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Separation and Recovery of Vanadium from Spent Vanadium Pentaoxide Catalyst by CYANEX 272

Archana Saily Painuly
Faculty of Chemical Sciences, Shri Ramswaroop Memorial University, Lucknow, India.

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ABSTRACT

The contact process preferably used vanadium pentaoxide as catalyst to increase the rate of reaction of producing sulphuric acid. Sulfuric acid plants regularly require catalyst replacement in order to cope with process improvements. The spent catalyst considered as hazardous solid waste and cannot be discarded untreated owing to presence of high amount of vanadium and other associated metal. Because of significant environment implications of spent catalyst wastes it is imperative to recover valuable metals present in them. The recovery of precious materials or metals from waste will not only help in mitigating environment problem due to metal pollution but also improve the economy of the country. The purpose of this research work is to develop method to recover vanadium from spent V_2O_5 catalyst. The detailed study of extraction, separation and recovery of vanadium from leached spent catalyst solution of composition; V, 3.6% ; Al,2.1%; Fe, 1.3 Ti, 0.8 and less than 1 % of Cr and Pb is reported in this paper. Cyanex 272 (bis (2, 4, 4-trimethylpentyl) phosphinic acid) has been explored for the recovery of vanadium from spent V_2O_5 catalyst. The effects of different parameters like, pH, solvent concentration, organic to aqueous ratio etc were optimised for the complete extraction and recovery of vanadium. The proposed procedure gives high purity vanadium with almost a quantitative yield (~99%) and of course free from closely associated metals. The extractants could be reused up to ten cycles with no significant change in the extraction capability.

Introduction

Vanadium is metal which is generally used for alloying steel and iron and in the production of oxidation catalysts. The metal has seen a steady rise in demand from the steel construction industry as building regulations increasingly call for improved strength and lighter construction materials. More recently the development of large-scale vanadium-redox flow batteries (VRFBs) for use in energy grid storage applications has open up a new demand stream for vanadium (Gan and Dong, 2010; Lazenby, 2012) .With increasing demand and gradual depletion in natural resources containing V, has encouraged to explore the search for secondary resources such as industrial or electronic waste and by products. Of the secondary resources, spent catalyst is the most important one. V is widely used as a catalyst in petroleum refinery and many industrial processes. The life of a catalyst varies from 3 to 6 years depending upon the impurities in the feed and number of cycles used (Park et al., 2006) . The deactivated catalysts are activated and reused. After a number of deactivation–activation cycles, the catalysts are discarded as a waste (Furimsky, 1996) .The waste catalysts are regarded as hazardous materials (Rapaport, 2000) and are therefore, either stored properly or further treated to recover the metal values. The second alternative is more advantageous as in the process valuable metals can be recovered from a hazardous material. The recovery of precious materials or metals from waste will not only help in mitigating environment problem due to metal pollution but also improve the economy of the country.

A significant effort has been made to recover vanadium from aqueous solutions by solvent extraction technique using various extractants. During the latter half of the twentieth century, reagents like –diketones, oxines, oximes, dithizones, dithiocarbamates, dithiols, high molecular weight amines (HWWA) and organophosphors compounds came into prominence. Among these HMWA and a few organophorous compounds emerged out as popular commercial extractants for vanadium. However, HMWA suffer from some limitations. The most usually encountered problem with long chain alkylamines is of emulsion formation (Saily, 1997). As of now alkylphosphorous compounds are more or less dominating the market of extractants. Among organophosphorous DEHPA (bis (2-ethylhexyl) phosphoric acid) and TOPO (Tri-n-octylphosphine oxide) have been extensively used for extraction behaviour of vanadium (Hughes and Biswas, 1991; Islam and Biswas, 1980; Juang and Lo, 1993; Li et al., 2011; Sato et al., 1980). However, there are few problems with these solvents such as DEHPA which readily form an emulsion or a third phase during stripping of Mo and V from the loaded solvent with the ammonia solution. Poor selectivity is another disadvantage of such extractants since it can co-extract several metals, including impurity elements such as iron and aluminium even at low pH (Sahu et al., 2013).TOPO shows high extraction coefficients but poor selectivity. It is known to extract approximately 30 metal ions from aqueous solutions (Shaeri et al., 2014).

Cyanex reagents are different, in that alkyl groups are bonded directly to the phosphorus atoms through P-C bonds rather than P-O-C bonding which exist in other commercial available organophosphorous reagents (e.g. D2EHPA, DDPA, TBP, EHPEHPA etc.). The presence of P-C bonding in Cyanex reagents renders them to be less susceptible to hydrolysis and less soluble in water than other reagents (Saily and Tandon, 1998).

Extraction equilibria studies of vanadium using Cyanex 272 (bis (2, 4, 4-trimethylpentyl) phosphinic acid) have been

Tele:
E-mail addresses: archana.cy@srmu.ac.in

reported by researchers (Li et al., 2012; Saily and Tandon, 1998; Zang et al., 1996; Zeng and Cheng, 2009) and few studies have also been conducted on its recovery from wastes. Most of separation and recovery was done employing synergetic effects of two or more extractants (Noori et al., 2014; Shaeri et al., 2014; Tavakoli and Dreisinger, 2014; Wu et al., 2012) , however, the occurrence of a white turbidity and a third phase formation was the major problems observed during stripping of V from the loaded organic (Li et al., 2011; Sahu et al., 2013). The present study focussed on the extraction studies of V along with closely associated metal ions from nitrate solutions and its quantitative recovery from spent V_2O_5 catalyst employing Cyanex 272 without synergetic effect, which certainly enhance financial viability of methodology. A complete separation scheme for the recovery of vanadium from spent V_2O_5 catalyst was developed and designed in a way so that impurities extracted in the organic phase leaving behind vanadium in raffinate to overcome the problem of turbidity and third phase formation during stripping.

Experimental

Cyanex 272 was obtained from Cytec, USA and was used without further purification. The sample of spent V_2O_5 catalyst was obtained from Projects and Development India Limited (PDIL), Sindri (India). All chemicals used were of analytical purity. Stock solutions of metal ions were standardized by usual complexometric titrations (Meites, 1963; Schwarzenbach and Flaschka, 1969).

C.a 1g of the powdered spent V_2O_5 catalyst (V, 3.5% ; Al, 2.0%; Fe, 1.3 ,Ti, 0.8%; and less than 1 % of Cr and Pb) was repeatedly (four times) digested with aqua-regia. The residue was treated with 10 ml of concentrated HNO_3 and filtered. The filtrate was boiled with nitric acid, cooled and made upto a final volume of 100 ml .The metal ion concentrations in the leach solution of catalyst agree fairly well with the composition data provided by the supplier. In order to get a representative value five separate samples of the catalyst were dissolved and processed by the proposed extraction procedure.

The solvent extraction and stripping experiments were carried out by shaking the required volumes of aqueous and organic phase at room temperature (25± 2^0C) for 3 minutes to ensure euiliribration. After phase separation the metal concentration in aqueous and stripped organic phase were analysed by Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The different results reported in the paper are the average of minimum of two determinations. Blank determinations were carried out wherever necessary and the corrections were made if required. During the analysis for different parameters blanks, duplicates, spikes and standards were processed on 5% basis. The percentage recovery for spiked samples in metal determinations ranged from 94 to 104%, which indicate that the results are accurate and unbiased. Relative percent difference of duplicate measurements was less than 10%, which is a satisfactory precision.

Result and Discussion

Effect of solvent concentration on metal extraction

The concentration of Cyanex 272 was varied from 0 to 30 % (v/v), to optimize the concentration of the solvent for the extraction of metals from leached spent V_2O_5 catalyst solution. The pH of leach solution and O/A ratio were maintained at a constant of 2 and 1, respectively. The percentage extraction of metal ions was found to increase with an increase in solvent concentration from 5 to 25 % (Fig 1) and came constant after that. Cyanex 272 shows a greater affinity for titanium over iron at a lower solvent concentration. For all further experiments 30% of the solvent was used.

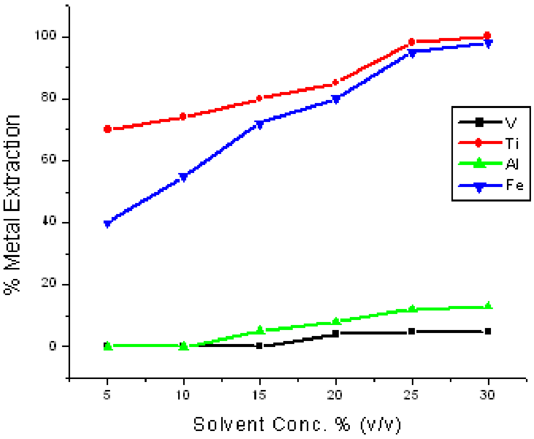

Fig 1. Effect of solvent concentration for the extraction of metal ions from leached solution of spent V_2O_5 catalyst containing (mg/L) V

Effect of pH on the extraction

Extraction efficiency of vanadium is highly dependent on pH because it forms different anionic complexes at low pH (Zeng and Yong Cheng, 2009). The extraction behaviour was studied at different pH from 0 to 3. The other experimental conditions were fixed as O/A 1:1, Cyanex 272 concentration, 30% (v/v). The extraction behaviour of V alongwith Al, Fe, Ti, Cr and Pb are shown in Fig. 2. The extraction of Fe and Al increased with increasing pH, however, V follows reverse pattern that is extraction efficiency increased with decreasing pH. Extraction of Ti is constant (80%) at lower pH and shows a quantitative increase at higher pH from 1 to 3. Co-extraction of Cr and Pb is almost negligible (< 5 %) and are not shown. At the equilibrium pH of 3, the distribution ratios for V, Al, Fe and Ti were found to be 0.04, 21, 64 and 37, respectively. The separation factor of Ti/V, Al/V and Fe/V were determined to be 880, 500 and 1523, respectively, which is a good separation value. To separate V from Fe Al and Ti from the leached solution the pH was fixed to 3.

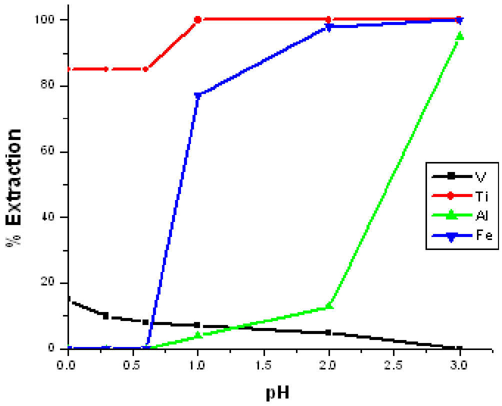

Fig 2. Effect of pH on the extraction of metal ions from leached solution of spent V_2O_5 catalyst (conditions 30%(v/v) Cyanex 272 in kerosene, O/A phase ratio-1:1)

Saturation loading capacity of Extractant

At pH 3 the 30% (v/v) Cyanex 272 was contacted with the leach solution of composition V- 366 mg/L, Al-215 mg/L, Fe-129 mg/L and Ti-75 mg/L, in a multiple contact mode. The O/A phase ratio was maintained at 1:1 to study the saturation loading capacity of the solvent. The metal uptake from the aqueous phase continued to increase after each contact, however, from third contact onwards, the extracted metals showed precipitation at the interface of aqueous and organic layer (Fig. 3). The solvent was loaded with about 660 mg/L of Al, 453 mg/L of Fe and 256 mg/L of Ti after the fourth cycle, which was assumed as the saturated loading capacity of 30 % Cyanex 272 for Al, Fe and Ti. The vanadium uptake was found negligible in multiple contact modes as at pH 3 the extraction of vanadium is less than 5 % (Fig. 2) and most enabled condition for the separation of vanadium from Al, Fe and Ti.

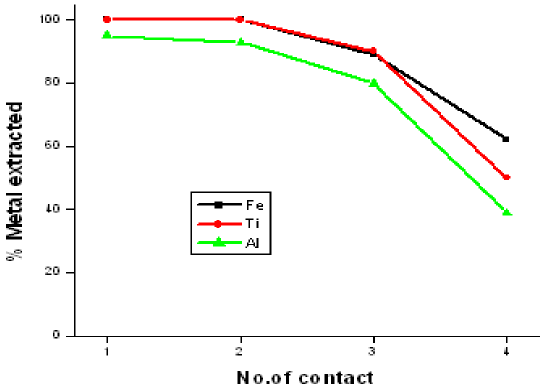

Fig 3. Saturation loading of Fe, Ti and Al by Cyanex 272 (30%), Aqueous feed (mg/L) V- 366, Ti-75, Al-215 and Fe-129, pH- 3, O/A ratio -1:1

Effect of O/A phase ratio

The distribution of V, Al, Fe and Ti present in leached solution was carried out at a different O/A ratio (organic to aqueous) using 30 % Cyanex 272 at pH 3 to determine the condition for the maximum extraction and subsequent separation of these metals. The O/A phase ratio was varied from 1:5 to 5:1. The solution containing V- 366 mg/L, Al-215 mg/L, Fe-129 mg/L and Ti-75 mg/L with pH 3 was used for the experiment. It was observed that with increase O/A phase ratio from 0.2 to 3.0, extraction of Fe, Ti and Al also increased (Table 1).

Table 1. Percentage extraction of Fe, Ti and Al at different organic/aqueous ratio study from leached solution of spent V_2O_5 catalyst

O/A ratio	% Extraction		
	Fe	Ti	Al
0.2	60	65	40
0.25	67	70	60
0.33	77	80	70
0.5	90	95	85
1	98	100	90
2	99	100	95
3	99	100	95

In order to determine the extraction isotherms, the McCabe –Thiele plot was constructed from phase ratio variation study for Fe and Al. The McCabe –Thiele plot represented in Fig 4 and 5 for Fe and Al, respectively, predicted requirement of 2 theoretical stages at O/A ratio at 1:2 for complete extraction of associated metal ions (Al, Fe, and Ti) and subsequent separation of vanadium from leached solution of spent V_2O_5 catalyst.

In order to validate the number of stages determined from the McCabe –Thiele plots (Fig 4 and 5) counter current simulation study for the complete extraction of Fe and Al from the leached solution was carried out. It was observed that 99% of Fe and 95 % of Al could be extracted in two stages leaving behind vanadium in aqueous phase using 30% Cyanex 272 with O:A ratio of 1:2 at an aqueous phase pH of 3. The problem in stripping of vanadium from loaded Cyanex 272 encountered by other researchers due to turbidity and third phase formation could be overcome in this investigated process as vanadium remains in aqueous phase.

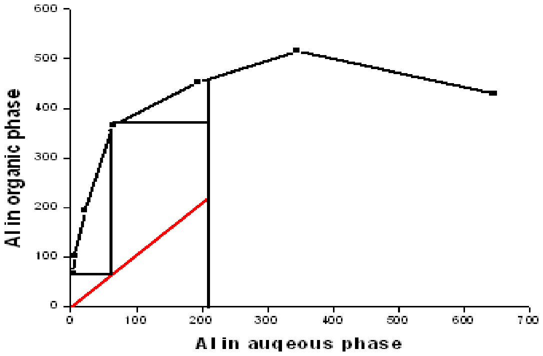

Fig 4. McCabe-Thiele diagram for determination of number of stages for complete extraction of aluminium from leached solution of spent V_2O_5 catalyst (conditions 30%(v/v) Cyanex 272 in kerosene, pH-3)

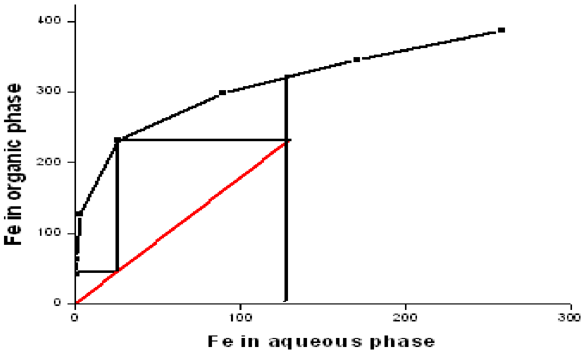

Fig 5. McCabe-Thiele diagram for determination of number of stages for complete extraction of iron from leached solution of spent V_2O_5 catalyst (conditions 30%(v/v) Cyanex 272 in kerosene, pH-3)

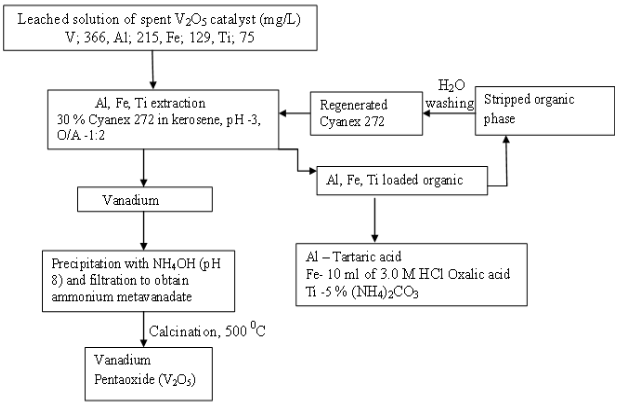

Fig 6. Flow sheet for the recovery of vanadium from leached solution of spent V_2O_5 catalyst using Cyanex 272

Stripping of iron, titanium and aluminium from loaded Cyanex 272

Leached solution of spent V_2O_5 catalyst containing V, Al, Fe and Ti loaded to the Cyanex 272 by two stage counter current process as determined by McCabe –Thiele plot (Fig 4 and 5) using O/A phase ratio of 1:2. The loaded organic containing Al; 730 mg/L, Fe; 262 mg/L, and Ti 155mg/L was washed first with 5% $(NH_4)_2CO_3$ for selective stripping of Ti from Fe and Al. After the removal of Ti, Fe was stripped from organic phase by washing it first with10 ml of 3.0 M HCl and then with 10 ml of 0.10 M oxalic acid. Al left behind after Ti and Fe removal was stripped from organic phase by washing it with 10 ml of 0.1 M tartaric acid. The percentage recovery of Al, Fe and Ti are 98, 99 and 99, respectively.

The organic phase, after removal of Fe, Ti and Al can be regenerated by washing it twice with water. The regeneration capacity of this extraction system was tested by carrying out successive extraction stripping cycles of kerosene solution of Cyanex 272. The results show no significant change in the extractability of reagents upto ten cycles.

Process flow sheet of vanadium recovery from spent V_2O_5 catalyst

Based on above investigation, a process flow sheet was developed for the recovery of vanadium from leached solution of spent V_2O_5 catalyst (Fig 6). In this flow sheet, vanadium can be effectively separated from Al, Fe and Ti in two stages counter current extraction process using 30 % Cyanex 272. Vanadium rich raffinate which was almost free from Al, Fe and Ti was precipitated with NH_4OH at a pH about 8. The precipitate was filtered and calcined at 500^0 C for 1 hr to produce corresponding oxide in pure form.

The above investigations project the potential of Cyanex 272 for the recovery of vanadium from spent V_2O_5 catalyst of composition V- 366 mg/L, Al-215 mg/L, Fe-129 mg/L and Ti-75 mg/L. In the proposed extraction process vanadium remains in aqueous phase which has two major advantages first it overcome the problem of turbidity and third phase formation which was encountered by past researchers during the stripping of vanadium from loaded Cyanex 272 and second the possibility of loss of vanadium is negligible as during the extraction processes vanadium is in aqueous phase. Cynex 272 is promising reagent; besides vanadium the extraction process also recovered aluminium, iron and titanium which are present in significant amount. The extraction isotherm, constructed at pH 3 with O:A phase ratio of 1:2 through McCabe-Thiele plot predicted two stages counter current process. Vanadium free from Al, Fe and Ti was selectively recovered as their ammonium salt, which was calcined at 500^0 C to get the vanadium as oxide (V_2O_5). Recovery of vanadium as V_2O_5 was found to be 99%. The extractants could be reused simply by washing with water upto ten cycles with no significant change in the extraction capability.

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