IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 9, November 2014.
www.ijiset.com
ISSN 2348 – 7968

# Recovery of Vanadium from sulfuric acid medium by micro extraction by tri-C8-C10 –alkyl (Amines)

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## Abstract
The behavior of vanadium (V) extracted from sulfuric acid solution was investigated using Amines as an extractant. The effects of the concentration of Amines and the pH of the solution were studied. The extraction of vanadium (V) increases with the increase of Amines concentration. Amines can extract vanadium (V) from sulfuric acid solution at low pH conditions, and the best pH conditions for extraction of vanadium (V) are at pH 1.0-2.0. The species extracted into the organic phase is VO2HSO4 with one molecule of Amines. Equilibrium time for extraction is 100s and best kerosene ratio in organic phase is 40%. The economic and best O/A for vanadium extraction is O/A=1

.***Keywords:*** *vanadium, liquid- liquid extraction, tri-C8-C10 –alkyl (Amines).*

## 1. Introduction

Today, vanadium is one of the strategic metal. Some 90% of the vanadium consumed globally is for use as an alloying agent for carbon steels, tool steels and high-strength, low-alloy steels. Advanced titanium-aluminum-vanadium alloys are seeing application in the aerospace industry. Small, but ever growing amounts, are finding application as catalysts or in electronics. New uses are continually being discovered for this metal. One example of a new application is the vanadium-redox battery for use in generation plants and back-up power sources. Vanadium is the 22nd most abundant element in the earth's crust (Baroch 2006).

Vanadium is commercially important as a constituent of several alloys and catalysts. Usually, vanadium exists in the combination with various minerals which include carnotite, roscoelite, vanadinite, mottramite and patronite as important sources of the metal. Because of the low grade of vanadium in the processed ores and the depletion of concentrated ore deposits in the world, many industrial subproducts, including the converter and smelter slag [1-3], spent catalysts [4], and oil fly ash[5-13], are becoming interesting sources for the recovery of vanadium in industry.

Recently, Lozano and Juan [14] have reported a solvent extraction process for the recovery of vanadium from spent sulphuric acid catalyst using Primene 81R in kerosene as an extractant. Nekovar and Schrotterova [15] have studied the extraction of vanadium (V) from acidic sulphate solutions using Primene JMT and found that extraction efficiency was higher in the pH range in which polymeric anionic species of vanadium (V) are present.

Tertiary amines were found to be better extractants for vanadium in the PH range 1.5 to 4.0 [16]. On the other hand, quaternary amines were found to be effective extractants for vanadium in the PH range 1.5 to 12 reaching optimum values between pH 6-9 [17]. Tricaprylrnethyl ammonium chloride (Aliquat 336), a liquid anion exchanger has been used for the commercial recovery of vanadium and chromium from alkaline leach liquors obtained from titaniferrous magnetite ore [18]. Separation is based on preferential extraction of vanadium at pH 9.0 and chromium at pH 13.5. Chromium is first extracted and stripped with NaCl. The raffinate is then used for vanadium extraction using Aliquat 336 followed by stripping with NaCl solution.

Alamine 336 has been used commercially for the recovery of vanadium from uranium circuits involving sulphuric acid leach liquors of the carnotite ores [19]. This separation method involves simultaneous extraction of uranium and vanadium at pH 2.0 followed by selective stripping of vanadium by $H_2S0_4$ and that of uranium by 1.0 mol/dm" $Na_2C0_3$.

The purpose of the present work is to study the behavior of amines for the extraction of vanadium (V) in a sulfuric acid medium to obtain a more economic and effective extraction reagent and set the best conditions for extraction.

## 2. Experimental

### 2.1. Reagents and solutions

Vanadium (V) solutions were each prepared by dissolving a certain weight of vanadium pentoxide giving 0.055 g/L in acid medium with heating. Tri-C8-C10 –alkyl (Amines), were supplied by Merck. Kerosene with a flash point of

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76°C used as diluents. Ethanol. $H_2SO_4$ and $V_2O_5$ and all other chemicals used were of analytical reagent grade.

### 2.2. Apparatus

A Varian atomic absorption spectrometer (Spectra AA-200, USA) was used for the measuring of vanadium ion in an air-acetylene flame. The operating conditions were as follows: wavelength, 670.8 nm; lamp current, 5.0 mA and spectral bandwidth, 0.5 nm.
The pH values were measured with a Schot pH-meter (CG 841) supplied with a glass-combined electrode. Phase separation was assisted using a centrifuge (Mistral 1000, MSB 100/CE 1.4).

### 2.3. Experimental procedure

Solvent extraction were carried out by mechanical shaking equal volumes of aqueous and organic phases in glass-stoppered vials at room temperature for the necessary time to achieve equilibrium. After phase separation, the concentration of vanadium left in the aqueous phase was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).
The amount for tests at all stages of solution containing vanadium pentoxide and sulfuric acid in water at aqueous solution (Aq) is 7-5 mL and the amount of extractant (Ex) is 0.1-2 mL and the required amount of disperser is used, after mixing the aqueous and organic phase of each sample manually shaken for 5 min and then 10 min centrifuges by 6000 rpm speed. After this 3 mL of the aqueous phase separated would be sent for the analysis. The extraction procedure was performed by shaking equal volumes (7mL) of the aqueous and (3mL) of organic phases in stoppered glass tubes for 5 min using manual shaking. Preliminary experiments showed that a contact time of 5 min is sufficient to reach the extraction equilibrium for vanadium. The extraction yield was calculated from the equation:

$$\%E = \frac{C0 - C1}{C0} \times 100 \qquad (1)$$

Where, Co is the initial metal concentration in the aqueous phase before extraction and C1 is the metal concentration in the aqueous phase after extraction.
The results show that only when the extraction rate shocks are very different two phases separate without shocking through centrifuges.

## 3. Results and discussion

### 3.1. Select the best method for extraction

The effect of Extraction of vanadium from the leaching solution with organic phases made up of Amines , Kerosene As the diluter , ethanol as disperser and mix of both using an organic/aqueous (O/A) phase ratio of 1:2.5 is shown in Fig. 1. The shaking time used in these experiments was 5 min.

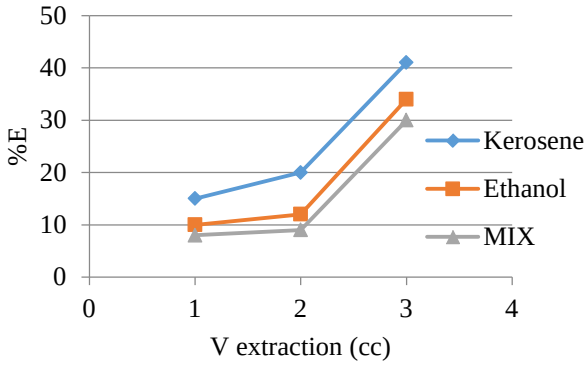


Fig 1 Comparison of vanadium extraction with kerosene, ethanol and mix both

According to Figure 1 the best method for extraction is extraction with diluent and when use mix disperser and diluter have a Negative effect on extraction.

### 3.2 Effect of kerosene ratio in organic phase

The fact that the choice of organic diluent is important for a solvent extraction process goes without saying. Several factors, such as e.g. price, flash point, viscosity, polarity etc. each have their place in the planning of a solvent extraction system.
Volume percent of diluent was the other parameter that has been studied. Fig. 2 shows the effect of Volume percent of diluent on the extraction yield of vanadium (V).

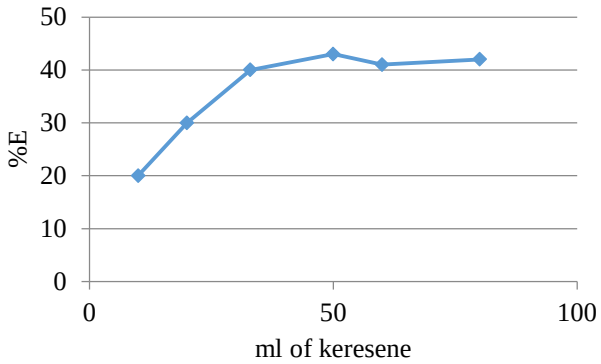


Fig 2 kerosene ratio in organic (2ml Amines)

According to Figure 2 the best of diluent volume is 50%. Adding more diluent is not only higher extraction rate, but also has a negative effect.

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### 3.3. Effect of shaking time

Fig. 3 shows the effect of shaking time on the extraction yield of vanadium (V). The organic phases were made up of Amines (50vol. %) And kerosene (50 vol. %). It is clearly shown that the vanadium extraction yield increases with an increase in shaking time, and after about 100s, the increase trend in vanadium extraction yield is no longer obvious with prolonging shaking time.

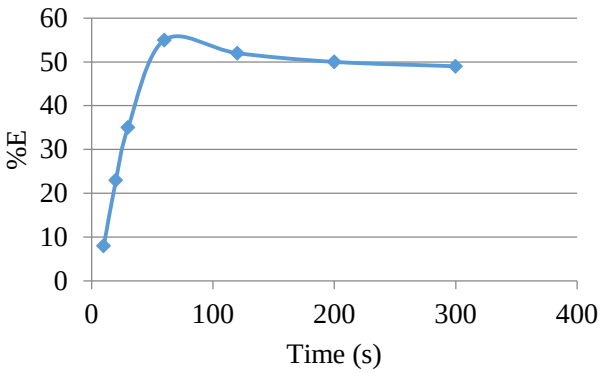

Fig 3 effect of shaking time

When the two immiscible phases were equilibrated for a period of (1 min to 12 min), the extraction was quantitative over a period of 1 to 2 min. For the proposed method, 100s equilibration time was recommended in order to ensure complete extraction of vanadium [Fig. 3].

### 3.4. Effect of pH value

The extraction yield of vanadium (E) from the leaching solution with organic phases made up of Amines and kerosene using an organic/aqueous (O/A) phase ratio of 1:2.5 is shown in Fig.4. The shaking time used in these experiments was 100 second.

Table 1 Effect of pH on the extraction yield of V (V).

| r | pH | Ex ml | K ml | Aq ml | %E |
|---|---|---|---|---|---|
| 1 | 0.7 | 2 | 2 | 7 | 97.25 |
| 2 | 0.9 | 2 | 2 | 7 | 97.14 |
| 3 | 1.1 | 2 | 2 | 7 | 97.02 |
| 4 | 1.9 | 2 | 2 | 7 | 93.93 |
| 5 | 3 | 2 | 2 | 7 | 87.31 |
| 6 | 4 | 2 | 2 | 7 | 18.17 |
| 7 | 5.5 | 2 | 2 | 7 | 6.26 |

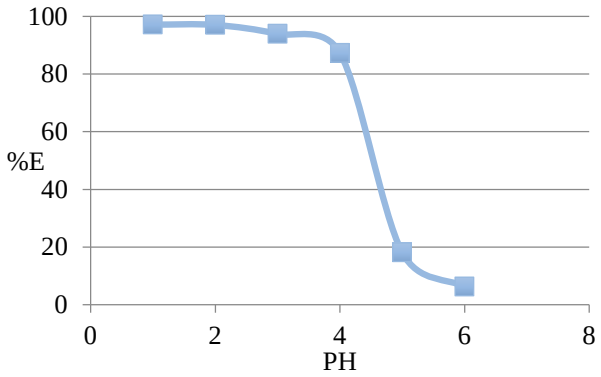

Fig. 4. Effect of pH on the extraction yield of V (V).

The effect of pH on vanadium extraction yield is not obvious in pH range of 0 to 1.0, and the vanadium extraction yield is about 97%. With an increase in pH, the vanadium extraction yield obviously increases and shows an optimum range (pH between 1.0 and 2.0). When the pH values are beyond 4.0, the vanadium extraction yield decreases sharply.

### 3.5. Effect of extraction concentration

The effect of amines concentration on vanadium (V) extraction has been studied at constant vanadium
Concentration, and the results are shown in Fig. 5. The extraction of vanadium (V) increases with an increase in extractant concentration. The E versus amines shows. Here, E is the extraction yield. Organic phases ranged between 40% amines using sulfonated kerosene as diluent. The results shows, indicating the ratio of the extractant to the metal species at this pH value.
The effect of O/A phase ratio upon Vanadium extraction from the working liquor using 60% Amines /kerosene was investigated at O/A phase ratios ranged from 1/7 to 10/7. The results in Table (2) clarified that, maximum vanadium extraction (80.7%) obtained at an O/A phase ratio of 1.42. The economic and best O/A for vanadium extraction was O/A= 1.

Table 2 Effect of extraction concentration on the extraction yield of V (V).

| r | pH | Ex ml | kerosene ml | Aq ml | 0/A | %E |
|---|---|---|---|---|---|---|
| 1 | 1.1 | 0.6 | 0.4 | 7 | 0.14 | 16.2 |
| 2 | 1.1 | 1.8 | 1.2 | 7 | 0.42 | 28.8 |
| 3 | 1.1 | 3 | 2 | 7 | 0.71 | 52.5 |
| 4 | 1.1 | 4.2 | 2.8 | 7 | 1 | 73.6 |
| 5 | 1.1 | 5.6 | 3.4 | 7 | 1.28 | 77.3 |
| 6 | 1.1 | 6 | 4 | 7 | 1.42 | 80.7 |

ISSN 2348 – 7968

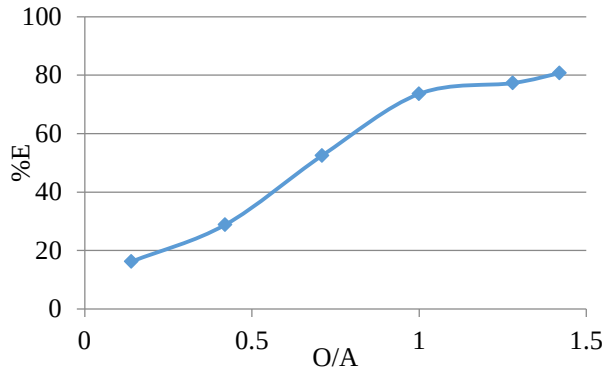


Fig.5. Effect of amines concentration on vanadium (V) extraction.

**4. Conclusions**

The extraction procedure was performed by shaking equal volumes (7 ml) of the aqueous and (3ml) of organic phases in stoppered glass tubes for 5 min using a thermostated shaking water bath adjusted at 25 °C.

The results obtained with amines dissolved in kerosene indicate that this reagent can be used to extract vanadium (V) from sulfuric acid media at low acid pH values.

The extraction of vanadium (V) increases with the increase of Amines concentration. Amines can extract vanadium (V) from sulfuric acid solution at low pH conditions, and the best pH conditions for extraction of vanadium (V) are at pH 1.0-2.0. The species extracted into the organic phase is $VO_2HSO_4$ with one molecule of Amines. Equilibrium time for extraction is 100s and best kerosene ratio in organic phase is 40% and the economic and best O/A for vanadium extraction is O/A= 1.

Amines is shown to be an efficient extractant agent for vanadium (V) ions that quantitatively extracts vanadium from acidic sulfuric acid media at optimum pH (1-2).

Thus, Amines is an efficient extractant agent for the recovery of the vanadium (V) ions from sulfate media and provides an alternative to the widely known extractant agent TOA.

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