Extraction and separation of molybdenum and vanadium from alkaline leaching

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Abstract

Extraction of vanadium and molybdenum from alkaline leaching solution of boiler ash was investigated. The ash coming from heavy oil-fired electrical power station was leached with 8 mol dm^{-3} sodium hydroxide at 373 K. The leaching solution was cooled to 278 K; an alkali-precipitate was precipitated. The precipitate was dissolved in sulfuric acid and a selective solvent extraction process was applied. First, almost all the molybdenum was extracted with 1.5% (v/v) tri-n-dodecylamine/kerosene, stripped with 0.5 mol dm^{-3} NaOH and precipitated with CaCl$_2$ as CaMoO$_4$, then acidified with 30% HNO$_3$, the resulting H$_2$MoO$_4$.H$_2$O was calcinated at 723 K for 4 hours to give molybdenum oxide, next the vanadium was extracted from the raffinate coming from the first solvent extraction with 25% (v/v) tri-n-dodecylamine/kerosene at pH 1.8, stripped with 0.5 mol dm^{-3} NaOH, precipitated with (NH$_4$)$_2$SO$_4$ at pH between 7.5–8.5 as ammonium metavanadate and calcinated at 773 K for twenty four hours to yield 99.9% vanadium pentoxide.

Keywords

Fly ash · extraction · molybdenum · vanadium · tri-n-dodecylamine

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1 Introduction

There are increasing environmental concern in the world regarding the possible leaching of heavy metals from fly ash and boiler ash, generated by the electrical power stations that use heavy oil as a source of fuel, into land and ground water. Several studies showed that Cr, V and Mo were found to be leached out of the waste ash contaminating water and soil [1]-[3]. At the same time, ash contains some valuable metals especially V, Ni and Mo which can be leached with acidic and alkaline solutions, then selective precipitation is applied to separate the desired elements. Moreover, to produce pure V it is necessary to go through the solvent extraction technique. It is well known that each ash has its own identity depending on the characteristics of the burned oil and the place of ash formation, which involves development of an appropriate treatment to recover and purify the desired elements.

Considerable researches have been devoted to recover V and Mo from aqueous solutions by solvent extraction in view of the industrial and economic value of the recovered metals and elimination a pollution source [4, 5]. Many extractants have been used for V and Mo purification. Among these, Di-(2-ethylhexyl) phosphoric acid, Tributyl phosphate and amines [4, 6]-[11].

Ottartoun and Strandell [11] used H$_2$SO$_4$ to leach the ash produced by heavy oil-fired electrical power stations. During leaching, V was kept in its tetravalent states by feeding SO$_2$ to the solution and recovered by solvent extraction. A mixture of 20% Di-(2-ethylhexyl) phosphoric acid and 15% Tributyl phosphate was used. Vanadium was stripped from loaded organic phase with 1.5 mol dm^{-3} sulfuric acid.

Bal et al [12] studied the influence of temperature, NaOH concentration, and the pH on the stripping of V from Aliquat 336. He indicated that the limiting step of the stripping process consists in the slow transformation of the extracted polyoxometallate species (H$_2$V$_{10}$O$_{28}^{4-}$) into HVO$_4^{2-}$.

Chen et al [13] indicated that the Mo and V containing in leach liquor obtained by roasting of spent catalyst with soda carbonate at 1023 K were extracted by using 20% (v/v) trialkylamine (N235, R$_3$N, R = C8 – C10) and 10% (v/v) secondary octyl alcohol in kerosene. 10% (w/w) ammonia/water was used

as stripping agent. 0.375 mol dm^{-3} NH$_4$NO$_3$ was added to the stripping solution, over than 99% of V can be crystallized as ammonium metavanadate at pH$=7$–8.5 and over than 98% of Mo can be crystallized as ammonium polymolybdate at pH between 1.5–2.5.

The leaching solutions indicated in the literature and used to recover V and Mo from ashes and spent catalysts were H$_2$SO$_4$, H$_3$PO$_4$, HNO$_3$, HCl, HClO$_4$, NH$_4$OH, Na$_2$CO$_3$ and NaOH. It was found that H$_2$SO$_4$ and NaOH were the best leaching agents, and using NaOH leads to a negligible content of iron in the leach liquor comparing to H$_2$SO$_4$. The principal extractants used to recover V and Mo from the leach liquors were (D2EHPA+TBP, quaternary amine, tertiary amine). The synergistic mixture of D2EHPA+TBP is effective to extract V in its tetravalent state, so it is necessary to add a redox (feeding SO$_2$ gas) to the leach liquor, and this will complicate the process. Quaternary amines are effective extractants but they are expensive and the stripping of V and Mo is difficult. Tertiary amines are also attractive and effective for V and Mo extraction but they need to add a modifier to the organic phase to prevent third phase formation. But at the same time, using long chain aliphatic amines has some advantages: (low solubility in the aqueous phase, moderate cost of extraction processing and the stripping of the extracted elements by alkaline solutions is so easy).

The main purpose of this paper is developing an appropriate solvent extraction system, in laboratory scale, using (tri-n-dodecylamine + octanol-2/kerosene) as extractant to recover and separate Mo and V from alkaline leaching solutions that could offer an effectively and economically viable process.

2 Experimental

2.1 Reagents

The tri-n-dodecylamine (TDA) used as extractant agent was from Merck-Schuchardt with purity $> 95\%$, the Kerosene used as diluent was from PEMCO Chemicals and has as main properties: specific gravity 0.8; flash point 343 K; aromatics $< 1\%$, initial boiling point 473 K; final boiling point 523 K; sodium hydroxide (99%) used as leaching agent was from Analar, sulfuric acid (96%) from Fluka, ammonium sulfate (99%) from Sharlau, Octanol-2 (96%) used as a modifier was from Merck.

2.2 Digestion procedure of boiler ash and analysis
2.2.1 Digestion procedure

Boiler ashes were collected from Damascus thermal power station from the radiant furnace (local temperature 1673-1873 K). Prior to leaching, a mass of boiler ash was ground and mixed during 12 hours time to render the solid homogeneous, three samples (0.5 g each) from this mass were digested, at the same conditions in closed Teflon vessels (volume 100 cm^3) using a 10 cm^3 of aqua regia. Then 1 cm^3 of concentrated hydrofluoric acid was added and heated until the mixture became viscous, then 25 cm^3 of triple distilled water was added and heated again, before the dryness a mixture of (1 cm^3 HNO$_3$ + 1cm^3 HClO$_4$) was

added and heated for 2 minutes, finally the mixture was diluted to 100 cm^3 by triple distilled water.

2.2.2 Analysis of boiler ash

All standard solutions were prepared from Merck stock solutions containing 1000 mg dm^{-3} of each analyzed element. The working standards and the blank were prepared in a solution containing all reagents used in the digestion of the boiler ash sample and at the same concentration. Vanadium, nickel, molybdenum, iron, chromium, magnesium, cobalt, calcium, silicon, phosphorus were determined in the digested samples by Atomic Absorption Spectrometer (AAS vario 6, from Analytik-Jena, Germany), while sulfur was determined by Elemental analyzer (EA-3000, Italy) using BBOT reference material (EU-ROVECTOR, Italy). The chemical composition of boiler ash is presented in Table 1.

2.3 Leaching procedure of boiler ash

A block diagram for the recovery of vanadium and molybdenum from boiler ash is given in Fig. 1. Leaching test was performed in a 250 cm^3 three-necked Pyrex flask equipped with a thermometer, a mechanical stirrer and a reflux condenser for 4 hours using 8 mol dm^{-3} sodium hydroxide at 373 K and liquid to solid ratio (L/S) equal to 5 [14]. The alkali leaching solution was cooled to 278 K and a white alkali-precipitate containing V and Mo was precipitated. The precipitate was separated from the leach solution by filtration, more than 95% of the leached vanadium and molybdenum was precipitated.
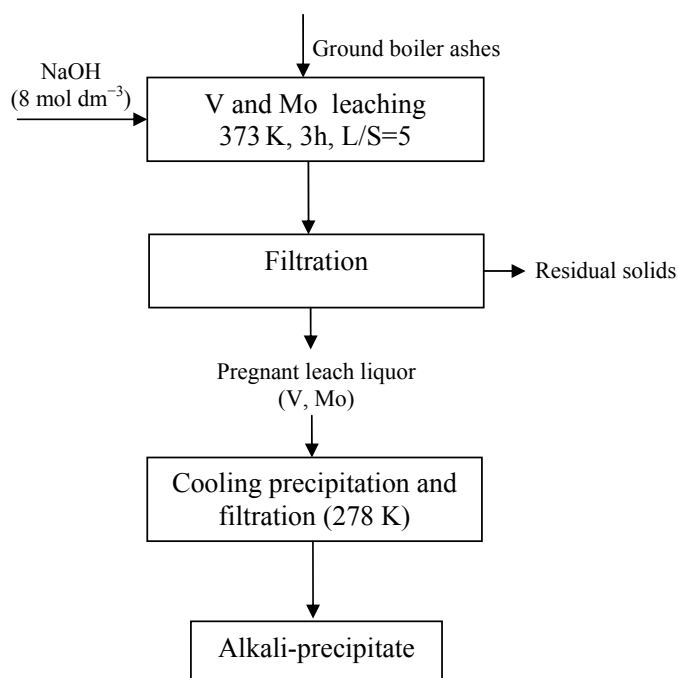

Fig. 1. Flow sheet for the recovery of V and Mo from boiler ash by NaOH leaching.

The main chemical compositions of the alkali-precipitate are reported in Table 2.

Tab. 1. Chemical composition of boiler ash.

Elements	Moisture	V	Ni	Mo	Fe	Cr
Wt(%)*	0.16±0.003	5.00±0.25	1.54±0.06	0.350±0.014	22.05±0.66	0.80±0.06
Elements	Mg	Co	Ca	Si	P	S
Wt(%)*	0.20±0.01	0.220±0.013	0.73±0.04	4.8±0.5	0.40±0.02	5.36±0.21

the mean value of three samples.

Tab. 2. Main chemical compositions of the alkali-precipitate.

Elements	V	Mo	Fe	S	Ni
Wt (%)	13.50±0.67	0.100±0.004	$\sim 0^*$	$\sim 0^{**}$	0.027±0.001
Elements	P	Ca	Si	Cr	Mg
Wt (%)	0.0050±0.0002	0.100±0.006	0.050±0.005	0.010±0.0007	0.010±0.0005

*,** *Undetectable by Atomic absorption and elemental analyzer techniques respectively.*

2.4 Preparation of aqueous and organic phases for solvent extraction

The aqueous phase was prepared by the addition of 50 g of the white alkali-precipitate with 10% sulfuric acid, in order to obtain nearly 0.137 mol dm^{-3} V and 1.042.10^{-2} mol dm^{-3} Mo.

Organic phases were prepared by dissolving the necessary amount of tri-n-dodecylamine and octanol-2 in kerosene in order to obtain mixtures with a range of concentrations from 1% to 30% on v/v basis. The addition of octanol-2 as a modifier to the organic phase was imperative to prevent the formation of a third phase (second organic phase) during the extraction process and accelerate phase separation. Before the extraction the solvent was pre-equilibrated with 5% sulfuric acid in order to convert TDA to the appropriate amine salt to provide an anion to exchange with metal species.

2.5 Solvent extraction procedure

The extraction was carried out, by stirring equal volumes (25 cm^3) of organic and aqueous phases for a fixed time of 10 min in a thermo-static water bath; the mixtures were allowed to settle for 1h, then the two phases were separated. The concentration of V and Mo in the aqueous phases were determined by AAS technique at wavelengths 318.5 nm and 313.3 nm respectively, while concentrations of V and Mo in the organic phases were calculated by material balance.

Since, the organic to aqueous phase ratio was (O/A=1), the yield of vanadium (Y$_V$ %) and molybdenum (Y$_{Mo}$ %) extraction were calculated from the following equation:

$$Y_M\% = \frac{[M]_{org} \times 100}{[M]_{i,aq}} = \frac{\{[M]_{i,aq} - [M]_{aq}\} \times 100}{[M]_{i,aq}} \quad (1)$$

$[M]_{i,aq}$ is the initial concentration of the metal M in the aqueous phase (mol dm^{-3}).

$[M]_{aq}$, $[M]_{org}$ are the equilibrium concentration of the metal M in the aqueous and organic phase (mol dm^{-3}) respectively.

While the yield of vanadium (Y$'_V$ %) and molybdenum (Y$'_{Mo}$

%) stripping were calculated as follows:

$$Y_M^{`}\% = \frac{\{[M]_{aq} \times \frac{A}{O}\} \times 100}{[M]_{i,org}} = \frac{4[M]_{aq} \times 100}{[M]_{i,org}}, \text{ since }, \frac{A}{O} = 4 \quad (2)$$

Where, $[M]_{aq}$ and $[M]_{i, org}$ are the equilibrium concentration of the metal M (mol dm^{-3}) in the aqueous phase and the initial concentration of the metal M in the organic phase respectively.

The pH of the aqueous solutions was measured by a Mettler Toledo, MP 230 pH meter.

3 Results and discussion

Preparatory tests were performed to determine the principal parameters controlling the extraction of V and Mo from sulfate solution (mixing time, octanol-2 (%) in the organic phase, pH of the aqueous phase, TDA concentration, concentration of V in aqueous solutions, temperature).

3.1 Effect of mixing time

Equal volumes (25 cm^3) of aqueous phase containing about (0.137 mol dm^{-3} V and 1.042.10^{-2} mol dm^{-3} Mo) at pH=2.2 and organic phase of 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene were mixed vigorously together at 298 K and at organic to aqueous phase ratio O/A=1 for different period of time (15, 30, 60, 90, 120 and 150 s). Fig. 2 shows that the 90 second of mixing is the minimum time to reach the equilibrium.

3.2 Effect of the modifier on V and Mo extraction

Unfortunately, mixing tertiary amine/aliphatic diluent with aqueous acidic solution gives a third phase, which is not tolerated in solvent extraction process, so the addition of small amount of high molecular weight long-chain alcohols to the tertiary amines will prevent third-phase formation without affecting the metal ion extraction or phase disengagement [15, 16].

Tests have proved that the addition of the octanol-2 in the range of 5-15% (v/v) to the organic phase (TDA/kerosene) did not affect the extraction of V and Mo (Fig. 3) and it was found that 5% (v/v) of octanol-2 is the minimum required concentration to prevent third-phase formation.
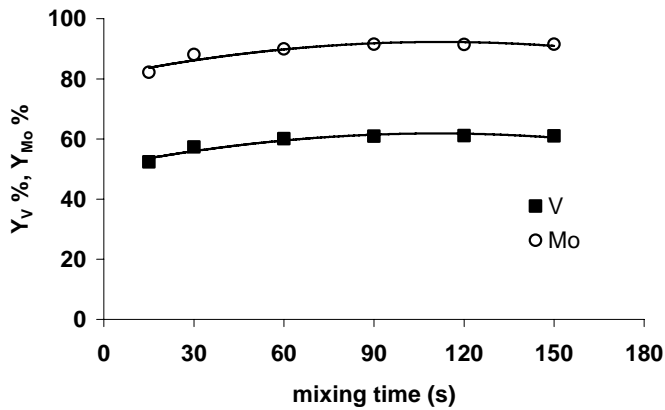
Fig. 2. Effect of mixing time on V and Mo extraction (O/A=1, pH = 2.2, T=298 K, 25 % (v/v) TDA + 5% (v/v) octanol-2 / kerosene)
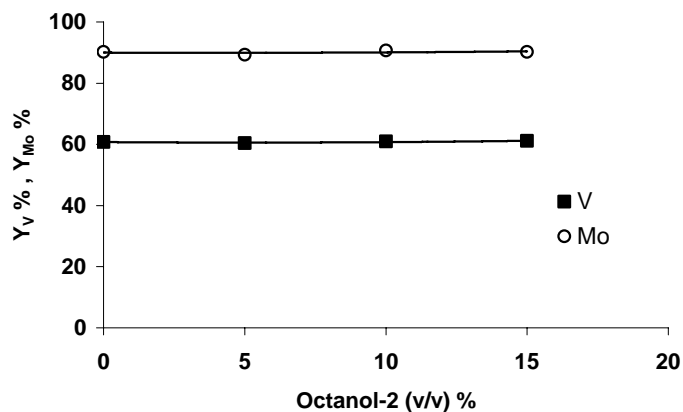

Fig. 3. Effect of octanol-2 on V and Mo extraction (T=298 K, pH=2.2, 25 % (v/v) TDA + (0, 5, 10, and 15%) (v/v) octanol-2/kerosene, O/A=1).

3.3 Effect of the pH of the aqueous phase on V and Mo extraction

Fig. 4 represents the effect of the pH of the aqueous phase on the yield of V and Mo extraction. We remark that, the V and Mo extraction yield decreases rapidly with increasing the pH of the aqueous phase. The extraction curves of V and Mo are nearly similar, they present the same behavior at different values of pH; the yield of extraction was almost complete for both at pH 1.8. At pH 2.2 the yield of extraction drops rapidly to 60% for the V, and 90% for the Mo, and at pH 6 the extraction is null. In our study all the experiments have been done at pH 2.2 to observe clearly the effect of each parameter on the extraction.

3.4 Effect of TDA concentration on V and Mo extraction

Fig. 5 shows that at very low TDA concentration almost all the Mo will be first extracted. In the competition for the available TDA the element with the highest extraction power or distribution coefficient will be preferentially extracted. With decreasing TDA concentration in the organic solution and since the yield of the extracted metal Y_M % is proportional to the distribution coefficient k_d, the Mo which has the highest distribution coefficient will be preferentially associated with the solvent.
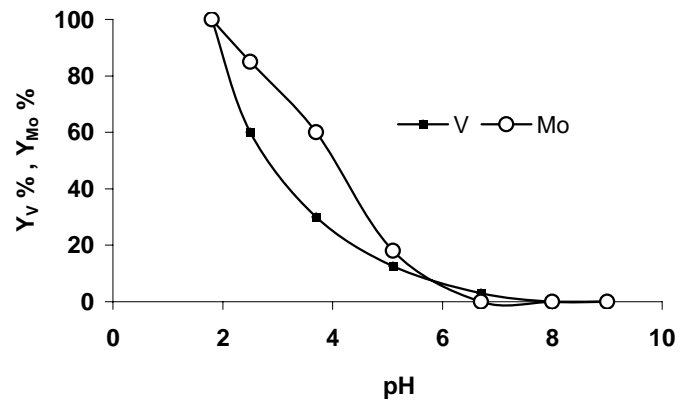

Fig. 4. Effect of pH on vanadium and molybdenum extraction (25% (v/v) TDA + 5% (v/v) octanol-2)/Kerosene.O/A=1, T=298 K.
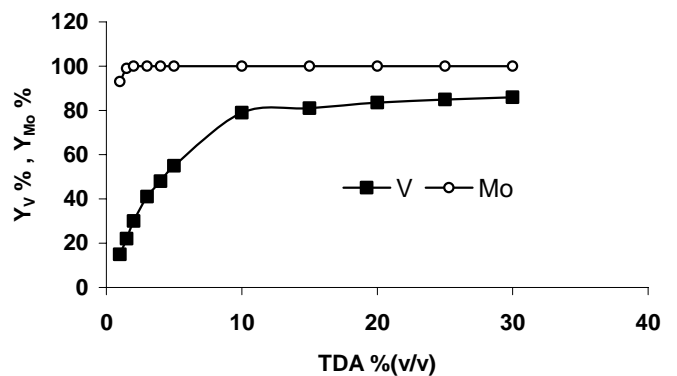

Fig. 5. Effect of TDA concentration on vanadium and Molybdenum extraction. pH=2.2, O/A=1, T=298 K.

3.5 Effect of initial V concentration in aqueous solutions on V and Mo extraction.

Fig. 6 shows that, whatever is the initial concentration of V in the aqueous phase the Mo will be first extracted from the solution by the TDA and afterwards the available TDA will be occupied by the V.
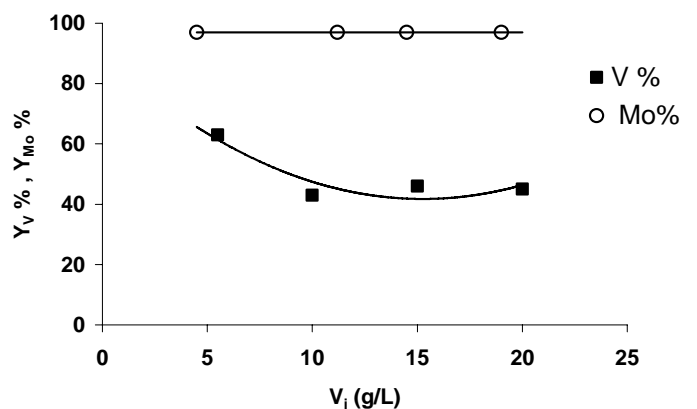

Fig. 6. Effect of initial V concentration in the aqueous phase on Vanadium and Molybdenum extraction. (25% (v/v) TDA + 5% (v/v) octanol-2)/Kerosene. pH=2.2, O/A=1, T=298 K.

3.6 Effect of temperature on V and Mo extraction

Fig. 7 shows the effect of temperature in the range 293-323 K on V and Mo extraction. It can be clearly seen that the yield

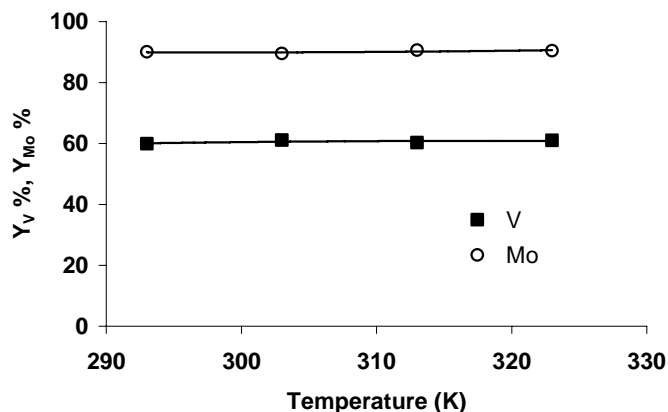of V and Mo extraction is not influenced by the temperature but the separation of the two phases was improved.

Fig. 7. Effect of temperature on the extraction of V and Mo (pH = 2.2, 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene, O/A=1).

3.7 Stripping of V and Mo from the loaded solvent

Since TDA is a weak base, the vanadium and molybdenum stripping from the loaded solvent is reversed by basic solutions. As indicated in Fig. 8, Four stripping agents at the concentration of 1 mol dm^{-3} were tested (NaOH, $(NH_4)_2CO_3$, Na_2CO_3 and $(NH_4)_2SO_4$) to strip V and Mo from the organic phase 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene. The yield of Mo stripping (Y'_{Mo}) was a little bit greater than the yield of V stripping (Y'_V), but they follow the same order:

$$NaOH > (NH_4)_2CO_3 > Na_2CO_3 >> (NH_4)_2SO_4$$
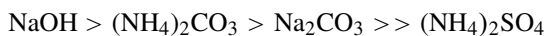
$(NH_4)_2CO_3$ was rejected since the ammonium metavanadate produced was precipitated in the mixer as well as $(NH_4)_2SO_4$ because of its low stripping yield. Consequently, sodium hydroxide is considered as the best stripping agent in comparison with sodium carbonate.
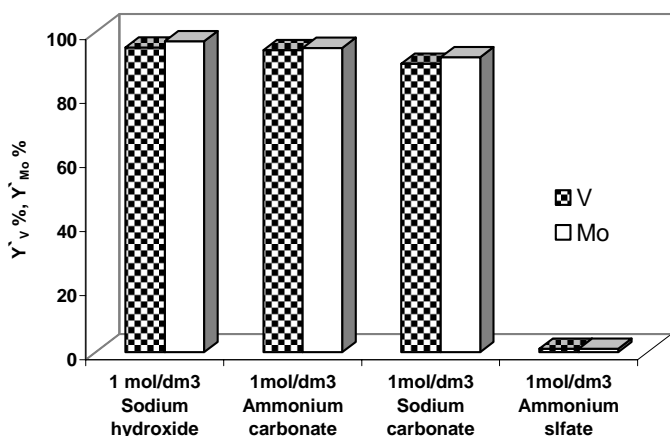

Fig. 8. Determination of the best stripping agent of the organic phase 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene ([Stripping agent concentration] = 1mol dm^{-3}, A/O=4, T = 298 K).

Tests have proved that no effect of temperature on the stripping process (Fig. 9) and 0.5 moldm^{-3} of NaOH was enough

(Fig. 10) to strip 95% of vanadium and molybdenum. The equilibrium between organic and aqueous phases was reached in 3 minutes at 298 K and A/O= 4.

Fig. 9. Effect of temperature on the stripping of vanadium and molybdenum from the organic phase 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene (A/O = 4, [NaOH] = 0.5 mol dm^{-3})
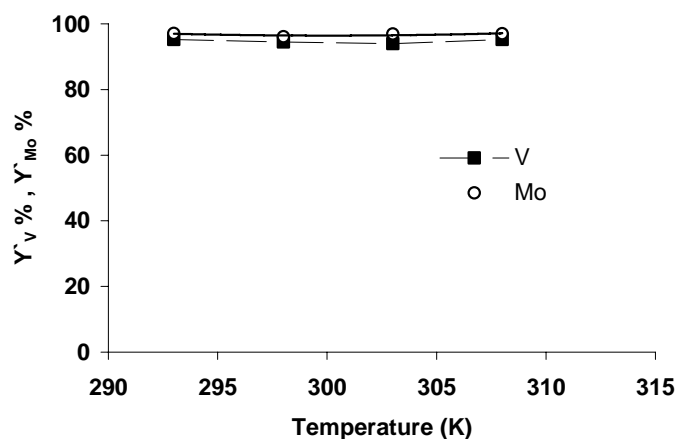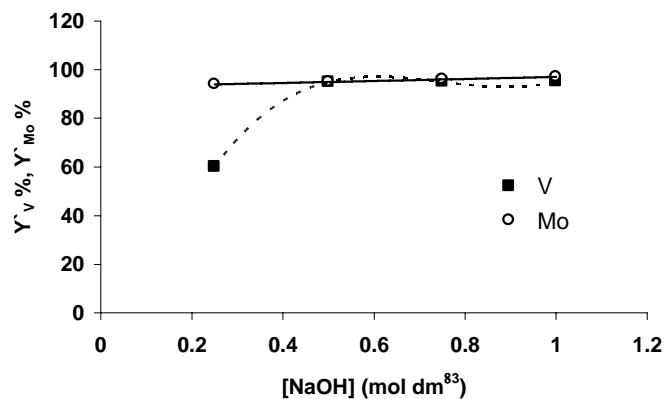

Fig. 10. Effect of NaOH concentration on the stripping of vanadium and molybdenum from the organic phase 25% (v/v) TDA + 5% (v/v) octanol-2/kerosene (A/O=4, T=298 K).
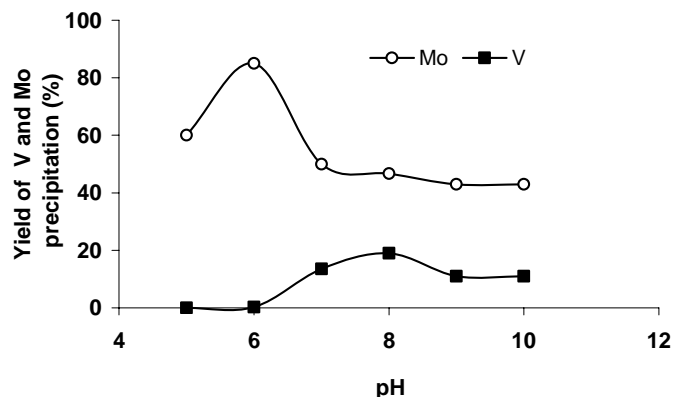

Fig. 11. Effect of pH on the precipitation of Mo and V with $CaCl_2$. T = 358 K.

Alkali precipitate Coming
from the leaching circuit

V and the rest of Mo

10% H_2SO_4

Dissolution stage
pH = 1.8

0.137 mol dm^{-3} V
$1.042.10^{-2}$ mol dm^{-3} Mo

Loaded organic
$1.042.10^{-2}$ mol dm^{-3} Mo
$\sim1.963.10^{-2}$ mol dm^{-3} V

NaOH
(0.5 mol dm^{-3})

First Solvent extraction
1.5% tri-n-dodecylamine

Stripping
O/A = 4

$5.212.10^{-4}$ mol dm^{-3} Mo
$9.815.10^{-4}$ mol dm^{-3} V

$7.46.10^{-2}$ mol dm^{-3} V
$3.96.10^{-2}$ mol dm^{-3} Mo

First raffinate (V)

0.118 mol dm^{-3} V
$5.212.10^{-5}$ mol dm^{-3} Mo

Barren organic

H_2SO_4

($CaCl_2.2H_2O$)

Raffinate
$1.178.10^{-3}$ mol dm^{-3} V

Second Solvent extraction
25% tri-n-dodecylamine

pH=6
Precipitation and
filtration

Filtrate

$7.46.10^{-2}$ mol dm^{-3} V
$5.212.10^{-3}$ m^{-3} Mo

Barren solvent

Loaded solvent
0.117 mol dm^{-3} V
$5.212.10^{-5}$ mol dm^{-3} Mo

NaOH
(0.5 mol dm^{-3})

Stripping
O/A = 4

$CaMoO_4$

30% HNO_3

Acidification
pH=1, t=363 K

Loaded stripping agent
0.443 mol dm^{-3} V
$\sim2.085.10^{-4}$ mol dm^{-3} Mo

$(NH_4)_2SO_4$

pH = 8
NH_4VO_3 crystallization and
calcination (773 K)

$H_2MoO_4.H_2O$
Calcination (723 K)
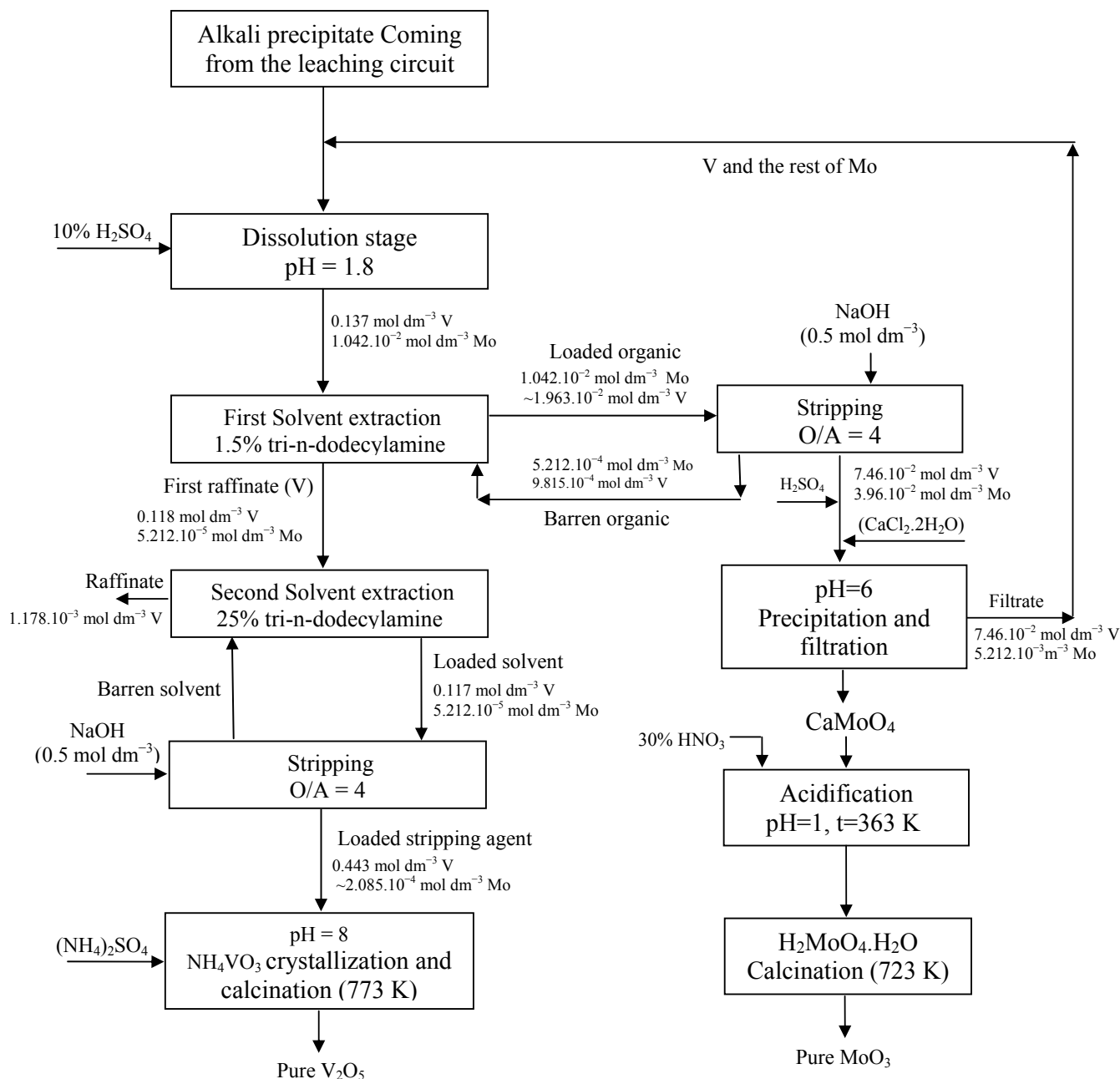
Pure V_2O_5

Pure MoO_3

Fig. 12. Flow sheet for the recovery of V and Mo by tri-n- dodecylamine/kerosene.

3.8 Procedure to recover and separate Mo and V.

3.9 Separation of molybdenum from vanadium by precipitation.

The molybdenum can be precipitated from the pregnant stripping solution by chemical precipitation with $CaCl_2.2H_2O$ in stoichiometric amounts according to Eq. 3.

$$CaCl_2.2H_2O + Na_2MoO_4 \longrightarrow CaMoO_4 + 2NaCl + 2H_2O \quad (3)$$
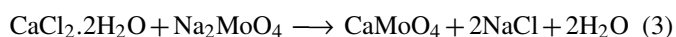
Fig. 11 shows that at pH 6, T=358 K and a mixing time of 60 minutes, over than 85% of the Mo will be precipitated as $CaMoO_4$, while the vanadium remains soluble in the solution.

Fig. 12 represents a procedure to separate V and Mo from the acidic leach liquor by solvent extraction. The alkali precipitate coming from the leaching circuit is dissolved in 10% sulfuric acid in order to obtain nearly 0.137 mol dm^{-3} V and $1.042.10^{-2}$

mol dm^{-3} Mo, the pH is adjusted to 1.8. Mo and V are separated and recovered from the leach liquor by solvent extraction in separate circuit. First the Mo is selectively extracted from the feed solution by 1.5% (v/v) TDA in kerosene (T=298 K, O/A=1), more than 99% of the Mo is extracted and 15% of the V co-extracted. V and Mo are stripped from the pregnant organic phase with 0.5 mol dm^{-3} NaOH, the pH of the loaded stripping agent is adjusted to 6 by 10% (v/v) sulfuric acid, followed by the addition of calcium chloride in stoichiometric amounts, more than 85% of the Mo is precipitated as $CaMoO_4$.

The stripping agent containing vanadium and the rest of the molybdenum is sent to the dissolution stage. The calcium molybdate is acidified with 30% nitric acid to adjust the pH to 1 and heated to 353–363 K. Consequently, Mo is precipitated as molybdic acid ($H_2MoO_4.H_2O$) and calcined at 723 K for 4

hours to give molybdenum oxide (MoO_3).

The first raffinate containing the V, coming from the first extraction is submitted to the second solvent extraction with 25% (v/v) TDA in kerosene (T=298 K, O/A=1), more than 99% of the V will be extracted. V is stripped from the loaded solvent with 0.5 mol dm^{-3} NaOH, the pH is adjusted to the range 7.5–8.5 followed by the addition of $(NH_4)_2SO_4$ to the loaded stripping agent. After two hours of mild agitation, a crystal of ammonium meta vanadate produced will be precipitated, separated by filtration and decomposed at 773 K for 24 hours to yield a pure vanadium pentoxide.

4 Conclusion

The extraction of vanadium and molybdenum from alkaline leaching solution of boiler as has been studied using tri-n-dodecylamine/kerosene containing 5% (v/v) octanol-2 as modifier.

The percentage of octanol-2 in the organic phase in the range (0-15%) and the temperature in the range (293-323 K) had no effect on vanadium and molybdenum extraction.

The pH of the aqueous phase and the concentration of tri-n-dodecylamine/kerosene in the organic phase play an important role in the extraction of vanadium and molybdenum as well as their separation from each other.

Sodium hydroxide was found to be the best stripping agent of vanadium and molybdenum from the organic phase tri-n-dodecylamine/kerosene and more than 95% of both elements can be stripped in one stage using 0.5 mol dm^{-3} of NaOH.

A simple process to recover a high purity vanadium and molybdenum was proposed. First V and Mo were leached out from the boiler ash by alkaline solution, then separated by solvent extraction in separate circuit in two extraction stages using two different concentrations of TDA (1.5% (v/v) and 25% (v/v)) in kerosene.

The proposed method is simple, cheap and can be, continuously examined on a micro-pilot scale.

The remaining boiler ash after the leaching process will become less dangerous to the environment.

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