A review of the valorization and management of industrial spent catalyst waste in the context of sustainable practice: The case of the State of Kuwait in parallel to European industry

Sultan Majed Al-Salem[1] [iD], Achilleas Constantinou[2,3], Gary Anthony Leeke[4], Sanaa Hafeez[2], Tayeba Safdar[2], Hajar Jawad Karam[1], Masumah Al-Qassimi[1], Ayyad Toman Al-Dhafeeri[5], George Manos[3] and Umberto Arena[6]

Abstract

Industrial solid waste management encompasses a vital part of developed and developing countries strategies alike. It manages waste generated from vital industries and governs the hazardous waste generated as a major component of integrated waste management strategies. This article reviews the practices that govern the management approaches utilized in the developed world for industrial spent catalysts. It critically assesses the current situation of waste management within the developing world region focusing on the industrial waste component, in a novel attempt to crucially develop a strategy for a way forward based on best practices and future directions with major European industries. The review also draws parallels with European countries to compare their practices with those of the State of Kuwait, which rely solely on landfilling for the management of its industrial waste. Spent catalysts recovery methods are discussed at length covering conventional methods of valuable metals and chemicals recovery (e.g., hydrometallurgical, solid–liquid and liquid–liquid extraction) as well as biological recovery methods. A major gap exists within regulations that govern the practice of managing industrial waste in Kuwait, where it is essential to start regulating industries that generate spent catalysts in-view of encouraging the establishment of valorization industries for metal and chemical recovery. This will also create a sustainable practice within state borders, and can reduce the environmental impact of landfilling such waste in Kuwait.

Keywords

Spent catalysts, industrial waste, hydrometallurgical treatment, extraction, waste management

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Introduction

Solid waste management (SWM) has become the centre of attention within research and academic circles in recent years due to its paramount importance from environmental, social and economic points of view. SWM covers the concept of waste reduction and reuse as well as the processes and technologies of recycling, valorization/recovery, aerobic or anaerobic treatment, thermal treatment with or without energy recovery, fuel production and landfilling. Typically, solid waste (SW) is classified as municipal solid waste (MSW), industrial solid waste (ISW), agriculture waste or commercial waste. In general, MSW refers to the mixture of residential and commercial refuse such as garden and food waste, paper, textiles and plastics film/rigid products. On the other hand, ISW refers to the waste generated by the industrial, and on a lesser extent, the institutional sector (Dixon and Jones, 2005; Prabakar al., 2018). The inclusion of various ISW components is a subjective matter, where construction and demolition solid waste, chemicals from the medical and pharmaceutical industry and wastewater are not always included in assessment reports. The ISW contains valuable metals that could be valorized to boost economic returns of countries and societies, as well as, reduce its associated environmental burdens that stem out of mismanaged ISW components.

[1]Environment and Life Sciences Research Centre, Kuwait Institute for Scientific Research, Safat, Kuwait
[2]Division of Chemical and Petroleum Engineering, School of Engineering, London South Bank University, London, UK
[3]Department of Chemical Engineering, University College London, London, UK
[4]School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham, UK
[5]Water Research Centre, Kuwait Institute for Scientific Research, Safat, Kuwait
[6]Department of Environmental, Biological Pharmaceutical Sciences and Technologies – University of Campania "Luigi Vanvitelli", Caserta, Italy

Corresponding author:
Sultan Majed Al-Salem, Environment and Life Sciences Research Centre, Kuwait Institute for Scientific Research, PO Box: 24885, Safat, 13109, Kuwait.
Email: ssalem@kisr.edu.kw

Table 1. Industrial waste classification.

Products	Hazardous wastes
Medicine	Organic solvents and residues, heavy metals (mercury and zinc)
Metals	Heavy metals, fluorides, cyanides, acids, alkaline clearness and pigments
Paints	Heavy metals, pigments, solvents and organic residue
Leather	Heavy metals and organic solvents
Oil/gas	Oil, phenols, organic compounds and heavy metals
Pesticides	Organic chlorine compounds and organic phosphate compounds
Plastics	Organic chlorine compounds, fire retardants, bromine compounds and fluorine
Textiles	Heavy metals, dyes, organic chlorine compounds and solvents

Sources: Biology Discussion Forum (2018); Hahladakis and Iacovidou (2018).

Typically, ISW originates from chemical plants, paint industries, cement factories, thermal power plants, metallurgical plants, the pharmaceutical industry, textile industries, food processing and the petroleum industry. ISW can be divided into two main categories which are hazardous and non-hazardous waste (HW). The latter is produced from food processing plants, cotton mills, paper mills and textile industries. On the other hand, HW is the waste portion produced from industries other than the aforementioned. Common examples of HW are metals, chemical, drugs, lather, electroplating and rubbers. Table 1 shows a classification of ISW with respect to type and source (Biology Discussion Forum, 2018).

The State of Kuwait (29°30'N latitude and 47°45' E longitude) is an oil-dependent state within the Gulf Council Countries (GCC) region of West Asia. The country is inhabited by 4.1 million residents of both nationals and expatriates within a total area of 17,818 km^2. It has been reported to be the highest per capita generator of MSW with conflicted reports showing a per capita generation range between 1.55 to 5.74 kg per day according to recent estimates (Hoornweg and Bhada-Tata, 2012; Kaza et al., 2018). Kuwait has also been reported to be the second most toxic country in the world (Whittaker-Wood, 2018). The current infrastructure does not support waste management (WM) activities in an integrated manner and governmental parties at the moment are defining criteria to develop sustainable and up-to-date plans to do so (Kaza et al., 2018). The sole method of SW disposal in the country is unsanitary landfilling in open dumps (Al-Salem, 2009). Kuwait is divided into six governorates that host major industries, mainly revolving around chemicals and petrochemicals conversion processes. The focus of the State of Kuwait has shifted in recent years towards MSW and ISW management due to the nature of the country's industrial activities and social behaviour. The country has also embarked on various mega-scale industrial projects including the new refinery project (NRP) which is designed to process over 600 MMbpd of crude oil (Al-Salem, 2015). The NRP has been announced to be one of the largest in the world that will host catalytic upgrading units, including fluidized catalytic cracking (FCC) and atmospheric residue desulphurization (ARDS) units using up-flow reactor technology (Richmond, 2010). Such industrial ventures will necessarily result in the accumulation of more ISW, namely industrial grade catalysts. A similar situation can be observed across Europe. Countries such as France, Germany and Sweden are leaders in their respective industries, thus they generate a substantial amount of waste. The majority of Europe's waste is generated from the following industrial sectors, which all make the management of ISW more critical: agriculture; mining and quarrying; plastics and rubbers; manufacturing; energy production; water distribution and treatment; and construction. Typically, MSW constitutes 15% of the total SW generated across European countries, whilst ISW represents some 40% of the total waste load (Jordan and Heidorn, 2003). On an average per capita assessment by recent published estimates of the World Bank (Kaza et al., 2018), ISW is generated in high income countries (e.g., Kuwait) by 42.62 kg per day. Comparatively, MSW and electronic waste are produced (on average) at a rate of 0.81 and 0.05 kg per capita per day, respectively. These estimates also represent some 950 kg of ISW for every 1000 Euros of added value.

The industry in Kuwait mostly falls under oil and gas activities. Currently, Kuwait processes about 1000 M bpd of crude oil within its country limits representing a feedstock for the light derivatives and petrochemical industries. It also exports over 3.1 MM bpd of crude oil as it is one of the oldest members of the Organization of the Petroleum Exporting Countries. Al-Muzaini (1998) stated that there were twelve industries located in Shuaiba Industrial Area, which is the largest industrial area in the Arabian Gulf hosted on the western coastal line of Kuwait. The total production of industrial wastewater alone is 23,000 m^3 d^{-1}, which carry heavy metals, organic chemicals and suspended solids and mostly end up in the Arabian Gulf. Different technologies of treating such waste are based on physical, chemical and biological aspects (Syed, 2006). Industrial activities have grown considerably in Kuwait within the past decade. Alhumoud and Al-Kandari (2008) showed in their work that a drastic increase of industrial waste (IW) was noted in Kuwait between the years 2000 (12,660 metric tonnes) and 2005 (47,169 metric tonnes). Figures 1 and 2 show approximately the percentages of factories by type and the percentage of hazardous ISW, respectively. In WM, one of the main classifications is identifying the waste regarding to its harshness to fall either under the hazardous or non-hazardous categories. On an annual basis, HW formulates 18.86% of the total production of IW generated in Kuwait (≈ 8,895 metric tonnes), including heavy oil sludge, asbestos and
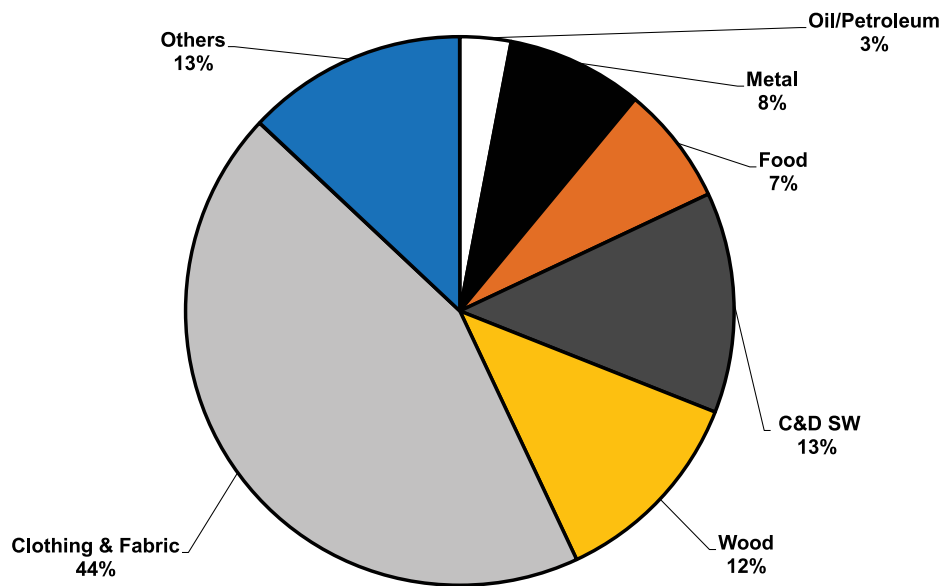
Figure 1. Approximate percentages of factories by type of activity in the State of Kuwait. Adapted from Alhummod and Al-Kandari (2008).
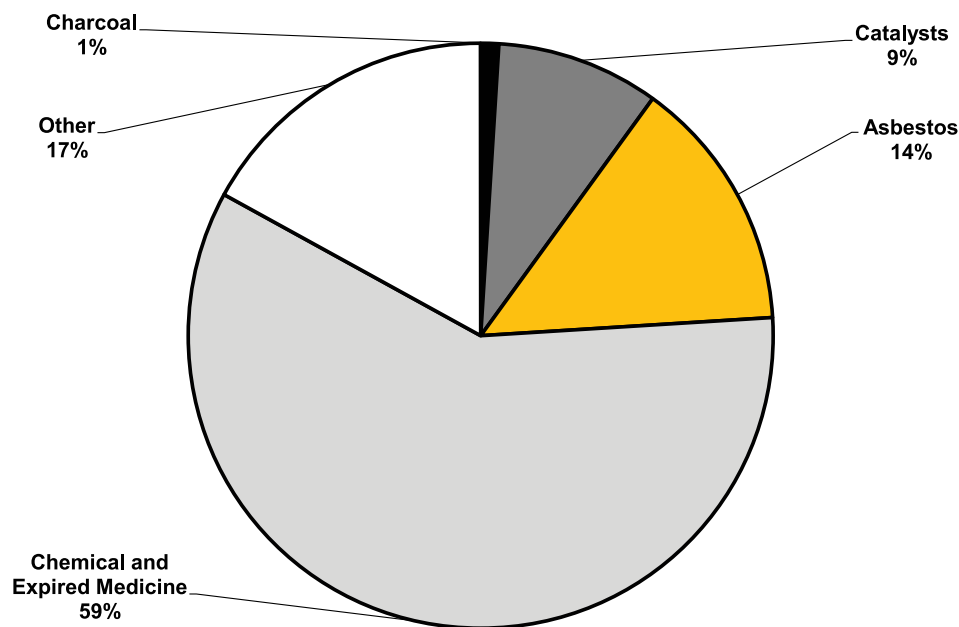C&D SW: construction and demolition solid waste.

Figure 2. Approximate percentages of industrial solid waste in the State of Kuwait. Adapted from Alhummod and Al-Kandari (2008).

expired chemicals (Alhumoud and Al-Kandari, 2008; Al-Qallaf et al., 2016).

Petroleum refining is considered to be the most significant pillar of the economy, due to Kuwait's oil-based and gas-based industry. Despite the strength of the financial return, oil and gas industries may cause various environmental problems. Petroleum waste contains high concentrations of heavy and toxic metals (Obiajunwa et al., 2002). To manage the potential side effects of petroleum waste, Mansour et al. (2016) examined petroleum-based waste such as sludge and sand. Over 17 elements including metals were recorded in their findings. The samples were derived

from petroleum companies' waste in Kuwait. The results reflect six samples that were dried for one day under 110°C. The volume of elements was detected through the technique of X-ray fluorescence. The level of iron (Fe) was very high in both sludge and sand samples in addition to manganese (Mn) and calcium (Ca). Manganese was noted to be consistent with previous studies (0.25%–0.28%), whereas Ca is higher (0.9%–1.02%) (Table 2). A study published in Kuwait (Alshammari et al., 2008) declared that all industrial oil and gas plants plan to dispose of some 240 ktpa of IW, in order to achieve an integrated WM strategy in the refining industry. To deal with this waste, they classified HW as

incinerable and non-incinerable. Catalysts are one of non-incinerable HW, which contain various metals (e.g., platinum, cobalt, copper, molybdenum, iron, zinc, nickel, and aluminium). Typical catalysts composition is presented below for the three main operating refineries within state borders of Kuwait, namely Mina Al-Ahmadi, Mina Abdullah and Shuibah refineries (Table 3).

According to the official European Statistics published by EUROSTAT, the European Union (EU) generated a total of 58 million metric tonnes of HW back in 2002 which includes HW from all economic sectors encompassing hazardous municipal waste (European Commission, 2005). This estimate increased to 100 million metric tonnes in 2016 comprising 4% of the total generated waste across the 28 EU Member states (Euro Statistics, 2019). The UK alone generates 335 million metric tonnes of waste per year (mtpa) of which 225 million metric tonnes are MSW (Lupa et al., 2011). Due to the environmental impact of waste accumulation, recycling has gained increasing interest across the EU in recent years (Beigl et al., 2004; Pires et al., 2011).

Even though the EU industry is different to that of Kuwait, heavy metal waste is still generated from different industries in the UK and Europe. Mercury (Hg) arising from the industrial sector, lead (Pb) mainly from road transport, cadmium (Cd) due to abatement technologies, and chromium (Cr) are some of the most commonly generated heavy metals that pose numerous environmental and health risks. One of the major contributors of such toxins is the waste generated from the construction industry, as well as mining and extraction (European Commision, 2002). Due to recent awareness of the negative effects of these metals, governments are devising models and implementing plans to lower the amount of heavy metal waste. For example, Pb associated waste has been reduced by 93% in the last 26 years across Europe. This was achieved by phasing out leaded petroleum which currently accounts for one-third of total waste emissions around the world (European Environmental Agency, 2017). Despite the awareness of and overall decrease in heavy metal emissions, in the last few decades, there is still a dire need for SWM, further reducing emissions and developing metal recovery methods. Regression models' results, baseline studies and the development of integrated frameworks to reduce waste accumulation, have also been adopted recently in Kuwait taking into consideration EU strategies (Al-Salem et al., 2018a). In addition, strategies to mitigate plastic solid waste (PSW) and the development of standards to govern the use of polymeric products, are also considered two main highlights of Kuwait's recent WM strategies development by governing bodies (Al-Salem et al., 2018b). Taking into consideration the aforementioned, this review showcases the major ISW management activities and potential of valorization within the State of Kuwait with an emphasis on spent catalysts as a waste component. The work also draws parallels with the EU in reviewing ISW activities and major valorization techniques that can relate to the case of Kuwait, especially in the petroleum industry (e.g., spent catalysts). It critically assesses the current situation of WM within the developing world region focusing on the IW component, in a novel attempt to crucially develop a strategy for the way forward based on best practices and future directions within major European industries. The work in this review can pave the way for the governmental parties, in both Kuwait and other industrial countries, in targeting the main SW components that can reduce environmental burdens in industry. An examination of the main

Table 2. Percentile (wt.%) of elements found in Kuwait petroleum waste.

Element	Kuwait	
	Sludge	Sand
Si	1.07	45.7
P	6.7	No data (nd)
S	10.58	13.12
K	26.15	6.4
Ca	15.83	20.36
Mn	0.28	0.12
Fe	38.07	7.53
Zn	nd	nd
As	nd	nd
Br	0.57	nd
Sr	0.61	0.24
Rh	nd	0.04
Ba	nd	nd
Ho	nd	nd

Source: Mansour et al. (2016).

Table 3. Characteristics of industrial spent catalysts exposed to thermal, chemical, and physical treatment.

Source	Chemical constituents	Maximum quantity (tpa)
Shuibah refinery	Co, Ni, Mo, Fe, Cr, Zn, Al	1900
Petrochemical Industries Co. fertilizer plant	Co, Mo, ZnO, NiO, Fe_2O_3, CuO, FeO	205
Mina Abdullah refinery	Co, Mo, NiO, Al_2O_3, ZnO, CoO, MoO, Fe_2O_3, Cr_2O_3, CuO, SiO, CaO, FeO, Ni, W	2500
Mina Al-Ahmadi refinery	Co, CoO, Mo, MoO, Ni, NiO, FeO, Fe, ZnO, Zn, Al_2O_3, Fe_2O_3, Cr_2O_3, CuO, SiO, CaO, V	6185
Total		10,790

Source: Alshammari et al. (2008).

Table 4. Properties of petroleum spent catalyst waste.

Main reported property	Mina Al Fahal refinery	Sohar refinery
Physical state	Solid	Solid
Colour	White to off-white	Grey
Shape	Spheres or granules	Crystalline powder
Odour	Acidic smell and reacts very vigorously in water	Odourless
Solubility	Insoluble in water, oil and solvents	Insoluble in water, oil and solvents
Liquid limit (%)	51.9	72.8
Bulk specific gravity	2.79	2.60
Sand equivalent (%)	92.6	Not applicable (NA)
Los Angeles abrasion test (%)	72.4	NA
Absorption (%)	31.2	NA
Surface area ($cm^2\ g^{-1}$)	3235	900

Source: Taha et al. (2011).

recovery techniques utilized in spent catalysts is also reported in this work.

Spent catalysts in the context of IW management and operational challenges

Spent catalysts are non-active, used and/or regenerated catalysts (containing metals/metal oxides) that are discarded as ISW. Approximately 4% of them are petroleum refinery waste regarded largely as a HW component. The amount of spent catalyst waste is in direct correlation with the amount of fresh catalysts used and the regeneration cycles of unit operations. The spent waste can be managed via chemical/microbial treatment, regeneration and reuse or landfilling (Akcil et al., 2015). The petroleum industry is responsible for the generation, accumulation and disposal of spent catalysts. There are three main contributing sectors to spent catalyst waste: hydroprocessing (hydrotreating and hydrocracking); FCC; and reforming catalysts along with any desulphurizing processes. Hydroprocessing is the name given to processes that are used to refine and treat fuels. In particular, hydrotreating is used to eliminate hetero atoms and saturated carbon–carbon bonds through removing sulphur, nitrogen, oxygen and other metals. On the other hand, hydrocracking is used to form smaller molecules by breaking carbon–carbon bonds as well as increasing the fuel yield. To carry out these processes, hydroprocessing catalysts are utilized. In recent years, there has been a substantial increase in spent catalysts, with an annual expected rise of 4.4% in hydrotreatment catalysts. The following factors are responsible for this increase: higher demands of low-sulphur fuel (via distillates hydrotreating capacity); reduction of catalyst cycles to overcome operational challenges in diesel hydrotreating units; and processing of more viscous feedstock and unavailability of catalyst reactivation processes (Marafie and Stanislaus, 2008).

The hydrodesulphurization (HDS) method is used to remove sulphur from different kinds of organic materials. The catalysts utilized usually are a combination of bimetallic of Ni/Co on an aluminium oxide support. Fly ash is a residue of coal from thermal power plants, accounting for up to a maximum of 20% of the

Table 5. Composition of petroleum spent catalyst waste.

Chemical compound	Composition (%)	
	Mina Al Fahal refinery	Sohar refinery
SiO_2	1.71	39.21
Al_2O_3	66.66	37.68
Fe_2O_3	0.07	0.66
CaO	0.08	0.05
MgO	0.02	0.26
Na_2O	8.29	0.43
K_2O	0.26	0.06
Loss on ignition value	26.13	2.43

Source: Taha et al. (2011).

original coal feed, containing catalysts as well. Approximately 750 million metric tonnes of fly ash are generated each year and almost all of it is disposed of into landfill. HDS and fly ash disposal further contribute to the spent catalyst disposal challenge, as well as causing further strain on the environment (Akcil et al., 2015). To overcome this, many refineries are looking into recycling fly ash into the cement industry by potentially using it as a raw feedstock material.

The FCC units, used to optimize the yield of petroleum (with high octane number) from crude oil, are another major source of spent catalysts. FCC is used to convert distillates into petroleum range hydrocarbons (HCs) (Gianetto et al., 1994). FCC catalysts are usually made from active silica dioxide (SiO_2) and aluminium oxide (Al_2O_3). The leading Oman refineries (e.g., Sohar and Mina Al-Fhal refineries) which are located in the same region as Kuwait (i.e., GCC), produce approximately 20 metric tonnes per day of FCC catalysts' waste and an average of 250 kg of spent alumina waste. The majority of which is disposed of onsite or at various disposal sites leading to environmental issues (Taha et al., 2011). Tables 4 and 5 show the generic properties and composition of spent catalyst waste produced from Oman refineries (Al-Jabri et al., 2013). FCC spent catalyst metal composition can vary across the world. Metals such as vanadium (V) and nickel (Ni) are also commonly present amongst the ones listed in Table 4.

A typical FCC catalyst is a mixture of an inert matrix of kaolin, alumina and silica. Different kinds of zeolites are also applied such as types X, Y and ZSM-5. Approximately 750 ktpa of spent catalyst waste is generated worldwide through FCC processing (Kasliwal et al., 2015). In extension to this, FCC catalysts have recently been utilized for cement production and as a cement additive (for aluminate calcium cement). These catalysts contain additional cobalt metals. In India, FCC spent catalysts are also known for being used as a refractory for furniture manufactured from a clay-based kiln. The particle size ranges from 60 to 100 μm (Ramezani et al., 2017). The generation and untreated disposal of such fine particles causes major environmental concerns due to wide and uncontrolled dispersion of harmful metals present in the catalysts. Recently, Su et al. (2019) showed that spent FCC displays advanced desulphurization properties. The seriousness of spent catalyst waste disposal has brought forth a new research potential for spent catalysts disposal along with recovery and reuse of metals. Amongst which molybdenum has gained substantial attention to be recovered from hydrogenation plant wastes. This transition metal is widely applied in the desulphurization of petrochemicals and coal-based liquids/fuels (Kar et al., 2004). Due to the toxicity of catalysts, the United States Environmental Protection Agency has classified all these metals and catalysts as HW (Marafi and Rana, 2016). Metals such as V, Ni, Mo and Co get leached by water and pollute the environment as well as generating harmful toxic gases such as hydrogen cyanide (Marafi and Stanislaus, 2008). The hydrotreating of spent catalysts can have a life cycle between three to four years and FCC catalysts get lost in the atmosphere daily and are offloaded daily/fortnightly (dependent upon the use and requirement) (Chiranjeevi et al., 2016). The increased exposure, toxicity and disposal has developed numerous spent catalysts recovery methods, which are discussed in the following sections.

Recovery methods used in IW managementM

Hydrometallurgical and liquid–liquid extraction process

The hydrometallurgical process is defined as the recovery of metals in the post-chemical leaching in aqueous solutions aimed at recovering metals from ISW (Al-Qassimi et al., 2018; Kentish and Stevens, 2001). Hydrometallurgical pre-treatment is typically applied to recover metals such as iron, steel, copper and aluminium from electric and electronic waste (Tuncuk et al., 2012). The procedure follows three consecutive stages starting with leaching followed by purification of solution and concentrate of metals; and finally the process of recovering (electrolysis) recuperates the desired metals (Brandl et al., 2001; Cerruti et al., 1998; Xu et al., 2007). This method has low environmental impact, capital and high metal recoveries, as well as having the ability to be applied for small-scale projects which makes it versatile and efficient.

Molybdenum (Mo) and platinum (Pt) are commonly used as catalysts with other base metals, rooted (entrenched) upon catalysts pores supported on various materials such as aluminium oxide (Al_2O_3). Vanadium (V) and Mo are valuable metals that can be recovered from different processes such as desulphurization catalyst, oil sands, slags, ashes and lean ores. Extensive research was conducted in recovering V and Mo from waste catalysts from heavy oil desulphurization in Japan, Germany and the USA. The common catalyst used in this process is MoO_3 promoted with CoO on a Υ-Al_2O_3 base. It is reported that the experimental procedure follows four main steps: pretreatment of waste catalyst (washing with ligroin and drying); sodium chloride–water vapour roasting of the calcined catalyst; leaching of the roasted catalyst; and liquid–liquid extraction, stripping and precipitation (Biswas, 1985). To convert the metal values selectively (V and Mo) into the water-soluble form in the second step, NaCl–H_2O vapour is used to roast the catalyst (calcined at 630°C). Since the thermal hydrolysis of NaCl is much faster above its melting point (i.e., 800°C), experiments are conducted above this temperature. The roasting reaction is measured by the absorption of HCl gas in NaOH solution at pH 10.5 and correcting the pH by adding 1 M NaOH solution. Dried NaCl (400°C) is weighed and ground in a mortar to 152 μm then placed in the furnace. The temperature of the furnace is maintained within ±10°C. When the desired temperature is reached ($\approx$ 630°C), the saturated gas with water vapour is passed through the furnace (Biswas, 1985).

Metal recovery using solvent and liquid–soil extraction

LIX 84-I (2-hydroxy-5-nonylacetophenone oxime) is a chelating organic extract. Solvent extraction with LIX 84-I dissolved in kerosene at an O:A phase ratio of 1 to 1, is a technique applied to catalyst leachate solutions containing up to 10 g L^{-1} Mo, 27 g L^{-1} Al and 2 g L^{-1} Ni to extract Mo(VI) (Park et al., 2010). The procedure is carried out to extract Mo(VI) from leached liquor with an initial pH range of 0.5–3.0. The leaching solution is typically performed after baking the spent catalyst then leaching it with sulphuric acid (H_2SO_4). By using a separating funnel for 5 minutes to equilibrate both aqueous and organic solutions in equal volume, the trace content of the organic component present in the solution is separated and pH is measured for raffinates. Afterwards, the raffinate is diluted to reach a suitable concentration with 1% HNO_3 where the organic sample is stripped with 1 M NH_4OH (Park et al., 2010). The work aforementioned covered the effect of different variables on the process such as pH, concentration of LIX 84-I, different stripping reagents, phase ratio and diluents. The extraction of Mo(VI) increased with a decrease in equilibrium pH and increased with an increase in LIX 84-I concentration.

A different technique to recover V, Mo and Ni from waste catalyst produced from heavy gasoil hydrodesulphurization is by using caustic soda solution (Rojas-Rodríguez et al., 2012). Spent catalyst with a particle size between 1.5 and 7.3 mm is calcinated at temperatures up to 450°C. The reactions lead to the removal of the sulphur, carbon, and the oxidation of vanadium sulphide. V and Mo are precipitated as vanadium pentoxide and molybdenum
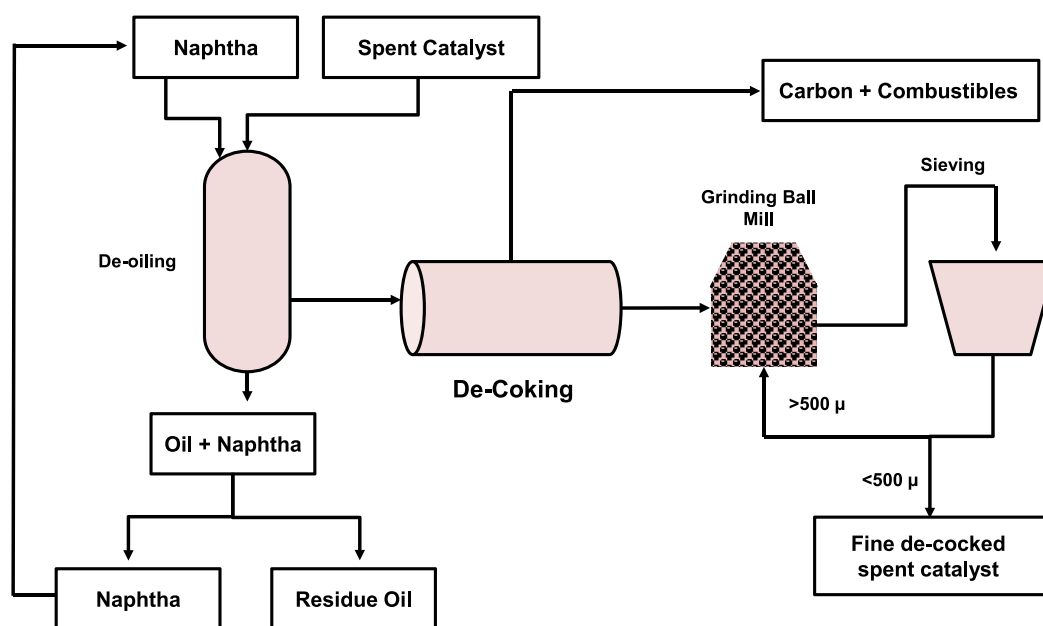
Figure 3. Pretreatment stages applied for spent catalyst. Adapted from Marafi and Rana (2016).

trioxide, respectively. Nickel aluminate is obtained from the residue after the removal of vanadium and molybdenum. The recovery achieved is up to 95.1% and 95.5% for the V and Mo, respectively.

Solid–liquid extraction is also used to recover valuable metals from spent catalysts. The procedure published previously by Rojas-Rodríguez et al. (2012) shows that a temperature between 20°C and 100°C is typically employed in the hydrometallurgical extraction process, which uses citric acid for leaching purposes. Firstly, the catalyst is exposed to citric acid after washing with distilled water for 30 minutes at 64°C . Spent catalyst is also autoclaved and rewashed with de-ionized water. Al, Ni, and Mo recovery are achieved during this process with temperatures around 80°C. The importance of spent catalysts is notable in several ways in catalyst preparation or for use in the metal industries. Marafi and Rana (2016) showed that catalyst derived from ARDS can be treated in five stages: de-oiling; drying; grinding; sieving; and de-coking. In fact, the spent catalyst is a mixture obtained from four reactors in fixed portions suitable for metal recovery (Marafi et al., 2007; Sheeha et al., 2013). When spent catalyst reaches the de-coking process, the catalyst is combusted (with oxygen) for 8 hours under a temperature range 300°C–600°C. Figure 3 shows the five stages of pretreatment of spent catalyst typically used in ARDS processes.

Soda roasting and metal leaching

Soda roasting is used to extract high yields of V and Mo. High pressure is applied to recover Ni(CO) as a solid using NaOH. Mo and V are recovered in high percentages reaching 95% when a roasting temperature of 550°C is applied (Marafi and Stanislaus, 2011). In this process, leaching reagents which are basic in nature, such as ammonium salts, are typically used. Ammonium per-sulphate (APS) is an example of high efficiency leaching

agents, due to its ability to oxidize and increase Ni and Al extraction percentages. APS is formed of 7 wt% of active oxygen which release free radicals that promote metal recovery especially for V, Ni, and Al; however, the acidic nature minimizes the ability of extracting Mo. Valuable metals (e.g., Co, Cr, Cu, Ni, Mo, Ti, V, and W) form the majority of catalysts used in industrial sectors with an estimate of 35 wt.%. A study performed by Gaballah et al. (1994) investigated the degree of metal recovery by monitoring selective chlorination over a wide range of temperatures (300°C–600°C). Mixtures of chlorinated gas were able to recover 98% of Ni and Co from chloronated deposits, 98%% of Mo, Ti, and W and 80% of vanadium compounds. Thermal cracking between 20°C and 1000°C was applied on hydrodesulphurization spent catalysts followed by the process of cholorination (Gaballah and Kanari, 1990). The volatiles were condensed through two condensers at different temperatures as shown in Figure 4.

A note on the spent catalysts generated through thermal cracking and SW upgrading

Both ISW and MSW have been researched extensively over the past few decades, namely in fuel and energy recovery processes. These processes will typically utilize various types of catalysts for upgrading products and distillates such as HZSM-5 and PZSM-5 (Demirbaş, 2005). These processes also revolve around the concept of oils and HC cracking to achieve the desired products acceptable to the marketplace and standards (Al-Salem, 2019; Chandrasekaran and Sharma, 2019a; Vasile et al., 2001). Further upgrading for the generated products can also be achieved with catalytic reforming in the petroleum downstream industry (Hafeez et al., 2019; Muhammad et al., 2015; Sharma and Bansal, 2016; Sharma et al., 2014; Sharuddin et al., 2016). All of which combined can lead to the accumulation of spent catalysts that is
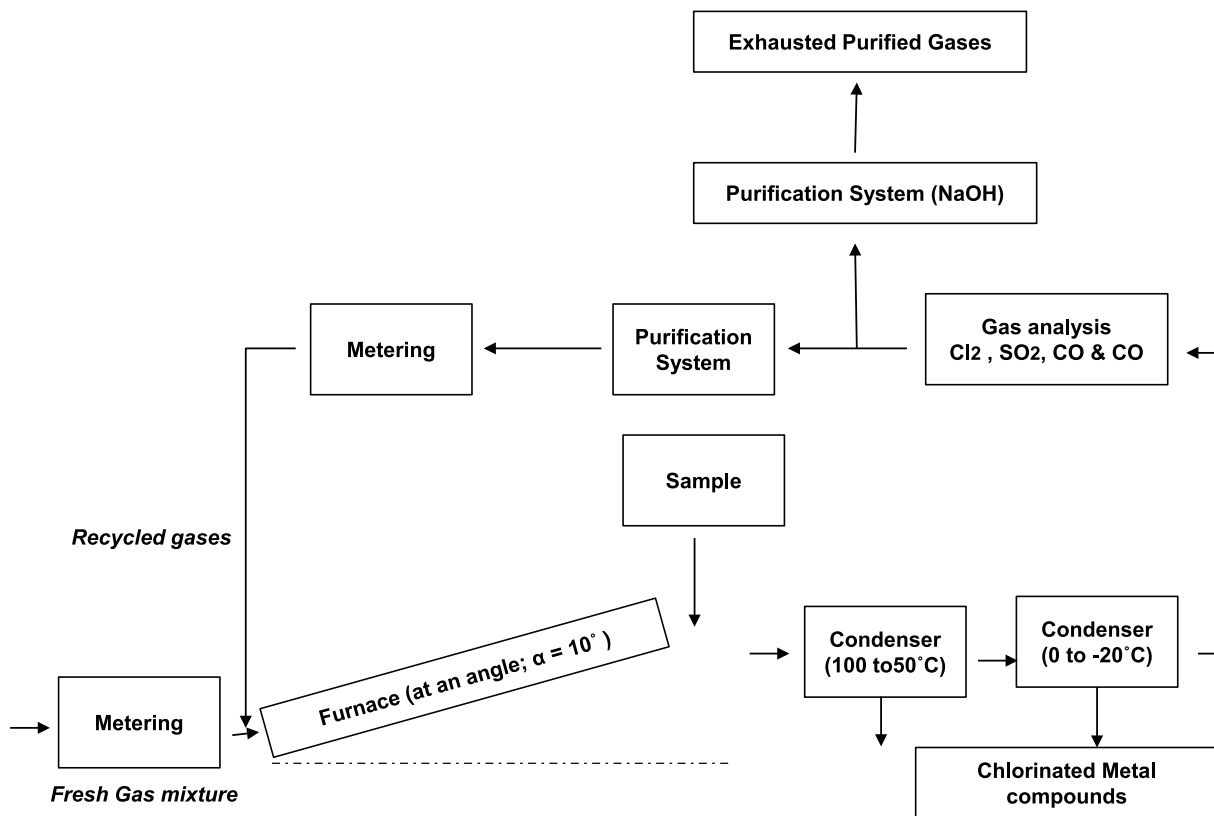
Figure 4. Selective chlorination for the recovery of metals. Adapted from Gaballah et al. (1994).

not typically accounted for in integrated solid waste management (ISWM) surveys, strategy development and studies. It is essential to understand the possible routes of spent catalysts accumulation as an ISW component within such upgrading technologies. This will enable the determination of the best course of action for future developmental plans in IW mitigation and management strategies. The types of catalysts used in such processes will be the focus of this section where the aforementioned recovery techniques in the previous two sections can be successfully applied to extract valuable metals and products.

A prominent example of ISW upgrading and management in petroleum downstream industries is the process of pyrolysis. This is directed (mainly) towards producing valuable oils and tars that are free of metals (Muhammad et al., 2015). Pyrolysis subjects a feedstock to inert gas deterioration at elevated temperatures typically between 500°C to 800°C. Once catalytic pyrolysis is considered, some 300°C to 400°C reduction in the operating temperature is achieved whilst obtaining cleaner distillates and products (Xue et al., 2015). Pyrolysis has also been applied in the past as a replacement to direct combustion for IW oil treatment (Demirbaş, 2005).

In an effort to study the possibility of integrating cracking technologies with the petroleum downstream industry, Chandrasekaran and Sharma (2019b) have detailed a plan to consider pyrolytic units treating PSW as a feedstock for fuel production whilst integrated to existing industrial infrastructure. Butler et al. (2011) have also proposed to integrate both thermal and catalytic pyrolysis in petroleum downstream industries to

upgrade and produce petroleum and diesel; while utilizing a feedstock from PSW. Catalysts that are usually used in such processes are zeolite-based ones. Bargi and Williams (2002) showed the effect of using Y-zeolite on the pyrolysis of polyethylene in a two-stage fixed bed reactor system. The evolved gases and oil generated consisted mainly of aliphatic compounds. Lin et al. (2012) used a hybrid FCC series catalyst to pyrolyse a mixed PSW feedstock under an operating temperature between 330°C and 450°C. Oil produced was estimated to be 87 wt.% of the total product yield. Table 6 also depicts major studies conducted in recent years using catalytic pyrolysis to upgrade SW. On the other hand, gasification technology where sub-oxygen content of carrier gas is applied in the degrading media, has also been used with aid of catalysts to upgrade various feedstock. Readers are referred to Wu and Williams (2010), Arena (2012) and Al-Salem et al. (2017) for additional content on both pyrolysis and gasification of various organic substances.
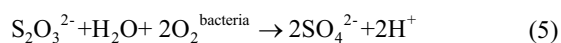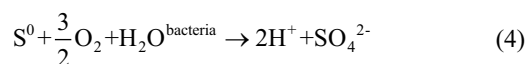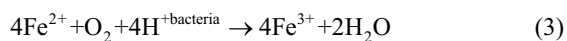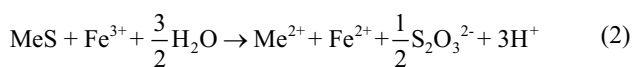
Biotechnological processes

Biotechnological processes require longer leaching times to gain efficient extraction when compared to other conventional methods. They are typically directed at winning processes for copper (Cu) recovery. On the other hand, bioleaching methods are more cost-effective and environmentally friendly than other conventional recovery techniques. They have been investigated on a small scale for exhaust catalysts to study their potential as a recovery process. The following reactions show a simplified

Table 6. A review of main thermo-chemical conversion conducted in recent years using catalytic processes.

Operation in pyrolysis mode

Reference	Feedstock/catalyst used	Operating conditions	Notes
Cardona and Corma (2000)	Catalytic cracking of polypropylene (PP) using zeolites, amorphous/silica–aluminas and a spent equilibrium fluidized catalytic cracking (FCC) commercial catalyst	250°C to 400°C in a stirred bed reactor	Spent catalysts were used
Zhang et al. (2009)	Biomass conversion was achieved using recovered FCC spent catalyst	Operating temperature at around 400°C	Fluidization media used was sand with different catalyst percentages.
Seo et al. (2003)	High density polyethylene using powder and pellets catalysts of mordenite, zeolite-Y and ZSM-5	Catalytic degradation yielded more light hydrocarbons (C6–C12) than thermal degradation	
Sarker et al. (2011)	Waste polyethylene terephthalate using Ca(OH)2 catalyst	405°C in a distillation unit	
Ali et al. (2002)	HDPE pyrolysis using HZSM-5, USY and an equilibrated FCC catalyst	Fluidized bed reactor used at 450°C	Petroleum was main product obtained
Mertinkat et al. (1999)	Polyethylene on an FCC catalyst at 515°C in a fluidized bed reactor		Yield of waxes was below 1%
Donaj et al. (2012)	Ziegler–Natta catalyst (TiCl4/MgCl2) in the pyrolysis of a mixture of polyolefins at 650°C		Increase in gas produced with catalyst employed
Gasification process			
He et al. (2009)	Catalytic steam gasification of municipal solid waste (MSW) with calcined dolomite catalyst	Bench-scale fixed bed reactor temperature range of 750–950°C with a steam to MSW ratio of 0.77	
Ro et al. (2007)	Review of wet waste including manure as a feedstock to gasification technologies recommending the use of spent catalysts to reduce cost		
Nanda et al. (2019)	Waste cooking oil was gasified in supercritical water over Ru/Al2O3		Glycerol and propionic acid were obtained

mechanism for metal sulphide recovery from exhaust catalyst in a solid matrix form. Equation (1) represents direct *bio-oxidation* of metal sulphides onto the matrix. Equation (2) shows the chemical oxidation by iron which is generated by bio-oxidation in Equation (3). Equations (4) and (5) show the formation of sulphide ion through bio-oxidation of sulphur and thiosulphate, respectively, for a complete reaction case.

$$MeS + \frac{1}{2}O_2 + 2H^{+\text{bacteria}} \rightarrow Me^{2+} + S^0 + H_2O \quad (1)$$

$$MeS + Fe^{3+} + \frac{3}{2}H_2O \rightarrow Me^{2+} + Fe^{2+} + \frac{1}{2}S_2O_3^{2-} + 3H^+ \quad (2)$$

$$4Fe^{2+} + O_2 + 4H^{+\text{bacteria}} \rightarrow 4Fe^{3+} + 2H_2O \quad (3)$$

$$S^0 + \frac{3}{2}O_2 + H_2O^{\text{bacteria}} \rightarrow 2H^+ + SO_4^{2-} \quad (4)$$

$$S_2O_3^{2-} + H_2O + 2O_2^{\text{bacteria}} \rightarrow 2SO_4^{2-} + 2H^+ \quad (5)$$
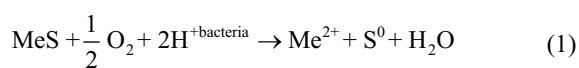
In the process, the HCs from the catalysts are first removed by washing with ethyl alcohol. The microorganism culture, containing Fe/S oxidizing bacteria, are cultivated under acidic conditions and the bioleaching is carried out by incubation at 30°C. Results show that Ni and V could be successfully extracted

Beolchini et al., 2010). This process is a cost-effective and environmentally friendly method for spent metal recoveries.

Precious metal recovery via AquaCat. AquaCat is a method to recover metals from spent heterogeneous and homogeneous catalysts using a process based on supercritical water oxidation which converts carbonaceous material to less noxious compounds, leaving the precious metals as their oxides (Grumett, 2003). The technology was commissioned at Johnson Matthey's Brimsdown (UK) facility in 2002 and operated until 2007 when the process and technology rights were purchased by Supercritical Fluids International (Smith et al., 2013). It consists of two stages, the determination of the metal content by direct sampling and the utilization of supercritical oxidation to convert carbon materials into less harmful compounds. This method targets organometallic-based catalysts which have historically been treated by high energy intensive methods such as combustion. In the direct sampling, the spent catalyst in the form of a wet filtered cake (between 5 μm and 500 μm particle size) is added to water and a surfactant in a vessel and agitated to form a homogeneous dispersed mixture, which is analysed to determine the metal content. The water-based slurry is then pumped to the feeding tank where the supercritical water oxidation takes place. Water becomes supercritical above 374°C and 221 bars, and by that stage its viscosity will be close to that of its vapour combined with a higher fluid density. At this stage, the organic substances become soluble and the water will act as a solvent for the oxidation.

For homogeneous catalysts, high pressure water is fed into the economizer. The catalyst is inserted directly into the reactor after oxygen injection as it does not mix with the supercritical water. The AquaCat process requires less energy and exhibits lower carbon dioxide emissions and does not give rise to SOx and NOx emissions as opposed to incineration. Direct sampling allows safer handling and treatment of hazardous materials as it can be collected in bulk (Grumett, 2003). The precious metals are recovered in a separator.

Bio-hydrometallurgical process. In this process, microorganisms have the primary role of leaching instead of using reagents to do this activity. Microorganisms (e.g., bacteria and fungi such as *Bacillus* sp., *Aspergillus niger, Penicillium simplicissimum, Saccharomyces cerevisiae*, and *Yarrowia lipolytica*) interact with metals for the purpose of solubilization. Previous studies were conducted on the biological recovery of metals from sludge, fly ashes, batteries, and electronic waste (Bayat and Sari, 2010; Carranza et al., 2009; Lombardi and Garcia, 2002; Wu and Tin, 2009; Xin et al., 2009; Zheng et al., 2009). Gaballah et al. (1994) showed that various hydrometallurgical processes are available for metal recovery. They recovered metals when catalyst roasting is the typical recovery route. After biological uptake, it was reported that chlorides of Mo and V were volatilized at 500°C whilst those of Co and Ni remained at solid state until 700°C was reached. During bio-uptake hazardous compounds such as HCL, H_2SO_4 and alkalis were separated from valuable metals (e.g., Mo, V, and Al).

Pyrometallurgical process. The pyrometallurgical process is a nominal choice when physical properties are negligible. It recovers metals from IW after thermal treatment (smelting, roasting, and refining). In synthesis gas production, especially in low temperature processes of carbon monoxide conversion with steam to form hydrogen for the production of ammonia or methanol, the $CuO–ZnO–Al_2O_3$ catalyst was considered by Malecki and Gargul (2018). The spent catalyst could be a valuable source of metal using pyrometallurgical and hydrometallurgical processes to recover more than 66% of the Cu in metal form and 70% of zinc as ZnO. The objective in the pyrometallurgical process is to maximize the yields of Cu and zinc (Zn) extracted from the spent catalyst in the recovery process so test melting is initially performed. Slag-forming additives are needed in the recovery process to obtain the lowest melting point of the slag which also has a meaningful effect on the recovery of Cu to alloy and Zn to dust. In the additives CaO, SiO_2, and Na_2O were shown to give the lowest melting point when the components were in the same weight percentage. The catalyst was loaded into a graphite crucible and placed in an induction furnace at a temperature range of 1100°C–1300°C to obtain the maximum stripping of zinc and the formation of liquid copper. Coal is added to the process to reduce CuO and ZnO. After melting, the liquid products were cooled, separated and weighed for chemical analysis. On the other hand, the hydrometallurgical method consists of two main processes,

leaching and filtration. The zinc oxide and copper oxide leaching process follows two stages: leaching in NaOH solution (temperature 75°C for 120 minutes, NaOH concentration = 200g dm^{-3}, 1/s = 10) followed by leaching in H_2SO_4 solution (temperature 60°C, for 120 minutes, H_2SO_4 concentration = 180 g dm^{-3}, 1/s = 10). Zinc has high resistance to both acid and alkaline so after leaching an insoluble residue is formed, which was filtered to separate the precipitate. The resulting yield of copper in the solution is about 98% with 62% zinc in the alkaline solution.

Recovery of catalysts from automotive catalyst deposits. The use of platinum group metals in automotive catalysts is widespread. There are numerous reports in the literature on the fate of these metals in the environment and on human health from countries around the world (Gao et al., 2012; Khan and Strand, 2018; Sen et al., 2013; Spaziani et al., 2008). Road dust containing these metals has been assessed as an anthroprogenic resource and methods have been established to recover the spent catalyst. Methods include leach solutions such as aqua regia to solubilize the metals as well as a microwave-assisted leaching method (Yong et al., 2003).The microwave approach gave 80% metals recovery, with the leach time reduced from 2 hours to 15 minutes using 50% (aq.) diluted aqua regia compared to conventional acid leaching to give potentially a more biocompatible leachate. Some researchers have used aqua regia leachates rich in platinum group metals as feedstock for bacteria such as *Desulfovibrio desulfuricans, Cupriavidus metallidurans* or *Escherichia coli* (Murray et al., 2017; Yong et al., 2003) which reduces the soluble metals to cell-bound insoluble base metals, for example, Pd(II) to Pd(0)). It was reported that bacteria immobilized in a biofilm preloaded with Pd(0) loaded in a flow-through electrobioreactor performed better as chemical catalysts for the reductive recovery of precious metals when compared to free cells with a recovery of spent automotive catalysts of up to 90% efficiency at a residence time of 15 minutes. Model solutions were found to give better results than real automotive leachate and from crushed spent automotive catalyst due to interference by other contaminants. The bacterial Pd(0) functioned as a superior chemical catalyst in a test reaction which liberated hydrogen from hypophosphite (Yong et al., 2002). These catalysts have also been tested as cheap nanocatalysts for fuel cell electrodes (Yong et al., 2010).

Recovery of catalysts from in situ heavy oil upgrading. In situ methods to recover heavy oil fractions are gaining momentum. These are largely based on combustion methods but *in situ* catalytic upgrading processes such as catalytic petroleum recovery *in situ* are employed to further improve the upgrading of the heavy oil. The catalyst is typically packed into an annulus around the horizontal production well; however, some researchers have investigated the use of dispersed catalysts to improve the issues of deactivation associated with packed bed catalysis (Al-Marshed et al., 2016). The recovery of spent catalyst from *in situ* recovery processes poses challenges. The catalyst can be retained in the formation and it has been suggested that dispersed catalyst

injected in the form of nanoparticles may either agglomerate into larger particles or adsorb to the rock surface especially at the temperature and pressure conditions. To negate this, ultradispersed suspensions with high stability and selectivity are needed (Guo et al., 2016). Spent dispersed catalysts can be recovered from the oil using conventional demetallization processes that are used to remove metals from heavy oil. Demetallization processes are valuable in their own right as metal recovery processes; a third of all vanadium produced by Russia stems from demetallization of heavy oil and 8% the world production of vanadium comes from oil feedstocks. Demetallization takes place in the electrostatic desalter at a refinery although this process is typically modified to deal with stable organometallics with electrolysis cells and polymeric sorbents being used to recover metals (Magomedov et al., 2015).

Regulations governing spent catalysts handling and IW

EU regulations

The EU has some of the highest WM standards in the world. The EU WM Regulations and Directives EC 1013/2006 and 2008/98/EC aim to protect the environment and human health through highlighting the importance and emphasizing the application of waste recovery and recycling techniques (European Commission, 2006, 2008). These regulations also govern the shipment and handling of ISW and spent catalysts trade between EU countries. To implement this, the original waste producer must pay for the costs of proper and adequate WM as well as introduce extended producer responsibility. This is where the manufacturer accepts and disposes of products that are returned after use. The producers of waste are required to treat the waste before disposing of it or have it professionally tested; this is tracked by regular inspections (European Union, 2008).

The EU regulations for waste have been divided into various sections. The Directive of landfill waste (EC/35) aims to reduce and prevent disposal as much as possible, to have little to *no impact* on surface water, groundwater, soil or human health. To achieve this, specific guidelines have been set. EU landfill sites are usually split into three different sections: HW; non-HW; and inert waste (non-incinerable/decomposable waste). Biodegradable waste is discouraged and used tyres, liquid waste, flammable waste, explosive or corrosive waste are not allowed in landfill sites. Only treated waste can enter landfill sites. This is tracked by issuing permits and regular operator checks (European Union, 2004).

The HW regulations were set by the European Economic Community and the Basel Convention. This regulates the boundaries for which the HW disposal must abide by. It consists of three main sections: minimizing transported quantities, treatment and disposal of wastes as close to the place of generation and to prevent/ minimise the generation of waste from the beginning (European Economic Community, 1993). Due to the recent

increase in ISW generation, the waste safety and guidelines have become more severe. The EU also gave formal consent for a ban prohibiting the export of waste to non-Organisation for Economic Co-operation and Development (OECD) countries a while ago (Hackett, 1989).

To control industrial emission, the EU has devised a framework of interconnected permitting. This is where the emission permit must take into consideration the industrial plant's whole environmental performance (from start up to shut down) and to avoid the pollution shift between mediums (such as air, water and land). Priority is given to prevent pollution by intervening at the generation point and ensuring efficient and sustainable use/management of natural resources. This legislation covers the following industrial sectors: energy; metal production/processing; minerals; chemicals; and WM. This allows the public to be given an early opportunity to contribute to the permitting process and installations (European Union, 2010).

The European Catalysts Manufacturers Association has set guidelines for the management of spent catalysts, which was established back in 1993. The association abides by the rules of the European Chemical Industry Council. The guidelines state that whilst the catalyst is in use, the user is required to pay attention to precautions and safety measures that will be required once the catalyst has been deactivated and devise an adequate disposal plan. The hazardous proprieties of the catalyst should be well-known to the user to help aid the disposal plan. Once the catalyst has been discharged, it can either be reused (via off-site regeneration) or directed towards metals recovery. Regeneration of a catalyst usually involves international movement, which has to be carried out by adhering to the EU Waste Transportation Act (European Commission, 2006). According to the OECD decision, transportable waste has been coded, Green and Amber. The Green coding includes wastes that have low risk for humans and the environment and thus fall under normal commercial transactions. The Amber code refers to waste that has sufficient risk to being borderline under the satisfaction of the OECD control. This requires advance notice for all the concerned authorities along with a tracking document. A Green coded spent catalyst can be treated as Amber should it contain impurities or contaminates that might prevent recovery (Cefic Group, 2001). The EU also promotes the activities of its governing agency of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) which adopts regulations to protect health and environment of EU countries. Chemical substances and metals recovered from ISWM are approved through this programme for trading amongst EU countries (EU REACH, 2006).

Governing standard within the State of Kuwait and lessons learnt

The governing body within the State of Kuwait concerning the handling and disposal of waste is the Kuwait Environment Public Authority (KEPA). One of the first things that comes to mind concerning the issue of ISWM and waste standards within

Kuwait, is the fact that various components of waste fall under the jurisdictions and responsibilities of various sectors. A prime example is the fact that MSW is managed by Kuwait Municipality, whereas ISW with the exception of the oil and gas industries fall under the responsibilities of the Public Authority for Industry. Each petroleum refinery is contracted to manage its own waste through national landfill sites, and industrial wastewater is managed by a different sector of the government through the Ministry of Public Works. This trend goes on to create major controversy among various parties in Kuwait, and there exists no governing body to liaise between all responsible parties. On the other hand, the regulations that KEPA have developed are being revised and improved constantly. The current regulations within Kuwait also present major gaps and are not descriptive enough. Major technical and scientific input is required to have a comprehensive regulation by KEPA for governing WM activities within Kuwait. Generally, the management of SW is governed and regulated by Law No. 16/1996 and by-law Directive 210/2001 (Kuwait Al Youm, 2001). These laws assign waste in Kuwait to the categories of hazardous and non-hazardous based on the Basel Convention (Basel Convention, 1989). Private and cottage industries in Kuwait have to abide by these regulations by law. In addition, KEPA Directive (law) No. 5/2016 identifies various definitions and aspects with regards to WM, and law No. 6/2017 sets regulations for managing waste generated from medical and hazardous sources. It also regulates radioactive waste within the country (Kuwait Al Youm, 2016, 2017). By comparison to the case of the EU, and examining the aforementioned generation trends of ISW in Kuwait, a number of recommendations can be inferred as a strategy for the country. The State of Kuwait can benefit immensely by supporting the establishment of governmental and private industries alike, in creating a market for ISW valorization. These industries also can benefit immensely and within state borders by trading recovered metals and chemicals from ISW, namely spent catalysts. The regulations in Kuwait can also start to accommodate such industrial practice, and one governing body can be responsible for managing the various WM aspects in the country, instead of the current situation that creates confusion between waste generating sectors. The sustainability of the development of such practice is also something that cannot be neglected. The sole method of disposal for ISW in Kuwait is landfilling in a governmental site. This is a major cause of land loss, generation of environmental and social associated burdens, and land reclamation/rehabilitation costs. These issues can be eliminated by establishing both the appropriate standards and industry to govern ISW, moreover including spent catalyst which Kuwait consumes by a large amount due to its industrial nature.

Conclusion

Improper management of ISW is beginning to be recognized by many business sectors; however, the action to address the problem in an efficient and sustainable manner is yet to be established.

Manufacturers are gradually shifting towards the reuse of spent catalyst and have developed recovery methods such as: hydrometallurgical and the liquid–liquid extraction process (chemical leaching method post-metal recovery, commonly used to recover Mo and V); solvent and liquid–soil extraction (solvent extraction with LIX-84-1 dissolved in kerosene, commonly used to recover V, Mo and Ni); and soda roasting and metal leaching (used to extract V and Mo at high percentages but at the expense of a temperature range of 500°C–700°C). Biotechnological processes are also commonly used to extract V, Mo and Ni, at the expense of longer leaching time; however, these methods prove to be more cost-effective than conventional ones (including thermal cracking, gasification and pyrolysis). All of these proposed and applied processes mostly aim at a small number of precious metals, making them limited to the recovery of catalysts that may contain V, Mo and Ni. Other valuable metals such as Pt, Al, and Zi, may not be compatible. Legal guidelines across Europe and Kuwait have set strict guidelines in regard to ISW and its management, based on the hazardous properties of catalysts. Regeneration of spent catalyst/metal recovery requires international transport and numerous post-treatment and pre-treatment steps. The transport across different borders is one the biggest drawbacks as different countries have different rules, regulations and standards, thus making the management plan harder to execute and successfully implement.

ORCID iD

Sultan Majed Al-Salem https://orcid.org/0000-0003-0652-4502

References

Akcil A, Francesco V, Ferella F, et al. (2015) A review of metal recovery from spent petroleum catalysts and ash. *Waste Management* 45: 420–433.

Alhumoud JM and Al-Kandari FA (2008) Analysis and overview of industrial solid waste management in Kuwait. *Management of Environmental Quality: An International Journal* 19: 520–532.

Ali S, Garforth AA, Harris DH, et al. (2002) Polymer waste recycling over used catalysts. *Catalysis Today* 75: 247–55.

Al-Jabri K, Baawain M, Taha R, et al. (2013) Potential use of FCC spent catalyst as partial replacement of cement or sand in cement mortars. *Construction and Building Materials* 39: 77–81.

Al-Marshed A, Hart A, Leeke GA, et al. (2016) Effectiveness of different transition metal dispersed catalysts for *in-situ* heavy oil upgrading. *Industrial & Engineering Chemistry Research* 54: 10,645–10,655.

Al-Muzaini S (1998) Industrial wastewater management in Kuwait. *Desalination* 115: 57–62.

Al-Qallaf Y, Al-Kandari S, Yousef K, et al. (2016) Analysis and improvement possibilities of waste management at Kuwait Oil Company (KOC). In: *Proceedings of the Wessex Institute of Technology (WIT) Transactions of the 8th International Conference on Waste Management and The Environment (WM 2016)*, Valencia, Spain, 7–9 June 2016. Southampton, UK: WIT Press, 73–84.

Al-Qassimi M, Sultan H and Al-Salem SM (2018) Futuristic overview of waste from electronics & electrical equipment (WEEE). In: Al-Salem SM (ed.) *The State of Kuwait*. Kuwait: Kuwait Institute for Scientific Research (KISR) Book of Proceedings, pp.13–33.

Al-Salem SM (2009) Establishing an integrated databank for plastic manufacturers and converters in Kuwait. *Waste Management* 29: 479–484.

Al-Salem SM (2015) Carbon dioxide (CO_2) emission sources in Kuwait from the downstream industry: Critical analysis with a current and futuristic view. *Energy* 81: 575–587.

Al-Salem SM (2019) Feedstock and optimal operation for plastics to fuel conversion in pyrolysis. In: Al-Salem SM (ed.) *Plastics to Energy: Fuel, Chemicals and Sustainable Implications*. 1st edn. Amsterdam: Elsevier, 117–146.

Al-Salem SM, Antelava A, Constantinou A, et al. (2017) A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *Journal of Environmental Management* 197: 177–198.

Al-Salem SM, Al-Nasser A and Al-Dhafeeri AT (2018a) Multi-variable regression analysis for the solid waste generation in the State of Kuwait. *Process Safety and Environmental Protection* 119: 172–180.

Al-Salem SM, Al-Nasser A, Al-Wadi M, et al. (2018b) Biodegradable Films Physical Properties Change With Respect To Degradation Exposure To Various Media. In: Nzihou A and Stehlik P (eds) *Proceedings of 7th International Conference on Engineering for Waste and Biomass Valorisation*, Prague, Czech Republic, 2–5 July 2018. Kuwait: Kuwait Institute for Scientific Research (KISR) Book of Proceedings, pp.272–282.

Alshammari JS, Gad FK, Elgibaly AA, et al. (2008) Solid waste management in petroleum refineries. *American Journal of Environmental Science* 4: 353–361.

Arena U (2012) Process and technological aspects of municipal solid waste gasification. A review. *Waste Management* 32: 625–639.

Bagri R and Williams PT (2002) Catalytic pyrolysis of polyethylene. *Journal of Analytical and Applied Pyrolysis* 63: 29–41.

Bayat B and Sari B (2010) Comparative evaluation of microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge. *Journal of Hazardous Materials* 174: 763–769.

Basel Convention (1989) Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal. Geneva: UNEP. Available at: https://www.basel.int/Portals/4/Basel%20Convention/docs/text/BaselConventionText-e.pdf (accessed 20 September 2019).

Beigl P, Wassermann G, Schneider F, et al. (2004) Forecasting municipal solid waste generation in major European cities. In: *Proceedings 9th International Congress on Enviormental Modelling & Software*, Osnabrück, Germany, 1 July 2004. Available at: https://pdfs.semanticscholar.org/6d33/e9d43a906be1dfe52f97b1fea27375183a78.pdf (accessed 25 September 2019).

Beolchini F, Fonti V, Ferella F, et al. (2010) Metal recovery from spent refinery catalysts by means of biotechnological strategies. *Journal of Hazardous Materials* 178: 529–534.

Biology Discussion Forum (2018) Biology Discussion Forum. Wastes: Sources, Classification and Impact (2018). Available at: http://www.biologydiscussion.com/wastes/wastes-sources-classification-and-impact/7091 (accessed 20 September 2019).

Biswas RK (1985) Recovery of vanadium and molybdenum from heavy oildesulphurization waste catalyst. *Hydrometallurgy* 14: 219–230.

Brandl H, Bosshard R and Wegmann M (2001) Computer-munching microbes: Metal leaching from electronic scrap by bacteria and fungi. *Hydrometallurgy* 59: 319–326.

Butler E, Devlin G, Meier D, et al. (2011) A review recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews* 15: 4171–4186.

Cardona SC and Corma A (2000) Tertiary recycling of polypropylene by catalytic cracking in a semibatch stirred reactor: Use of spent equilibrium FCC commercial catalyst. *Applied Catalysis B: Environmental* 25 151–162.

Carranza F, Romero R, Mazuelos A, et al. (2009) Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests. *Hydrometallurgy* 97: 39–45.

Cefic Group (2001) Guidelines For The Management Of Spent Catalysts. August 2001. Available at: https://www.catalystseurope.eu/images/Documents/Guidelines_for_the_management_of_spent_catalysts.pdf (accessed 20 September 2019).

Cerruti C, Curutchet G and Donati E (1998) Bio-dissolution of spent nickel–cadmium batteries using *Thiobacillus ferrooxidans*. *Journal of Biotechnology* 62: 209–219.

Chandrasekaran SR and Sharma BK (2019a) Fuel properties associated with catalytic conversion of plastics. In: Al-Salem SM (ed.) *Plastics to Energy: Fuel, Chemicals and Sustainable Implications*. 1st edn. Amsterdam: Elsevier, 173-220.

Chandrasekaran SR and Sharma BK (2019b) From waste to resources: How to integrate recycling into the production cycle of plastics. In: Al-Salem SM (ed.) *Plastics to Energy: Fuel, Chemicals and Sustainable Implications*. 1st edn. Amsterdam: Elsevier, 345–364.

Chiranjeevi T, Pragya R, Gupta S, et al. (2016) Minimization of waste spent catalyst in refineries. *Procedia Environmental Sciences* 35: 610–617.

Demirbaş A (2005) Recent advances in recycling and re-refining processes of petroleum based wastes (PBW). *Energy Sources* 27: 261–269.

Dixon N and Jones DRV (2005) Engineering properties of municipal solid waste. *Geotextiles and Geomembranes* 23: 205–233.

Donaj PJ, Kaminsky W, Buzeto F, et al. (2012) Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Management* 32: 840–846.

European Commision (2002) Heavy Metals in Waste. Final Report Project ENV.E.3/ETU/2000/0058. Available at: https://ec.europa.eu/environment/waste/studies/pdf/heavy_metalsreport.pdf (accessed 20 September 2019).

European Commission (2005) Press Release statement. Available at: http://europa.eu/rapid/press-release_MEMO-05-496_en.htm (accessed 20 September 2019).

Euopean Commission (2006) Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June (2006) on shipments of waste. Available at: https://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX%3A32006R1013 (accessed 20 September 2019).

European Commission (2008) Directive 2008/98/EC on waste (Waste Framework Directive). Available at: https://ec.europa.eu/environment/waste/framework/ (accessed 20 September 2019).

European Economic Community (1993) Council Regulation (EEC) No. 259/93 on the supervision and control of shipments of waste within, into and out of the European Community. Available at: https://publications.europa.eu/en/publication-detail/-/publication/ba7c954f-4bbc-44f3-9dfc-68aaf3b1ab8f (accessed 20 September 2019).

European Environmental Agency (2017) Heavy Metal Emissions: Indicator Assessment. Available at: https://www.eea.europa.eu/data-and-maps/indicators/eea32-heavy-metal-hm-emissions-1/assessment-9 (accessed 29 September 2019).

EU REACH (2006) Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32006R1907 (accessed 29 September 2019).

Euro Statistics (2019) Waste Statistics: Statistics Explained. Updated May 2019. Available at: https://ec.europa.eu/eurostat/statistics-explained/pdf-scache/1183.pdf (accessed 20 September 2019).

European Union (2004) Official Journal of the European Communities, L 269 (September 2000), pp. 1–15. Available at: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:en:PDF (accessed 20 September 2019).

European Union (2008) Official Journal of the European Union (EC) No 1126/2008 of 3 November 2008 adopting certain international accounting standards in accordance with Regulation (EC) No 1606/2002 of the European Parliament and of the Council (Text with EEA relevance). Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0098&from=EN (accessed 20 September 2019).

European Union (2010) Official Journal of the European Communities. Available at: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:en:PDF (accessed 7 December 2018).

Gaballah I and Kanari N (1990) A survey of binary chloride compounds MxNyClz (M = R.E., R.M., P.M., T.M.). In: *Proceedings 7th National Conference on Metallurgical Science and Technology*, Madrid, Spain, 3–5 October 1990, vol. 1, pp.377–386.

Gaballah I, Djona M, Mugica JC, et al. (1994) Valuable metals recovery from spent catalysts by selective chlorination. *Resources, Conservation and Recycling* 10: 87–96.

Gao B, Yu Y, Zhou H, et al. (2012) Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China. *Environmental Toxicology and Chemistry* 31: 1231–1238.

Gianetto A., Farag HI, Blasetti AP, et al. (1994) Fluid catalytic cracking catalyst for reformulated gasolines: Kinetic modeling. *Industrial & Engineering Chemistry Research* 33: 3053–3062.

Grumett BP (2003) Precious metal recovery from spent catalysts. *Platinum Metals Review* 47: 163–166.

Guo K, Li H and Yu Z (2016) *In-situ* heavy and extra-heavy oil recovery: A review. *Fuel* 185: 886–902.

Hackett DP (1989) Assessment of the basel convention on the control of transboundary movements of hazardous wastes and their disposal. *The American University Journal of International Law and Policy* 5: 291–323.

Hafeez S, Pallari E, Manos G, et al. (2019) Catalytic conversion and chemical recovery. In: Al-Salem (ed.) *Plastics to Energy: Fuel, Chemicals and Sustainable Implications*. 1st edn. Amsterdam: Elsevier, 147–172.

Hahladakis JN and Iacovidou E (2018) Closing the loop on plastic packaging materials: What is quality and how does it affect their circularity? *Science of the Total Environment* 630: 1394–1400.

He M, Hu Z, Xiao B, et al. (2009) Hydrogen-rich gas from catalytic steam gasification of municipal solid waste (MSW): Influence of catalyst and temperature on yield and product composition. *International Journal of Hydrogen Energy* 34: 195–203.

Hoornweg D and Bhada-Tata P (2012) What a Waste: A Global Review of Solid Waste management. World Bank's Urban Development Series Knowledge Papers no.15, March 2012. Available at: https://siteresources.worldbank.org/INTURBANDEVELOPMENT/Resources/336387-1334852610766/What_a_Waste2012_Final.pdf (accessed 20 September 2019).

Jordan K and Heidorn C (eds) (2003) Waste Generated and Treated in Europe: Data 1990–2001. Luxembourg: Office for Official Publications of the European Communities. Available at: https://ec.europa.eu/eurostat/documents/3217494/5646057/KS-55-03-471-FR.PDF/43418c26-d661-41fa-ae1e-4d999edeb9a5?version=1.0 (accessed 20 September 2019).

Kar BB, Datta P and Misra VN (2004) Spent catalyst: Secondary source for molybdenum recovery. *Hydrometallurgy* 72: 87–92.

Kasliwal PK, Prabhu KM, Kumar B, et al. (2015) Challenges and Opportunities in disposal of spent FCC/RFCC catalyst. Symposium on regeneration, reactivation and reworking of spent catalysts, 205 meeting of ACS. Available at: https://www.semanticscholar.org/paper/Challenges-and-Opportunities-in-disposal-of-spent-%2F-Kasliwal-Prabhu/72e52c18a8aef6b341f43f316f680bf8c2b72d19 (accessed 20 September 2019).

Kaza S, Yao L, Bhada-Tata P, et al. (2018) *What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050*. Urban Development Series. Washington, DC: World Bank.

Kentish SE and Stevens GW (2001) Innovations in separation technology for the recycling and re-use of liquid waste streams. *Chemical Engineering Journal* 84: 149–159.

Khan RK and Strand MA (2018) Road dust and its effect on human health: a literature review. *Epidemiology and Health* 40: e2018013. Epub ahead of print 10 April 2018. DOI: 10.4178/epih.e2018013.

Kuwait Al Youm (2001) Decision No. 210/2001. Appendix of Issue No. 533.

Kuwait Al Youm (2016) Decision No. 5/2016. Appendix of Issue No. 1298.

Kuwait Al Youm, 2017. Decision No. 6/2017. Appendix of Issue No. 1344.

Lin YH, Wei TT, Yang MH, et al. (2012) Postconsumer plastic waste over post-use cracking atalysts for producing hydrocarbon fuels. *Journal of Energy Resources Technology* 135: 1–8.

Lombardi AT and Garcia O (2002) Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by *Thiobacillus ferrooxidans* and its effect on metal partitioning. *Water Research* 36: 3193–3202.

Lupa CJ, Ricketts LJ, Sweetman A, et al. (2011) The use of commercial and industrial waste in energy recovery systems – A UK preliminary study. *Waste Management* 31: 1759–1764.

Magomedov RN, Popova AZ, Maryutina TA, et al. (2015) Current status and prospects of demetallization of heavy petroleum feedstock (Review). *Petroleum Chemistry* 55: 423–443.

Małecki S and Gargul K (2018) Low-Waste Recycling of Spent CuO-ZnO-Al2O3 Catalysts. *Metals* 8. Available at: https://www.semanticscholar.org/paper/Low-Waste-Recycling-of-Spent-CuO-ZnO-Al2O3-Ma%C5%82ecki-Gargul/89d9545b1bb0feb56181e73fc27afc7dbb6df156 (accessed 20 September 2019).

Mansour NA, Hassan NM, Abd Elaal SA, et al. (2016) On the comparison of metals, heavy and toxics elements in waste petroleum of Egypt and Kuwait. *International Journal of Advancement in Engineering Technology, Management and Applied Science* 3: 34–44.

Marafi M, Al-Omani S, Al-Sheeha H, et al. (2007) Utilization of metal-fouled spent residue hydroprocessing catalyst in the preparation of an active HDM catalyst. *Industrial & Engineering Chemistry Research* 46: 1968–1974.

Marafi M and Rana MS (2016) Refinery waste: The spent hydroprocessing catalyst and its recycling options. In: *WIT Transactions on Ecology and the Environment*, Volume 2002. Southampton, UK: WIT Press, 219–230.

Marafi M and Stanislaus A (2008) Spent catalyst waste management: A review. Part I – Developments in hydroprocessing catalyst waste reduction and use. *Resources, Conservation and Recycling* 52: 859–873.

Marafi M and Stanislaus A (2011) Alumina from reprocessing of spent hydroprocessing catalyst. *Catalysis Today* 178: 117–123.

Mertinkat J, Kirsten A, Predel M, et al. (1999) Cracking catalysts used as fluidized bed material in the Hamburg pyrolysis process. *Journal of Analytical and Applied Pyrolysis* 49: 87–95.

Muhammad C, Onwudili JA and Williams PT (2015) Catalytic pyrolysis of waste plastic from electrical and electronic equipment. *Journal of Analytical and Applied Pyrolysis* 113: 332–339.

Murray AJ, Zhu AJ, Wood J, et al. (2017) A novel biorefinery: Biorecovery of precious metals from spent automotive catalyst leachates into new catalysts effective in metal reduction and in the hydrogenation of 2-pentyne. *Minerals Engineering* 113: 102–108.

Nanda S, Rana R, Hunter HN, et al. (2019) Hydrothermal catalytic processing of waste cooking oil for hydrogen-rich syngas production. *Chemical Engineering Science* 195: 935–945.

Obiajunwa EI, Pelemo DA, Owolabi SA, et al. (2002) Characterisation of heavy metal pollutants of soils and sediments around a crude-oil production terminal using EDXRF. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 194: 61–64.

Park K, Kim H and Parhi PK (2010) Recovery of molybdenum from spent catalyst leach solutions by solvent extraction with LIX 84-I. *Separation and Purification Technology* 74: 294–299.

Pires A, Martinho G and Chang N (2011) Solid waste management in European countries: A review of systems analysis techniques. *Journal of Enviromental Management* 92: 1033–1050.

Prabakar D, Manimudi VT, Suvetha KS, et al. (2018) Advanced biohydrogen production using pretreated industrial waste: Outlook and prospects. *Renewable and Sustainable Energy Reviews* 96: 306–324.

Ramezani A, Emami SM and Nemat S (2017) Reuse of spent FCC catalyst, waste serpentine and kiln rollers waste for synthesis of cordierite and cordierite-mullite ceramics. *Journal of Hazardous Materials* 338: 177–185.

Richmond CA (2010) Chevron Lummus Global Selected by Kuwait National Petroleum Corporation to Build World's Largest Residuum Hydrotreater Complex. Media Release, Chevron Lummus Global. Available at: https://www.chevrontechnologymarketing.com/Documents/KNPC%20Media%20Release%20_2_.pdf (accessed 20 September 2019).

Ro KS, Cantrell K, Elliott D, et al.(2007) Catalytic wet gasification of municipal and animal wastes. *Industrial Engineering & Chemistry Research* 46: 8839–8845.

Rojas-Rodríguez AD, Flores-Fajardo O, González FSA, et al. (2012) Chemical treatment to recover molybdenum and vanadium from spent heavy gasoil hydrodesulfurization catalyst. *Advances in Chemical Engineering and Science* 2: 408–412.

Sarker M, Kabir A, Rashid MM, et al. (2011) Waste polyethylene terephthalate (PETE-1) conversion into liquid fuel. *Journal of Fundamental Renewable Energy Application* 1: 1–5.

Sen IS, Peucker-Ehrenbrink B and Geboy N (2013) Complex anthropogenic sources of platinum group elements in aerosols on Cape Cod, USA. *Environmental Science & Technology* 47: 10188–10196.

Seo YH, Lee KH and Shin DH (2003) Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. *Journal of Analytical and Applied Pyrolysis* 70: 383–398.

Sharma BK, Moser BR, Vermillion KE, et al. (2014) Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. *Fuel Processing Technology* 122: 79–90.

Sharma R and Bansal RP (2016) Use of different forms of waste plastic in concrete – A review. *Journal of Cleaner Production* 112: 473–482.

Sharuddin SDA, Abnisa F, Daud WMAW, et al. (2016) A review on pyrolysis of plastic wastes. *Energy Conversion and Management* 115: 308–326.

Sheeha H, Marafi M, Raghavan V, et al. (2013) Recycling and recovery routes for spent hydroprocessing catalyst waste. *Industrial & Engineering Chemistry Research* 52: 12794–12801.

Smith R, Inomata H and Peters C (2013) *Introduction to Supercritical Fluids: A Spreadsheet-Based Approach*. Amsterdam: Elsevier.

Spaziani F, Angelone M, Coletta A, et al. (2008) Determination of platinum group elements and evaluation of their traffic-related distribution in Italian urban environments. *Analytical Letters* 41: 2658–2683.

Su BC, Shi L, Meng X, et al. (2019) From waste to best: Excellent desulfurization performance of spent FCC catalyst. *Journal of Sulfur Chemistry* 40: 75–87.

Syed S (2006) A green technology for recovery of gold from non-metallic secondary sources. *Hydrometallurgy* 82: 48–53.

Taha R, Al-Kamyani ZS, Al-Jabri K, et al. (2011) Use of waste spent catalyst in construction. In: *Proceedings of the 1st Annual International Conference on Construction*, Athens, Greece, 20–23 June. Available at: https://www.researchgate.net/publication/260086590_Use_of_Waste_Spent_Catalyst_in_Construction (accessed 25 September 2019).

Tuncuk A, Stazi V, Akcil A, et al. (2012) Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling. *Minerals Engineering* 25: 28–37.

Vasile C, Pakdel H, Mihai B, et al. (2001) Thermal and catalytic decomposition of mixed plastics. *Journal of Analytical and Applied Pyrolysis* 57: 287–303.

Whittaker-Wood F (2018) Dirty Cars, Dirty Air: Who are Europe's Most Toxic Drivers?. *Ecoexperts*, 12 February 2018. Available at: https://www.theecoexperts.co.uk/most-toxic-countries (accessed 20 September 2019).

Wu C and Williams PT (2010) Pyrolysis–gasification of plastics, mixed plastics and real-world plastic waste with and without Ni–Mg–Al catalyst. *Fuel* 89: 3022–3032.

Wu HY and Tin YP (2009) Metal extraction from municipal solid waste (MSW) incinerator fly ash-chemical leaching and fungal bioleaching. *Enzyme and Microbial Technology* 38: 839–847.

Xin BP, Zhang D, Zhang X, et al. (2009) Bioleaching mechanism of Co and Li from spent lithium–ion battery by the mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria. *Bioresource Technology* 100: 6163–6169.

Xu K, Deng T, Liu J, et al. (2007) Study on the recovery of gallium from phosphorous flue dust by leaching with spent sulfuric acid solution and precipitation. *Hydrometallurgy* 86: 172–177.

Xue Y, Zhou S, Brown RC, et al. (2015) Fast pyrolysis of biomass and waste plastic in a fluidized bed reactor. *Fuel* 156: 40–46.

Yong P, Mikheenko IP, Deplanche K, et al. (2010) Biorefining of precious metals from wastes: an answer to manufacturing of cheap nanocatalysts for fuel cells and power generation via an integrated biorefinery? *Biotechnology Letters* 32: 1821–1828.

Yong P, Rowson NA, Farr JPG, et al. (2002) Bioreduction and biocrystallization of palladium by *Desulfovibrio desulfuricans* NCIMB 8307. *Biotechnology and Bioengineering* 80: 369–379.

Yong P, Rowson NA, Farr JPG, et al. (2003) A novel electrobiotechnology for the recovery of precious metals from spent automotive catalysts. *Environmental Technology* 24: 289–297.

Zhang H, Xiao R, Wang D, et al. (2009) Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized fatalytic cracking (FCC) catalysts. *Energy & Fuels* 23: 6199–6206.

Zheng G, Zhou L and Wang S (2009) An acid-tolerant heterotrophic microorganism role in improving tannery sludge bioleaching conducted in successive multi-batch reaction systems. *Environmental Science & Technology* 43: 4151–4156.