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## Sequential recovery processes of tungsten from hubnerite mineral concentrate of Qash Amir mineralized quartz veins, South Eastern Desert, Egypt

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**Abstract:** A hubnerite ( $MnWO_4$ ) mineral concentrate was prepared from the mineralized quartz veins of Gabal Qash Amir muscovite granite. This W- concentrate was chemically processed to obtain the more economic highly pure tungsten oxide. To accomplish this goal, two successive atmospheric agitation leaching processes were conducted. The first includes HCl acid agitation leaching to breakdown hubnerite mineral structure. The purpose was also to get rid of the associated Mn and Fe contents from one hand, and to prepare the more important intermediate tungstic acid from the other hand. From the latter, a sodium tungstate ( $Na_2HWO_4$ ) leach liquor was adequately prepared after applying the second atmospheric NaOH agitation leaching process using the optimum conditions of 40% caustic soda concentration at solid/ liquid ratio of 1/3, 180°C for 2h. Finally, 7% Alamine 336 in kerosene was used for extracting 93.7% of W content under the studied optimum conditions of O/A ratio of 1/1, contact time 7 min at room temperature ( $20\pm 5^\circ C$ ) and pH of 8.

**Keywords:** sequential leaching processes, tungsten recovery, hubnerite mineral concentrate, mineralized quartz veins, NaOH agitation leaching, Alamine 336

### 1. Introduction

In the extreme south eastern part of Egypt namely; Halaib environ, a new tungsten mineralization has been lately discovered within muscovite granite of Gabal (G.) Qash Amir. This discovery adds to the economic importance of this region as it was very famous for its Mn-oxide ore of G. Elba, Mn- U of G. Qash Amir and G. El Sella. G Qash Amir younger granites pluton is located at about 20 km west of Abu Ramad City covering an area of about 3.0 km<sup>2</sup>. This pluton is invaded by numerous mineralized quartz veins of fluctuates in width and length (El Agami, et al., 1999; El Gammal and Sherief, 1999; El Agami (2004).

In 2014, the European Union identified 20 raw materials as critical concerning the supply risk and economic importance. Tungsten is one of those critical raw materials, because of the high economic importance and the high supply risk when depending on imports (European Commission, 2014; Reichl et al., 2016; Willersinn and Bart, 2017). Tungsten is extraordinary important for a broad range of industrial processes because of its unique physicochemical properties and excellent performance. It has the highest melting point of all metals (3422 °C) and a high density of 19.3 g/cm<sup>3</sup> make it suitable for military applications in penetrating projectiles. Tungsten carbide is known as one of the stiffest materials (Lassner et al., 2000; Brown et al., 2013). Tungsten as a national strategic metal and tungsten compounds has been widely applied in the fields of machinery manufacture, petrochemical catalysts process, filaments, aerospace and nuclear industries (Rout et al., 2017; Forsén and Aromaa, 2016; Zhihua et al., 2019). In this context, tungsten used to protect against radiation such as gamma and x-ray (as shielding) or as a collimator for concentrating radiation beams directly to target. Tungsten-based composites are a significant in the field of nuclear materials. They can improve mechanical properties,

oxidation resistances, irradiation resistance, strength and microstructural stability (Waseem and Ryu, 2016).

In general, tungsten-bearing ores are generally classified in two mineral groups: the wolframite and scheelite groups. In the first, wolframite [(Fe, Mn)WO<sub>4</sub>] includes the solid solution series between ferberite (FeWO<sub>4</sub>) and hubnerite (MnWO<sub>4</sub>) (Horsnail 1979; Sengupta et al., 1987; Gbaruko and Igwe 2007; McClenaghan et al., 2014; Srivastava et al., 2019). The second group, scheelite (CaWO) itself is the only commercially important member of the scheelite group (Martins 2013). Wolframite is the most common tungsten mineral in Central Africa and is widely originate in quartz vein deposits found in hydrothermal systems (Goldmann et al., 2013; Harzanagh etl., 2017).

In hydrometallurgical recovering tungsten from concentrate, tungstic acid produced in a strong mineral acid solution at atmospheric pressure, such as a solution of H<sub>2</sub>SO<sub>4</sub>, HCl or HNO<sub>3</sub>, at a temperature ranging of from 40 to 100°C for 1-4 hrs. in the presence of an inorganic complexing salts, and adding an ammonium salt compound for precipitating the tungsten. The precipitate is then dissolved in NH<sub>4</sub>OH solution under pressure and the tungsten recovered as ammonium paratungstate (APT) (Lundquist 1979; Martins, 1983).

Alternately, alkali leaching (NaOH or Na<sub>2</sub>CO<sub>3</sub>) is widely used to process tungsten concentrates under high temperature and pressure conditions (Hairunnisha et al., 2007; Zhao et al., 2011; Liu et al., 2020). Na<sub>2</sub>CO<sub>3</sub> is the most cited reactant in the literature (Paulino et al., 2012). Concentrates of tungsten ores are chemically processed to recover tungsten by leaching with Na<sub>2</sub>CO<sub>3</sub> in autoclave forming soluble sodium tungstate (Shamsuddin and Sohn, 1981; Queneau et al., 1982; Martins, 1996; Pandey et al., 2008; Martins, 2013). Tungsten can be extracted from wolframite with a high recovery rate (around 98%) under the following conditions: temperature range of 190–250°C, 12– 26 bar pressure, 10–18% Na<sub>2</sub>CO<sub>3</sub>, 2.5–4.5 weight ratio of Na<sub>2</sub>CO<sub>3</sub>/WO<sub>3</sub> (Bohlouli et al., (2016).

Recently, new processes were developed on industrial scale for the solvent extraction (SX) to recover W from alkaline media (Zhang et al., 2016). So, solvent extraction is an extremely useful technique to recover tungsten from its leachates (Lassner, 1995; Pandey et al., 2001). As extractants, aliphatic amines have long history of use (Palant et al., 1998). In general, the amine's efficiency decreases in the order quaternary>tertiary >secondary>primary under the same experimental conditions. Tertiary amines are the most cited in the literature (Gerhardt et al., 2001; Nguyen and Lee (2016); Song et al., 2019) [33-35]. Paulino et al. (2012) extracted about 99.9 of W from alkaline solution using Aliquat 336 as quaternary ammonium salt in one stage.

However, in Egypt there is a research deficit as it relates to W- bearing minerals extractive metallurgy. Then, there is a requirement to conduct studies that can lead to a better understanding and to develop extraction processes for the metal of interest. To achieve this goal, the present work attentive mainly upon comprehensive characterization of W- bearing ore material (veins type deposit) and shifted toward the extraction of this interesting valuable element. For this purpose, a representative sample was collected from mineralized quartz veins invaded G. Qash Amir muscovite granite for the required physical and chemical processing.

## 2. Materials and methods

These include applying either physical and chemical processes upon the studied mineralized quartz veins sample. The former includes mineralogical characterization and physical beneficiation procedures using shaking tabling and magnetic separator techniques. The attained heavy mineral concentrate was then subjected to chemical processing for recovering tungsten (Fig. 1).

### 2.1. Mineralogical characterization of mineralized quartz veins

To investigate the mineralogical composition of the quartz veins representative sample from Qash Amir, heavy mineral separation procedures were applied. For this purpose, the whole disaggregated concentrate was deslimed by washing and decantation. After drying, the dry fraction was then sieved into the size -0.1 to +0.063 mm. The light and heavy fraction was separated by bromoform (sp. gr. 2.8 gm/cm<sup>3</sup>). The heavy mineral fractions were obtained and investigated under the binocular microscope and picked mineral grains were identified by X-ray diffraction technique (XRD). The latter was associated with Device model Malvern Panalytical Empyrean, (2020) (Netherland) a diffractometer with

automatic sample changer, (21 position). The X-ray radiation used is Cu-target tube (Anode material) at generator setting of 40 kV and 30 mA. This instrument is connected to a computer system and ASTM cards for mineral identification. The Environmental Scanning Electron Microscope (ESEM) a Philips Model EXL 130 supported by an energy dispersive X- ray EDAX unit for semi-quantitative analysis was used to examine some of the separated grains.

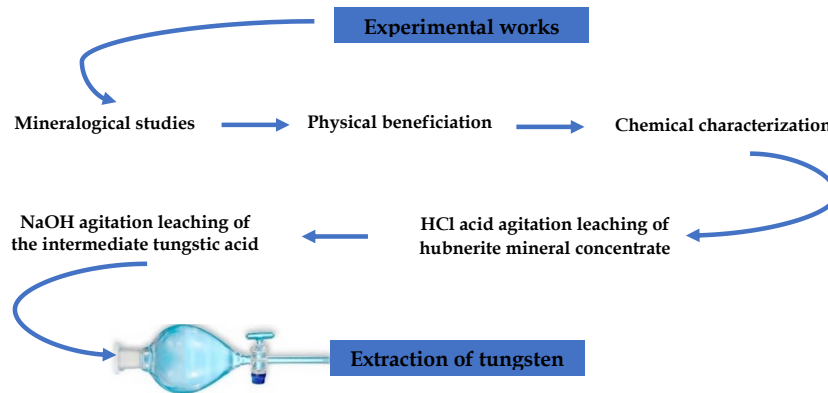


Fig. 1. Schematic diagram summarizes the applying experimental work

## 2.2. Physical beneficiation of mineralized quartz veins

The collected representative sample from mineralized quartz veins invaded within G. Qash Amir muscovite granite was firstly subjected to crushing–grinding to liberation size. A bulk sample weight of 20 Kg assays 0.43%  $WO_3$  was subjected to control and reduce its size using a combination of jaw crushers and a roll mill crusher to pass 1.0 mm screen. The deslimed fraction was dried and fractionated using a set of screens starting from -1.000 down to +0.063 mm which is suitable for the physical beneficiation technique. On the other hand, gravitative technique was approved out utilizing the laboratory wet Wilfely shaking table (No.13, Germany) to obtain hubnerite and pyrite concentrate. The obtained concentrate would then be magnetically treated by the high intensity Induced roll magnetic separator (Carpco Model MLH (13) III-5, USA) to attain the required W- concentrate.

## 2.3. Chemical characterization of W-concentrate

The chemical composition of the working W-concentrate beside the obtained tungstic acid were analyzed by Axios advanced WDXRF-PAN analytical (Netherland) XRF for major and trace elements. On the other hand, an atomic absorption spectrometer (Unicame 969) was used for Mn determination at  $\lambda$  403 (Weltz and Sperling 1999). While Fe determine using titration method against sulfosalicylic acid according to Shapiro and Brannock (1962). Alternately, W and Nb were analyzed during the leaching experiments using simultaneous inductively coupled plasma emission spectrometer (720 ICP- OES, Agilent Technologies).

## 2.4. Sequential atmospheric agitation leaching processes

Two successive atmospheric agitation leaching process were carried out upon the studied W-concentrate beginning with HCl acid leaching to breakdown the hubnerite mineral structure and to get rid of Mn and Fe elements. This process was followed by atmospheric alkali agitation leaching using NaOH to dissolve the obtained tungstic acid.

### 2.4.1. Atmospheric HCl acid agitation leaching process of hubnerite mineral concentrate

Several breakdown experiments have been achieved by agitating 5g of the ground W- concentrate sample (53-40 $\mu$ ) with HCl acid of different concentrations at different solid/liquid (S/L) ratios, different periods of time and different temperatures. A hot plate with a magnetic stirrer was used in these experiments, and precautions were taken to avoid contamination and acid evaporation. After leaching,

the slurry was obtained then cooled, filtered, washed with distilled water and volumized. Mn and Fe were estimated in all agitation leaching streams to calculate their leaching efficiencies.

#### 2.4.2. Atmospheric NaOH agitation leaching process of the intermediate tungstic acid

After applying the above mentioned HCl agitation leach process, a stock of solid tungstic acid was prepared using the obtained optimum leaching conditions. The purpose was to operate the subsequent recovery procedures. For the latter, a series of atmospheric NaOH agitation leaching experiments were conducted. Each leaching experiment has been achieved by agitating a weight of tungstic acid with different NaOH concentrations, different solid/liquid ratio (S/L) for different periods of time at different temperatures. A hot plate with a magnetic stirrer was used in these experiments, and precautions were taken to avoid contamination and evaporation. The obtained slurry was then cooled, filtered, washed with distilled water and made up to volume for analyzing the dissolved W content.

### 2.5. Extraction of tungsten

#### 2.5.1. Preparation of pregnant solution and Solvent extraction of W

The working sodium tungstate leach liquor required for W extraction was prepared via mixing 100g of the tungstic acid with 40% NaOH at the optimum agitation leaching conditions. After filtration and washing with distilled H<sub>2</sub>O the final volume of the prepared sodium tungstate leach liquor attained 1L at pH =12.3. In this regard, solvent extraction technique via Alamine 336 in kerosene and octanol as a modifier was applied for W extraction at the optimum extraction conditions.

### 3. Results and discussion

In fact, the rate of valuable metal dissolution and recoveries are mainly controlled by the nature and mode of occurrence of a mineralization, as well as its associated gangues. The following is a brief description of the mineralogical and chemical properties of the studied mineralized quartz veins.

#### 3.1. Mineralogical characteristics of the studied mineralized quartz veins

In the studied sample, hubnerite is recorded as parent W mineral in association with pyrite. It is worthy to mention herein that, hubnerite masses can be observed by naked eye in quartz veins invaded with muscovite granite reach up to about 1 cm (Fig. 2).

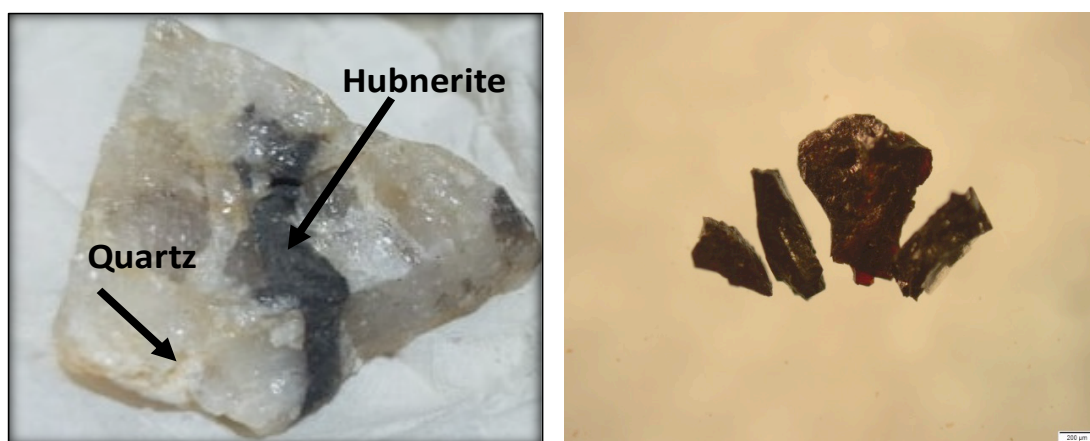


Fig. 2. Close up photograph of hubnerite mineral associated to quartz vein present as large black grains (left), stereophotograph of picked hubnerite grains (right) X=10

In this context, the detailed mineralogical study of the working sample of Qash Amir quartz veins by means of XRD analysis revealed that hubnerite is the main valuable mineral (Fig. 3). Hübnerite or hubnerite is belongs to rare group wolframite. According to (Errandonea and Segura, 2010), wolframite (Fe, Mn)WO<sub>4</sub> forms a solid solution series between the two endmembers ferberite (FeWO<sub>4</sub>) and hübnerite (MnWO<sub>4</sub>). It is the Mn- endmember (Hu et al., 2010) has reddish brown to

black prismatic submetallic crystals. It is mainly occurs as high temperature hydrothermal vein deposits and pegmatites. Also, the EDX data for two samples, provided that hubnerite contains an average 62.17 wt. % W and 25.1 wt. % Mn. It contains considerable amounts of Nb, reach about 0.27 wt. % (Fig. 4).

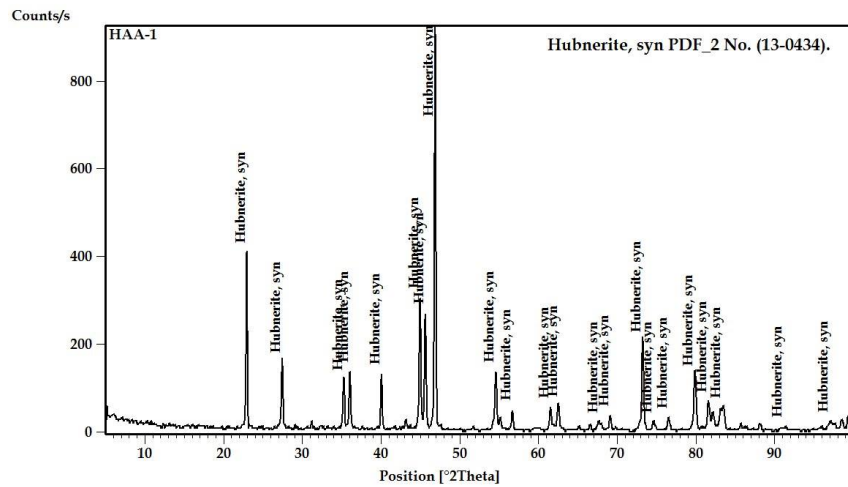


Fig. 3. X-Ray diffractogram data of hubnerite mineral

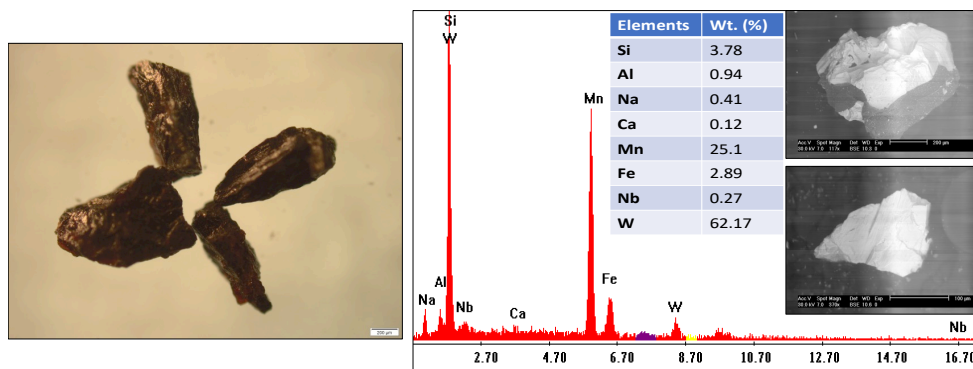


Fig. 4. Photograph of picked hubnerite grains (left), EDX analysis data and BSE image of hubnerite grain (right)

### 3.2. Physical upgrading of Qash Amir mineralized quartz veins

The suitable size is the most effective parameter affecting separation and upgrading procedures (Gaudin, 1980). From sieving analysis data of the studied sample (Table 1) it can conclude that, about 45 wt.% of bulk sample related  $-1\text{mm}+0.5\text{mm}$  which confirmed the importance of grinding step to liberate the W- mineral before hydrometallurgical work. Also, 91.7% of heavy minerals is concentrated in about 90% of the bulk sample. It is worthy to mentioned herein that, the crushing operation is effective method for saving the majority of heavy mineral content in size fraction between  $-1\text{mm}$  and  $+0.063\text{mm}$ .

Table 1. The distribution of heavy minerals in different size fractions

Sieving size	Bulk sample Wt. (%)	Heavy minerals (Wt. %)	Distribution (%)
-1+0.7 mm	24.2	1.2	11.8
-0.7+0.5 mm	20.7	1.1	12.4
-0.5+0.25 mm	14.6	1.5	14.8
0.25+0.125 mm	17.8	1.6	22.6
-0.125+0.063 mm	12.4	2.3	31.1
Sum (-1+0.063mm)	89.7	-	91.7
-0.063 mm	10.3	1.3	8.2
Bulk sample	100	1.3	99.9

Depending on the differences in the specific gravities between the hubnerite mineral (Sp.gr.7.12-7.18) and the associated gangue minerals (mainly quartz Sp. gr. 2.65) would make the gravitational concentration by shaking table an effective tool for their primary separation. In the meantime, preparation of a suitable feed size of separation is very useful for attaining the maximum efficiency of the used shaking table. Accordingly, about 20Kg of bulk sample was prepared in size range from -1 to +0.063 mm fraction size and then was feed upon the Wilfely shaking table. This procedure conditions were optimized by using fewer quantities of feed fractions, a reduced amount of water, less tilt as much as possible (Raslan and Fawzy, 2017). The obtained pure concentrate mainly composed of hubnerite associated with pyrite mineral. It is worthy to mentioned herein that, the shaking table recovery efficiency was 89.7%.

In this context, obvious variations in the magnetic susceptibilities between hubnerite and pyrite would constitute the basis for their final magnetic separation. The purpose was to purified the W-concentrate from free magnetite and pyrite. A proper magnetite free- feed (about 138 g) was then prepared and directed to magnetic separation using high Intensity Lift type magnetic separator (Carpco Model MLH (13) III-5). The obtained data illustrated that the ultimate non-magnetic concentrate at 1.7 amp mainly contains pyrite while magnetic concentrate at 0.2-0.7 amp of feed having 63.54%  $WO_3$ . Finally, a flowsheet represented the sequence of processes following the upgrading operation was given in Fig. 5.

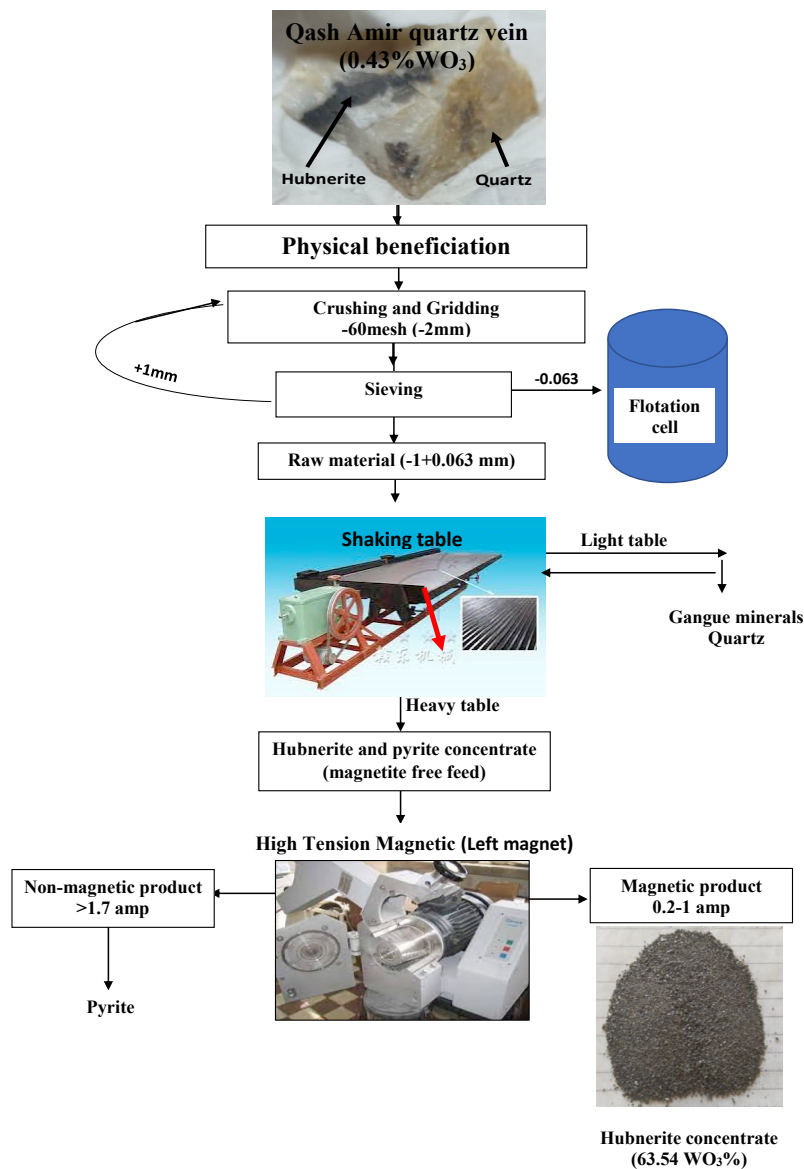


Fig. 5. A flow sheet illustrates the physical upgrading processes of G. Qah Amir mineralized quartz veins

### 3.3. Chemical composition of the studied tungsten concentrate

The working hubnerite W-concentrate of G. Qash Amir has first been chemically analyzed for their major and trace elements constitution (Table 2).

Table 2. XRF analysis and complete chemical composition of the studied concentrate

Major Constituents	(Wt. %)	Constituents	Wt. (%)
SiO <sub>2</sub>	3.14	WO <sub>3</sub>	63.54
TiO <sub>2</sub>	0.05	Nb <sub>2</sub> O <sub>5</sub>	0.39
Al <sub>2</sub> O <sub>3</sub>	0.78	Ta <sub>2</sub> O <sub>5</sub>	0.112
Fe <sub>2</sub> O <sub>3</sub> <sup>tot</sup>	3.19	CuO	0.03
CaO	1.43	ZnO	0.027
MgO	0.11	SrO	0.007
Na <sub>2</sub> O	0.55	Y <sub>2</sub> O <sub>3</sub>	0.038
K <sub>2</sub> O	0.53	ZrO <sub>3</sub>	0.016
MnO	24.53	PbO	0.191
SO <sub>3</sub>	0.13		
F-	0.23		
Cl-	0.04		
*L.O.I	0.02		
Total	34.72		64.351

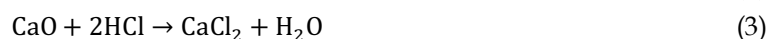
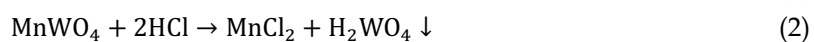
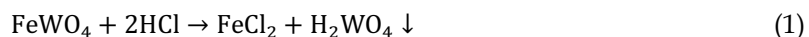
\*L.O.I. Loss Of Ignition

From the obtained major oxides of the working concentrate given in Table 2, it is clearly evident that, the concentrate is mainly composed of WO<sub>3</sub> (63.54%), MnO (24.53%) and SiO<sub>2</sub> (3.14%) besides Al<sub>2</sub>O<sub>3</sub> (0.78%) and low total iron oxides (3.19%). These oxides are chiefly allotted as wolframite series minerals due to the deficiency of CaO (1.43%). With respect to the valuable metals of the study concentrate, it was found that, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> amounted to 0.39% and 0.11%, respectively which reflects the significant high-grade type of concentrate and reflect the importance of their recovery.

Finally, from the mineralogical and chemical attendances of the studied W- concentrate, it can be concluded that, it might be in favor to apply HCl acid leaching process to get rid of associated impurities namely; (Fe, Mn, Ca, Na and K) from one hand, and to increase valuable WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> concentration from the other hand.

### 3.4. Results of sequential atmospheric agitation leaching processes

Due to the importance of hubnerite mineral as a main source of W element, it was found necessary to study the leaching potentialities of this important mineral in a trial to obtain a highly pure W- products. The following is a brief clarification about the used leaching process. In this respect, the expected reactions between HCl acid and the studied concentrate were shown in equations (1-3) to produce the soluble chloride of metals of interest e.g. Mn and Fe beside insoluble tungstic acid.



#### 3.4.1. Results of atmospheric HCl acid agitation leaching

##### 3.4.1. 1. Effect of HCl concentration

Different HCl acid concentrations ranged from 15 to 36 % were used to investigate the effect of acid concentration upon the leaching efficiencies of the studied metal values. The other leaching conditions were fixed at 100°C for 2h, 53-40μ concentrate size and S/L ratio of 1/2. From the obtained results (Fig. 6A), it was found that, the leaching efficiencies of Mn and Fe increased from 39.1 and 72.4% to 62.3 and 89.4%, respectively by increasing the acid concentration from 20 to 30%. While, more increasing in acid



concentration indicated no considerable effect upon their leachability. On the other hand, the leaching efficiencies of W and Nb is not satisfactory. This may be owing to the formation of insoluble tungstic acid.

### 3.4.1. 2. Effect of solid/ liquid ratio (w/v)

The effect of S/L ratio upon the leaching efficiencies of the metals of interest were studied at S/L ratio ranging from 1/1 to 1/2.5 using 30% HCl acid at 100°C for 2h. The obtained data (Fig. 6B) indicated that, the leaching efficiencies of Mn and Fe increased by decreasing the S/L ratio from 1/1 to 1/1.5. On the other hand, more decreasing in S/L ratio than 1/1.5 showed no significant effect upon the leachability of both of Mn and Fe. The high consumption of HCl results from the reaction is controlled kinetically by diffusion of HCl reagent, meanwhile the porosity of the tungstic acid coating formed on the particles is extremely low (Martins, 2014).

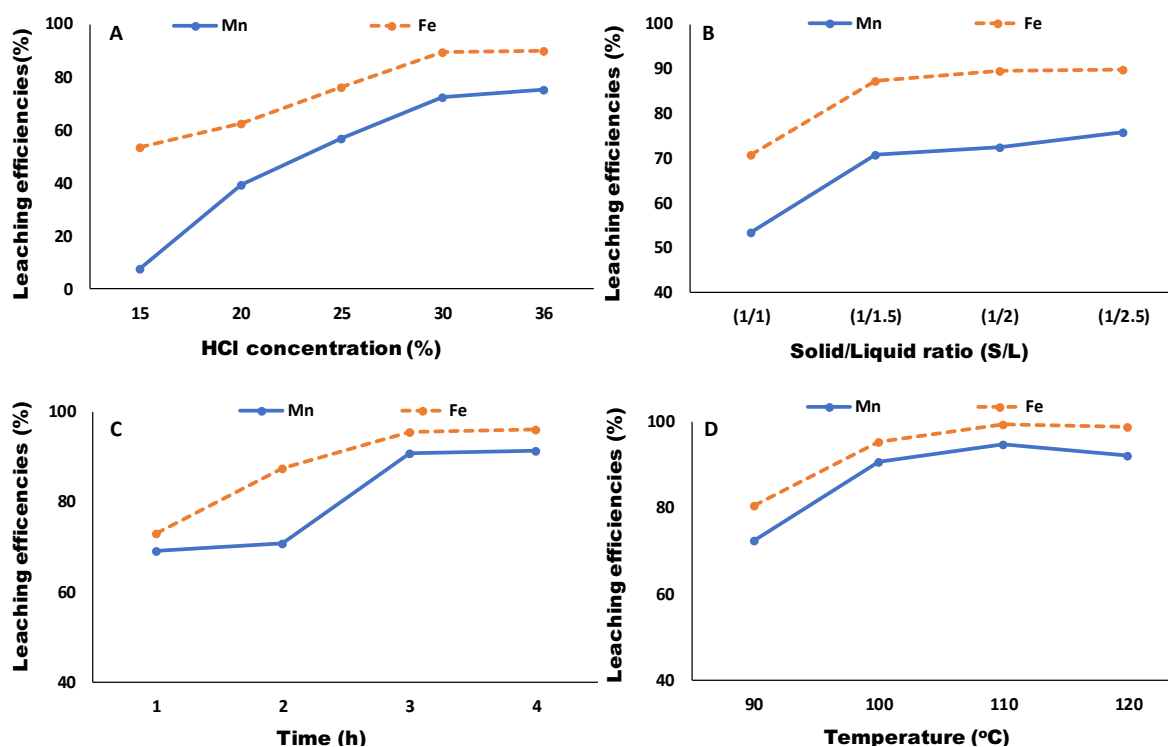


Fig. 6. The effect of HCl Conc. (A), S/L ratio (B), time (C) and temperature (D) upon leaching efficiencies of Mn and Fe

### 3.4.1.3. Effect of leaching time

It was considered in the various times ranging from 1 to 4 hours. The other leaching conditions were established at 30% HCl, S/L ratio of 1/1.5 and 100 °C. The corresponding leaching efficiencies (Fig. 6C) indicated that, the studied W- concentrate required long periods of time to be leached. The Mn and Fe leaching efficiencies were 90.6 and 95.4%, respectively at 3 h. Increasing the leaching time more than 3h show slight increase in the leaching efficiencies of all the metals of interest.

### 3.4.1.4. Effect of leaching temperature

The effect of leaching temperature upon the leaching efficiencies of the studied metal values was investigated in the range from 90 to 120°C. The other leaching conditions were kept constant at acid concentration of 30% HCl, S/L ratio of 1/1.5 and leaching time of 3h. The obtained data (Fig. 6D) indicated that the studied W- concentrate has required high temperature exceeding 100°C as indicated from the dissolution of Mn and Fe which reached to 94.6 and 99.4% respectively at 110°C.

Finally, from the foregoing HCl acid agitation leaching study, it can be concluded that, the dissolution efficiencies of Mn and Fe are satisfactory where they reached 94.6 and 99.4% respectively at



the following optimum conditions: 30% HCl concentration, 1/1.5 S/L ratio and 3h agitation time at 110°C. At these conditions, it is worthy to mention herein that, the leaching efficiencies of both W and Nb not exceed than 0.09 and 0.02% respectively.

### 3.4.2. Results of atmospheric NaOH agitation leaching of the obtained tungstic acid

This process was carried out by applying the atmospheric HCl acid agitation leaching optimum conditions upon 100 g of hubnerite mineral concentrate grounded to 53-40 $\mu$ . The obtained yellow tungstic acid (H<sub>2</sub>WO<sub>4</sub>) was identified using both EDX and XRD analysis (Fig. 7AB) and chemically analyzed using XRF technique (Table 3) in order to ascertain its chemical composition. The purpose was to determine the prepare subsequent alkaline leaching process. The following equations (4-6) illustrate the expected reaction between NaOH and the obtained insoluble tungstic acid.

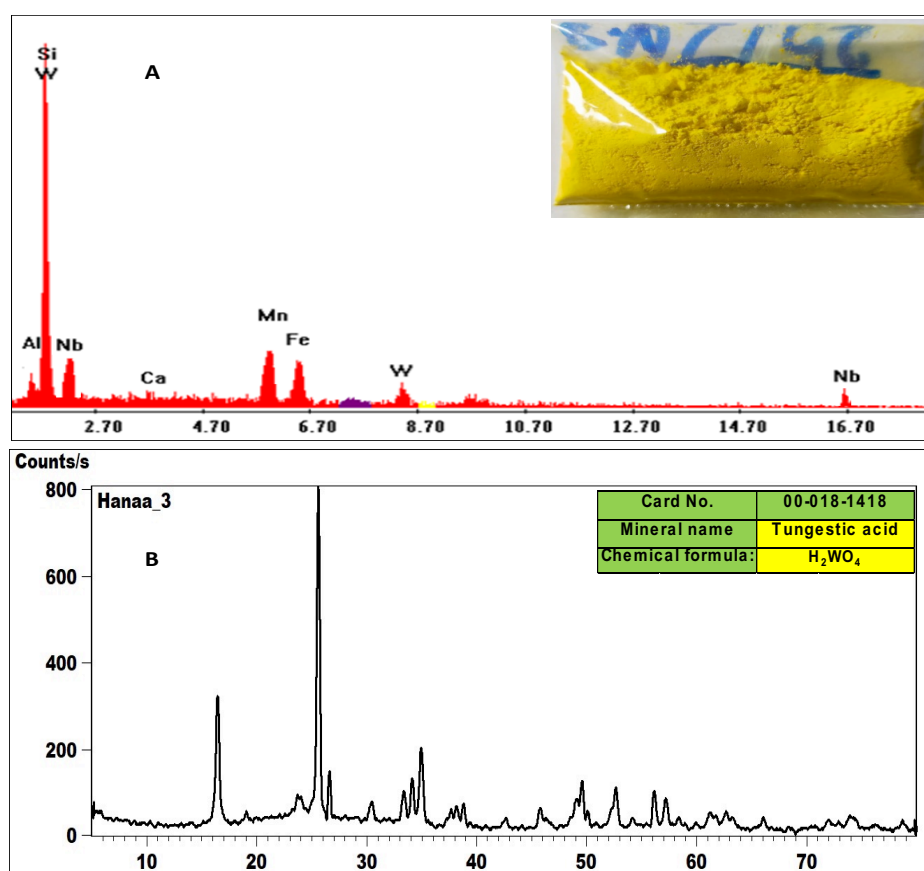
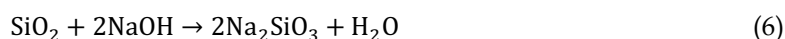
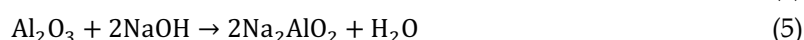
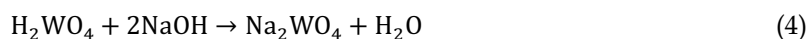


Fig. 7. EDX analysis of yellow precipitate (A), XRD chart of intermediate tungstic acid (B)

Table 3. XRF analysis of the obtained tungstic acid

Constituents	(Wt. %)
WO <sub>3</sub>	86.99
Nb <sub>2</sub> O <sub>5</sub>	0.59
Ta <sub>2</sub> O <sub>5</sub>	0.21
SiO <sub>2</sub>	3.86
Al <sub>2</sub> O <sub>3</sub>	0.91
Fe <sub>2</sub> O <sub>3</sub> <sup>tot</sup>	0.02
CaO	1.5
MnO	1.64

### 3.4.2.1. Effect of NaOH concentration

A series of leaching experiments were conducted using different concentration of NaOH ranging from 20 to 45%, while the other leaching factors were fixed at 1/2 of S/L ratio and agitation time of 2h at 120°C. Data in Fig. 8A showed that, the leaching efficiencies of W and Nb increased gradually from 56.9 and 1.3% to 84.1 and 5.7%, respectively by increasing the NaOH concentration from 20 to 40%, beyond this concentration a limit increase in the leaching efficiencies of the metals of interest took place.

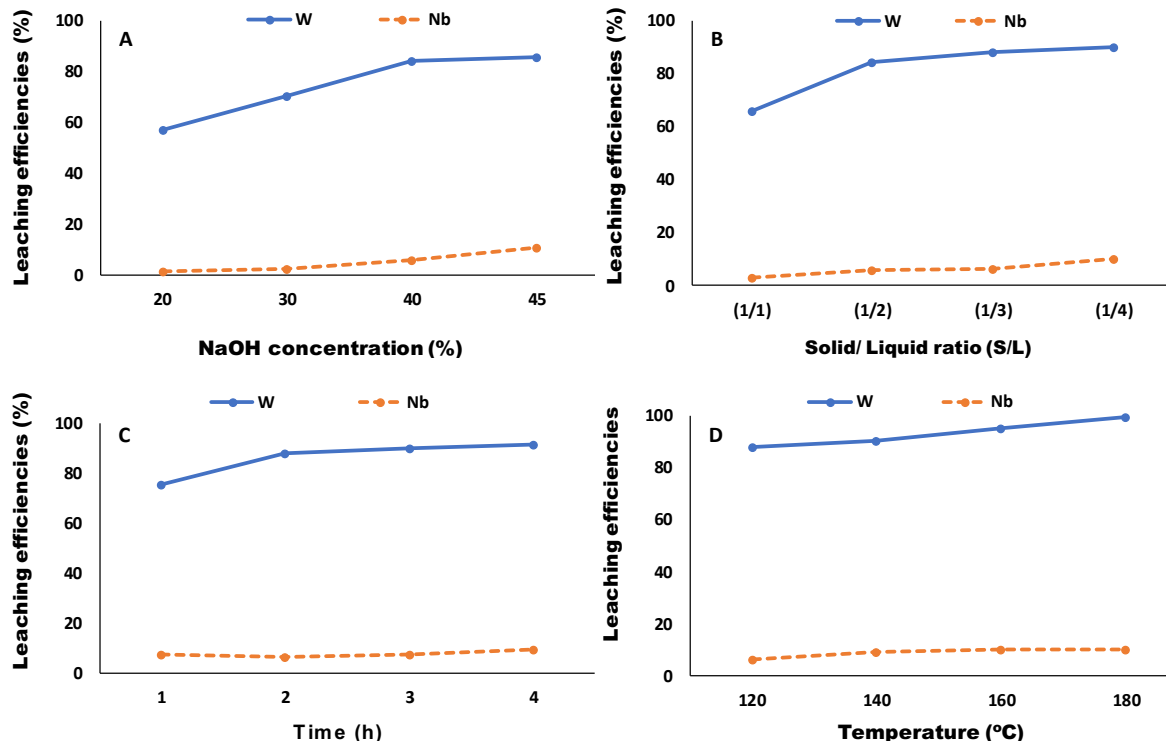


Fig. 8. The effect of NaOH Conc. (A), S/L ratio (b), time (c) and temperature D) upon leaching efficiencies of W and Nb

### 3.4.2.2. Effect of solid/ liquid ratio

The impact of S/L ratio upon the leaching efficiencies of W and Nb was examined at different ratio ranged from 1/1 to 1/4 using 40% NaOH at 120°C and stirring time for 2h. The obtained data plotted in Fig. 8B indicated that, by decreasing the S/L ratio from 1/1 to 1/3 the leaching efficiency of W increased significantly from 65.8 to 87.9% and then slightly increased to 89.9% at S/L ratio of 1/4. On the contrast, the leaching efficiency of Nb recorded only 6.4% at S/L ratio of 1/3 and this may attribute to the less affinity of Nb toward NaOH.

### 3.4.2.3. Effect of leaching time

The influence of agitation time upon the leaching efficiencies of the elements of interest was studied using the fixed conditions of 40% NaOH, 1/3 as S/L ratio at 120°C while varying the leaching time from 1 to 4h. The obtained results (Fig. 8C) emphasized that, the agitation time of 2h represented the optimum one for dissolving of both of W and Nb with efficiencies of 87.9 and 6.4%, respectively. Beyond 2h no significant effect upon the leaching efficiencies of W took place and this can be attributed to the fact that, the reaction time at elevated temperature will tend to increase NaOH losses through volatilization which may cause the gelatinous and colloidal solution (Luo et al., 2003 and Paulino et al., 2012).

### 3.4.2.4. Effect of leaching temperature

The influence of leaching temperature upon the leaching efficiencies of either W and Nb was studied at temperature ranging from 120 to 180°C. The other leaching factors were fixed at 40% NaOH, 2h agitation

time and 1/3 S/L ratio. The obtained results Fig. 8D proved that, the leaching efficiencies of both of W and Nb increased from 87.9 and 6.4% to 99.1 and 10.1% respectively, as the temperature increased from 120 to 180°C.

### 3.5. Results of tungsten extraction process

#### 3.5.1. Preparation of pregnant solution and Solvent extraction of tungsten

The working alkaline leach liquor required for W extraction was prepared via mixing 100g of the tungstic acid with 40% NaOH at the optimum agitation leaching conditions of 1/3 S/L ratio, agitation time 2h and agitation temperature 180°C. After filtration and washing with distilled water the final volume of the prepared sodium tungstate leach liquor attained 1L and its pH value was 12.3. The chemical specification of the prepared sodium tungstate solution is given in Table 4.

Table 4. Chemical specification of the working sodium tungstate pregnant solution at pH =12.3

Major Constituents	(g/L)
W	48.79
Si	0.63
Nb	0.041
Ta	0.017
Na	73.2
Ca	0.029

In this regard, solvent extraction technique using Alamine 336 in kerosene and octanol as a modifier was applied for W extraction and its separation from the associated interfering elements e.g. Si and Na at the optimum extraction conditions. To achieve this goal, direct solvent extraction had been carried out using Alamine 336 in kerosene after pH controlling to 8 using diluted HCl acid. About 94% of tungsten was recovered from sodium tungstate pregnant solution when using 7% Alamine 336 in kerosene, 7 min equilibrium time, O/A ratio 1/1 at room temperature (Palulino, 2012). It is important to mention herein that, the loaded Alamine 336 was scrubbed with distilled water to get rid of co-loaded impurities especially Na and Si (Zhang et al., 2016). So, both raffinate and scrubbing solutions was directed to leach liquor in recycling process.

#### 3.5.2. Stripping process and preparation of ammonium paratungstate

After loading, stripping process was performed for regeneration of the loaded organic solvent to obtain W rich solution. In this context, stripping of tungsten from loaded Alamine336 was performed using NH<sub>4</sub>OH solution at the optimum conditions of: 5 % NH<sub>4</sub>OH solution, A/O ratio of 1/1 and equilibrium time 7 min yields highly pure ammonium tungstate solution realizing stripping efficiency of more than 97.9%. The strip solution was then slowly evaporated at 50 °C under atmospheric pressure and crystallized to recover tungsten as ammonium paratungstate (APT), ((NH<sub>4</sub>)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>].4H<sub>2</sub>O). In this context, all impurities have much higher solubilities than APT, crystallization process is not only used to recover tungsten in solid APT form, but it is also used as the final step in purification. Accordingly, about 90% tungsten was recovered throughout the crystallization process. In the present work, it was possible to produce an important intermediate W-compound APT of 99.97% purity (Fig. 9) by applying this process route. The transformation of crystallized white APT to yellow WO<sub>3</sub> oxide take place at temperatures of 750°C (Fig. 10). Finally, a proposed flowsheet represented the preparation of the pure product of W- metal oxide (WO<sub>3</sub>) was represented in Fig. 11.

## 4. Conclusions

In the extreme south eastern part of Egypt namely; Halaib environ, a new tungsten mineralization has been lately discovered within quartz veins invaded in muscovite granite of Gabal (G.) Qash Amir. From the latter, a hubnerite mineral concentrate of 63.54% WO<sub>3</sub> was prepared using the Wilfy shaking table followed by magnetic separation procedures. The recovery of tungsten oxide from the prepared

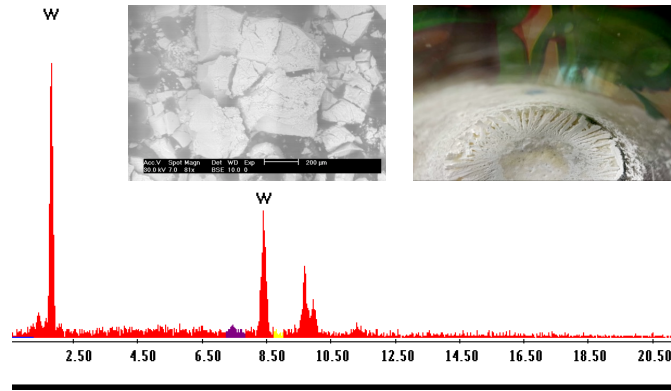


Fig. 9. EDX analysis data of the prepared highly pure APT

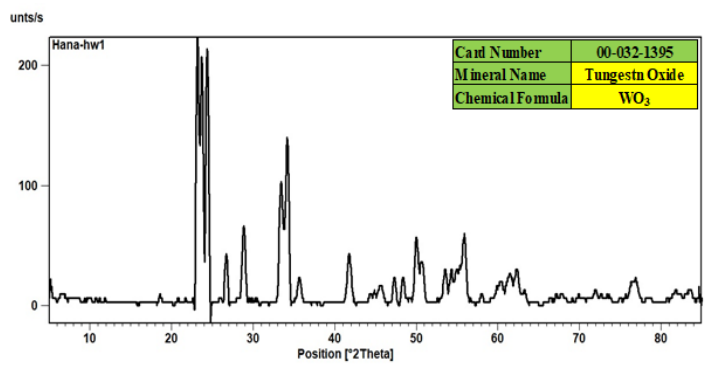


Fig. 10. XRD chart of highly pure WO<sub>3</sub>

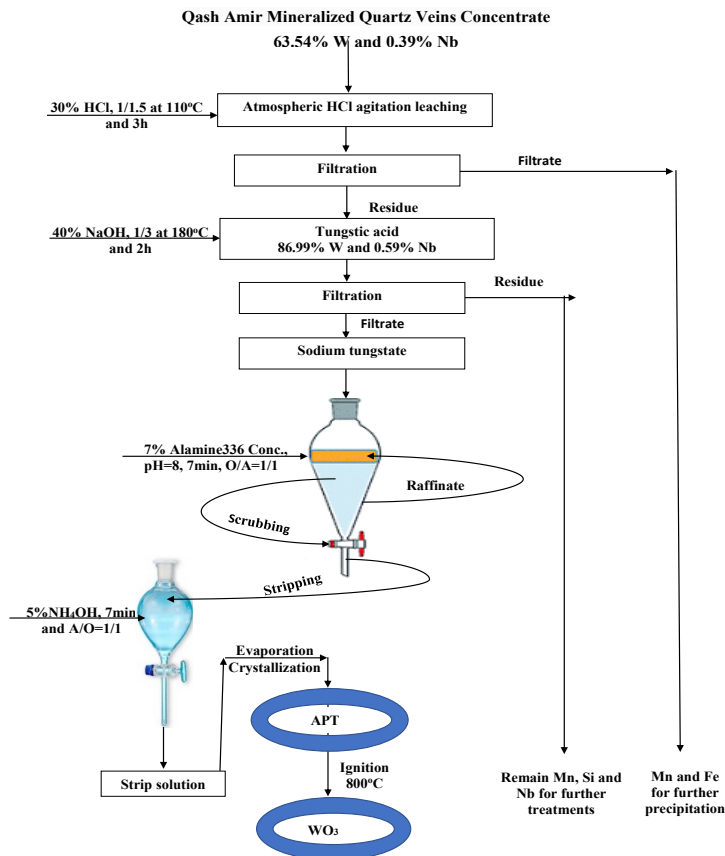


Fig. 11. Working flowsheet summarized the all chemical processing for preparation APT and pure WO<sub>3</sub>

hubnerite mineral concentrate was achieved after applying two successive atmospheric agitation leaching processes namely; HCl acid to produce tungstic acid followed by NaOH leaching process. From the latter, 99.1% of tungsten was leached as Na<sub>2</sub>WO<sub>4</sub> using 40% NaOH, 1/3, S/L ratio at 180°C for 2 h. Also, about 94% of tungsten was extracted by 7% Alamine 336 in kerosene, equilibrium time 7 min, O/A ratio 1/1. On the other hand, stripping was easily performed using 5% NH<sub>4</sub>OH solution at A/O of 1/1 at room temperature. Tungsten was recovered in the form of the marketable ammonium paratungstate (APT) which was then transformed by ignition into WO<sub>3</sub> at temperature of 750°C.

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