



Sequential Leaching of Vanadium from Heavy Fuel Oil Fly Ash Generated from Saudi Arabia Thermal Power Plants

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

The leaching characteristics of vanadium (V), iron (Fe) and nickel (Ni) from fly ash (FA) waste of power station in Saudi Arabia were studied. The kinetics and thermodynamic characteristics of V leaching from FA using a series of leaching agents (H₂O, NH₄OH, HCl, H₂SO₄) were studied. The rate of leaching of V was fast; reached equilibrium in a short time and followed a first-order rate equation with an overall rate constant k of 0.076 min⁻¹. The thermodynamic parameters of V leaching in different leaching agents were critically investigated. The negative values of ΔH and ΔG were interpreted as the exothermic and spontaneous reaction of V leaching onto the leaching solution. Sequential proposed scheme for V leaching is also included.

Keywords: *Characterization; heavy fuel oil fly ash; leaching; trace elements (V, Fe and Ni); kinetics and thermodynamics; metal recovery; thermal power plants.*

1. INTRODUCTION

Oil fuel and coal are the most employed fuel for thermal power generation in many countries [1]. However, heavy fuel oil, diesel and natural gas are also used for power generation [2]. Upon burning heavy fuel oil and coal, fly and bottom ash are generated [3]. Currently, Saudi Arabia power stations are powered by heavy fuel oil, diesel, and/or natural gas [4]. Large amount of fly ash (FA) is directly discharged as landfills and ash ponds, whereas an approximate percentage (20 %) of FA is used in concrete production, road basement material, waste stabilization/solidification, cement clinkers, amendments of soft soil, and more recently in geo polymers [5]. FA of coal origin is characterized by the high content of Si and Al which make it a suitable ingredient for normal Portland cement and an excellent starting material for geo polymers [6-8]. On the other hand, heavy oil FA (HOFA) is characterized by a high C content and low Si/Al content [9]. The chemical composition of FA is dependent upon the nature of the feeding fuel, either coal or petroleum material. Besides Al, Si, Fe and Ca, FAs of coal origin are also rich in metals like As, Be, B, Cd, Cr, Co, Mg, Mo, Pb, Se and V [8]. FA of heavy fuel oil has received less attention, and the published studies are mainly limited to surface characterization [10].

Limited studies have addressed characterization and utilization of heavy oil FA [10]. The generated FA in the stations was estimated to be 418.5 tons in 2009 [11], however, an increase in the FA amount is expected due to the growth rate of energy demand. Public agencies have addressed the potential risk of FA generated in the local power stations, since FA is a toxic material and should not directly discharge into the environment [11-13]. Coal fly ash (CFA) and heavy oil fuel fly ash (HOFA) residues from different power plant stations contains considerable amounts of V, Fe and Ni [14]. Some heavy metals can potentially be released into soil, surface water and groundwater by leaching processes, resulting in environmental health concerns [15]. pH and oscillation time are the important factors affecting metal leaching from FA [12,16-18]. The composition of FA depends on the composition of source of CFA or HOFA and co-feed materials, combustion technology, pollution control technology and handling technology of FA [19,20]. Several hazardous elements e.g. As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, and Se, are present in small

quantities in HOFA [20]. Thus, extraction of heavy metals from fly ash using leaching agents has been considered to be a proper way to control metal contamination and resource recovery [12,21]. A series of leaching agents e.g. EDTA, acetic acid and various acids has been used for metal (Zn, Pb) leaching from fly ash [12, 22]. The U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) is the regulatory method required when determining whether a solid waste is hazardous after leaching from hazardous pollutants [23].

A wide range of standardized leaching tests with variable agitation method, liquid to solid ratio (L/S), complexity, reagents, temperature, contact time along with some others non-standardized method have been reported [14,24]. A detailed discussion on the worldwide standard leaching tests is out of the scope of this study and can be found elsewhere [24,25]. Any attempt to integrate the outcomes of such a wide range of leaching conditions must be undertaken with due care. Based on the significant growth in Saudi Chemical industries [23-27], the present study focused on: i) Evaluation of the leachability of V, Fe and Ni from fly ash samples derived from three thermal power plants to phase out total V, Fe and Ni in FA caused by these industrial activities to monitor and hamper these metal ions and to prevent their subsequent effects in Saudi inhabitants; ii) Assigning the kinetics of leaching V from the fly ash samples and finally iii) Studying the thermodynamic characteristics of V, Fe and Ni using solvent extraction.

2. EXPERIMENTAL

2.1 Instrumental and Apparatus

A Perkin Elmer inductively coupled plasma – optical emission spectrometer (ICP- OES, Optima 4100 DC (Shelton, CT, USA) was used and operated at the optimum operational parameters for V, Fe and Ni determination. The ICP-OES instrument is optimized daily as recommended by the manufacturer. A Perkin Elmer ICP-MS Sciex model Elan DRC II (California, CT, USA) was also used to measure the ultra trace concentrations of Ni, Fe and V in the leachant liquor. All samples are analyzed first using the optima 4100 DV ICP-OES spectrometer. If the resulting concentration of V, Fe and Ni in the leachant liquor was below $1.0 \mu\text{g mL}^{-1}$, ICP-MS is performed to analyze analyte concentration with acceptable accuracy. A Milli-Q

Waters Plus system (Milford, MA, USA) and a Thermo Fisher Scientific Orion model 720 pH Meter (Milford, MA, USA) were also used.

2.2 Reagents and Materials

All chemicals and solvents used were of analytical reagent grade and were used without further purification. Deionized Water was used through the work. Standards of nickel, iron and vanadium nitrate salts were purchased from Aldrich Chemicals Co Ltd, (Milwaukee, WI, USA) and were used for preparation of stock solutions ($1000.0 \mu\text{g mL}^{-1}$) of nickel, iron and vanadium. More diluted solutions ($1.0 - 100 \mu\text{g L}^{-1}$) of these elements were prepared by suitable dilution of the stock. Stock solutions were stored in low density polyethylene bottles (LDPE) in dark. Stock solutions ($0.1-1\%$ w/v) of dimethylglyoxime, sodium diethyldithiocarbamate (Na-DDTC) and ammonium pyrrolidind diethyldithiocarbamate (Merck, Darmstadt, Germany) were prepared in ethanol-water. Methylisobutylketone, (MIBK) was purchased from Fluka, AG (Buchs, Switzerland).

2.3 Sampling

Rabigh is a small towns in Saudi Arabia and has one of the lowest populations. It lies at latitude 23° N and longitudes $400 30'E$ along the Red Sea coast in the west central part of the Arabian Shield, Saudi Arabia. HOFA samples of heavy fuel oil (Vacuum gas oil, Bunker "C") generated from Rabigh water desalination power station were randomly collected from three locations around the station. The samples were then air dried for 21 days and sorted to remove unwanted materials. FA samples were washed with HCl solution (1.0 mol L^{-1}) for 16-17 h at 25°C where mixed with HCl ($37\%v/v$) solution at FA waste/HCl weight ratio of 1: 20 (m/v) in a polytetrafluoroethylene beaker. The mixture solutions were filtered and washed several times with deionized water just to remove the water-soluble impurities and the adhered particles on the surface. The samples were dried in oven at 105°C for 24 h and kept in the desiccators prior to activation. Three replicate samples were collected from the same site and analyzed separately.

2.4 Experimental Procedures

2.4.1 Analysis of the certified reference material (IAEA- Soil-7)

An accurate weight ($0.14 - 0.18 \pm 0.01\text{g}$) of the CRM (IAEA-Soil-7) sample was transferred into a

Teflon beaker (50.0 mL) containing HF (7.0 mL), concentrated HCl (2.0 mL), and concentrated HNO_3 (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture heated slowly for 1h at $100-150^{\circ}\text{C}$ on a hot plate. After the evolution of NO_2 fumes had ceased, the reaction mixture evaporated almost to dryness and mixed again with concentrated HNO_3 (5.0 mL). The process was repeated thrice and the mixture was again evaporated to dryness. After evaporation, the solid residue was then re dissolved in dilute nitric acid (10.0 mL , 1.0 mol L^{-1}). The resulting mixture filtered through a Whatman 41 filter paper, transferred to volumetric flask (25.0 mL) and the solution was completed to the mark with deionized water. Metal concentrations were determined using the ICP-OES and/ or ICP-MS except potassium measured with flame atomic absorption spectrometry. Similarly, the aqueous solutions of the collected soil samples were prepared following the same procedure applied to the certified reference material.

2.4.2 Wet digestion for determination of total V, Fe and Ni content in fly ash

The sample preparation procedure by Narin et al [28] was applied for the leaching of trace metals from the soil samples. FA samples were dried at 110°C for 2h, ground through a 200 mesh sieve and homogenized for analysis. HOFA samples were dried to a constant weight at 110°C . The water content was close to 1%. Several representative aliquots (100, 200 and 300 mg) were mineralized (in duplicate) using aqua regia (20 mL) in a microwave furnace, model MAR5X (CEM, USA). The volume was adjusted to 250 mL and filtered, and the filtrate was analyzed for V, Fe and Ni. The V, Fe and Ni content was 1.6% (in weight). The C element content of the oil fly ash (inclusive carbonate, carbon and residual oily material) was evaluated by thermal decomposition at 1000°C . The weight loss from thermal decomposition at 1000°C for 6 h was about 85%. Silicon content was evaluated at between 3% and 4% by X-ray fluorescence analysis.

Alternatively, an accurate weight ($0.5 - 0.6 \pm 0.01\text{g}$) of the FA sample was transferred into a glass beaker containing conc. HCl (2.0 mL), HClO_4 (5.0 mL) and nitric acid (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture was then heated slowly at 100°C for 1h on a hot plate with constant stirring. After complete evolution of nitrogen oxides fumes, the reaction mixture was

evaporated almost to dryness. To the solid residue was then mixed with conc. HNO₃ (5.0 mL). The digestion step was repeated three times and the mixture was again evaporated to complete dryness. The solid residue was re dissolved in dilute HNO₃ (5.0 mL, 1.0 mol L⁻¹) and the resulting solution mixture was filtered through a Whatman 41 filter paper, transferred to volumetric flask (25.0 mL). The solution was finally completed to the mark with deionized water and analyzed by ICP-OES under the optimized operational parameters for the determination of V, Fe and Ni (Table 1). A blank experiment was also carried out and analyzed by ICP-MS. The average concentration (µg g⁻¹) of the tested V, Fe and Ni was determined by difference employing the following equation:

$$\text{Average V concentration, } \mu\text{g.g}^{-1} = (\text{C}-\text{B}) \times \text{V}/\text{m} \quad (1)$$

where C is the average element concentration in sample solution (µg mL⁻¹) of the FA sample; B is the blank reading; V is the sample volume (mL) and m is the mass of fly ash samples in grams. Quantification of the tested elements was performed for each fly ash sample with the aid of the corresponding standard calibration graph. If the resulting concentration of the element is below 1.0 µg/mL, ICP-MS is performed to determine the concentration with great accuracy. The measurements were validated by analysis of certified reference concentrations of each ion under the operational conditions of ICP-OES or ICP-MS instrument.

2.4.3 Recommended leaching experiments

2.4.3.1 Effect of leaching agents (H₂O, NH₃, HCl, HNO₃, and H₂SO₄) on V leaching

An accurate weight (0.5±0.001 g) of dry fly ash sample was shaken individually well with various the leaching agents H₂O, NH₃, HCl, HNO₃, and

H₂SO₄ (1.0 M) for 3 hrs. After filtration and separation of the fly ash residues, the filtrate and the washings of the leachate solutions were critically separated out and analyzed for nickel, iron and vanadium using ICP-OES. Metal ions leached at equilibrium (q_e) and the distribution ratio (D) of the metal ions leached on the test solutions were then calculated as reported [29].

2.4.3.2 Effect of leaching agents concentration on V leaching from fly ash

An accurate weight (0.5±0.001 g) of fly ash was shaken individually well with ammonia, HCl, HNO₃ and H₂SO₄ concentrations at various concentrations (0.25 -7.5 M) for 2h at room temperature. After separation of the solid residue, the filtrate solutions and the washings were filtered and analyzed for nickel, iron and vanadium by ICP-OES.

2.4.3.3 Influence of leaching time on V leaching

To investigate the influence of contact time of the fly ash with the leaching agents tested, accurate weights (0.5±0.001 g) of the fly ash sample (Shoiba, Jeddah, and Rabigh) were left in contact with the leaching agents: H₂O, NH₃, HCl, HNO₃, and H₂SO₄ (1.0 M) for various time intervals (1-7 h) individually. After equilibrium, the solid fly ash residue was separated out by filtration. The filtrate solutions and the washings were successfully collected and analyzed for nickel, iron and vanadium at the optimum operational parameters an accurate weights (0.5±0.001 g) of the fly ash sample (Shoiba and Rabigh) were left in contact with the leaching agents agent water, HCl, ammonia solution, sulfuric acid and nitric acid (1.0 M) for various time intervals (1-7h) individually. After equilibrium, the solid fly ash was separated out by filtration and finally the filtrate solutions were analyzed for Fe, Ni and V at the optimum operational parameters of ICP-OES.

Table 1. ICP-OES operational conditions and wavelength (nm) for trace metal determination

Parameter	
Rf power (kW)	1050
Plasma gas (Ar) flow rate, Lmin ⁻¹	15
Auxiliary gas (Ar) flow rate, Lmin ⁻¹	0.2
Nebulizer gas (Ar) flow rate, Lmin ⁻¹	0.80
Pump rate, mL min ⁻¹	1.5
Observation height, mm	15
Integration time, S	10
Radial view	20
Wavelength, nm	Ni: 231.604 nm Fe: 238.204 nm V: 290.88 nm

2.4.3.4 Sequential leaching of V from fly ash samples

Sequential leaching of the fly ash was carried out in three steps according to the following recommended procedures [29] as follows:

- i. An accurate weights (0.5 ± 0.001 g) of the fly ash sample (Shoiba or Rabigh) were left in contact for 24 h with the leaching agent (water, 100 mL) with constant stirring in a mechanical shaker. After 24 h, the solid residue was separated out and the filtrate was analyzed for iron, nickel and vanadium under the recommended operational parameters of ICP-OES. The resultant solid residue was then subjected to leaching with ammonium acetate (100 ml, 1.0 mol L^{-1})
- ii. The solid residue of water leaching step was sequentially treated with ammonium acetate (100 mL, 1.0 mol L^{-1}) as leaching agent and left in contact for 24 h with constant stirring in a mechanical shaker. After 24 h, the solid residue was separated out and the filtrate was analyzed for iron, nickel and vanadium under the recommended operational parameters of ICP-OES. The resultant solid residue was then subjected to leaching with HCl (100 ml, 1.0 mol L^{-1})
- iii. The resultant solid residue of fly ash after ammonium acetate leaching step was sequentially treated with HCl (100 mL, 1.0 mol L^{-1}) as leaching agent and left in contact for 24 h with constant stirring in a mechanical shaker. After 24 h, the final solid residue was separated out and the filtrate was subjected to analysis for V, Fe and Ni.

2.4.4 Extraction experiments

2.4.4.1 Sequential extraction of V, Fe and Ni from fly ash by solvent extraction

Solvent extraction was performed by mixing 20 mL of leachate with 20 mL of the organic phase for 30 min [64]. The organic phase was prepared by dilution of the extractant in kerosene (Fluka). Isodecanol (Fluka) was added to the solution to give a 5% (v/v) concentration in order to prevent the formation of a third phase during the extraction process. The extractant concentration was adjusted to the selected values. Preliminary experiments were performed with synthetic V, Fe

and Ni ions solutions (close to $50 \mu\text{g/ mL}$) in order to define the optimum experimental conditions. The concentration of iron, nickel or vanadium in the aqueous phase was determined by ICP-OES. The results were then applied to the leachates when relevant (for Fe, Ni and / or V concentrations higher than 200 mg L^{-1}). The leachates were submitted to a pre-treatment with hydrogen peroxide in order to oxidize any fraction of vanadium that could be in a reduced form (IV), less extractable): a 50% excess of hydrogen peroxide was added compared to the total amount of V. The pH of the leachate was then controlled at the suitable value (generally pH 3). Stripping was performed by contacting equal volumes of the organic and stripping phases (NaOH, NH_3 , $\text{NH}_4\text{Cl}/\text{NH}_3$, NH_4NO_3) at known concentration for 30 min. The concentration of vanadium in the aqueous phase was used in the mass balance equation for the determination of the stripping efficiency. Alternatively, an accurate volume (500.0 mL) of leachate solution was shaken well with chloroform (15.0 mL) in the presence of ammonium pyrrolidine dithiocarbamate (5 mL, 0.5% m/v) for 5 min. After equilibrium and layer separation, the organic extract was separated out. Nickel, iron and vanadium were then stripped from the organic extract by shaking well with 10 mL of nitric acid (10 mL) containing mercuric (II) ions. The Ni, Fe and Fe was then stripped in the nitric acid layer and analyzed by ICP-OES. The exact concentrations of metals were then determined after considering the preconcentration factor.

2.4.4.2 Recovery of total V and Fe

After separation of nickel by dimethylglyoxime [30], an accurate volume (500.0 mL) of the HCl leachate solution was shaken well with ammonium pyrrolidine dithiocarbamate (APDC) at pH 3 and shaking with chloroform (15.0 mL) for 5 min. After equilibrium and layer separation, the organic extract containing total V and Fe was separated out. Vanadium and iron were then stripped from the organic extract by shaking well with 10 mL of nitric acid (10 mL) and analyzed by ICP-OES. The exact concentration of metals was then determined after considering the preconcentration factor. Attempts to isolate iron(III) after reduction to iron(II) with sodium sulphite in HCL media from the vanadium solution was achieved by shaking with 1, 10 phenanthroline and rose bengal as counter in chloroform as described [30].

3. RESULTS AND DISCUSSION

3.1 Total Digestion of Fly Ash Samples

Preliminary investigations on the chemistry of fly ash in the different sources (Jeddah, Shouiba and Rabigh power stations) of fly ash resulting from various power stations in Kingdom of Saudi Arabia have revealed considerable content of trace metal ions particularly nickel, iron and vanadium. Therefore, detailed investigation on the chemical composition of dry fly ash at three different locations of water treatment station in Jeddah city was critically carried out at water treatment station at Jeddah, Rabigh and Shuiba water treatment stations. For this purpose various fly ash samples were carefully collected from the selected water plant stations and the samples were critically digested by concentrated HCl-HNO₃ (1:3 v/v) system following the recommended procedures [28]. The results are given in Table 2. The results revealed considerable amount of vanadium, iron and nickel in the three fly ash samples. The content of iron, nickel and vanadium lies in the range 4057.0 -9913.9; 751.2- 2632.9 and; 75.12-429.49 and 3625.1- 5601.3 µg/ g, respectively. These values are comparable well level content in the study reported by other authors except for nickel [31,32]. It is well known that nickel species are able to form stable complex and / or organo nickel compounds with the oxygenated and organo- carbon species in the fly ash samples. Complete digestion of this class of compounds is too tedious and required enough digestion. Therefore, the low value of nickel is most likely attributed to the incomplete digestion of total fly ash. Thus, it is recommended to carry out the digestion step in a vacuum step to achieve complete digestion and conversion of total metal ions to simple.

3.2 Influence of Leaching agent on V Leaching from Fly Ash Samples

Based on the preliminary investigations on the content of total iron, nickel and vanadium in the various fly ash samples resulting from Jeddah, Shouiba and Rabigh power stations, detailed investigation on the use of acid and alkaline leaching agent was critically carried out at water treatment station at Jeddah , Rabigh and Shuiba water stations. Changing the type of leaching agent may change the efficiency of the leaching process, the selectivity of metal leaching and may also the speciation of the metals, which in

turn may affect their behavior in terms of solvent extraction and precipitation. Based on the speciation of vanadium in solution [33-37], vanadium is expected to be in the form of VO₂⁺ in acidic solutions and in the form of VO₃(OH)²⁻ and VO₄³⁻ in alkaline solutions . Thus, for this purpose various leaching agents (HCl, HNO₃, H₂SO₄), and alkaline solutions (ammonia solution) agents were used. Several analytical procedures (pH-calorimetric measurements, ionic chromatography and proton-induced X-ray emission analysis) have been carried out to identify extractable Fe, Ni and V species [37]. However, in the present study, ICP-OES was critically used for the measurements of the total iron, nickel and vanadium in the leachant solution at the optimum operational parameters of each element.

3.2.1 Acid leaching of V from FA samples

The acidic leaching was performed using various concentrations of HCl, HNO₃ and H₂SO₄. Taking into account the composition of HOFA samples and the experimental procedure for the leaching process, it was possible to calculate the extraction percentage and the distribution ratio for the various metal ions (Fe, Ni and V) in relation to total amount in oil fly ash. The fact that, fly ashes are treated by means of one of the following four methods [36,37], cement solidification, chemical stabilization, melting treatment, and acid extraction. Usually the leaching is the first important operation for the whole treatment process.

A limited number of research works of leaching with HCL have been reported to date [38,39]. Thus, we conducted a fundamental study for systematic investigation on the application of a series of acid leaching employing H₂SO₄, HCl and HNO₃ to the leaching process of heavy metal from fly ash in present work. Hence, the effect of mineral acids and their concentrations on V, Fe and Ni extraction from the fly ash was examined at a liquid/solid ratio of 50:1, contact time of 180 min at room temperature. The results obtained are summarized in Tables 3-5 and representative data for leaching of V in HNO₃ and HCl are shown in Fig. 1. The extraction rate for the tested metal ions (V, Fe and Ni) decreased with lowering acidity value. This suggests that the leaching can be regarded as some kind of ions exchanging process, that is, metal elements will be replaced by H⁺ and dissolved into the solution from the fly ash particles. Thus, it can be concluded that, the acid

leaching is dependent of the metal involved. Acidic leaching extracted the metals to various extents, but non-negligible concentrations of each of them were also present in the rinsing baths. Considering the leaching efficiency, acidity in the range 1-3 M is recommended.

Table 2. Analysis of total V, Fe and Ni in fly ash samples by wet digestion in Jeddah, Rabigh and Shuaiba power stations[†]

Source fly ash	Concentration, $\mu\text{g g}^{-1}$		
	Fe	Ni	V
Jeddah power station	9913.9 \pm 23.2	751.2 \pm 13.7	3625.1 \pm 21.8
Rabigh power station	4057.0 \pm 32.7	2632.9 \pm 41.2	5601.3 \pm 27.6
Shuaiba power station	7946.2 \pm 13.2	2610.0 \pm 53.2	5519.6 \pm 28.1

[†] The results are the average of three measurements.

Table 3. Effect of various leaching agents HCl, H₂SO₄, HNO₃ and H₂O on V, Fe and Ni dissolution from fly ash collected from Jeddah power station[†]

Leaching medium	Leaching time	Fe (ppm)	Ni (ppm)	V (ppm)
Water	1h	3569.1	1596.3	1581.7
	3h	3557.1	1878.5	1875.2
	5h	5847.9	1691.9	2304.1
	7h	5984.1	2101.6	2365.2
HNO ₃	1h	33377.7	1581.4	13990.0
	3h	68818.6	2857.2	20625.6
	5h	78668.9	3616.0	26369.4
	7h	86389.4	4461.2	33856.9
HCl	1h	55149.5	2047.1	16531.6
	3h	67309	3056.5	18119.6
	5h	72558.1	3420.6	20770.8
	7h	75481.7	3485.1	20830.6
H ₂ SO ₄	1h	39719.7	1355.4	10864.2
	3h	44700.4	1591.9	11737.7
	5h	45512.7	1652.5	13202.4
	7h	46085.2	1653.8	12363.5

[†] The results are the average of three measurements.

Table 4. Effect of various leaching agents (HCl, H₂SO₄, HNO₃) (mol L⁻¹) and H₂O on V, Fe and Ni dissolution ($\mu\text{g/g}$) from fly ash collected from Rabigh water power station[†]

Leaching medium	Leaching time	Fe	Ni	V
Water	1h	900.5	1703.2	2840.0
	3h	262.9	1636.6	3342.4
	5h	410.6	1906.8	4998.3
	7h	599.7	2210.3	3988.0
HNO ₃	1h	1474.4	1293.8	5561.0
	3h	1357.8	1452.4	6220.5
	5h	2053.3	1980.0	8441.0
	7h	2355.8	2293.8	10033.3
HCl	1h	1545.9	1457.4	5767.6
	3h	1598.5	1587.2	6177.1
	5h	1763.6	1601.2	6332.2
	7h	1926.2	1944.7	7769.6
H ₂ SO ₄	1h	967.4	801.1	3873.6
	3h	n.d.	n.d.	n.d.
	5h	n.d.	n.d.	n.d.
	7h	1197.6	914.8	4434.5

[†] The results are the average of three measurements.

Table 5. Effect of various leaching agents HCl, H₂SO₄, HNO₃ (mol L⁻¹) and H₂O on V, Fe and Ni dissolution (µg/g) from FA collected from Shouiba power station[†]

Leaching medium	Leaching time	Fe	Ni	V
Water	1h	221.7795	436.919	1819.389
	3h	7.968127	45.81673	10737.05
	5h	0	51.79283	11188.58
	7h	61.08898	1601.594	18154.05
HNO ₃	1h	2106.738	3967.979	13909.27
	3h	4078.052	7505.003	28519.01
	5h	5270.847	9426.284	37378.25
	7h	5648.432	9879.92	39052.7
HCl	1h	3177.845	6221.555	22275.61
	3h	3595.596	6860.194	24244.24
	5h	4015.349	7534.201	26800.13
	7h	4500.501	8575.242	30083.42
H ₂ SO ₄	1h	2999.667	3842.928	16712.15
	3h	2969.717	3971.381	17111.48
	5h	3268.552	4117.804	18216.31
	7h	3456.24	4510.483	20066.56

[†] The results are the average of three measurements.

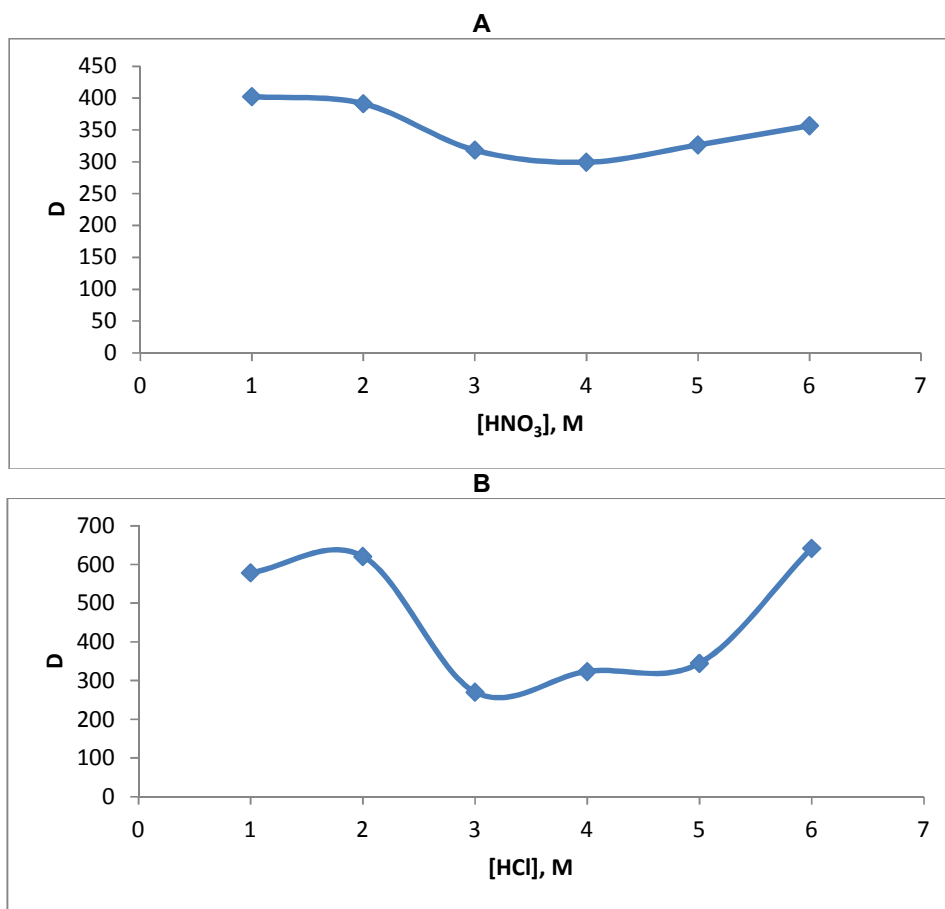


Fig. 1. Plot of distribution ratio of vanadium leaching in Shouiba vs mineral acids (HNO₃ and HCl) as leaching reagent at various concentrations

3.2.2 Alkaline leaching

Alkaline leaching agents e.g. ammonia and sodium hydroxide solutions may be appropriate since they are able to leach vanadium while maintaining Fe and Ni precipitation. Sequential leaching has been suggested as an alternative for the separation of V, Fe and Ni, according to their solubility/precipitation and redox properties. Two different alkaline reagents were used for alkaline leaching in this study. Representative results for V leaching in NH_4OH at different concentrations are shown in Fig. 3, where good was achieved maximum ($D= 600 \text{ mL/g}$) at 3 M NH_4OH , while the values of D were found in the range of 1-2 and 8-48 mL/g . The ability of vanadium(VI and V) to form vanadium ammonia complex are most likely stable compare to nickel and iron amine complex.

3.3 Effect of Contact Time of HNO_3 , HCl , H_2SO_4 and Ammonia Solutions (1.0 M) on Leaching

The effect of leaching time on heavy metals extraction from the fly ash was examined at liquid/solid ratio of 50:1 at room temperature in water, HNO_3 , HCl , H_2SO_4 and NH_4OH solutions (1.0 M). The results are summarized in Tables 3-5 and representative data for V are demonstrated in Fig. 3. Maximum metal extraction rate is obtained at 20 min, and further leaching is not necessary. The performance of Ni leaching followed the order: $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{H}_2\text{O}$, while for V and Fe the leaching followed the order: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{H}_2\text{O}$. Thus, in the next work, HCl was used as a proper leaching agent for V from the various FA samples.

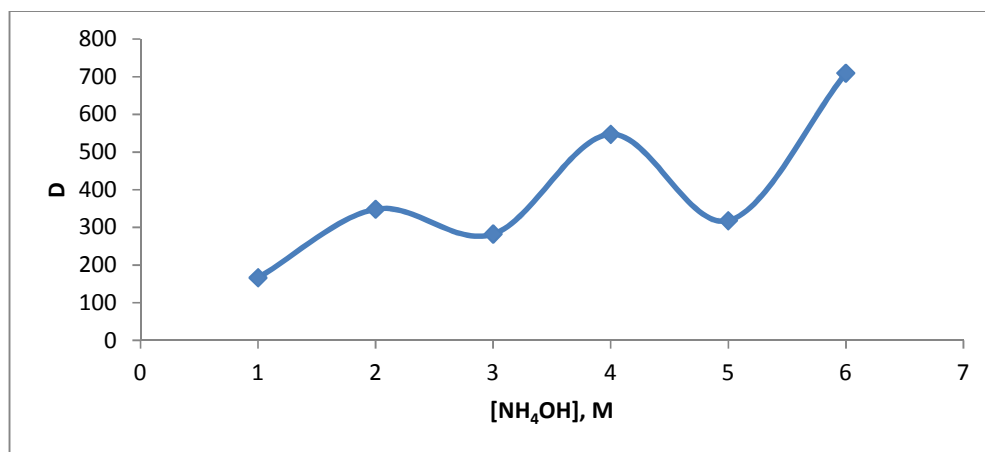


Fig. 2. Plot of distribution ratio of vanadium leaching in Shouiba vs NH_4OH as leaching reagent at various concentrations

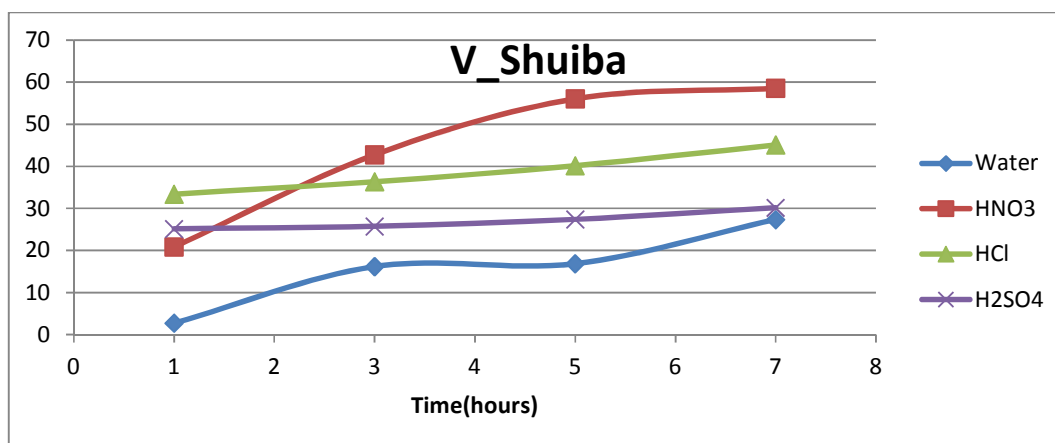


Fig. 3. Effect of contact time on the extraction of V from fly ash samples of Shouiba power station using HCl , H_2SO_4 , HNO_3 (1.0 mol L^{-1}) and water

3.4 Kinetic Behavior of Leaching V from FA:

The influence of shaking time (1-7 hour) on V leaching from fly ash in the presence of various leaching agents ammonia solution, HCl, HNO₃ and H₂SO₄ (1.0M) and water was critically investigated. The leaching profiles of vanadium was fast at the early stages and reached equilibrium 6 hours of shaking time. This conclusion was supported by calculation of the half-life time ($t_{1/2}$) of V leaching on the used leaching agents. The values of $t_{1/2}$ calculated from the plot of $\log C/C_0$ vs. time for V leaching was found to be in the range of 0.5 h in agreement with the values of $t_{1/2}$ reported earlier [40]. Thus, gel diffusion is not only the rate-controlling step for vanadium leaching and the kinetic of iron, nickel and vanadium leaching depends on film and intraparticle diffusion where, the more rapid one controls the overall rate of transport. The leached iron, nickel and vanadium leaching species were subjected to Weber–Morris model [40,41]:

$$q_t = R_d(t)^{1/2} \quad (2)$$

where, R_d is the rate constant of intraparticle transport in $\mu\text{mole g}^{-1} \text{h}^{-1/2}$ and q_t is the iron, nickel and vanadium leaching concentration ($\mu\text{mole g}^{-1}$) in various leaching agents HNO₃, HCl, H₂SO₄ (1.0M) and water at time t . Representative Weber – Morris plot for V

leaching of Shuiba power station in HNO₃ (1.0 mol L⁻¹) vs. square root of time is shown in Fig. 4. The plot of q_t vs. time in most leaching agents for V was found linear at the initial stage of leaching up to 5.29 h \pm 0.05 h and deviate on increasing the shaking time. Thus, the rate of the leaching step of V onto the leaching agent solution from fly ash sample is film diffusion at the early stage of extraction [40,41]. The values of R_d computed for V leaching from the two distinct slopes of Weber – Morris plot (Fig. 4) were found equal 3.076 ± 1.01 and $0.653 \text{ mmol g}^{-1}$ with $R = 0.989$ and 0.995 , respectively. The observed change in the slope of some linear plots is most likely attributed to the different pore size [41]. Thus, intra-particle diffusion step is most likely the rate determining step. In most plots the straight lines do not pass through the origin revealing that, particle diffusion mechanism is not only responsible for the kinetic of metal leaching onto the leaching agent solutions. Thus, V, Fe and Ni leaching is most likely involved three steps: i- bulk transport of metal ions in solution, ii- film transfer involving diffusion of metal ions within the pore volume of the solution and finally iii- formation of the complex ion species. Therefore, the actual iron, nickel and vanadium leaching onto the interior surface is rapid and hence it is not the rate determining step in the sorption process. Thus, film and intraparticle transport might be the two main steps controlling the leaching step.

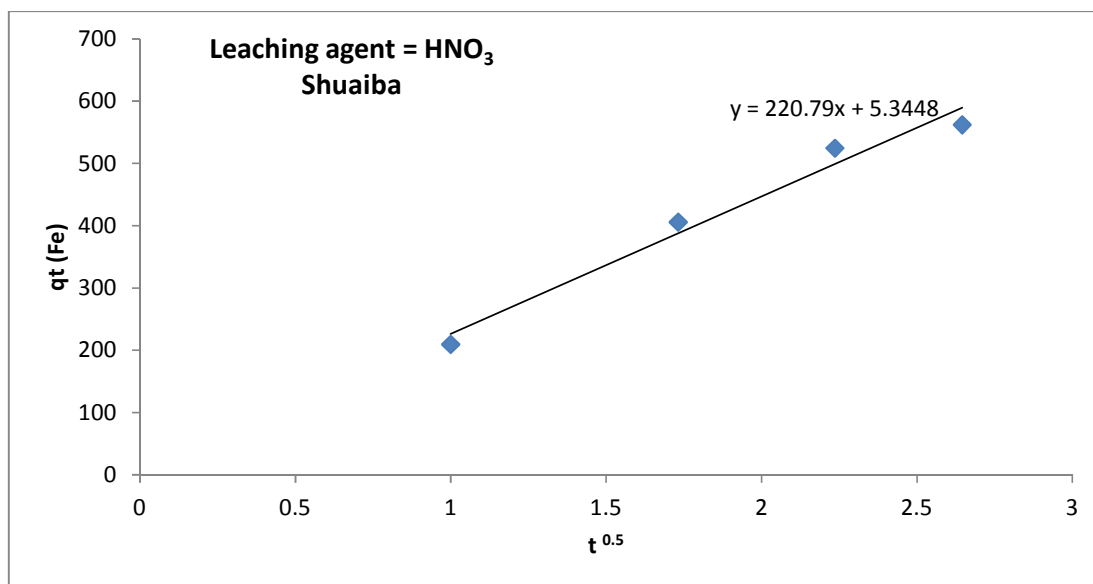


Fig. 4. Weber – Morris plot of V leaching from FA in nitric acid (1.0 mol L⁻¹) vs. square root of time

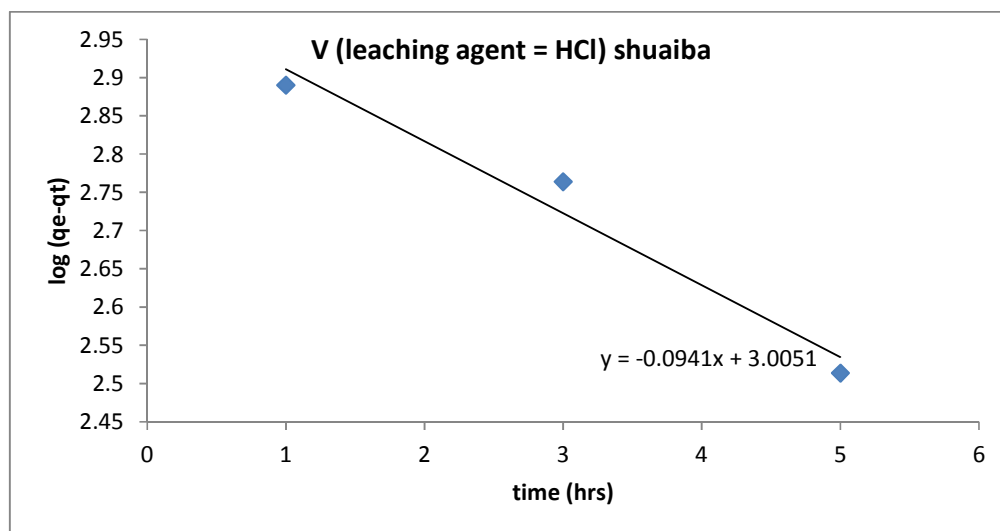


Fig. 5. Lagergren plot of V leaching of FA by aqueous HCl (1.0 mol L⁻¹) solution at room temperature versus time

The leaching of V was also subjected to Lagergren model [41]:

$$\log (q_e - q_t) = \log q_e - \frac{K_{Lager}}{2.303} t \quad (3)$$

where, q_e is the amount of V leached at equilibrium per unit mass of sorbent ($\mu\text{moles g}^{-1}$); K_{Lager} is the first order overall rate constant for the retention process and t is the time in hour. The results are demonstrated in Fig. 5. The value of K_{Lager} calculated from the linear plot of $\log (q_e - q_t)$ vs. time was found equal to $0.132 \pm 0.033 \text{ h}^{-1}$ for V suggesting first order kinetics for leaching of V towards HCl leaching agent. The influence of vanadium concentration was investigated and the results indicate also that, the value of K_{Lager} increases with increasing adsorbate concentration confirming the formation of mono - layer of the leached iron, nickel and vanadium species onto the used leaching agent as well as the first order kinetic nature of the retention process [41].

3.5 Thermodynamic Characteristics of V, Fe and Ni Leaching from FA in HCl

V leaching in HCl (3.0 M) from fly ash was critically studied over wide range of temperature ((293- 323 K) to determine the nature of leaching species at the established conditions. The effect of temperature on V leaching from the fly ash samples was examined at a liquid/solid ratio of 50:1, contact time of 3h in HCl (pH=0.0). Raising

temperature from 293 to 323 K, showed slight increase on the leaching rate of V as shown in Fig. 6. Thus, it can be concluded that, the leaching reaction of V is slightly temperature-dependent and room temperature is suitable. The thermodynamic parameters (ΔH , ΔS , and ΔG) were calculated using the following equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$\Delta G = -RT \ln K_c \quad (6)$$

where, ΔH , ΔS , ΔG , and T are the enthalpy, entropy, Gibbs free energy changes and temperature in Kelvin, respectively and R is the gas constant ($\approx 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$) and K_c is the equilibrium constant depending on the fractional attainment (Fe) of the sorption process. The values of K_c of iron, nickel and vanadium leaching ions from the test fly ash at equilibrium onto HCl (3.0M) were calculated using the equation [39-41]:

$$K_c = \frac{Fe}{1 - Fe} \quad (7)$$

The plot of $\ln D$ i.e. $\ln K_c$ versus $1000/T$ for leaching of iron, nickel and vanadium from Shoiba and Rabigh fly ash samples using HCl (1.0M) are demonstrated in Figs. 56-58 and Figs

59-61, respectively. The plots are linear over the temperatures range (293- 323 K). The values of the equilibrium constants decreased on increasing temperature, revealing that, the leaching processes of iron, nickel and vanadium species from fly ash onto the leaching agent (HCl) are exothermic process. The numerical values of ΔH , ΔS , and ΔG calculated from the slope and intercept of the linear plot of $\log K_C$ against $1000/T$ (Figs. 56-61) were found to be in the range -18.72 ± 1.01 -32.8 kJ mol^{-1} , 54.57 ± 0.5 -67.9 ± 3.9 $\text{J mol}^{-1} \text{K}^{-1}$ and -2.46 ± 0.1 -7.6 kJ mol^{-1} (at 298 K), respectively with correlation factor of 0.998.

Considering the Van't Hoff model, the distribution coefficient (K_d) of iron, nickel and vanadium leaching from fly ash samples into HCl is correlated with temperature according to the following expression [41]:

$$\log K_d = \frac{-\Delta H}{2.30 RT} + C \quad (8)$$

where, C is constant. The plots of $\log K_d$ versus $1/T$ for vanadium species leached onto the HCl leaching agent was linear. The value of ΔH for V leaching determined from the slope of the linear plot is in good agreement with the value obtained from equations 7.

The negative value of ΔH and the data of K_d and K_C reflect the exothermic behavior of V leaching and non-electrostatics bonding formation between the leachate and FA. The negative values of ΔS may be indicative of the moderated leaching step of V leaching and ordering of ionic charges without a compensatory disordering of the leached species in HCl media. Thus, the freedom of V motion is more restricted in the HCl solution than in solid fly ash. Since the leaching processes involve a decrease in free energy, the ΔH is expected to be negative as confirmed earlier. Moreover, on raising the temperature, the physical structure of the fly ash may be changing, thus affecting the strength of the intermolecular interactions between the analytes in the fly ash matrices. Thus, the high temperature may make the membrane matrix become more unstructured and affect the ability of the polar segments to engage in stable hydrogen bonding with analyte species, which would result in a lower leaching. The negative of ΔG at 295 K implies the spontaneous and physical sorption nature of leaching onto HCl. The decrease in ΔG values on decreasing temperature confirms the spontaneous nature of the leaching step and iron, nickel and vanadium leaching is more favorable at low temperature confirming the exothermic leaching processes.

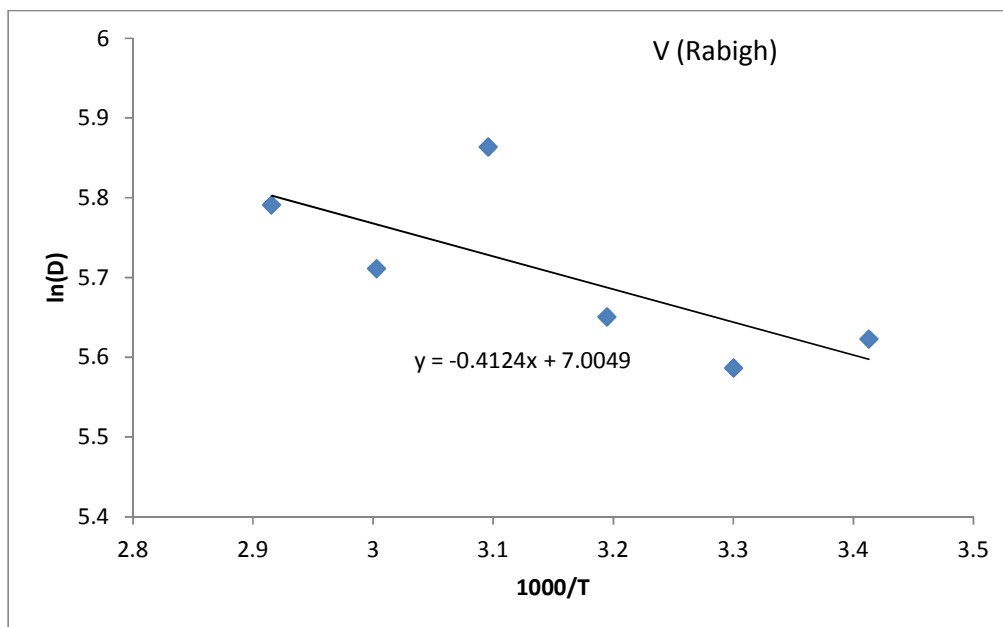
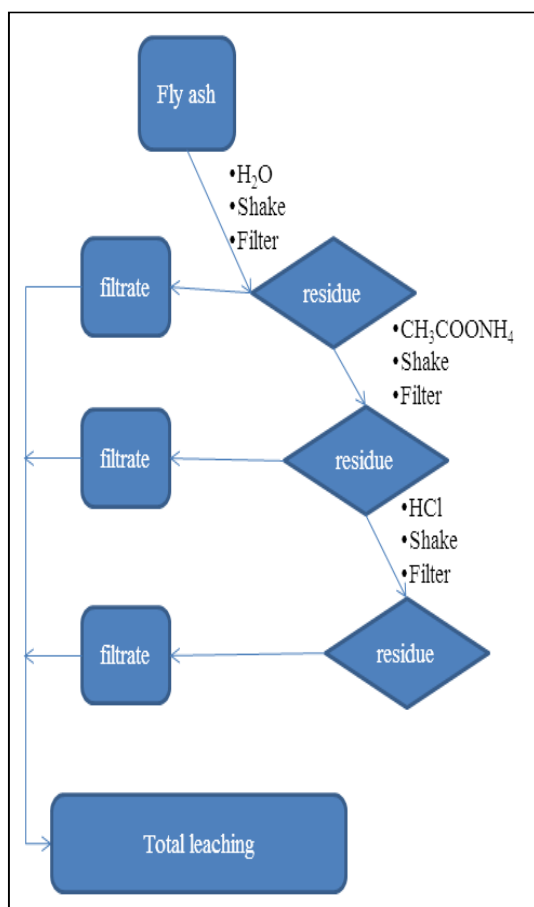


Fig. 6. Plot of $\ln K_C$ of V leaching from fly ash by HCl (1.0 mol L^{-1}) vs. $1/T$ (K^{-1})



Scheme 1. A proposed flow chart for leaching of V, Fe and Ni from FA samples

3.6 Sequential Leaching

A series of leaching agents were used in the sequential leaching steps. The first step in the study was aimed at selecting water as proper leaching agent in the leaching step at fly ash: water (0.5 g:100 mL) ratio. An acceptable leaching percentage was achieved for iron, nickel

and vanadium in the water extract after 24 h contact time (Table 6). The solid residue was then leached with ammonium acetate (1.0M) solution for 24 h at fly ash: ammonium acetate (0.5 g: 100 mL) ratio. After 24 h contact with ammonium acetate, the solid residue was separated out and the filtrate was analyzed for V, Fe and Ni. Finally, the solid residue of fly ash was shaken with HCl (1.0M) at fly ash: HCl (0.5 g: 100 mL) ratio for 24 h and the leachate solution was analyzed for V, Fe and Ni. The results of the V, Fe and Ni leaching from FA samples are summarized in Tables 6, 7. A representative flow chart describing all leaching steps of FA samples for V, Fe and Ni is demonstrated in Schemes 1 & 2.

3.7 Solvent Extraction and Recovery of V, Fe and Ni

Preliminary experiments were performed with synthetic mixture of V, Fe and Ni solutions (close to 50 mg/L) in order to define the optimum experimental conditions. The concentration of V, Fe and Ni in the aqueous phase was determined by ICP-OES. The results were then applied to the leachates when Fe, Ni, and V concentrations higher than 200 mg/L. The leachates were pre-treatment with hydrogen peroxide to oxidize any fraction of vanadium (IV or III) The pH of the leachate was then controlled at pH 3 and was shaken well with ammonium pyrrolidine dithiocarbamate in chloroform. The solution was shaken well for 5 min. After equilibrium and layer separation, the organic extract was separated out. The results revealed complete extraction of the tested metal ions in the chloroform phase. V, Fe and Ni were then stripped from the organic extract by shaking well with HNO₃ (10 mL, 1 M)) containing Hg²⁺ ions and analyzed. Total content of V, Fe and Ni was completely stripped and analyzed.

Table 6. Results of sequential leaching of Fe, Ni and V in the Shouiba fly ash samples using water, ammonium acetate and hydrochloric acid after 24 h contact time (solid residue)

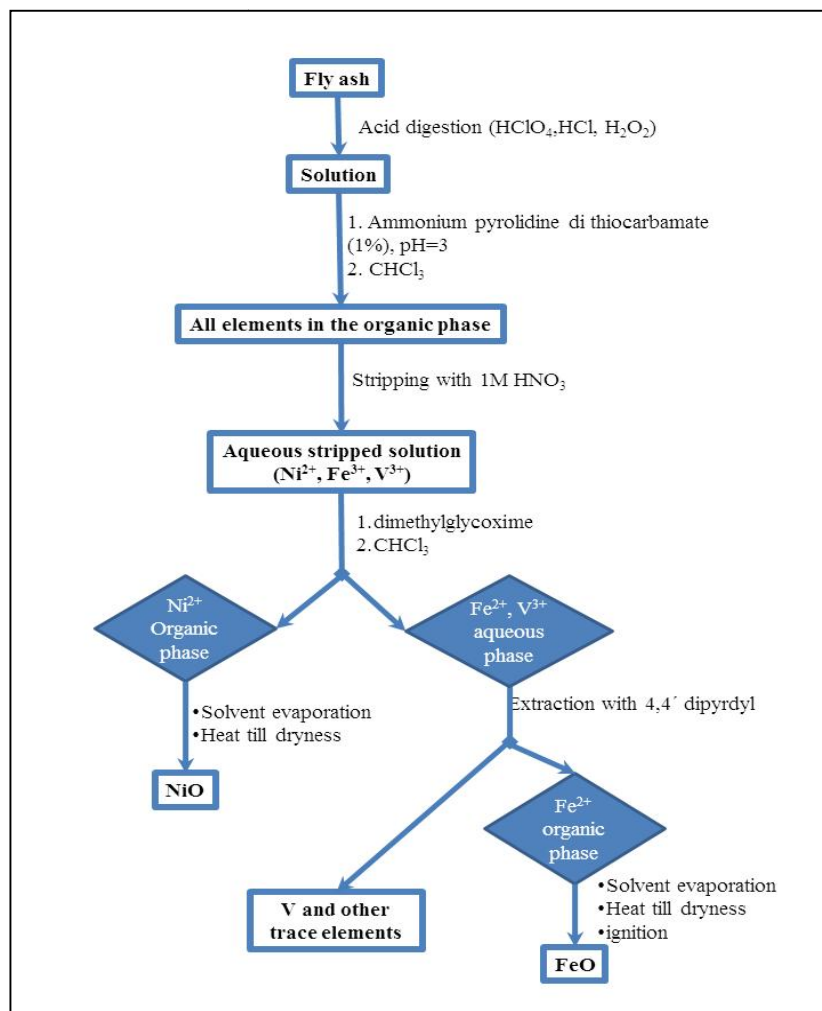
Element	Fe	Ni	V
Leaching agent			
H ₂ O	4.4	4.9	9.0
CH ₃ COONH ₄	0.50	1.9	3.8
HCl	2.7	0.5	1.8

Table 7. Results of sequential leaching of Fe, Ni and V in the Shouiba fly ash samples using water, ammonium acetate and hydrochloric acid after 24 h contact time (leachate residue)

Element Leaching agent	Fe	Ni	V
H ₂ O	4.5	64.8	20.2
CH ₃ COONH ₄	0.1	1.4	36.0
HCl	19.8	8.7	25.5

Total Ni in the stripped nitric acid solution was then extracted with dimethylglyoxime at pH5-6 in chloroform and analyzed for Ni. The stripped solution was then treated with 4,4 pypyridyl to extract Fe quantitatively and finally vanadium. Other trace metal ions were remained in the aqueous phase and analyzed by ICP-OES. Representative flow charts summarized all steps are illustrated in schemes 1 & 2. Satisfactory recovery of nickel was achieved close to the

values mentioned for total digestion. The Fe content in leachate solution (or the resultant solution of total digestion of fly ash by wet digestion) was reduced to iron(II) and shaken with 1, 10 phenanthroline in the presence of rose bengal and chloroform. After equilibrium and separation of layers, the organic extract was separated out. Complete extraction of iron was achieved while the remained aqueous solution contains only vanadium.



Scheme 2. A proposed flow chart for leaching of V, Fe and Ni from FA samples

4. CONCLUSION

The occurrence of trace elements in fly ash plays a primary role in the distribution of elements within ash particles. The elements enriched in the core of FA particles are not directly exposed to leaching, whilst surface-associated elements are more accessible to leaching in an aqueous environment. The study offers a snapshot of the field of metal recovery from FA solid waste at this critical stage. More work is necessary to: i) predict the performance of leaching of V, Fe and Ni from FA samples in the leachate solutions and finally; ii) Understand the most probable mechanism of metal leaching.

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COMPETING INTERESTS

Author has declared that no competing interests exist. The company name used for this research is commonly and predominantly selected in our area of research and country. It is absolutely no conflict of interest between the author and company because we do not intend to use this company as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the company rather it was funded by personal efforts of the author.

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