# RECOVERY OF VANADIUM FROM SCALE RESIDUES OF OIL-FIRED POWER STATIONS

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## ABSTRACT

*The aim of the present research is concerned with study of the leaching unit in a pilot plant, using the alkaline leaching process for the recovery of vanadium from scales of oil-fired power stations in Iraq.*

*An investigation was conducted to study the effects of process variables such as temperature, particle size of scale, molarity of sodium hydroxide and leaching time on the percentages of vanadium recovery.*

*A complete vanadium recovery was achieved at the following conditions: (1) 100°C, 125μm, 3 hr, and 4 M NaOH. (2) 100°C, 150μm, 4 hr, and 4 M NaOH.*

*Fluid film resistance, ash resistance and chemical reactions resistance were investigated to evaluate the controlling step. It was found that the resistance to diffusion through the ash layer is the controlling step.*

## INTRODUCTION

Vanadium is significantly increases the strength and improves the toughness and ductility of carbon steel used for constructing bridge and pipelines.

Vanadium compounds have been found effective for catalyzing both inorganic oxidation and reaction, such as in the manufacturer of sulfuric acid by the contact process [1].

In medicine, vanadium compounds have been used in minute amounts to achieve divers therapeutic effects. Vanadium has also important applications such as dyeing industries, glass making, and in analytical chemistry [2].

In Iraq, the fuel oil used in electric power stations release off composition gasses, which contain vanadium that could constitute a good source of this metal. Table (1) gives the results of element analysis of samples taken from scale and ash residues in the south of Baghdad power station, and these results indicate the high vanadium content in the scale residues which is proved to be higher than anyone of the known vanadium ores [3].

In 1966, it was reported that there were eleven solvent extraction plants in the United States of America for recovering vanadium from ores or slugs [4]. Some extraction processes have been described by Ritcey [5].

A Swedish process has been designed to recover vanadium from oil-fired power station residues.

An extraction plant has been in operation with capacity of 2000 tons of ash per year, corresponding to about 100 tons of vanadium (5% content).

The flow sheet contains an acid leaching in two stages followed by a solvent extraction step to recover vanadium from the leaching solution. The solvent extraction of vanadium was performed with 20% DEHPA and 15% TBP in three small-scale mixer-settler stages [6].

Table (1) The elemental analysis of scale and ash residue in the South Baghdad Power Station

| Residue | V% | Ni% | Fe% | Na% |
|---|---|---|---|---|
| Scale | 24.0 | 6 | 1.49 | 2.8 |
| Ash | 3.5 | 5 | 1.8 | 0.8 |

## EXPERIMENTAL

### Application of Box-Wilson Method to the Experiments

Leaching of scale by sodium hydroxide was studied. The effect of four variables such as reaction temperature, sodium hydroxide molarity, particle size, and time of leaching on the vanadium recovery was investigated and analyzed by using the experimental design. Box Wilson central composite design was adopted to find a useful relationship between the four controllable variables and the

observed response (vanadium recovery percentage). $X_1$=temperature (60°C to 100°C), $X_2$=particle size (100 to 200μm), $X_3$=time of leaching (1 to 8 hr), and $X_4$=molarity of sodium hydroxide (1 to 4 Molar).

## Materials

### Sodium hydroxide

Sodium hydroxide (manufactured in Saudi Arabia).

### Scale residues

The term scale residue is used to describe the hard material adhering to the inside surface of the chimney. Scale was taken randomly from four power stations in Iraq (Al-Musaiab, South of Baghdad, Al-Dura, and Beiji Power Station).

### Laboratory experimental unit

Experiments were carried out in cylindrical Pyrex tank supplied with mixer of four baffles equally spaced (the reason for using Pyrex tank is to allow visual observations). The diameter of the tank was 14 cm, and the height was 20 cm.

The width and thickness of the baffles were (1/10) of the tank diameter. The mixer was consists of stainless steel shaft o.5 diameter, which was screwed with four pitches turbine blades impeller, the diameter of impeller was 4.5 cm.

Impeller is mounted on a centered vertical screwed shaft by means of two stainless steel nuts. The other end of the shaft was coupled to AC motor by means of brass coupling.

The motor was connected in series with a variance to give the desired speed of impeller (720 rpm).

A schematic diagram of the equipment in figure (1).

### Experimental procedure

Scale was obtained from as solidified blocks taken randomly from several stations was milled in laboratory stainless steel ball mill and sieved by means of laboratory sieve to obtain a particles size (100-200$\mu m$).

The required [1-4] molar solution of sodium hydroxide was prepared in the experimental tank. The solution was then heated to the desired temperature (60-100°C) while the stirrer was switch on. 150 gm of scale with particle size in the range (100-200μm) added to the aqueous solution of sodium hydroxide, and after the desired time (1-8 hr) the solution was filtered to remove the unreacted vanadium and impurities.

For experiments conducted at high temperatures (80-100°C), it was necessary to make up the volume correction by adding appropriate amount of water to compensate for the evaporation during the specified times of experiments. In this way, a fixed volume of (1.5 liter) was assured throughout all experiments. Figure (2) shows the processes.

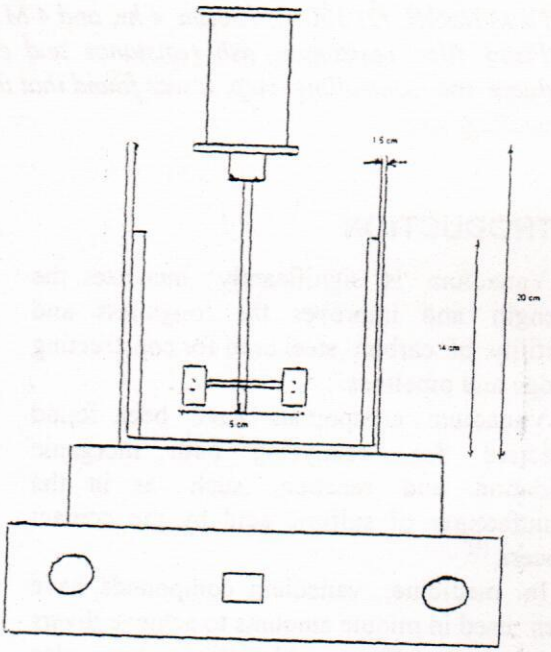

Fig. (1) A schematic diagram of the equipment

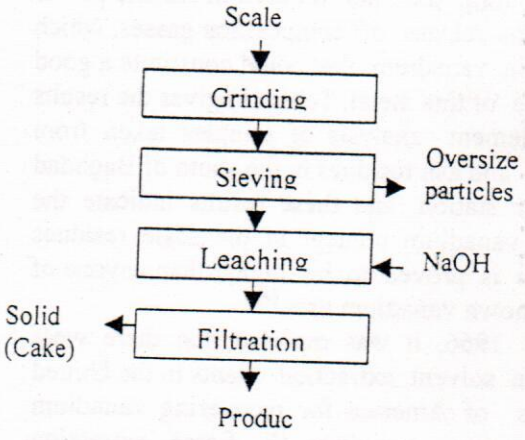


Fig. (2) Experimental procedure block diagram

Solid samples of the powder stock, which was used in this work, were analyzed for vanadium content and the average percentage was found to be equal to 30%. This value was used in the calculation of vanadium recovery for each experiment.

Samples of solutions from all experiments were analyzed for vanadium by means of Atomic Absorption Spectrometry.

Twenty five experiments were carried out according to the experimental design.

## RESULTS AND DISCUSSION

### Mathematical Modeling

A mathematical expression was found by utilizing the experimental data summarized in table (2), to relate the effect of variables studied on the percentage of recovery. This was achieved be relating the various variables ($X_1$, $X_2$, $X_3$, and $X_4$) by a simple multivariable polynomial, which has the general form:

Table (2) Vanadium recovery of Box-Wilson method experiments

| | Coded Variables | | | | Real Variables | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Run No. | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $X_1$ | $X_2$ | $X_3$ | $X_4$ | Y% |
| 1 | 1 | 1 | 1 | 1 | 90 | 175 | 6.25 | 3.25 | 54.7 |
| 2 | -1 | 1 | 1 | 1 | 70 | 175 | 6.25 | 3.25 | 51.2 |
| 3 | 1 | -1 | 1 | 1 | 90 | 125 | 6.25 | 3.25 | 77.9 |
| 4 | 1 | 1 | -1 | 1 | 90 | 175 | 2.75 | 3.25 | 71.9 |
| 5 | 1 | 1 | 1 | -1 | 90 | 175 | 6.25 | 1.75 | 54.7 |
| 6 | -1 | -1 | 1 | 1 | 70 | 125 | 6.25 | 3.25 | 61.6 |
| 7 | -1 | 1 | -1 | 1 | 70 | 175 | 2.75 | 3.25 | 48.6 |
| 8 | -1 | 1 | 1 | -1 | 70 | 175 | 6.25 | 1.75 | 44.0 |
| 9 | 1 | -1 | -1 | 1 | 90 | 125 | 2.75 | 3.25 | 54.7 |
| 10 | 1 | -1 | 1 | -1 | 90 | 125 | 6.25 | 1.75 | 40.0 |
| 11 | 1 | 1 | -1 | -1 | 90 | 175 | 2.75 | 1.75 | 60.0 |
| 12 | -1 | -1 | -1 | 1 | 70 | 125 | 2.75 | 3.25 | 52.7 |
| 13 | -1 | -1 | 1 | -1 | 70 | 125 | 6.25 | 1.75 | 38.2 |
| 14 | -1 | 1 | -1 | -1 | 70 | 175 | 2.75 | 1.75 | 48.0 |
| 15 | 1 | -1 | -1 | -1 | 90 | 125 | 2.75 | 1.75 | 45.8 |
| 16 | -1 | -1 | -1 | -1 | 70 | 125 | 2.75 | 1.75 | 35.0 |
| 17 | 2 | 0 | 0 | 0 | 100 | 150 | 4.5 | 2.50 | 56.9 |
| 18 | 0 | 2 | 0 | 0 | 80 | 200 | 4.5 | 2.50 | 48.7 |
| 19 | 0 | 0 | 2 | 0 | 80 | 150 | 8.0 | 2.50 | 47.9 |
| 20 | 0 | 0 | 0 | 2 | 80 | 150 | 4.5 | 4.00 | 69.3 |
| 21 | -2 | 0 | 0 | 0 | 60 | 150 | 4.5 | 2.50 | 50.8 |
| 22 | 0 | -2 | 0 | 0 | 80 | 100 | 4.5 | 2.50 | 45.4 |
| 23 | 0 | 0 | -2 | 0 | 80 | 150 | 1.0 | 2.50 | 58.5 |
| 24 | 0 | 0 | 0 | -2 | 80 | 150 | 4.5 | 1.00 | 43.0 |
| 25 | 0 | 0 | 0 | 0 | 80 | 150 | 4.5 | 2.50 | 53.5 |

$$Y = A_o + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} B_i X_i^2 + \sum_{i=1}^{n}\sum_{j=1}^{n} C_{ij} X_i X_j \quad (1)$$

Equation (1) can be represented as follows:

$$Y = A_0 + A_1 T + A_2 P.S + A_3 t + A_4 M + A_5 T_i^2 + A_6 P.S^2 + A_7 t^2 + A_8 M^2 + A_9 P.S.T + A_{10} T.t + A_{11} T.M + A_{12} P.S.t + A_{13} P.S.M + A_{14} t.M \quad (2)$$

The least squares method for multivariable was adopted to estimate various coefficient, the results are summarized in table (3).

Table (3) Least squares coefficients

| Function | Coefficient | Symbol | Variable |
|---|---|---|---|
| 1 | 62.127 | $A_o$ | |
| 2 | -3.242 | $A_1$ | T |
| 3 | 0.860 | $A_2$ | p.s |
| 4 | 6.868 | $A_3$ | t |
| 5 | 3.474 | $A_4$ | M |
| 6 | $1.092*10^{-2}$ | $A_5$ | $T^2$ |
| 7 | $-2.907*10^{-3}$ | $A_6$ | $p.s^2$ |
| 8 | -0.3005 | $A_7$ | $t^2$ |
| 9 | -1.110 | $A_8$ | $M^2$ |
| 10 | $9.784*10^{-3}$ | $A_9$ | T.p.s |
| 11 | $-4.4816*10^{-2}$ | $A_{10}$ | T.t |
| 12 | 0.3099 | $A_{11}$ | t.M |
| 13 | $-3.7*10^{-2}$ | $A_{12}$ | p.s.t |
| 14 | -0.21731 | $A_{13}$ | p.s.M |
| 15 | 1.895 | $A_{14}$ | t.M |

*Average error=30%, Correlation coeff.=0.951, F-value=4.789, Est. Std. Deviation of Y=4.156*

### Effect of Different Variables on the Percentage of Vanadium Recovery

#### *Effect of particle size*

It can be seen from figures (3, 4) that the vanadium recovery increase as the particle size decrease. The particle size influences the vanadium recovery in a number of ways. The smaller the size the greater is interfacial area between the solid and liquid, the rate of reaction and the rate of transfer of material are higher.

A reduction in particle size usually results in a decrease in the average time of passage of solvent from the surface to the interior of the particle and decrease the average time of passage of solute molecules from the dissolving point in the interior of the solid particle to the surface of the particle.

The effect of temperature on the choice of optimum particle size can not be neglected. This can be seen clearly in figures (3, and 4).

Referring to figure (4), it can be seen that at 60°C and 4 molar NaOH solution, the optimum particle size is 100μm while at 100°C, maximum recovery of vanadium was obtained with particles of 150μm. This phenomena is in a very good agreement with figure (11) in which plotting the conversion (x), $1-(1-x)^{1/3}$, or $x-3(1-x)^{2/3}+2(1-x)$ versus the time at 100°C and 150μm the inverse of the slope represented the time for complete conversion, it can be seen from this figure that after three hours the time for complete conversion (ash resistance controlling, chemical reaction controlling, and fluid film controlling) is minimum and have the same values.

In practice very fine particles should be avoided because of the expected difficulties in filtration system, i.e., smaller particle size is advantageous for the leaching process but it is rather unfavorable for the filtration process.

### Effect of temperature

Examining figures (5, and 6), it can be shown that increasing the temperature will increase the vanadium recovery. The temperature influences the vanadium recovery in number of ways. Firstly as the temperature increases the mobility of the molecules will increase due to more energy gain, secondly the effective diffusivity increases with the increase in the temperature (this is coincided with the definition of the diffusivity).

Referring to figure (6), which clearly illustrates the interaction between temperature and particle size, the percentage recovery of vanadium at 60°C and 200μm is 28%, increasing to 60% for 150μm at the same temperature. This can be explained by referring to figures (12, and 13) , by utilizing 60°C and 150μm where the value of tou is smaller than the case utilizing 60°C and 200μm regardless of the step which is controlling the process.

Examining figures (14 and 15), it can be seen that changing the temperature from 80°C to 100°C while keeping molarity and particle size constant the controlling step will change from ash resistance controlling to the reaction controlling resistance.

### Effect of NaOH molarity

Figures (7, and 8) show the vanadium recovery increase as the molarity of NaOH increases, and that due to the external diffusion rate, diffusion through ash layer and the reaction rate dependent greatly on NaOH concentration.

Figure (8), shows that percentage recovery of vanadium increases with molarity increasing at all temperatures studied for particle size 175μm and 8 hr leaching time.

Figure (7) indicates that for a particle size 125μm there is a linear relationship between percentage recovery and NaOH molarity at all temperatures. A small increase in the slope of straight lines for temperatures 80°C, 90°C, and 100°C was observed.

### Effect of time of vanadium recovery

It is clear from figures (9, and 10) that best leaching time which lead to maximum recovery of vanadium is greatly dependent on the specific conditions of test, i.e , particle size, molarity of NaOH and temperature of test. For example, referring to figure (9), at 150μm and 4 molar NaOH and 60°C the best leaching time was found to be 8 hours while it was only 3 hours at 100°C.

Examining figure (10), it can be seen that for 150μm, 3.5 molar NaOH, and 60°C the time required for maximum recovery may be greater that 8 hours, and at 80°C, the time was 8 hours while at 100°C the best leaching time was about 6 hours.

### Kinetic

In heterogeneous reaction there are free resistance that may control the process (fluid-film, ash layer, and chemical reaction), such cases can be represented by the following equations:

$$\frac{t}{\tau} = X_B \qquad (3)$$

$$\frac{t}{\tau} = 1-(10X_B)^{1/3} \qquad (4)$$

$$\frac{t}{\tau} = 1-3(1-X_B)^{2/3}+2(1-X_B) \qquad (5)$$

These equations were plotted in figures (11 to 14), and the inverse of the slope represented a time for complete conversion.

## SYMBOLS

| | |
|---|---|
| M | Molarity (mol/L) |
| P-s | Particle size (m) |
| T | temperature (°C) |
| t | Time (s) |
| X | Conversion |
| Y | Vanadium recovery percentage |
| τ | Time for complete conversion (s) |

## CONCLUSIONS

1. From the present investigation, it was concluded that the percentage of vanadium recovery increased when: (i) Increasing temperature, (ii) Increasing NaOH molarity, (iii) Decreasing particel size.
2. The optimum leaching time depends greatly on specific conditions of test, i.e., temperature, particle size, and NaOH molarity.
3. The selectivity of NaOH solution for the recovery of vanadium from scales was excellent.
4. At a given particle size and NaOH molarity, it was found that less than 80°C, the controlling step was a diffusion through ash layer. This is due to the (τ) for the ash layer is greater than that for fluid film and chemical reaction.
5. A complete vanadium recovery was achieved at (i) 100°C, 125μm, 3hr, and 4M NaOH, (ii) 100°C, 150μm, 4hr, 4M NaOH.
6. A correlation was proposed relating the above variables to the percentage of vanadium recovery.

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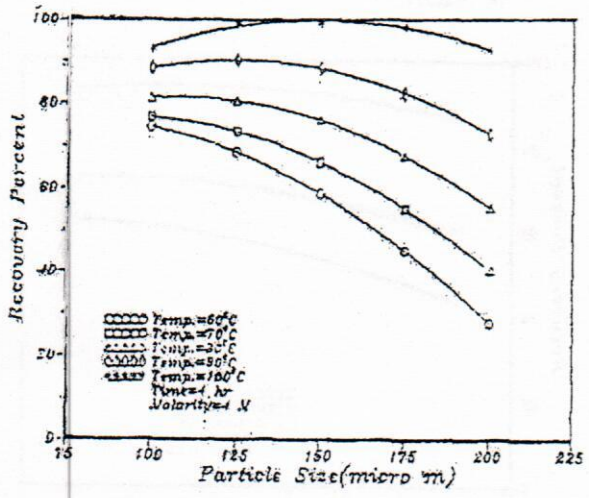


Fig. (3) Effect of particle size on vanadium recovery at different temperatures for 4 hr and 4M.

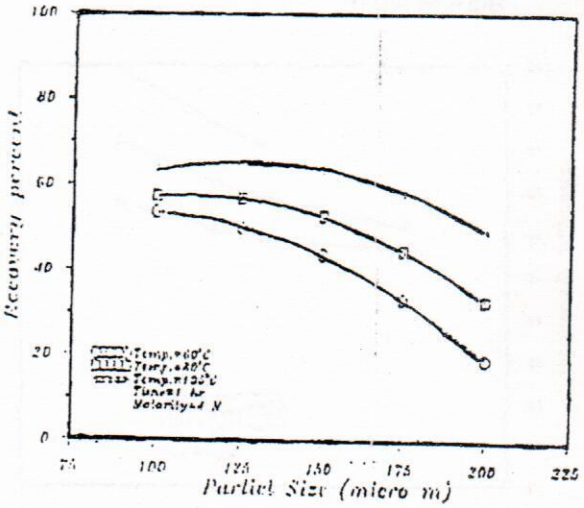


Fig. (4) Effect of particle size on vanadium recovery at different temperatures for 1 hr and 4M.

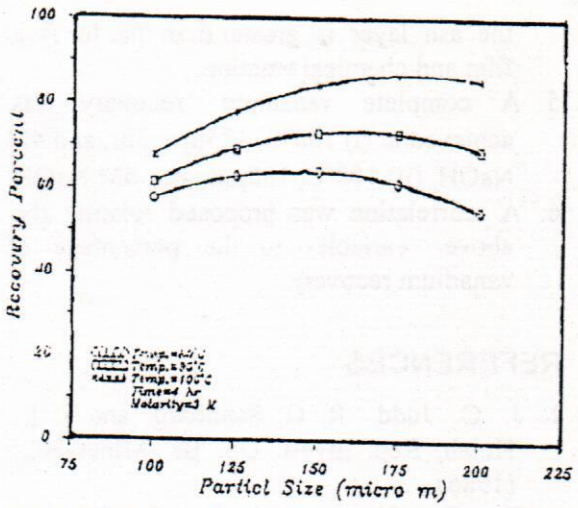


Fig. (3) Effect of particle size on vanadium recovery at different temperatures for 4 hr and 4M.

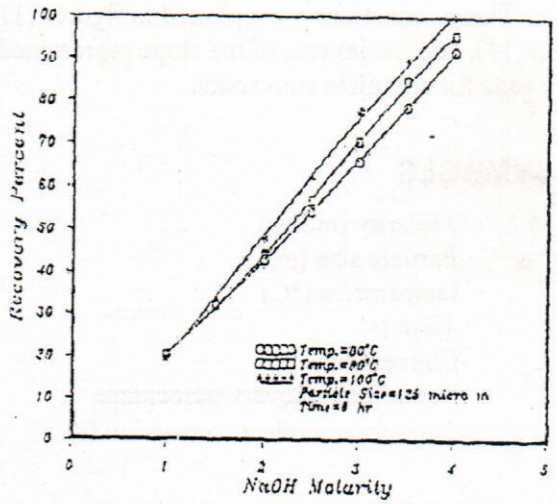


Fig. (8) Effect of NaOH molarity on vanadium recovery at different temperatures for 8 hr and 125 micron.

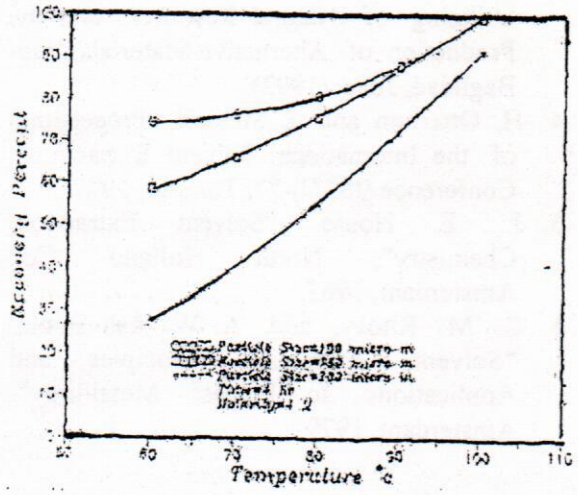


Fig. (6) Effect of temperature on vanadium recovery at different particle size for 5 hr and 4 M NaOH.

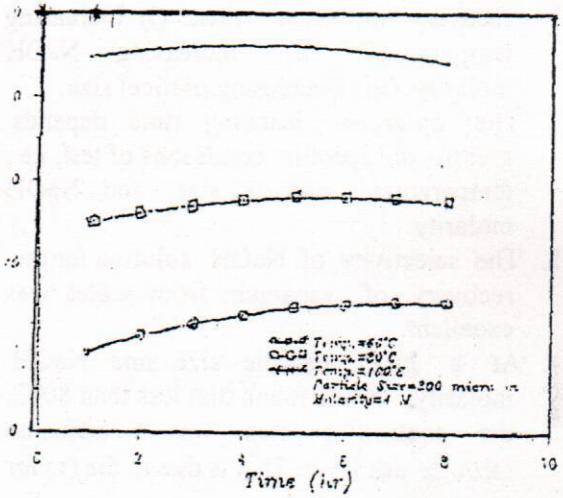


Fig. (9) Effect of time on vanadium recovery at different temperatures for 200 micron and 4 M NaOH.

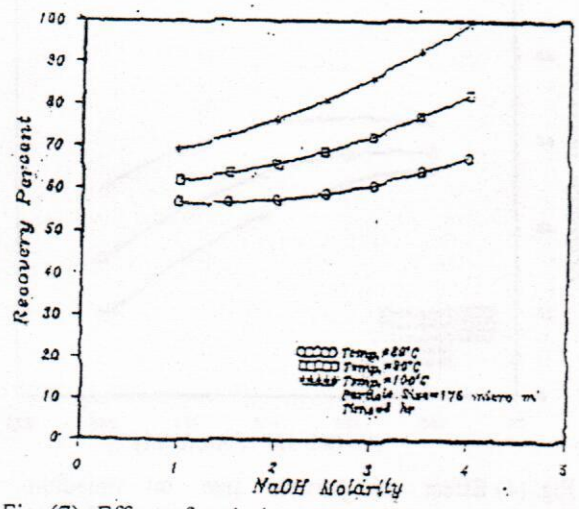


Fig. (7) Effect of molarity on vanadium recovery at different temperatures for 8 hr and 175 micron.

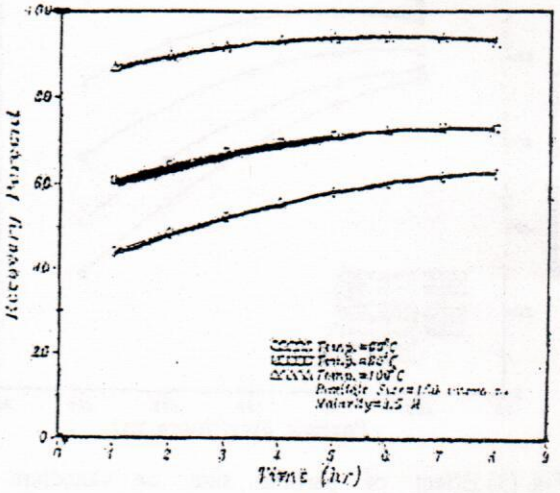


Fig. (10) Effect of time on vanadium recovery at different temperatures for 3.5 M NaOH and 150 micron.

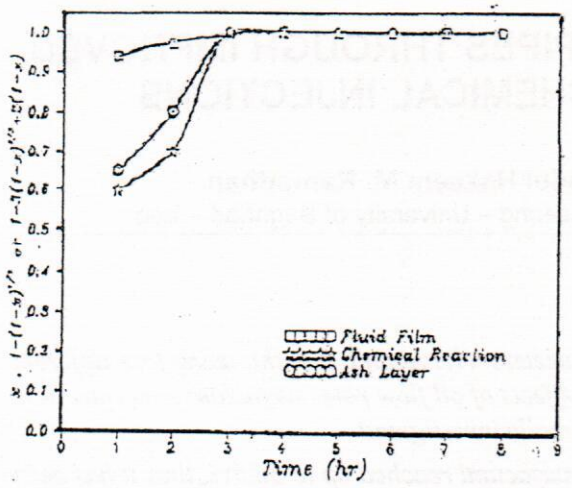


Fig. (11) Illustration of different resistances on vanadium recovery for 100°C, 150 micron, and 4M NaOH.

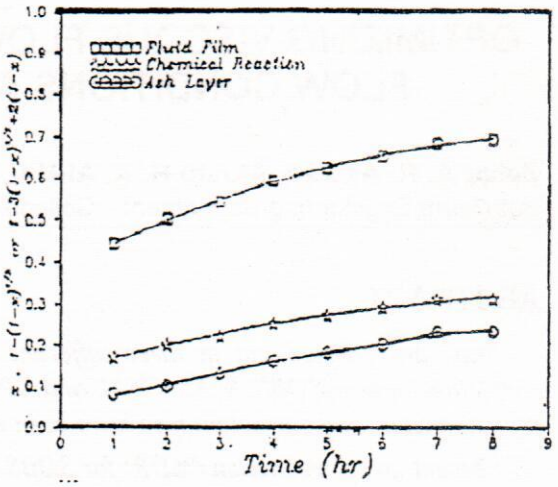


Fig. (13) Illustration of different resistances on vanadium recovery for 60°C, 150 micron, and 4M NaOH.

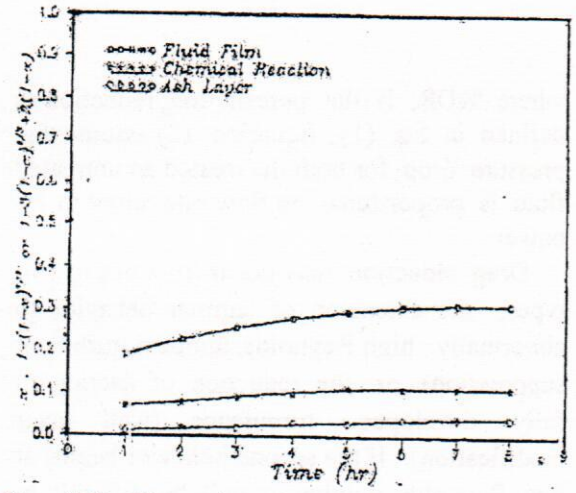


Fig. (12) Illustration of different resistances on vanadium recovery for 60°C, 200 micron, and 4M NaOH.

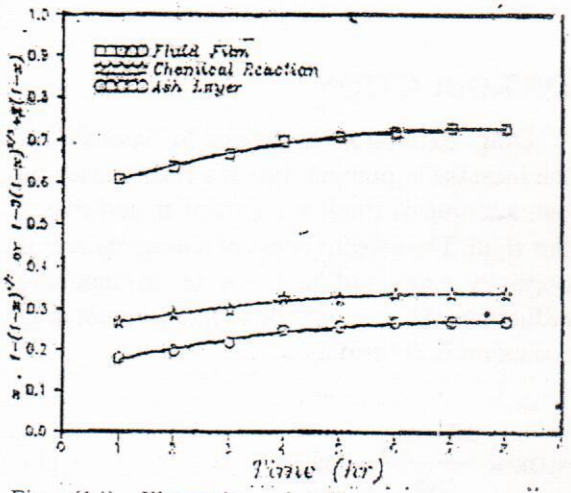


Fig. (14) Illustration of different resistances on vanadium recovery for 80°C, 150 micron, and 3.5 M NaOH.