VANADIUM EXTRACTION FROM RESIDUAL OF FIRED CRUDE OIL IN POWER PLANTS

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ABSTRACT :-

The chemical compositions of Iraqi crude oil often have a high concentration of the vanadium and nickel elements. The quantity of waste resulting from the burning of crude oil in electrical generation stations (power plants) in Iraq, including more than 10thousand tons per year of vanadium and nickel. The percentage of these elements was between 25and 35% depending

This paper at hand deals with the extraction of vanadium metal from residual of fired crude oil in electric power station. The residual were pretreated by grinding and sieving. Vanadium and nickel then concentrated by particle size. Magnetic helps to separate the iron exist in crude oil residual as magnetite form. The results show the ability of separating will be 83 % of iron, vanadium also can be recovered from the residual by alkaline leaching method by using sodium hydroxide solution. Thereafter resulted in the leaching 98% of vanadium, and an increasing nickel concentration to 17.37%.

The establishment of industrial units of this technology allows for Iraq and other regional countries to assume a leading position world wide in the production of vanadium.It is noted that vanadium pentoxide (V_2O_5), does not produce locally now in Iraq.

KEYWORDS:
Vanadium, Crude Oil, Extraction,Residual, Fuel

استخلاص الفناديوم من مخلفات حرق النفط خام في محطات توليد الطاقة .

على الغالب يحتوي النفط الخام العراقي على تراكيز عالية من عنصري الفناديوم والنيكل. المخلفات الناتجة من حرق النفط الخام في محطات توليد الطاقة الكهربائية في العراق يقدر لأحتوائها على أكثر من عشرة آلاف طن بالسنة من النيكل والفناديوم، النسبة الوزنية لهذين العنصرين تترواح بين 20–35 % بالأعتماد على نوعية النفط الخام المستخدم.

في هذا العمل استخلص معدن الفناديوم مخلفات حرق النفط الخام في (محطة القدس الغازية)، تم تحضير المخلفات بتجفيفها من مواد غسل هذه المخلفات من ريش التوربباين العالقة به، بهذه الطريقة يتم تركيز عنصري الفناديوم والنيكل بواسطة الطحن والفصل بحجم الجزيئات، بعدها الفصل المغناطيسي ساعد على فصل الحديد الموجود بشكل مغانيط بنسبة فصل 83 % من الحديد. استعادة الفناديوم من المخلفات تم بواسطة هيدروكسيد الصوديوم المذيب الأنتقائي للفناديوم بنسبة استخلاص 98 % وزيادة تركيز النيكل إلى 17.3 %.

إن إقامة وحدات صناعية لهذه التقنية يسمح للعراق وغيرها من الدول العربية أن تتبوأ موقعا متقدما على مستوى العالم فى إنتاج الفناديوم ، أذا ما علمنا أن خامس أوكسيد الفناديوم لا ينتج محلياً في العراق.

1. INTRODUCTION :-

Current consumption of crude oil just in Al-Qudus Gas Station (In Iraq, north of Baghdad) is approximately 10 million cubic meters per year. It is used as fuel in power stations or as heating source in industrial boilers[Al-Qudus, 2012].

Crude oil burn's residual contain number of metals. Some of these metals like Vanadium were extracted from residuals and crudes in past years.

In 1989, the researches (P. B. Queneau) with othersconducted study on nickel and vanadium extracting from coal by using pressure container to oxidize the residuals under 300 °C and pressure 2500 psig with presence of (N_2, CO_2, O_2) and adding (60 – 110 gm/lit.) sodium carbonates to the residuals to obtain $Fe_3(VO_3)$. Then the researcher solved $NiCO_3$ by using sulpheric Acid to obtain nickel sulphates.

Some of the oil ashes produced in the combustion are residues in the furnace pipes which is called the slag; those that rise through funnels and are collected by a washing. Based on the ash production model established by the authors, there should be approximately 43000 tons of fly ash produced per year[Tsai S., 1997]; of this, fly ash produced by fuel oil power stations is approximately 9000 tons; The fly ash mainly consists of porous unburned carbon, oxides of vanadium, nickel and iron, and water-soluble sulfates. Sulfates tend to be dissolved easily when in contact with water resulting in the release of heavy metal ions (such as vanadium, nickel, etc.) [Mamane Y, 1986].In 1981, the amount of vanadium recovered from oil ashes (the name for both oil-fired fly ashes and slag) in the US was 23% of total vanadium production [Kuck PH, 1983]. Similarly, 14% of Japanese vanadium came from oil ash in 1986 [Tsuboi I, 1987]. Subsequently, ammonium salts wereadded to the filtrateat pH (8 –9) to precipitate and recover the ammonium metavanadate. Canada's Petrofina Company had designed a 6000 -lb/day pilot plant to recover vanadium [Whigham W., 1965]. vanadium pentoxide that was 99% pure could be recovered. A process for the recovery of vanadium and nickel in Japan used water to dissolve the soluble metal salts in fly ash [JP:Tokyo, 1974]. Park adopted the method of leaching in sulfuric acid, where sodium chlorate solution was added to the leaching liquid to oxidize vanadium ions into a pentavalent state [Kyning Ho Park, 1993]. Parton et al. also used the method of leaching in sulfuric acid and selective precipitation to recover vanadium, nickel, iron, magnesium hydroxide and carbon material in fly ash [Parton G, 1993].

Annual production of oil-fired fly ash in Taiwan is approximately 43000 tons, of this approximately 13000 tons is electrostatically precipitated, the rest is cyclonically collected. Structure wise, both consist of porous unburned carbon, vanadium and nickel oxide, and water-soluble sulfate. Electrostatically precipitated fly ash contains large amounts of ammonium sulfate. When leached in 2 M sodium hydroxide solution, the extraction of vanadium was 80%, and the extraction of nickel was negligible. If leached in an ammonia water, the extraction of nickel increased, along with an increase in the concentration of ammonia in water. When leached with 4 N ammonia water, the extraction of nickel was 60%, the extraction of vanadium was less than that obtainable from leaching in sulfuric acid solution or in sodium hydroxide solution (see Fig.(1))[Shang-Lin Tsai, 1998].

A comparative study of the solvent extraction of vanadium (V) from hydrochloric acid and sodium hydroxide media was separately carried out using liquat-336 (methyltrioctylammonium chloride) extractant dissolved in kerosene containing 10% n-octanol as phase modifier, has been studied [Y.A. El-Nadi, 2009].

2. EXPERIMENTAL :-

2.1 Materials

Crude oil used as fuel in electrical power stations was supplied by Al-Qudus Gas Station (North of Baghdad), Iraq. The chemical composition was determined by energy dispersive X-ray fluorescence (XRF) in cooperationwith the Ministry ofScience andTechnology and is given in Table (1). All chemicals and reagents used were analytical reagent grade. Sodium hydroxide, nitric acid, and ammonium hydroxide werepurchasedfrom local markets.

2.2 Work Method

The crude oil's residuals were processed by using base solution to solve vanadium. The solution was done by adding (100 gm) of residuals (after magnetic separation for Fe) to (500 ml) of sodium hydroxide solution of (2 M) concentration as sodium hydroxide is good and selective solvent for Vanadium.

The solution process was done in (500 ml) glass reactor along with condensation process to prevent losing in solvent solution.

The solution process was done under (50-110 °C) for (30-18 min.) to study the effect of temperature on vanadium solving and to determine the optimal time needed to achieve highest solution percentage. Later, filtering process was done to separate non-solved solid materials from Vanadium-laden solution resulted from solving process.

The sample of vanadium-laden solution was analyzed to gauge the percentage of solved Vanadium. The sample of non-solved solid residuals was analyzed, too, to gauge Nickel concentration in residuals resulted from the solving process and to find out the percentage of full Vanadium solution.

50 ml was taken from Vanadium-laden solution and poured into conical flux to equivalent acidity as the vanadium-laden solution was of (pH 12) when drops of Nitric acid of (0.5 M) concentration were added while continuing stirring process by using magnetic stirrer with (20 r.p.m) sinning to make solution acidity at (pH 2) by adding (22 ml) of Nitric acid for each (50 ml) of the V-laden solution. Then, precipitation process was done by adding ammonium hydroxide of (4 M) concentration while continuing stirrer to obtain (NH_4VO_3 ammonium metavanadate) was kept in ceramic container and then it was put in the oven for calcination process under (690 °C) for 30 minutes [Daniel Kittelty, 2001]. The calcination resulted in (V_2O_5), as shown in diagram (Fig. (2)).

3. RESULTS &DISCUSSION :-

3.1 Temperature Effect of Vanadium Extraction

In the light of the results obtained from experiment, the relationship between the temperature and extraction percentage can be shown in Fig. (3), which demonstrates the optimal temperature (100 °C) at which highest percentage of vanadium can be extracted with 98 %.

3.2 The effect of sodium hydroxide concentration in Vanadium extraction.

Figure (4) shows the relation between sodium hydroxide concentration and extraction percentage, this figure clarifies that when concentration of sodium hydroxide is more than (2M), the vanadium concentration percentage is lower and this due to effect of hydroxide ion which causes vanadium precipitation from solving solution. When the concentration is increased the solution viscidity increased and that will consequently reduce the solving average which results in reducing extraction percentage.The maximum vanadium extraction has been at (2 M) as shown in this figure.

3.3 Effect of solving time in vanadium extraction

Figure(5) shows the relation between solving time and vanadium extraction percentage. The maximum vanadium extraction (98%) has been achieved at two hours of extraction time. The extraction percentage will be decreased when the solving time is increased as time increasing leads to increasing evaporation and consequently the solving solution will be decreased, this will lead to increasing concentration of the solution while solving average will be decreased and this will lead to decreasing extraction.

Results of some researches like in [Kyning Ho Park, 1993, Daniel Kittelty, 2001,and (2000 وحسين محمد 1992 مؤيد كاصد)] may be different from results of our research due to continuous losing of sodium hydroxide solution which leads to changing its concentration; therefore the process looks unsteady state with regard to solvent amount and its concentration. This will complicate preparing optimal conditions to extract as much as possible of vanadium, therefore the problem has been tackled by conducting full and continuous condensing for all evaporations resulted from heating process to prevent losing sodium hydroxide and to maintain its full volume (amount) and concentration in the reactor and this will facilitate observing the effect of temperature changing on extraction process in addition to other main variables like concentration and extraction time which have been studied in this research.

4. CONCLUSIONS :-

1. Liberate tests for crude oil which contains relatively high percentage of sulphate showed that the oil contains vanadium (45-66 ppm), before burning, while vanadium percentage become (30.6 %) after burning, in addition to other elements like ferro, nickel, chrome, and Pb.
2. Vanadium couldn't be separated from other elements in the residual by sieving process.
3. In separation process by solving, it was found out that the conditions at which best extraction percentage (98%) was obtained when sodium hydroxide solution of concentration (2 M) was used under (100 °C) for two hours. The results showed that when the concentration of solvent solution is more than (2 M), this will lead to decreasing in extraction percentage, and the decrease take place, too when solving time is increased.

5. RECOMMENDATIONS :-

1. Studying Nickel extraction from crude oil burn's residual in power generating plants.
2. Studying interaction effects of the variables of temperature, concentrations, and time to optimal conditions by using modern suitable method in order to extract highest extraction percentage of vanadium from the crude oil burn's residual in power generating plants.

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Table (1): Main chemical composition of the residual of crude oil burning.

Element	V	Ni	Fe	Mg	Su	Si	Co	K	Ba	C
Concentration, %	30.6	10.61	2.41	2.31	2.23	1.57	0.021	0.016	0.006	Bal.

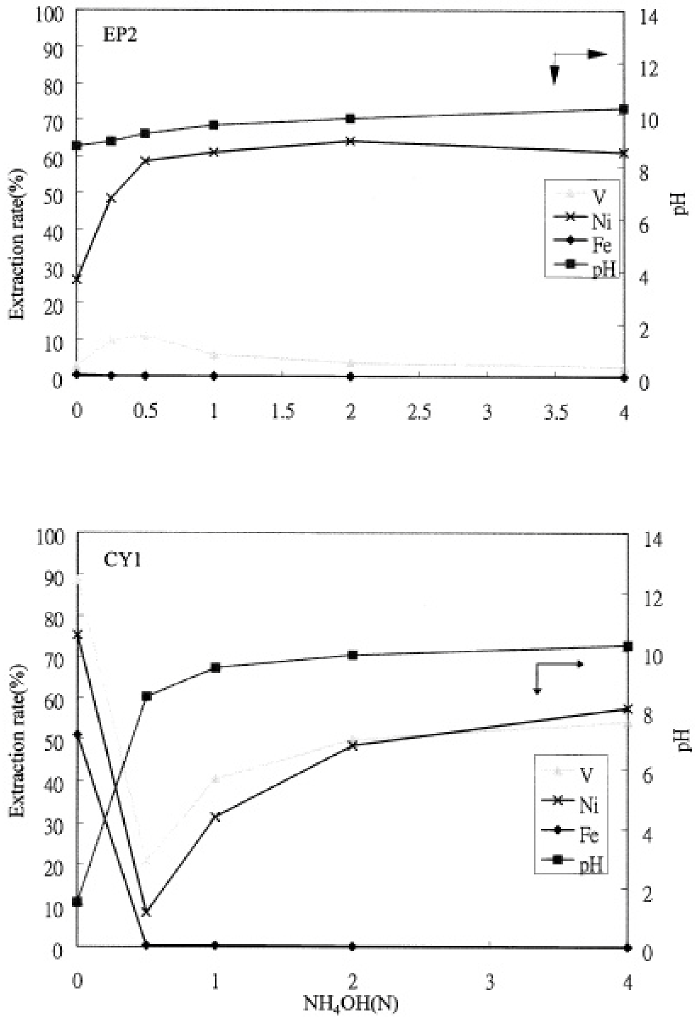

Fig. [1]: The effects of NaOH concentration on extraction rate of fly ash leached (100 g/500 ml;temp.=30°C; time=2 h).

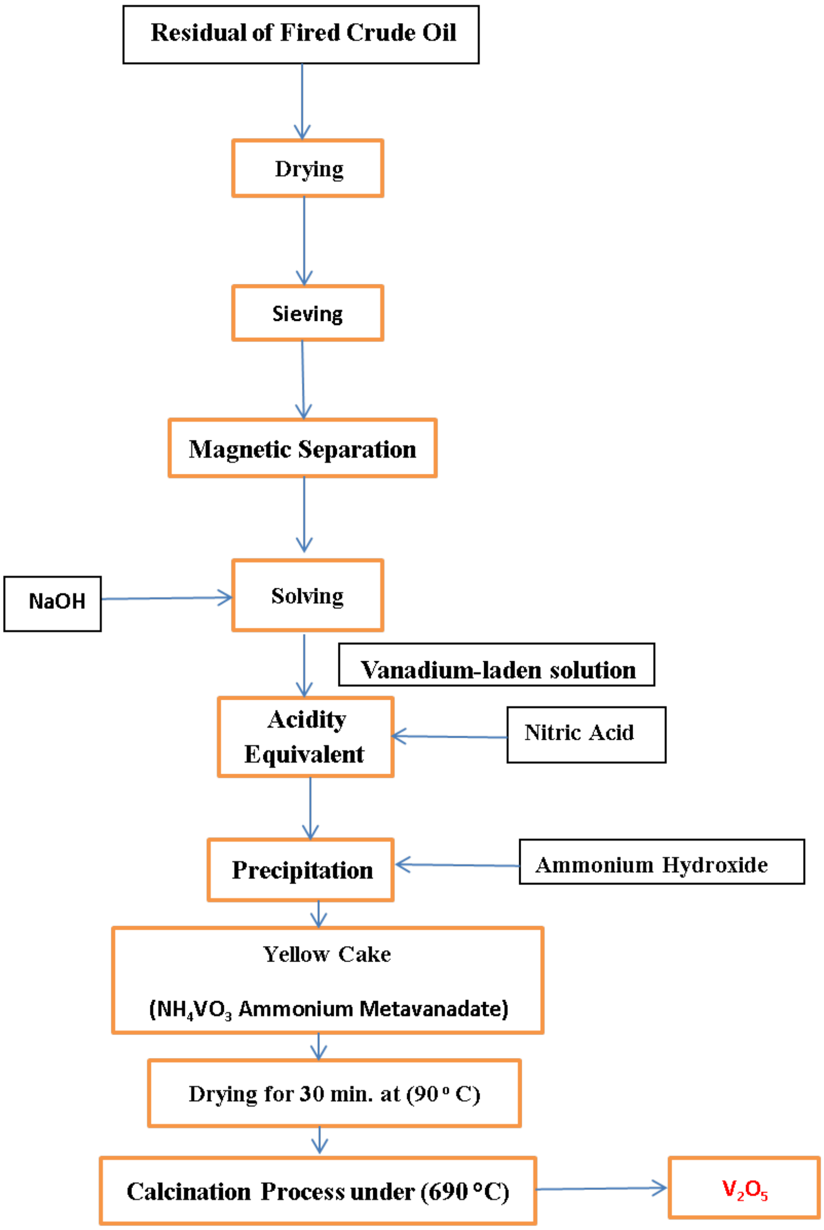

Fig. (2): Diagram of Experimental work

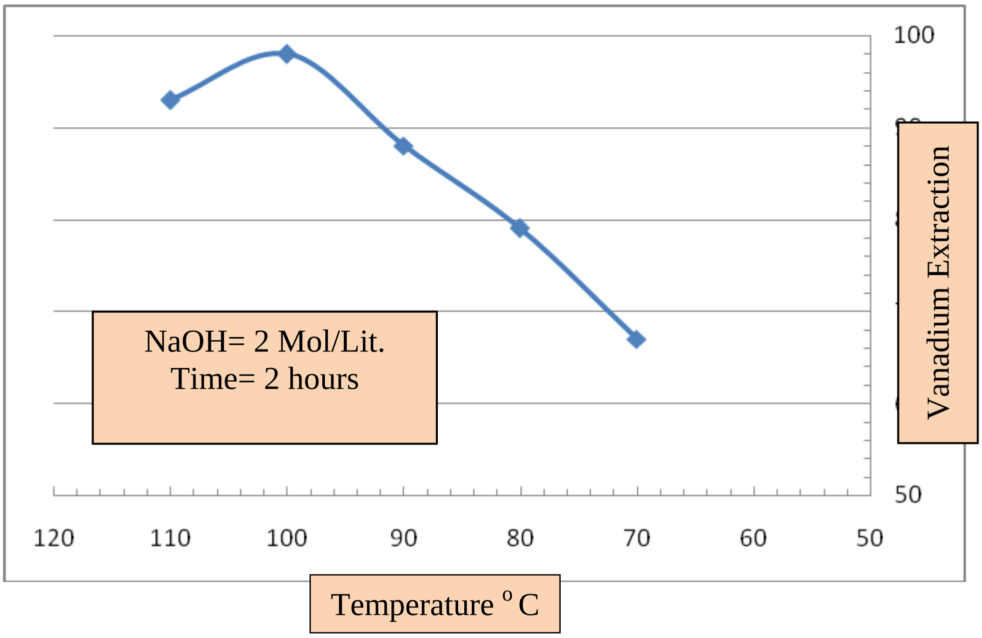

Fig. (3) Relationship between Temperature & Vanadium

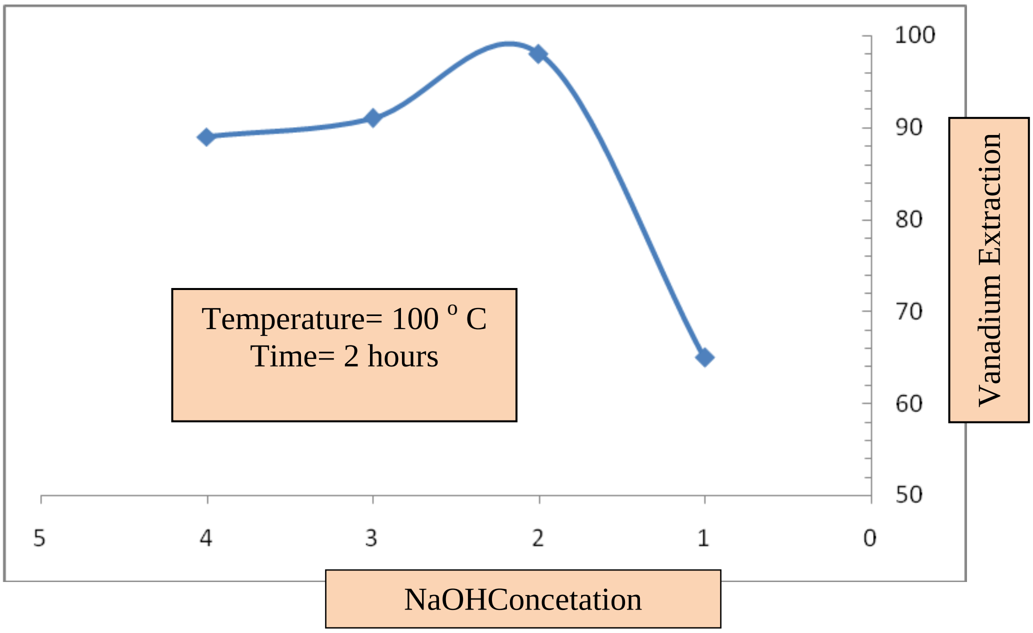

Fig. (4) Relationship between NaOH Concentration& Vanadium

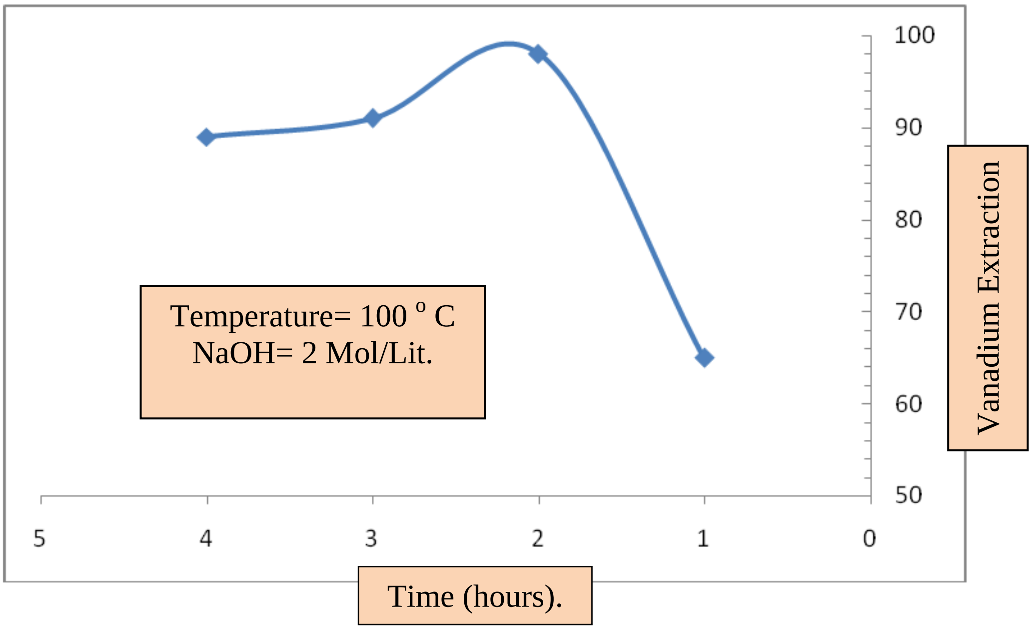

Fig. (5) Relationship between the Time& Vanadium Extraction

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