

Review

Vanadium and Nickel Recovery from the Products of Heavy Petroleum Feedstock Processing: A Review

Aleksey Vishnyakov ^{1,2,†,‡} ¹ Skolkovo Institute of Science and Technology, Moscow 121205, Russia; avishnja@polly.phys.msu.ru² Department of Physics, Moscow State University, Moscow 119991, Russia

† Organization where the project was carried out.

‡ Current addresses: Institute of Solutions Chemistry RAS, Ivanovo 153038, Russia.

Abstract: The steadily growing demand for non-ferrous metals, a shift to heavier crude oil recovery and tightened environmental standards have increased the importance of heavy petroleum feedstock (HPF) as a raw source of metals. This paper reviews the recent developments in the recovery of vanadium and nickel from HPF. During crude oil processing and the application of its products, HPF is converted to various metal-enriched byproducts (“heavy oil”, petcoke, ashes and slags) from which the metals can be recovered. This paper briefly describes the sources and recovery pathways (both mainstream and exotic), and discusses the economic viability and possible future directions. Particular attention is paid to (i) the electrochemical recovery of metals from petrofluids and alternative approaches; (ii) pre-combustion metal recovery from petcoke; and (iii) metal reclamation from fly ash from heavy fuel oil or petroleum coke combustion: hydro- and pyro-metallurgical and bio-based techniques. The current stage of development and prospects for the future are evaluated for each method and summarized in the conclusion. Increasing research activity is mostly observed in traditional areas: metal extraction from fly ash and the reduction of metals from the ash to V–Fe and Ni–Fe alloys. Bioengineering approaches to recover vanadium from ashes are also actively developed and have the potential to become commercially viable in the future.

Keywords: vanadium; nickel; heavy oil; reclamation

Citation: Vishnyakov, A. Vanadium and Nickel Recovery from the Products of Heavy Petroleum Feedstock Processing: A Review. *Metals* **2023**, *13*, 1031. <https://doi.org/10.3390/met13061031>

Academic Editors: Lijun Wang and Shiyuan Liu

Received: 25 January 2023

Revised: 12 May 2023

Accepted: 23 May 2023

Published: 27 May 2023



Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Metal ions, which are abundant in heavy petroleum feedstock (HPF), are pollutants, and research on the techniques for petroleum demetallization never stops. Metal ions irreversibly poison the catalysts employed in oil processing and increase equipment corrosion. Furthermore, many metal compounds, including nickel oxides and, possibly, vanadium oxides, are carcinogens [1]. At the same time, the non-ferrous metals contained in HPF are a valuable resource.

The most abundant metal in HPF is vanadium. In Russia, the vanadium content of heavy petroleum recovered every year amounts to one third of the current annual production using traditional methods. Nickel is a distant second, and cobalt is found in sizable concentrations. Vanadium is of special interest: although it is ubiquitous in the Earth’s crust in the forms of oxides, sulfides and phosphates, and is associated with other metals (iron, titanium, uranium, etc.), the vanadium grade is typically too low for direct production. Almost 70% the vanadium produced worldwide is extracted from slag formed in the process of steel production. The world demand for vanadium amounted to 120,067 mt in 2021, and only 8% of that originated from HPF. In the US, vanadium produced from petroleum feedstock amounted to 20% of the total in 2007 [2]. It should be noted that vanadium supply is key for the transition to a circular economy: vanadium redox batteries are regarded as the best option in stationary, long duration, high power applications for their ability to sustain nearly unlimited charge–discharge cycles, safety features and the

ease of reuse/recycling of the components and the electrolyte. The factors limiting their application are vanadium toxicity and high vanadium costs. The transition to a circular economy and the steady demand from the steel and biomedical industries are expected to drive the vanadium market up at an annual rate of 8.5% through to 2033 [3]. The demand for nickel is expected to grow by 44% by 2030 [4].

Metal recovery from crude oil demetallization waste is by no means a new field. The efforts to recover metals started in the 1940s and have been progressing ever since. Whilst it cannot be said that the metal recovery from HPF processing waste is rapidly growing, the situation is changing slowly, but surely. What was considered as waste in the 1940s has now become treasure. The three main factors in that evolving landscape are:

(i) Low-hanging fruits have mostly been reached: the depletion of fields with light and medium oils forces the recovery of heavy oil, which constitutes 70% of all resources that are available now [5]; the metal concentration generally grows with the asphaltene content in the crude, which makes metal recovery more attractive;

(ii) Improvements in oil processing technologies increase the share of the crude that is converted to fluid products, thus increasing the metal content in the residues;

(iii) The ever-tightening environmental regulations drive the search for safer and environmentally benign techniques of metal production.

As a result, both academic and industrial research has substantially intensified over the last 5–8 years. Remarkably, more efforts are invested in the traditional areas, e.g., the hydrometallurgic recovery of metals from the ashes. It is worth noting that the methods originally developed for metal recovery from mineral oils are now extended to spent refinery catalysts, municipal waste and other sorts of refuse.

Over the last several years, several comprehensive reviews were published on neighboring topics. In particular, Magomedov et al. [6] reviewed the methods of petroleum demetallization. Kurniawan et al. [7] considered the chemistry, origins and removal of metalloporphyrins; Yuan et al. [8] considered vanadium extraction techniques from all possible sources. Yet, none of them actually cover the metals recovery from HPF demetallization residues in reasonable detail. The recovery of metals from spent catalysts and ashes was reviewed eight years ago by Akcil et al. [9]. Spent catalysts recovery has certainly progressed towards full-scale commercial implementation. A very recent work by Baritto et al. [10] presented an economic evaluation of the recovery of vanadium from a spent catalyst employed in the catalytic reforming of bitumen. Data intensive process models developed for mass and energy balances allowed for the estimation of capital and operating costs. It was concluded that the recovery of vanadium from a spent catalyst obtained from bitumen upgrading the operations is potentially profitable considering the current vanadium market price. Spent catalysts from oil processing will not be considered here in detail, because hydrometallurgical pathways are similar to those applied for ashes and have not drastically changed since 2015, while novel biomethods were reviewed by Pathak et al. [11]. Wastewater deserves mentioning as well, because oil conditioning and desalting leaches substantial amounts of metals. Some additives, e.g., phosphoric acid, facilitate demetallization during oil pre-treatments, resulting in a high metal content in the wastewaters [12]. The methods applied to wastewater are drastically different from those reviewed in this paper and were recently described elsewhere [13].

This paper aims at providing a critical review of the existing methodologies of metal extraction from HPF, describing the current trends in the academic and industrial literature, and providing an outlook for further developments in the market, which is expected to grow [3,4]. The focus of this review is the recovery of vanadium and nickel, as they are most abundant in HPF, and most of the research efforts focus on them. The approaches to recovery are divided into two main categories: pre-combustion and post-combustion (recovery from ashes). We try to cover both major pathways and alternative ideas.

2. Vanadium and Nickel in Crude Oil

Vanadium and nickel compounds in crude oil are called “molecular fossils” due to their origin from heme and chlorophyll. Just as in living cells, in petroleum they are found in various coordination complex compounds, with metal porphyrins being the most known (Figure 1). The polyaromatic structures are flat and interact favorably with other polyaromatics via dispersion and π - π forces. Polyaromatic asphaltenes form the most hydrophilic fraction of crude (e.g., [14]), and the metal-containing complexes shown in Figure 1a are more hydrophilic in comparison with typical asphaltene molecules. In oil-water emulsions, they are located near the oil-water interface, which is important in some prospective recovery processes. In general, the metal content in crude oils increases with the density (and with the asphaltene content, correspondingly) [15]. The vanadium content grows with density faster than the nickel content (Figure 1b). Upon de-asphalting with heptane, most metals remain with the asphaltene fraction: vanadium content reached 1% of the total asphaltene mass precipitated from the heaviest oil samples (Figure 1c) [15]. As the asphaltene content in the petroleum feedstock increases, more effort has to be invested in demetallization, and in turn the demetallization waste becomes more valuable as a source of metals.

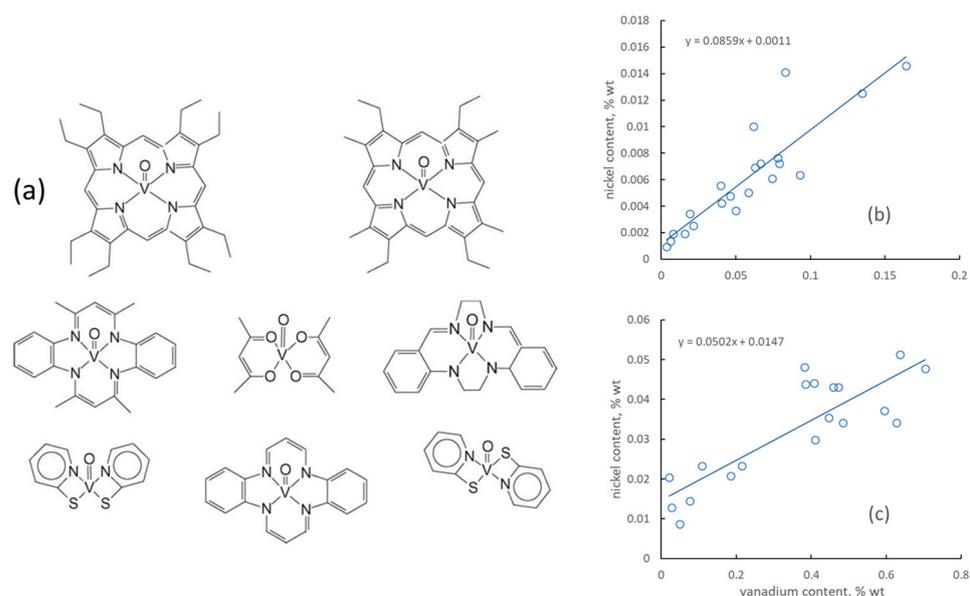


Figure 1. (a) Chemical structures of vanadium compounds in crude oil [16] (reproduced from ref. [16] with a permission from Elsevier), (b) vanadium to nickel ratio as a function of total vanadium content in the crude oil for different oil fields in Russia, (c) vanadium to nickel ratio in asphaltene fraction for the same oil samples upon standard extraction with heptane. Vanadium content in the asphaltene fraction reaches 1% mass, nickel mass is about twenty times as low (redrawn using data from ref. [17]).

The metal-containing molecules with strong coordination bonds between the metal and the surrounding organics are separated from the lighter components by fluid/critical/supercritical extraction and broken in the processes of thermal and catalytic cracking of the HPF, hydrogenation, coking and gasification. Each process listed above generally yields a lighter fraction, is more or less conveniently usable (as fuel, in organic synthesis, etc.), and has a denser “residue”, enriched with carbon and heteroatoms. Metals always tend to stay with the residue. Each of the stages of oil processing can therefore be regarded as a demetallization process, which produces the desired product and “waste”, which is often the raw material for the next stage. The heavier products, which are of interest as sources of metals, are:

- (i) Heavy fuel oil. Although attempts to recover metals from heavy oil without combustion exist, there are few and these methods are not well established.

- (ii) Asphalt, a solid or semi-solid bituminous residue from mostly critical and supercritical extraction. Asphalt can be coked and gasified, or can be used for metal recovery as is.
- (iii) Cokes from delayed coking and flexicoking; also, coke gasification produces soot enriched with metals, which can also be used as a source of metals.
- (iv) Ashes from heavy oil and coke combustion.

Below, we describe the techniques for metal recovery at each stage. The conclusion gives a summary comparison of the approaches.

3. Pre-Combustion Metal Recovery from Fluid Oil

3.1. Electrochemical Approaches

The electrochemical methods described here attempt to break the metal complexes in the liquid phase, and thus do away with any thermal-based demetallization treatment. Despite the hydrophobicity of the complexes, they can be either dissolved in a non-aqueous medium of a reasonable conductivity or dispersed in water (say, as a fine emulsion or a micellar solution), where they can be subjected to electrochemical oxidation or reduction. It is important that the organometallic compounds are among the most polar in the crude.

Electrochemical approaches are versatile, eco-benign and the metals can potentially be obtained in pure, easily usable forms. The fundamental possibility of the electrochemically assisted demetallization of porphyrins has been explored since the 1960s [18–20]. The efficiency depends on the composition of the electrolytic medium, the electrode material and the applied voltage. Ovales et al. [21] systematically studied the electrochemically assisted processing of HPF, including the reduction of polyaromatic compounds, demetallization and desulfurization. Demetallization and desulfurization of the real crudes could not be achieved simultaneously (high metal yields corresponded to low sulfur yields). Up to 81% of metals were successfully removed from bitumen residues, but the currents were as low as 0.01–0.02 A/cm² of the electrode surface, with an approximate maximum of 0.002 eq. of metals per m² s.

Jorge et al. [22] investigated the electrochemical decomposition of vanadyl tetraphenylporphyrins dissolved in xylene and dispersed in aqueous solutions of K₂SO₄. The electrolysis of the two-phase system was carried out potentiostatically. A steady-state regime with a constant current density was reached. The demetallization mechanism included vanadyl oxidation followed by the formation of cationic and zwitterionic radicals which led to the destruction of the porphyrin cycle. This work demonstrated a possibility for vanadium extraction via the electrolysis of a fine liquid emulsion. Welter et al. [23] attempted the demetallization of two synthetic compounds, vanadyl (IV) meso-tetraphenylporphyrin and vanadyl (IV) octaethylporphyrin, as well as Ayacucho Venezuelan crude oil samples by electrochemical techniques. They found that a protonated medium was essential for metal removal. Metal extraction resulted in the formation of free porphyrins that were not destroyed by the electrolysis. The cycling voltammograms were measured in a wide range of applied voltages (−2.3 to 0 V vs. Ag/Ag⁺) and were quite complex (Figure 2). The best metal extraction from commercial petroporphyrins (84%) was obtained on the glassy carbon electrode at −2.3 V in 0.1M HClO₄ solution in 4/1 vol. mixture of tetrahydrofuran and CH₃OH. For crude oil samples, the best metal yield was 66.4% of graphite, while for direct electrolysis on crude, the yields were 7.5% of vanadium, 8.2% of nickel and 79.6% of iron in charge efficiency. The ambitious goal of precipitating different metals in relatively pure forms with a successive step-by-step reduction at different voltages was not achieved because of very slow reduction kinetics. To increase the current, the authors had to increase the overpotential, which resulted in different reduction reactions running concurrently. According to the paper, “the results of commercial interest related to direct demetallization in crude oil still remains as an open challenge for electrochemists.” As far as we understand, this challenge still remains open as of today. A somewhat similar attempt was made by Kurbanova and co-authors [24]. The authors used ethanol as a solvent, and the currents were significantly higher than in previous studies, 0.035 A/m² (assuming we understood the text correctly). It should be noted that as soon as the crude oil (rather

than the extracted porphyrins) is diluted with expensive solvents [24], the process becomes economically non-viable.

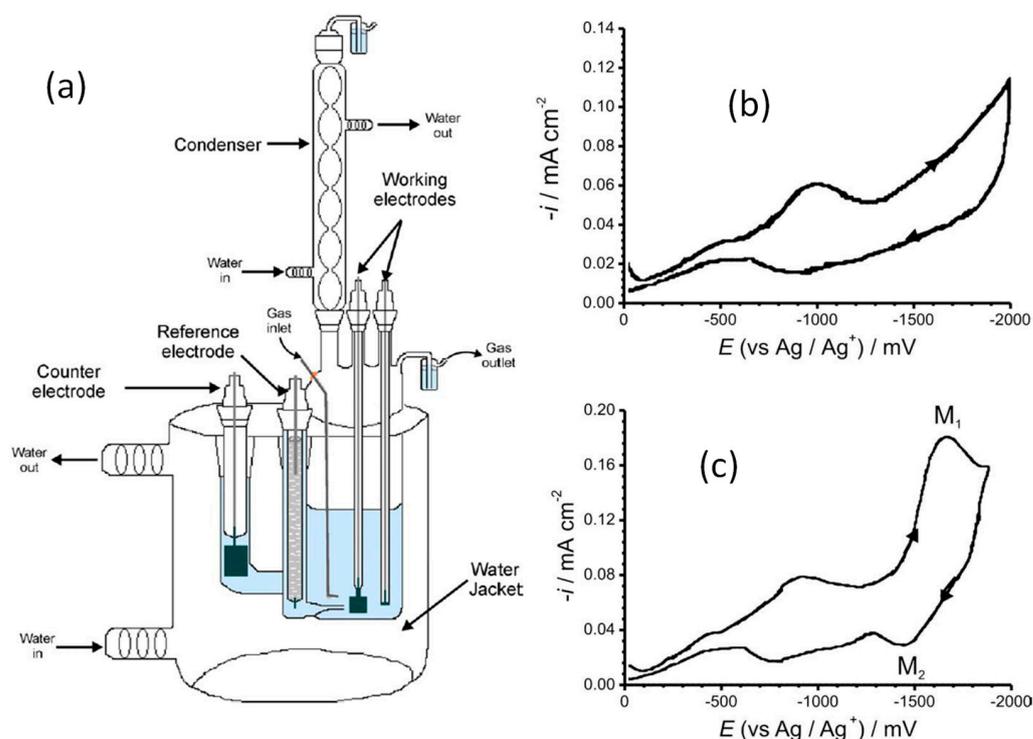


Figure 2. (a) Electrochemical cell used for electrolysis of metal–porphyrin compounds in polar non-aqueous solvents. (b) Cyclic voltammograms of mesotetraphenyl in THF/LiClO₄/MeOH/HClO₄ solution on platinum, voltage change rate of 50 mV/s, ambient conditions. (c) Cyclic voltammograms of vanadyl mesotetraphenyl at the same conditions. M₁ reduction wave at -1 V is associated with direct electron transference to the porphyrin nucleus and is reversible. M₂ is related to metal oxidation and is not fully reversible. Reproduced from ref [23] with permission from Elsevier.

Afanasieva et al. [25] applied electrolysis to a micellar solution of metal-containing asphaltenes. The authors experimented with both synthetic porphyrins and Castilla crude oil. The oil was mixed with either 0.2M LiClO₄ solution in THF and methanol (70/20 vol) or 0.5% H₃PO₄ + 0.1 M LiClO₄ in the mixture of THF and acetonitrile, and then the solution was electrolyzed. Cyclic voltammograms were measured at potentiostatic conditions between -2 V and 0 V vs. Ag/Ag⁺. As a result, 80%+ of the metals (V, Ni and Fe) precipitated on the carbon electrode. Theoretically, such a method can separate the different metals contained in the asphaltene mixture. The kinetics, however, was also a serious problem: the currents were so low that metal separation was not achieved even in the laboratory experiment, and the conclusion made by the authors indicated that as of 2015, the electrochemical route was not viable. This was not surprising since the electrolysis was performed with a non-aqueous micellar solution. Increasing the overpotential in order to improve the kinetics was hardly reasonable due to numerous side reactions.

Electrolysis was also applied to the products of asphaltene reduction in an effort to extract vanadium and nickel [26]. Portions of the Boscan asphaltenes were treated with Raney nickel (a fine-grained solid composed mostly of nickel derived from a nickel–aluminum alloy [27]) and electrolyzed in LiCl solution in ethylenediamine. According to the study, the loss in vanadium was proportional to the loss of metalloporphyrins. While interesting, this technique does not seem economically promising: the process is quite complex, requires the re-solubilization of asphaltenes and does not promise much in terms of kinetics.

Electrochemical techniques can also assist metal extraction by hydrogenation. For example, Acevedo et al. [28] deposited vanadium and nickel from tetraphenylporphyrins

dissolved in CH_3Cl . Hydrogen was generated by electrolysis and diffused through a Pd electrode which served as a catalyst in non-aqueous hydrogenation.

In summary, electrochemical methods are attractive for several reasons, and efforts to make them viable have not ceased. The hydrophobicity of porphyrin structures still makes electrochemical deposition very slow for the necessity to use non-aqueous solvents or colloidal solutions. As of today, electrochemical extraction provides moderate to high yields, but the kinetics are always questionable. The slow kinetics problem has not been resolved, and electrochemical methods, often called “most promising” are in fact not close to commercial applications.

3.2. Bioengineering Approaches

This section describes interesting ideas, each of which was reported in a single or in very few research papers and/or patents. These methods are apparently far from any commercial implementation, but deserve attention as interesting concepts for the future. Bioengineering approaches are inspired by the vigorous efforts invested into the biodegradation of crude oil (e.g., [29]). Metalloporphyrins are specifically targeted in a number of studies [7]. As a result of the biodegradation of the metalloporphyrins, metal ions are leached from the extremely stubborn asphaltene precipitate to forms that are more or less accessible to electrochemical and other methods. Preliminary studies were carried out on pure substances—surrogates of petroleum organometallic compounds. For example, in ref. [30], fungal cultures of *aspergillus* were used to decompose vanadyl-oxido octaethylporphyrin. The protoporphyrins of nickel were decomposed [31] by a very complex process using an enzyme obtained from *P. azelaica* YA-1 cultures. As means to obtain metals, bacterial and yeast cultures are hardly promising as of today: it is not even exactly clear as to what raw source they should be applied to. Yet, it is not impossible that crude oil biotransformation will also lead to metals in reasonable forms and quantities.

3.3. Other Alternative Approaches

Shiraishi et al. [32] proposed a photochemical process to destroy the most stable bonds between metal and porphyrin rings. The authors first considered a simultaneous photoreaction and extraction in a two-phase oil/water system (Figure 3). The results obtained for vanadium (IV) and nickel (II) tetraphenyl porphyrins dissolved in tetralin were compared with the results obtained for the residues from the atmospheric distillation of a crude oil samples. It was found that the first process was able to demetallize the “free” metalloporphyrins, but experienced difficulties in demetallizing “bound” metalloporphyrins, which are strongly associated with asphaltene molecules in the oil residue. In order to weaken this association and thus convert bound metalloporphyrins into free ones, a protonating solvent, 2-propanol, was added to the residual oil and subjected to photoemission. Then, the 2-propanol was evaporated, and the resulting oil residue was processed with an aqueous HCl solution, into which the vanadium and nickel successfully dissolved. In total, 93% of vanadium and 98% of nickel were extracted from the atmospheric residue; 73% of vanadium and 85% of nickel were extracted from the vacuum residue, respectively [32]. This method looks interesting, but suffers from the same problems as the electrochemical methods: the photochemical process is rather slow and the procedure requires relatively expensive solvents.

Lebedev et al. [33] proposed metal extraction using a microwave discharge. The focusing lens was placed against the side wall of the oil tank, and an antenna wire was inserted into the tank. As a result of the expansion and formation of plasma around the antenna, a solid residue of a fractal structure was formed on the wire. The residue contained metals in high concentrations (order of magnitude greater than in the parent bitumen); the metals were easy to leach with an acid. The practical significance of the idea is unclear, since: (i) metals still have to be extracted from the residue; (ii) the scalability of the process is dubious; and (iii) the process leads to the formation of conductive carbon particles in the liquid phase, thus preventing the process from being repeated. Garyfzyanova [34] also

proposed the application of a plasma arch to cause the pyrolysis of heavy oil products into lighter hydrocarbons with the deposition of a residue containing soot and metal oxides. Trutnev et al. [35] proposed sonication to facilitate the recovery of metals (V, Ni, Cr and W) during the thermal cracking of crude oil. Finely dispersed metal oxide particles were introduced to the liquid-like residue obtained by thermal cracking and heated to a temperature of 380–420 °C. The application of an acoustic field to the dispersion is supposed to facilitate the precipitation of the particles and separation of the metal-containing fraction, which is periodically removed and subjected to calcination and purification, thus recovering both metal particles and porphyrins. We are not aware of any practical application of this idea.

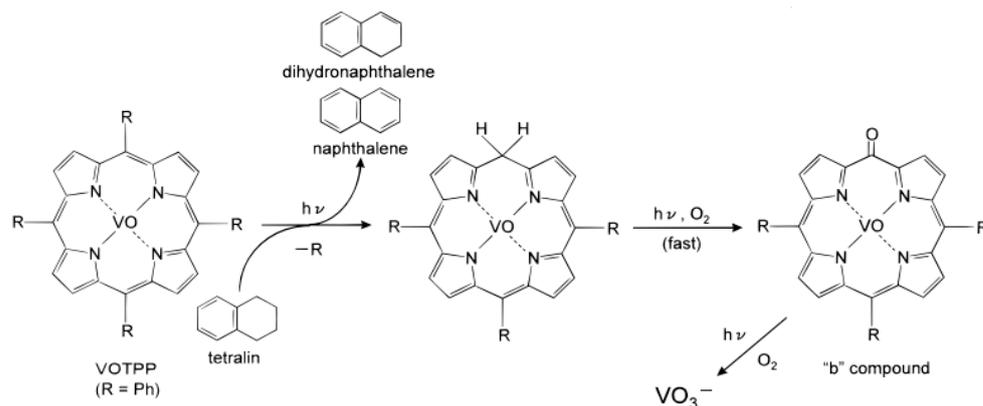


Figure 3. The proposed photodecomposition pathway for vanadyl (IV) tetraphenylporphyrin by photoirradiation to the tetralin + vanadyl (IV) tetraphenylporphyrin/water two-phase system [32] (reproduced with permission).

4. Pre-Combustion Metal Recovery from Petroleum Cokes

4.1. Metal Content in Petcoke

Petcoke results from the thermal cracking of heavy petroleum feedstock and is used as a fuel and in metallurgy. As always, in coking processes the coke is a “residue” enriched with metals, which are undesirable pollutants in metallurgy and energy production. A DTE petcoke technical data sheet (according to ref. [36]) estimated the vanadium content in petcoke at 0.12% and nickel content as 0.025% wt. in 2009. A recent thesis [37] cites a vanadium content of 0.1 to 0.2% and nickel content from 0.0035% to 0.06%. The current standard for the needle coke used in metallurgical electrode production is <0.025% vanadium, and the actual content is even lower [38]. ExxonMobile advertises the coke from flexicoking units for metal reclamation [39]. This section reviews the techniques of pre-combustion metal removal. Processing with acids, bases, sintering with salts and oxidation are mainstream methods in the published efforts. It is worth noting that similar methods are applied in metal extraction from stone coal, spend catalysts and other industrial waste materials [40–43].

4.2. Pre-Combustion Metal Leaching from Petcoke

Hepworth and Slimane [44] extracted vanadium and nickel from flexicoke obtained from Orinoco crude by leaching with acids at atmospheric pressure followed by extraction and crystallization. They obtained 99.6% pure V_2O_5 . Acid leaching is more effective for a lower valence state of vanadium (V_2O_3) than for a higher valence (V_2O_5). The effect of vanadium re-leaching following the heat treatment using H_2SO_4 or NaOH was also studied. Vanadium recovery increased up to 98% by repeated leaching with 2M NaOH. Ultrasound also facilitated vanadium recovery. Alvarado et al. [45] treated coal and petroleum coke from Venezuelan oil with HNO_3 solutions (!) and subjected the result to a heat treatment in a microwave oven. In total, 93% to 98% of vanadium was recovered from the different samples. Sitnikova et al. [46] extracted vanadium from cokes produced by delayed coking

and flexicoking from West Siberian HPF samples. Similarly to ref. [45], leaching was carried out with an oxidative solution ($\text{H}_2\text{SO}_4 + \text{NaClO}$) for 4 h at 70–80 °C. Here, 99% of vanadium was extracted from flexicoke, and only 40% of the available vanadium was extracted from the cokes produced by delayed coking. Ryumin et al. [47] leached vanadium from petroleum coke with H_2SO_4 . The coke was pulverized to <100 μm particles, heated at 380–420 °C in air for 2–6 h, then processed with a H_2SO_4 solution for 2–3 h at 90–100 °C. Depending on the acid concentration, temperature and duration, 69–92% of the available vanadium was extracted with 40–70% (!) carbon mass loss. Rudko et al. [48,49] treated a lab sample of coke obtained from asphaltenes of West Siberian crudes with H_2SO_4 and $\text{H}_2\text{SO}_4\text{--HNO}_3$ mixtures of different concentrations. Coke that was manually crushed to 100 μm particles was exposed to leaching agents for 1–2 h at 100 °C. The degree of extraction reached 90%, which looks good, but no data on the carbon losses were provided.

The kinetics of alkaline leaching of vanadium from flexicoking residues was also explored. For example, in ref [50], flexicoke pulverized to 0.09–0.106 μm -sized particles was exposed to concentrated solutions of Na_2CO_3 and NaOH in the presence of a H_2O_2 oxidant over 5 h at 100 °C. The ratio of liquid and solid phases was 6 to 1. A 72.7% degree of demetallization was achieved.

Vanadium can be extracted from petrocokes by sintering with alkali metal salts at temperatures below salt melting, and then leaching in aqueous media with acids or bases. Patent [51] considers flexicokes, although does not limit the application to this specific source. The disadvantage of this method is the loss of a significant part of the carbon mass of the coke as a result of the process. Paper [52] applies a similar method for concurrent sulfur removal and vanadium extraction. Only 60% of vanadium was extracted.

In general, the attempts to “have your cake and eat it” (that is, to extract metals and efficiently use the carbon as a fuel or otherwise) have a long history and have not ceased. The problem is the high carbon loss, which increases the cost and, in many cases, low degree of extraction. A more subtle route to do away with the oxidation step is leaching metals from coke or asphalt gasification residue, rather than from the coke itself [53,54]. Gasification is the processing of a dried residue (coal, coke or asphalt) with steam and oxygen at high temperatures leading to a syngas (CO , H_2 or CO_2) and carbon soot enriched with metals (review [55]). By thermodynamic and kinetic modeling, the authors [53,54] attempted to find conditions that would lead to easy-to-extract metal compounds in the resulting soot residue. The authors found that only a small fraction of molybdenum and nickel would be reduced to pure metals; rather they would form carbides. Vanadium would be reduced to V_2O_3 , especially at lower gasification temperatures. The resulting compounds are rather difficult to dissolve (vanadium dissolves in water in vanadate forms only), and thus the process would require an extra oxidation step. As an alternative, the authors explored controlled soot burnout to an ash and concluded that burnout was superior as a method for metal recovery.

4.3. Conversion of Metals Contained in Petcokes to Other Products without Prior Leaching

There are exotic ideas that target metal conversion to useful products without the isolation and purification of vanadium and nickel compounds. Abdrabo and Husein [56] proposed the conversion of oil demetallization waste (namely, the gasification residue) to the dispersion of metal oxide nanoparticles in heavy oil. This interesting idea does not however fully qualify as a technique for metal recovery. Finally, Zhan et al. [57] synthesized a vanadium-based metal organic framework (MOF) from vanadium-containing waste: carbon black from an oil refinery. This idea is demonstrated in Figure 4. No matter how interesting this idea is (it is!) as a method of *vanadium recovery*, this work is not very convincing, because vanadium has to be converted in a reasonably usable form before MOF synthesis.

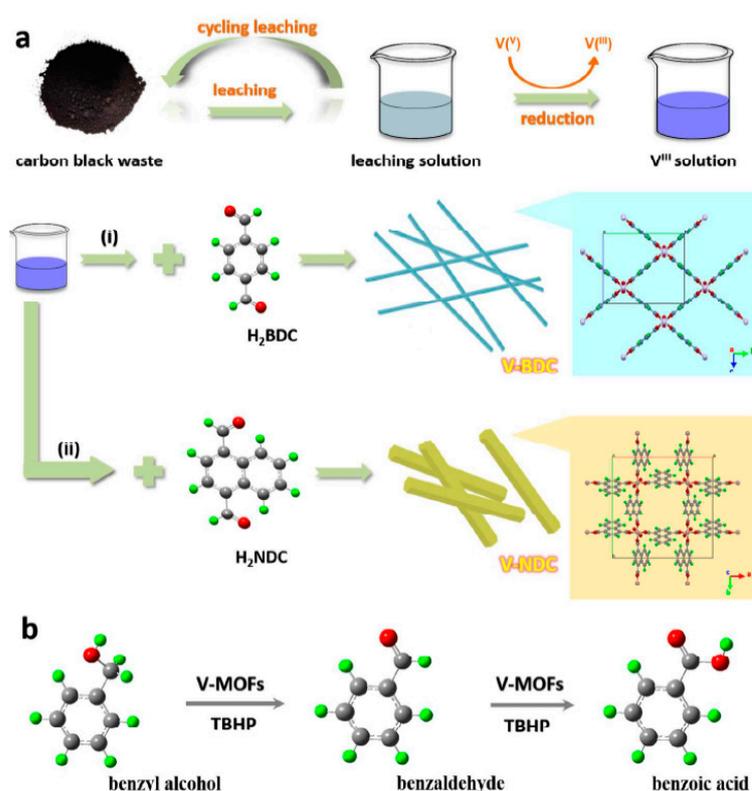


Figure 4. (a) Schematic illustrations of vanadium recovery from carbon black waste into V-MOFs: (i) synthesis of vanadium–benzene dicarboxylate, and (ii) synthesis of vanadium–naphthalenedicarboxylate nanorods. The cycling leaching process represents the usage of the first leachate as a leaching agent in order to increase the concentration of vanadium in the second leachate. (b) The reaction route of catalytic benzyl alcohol oxidation over the vanadium-MOF catalyst. Color codes in molecular structures and ball–stick models: green balls (hydrogen atoms), gray balls (carbon atoms), red balls (oxygen atoms) and pink balls (vanadium atoms). (Reproduced from ref. [57] with permission from ACS).

5. Ashes from Heavy Fuel Oil, Petroleum Coke and Asphalt as Sources of Metals

5.1. Fly Ash from Heavy Fuel Oil and Coke Combustion

Unlike CO₂ and water, metal oxides are relatively non-volatile. During the combustion of hydrocarbon fuel, they concentrate in the solid residue, aka ashes (Figure 5). The recovery of metals from combustion products attracts intensive efforts and is (as of today) the only path that is industrially implemented. The implementation started back in the 1970s. The literature review in thesis [58] already described a long research history, and as of 1988, eight units of vanadium recovery from combustion residue operated in Canada and Venezuela (according to review [6]).

As sources of metals, heavy oil (or “heavy fuel”) fly ash (HOFA) and ashes from petcoke combustion are of special interest. Since most metals (V, Ni, Co and Fe) are chemically bonded to the polyaromatic fragments of the asphaltenes, they are found in the fly ash rather than the bottom ash of the pulverized or fluidized petcoke furnaces. Metal-containing ash is a waste and substantial efforts are being invested into its utilization (see special issue [59] and review [60]). The most common applications for fly ash are composites [61], waste stabilization [62] and construction materials [63]. Still, about half of the fly ash in the US is currently landfilled [64]. Using fine heavy oil and petcoke fly ash in concrete and asphalt concrete is safer compared to landfill depositing, as metal emissions to the environment are much slower when the metal-containing particles remain in a stabilized form [65]. The prospective applications of fly ashes include even soil improvement [66].

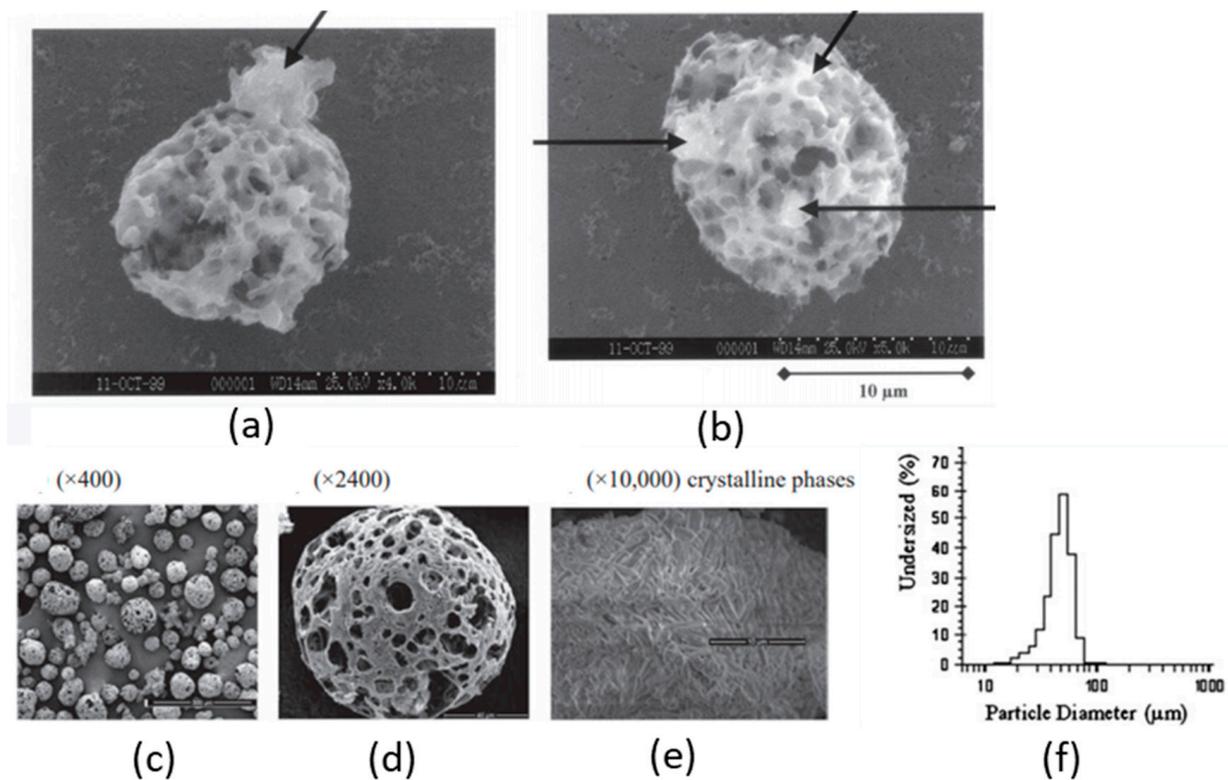


Figure 5. Top row (a,b) particles of fly ash from semi-solid asphalt combustion. The arrows indicate metal-rich inorganic inclusions; the carbon phase is darker gray (reproduced from ref. [67] with permission from T&F). Bottom row (c–e) ash particles formed during the combustion of heavy fuel oil in boilers and (f) the particle size distribution (reproduced from ref [68] with permission from Elsevier).

5.2. Controlled Combustion and Gasification of Petcoke to Obtain Ash Enriched with Metals

Although power plants are the main sources of fly ash, sometimes it makes sense to burn refuse polluted coke or solid asphalt resulted from demetallization via critical or supercritical extraction. The controlled oxidation generates ash that is easy to collect and transport.

In 1945, a patent was granted [69] in the US for a method of vanadium recovery from oil, which involved separation of the high boiling solid or semi-solid fraction (asphalt) from the feed oil, burning and further oxidation of the product in a controlled manner and leaching the metal from the resulting ash. The patent schematically presented the construction of the furnace for the controlled burning of the asphalt. Note that metal recovery is the specific target of asphalt oxidation here, rather than a byproduct of power generation.

Jack and co-authors [70] studied the possibility of the extraction of iron, vanadium, nickel and titanium by hydrometallurgical methods from petroleum coke obtained during flexicoking from the Athabasca oil bitumen sands. When treated with strong acids, the extraction of vanadium, iron and nickel was more than 50%, while only 20% of titanium was extracted. By means of weak acid leaching, nickel extraction was about 30%, but no transition to a solution of other metals was achieved. If coke obtained from the bitumen of Athabasca oil sands by flexicoking or the usual method of delayed coking is oxidized by air at temperatures below 500 °C, then the vanadium and nickel remaining in the ash are easily leached by acid: the solid residue is treated with acids, as a result of which the metals pass into the solution. Nickel and cobalt are extracted as cations $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, and vanadium is extracted in the form of isopolymers; for example, $(\text{V}_2\text{O}_7)^{4-}$, $(\text{V}_3\text{O}_9)^{3-}$, etc.

A straightforward method of extracting vanadium from petroleum coke proposed by Gardner [71] is based on the complete gasification of coke, the production of ash and

combustible gas and the extraction of vanadium from the ash. For the flexicoking residue specifically mentioned by the author, such an approach may be fully justified. For example, two Canadian companies, MGX Minerals and Highbury Energy, announced a venture to recover metals from excessively vast petcoke stockpiles close to the Athabasca region in Alberta, Canada [72]. Gasification units were developed specially for the project. According to the report [73], MGX studied thirteen coke samples from two different stockpiles. The two stockpiles contained 0.042% and 0.046% of vanadium (wt% of dry petcoke). The ashes contained 6.6% and 45% of V_2O_5 , correspondingly.

5.3. Hydrometallurgical Approaches for Metal Extraction from Ash

Heavy oil fly ash (HOFA) is a by-product generated in power plants by the burning of heavy fuel oil. The main constituent of HOFA is unburned carbon; it also contains other elements such as As, Cd, Co, Cr, Hg, Ni, Pb, Cu, Zn, Se, Ca, Mg, Na and Si. The composition and physico-chemical characteristics of HOFA were studied quite comprehensively. HOFA particles have a typical size of 10–100 μm [74], although the size depends heavily on the process. The bulk density of HOFA varies from 0.50 to 1.50 g/cm^3 and the porosity is estimated as 10.31% [75]. A comparison of the BET [76] surface area and the particle size reported in ref. [77] also suggests a substantial porosity. The metal content of HOFA varies widely (depending on the raw material and the combustion process), but is always significant. HOFA consists mostly of carbon [78] and contains large amounts of sulfur. Besides vanadium and nickel, HOFA samples can contain substantial amounts of zinc and iron, and traces of cobalt, chromium, lead and copper [68]. Carbon soot is the most significant constituent of HOFA; the total metal content can approach 5% [68,79–82]. For example, Jung and Mishra measured the metal content by inductively coupled plasma atomic emission spectroscopy and X-ray fluorescence. Their samples of HOFA contained 2.2% wt vanadium, 1.9% germanium and 0.4% nickel. Carbon constituted >93% wt of the total HOFA mass. Vanadium is mostly present in HOFA in the $\text{Mg}_3\text{V}_2\text{O}_8$ form. It is worth mentioning that the V/Ni ratio does not obey the relationships common to heavy oil [83], possibly suggesting metal loss.

The metal content in ashes depends on the combustion process and on the ability to collect the fly ash (by electromagnetic traps). Linak and Miller [84] burned gasified coals and fuel oil in laboratory installations simulating power plants. Coals with various sulfur and metal contents were used: the vanadium content ranged from 2.25 to 13 $\mu\text{g}/\text{g}$, and the nickel content ranged from 0 to 6.4 $\mu\text{g}/\text{g}$ of the raw materials. The highest content was in a high grade fuel oil sample, 220 $\mu\text{g}/\text{g}$. Next, the metal content in the trapped particles formed during combustion was measured. The type of combustion equipment played an important role: during the combustion of fuel oil in narrow tubes surrounded by water, which led to the rapid cooling of the combustion products, a large number of very small non-trappable particles formed, and the metal content in the trapped ash was lower. The metal content in the smaller particles was always higher than in the larger ones. When combustion occurred in a larger volume (water was supplied in the tubes, burning was conducted in the surrounding space), the combustion products cooled more slowly, which led to larger particles and a vanadium content up to 13.6%. Since the processes of burning coal and petroleum coke are similar, it is expected that in ash with a particle size smaller than 2.5 μm , the metal content in the fine ash fraction is increased by 25–100 times compared to the original coke. For HOFA, we might expect the ratio of 250+ times.

The main approaches to metal extraction are based on solvent extraction/leaching, roasting/calcination with salts also followed by leaching and controlled oxidation to burn out the carbon and obtain metal oxide mixture to an almost-pure form. The degree of recovery and the selectivity are two main targets. The straightforward approach is a “hydrometallurgical” recovery of vanadium and nickel directly from HOFA by acids [85–89], bases [90–93] or water [94] leaching. Vanadium is oxidized to vanadate forms (by O_2 [85], H_2O_2 [90,95], HClO [8,96], etc. [86,87]) and precipitated with non-alkali cations or an ion exchange [97]. Then, it can be isolated and purified with recrystallization or solvent extraction [88,89]. We

will not describe all these studies here; a comprehensive review can be found in [98] with the focus on the removal rather than the recovery. The process can be assisted by sonication [99]. The straightforward procedure promises moderate success. Al-Degs et al. [68] used various solvents (HNO_3 , NaOH , EDTA, etc.), as well as acid and base solutions on a set of HOFA samples to extract different metals (Ni, V, Mo, Cr, Zn, Cu and Mg) and recovered up to 95% of the total magnesium and up to 15% of the total vanadium, for which the yields were notably low. Other published studies report a somewhat higher recovery [100]. For example, in paper [101] leaching HOFA with 0.5 N sulfuric acid resulted in the extraction of 65% vanadium, 60% nickel and 42% iron. During leaching in a 2M NaOH , vanadium recovery was 80%, and nickel recovery was insignificant, which allows for the selective recovery of metals. Selective nickel extraction was achieved with a mixture of ammonium water and ammonium sulfate. Paper [102] followed similar pathways of vanadium extraction from HOFA, but explored in finer details the influence of process parameters, such as the solvent composition, time, particle size and mixing rate. Navarro and co-authors [103] treated HOFA with alkalis to selectively separate vanadium in the form of soluble vanadates, from which insoluble forms were precipitated with non-alkaline metal ions. Generally, leaching at a high pH is selective to vanadium, while other metals, including nickel and cobalt, are leached by acids. A three-step process of metal extraction from Orimulsion fly ashes was presented by Vitolo et al. [80].

5.4. Roasting with Salts and Controlled Oxidation

Fly ash sintering (roasting, calcination) with salts in order to convert metals (vanadium and nickel, first of all) to forms better suitable to leaching makes another group of traditional methods that can be traced back to at least early 1980 [58]. Gomez-Bueno et al. [104] roasted the ashes from Athabasca HPF combustion with NaCl at 875–950 °C prior to leaching with an alkali at boiling temperatures. The authors recovered 85% of the available vanadium. Holloway et al. applied a very similar approach to oil sands fly ash [105]. The same group examined the selectivity of vanadium extraction and found that roasting with high amounts of Na_2CO_3 allowed for the selective recovery of vanadium, and somewhat later, they proposed the production technology [106]. Recent developments include roasting oxidation for the selective recovery of vanadium that could be leached by water, and nickel that could only be recovered with acids [107]. More than 80% of the available vanadium was recovered as a result.

The approaches to fly ash from petcoke combustion are similar. Vasilyeva et al. [108] studied the elemental composition of ash produced by the combustion of petcoke of Syrian origin. The very scheme of leaching vanadium compounds dates back to a very old patent [109]. Most attempts to isolate metals involve the roast-and-leach approach [110]. For example, Rezaei et al. [111] recently applied roasting with Na_2CO_3 and nitric acid leaching to extract a wide group of metals from coal coke. Ziyadanoğullari [112] applied the roast-and-leach approach to asphalt residue after critical solvent extraction and was able to recover 70%+ of the available vanadium. Petcoke is more often subjected to controlled oxidation prior to calcination with salts in order to remove most of the remaining carbon [113,114]. Kadhim [115] applied a two-stage process: first, the ash was treated with air at 650 °C and 850 °C in order to reduce the carbon content. Then, the product was processed with NaOH to extract the vanadium. Vitolo et al. [80] also conducted preliminary oxidation with air at 650 to 1150 °C, below the initial deformation temperature of the fly ash. The temperature of the preliminary burning step substantially influences the outcome. Above 950 °C, the volatilization of vanadium and the formation of V–Ni refractory compounds adversely affected the recovery of vanadium. The burning temperature of 850 °C was found to be the optimum as a result of the trade-off between the overall vanadium recovery yield (83%) and the V_2O_5 weight percentage in the precipitate (84.8%). For coke from oil obtained from the oil sands of Western Canada, a complex process was proposed [116], including: (i) the burning of ash in the presence of oxygen and NaCl (5 to 35% wt of the petcoke) at temperatures ranging from 700 °C to 950 °C; (ii) leaching of the residue with aqueous

solutions at pH = 5–12 and temperatures ranging from room to boiling until a significant portion of the vanadium dissolves; and (iii) precipitation of metavanadate ammonium with a solution of ammonium chloride or sulfate acidified to a pH = 2–3.

Volkov et al. [82] published a detailed analysis of HOFA roasting with Na_2CO_3 followed by aluminothermic melting. The process leads to a “slag” enriched with V, Ni and Fe in various forms ($\text{NaMg}_4(\text{VO}_4)_3$, NaVO_3 , $\text{Ca}_x\text{Mg}_y\text{Na}_z(\text{VO}_4)_6$; (FeV_2O_4) , $\text{V}_{2-x-y-z}\text{Fe}_x\text{Al}_y\text{Cr}_z\text{O}_3$, $\text{Mg}_{1-x-y-z}\text{Ni}_x\text{Fe}_y\text{V}_z\text{O}$). The metals were leached with either acid or base solutions. Leaching from the slug was far more effective compared to the direct leaching from the HOFA source (72.3–96.2% V and about 90% Ni was recovered with H_2SO_4). A somewhat similar method was previously applied to vanadium-containing sludge, which is a byproduct of vanadium pentoxide obtained by hydrometallurgical methods. Vanadium was mostly in the $\text{FeO}\cdot\text{V}_2\text{O}_3$ form. The authors explored various oxidation roasting methods for a sludge treatment to facilitate vanadium extraction. Oxidation roasting of the sludge at 1000 °C with 1% CaCO_3 increased the acid-soluble V_2O_5 from 1.5% to 3.7% and lowered the content of $\text{FeO}\cdot\text{V}_2\text{O}_3$ from 3% to 0.4% [117]. Vanadium and nickel from flexicoking waste were isolated by Queneau et al. [118] by pressure oxidation: steam with a pH = 9.5 was supplied under pressure in an industrial-type facility. Exothermic reactions produced enough steam to generate enough electricity to make the process self-sustainable. Vanadium and nickel are concentrated in some kind of ash in carbonate forms and converted to high purity salts and then oxides with extraction and crystallization. The general scheme of vanadium and nickel extraction from fly ash is shown in Figure 6.

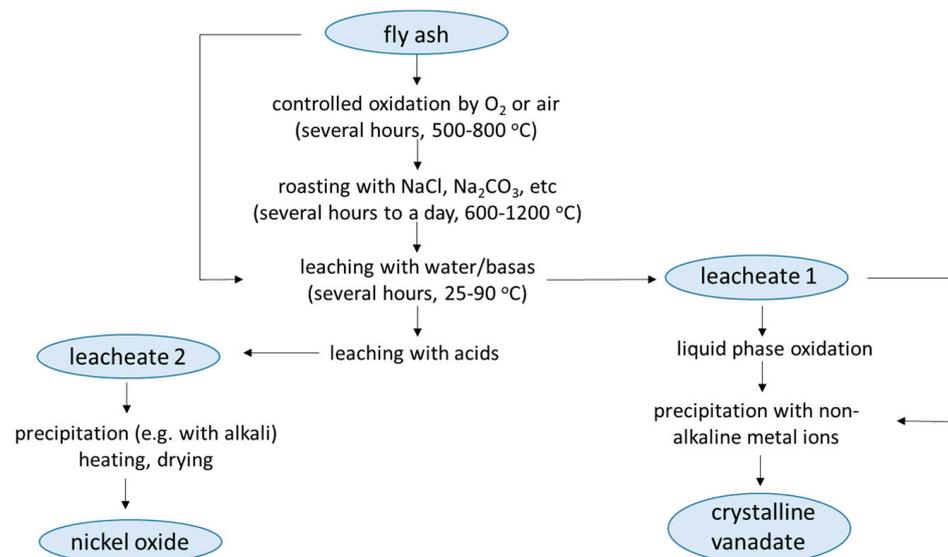


Figure 6. Composite scheme of hydrometallurgical vanadium and nickel recovery from fly ash, according to the literature. There are many modifications of this process; for example, Liu et al. [8] describe chlorination-based methods.

5.5. Pyrometallurgical Methods

Pyrometallurgical approaches [119–122] are qualitatively different from sintering with salts or controlled oxidation; their products are alloys of the target metals with a less expensive metal, usually Fe. For example, Xiao et al. [120] suggested an interesting pyrometallurgical method to recover vanadium by obtaining a ferrovanadium alloy from two industrial waste resources: petcoke fly ash and flue dust. A ferrovanadium alloy with about 20 wt% vanadium was obtained at 1550 °C. On average, about 30% of the metal yield was obtained during smelting of the mixture of petroleum fly ash to flue dust in a 4/5 weight ratio. Sun et al. [122] proposed a pyrometallurgical process to recover nickel in the form of an Fe–Ni alloy from coal fly ash, spent petroleum catalyst, CaO, Fe powder and H_3BO_3 .

Finally, Tectonics' DC operates a plasma arc melting furnace (PAF) to recover metals from the ash that is used just as any ore [123]. In PAF, the content is melted under an inert gas atmosphere at an ambient pressure with the plasma arc torch column which provides temperatures sufficient for the production of metals. Wet materials containing substantial amounts of water can be heated safely and effectively in a plasma arc smelting furnace. The recovery of nickel as an Fe–Ni alloy and a vanadium-rich slag is achieved with a carbothermic reduction process common in pyrometallurgy: nickel and iron oxides are reduced by carbon. Then, vanadium as an Fe–V alloy from the first stage slag is obtained via reduction with aluminum. Nickel and vanadium are thus obtained separately in this two-stage process. Further processing of the alloys (especially the first stage Fe–Ni alloy) may be required to meet the standard ferroalloy specifications.

5.6. Bioengineering-Based Approaches to Post-Combustion Extraction Metals

Bioengineering approaches to vanadium and nickel separation from ashes appear to be far from production but potentially promising [124]. Li and co-authors [125] studied the metabolism of vanadium in technologies where coke was mixed with an organic matter of biological origin. It must be said that the bio-demetalization of coal combustion products has been studied for quite a long time, and it is based on the consumption of carbon residues by microorganisms. Rasulnia and Mousavi [126] applied fungal microorganisms, including ordinary penicillin, to produce vanadium and nickel from ashes (Figure 7). The utilization of carbon for the vital activity of fungi leads to the release of metals, because microorganisms do not absorb metal ions, which in high concentrations are harmful to them. Fungal cultures are introduced to fairly dense suspensions of ash in water. Metal ions can be precipitated into insoluble forms. At a temperature of 60 °C, 90% of vanadium and about half of nickel were extracted within a week. The process is long but environmentally benign. Generally, the idea of the biological extraction of metals received wide interest, including applications to metallurgical slag [127], the ash from municipal waste [128–130], wastewater treatment and the extraction of metals from the wreckage of electronic devices (review [131]).

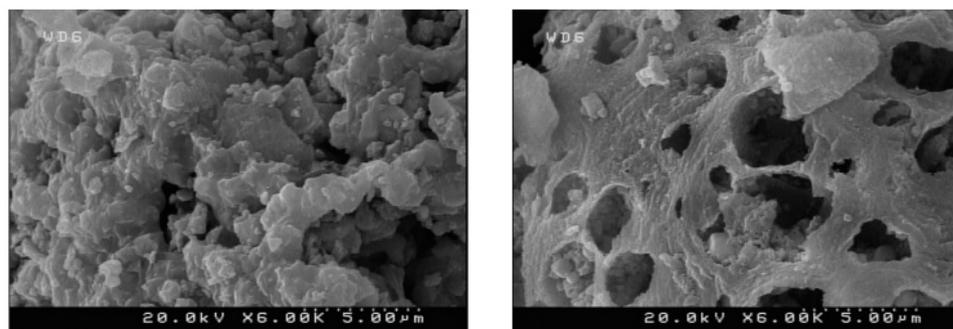


Figure 7. The effect of bioleaching in FE-SEM images of the surface morphology of the original HOFA particles (left) and the before and after bioleaching at $\times 6.00$ K magnification (right). Reproduced from ref. [126] with permission from RSC.

6. Conclusions

Table 1 lists the main approaches to metal reclamation from the products of HPF processing, their advantages and disadvantages, the stages of development and commercialization. The successful commercial projects of metal extraction from HPF have existed for decades. Nevertheless, they remain relatively small and “local”: metal reclamation seems to have not reached the scale comparable with traditional sources—the slag from steel production and the direct production from vanadium-bearing ores. Post-combustion metal extraction from power plant ashes and gasification residues is the only route of metal recovery from the HPF commercially explored on a regular basis as of today. Metal-polluted ash is really a waste that needs to be safely disposed of. In general, the approaches to recov-

ery are somewhat similar to those applied to the metal extraction from slag. The important difference is the high carbon content of the fly ashes, while the slag consists primarily of metal oxides, silicates and phosphates, [132] with V_2O_5 content up to 20 wt% [133] (we did not review the vanadium extraction from the slag since it is mostly of non-petroleum origin and was described extensively [133,134]). The environmental challenges specific to the fly ashes are related to the ash capture (as we showed, metals are contained in a small particle fraction that needs to be captured), storage and transportation. Pyrometallurgy is energy-intensive, but relies on relatively traditional smelting technologies. The hydrometallurgical route is the most studied in the literature and can be easily adjusted to the various types of raw materials. Most research efforts are also concentrated in these traditional and mature areas. The progress is mostly incremental and follows the prospective industrial demand.

Table 1. Summary of the main methods of vanadium and nickel extraction from HPF demetallization residues.

Source	Method	Advantages	Disadvantages	
Heavy oil	Electrochemical: Emulsification/solvation in non-aqueous solvent, electrolysis	Convenient, environmentally benign, potentially selective	Very slow	Very unlikely to reach industrial implementation
Coke	Leaching with acids, solvents	Simple	Loss of reagents on carbon oxidation	In perspective, inferior to other methods
Coke or solid asphalt	Oxidation or gasification to ash	Produces syngas		Good way to utilize low quality or refuse material Implementation underway
Ash from heavy oil and coke combustion	Hydrometallurgy: oxidation–roasting–leaching–precipitation	Source is really a waste; Extraction is a low energy process	Complex, multi-stage; fly ash collection, storage and transportation is difficult	Most used and studied, will remain for a while
	Pyrometallurgy: reduction to V–Fe and Ni–Fe alloys	Metals obtained in convenient form	Energy consumption, expensive equipment	Ready technology, will remain for a while
	Bioengineering	Environmentally benign	Slow, not studied enough	Years of research needed, but potentially viable

Where we may expect serious developments is metal reclamation from the residues resulted from the on-site supercritical extraction of the lighter components from heavy oil. The on-site extraction and hydrocracking of super heavy oils are aimed at resolving the transportation problem: currently, very viscous heavy oil is often diluted with lighter oils just to be transported to refineries. The on-site extraction yields liquid and solid products that are much easier to deal with. Whether the semi-solid asphalt obtained on-site is worth further cracking processing depends on the original crude and the extraction conditions, which can be tailored to deeper extractions (less saturates and lower aromatics on the residue; more organometallic compounds in the deasphaltate) or shallower extractions (deeper demetallization; more SAR in the residue). In the case of a deeper extraction, the asphalt might likely be treated similarly to petcoke with gasification and hydrometallurgical extraction, but further research to optimize the extraction and metal reclamation is needed.

The other area of actively increasing research activity is bio-extraction from ashes with fungi species known to accumulate vanadium and/or consume the carbon fraction of the ashes. How long it may take to develop into ready technologies is hard to predict; it is possible that the bioengineering methods will never become commercially viable. As we may see from the review, the pre-combustion extraction of metals from petcoke, electrochemical extraction and exotic methods are very far from commercial application and are unlikely to develop into real technologies anytime soon.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Luz, A.L.; Wu, X.; Tokar, E.J. Chapter One—Toxicology of Inorganic Carcinogens. In *Advances in Molecular Toxicology*; Fishbein, J.C., Heilman, J.M., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; Volume 12, pp. 1–46.
2. Raja, B.V.R. Vanadium market in the world. *Steelworld* **2007**, *13*, 19–22.
3. FacrMR. Vanadium Market Growth Outlook (2023–2033). Available online: <https://www.factmr.com/report/vanadium-market> (accessed on 20 January 2023).
4. Samora, R.; Bell, A. Vale Sees 44% Increase in Global Nickel Demand by 2030. Available online: <https://www.reuters.com/markets/commodities/vale-sees-44-increase-global-nickel-demand-by-2030-2022-09-07/> (accessed on 20 January 2023).
5. Kornienko, V.; Avtonomov, P. Application of Neutron Activation Analysis for Heavy Oil Production Control. *Procedia Soc. Behav. Sci.* **2015**, *195*, 2451–2456. [CrossRef]
6. Magomedov, R.; Popova, A.; Maryutina, T.; Kadiev, K.M.; Khadzhiev, S. Current status and prospects of demetallization of heavy petroleum feedstock. *Pet. Chem.* **2015**, *55*, 423–443. [CrossRef]
7. Kurniawan, Y.S. The Origin, Physicochemical Properties, and Removal Technology of Metallic Porphyrins from Crude Oils. *Indonesian J. Chem.* **2021**, *21*, 1023–1038.
8. Liu, S.; Xue, W.; Wang, L. Extraction of the Rare Element Vanadium from Vanadium-Containing Materials by Chlorination Method: A Critical Review. *Metals* **2021**, *11*, 1301.
9. Akcil, A.; Vegliö, F.; Ferella, F.; Okudan, M.D.; Tuncuk, A. A review of metal recovery from spent petroleum catalysts and ash. *Waste Manag.* **2015**, *45*, 420–433. [CrossRef]
10. Baritto, M.; Oni, A.O.; Kumar, A. The development of a techno-economic model for the assessment of vanadium recovery from bitumen upgrading spent catalyst. *J. Clean. Prod.* **2022**, *363*, 132376. [CrossRef]
11. Pathak, A.; Kothari, R.; Vinoba, M.; Habibi, N.; Tyagi, V.V. Fungal bioleaching of metals from refinery spent catalysts: A critical review of current research, challenges, and future directions. *J. Environ. Manag.* **2021**, *280*, 111789. [CrossRef]
12. Kukes, S.G.; Battiste, D.R. Demetallization of Heavy Oils with Phosphorous Acid. U.S. Patent 6,655,113, 11 June 1985.
13. Taghvaie Nakhjiri, A.; Sanaeepur, H.; Ebadi Amooghin, A.; Shirazi, M.M.A. Recovery of precious metals from industrial wastewater towards resource recovery and environmental sustainability: A critical review. *Desalination* **2022**, *527*, 115510. [CrossRef]
14. Zheng, F.; Shi, Q.; Vallverdu, G.S.; Giusti, P.; Bouyssièrè, B. Fractionation and Characterization of Petroleum Asphaltene: Focus on Metalopetroleomics. *Processes* **2020**, *8*, 1504. [CrossRef]
15. Yakubov, M.R.; Milordov, D.V.; Yakubova, S.G.; Borisov, D.N.; Ivanov, V.T.; Sinyashin, K.O. Concentrations of vanadium and nickel and their ratio in heavy oil asphaltenes. *Pet. Chem.* **2016**, *56*, 16–20. [CrossRef]
16. Amorim, F.A.C.; Welz, B.; Costa, A.C.S.; Lepri, F.G.; Vale, M.G.R.; Ferreira, S.L.C. Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. *Talanta* **2007**, *72*, 349–359. [CrossRef]
17. Yakubov, M.R. Composition and Properties of Asphaltenes from Heavy Oils with High V and Ni Content. Ph.D. Thesis, Kazan Research Center RAS, Ufa, Russia, 2019. [CrossRef]
18. Sugihara, J.M.; Okada, T.; Branthaver, J.F. Reductive Desulfuration on Vanadium and Metalloporphyrin Contents of Fractions from Boscan Asphaltenes. *J. Chem. Eng. Data* **1965**, *10*, 190–194. [CrossRef]
19. Lanese, J.G.; Wilson, G.S. Electrochemical studies of zinc tetraphenylporphin. *J. Electrochem. Soc.* **1972**, *119*, 1039–1043. [CrossRef]
20. Khanova, L.A.; Lafi, L.F. Adsorption characteristics of tetraphenylporphyrins on an amalgamated platinum electrode. *J. Electroanal. Chem.* **1993**, *345*, 393–411. [CrossRef]
21. Ovalles, C.; Rojas, I.; Acevedo, S.; Escobar, G.; Jorge, G.; Gutierrez, L.B.; Rincon, A.; Scharifker, B. Upgrading of Orinoco Belt crude oil and its fractions by an electrochemical system in the presence of protonating agents. *Fuel Process. Technol.* **1996**, *48*, 159–172. [CrossRef]
22. Jorge, G.A.; Garcia, E.; Scott, C.E. Electrolysis of V(IV) and free meso-tetraphenyl porphyrin in two immiscible liquids. *J. Appl. Electrochem.* **2002**, *32*, 569–572. [CrossRef]
23. Welter, K.; Salazar, E.; Balladores, Y.; Marquez, O.P.; Marquez, J.; Martinez, Y. Electrochemical removal of metals from crude oil samples. *Fuel Process. Technol.* **2009**, *90*, 212–221. [CrossRef]
24. Kurbanova, A.N.; Akhmetov, N.K.; Yeshmuratov, A.; Zulkharnay, R.N.; Sugurbekov, Y.T.; Demeuova, G.; Baisariyev, M.; Sugurbekova, G.K. Removal of nickel and vanadium from crude oil by using solvent extraction and electrochemical process. *Phys. Sci. Technol.* **2017**, *4*, 74–80. [CrossRef]
25. Afanasjeva, N.; Lizcano-Valbuena, W.H.; Aristizabal, N.; Mañozca, I. V and Ni electrochemical deposition from asphaltenes in heavy oils. *Ing. Compet.* **2015**, *17*, 9–17. [CrossRef]
26. Farag, A.S.; Sif El-Din, O.I.; Youssef, M.H.; Hassan, S.I.; Farmawy, S. Solvent demetalization of heavy oil residue. *Hung. J. Ind. Chem.* **1989**, *17*, 289–294.

27. Billica, H.; Adkins, H. Catalyst, Raney Nickel, W6 (with high contents of aluminum and adsorbed hydrogen). *Org. Synth.* **1949**, *29*, 24. [CrossRef]
28. Acevedo, D.; Camacho, L.F.E.; Moncada, J.; Puentes, Z. Electrochemically assisted demetallisation of model metalloporphyrins and crude oil porphyrinic extracts in emulsified media, by using active permeated atomic hydrogen. *Fuel* **2012**, *92*, 264–270. [CrossRef]
29. Khandelwal, A.; Singh, S.B.; Sharma, A.; Nain, L.; Varghese, E.; Singh, N. Effect of surfactant on degradation of *Aspergillus* sp. and *Trichoderma* sp. mediated crude oil. *Int. J. Environ. Anal. Chem.* **2021**, *103*, 1667–1680. [CrossRef]
30. Salehizadeh, H.; Mousavi, M.; Hatamipour, S.; Kermanshahi, K. Microbial Demetallization of Crude Oil Using *Aspergillus* sp.: Vanadium Oxide Octaethyl Porphyrin (VOOEP) as a Model of Metallic Petroporphyrins. *Iran. J. Biotechnol.* **2007**, *5*, 31.
31. Dedeles, G.R.; Abe, A.; Saito, K.; Asano, K.; Saito, K.; Yokota, A.; Tomita, F. Microbial demetallization of crude oil: Nickel protoporphyrin disodium as a model organo-metallic substrate. *J. Biosci. Bioeng.* **2000**, *90*, 515–521. [CrossRef]
32. Shiraiishi, Y.; Hirai, T.; Komasa, I. A novel demetallation process for vanadyl- and nickelporphyrins from petroleum residue by photochemical reaction and liquid-liquid extraction. *Ind. Eng. Chem. Res.* **2000**, *39*, 1345–1355. [CrossRef]
33. Lebedev, Y.A.; Averin, K.A. Extraction of valuable metals by microwave discharge in crude oil. *J. Phys. D-Appl. Phys.* **2018**, *51*, 5. [CrossRef]
34. Garifzyanova, G.G.; Garifzyanov, G.G. Pyrolysis of vacuum resid by the plasma chemical method. *Chem. Tech. Fuels Oils* **2006**, *42*, 172–175. [CrossRef]
35. Trutnev, J.A.; Mufazalov, R.S.; Mukhtorov, N.J.; Zaripov, R.K. Method and Apparatus for Demetallization of Crude Oil. RU Patent 2133766C1, 27 July 1999.
36. Fan, X. The Fates of Vanadium and Sulfur Introduced with Petcoke to Lime Kilns. Ph.D. Thesis, University of Toronto, Toronto, ON, Canada, 2010.
37. Abdolahnezhad, M. Metal Leaching from Oil Sands Fluid Petroleum Coke under Different Geochemical Conditions. Master's Thesis, University of Saskatchewan, Saskatoon, SK, Canada, 2020.
38. Lukoil. Coke. Available online: <https://lukoil.ru/Products/business/petroleumproducts/coke> (accessed on 20 January 2023).
39. ExxonMobile. Resid Conversion: Flexicoking. Available online: <https://www.exxonmobilchemical.com/en/catalysts-and-technology-licensing/resid-conversion> (accessed on 20 January 2023).
40. Cai, Z.; Zhang, Y.; Liu, T.; Huang, J. Mechanisms of vanadium recovery from stone coal by novel BaCO₃/CaO composite additive roasting and acid leaching technology. *Minerals* **2016**, *6*, 26. [CrossRef]
41. Mishra, B.; Jung, M. Recovery and Recycling of Valuable Metals from Fine Industrial Waste Materials. *Int. J. Soc. Mater. Eng. Resour.* **2018**, *23*, 105–108. [CrossRef]
42. Szymczycha-Madeja, A. Kinetics of Mo, Ni, V and Al leaching from a spent hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide. *J. Hazard. Mater.* **2011**, *186*, 2157–2161. [CrossRef]
43. Kinoshita, T.; Yamaguchi, K.; Akita, S.; Nii, S.; Kawaizumi, F.; Takahashi, K. Hydrometallurgical recovery of zinc from ashes of automobile tire wastes. *Chemosphere* **2005**, *59*, 1105–1111. [CrossRef]
44. Hepworth, M.; Slimane, R. Recovery of vanadium, nickel, and carbon from Orinoco crudes via flexicoking. *J. Solid Waste Techn. Manag.* **1997**, *24*, 104–112.
45. Alvarado, J.; Alvarez, M.; Cristiano, A.R.; Marcó, L. Extraction of vanadium from petroleum coke samples by means of microwave wet acid digestion. *Fuel* **1990**, *69*, 128–130. [CrossRef]
46. Sitnikova, G.Y.; Rastova, N.V.; Davydova, S.L. Role of thermal oxidation in the process of vanadium extraction from refinery coke (solid oil residues). *Petrol. Chem. USSR.* **1990**, *30*, 172–175.
47. Ryumin, A.; Belonin, A.; Gribkov, V. Method of Extraction of Vanadium from Petroleum Coke (Способ Извлечения Ванадия из Нефтяного Кокса). RU Patent 2070940C1, 27 December 1996.
48. Rudko, V.A.; Kondrasheva, N.K.; Lukonin, R.E. Influence of acid leaching parameters on the extraction of vanadium from petroleum coke. *Bullet. S. Petersb. Technol. Inst.* **2018**, *42*, 43–48.
49. Kondrasheva, N.K.; Rudko, V.A.; Lukonin, R.E.; Derkunskii, I.O. The influence of leaching parameters on the extraction of vanadium from petroleum coke. *Pet. Sci. Technol.* **2019**, *37*, 1455–1462. [CrossRef]
50. Zhang, Y.; Yang, L. Alkali leaching of vanadium from petroleum coke and kinetics analysis. *Int. J. Environ. Eng.* **2015**, *7*, 90–100. [CrossRef]
51. McCorrison, L.L. Process Using Sulphate Reagent for Recovering Vanadium from Cokes Derived from Heavy Oils. U.S. Patent 4,389,378, 21 June 1983.
52. Shlewit, H.; Alibrahim, M. Extraction of sulfur and vanadium from petroleum coke by means of salt-roasting treatment. *Fuel* **2006**, *85*, 878–880. [CrossRef]
53. Visaliev, M.Y.; Shpirt, M.Y.; Kadiev, K.M.; Dvorkin, V.I.; Magomadov, E.E.; Khadzhiev, S.N. Integrated conversion of extra-heavy crude oil and petroleum residue with the recovery of vanadium, nickel, and molybdenum. *Solid Fuel Chem.* **2012**, *46*, 100–107. [CrossRef]
54. Shpirt, M.; Nukenov, D.; Punanova, S.; Visaliev, M. Principles of the Production of Valuable Metal Compounds from Fossil Fuels. *Solid Fuel Chem.* **2013**, *47*, 71–82. [CrossRef]
55. Murthy, B.N.; Sawarkar, A.; Deshmukh, N.; Mathew, T.; Joshi, J. Petroleum coke gasification: A review. *Can. J. Chem. Eng.* **2014**, *92*, 441–468. [CrossRef]

56. Abdrabo, A.E.; Husein, M.M. Method for Converting Demetallization Products into Dispersed Metal Oxide Nanoparticles in Heavy Oil. *Energy Fuels* **2012**, *26*, 810–815. [CrossRef]
57. Zhan, G.W.; Ng, W.C.; Lin, W.Y.; Koh, S.N.; Wang, C.H. Effective Recovery of Vanadium from Oil Refinery Waste into Vanadium-Based Metal-Organic Frameworks. *Environ. Sci. Technol.* **2018**, *52*, 3008–3015. [CrossRef]
58. Griffin, P.J. Extraction of Vanadium and Nickel from Athabasca Oil Sands Fly Ash. Ph.D. Thesis, University of Alberta, Edmonton, AB, Canada, 1981.
59. Valeev, D.; Kondratiev, A. Current State of Coal Fly Ash Utilization: Characterization and Application. *Materials* **2023**, *16*, 27. [CrossRef]
60. Basha, S.I.; Aziz, A.; Maslehuddin, M.; Ahmad, S.; Hakeem, A.S.; Rahman, M.M. Characterization, Processing, and Application of Heavy Fuel Oil Ash, an Industrial Waste Material—A Review. *Chem. Rec.* **2020**, *20*, 1568–1595. [CrossRef]
61. Qaidi, S.; Najm, H.M.; Abed, S.M.; Ahmed, H.U.; Al Dughaiishi, H.; Al Lawati, J.; Sabri, M.M.; Alkhatib, F.; Milad, A. Fly ash-based geopolymer composites: A review of the compressive strength and microstructure analysis. *Materials* **2022**, *15*, 7098. [CrossRef]
62. Kanhar, A.H.; Chen, S.; Wang, F. Incineration Fly Ash and Its Treatment to Possible Utilization: A Review. *Energies* **2020**, *13*, 6681. [CrossRef]
63. Herath, C.; Gunasekara, C.; Law, D.W.; Setunge, S. Performance of high volume fly ash concrete incorporating additives: A systematic literature review. *Constr. Build. Mater.* **2020**, *258*, 120606. [CrossRef]
64. UnionProcess. Coal, Coke & Fly Ash Applications for Particle Size Reduction Equipment. Available online: <https://www.unionprocess.com/industries-applications/energy/coal-coke-fly-ash/> (accessed on 20 January 2023).
65. Mofarragh, A.; Husain, T.; Danish, E.Y. Investigation of the Potential Use of Heavy Oil Fly Ash as Stabilized Fill Material for Construction. *J. Mater. Civ. Eng.* **2012**, *24*, 684–690. [CrossRef]
66. Sett, P. Flyash: Characteristics, Problems and Possible Utilization. *Adv. Appl. Sci. Res.* **2017**, *8*, 32–50.
67. Huffman, G.P.; Huggins, F.E.; Shah, N.; Huggins, R.; Linak, W.P.; Miller, C.A.; Pugmire, R.J.; Meuzelaar, H.L.C.; Seehra, M.S.; Manivannan, A. Characterization of fine particulate matter produced by combustion of residual fuel oil. *J. Air Waste Manag. Assoc.* **2000**, *50*, 1106–1114. [CrossRef]
68. Al-Degs, Y.S.; Ghair, A.; Khoury, H.; Walker, G.M.; Sunjuk, M.; Al-Ghouti, M.A. Characterization and utilization of fly ash of heavy fuel oil generated in power stations. *Fuel Process. Technol.* **2014**, *123*, 41–46. [CrossRef]
69. Noel, H.M. Recovery of Vanadium. U.S. Patent 2,372,109, 20 March 1945.
70. Jack, T.R.; Sullivan, E.A.; Zajic, J.E. Leaching of vanadium and other metals from Athabasca Oil Sands coke and coke ash. *Fuel* **1979**, *58*, 589–594. [CrossRef]
71. Gardner, H.E. Recovery of Vanadium and Nickel from Petroleum Residues. U.S. Patent 4816236A, 28 March 1989.
72. Junior_Gold_Report. MGX Minerals Partners with Highbury Energy to Extract Nickel, Vanadium, and Cobalt from Petroleum Coke. Available online: <https://juniorgoldreport.com/mgx-minerals-partners-with-highbury-energy-to-extract-nickel-vanadium-and-cobalt-from-petroleum-coke/> (accessed on 20 January 2023).
73. Kikauka, A. *MGX Minerals and Highbury Energy Produce 45% Vanadium Concentrate from Petroleum Coke Ash*; MGX Minerals: Vancouver, BC, Canada, 2017.
74. Saeed, A.; Banoqitah, E.; Alaqab, A.; Alshahrie, A.; Saleh, A.; Alhawsawi, A.; Damoom, M.; Salah, N. Epoxy Flooring/Oil Fly Ash as a Multifunctional Composite with Enhanced Mechanical Performance for Neutron Shielding and Chemical-Resistance Applications. *ACS Omega* **2022**, *8*, 747–760. [CrossRef]
75. Kwon, W.-T.; Kim, D.-H.; Kim, Y.-P. Characterization of heavy oil fly ash generated from a power plant. *Adv. Technol. Mater. Mater. Process. J.* **2004**, *6*, 260–263.
76. Brunauer, S.; Emmett, P.H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319. [CrossRef]
77. Kamil, F.H.; Abood, W.M.; Mohammed, Y.; Khedair, Z. Heavy Oil Fly Ash as an Adsorbent for Methylene Blue Removal from Aqueous Solution. *Iraqi J. Ind. Res.* **2022**, *9*, 48–56. [CrossRef]
78. Dalhat, M.A.; Al-Abdul Wahhab, H.I. Sulfur extended heavy oil fly ash and cement waste asphalt mastic for roofing and waterproofing. *Mater. Struct.* **2015**, *48*, 205–216. [CrossRef]
79. Akita, S.; Maeda, T.; Takeuchi, H. Recovery of vanadium and nickel in fly ash from heavy oil. *J. Chem. Technol. Biotechnol. Int. Res. Process Environ. Clean Technol.* **1995**, *62*, 345–350. [CrossRef]
80. Vitolo, S.; Seggiani, M.; Filippi, S.; Brocchini, C. Recovery of vanadium from heavy oil and Orimulsion fly ashes. *Hydrometallurgy* **2000**, *57*, 141–149. [CrossRef]
81. Al-Ghouti, M.A.; Al-Degs, Y.S.; Ghair, A.; Khoury, H.; Ziedan, M. Extraction and separation of vanadium and nickel from fly ash produced in heavy fuel power plants. *Chem. Eng. J.* **2011**, *173*, 191–197. [CrossRef]
82. Volkov, A.; Kologrieva, U.; Stulov, P. Study of Forms of Compounds of Vanadium and Other Elements in Samples of Pyrometallurgical Enrichment of Ash from Burning Oil Combustion at Thermal Power Plants. *Materials* **2022**, *15*, 8596. [CrossRef]
83. Bakirova, S.; Kotova, A.; Yag'yaeva, S.; Fedorova, N.; Nadirov, N. Structural features of vanadyl porphyrins of petroleum of West Kazakhstan. *Pet. Chem. USSR* **1984**, *24*, 733–738. [CrossRef]
84. Linak, W.P.; Miller, C.A. Comparison of particle size distributions and elemental partitioning from the combustion of pulverized coal and residual fuel oil. *J. Air Waste Manag. Assoc.* **2000**, *50*, 1532–1544. [CrossRef]
85. Amer, A.M. Processing of Egyptian boiler-ash for extraction of vanadium and nickel. *Waste Manag.* **2002**, *22*, 515–520. [CrossRef]
86. Whigham, W. New in extraction: Vanadium from petroleum. *Chem. Eng.* **1965**, *72*, 64.

87. Park, K. Recovery of vanadium and nickel from heavy oil fly ash. In Proceedings of the 2nd International Symposium on East-Asian Resources Recycling Technology, Seoul, Republic of Korea, 30 June 1993; p. 211.
88. Tsuboi, I.; Kasai, S.; Kunugita, E.; Komasaawa, I. Recovery of Gallium and Vanadium from Coal Fly Ash. *J. Chem. Eng. Jpn.* **1991**, *24*, 15–20. [[CrossRef](#)]
89. Tsuboi, I.; Kasai, S.; Yamamoto, T.; Komasaawa, I.; Kunugita, E. Recovery of Rare Metals from Coal Fly Ash. In *Process Metallurgy*; Sekine, T., Ed.; Elsevier: Amsterdam, The Netherlands, 1992; Volume 7, pp. 1199–1204.
90. Chmielewski, A.G.; Urbański, T.S.; Migdał, W. Separation technologies for metals recovery from industrial wastes. *Hydrometallurgy* **1997**, *45*, 333–344. [[CrossRef](#)]
91. Edwards, C.R. The recovery of metal values from process residues. *JOM* **1991**, *43*, 32–33. [[CrossRef](#)]
92. Lakshmanan, V.I.; McQueen, N. Recovery of Vanadium from Suncor Flyash—Flowsheet Development. *Proc. Second. Int. Conf. Sep. Sci. Technol.* **1989**, *2*, 525–531.
93. Aydin, A. Recovery of vanadium compounds from the slags and fly ashes of power plants. *Chim. Acta Turc.* **1988**, *16*, 153–182.
94. Akaboshi, T.; Kaneko, N.; Sakuma, A.; Sugiyama, T. Recovery of ammonium metavanadate from petroleum-combustion residues. *Jpn. Kokai Tokkio Koho JP* **1987**, *62*, 298.
95. Tsygankova, M.V.; Bukin, V.I.; Lysakova, E.I.; Smirnova, A.G.; Reznik, A.M. The recovery of vanadium from ash obtained during the combustion of fuel oil at thermal power stations. *Russ. J. Non Ferr. Met.* **2011**, *52*, 19–23. [[CrossRef](#)]
96. Murase, K.; Nishikawa, K.-i.; Ozaki, T.; Machida, K.-i.; Adachi, G.-y.; Suda, T. Recovery of vanadium, nickel and magnesium from a fly ash of bitumen-in-water emulsion by chlorination and chemical transport. *J. Alloys Compd.* **1998**, *264*, 151–156. [[CrossRef](#)]
97. Tokuyama, H.; Nii, S.; Kawaizumi, F.; Takahashi, K. Process development for recovery of vanadium and nickel from heavy oil fly ash by leaching and ion exchange. *Sep. Sci. Technol.* **2003**, *38*, 1329–1344. [[CrossRef](#)]
98. Meer, I.; Nazir, R. Removal techniques for heavy metals from fly ash. *J. Mater. Cycles Waste Manag.* **2018**, *20*, 703–722. [[CrossRef](#)]
99. Rahimi, G.; Rastegar, S.; Chianeh, F.R.; Gu, T. Ultrasound-assisted leaching of vanadium from fly ash using lemon juice organic acids. *RSC Adv.* **2020**, *10*, 1685–1696. [[CrossRef](#)]
100. Liu, J. Recovery of Vanadium and Nickel from Oil Fly Ash. Ph.D. Thesis, Memorial University of Newfoundland, St. John's, NL, Canada, 2017.
101. Tsai, S.L.; Tsai, M.S. A study of the extraction of vanadium and nickel in oil-fired fly ash. *Resour. Conserv. Recycl.* **1998**, *22*, 163–176. [[CrossRef](#)]
102. Parvizi, R.; Khaki, J.V.; Moayed, M.H.; Ardani, M.R. Hydrometallurgical Extraction of Vanadium from Mechanically Milled Oil-Fired Fly Ash: Analytical Process Optimization by Using Taguchi Design Method. *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **2012**, *43*, 1269–1276. [[CrossRef](#)]
103. Navarro, R.; Guzman, J.; Saucedo, I.; Revilla, J.; Guibal, E. Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. *Waste Manag.* **2007**, *27*, 425–438. [[CrossRef](#)] [[PubMed](#)]
104. Gomez-Bueno, C.; Spink, D.; Rempel, G. Extraction of vanadium from Athabasca tar sands fly ash. *Metall. Trans. B* **1981**, *12*, 341–352. [[CrossRef](#)]
105. Holloway, P.C.; Etsell, T. Salt roasting of suncor oil sands fly ash. *Metall. Mater. Trans. B* **2004**, *35*, 1051–1058. [[CrossRef](#)]
106. Holloway, P.; Etsell, T. Process for the complete utilization of oil sands fly ash. *Can. Metall. Q.* **2006**, *45*, 25–32. [[CrossRef](#)]
107. Goncharov, K.; Kashekov, D.Y.; Sadykhov, G.; Olyunina, T. Processing of fuel oil ash from thermal power plant with extraction of vanadium and nickel. *Non Ferr. Metals* **2020**, *1*, 3–7. [[CrossRef](#)]
108. Vassileva, C.; Vassilev, S.; Daher, D. Preliminary results on chemical and phase-mineral composition of Syrian petroleum coke and ash. *Comptes Rendus L'acad. Bulg. Sci.* **2010**, *63*, 129–136.
109. Guillaud, P. Process for Treatment of Vanadium Containing Fly Ash. U.S. Patent 3873669A, 3 March 1975.
110. Kudinova, A.; Kondrasheva, N.; Rudko, V. Influence of leaching parameters on the vanadium extraction from petroleum coke. *E3S Web Conf.* **2021**, *266*, 08002. [[CrossRef](#)]
111. Rezaei, H.; Shafaei, S.Z.; Abdollahi, H.; Shahidi, A.; Ghassa, S. A sustainable method for germanium, vanadium and lithium extraction from coal fly ash: Sodium salts roasting and organic acids leaching. *Fuel* **2022**, *312*, 122844. [[CrossRef](#)]
112. Ziyadanoğullari, R.; Aydın, I. Recovery of uranium, nickel, molybdenum, and vanadium from floated asphaltite ash. *Sep. Sci. Technol.* **2004**, *39*, 3113–3125. [[CrossRef](#)]
113. Jia, L.; Anthony, E.J.; Charland, J.P. Investigation of vanadium compounds in ashes from a CFBC firing 100% petroleum coke. *Energy Fuels* **2002**, *16*, 397–403. [[CrossRef](#)]
114. Jung, M.; Mishra, B. Vanadium Recovery from Oil Fly Ash by Carbon Removal and Roast-Leach Process. *Jom* **2018**, *70*, 168–172. [[CrossRef](#)]
115. Kadhim, M.J.; Hafiz, M.H.; Abbas, R.A. Optimization for leaching kinetics of vanadium pentoxide from thermal power plants fly ash using Taguchi approach. *Dijlah J.* **2019**, *2*.
116. Etsell, T.H.; Griffin, P.J. Vanadium Recovery from Ash from Oil Sands. CA Patent 1221243A, 5 May 1987.
117. Kologrieva, U.; Volkov, A.; Zinoveev, D.; Krasnyanskaya, I.; Stulov, P.; Wainstein, D. Investigation of Vanadium-Containing Sludge Oxidation Roasting Process for Vanadium Extraction. *Metals* **2021**, *11*, 100. [[CrossRef](#)]
118. Queneau, P.B.; Hogsett, R.F.; Beckstead, L.W.; Barchers, D.E. Processing of petroleum coke for recovery of vanadium and nickel. *Hydrometallurgy* **1989**, *22*, 3–24. [[CrossRef](#)]
119. Abdel-latif, M.A. Recovery of vanadium and nickel from petroleum flyash. *Miner. Eng.* **2002**, *15*, 953–961. [[CrossRef](#)]

120. Xiao, Y.; Mambote, C.R.; Jalkanen, H.; Yang, Y.; Boom, R. Vanadium recovery as FeV from petroleum fly ash. In Proceedings of the Twelfth International Ferroalloys Congress Sustainable Future, Helsinki, Finland, 6–10 June 2010; pp. 6–9.
121. Howard, R.; Richards, S.; Welch, B.; Moore, J. Pyrometallurgical processing of vanadiferous slag using plasma/induction heating. *INFACON* **1992**, *1*, 225–231.
122. Sun, S.; Yang, K.; Liu, C.; Tu, G.; Xiao, F. Recovery of nickel and preparation of ferronickel alloy from spent petroleum catalyst via cooperative smelting-vitrification process with coal fly ash. *Environ. Technol.* **2021**, *42*, 1–11. [[CrossRef](#)]
123. Johnson, T.P. Recovery of Nickel and Vanadium from Heavy Oil Residues Using DC Plasma Smelting. In *Extraction 2018*; Springer: Berlin/Heidelberg, Germany, 2018; pp. 1017–1028.
124. Seddiek, H.A.; Shetaia, Y.M.; Mahamound, K.F.; El-Aassy, I.E.; Hussien, S.S. Bioleaching of Egyptian Fly Ash Using *Cladosporium cladosporioides*. *Ann. Biol.* **2021**, *37*, 18–22.
125. Li, J.Z.; Wang, X.Y.; Wang, B.; Zhao, J.T.; Fang, Y.T. Investigation on the fates of vanadium and nickel during co-gasification of petroleum coke with biomass. *Bioresour. Technol.* **2018**, *257*, 47–53. [[CrossRef](#)] [[PubMed](#)]
126. Rasoulnia, P.; Mousavi, S.M. V and Ni recovery from a vanadium-rich power plant residual ash using acid producing fungi: *Aspergillus niger* and *Penicillium simplicissimum*. *RSC Adv.* **2016**, *6*, 9139–9151. [[CrossRef](#)]
127. Mirazimi, S.M.J.; Abbasalipour, Z.; Rashchi, F. Vanadium removal from LD converter slag using bacteria and fungi. *J. Environ. Manag.* **2015**, *153*, 144–151. [[CrossRef](#)] [[PubMed](#)]
128. Krebs, W.; Bachofen, R.; Brandl, H. Growth stimulation of sulfur oxidizing bacteria for optimization of metal leaching efficiency of fly ash from municipal solid waste incineration. *Hydrometallurgy* **2001**, *59*, 283–290. [[CrossRef](#)]
129. Wu, H.Y.; Ting, Y.P. Metal extraction from municipal solid waste (MSW) incinerator fly ash—Chemical leaching and fungal bioleaching. *Enzym. Microb. Technol.* **2006**, *38*, 839–847. [[CrossRef](#)]
130. Yang, J.; Wang, Q.H.; Wang, Q.; Wu, T.J. Heavy metals extraction from municipal solid waste incineration fly ash using adapted metal tolerant *Aspergillus niger*. *Bioresour. Technol.* **2009**, *100*, 254–260. [[CrossRef](#)]
131. Rasoulnia, P.; Barthen, R.; Lakaniemi, A.M. A critical review of bioleaching of rare earth elements: The mechanisms and effect of process parameters. *Crit. Rev. Environ. Sci. Technol.* **2020**, *51*, 378–427. [[CrossRef](#)]
132. Mirazimi, S.M.J.; Rashchi, F.; Saba, M. A new approach for direct leaching of vanadium from LD converter slag. *Chem. Eng. Res. Des.* **2015**, *94*, 131–140. [[CrossRef](#)]
133. Lee, J.-C.; Kurniawan, Kim, E.-Y.; Chung, K.W.; Kim, R.; Jeon, H.-S. A review on the metallurgical recycling of vanadium from slags: Towards a sustainable vanadium production. *J. Mater. Res. Technol.* **2021**, *12*, 343–364. [[CrossRef](#)]
134. An, Y.; Ma, B.; Li, X.; Chen, Y.; Wang, C.; Wang, B.; Gao, M.; Feng, G. A review on the roasting-assisted leaching and recovery of V from vanadium slag. *Process Saf. Environ. Prot.* **2023**, *173*, 263–276. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.