OPTIMUM PARAMETER FOR THE SOLVENT EXTRACTION OF VANADIUM FROM ITS IMPURITIES

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Abstract—Acid leaching has been widely used in the recovery process of vanadium due to its efficient selectivity. It was necessary to further separate vanadium from hydrochloric acid leaching solution. Two extractants Alkyl phosphoric acid (D2EHPA based) and other one is an Alkyl phosphinic acid (CYANEX based)were carried about at optimum PH. For extraction of vanadium from a simulated hydrochloric acid solution, and it is concluded that at lower pH (1-3) there is no selective extraction. Both Vanadium and Tungsten are getting extracted. But at higher pH, selective extraction of Vanadium occurs for both the extract ants. So, for selective extraction of Vanadium, the pH should be in the range 5-8.The single-stage extraction efficiency of vanadium reached more than 90% with a pH value of 2.0, extraction time of 5 min. This technology was a more efficient process for extraction of vanadium from hydrochloric acid solution.

Keywords—Solvent Extraction,Alkyl phosphoric acid,Alkyl phosphinic acid,VanadiumTungsten

I. Introduction

Vanadium could be amove refractory metal with a tallsoftening point that's troublesome to oxidize in discuss but is steady in soluble base and corrosive. [1] As a result, vanadium is as often as possibleutilized as ferrovanadium, vanadium compounds, and metal vanadium in metallurgy, aviation, chemical catalysts, batteries, and other businesses. [2,3].As is commonly known, vanadium saves are for the most partproduced from vanadium titan magnetite. [4]. Vanadium may too be found in phosphoritemetal, siltstone, bauxite, carbonaceous rough oil, coal, and shale. [5−7] The method of pretreatment, filtering, division, and enhancement based on the physical, chemical, and mineral composition highlights of crude

materials is presently the vital vanadium extraction method, with sulfuric corrosive filtering being commonly utilized due to its tall vanadium recuperation. [8,9].As a result, variousanalysts have hypothesized that specific vanadium filteringcan befulfilled by filtering vanadium titan magnetite, bauxite, ruddy mud, vanadium squander catalyst, and other crude materials with hydrochloric acid.[10-13] For case, the filteringeffectiveness of vanadium and press was more than 80%, whereas titanium filteringeffectiveness was less than 5% from vanadium titan magnetite by corrosivefiltering with an fitting concentration of hydrochloric corrosive, permitting for the viablepartition of titanium and vanadium.[14]

Solvent extraction technique is a part of analytical chemistry which refers to the distribution of a solute between two immiscible liquid phases in contact with each other. It is a two phase distribution of solutes from which one phase is organic and other one is generally inorganic. As the organic phase is lighter it forms the upper layer and having more density, the inorganic phase remains below. It is shown in figure 1.
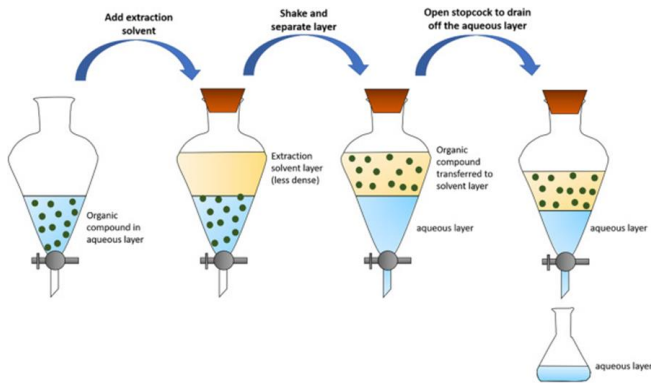
Figure 1. Solvent extraction technique

The solute A, which is initially dissolved in only one phase, eventuallydistributed in both the phases by stirring, shaking etc. when this distributionreaches equilibrium, the distribution ratio of the solute-

D = [A]org/ [A]aq

Where, [A]org – Conc. of A in organic layer

[A]aq – Conc. of A in Aqueous layer

Solvent extraction technique has various applications in industrial separations, in analytical chemistry, in pharmaceutical and in biochemicalindustries. Being very simple, easy and efficient, it is one of the broadly usedtechniques in metal recovery. Here, our focus is only on extraction of certain metalby solvent extraction technique. Generally, there are 3 steps i.e. 1. Extraction 2.Scrubbing, 3. Stripping. The transfer of metal ions from the aqueous to the organicphase is called Extraction. The loaded organic phase comes with contact of anaqueous solution to remove impurity. This is called Scrubbing. The scrubbedorganic phase comes contact with an stripping reagent to recover the metal fromthe organic phase. This process is called Stripping. This is shown in figure 2.
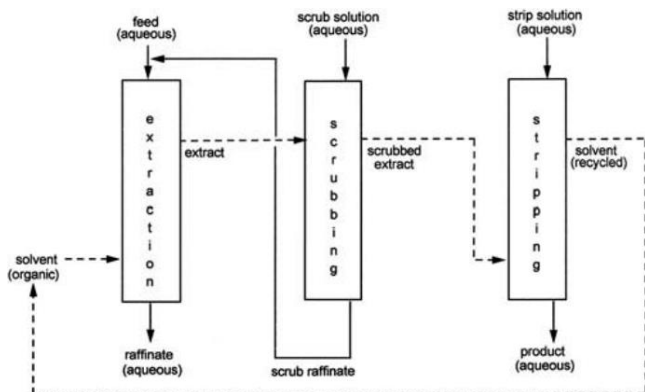

Figure 2. Stripping.

I.1.0 Factor Affecting Solvent Extraction

I.1.0.1 Choice of Solvent

To choose a suitable solvent, two things are to be considered. The most important consideration is the extractability of a metal by that solvent. The second thing is the ease of recovery of the solute from the solvent. Also, the degree of miscibility of the two phases, the relative specific gravities and viscosities should be considered. Since some metals are very selectively extracted by the extractant, choice of a suitable solvent is very important.

I.1.0.2 pH of the aqueous phase

The extractability of metals are very much affected by the acidity of the aqueous phase in which the metal exists. The optimum concentration of H+ is to be ensured for maximum extraction.

I.1.0.3 Stripping

Stripping is the removal of the extracted metal from the organic phase to another aqueous phase. This is important because generally we can't determine the concentration of metal extracted in organic phase. By stripping we provide the metal a stable medium from which we can perform the analysis. For stripping different stripping agent can be used. The stripping agent can be acidic viz. HCl, H2SO4, HNO3 etc. or it can be basic viz. NaOH, NH3 etc. For better stripping, compound stripping agent (mixture of a salt and base or acid) also be taken. Ex- NaOH+NaCl, NH3+(NH4)2CO3 etc. Stripping of metal totally depends on the choice of stripping agent. We have to analyze different stripping agent and should take the one with maximum recovering capacity. Howsoever concentration of the stripping agent also affects the stripping percentage. Optimum concentration results maximum stripping.

I.1.0.4 Variation of Oxidation State

The percentage of extraction can be increased by modification of oxidation states of interfering ions to prevent the formation of their extractable metal form. For example, Iron(III) present as impurity is reduced to Iron(II) which is not extractable. On the other hand, preparation of extractable metal in its proper oxidation state is equally important for complete extraction.

I.1.0.5 Ratio of Organic and Aqueous phase

The ratio of Organic and Aqueous phase which are in contact is an important factor of extraction. Optimum ratio is to be maintained for maximum extraction of metal. Generally, the aqueous phase is taken in greater ratio because organic solvent is costly and non-generative.

Principle of Solvent Extraction

Solvent extraction principle is based on subjecting the aqueous solution carrying metal ion to an organic solvent called as extractant. Metal ion is somewhere dispersed between the 2 layer.

Under equilibrium,

$$D = \frac{\text{Conc. of metal ion in organic phase } (C_o)}{\text{Conc. of metal ion in aqueous phase } (C_a)}$$

This relation holds good if there is no association or dissociation in either phase. Now if we consider the association and dissociation in both phase. Let us assume α_o and α_a are the association or dissociation coefficient in organic and aqueous phase respectively then the reaction is altered as,

$$D = \frac{C_o(1-\alpha_o)}{C_a(1-\alpha_a)}$$

This coefficient would help in accessing the extent of extraction in a given number of stages.

After extraction, metal recovered from the LO (Loaded Organic) phase through stripping, where the solvent is subjected to a suitable aqueous stripping solution. Instead of using all the solvent at a time, it is used in a number of volume fractions so that maximum extraction is achieved. After n extractions, the conc. of solute in aqueous solution, $(C_a)n$ is given by,

$$(C_a)_n = (C_a)_i \left[\frac{1}{1 + D(\nu_o/\nu_a)} \right]$$

Where ν_o and ν_a are volume of organic phase and volume of aqueous phase respectively.

Let us consider a reaction in extraction of metal(M),

$$(M^{2+})_{aq} + 2(RH)_{org} = (R_2M)_{org} + (2H^+)_{aq}$$
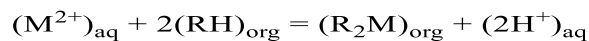
So the equilibrium constant will be,

$$K = \frac{[R_2M]_{org}\ [H^+]^2_{aq}}{[RH]^2_{org}\ [M^{2+}]_{aq}}$$

So the distribution coefficient can be expressed as,

$$D = \frac{K[RH]^2_{org}}{[H^+]^2_{aq}}$$

Therefore,

Log D = log K + 2log [RH]org + 2pHaq

Hence the dissemination coefficient depends on the pH of the arrangement as well as on the conc. of the extractant in naturalphase.The concept of metal extraction includes the chemistry of metal complexes in natural and watery media. By and large, a metal particle exists as a hydrated particle in anwateryarrangement. So to change over a metal particle to an extractable species which needs neutralization. So the hydrated portionmust be supplanted by a fewparticle or particle, which is accomplished by complexing the metal particle with another particle of inverse charge to makeaunbiased species, which can supplanta few or all water of hydration around the metal particle. Extraction of metal takes put when complexation happens at the interphase of the natural and aqueous stages in which the ionic portion of the extractantatom is foundwithin thefluidstage and the non-polar portionwithin thenaturalstage. The uncharged complex is extricatedwithin thenaturalstage.

In dissolvable extraction, a metal-containing fluidstage is reached with a water-immiscible naturalstage comprising an extractant, a diluent, and every so often a modifier. The extractantatomresponds with the metal displaywithin thefluidstage, making a hydrophobic species dissolvablewithin thenaturalstage. The extractants can be separated into three primarybunches:

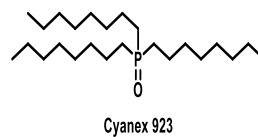Acidic extractants (D2EHPA)

DEHPA
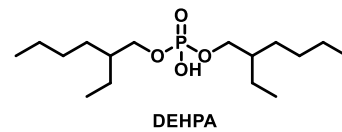
Basic extractants (Aliquat 336)

Aliquat 336
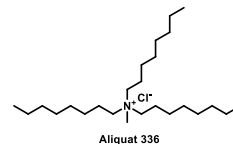
Solvating extractants (CYANEX 923)

Cyanex 923

II.EXPERIMENTAION

pH of the aqueous solution plays an important role in metal-chelates formation and the subsequent extraction. Extraction of the metal is different in different pH. Hence percentage extraction at different pH was calculated for two different extractant. One extractant is an Alkyl phosphoric acid (D2EHPA based) and other one is an Alkyl phosphinic acid (CYANEX based).First 3 liters of aqueous solution is prepared where Tungsten(W) present is 4.6g/L and Vanadium(V) present is 0.23g/L. It was well stirred with the magnetic stirrer. 0.02M CYANEX based and 0.02 D2EHPA based extractants were prepared, 200mL each, by taking kerosene as the diluent.

The pH of aqueous solution was found to be 8.12. 40mL of aqueous solution was taken and its pH was brought to 1 by adding conc. HCl. 10mL of each extractant were taken in two 25mL separating funnel. 10mL of the pH maintained aqueous solution was added in each separating funnel. It was shaken 10 minutes. Aqueous phase was collected and diluted 100 times. The pH of aqueous solution was brought to 2. The above procedure was repeated for pH=2 to pH=8. Since the extraction is done the aqueous solution

collected can be considered as raffinate. All the diluted raffinate was sent to ICP for analysis. Concentration of both V and W were determined. The initial concentration of Vanadium was found to be 0.23g/L. The initial concentration of Tungsten was found to be 4.615g/L.

III. Result and Discussion

Table 1.1 (Extraction of V by CYANEX based extractant)

Sl. No.	pH of aqueous phase	Conc. of V in the raffinate (x) (In g/L)	Percentage extraction [(0.23-x)/0.23]*100
1	1	0.0403	82.47%
2	2	0.0017	99.26%
3	3	0.0016	99.30%
4	4	0.0858	62.69%
5	5	0.0912	60.34%
6	6	0.0039	98.30%
7	7	0.0145	93.69%
8	8	0.0131	94.30%

Table 1.2 (Extraction of V by D2EHPA based extractant)

Sl. No.	pH of aqueous phase	Conc. of V in the raffinate (x) (In g/L)	Percentage extraction [(0.23-x)/0.23]*100
1	1	0.0403	82.47%
2	2	0.0031	98.65%
3	3	0.0028	98.78%
4	4	0.1299	43.52%
5	5	0.1390	39.56%
6	6	0.1385	39.78%
7	7	0.1452	36.86%
8	8	0.1453	36.82%

Table 1.3 (Extraction of W by CYANEX based extractant)

Sl. No.	pH of aqueous phase	Conc. of W in the raffinate (x) (In g/L)	Percentage extraction [(4.61-x)/4.61]*100
1	1	0.0020	99.95%
2	2	0.0013	99.97%
3	3	0.0010	99.97%
4	4	0.8957	80.57%
5	5	0.8626	81.28%
6	6	1.4441	68.67%
7	7	2.1542	53.27%
8	8	3.9594	14.11%

Table 1.4 (Extraction of W by D2EHPA based extractant)

Sl. No.	pH of aqueous phase	Conc. of W in the raffinate (x) (In g/L)	Percentage extraction [(4.61-x)/4.61]*100
1	1	0.0060	99.86%
2	2	0.0032	99.93%
3	3	0.0017	99.96%
4	4	1.5515	66.34%
5	5	1.4741	68.02%
6	6	2.7098	41.21%
7	7	3.0377	34.10%
8	8	3.9938	13.36%

By plotting graphs of table 1.1 to table 1.4, we can perceive it better. The plots are given below.
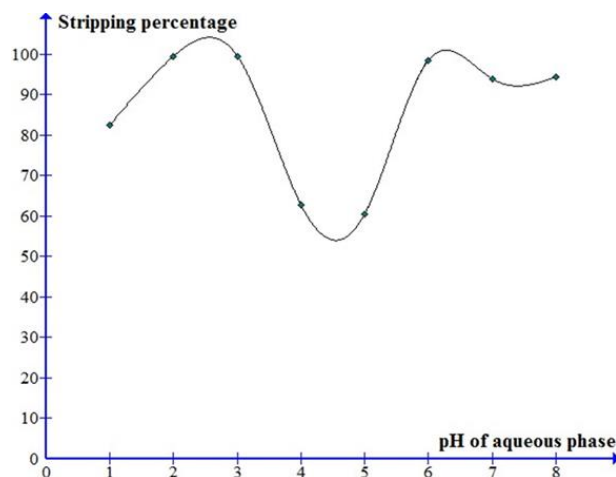

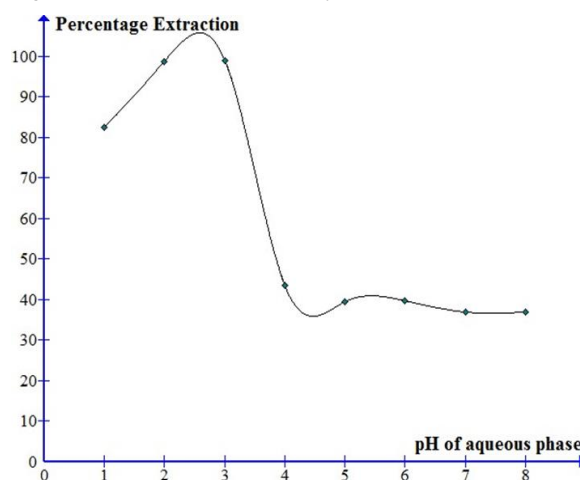Fig.1- Extraction of Vanadium by CYANEX based extractant

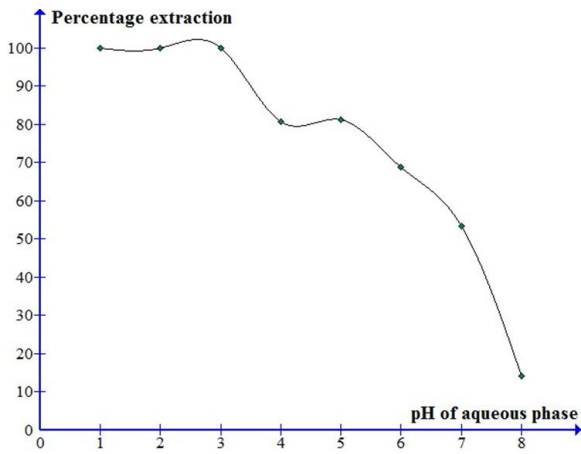Fig.2- Extraction of Vanadium by D2EHPA based extractant

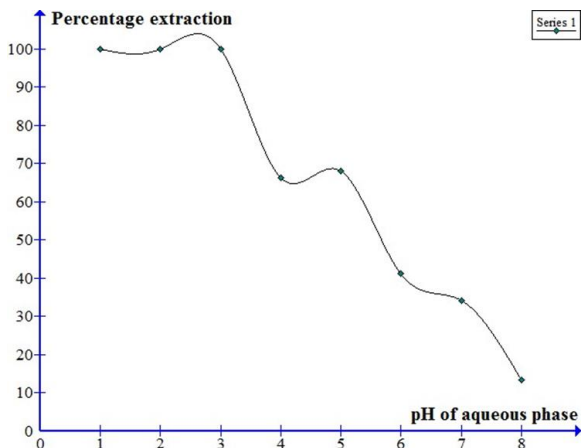Fig.3. Extraction of Tungsten by CYANEX based extractant

Fig.4. Extraction of Tungsten by D2EHPA based extractant

III. CONCLUSION

From the study it was found out that, at lower pH (1-3) there is no selective extraction. Both Vanadium and Tungsten are getting extracted. But at higher pH, selective extraction of Vanadium occurs for both the extractants. So, for selective extraction of Vanadium, the pH should be in the range 5-8. Also, it can be concluded that, for extraction of Vanadium CYANEX based extractant is morepreferable than D2EHPA based extractant.

The irregularities in the plots may cause from various errors like mechanical error, instrumental error, error in dilution etc.To avoid such errors, shaking should be doneperfectly and uniformly. Dilution should be done accurately.

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