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Recovery of vanadium from spent catalysts of sulfuric acid plant by using inorganic and organic acids: Laboratory and semi-pilot tests

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ABSTRACT

Catalysts are used extensively in industry to purify and upgrade various feeds and to improve process efficiency. These catalysts lose their activity with time. Spent catalysts from a sulfuric acid plant (main elemental composition: 5.71% V₂O₅, 1.89% Al₂O₃, 1.17% Fe₂O₃ and 61.04% SiO₂; and the rest constituting several other oxides in traces/minute quantities) were used as a secondary source for vanadium recovery. Experimental studies were conducted by using three different leaching systems (citric acid with hydrogen peroxide, oxalic acid with hydrogen peroxide and sulfuric acid with hydrogen peroxide). The effects of leaching time, temperature, concentration of reagents and solid/liquid (S/L) ratio were investigated. Under optimum conditions (1:25 S/L ratio, 0.1 M citric acid, 0.1 M hydrogen peroxide, 50 °C and 120 min), 95% V was recovered in the presence of hydrogen peroxide in citric acid leaching.

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1. Introduction

Catalysis has been defined as the process by which chemical reaction rates are altered by the addition of the catalyst. Catalysts have very wide range and the number of uses is increasing everyday. However, the catalysts deactivate by and by. When the activity of the catalyst declines below the acceptable level, that catalyst is usually regenerated and reused, but regeneration is not possible every time (Furimsky, 1996; Marafi and Stanislaus, 2008a). After a few cycles of regeneration and reuse, the catalyst activity may decrease, and further regeneration may not be economically feasible (Wahoud et al., 2011). The U.S. Environmental Protection Agency classifies spent catalysts as hazardous wastes (USEPA, 2003).

Spent catalysts considered as secondary resources would decrease the consumption of primary resources and would provide great economic benefits. Valuable metals (V, Ni, Mo, Co, etc.) in the form of oxides or sulfides are usually extracted from primary ores at very low concentrations (a few ppm). Excavation of huge amounts of rock with the water and energy consumption required for processing such ores makes the recovery from oil-refining

residues economical in terms of natural resources saved. Furthermore, the concentration of those metals in the spent catalysts is much greater than the concentration of those metals in primary ores. Due to strict environmental regulations for disposal, different processes have been examined to treat waste catalysts in a meaningful way. One effort is to recover valuable metals through economically and environmentally sustainable techniques (Marafi and Stanislaus, 2008a; Akcil et al., 2015).

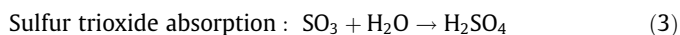
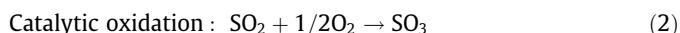
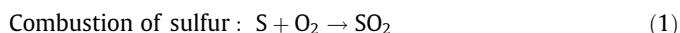
Vanadium (V) especially has strategic and industrial importance due to its applications in many technological fields (Moskalyk and Alfantazi, 2003). V has many and continually increasing industrial applications. Today, vanadium consumption in steel industry amounts to 85% of its total consumption; other applications are in vanadium bearing titanium alloy, chemical industries and an alloying agent to produce ferro-vanadium. V is employed for the manufacture of a variety of V compounds, many of which in turn are employed to prepare catalysts such as hydrocarbon oxidation catalysts and catalysts for the manufacture of sulfuric acid (H₂SO₄) (Khorfan et al., 2001). The common grade of V in processed ores is usually less than 2%. As a result, many industrial sub-products have been investigated and used for V recovery, including converter and smelter slag, or spent catalysts (Gupta and Krishnamurthy, 1992). Vanadium is never found in its pure state and present primary resources are not sufficient to satisfy V

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demand (Liu et al., 2003) and to ease an insufficient supply of domestic resources; many countries comprehensively utilize secondary resources containing V (Shao et al., 2009).

Average service life of vanadium catalysts is 1–2 years. For this reason, 7770 tons of spent catalyst is revealed from sulfuric acid plant per year in Turkey (Eti Mine Company, 2013). The H_2SO_4 production process can be divided into three main reactions, namely (Tveit, 2003);



When producing H_2SO_4 through the contact process, an important step is to produce sulfur trioxide by passing a gas mixture of sulfur dioxide and oxygen over a catalyst (Eq. (2)). The oxidation of SO_2 to SO_3 is slow and needs a very high temperature to have a realistic rate without the use of a catalyst (Ognyanova et al., 2009).

Most industrial waste is now treated as a substance for reuse and as a source of valuable raw materials. Such type of waste is spent V catalyst – the amount of spent V catalyst accumulated in Poland is estimated to be approximately 3000 Mg (Grzesiak, 2006). The problem of deactivated and decommissioned industrial catalysts is very serious and has not been solved yet in a comprehensive manner (Mazurek et al., 2010; Mazurek, 2012, 2013).

Extraction of the V present in spent catalysts by leaching method has been studied by many researchers, as indicated by the summary of the studies shown in Table 1. Aqueous solutions of ammonia and ammonium salts, various concentrations of inorganic acids (e.g., HCl, H_2SO_4 , HNO_3), oxidants and alkalis have been used as leaching solutions.

Among organic reagents (e.g., citric acid, oxalic acid), water-soluble organic acids have been attracted more attention (Marafi and Stanislaus, 2008b). Lee et al. (1992) and Zeng and Cheng (2009) reported that oxalic acid can be used as a complexing agent to selectively extract V from the spent HDS catalysts. Beuther and Flinn (1963) compared the efficiencies of many organic acids such as oxalic acid, lactic acid, citric acid, glycolic acid, phthalic acid, malonic acid, succinic acid, salicylic acid and tartaric acid for leaching metals (V, Mo, Ni and Co) from a spent hydrotreating catalyst. Aqueous solutions of the acids (1%) were used at ambient

temperature and pressure in this study. Oxalic acid was found to show the highest efficiency for leaching all four metals. The metals V (47%), Mo (59%), Co (60%) and Ni (56%) were leached by 1 wt% oxalic acid solution. The effect of reagent concentration and other conditions of leaching were not investigated and optimized.

A study published by Mulak et al. (2006) was studied on optimizing the parameters for the extraction of Mo, Ni, V and Al from a spent HDS catalyst using aqueous oxalic acid solution mixed with hydrogen peroxide (H_2O_2). The results showed that addition of H_2O_2 to oxalic acid up to 3.0 M H_2O_2 enhanced the leaching of metals remarkably, and thereafter the leaching remained relatively stable. The highest extraction of metals from the spent catalyst (at 50 °C with a solution of 0.5 M oxalic acid with 3.0 M H_2O_2) was found to be 90% Mo, 94% V, 65% Ni and 33% Al in 4 h of leaching.

In another study, ammonium metavanadate was precipitated from the purified solutions at pH 7.2–7.6, a ratio of $(\text{NH}_4)_2\text{SO}_4/\text{V}_2\text{O}_5$ and at room temperature. Increasing the sulfate concentration was shown to adversely affect the precipitation of ammonium metavanadate. Conversion of metavanadate into polyvanadate was achieved by repulping in hot distilled water (90–95 °C) and in pH 2. Vanadium pentoxide (98.8% V_2O_5) was produced by firing polyvanadate precipitate at 560 °C (Gladyshev et al., 2015).

At the same time, bioleaching has been applied for the recovery of spent catalyst, and several studies have recently been focused on spent catalyst (Beolchini et al., 2012). Bioleaching is today considered a novel approach for metal mobilization from various solid matrices: mineral ores, fly ash, sewage sludge, spent batteries and electronic scrap materials. Spent catalysts are only some of the solid wastes that can potentially be treated by means of bioleaching (Santhiya and Ting, 2005; Marafi and Stanislaus, 2008b). In a study conducted by Beolchini et al. (2012), Fe/S-oxidizing bacteria were applied to spent refinery catalysts to assess the performance of bioleaching in metal mobilization. For spent refinery catalysts, the improvement in metal extraction observed in the presence of microbial activity confirms the key role of Fe/S-oxidizing bacteria and ferrous iron with 1% solid content (w/v). They were showed that recovered Ni, V, Mo of 83%, 90% and 40%, respectively.

The main purpose of the present work was to investigate the recovery of V from the spent catalyst with H_2SO_4 , oxalic acid and citric acid leaching. Metals are able to form soluble metal complexes, with the addition of H_2O_2 as effective reagent. The studied

Table 1
Summary of some studies carried out on recovery of V from spent catalyst.

Source of waste	Leaching conditions	V recovery (%)	References
Spent catalyst	In a solution of 0.05 N sodium nitrate (NaNO_3), pH 8.00, at 25 °C and 1:15 S/L ratio	39	Lai and Liu (1997)
Spent H_2SO_4 catalyst	H_2SO_4 leaching (15% H_2SO_4 ; 1 h; 100 °C; 1/5 S/L ratio) + Oxidative precipitation (73% efficiency)	96.6	Khorfan et al. (2001)
Spent Hydro-desulfurization (HDS) catalysts	The leaching step with acid mixture (50 mL 70% HNO_3 + 25 mL of 96% H_2SO_4 + 25 mL of 37% HCl) in 2 h at 70 °C	99	Lai et al. (2008)
Spent H_2SO_4 catalyst	The roasting step (400 °C)	78	Ognyanova et al. (2009)
Spent catalyst (Ni–Mo/ Al_2O_3)	The acidic leaching step (0.3 M H_2SO_4) in 6 h at 80 °C and 1:10 S/L ratio	80	Madeja (2011)
Spent V catalyst	The alkaline leaching step (4 M NaOH) in 2 h, followed by acidic leaching (0.5 M H_2SO_4) In a solution of 0.50 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and 0.66 M H_2O_2 , at 70 °C A 180–250 μm catalyst in 4 h at 323 K in the presence of 2% oxalic acid solution at 1:25 S/L ratio	91	Mazurek (2013)
V cake	2 M H_2SO_4 and 40 g/L Na_2SO_3 at 40% pulp density, 70 °C for 1 h	93.1	Okudan et al. (2015)
Selective catalytic reduction (SCR) catalysts	5 M NaOH solution, 1:5 S/L ratio at 393 K for 3 h (continuous air stirring, 10 mL/min, 0.05 MPa)	96.5	Huo et al. (2015)
Spent selective catalytic reduction (SCR) catalyst	2 M NaOH, 0.2 M Na_2CO_3 , 300 °C, and 1:20 S/L ratio	86.6	Kim et al. (2015)
Spent diesel exhaust catalyst	The ammonia concentration of 4.5 M, leaching temperature of 413.15 K, reaction time of 2 h, the H_2O_2 solution concentration of 1.0 M and 1:20 S/L ratio	46.25	Zhao et al. (2015)

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