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EFFECTIVE ISOLATION AND RETRIEVAL OF VANADIUM FROM IMPURITIES USING HYDROCHLORIC ACID

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Abstract: Acid leaching is commonly employed in vanadium recovery due to its high selectivity. However, further separation of vanadium from the hydrochloric acid leachate is required. Two extractants were tested under optimal pH conditions: one based on alkyl phosphoric acid (D2EHPA) and the other on alkyl phosphinic acid (CYANEX). The extraction of vanadium from a simulated hydrochloric acid solution showed that at low pH levels (1-3), there is no selective extraction, with both vanadium and tungsten being extracted. However, at higher pH levels, selective extraction of vanadium occurs with both extractants, suggesting that a pH range of 5-8 is ideal for vanadium extraction. The single-stage extraction efficiency of vanadium exceeded 90% at a pH of 2.0 and an extraction time of 5 minutes, demonstrating that this method is highly efficient for extracting vanadium from hydrochloric acid solutions.

***Keywords*— Solvent Extraction, Alkyl phosphoric acid, Alkyl phosphoric acid, Vanadium, Tungsten**

1. Introduction:

Vanadium is considered a refractory metal with a high melting point and is resistant to oxidation in air but remains stable in alkaline and acidic environments [1]. As a result, vanadium is frequently used in the production of ferrovanadium, vanadium compounds, and metallic vanadium, which find applications in metallurgy, aerospace, chemical catalysts [2, 3], batteries, and other industries. It is well known that vanadium is primarily obtained from vanadium-titanium magnetite deposits. However, vanadium is also present in phosphate ores, siltstone, bauxite, crude oil, coal, and shale [4]. The extraction process for vanadium typically involves steps like pretreatment, leaching, separation, and purification, based on the physical, chemical, and mineral properties of raw materials [5-7]. Among these methods, sulfuric acid leaching is widely used because of its high vanadium recovery rate [8-9]. Consequently, various researchers have proposed that vanadium can be effectively leached from vanadium-titanium magnetite [10], bauxite, red mud, vanadium waste catalysts [11-12], and other raw materials using hydrochloric acid. For example, vanadium and iron extraction efficiencies of over 80% have been achieved from vanadium-titanium magnetite [13], while titanium extraction remained below 5%, enabling effective separation of titanium and vanadium [14].

The solvent extraction technique, a key method in analytical chemistry, refers to the process of distributing a solute between two immiscible liquid phases in contact with each other. In this two-phase system, one phase is organic, and the other is typically inorganic. The organic phase, being less dense, forms the upper layer, while the denser inorganic phase settles below. This is illustrated in figure 1.

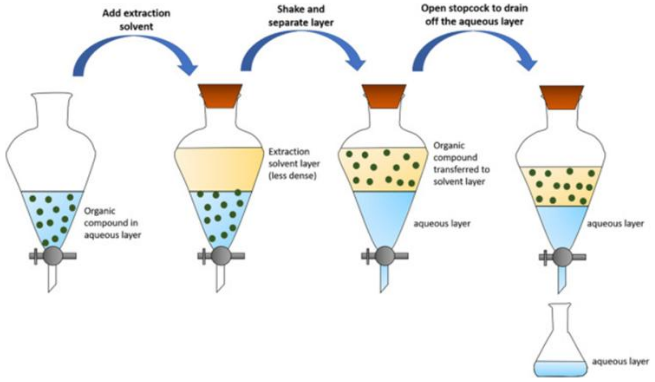

Figure1. Solvent extraction technique

The solute A, initially present in only one phase, eventually distributes between both phases after stirring or shaking. Once equilibrium is reached, the distribution ratio of the solute is defined as:

$D = [A]org / [A]aq$

Where:

- [A]org is the concentration of solute A in the organic phase
- [A]aq is the concentration of solute A in the aqueous phase

Solvent extraction is widely used across industries for separations, including industrial, analytical chemistry, pharmaceutical, and biochemical applications. Its simplicity, ease of use, and efficiency make it one of the most popular methods for metal recovery. In metal extraction, the process typically involves three steps: 1. Extraction, 2. Scrubbing, and 3. Stripping. During extraction, metal ions are transferred from the aqueous phase to the organic phase. In the scrubbing step, the loaded organic phase is treated with an aqueous solution to remove impurities. Finally, the metal is recovered from the organic phase by bringing it into contact with a stripping reagent, in a process called stripping. This is illustrated in figure 2

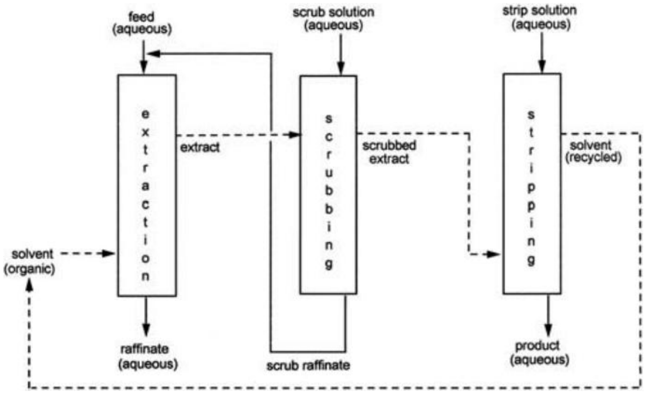

Figure 2. Stripping.

2. Principle and Factors Influencing Solvent Extraction :

The principle of solvent extraction involves exposing an aqueous solution containing metal ions to an organic solvent, known as the extractant. The metal ion becomes distributed between the two phases. Under equilibrium conditions, the distribution follows this relationship (without any association or dissociation in either phase). However, if association or dissociation occurs, the extraction process is modified by the

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respective association/dissociation coefficients in the organic (α_o) and aqueous (α_a) phases.

After extraction, the metal is recovered from the loaded organic (LO) phase by stripping it with a suitable aqueous solution. To maximize extraction efficiency, the solvent is applied in multiple fractions rather than all at once. After "n" extractions, the concentration of the solute in the aqueous phase (C_a) can be calculated as:

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,

$$D = \frac{Conc\ of\ metal\ ion\ in\ organic\ Phase\ (C_0)}{Conc\ of\ metal\ ion\ in\ aqueous\ Phase\ (C_a)} \tag{1}$$

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 αo and αa 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, (Ca)n is given by,

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

Where υo and υa are volume of organic phase and volume of aqueous phase respectively.

2.1.1. Solvent:

Choosing an appropriate solvent requires considering two main factors. First, the solvent's ability to effectively extract the metal is crucial. Second, the ease with which the solute can be recovered from the solvent should be evaluated. Additionally, factors such as the miscibility of the two phases, their relative densities, and viscosities need to be taken into account. Since certain metals are selectively extracted by specific solvents, selecting the right solvent is essential.

2.1.2. PH of the Aqueous Phase:

The extractability of metals is significantly influenced by the acidity (pH) of the aqueous phase in which the metal is present. For optimal metal extraction, it is important to maintain the right concentration of hydrogen ions (H^+).

2.1.3. Stripping:

Stripping refers to the process of removing the extracted metal from the organic phase and transferring it to another aqueous phase. This step is critical because it allows for analysis of the extracted metal, which is difficult to measure directly in the organic phase. Various stripping agents, such as acids (e.g., HCl, H2SO4, HNO3) or bases (e.g., NaOH, NH3), can be used for this purpose. Compound stripping agents (mixtures of salts and acids or bases) like NaOH+NaCl or NH3+(NH4)3CO2 can also enhance stripping efficiency. The effectiveness of the stripping process depends on the choice and concentration of the stripping agent; an optimal concentration maximizes the recovery of the metal.

2.1.4. Oxidation State Variation:

Altering the oxidation state of interfering ions can improve extraction efficiency by preventing the formation of extractable metal forms. For example, iron (III) impurities can be reduced to iron(II), which is not extractable. Likewise, ensuring that the metal to be extracted is in the correct oxidation state is essential for complete extraction.

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2.1.5. Organic-to-Aqueous Phase Ratio:

The ratio of the organic and aqueous phases in contact during extraction plays a crucial role in the process. An optimal phase ratio ensures maximum metal extraction. Typically, the aqueous phase is used in a larger proportion, as organic solvents tend to be more expensive and non-reusable.

3. EXPERIMENTAION:

P^H 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.

4. Result Analysis

Table 4.1 (Extraction of V by CYANEX based extractant)

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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 4.2 (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 to table 1.4, we can perceive it better. The plots are given below.

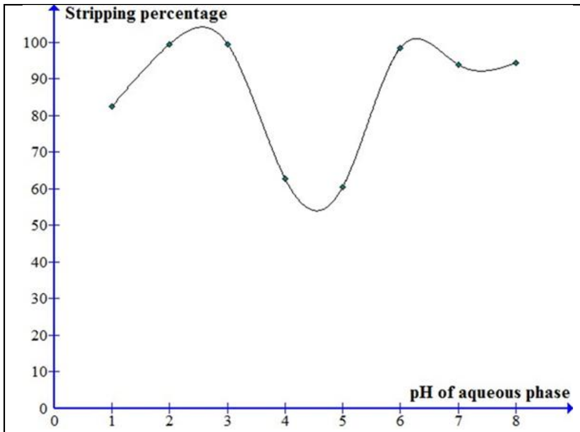

Figure.3- Extraction of Vanadium by CYANEX based extractant

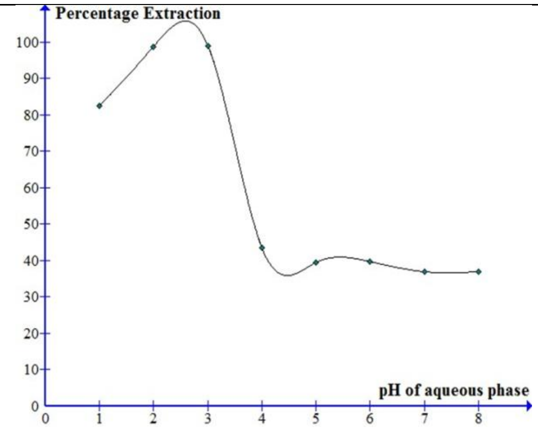

Figure.4- Extraction of Vanadium by D2EHPA based extractant

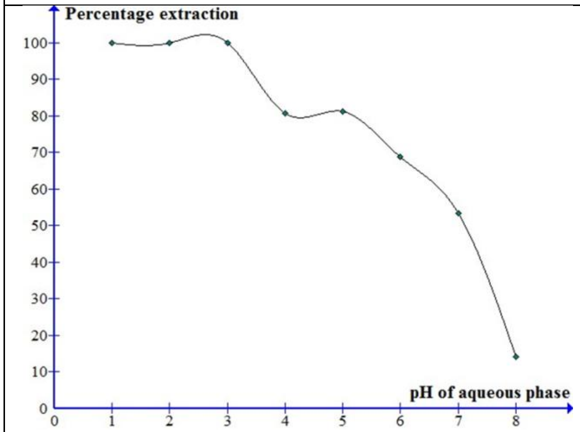

Figure.5. Extraction of Tungsten by CYANEX based extractant

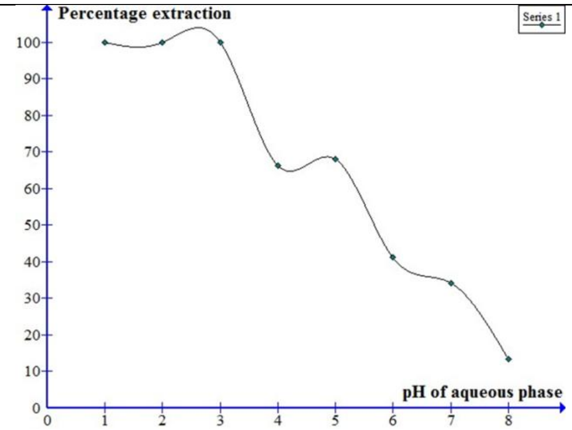

Figure.6. Extraction of Tungsten by D2EHPA based extractant

5. Conclusion

In summary, the process of isolating and recovering vanadium from impurities using hydrochloric acid demonstrates a highly efficient and selective method. The key to success in this approach lies in controlling factors such as pH, solvent choice, and extraction conditions, which significantly influence the selectivity and efficiency of vanadium extraction.

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At lower pH levels, both vanadium and its impurities, such as tungsten, are co-extracted, leading to non-selective extraction. However, by carefully adjusting the pH to an optimal range (typically between 5 and 8), the process enables selective extraction of vanadium with minimal contamination from other elements. This makes the technique particularly suitable for high-purity vanadium recovery in various industrial applications.

Among the extractants tested, CYANEX-based extractants have proven to be more effective than D2EHPA-based alternatives in terms of selectivity and overall recovery of vanadium. The findings also suggest that careful attention to operational details, such as accurate pH control, proper mixing, and precise dilution, is essential to avoid potential errors that could affect the results, such as mechanical or instrumental errors.

In conclusion, this method offers a promising and scalable solution for vanadium extraction from complex matrices, providing industries such as metallurgy, chemical production, and energy storage with a reliable and cost-effective means of obtaining high-purity vanadium. The study underscores the importance of refining extraction techniques to enhance both the efficiency and the selectivity of metal recovery processes.

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