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Research Paper

A Kinetic Study of Vanadium Dissolution During Acetic Acid Leaching of Steel Making Converter Slag

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ABSTRACT

Steelmaking slags are known as the secondary product of steel making process. Regarding the high rate of slag production and the existence of a noticeable amount of toxic and valuable metals such as vanadium in this material; recovery of vanadium from this product is necessary. In this study, steel making converter slag (containing about 1.96 wt.% V_2O_5) was ground to a mean size of 85 µm, and recovery of vanadium was carried out using acetic acid leaching. The effects of time (in the range of 0 to 120 min) and temperature (in the range of 0 to 80 ^{0} C) in fixed acetic acid concentration (1 molal) and solid to liquid weight ratio (one gram slag in 200 ml) on the leaching process were investigated. The results showed that the increase in time and decrease of temperature (activation energy was equal to -11.4 kJ/mol) increases vanadium leaching efficiency. Maximum leaching efficiency was reached at 0 ^{0} C and 90 min. Kinetics studies showed that heat diffusion through the solid layer is the controlling step of vanadium dissolution in acetic acid. Furthermore, thermal conductivity (ka) decreases by increasing temperature (ka=21877.6/T3), so the heat moves away from the reaction zone to the particle's surface at a slower rate.

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1. Introduction

Vanadium is present in the earth's crust at an average grade of 150 grams per ton and is very significant. However, due to its wide distribution in nature, it is still a scarce element to this day. Additionally, because of its special chemical properties, vanadium is not found as an independent ore but is found with other oxides, especially iron oxide [1]. Approximately 50% of the vanadium sources are present in the titaniferous magnetite ore [2]. Commercial extraction of this metal is often carried out from secondary materials (by-products of other processes such as fly ash) as the concentration of vanadium in the primary sources is low [3].

Slag is a by-product of the iron and steel production process and currently accounts for 80% of vanadium production [4]. Huge quantities of steel slag are produced each year in different countries. In addition, the presence of valuable elements such as vanadium, its use for various purposes has been investigated. In Sweden, in a factory that used steel making converter slag to produce agricultural fertilizers, some died due to vanadium poisoning, so it is forbidden for fertilizer production. Therefore, vanadium recovery from a steelmaking converter slag is both economically and environmentally important [4; 5].

The most common methods of vanadium extraction involve four steps: salt roasting (with sodium carbonate, sodium chloride, or sodium sulfate), leaching, solution purification, and precipitation of V_2O_5. Direct leaching can be an alternative to salt roasting. Acid or base leaching has been used commercially for vanadium recovery from uranium-containing ore, spent catalyst, and fuel ash [2; 6].

By sodium carbonate roasting and hot water leaching, the vanadium recovery of about 85% was reported [7]. Aarabi et al. used sodium carbonate roasting and sulfuric acid leaching to recover vanadium from steel converter slag and recovered more than 90% of vanadium [8].

Mahdavian et al. used salt roasting with sodium carbonate and leaching with sodium carbonate-sodium hydroxide solution, achieving an efficiency of about 80% [1]. The extraction of vanadium oxide from fuel ash using two methods was investigated: a combined pyro-hydrometallurgical process and a hydro-metallurgical process. In the combined pyro-hydro-metallurgical process, the ash was the first alkaline melted. The resulting product was dissolved in water, and the vanadium compounds were precipitated and calcined. In the hydrometallurgical process, the ash was dissolved in sodium hydroxide, and then vanadium was recovered as an oxide [9]. Several studies have been performed on the direct separation of vanadium oxide from slag [10]. Xiao et al. used a method to recover vanadium based on selective silica separation from a vanadium-containing steel slag using sodium hydroxide leaching [11].

Since vanadium is mainly trapped in the calcium oxide structure [12; 13], it is necessary to review the dissolution behavior of calcium oxide compounds. Iwama et al. showed that citric acid could dissolve up to 74% of the calcium oxide in the slag [14]. In a study by Eloneva et al. aimed at dissolving the calcium content of steel converter slag and calcium carbonate precipitation from that solution, 16 different solvents were investigated to find the appropriate calcium solvent in a steel converter slag. Their experiments showed that acetic acid is a suitable solvent with the highest calcium dissolution efficiency [15]. Gharabaghi et al. used acetic acid leaching to remove carbonate ganglion and increase the P2O5 percentage in calcareous phosphate ore. The reaction of acetic acid with calcareous materials is expressed as reaction (1) [16]:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O \qquad (1)$$

Teir et al. investigated the leaching of steel slag in acetic acid to precipitate calcium carbonate. The reaction of acetic acid with calcium silicate is expressed as reaction (2) [17]:

$$CaSiO_3 + 2CH_3COOH \rightarrow Ca^{2+} + 2CH_3COO^- + SiO_2 + H_2O \qquad (2)$$

After filtering the silica from the solution, the CO_2 gas is pumped into the solution, and calcium carbonate is formed and precipitated:

$$Ca^{2+} + 2CH_3COO^- + CO_2 + H_2O \rightarrow CaCO_3 (\downarrow) + 2CH_3COOH \qquad (3)$$

At this step, acetic acid is recovered and reused. The Gibbs free energy change of each step is negative and, therefore, does not require high input energy. It was found that calcium extraction from iron and steel slag is very fast. Almost all the calcium in the slag can be dissolved. Increasing the acetic acid concentration and decreasing the dissolution temperature results in the increased dissolution of calcium in acetic acid. Thermodynamic calculations also showed that the dissolution of calcium in the acetic acid is exothermic [17]. There is not any comprehensive kinetic study on the vanadium recovery from steel converter slag by acetic acid. Therefore kinetics of vanadium dissolution in acetic acid during the leaching process of steel converter slag is the purpose of the present study.

2. Materials and methods

2.1. Materials

- Laboratory acetic acid (Merck) with a purity of 98% and a density of 1050 gr/liter and a molecular weight of 60.05 gr/mol.

- Steelmaking converter slag from Isfahan Steel Company. This slag was available in course size, which was used after grinding to -246 µm. The particle size distribution of this product (which is used as raw material in leaching tests) was obtained as presented in Table 1. Weight average diameter [18] was calculated equal to 85 µm.

Table 1. Particle size distribution of ground steel converter slag.

Particle size (μm)	Weight present
147-246	13.750
88-147	24.325
61-88	18.510
43-61	9.250
38-43	20.745
-38	13.420

X-ray fluorescence (XRF) of steelmaking slag in table 2 shows its approximate chemical analysis.

Table 2. XRF analysis of steel converter slag.

compound	CaO	Fe_2O_3	SiO_2	P_2O_5	MnO	TiO_2	V_2O_5	Al_2O_3	MgO
Wt.%	49.26	20.30	9.67	1.54	4.53	1.66	1.79	1.20	1.50

To determine the exact concentration of vanadium in steelmaking slag; 1 gram of slag powder with 10 gram of NaOH and 1 gram of Na_2O_2 were mixed and heated in a nickel crucible until they melted completely. The melt was then poured into distilled water, and the pulp was stirred for 1 hour [19]. After filtering the pulp, the solution was analyzed by the ICP method. The result shows 1.96 wt.% V_2O_5 in the converter slag.

X-ray diffraction (XRD) analysis was performed to study the phases of the steel converter slag, and the results are shown in Fig. 1. The identified phases include $Ca(OH)_2$, $Ca_2Fe_2O_5$, Ca_2SiO_4, $Ca_2Mn_2O_5$ and Fe_2O_3.

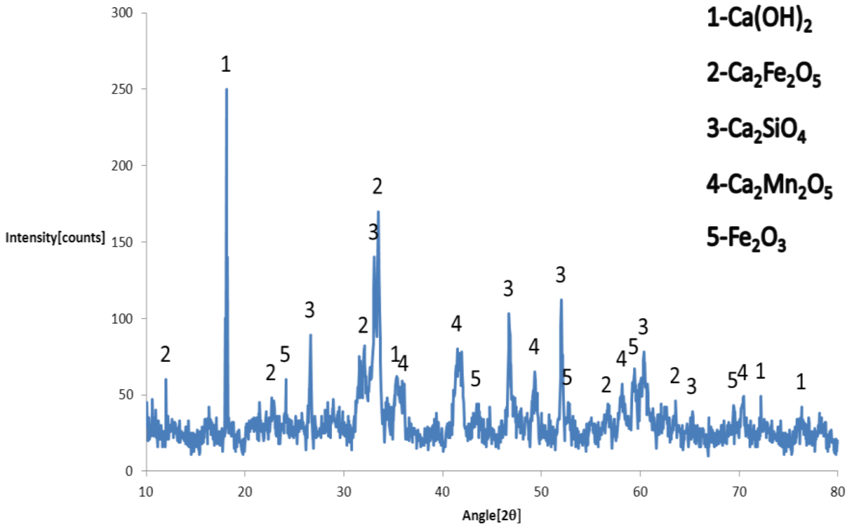

Fig. 1. X-ray diffraction pattern of the steel converter slag

FE-SEM micrograph of the raw material and leaching residual were given in Fig. 2 and showed a random morphology.

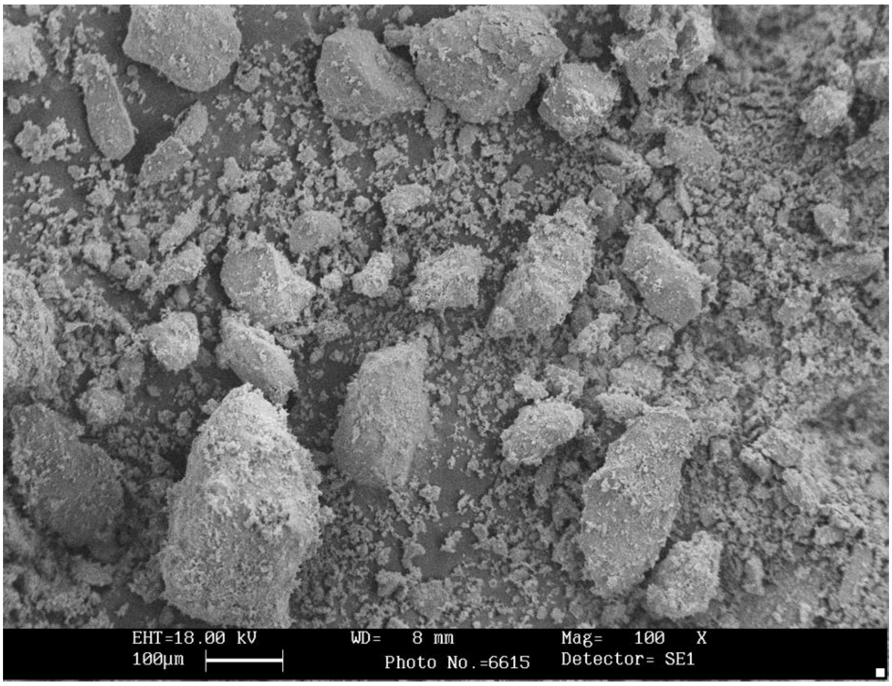

Fig.2. morphology of the raw material

2.2. Equipment

- Sieve analysis (Manufactured by Damavand Co., Iran).
- XRF analysis (Bruker, S4 pioneer, Germany).
- XRD analyzer (X-pert) with 30 mA current and 40 kV voltage, Cu-Kαradiation with a wavelength of 1.5406 angstroms (Manufactured by Philips, Netherlands).
- FE-SEM (Cam Scan model MV2300)
- ICP analyzer (optima 7300DV) for concentration analysis of solutions (Manufactured by Perkin-Elmer, USA).

2.3. Method of Experiments

A homogeneous slag sample using the quartering method [20] was prepared for each experiment. Leaching temperature was changed from zero to 80 degrees Celsius, and leaching time was changed from 10 to 120 min.

After each test, the pulp was filtered, and vanadium concentration was measured by ICP, and vanadium recovery was calculated (concentration measured in each experiment divided by the total vanadium soluble concentration in the sample).

The constant conditions in these experiments were as follows:

- Pulp density (solid to liquid ratio) of one gram slag in 200 ml of solvent.
- Solution stirring speed of 200 rpm.
- Acid concentration of 1 molal.

3. Results and discussion

As can be seen in Fig.3, decreasing the temperature and increasing the time resulted in an increase in vanadium dissolution fraction. It is also observed that the highest solubility fraction is obtained at 0 °C and 90 min.

3.1. Determining the process controlling step

The micrograph of residual solid after leaching in Fig.4 shows no significant change in particles size compared to raw materials. So it is inferred that there is a product layer on the shrinking core.

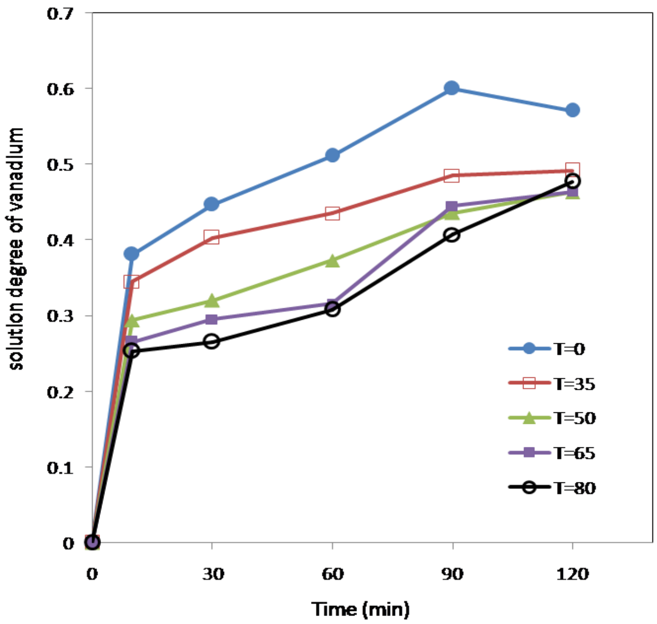

Fig. 3. Effect of temperature and time on the solubility of vanadium from steel converter slag in 1 molal acetic acid solution (temperature in degrees Celsius)

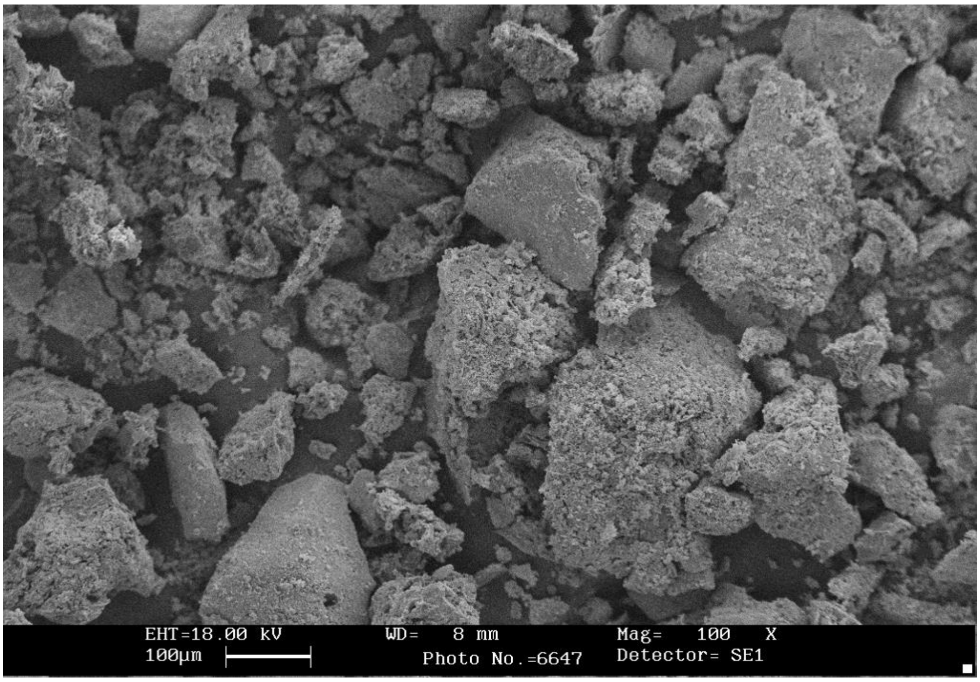

Fig. 4. Micrograph of residual salid after leaching.

According to the shrinking core model, the steps of a dissolution process are as follows:

a) Solvent transfer to the particle surface.

b) Solvent diffusion from the surface of the solid product reacted to the product-raw material interface.

c) Chemical reaction.

d) The diffusion of reaction products from through the product layer to the particle surface.

e) Reaction products transfer from the surface of the particle to areas far from the surface.

Any of the above steps that have the most resistance to the overall dissolution process (have the slower rate) will be the rate-controlling of the process.The following hypotheses have to be taken into account for the kinetic investigation of the shrinking core model:

- Steady-state conditions.
- Isothermal conditions.
- The initial size of the solid particle does not change during the reaction.

Table 3 summarizes the relationships of the shrinking core model for a sphere particle. The term X is the dissolution fraction, t is time, and τ is time for the complete reaction [21; 22].

Table 3. The relationships of the shrinking core model for a sphere particle [21; 22].

$\mathrm{f(X)}: a\ fanction\ of\ X$	Controlling step
$\mathrm{X} = \frac{\mathrm{t}}{\tau}$	Transfer
$1 - 3(1 - \mathrm{X})^{2/3} + 2(1 - \mathrm{X}) = \frac{t}{\tau}$	Diffusion
$1 - (1 - \mathrm{X})^{1/3} = \frac{\mathrm{t}}{\tau}$	Chemical reaction

The results of the kinetic studies of vanadium dissolution of steel converter slag on 1 molal acetic acid at 0, 35, 50, 65, and 80 °C are shown in Fig.5. In these figures, R is the correlation coefficient. As can be seen in this figure, at all temperatures, the process is diffusion control.

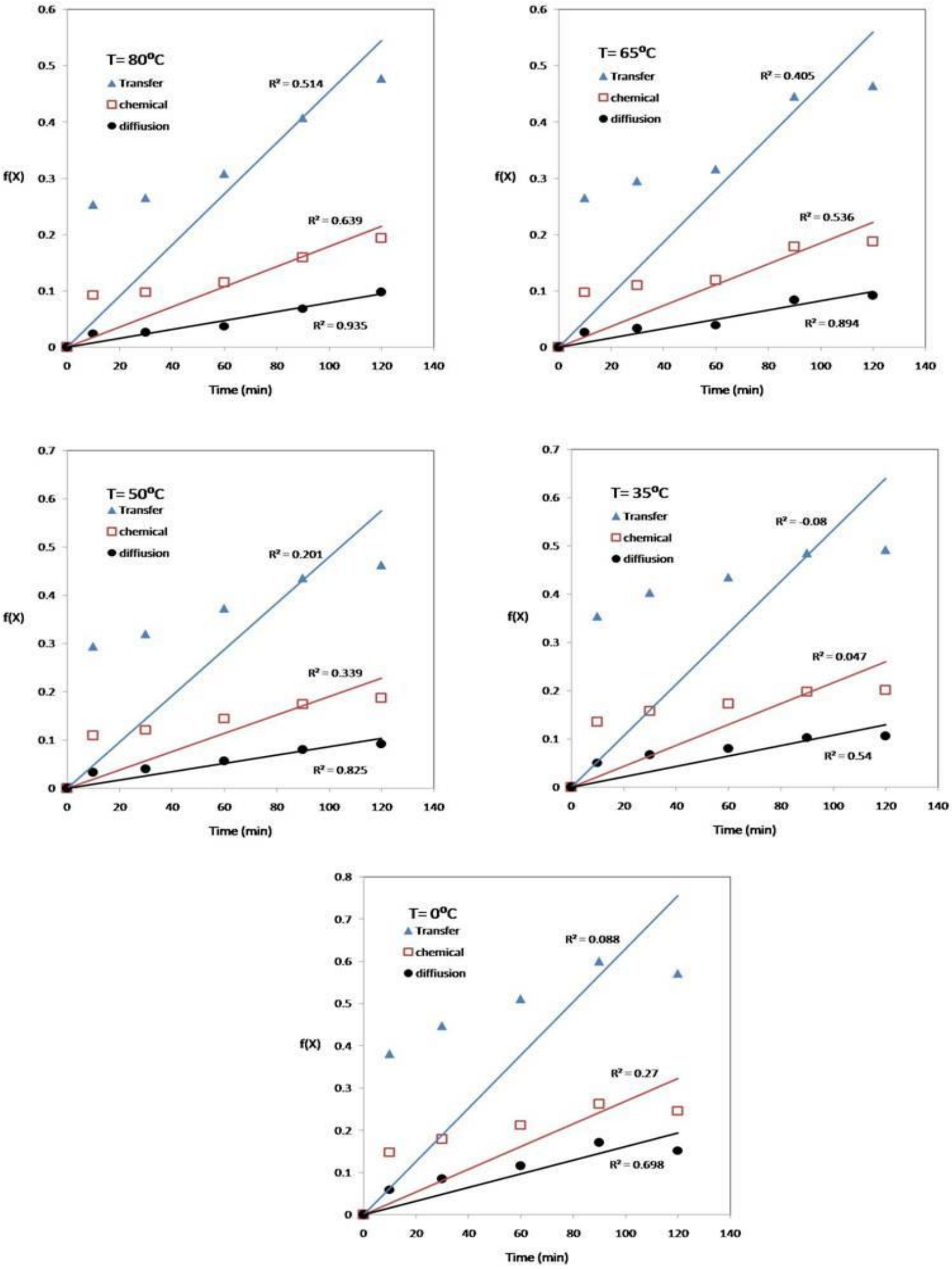

Fig. 5. Fitting of the experimental data to the kinetic models

3.2. Effect of temperature on the reaction kinetics

Fig.3 shows a decrease in leaching efficiency as the temperature increases, which is in agreement with other investigations [17]. The slope values of the lines f(X) versus t, which are indicated by k_a, were given in Table 4. k_a is equal to 1/τ and is called the apparent rate coefficient.

Table 4. The values of apparent rate coefficient in different temperature.

T (°C)	0	35	50	60	80
$k_a\ (min^{-1})$	1.61×10^{-3}	1.08×10^{-3}	8.55×10^{-4}	8.22×10^{-4}	7.84×10^{-4}

The activation energy of this process was calculated using Arrhenius equation [21] in fig.6 and was equal to $-11.4\ kJ/mol$.

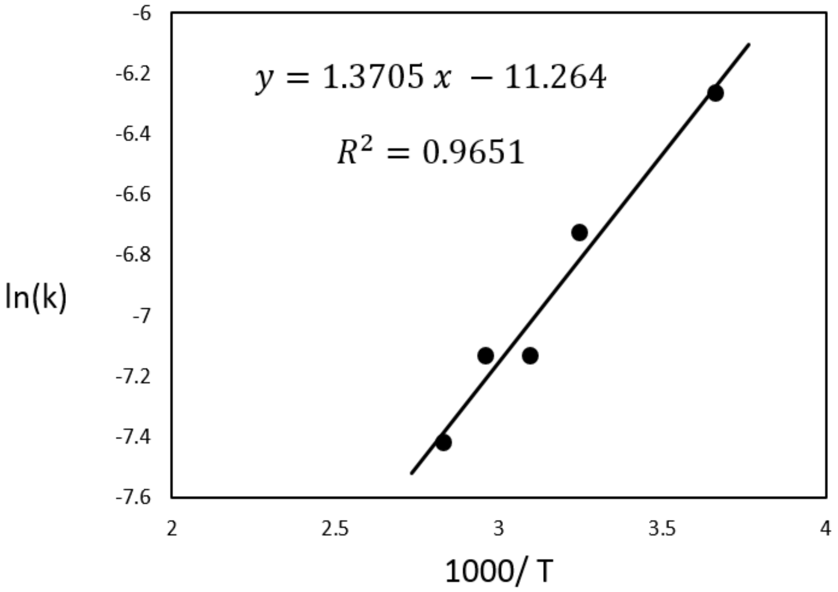

Fig. 6. Plotting of Arrhenius equation.

The rate of a diffusion control process is proportional to the diffusion coefficient [21]. However, the mass diffusion coefficient always increases with increasing the temperature [23]. So, in spite of the fact that the process is diffusion control, it is not mass diffusion. Here it should be noted that:

Firstly, as it is mentioned earlier, vanadium is trapped in calcium oxide structures [12; 13].

Secondly, the reaction of lime dissolution in acetic acid is an exothermic reaction [17].

Therefore, the dissolution of vanadium requires the dissolution of calcareous structures, which is, of course, an exothermic reaction. Therefore, the continuation of the process depends on the diffusion of this heat from inside the particles to their surface. However, according to phase analysis (Fig.1), this layer consists of ceramic materials. However, it has been theoretically and empirically confirmed that the thermal conductivity of ceramic materials decreases with increasing temperature [24-26]. As a result, when temperature increases, thermal conductivity decreases, and, consequently, the heat moves away from the reaction zone to the surface of a particle at a slower rate. Therefore, the overall process speed decreases with increasing the temperature. Fig. 7 shows the hyperbolic variation of the apparent rate coefficient with temperature. By plotting it logarithmically, Fig. 8 shows that a straight line corresponds well to these data, and equation (4) can be derived.

$$k_a = \frac{10^{4.34}}{T^3} \tag{4}$$

The relationship between the time for complete reaction (τ) and other parameters is in the form of equation (5), where d_0 is the initial particle diameter, ρ_B the product layer density, k is the thermal conductivity of the product layer, ΔC is the fluid reactant (here the acid solution) concentration difference between the bulk of solution and particle surface and M_B is the molecular weight of the product layer [27].

$$\tau = \frac{d_0^2\,\rho_B}{24\,k\,\Delta C\,M_B} \tag{5}$$

Because of $k_a = 1/\tau$, then $k_a \propto k$. On the other hand, since the other parameters in equation (5) are temperature independent, changes in the apparent rate coefficient of temperature can be attributed to changes in the thermal conductivity coefficient of temperature as relationship (6).

$$k \propto \frac{1}{T^3} \tag{6}$$

This relation is in accordance with the general relationship presented for the thermal conductivity coefficient in expression (7) [28].

$$k \propto \frac{1}{T^x} \tag{7}$$

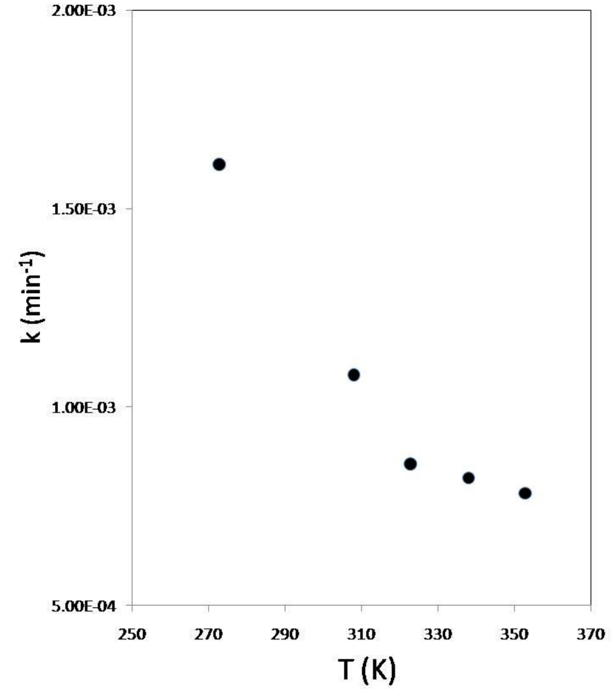

Fig. 7. Apparent rate coefficient versus temperature

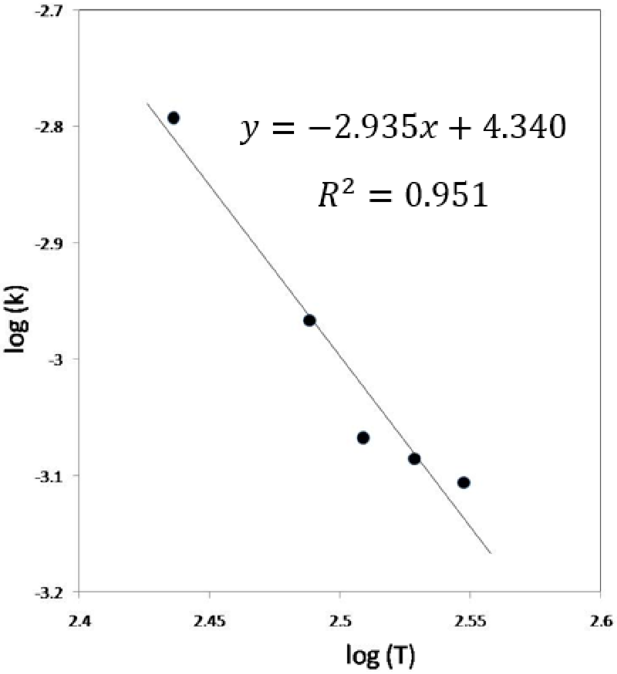

Fig. 8. Logarithmic changes of apparent rate coefficient from temperature logarithm

4. Conclusions

- Acetic acid can be selected as a suitable solvent for the dissolution of vanadium in the steel converter slag. Dissolution increased with increasing the time and decreasing the temperature so that the highest dissolution was obtained at 90 min and 0 °C.
- The kinetics of vanadium dissolution in the acetic acid leaching of steel converter slag is diffusion control, according to the shrinking core model.
- The rate-controlling step of the dissolution process is the diffusion of heat generated by the reaction from inside the particles to their surface.

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