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Recovery of vanadium and nickel from heavy oil fly ash (HOFA): a critical review

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Heavy oil fly ash "HOFA" is the fly ash generated in power stations using heavy oil as fuel. HOFA is considered a hazardous waste because it contains considerable amounts of heavy metals. However, it contains significant amounts of vanadium "V" and nickel "Ni", which are precious metals for manufacturing processes. This paper presents a critical review of various approaches described in the literature for the recovery of V and Ni from HOFA, including processes of leaching, chemical precipitation, solvent extraction, and ion exchange. The optimum operational parameters and their effects on recovery efficiency are discussed. The digestion mixtures of strong mineral acids used for dissolving all metals present in HOFA are also highlighted. The leaching processes of V and Ni use mainly acidic and alkaline solutions. Bioleaching is a promising environmentally friendly approach for the recovery of V and Ni through using appropriate bacteria and fungi. After leaching, V and Ni compounds are recovered and purified using various techniques, including chemical precipitation, solvent extraction, and ion exchange. In most cases, V and Ni are recovered as thermally decomposable compounds that undergo calcination to produce V_2O_5 and NiO. Eventually, V and Ni are recovered as pure oxides in most approaches, but pure metals are obtained in exceptional procedures.

1. Introduction

Heavy oil fly ash (HOFA) is a waste product resulting from the combustion of heavy fuel oil. Heavy oil is the most used fuel for heating boilers at power stations and water desalination plants in Saudi Arabia and many countries worldwide. For instance, the annual consumption of heavy oil in power stations and desalination plants is more than 40 million tons in Saudi Arabia, and more than 4 thousand tons in thermal power stations in Egypt.[1] The combustion of heavy fuel in power stations generates great amounts of fly ash, which is expected to increase in the next few years due to the growing rate of energy demand. Burning 1000 liters of heavy oil generates about 3 kg of fly ash.[2] The HOFA produced is mainly composed of unburned carbon, with a great percentage of 64–97,[3] and inorganic compounds, including oxides of vanadium, nickel, magnesium, aluminum, zinc, iron, and others. Sulfates of those metals might be included too.[4]

Vanadium(V) and nickel (Ni) are considered the most toxic metallic species present in HOFA.[5,6] They are easily leachable by rainwater in disposal landfills. On the other hand, V and Ni have wide applications in the industry; they are used as alloying elements in steel and other special alloys.[7,8] Therefore, the recovery of V and Ni from industrial wastes is of great interest in terms of environmental and economic aspects. In general, V and Ni are present in HOFA with contents of 2–5 wt% according to many studies characterized the fly ash.[9–11] The chemical composition of HOFA varies depending on the composition of the heavy oil fuel, the operating conditions, and the reagents added. However, higher levels of V and Ni were detected in heavy oil fly ashes (HOFAs) produced worldwide in various power stations.[12]

Both V and Ni are considered precious metals and their rapid and continuously increasing demand is countered by their low concentrations in raw minerals. V is usually recovered from the raw materials produced as a by-product during the extraction of other metals. V is used in a wide range as an alloying element for a diverse range of super alloys of steel, stainless steel, nickel, and titanium.[7,13,14] Many applications are contributing to the increased demand for V, for example, V redox battery (V flow battery) is a promising solution for the global problem of seeking large scale energy storage.[15–17]

Heavy oil fuel is the major fuel used in Saudi Arabia, it contributes to more than 70% of national energy production.[3,18] The bulk density of HOFA ranges from 0.26 g cm^{-3} (ref. 19) to 0.52 g cm^{-3}.[20] However, most studies reported that HOFA has a density of around 0.33 g cm^{-3}. This means that the specific volume of HOFA is about 3 cm^3 g^{-1}. Consequently, the dumping

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of HOFA needs spacious landfill sites that increase the environmental consequences. The large quantity of HOFA generated along wide Saudi Arabia has become a pressing concern from a safe disposal point of view.

Although the HOFA contains V and Ni in economical concentrations comparable to that found naturally in mineral recourses, its disposal in landfills leads to the leaching of V and Ni that poisons the soil. Consequently, real efforts have to be directed to allow the recovery of these valuable metals and the safe re-utilization of fly ash residue.

2. Digestion and chemical composition of HOFA

Digestion aims at the dissolution of various metals (major and trace) present in HOFA in an aqueous solution that can be undergone subsequent analysis using atomic spectrometric techniques. Mixtures of strong inorganic acids such as HCl, HNO_3, HF, and H_2SO_4 are the most commonly used dissolvents for the direct digestion of fly ash. It is reported that HCl digestion can completely dissolve all cations, except for Si and partly Ti. However, HF acid can dissolve silicates and completely extract Si and Ti.[21,22] The mixture of 1 : 1 concentrated HCl–HNO_3 with water, dissolved 49 elements.[23] The most common digestion methods of fly ash for extraction of heavy metals involve the use of aqua regia solution (3 : 1 HCl–HNO_3) and reverse aqua regia solution (1 : 3 HCl–HNO_3). Digestion procedures include using a hot plate, a microwave oven and ultrasonic baths. With the aid of microwave and ultrasonic techniques, the digestion time can be reduced with higher dissolution efficiency.[24] Digestion is commonly preceded by the preparation of ash samples through drying at elevated temperatures. Table 1 summarizes some digestion procedures used for the chemical analysis of HOFA elements.

The mostly used spectrometric techniques are atomic absorption spectrometry "AAS", inductively coupled plasma-optical emission spectrometry "ICP-OES", and inductively coupled plasma-mass spectrometry "ICP-MS".[24,25] ICP-OES has widely been used to analyze an enormous range of coal and fly ashes. The main superiority of ICP over AAS techniques include its capability of conducting simultaneous multi-element analysis with higher sensitivity and reliability.[24] The carbon content in the fly ash (found as carbon, carbonate, and residual oily substance) is evaluated by thermal decomposition for 6 h at 1000 °C. The weight loss is considered to be the carbon content that is found to be 85% in a HOFA sample.[26,27] However, Tsai and Tsai[28] measured the contents of carbon, hydrogen, and nitrogen in the fly ash using the elemental analyzer (Heraeus CHNRapid Elemental analyzer). The sulfur content in the fly ash is determined using X-ray fluorescence spectrometer according to old and recent researches,[29,30] but Tsai and Tsai[28] measured the sulfur in the fly ash by a Tacussel Coulomax 78 Elemental analyzer.

The chemical analysis of HOFA shows that it is composed mainly of carbon, in addition to some metallic elements. Table 2 reveals the chemical composition of fly ash samples produced by burning heavy oil in different power plants and desalination plants. The ash contains high levels of V and Ni, and highly toxic elements such as arsenic, cadmium, cobalt, chromium, lead, and selenium. V content reaches up to 5 wt%,[11] but the maximum content of Ni is 1.8 wt%.[31]

3. Leaching of V and Ni from HOFA

Leaching of HOFA is the first main step for the recovery of V and Ni. The recovery procedure varies with the type of ash depending on its own physicochemical properties, particularly the chemical composition.[32] Research is directed to reach optimal leaching conditions, which include the leaching agents, temperature, residence time (contact time), agitation speed, particle size, and solid to liquid ratio (S/L).[22]

Aburizaiza[26] studied the leachability of V, Ni, and Fe from HOFA generated in three different power and desalination plants using various leaching agents, including water, H_2SO_4, HNO_3, and HCl. It was found that the most leachable metal is V with exothermic and spontaneous dissolution reactions. For a comparison investigation of the used agents' leachability, acidic solutions were tested with a concentration of 1 M and S/L ratio of 1/50 g ml^{-1} at room temperature. Considerable metal recovery is obtained at 20 min. Within this time, the leachability for Ni follows the order; HCl > H_2SO_4 > HNO_3 > H_2O. For V and Fe, the leaching agents are ranked as H_2SO_4 > HCl > HNO_3 > H_2O. However, a longer time for 1 h ranks HCl and HNO_3 in a higher rank former to H_2SO_4.[26] On the other hand, alkaline leaching using sodium hydroxide "NaOH" and ammonium hydroxide "NH_4OH" have the advantage to leach V leaving Ni and Fe undissolved in the ash.[26,28]

An overall review of the literature shows that the approaches proposed for the recovery of V and Ni are mainly performed through acidic or alkaline leaching processes. Therefore, the recovery methods can be classified, according to the leaching solution used, to be acidic and alkaline processes. Additionally, water leaching and bioleaching are recently researched in systematic approaches to recover V and Ni from fly ash.

3.1. Acidic leaching

H_2SO_4 is widely used in leaching processes by the virtue of its high economically advantageous due to its distinct lower cost.[22,33] H_2SO_4 acid dissolves most of the metallic cations, such as V, Ni, Fe, Mg, and others, forming metal sulfates. V compounds can be then precipitated by adding various agents. Ni can also be precipitated as Ni compounds, or pure Ni can be electrochemically deposited from a Ni sulfate solution.

Amer[34] studied the selective recovery of V and Ni by direct H_2SO_4 leaching of Egyptian boiler ash under oxygen pressure to produce $V_2(SO_4)_3$ and $NiSO_4$. The dissolution of V and Ni is explained in the next two equations:

$$V_2O_3 + 3H_2SO_4 = V_2(SO_4)_3 + 3H_2O \tag{1}$$

$$NiO + H_2SO_4 = NiSO_4 + H_2O \tag{2}$$

Table 1 A summary of some digestion procedures used for chemical analysis of HOFA

Digestion solution	Preparation of the ash	Temp., °C	Time	S/L ratio	Assisting technique	Analysis technique	Ref.
Conc. HCl (2.0 mL) + $HClO_4$ (5.0 mL) + HNO_3 (5.0 mL)	Drying at 110 °C for 2 h, ground + −200 mesh seiving	Room temperature		1 : 20 g ml^{-1}	Heating slowly at 100 °C for 1 h on a hot plate with constant stirring till drying, then conc. HNO_3 + drying (3 times). Finally the solid residue was redissolved in dilute HNO_3	ICP-OES	26
Aqua regia	Drying at 110 °C for 2 h, ground + −200 mesh seiving				The cooled solution was filtered in a 100 mL volumetric flask and diluted with distilled water before analysis		26
Reverse aqua regia solution (1 : 3 HCl–HNO_3)	Crushing + sieving (−100 μm)	250 °C	300 min	1 : 5 g ml^{-1}		ICP-AES	51
A mixture of acids composed of $HClO_4$, H_2SO_4 and HNO_3							35
Aqua regia	Drying t 110 °C + sieving (−500 μm)			0.005–0.015 g ml^{-1}	Microwave furnace	ICP-AES	27
Hydrofluoric acid + aqua regia	Burned at 550 °C for 24 h				Hydrofluoric acid and aqua regia	AAS	28
H_2SO_4						ICP-OES & titration	37
3 : 1 HNO_3–Hf solution	Drying at 105 °C	120 °C	120 min	1 : 40 g ml^{-1}	Autoclave	ICP-AES & titration	38
HNO_3–Hf solution	Drying at 105 °C	120 °C	120 min		Autoclave	ICP-AES	40
Hydrofluoric acid (2.5 mL) and nitric acid (7.5 ml)				1 : 10 g ml^{-1}		ICP-AES	69
25% nitric acid solution	0.1 g of fly ash was mixed with 1 g lithium borate mixture + heating at 1000 °C for 1 h	60 °C				ICP-AES	52
Hot mixed acid composed of concentrated $HClO_4$, H_2SO_4, and HNO_3						ICP-AES	31
Aqua regia	Crushing + sieving (−75 μm) + washing with hexane and acetone + drying for 30 min at 70 °C	50 °C	24 h			ICP-OES	46
Aqua regia	Drying 120 °C, 24 h	100 ± 5 °C	2 h	1 : 10 g ml^{-1}	Digestion was repeated thrice using a hot plate with magnetic stirrer, a flask, and a condenser	ICP-OES	47

Table 2 Chemical composition of HOFA reported in various references[a]

	Reference								
Element	Ref. 20, PP	Ref. 20, DP	Ref. 19	Ref. 9	Ref. 11	Ref. 40	Ref. 10	Ref. 31	Ref. 47
Carbon (%)	94.40	56.70	85.56	51.86		67.4		77.40	
Sulfur (%)	7.77	27.18	ND			8.6		7.10	
Vanadium (ppm)	**9072**	**31 044**	**2958**	**34 487**	**50 000**	**38 000**	**7670**	**12 900**	**3540**
Nickel (ppm)	**2382**	**13 633**	**1762**	**11 852**	**15 400**	**16 000**	**18 000**	**6800**	**1055**
Cadmium (ppm)	1.65	3.7	3.28	1.59					60.4
Arsenic (ppm)	2.54	1846	2.24	68.29					128.5
Cobalt (ppm)	2.88	12.33	3.28	247.79	2200				60.7
Chromium (ppm)	36.79	113.09	4.06	107.60	8000				70.4
Selenium (ppm)	1.00	6.81	11.60	13.20					7.25
Lead (ppm)	17.09	13.94	11.00	116.10					27.85
Zinc (ppm)	21.92	118	130	592.10			1110	4000	65.5
Copper (ppm)	10.44	50.40	170.4	120.30				17 000	57.12
Iron (ppm)	7210	8771			220 500	8000	59 800	1400	176.5
Magnesium (ppm)	6971	94 608			2000		3430	14 100	3615
Manganese (ppm)	23.9	149.26							12.8
Calcium (ppm)	582.3	4121.2						2300	3380
Sodium (ppm)	1395	7555				19 000			1310
Alumnium (ppm)	3541	1041.8				1040	2870	2500	642.4
Barium (ppm)	7.42	49.68							69.0
Others (ppm)			Hg, 0.25		Mo, 3500	Si, 8000		Si, 800; O, 93 200	

[a] PP = power plant; DP = desalination plant.

The optimum parameters for leaching are established to be: temperature of 200 °C, leaching period of 15 min, O_2 pressure of 15 bar, H_2SO_4 concentration of 60 g l^{-1}, and S/L ratio of 1. V is precipitated from the acidic sulfate solution as vanadium hydroxide "$V(OH)_3$" by adding NH_4OH and neutralization. On the other hand, Ni metal can be electrodeposited from $NiSO_4$ electrolyte. Leaching under O_2 pressure is applied to oxidize ferrous sulfate to ferric sulfate (eqn (3)). The latter hydrolyzes thereafter and leads to Fe precipitation as ferric oxide (eqn (4)), leaving V and Ni in the leaching solution.

$$2FeSO_4 + H_2SO_4 + 1/2\ O_2 = Fe_2(SO_4)_3 + H_2O \tag{3}$$

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4 \tag{4}$$

Barik *et al.*[35] developed a process for recovering V and Ni from an industrial Ni and V-rich solid waste. The process includes H_2SO_4 leaching, solvent extraction, precipitation, and crystallization. Both V and Ni were leached out with 98% recovery by 1.35 M H_2SO_4 at 40 °C for 90 min. V is selectively extracted from the liquor with 40% LIX 84-I at pH 0.5 and precipitated as ammonium metavanadate "NH_4VO_3" by adding NH_4OH. The Ni dissolved in the raffinate is selectively separated as Ni oxalate "NiC_2O_4" by using ammonium oxalate "$(NH_4)_2C_2O_4$". Finally, pure Ni oxide "NiO" is obtained by calcination of Nickel oxalate "NiC_2O_4" at 450 °C for 2 h. On the other hand, the NH_4VO_3 can be calcined to give V pentoxide "V_2O_5".[36]

Nazari *et al.*[37] optimized the parameters of the H_2SO_4 leaching process to maximize the recovery of V and Ni. The optimum conditions for the highest recovery obtained, for V of 94% and for Ni of 81% are: H_2SO_4 concentration of 19.5%, temperature of 80 °C, S/L ratio of 9.15 wt%, and leaching time of 2 h.

Vitolo *et al.*[38] recovered V as V_2O_5 from fly ash, through a three-step process consisting of H_2SO_4 leaching, oxidative precipitation, and washing. The operating parameters of leaching are reported to be boiling H_2SO_4 of 1 M concentration for 30 min with L/S ratio of 3 ml g^{-1}. The recovery of V is around 90%. The oxidative precipitation process is performed by adding sodium chlorate "$NaClO_3$" as an oxidative agent of $V^{(IV)}$ to $V^{(V)}$.[39] This oxidation of V is accompanied with the evolution of H and consequently leads to a decrease in pH. Na_2CO_3 is added to keep the ideal pH for V_2O_5 precipitation. Finally, the V_2O_5 precipitated is washed with an acidic solution to remove Na and other impurities.

Vitolo *et al.*[40] developed their three-step process[38] by preceding it with a controlled burning of fly ash in order to reduce its carbon content. The reduction of carbonaceous fraction in the fly ash increases the V recovery in the following leaching step to reach 97%. The optimum temperature of the burning step is found to be 850 °C and leads to greater overall V recovery (83%) in the form of V_2O_5 with lower content of impurities. Higher burning temperature (above 950 °C) leads to lower V recovery due to the fusion and volatilization of V and the formation of complicated V–Ni refractory compounds.

Navarro *et al.*[27] conducted leaching experiments of HOFA in 0.5 M H_2SO_4 solution with L/S ratio of 4 ml g^{-1} for 24 h at room temperature and an agitation speed of 200 rpm. The leaching step was followed by rinsing for 1 h in water with L/S ratio of

4 ml g^{-1}. V recovery is recorded to be 98%, while Ni recovery is close to 12%.

Aburizaiza[26] illustrated a multi-step procedure for leaching and extraction of Ni, V, and Fe from HOFA, following the next steps:

(1) Acidic leaching of fly ash in digestion solution composed of mineral acids (perchloric acid "$HClO_4$" and/or HCl), and hydrogen peroxide "H_2O_2".

(2) Organic extraction of metals; in this step, the leachate is mixed and stirred with ammonium pyrollidine dithiocarbomate "$C_5H_9NS_2 \cdot NH_3$" in chloroform "$CHCl_3$". After equilibrium, a layer of an organic phase – containing the metallic cations – is formed. The results reveal compete extraction of aimed metal ions (V, Ni, and Fe) in the organic phase.

(3) Stripping of V, Ni, and Fe from the organic phase by mixing it with 1 M HNO_3 containing Hg^{2+} ions. Thus, the resultant aqueous nitric acid solution contains metallic cations (V^{3+}, Ni^{2+}, Fe^{2+}).

(4) Extraction of total Ni in the stripped nitric acid solution by adding dimethylglyoxime "$C_4H_8N_2O_2$" in chloroform, that forms again an organic phase containing Ni^{2+} ions and leave V^{3+} and Fe^{2+} ions dissolved in the aqueous nitric acid solution phase. The Ni-contained organic phase is separated and evaporated till dryness to recover nickel in the form of NiO.

(5) Extraction of total Fe in the aqueous nitric acid solution phase (remained in step 4) by treating with 4,4-pypyridyl. The Fe-contained organic phase is separated and undergoes evaporation and ignition to obtain Fe in the form of FeO.

(6) The remained aqueous solution contains vanadium as V^{3+} and other trace elements.

Analysis and materials balance reveal higher recovery values of Ni and Fe when their extracted concentrations are compared with that in the digestion solution. However, the study does not suggest an approach to extract V from the final aqueous solution. Moreover, the approach consumed a lot of chemicals to treat a small quantity of fly ash.[26]

Aiming at recovering of V and Ni and making the fly ash harmless, Tokuyama *et al.*[31] leached HOFA in two steps. The first step uses water to dissolve Ni, Zn, Mg, Al, and Fe; and the second utilizes H_2SO_4 to dissolve V. The authors also found that the leaching efficiency of H_2SO_4 is comparable to that of HCl. On the other hand, the authors reported that selective leaching of V can be achieved by leaching with concentrated NaOH.

Tsygankova *et al.*[12] reported that the leaching process of HOFA depends not only on its chemical composition but also on its phase composition. They presented the results of acidic leaching for three fly ash types with different chemical and phase compositions. Each fly ash has its own optimum leaching parameters in acidic solutions, that range from 5 to 9% H_2SO_4 concentration at temperatures between 20 and 80 °C for time periods extending to 30 and 60 min. V is precipitated as V_2O_5 through oxidation of the leaching solution with H_2O_2 at 20 °C for 30 min. Precipitation is completed by subsequent heating at 95 °C and pH of about 1.8 to 2.

Khalafalla *et al.*[41] leached the concentrate of petroleum fly ash in H_2SO_4 solution with the aim at recovering V, Ni, and Zn. The fly ash is physically concentrated using high tension left magnet to raise the contents of V_2O_5, NiO, and ZnO to 18.1%, 11.18%, and 8.11%, respectively. Thereafter, the leaching process, with 180 g per l H_2SO_4 in the presence of 4% MnO_2 as an oxidant at 80 °C for 10 h, is conducted to leach 96.5 of V, 94.8% of Ni, and 99.1% of Zn. Eventually, V is recovered from the leach liquor by solvent extraction with 3% Alamine 336 in kerosene, leaving Ni and Zn dissolved in the raffinate solution. V is then stripped from the organic phase by adding H_2SO_4 and precipitated as $V_2O_5 \cdot H_2O$ compound. On the other hand, Ni and Zn are co-precipitated, by adding Na_2S to the raffinate solution, forming (Zn–Ni) sulfide cake, which can be suggested to undergo hydrometallurgical and solvometallurgical[42] approaches for recovery and separation of Zn and Ni.[43–45]

Rahimi *et al.*[46] developed a novel approach for extracting V from HOFA using lemon juice by the leaching effect of organic acids contained therein. Lemon juice contains 90 mg g^{-1} citric acid, 0.86 mg g^{-1} malic acid, and 1.24 mg g^{-1} ascorbic acid. The concept was to use an environmentally friendly approach to get organic acids alternative to the creation of such acids by the very slow microbial growth in bioleaching. The authors[46] dissolved V with the highest recovery of 88.7% using optimal conditions of 2 h ultrasound leaching of HOFA in 27.9% lemon juice solution containing 10% H_2O_2 at 35 °C and S/L ratio of 0.01%. After the leaching step, sodium carbonate "Na_2CO_3" is added to raise pH to 9–10, and $CaCl_2$ is put in the liquor to precipitate Al and Fe. Thereafter, V is precipitated as highly pure NH_4VO_3 by adding ammonium chloride "NH_4Cl". Eventually, NH_4VO_3 is calcined at 500 °C to produce vanadium pentoxide "V_2O_5". The assisting leaching agents, both H_2O_2 and ultrasound, are found to have an essential effect in accelerating the V dissolution kinetics.

The approach to leach HOFA by the organic acids in lemon juice is novel and environmentally friendly. Nevertheless, the S/L ratio used of only 0.01% necessitates using great amounts of lemon juice. Moreover, the results lack more research to be more reliable.

3.2. Alkaline leaching

Many studies on alkaline leaching of HOFA reported that Ni is insoluble in alkali solutions, which have the superiority for selective leaching of V with higher recovery efficiency. (*e.g.* Ref. 26, 28, 31 and 47). Tsai and Tsai[28] suggested a two-stage leaching method for HOFA. In the first stage, Ni is recovered by leaching the fly ash in ammonia water containing ammonium sulfate "$(NH_4)_2SO_4$". In the second stage, the ash residue is leached in an alkaline (NaOH) solution to recover V. However, the approach was not adopted in recent studies because of the lower recovery of Ni (60%) in the ammonia/$(NH_4)_2SO_4$ solution, which dissolves also 8% of V in the first stage. Moreover, the study didn't conduct or suggest an approach for the final recovery of V and Ni from the leaching solution.

Al-Zuhairi[48] extracted V with a high recovery yield (98%) from the residual of fired crude oil in a power station by alkaline leaching method using sodium hydroxide "NaOH" solution. The conditions for maximum extraction of V are reported to be 2 M NaOH concentration at 100 °C for 2 h. The leachate is then acidified, to lower its pH, and treated with ammonium hydroxide "NH_4OH" in order to precipitate V as NH_4VO_3. The latter is calcined at a temperature of less than 690 to produce V_2O_5.

Navarro *et al.*[27] reported that alkaline leaching of HOFA by NaOH is preferred to acidic leaching because it is more selective for V, although alkaline leaching has lower leaching efficiency compared to acidic leaching by H_2SO_4. Alkaline leaching by NaOH is performed using 2 M NaOH solution with L/S ratio of 4 ml g^{-1} for 24 h at room temperature and agitation of 200 rpm. Leaching is followed by 1 h water rinsing 3 times. Vanadium recovery reaches 90%, but successive leaching and rinsing for 6 times, 1 h for each time, increases V recovery to 98%. The temperature is found to have a very limited influence on the efficiency and kinetics of V leaching when the contact time reaches 12 h. Sodium carbonate "Na_2CO_3" is also tested for leaching HOFA with the aim of increasing the selectivity V recovery with avoiding Si leaching. However, 80% of V is recovered by leaching treatment using 0.66 M Na_2CO_3 solution at the same condition applied for NaOH leaching. Compared to NaOH leaching, Na_2CO_3 leaching shows higher vanadium selectivity with lower leaching efficiency.

Hakimi *et al.*[49] established a flowchart for the extraction of V with a high recovery yield through alkaline leaching of V-rich HOFA using NaOH solution at 95 °C for 4 h. After the leaching, the alkaline leachate is neutralized by adding 4.5 M H_2SO_4 solution. When the pH is adjusted to 8, dissolved Al and Si are deposited leaving V dissolved as sodium vanadate in the filtrate. The latter is treated with an ammonium compound to precipitate V as NH_4VO_3, which is calcined at 450 °C for 1 h to produce V_2O_5.

Akita *et al.*[50] studied the recovery of nickel and vanadium from oil fly ash in a two-step leaching process. Ni is leached with NH_4Cl solution in the first step, followed by Na_2CO_3 leaching of the residual ash to dissolve vanadium in the second step. Vanadium is then recovered by solvent extraction with TOA/toluene solution followed by precipitation as NH_4VO_3 with NH_4Cl. On the other hand, Nickel is recovered as NiS from its leach liquor by precipitation with Na_2S.

Al-Ghouti *et al.*[51] conducted leaching of HOFA in a two main steps process for recovery of nickel and vanadium. In the first step, Ni is selectively extracted using NH_4Cl/NH_3 solution composed of 2 M NH_4CL and 2 M NH_3, at 50 °C with L/S ratio of about 19 ml g^{-1}, under agitation for 6 h. The leachate is then treated with sodium sulfide "Na_2S" to precipitate Ni as NiS with a recovery yield of 56%. In the second step, V is extracted from the Ni-free residual ash by leaching in an aqueous solution of sodium carbonate with a concentration of 2 M Na_2CO_3 at 70 °C and pH 5.5 under agitation for 6 h. However, Na_2CO_3 solution strips other cations like Fe, Mg, and Ca along with V. Selective extraction of V is conducted by adding tri-ethylamine/toluene solution "0.1 M of $(CH_3CH_2)_3N$ in toluene" to the Na_2CO_3 solution. The organic layer is separated and mixed again with a new 2 M Na_2CO_3 solution for 3 h to extract V in an aqueous layer. The extracted V is precipitated with a maximum recovery of 45% by mixing the resulting aqueous layer with 1.3 M NH_4Cl for 20 h.

Stas *et al.*[11] established a two-stage leaching process for the recovery of vanadium, nickel, and molybdenum from HOFA. In the first stage, namely alkaline leaching, V and Mo are recovered using NaOH solution. The residual fly ash is then leached within the following second leaching stage (acidic leaching) by H_2SO_4 to recover Ni. The highest V recovery (∼90%) is achieved in 8 M NaOH solution with L/S ratio of 5 ml g^{-1} at 100 °C for 3 h. The resultant alkaline leaching solution containing V and Mo is cooled with mild agitation to 5 °C for 1 h to precipitate V as sodium vanadate, which is separated by filtration leaving the filtrate containing sodium molybdate. The latter filtrate is acidified with HNO_3 and heated to 90 °C to precipitate Mo as H_2MoO_4. On the other hand, the sodium vanadate is re-dissolved in 5% HNO_3 solution (pH = 8), and $(NH_4)_2SO_4$ is added to the solution to precipitate V as NH<sub4></sub>VO<sub3></sub>. The NH<sub4></sub>VO<sub3></sub> transforms to V_2O_5 by calcination at 500 for 24 h. In the second stage (acidic leaching), the residual ash is leached by 5 M H_2SO_4 solution for 3 h at 100 °C and L/S ratio of 4 ml g^{-1} to extract Ni with a recovery yield of 80%. The acidic leachate is then treated with NaOH solution in two steps to raise the pH and precipitate Fe and the remaining V. Eventually, sodium carbonate "Na_2CO_3" is added to precipitate Ni as nickel carbonate "$NiCO_3$".

Howsawi *et al.*[47] conducted alkaline leaching experiments for recovery of V from HOFA sample delivered from a power station plant in Saudi Arabia. 2 M NaOH solution dissolves 94.4% of V found in HOFA in a leaching experiment for 2 h at 110 °C and L/S ratio of 8 ml g^{-1}. A Graham condenser is used to cool and condense vapor back to the leaching solution. The filtrate is acidified to pH 2 by adding HNO<sub3></sub>, and then NH_4OH is gradually added until pH 7 to precipitate V as NH_4VO_3.

3.3. Water leaching

A three-step process, beginning with carbon burning and followed by salt roasting and water leaching, was conducted on HOFA containing 85 wt% unburned C and 2.2 wt% V.[52] The burning step for 4 h at 650 °C removes the most of carbon and consequently raises the V content up to 19 wt%. Then, the burned ash (enriched with V) is roasted for 4 h at 650 °C with sodium carbonate "Na_2CO_3" in order to convert V oxides to sodium metavanadate "$NaVO_3$" (eqn (5) and (6)), which is a water-soluble vanadium compound.[52,53]

$$V_2O_5 + Na_2CO_3 = 2NaVO_3 + CO_2\ (g) \tag{5}$$

$$V_2O_3 + Na_2CO_3 + O_2\ (g) = 2NaVO_3 + CO_2\ (g) \tag{6}$$

The roasted ash, containing V as water-soluble $NaVO_3$, is leached with water for 4 h at 60 °C with L/S ratio of 50 ml g^{-1}. Water leaching selectively dissolves V, leaving Fe and Ni compounds undissolved in the ash residue, and 92 wt% of V is recovered. After the leaching process, V is precipitated as NH_4VO_3 from the leaching solution by adding $NH_4)_2SO_4$.[49] The precipitated NH<sub4></sub>VO<sub3></sub> is separated by filtration, dried, and calcined to produce vanadium oxide

"V_2O_5" according to the next precipitation and calcination reaction equations:

Precipitation:

$$2NaVO_3 + (NH_4)_2SO_4 = 2NH_4VO_3 + Na_2SO_4 \tag{7}$$

Calcination:

$$2NH_4VO_3 = V_2O_5 + 2\ NH_3 + H_2O \tag{8}$$

A more recent approach for converting V compounds into water-soluble $NaVO_3$ through roasting with NaCl is reported by Ibrahim *et al.*[54] The authors leached vanadium in distilled water, at L/S ratio of 10 ml g^{-1}, with a high recovery (95.3%) from HOFA that was previously roasted with 20 wt% NaCl for 2.5 h. The roasting temperature is optimized, and 850 °C is found to be the appropriate temperature for the reaction of sodium chloride with vanadium-bearing minerals in the presence of excess oxygen to form $NaVO_3$ according to the equations (eqn (9) and (10)):

$$2NaCl + 2VO_2 + O_2 \rightarrow 2NaVO_3 + Cl_2\uparrow \tag{9}$$

$$2NaCl + V_2O_5 + 1/2\ O_2 \rightarrow 2NaVO_3 + Cl_2\uparrow \tag{10}$$

$$2NaCl + 2Fe_2VO_4 + 2O_2 \rightarrow 2NaVO_3 + 2Fe_2O_3 + Cl_2\uparrow \tag{11}$$

However, higher temperature up to 1000 °C leads to the formation of refractory compounds due to the sintering of V, Ni, Al, and Fe compounds and the melting of NaCl.[55] Eventually, the study showed that V can be easily extracted from $NaVO_3$ through water leaching. The solid residue can undergo a further acidic leaching process to extract Ni.

3.4. Bioleaching

Bioleaching is a developed approach for extraction of valuable metals from fly ashes with the advantage of avoiding high amounts and concentrations of chemical reagents used in acidic and alkaline leaching processes.[56–59] In bioleaching, several kinds of microorganisms including various species of bacteria and fungi are utilized to leach and recover a variety of metals from solid materials. The most common bacteria used in bioleaching belong to the thiobacilli genus, which are considered as acidophilic species, such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*.[60]

Rastegar *et al.*[60] optimized the recovery of V, Ni, and Cu from HOFA using *Acidithiobacillus ferrooxidans* bacteria "*A. ferrooxidans*". The bacteria were allowed to grow in a medium containing 3 g per l $(NH_4)_2SO_4$, 0.5 g per l $MgSO_4\cdot 7H_2O$, 0.5 g per l $K_2HPO_4\cdot 3H_2O$, 0.1 g per l KCl, 0.01 $Ca(NO_3)_2$, and 44.22 g per l $FeSO_4\cdot 7H_2O$. The fly ash is added to this medium with S/L ratio ranging between 1% and 4%. Vanadium, nickel, and copper are simultaneously leached with maximum recoveries of 74%, 95%, and 88%, respectively, using optimum parameters; including Fe^{2+} concentration of 2.6 g l^{-1}, pH of 1.3, S/L ratio of 0.01 (w/v). After bioleaching step, Ni and Cu are separated from the leachate liquid by raising its pH up to 9–10 using NaOH. V is then precipitated as NH_4VO_3 by adding NH_4Cl. Pure V_2O_5 is obtained by calcination of NH_4VO_3 for 4 h at 550 °C.

Additionally, the authors[60] investigated a hydrothermal method for producing NaV_6O_{15} nanorods, which can be used in the synthesis of rechargeable lithium batteries. A suspension of V_2O_5 powder, in water with additions of H_2O_2 and NaCl, is undergone vigorous stirring for 2 h until obtaining an orange suspension of NaV_6O_{15} nanorods that are washed, dried, and annealed at 500 °C.

Wei *et al.*[61] reported that *A. ferrooxidans* bacteria utilize sulfur and ferrous sulfate for growth and produce H_2SO_4. The authors investigated *A. ferrooxidans* for bioleaching of V from a V-containing shale. Maximum recovery of 62% V is achieved with S/L ratio of 0.02, 5 g l^{-1} initial Fe^{2+} concentration, pH 2, 10% inoculum percentage, and 1.2 days bioleaching time.

Rasoulnia *et al.*[62] studied the bioleaching of HOFA using the fungus *Penicillium simplicissimum*, which produces high amounts of organic acids (citrate, gluconate, oxalate). The fungus is activated and cultivated on PDA (potato dextrose agar) Petri dishes for 7 days as incubation time at 30 °C. The fungus is inoculated to bioleaching medium with the following composition: 100 g per l sucrose, 1.5 g per l $NaNO_3$, 0.5 g per l KH_2PO_4, 0.025 g per l $MgSO_4\cdot 7H_2O$, 0.025 g per l KCl, and 1.6 g per l yeast extract. Bioleaching experiments of the ash are conducted in 100 ml of *Penicillium simplicissimum* medium with S/L ratio of 0.01 g ml^{-1} at 30 °C under stirring with 130 rpm. Among three leaching methods studied by the authors, the method, namely spent-medium leaching, is found to achieve the highest recovery of V and Ni. In this method, the fungus is endowed to grow for 15 days and create organic acids. The ash sample is then added to the bioleaching medium and undergoes leaching by the organic acids produced by fungus. The subsequent analysis of the filtrate showed that the recovery of V is 96.3% and of Ni is 40.1%. Fe is also extracted but with a lower recovery yield, which can be increased to be 48.3% if the original ash was preheated at 400 °C. However, the thermal pretreatment of the ash reduces the recovery of V and Ni due to the formation of less soluble compounds.

In a comparison study between the bioleaching efficiency of the acid producing fungi, *Aspergillus niger* and *Penicillium simplicissimum*, Rasoulnia and Mousavi[63] found that the maximal recovery of V (97%) and Ni (50%) is obtained using *Aspergillus niger*. The higher bioleaching efficiency of *Aspergillus* enables using higher pulp density of added ash with S/L ratio of 3.2% (w/v) under optimal conditions of 7 days leaching duration and 60 °C leaching temperature.

Another fungal bioleaching approach was recently investigated by Seddiek *et al.*[64] The fungal isolate *Cladosporium cladosporioides* is grown on Czapek's Dox agar medium with a composition of 30 g sucrose, 15 g agar, 1 g KH_2PO_4, 2 g $NaNO_3$, 0.5 g KCl, 0.5 g $MgSO_4\cdot 7H_2O$, traces $FeSO_4\cdot 5H_2O$, and 5 g yeast extract in 1 liter. The main organic acid produced by this fungus is malic acid. The optimum parameters for bioleaching of V and Ni from HOFA are; the fly ash concentration is 1% (w/v), pH is 6 for V and pH is 8 for Ni, and the bioleaching time is 10 days. The maximum recovery obtained for V and Ni is 65.4% and 74.6%, respectively. The thermal roasting pretreatment preceding the

Table 3 A summary of various leaching approaches for HOFA

Approach	Preparation of the ash	Leaching agent	Temp., °C	Time	S/L ratio	Leaching recovery efficiency	Extraction approach	Final product	Ref.
Acidic leaching	The ash was crushed, ground and sieved (−250 μm)	H_2SO_4 (60 g l^{-1}), under O_2 pressure of 15 bar	200 °C	15 min	1	95%	*Precipitation* of V as $V(OH)_3$ by adding NH_4OH electrodeposition of Ni	V_2O_5 & Ni	34
Acidic leaching		H_2SO_4 (1.35 M), with stirring 300 rpm	40 °C	90 min	1/5 g ml^{-1}	98% V, 98% Ni	*Solvent extraction* of V by LIX 84-I at pH 0.5; followed by precipitation as NH_4VO_3 by adding NH_4OH *Precipitation* of Ni as NiC_2O_4 by adding $(NH_4)_2C_2O_4$ to the raffinate	V_2O_5 & NiO	35
Acidic leaching	Crushing + sieving (−75 μm)	H_2SO_4 (conc. 19.5%)	80 °C	120 min	9.15 wt%	94% V, 81% Ni			37
Acidic leaching		Boiling H_2SO_4 (conc. 1 M)	Boiling (∼100 ° C)	30 min	1/3 g ml^{-1}	∼90%	*Precipitation* of V as V_2O_5 by adding $NaClO_3$ + Na_2CO_3	V_2O_5	38
Acidic leaching	Burning of the ash at 850 °C	Boiling H_2SO_4 (conc. 2 M)	Boiling (∼100 ° C)	60 min	1/7 g ml^{-1}	97%	*Precipitation* of V as V_2O_5 by adding $NaClO_3$ + Na_2CO_3	V_2O_5 with higher purity	40
Acidic leaching	Drying t 110 °C + sieving (−500 μm)	H_2SO_4 (conc. 0.5 M)	RT, agitation speed 200 rpm	24 h	1/4 g ml^{-1}	98% V; 68% al; 42 Fe; 12% Ni; 4% Si	*Precipitation* of V as NH_4VO_3 by adding NH_4Cl (1 M) pH 5 + agitation for 7 days	NH_4VO_3	27
Acidic leaching		($HClO_4$ + HCl + H_2O_2)				High recovery of V, Ni, and Fe	*Solvent extraction* using organic compounds and HNO_3 in sequential procedure	NiO and FeO in two separation steps, leaving V dissolved in aqueous solution	26
Water leaching + acidic leaching		Water to dissolve Ni, Zn, mg, al, and Fe; followed by H_2SO_4 (1 M) to dissolve V	25 °C	360 min	1/25 g ml^{-1}		*Precipitation* of Al and Fe after water leaching by adding NaOH + *ion exchange* to recover Ni, Zn, and V		31
Acidic leaching		H_2SO_4 (conc. 5–9%)	20–80 °C	30–60 min	1/4 g ml^{-1}		*Precipitation* of V as V_2O_5, after oxidation by H_2O_2, by static heating for 2 h at 95 ° C and pH 1.8–2	V_2O_5	12
Acidic leaching	Physical concentration using high tension magnetic separation	H_2SO_4 (180 g l^{-1}) + 4% MnO_2	80 °C	600 min	1/10 g ml^{-1}	96.5% V, 94.8% Ni	*Solvent extraction* of V using Alamine 336/kerosine and H_2SO_4 stripping; *precipitation* of Ni & Zn by adding Na_2S	$V_2O_5 \cdot H_2O$; Zn–Ni sulfide cake	41
Ultrasound-assisted acidic leaching	Crushing + sieving (−75 μm) + washing with hexane and acetone + drying for 30 min at 70 ° C	27.9% lemon juice solution containing 10% H_2O_2	Initial = 35 °C	120 min	0.01%	88.7%	*Precipitation* of V as NH_4VO_3 by adding NH_4Cl	V_2O_5	46

Table 3 (*Contd.*)

Approach	Preparation of the ash	Leaching agent	Temp., °C	Time	S/L ratio	Leaching recovery efficiency	Extraction approach	Final product	Ref.
Acidic leaching	Drying at 105 °C	H_2SO_4 (0.5 N), pH 1	30 °C	120 min	1/5 g ml^{-1}	65% for V 60% for Ni, 42% for Fe			28
Alkaline leaching	Drying at 105 °C	NaOH (2 N), pH 14	30 °C	120 min	1/5 g ml^{-1}	80% for V			28
Alkaline leaching	Drying at 105 °C	NH_4OH (4 N), pH 10	30 °C	120 min	1/5 g ml^{-1}	50% for V 60% for Ni			28
Alkaline leaching	Drying at 105 °C	(NH_4OH (0.25 N) + $(NH_4)_2SO_4$ (4 N); pH 8.5	30 °C	120 min	1/5 g ml^{-1}	80% for V 60% for Ni			28
Alkaline leaching		NaOH, 2 M	100 °C	120 min		V (98%)	*Precipitation* of V as NH_4VO_3 by adding NH_4OH'' after acidification by HNO_3	NH_4VO_3 is calcined at <690 °C to produce V_2O_5	48
Alkaline leaching	Drying at 110 °C + sieving (−500 μm)	NaOH, 2 M + water rinsing of residual ash (for 1 h, 3 times)	RT, agitation speed 200 rpm	24 h + 6 times repeating washing/rinsing step	1/4 g ml^{-1}	V (98%)	Controlling pH to be 8 for precipitation of Al. Then, adding NH_4CL (1 M, pH 5) for *precipitation* of V (99 % V)	NH_4VO_3	27
Alkaline leaching	Drying at 110 °C + sieving (−500 μm)	Na_2CO_3 0.66 M + water rinsing	RT, agitation speed 200 rpm	24 h + 6 times repeating washing/rinsing step	1/4 g ml^{-1}	V (80%)	*Precipitation* of V by adding NH_4CL (1 M, pH 5)	NH_4VO_3	27
Alkaline leaching		NaOH, 2.5 M	100 °C	240 min	1/2.7 g ml^{-1}	V (99.6%)	*Precipitation* of V as NH_4VO_3 by adding of NH_4NO_3 (pH = 6–7, 100 °C, 4 h)	NH_4VO_3 is calcined at 450 °C to produce V_2O_5	49
Alkaline leaching		2 M NH_4Cl + NH_4OH	50 °C	300 min		Ni (59.1%)	*Precipitation* of Ni by adding Na_2S	NiS	50
Alkaline leaching	Leaching in NH_4Cl/NH_4OH solution for recovering Ni	2 M Na_2CO_3 solution	70 °C	420 min		V (63%)	*Solvent extraction* of V is conducted using TOA/toluene + *precipitation* of V by adding NH_4CL	NH_4VO_3	50
Alkaline leaching NH_4Cl/NH_3 solution	Crushing + sieving (−100 μm)	2 M NH_4Cl + 2 M NH_3	50 °C	300 min	1/19 g ml^{-1}	Ni (56%)	*Precipitation* of Ni by adding Na_2S	NiS	51
Alkaline leaching Na_2CO_3 solution	Leaching in NH_4Cl/NH_3 solution for recovering Ni	2 M Na_2CO_3 solution	70 °C	300 min	1/20 g ml^{-1}	V (45%)	*Solvent extraction* of V is conducted using tri-ethylamine/toluene + *precipitation* of V by adding NH_4CL	NH_4VO_3	51

Table 3 (*Contd.*)

Approach	Preparation of the ash	Leaching agent	Temp., °C	Time	S/L ratio	Leaching recovery efficiency	Extraction approach	Final product	Ref.
Alkaline leaching		NaOH, 8 M	100 °C	180 min	1/5 g ml^{-1}	V (90%)	Cooling to 5 °C + gentle agitation to precipitate $NaVO_3$, that is dissolved in HNO_3 + adding $(NH_4)_2SO_4$ to precipitate NH_4VO_3	NH_4VO_3 is calcined to produce V_2O_5	11
Acidic leaching	Leaching in NaOH for recovering V & Mo	H_2SO_4, 5 M	100 °C	180 min	1/4 g ml^{-1}	Ni (80%)	*Precipitation* of Ni as $NiCO_3$ by adding Na_2CO_3	$NiCO_3$	11
Alkaline leaching		NaOH, 2 M	110 °C	120 min	1/8 g ml^{-1}	V (94.4%)	*Precipitation* of V as NH_4VO_3 by adding of NH_4OH (pH = 6–7, 100 °C, 4 h)	NH_4VO_3	47
Water leaching	Burning for 4 h at 650 °C + roasting for 4 h with Na_2CO_3 at 650 °C	H_2O	60 °C	240 min	1/50 g ml^{-1}	92%	*Precipitation* of V as NH_4VO_3 by adding $(NH_4)_2SO_4$	V_2O_5	52
Water leaching	Roasting for 2.5 h with 20 wt% NaCl at 850 °C	H_2O	RT	90 min	1/10 g ml^{-1}	95.3%	*Precipitation* of V as NH_4VO_3 by adding NH_4Cl	NH_4VO_3	54

bioleaching process reduce the recovery efficiency of both V and Ni. This is attributed to the fact that the increase in the concentration of metallic elements in the ash due to the thermal pretreatment has an inhibitory effect on the growth of fungus.[62,64]

4. Recovery of V and Ni from the leaching solutions

Leaching processes dissolve V and Ni with other metals in aqueous solutions. V and Ni can be extracted through main methods, including chemical precipitation, solvent extraction, and ion exchange.

4.1. Chemical precipitation

Chemical precipitation is conducted by adding an ammonium compound (*e.g.* NH_4OH, NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_8$, or NH_4NO_3) to the leaching solution to precipitate V as NH_4VO_3 at pH 7 to 9, see Table 3. NH_4Cl is preferred to use because of its low cost. Also, an increasing the amount of NH_4Cl induces the precipitation of NH_4VO_3 and decreases its solubility.[65] NH_4VO_3 can be directly processed to fabricate NaV_6O_{15}, which is investigated as a high-performance cathode in lithium ion batteries, sodium ion batteries, and zinc ion batteries.[66–68]

Hakimi *et al.*[49] optimized the precipitation of V as NH_4VO_3 compound by adding an ammonium compound to the filtrate after the leaching process. They compared individual use of three ammonium compounds, namely $(NH_4)_2SO_4$ ammonium persulfate "$(NH_4)_2S_2O_8$", and ammonium nitrate "NH_4NO_3". The highest yield of V extraction (99.6%) is obtained by using NH_4NO_3, because the nitrate anion is a strong oxidizing agent that completely oxidizes the V cations to the highest oxidation state of V^{5+}. Otherwise, H_2O_2 can be added to complete the oxidation state of V compounds to the valence state of +5 as recommended by many studies.[12,34,37] Oxidation increases the recovery efficiency of V and facilitates the precipitation of V compounds because V^{5+} is less soluble than V^{4+}.

V, in the form V^{5+} cations, is precipitated as NH_4VO_3, which is subsequently calcined to produce the prevalent final product "V_2O_5". However, Vitolo *et al.*[38,40] precipitated V_2O_5 directly from H_2SO_4 leachate by adding $NaClO_3$, as an oxidant, with adjusting pH at about 2 or 3. However, adjusting pH with Na_2CO_3 pollutes the V_2O_5 precipitated with some Na. This necessitates repeat washing with an acidic solution to remove Na. Consequently, the oxidant H_2O_2 is preferred to eliminate contamination with alkali elements.[12]

Nickel is dissolved as $NiSO_4$ in H_2SO_4 leaching solutions. Some studies[34,69–71] suggested the application of electrowinning technique to obtain pure Ni. Nevertheless, these studies didn't conduct electrodeposition experiments and were confined to suggestions. However, the electrochemical deposition of Ni from $NiSO_4$ electrolyte is well known process.[72–76]

Ni is precipitated as $NiCO_3$ from pH-modified H_2SO_4 leaching solution by adding Na_2CO_3.[11] Also, Ni is precipitated from alkaline NH_4Cl/NH_3 leaching solution as NiS by adding Na_2S.[51] Nickel oxalate "NiC_2O_4", which can be easily transformed to

NiO by calcination, is precipitated after adding ammonium oxalate "$(NH_4)_2C_2O_4$" to H_2SO_4 leaching solution.[35]

4.2. Solvent extraction

Solvent extraction is the process in which the element or compound aimed to be extracted transfers from one solvent to another due to the difference in solubility or distribution coefficient between these two immiscible (or slightly soluble) solvents.[77–79] It has a greater separation efficiency than chemical precipitation and a higher selectivity degree than the ion exchange method with faster mass transfer. Therefore, solvent extraction has long been utilized for vanadium extraction (since 1950s).[80]

The extractants used are decided according to the leaching solution, its pH, and the dissolved metal valency. Vanadium is generally found as V^{4+} or V^{5+} cations in the leaching solutions of HOFA. For extracting V^{4+}, organophosphorus acids, such as D2EHPA "di(2-ethylhexyl)phosphoric acid", Cyanex 272 "bis(2,4,4-trimethylpentyl)phosphinic acid", and EHEHPA "2-ethylhexylphosphonic acid mono-2-ethyl hexyl ester" are used. On the other hand, TOA "trioctylamine", Alamine 336 "trialkylamine", LIX 860-I "trialkylamine", and NBEA "*N*-(2-hydroxy-5-nonylbenzyl)-β,β-dihydroxyethylamine" are used for extracting V^{5+}.[80,81] Ionic liquids "ILs" are recently used as extractants for vanadium from aqueous solutions; Examples of such novel ILs are trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate "Cyphos IL 104"[82] and 1-octyl-3-methylimidazoliumchloride "[Omim]Cl".[83] Table 4 summarizes some procedures and solvent extraction conditions for V and Ni reported in the literature.

The solvent extraction efficiency is influenced by the vanadium complex, which is determined by the solution pH and the concentration of V. Zeng and Cheng[84] reported that the pH in the range between 1.5 and 2.5 is optimum to extract V(IV) by D2EHPA with a concentration of 5–20% in kerosene. However, Liu *et al.*[85] found that the solution pH must be in the range from 2.5 to 2.8 to extract V(IV) by D2EHPA, and that further increase in the pH leads to co-extraction of Fe and Al. Noori *et al.*[86] used a mixture of 0.25 M D2EHPA and 0.35 M Cyanex 272 to extract V(IV) at pH 2.5 and extract Ni(II) at pH 5.5. Tang *et al.*[87] illustrated the chemical behavior of V extraction from the aqueous leachate of stone coal. The authors reported that the extraction efficiency increases as the pH increases up to 2.5. The leachate should be treated with SO_2 before extraction to reduce V(V) to V(IV) which is extracted more efficiently by D2EHPA.

Barik *et al.*[35] used the commercial solvent extractant LIX 84-I "2-hydroxy-5-nonylacetophenone oxime" diluted with kerosene (40% v/v) to selectively recover V from an acidic aqueous solution. V is extracted with a recovery efficiency of 99.9% when the ratio of organic phase to aqueous phase "O : A ratio" is 1 : 1, and pH is 0.5 at 25 °C. Then, V is stripped from V-loaded LIX84-I as NH_3VO_3 by equilibration with 15% NH_4OH aqueous solution with O : A ratio of 1 : 3. Eventually, NH_3VO_3 is crystallized by evaporation of the stripped solution.

Table 4 A summary of some solvent extraction conditions reported in literature for recovery of V and Ni

Solvent	Target metal valence	Solvent composition	O/A ratio	Proper pH	Extracting efficiency	Stripping agent	Stripping O/A ratio	Stripping efficiency	Ref.
LIX 84-1	V(V)	40% LIX 84-1 in kerosene	1 : 1	0.35–1.0	>99.9%	15% NH_4OH	1 : 3	99.9%	35
Aliquat 336	V(V)	0.06 M aliquat 336 in kerosene +5% isodecanol	1 : 1	3.0	99.0%	NH_4OH/NH_4Cl	1 : 1	48.0%	27
NBEA	V(V)	0.2 M NBEA in octan	1 : 1	3.5	98.0%				81
D2EHPA	V(IV)	10% D2EHPA + 5% TBP,+ 85% sulfonated kerosene	1 : 2	2.5–2.8	99.0%	1.5 M H_2SO_4	1 : 5	99.0%	85
D2EHPA	V(IV)	10% D2EHPA + 5% TBP,+ 85% sulfonated kerosene	1 : 4	≤2.5	96.12%				87
D2EHPA + Cyanex 272	V(IV)	20% V (0.25 M D2EHPA and 0.35 M Cyanex 272) + 80% V kerosene	1 : 1	2.5	80%	n/a			86
D2EHPA + Cyanex 272	Ni(II)	20% V (0.25 M D2EHPA and 0.35 M Cyanex 272) + 80% V kerosene	1 : 1	5.5	90%	n/a			86
Cyphos IL 104	V(V)	Cyphos IL 104	1 : 3	0.5–2	99.07%	1.5 M HNO_3	3 : 1	>99.99%	82
[Omim]Cl IL	V(V)	0.2 M of [Omim]Cl IL in 1 L of *n*-pentanol	1 : 1	8.05	97.93%				83
HBL110	Ni(II)		1 : 1		98%	Dilute H_2SO_4 solution + electrowinning	1 : 1	95%	71

With the aim of extracting vanadium from the NaOH alkaline leachate, Navarro *et al.*[27] applied two different procedures; one is named as selective precipitation, and the other is termed as solvent extraction. In the selective precipitation procedure, the alkaline leachate is neutralized by adding H_2SO_4 to control the pH to 8 in order to precipitate Si and Al, leaving V in the solution. Further pH lowering of the alkaline leachate to be 5 by extra H_2SO_4, with the addition of 1 M NH_4Cl solution, leads to the precipitation of vanadium as ammonium vanadate. On the other hand, solvent extraction is conducted by using Aliquat 336 which extracts metals by acting as a liquid anion exchanger. Aliquat 336 is added to kerosene with a concentration of 0.06 M and 5% isodecanol, forming an organic phase that is mixed with the same volume of H_2O_2-pretreated alkaline leachate for 30 min at pH controlled to be 3. The solvent extraction procedure results in significant extraction of V but is contaminated with Al. Also, it is difficult to strip V from the organic phase. Therefore, a selective precipitation procedure using NH_4Cl solution is endorsed as the final step after alkaline leaching.

Mahandra *et al.*[82] extracted V(V) from the leaching solution of spent V_2O_5 catalyst using Cyphos IL 104. HNO_3 is used as a stripping agent to strip V from the organic phase. The A/O ratio for extraction is 3/1 but for stripping is 1/3.

Zeng *et al.*[71] proposed a new approach for the direct extraction of Ni from H_2SO_4 leach solutions of low grade Ni resources using a novel solvent extractant HBL110. This extractant can selectively recover Ni with an efficiency of 98% leaving Fe, Al, Mn, Cr, and Ca in the leaching solution. The Ni-loaded organic solution is stripped by dilute H_2SO_4 solution. The O/A ratio of extraction and of stripping is 1. Ni can be eventually extracted by electrowinning with an overall recovery of 95%. The process is advantageous because it consumes low chemicals with a short flowchart procedure and achieves high recovery of Ni with efficient removal of impunities. Therefore, the authors reported that the process shows proper economical and environmental advantages.

4.3. Ion exchange

The ion exchange approach is a process to separate and extract selected metals from their solutions using ion exchange resins. The ion exchange processes have the advantage of the separation of target ions without using an excess of chemicals, with enabling the application of closed water recycling systems that eliminate additional equipment for wastewater treatment. The ion exchange resins used to adsorb vanadium are generally classified as anionic exchange resins and chelating resins. Anionic resins react with and separate pentavalent vanadate ions "V(V)" from other impurities in aqueous solutions, but chelating resins are used to extract V(IV) from acidic solutions.[80,88] Although there are several papers on using ion exchange resins for the separation of vanadium ions from other impurities in various media, the literature on the extraction of vanadium from fly ash leachate is limited. However, ion exchange technology is primarily applied on the experimental scale and is rarely applied in the industry.[88]

Tokuyama *et al.*[31] developed a process to recover V and Ni and to make the fly ash less harmful. The process includes two-step leaching and ion exchange. The first leaching step uses water to dissolve Ni, Zn, Mg, Al, and Fe. The second leaching step is applied to dissolve V using H_2SO_4. The solution after water leaching is treated with NaOH to reach pH 5 to precipitate Al and about 80% of Fe. The remaining Fe dissolved as Fe(II) is oxidized to Fe(III) by adding H_2O_2. Recovery of Ni and Zn is then conducted by ion exchange with CR20 resin. Nickel can be selectively recovered from the resin because of a distinct inequality in the ion exchange isotherm between Ni and Zn. On the other hand, vanadium is selectively recovered from the second acidic leachate by using the resin C467, because this resin has the highest selectivity for V against Fe.

Yu *et al.*[89] utilized trioctyl methyl ammonium chloride-impregnated resins "TOMAC-IRs" to extract vanadium from a V-containing acidic solution. TOMAC-IRs adsorbed V(V) with a higher efficiency from V-containing solution with initial pH of 1.8 and S/L ratio of $1:200$ g ml^{-1} in a contact time of 4 h. The adsorbed vanadium in TOMAC-IRs is then desorbed with 6 mol l^{-1} NaOH solution.

Seggiani *et al.*[69] investigated the extraction of nickel from sulfate solution leachate of Orimulsion fly ash after vanadium recovery using ion exchange chelating resins. Three commercial chelating resins, namely Lewatit TP-207, Purolite S-930 and Amberlite IRC-748, are examined for uptake of Ni from the fly ash leachate at pH 4. The results showed that TP207 resin displays higher extraction of Ni(II) with the recovery of 92–95%. Nickel is then stripped from the resin by 10% H_2SO_4 solution. Nickel can be eventually recovered from the resultant solution containing $NiSO_4$, as metallic nickel by electrowinning.[70,90]

5. Calcination

In consequence of the recovery of V and Ni in the form of their chemical compounds (NH_4VO_3 and NiC_2O_4), as mentioned above, calcination is conducted to produce V_2O_5 and NiO. Vanadium pentoxide "V_2O_5" is widely used in the synthesis of modern high-performance batteries, electrochromic devices, sensors, and photocatalysts.[91–93] Nickel oxide "NiO" has a variety of specialized applications in thin film solar cells, superior rechargeable batteries, and electrochromic devices.[93,94] Both V_2O_5 and NiO, even with low purity grades, are widely used in the production of steel alloys.[93,95]

The precipitated NH_4VO_3 is separated from the leaching solution by filtration, dried, and calcined to produce V_2O_5 according to eqn (8) "$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3 + H_2O$". Liu *et al.*[96] reported that the optimum conditions for calcination of NH_4VO_3 to obtain V_2O_5 are to be 400 °C for 36 min, based on experimentation of a sample weighing 4.25 g. Nevertheless, most of the studies conducted the calcination process of NH_4VO_3 at higher temperatures and for longer times. Stas *et al.*[11] calcined NH_4VO_3 at 500 °C for 24 h. However, most of the old and recent studies conducted the calcination process in shorter times at the temperature range of 500–690 °C, *e.g.* 1 h at 500 °C,[97] 30 min at 690 °C,[48] 4 h at 550 °C 46, 1 h at 450 °C.[49]

Nickel is recovered from the acidic leachate of HOFA as NiC_2O_4 by adding $NH_4)_2C_2O_4$.[35] Nickel oxide "NiO" is obtained by calcination of NiC_2O_4 at 450 °C for 2 h. The thermal

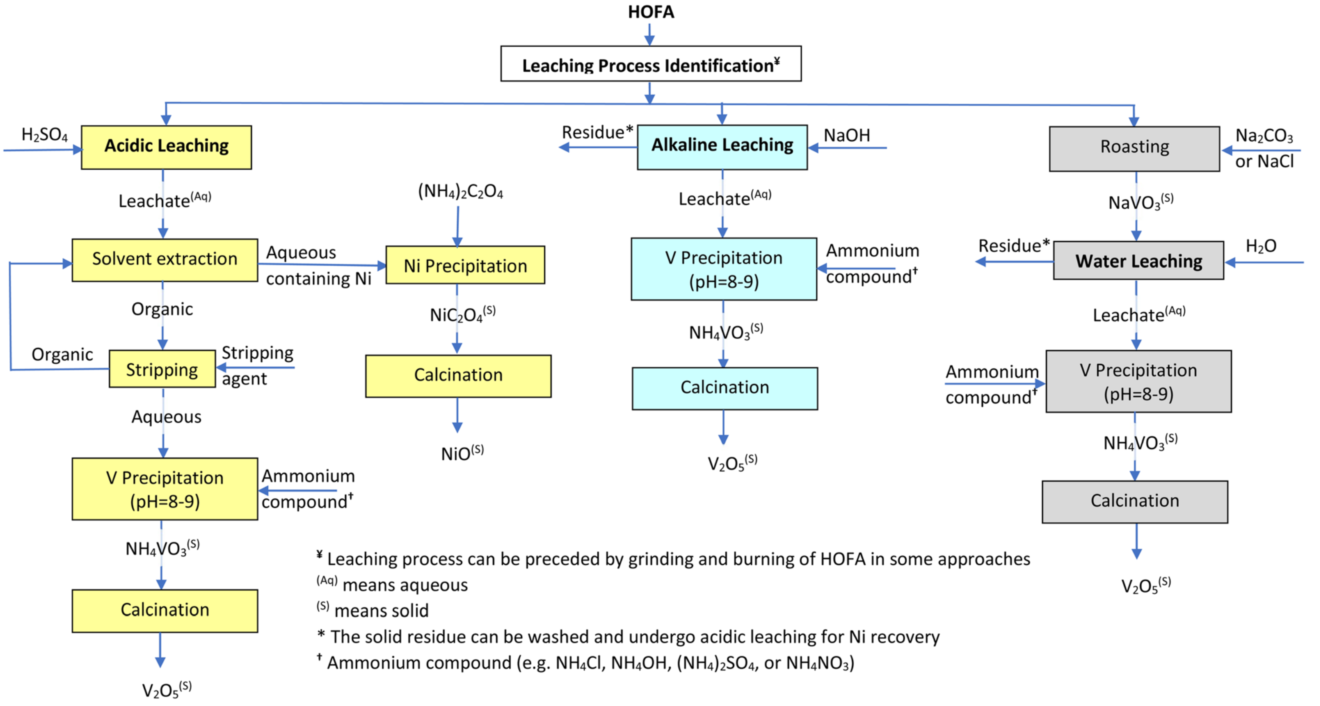

Fig. 1 Overall flowchart of the recovery of V and Ni from HOFA showing the most common steps following the main three optional leaching approaches.

decomposition of $(NH_4)_2C_2O_4$ has been demonstrated to occur following the next reactions:[98]

$$NiC_2O_4 \rightarrow NiO + CO + CO_2 \quad (12)$$

$$NiO + CO \rightarrow Ni + CO_2 \quad (13)$$

Du *et al.*[98] fabricated Ni/NiO nanocomposite by direct calcination of NiC_2O_4, and controlled the Ni metal content in the NiO by controlling the temperature and atmosphere of the calcination. The produced Ni/NiO composite demonstrated high electrochemical performance as an anode in lithium-ion battery. However, Rakshit *et al.*[99] and Gomaa *et al.*[100] reported that the calcination in air, where excess of O_2, converts NiC_2O_4 into NiO.

Also, $NiCO_3$, precipitated by the addition of Na_2CO_3 to the acidic leachate of HOFA 11, can also undergo thermal decomposition at 450 °C to produce NiO, according to the equation "$NiCO_3 \rightarrow NiO + CO_2$".[101,102]

6. Concluding summary and recommendations

In summary, Fig. 1 displays an overall flowchart of the recovery of V and Ni from HOFA with showing the most common steps following the main three optional leaching approaches (acidic leaching, alkaline leaching, and water leaching). Also, Table 5 summarizes the advantages and limitations of all leaching and recovery processes reviewed in this paper.

The recovery of V and Ni from HOFA commences with the leaching process, which is considered as the first main step in recovery. The leaching processes mostly applied are classified as acidic processes and alkaline processes, in addition to the water leaching process.

Although acidic leaching can be performed by one of the strong mineral acids such as HCl, H_2SO_4, or HNO_3, and studies reported that HCl and H_2SO_4 have comparable leaching efficiencies, H_2SO_4 is preferred due to its significantly lower cost and its wide application in leaching of many metals. In addition to V and Ni, H_2SO_4 dissolves almost all metals present in HOFA, such as Mo, Mg, Mn, and others.

However, alkaline leaching using NaOH has the advantage of selective leaching of V, leaving Ni undissolved in the ash because it is insoluble in alkaline solutions. Although NH_4OH and Na_2CO_3 solutions were investigated in some studies as alkaline leaching agents, NaOH has the highest selectivity with the highest leaching efficiency for V.

Based on the advantage of selective solubility of V by NaOH solution, a two-stage leaching process has been developed and can be adopted to recover V and Ni; In the first stage (alkaline leaching), V is recovered by NaOH solution. The residual solid fly ash is then leached by H_2SO_4 solution (acidic leaching) to recover Ni.

Water leaching is significantly weak if compared with acidic and alkaline leaching. However, the approaches reported on water leaching of HOFA preceded the leaching process with a roasting step. The roasting of ash with Na_2CO_3 salt or NaCl salt converts vanadium compounds into $NaVO_3$ which is a water-soluble compound. The roasting temperature should not be too high to bring about sintering of V and Ni compounds.

Bioleaching is an environmentally friendly approach that utilizes specific species of bacteria and fungi for yielding acidic

Table 5 A summary of the advantages and limitations of all methods for leaching and recovery of vanadium and nickel from HOFA

Process	Type	Advantages	Limitations
Pre-treatment of HOFA	**Burning** (400–850 °C)	Reduces the C content of HOFA	Gaseous emissions
		Reduces the volume of HOFA	Possible volatilization of V compounds
		Increases the V & Ni contents in the ash	Possible fusion and formation of V–Ni refractory compounds at higher temperatures (>900 °C)
		Increases the V & Ni recovery, and decreases the consumption of chemical agents in the leaching process	Changes the ash pH that may adverse the V & Ni recovery in bioleaching process
		Possibility of recovering the heat of combustion of carbonaceous constituents of HOFA	
	Roasting (mostly with Na_2CO_3 or NaCl, at 650–850 °C)	Is necessary prior to water leaching to produce water soluble $NaVO_3$ compound	Gaseous emissions
		Leads to selective recovery of V	Possible sintering of V & Ni at high temperatures
		Reduces the volume of HOFA	Possible fusion of NaCl at high temperatures
Leaching	**Acidic leaching** (H_2SO_4 is widely used)	Higher extraction rate	No selectivity
		Lower cost	More waste solutions
		Dissolves all metals, so residual HOFA can be reused in some applications	More complicated steps for selective recovery of V and Ni
	Alkaline leaching (NaOH is widely used)	Selective recovery of V	Ni is nonrecoverable
		Good extraction rate	For Ni recovery, the ash should undergo a next acidic leaching process
		Simple flowchart process	The solid ash residue keeps its polluting metals
	Water leaching	Lower cost and wide availability	Should be preceded by a roasting step
		Avoids high amounts of chemical reagents	Lower recovery efficiency
		Simple flowchart process	No attempts to recover Ni
	Bioleaching	Environmentally friendly	Very slow
		Avoids high amounts of chemical reagents	The S/L ratio is very low
Recovery	**Chemical precipitation** (using ammonium compounds)	Lower cost	Weak selectivity
		Straightforward process	Lower metal purity
	Ion exchange	Avoids using excess of chemicals	Lower selectivity degree
		Good recovery rate	Resin needs refreshening
			Long flowchart process
	Solvent extraction	Greater separation efficiency	Narrow pH range
		Higher selectivity degree	Is influenced by the metal valency
		Faster extraction rate	Long flowchart process
Calcination		Simple process	Gaseous emissions
		Extraction of vanadium pentoxide and nickel oxide that have great and modern applications	Extraction of metal oxide, not pure metal

media that leach V and Ni from HOFA. "*Acidithiobacillus ferrooxidans*" bacteria utilize sulfur and ferrous sulfate for the production of H_2SO_4, which leaches V and Ni from HOFA, but with much lower recovery efficiency than traditional acidic leaching.

The fungi "*Aspergillus niger*" and "*Penicillium simplicissimum*" are endowed to grow for days and create organic acids (citrate, gluconate, oxalate), that leach V and Ni when mixed with the ash. The fungal isolate *Cladosporium cladosporioides* yields malic acid that extracts V and Ni from HOFA.

Alternatively to the bioleaching approach which is very slow, another environmentally friendly trial used lemon juice – which contains few contents of citric acid, malic acid, and ascorbic acid – to recover V from HOFA with a considerable recovery efficiency. However, the leaching experiment has a very low pulp density of added ash, and further research is recommended to conduct to have more reliable results.

Recovery of V and Ni from the leaching solution can be conducted by chemical precipitation, solvent extraction, or ion exchange. Direct chemical precipitation of V as NH_3VO_3 is achieved by adding an ammonium compound (*e.g.* NH_4OH, NH_4Cl, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_8$, or NH_4NO_3) to the leaching solution with pH of 8 to 9. NH_4Cl is preferred more than other compounds because of its lower cost. However, NH_4NO_3 yields the highest V recovery because of its oxidizing effect on V cations to V^{5+}. On the other hand, Ni is precipitated as $NiCO_3$ from pH modified H_2SO_4 leaching solution by adding Na_2CO_3, and as nickel oxalate "NiC_2O_4" by adding $(NH_4)_2C_2O_4$. Solvent extraction has a higher recovery efficiency than chemical precipitation and a higher degree of selectivity than the ion exchange method with faster mass transfer.

The recovered NH_4VO_3 is straightforwardly calcined at temperatures ranging from 400 °C to 550 °C to produce vanadium pentoxide "V_2O_5". On the other hand, NiC_2O_4 is easily transformed into NiO by calcination at 450 °C. Also, Ni leached as $NiSO_4$ in an H_2SO_4 leaching solution can be electrodeposited as a pure metal. Both V_2O_5 and NiO are used widely in the synthesis of modern high-performance batteries and electrochromic devices, and in other superior applications, as well as in the production of special alloy steel.

HOFAs generated from several power stations and desalination plants have diverse chemical compositions, as well as having low to tiny contents of V and Ni. Therefore, there is no recovery method has been yet adopted to be the best approach. In this regard, further research is recommended to optimize the recovery approach individually adopted for a particular HOFA.

It is also recommended to direct further research to increase the recovery efficiency with lowering pollution through reducing the chemical agents used, reutilizing the waste solutions, and minimizing gaseous emissions. For example, the utilization of ultrasound can reduce the time, temperature, and chemical agents of leaching processes. Also, using seawater instead of fresh water in water leaching can be experimented to raise the recovery efficiency. Moreover, pre-water-washing of HOFA preceding the roasting can be suggested to dissolve metal sulfates that will reduce emission of sulfur oxides.

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Conflicts of interest

There are no conflicts to declare.

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