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Study on Vanadium Recovery from Spent Catalyst Used in the Manufacture of Sulfuric Acid

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Abstract

Spent catalysts for sulfuric acid production have large amount of vanadium and due to environmental authority it is required to reduce the vanadium contain of the spent catalyst. Experimental investigation was conducted to study the vanadium recovery from spent catalyst via leaching process using sodium hydroxide to study the effect of process variables (temperatures, sodium hydroxide molarities, leaching time and particle size) on vanadium recovery. The effect of process variables (temperature, particle size,molarities of sodium hydroxide and leaching time) on the percentages of vanadium recovery were investigated and discussed .It was found that the percentage of vanadium recovery increased with increasing temperature up to 100 ℃ , increasing sodium hydroxide molarity from 2 to 4M, increasing leaching time, decreasing particle size from mesh 150, 100 and 65. A complete vanadium recovery was achieved at the following conditions: temperature (100˚c), particle size (150 mesh) molarity of Na OH(4 molar) and leaching time(5 h).
Key words: vanadium, spent catalysts, sulfuric acid

Introduction

Vanadium is employed for the manufacture of a variety of vanadium compounds. Vanadium compounds have been found effective for catalyzing both organic oxidation and reduction. The oxides of vanadium have found many applications as catalysts especially in vapor-phase reductions. Vanadium pentoxide is the most common commercial form of vanadium. It can be used as a dye and color-fixer, and it's used as a catalyst in the production of sulfuric acid by Contact Process. Catalysts based on vanadium pentoxide are widely used in the conversion of naphthalene to phthalic anhydride. Vanadium is also used as catalyst in the process of CO_2 removal from the gas mixture in ammonia synthesis West [1]. Haoran et al. ,[2]; studied recovery of vanadium from clay vanadium mineral using an acid leaching method

References and further reading may be available for this article. To view references and further reading you must purchase this article.. A technique is including direct acid leaching. Stas et al., [3] studied the recovery of vanadium, nickel and molybdenum from fly ashes produced from heavy oil-fired electrical power station using two stages leaching process which consisted of an alkaline leaching to dissolve vanadium and molybdenum followed by sulfuric acid leaching to recover nickel. Lozano, and Godínez ,[4] studied the solvent extraction of Vanadium in sulphate media using primary amine and tertiary amine dissolved in kerosene has been carried out. Luis and Cury ,[5] studied the catalyst leaching in order to reduce its vanadium content so that it can be safely disposed. Factorial experimental design was used and the process variables studied were particle size, temperature, acid concentration and agitation intensity. Results showed strong dependency between remaining vanadium content and particle size. Temperature has shown lesser influence. The latter indicates an intra particle diffusion controlled process. Conventional method for recovering vanadium from vanadium containing ores was studied by Hansen, [6]. This method included as an initial step the roasting of the vanadium ore with a sodium salt to form roasted products which contain sodium vanadate in solid form. The roasted material was then cooled, crushed, ground and water leached in agitation leach tank in a conventional manner. The solubilized sodium vanadate in solution was recovered from the solids through

convential solid-liquid separation such as filtration or counter current decantation. Jassim,[7] used a solvent extraction technique as a separation method to separate a vanadium from the leach solution of the ashes of burned fuel oil at Electrical Power Station . Tributyl phosphate (TBP) was used as an extracting agent through mixer-settler batteries. Some Parameters, which influenced vanadium extraction, were studied in detail, such as chloride ion concentration and the acidity of the mother solution, in addition to the number of extraction, stripping stage and phase ratios. Mousa [8] recovered vanadium from scale residues of oil-fired power stations by alkaline leaching method using sodium hydroxide solution . Spent catalysts for sulfuric acid production have large amount of vanadium and due to environmental authority it is required to reduce the vanadium contain of the spent catalyst[Khorfan et al. , [9] studied the recovery of vanadium pentoxide from spent sulfuric acid catalysts ,using a three-step process involving acid leaching, oxidation and precipitation. Several different acids were used in the leaching, sulfuric acid was used in various concentrations, solid to liquid ratios, stirring times and temperatures. A high solid/liquid ratio in the leaching stage was used to obtain high concentration of vanadium pent oxide and low acid consumption that allowed direct precipitation without the use of extraction by rather expensive organic solvents. Sodium carbonate solution of one mole/liter concentration was used in the precipitation stage. Sulfuric acid was found to be the best leaching solution.

The aim of this work is to study the possibilities of vanadium recovery from spent catalyst used via leaching process using sodium hydroxide due to selectivity of sodium hydroxide to vanadium, and study the factures affecting the leaching process.

Experimental Apparatus

Experiments were carried out in 1 litter glass reactor, the diameter of glass reactor was 12cm and the height was 10 cm applying on heating mantle with thermostat and a mixer consisted of stainless steel shaft, screwed with four pitched turbine blades impeller , the diameter of impeller was 4 cm. The stirrer rotated by means of an electrical motor coupled to variable resistor to achieve 600 rpm .

A schematic diagram of the reactor system is show in Fig. 1.

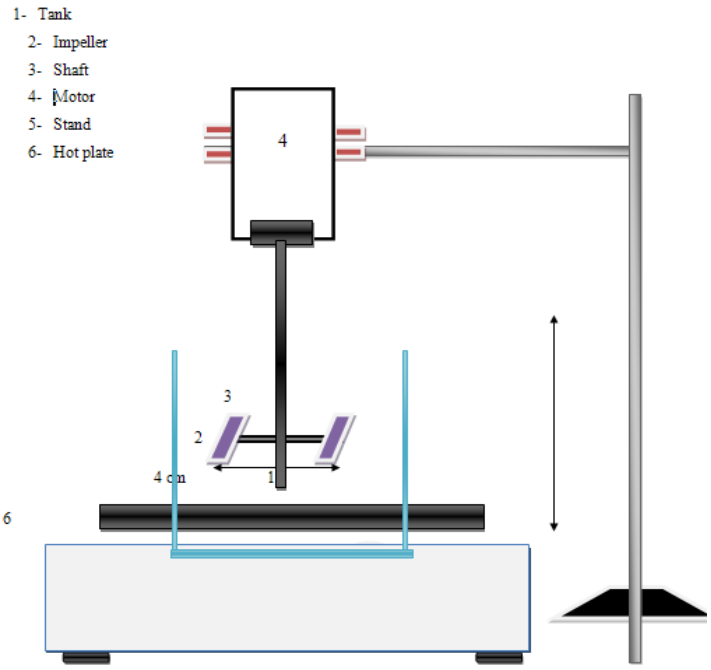

Fig. 1 A schematic Diagram of the Reactor system

Experimental procedure

The sample of spent catalyst used in this experimental procedures was obtained from (Al-Sadra Company in the west of Baghdad) taken randomly, grinded in laboratory ball mill and sieved by means of laboratory sieve supplied by Retsch company to obtain particle size (150 mesh=104 µm ,100 mesh=147 µm and 65 mesh=208 µm). Sodium hydroxide as applet supplied by BDH Company (98%) was used due its selectivity of vanadium. The required (2-4) molar solution of sodium hydroxide was prepared in the experimental tank as fallow.

$$\text{No. of mole} = \frac{weight}{moleculer\ weight}$$

Molar = mole / litter

$$2\,M = \frac{x}{40} \Big/ \frac{500\ ml}{1000} \qquad \Rightarrow x = \frac{40}{0.98} = 48.8gm$$ of NaOH

The solution was then heated to the desired temperature (60-100ºC) while stirrer at 600 rpm, the rpm was achieved by means of variance coupled with motor .100 gm of spent catalyst with particle size in the rang (mesh 150 to 65) was added to the aqueous solution of sodium hydroxide in each run .The reaction as follow.

$$V_2O_5 + 2\,NaOH \rightarrow 2\,NaVO_3 + H_2O$$

After the desired time (1-5 hr) the solution was filtered to remove the unreacted vanadium and impurities.
A fixed volume of 500 ml was used for all experiments. The block diagram of Fig. 2 shows the processes. Solid samples of the powder stock, which was used in this work were analyzed for vanadium content and the average percentage was found to be (37 %). This value was used in the calculation of vanadium fraction recovery for each experiment.
Samples of solutions from all experiments were analyzed for vanadium by means of Atomic Absorption spectrometry at the analytical laboratory of Ibn Cina Company.

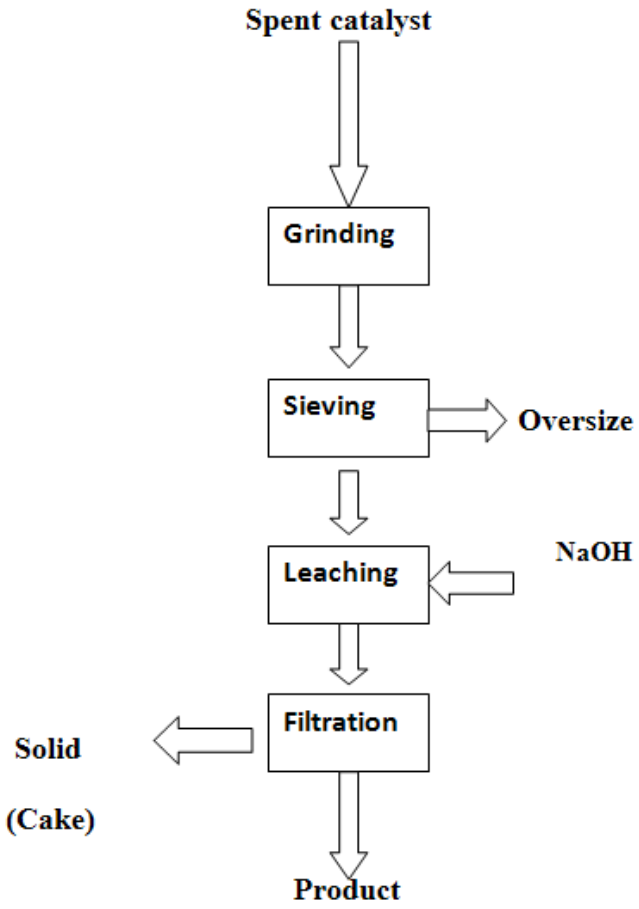

Fig.2. Experimental Procedure Block Diagram

Results and Discussion

The effect of temperature on vanadium recovery at different molarity at a given mesh size is shown in figures 3 and 4.
Observing these figures it can be shown that increasing the temperature will increase the vanadium recovery, the temperature influences the vanadium recovery in number of ways. Firstly as the temperature increases the mobility of the molecules will increase due to more energy gain, secondly the effective diffusivity increases with the increase in the temperature. This coincides with the definition of the diffusivity.
The main resistances to leaching are: kinetic of the process, intra-particle mass transfer and mass transfer from particle surface to surrounding. The chemical step is usually much more temperature-sensitive than the physical steps. Levenspiel,[10].
Since the change in temperature affected the fraction recovery one can say that the chemical reaction step is dominate.
Comparing with the results of Luis and Cury [5] reveals that the leaching velocity of residual vanadium content influenced by temperature where tested values from 25 to 55˚c,where vanadium recovery was 1310 ppm at(35 mesh size ,25˚c and 1% sulfuric acid concentration),while 1190 ppm at (35 mesh size ,55˚c and 1% sulfuric acid). Khorfan et. al.[9] showed that the temperature affects the vanadium recovery up to 80˚c, above this value no effected was noted.

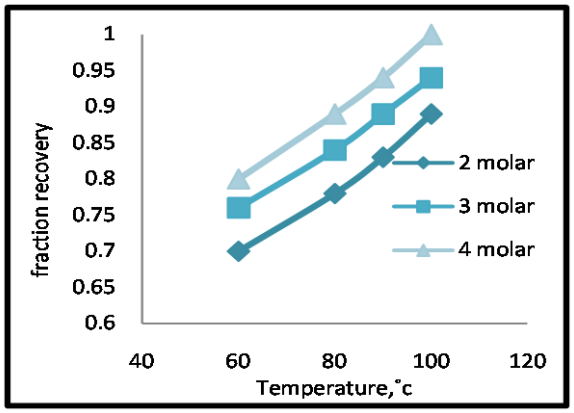

Fig. 3 Effect of temperature on vanadium fraction recovery at different time for 5molar and 150 mish size

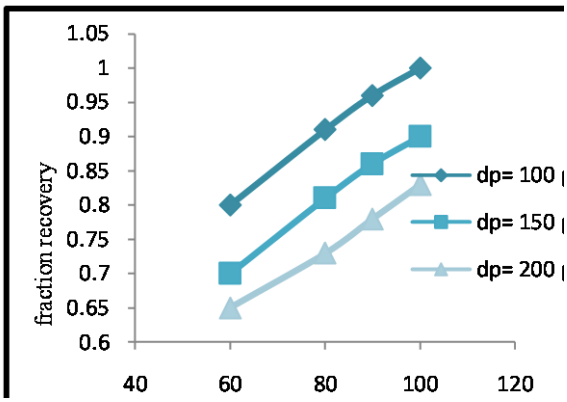

Fig. 4 Effect of temperature on vanadium fraction recovery at different time for 3 molar and 150 mish sizes

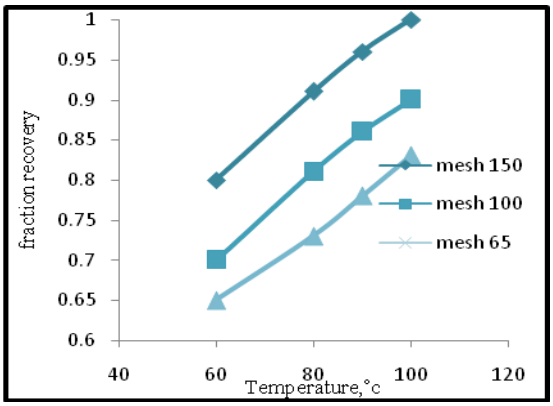

Fig 5 Effect of temperature on vanadium fraction recovery for 4 molar and 5 h

The effect of particle size on vanadium recovery at different temperature at a given time is shown in Fig 5. In this figure it can be seen that the fraction recovery increase as the particle size decrease (increasing mesh size).

The particle size influences the fraction recovery in a number of ways. The smaller the size is the greater interfacial area between the solid and liquid, the rate of reaction and the rate of transfer of material are higher. A reduction in particle size usually results in a decrease in the average time of passage of solvent from the surface to the interior of the particle and decrease the average time of passage of solvent from the surface to the interior of the particle and decrease the average time of passage of solute molecules from the dissolving point in the interior of solid particle to the surface of the particle ,Rickles,[11] .The effect of NaOH molarity on vanadium fraction recovery is shown in Fig.6 The figure shows that vanadium recovery increase as the molarity of NaOH increases. Comparing with result of Luis &Cury,[5] on which, the results shows that the vanadium recovery does not effected by sulfuric acid concentration, where the vanadium recovery constant at 1110 ppm in spite of changing the concentration from 1% to 10% while the other conditions are constant(65 mish size and 25˚c).

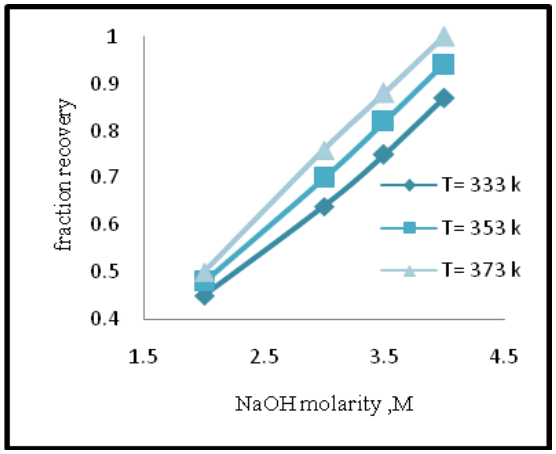

Fig. 6: Effect of NaOH molarity on vanadium fraction recovery for 5 h and 150 mish size.

Figures 7, 8 and9 shows the plots of fraction of vanadium recovery versus time for different temperatures and a given mesh size and NaOH molarity. It is clear from these figures that the best leaching time which lead to maximum recovery of vanadium is greatly dependant on the specific conditions of test i.e particle size, molarity of NaOH and temperature of test. Examination of figure 6 shows that the maximum fraction recovery was 150 mesh size and 4 molar NaOH, where the best leaching time was found to be 5 h at 100˚c.

Khorfan et al,[9] showed that the leaching was carried out by varying the time of mixing from 10 min to 4 hours while keeping other conditions constant (T = 100 ◦C,solid/liquid = 1/10 g/ml, sulfuric acid 15% v/v). The efficiency was constant after 30min so it is enough to fix the mixing time at one hour for other experiments.

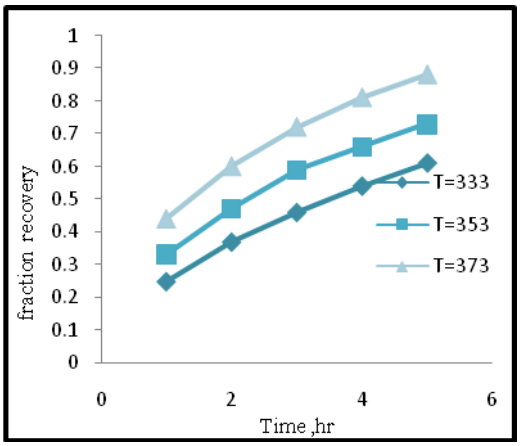

Fig. 7 effect of time on vanadium fraction recovery for 65 mesh size and 4 molar NaOH

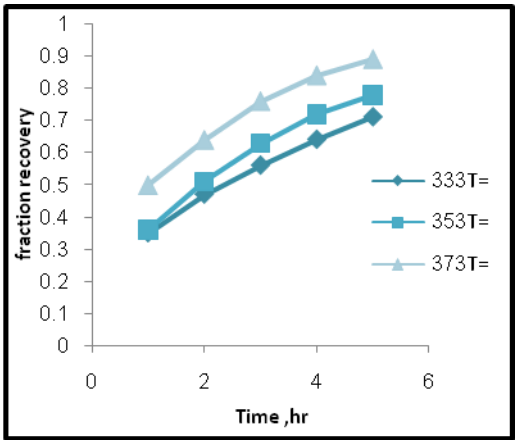

Fig. 8 effect of time on vanadium fraction recovery at different temperatures for 100 mesh size and 4 molar NaOH.

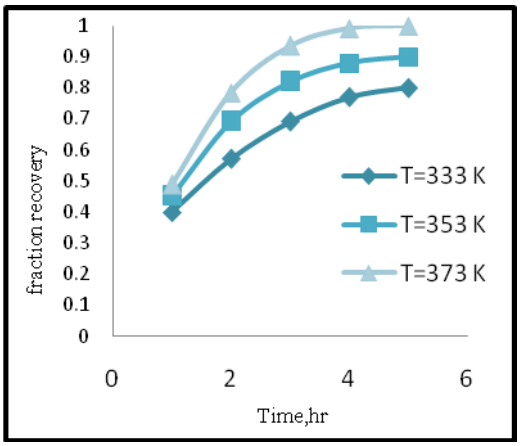

Fig. 9 effect of time on vanadium fraction recovery for 150 mesh size and 4 molar NaOH

Conclusions:

1.From the present investigation it was concluded that the fraction of vanadium recovery increasing with increasing of temperature ,NaOH molarity ,leaching time and decreasing with particle size increasing.:

2.The optimum leaching time depended greatly on specific conditions of test ;temperature, particle size and NaOH molarity.

3.The selectivity of NaOH solution for the recovery of vanadium from spent catalyst was excellent.

4.A complete vanadium recovery was achieved at the following conditions: temperature (100˚c), partical size(150 mesh), molarity of NaOH(4 molar) and leaching time(5 h).

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الخلاصة

تعتبر عملية استرداد الفناديوم من العامل المساعد المستهلك والمستخدم في صناعة حامض الكبريتيك من الامور المهمة لكونة يعتبرمصدر جيد للحصول على الفناديوم وكذلك لاهمية الموضوع من الناحية البيئية وذلك لظرورية خفض نسبة الفناديوم في المخلفات قبل طمرها. اهتم هذا البحث بدراسة استرداد الفناديوم من مخلفات المحفز المستهلك المستخدم في صناعة حامض الكبريتيك بواسطة محلول هيدروكسيد الصوديوم .

تم دراسة تأثير عدة متغيرات هي درجة الحرارة ،الحجم الحبيبي للمخلفات ، مولارية هيدروكسيد الصوديوم و زمن الهظم .