



## SELECTIVITY OF VANADIUM OVER IRON DURING THE EXTRACTION OF VANADIUM BY TOA FROM AQUEOUS H<sub>2</sub>SO<sub>4</sub> LEACHING LIQUOR

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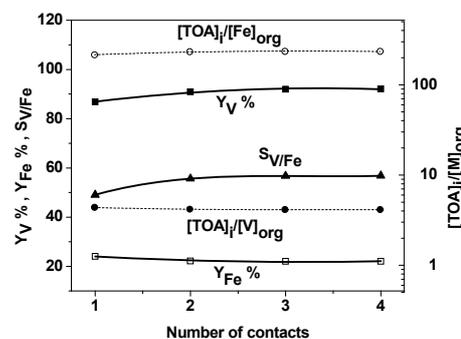
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The extraction of V by trioctylamine (TOA)/kerosene containing 1-octanol or TBP as modifier from aqueous H<sub>2</sub>SO<sub>4</sub> leaching solution (ASLS) resulted from the treatment of spent catalyst used for H<sub>2</sub>SO<sub>4</sub> production in Triple Super Phosphate Fertilizer Company (Homs) by 20% w/v H<sub>2</sub>SO<sub>4</sub> in a batch leaching process was studied. All parameters influencing the extraction of V and Fe by TOA (mixing time, extractant concentration, pH of the aqueous phase, organic to aqueous phase ratio, temperature, modifier percentage in the organic phase) as well as the selectivity of V over Fe were investigated. TOA/kerosene was found to be very effective in extracting V from ASLS. The percentage of Fe transferred to the organic phase can be reduced by increasing TBP or 1-octanol percentage in the organic phase and reducing the organic to aqueous phase ratio and increasing the number of contacts of ASLS with TOA/kerosene.

Temperature has negative effect on V extraction and selectivity.



### INTRODUCTION

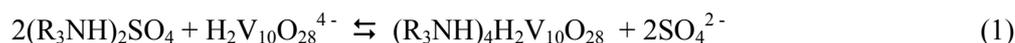
Vanadium consumption in the world has increased in the last few years as a result of increasing demand for steel which is the base of the most recent industries and exploring a new horizon for the use of this important metal specially in aerospace and chemical industry, many of other application of vanadium are: alloys, catalyst in H<sub>2</sub>SO<sub>4</sub> production, ink dye, paint, photography, pharmaceutical, vanadium battery.... *etc.*<sup>1-4</sup> The recovery of vanadium from its secondary resources (spent catalysts, fly ash, bottom ash, petroleum coke, industrial wastes) using hydrometallurgical methods, became attractive from environmental and economical point of view, solvent extraction have many advantages : No need for high-tech instruments, low temperature and low electrical consumption,

providing vanadium with high purity, and transforming the dangerous wastes to a safer waste.<sup>5-9</sup> Organophosphorous extractant di-(2-ethyl hexyl) phosphoric acid (D2EHPA) was extensively used to recover vanadium (IV) from aqueous acidic solutions (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>).<sup>10-14</sup> The synergistic mixture of D2EHPA and TBP was used by Merrit<sup>15</sup> and showed that six extraction stages are necessary to recover vanadium from H<sub>2</sub>SO<sub>4</sub> solutions. LI Xing-bin *et al.*<sup>16</sup> studied the extraction of vanadium (IV) from H<sub>2</sub>SO<sub>4</sub> solution by a group of organophosphorous compounds (D2EHPA, EHEHPA, CAYANEX 272) and found that D2EHPA is the best extractant for vanadium extraction and the extracted species are in the form VOR<sub>2</sub>(HR)<sub>2</sub> at low pH values while at high pH value the extracted species are in the form VOR<sub>2</sub>. Painuly<sup>9</sup> proposed a process to recover vanadium from vanadium pentoxide spent catalyst using

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Cyanex 272 as extractant diluted in kerosene with almost a quantitative yield (~ 99%). He mentioned that the extractant can be reused up to ten cycles with no significant change in its extraction capability. Many amines extractants were also tested to extract vanadium from aqueous solutions. Lozano *et al.*<sup>17,18</sup> studied the recovery of vanadium from a spent catalysts leaching process using primary amine (Primene 81R), resulting in an industrial multistage process for the treatment of these effluents and vanadium was precipitated as ammonium metavanadate. Aliquat 336 (methyltrioctylammonium chloride) was tested by El-Nadi *et al.*<sup>19</sup> and proven to be effective in extracting vanadium from HCl and NaOH media. This method was applied for treatment of the spent catalyst used in manufacturing H<sub>2</sub>SO<sub>4</sub> giving a recovery of 93% for vanadium in the whole process. Palant *et al.*<sup>20</sup> investigated the extraction of vanadium from sulfate media with

diisododecylamine (DIDA) in toluene and kerosene. He mentioned that vanadium(V) can be efficiently recovered from weakly acidic solution of (pH 5-6) yielding a DIDA:V=1:2.5 (mol/mol) complex in the organic phase and vanadium can be completely reextracted from the organic phase by NH<sub>4</sub>OH solution. Changes *et al.*<sup>21</sup> investigated the speciation of vanadium (V) extracted from acidic sulfate media by protonated trioctylamine in n-dodecane modified with 5% (wt) 1-tridecanol using FTIR technique and <sup>51</sup>V NMR spectroscopy. He indicated that vanadium (V) exists in the organic phases as polyvanadates, likely decavanadates. Kurbatova *et al.*<sup>22</sup> indicated that vanadium extraction by TOA takes place in the pH range 2-3.5 and the extracting complex contains decavanadate anion H<sub>2</sub>V<sub>10</sub>O<sub>28</sub><sup>4-</sup> and four molecules of the extraction agent. The extraction reaction of vanadium by TOA<sup>22</sup> and Alamine 336<sup>23</sup> can be respectively described as follows:



This paper will focus on vanadium and iron extraction from aqueous H<sub>2</sub>SO<sub>4</sub> leaching solution of spent V<sub>2</sub>O<sub>5</sub> catalyst using trioctylamine/kerosene modified with TBP or 1-octanol and studying in detail the selectivity of vanadium extraction over iron (S<sub>V/Fe</sub>) by investigating the effect of all parameters influencing the extraction of vanadium on the selectivity.

## EXPERIMENTAL

### Reagent

All the chemicals used in this study were of analytical grade reagent. Tri-n- octylamine (TOA) was obtained from Fluka with a purity of 98% and used as extractant without any further treatment. The diluent used was the kerosene PEMCO SOLV 110 from PEMCO Chemicals Company, which has a density of 800-810 kg/m<sup>3</sup> at 15 °C, with a boiling point range 200-250 °C, and flash point > 70 °C, with aromatic content of max 0.5% (v/v). 1-Octanol and tri-n- butyl phosphate (TBP) were used as modifiers and obtained from MERCK with a purity of 99% for each.

The aqueous solutions of sulfuric acid were prepared by diluting concentrated sulfuric acid (95-97%) from Fluka, with double distilled water.

The organic phases of TOA were prepared by diluting it with kerosene, 1-Octanol, or tri-n- butyl phosphate were added to the organic phases to prevent third phase formation.

### Leaching of V and Fe from spent catalyst

Before starting the leaching experiments, V and Fe in the spent catalyst (SC) brought from Triple Super Phosphate

Fertilizer Company (Homs) were determined by Atomic Absorption Spectrometry after complete acidic digestion of a known amount of SC. 900 grams of spent catalyst were put in contact with 3 liters of sulfuric acid (20% w/v) at 50 °C for 1/2 hour with continuous mechanical stirring. Then the leachate was separated by filtration. The aqueous phase rich in vanadium and containing iron as impurity was used for vanadium extraction by tri-n-octylamine/kerosene.

### Solvent Extraction procedure and analysis

Solvent extraction experiments were carried out at a constant temperature by stirring equal volumes (25 mL) each of aqueous leaching solution of H<sub>2</sub>SO<sub>4</sub> and organic phase (TOA/kerosene) in a stirring bath thermostat; After reaching the equilibrium, the phases were allowed to settle and separated.

Vanadium and iron in the aqueous phases before and after extraction were analyzed using an Analytik Jena model novAA 300 atomic absorption spectrometer. Two calibration curves have been constructed by measuring the absorbance of a series of standard solutions of vanadium and iron in the range of (0-100 ppm) and (0-6 ppm). The calibration curves obtained for vanadium and iron were (Y<sub>V</sub> = 0.002×C<sub>V</sub>; r = 0.9998) and (Y<sub>Fe</sub> = 0.0625×C<sub>Fe</sub>; r = 0.9999) respectively. The relative standard deviation of iron and vanadium determination for all analyzed samples was ≤ 4%. (n=3). The pH values of the aqueous phases were measured using Mettler Toledo pH meter equipped with a glass-combined electrode.

The distribution ratio (K<sub>d</sub>), and the yield of vanadium and iron extraction (Y<sub>V</sub> % and Y<sub>Fe</sub> %) were calculated as follows:

$$K_d = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}, \quad Y_M\% = [\text{M}]_{\text{org}} \times 100/[\text{M}]_i$$

where M is V or Fe and [M]<sub>org</sub>, [M]<sub>i</sub>, [M]<sub>aq</sub> refers to concentration of M in the organic phase, initial aqueous phase and aqueous phase after extraction respectively.

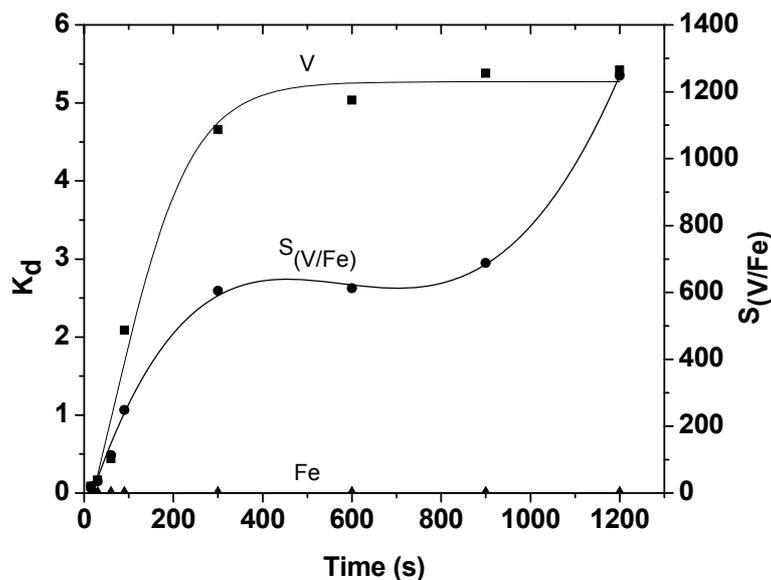


Fig. 1 – Effect of time on V and Fe extraction by TOA/kerosene;  $(V)_i = 6.7$  g/L,  $(Fe)_i = 0.54$  g/L,  $[TOA]_i = 0.5$  M + 10% (v/v) 1-octanol; pH = 2,  $V_{org}/V_{aq} = 1$ ,  $t = 25 \pm 0.1$  °C.

Selectivity of vanadium over iron was calculated using the following equation:

$$S_{(V/Fe)} = \frac{\text{Molar concentration of V in the organic phase}}{\text{Molar concentration of Fe in the organic phase.}} \\ = [V]_{org}/[Fe]_{org}$$

## RESULTS AND DISCUSSION

### Effect of contact time

The effect of time on V and Fe extraction from  $H_2SO_4$  leaching liquor was tested by mixing the aqueous phase with 0.5 M TOA/kerosene containing 10% 1-octanol for different periods of time (0-1200 s). The results presented in the form of distribution ratio ( $K_d$ ) of V and Fe and selectivity of vanadium over iron ( $S_{(V/Fe)}$ ) against time (Fig. 1).

It is clear from Fig. 1 that the extraction of Fe is very low comparing to the extraction of V and the extraction reaction of V and Fe reaches equilibrium at  $\approx 900$  s. The selectivity of vanadium extraction over iron increased with time to reach its maximum value  $S_{(V/Fe)} = [V]/[Fe] = 1247.5$  at 1200 s.

### Effect of TOA concentration and pH of aqueous phase on V and Fe extraction

A series of experiments were conducted to study the effect of tri-n-octylamine /kerosene on V and Fe extraction at different pH values (0.5, 0.75, 1, 1.25, 1.5 and 2) of aqueous phase and at different TOA concentration ranging from 0.2-0.6

M in kerosene containing 10% of 1-octanol as modifier to prevent third phase formation while the organic to aqueous phase ratio was kept constant ( $V_{org}/V_{aq} = 1$ ). The extraction procedure was done by mixing the aqueous and organic phases at  $25 \pm 0.1$  °C.

It can be seen from Figs 2a and 2b that the yield of V and Fe extraction is increasing with the increase of initial TOA concentration in the organic phase and  $Y_V \% \gg Y_{Fe} \%$ . The effect of pH on the extraction of V was observed clearly and had a positive effect on  $Y_V \%$  in the range of pH = 0.5-1.5 then  $Y_V \%$  decreased at pH = 2. Concerning the extraction of iron as shown in Fig. 2b, the maximum values around 50% were for Fe extraction yield was obtained at pH 0.75 and 1.5 whatever TOA concentration in the organic phase.

It can be seen from Fig. 3 that the best selectivity of vanadium over iron was observed at pH = 1 and  $[TOA]_i = 0.3$  M at which the  $Y_V \%$  is however relatively low and equal to 42.3%, and the selectivity sharply decreased after this concentration of amine, this result can be explained by the fact that at high amine concentration ( $>0.3$  M) there is more free amine available to extract more iron which consequently reduces the selectivity, while at low amine concentration vanadium will be preferentially extracted but with low  $Y_V \%$  where there is not too much available free amine to extract iron leading to increase of the selectivity. The effect of pH on the selectivity is most significant at pH = 1, since most vanadium is in an anionic form while iron is in the cationic form and amine in general plays the role of anionic exchanger.

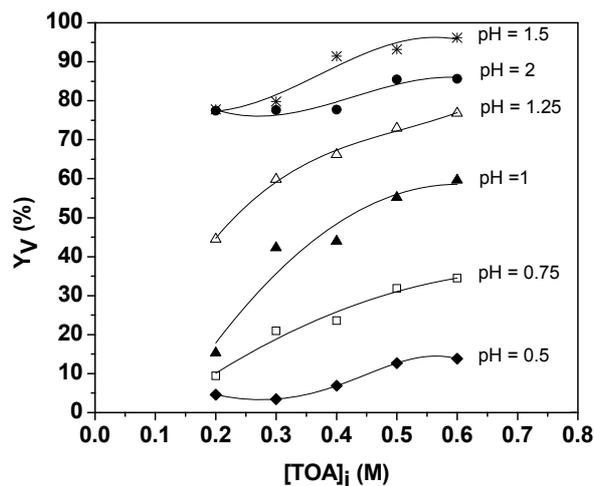


Fig. 2a – Effect of TOA concentration and pH of the aqueous phase on the yield of V extraction;  $[TOA]_i = 0.2-0.6$  M/kerosene + 10% 1-octanol,  $t = 25$  °C; pH = 0.5, 0.75, 1, 1.25, 1.5, 2;  $V_{org}/V_{aq} = 1$ .

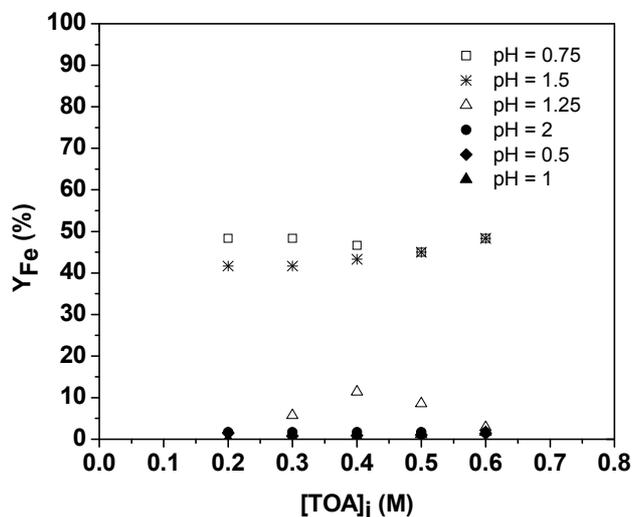


Fig. 2b – Effect of TOA concentration and pH of the aqueous phase on the yield of Fe extraction;  $[TOA]_i = 0.2-0.6$  M/kerosene + 10% 1-octanol,  $t = 25$  °C; pH = 0.5, 0.75, 1, 1.25, 1.5, 2;  $V_{org}/V_{aq} = 1$ .

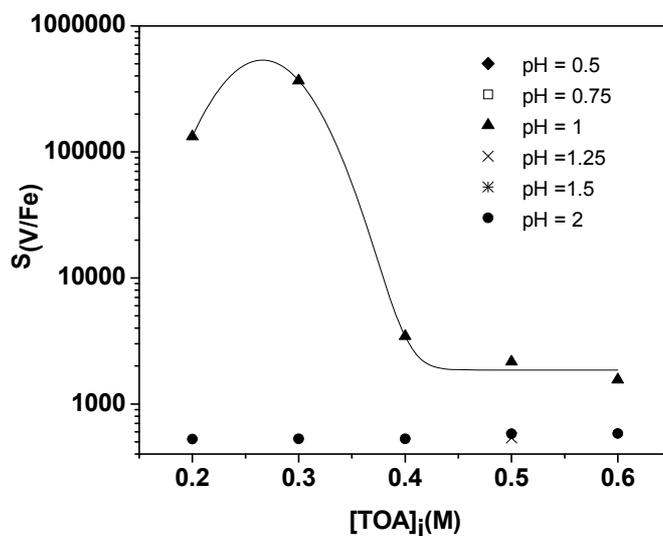


Fig. 3 – Effect of TOA concentration and pH of aqueous phase on the selectivity;  $[TOA]_i = 0.2-0.6$  M/kerosene + 10% 1-octanol,  $t = 25$  °C; pH = 0.5, 0.75, 1, 1.25, 1.5, 2;  $V_{org}/V_{aq} = 1$ .

### Effect of modifier on V and Fe extraction

The effect of modifier (1-octanol and TBP) was investigated by mixing two series of organic phases. The first series contains 0.5 M TOA/kerosene and different percentage of 1-octanol ranging from 4 to 20% (v/v) while the other series contains 0.5 M TOA/kerosene and different percentage of tributyl phosphate ranging from 4 to 20% (v/v) with aqueous  $H_2SO_4$  leaching liquor at the following experimental procedures ( $pH = 2$ ,  $V_{org}/V_{aq} = 1$ ,  $t = 25^\circ C$ ). The results were presented in Figs. 4a and 4b and 5 in the form of yield of extraction of V and Fe and the selectivity against modifier percentage in the organic phase.

From Figs. 4a and 4b it can be seen that vanadium is extracted strongly while most iron remained in the aqueous phase. 1-Octanol and TBP percentage in the organic phase in the range of (6-12%) does not show a significant effect on V and Fe extraction yield while in the range of (15-20%) the effect was negative and  $Y_V\%$  and  $Y_{Fe}\%$  decreased especially when 1-octanol was used as a modifier. The selectivity of vanadium over iron was presented in Fig. 5 as a function of 1-octanol and TBP % in the organic phase. The selectivity increased with increasing both 1-octanol and TBP percentage in the organic phase and TBP played a slightly increased positive effect on the selectivity in comparison to 1-octanol.

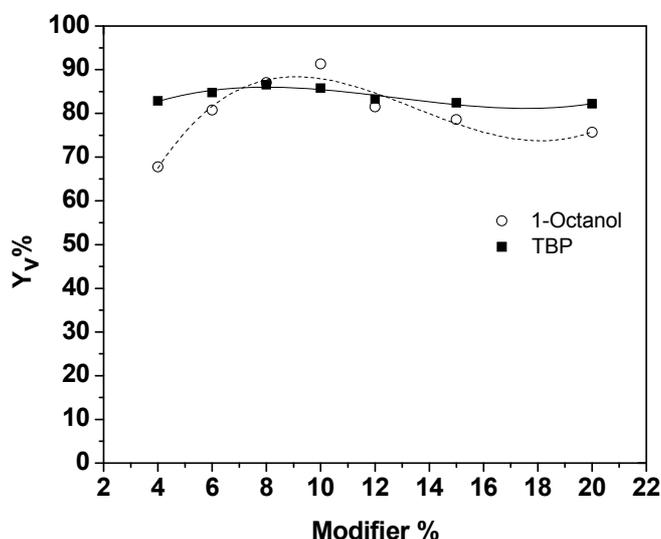


Fig. 4a – Effect of 1-octanol and TBP % on the yield of V extraction;  $[TOA]_i = 0.5\text{ M /kerosene} + (4\text{-}20\%)\text{ v/v 1-octanol}$ ;  $[TOA]_i = 0.5\text{ M /kerosene} + (4\text{-}20\%)\text{ v/v TBP}$ ;  $pH = 2$ ,  $t = 25^\circ C$ ,  $V_{org}/V_{aq} = 1$ .

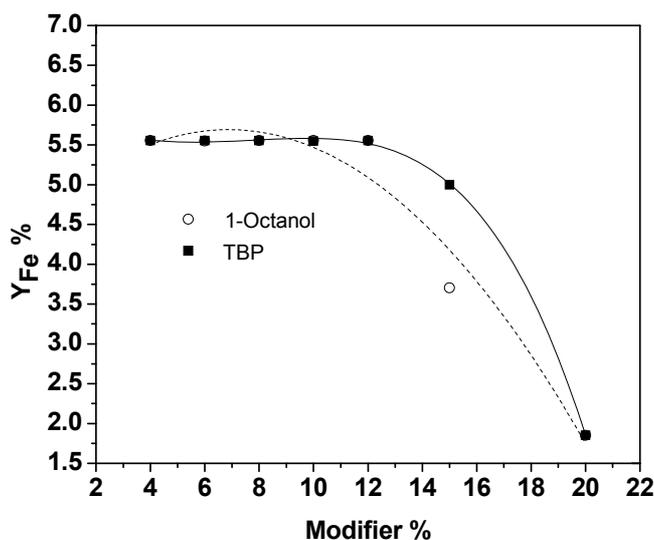


Fig. 4b – Effect of 1-octanol and TBP % on the yield of Fe extraction;  $[TOA]_i = 0.5\text{ M /kerosene} + (4\text{-}20\%)\text{ v/v 1-octanol}$ ;  $[TOA]_i = 0.5\text{ M /kerosene} + (4\text{-}20\%)\text{ v/v TBP}$ ;  $pH = 2$ ,  $t = 25^\circ C$ ,  $V_{org}/V_{aq} = 1$ .

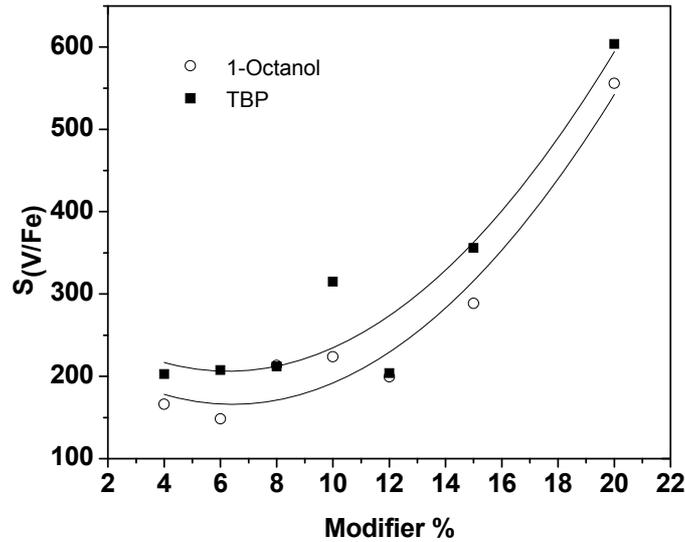


Fig. 5 – Effect of modifier % on the selectivity of vanadium over iron;  $[TOA]_i = 0.5 \text{ M /kerosene} + (4\text{-}20\%) \text{ v/v 1-octanol}$ ;  $[TOA]_i = 0.5 \text{ M /kerosene} + (4\text{-}20\%) \text{ v/v TBP}$ ;  $\text{pH} = 2$ ,  $t = 25 \text{ }^\circ\text{C}$ ,  $V_{\text{org}}/V_{\text{aq}} = 1$ .

So, the optimum yield and reasonable selectivity for V extraction can be obtained at the following operating conditions (0.5 M TOA/kerosene + 20% TBP;  $t = 25 \text{ }^\circ\text{C}$ ;  $\text{pH} = 2$ ;  $V_{\text{org}}/V_{\text{aq}} = 1$ ).

#### Effect of temperature on V and Fe extraction

The effect of temperature in the range of (25-50  $^\circ\text{C}$ ) on V and Fe extraction and selectivity was studied by mixing the organic phase 0.5 M TDA/kerosene + 10% 1-octanol with aqueous  $\text{H}_2\text{SO}_4$  leaching solutions at the following

operation conditions ( $V_{\text{org}}/V_{\text{aq}} = 1$ ,  $\text{pH} = 2$ ). The results of V and Fe extraction yield and selectivity against temperature and the variation of  $\text{Log } K_d$  against  $1/T$  were presented in Fig. 6. It can be seen from fig. 6 that the  $Y_V \%$  is decreasing with the increase of temperature which indicate that the extraction reaction of V by TOA is exothermic and the selectivity is also decreasing with increasing temperature. Consequently working at low temperature (25  $^\circ\text{C}$ ) is necessary to have better  $Y_V \%$  and selectivity as well as reducing the cost of V recovery from SC.

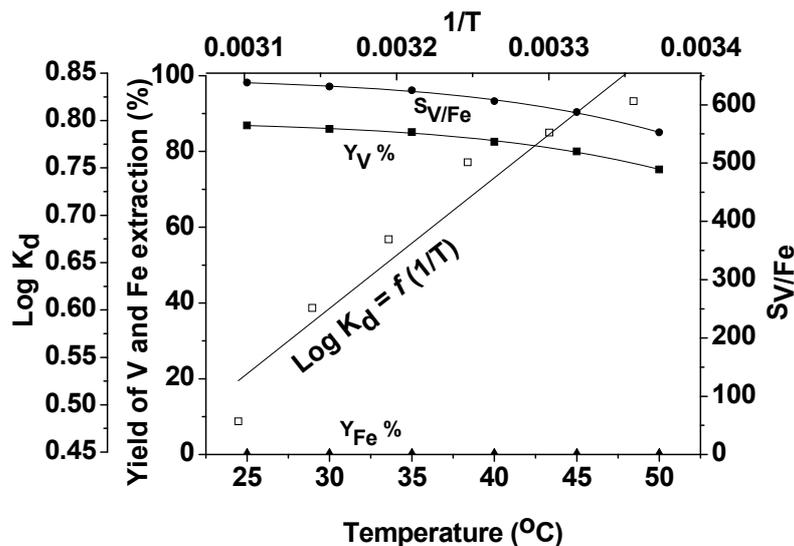


Fig. 6 – Effect of temperature on V and Fe extraction and selectivity;  $[TOA]_i = 0.5 \text{ M /kerosene} + 10\% \text{ 1-octanol}$ ;  $V_{\text{org}}/V_{\text{aq}} = 1$ ,  $t = 25\text{-}50 \text{ }^\circ\text{C}$ .

### Effect of phase ratio on V and Fe extraction

The effect of organic to aqueous phase ratio ( $V_{org}/V_{aq}$ ) on V and Fe extraction was studied by mixing the organic phase 0.5M TOA/kerosene + 10% 1-octanol with aqueous  $H_2SO_4$  leaching liquor at 25 °C at different organic to aqueous phase ratios ranging from 0.25 to 4. The results were presented in Fig. 7 in the form of  $Y_V$  % and  $Y_{Fe}$  % and selectivity against the phase ratios. It can be seen from fig. 7 that the yields of vanadium and

iron extraction are increasing with increasing  $V_{org}/V_{aq}$  ratio until  $V_{org}/V_{aq} = 1.5$  after that the  $Y_V$  % and  $Y_{Fe}$  % remains constant. The yield of vanadium extraction is always greater than the yield of iron extraction in the range of  $V_{org}/V_{aq}$  studied, while the selectivity is rapidly decreasing with the increase of  $V_{org}/V_{aq}$ . From the results presented in fig. 7 it can be concluded that the best phase ratio for good vanadium extraction yield and good selectivity is  $V_{org}/V_{aq} = 1.5$ .

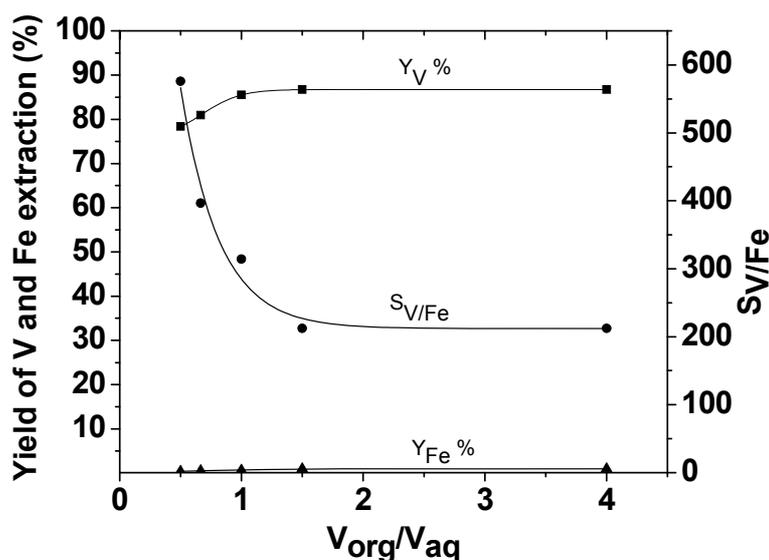


Fig. 7 – Effect of phase ratio on V and Fe extraction and selectivity;  $[TOA]_i = 0.5$  M /kerosene + 10% 1-octanol;  $t = 25$  °C,  $V_{org}/V_{aq} = 0.5, 0.666, 1, 1.5, 4$ .

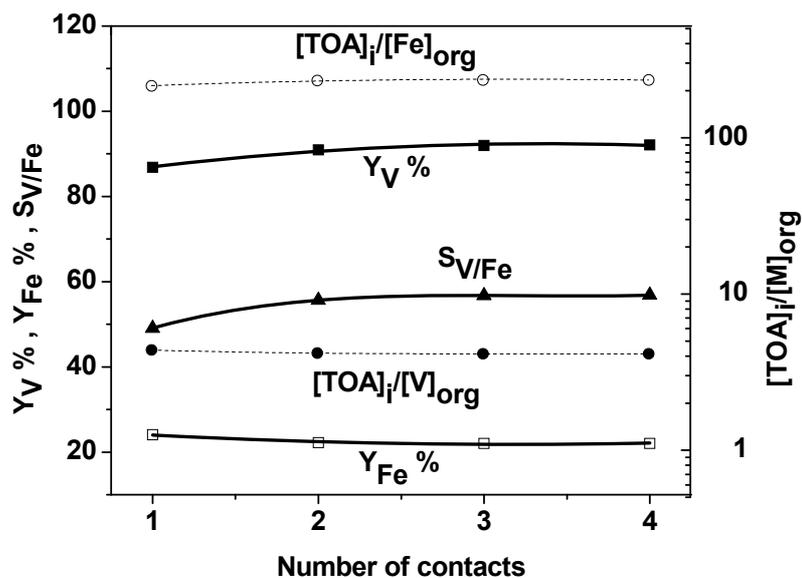


Fig. 8 – Variation of  $Y_V$  %,  $Y_{Fe}$  %,  $S_{V/Fe}$  and  $[TOA]_i/[M]_{org}$  against number of contacts;  $[TOA]_i = 0.5$  M /kerosene + 10% 1-octanol;  $pH = 2$ ,  $V_{org}/V_{aq} = 1$ ,  $t = 25$  °C.

### Loading of the organic phase

Maximum loading of the organic phase 0.5 M TDA/kerosene + 10% 1-octanol by vanadium was investigated by mixing it with aqueous H<sub>2</sub>SO<sub>4</sub> leaching solution (ASLS) at 25 °C and V<sub>org</sub>/V<sub>aq</sub> = 1 for four successive times. The results of extraction yield of V and Fe, selectivity and [TOA]<sub>i</sub>/[M]<sub>org</sub> against the number of contacts (N) were presented in Fig. 8. It can be seen from Fig. 8 that Y<sub>V</sub> % >> Y<sub>Fe</sub> % and increased slowly with N while Y<sub>Fe</sub> % was decreased slightly. So, increasing N will be in the favor of improving the selectivity S<sub>V/Fe</sub> and increasing N from 1 to 4 will increase Y<sub>V</sub> % from 86.9% to 92.2% and S<sub>V/Fe</sub> from 49.1 to 56.8 and reduce the contamination of V extracted into the organic phase by Fe to less than 2%. It is important to note that the ratios [TOA]<sub>i</sub>/[V]<sub>org</sub> and [TOA]<sub>i</sub>/[Fe]<sub>org</sub> at the saturation of TOA by V were found to be 4.13 and 214.8 respectively.

### CONCLUSION

From the results presented in this work the following conclusions can be drawn:

Vanadium can be extracted from the aqueous H<sub>2</sub>SO<sub>4</sub> leaching liquor effectively with good selectivity using TOA/kerosene.

The best operation conditions to have good yield of V extraction and reasonable selectivity are: (V<sub>org</sub>/V<sub>aq</sub> = 1; t = 25 °C; pH = 2; 0.5 M TOA/kerosene + 20% 1-octanol or 20%TBP). While using the following operation conditions (V<sub>org</sub>/V<sub>aq</sub> = 1; t = 25 °C; pH = 1; 0.3 M TOA/kerosene + 20% 1-octanol or 20% TBP) will give the highest selectivity but with low vanadium extraction yield.

Temperature has negative effect on V extraction indicating that extraction reaction of V by TOA is exothermic and ΔH° was found to be ~24.37 kJ/mol and the selectivity was also affected negatively.

1-Octanol and TBP have negative effect on V extraction but their effect on selectivity was positive specially in the range 15-20% of modifier percentage in the organic phase, with the remark that TBP is more advantageous compared to 1-octanol.

The number of contacts of organic phase with aqueous H<sub>2</sub>SO<sub>4</sub> leaching solution increases the yield of V extraction and improves the selectivity.

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