

Using of industrial wastes as secondary resources for metal recovery

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The increasing demand for metals in the world has required intensive studies for the extraction of metals from low-grade ores and/or secondary resources.

The recovery of base metals from industrial wastes by acidic and alkaline leaching yields solutions rich in metals, such as Molybdenum, Cobalt, Nickel and Vanadium in addition to Alumina or Silica, up to the studied material.

Extraction of these metals was performed from secondary resources like: spent catalyst from manufacture of sulfuric acid (SSAC), as well as some petrochemical industrial waste matters: spent hydrodesulphurization (HDS) catalyst, LC finer and boiler ash.

In the current work are presented in details results regarding Vanadium recovery from SSAC by means of alkaline leaching. Statistical design of experiments and analysis of variance (ANOVA) were performed in order to determine the main effects and interactions of the factors under research, which were temperature of roasting, pulp concentration and concentration of the leaching reagent (NaOH). For optimizing the extraction yield of V, further leaching tests were performed using one-factor at a time method, considering the factors with significant effect.

Passwords: Industrial wastes; Vanadium recovery; alkaline leaching

1. Introduction

With the ceaseless exploitation of resources in the world, high grade ore is exhausted day by day, with primary sources presently insufficient to supply demand and secondary sources increasingly exploited for recovery of metals.

Vanadium has many and continuously increasing industrial uses. Today over 85% of the world production of vanadium is consumed in carbon and stainless steel-production, as 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 catalyst and catalysts for the manufacture of sulphuric acid.

The process of making sulfuric acid can be divided into three main reactions:

- combustion of sulfur: $S + O_2 \rightarrow SO_2$ (1)
- catalytic oxidation: $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$ (2)
- sulfur trioxide absorption: $SO_3 + H_2O \rightarrow H_2SO_4$ (3)

When producing sulfuric acid by 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). Without a catalyst this reaction needs a very high temperature to have a realistic rate. Commercial catalyst contains 4-9 wt % V_2O_5 , as the active component, together with alkali-metal sulfate promoters (potassium sulfate or cesium sulfate). The supporting material is silica in different forms. The average service life for the catalyst is about 10 years. There are two methods for disposing of spent catalyst: metal recovery and landfill disposal (Ullmann's, 1994).

A number of hydro- and pyro-metallurgical processes have been proposed for metal recovery from spent catalyst, fly ash and boiler ash. In both cases the metals are recovered as mixed solutions and then separated by conventional separation techniques (solvent extraction, selective precipitation and ion-exchange).

Regarding other works on spent catalyst from manufacture of sulfuric acid production, Lozano and Juan (2001) stated that Vanadium could be recovered from sulfate solutions by means of solvent extraction with primary aliphatic. Khorfan et al. (2002) described a three-step process involving acidic leaching, oxidation and precipitation for recovery of vanadium pentoxide from spent sulfuric acid catalyst with efficiency of 70%.

Ho et al. (1994) reported that alkaline leaching is selective for vanadium over iron but dissolves some silica and it is more costly in terms of reagents.

In the present work, a preliminary study to recover V from SSAC is reported: a hydrometallurgical operation in which sodium hydroxide leaching is the main step of the overall process. Full-factorial experiment was carried out to study the effect of roasting process, NaOH concentration and pulp concentration on the leaching extraction yield. ANOVA was used for predicting the effects of operating conditions to the V extraction yield and concentration in a wide range. For optimizing the extraction yield of V, further leaching tests were performed using one-factor at a time method, considering the factors with significant effect.

2. Materials And Methods

2.1 Characterization of the sample

The material, used in this study, was kindly provided by ORIM S.P.A., Macerata, Italy. The samples were dried at 105°C for 24h and ground. V content were determined with acid attack using aqua regia containing 1:3 ratio of HNO_3 and HCl. 3.5% V were read by Varian SpectraAA 200 atomic absorption spectrophotometer. XRD analysis, carried out on SSAC before roasting, has showed that the main phases are V_2O_5 , $K(Fe,V)(SO_4)_2$ and SiO_2 .

Table 1. Factors and levels investigated in the factorial experiment (80°C temperature of leaching)

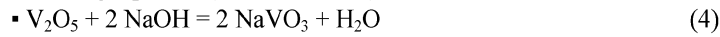
Factor		Levels	
		Low	High
A	Temperature of roasting, °C	105	400
B	Pulp concentration, % w/v	10	20
C	NaOH concentration, M	2	4

2.2 Leaching tests

After drying the sample was roasted at a desired temperature for 4h in furnace, followed by alkaline leaching process. In the present study, a 2³ full factorial design involving 8 treatment combination and 3 replications of the central point was chosen for conducting the alkaline system. Three factors and two levels studied are shown in Table 1.

The leaching tests were carried out by using 250 ml bottom flask, fitted with a seal to avoid evaporation loss, fixed in a Dubnoff water bath with a mechanical stirring (200 rpm). For all leaching experiments the process time was 6h. Several samples were collected at 30 min, 1h, 2h, 4h and 6h, filtrated and diluted (1:10). The concentration of V in the leach liquors was determined by AAS.

In alkaline solution, the chemical reaction for V that can be hypothesized is given by the following equation (Pourbaix, 1974):



2.3 Data analysis

A systematic check by Yates' algorithm (Montgomery, 1991) was used in the interpretation of the experimental results obtained from the factorial design at two levels. This permitted an assessment of the main effects of factors and the interactions among them. The effect of the factor is defined to be the change in response produced by a change in the level of the factor (Montgomery, 1991).

3. Results And Discussion

3.1 Leaching results and ANOVA analysis

For alkaline leaching of SSAC, full factorial design was performed. Table 2 presents the results of alkaline leaching, in terms of V concentration (mg.L⁻¹) and extraction yield (%). Vanadium extraction reached 78% in *ac* treatment; mean concentration: 2742 mg V L⁻¹ (10% pulp concentration, 400°C roasting temperature, 80°C leaching temperature, 4M NaOH for 2 h). Further increase in time does not affect the extraction of vanadium; on the contrary, it may lead to leaching of more alumina and silica.

Table 2. Results of the alkaline leaching full factorial experiment in, in terms of V concentration (mg. L⁻¹) and extraction yield (%)

Treatment	A, °C	B, %	C, M	Conc. (mg L ⁻¹)				Extraction Yield (%)			
				0.5 h	1 h	2 h	4 h	0.5 h	1 h	2 h	4 h
1	105	10	2	1363	1550	1705	1760	39	44	49	50
a	400	10	2	1934	2335	2538	2570	55	67	73	73
b	105	20	2	2134	2695	3063	3232	30	39	44	46
ab	400	20	2	3046	3446	3694	4218	44	49	53	60
c	105	10	4	1467	1655	1807	1916	42	47	52	55
ac	400	10	4	2190	2483	2742	2646	63	71	78	76
bc	105	20	4	2930	3262	3720	3770	42	47	53	54
abc	400	20	4	3568	3790	4576	4880	51	54	65	70
I	300	15	3	2938	2960	3210	3408	56	56	61	65
II	300	15	3	2710	3020	3194	3226	52	58	61	61
III	300	15	3	2718	2776	3100	3158	52	53	59	60

These results are basically consistent with those presented by Tsai and Tsai (1998) and Navarro et al. (2007) using an oil fly ash, who found that vanadium extraction, exceeded 80% with 2 M NaOH leaching solutions.

The effect of the studied factors on the extraction yield of V is shown in Fig. 1. The vertical line represents the value of V effects which matches 95% significant level: it means that every factor higher than this line is significant, according to *F*-test utilized. The corresponding line on the negative effect plane is not reported, because there are no factors with negative significant effect.

- Factor A (temperature of roasting; tested values: 105°C and 400°C) has a positive effect on the extraction of V. The temperature of roasting has to be below 600°C to prevent of species which would adversely affect recovery of V (Gardner, 1989).

- Factor B (pulp concentration; tested values: 20% and 10%) has a negative effect on the extraction of vanadium. This might be due to insufficient mixing through mechanical stirring.

- Factor C (concentration of sodium hydroxide; tested values: 2M and 4M) does not show a significant effect on the extraction. Therefore concentration of NaOH lower than 4 M can be used in our further work.

Nevertheless, the maximum yield [%] for V extraction was achieved using 4 M NaOH for alkaline leaching step (*ac* treatment combination). Yet when comparing the results on Table 2 the columns presenting V extraction yield in *ac* and *a* treatment combination, they appear very similar: 76% and 73% V extraction yield after 4h leaching with respectively 4M and 2M NaOH. A stronger positive effect of this factor is observed after 30 min. of leaching time.

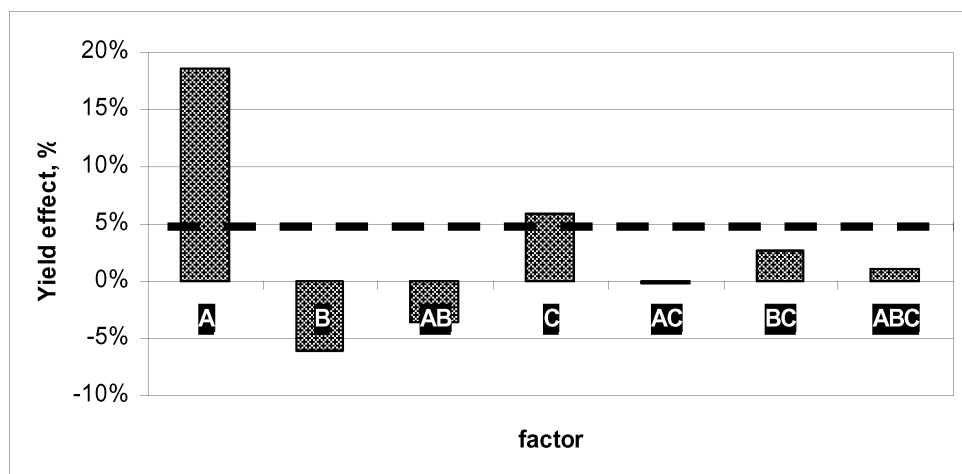


Fig. 1. Main effects of the investigated factors and of the interactions among them on the extraction yield of V, according to alkaline leaching of SSAC (See Table 1 for the studied factors).

3.2 One-Factor at a time method

For optimizing the extraction yield of V, further leaching tests were performed using one-factor at a time method, considering the factors with significant effect. These tests were conducted treating SSAC with initial concentration of 7% V.

3.2.1 Temperature of roasting

The effect of roasting temperature was studied by varying the temperature from 105°C to 600°C with other conditions constant (10% pulp concentration, 3M NaOH and 80°C leaching temperature). The measured weight loss after drying (at 105°C) was about 3.5% and other 2% after further roasting (at 200°C and more).

The results of this experiment (not presented here) show that roasting step is not necessary. The sample changed its color after treating at different temperature of roasting, but the amount of Vanadium after leaching was approximately the same in all the cases (95%; mean concentration: 6670 mg V L⁻¹), moreover that the measured weight loss after alkaline leaching was the same (about 80%).

A possible explanation is that the spent catalyst used in this study had already been exposed to high temperatures (410-430°C) in the SO₂ oxidation reactor (Tor-Martin Tveit, 2003).

3.2.2 Concentration of NaOH

Different concentrations of the leaching reagent were tested, ranging from 0.5M to 4M NaOH, using dried sample of SSAC. The results are presented in Fig. 2, where is demonstrated that Vanadium extraction yield is in accordance with the measured weight loss after alkaline leaching. More than 95% of V was dissolved by means of NaOH with higher concentration than 3M, but in this condition a lot of silica is dissolved as well.

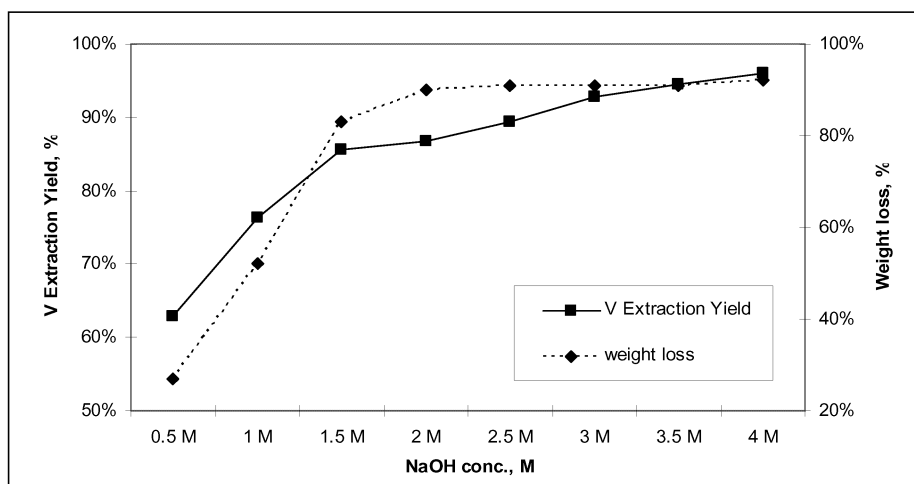


Fig. 2. Weight loss and Vanadium Extraction Yield at different NaOH concentrations (without roasting; 80°C leaching temperature; 10% pulp concentration)

Eatough et al. (1984) carried out several analytical procedures (pH-calorimetric measurements, ionic chromatography and proton-induced X-ray emission analysis) to identify extractable V species. They concluded that vanadium was present as both VO_2^+ and VO^{2+} in the leach liquor.

In order to have only vanadium ions in the alkaline leach solution, the impurity of Si and P can be removed by chemical precipitation with the addition of $\text{Mg}(\text{NO}_3)_2$ and ammonia (Yun Chen et al., 2006) or by adding calcium oxide to precipitate silica (Goddard, 1987).

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