

# Sequential leaching of V from heavy fuel oil fly ash generated from Saudi Arabian thermal power plants and analytical applications: Kinetics and thermodynamics characteristics of V leaching

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## Abstract:

The kinetics and thermodynamic characteristics of V leaching from fly ash waste generated from Ra-high thermal power station of Saudi Arabia in a series of leaching agents ( $\text{H}_2\text{O}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) were studied. The rate of leaching step of V was fast; reached equilibrium in a short time from and followed a first-order rate equation with an overall rate constant  $k$  of  $0.076 \text{ min}^{-1}$ . The thermodynamic parameters of V leaching in different leaching agents were critically investigated. The negative values of  $\Delta H$  and  $\Delta G$  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:** Fly ash; Heavy oil fuel fly ash; Leaching; V, Fe and Ni; Kinetics; Recovery; Power plants.

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## 1. Introduction

Heavy 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]. 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]. Fly ash of heavy fuel oil has received less attention, and the published studies are mainly limited to surface characterization [9]. Heavy oil FA (HOFA) is characterized by a high C content and low Si/Al content [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

have been reported [14, 24, 25]. Based on the significant growth in Saudi Chemical industries [23-27], the present study focuses on: i) Evaluation of the leachability of V, Fe and Ni from fly ash samples derived from Rabigh thermal power plant 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 and finally ii) Studying 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, WC, 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 pyrrolidine 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 town in Saudi Arabia and has one of the lowest populations. It lies at latitude 23° N and longitude 40° 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<sup>-1</sup>) 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±0.01g) 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<sub>3</sub> (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture heated slowly for 1h at 100-150°C on a hot plate. After the evolution of NO<sub>2</sub> fumes had ceased, the reaction mixture evaporated almost to dryness and mixed again with concentrated HNO<sub>3</sub> (5.0 mL). The process 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<sup>-1</sup>). The result-

ing 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 FA samples were prepared following the same procedure applied for the CRM.

#### **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 ( $0.5 - 0.6 \pm 0.01$ g) of the FA sample was transferred into a glass beaker containing conc. HCl (2.0 mL), HClO<sub>4</sub> (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. HNO<sub>3</sub> (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 HNO<sub>3</sub> (5.0 mL, 1.0 mol L<sup>-1</sup>) 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 optimum operational parameters of vanadium, iron and nickel summarized in Table 1. A blank experiment was also carried out and analyzed by ICP-MS. The average concentration ( $\mu\text{g g}^{-1}$ ) of the tested V, Fe and Ni was determined by difference employing the following equation:

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

where C is the average element concentration in sample solution ( $\mu\text{g mL}^{-1}$ ) 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  $1.0 \mu\text{g/mL}$ , 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. Effect of leaching agents ( $\text{H}_2\text{O}$ , $\text{NH}_3$ , $\text{HCl}$ , $\text{HNO}_3$ , and $\text{H}_2\text{SO}_4$ ) on V leaching**

An accurate weight ( $0.5 \pm 0.001 \text{ g}$ ) of dry FA sample was shaken individually well with various the leaching agents  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  (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]. Similarly, the influence of leaching agents concentration (0.25 -7.5 M) and leaching time for various time intervals (1-7 h) was critically studied.

#### **2.4.4. Sequential leaching of V from FA samples**

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

- i. An accurate weights ( $0.5 \pm 0.001$  g) of the fly ash sample 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,  $1.0 \text{ mol L}^{-1}$ )
- ii. The solid residue of water leaching step was sequentially treated with ammonium acetate (100 mL,  $1.0 \text{ mol L}^{-1}$ ) 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,  $1.0 \text{ mol L}^{-1}$ )
- iii. The resultant solid residue of FA after ammonium acetate leaching step was sequentially treated with HCl (100 mL,  $1.0 \text{ mol L}^{-1}$ ) and left in contact for 24 h with constant stirring in a shaker. The final solid residue was separated out, filtrated and subjected to for V, Fe and Ni determination.

#### **2.4.5. Sequential extraction of V, Fe and Ni from FA 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 V, Fe and Ni in the aqueous phase was determined by ICP-OES. The results were applied to the leachates when relevant ( Fe, Ni and / or V) concentrations higher than  $200 \text{ mg L}^{-1}$ ). The leachates were submitted to a pre-treatment with hydrogen peroxide in order to oxidize any fractions of V that could be in a reduced form  $\text{V}^{4+}$  vanadium(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<sub>3</sub>, NH<sub>4</sub>Cl/NH<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>) at known concentration for 30 min. The V concentration 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 pyrolidine 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.

#### **2.4.6. Recovery of total V and Fe**

After separation of Ni by dimethylglyoxime [30], an accurate volume (500.0 mL) of the HCl leachate solution was shaken well with ammonium pyrolidine 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. V and Fe 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 [64].

### **3. Results and discussion**

#### **3.1. Total digestion of fly ash samples**

Preliminary investigations on the chemistry of FA resulting from the power station in Kingdom of



Saudi Arabia have revealed considerable content of trace metal ions particularly V, Fe and Ni. Therefore, detailed investigation on the chemical composition of dry FA was critically carried out at water treatment station at Rabigh water treatment station. 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-HNO<sub>3</sub> (1:3 v/v) system following the recommended procedures [28]. The results are given in Table 2. Considerable amount of V, Fe and Ni in the FA samples. The content of V, Fe and Ni lies in the range 3625.1 ±21.8 - 5601.3 ±27.6; 4057.0±32.7 - 9913.9 ±23.2 and 751.2 ±13.7-2632.9 ±41.2 µg/ g, respectively (Table 2). These values are comparable well level content in the study reported by other authors except for Ni [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 FA samples. Complete digestion of this class of compounds is too tedious and required enough digestion. Thus, low value of Ni is most attributed to the incomplete digestion of total FA. Thus, digestion step was carried out in a vacuum step to achieve complete digestion.

### **3.2. Influence of leaching agent on V leaching from FA samples**

Based on the preliminary investigations on the content of total iron, nickel and vanadium in the various fly ash samples resulting from Rabigh power stations detailed investigation on the use of acid and alkaline leaching agent was critically carried out at water treatment station. 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 V in solution [33-37], it is expected to be in the form of VO<sub>2</sub><sup>+</sup> in acidic solutions and in the form of VO<sub>3</sub>(OH)<sup>2-</sup> and VO<sub>4</sub><sup>3-</sup> in alkaline solutions . Thus, for this purpose various leaching agents (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>), 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. General characteristics of acid leaching of V from FA samples**

The acidic leaching was performed using various concentrations of HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. 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. In practice, leaching methods, such as hydrothermal, subcritical water treatment and fungal bioleaching, were seldom considered for the practical process due to their too strict operation conditions and high cost or too long operation time, so the process performed at ambient temperature should be preferentially considered, and selection of the most suitable lixiviant is essentially significant.

A limited number of research works of leaching with HCL have been reported to date [38, 39] we conducted a fundamental study for systematic investigation on the application of a series of acid leaching employing H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub> to the leaching process of heavy metal from fly ash in present work. Thus, 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 data are summarized in Tables 3-5 and representative data for leaching of V are shown in **Figures 1**. The extraction rate for all the metals generally 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<sup>+</sup> and dissolved into the solution from the fly ash particles. Considering the leaching efficiency, acidity in the range 1-3 M is recommended.

The extraction behavior appeared to be independent 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. It is especially important to take into account the objective of the process, i.e., the selective recovery of vanadium. The presence of several metals in the leachates increases the difficulty of separating the metals for the subsequent processing steps (i.e., solvent extraction and/or precipitation). For this reason it is important to find another leaching agent that could avoid the simultaneous leaching of some of these metals, especially iron and nickel. These metals precipitate in the same pH range as V.

### **3.2.2. Alkaline leaching**

Alkaline leaching agents e.g. ammonia and sodium hydroxide solutions may be appropriate since they are able to leach V 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. Ammonia and sodium hydroxide solutions were used for alkaline leaching in this study. Representative are shown in **Figure 2** where good leaching of V was achieved compare to nickel and iron. The distribution ratio of V was achieved maximum ( $D=600 \text{ mL/g}$ ) at 3 M ammonia. The ability of  $V^{4+}$  and  $V^{5+}$  species to form complexes with ammonia are most likely stable compared to Fe and Ni 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 FA was examined at liquid/solid ratio of 50:1 at room temperature in water,  $HNO_3$ ,  $HCl$ ,  $H_2SO_4$  and ammonia solutions (1.0 M). Maximum metal extraction rate is obtained at 20 min, and further leaching is not necessary. Based on the results of total digestion and analysis of V, Fe and Ni in FA demonstrated in Tables 3-5. Representative data for V are demonstrated in Figure 4. Based on the data given in Tables 3-5 revealed that, the performance of V and Fe leaching followed the order:  $H_2SO_4 > HCl > HNO_3$

>H<sub>2</sub>O while for Ni, the following order HCl > H<sub>2</sub>SO<sub>4</sub> > >HNO<sub>3</sub> >H<sub>2</sub>O, was achieved. Thus, in the subsequent work, HCl was used as a proper leaching agent for V from the various fly ash samples at the employed concentrations.

### 3.4. Kinetic behavior of leaching V, Fe and Ni from FA:

The influence of shaking time (1-7 h) on V, Fe and Ni leaching from fly ash in the presence of various leaching agents ammonia solution, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1.0M) and water was critically investigated. The leaching profiles of ions V, Fe and Ni was fast at the early stages and reached equilibrium 6 h of shaking time. This conclusion was supported by calculation of the half-life time ( $t_{1/2}$ ) of iron, nickel and vanadium leaching on the used leaching agents. The values of  $t_{1/2}$  calculated from the plots of  $\log C/C_0$  versus time for V, Fe and Ni leaching. The values of  $t_{1/2}$  for iron, nickel and vanadium leaching was found to in the range be 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 iron, nickel and vanadium leaching and the kinetic of V, Fe and Ni leaching depends on film and intraparticle diffusion where, the more rapid one controls the overall rate of transport. The leached V, Fe and Ni leaching species were subjected to Weber–Morris model [40, 41]:

$$q_t = R_d (t)^{1/2} \quad (4)$$

where,  $R_d$  is the rate constant of intraparticle transport in  $\text{mol g}^{-1} \text{h}^{-1/2}$  and  $q_t$  is the V, Fe and Ni leaching concentration ( $\text{mole g}^{-1}$ ) in various leaching agents HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> (1.0M) and water at time t. Representative results of Weber – Morris plot of V leaching of Shuiba power station in nitric acid ( $1.0 \text{ mol L}^{-1}$ ) vs. square root of time (Figure 3). The plots of  $q_t$  versus time in most leaching agents for V, Fe and Ni were found linear ( $R^2 = 0.989$ ) at the initial stage of V, Fe and Ni leaching up to  $6 \text{ h} \pm 30 \text{ min}$  and deviate on increasing the shaking time. Thus, the rate of the leaching step of V step onto the leaching agent solution from fly FA 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 plots were found equal  $(3.076 \pm 1.01) \times 10^{-3}$  and  $65.3 \times 10^{-5} \text{ mol g}^{-1}$  with

R= 0.989 and 0.995, respectively (Figure 4). The observed change in the slope of some linear plots is most likely attributed to the different pore size [41, 42]. 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 V, Fe and Ni 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 sorption step. Moreover, V, Fe and Ni leaching will also subjected to pseudo first order model [41]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where,  $q_e$  is the amount of Fe, Ni or V leached at equilibrium per unit mass of sorbent ( $\text{mol g}^{-1}$ );  $k_1$  is the first order overall rate constant for the retention process per min and  $t$  is the time in hour. Representative results are demonstrated in Figure 5. The value of  $k_1$  calculated from the linear plots of  $\log(q_e - q_t)$  versus  $t$  (Figure 6) was found equal  $0.132 \pm 0.033 \text{ h}^{-1}$ . Thus, first order kinetic for V, Fe and Ni species towards HCl leaching agent is the most probable kinetic model describing their leaching in HCl. The value of  $k_1$  increases with increasing V, Fe and Ni concentration confirming the formation monolayer 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 , and pH=0.0. Representative results of V leached at various temperatures

from Shouba are demonstrated in **Figure 6**. It is found from that temperature shows very slight effect on the extraction rate, suggesting that the leaching reaction for the metals is temperature-dependent. The thermodynamic parameters ( $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ) were calculated using the equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\Delta G = -RT\ln K_c \quad (8)$$

where,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ , 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 V, Fe and Ni leaching ions from the FA at equilibrium onto HCl (3.0M) were calculated as reported [39-41]. The plot of  $\ln K_C$  versus  $1000/T$  for leaching of V, Fe and Ni were found linear from FA samples using HCl (1.0M) over the temperatures range (293- 323 K). Representative results are shown in Figure 6. The values of  $K_C$  decreased on increasing temperature, revealing the exothermic process of V, Fe and Ni leaching from FA in HCl. The numerical values of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  calculated from the slope and intercept of the linear plot of  $\log K_C$  against  $1000/T$  for V were found in the range -  $18.72 \pm 1.01$  -32.8 kJ mol<sup>-1</sup>,  $54.57 \pm 0.5$  -67.9 $\pm 3.9$  J mol<sup>-1</sup> K<sup>-1</sup> and  $-2.46 \pm 0.1$  -7.6 kJ mol<sup>-1</sup> (at 298 K), respectively with correlation factor 0.998. The negative value of  $\Delta H$  and the data of  $K_d$  and  $K_C$  reflect the exothermic behavior of V leaching. The negative values of  $\Delta S$  may be indicative of the moderated sorption step of Fe, Ni and V leaching and ordering of ionic charges without a compensatory disordering of the leached species in HCl extraction media. Thus, the freedom of V, Fe and Ni motion is more restricted in HCl media than in solid FA. The physical structure of the FA may be changing on raising temperature, thus affecting the strength of the intermolecular interactions between the analytes in FA matrices. The negative of  $\Delta G$  at 295 K implies the spontaneous and physical sorption nature of leaching onto HCl. The decrease in  $\Delta G$  values on

decreasing temperature confirms the spontaneous nature of the leaching step of V, Fe and Ni and the leaching step is exothermic and favorable at low temperature.

### **3.7. 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. 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.

### **3.8. 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-treated 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 HNO<sub>3</sub> (10 mL, 1 M) containing Hg<sup>2+</sup> ions and analyzed. Total content of V, Fe and Ni was completely stripped and analyzed.

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 pyridyl 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.

## **Conclusion**

The mode of occurrence of trace elements in fly ash plays a primary role in the mode of occurrence in FA and 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 utilization of FA solid waste at this critical stage. The method could be extended to pico-mole regime via online preconcentration methods. 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.

## **Competing Interests Disclaimer:**

Authors have 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. There is absolutely no conflict of interest between the authors 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 authors.



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## Adsorption System Boundary

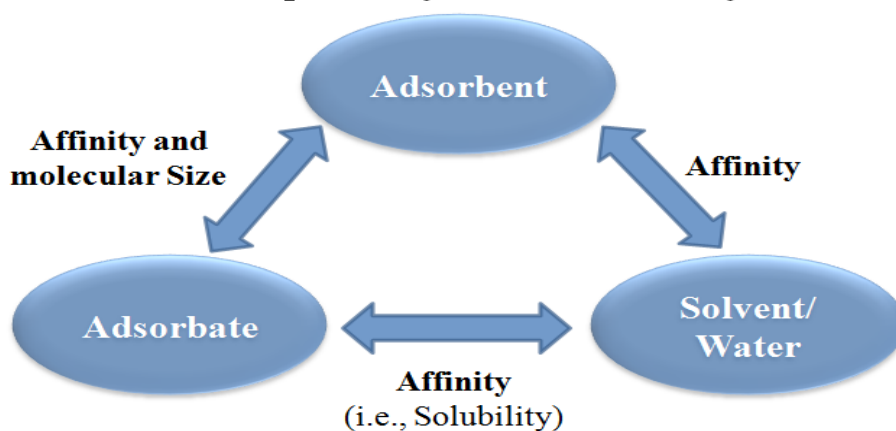


Figure 1. Schematic diagram representing the adsorbent-adsorbate-extraction media interactions on long-term batch leaching experiment.

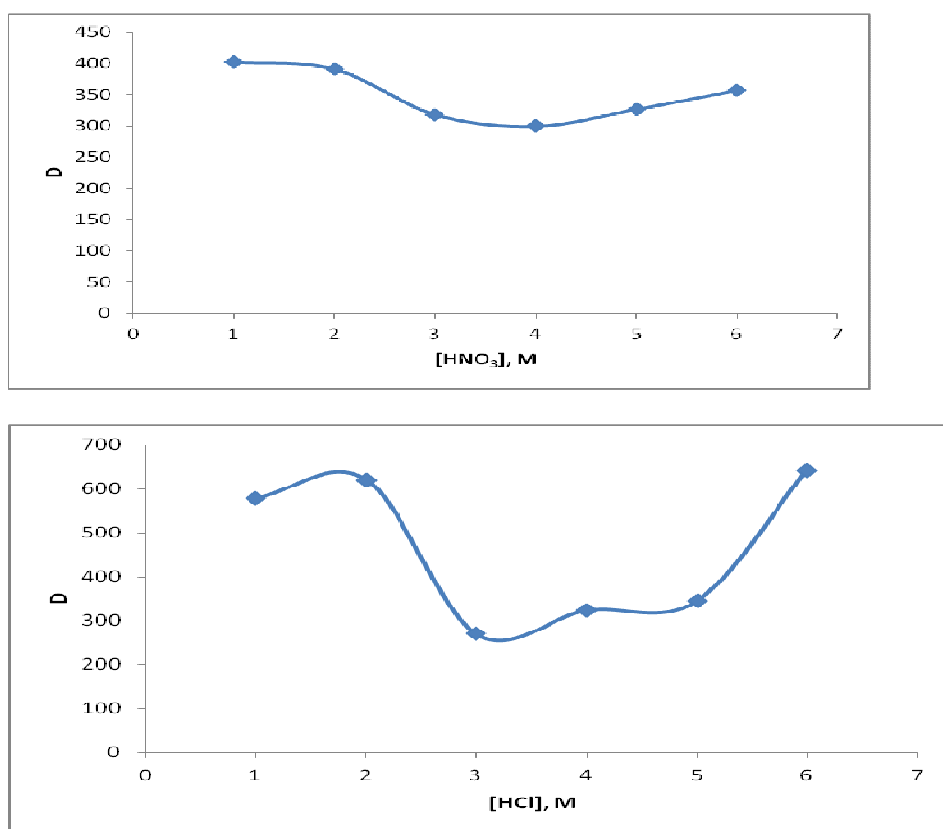


Figure 2. Plot of distribution ratio of vanadium leaching in Shouiba vs mineral acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ) as leaching reagent at various concentrations.

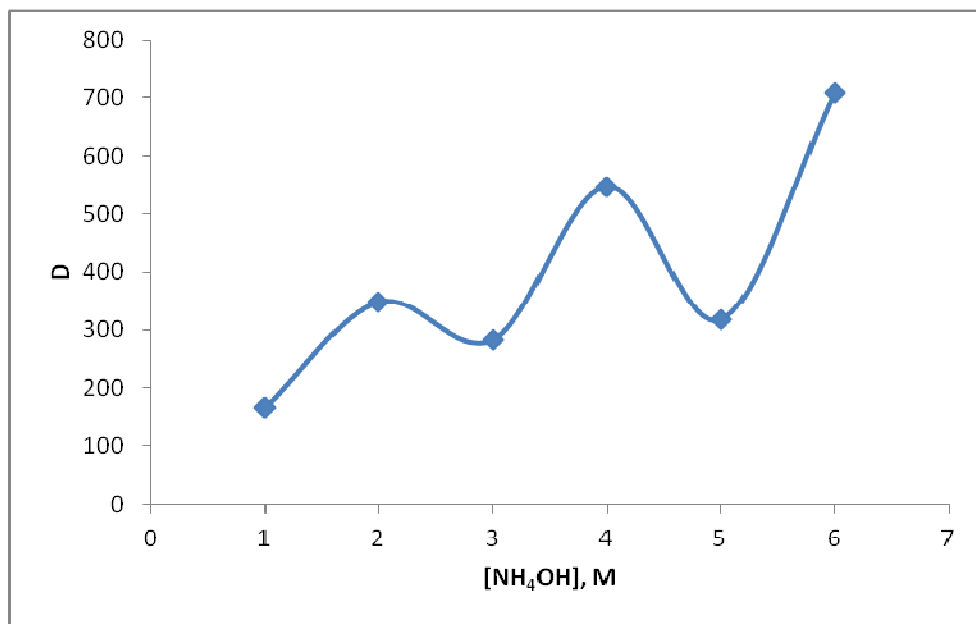


Figure 3. Plot of distribution ratio of vanadium leaching in Shouiba vs.  $\text{NH}_4\text{OH}$  as leaching reagent at various concentrations.

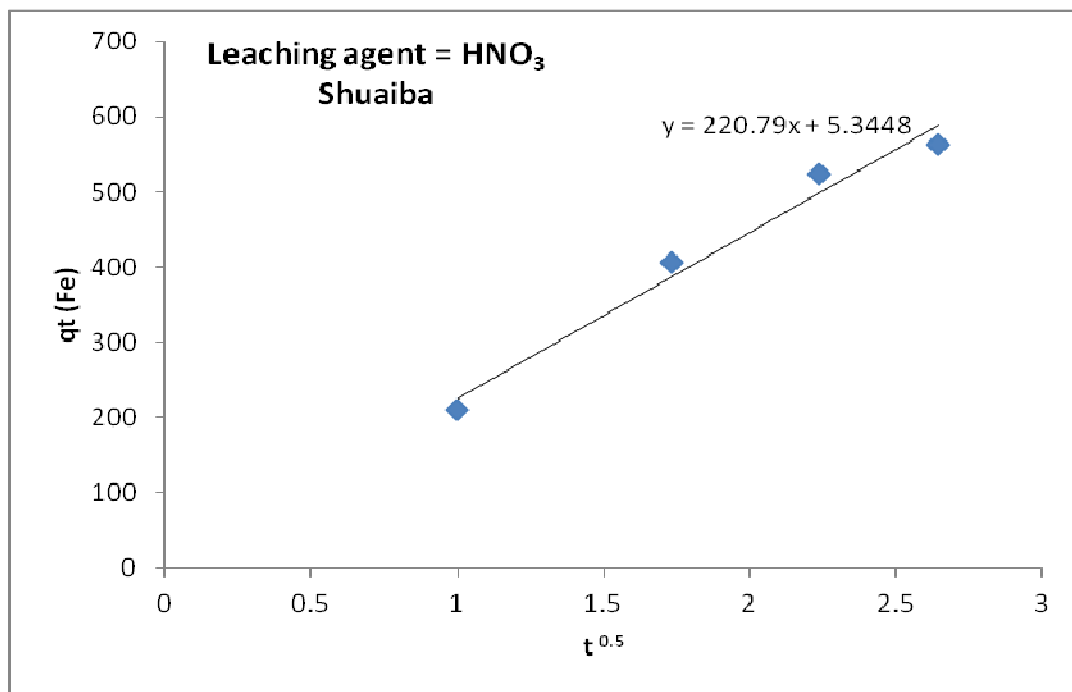


Figure 4. Weber – Morris plot of vanadium leaching of Shuaiba power station in nitric acid (1.0 mol  $\text{L}^{-1}$ ) vs. square root of time.

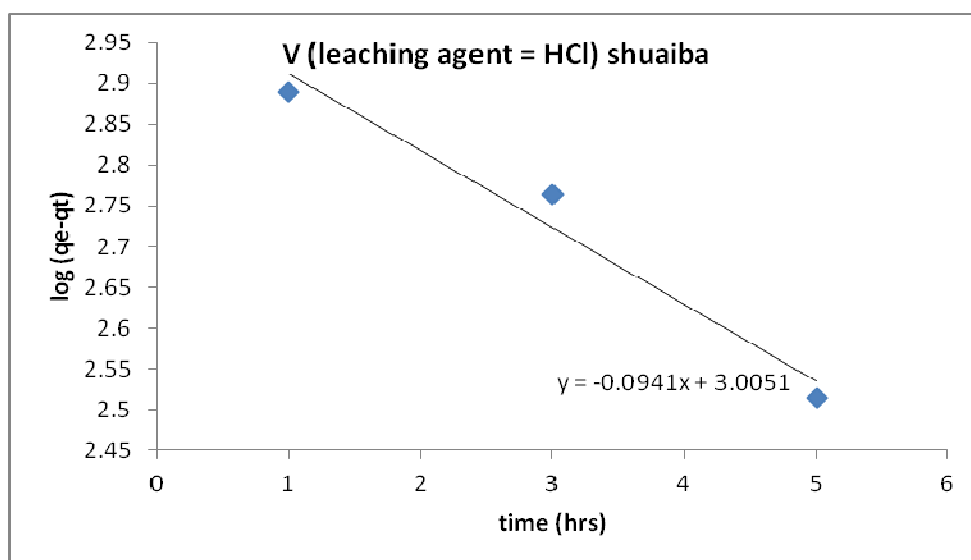


Figure 5. Lagergren plot of vanadium leaching of Shuiba power station by aqueous HCl (1.0 mol L<sup>-1</sup>) solution of Shouba fly ash at room temperature versus time.

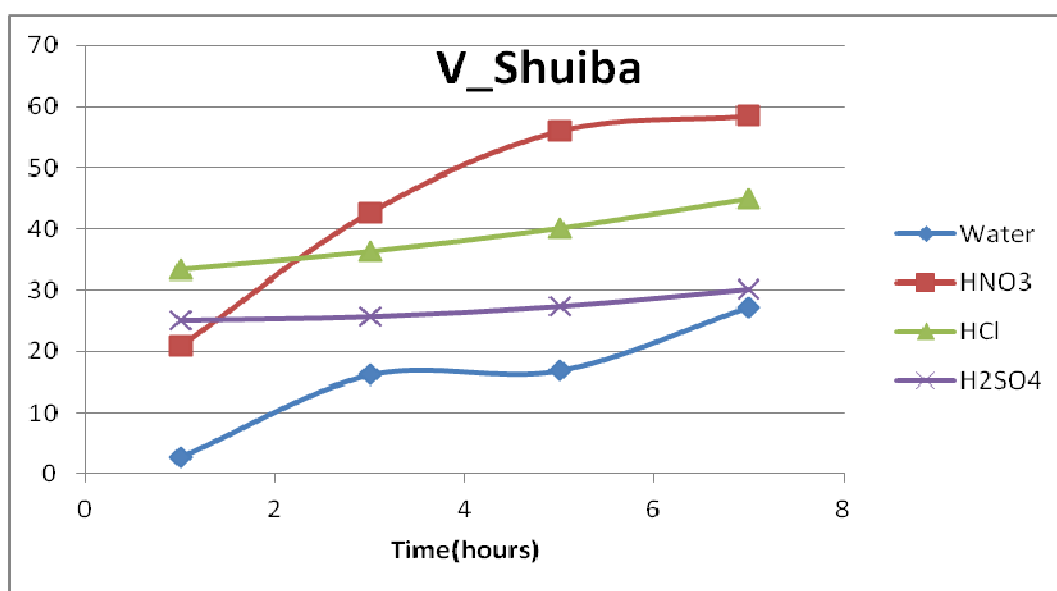


Figure 6. Effect of contact time on the extraction of V from fly ash samples of Shuiba power station using HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (1.0 mol L<sup>-1</sup>) and water.

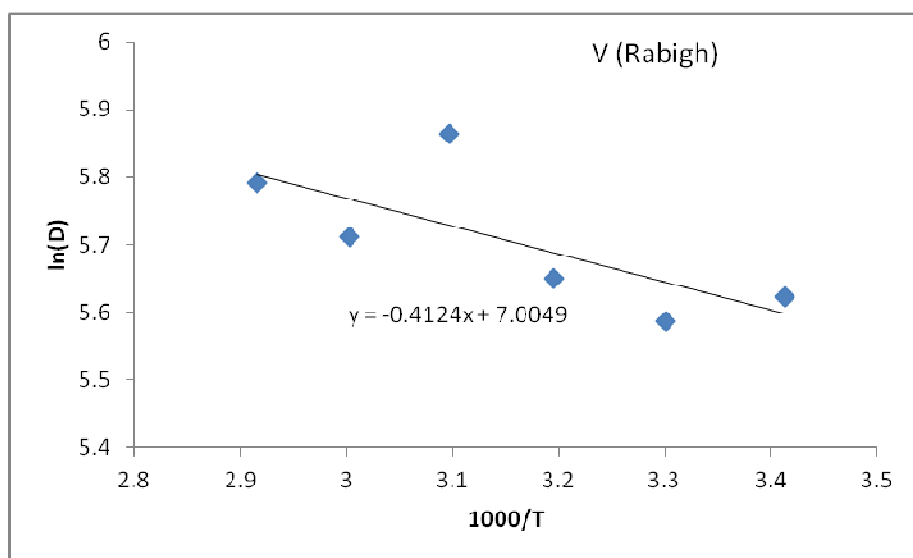


Figure 7. Plot of  $\ln K_C$  of V leaching from Rabigh fly ash HCl (1.0 mol L<sup>-1</sup>) vs.  $1/T$  (K<sup>-1</sup>).

**Table 1** ICP-OES Operational conditions and wavelength (nm) for trace metal determination

Parameter	
Rf power (kW)	1050
Plasma gas (Ar) flow rate, Lmin <sup>-1</sup>	15
Auxiliary gas (Ar) flow rate, Lmin <sup>-1</sup>	0.2
Nebulizer gas (Ar) flow rate, Lmin <sup>-1</sup>	0.80
Pump rate, mL min <sup>-1</sup>	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



Table 2. Analysis of total nickel, iron and vanadium in fly ash samples by wet digestion in Jeddah, Rabigh and Shuaiba power stations<sup>†</sup>

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

<sup>†</sup> The results are the average of three measurements.

Table 3. Effect of various leaching agents HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and H<sub>2</sub>O on the dissolution of iron, nickel and vanadium from fly ash collected from Jeddah power station<sup>†</sup>

Leaching medium	Leaching time	Fe (ppm)	Ni (ppm)	V (ppm)
<b>Water</b>	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
<b>HNO<sub>3</sub></b>	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
<b>HCl</b>	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
<b>H<sub>2</sub>SO<sub>4</sub></b>	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

<sup>†</sup> The results are the average of three measurements.

Table 4 Effect of various leaching agents HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (mol L<sup>-1</sup>) and H<sub>2</sub>O on V, Fe and Ni dissolution (µg/g) from fly ash collected from Rabigh water power station<sup>†</sup>.

Leaching medium	Leaching time	Fe	Ni	V
<b>Water</b>	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
<b>HNO<sub>3</sub></b>	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
<b>HCl</b>	<b>1h</b>	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
<b>H<sub>2</sub>SO<sub>4</sub></b>	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

<sup>†</sup> The results are the average of three measurements.

Table 5 Effect of various leaching agents HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (mol L<sup>-1</sup>) and H<sub>2</sub>O on V, Fe and Ni dissolution (µg/g) from FA collected from Shouiba power station<sup>†</sup>

Leaching medium	Leaching time	Fe	Ni	V
<b>Water</b>	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
<b>HNO<sub>3</sub></b>	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
<b>HCl</b>	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
<b>H<sub>2</sub>SO<sub>4</sub></b>	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

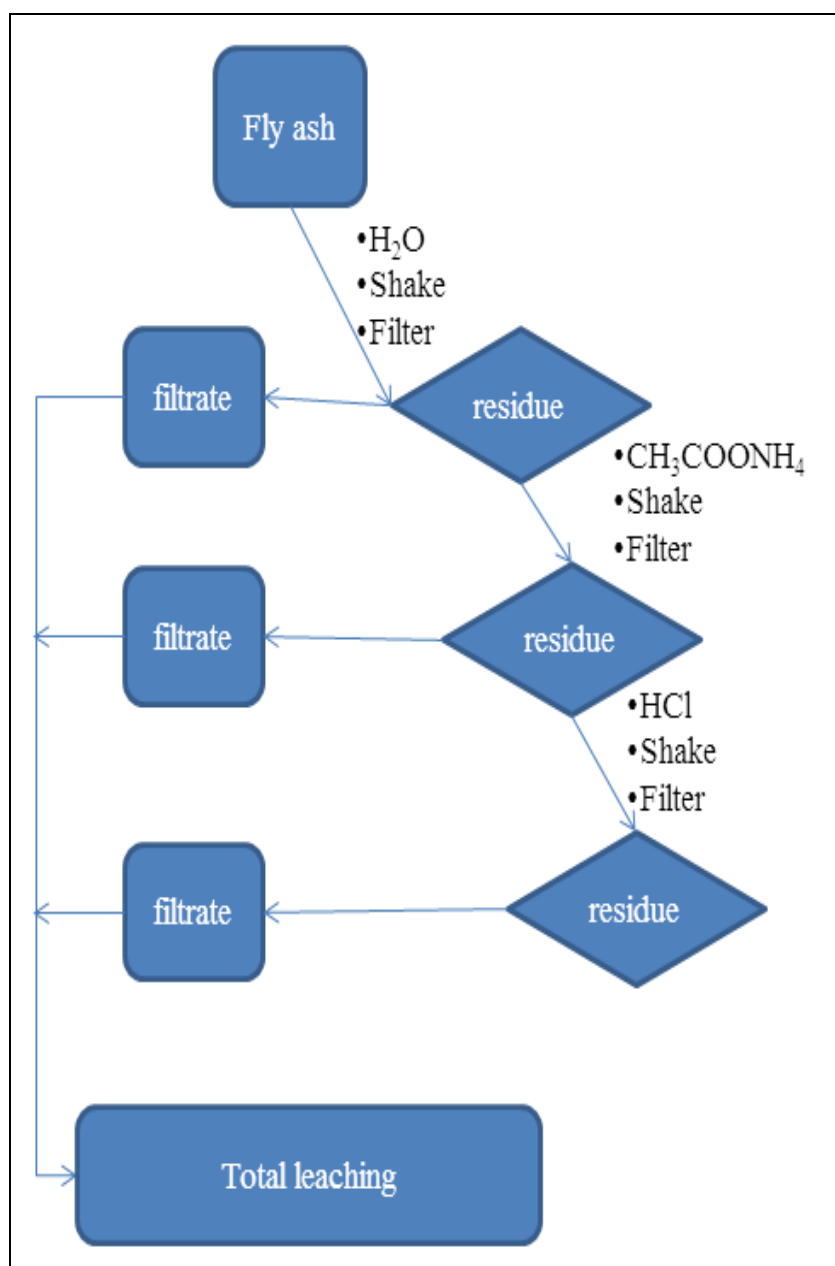
<sup>†</sup> The results are the average of three measurements.

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

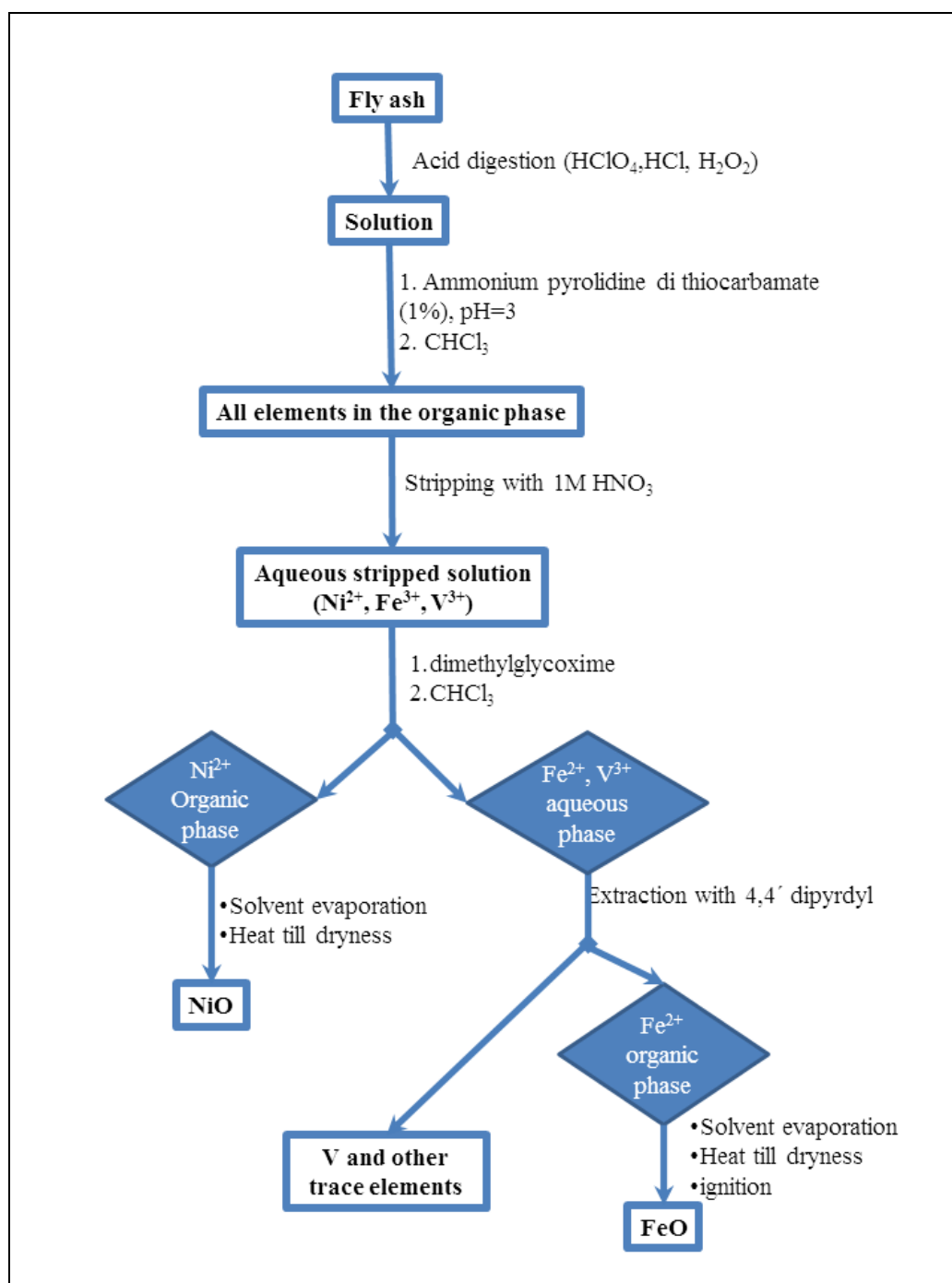
Element Leaching agent	Fe	Ni	V
H <sub>2</sub> O	4.4	4.9	9.0
CH <sub>3</sub> COONH <sub>4</sub>	0.50	1.9	3.8
HCl	2.7	0.5	1.8

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

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



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



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