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Effect of parameters on vanadium recovery from by-products of the Bayer process

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ABSTRACT

Leach solutions and wastes of the Bayer process are important resources for metals such as aluminum and vanadium. Despite the fact that vanadium is precipitated as cake and removed in the Seydisehir Eti Aluminum Facility (Turkey), it cannot be used due to low metal content and impurities it contains. Within the scope of this study, research and development of environmentally acceptable, technically sound and low-cost chemical leaching and recovery methods were conducted for the recovery of vanadium from the by-product cake of the Bayer process. In the conducted studies, a sample of vanadium cake was used after its detailed characterization. Roasting tests were performed in order to remove the arsenic from the vanadium cake; however, it was found that roasting was not effective for arsenic removal. The performances of different reagents were examined in chemical leaching tests (H_2O and H_2SO_4 leaching, H_2SO_4 leaching with the addition of $NaSO_3$, and NH_4F); in the H_2SO_4 leaching tests performed with the addition of Na_2SO_3, the effects of concentrations of reagents and temperature on the efficiency of vanadium recovery (max. 93.09%) were determined with the full factorial experimental design method. The results were evaluated with ANOVA (variance analysis) method, and empirical models were formed. In lab and semi-pilot scale leaching tests, vanadium recoveries were 96.34% and 94.76% respectively. Vanadium was precipitated with NaOH and $FeSO_4$ and almost all vanadium (95.8%) was obtained as $Fe_3(VO_4)_2$. Cost analysis and economic evaluation have shown the economic feasibility of the leaching and recovery processes proposed.

1. Introduction

The Bayer process is a keystone method of the aluminum production industry used in producing quality alumina for bauxite refining worldwide. Despite the fact that the process is well understood, the existence of impurities in the solution affects the product quality and causes a significant cost in the industry (Sonthalia et al., 2013).

Bauxite ores contain strategically important metals such as vanadium as well as aluminum. In the Bayer process, vanadium in the ore is dissolved with the leaching procedure and the concentration of vanadium in the leach solution increases with time. Vanadium is removed from loaded leach solutions as vanadium cake (16–17% V_2O_5) in the evaporation unit. Vanadium cake, which also contains gallium (30–40 ppm), cannot be efficiently used due to the relatively low content of vanadium and high levels of impurities it contains (Mahanty et al., 1967; Mukherjee et al., 1990).

It is estimated that approximately 10,000–50,000 tons of vanadium in bauxite are extracted through the Bayer process during global annual alumina production. In 2010, the global vanadium production amount was only 64,000 tons (Zhao et al., 2012). Vanadium is one of the strategically important metals used as a catalyst in manufacturing sulfuric acid and in titanium alloys in the steel, automobile, and spacecraft and airplane industries (Perron, 2001; Moskalyk and Alfantazi, 2003; Archana, 2005; Raja, 2007; Koltuniewicz et al., 2014). Vanadium alloys have begun to be used recently in offshore oil drilling pipes in the USA. Vanadium alloys, which are used in manufacturing high-pressure gas pipes in Russia but the use of which is gradually decreasing in this area, are used in manufacturing special pipes (submarines) because they increase the resistance of other alloys with carbon and manganese against corrosion. The most recently developing areas for the use of vanadium are the manufacture of eyeglasses, filtration of window glasses of big buildings against ultraviolet lights, and manufacturing of Vitamin A tablets (catalyst) (Moskalyk and Alfantazi, 2003; Kar et al., 2004).

Solvent extraction (Navarro et al., 2007; Li et al., 2009; Zeng and Cheng, 2010) and ion exchange (Hu et al., 2009; Yeom et al., 2009; Zeng et al., 2009; Li et al., 2011) are two very effective methods for recovering vanadium from solutions. It is very difficult, however, to recover vanadium directly from these solutions due to the strongly basic structure of the Bayer leach solutions and the low concentration of vanadium.

An optional method is recovery by precipitation of vanadium in the Bayer solution (Ye et al., 2012). Bayer liquor is a complex solution, containing $Al(OH)_4^-$ in major amounts along with impurities such as

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Table 1
The conditions of the roasting tests for the vanadium cake sample with the ashing furnace (VCF — Vertical Chamber Furnace) and microwave oven (VCMW).

Sample code (VCF)[a]	Temperature (°C)	Sample code (VCMW)[b]	Roasting duration (min)
VCF-1	200	VCMW-1	3
VCF-2	400	VCMW-2	5
VCF-3	500	VCMW-3	8
VCF-4	600	VCMW-4	10

[a] VCF roasting time: 60 min.
[b] VCMW roasting power unit: 360 W.

$SiO_2(OH)_2^{2-}$, CO_3^{2-}, and VO_4^{3-}. Therefore, it is very difficult for an efficient precipitation of vanadium (Zhao et al., 2012). Lime is a good precipitant as it forms a low soluble product of calcium vanadate (Wang, 1992). In addition to this, methods have been developed for recovery of vanadium from calcium vanadate, and their viability has been proven by many researchers (Huang and Wang, 1992; Liu et al., 2003; Lin et al., 2004).

Vanadium, >90% of which is V^{3+} in Al–Si volatile ash matrix, is oxidized to V^{4+} and V^{5+} during NaOH leaching and they can be extracted as vanadates with concentrated alkaline solution (Burriel et al., 1992; Moskalyk and Alfantazi, 2003; Font et al., 2007).

Alkaline solutions containing vanadium may be treated to selectively separate V from Si, Al and P. From a solution containing Si, Al, P and V, a vanadium containing solution was obtained by a two-stage process: addition of H_2SO_4 to adjust the pH to 8–9 and then addition of $Mg(NO_3)_2$ and ammonia to precipitate $MgNH_4PO_4$ and $MgSiO_3$ after heating recovered 94% of the vanadium (He et al., 2007).

In order to obtain vanadium pentoxide as a by-product from the Bayer process sodium aluminate solution, Mahanty et al. (1967) recovered 90% of the vanadium by precipitating it with NH_4Cl as ammonium vanadate and transforming it to V_2O_5 at 300 °C. Mukherjee et al. (1990) obtained V_2O_5 with a purity percentage of 99 as a result of leaching, adsorption, desorption, precipitation, and calcination procedures in the study they conducted to obtain pure vanadium oxide from the Bayer process sodium aluminate solution that contains approximately 18–20% V_2O_5.

Yüzer et al. (1990) conducted studies on the production of vanadium pentoxide from vanadium cake that was enriched in the system during alumina production in Etibank Seydişehir Aluminum Facilities and was stocked by removing from the system from time to time. They obtained vanadium pentoxide from vanadium mud that contained 11.01% V_2O_5, 5.94% free-NaOH, 5.61% F, 3.30% P_2O_5, 3.20% As_2O_5, 3.00% Al_2O_3 and 42.80% water. At the same time, free-NaOH and Al_2O_3 in the vanadium mud were recovered at 55% and 45%, respectively. The concentration of vanadium pentoxide, which was dissolved as Na-NH_4 polyvanadate in the main solution, decreased to 0.1–0.3 g/L and its transferred volume was minimized. The grade of the product that was obtained under the best circumstances was 99.5% V_2O_5 and the efficiency was 95%.

Chen et al. (2010) investigated the effect of acid concentration, temperature, and leaching period parameters with H_2SO_4 leaching on hard coal that included (1.09% V_2O_5). They obtained 96% vanadium extraction efficiency under optimum conditions. Tavakoli et al. (2014) studied solubility of vanadium in sulfuric acid media up to 90 °C. They showed that reductive agents in acidic pH range can increase leaching efficiency significantly; V_2O_5 can be leached at pH = 5 as decavanadate in around 2 h at 90 °C, and dissolved at pH = 8 as metavanadate in about an hour at 90 °C. Roasting of a similar material, stone coal (anthracite), at 850 °C for 3 h was enough to convert the vanadium-bearing phase to V_2O_5 (He et al., 2007). Li et al. (2009) and Chen et al. (2010) investigated NaClO and MnO_2, respectively, as an oxidizer to increase vanadium recovery in leaching. Furthermore, Okuwaki et al. (1988) and Li et al. (2010) studied H_2SO_3 and $FeSO_4$, respectively, as a reductive agent to increase leaching recovery. Moreover, Li et al. (2009) showed that $FeSO_4$ has no effect on vanadium leaching while Chen et al. (2010) reported that $FeSO_4$ decreases vanadium recovery.

Table 2
The factors investigated in full factorial experiments conducted with H_2SO_4 leaching with the addition of Na_2SO_3.

Factors	Symbol	Level	
		Low	High
H_2SO_4 concentration (M)	A	0.5	2
Na_2SO_3 concentration (g/L)	B	0	40
Temperature (°C)	C	70	90

Table 3
2^3 full factorial design experimental conditions for H_2SO_4 leaching with the addition of Na_2SO_3.

Test no	Treatment combinations[a]	A	B	C	A	B	C
1	(1)	−	−	−	0.5	0	70
2	a	+	−	−	2	0	70
3	b	−	+	−	0.5	40	70
4	ab	+	+	−	2	40	70
5	c	−	−	−	0.5	0	90
6	ac	+	−	−	2	0	90
7	bc	−	+	−	0.5	40	90
8	abc	+	+	−	2	40	90
9	I	0	0	0	1.25	20	80
10	II	0	0	0	1.25	20	80
11	III	0	0	0	1.25	20	80

[a] Pulp density: 40%.

In this study, efficient leaching and metal recovery methods/reagent systems were investigated with laboratory and semi-pilot tests regarding recovering vanadium from vanadium cake, which is strategically important in terms of the industry, from the Bayer process waste by-products in the Seydisehir Eti Aluminum Facility.

2. Experimental

2.1. Vanadium cake

Vanadium cake sample was collected systematically from the points where the evaporation unit of the Seydisehir Aluminium Plant (Cengiz Holding, Konya, Turkey) could be represented in general. Initially, the sample was allowed to settle and then the water on top was removed. This was repeated for 10 days and the cake was then dried at 50 °C in the drying oven for 3 days.

Physical and chemical analyses of the vanadium cake sample were performed. Moreover, XRD (Siemens D500) analyses were performed in order to be able to determine the mineralogical compounds. DTA-TG device (SEIKO 6300) was used in order to determine the thermogravimetric changes that occur in the vanadium cake due to the increase in temperature.

2.2. Roasting of vanadium cake prior to leaching

Vanadium cake sample was exposed to the roasting procedure for 1 h at different temperatures (200, 400, 500 and 600 °C) in an ashing furnace before the leaching experiments in order to vaporise the harmful elements it contained such as arsenic. The samples were weighed (KERN ABJ 220-4M) before each process and they were transferred to heat resistant crucibles and placed into an ashing furnace (Electro-Mag M 1811) for roasting. The crucibles were weighed again after roasting and the amount of loss of the volatile substance was determined. The roasting of the cake was also performed with a microwave oven (MW) for a specific period of time (3–5–8–10 min, 360 W). The