Leaching Kinetics and Recovery of Vanadium from Egyptian Boiler Ash Under Alkaline Oxidizing Conditions

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ABSTRACT

Processing of Egyptian boiler ash in potassium hydroxide solution using potassium perchlorate as an oxidant has been investigated. The results showed that leaching temperature, potassium perchlorate, potassium hydroxide concentration, leaching time, liquid-to-solid ratio and agitation speed, have a significant effect; optimum process operating parameters were established as follows: temperature: 95 °C; concentration of KClO₃: 2%; potassium hydroxide concentration: 2 M; time: 3 h; liquid-to-solid ratio: 5:1; agitation speed: 600 rpm. Under these experimental conditions, the extraction efficiencies of Vanadium attained 99% with no co-extraction of Nickel and Iron. 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 32.393 kJ/mol. Direct precipitation of pure Vanadium pentoxide from the obtained leach liquor with no co-extraction of Nickel and Iron had been done also, no need to use solvent for extraction. In fact this method will be the best to be applied to the Industrial-scale.

KEYWORDS
Oxidative Leaching, Vanadium, Leaching of Vanadium, Kinetics, Recovery.

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INTRODUCTION

Vanadium, as a very important material, is widely used in various fields (Liao, et al. 1985).

Vanadium is an important rare metal so, it is exposed to a rapid depletion of its based ores. However, renewed sources for Vanadium production have to be established to face the continuous need of Vanadium. For this reason, the recovery of Vanadium from fly and boiler ashes has received attention in recent years and high priority. On the other hand, the disposal and accumulation of this industrial waste may lead to environmental problems. Several methods have been used to recover Vanadium from fly and boiler ashes using hydrometallurgical processes. The recovery may be carried out directly by acid (Tsai et al., 1998, Vitolo et al., 2000, 2001; Navarro et al., 2007) alkaline (Akita et al., 1995) or water (Akaboshi et al., 1987) leaching; this may be followed by an oxidation of Vanadium using air (Akaboshi et al., 1987), NaClO (Whigham, 1965), NaClO (Schemel, 1985), or oxygen (Goddard, 1987). Vanadium in the attained leach liquor may be separated using precipitation (Vitolo et al., 2000), ion exchange (Tokuyama et al., 2003), or solvent extraction (Lozano and Juan, 2001, Miura et al., 2001 and Guibal et al., 2003).

Kinetic study of any chemical reaction is an indispensable part in designing the chemical process at leaching stage. Most of the leaching processes are reactions occur between liquid and solid phases. The models that have been used to express kinetics of non-catalytic liquid-solid reactions are the homogeneous, grain, uniform pore and random pore models, shrinking (including shrinking particle and shrinking core), (Gbor and Jia, 2004; Georgiou and Papangela-kis, 1998).

The aim of this work is to investigate a simple leaching process of the Egyptian boiler ash from El-Korimat thermal power station by KOH solution in the presence of KClO₃ as oxidizing agent. The effects of the main system variables on the leaching rate are examined. Moreover, the kinetic aspects of leaching Vanadium which provided a theoretical basis for the industrial application in the future had been studied.

EXPERIMENTAL

1. Chemical analysis 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% SiO₂, 2.93% Al₂O₃, 12.49% Fe₂O₃, 5.81% CaO, 9.65% MgO, 3.51% K₂O, 2.85% Na₂O. Beside the presence of 10.51% Vanadium and 8.01% Nickel. All the chemicals used in this study were of analytical grade.

2. Analytical procedures

The ore was analysed for its major and minor elements using the proper analytical methods (Marczenko. et al., 1986; Welz et al., 1999).

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 KOH solution and KClO₃ 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.

RESULTS AND DISCUSSION

1. Leaching results

1.1. Effect of stirring speed

Fig (1) presents the effect of stirring speed under the conditions of ~74 µm particle size, 2.5 M KOH, 2% KClO₃ and 1:5 solid/liquid ratio at 95°C for 3 h. The results indicated that, the leaching rate of Vanadium increases quickly below 400 rpm and remains almost constant after 600 rpm. Clearly, stirring speed
improves leaching efficiency of Vanadium; increase stirring speed usually increases the rate of leaching due to the suspension of the compound 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.

1. 2. **Effect of KOH concentration**

![Fig.(1): Effect of stirring speed upon the leaching efficiencies of V(IV) (2.5 M KOH, 2% KClO₃ and 1:5 solid/liquid ratio at 95°C for 3 h).](image1)

Extraction of Vanadium is affected by KOH concentration. A concentration range from 0.25 to 2.5 M was tested under the conditions of -74 µm particle size, 2% KClO₃ and 1:5 solid/liquid ratio at 95°C for 3 h with stirring speed 600 rpm. From the obtained leaching efficiencies as plotted in Fig (2), it was observed that, Vanadium extraction efficiencies increases from 35.11% to 99% when the KOH concentration is increased from 0.25 to 2 M. A further increase in KOH concentration to 2.5 M resulted in very little increase in the extraction efficiency of Vanadium. Therefore, the optimum KOH concentration appears to be 2 M and all further experiments were carried out at this KOH concentration.

![Fig.(2): Effect of KOH concentration upon the leaching efficiencies of V(IV), Ni(II), and Fe(II) at (2% KClO₃ and 1:5 solid/liquid ratio at 95°C for 3 h).](image2)

1. 3. **Effect of KClO₃ concentration**

The effect of KClO₃ concentration was examined in the absence and presence of different concentrations of KClO₃ varying from 1 to 3%. The other leaching conditions were fixed at -74 µm particle size, 2 M KOH, and 1:5 solid/liquid ratio at 95°C for 3 h. From the obtained leaching efficiencies as plotted in Fig (3), it was observed that, KClO₃ concentration play a critical role in dissolution of Vanadium. Hence the dissolution of Vanadium increases from 84% to 99%, when the KClO₃ concentration is increased from 0 to 2%. With increase in KClO₃ concentration to 3% the extraction efficiency of Vanadium sharply decreased to 90.50%. Therefore, the optimum KClO₃ concentration appears to be 2%.

![Fig.(3): Effect of KClO₃ concentration upon the leaching efficiencies of V(IV), at (2 M KOH, and 1:5 solid/liquid ratio at 95°C for 3 h).](image3)

1. 4. **Effect of time**

In order to evaluate the effect of time, a series of leaching experiments was carried out at different times ranging from 30 to 180 min. In these experiments, the other leaching conditions were kept fixed; namely, 2 M KOH, 2% M KClO₃, and 1:5 solid/liquid ratio at 95°C. From the results obtained, it is evident that, at only 30 min leaching time, the leaching efficiencies of Vanadium has been decreased to 36.30%. With increasing leaching time, the extraction efficiency of Vanadium sharply increased to reach 99%.

Therefore, 180 min leaching time would be adequate and could be considered as optimum for Vanadium extraction.

3. 1. 5. **Effect of temperature**

Four leaching experiments were carried out at room temperature, 50, 75, and 85°C under the same
conditions previously used at 95°C. The resultant extraction efficiencies plotted in Fig. (4) Indicates that, the temperature plays a critical role in leaching Vanadium. For example, working at room temperature, the obtained extraction efficiency for Vanadium was decreased to only 21.51. By increasing temperature to 75°C the extraction efficiency of vanadium will reach 80.01, a further increase in temperature to reach 95°C the extraction efficiency of Vanadium become 99 %. Therefore, it can be concluded that 95°C leaching temperature would be adequate and considered optimum.

2. Leaching kinetics of vanadium

2.1. Kinetic analysis

Leaching reactions do not often obey simple first- and second-order kinetics. A kinetic analysis of leaching reactions are generally expressed by non-catalytic heterogeneous reaction models. A kinetic analysis of leaching reactions is essential for the effective design of leaching reactors to be used in a hydrometallurgical plant.

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. (Ibrahim et al., 2013; Levenspiel, 1999).

These rate equations can be expressed as follows:

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

\[ X = k_1 t \]  

(2)

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

\[ 1 - 2/3X - (1-X)^{1/3} = K_d t \]  

(3)

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

\[ 1 - (1-X)^{1/3} = K_c t \]  

(4)

where \( X \) is the conversion fraction of solid particle, \( k_1 \) is the apparent rate constant \( (\text{min}^{-1}) \) for diffusion through the fluid film, \( k_d \) is the apparent rate constant \( (\text{min}^{-1}) \) for diffusion through the product layer, \( k_c \) is the apparent rate constant \( (\text{min}^{-1}) \) for the
surface chemical reaction, and \( t \) is the reaction time.

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 2 M KOH, 2% KClO₃, and 1:5 solid/liquid ratio from 0 to 180 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.

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

\[
k = A \exp(-\frac{E_a}{R \cdot T}) \tag{5}
\]

or \( \ln k = \ln A - \frac{E_a}{RT} \) \tag{6}

Where \( k \) is a reaction rate constant, \( A \) is the frequency factor, \( E_a \) 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 (\( E_a \)) was, hence, determined to be 32.393 kJ/mol.

![Fig.(6): Effect of temperature on leaching rate of Vanadium at (2 M KOH, 2% KClO₃ and 1:5 solid/liquid ratio).](image)

![Fig.(7): Relationship between \([1-(1-X)^{1/3}]\) and leaching time for Vanadium leaching at various temperature at (2 M KOH, 2% KClO₃ and 1:5 solid/liquid ratio).](image)

![Fig.(8): Arrhenius plot for Vanadium leaching at (2 M KOH, 2% KClO₃ and 1:5 solid/liquid ratio).](image)

![Fig.(9): XRD analysis of the pure Vanadium pentoxide (\( V_2O_5 \)) product.](image)

RECOVERY OF \( V_2O_5 \)

Before precipitating vanadium, Ammonium chloride in a solid/liquid ratio of 5 g NH₄Cl/250 ml solution was added to the filtered leach liquor containing either 0.01 M oxidizing agents HClO₄ or HNO₃.
The obtained precipitate (ammonium meta vanadate) is dried at 110°C for 2 h, the product obtained was undergoing thermal decomposition at 400°C for 4 h. A pure form of Vanadium pentoxide (V₂O₅) was obtained as indicated by XRD, EDAX analysis as shown in Fig (9), Fig (10).

Based on the experimental results of the present investigation a technological flow sheet, describing the alkaline leaching, Vanadium and silica separation and the recovery of V₂O₅ by precipitation followed by thermal decomposition of the obtained crystals, was presented in Fig. 11.

**CONCLUSION**

It is clear from the experiments that Vanadium can be easily leached from Egyptian boiler ash by using KOH in presence of KCIO₃ as oxidant. The results shows that, working 2 M KOH; 2% KCIO₃; stirring speed 600, solid/liquid ratio 1:5 at 95°C for 3 h, the extraction efficiency of Vanadium attained about 99%, with no co-extraction of Nickel and Iron. Recovery of pure V₂O₅ from the resultant leach liquor is done to establish a good separation method of Vanadium pentoxide from the Egyptian boiler ash.

The leaching kinetics of Vanadium shows that, the rate of Vanadium leaching using KOH in presence of KCIO₃ as oxidant is chemically controlled and follows the shrinking core model 1− (1−X)³/₅=kt with an apparent activation energy of 32.393 kJ/mole.

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**Table:**

<table>
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<th>Element</th>
<th>Mass %</th>
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**Fig. (10):** Scanning Electron Microscopy and Energy Dispersive Spectroscopy analysis of Vanadium pentoxide.

**Fig. (11):** Flow sheet for the process of recovery of V₂O₅ from El-Korimat boiler ash leach liquor.


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