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Manufacture of Vanadium pentoxide and nickel sulfate from heavy oil fly ash

Kyung-Ho Park
Minerals Utilization Division, Korea Institute of Geology, Mining & Materials.

ABSTRACT

This work is carried out to develop the recovery process of vanadium as vanadium pentoxide and nickel as nickel sulphate from the leaching solution of heavy oil fly ash. First, sodium chlorate solution was added to the leaching solution to oxidize vanadium ions. With adjusting pH of the solution and heating, vanadium ions(V) is hydrated and precipitated as red cake of V_2O_5 from the solution. After recovering vanadium, nickel is recovered as ammonium nickel sulfate with crystallization process. From this nickel salt, nickel sulfate which meets the specifications for the electroplating industry can be produced economically. More than 85% of vanadium and nickel in the fly ash are recovered in this process.

1. INTRODUCTION

Heavy oil fly ash is the industrial waste deposited between the radiant furnace outlet and the stack tip in the power stations and is usually collected from the electrostatic precipitators. This ash is deposited as oxides and sulphates of metals contained in the fuel oil and its additives. The valuable metals such as vanadium and nickel are usually found in the ash as major components along with carbon. As a result of strict environmental laws and regulations, heavy fly ash is classified as a specified waste and the disposal in landfills is not allowed. Therefore the recovery of vanadium and nickel from heavy oil fly ash has become major interest from the standpoints of environmental protection and the recycling of resources. Salt roasting-leaching process has been known as the common method to recovery vanadium from heavy oil fly ash[1,2,3]. However this process has two disadvantages : high energy cost in roasting process and necessity of another process to recovery nickel. To solve these problems, this study was carried out to develop the recovery process of vanadium and nickel from fly ash with a direct wet process and the proposed flow-sheet is shown in Fig. 1. Vanadium and nickel are extracted from the fly ash by leaching with sulfuric acid in the agitated vessel. More than 90% of them were dissolved in this process. The experimental result of this leaching process was already published[4]. In this paper, we investigate and discuss the recovery process of vanadium as vanadium pentoxide and nickel as nickel sulphate from the leaching solution of heavy oil fly ash.

2. MATERIALS AND EXPERIMENTAL

2.1. Materials

The solution used in this study was leaching solution of heavy oil fly ash with sulfuric acid and the chemical composition is shown in Table 1.

2.2. Experimental

All of the tests were performed in a 1 liter three necked glass vessel fitted with a two-bladed teflon stirrer and a reflux condenser. Heat was supplied using a heating mantle fitted with an energy regulator. Temperature of the solution was monitored with a thermocouple and a digital temperature indicator. For each run, 500 ml of leaching solution was used and some chemicals were added if required. In all experiments, the speed of stirring kept constant (400 rpm). Aliquots

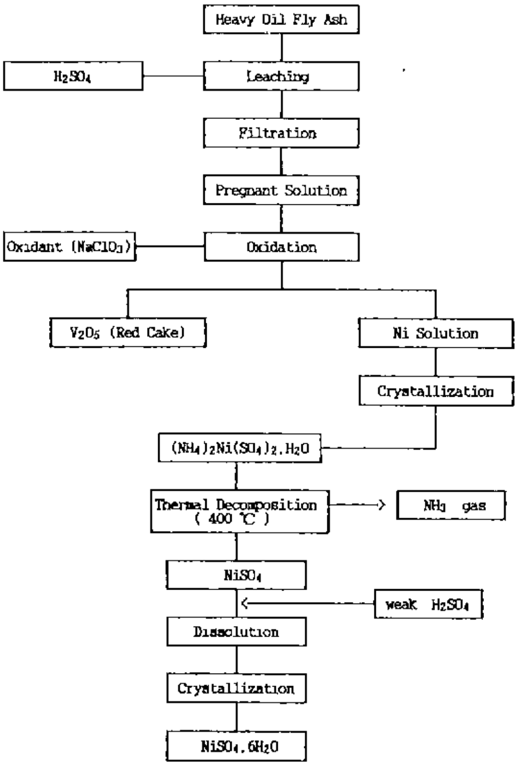

Fig. 1. Simplified flow sheet of reclaiming vanadium and nickel from heavy oil fly ash.

Table 1. Chemical composition of leaching solution

component	V	Ni	Zn	Al	Na
wt. %	4.14	2.13	0.10	0.093	2.54
component	Fe	Ca	Cu	Cr	Pb
wt. %	1.71	0.041	132 ppm	550 ppm	45 ppm

(5 ml) of the solution were withdrawn at appropriate time intervals for chemical analysis.

3. RESULTS AND DISCUSSION

3.1. Production of vanadium pentoxide (Red cake)

Fig. 2 presents the well known Pourbaix diagram[5] for vanadium ions and the compounds in aqueous media. This diagram indicates the Eh-pH ranges for precipitation of vanadium in its various oxiforms. With controlling Eh and pH of the solution, the vanadium can be precipitated selectively as vanadium pentoxide

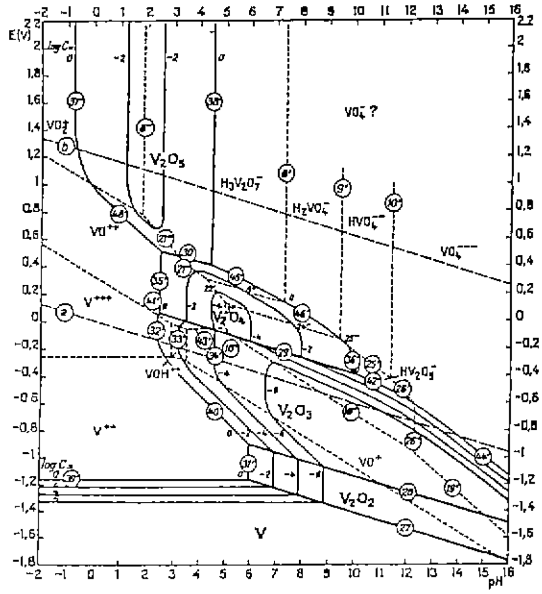

Fig. 2. Potential-pH equilibrium diagram for the system vanadium-water at 25℃ [5].

and recovered from the solution. As almost all vanadium ions in the leaching solution exists as vanadium (IV), it should be oxidized to vanadium (V) with adding the oxidant such as $NaClO_3$ as equation (1).

$$6VO^{++}+NaClO_3+3H_2O=6VO_2^{+}+6H^{+}+NaCl \quad (1)$$

With adjusting pH of the oxidized solution and heating, vanadium pentoxide is precipitated as a result of hydrolysis as given in equation (2).

$$2x(VO_2^{+})+(x+y)H_2O=(V_2O_5)_x(H_2O)_y+2x(H^{+}) \quad (2)$$

As explained above, the vanadium recovery process can be devided into three parts : oxidation of vanadium ions, pH control of solution and hydrolysis of vanadium (formation of vanadium pentoxide).

The oxidation of vanadium was conducted using $NaClO_3$ which is an effective oxidizing agent in acid medium. The experiments were carried out to define the minimun amount of $NaClO_3$ compatible with complete oxidation of vanadium at initial pH 0.4, 80℃ and the results gives in Fig. 3. An amount of 512 g $NaClO_3$ per 1 kg vanadium was found necessary to achieve 100% oxidation of vanadium with redox potential of about

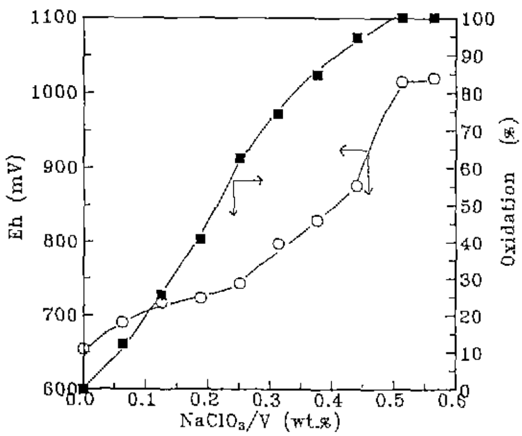

Fig. 3. Effect of the amount of oxidant($NaClO_3$) on the vanadium oxidation.

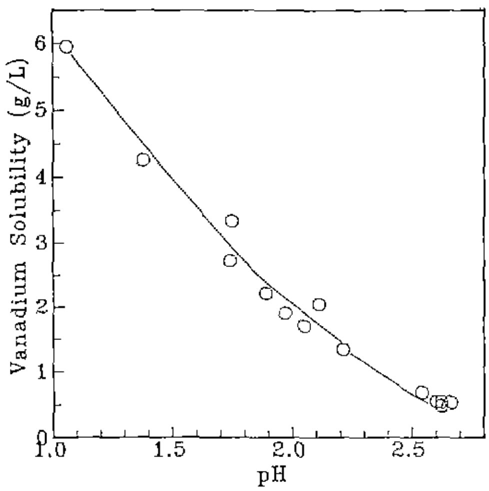

Fig. 4. Effect of pH on the vanadium solubility.

1000 mV. If the reaction temperature was lower than 60℃, the oxidation of vanadium did not almost occur.

pH of the solution gives a great influence on the yields of vanadium (the amount of vanadium pentoxide precipitated) as expected in Fig. 2 and is the most important factor to control. In order to study the effect of pH on the solubility of vanadium, a series of tests had been performed. The final pH of the leaching solution was changed by adding amounts of NH_4OH. The results in Fig. 4 show that the amount of vanadium dissolved in the solution decreased with increasing pH up to 2.60. Further increases in the pH had no effect on the vanadium solubility. With oxidation and hydrolysis processes explained above, the vanadium in the leaching solution was precipitated as vanadium pentoxide(red cake) and could be separated from solution by filtration.

Another experimental results show that optimum hydrolysis condition of vanadium could be obtained at reaction time of 1 hour and temperature of 80℃.

After this process, the filtrate contains only small amount of vanadium and most of nickel was left in the solution. Table 2 shows the chemical composition of vanadium pentoxide(red cake) and the recovery rate of vanadium was 86.7%.

3.2. Production of nickel sulfate

The nickel reclamation process can be divided into two parts. The first part of the processing is manufacturing ammonium nickel sulfate from the filtrate by crystallization method. The second part is production of nickel sulfate from ammonium nickel sulfate by thermal decomposition, dissolution and crystallization methods as shown in Fig. 1.

By adding NH_4OH in the leaching solution to control pH, the nickel exists as ammonium nickel sulfate. Cooling the filtrate from 80℃ to room temperature results

Table 2. Chemical composition of vanadium pentoxide produced

Component	V_2O_5	Fe	Al	Ca	K	Mg	Ni	Cu	Mn	Na
Wt. %	80.15	12.35	0.22	0.24	0.30	0.14	0.19	0.005	0.018	1.42

Table 3. Chemical composition of ammonium nickel sulfate crystallized

Component	Ni	V	Zn	Al	Na	Fe	Ca	Cu	Cr	Pb
Wt. %	13.3	0.003	0.44	0.009	0.028	0.012	0.041	0.019	0.005	0.017

Table 4. Chemical composition of nickel sulfate produced

Component	Specification(KS M 1115)		Production
	1 class	2 class	
Ni+Co(%)	> 21.0	> 18.0	18.6
Fe(%)	< 0.01	< 0.03	0.003
Cu(%)	< 0.02	< 0.04	0.007
Mn(%)	< 0.02		0.002
Zn(%)	< 0.05		0.28
Pb(%)	< 0.01		0.017

in crystallization of ammonium nickel sulfate because the large solubility difference of this material between these two temperatures(38.5 g/*l* at 80℃, 6.2 g/*l* at 15℃). After crystallization process, the contents of vanadium and nickel in the crystal produced are shown in Table 3. By repeating crystallization process several times, high purity ammonium nickel sulfate and high yield of nickel can be obtained.

The ammonium nickel sulfate is not a common chemical and was used as a raw material to prepare nickel sulfate in this work. The chemical compostion of the nickel sulfate manufactured by this process is shown in Table 4 and this meets specifications of the electroplating industry.

4. CONCLUSION

This study is carried out to develop the recovery process of vanadium as vanadium pentoixde and nickel as nickel sulfate from the leaching solution of heavy oil fly ash. The important results obtained from this study are as follows:

(1) Vanadium pentoxide was obtained with oxidation of vanadium ions, control of pH of about 2.5 and hydrolysis at 1 hr, 80℃.

(2) Nickel was recovered as ammonium nickel sulfate from the filtrate removed vanadium with crystallization.

(3) Nickel sulfate was obtained from ammonium nickel sulfate by thermal decomposition, dissolution and crystallization and mets the specifications for the electroplating industry.

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