

1 **A Review of The Valorisation and Management of Industrial Spent Catalyst Waste in The Context**
2 **of Sustainable Practice: The Case of The State of Kuwait in Parallel to European Industry**

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28 **Abstract**

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

45 **Keywords:** Spent catalysts, Industrial Waste, Hydrometallurgical treatment, Extraction, Waste
46 management.

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56 1. Introduction

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

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

80 The State of Kuwait (29°30'N *lat.* and 47°45' *E long.*) is an oil-dependent state within the Gulf Council
81 Countries (GCC) region of West Asia. The country is inhabited by 4.1 million residents of both national
82 and expatriates within a total area of 17,818 km². It has been reported to be the highest per capita
83 generator of MSW with conflicted reports showing a per capita generation range between 1.55 to 5.74 kg
84 per day according to recent estimates (World Bank, 2012, Kaza et al., 2018). Kuwait has also been
85 reported to be the second most toxic country in the world (Whittaker-Wood, 2017). Current infrastructure
86 doesn't support waste management (WM) activities in an integrated manner and governmental parties at
87 the moment are defining criteria to develop sustainable and up-to-date plans to do so (Kaza, 2018). The
88 sole method of SW disposal in the country is unsanitary landfilling in open dumps (Al-Salem, 2009).

89 Kuwait is divided into six governorates that host major industries, mainly revolving around chemicals and
90 petrochemicals conversion processes. The focus of the state of Kuwait has shifted in recent years
91 towards MSW and ISW management due to the nature of the country's industrial activities and
92 social behaviour. The country has also embarked on various mega-scale industrial projects including
93 the new refinery project (NRP) which is designed to process over 600 MMbpd of crude oil (Al-
94 Salem, 2015). The project has been announced to be one of the largest in the world that will host
95 catalytic upgrading units, including fluid catalytic cracking (FCC) and atmospheric residue
96 desulphurisation (ARDS) units using up-flow reactor technology (Richmond, 2010). Such industrial
97 ventures will necessarily result in the accumulation of more ISW namely industrial grade catalysts.
98 A similar situation can be observed across Europe. Countries such as France, Germany and Sweden are
99 leaders in their respective industries, thus generate substantial amount of waste. The majority of Europe's
100 waste is generated from the following industrial sectors: Agriculture, mining and quarrying, plastics and
101 rubbers, manufacturing, energy production, water distribution and treatment and construction, which all
102 make the management of ISW more critical. Typically, MSW constitutes 15% of the total solid waste
103 generated across European countries, whilst ISW represents some 40% of the total waste load (Jordan and
104 Heidorn, 2003) . On an average per capita assessment by recent published estimates of the World Bank
105 (Kaza et al., 2018), ISW is generated in high income countries (e.g. Kuwait) by 42.62 kg per day.
106 Comparatively, MSW and electronic waste are produced (on average) at a rate of 0.81 and 0.05 kg per
107 capita per day, respectively. These estimates also represent some 950 kg of ISW for every 1000 Euros (€)
108 of added value.

109 The industry in Kuwait mostly falls under oil and gas activities. Currently, Kuwait processes about
110 1000 M bpd of crude oil within its country limits representing a feedstock for the light derivatives
111 and petrochemical industries. It also exports over 3.1 MM bpd of crude oil as it is one of the oldest
112 members of the Organization of the Petroleum Exporting Countries (OPEC). Al-Muzaini (1998)
113 stated that there were twelve industries located in Shuaiba Industrial Area (SIA), which is the largest
114 industrial area in the Arabian Gulf hosted on the western coastal line of Kuwait. The total production
115 of industrial wastewater alone is 23,000 m³ d⁻¹, which carry heavy metals, organic chemicals and
116 suspended solids and mostly ends up in the Arabian Gulf. Different technologies of treating such
117 waste is based on physical, chemical and biological aspects (Syed, 2006). Industrial activities grew
118 considerable in Kuwait within the past decade. Alhumoud and Al-Kandari (2008) showed in their
119 work that a drastic increase of industrial waste was noted in Kuwait between the years 2000 (12,660
120 tonnes) to 2005 (47,169 tonnes). Figs.1-2 show approximately the percentages of factories by type
121 and the percentage of hazardous industrial solid waste, respectively. In waste management, one of
122 the main classifications is identifying the waste regarding to its harshness to fall either under the

123 hazardous or non-hazardous categories. On an annual basis, hazardous waste formulates 18.86% of
124 the total production of industrial waste generated in Kuwait (\approx 8,895 tonnes), including heavy oil
125 sludge, asbestos and expired chemicals (Alhumoud and Al-Kandari, 2008, Al-Qallaf et al., 2016).

126 Petroleum refining is considered to be the most significant pillar of the economy, due to Kuwait's oil
127 and gas based industry. Despite the strength of the financial return, oil and gas industries may cause
128 various environmental problems. Petroleum waste contains high concentrations of heavy and toxic
129 metals (Obiajunwa et al., 2002). To manage the potential side effects of petroleum waste, Mansour
130 et al. (2016) examined petroleum-based waste such as sludge and sand. Over 17 elements including
131 metals were recorded in their findings. The samples were derived from petroleum companies waste in
132 Kuwait. The results reflect six samples that were dried for one day under 110°C. The amount of
133 elements was detected through the technique of X-Ray Fluorescence (XRF). The level of iron (Fe)
134 was very high in both sludge and sand samples in addition to manganese (Mn) and calcium (Ca).
135 Manganese was noted to be consistent with previous studies (0.25-0.28%), whereas Ca is higher
136 (0.9-1.02%) (Table 2). A study published in Kuwait (Alshammari et al., 2008) declared that all
137 industrial oil and gas plants plan to dispose some 240 ktpa of industrial waste, in order to achieve an
138 integrated waste management strategy in the refining industry. To deal with this waste, they
139 classified hazardous waste as incinerable and non-incinerable. Catalysts are one of non-incinerable
140 hazardous waste, which contains various metals (e.g. platinum, cobalt, copper, molybdenum, iron
141 zinc, nickel and aluminium). Typical catalysts composition is presented below for the three main
142 operating refineries within state borders of Kuwait, namely Mina Al-Ahmadi (MAA), Mina
143 Abdullah (MAB) and Shuibah (SHU) refineries (Table 3).

144 According to the official European Statistics published by EUROSTAT, the EU generated a total of 58
145 million tonnes of hazardous waste back in 2002 which includes hazardous waste from all economic
146 sectors encompassing hazardous municipal waste (European Commission, 2005). This estimate increased
147 to 100 million tonnes in 2016 comprising 4% of the total generated waste across the EU-28 (Euro
148 Statistics, 2019). The UK alone generates 335 million tonnes of waste per year (mtpa) of which 225
149 million tonnes are MSW (Lupa et al, 2011). Due to the environmental impact of waste accumulation,
150 recycling has gained increasing interest across the EU in recent years (Beigl et al., 2004; Pires et al.,
151 2011).

152 Even though the EU industry is different to Kuwait, heavy metal waste is still generated from
153 different industries in the UK and Europe. Mercury (Hg) arising from the industrial sector; lead (Pb)
154 mainly from road transport; cadmium (Cd) due to abatement technologies and chromium (Cr) are
155 some of the most commonly generated heavy metals that pose numerous environmental and health

156 risks. One of the major contributors of such toxins is the waste generated from the construction
157 industry, as well as mining and extraction (European Commission, 2002). Due to recent awareness of
158 the negative effects of these metals, governments are devising models and implementing plans to
159 lower the amount of heavy metal waste. For example, Pb associated waste has been reduced by 93%
160 in the last 26 years across Europe. This was achieved by phasing out leaded petrol which currently
161 accounts for one third of total waste emissions around the world (EEA, 2017). Despite the awareness
162 and overall decrease in heavy metal emissions, in the last few decades, there is still a dire need for
163 SWM, further reducing emissions and developing metal recovery methods. Regression models
164 results, baseline studies and the development of integrated frameworks to reduce waste
165 accumulation, have also been adopted recently in Kuwait in-light of EU strategies (Al-Salem et al.,
166 2018a). In addition, strategies to mitigate plastic solid waste (PSW) and the development of
167 standards to govern the use of polymeric products, are also considered two main highlights of
168 Kuwait's recent waste management strategies development by governing bodies (Al-Salem et al.,
169 2018b). In light of the aforementioned, this review showcases the major ISW management activities
170 and potential of valorisation within the State of Kuwait with an emphasis on spent catalysts as a
171 waste component. The work also draws parallels with the EU in reviewing ISW activities and major
172 valorisation techniques that can relate to the case of Kuwait, especially in the petroleum industry
173 (e.g. spent catalysts). It critically assess the current situation of waste management within the developing
174 world region focusing on the industrial waste component, in a novel attempt to crucially develop a way
175 forward strategy based on best practices and future directions with major European industries. The work
176 in this review can pave the way for the governmental parties, in both Kuwait and industrial
177 countries, in targeting the main SW components that can reduce environmental burdens in industry.
178 An examination of the main recovery techniques utilized in spent catalysts is also reported in this
179 work.

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186 2. Spent Catalysts in the Context of Industrial Waste Management and Operational Challenges

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

205 The hydrodesulphurisation (HDS) method is used to remove sulphur from different kinds of organic
206 materials. The catalysts utilised usually are a combination of bimetallic of Ni/Co on an aluminium oxide
207 support. Fly ash is a residue of coal from thermal power plants, accounting up to a maximum of 20% of
208 the original coal feed, containing catalysts as well. Approximately 750 million tonnes of fly ash are
209 generated each year and almost all of it is disposed into landfill. HDS and fly ash disposal further
210 contribute to the spent catalyst disposal challenge, as well as, causing further strain on the environment
211 (Akcil et al., 2015). To overcome this, many refineries are looking into recycling fly ash into the cement
212 industry by potentially using it as a raw feedstock material.

213 FCC units, used to optimise the yield of gasoline (with high octane number) from crude oil, are another
214 major source of spent catalysts. FCC is used to convert distillates into gasoline range hydrocarbons
215 (Gianetto et al., 1994). FCC catalyst are usually made from active silica dioxide (SiO_2) and aluminium
216 oxide (Al_2O_3). The leading Oman refineries (e.g. Sohar and Mina Al-Fhal Refineries) which are located in
217 the same region as Kuwait (i.e. GCC), produce approximately 20 tonnes per day of FCC catalysts' waste
218 and an average of 250 kg of spent alumina waste. The majority of which is disposed of onsite or at

219 various disposal sites leading to environmental issues (Taha et al., 2011) . Tables 4 and 5 show the
220 generic properties and composition of spent catalyst waste produced from Oman refineries (Al-Jabri et al.,
221 2013) FCC spent catalyst metal composition can vary across the world. Metals such as vanadium (V) and
222 nickel (Ni) are also commonly present amongst the ones listed in Table 4.

223 A typical FCC catalyst is a mixture of an inert matrix of kaolin, alumina and silica. Different kinds of
224 zeolites are also applied such as types X, Y and ZSM-5. Approximately 750 ktpa of spent catalyst waste
225 is generated worldwide through FCC processing (Kasliwal et al., 2015) In extension to this, FCC catalyst
226 have recently been utilised for cement production and as a cement additive (for aluminate calcium
227 cement). These catalysts contain additional cobalt metals. In India, FCC spent catalyst are also known for
228 being used as a refractory for furniture manufactured from clay-based kiln. The particle size ranges from
229 60 to 100 μm (Ramezani et al., 2017). The generation and untreated disposal of such fine particles causes
230 major environmental concerns due to wide and uncontrolled dispersion of harmful metals present in the
231 catalysts. Recently, Su et al. (2019) showed that spent FCC displays advanced desulfurization properties.
232 The seriousness of spent catalyst waste disposal has brought forth a new research potential for spent
233 catalysts disposal along with recovery and reuse of metals. Amongst which molybdenum has gained
234 substantial attention to be recovered from hydrogenation plant wastes. This transition metal is widely
235 applied in the desulphurisation of petrochemicals and coal-based liquids/ fuels (Kar et al., 2004). Due to
236 the toxicity of catalysts, the United States Environmental Protection Agency (EPA) has classified all these
237 metals and catalysts as hazardous waste (Marafi and Rana, 2016). Metals such as V, Ni, Mo and Co get
238 leached by water and pollute the environment as well as generating harmful toxic gases such as hydrogen
239 cyanide (Marafi and Stanislaus, 2008). The hydrotreating of spent catalysts can have a life cycle between
240 three to four years and FCC catalysts get lost in the atmosphere daily and are offloaded daily/ fortnightly
241 (dependent upon the use and requirement) (Chiranjeevi et al., 2016). The increased exposure, toxicity and
242 disposal has developed numerous spent catalysts recovery methods, which are discussed in the sections
243 hereafter.

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251 3. Recovery Methods Used in Industrial Waste Management

252 3.1. Hydrometallurgical and Liquid-Liquid Extraction Process

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

262 Molybdenum (Mo) and platinum (Pt) are commonly used as catalysts with other base metals, rooted
263 (entrenched) upon catalyst pores supported on various materials such as aluminium oxide (Al_2O_3).
264 Vanadium (V) and Mo are valuable metals that can be recovered from different process such as
265 desulfurization catalyst, oil sands, slags, ashes and lean ores. Extensive research was conducted in
266 recovering V and Mo from waste catalyst from heavy oil desulphurization in Japan, Germany and
267 the USA. The common catalyst used in this process is MoO_3 catalyst promoted with CoO on Y-
268 Al_2O_3 base. It is reported that the experimental procedure follows four main steps: Pretreatment of
269 waste catalyst (washing with ligroin and drying), sodium chloride-water vapour roasting of the
270 calcined catalyst, leaching of the roasted catalyst and finally, liquid-liquid extraction, stripping and
271 precipitation (Biswas, 1985). To convert the metal values selectively (V and Mo) into the water-
272 soluble form in the second step, NaCl- H_2O vapour is used to roast the catalyst (calcined at 630°C).
273 Since the thermal hydrolysis of NaCl is much faster above its melting point (i.e. 800°C), experiments
274 are conducted above this temperature. The roasting reaction is measured by the absorption of HCl
275 gas in NaOH solution at pH 10.5 and correcting the pH by adding 1 M NaOH solution. Dried NaCl
276 (400°C) is weighed and grinded in a mortar to $152\ \mu\text{m}$ then placed in the furnace. The temperature
277 of the furnace is maintained within $\pm 10^\circ\text{C}$. When the desired temperature is reached ($\approx 630^\circ\text{C}$), the
278 saturated gas with water vapour is passed through the furnace (Biswas, 1985).

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283 3.2. Metal Recovery Using Solvent and Liquid/Soil Extraction

284 LIX 84-I (2-hydroxy-5-nonylacetophenone oxime) is a chelating organic extract. Solvent extraction
285 with LIX 84-I dissolved in kerosene at an O:A phase ratio of 1 to 1, is a technique applied to catalyst
286 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
287 al., 2010). The procedure is carried out to extract Mo(VI) from leached liquor with an initial pH
288 range of 0.5-3.0. The leaching solution is typically performed after baking the spent catalyst then
289 leaching it with sulphuric acid (H_2SO_4). By using a separating funnel for 5 minutes to equilibrate
290 both aqueous and organic solutions in equal volume, the trace content of the organic component
291 present in the solution is separated and pH is measured for raffinates. Afterwards, the raffinate is
292 diluted to reach a suitable concentration with 1% HNO_3 where the organic sample is stripped with 1
293 M NH_4OH (Park et al., 2010). The work aforementioned covered the effect of different variables on
294 the process such as pH, concentration of LIX 84-I, different stripping reagents, phase ratio and
295 diluents. The extraction of Mo(VI) increased with decrease in equilibrium pH and increased with an
296 increase in LIX 84-I concentration.

297 A different technique to recover V, Mo and Ni from waste catalyst produced from heavy gasoil
298 hydrodesulfurization is by using caustic soda solution (Rojas-Rodríguez et al., 2012). Spent catalyst
299 with a particle size between 1.5 and 7.3 mm is calcinated at temperatures up to 450°C . The reactions
300 lead to the removal of the sulphur, carbon, and the oxidation of vanadium sulphide. V and Mo are
301 precipitated as vanadium pentoxide and molybdenum trioxide, respectively. Nickel aluminate is
302 obtained from the residue after the removal of vanadium and molybdenum. The recovery achieved is
303 up to 95.1% and 95.5% for the V and Mo, respectively.

304 Solid/liquid extraction is also used to recover valuable metals from spent catalysts. The procedure
305 published previously by Rojas-Rodríguez et al. (2012) shows that a temperature between 20 and
306 100°C is typically employed in the hydrometallurgical extraction process, which uses citric acid for
307 leaching purposes. Firstly, the catalyst is exposed to citric acid after washing with distilled water for
308 30 min at 64°C . Spent catalyst is also autoclaved and rewashed with de-ionized water. Al, Ni, and
309 Mo recovery is achieved during this process with temperatures around 80°C . The importance of spent
310 catalysts is notable in several ways in catalyst preparation or for use in the metal industries. Marafi and
311 Rana (2016) showed that catalyst derived from atmospheric desulfurization (ARDS) can be treated in five
312 stages which were de-oiling, drying, grinding, sieving, de-coking. In fact, the spent catalyst is a mixture
313 obtained from four reactors in fixed portions suitable for metal recovery (Marafi et al., 2007; Sheeha et
314 al., 2013). When spent catalyst reaches the de-coking process, the catalyst is combusted (with oxygen) for

315 8 hours under a temperature range 300-600°C. Fig.3 shows the five stages of pretreatment of spent
316 catalyst typically used in ARDS processes.

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318 *3.3. Soda Roasting and Metal Leaching*

319 Soda roasting is used to extract high yields of V and Mo. High pressure is applied to recover Ni(CO)
320 as a solid using NaOH. Mo and V are recovered in high percentages reaching 95% when a roasting
321 temperature of 550°C is applied (Marafi and Stanislaus, 2011). In this process, leaching reagents which
322 are basic in nature, such as ammonium salts, are typically used. Ammonium per-sulphate (APS) is an
323 example of high efficiency leaching agents, due to its ability to oxidize and increase Ni and Al extraction
324 percentages. APS is formed of 7 wt% of active oxygen which release free radicals that promote metal
325 recovery especially for V, Ni, and Al, however, the acidic nature minimizes the ability of extracting Mo.
326 Valuable metals (e.g. Co, Cr, Cu, Ni, Mo, Ti, V, and W) form the majority of catalysts used in
327 industrial sectors with an estimate of 35 wt.%. A study performed by Gaballah et al. (1994)
328 investigated the degree of metal recovery by monitoring selective chlorination over a wide range of
329 temperatures (300-600°C). Mixtures of chlorinated gas were able to recover 98% of Ni and Co from
330 chlorinated deposits, 98% % of Mo, Ti, and W and 80% of vanadium compounds. Thermal cracking
331 between 20-1000°C was applied on hydrodesulfurization spent catalysts followed by the process of
332 chlorination (Gaballah et al., 1990). The volatiles were condensed through two condensers at different
333 temperatures as shown in Fig.4.

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348 3.4. A Note on the Spent Catalysts Generated Through Thermal Cracking and SW Upgrading

349 Both ISW and MSW have been researched extensively over the past few decades, namely in fuel and
350 energy recovery processes. These processes will typically utilise various types of catalysts for upgrading
351 products and distillates such as HZSM-5 and PZSM-5 (Demirbaş, 2005). These processes also revolve
352 around the concept of oils and hydrocarbon (HC) cracking to achieve the desired products acceptable to
353 the marketplace and standards (Vasile et al., 2001; Chandrasekaran and Sharma, 2019a; Al-Salem, 2019).
354 Further upgrading for the generated products can also be achieved with catalytic reforming in the
355 petroleum downstream industry (Sharma et al., 2014; Sharma and Bansal, 2016; Sharuddin et al., 2016;
356 Hafeez et al., 2019; Muhammad et al., 2015). All of which combined can lead to the accumulation of
357 spent catalysts that is not typically accounted for in ISWM surveys, strategy development and studies. It
358 is essential to understand the possible routes of spent catalysts accumulation as an ISW component within
359 such upgrading technologies. This will enable the determination of the best course of action for future
360 developmental plans in industrial waste mitigation and management strategies. The types of catalysts used
361 in such processes will be the focus of this section where the aforementioned recovery techniques in the
362 previous two sections can be successfully applied to extract valuable metals and products.

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

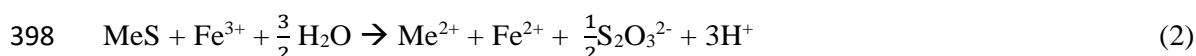
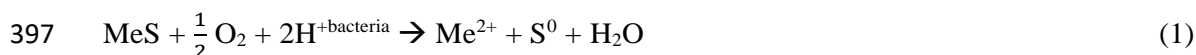
370 In an effort to study the possibility of integrating cracking technologies with the petroleum downstream
371 industry, Chandrasekaran and Sharma (2019b) have detailed a plan to consider pyrolytic units treating
372 Plastic Solid Waste (PSW) as a feedstock for fuel production whilst integrated to existing industrial
373 infrastructure. Butler et al. (2011) has also proposed to integrate both thermal and catalytic pyrolysis in
374 petroleum downstream industries to upgrade and produce gasoline and diesel; while utilising a feedstock
375 from PSW. Catalysts that are usually used in such processes are zeolite based ones. Bargi and Williams
376 (2002) showed the effect of using Y-zeolite on the pyrolysis of polyethylene (PE) in a two stage fixed bed
377 reactor system. The evolved gases and oil generated consisted mainly of aliphatic compounds. Lin et al.
378 (2012) used a hybrid FCC series catalysts to pyrolyse a mixed PSW feedstock under an operating
379 temperature between 330 to 450°C. Oil produced was estimated to be 87 wt.% of the total product yield.
380 Table 6 also depicts major studies conducted in recent years using catalytic pyrolysis to upgrade SW. On

381 the other hand, gasification technology where sub-oxygen content of carrier gas is applied in the
382 degrading media, has also been used with aid of catalysts to upgrade various feedstock. Readers are
383 referred to Arena (2012), Wu and Williams (2010) and Al-Salem et al. (2017) for additional content on
384 both pyrolysis and gasification of various organic substances.

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386 3.5. Biotechnological Processes

387 Biotechnological processes require longer leaching times to gain efficient extraction when compared
388 to other conventional methods. They are typically directed at winning processes for copper (Cu)
389 recovery. On the other hand, bioleaching methods are more cost effective and environmentally
390 friendly than other conventional recovery techniques. They have been investigated on a small scale
391 for exhaust catalysts to study their potential as a recovery process. The following reactions show a
392 simplified mechanism for metal sulphide recovery from exhaust catalyst in a solid matrix form.
393 Equation 1 represents direct *bio-oxidation* of metal sulphides onto the matrix. Equation 2 shows the
394 chemical oxidation by iron which is generated by bio-oxidation in Equation 3. Equations 4 and 5
395 show the formation of sulphide ion through bio-oxidation of sulphur and thiosulphate, respectively,
396 for a complete reaction case.



402 In the process, the hydrocarbons (HC) from the catalysts are first removed by washing with ethyl alcohol.
403 The microorganism culture, containing Fe/S oxidizing bacteria, are cultivated under acidic conditions and
404 the bioleaching is carried out by incubation at 30°C. Results show that Ni and V could be successfully
405 extracted of (Beolchini et al., 2010). This process is a cost effective and environmentally method for spent
406 metal recoveries.

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408 *3.5.1. Precious metal recovery via AquaCat*

409 AquaCat is a method to recover metals from spent heterogeneous and homogenous catalysts using a
410 process based on supercritical water oxidation which converts carbonaceous material to less noxious
411 compounds, leaving the precious metals as their oxides (Grumett, 2003). The technology was
412 commissioned at Johnson Matthey's Brimsdown (UK) facility in 2002 and operated until 2007 when
413 the process and technology rights were purchased by Supercritical Fluids International (Smith et al.,
414 2013). It consists of two stages, the determination of the metal content by direct sampling and the
415 utilisation of supercritical oxidation to convert carbon materials into less harmful compounds. This
416 method targets organometallic-based catalysts which have historically been treated by high energy
417 intensive methods such as combustion. In the direct sampling, the spent catalyst in the form of a wet
418 filtered cake (between 5-500 µm particle size) is added to water and a surfactant in a vessel and
419 agitated to form a homogenous dispersed mixture, which is analysed to determine the metal content.
420 The water based slurry is then pumped to the feeding tank where the supercritical water oxidation
421 takes place. Water becomes supercritical above 374°C and 221 bar, and by that stage its viscosity
422 will be close to that of its vapour combined with a higher fluid density. At this stage, the organic
423 substances become soluble and the water will act as a solvent for the oxidation. For homogenous
424 catalysts, high pressure water is fed into the economiser. The catalyst is inserted directly into the
425 reactor after oxygen injection as it does not mix with the supercritical water. The AquaCat process
426 requires less energy and exhibits lower CO₂ emissions and doesn't give rise to SO_x and NO_x
427 emissions as opposed to incineration. Direct sampling allows safer handling and treatment of
428 hazardous materials as it can be collected in bulk (Grumett, 2003). The precious metals are recovered
429 in a separator as depicted in the figure.

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442 3.5.2. Bio- hydrometallurgical Process

443 In this process, microorganisms have the primary role of leaching instead of using reagents to do this
444 activity. Microorganisms (e.g. bacteria and fungi such *Bacillus sp.*, *Aspergillus niger* and *Penicillium*
445 *simplicissimum*, *Saccharomyces cerevisiae*, *Yarrowia lipolytica*) interact with metals for the purpose
446 of solubilization. Previous studies were conducted on the biological recovery of metals from sludge,
447 fly ashes, batteries, and electronic waste (Lombardi et al., Wu and Tin, 2009; Carranza et al., 2009;
448 Xin et al., 2009; Bayat and Sari, 2010; Zheng et al., 2009). Gaballah et al. (1994) showed that
449 various hydrometallurgical processes are available for metal recovery. They recovered metals when
450 catalyst roasting is the typical recovery route. After biological uptake, it was reported that chlorides
451 of Mo and V were volatilised at 500°C whilst those of Co and Ni remained at solid state until 700°C
452 was reached. During bio-uptake hazardous compounds such as HCL, H₂SO₄ and alkalis were
453 separated from valuable metals (e.g. Mo, V and Al).

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455 3.5.3. Pyrometallurgical process

456 The pyrometallurgical process is a nominal choice when physical properties are negligible. It
457 recovers metals from industrial waste after thermal treatment (smelting, roasting, and refining). In
458 synthesis gas production, especially in low temperature processes of carbon monoxide conversion
459 with steam to form hydrogen for the production of ammonia or methanol, CuO-ZnO-Al₂O₃ catalyst
460 was considered by Malecki and Gargul (2018). The spent catalyst could be a valuable source of
461 metal using pyrometallurgical and hydrometallurgical processes to recover more than 66% of the
462 copper in metal form and 70% of zinc as ZnO. The objective in the pyrometallurgical process is to
463 maximize the yields of copper (Cu) and zinc (Zn) extracted from the spent catalyst in the recovery
464 process so test melting is initially performed. Slag-forming additives are needed in the recovery
465 process to obtain the lowest melting point of the slag which s also has a meaningful effect on the
466 recovery of Cu to alloy and Zn to dust. In the additives CaO, SiO₂ and Na₂O were shown to give the
467 lowest melting point when the components were in the same weight percentage. The catalyst was
468 loaded into a graphite crucible and placed in an induction furnace at a temperature range of 1100-
469 1300°C to obtain the maximum stripping of zinc and the formation of liquid copper. Coal is added to
470 the process to reduce CuO and ZnO. After melting, the liquid products were cooled, separated and
471 weighed for chemical analysis. On the other hand, the hydrometallurgical method consists of two main
472 processes, leaching and filtration. The zinc oxide and copper oxide leaching process follows two stages:
473 leaching in NaOH solution (temperature 75°C for 120 min, NaOH concentration = 200g dm⁻³, 1/s = 10)
474 followed by leaching in H₂SO₄ solution (temperature 60°C, for 120 min, H₂SO₄ concentration = 180 g dm⁻³

475 ³, 1/s = 10). Zinc has high resistance to both acid and alkaline so after leaching an insoluble residue is
476 formed, which was filtered to separate the precipitate. The resulting yield of copper in the solution is
477 about 98% with 62% zinc in the alkaline solution.

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479 3.5.4. Recovery of Catalysts from Automotive Catalyst Deposits

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

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508 *3.5.5. Recovery of catalysts from in situ heavy oil upgrading*

509 In situ methods to recover heavy oil fractions are gaining momentum. These are largely based on
510 combustion methods but in situ catalytic upgrading process such as CAPRI (Catalytic Petroleum
511 Recovery In situ) are employed to further improve the upgrading of the heavy oil. The catalyst is typically
512 packed into an annulus around the horizontal production well, however some researchers have
513 investigated the use of dispersed catalysts to improve the issues of deactivation associated with packed
514 bed catalysis (Al-Marshed et al., 2016). The recovery of spent catalyst from in situ recovery processes
515 poses challenges. The catalyst can be retained in the formation and it has been suggested that dispersed
516 catalyst injected in the form of nanoparticles may either agglomerate into larger particles or adsorb to the
517 rock surface especially at the temperature and pressure conditions. To negate this ultradispersed
518 suspensions with high stability and selectivity are needed (Guo et al., 2016). Spent dispersed catalysts can
519 be recovered from the oil using conventional demetallisation processes that are used to remove metals
520 from heavy oil. Demetallisation processes are valuable in their own right as metal recovery processes; a
521 third of all vanadium produced by Russia stems from demetallisation of heavy oil and 8% of vanadium
522 world production comes from oil feedstocks. Demetallisation takes place in the electrostatic desalter at a
523 refinery although this processes is typically modified to deal with stable organometallics with electrolysis
524 cells and polymeric sorbents being used to recover metals (Magomedov et al., 2015).

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536 **4. Regulations Governing Spent Catalysts Handling and Industrial Waste**

537 *4.1. European Union (EU) Regulations*

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

547 EU regulations for waste have been divided into various sections. The Directive of landfill waste (EC/35)
548 aims to reduce and prevent disposal as much as possible, to have little to *no impact* on surface water,
549 groundwater, soil or human health. To achieve this, specific guidelines have been set. EU landfill sites are
550 usually split into three different sections: hazardous waste, non-hazardous waste and inert waste (non-
551 incinerable/ decomposable waste). Biodegradable waste is discouraged and used tyres, liquid waste,
552 flammable waste, explosive or corrosive waste are not allowed in landfill sites. Only treated waste can
553 enter landfill sites. This is tracked by issuing permits and regular operator checks (EU, 2000).

554 Hazardous waste regulations were set by the European Economic Community and the Basel Convention.
555 This regulates the boundaries for which the hazardous waste disposal must abide by. It consists of three
556 main sections: minimising transported quantities, treatment and disposal of wastes as close to the place of
557 generation and to prevent/ minimise the generation of waste from the beginning (Community 1993). Due
558 to the recent increase in ISW generation, the waste safety and guidelines have become more severe. EU
559 has also given formal consent for a ban prohibiting the export of waste to non-OEDC countries a while
560 ago (Parties and This, 1987).

561 To control industrial emission, the EU has devised a framework of interconnected permitting. This is
562 where the emission permit must take into consideration the industrial plant's whole environmental
563 performance (from start up to shut down) and to avoid the pollution shift between mediums (such as air,
564 water and land). Priority is given to prevent pollution by intervening at the generation point and ensuring
565 efficient and sustainable use/ management of natural resources. This legislation covers the following
566 industrial sectors: energy, metal production/ processing, minerals, chemicals and waste management. This
567 allows the public to be given an early opportunity to contribute to the permitting process and installations
568 (EU 2004).

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

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599 4.2. *Governing Standard Within the State of Kuwait and Lessons Learnt*

600 The governing body within the State of Kuwait concerning the handling and disposal of waste is the
601 Kuwait Environment Public Authority (KEPA). One of the first things that comes to mind concerning the
602 issue of ISWM and waste standards within the state, is the fact that various components of waste fall
603 under the jurisdictions and responsibilities of various sectors. A prime example is the fact that MSW is
604 managed by Kuwait Municipality (KM), whereas ISW with the exception of oil and gas industries fall
605 under the responsibilities of the Public Authority for Industry (PAI). Each petroleum refinery is
606 contracted to manage its own waste through national landfill sites, and industrial wastewater is managed by
607 a different sector of the government through the Ministry of Public Works (MOPW). This trend goes on
608 to create major controversy among various parties in Kuwait, and there exist no governing body to liaise
609 between all responsible parties. On the other hand, the regulations that KEPA have developed are being
610 revised and improved constantly. The current regulations within the state also present major gaps and are
611 not descriptive enough. Major technical and scientific input is required to have a comprehensive
612 regulation by KEPA for governing WM activities within Kuwait. Generally, the management of SW is
613 governed and regulated by Law No. 16/1996 and by-law Directive 210/2001 (Kuwait Al Youm, 2001).
614 These laws assign waste in Kuwait to the categories of hazardous and non-hazardous based on the Basel
615 Convention (BC, 1989). Private and cottage industries in Kuwait have to abide by these regulations by
616 law. In addition, KEPA Directive (law) No. 5/2016 identifies various definitions and aspects with regards
617 to WM, and law No. 6/2017 sets regulations for managing waste generated from medical and hazardous
618 sources. It also regulates radioactive waste within the country (Kuwait Al Youm, 2016; 2017). By
619 comparison to the case of the EU, and examining the aforementioned generation trends of ISW in Kuwait,
620 a number of recommendations can be withdrawn as a strategy for the country. The State of Kuwait can
621 benefit immensely by supporting the establishment of governmental and private industries alike, in
622 creating a market for ISW valorisation. These industries also can benefit immensely and within state
623 borders by trading recovered metals and chemical from ISW namely spent catalysts. The regulations in
624 Kuwait can also start to accommodate such industrial practice, and one governing body can be
625 responsible for managing the various waste management aspects in the country, instead of the current
626 situation that creates confusion between waste generating sectors. The sustainability of the development
627 of such practice is also something that can't be neglected. The sole method of disposal for ISW in Kuwait
628 is landfilling in a governmental site. This is a major cause of land loss, generation of environmental and
629 social associated burdens and land reclamation/rehabilitation costs. These issues can be eliminated by
630 establishing both the appropriate standards and industry to govern ISW, more including spent catalyst
631 which Kuwait consumes by a large amount due to its industrial nature.

632 **Conclusion**

633 Improper management of industrial solid waste is beginning to be recognised by many business sectors
634 However, the action to address the problem in an efficient and sustainable manner is yet to be established.
635 Manufacturers are gradually shifting towards the reuse of spent catalyst and have developed recovery
636 methods such as hydrometallurgical and liquid-liquid extraction process (chemical leaching method post
637 metal recovery, commonly used to recover Mo and V); Solvent and Liquid/soil extraction (solvent
638 extraction with LIX-84-1 dissolved in kerosene, commonly used to recover V, Mo and Ni); soda roasting
639 and metal leaching (used to extract V and Mo at high percentages but at the expense of a temperature
640 range of 500°C – 700°C). Biotechnological processes are also commonly used to extract V, Mo and Ni, at
641 the expense of longer leaching time however, these methods prove to be more cost effective than
642 conventional ones (including thermal cracking, gasification and pyrolysis). All of these proposed and
643 applied processes mostly aim at a small number of precious metals, making them limited to the recovery
644 of catalysts that may contain V, Mo and Ni. Other valuable metals such as Pt, Al, Zi, may not be
645 compatible. Legal guidelines across Europe and Kuwait has set strict guidelines in regard to ISW and its
646 management, based on the hazardous properties of catalysts. Regeneration of spent catalyst/ metal
647 recovery require international transport and numerous post and pre-treatment steps. The transport across
648 different borders is one the biggest drawbacks as different countries have different rules, regulations and
649 standards thus making the management plan harder to execute and successfully implement.

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658 **Abbreviations**

659	Al ₂ O ₃ ;	Aluminium Oxide
660	ARDS;	Atmospheric Desulfurization
661	Cd;	Cadmium
662	Cr;	Chromium
663	EC;	European Commission
664	EU;	European Union
665	EU;	European Union
666	FCC;	Fluid Catalytic Cracking
667	GCC;	Gulf Council Countries
668	HDS;	Hydrodesulphurisation
669	ISW;	Industrial Solid Waste
670	KEPA;	Kuwait Environment Public Authority
671	KM;	Kuwait Municipality
672	Mo;	Molybdenum
673	MOPW;	Ministry of Public Works
674	MSW;	Municipal Solid Waste
675	Ni;	Nickel
676	OECD;	Organisation for Economic Co-operation and Development
677	OPEC;	Organization of the Petroleum Exporting Countries
678	PAI;	Public Authority for Industry
679	Pb;	Lead
680	PE;	Polyethylene
681	PSW;	Plastic Solid Waste
682	Pt;	Platinum
683	SiO ₂ ;	Silica Dioxide
684	SWM;	Solid Waste Management
685	V;	Vanadium

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