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## **PROCESSING OF EGYPTIAN BOILER-ASH FOR EXTRACTION OF VANADIUM AND NICKEL**

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Egyptian boiler ashes from thermal power stations contain up 20% vanadium and 22% nickel and thus they are valuable source for vanadium and nickel and their alloys as well as chemicals. The ash was directly leached with sulphuric acid under atmospheric pressure and in an autoclave. Atmospheric leaching leads to complete dissolution of vanadium and nickel together with iron. Separation of iron from vanadium is very difficult due to a narrow pH precipitation range of hydroxides of these metals, leaching under oxygen pressure leads to oxidation of iron and its precipitation as basic iron sulphate leaving vanadium and nickel in solution. Vanadium is thus precipitated as hydroxide by adjustment of pH value and then calcinated to vanadium penta-oxide. The leaching processes were thoroughly investigated and the optimum leaching conditions were determined.

*Key words: boiler ash, pressure leaching, vanadium, nickel*

### **INTRODUCTION**

Egyptian crude oil contains considerable amounts of vanadium and nickel. These metals are concentrated in the heavy fraction obtained from the fractional distillation process. The heavy fraction is used as a fuel in electrical power stations and consequently the metals (vanadium, nickel) are concentrated in the ash. The standard method applied for recovery of vanadium from vanadium containing slag

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consists of roasting the ash in a rotary kiln at 800 °C for 3 hr. followed by leaching with water to produced soluble sodium vanadate (Sastry, 1968; Solbodin, 1975; Cheng, 1987; Audin, 1988 and Chandra et al., 1998). The world consumption of vanadium increases in the last five years due to its utilization as special alloys such as ferrovandium and special steels. Steel industry consumes about 90% of vanadium production (Ruhle, 1981; Pawlek, 1983; Campbell, 1999; Halikia, 1991; Martins, 2000). The present investigation aims at optimizing the conditions of extraction of vanadium and nickel by hydrometallurgical processing of Egyptian boiler ash using aqueous sulphuric acid under atmospheric and oxygen pressure to produce leach liquor of sulphates of both vanadium and nickel free from iron. The parameters affecting the leaching process such as temperature, sulphuric acid concentration, time and oxygen partial pressure were systematically studied.

## EXPERIMENTAL

The Egyptian boiler ash samples were collected from different power stations which use fossil oil as fuel. The samples were crushed, ground and sieved to 100% (-250  $\mu\text{m}$ ). Chemical composition of studied sample is given in Table (1).

Table 1. Chemical analysis of studied boiler ash

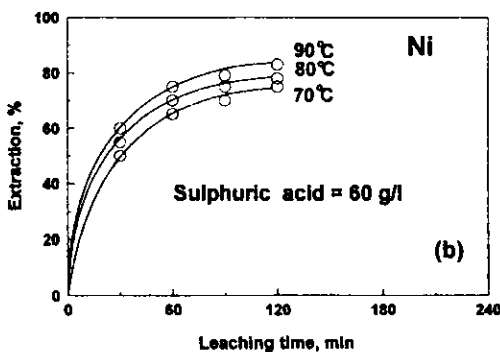
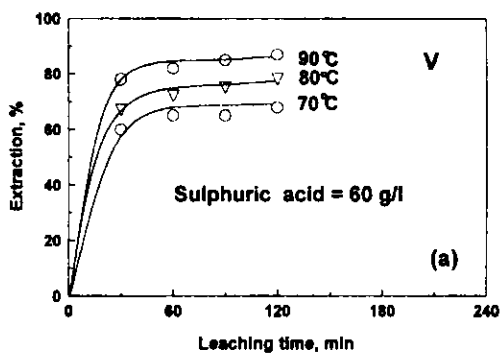
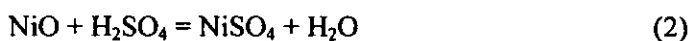
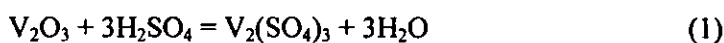
Composition	%
V	20.0
Ni	22.0
Fe (total)	4.67
CaO	3.10
SiO <sub>2</sub>	3.57
Al <sub>2</sub> O <sub>3</sub>	1.70
Cr <sub>2</sub> O <sub>3</sub>	1.50
MgO	1.10
ZnO	0.98
H <sub>2</sub> O (100°)	10.00
H <sub>2</sub> O (700°)	6.00

Atmospheric leaching was carried out in a glass reactor placed in a thermostatically controlled water bath. Pressure leaching experiments were carried out in a 2dm<sup>3</sup> capacity vertical autoclave gas inlet/outlet. The container is made of titanium to resist acid corrosion. The feed is first placed in the titanium container, which is then placed in autoclave. The pressure vessel was closed and thoroughly flushed with oxygen gas. The autoclave was heated to the required temperature at

agitation maintained a 1200 rpm. Oxygen gas was then introduced upon the attainment of the desired temperature (Hahn, 1965 and Amer, 1987). Samples were collected at various time intervals, filtered and analyzed for vanadium and nickel.

## RESULTS AND DISCUSSION

Dissolution of vanadium and nickel in sulphuric acid under the atmospheric conditions is explained as follows:



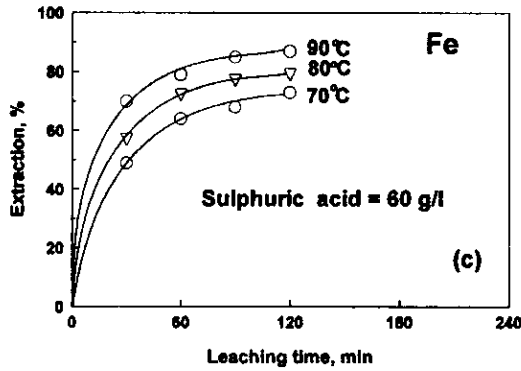


Fig. 1: Effect of leaching temperature upon the dissolution of vanadium nickel and iron under atmospheric conditions

Figure (1) shows the effect of temperature and time on leaching of boiler ash with 60 g/dm<sup>3</sup> sulphuric acid concentration at a solid-liquid ratio of 0.5. The degree of extraction of vanadium, nickel and iron increases with the increase of temperature. During the first 30 minutes, a sharp increase in recovery was observed, then the rate of dissolution becomes relatively slower till a constant recovery was achieved after 120 min.

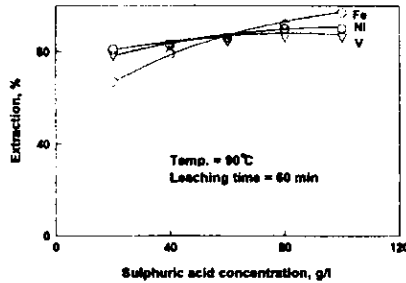


Fig. 2: Effect of sulphuric acid concentration upon dissolution of vanadium, nickel and iron under atmospheric conditions

Figure (2) shows the effect of sulphuric acid concentration on leaching of boiler ash at 90 °C and at solid-liquid ratio of 0.5 for 60 min leaching period. The percentage of vanadium, nickel and iron increases upon increasing acid concentration. Moreover, atmospheric leaching leads to 80% dissolution of iron. Separation of iron from vanadium is very difficult due to narrow pH range of precipitation of hydroxides of these two metals (vanadium and nickel).

Leaching under oxygen pressure was recommended for oxyhydrolysis of ferrous sulphate and iron precipitation as iron oxide leaving vanadium and nickel in solution. The mechanism of iron oxidation was given by many authors (Sohn, 1979; Anand, 1988). The most important variables affecting the leaching process are: temperature (160-220 °C), oxygen partial pressure (5-20 bar) and sulphuric acid concentration (40-80 g/L).

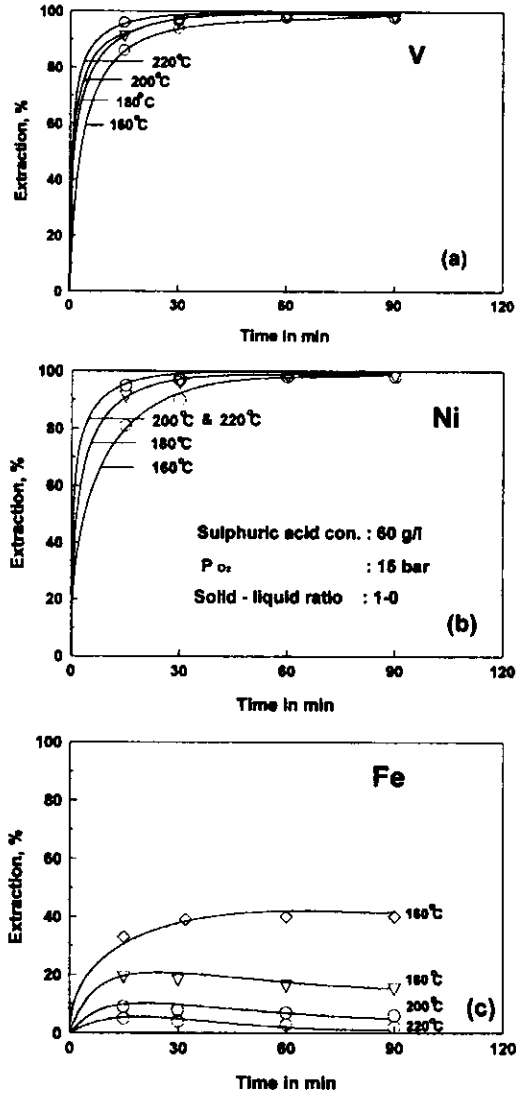


Fig. 3: Effect of temperature on the extraction of vanadium, nickel and iron under oxygen partial pressure

Figure (3) shows that the leaching rate of vanadium and nickel increases with increase of temperature in the range of 160-220°C. After 15 min at 220°C complete extraction of vanadium and nickel (97%) was reached with only 4% iron dissolution.

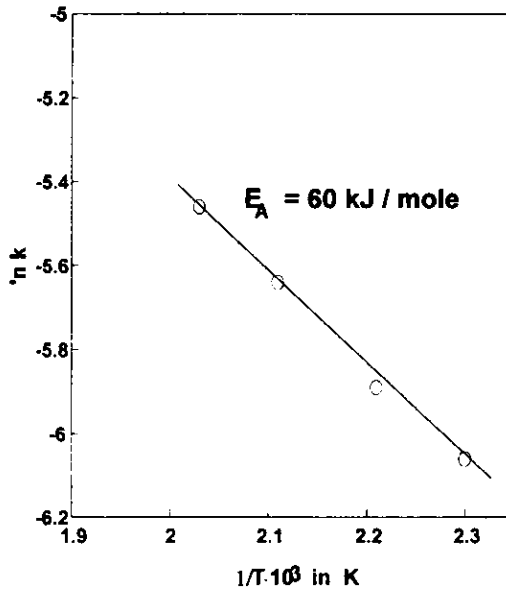
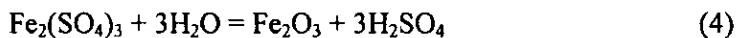
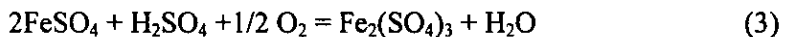


Fig. 4: Arrhenius plot for determination of apparent activation energy, data from Figure (3b)

From Arrhenius plot as shown in Fig. (4) the calculated value of apparent activation energy amounts 60 kJ/mole which is in good agreement with the value of 57 kJ/mole calculated from the oxidation of Fe (II) in aqueous sulphuric acid under oxygen pressure (Anand, 1989). The calculated value of apparent activation energy (60 kJ/mole) indicates that the reaction is chemically controlled (Sohn, 1979). The effect of partial oxygen pressure on the leaching rate is shown in Fig. (5). The leaching rate of both vanadium and nickel was slightly increased as the partial oxygen pressure increases from 5 up to 15 bar. The mechanism of oxyhydrolysis of iron sulphate is illustrated as follows:



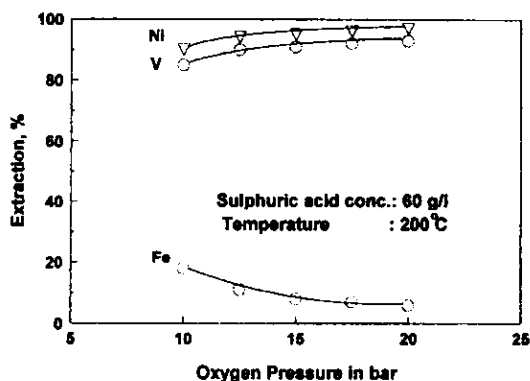


Fig. 5: Effect of oxygen partial pressure on the dissolution of vanadium, nickel and iron

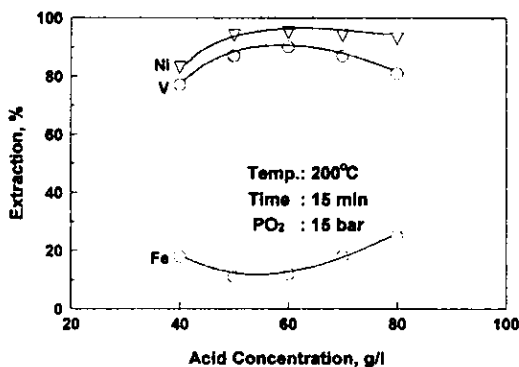


Fig. 6: Effect of sulphuric acid concentration on the extraction of vanadium, nickel and iron

The effect of sulphuric acid concentration on the leaching rate is shown in Fig. (6), the extent of vanadium and nickel recovery was about (95%) using acid concentration of 50 g/dm<sup>3</sup>. The extent of iron dissolution was slightly increased at sulphuric acid concentration above 60 g/dm<sup>3</sup>, however most of the iron (III) had precipitated as a result of hydrolysis. Vanadium and nickel were leached nearly completely at 50–60 g/dm<sup>3</sup> sulphuric acid concentration.

## CONCLUSION

Direct H<sub>2</sub>SO<sub>4</sub> processing of Egyptian boiler ash to produce both vanadium and nickel sulphate was achieved by pressure leaching under oxygen pressure. Iron is converted to basic iron sulphate which is then hydrolysed to iron oxide. The optimum conditions of pressure leaching process are; temperature 200 °C, partial

oxygen pressure 15 bar, sulphuric acid concentration 60 g/ dm<sup>3</sup> leaching period 15 min.

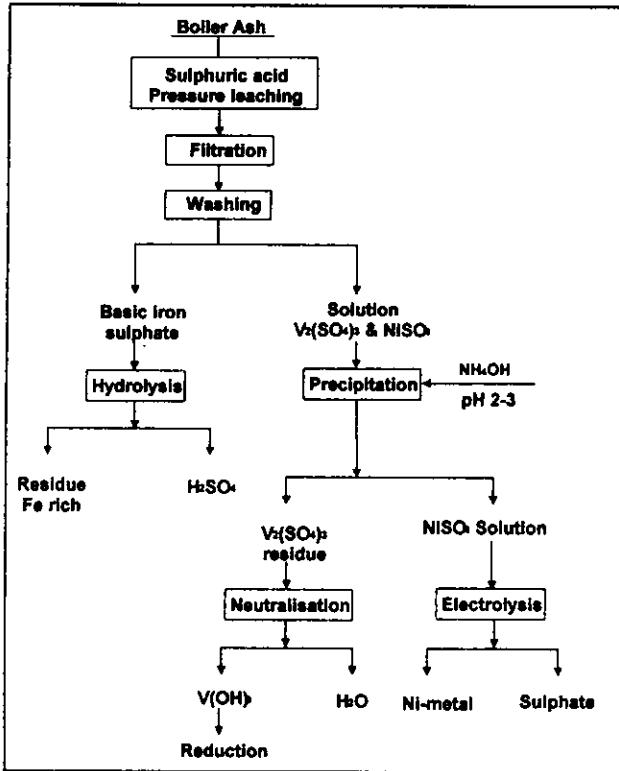


Fig. 7: Flow sheet of sulphuric acid pressure leaching of boiler ash

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Ashraf AMER, Przeróbka egipskich popiołów po spalaniu oleju opałowego dla odzysku wanadu i niklu, *Fizykochemiczne Problemy Mineralurgii*, 34, 153–161 (w jęz angielskim)

Egipskie popioły z elektrociepłowni zawierają do 20% V i 22% Ni. Popioły ługowano bezpośrednio pod ciśnieniem atmosferycznym oraz w autoklawie. Ługowanie pod ciśnieniem atmosferycznym prowadzi do całkowitego rozpuszczenia wanadu i niklu razem z żelazem. Separacja wanadu od żelaza jest trudna z powodu wąskiego zakresu pH wytrącania się wodorotlenków tych metali. Ługowanie pod ciśnieniem tlenu prowadzi do utleniania się żelaza i jego precypitacji w formie zasadowego siarczanu żelaza a V oraz Ni pozostają w roztworze. Vanad ulega następnie wytrąceniu jako wodorotlenek przez regulację pH i dalej jest kalcynowany do pięciotlenku. Proces ługowania był dokładnie przebadany i określono optymalne warunki procesu.