

## **RECOVERY OF SOME ELEMENTS FROM SOLID WASTE PRODUCED FROM FUEL COMBUSTION IN POWER PLANTS**

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### **ABSTRACT**

Solid waste residue generated in power stations that use heavy oil as the source of fuel poses a threat to the environment due to the presence of some heavy metals. At the same time, these metals include Vanadium (V) and Nickel (Ni) can be recovered and recycled. In this work Vanadium and nickel were recovered from solid waste residue (Furnace Bottom Sediments FBS) collected from the bottom of steam boiler. Four samples were selected and collected from different boilers. Solid samples were grinded to convert them to powdered form and sieved in 200 micrometer. The grinded samples were used for recovery. The recovery of vanadium and nickel was conducted in two stages. A first stage was acidification of the grinded (FBS) using 30 % sulfuric acid (dissolution of FBS) followed by alkali metal precipitation. The second stage is similar to first stage on the remaining solids from first stage. Determination of vanadium and nickel were conducted by two techniques, Energy Dispersive X-ray(EDX) and Inductive Coupled Plasma (ICP technique) .The effect of some operational parameters (liquid/solid, leaching, temperature, mixing time, acid and alkali concentrations) on the recovery of V and Ni was investigated. Conditions of precipitation of V and Ni from alkali solutions were established. The effect of different amount of ammonium hydroxide/ammonium chloride which gives deferent pH value from (2 to 10) at different temperatures (25, 40, 60, and 80 °C) were investigated. The maximum recovery of vanadium reached

96.3% at (pH 3.5), Nickel recovery was 95.8% at (pH 9.5) for reaction time 4 h.

**Keyword:** Furnace bottom sediments, Solid waste , Heavy fuel oil , Vanadium , Nickel.

## INTRODUCTION

Various types of fuel like liquid, solid and gaseous fuels are available for firing in boilers, furnaces and other combustion tools. The selection of right type of fuel depends on various factors such as cost, availability, storage, handling, and pollution. Solid and liquid fuel contain more ashes than gaseous fuel, so combustion of these types result in more residues that may be fly ashes or bottom residue. Most of developing country use these fuel types due to availability and price. The remaining solid waste, especially bottom ash, is buried in sanitary landfill Jung and Mishra (2018).

In Egypt, large amounts of solid wastes are produced as a result of firing heavy fuel in power plants. Without any treatment, these solid wastes are land filled. Extraction of metals from these wastes is an important industrial/environmental issue to assess metals' mobility and applications. Large amounts of elements (V, Ni, Fe, Ca, Mg, Na, and others) were leached from fly ashes under acidic, basic, and neutral conditions Young *et.al* (1993).

Extraction and separation of vanadium (V) and nickel (Ni) from fly ashes is achieved by many authors Grisafi, *et al.*,(1998).In the first step, Ni is selectively eluted from fly ashes using NH<sub>4</sub>OH solution and then

precipitated using (Sodium sulfide)  $\text{Na}_2\text{S}$ . On the other hand, V is extracted from Ni-free-fly ash using (Sodium Carbonate)  $\text{Na}_2\text{CO}_3$  solution, recovered by 0.1 M tri-ethylamine/toluene, and precipitated by (Ammonium Chloride) ( $\text{NH}_4\text{Cl}$ ). The adopted method showed a reasonable recovery for metals from fly ash, 56 and 45% from Ni and V, respectively

Tsai, & Tsai (1998). The earlier attempts indicated that separation of V/Ni by precipitation using  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  was not successful where both metals did not precipitate from solution in the presence of other elements Youngs *et al*(1993) Many other works dealt with the extraction of elements from fly ash Coudun&Hochpied (2005) , Vitolo *et al* (2000).

Bottom residues formed from complete combustion of heavy fuel oil, were expose to very high temperature inside the boiler so it differs from the fly ashes in its physical and chemical properties. This condition result in complete combustion of light nonmetals, evaporation of water content, formation of high density rock-like masses and formation of centric compounds. On the other hand, metals become more concentrated and more cost effective Leavens pile (1999). Recovery of some metals from bottom residues lead to decreasing of waste volume that land filled, and reuse of useful metals as Nickel and Vanadium.

To the best of our knowledge there is no previous work in literature dealt with the extraction of elements from bottom solid residue (Rock-like solid waste) produced from fuel combustion especially heavy fuel oil. In

this work some trials were carried out to extract some element from the solid waste remaining in the bottom of boilers furnace in power plant.

## MATERIALS AND METHODS

**1. Source of furnace bottom sediments samples:** The residue of FBS samples that were collected from steam boilers of heavy fuel in El-Kureimat (I), West Cairo (II), Shoubra El-Khema (III) and Ataka (IV) power stations.

### 2. Chemicals:

1. Commercial conc. sulfuric acid 98%
2. Sodium hydroxide (NaOH) was supplied by Koch-Light Laboratory Ltd, Colnbrook Bucks England Assay 98%.
3. Ammonium hydroxide/ammonium chloride by Arab lab products
4. Sodium carbonate by Arab lab products
5. All chemicals used in analysis and adjusting pH with laboratory grade.

**3. Recovery and determination of Nickel and Vanadium:** Recovery of vanadium and nickel from Furnace Bottom Sediment (FBS) was implemented using sulfuric acid for dissolution and ammonium hydroxide/ ammonium chloride for precipitation of vanadium and sodium hydroxide for precipitation of nickel in two stages. In the first stage various concentrations of sulfuric acid solutions were added to the solid waste furnace bottom sediment (FBS) at different solid liquid ratio in order to achieve soluble vanadium and nickel. The mixtures were then

stirred at 120 rpm at different time intervals (1, 2, 3 and 4 hours) at different temperature (25, 40, 60, and 80 °C). After the digestion time the final solutions (dissolution of vanadium and nickel metals) were conducted to measure the vanadium and nickel by using (ICP) instrument. The precipitation of vanadium from the aforementioned solutions were achieved by increasing the pH value of the solutions (from 2 to 9) using ammonium hydroxide/ ammonium chloride for vanadium precipitation. The filtrate treated with sodium hydroxide (20%) for nickel precipitation. The second stage is repeating to the first stage but on the remaining residue from first stage

#### **4. Analysis:**

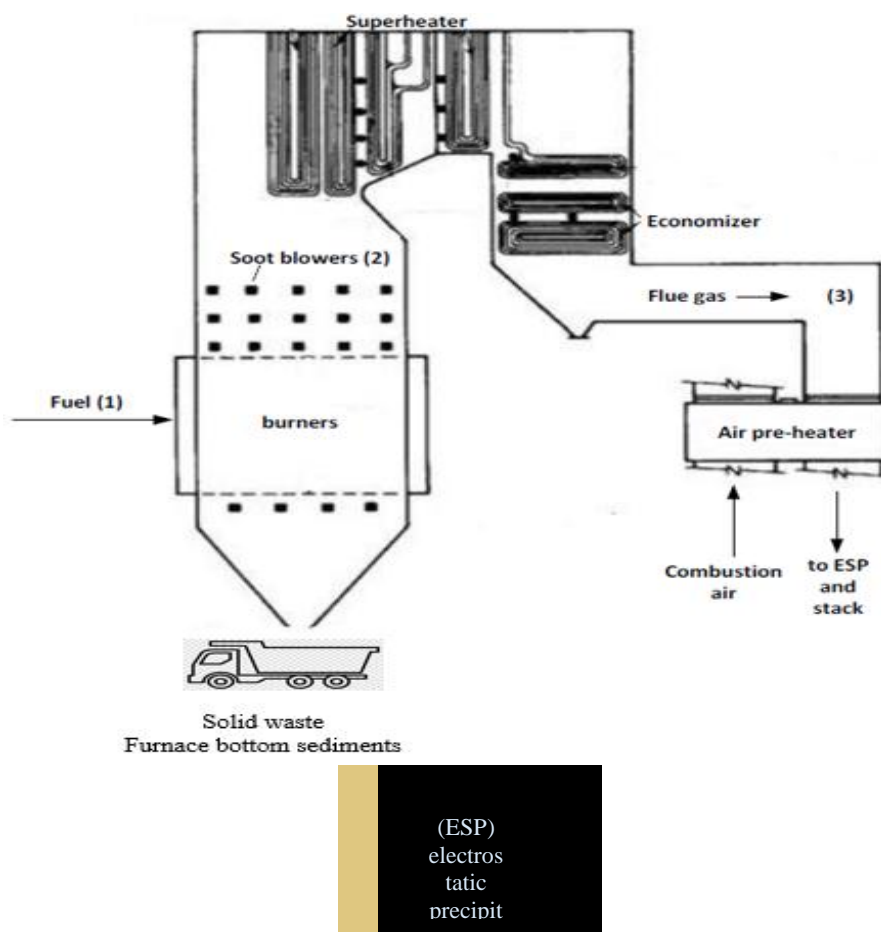
##### **a) Solid waste residue (Furnace Bottom Sediment) analysis:**

- **Thermo Gravimetric Analysis (TGA):** Thermo gravimetric analyses of the solid waste residue sample performed with thermo gravimetric analyser Leco: Mac-500.ST. Joseph, Michigan-USA. This apparatus provides a continuous measurement of sample weight at a range of temperatures between ambient and 900 °C. Samples were heated in an alumina cell to 900 °C at heating rate of 10°C/min with nitrogen as the circulating gas.
- X-ray analysis of solid waste residue: The dry solid waste residue was analysed using; Energy Dispersive X-ray System., ISIS Link Instrument P/C. Oxford Co.

- Ignition loss was measured by heating of solid waste residue from ambient temperature to 950 °C.
- Dried solid waste residue was grinded and sieved in 200 $\mu$  mesh and subjected to acid digestion at different (S/L ratio, temperature and time).
- Vanadium, Nickel and other elements in aliquot were quantified using Inductive Coupled Plasma (ICP) Spectrometer, Perkin Elmer 2100 DV Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

## **RESULTS AND DISCUSSION**

Many power boilers burn heavy fuel oil, such as mazout which produce large amounts of solid waste that must be handled and disposed of. The fuel boiler has a specially designed system to safely remove, transport and dispose of the produced solid waste generated during operation of the boiler. Figure (1) describes how solid waste is generated and the typical components used to remove this waste in a power boiler.



**Figure(1):** schematic diagram of steam boiler containing Solid waste removing system in power station

**1. Elemental analysis of Furnace Bottom Sediment (FBS) samples:** Nine Furnace Bottom Sediment samples were collected from some steam boilers of power stations in El- Kureimat (I), West Cairo (II), Shoubra

El-Khema (III) and Ataka (IV) power stations. The elemental analyses of these sediments are listed in table (1):

**Table (1):** Energy dispersive x-ray analysis (EDX) of nine-Furnace Bottom Sediment.

Element	S1	S2	S3	S4	S5	S6	S7	S8	S9
(O) Oxygen	30.46	27.07	21.76	46.45	41.28	4.81	36.63	26.98	32.79
(Al) Aluminium	9.61	8.37	4.87	--	2.45	0.73	0.39	--	--
(Si) Silicon	17.52	6.88	8.36	43.88	5.16	6.05	31.68	18.48	340
(K)Potasium	3.06	0.81	2.39	--	2.12	0.17	0.36	0.23	1
(Ca) Calcium	8.13	23.83	19.02	0.29	20.67	0.43	0.50	2.80	1.04
(Ti) Titanium	--	--	--	--	0.49	0.22	0.61	0.93	0.91
(V) Vanadium	2.66	3.73	3.28	--	0.52	3.33	3.30	4.83	3.40
(Fe) Iron	9.24	8.84	20.64	5.59	13.97	66.35	14.66	16.71	--
(Ni) Nickle	--	--	--	3.13	1.42	13.97	7.08	16.37	14.64
(Zn) Zinc	--	--	--	--	--	0.71	1.97	--	--
(S) Sulfur	17.74	20.47	19.67	--	10.00	0.06	--	0.77	--
(Cr) Chromium	--	--	--	--	--	--	--	2.76	--
(Mg) Magnesium	0.57	--	--	--	0.91	0.17	--	5.14	2.31
(Na) Sodium	1.01	--	--	0.34	1.02	--	--	--	0.50
(Cl) Chloride	--	--	--	0.32	--	--	--	--	0.56

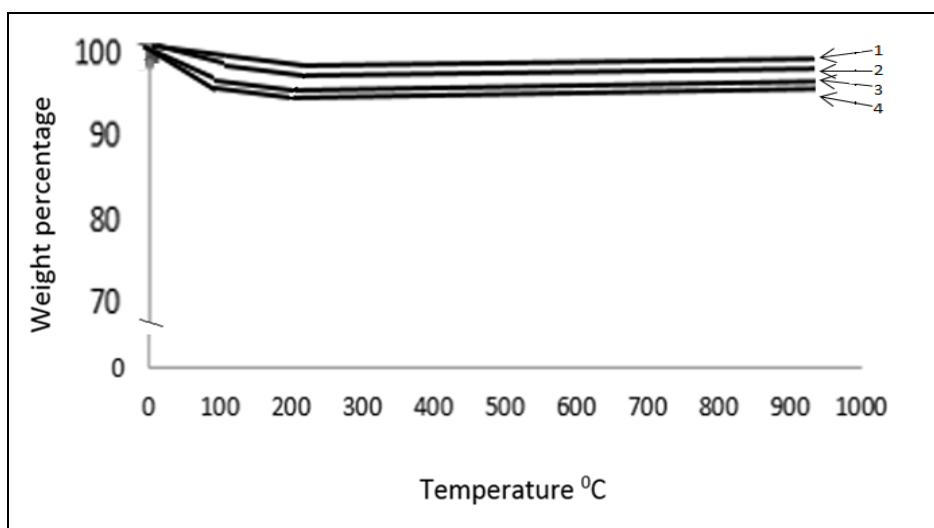
Table (1) show that there are four sediments (FBS) having higher contents of nickel and vanadium namely (S6, S7, S8 and S9). To carry out recovery experiment, the four samples were selected .

It can be noticed that the Ni concentration range from 1.42 to 16.37% while V recorded a range of 0.52 to 4.83%.

**2.Thermogravimetric analysis of (FBS) samples:** Fig.4. showed the thermo- gravimetric analysis for the four Furnace Bottom Sediments (FBS) samples. As it is evident, the results for the samples have three

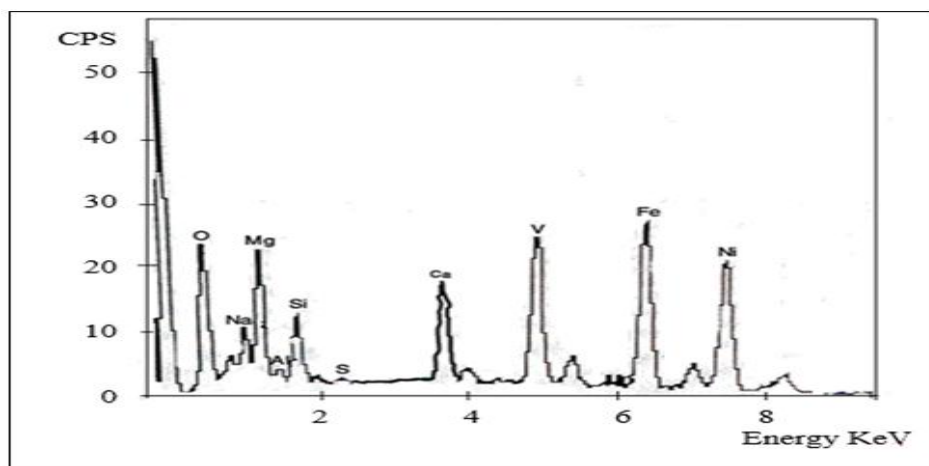


characteristic stages for decomposition. The first stage starts at 55 °C and end at 105°C with weight loss of 2.3 , 3.4 , 4,2 and 4.8% for S<sub>8</sub> , S<sub>7</sub> , S<sub>9</sub> and S<sub>6</sub> respectively. This could be recognized due to the moisture content of the (FBS) sample. The second stage which related to the main stage started at 105°C and end at 220°C with weight loss of 3.7, 5.4, 5.7 and 5.9 % for S<sub>8</sub>, S<sub>7</sub>, S<sub>9</sub> and S<sub>6</sub> respectively. This stage represented the hydrated hydroxide of metals components in (FBS). The thermogravimetric analysis showed that there is no decarbonization stage. The third stage is related to metal oxides stage which started at 220°C and ended at 900°C without increase in weight

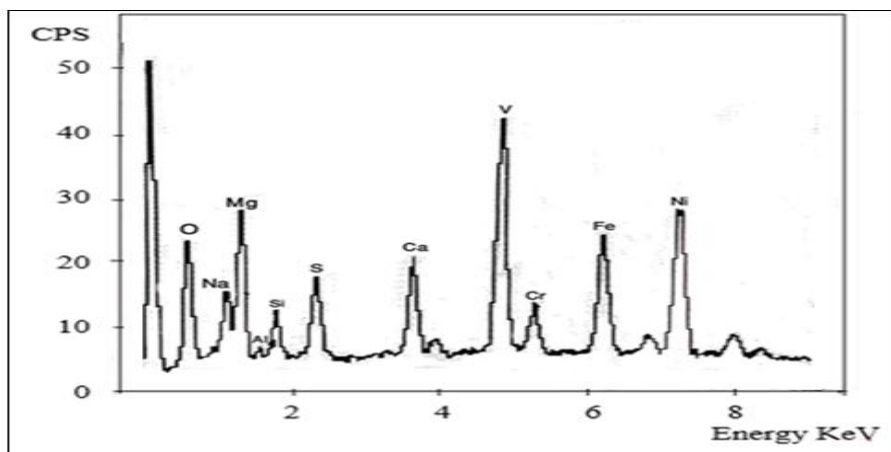


**Figure (4):** Thermo- gravimetric analysis of four Furnace Bottom Sediments (FBS) samples (1for S<sub>8</sub>), (2 for S<sub>7</sub>), (3 for S<sub>9</sub>) and (4 for S<sub>6</sub>).

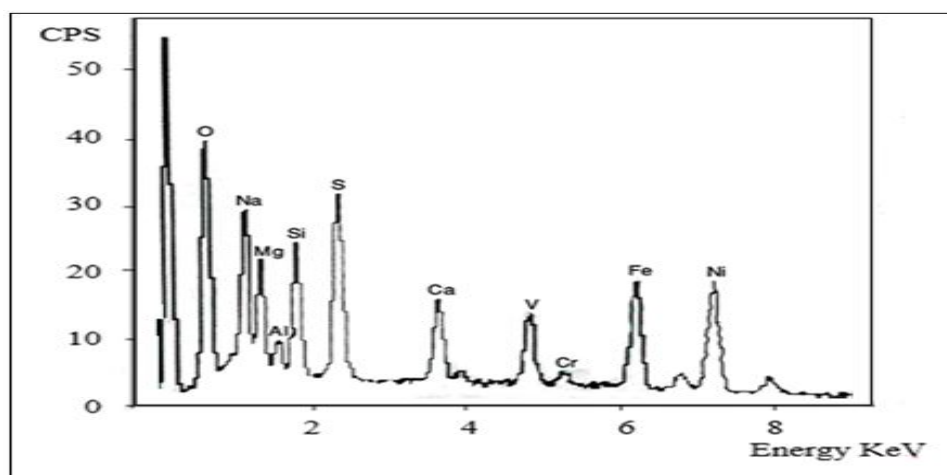
**3- X-ray analysis of the selected four samples:** The dry solid waste residue (FBS) was analysed using; Energy Dispersive X-ray System., ISIS Link Instrument P/C. Oxford Co. Figures from (5-8) shows x-ray spectra of these samples. It is clearly seen that the obtained results show that the amount of vanadium and nickel elements represented by the peak of figure (8) is higher one with respect to other (FBS) samples. Also figs.5-7 shows other element present in the different samples of (FBS) such as Al, Si, K, Ca, Ti, Fe, Zn, S, Cr, Mg, Na, Cl.



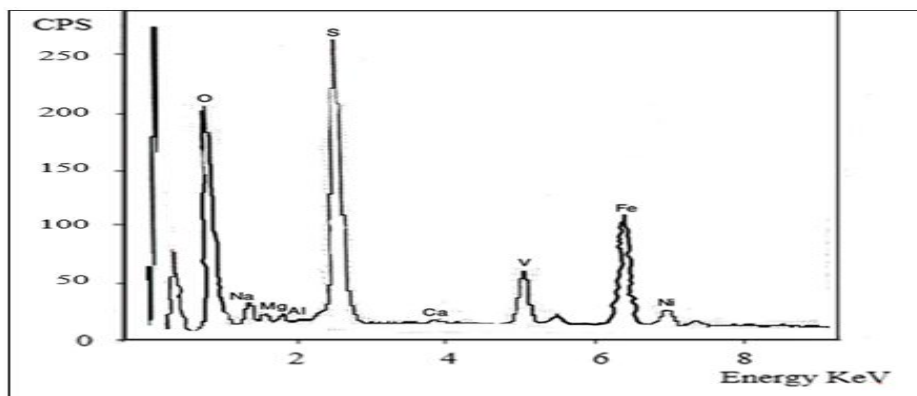
**Figure (5):** Energy dispersive X-Ray (EDX) of sample S<sub>5</sub>



**Figure(6):** Energy dispersive X-Ray (EDX) of sample S6



**Figure(7):** Energy dispersive X-Ray (EDX) of sample S7

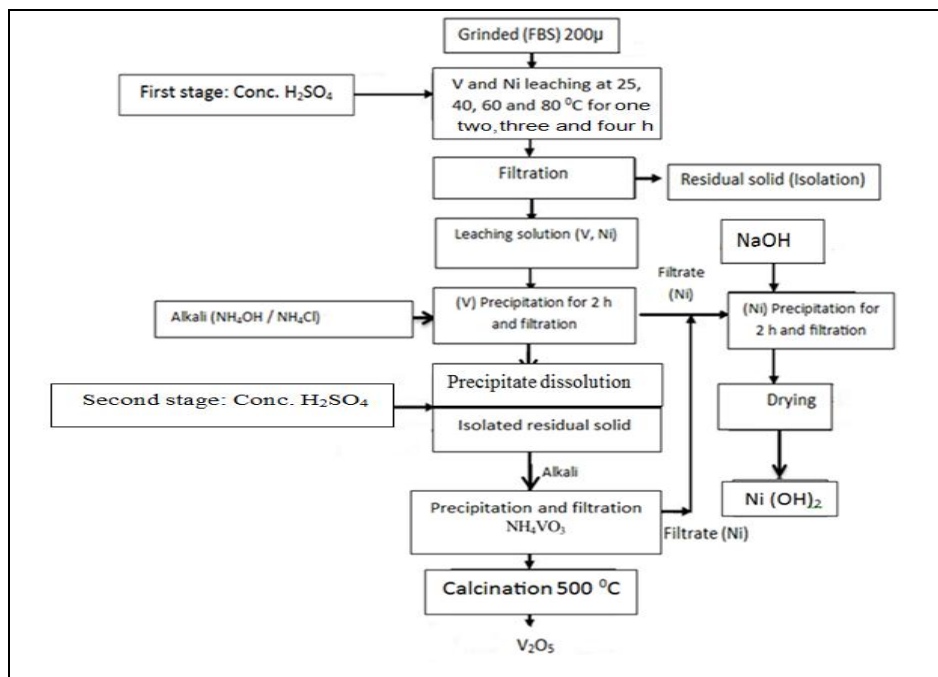


**Figure(8):** Energy dispersive X-Ray (EDX) of sample S8

The above-mentioned X-ray results revealed that the (FBS) with higher vanadium and nickel concentration which are the most important elements taken in consideration in this study.

**4- Extraction of vanadium and nickel:** In order to obtain a high selectivity and yield of vanadium and nickel recovery, two leaching stages were carried out.

- First stage leaching with sulfuric acid for dissolution then the precipitation by ammonium hydroxide / ammonium chloride. To leach out V and Ni from (FBS), preparatory tests performed to establish the best leaching operational parameters (Temperature, mixing time and pH).
- Second stage is repeating the first stage on the remaining residue.
- The following flow chart illustrates the two steps of leaching including dissolution and precipitation of vanadium and nickel elements from (FBS).



**Figure (10):** flow chart illustrates the two stage of leaching including dissolution and precipitation of vanadium and nickel elements from (FBS).

### 5 –Effect of leaching condition on the percentage recovery of vanadium and nickel:

The percentage recovery was detected according to the following equation:  $\% \text{ Recovery} = \frac{C_0 - C}{C_0} \times 100$

Where, (Co) is the initial concentration and (C) is the final concentration of (Vanadium and nickel) before and after leaching and precipitation process.

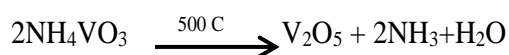
Leaching conditions were studied in the vanadium and nickel recovery, were as leaching agent sulfuric acid (98%), ammonium hydroxide/ ammonium chloride as alkali for pH adjustment and leaching temperature with continuous stirring at 200 rpm. Table (2) shows the effect of different parameter on the percentage recovery (precipitation efficiency).

**Table(2):** Effect of pH, time and temperature on the percentage recovery of vanadium and nickel from (FBS).

Elements	% Recovery															
	pH 2h at 25 0C								Time (h) pH = 3.5 at 25 0C				Temperature (0C) 4h and pH = 3.5			
	1.5	2.5	3.5	4.5	7.5	8.5	9.5	10.5	1	2	3	4	25	40	60	80
Vanadium	8.2	48.7	78	78	-	-	-	-	68	76	77	78	78	78.9	81.11	96.3
Nickel	pH 2h at 25 0C								Time (h) pH = 9.5 at 25 0C				Temperature (0C) 4h and pH = 9.5			
	2.5	3.5	4.5	6.5	7.5	8.5	9.5	10.5	1	2	3	4	25	40	60	80
	-	-	-	14	48	62	75	75	61	71	74	75	75	76.3	78.12	95.8

Vanadium precipitation efficiency was highly dependent on pH values. When the pH is 2.5-3.5, the vanadium precipitation efficiency reaches 96 % and this pH range is therefore suitable Navarro. *et.al* (2007).

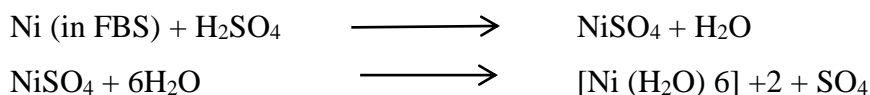
The produced yellow precipitate of ammonium metavanadate  $NH_4VO_3$  was roasted in a muffle furnace at 5000C for 1 h to obtain vanadium petoxide  $V_2O_5$  Akaboshi, *et.al* (1987).



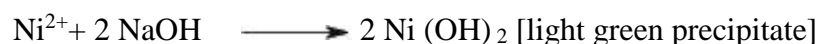
The  $V_2O_5$  purity reached 99%.

With respect to nickel the same manner was observed. It was found that the recovery of nickel increased with increasing pH value. The best pH value was in the range of 9.5-10.5. While there is no significant change in

nickel recovery with increasing temperature till 60°C.



When the pH is in the range of 9.5-10.5, the produced dissolute of  $[\text{Ni (H}_2\text{O)}_6]^{+2}$  was precipitated by adding NaOH to permanent green gelatinous precipitate of  $\text{Ni (OH)}_2$ .



The produced precipitated hydrated hydroxide of nickel  $[\text{Ni (H}_2\text{O)}_4(\text{OH})_2]$  was dried in a drying oven at 100°C for 1 h to obtain dried  $\text{Ni(OH)}_2$  Coudun and Hochepped (2005), Navarro. (2007).

## CONCLUSIONS

Vanadium and nickel can be leached and recovered from Furnace Bottom Sediment(FBS) by acid base method using sulfuric acid (30%) for dissolution and ammonium hydroxide/ammonium chloride and sodium carbonate/sodium hydroxide for precipitation. The best results in vanadium and nickel leaching rate obtained by using the following conditions:

Leaching agent sulfuric acid 30% temperature (80 °C), pH at (3.5-5.5) for vanadium recovery and (9.5-10.5) for nickel recovery, time (4hours) and agitation speed was maintained at 200 rpm. The results indicate that the best condition for recovering vanadium rate was 96.3% and nickel 95.8%.

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## استعادة بعض العناصر من النفايات الصلبة الناتجة عن احتراق الوقود في محطات القوى الكهربائية

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### المستخلص

تشكل بقايا النفايات الصلبة المتولدة في محطات القوى الكهربائية التي تستخدم الزيت الثقيل ( المازوت) كمصدر للوقود تهديداً للبيئة بسبب إحتوائها على بعض المعادن الثقيلة لذا فإن إستعادة العناصر المكونة لهذه الرواسب يعتبر حلاً مثالياً لمثل هذه النفايات . في هذا العمل، تم دراسة إمكانية إستعادة عنصرى الفاناديوم والنيكل من هذه النفايات الصلبة المترسبة في قاع فرن بعض غلايات إنتاج البخار في محطات القوى الكهربائية، حيث تم تجميعها وإجراء الدراسة عليها . تم اختيار تسع عينات من رواسب الفرن المجمعة لإجراء التحليل عليها لإختيار أعلاهم تركيز لعنصرى الفاناديوم والنيكل حيث أظهرت النتائج أربع عينات منهم فتم أختيارهم لإستخلاص هذه العناصر . تم طحن هذه العينات الصلبة لتحويلها إلى شكل مسحوق ونخله في منخل بحجم ٢٠٠ ميكرومتر . تم أستعادة الفاناديوم والنيكل على مرحلتين . المرحلة الأولى عن طريق تحميض الرواسب المطحونة في محلول حمض الكبريتيك لإذابتها ثم ترسيب هذه العناصر في محلول قلوى مكون من ( هيدروكسيد الامونيا / كلوريد الامونيا) . المرحلة الثانية تشبه المرحلة الأولى وتمت على المواد الصلبة المتبقية من المرحلة الأولى .

تم قياس عنصرى الفاناديوم والنيكل فى رواسب الفرن بطريقتين مختلفة الأولى بواسطة التحليل بإستخدام جهاز (EDX) والأخر بواسطة تقنية الليزر النبضى المزدوج (DP- LIBS) بالإضافة إلى قياس هذه العناصر فى محاليلهم بإستخدام جهاز (ICP )  
تم دراسة العوامل المؤثرة على عملية الترسيب والفصل لإستعادة V و Ni تم تحديد الظروف المثلى لترسيب V و Ni من المحاليل القلوية . تم دراسة تأثير كميات مختلفة من هيدروكسيد الأمونيوم / كلوريد الامونيوم عند درجات حرارة مختلفة ( ٢٥ و ٤٠ و ٦٠ و ٨٠ ) درجة مئوية حيث بلغت أقصى نسبة فصل للفاناديوم ٩٦,٣% عند (الأس الهيدروجيني ٣,٥) بينما بلغ نسبة استعاد النيكل ٩٥,٨ عند ( الأس الهيدروجيني ٩,٥) عند درجة حرارة ٨٠ لمدة أربع ساعات  
**الكلمات الدالة :** رواسب قاع الفرن، النفايات الصلبة، زيت الوقود الثقيل، الفاناديوم، النيكل