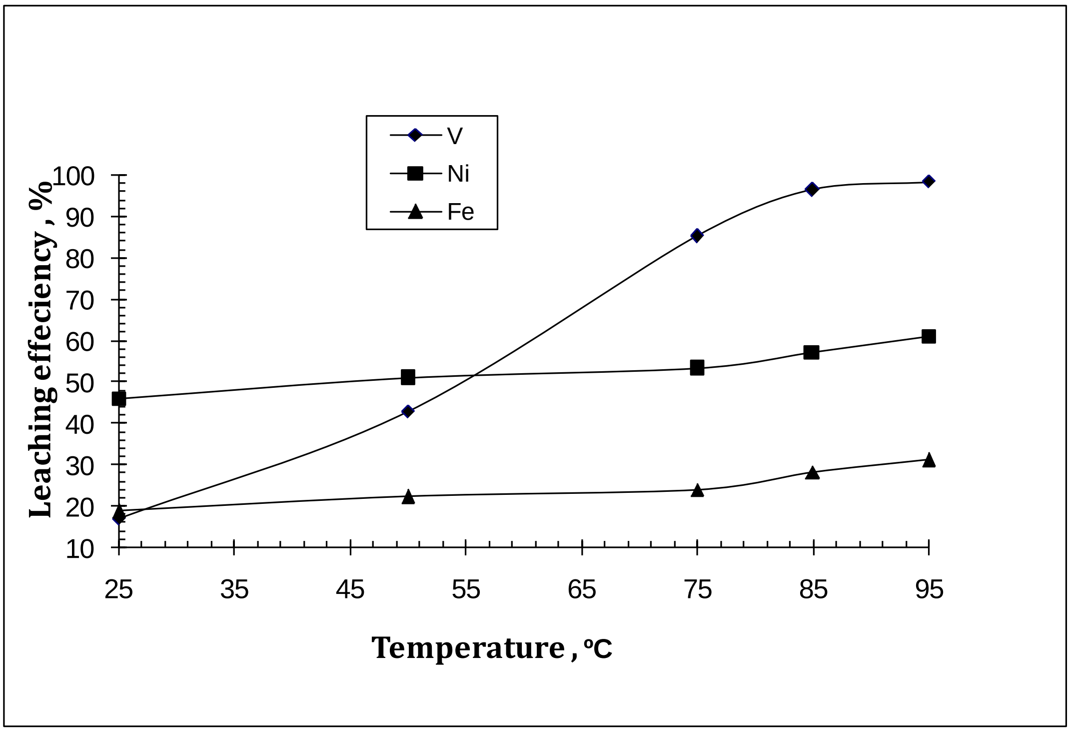

Fig. (4): Effect of temperature upon the leaching efficiencies of V(IV), Ni(II), and Fe(II) at (1.5 M H_2SO_4, 0.5 M H_2O_2, 1:5 solid/liquid ratio, 2 h).

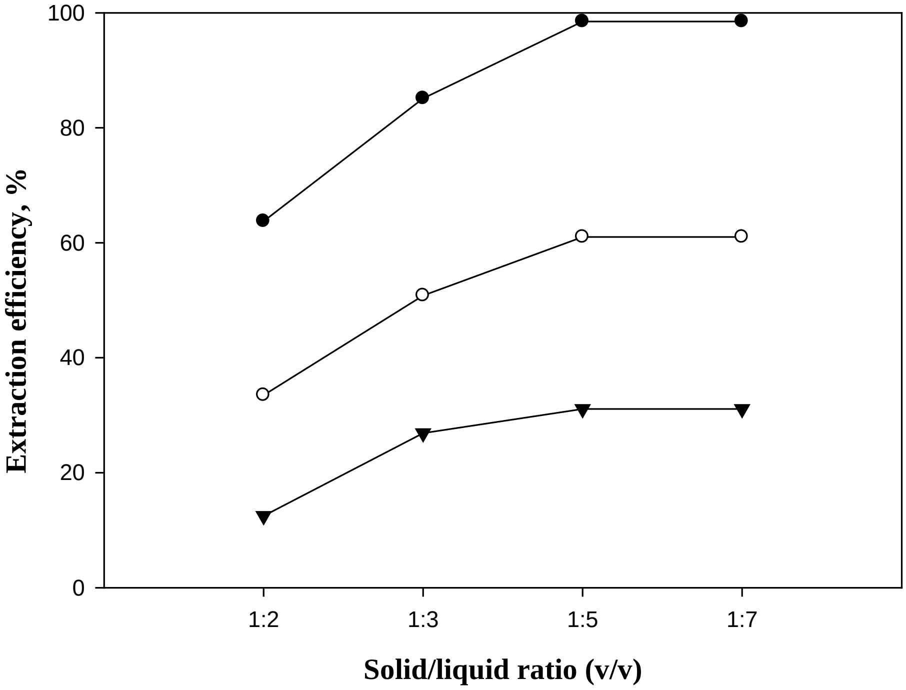

Fig. (5): Effect of solid/liquid ratio upon the leaching efficiencies of V(IV), Ni(II), and Fe(II) at (1.5 M H_2SO_4, 0.5 M H_2O_2, 95°C, 2h).

3.2 Leaching kinetics of vanadium

3. 2. 1. Kinetic analysis

Increasing attention is being paid to the study of the chemical kinetics of nonhomogeneous systems. In the classic homogeneous systems, the usual rate laws of first- and second-order kinetics are often sufficient to explain and analyze the experimental data. Leaching is a central unit operation in the hydrometallurgical treatment of ores, and the reactions occurring during the leaching process are typically heterogeneous. Thus, leaching reactions do not often obey simple first- and second-order kinetics. A kinetic analysis of these kinds of reactions is generally performed by noncatalytic heterogeneous reaction models. A kinetic analysis of leaching reactions is required for the effective design of leaching reactors for use in a hydrometallurgical plant. The leaching reaction of mineral particles by a reagent (a solid–fluid reaction) can be represented by the following reaction:

$$A_{fluid} + bB_{solid} \rightarrow \text{fluid and/or solid products} \qquad (1)$$

where A, B, and b represent the fluid reactant, the solid undergoing leaching, and stoichiometric coefficient, respectively. The kinetic of leaching reactions is often described by the shrinking core model. According to the shrinking core model, it is thought that the reaction between solid and fluid reactants takes place on the outer surface of solid. The solid reactant is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk fluid. As the reaction proceeds, the unreacted core of the solid shrinks toward the center of the solid, and a porous product layer forms around the unreacted core. However, it is assumed that the initial outside radius of the solid does not change while the leaching reaction continues [22].

The leaching rate of solid is governed by physical and chemical factors. The governing factors are the rate of transport of fluid reactant to and products from the particle surface (i.e., diffusion through the fluid film), the rate of diffusion of fluid reactant and products through the porous product layer that forms on the unreacted core of solid (i.e., diffusion through the product layer), and the rate of the reaction at the surface of unreacted core (i.e., surface chemical reaction). Each of these phenomena affects the rate of the overall leaching reaction. One or more of these factors might control the rate of reaction [18,19, 22].

For each step mentioned, the integrated rate equations derived from the shrinking core model are given in the literature. These rate equations can be written as follows:

If the leaching rate is controlled by the diffusion through the liquid film, then the integrated rate equation is:

$$X = k_1 t \qquad (2)$$

If the reaction rate is controlled by the diffusion through the ash or product layer, then the integrated rate expression is:

$$1 - 2/3X - (1-X)^{1/3} = K_d t \qquad (3)$$

If the leaching rate is controlled by the surface chemical reaction, then the integrated rate equation is:

$1 - (1\text{-}X)^{1/3} = K_ct$ (4)

where X is the conversion fraction of solid particle, k_l is the apparent rate constant (min^{-1}) for diffusion through the fluid film, k_d is the apparent rate constant (min^{-1}) for diffusion through the product layer, k_c is the apparent rate constant (min^{-1}) for the surface chemical reaction, and t is the reaction time.

3. 2. 2. Effect of temperature

The temperature is a factor of great importance for the leaching kinetics. The effect of reaction temperature was examined from 298 to 368 K under the conditions of 1.5 M H_2SO_4, 0.5 M H_2O_2, and 1:5 solid/liquid ratio from 0 to 120 min. The extraction efficiency curves obtained are shown in Fig. 6. It is clear that, the quantity of vanadium dissolved increases with increasing reaction temperature. In order to determine the kinetic parameters and rate controlling step, the experimental data as shown in Fig. (6) was analyzed on the basis of Eq. (2), Eq. (3) and Eq. (4) (shrinking core model) and the experimental data validity was tested by statistical and graphical methods and then the multiple regression coefficient obtained for the integral rate expression were calculated. The results showed that, the experimental results (in Fig. 6) fit the reaction model of Eq. (4), as shown in Fig. (7) which demonstrated that the reaction rate of vanadium leaching process is controlled by chemical reaction at the particle surface under the experimental conditions.

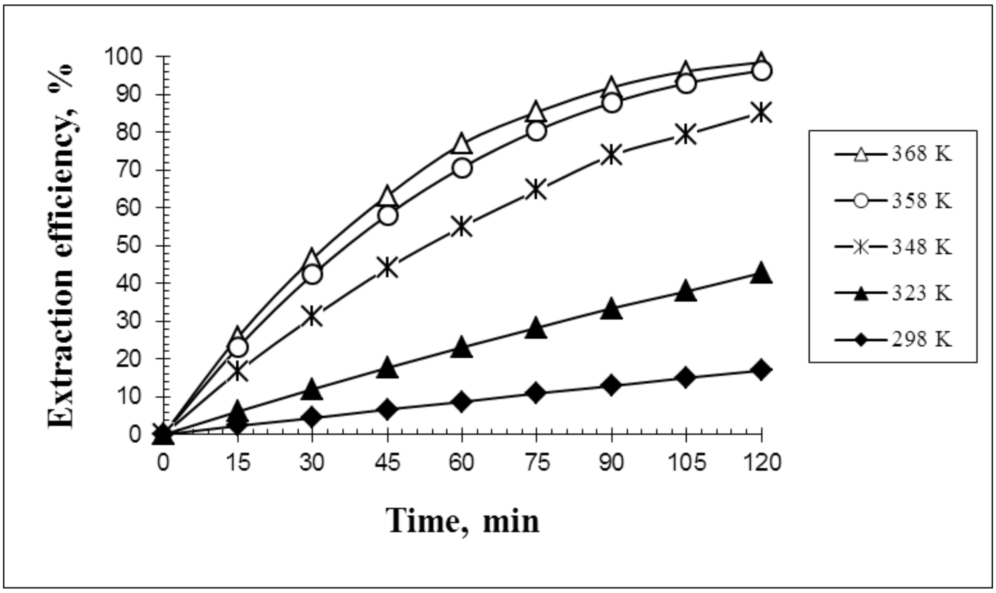

Fig. (6): Effect of temperature on leaching rate of vanadium at

(1.5 M H_2SO_4, 0.5 M H_2O_2, and 1:5 solid/liquid ratio).

The apparent activation energy was determined based on the Arrhenius equation:

$k = A \exp(-Ea/R^{-}T)$ (5)

or $\ln k = \ln A - Ea/RT$ (6)

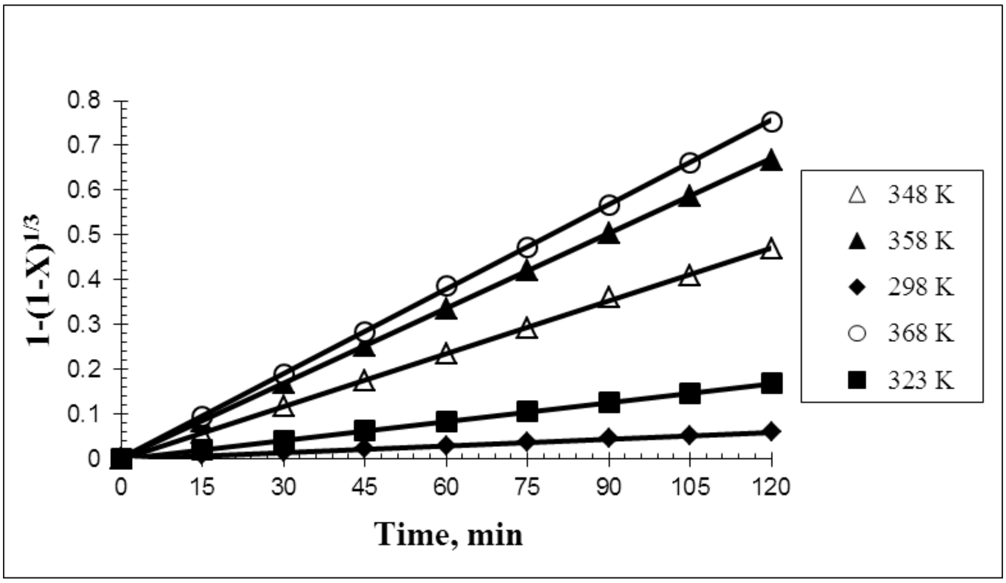

Fig. (7): Relationship between [1-(1-X) $^{1/3}$] and leaching time for vanadium leaching

at various temperature at (1.5 M H_2SO_4, 0.5 M H_2O_2, and 1:5 solid/liquid ratio).

Where k is a reaction rate constant, A is the frequency factor, Ea is the apparent activation energy and R is the gas constant. The data for the five temperatures are presented in Fig. (8), the regression analysis showed that the linear relationship is also significant. The apparent activation energy (Ea) was, hence, determined to be 34.35 kJ/mol.

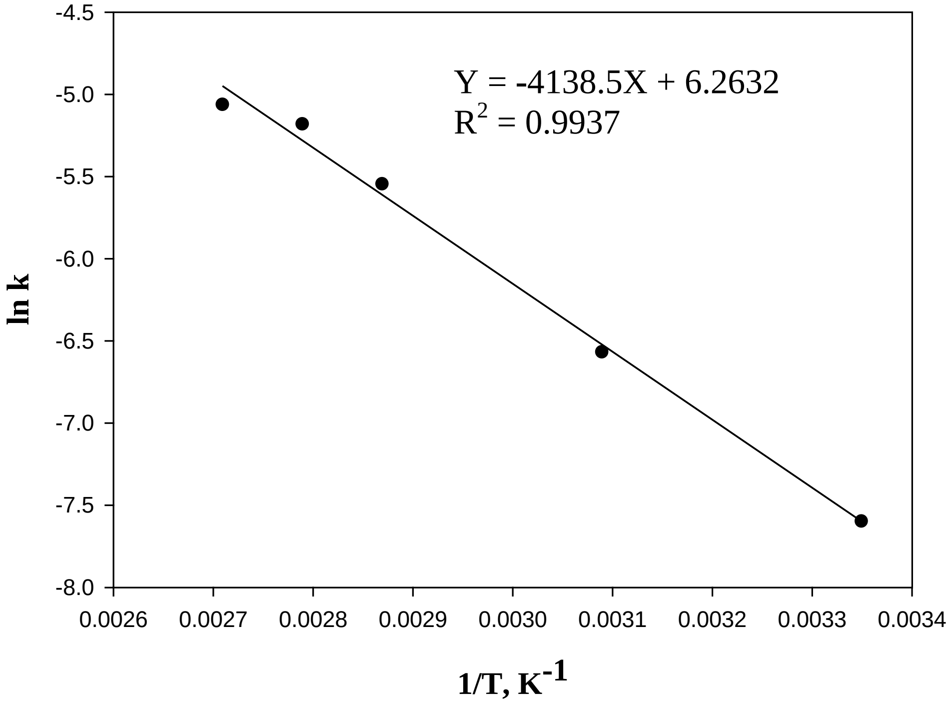

Fig. (8): Arrhenius plot for vanadium leaching at (1.5 M H_2SO_4, 0.5 M H_2O_2)

4. Conclusion

It is proved from the experiments that vanadium and nickel can be easily leached from Egyptian boiler ash by using H_2SO_4 acid in presence of H_2O_2 as oxidant. The results shows that, working 1.5 M H_2SO_4; 0.5 M H_2O_2; stirring speed 600, solid/liquid ratio 1:5 at 95°C for 2 h, the extraction efficiency of vanadium attained about 98.5%, whilst nickel and iron extraction reach 61% and 31% respectively.

The leaching kinetics of vanadium shows that, the rate of vanadium leaching using H_2SO_4 acid in presence of H_2O_2 as oxidant is chemically controlled and follows the shrinking core model $1-(1-X)^{1/3}=kt$ with an apparent activation energy of 34.35 kJ/mole.

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