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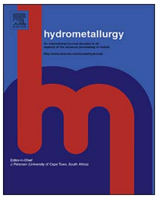

Technical note

# Application of lime in two-stage purification of leaching solution of spent vanadium catalysts for sulfuric acid production

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## ABSTRACT

Two-stage hydrolytic purification of acidic solution of reductive leaching of spent vanadium catalysts for sulfuric acid production from arsenic and iron impurities has been investigated. After oxidation of Fe(II) and As(III) with hydrogen peroxide and neutralization of vanadium (IV) solution with lime to pH 2.8 at 25 °C, the concentration of iron and arsenic has been reduced from 4.5 to 1.6 $g{\cdot}L^{-1}$ and from 1.0 to 0.6 $g{\cdot}L^{-1}$, correspondingly. After neutralizing excessive acidity to pH 8.5 at 60 °C and oxidation of vanadium, the concentration of iron and arsenic in obtained solutions of sulfates and vanadates of alkali metals does not exceed 0.1 $mg{\cdot}L^{-1}$. Lime's calcium ions are bound with excessive sulfate ions to form gypsum, which allows to preserve the composition of promoter salts and to return them into production of catalysts after vanadium separation. Washing of the second stage precipitation with initial leaching solutions allows to avoid vanadium losses, guarantees return of impurities to the first stage and their extraction in a convenient form for arsenic burial. The kinetic equation for an oxidation of vanadium (IV) solutions with atmospheric oxygen during their neutralization with lime in presence of ferric compounds has been acquired.

## 1. Introduction

Vanadium is an important product that is used almost exclusively in ferrous and non-ferrous alloys due to its physical properties such as high tensile strength, hardness and fatigue resistance (Moskalyk and Alfantazi, 2003; Archana, 2005). Vanadium is currently recovered as a by-product or, at best, a co-product from mineral resources: the former sources of concentrated ore deposits are now depleted. Usually, the vanadium content in processed ores is less than 2%. As a consequence, many industrial sub-products have been investigated and used for vanadium recovery, including converter and smelter slag or spent catalysts (Gupta and Krishnamurthy, 1992; Das et al., 2007). Reprocessing of secondary vanadium raw materials doesn't require ore mining and extraction and, in general, increases efficiency of valuable elements' extraction.

During production of sulfuric acid ($H_2SO_4$) about 40 thousand tons of spent vanadium catalyst (SVC) are produced annually worldwide (Mauskar, 2007). SVC is an example of product which after being spent, on one hand, creates a great pressure on the environment and on the other is the source of several valuable components. Cost efficiency of vanadium extraction from these raw materials is rather low and examples of industrial implementation of these processes are rare (Orehova et al., 2012), however, the ecological factors become increasingly strong argument for reprocessing instead of its disposal as a waste. At the same time, there is an urgent need of development and improvement of technologies of integrated reprocessing of SVC to ensure their economic attractiveness.

SVC is composed of an inert support with highly porous surface, typically of natural or synthetic cristobalites, with pores which contain a mix of potassium pyrosulfato-vanadates ($K_2S_2O_7{\cdot}V_2O_5$) and pyrosulfates of potassium ($K_2S_2O_7$), rubidium ($Rb_2S_2O_7$) or cesium ($Cs_2S_2O_7$) (Baltes, 2001). Content of vanadium varies from 2.2 to 4%, for alkali metal pyrosulfates it reaches 30–35%, whereas cristobalite content is 45–55% (Ullmann's, 1994). In addition, SVC contain admixtures of ferric compounds from 0.2 to 1.9% and arsenic (As) from $10^{-4}$ to 0.07% (sometimes, up to 1%) (Yanhai et al., 2009; Mazurek, 2012). Analysis of SVC components' value has shown that price of contained promoter is only slightly lower that of vanadium for potassium pyrosulfate catalysts, and is greater in case of catalysts based on cesium and rubidium salts (USGS Minerals Information, 2017). Thus, extraction of promoter salts allows to greatly increase economic attractiveness of SVC reprocessing. The majority of present day researches thoroughly study particular stage of hydrometallurgical reprocessing of vanadium raw materials, while complex reprocessing of SVC is the aim of a few of scientific works.

Ho et al. (1994) and Shao et al. (2009) have shown that basic

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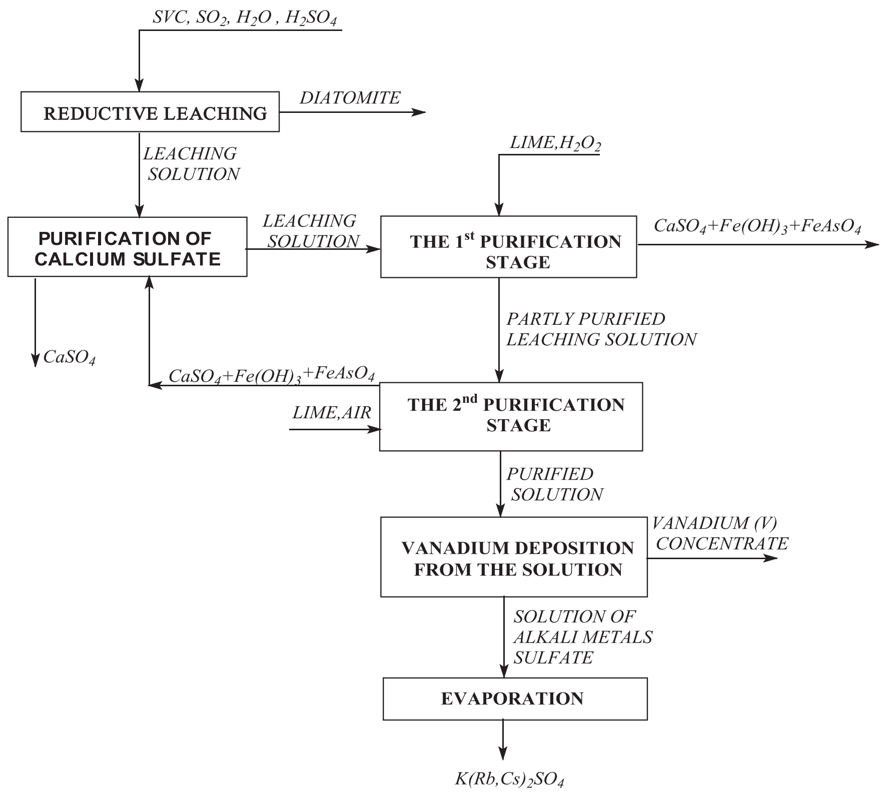

**Fig. 1.** Flowsheet of SVC for sulfuric acid production reprocessing.

vanadium leaching is selective towards iron, however leads to dissolution of silicate support and contamination of solutions with silicic acid. Ognyanova et al. (2009) have conducted a detailed study on leaching efficiency of sodium hydroxide (NaOH) solutions and achieved 78% vanadium recovery. During sulfuric acid leaching the silicate support does not dissolve and process can be carried out with obtaining of solution of vanadium (IV) and vanadium (V) compounds. Leaching with $H_2SO_4$ has been studied by Hong (1988) and Mazurek (2012). Lozano and Juan (2001a) have shown that 99% extraction of vanadium was achieved with three-stage process by 20% $H_2SO_4$. One-stage vanadium extraction in weakly-acidic medium can be achieved with reductive leaching. Owing to formation of highly soluble sulfates of vanadyl ($VOSO_4$), ferrous sulfates and arsenic acid, the method allows for complete separation of silicate support from other SVC components. When using reducer such as sulfurous acid ($H_2SO_3$) (Okuwaki et al., 1988; Mohanty, 2011; Nikiforova et al., 2016), hydrazine ($N_2H_4$) (Lasiewicz, 1989), oxalic acid $H_2C_2O_4$ (Badoiu et al., 1968), the change in solutions' ion compositions is negligible, which simplifies further utilization of contact mass.

For separation of vanadium from major part of impurities Sato and Takeda (1970), Giavarini (1982), Moussa et al. (2008), Li et al. (2009), Deng et al. (2010) and Li et al. (2011) have used solutions of di-2-ethylhexylphosphoricacid (D2EHPA) in kerosene. Despite good results for vanadium extraction, separation from iron is incomplete. In addition, re-extracts are contaminated with phosphor compounds, thus, additional purification stages are required. Biswas et al. (1985); Olazabal et al. (1992); Lozano and Juan (2001b); Chen et al. (2006); Navarro et al. (2007); Zeng and Yong Cheng (2009); have used extraction of V(V) with ammines, in acidic medium the vanadium is successfully separated from ferric ions, but not from arsenic. In addition, because of high redox potentials of solutions, the oxidation of ammines occurs, which limits this method for industrial applications.

Ho et al. (1994) mentioned that some of the iron can be precipitated selectively from vanadium by reducing the leach liquor to Fe(II) and V (IV) and then controlling the oxidation with peroxide to a redox potential around 800–900 mV. At this potential Fe(II) is oxidized (770 mV) but not V(IV) (1000 mV), and ferric hydroxide ($Fe(OH)_3$) precipitates at pH between 2 and 3. In addition, La Berre et al. (2007); Jia and Demopoulos (2008) and De Klerk et al. (2012) have shown, that upon neutralization with lime ($Ca(OH)_2$) of Fe(III) and As(V) solution to pH from 2 to 4, the arsenic is partially removed by ferric hydroxide, and at pH 8 it is fully precipitated.

Ability of V(V) to form highly soluble compounds in neutral and basic media allows for its separation from metal ions that are prone to hydrolysis under these conditions. At high V(V):Fe(III) ratio purification of vanadium solution from iron and other transitional metal impurities can be achieved with neutralization in a range of pH from 7 up to 9. However, the formed ferric hydroxides partially sorb vanadium, raising a problem of preliminary iron removal, if its concentration is high (Peacock and Sherman, 2004; Mazurek et al., 2010). Thus, difference in solubility of V(IV), V(V), Fe(III) and As(V) compounds upon pH changes, allows to make an assumption about possible separation of vanadium compounds from iron and arsenic by means of consequential hydrolytic precipitation.

Because extraction of alkali metal (K, Rb, Cs) sulfates can significantly improve cost-efficiency of catalysts reprocessing, it is not advised to introduce sodium ($Na^+$) or ammonium ($NH_4{}^+$) ions into solution upon neutralization. Rodriguez et al. (1985) have used potassium hydroxide (KOH) solution, but because of its high cost it is economically inadvisable. This draws attention to lime for neutralization of excessive acidity, calcium ions of which, can be removed from solution in form of slightly soluble sulfates. But because of possible coprecipitation of calcium sulfates and vanadates (Ivankin et al., 1976; Zhao et al., 2012), not enough attention has been paid to usage of lime for neutralization of sulfuric acid leaching solutions of SVC. However, sufficient solubility of calcium metavanadate ($Ca(VO_3)_2$) and high sulfate concentration in solution, can favor selective precipitation of calcium sulfate.

A condition for vanadium separation from impurity at high pH is its oxidation to pentavalent oxidation state. At a pH above 3 vanadium oxidation can be rapidly achieved with hydrogen peroxide ($H_2O_2$), but atmospheric oxygen can serve as a significantly cheaper oxidant in this