SOLID WASTE SPENT CATALYST'S METAL RECOVERY

FROM NORTH ATLANTIC REFINING LIMITED'S PETROCHEMICAL PLANT IN COME BY CHANCE, NEWFOUNDLAND AND LABRADOR

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1.   Acknowledgements

2.   Executive Summary

A hydrometallurgical process has been developed for metal recovery from spent HPCs. After analysing our catalyst, preliminary experiments showed that aqua regia is the most effective leaching agent to dissolve metals from our spent catalyst samples. Two amine-based extractants (Alamine308 & Alamine336), and one quaternary ammonium salt (Aliquat336) were diluted in toluene and were tested for cobalt, nickel, and molybdenum extraction from leached catalysts in aqua regia. A central composite design (CCD) was employed for our experimental design, and the best extractant was selected based on the ICP analysis on the efficiency, concentration requirement (cost-effectiveness), and required contact time for optimum metal removal. The effects of significant parameters on the extraction processes have been measured, and statistical models were developed using Design Expert software. ANOVA results were also studied to measure the accuracy and significance of the fitted models. Optimization of each solvent extraction process was completed and optimum points were determined for maximum metal removal from spent HPCs.

3. Glossary and acronyms

2FI	Two-Factor Interaction
AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
CCD	Central Composite Design
EDTA	Ethylene Diamine Tetraacetic Acid
EPA	Environmental Protection Agency
HDS	Hydrodesulphurization
HPC	Hydroprocessing catalyst
HYD	Hydrogenation
ICP-OES	Induced Coupled Plasma Optical Emission Spectrometer
MSDS	Material Safety Data Sheet
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SX	Solvent Extraction
TPO	Temperature-programmed oxidation
TSO	Time on stream
USEPA	United States Environmental Protection Agency

4.   Introduction

4.1 HPCs

4.1.1. Usage in petrochemical industries

HPCs (HPCs) are widely used in petrochemical industries, mostly to purify the hydrocarbon processing streams. These catalysts are mainly employed to enhance the efficiency of the process, remove sulphur from the stream, and to break the heavier hydrocarbons to short-chain sulphur-free hydrocarbons [1]. Spent HPCs are classified as hazardous solid wastes produced in petrochemical industries according to the United States Environmental Protection Agency (USEPA) due to the presence of hazardous materials including, but are not limited to, the heavy metals, metal oxides, and metal sulphides [2]. These catalysts have very high porosity and surface areas, in which coke can be deposited, to deactivate the catalyst. A sample of the spent HPCs which were used in this study is shown in Figure 1. Our sample was obtained from North Atlantic Refining Limited's Come By Chance petrochemical refinery.

Figure 1. Spent HPC in powder form before any treatment, as provided by North Atlantic Refining Limited. [3]

Recently, the use of HPCs has been drastically increasing due to the strict regulations on mandatory sulphur-free or ultra-low sulphur contents in petroleum products such as diesel and jet fuels [4]. For instance, the maximum sulphur content in on-road diesel fuel is 10-15 ppm [5]. All

indications suggest that the production and usage of HPCs are going to increase at least in the next ten years, and the market demand for these catalysts is estimated to grow with an annual rate of 4.4% [6]. The market for fresh hydrotreatment catalysts is currently around 120,000 tons per year. It has been declared that 50% of this amount (60,000 tons per year) are employed for cleaning the fuels produced as column distillates, and the remaining 50% are used to upgrade and purify the residues. The same trend is expected for the hydrocracking catalyst market, which is currently around 10,000 tons per year and is expected to grow at a rate of about 5% per year [4].

The increasing rate in fresh catalyst usage is the most significant factor for the increase of the discarded spent catalyst; however, there are many other factors upon which the total volume of spent HPCs discarded as solid waste depends. These parameters include, but are not limited to:

- Increasing need for fresh catalysts in hydroprocessing units to meet the increasing demand for production of ultra-low sulfur containing fuels
- Reduced cycle times due to severe operations in diesel hydrotreating units
- A constant growth in the distillation processing of heavier feed streams with much higher sulfur and metal contents
- Reduced catalyst deactivation times due to faster deactivation rate and unavailability of reactivation processes for residue HPCs

The amounts of spent catalysts discarded from the hydroprocessing units are always higher than those of the fresh catalyst amounts employed in that unit, due to the formation of coke and metal deposits on the catalyst surface [7]. These metal complexes and the metals present in the fresh catalysts in the first place, are both potential hazards, subject to the USEPA's environmental regulations.

4.1.2. Composition of HPCs

The composition of the HPCs depends largely on the type of catalysts and their supports used for a specific product stream. The composition of the catalysts employed for light and heavy feedstock is quite different. Light feeds do not usually contain metals and asphaltenes, and the catalyst composition is very critical in these situations. The choice of the catalyst and its

composition should be based on the type and content of sulphur and nitrogen heteroatoms. For heavier feedstock containing high concentrations of heavy metals and asphaltenes, the physical properties of the catalyst are much more important than the catalyst chemical composition, as the shape, size, and porosity of the catalysts are critical factors to achieve the full utilization of the catalyst. In some cases, different modifications may be necessary, depending on the type of the feedstock.

To date, various catalysts have been developed for hydroprocessing purposes, containing different types of metal complexes. The Mo(W)-containing supported catalysts, are typically promoted by cobalt and nickel, and have been employed in hydroprocessing units for decades. The predominant catalyst support for hydroprocessing processes has been γ-Al_2O_3; however, other supports have also been used such as silica-alumina, zeolites, Al_2O_3-TiO_2, and TiO_2 to increase the catalyst activity and enhance its performance. In $CoMo/Al_2O_3$ catalysts, several species can be found on the catalyst surface such as MoS_2, Co_9S_8, and Co/Al_2O_3. It should also be considered that the metals and metal complexes contained in spent HPCs not only depend on the synthesis of the fresh catalysts, but also largely depend on the feedstock composition and its heavy metals contamination. [8]

4.2. Deactivation and regeneration of HPCs

HPCs are used in various petrochemical processes such as hydrogenation (HYD), hydrodesulphurization (HDS), hydrocracking (breaking the C-C bonds), and many more catalytic processes. Hydrocracking catalysts mostly contain a molybdenum support on alumina as a typical carrier, and promoted by nickel and cobalt. Hydroprocessing reactions take place on the active metal sites on the sulphur vacancies located on the edge of the MoS_2 crystallites. These vacancies are much more active when promoted by cobalt and nickel also. [1]

Deactivation of HPCs is defined by the decline in the rate of hydroprocessing reactions with time on stream (TOS), and usually occurs when a strongly adsorbed molecule occupies an active vacancy. These molecules can be nitrogen compounds, coke molecules, metals, and any other basic molecules. Normally, deactivation takes place by multiple causes, with different strengths. These causes can be defined as active site blockage by strongly adsorbed species,

active site coverage by coke or different metals, and/or sintering at high temperatures. Some of these causes and their significance on the catalyst deactivation for three typical hydroprocessing processes are listed in Table 1 [1]. Deactivation is generally dependant on catalyst structure, operating conditions, and also the feedstock characterization. [5]

Table 1. Relative effects of coke and metals deposition on the deactivation of HPCs in three typical reactions

Catalyst function	Relative effect	
	Metals	Coke
Hydrodesulphurization (HDS)	Moderate	Moderate
Hydrogenation (HYD)	Weak	Strong
Hydrocracking (breaking C-C bonds)	Weak	Very strong

Different types of deactivation may occur with different degrees depending on the characteristics and compositions of the feedstock and are usually followed by the S-shaped curve of temperature vs. time-on-stream, illustrated in Figure 2 (*top*). This trends shows that the activity decline rate can be offset by increasing the temperature. The typical deactivation curve for activity loss vs. time is also shown in Figure 2 (*bottom*). Initially, coke deposition and adsorption of poisons can dominate the catalyst deactivation for a heavy feedstock, which can cause a rapid deactivation of the catalyst in several days. At this point, little contribution of metals to the overall catalyst activity loss may be observed. Deactivation by metal deposits usually occurs during a much longer period of almost stable activity (mostly linear increases with time on stream), until the drastic deactivation which is typically caused by pore restriction, sintering, and/or blockage of the pore structure at the end of the run [1,9]. When metals are deposited on the catalyst surface, they affect the permeability of the catalyst. For example, vanadium and nickel are gradually converted to sulphides. Permeability and metal deposition have adverse effects on each other, as the metal deposition increases, permeability is reduced, and the catalyst activity diminishes.
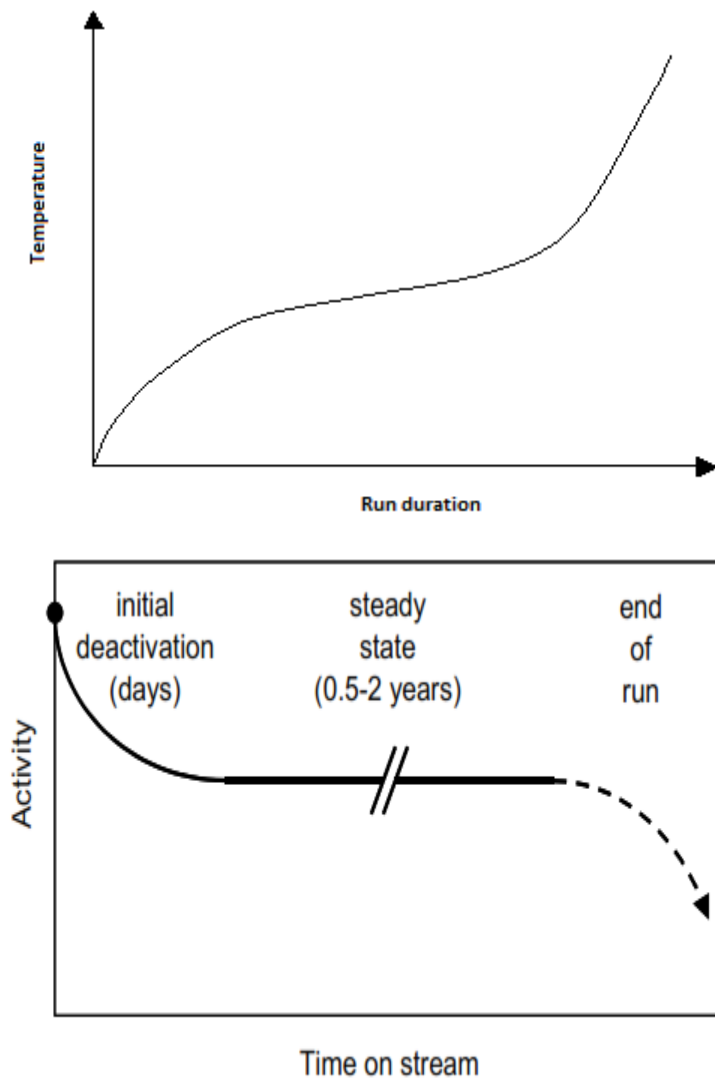
Figure 2. Typical S-shaped catalyst deactivation curve (*top*) [1], and typical activity loss curve for a HPC vs. time on stream (*bottom*). [9]

During the hydroprocessing of light feedstock, the catalyst can last for several years in operation; however, a prolonged exposure to high operating temperatures can cause catalyst recrystallization by modifying the porosity and surface area [5]. For distillate feeds, coke deposition and poisoning with nitrogen-containing compounds are the most significant factors causing the catalyst deactivation, sometimes occurring in parallel. As the boiling range of the feed increases, the coke deposition on the catalyst active sites increases too. For nitrogen-containing compounds, their strong adsorption to the active sites on the surface of the catalyst

can cause deactivation. As the feedstock goes heavier and the contained metals and asphaltenes increase, the coke deposition usually increases. The amounts of coke deposited on the catalyst active sites are governed by the feedstock resins and asphaltenes, as shown in Figure 3 [8].
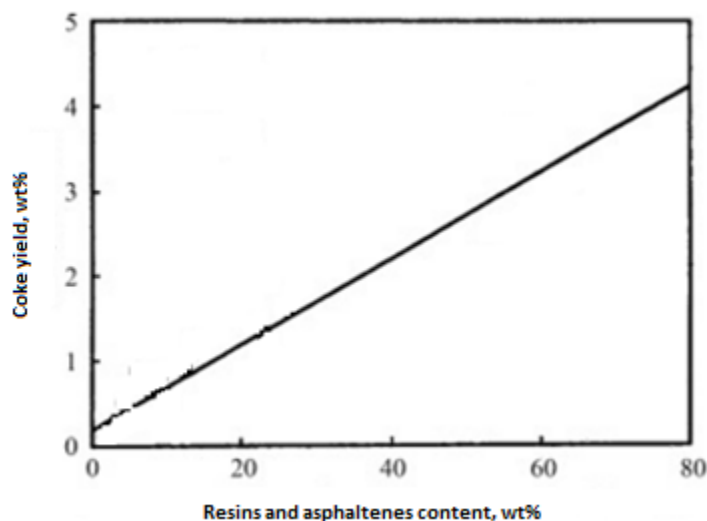
Figure 3. Deposited coke on HPCs as a function of the content of resins and asphaltenes according to three experimental samples for NiMo/Al$_2$O$_3$ catalysts at 8.5 MPa of H$_2$ and 673 K [8]

4.2.1. Extending the lifecycle of HPCs

Research and development is a key factor toward synthesis of improved HPCs, which require a clear, deep understanding of the catalyst key properties such as nature of the active sites and their structure, the textural characteristics of catalyst supports (alumina, carbon supported, etc.), and pore size distribution and its significant influence on the catalyst's performance.

Different methods have been proposed to extend the lifecycle time of HPCs; however, a patented successful method is developed to increase the life-time of these catalysts. The "React Technology" was introduced in 2003 by Albemarle and Nippon-Ketjen to restore the performance of spent HPCs close to their original levels [10]. Currently, more than 150 customers worldwide are using this patented method in more than 750 petrochemical units [10].

"React Technology" uses a proprietary regeneration process which is then followed by re-dispersion of the active metals on the catalyst surface. For HPCs, the active sites are recreated and protected by an organic coating. The "React Technology" treatment is capable of improving the catalyst performance, and also enhancing the activity of the catalyst, up to typically 95% of its initial value [10].

4.2.2. Regeneration of HPCs

When a catalyst is deactivated, its activity decreases, and its performance is lower than what is expected. Deactivation also causes poor catalyst stability and decreased conversion rate with time [1]. The first action required in order to achieve the minimum conversion rate required for the efficient process when deactivation occurs, is to gradually enhance the temperature of the catalyst bed. After some time, this method is no longer effective due to severe coke formation and undesirable product yields. Deposited coke can be of the soft or hard (refractory surface coke) types which are adsorbed weakly and strongly onto the active sites of the catalyst, respectively [1]. Temperature-programmed oxidation (TPO) can help the company to analyze the type of the produced coke.

As the catalyst activity goes below the minimum value required for the process, the first choice is to regenerate the catalyst, since disposal and/or landfilling should be considered as the last option. The regeneration process usually includes burning off the carbonaceous deposits by oxygen and inert gases under controlled temperatures [1]. Uncontrolled temperatures may lead to recrystallization and/or sintering of the catalytic active phases [8].

Complete regeneration of the catalyst is very difficult to achieve and is practically impossible; however, 80% recovery of the fresh catalyst activity is required for the regeneration process, to be considered desirable [8]. In most cases there are metal sulphides and other metal complexes on the catalyst active sites which cannot be burned off completely. In general, poisoning by metal deposition is irreversible, and vanadium and nickel oxides are also left on the surface of the catalyst after regeneration. It is possible to eliminate the metal deposits from the surface of the catalyst by mild chemical methods such as leaching (not very strong acids) without destroying the support and avoiding excess removal of molybdenum [1].

Another problem, which may occur during the oxidative regeneration processes, is the sintering and redistribution of the active metallic phase of the catalyst with the consequent loss of the catalyst's active sites. In order to restore the maximum catalytic activity possible in the regeneration process, careful handling of the catalyst, and control of the regeneration temperature and gas composition such as oxygen and nitrogen are significant factors to consider [1].

Another option to recover the deactivated catalyst's activity is reductive regeneration. In this case, at the end of the operation, the feed streams are discontinued, but the H_2 supply will be continued leading to the regeneration of the catalyst. There is far less information on reductive regeneration of HPCs which may be due to the fact that in most cases, oxidative regeneration has been the most effective option for catalyst activity restoration, and even in very high temperatures, reductive regeneration cannot compete with the oxidative regeneration in case of activity restoration [8]. Other regeneration processes such as regeneration with H_2O, CO_2, and NO_x have also been suggested in the published literature, which are not as effective and well-known as the oxidative regeneration and are described elsewhere [5].

4.3. Environmental aspects of spent HPCs

Production of HPCs has been increasing and thus, more and more metals should be extracted from mines and mining ores to be employed in catalyst production facilities. The extraction of these metals such as cobalt, molybdenum, vanadium, and specially nickel has several adverse impacts on the environment such as more acid mine drainage (AMD) produced in mining sites. On the contrary, operation of the HPCs in sulphur removing processes in petrochemical industries has several advantages to the environment. The most significant advantage is the reduction in the amount of sulphur present in produced fuel product such as diesel or jet fuels. Combustion of these petroleum refinery products produces hazardous gases and if the sulphur is present in higher amounts, toxic SO_x gases may be produced. Efficient operation of HPCs can reduce the amounts of SO_x gases released into the environment. Disposal of the solid waste HPCs, however, causes serious challenges for researchers in industry and academia as these hazardous wastes cannot be released into the landfill without proper treatment(s) [2]. Landfilling is the last option to consider and all efforts must be made to minimize the landfilling spent HPCs [5]. In this section, the hazardous nature of the spent HPCs,

how they are contaminated, and how to handle these solid wastes are presented. Finally, life cycle assessment and pollution prevention techniques are reviewed.

4.3.1. Disposal regulations

There are several strict regulations regarding the disposal and/or landfilling of spent HPCs, as they are considered hazardous solid wastes produced in petrochemical industries by the USEPA [2]. These regulations include, but are not limited to (directly quoted) [10]:

- No waste may be exported to any Third World countries having inadequate facilities
- No waste may be taken to a facility that is not properly equipped to recycle the hazardous solid wastes
- The country, state, and/or the province, where the waste requiring treatment is generated, is responsible for its treatment
- Hazardous waste for recycling may be shipped to authorize facilities anywhere in the world, but only under a highly regulated system

For spent HPCs, recycling may involve shipment of wastes to a company capable of regenerating spent catalysts for reuse. When HPCs are deactivated and can no longer be regenerated, they should be treated properly before disposal. Landfilling or disposal of these hazardous materials are strongly prohibited by environmental authorities. There are several hazardous metals available in the spent HPCs which are responsible for their toxicity, and which should be removed by efficient, easy-to-implement, and environmentally-friendly processes, before catalyst disposal and/or landfilling.

4.3.2. Catalyst contamination

After the catalysts are deactivated, and can no longer be regenerated, they are considered to be spent catalysts which are environmental hazards, as there are various contaminants on their surface. These contaminants can originate from different sources such as the feed (mainly vanadium, nickel, arsenic, sodium), or from additives employed in refining operations (silicon, lead), or from corrosion (iron) [11].

Nickel and vanadium, if present in feedstock, are included in larger-size molecules (with boiling points >500 °C) in the heavier fraction of vacuum gas oil. These larger molecules can easily be decomposed in the nickel and vanadium sulphides on the surface of the catalyst. However, it is more difficult to regenerate deactivated catalysts contaminated with vanadium due to their ultra-low activity, and reuse or regeneration of the catalyst is not recommended when they are deactivated with more than 1-3 wt. % vanadium [11].

Arsenic may also be present as a contaminating material in many crude oils. If present, there is usually a sharp steep arsenic gradient between the top and the bottom of the fixed-bed reactor, as they are extremely reactive in the conditions of hydroprocessing and thus easily decomposed and adsorbed on the surface of the catalyst. They become decomposed at the first stages but usually not beyond that. Arsenic is a serious and significant poison to the catalyst and can make a hydroprocessing catalyst deactivated in the very low concentrations of only 0.2-0.4 wt. % [11].

Other metals can also be considered serious contaminants. For example, sodium can be present in spent HPCs, if caustic soda is introduced in upstream operations. Another example is silicon in the feedstock, which can originate from different foaming agents, added in the lighter fractions of coker or visbreaker operations. Contamination with iron can also occur resulting from corrosion of upstream equipment.

When a catalyst is deactivated and cannot be regenerated, the amount of each contaminant such as vanadium, cadmium, arsenic, silicon, molybdenum, and sodium should be measured and compared to the USEPA regulations for disposal and/or landfilling. These solid waste spent catalysts should also undergo proper treatment(s) before their disposal into the environment [2].

4.3.3. Handling of spent HPCs

In many cases, when the catalyst performance decreases, the decline in catalyst activity can be offset by adjustment of some operating parameters (e.g. temperature). When this method is not capable of restoring the catalyst activity, the reactor operation has to be discontinued. The reason for this can be a high pressure drop caused either by solid accumulation on the front of the fixed bed or due to the attrition of catalyst particles and formation of clumps, which are caused

by temperature excursions. In most cases, catalysts have to be removed from the fixed bed reactor, which then should be reloaded with either fresh or regenerated catalysts. Many fixed bed reactors employed in hydroprocessing units are equipped with nozzles, specified for dumping the catalysts, as illustrated in Figure 4 [12]. In a few situations, refinery companies apply their own specific procedures; however, in most cases, to withdraw the spent HPCs, the nozzle is opened under a purge of nitrogen (N_2). Dry ice (CO_2) is also added to the filled containers to expel the remaining air. The removal of the last amounts of HPCs may require personnel to enter the reactor, taking into consideration all safety regulations, i.e. it is essential that in such cases, the personnel carry all mandatory safety equipment to prevent any serious harm or injuries.
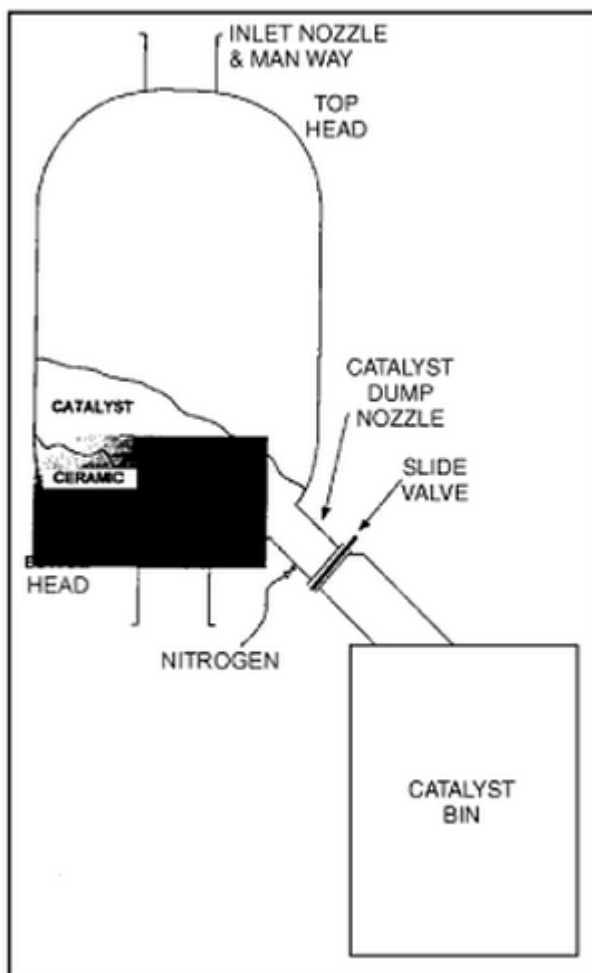
Figure 4. Schematic of the withdrawal system of spent HPCs from fixed bed reactors [12]

4.3.4. Pollution prevention techniques

Besides extending the lifecycle of catalysts, as previously discussed, many different techniques have been proposed to reduce the pollution effects produced by using HPCs. Many researchers suggest that using alternative catalysts with similar physical and chemical properties and equal efficiencies, but lower levels of toxicity can be an excellent option to reduce pollution (source reduction technique). Other techniques provide solutions regarding the optimization of the whole sulphur removal process, so the catalyst will last longer (increasing product life technique) in new facilities or optimized facilities available, designed for less environmental impacts.

In general, the quantity of spent hydroprocessing catalyst discarded as solid waste can be reduced, if the useful life of the catalyst before disposal can be extended for a longer period. This can be done in three ways [13]:

- Employing the catalyst with reduced performance in less demanding catalytic processes
- Regeneration and/or reuse using novel techniques
- Reducing catalyst consumption by using improved catalysts with longer life time such as nano catalysts with more surface area and porosity

4.3.5. From preparation to disposal ("cradle-to-grave approach")

The following flow-chart shown as Figure 5 shows the steps of production, use, and disposal of HPCs. The life cycle of a HPC starts with the initial production of fresh catalyst which is pre-sulphided prior to being employed in the refinery process. During its use, the catalyst deactivates mostly due to coke deposition on the catalyst active sites, and/or sintering. When the catalyst becomes deactivated, the catalyst cannot meet the performance targets within the limits of the reactor operating conditions, and thus the reactor is shut down. Depending on the degree and nature of catalyst contamination, it can be either directly regenerated, undergo an additional reactivation treatment, be recycled, disposed or landfilled [14].
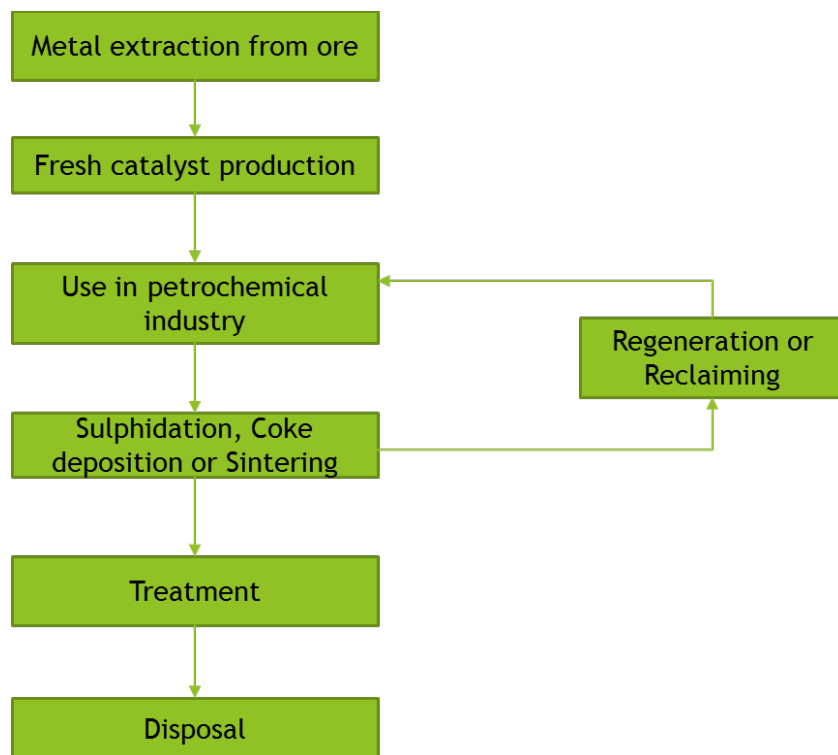
Figure 5. Hydroprocessing production to disposal [14]

The regeneration step is a vital step in pollution prevention. The deactivated catalyst can be regenerated several times before it becomes a waste. Therefore, optimizing the regeneration processes can be considered a significant technique to prevent pollution and to reduce the impact on the environment by improving the life-time of the HPCs in use (designed for less environmental impacts and more product life) [5].

A detailed "cradle-to-grave" approach is also illustrated in Figure 6. All of these detailed steps have their own impact on the environment, some being more significant than others. It should also be considered that recycling should only be considered when the regeneration does not work. Landfilling is also the last step to consider due to their hazard to the environment, and proper treatment(s) should be developed prior to disposal. In such a treatment(s), the metals should be removed and recovered from the spent catalysts which are not available for regeneration. These reclaimed metals from any catalyst disposed, can be reused for further catalyst synthesis and decrease the need for more metal mining from ores (recycle and reuse techniques) [14].
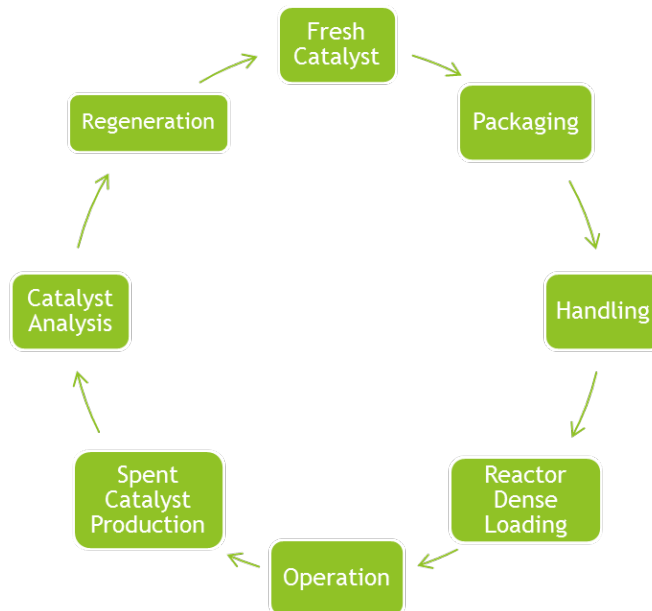
Figure 6. A cradle-to-grave approach for HPCs [14]

Typically, the catalyst life-cycle involves a long chain of operations, normally performed by different specialized companies. In addition to manufacturing, these operations include transportation, loading, change-out, regeneration, metal reclaiming, supplying different chemicals and materials, etc. Different factors, including the multiplicity of steps, the high number of different companies as well as technical, logistic and environmental issues involved, make it imperative to manage the catalyst life cycle in the most efficient and responsible way possible. Previously, each of the consecutive steps in the life-cycle of the catalyst was typically handled by a different company under the direct coordination of the refinery itself; however, leading catalyst manufacturers have currently started to provide "catalyst management'' services to their refinery customers.

4.4. Treatment of spent HPCs (metal removal and recovery)

The metal removal and recovery from spent HPCs can be studied from two different perspectives: environmental and economic aspects. As previously described, spent HPCs have

been classified as hazardous substances by USEPA definitions, and cannot be disposed into the environment, or landfilled without a proper treatment. From the economic perspective, metals in high concentrations may be isolated from other metals and be recovered for reuse. Studies have shown that in generic NiMo catalysts used in hydrocracking units (the catalyst sample used in the present study), molybdenum, cobalt and nickel are usually in the highest metal concentrations in the spent catalyst [8]. Cobalt is the most significant metal among these three to be considered for environmental issues; however, cobalt, nickel and molybdenum recovery can be studied for economic reasons as well [15], especially molybdenum which is considered a strategic metal [16].

4.4.1. Hydrometallurgical techniques

Extensive information is available in the literature for the removal and recovery of metals from different secondary sources using hydrometallurgical methods. In most cases, more than one metal is present in the solution when the secondary material's metals (in this case, spent catalysts' metals) are dissolved in the leaching agent(s). Solvent extraction (SX) has been proved to be a feasible and cost-effective method among all hydrometallurgical methods to remove the metals from synthetic and industrial solutions. Various organic solvents which should possess high selectivity towards the metal(s) of interest are also studied to be used in such processes. For nickel, molybdenum and cobalt, these extractants include, but are not limited to phosphate-based, amine-based, and different Cyanex extractants [17-24]. When the extraction of the targeted metals is optimized using different extractants, precipitation and/or stripping under controlled conditions can be used to obtain pure metal compound(s) [8].

In solvent extraction, the first step is usually to leach the spent HPC in acidic medium such as HCl, HNO_3, HSO_4, and aqua regia. There are several important factors needed to achieve complete dissolution, so the remaining inert support (usually Al_2O_3) can be discarded as an inert instead of a hazardous substance. When the leached solution is filtered, the organic solvent comes into contact with the leachate for a certain amount of time, and selectively isolates the hazardous metals.

4.4.2. Biosorption, the new progressive technology

Biosorption is defined as the adsorption of hazardous metals onto adsorbents produced from dead biomass or living organisms. There are two significant advantages of biosorption over conventional methods to remove and recover metals from secondary sources [12]:

- Biosorption is an environmentally-friendly process using biomass adsorbents which will not require any organic solvents. Therefore, it reduces the extra pollution which is usually caused in hydrometallurgical methods
- Biosorption is a very cost-effective method as it employs inexpensive biomass (especially dead biomass) materials to selectively separate the hazardous metals from other secondary sources and/or wastes

The significant limitation of this method is reported to be the slow adsorption of metals which has to be resolved for this method to be considered feasible for industrial applications. Furthermore, the only information available in the literature for biosorption is limited to lab-scale batch experiments. Other disadvantages of this method include, but are not limited to, the lack of sufficient knowledge of the mechanism(s) of the adsorption process, insufficient data on possible industrial applications in continuous processes, and the lack of reliable data on the most effective bioadsorbent to use.

5. Research methodology and approach
5.1. Apparatus and facilities

An Induced Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to quantify the trace metals in acidic solutions before and after the extraction process. Scanning Electron Microscope analysis (SEM, FEI Quanta 400) was also performed on the spent catalyst samples to develop a better understanding of metals present, and also the deactivated spots on the surface of the spent catalyst. A digital pH meter and an electric conductivity meter were also employed to measure the pH and electrical conductivity of the solutions, respectively.

5.2. Chemicals and reagents

The secondary spent HPCs were obtained from North Atlantic Refinery Limited's plant in Come by Chance, Newfoundland and Labrador. These catalysts were specifically used in the hydrocracking processes useful for jet fuel and gasoline production, by converting long-chain hydrocarbons to short-chain, sulphur-free hydrocarbons. The three reagents Aliquat336, Alamine308, and Alamine336 were provided by BASF, and were used without further purification. The chemical structures of these reagents are illustrated in Figures 7 and 8. The composition of our three reagents are provided in Table 2. Commercial-grade toluene was used as the diluent for all three extractants, to reach the desired concentrations.

Table 2. Composition of Aliquat336, used as hazardous metal removal reagent

Employed reagent	Chemical name	Content W/W %
Aliquat336	Tri-C8-10-alkylmethylammonium chlorides	85-95 %
	Octanol-1	3-7 %
	Decanol-1	3-7 %
Alamine308	Triisooctylamine	60 – 100 %
Alamine336	Amines, tri-C8-10-alkyl	100 %
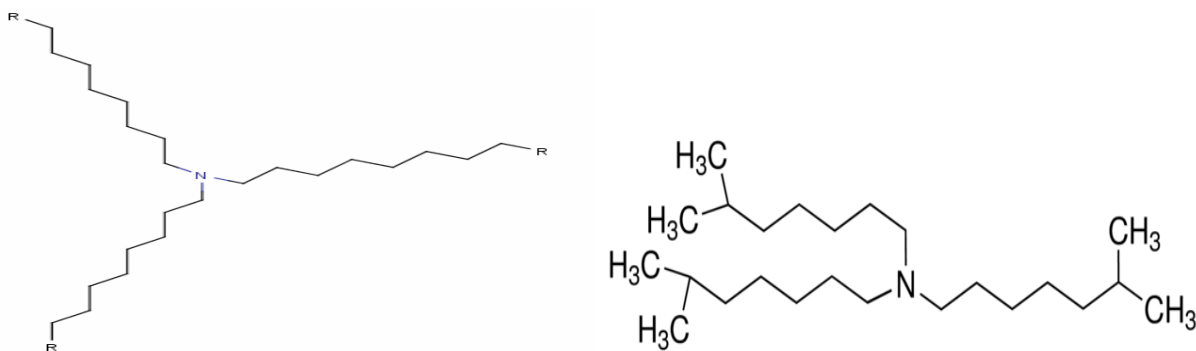
Figure 7. *Left*: Structure of tri-C8-10-alkyl amines (Alamine336), *Right*: triisooctylamine (Alamine308).
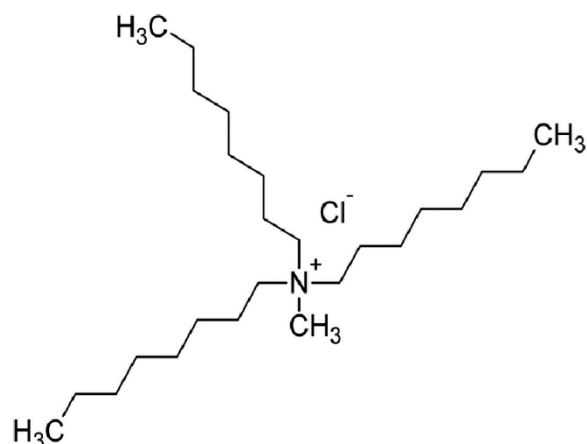
Figure 8. Chemical structure of Aliquat336 as a quaternary ammonium salt

5.3. Spent catalyst characterization

Spent catalyst samples were tested and analysed as received by the supplier. These spent catalyst samples were provided in powdered form, and mostly contain molybdenum, nickel, and cobalt as active sites of the catalyst on the surface of an inert support of Al_2O_3. These active sites are covered with coke and deposited metal complexes which are considered the main reasons for catalyst deactivation. Table 3 lists the composition of the spent catalyst and the metal concentration ranges, obtained from their MSDS.

Table 3. Information on solid spent HPC composition obtained from MSDS data provided by **North Atlantic Ltd.**

Ingredients	Wt. %
Aluminum Oxide	40 – 90 %
Cobalt Oxide	0.1-1 %
Cobalt Sulfide	0 – 10 %
Petroleum Coke	5 – 40 %
Hydrocarbon Mixture	0 – 20 %
Molybdenum Trioxide	0 – 1 %

Molybdenum Sulfide	0 – 25 %
Nickel Oxide	0.1 – 1.0 %
Nickel Sulfide	0 – 25 %
Phosphorus Pentoxide	0 – 10 %
Silicon Dioxide	0 – 20 %
Sulfur	0 – 15 %

Scanning electron microscope analysis (SEM) was also conducted to obtain a detailed two-dimensional scanned image of the catalyst surface, and to observe different metal availabilities on targeted areas, and the homogeneous nature of the catalyst. As can be seen in Figures 9 and 10, most of the active sites of the catalyst are covered with mostly coke and metal complexes which are the main causes of catalyst deactivation. Furthermore, the scanned image shows that the powder is fairly homogeneous which ensures the accuracy of the leaching experiments.
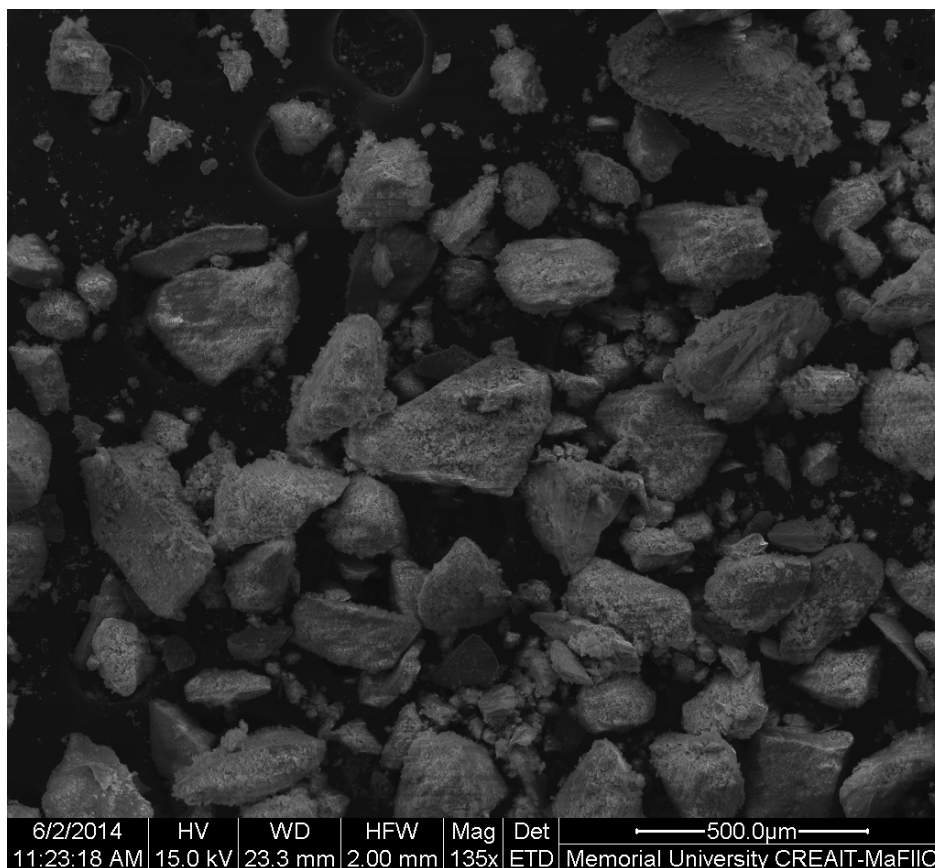
Figure 9. SEM image of powdered spent catalyst showing coke and metal deposition on active surface of HPC sample used in this study.
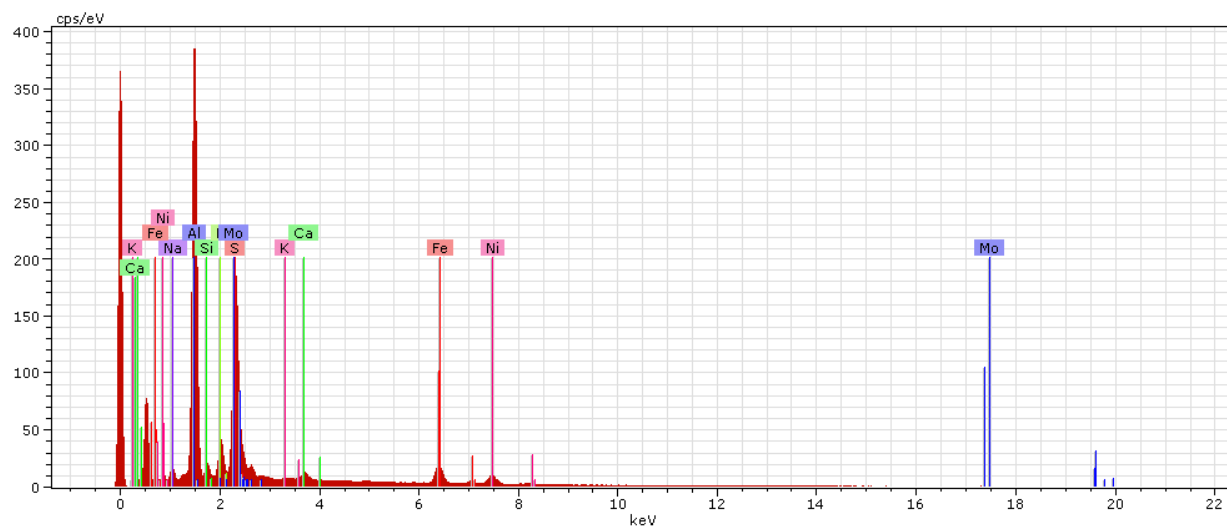
Figure 10. Results of SEM analysis on spent catalyst surface and matching metals with peaks

5.4. General experimental procedure

Initially, quantities of spent catalyst were dissolved in three different acidic media to measure the efficiency of leaching. Hydrochloric acid, nitric acid, and aqua regia were selected for leaching analysis. To obtain a complete dissolution of targeted metals, a solid: liquid ratio of 1:100 was considered and thus, 0.40 mg of spent catalyst samples were separately dissolved in 40 ml of the three different acidic solutions. The results were analysed by ICP-OES and the best leaching medium was selected. Aliquat336, Alamine308, and Alamine336 were employed as the three reagents to extract the hazardous metals. Each of these reagents were diluted in toluene to obtain the required concentrations according to the designed experimental matrix. Different volumes of acidic and organic solutions were then mixed according to the experimental design, and were stirred for certain amounts of time, using magnetic stirrers. The organic phases were separated from the aqueous phase using separator funnels, and the aqueous acidic solutions were sent to ICP-OES facility to calculate different metal removal efficiencies according to the following equations [25-27], were **m** represents metals, **D** is the distribution ratio, **C_m** is the concentration of metals in organic or aqueous solutions. **T**he extraction percentage of the targeted metals is represented as **E%**. All experiments were conducted in ambient temperature.

$$D_m = \frac{[C_m]org}{[C_m]aq} \qquad \text{Eq. 1}$$

$$E\% = \frac{D_m}{D_m + 1} \qquad \text{Eq. 2}$$

5.5. Design of experiments

Response surface methodology (RSM), has been widely used as a practical and economical method to optimize different metal extraction, ion-exchange, and hydrometallurgical processes. Three steps are defined in the RSM technique. The first one is to design the experiments to evaluate the effects of different factors on the efficiency of the process. The second one is to develop a polynomial model using the obtained experimental results, and evaluate the fitted model's suitability by applying a statistical test. The last step is to determine the optimum

conditions to achieve highest efficiencies [28]. In most cases, a second-order polynomial model is employed in the RSM. Details of such a model and how the coefficients are determined, are listed elsewhere [29, 30].

Central composite design (CCD) is the most popular second-order experimental design in the RSM technique. CCD does not require a huge number of experiments, thus minimizes the time and cost required for performing experiments, and also provides enough information for testing the fitness of the predicted model [28]. In the present study, face-centered CCD was employed as the main method to design the experiments, evaluate the effect of each parameter, provide a statistical model, and optimize the hydrometallurgical method.

In this study, three parameters were considered as the most significant factors affecting the process efficiency, including extractant concentration, organic/aqueous ratio, and contact time. These factors and their limit values were considered after preliminary literature review on research conducted on different hydrometallurgical processes. Tables 4 and 5 list the minimum and maximum levels for each parameter, and designed experiments using these parameter levels respectively. All these experimental parameters and the designed experiments were the same for all three extractants. Experiments were conducted on the basis of the design matrix of central composite design (CCD) with full horizontal design method containing six replicated points. All experiments were performed in random sequences to avoid or minimize the effects of uncontrolled factors.

Table 4. Process variables and their limit values

Name	Units	Type	Low	High
Aliquat conc. (A)	molar	Factor	0.01	0.6
O/A ratio (B)	ml/ml	Factor	0.5	3
stirring time (C)	min	Factor	10	120

Table 5. Designed experiments using face-centered central composite design

Run	Factor A: Aliquat conc.	Factor B: O/A ratio	Factor C: Stirring time
Unit(s)	Molar	ml/ml	min
1	0.01	1.75	65
2	0.305	1.75	10
3	0.6	1.75	65
4	0.305	1.75	65
5	0.6	3	120
6	0.01	0.5	10
7	0.01	3	10
8	0.305	1.75	120
9	0.01	0.5	120
10	0.305	0.5	65
11	0.6	3	10
12	0.6	0.5	10
13	0.305	1.75	65
14	0.6	0.5	120
15	0.305	1.75	65
16	0.305	1.75	65
17	0.01	3	120
18	0.305	3	65
19	0.305	1.75	65
20	0.305	1.75	65

6. Results and discussion

6.1. Leaching chemistry

Three different acidic solutions were prepared to leach the spent catalyst powder. ICP-OES results for targeted metal quantities are listed in Table 6. As can be observed, aqua regia can be considered to be the best leaching agent among these three leaching solutions. This can be due to the fact that strong oxidizers are formed in aqua regia such as chlorine and nitrosyl chloride according to the following reaction [31]:

$$HNO_{3 \ (aq)} + 3HCl_{(aq)} \rightarrow NOCl_{(g)} + Cl_{2 \ (g)} + 2H_2O_{(l)} \qquad \text{Eq. 3}$$

The pH and electrical conductivity of the produced aqua regia after the spent catalyst dissolution were measure as 0.10 and 1.828×10^5 µS respectively, which show the high acidity and great ionic activity of the solution. The leachate solution in aqua regia after vacuum filtration is illustrated in Figure 11.

Table 6. Leached amounts of spent HPCs metals in three different acidic solutions

Metals / Type of acid	Cobalt (mg/L)	Molybdenum (mg/L)	Nickel (mg/L)
Aqua regia	3643	840	1666
Nitric acid	<125	557	411
Hydrochloric acid	<125	<125	565
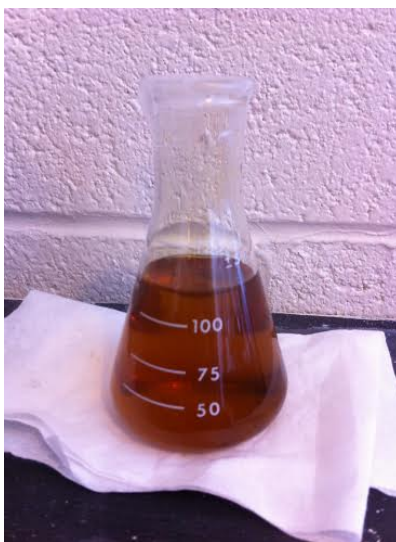
Figure 11. Spent HPC in aqua regia

Aliquat336, as a quaternary ammonium salt, is capable of extracting both anionic and cationic species; thus it has found a great deal of application in various areas. It has been suggested that an ammonium salt can isolate metal complexes by both anion and cation exchange mechanisms. Alamine308 and Alamine336 both contain a basic nitrogen atom, which can react with different types of acids such as HCl to form amine salts. These produced amine salts are able to do ion-exchange reactions with different types of anionic and cationic ions [20].

6.2. Solvent extraction results

Table 7 lists the results for cobalt, nickel, and molybdenum extraction percent for all three employed extractants. It can be inferred from the table that cobalt is the easiest hazardous metal among the three to be removed by all three extractants. Aliquat336 was able to extract cobalt and molybdenum up to more than 99%; however, showed difficulty on the removal of nickel with the best efficiency of 53.1%. On the other hand, both amine-based extractants were able to remove all three hazardous metals very well; however, molybdenum and nickel are the most difficult metals to be extracted with Alamine308 and Alamine336 respectively, as there are four extraction values under 60% for these metals in the table.

Table 7. Experimental results for cobalt, nickel and molybdenum extraction using three different extractants obtained by ICP-EOS

Run	Aliquat336			Alamine308			Alamine336		
	Cobalt %	Nickel %	Molybdenum %	Cobalt %	Nickel %	Molybdenum %	Cobalt %	Nickel %	Molybdenum %
1	99.8	51.9	46	99.62	94.36	54.43	99.62	83.21	77.26
2	99.8	51.2	97.7	99.62	94.10	96.16	99.63	42.15	88.14
3	96.7	51.3	99.2	99.62	82.91	98.02	99.62	83.33	98.12
4	99.8	51.8	97.6	99.62	82.76	96.71	99.95	84.25	96.52
5	99.8	49.8	99.7	99.62	82.27	96.36	99.60	37.66	99.41
6	99.8	52.6	31	99.62	94.18	50.04	96.85	92.99	50.94
7	99.8	53.1	55.2	99.62	94.30	56.55	99.62	81.05	10.01
8	99.8	51.6	97.9	99.62	82.98	96.50	99.85	81.43	89.29
9	97.9	47.3	25	99.62	94.29	50.79	99.62	94.41	51.49
10	99.8	50.7	89.2	99.62	94.11	86.08	99.96	94.49	85.41
11	99.8	50.3	99.7	99.62	82.16	96.06	99.88	79.98	99.42
12	99.8	52	89.4	99.62	94.08	91.50	99.62	81.37	78.29
13	96	48.7	97.8	99.62	83.30	96.71	99.55	40.30	91.57
14	99.8	51.3	95.9	99.62	83.38	94.89	99.62	94.37	92.48
15	99.8	50.3	97.9	99.62	82.58	96.52	99.62	94.38	96.21
16	99.8	50.4	97.8	99.62	82.40	96.42	99.62	94.10	95.39
17	99.8	51.7	61	99.62	83.46	78.73	99.62	83.49	78.52
18	99.8	50.1	99.1	99.62	93.98	97.56	99.65	41.50	96.11
19	99.8	51.2	97.8	99.62	82.84	96.44	99.62	92.20	95.26
20	99.3	51	97.8	99.62	82.97	96.61	99.62	87.43	96.30

6.3. Effect of Aliquat336 on hazardous metal removal

According to the results, it is obvious that cobalt can be extracted up to complete amounts of efficiency even by using a diluted organic phase of Aliquat336. Various parameters have no effect on cobalt extraction which shows that the mass transfer resistance is pretty low, the

extraction of cobalt by Aliquat336 occurs very rapidly and the maximum efficiency of cobalt extraction into the organic phase is reached in the first 10 minutes. The same patterns were observed for both nickel and molybdenum.

6.3.1. Effect of contact time

As illustrated in Figure 12, the zero or negative slope after the 10th minute means that the stirring time has no or adverse effect on efficiency. Stirring was conducted at a speed with which the optimal mixing occurred. Only in the nickel extraction case, a drastically decrease is observed which suggests that maximum nickel extraction can be reached in 10 minutes.
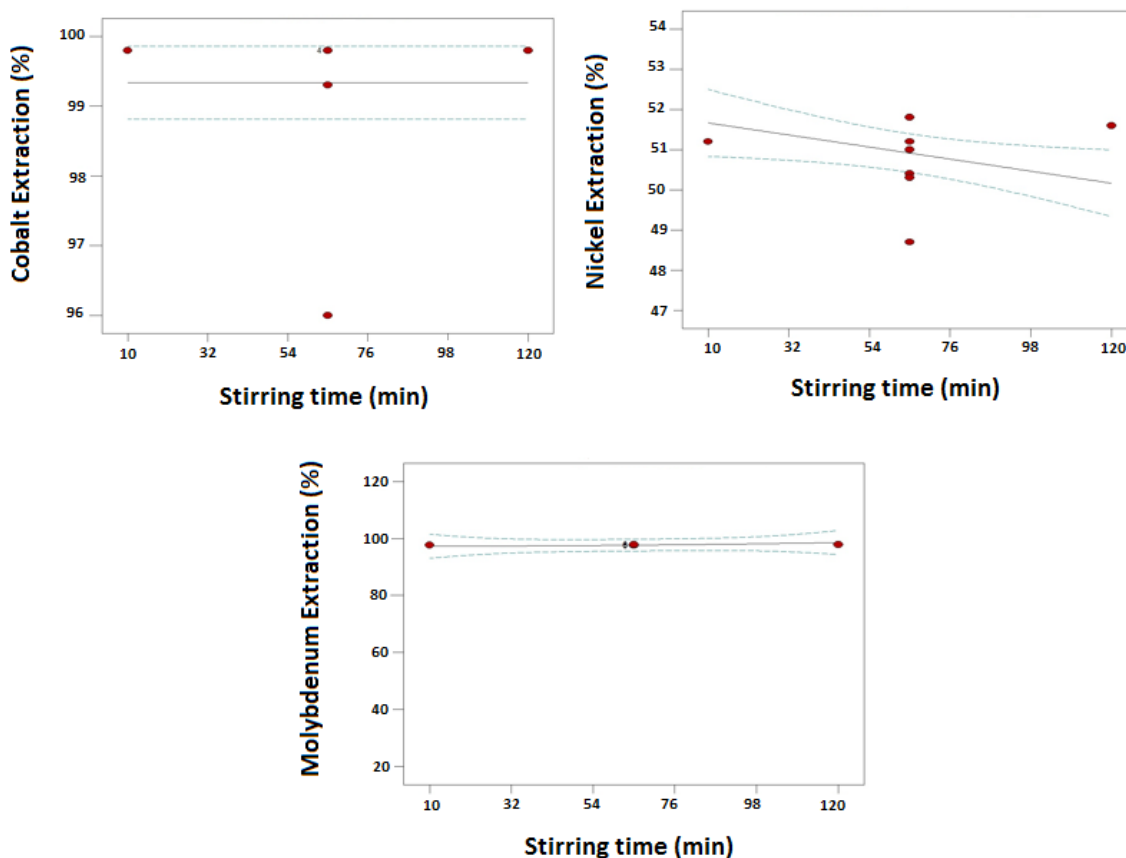
Figure 12. Metal extractions vs. time of stirring for (*left*) cobalt, (*right*) nickel and (*center*) molybdenum (Aliquat336 conc: 0.305M and O/A ratio 1.75)

6.3.2 Effect of reagent concentration

As can be seen in Figure 13, with increasing Aliquat336 concentrations, the nickel and cobalt extraction efficiencies remain unchanged; however, the molybdenum extraction increases to reach a maximum value, and then decreases. The optimum amount is shown to be ~0.48 M.
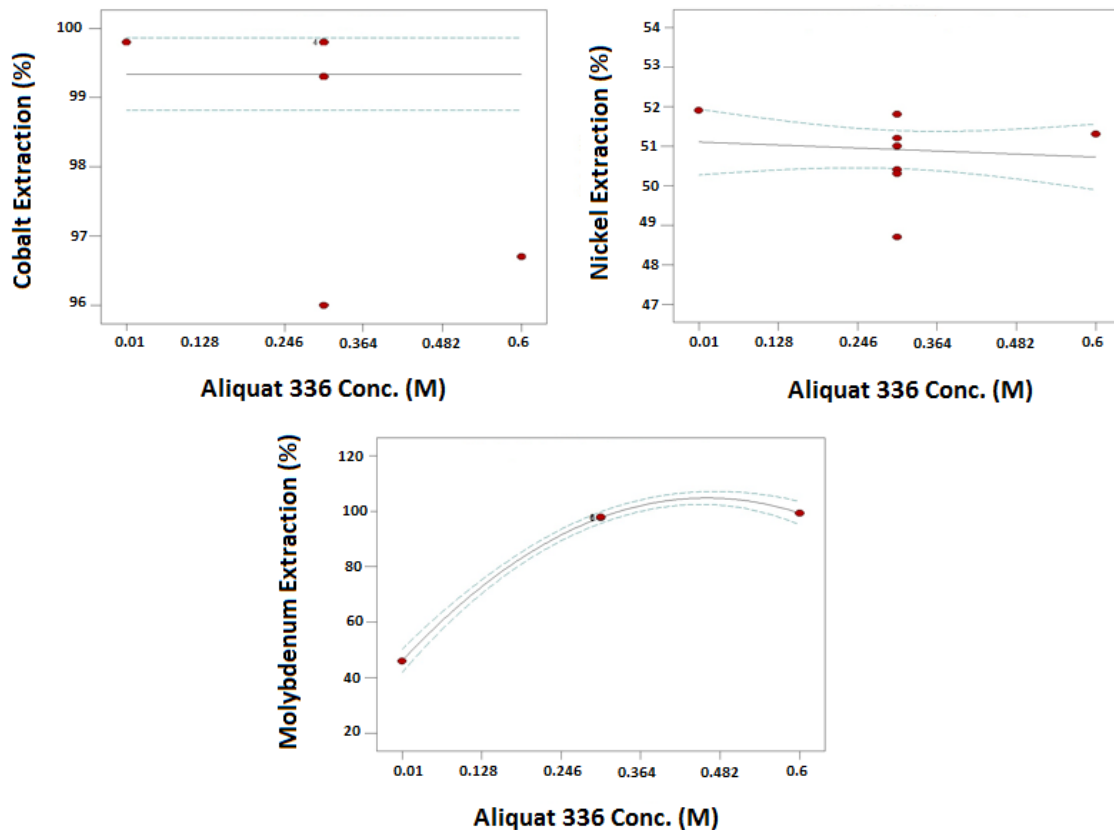
Figure 13. Changes of extraction efficiencies for different metals with the changes in Aliquat concentrations (O/A ratio 1.75 and stirring time 65 min)

6.3.3 Effect of organic/aqueous ratio

Figure 14 illustrates the effect of the O/A ratio on different extractions. Similar extraction values were observed for cobalt and nickel as there is little change when the O/A ratios change; however, for molybdenum, the extraction efficiency increases by enriching the organic phase with Aliquat336, until a maximum amount is reached.
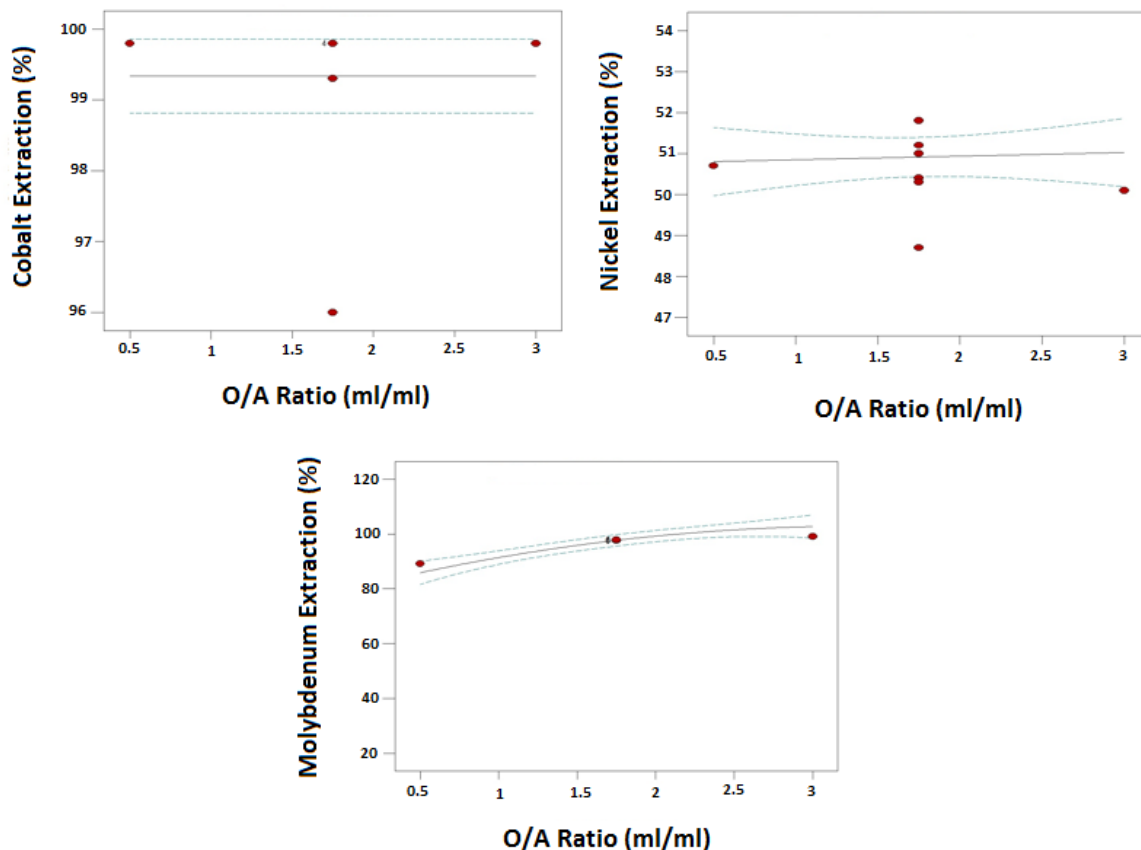
Figure 14. Effect of O/A ratio for various metal extractions

(Aliquat336 conc. 0.305M and stirring time 65 min)

6.3.4. Statistical modeling

Since cobalt extraction shows only slight changes with all of the modeled factors, there is no statistical model developed for cobalt extraction efficiency and the system suggested only a consistent mean value for it. As for nickel, a two-factor interaction (2FI) and for molybdenum, a quadratic model were suggested due to the results and the R^2 values were calculated to be 0.61 and 0.99 for nickel and molybdenum respectively which show that the most accurate model is produced for the molybdenum extraction. All the models (in term of coded factors) are listed below for nickel and molybdenum extractions (Equations 4 and 5, respectively). The

molybdenum extraction was found to be problematic since there are many factor interactions. Statistical modeling obtained by the Design Expert using a CCD approach shows that the nickel and molybdenum solvent extractions are not solely dependent on the main factors but also depend on the interactions.

The coefficients represent the significance of various parameters, and according to the following equations, the most important interactions between these factors for nickel are those between the Aliquat336 concentration and the O/A ratio. The same pattern was obtained for molybdenum extraction. The obtained results help us to make predictions for the efficiencies when changes occur with some factors.

Ni E% = [50.92 + (-0.19×A) + (0.11×B) + (-0.75×C) + (-1.01×AB) + (0.69× AC) + (0.51×BC)]   Eq. 4

Mo E% = [83.64 + (26.57×A) + (8.42×B) + (0.65×C) + (-5.76×AB) + (0.84×AC) + (0.66×BC)]   Eq. 5

6.3.5. ANOVA results

A least-squares fit procedure was applied to estimate the coefficients of the polynomial for metal extraction using Aliquat336, and then based on the fitted surface response, analysis was performed. The generated models developed by Design Expert software and their statistical importance were evaluated by the Fisher test (F-test) which is calculated by dividing the Model Mean Square by its Residual Mean Square for the analysis of variance (ANOVA).

ANOVA results for the nickel and molybdenum extraction efficiency models are presented in Tables 8 and 9 respectively. For these two, a very low probability value implies that these models are significant for the 95% confidence interval as the P-value less than 0.05 indicates significance. As the P-value decreases, it becomes less likely the effect is due to change, and more likely that there was a real cause. There is only a 3% and 0.01% chance that a "Model F-value" having the same great magnitude could occur due to noise.

Table 8. Analysis of variance results for nickel extraction by Aliquat336 ($R^2 = 0.61$)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	20.19	6	3.37	3.40	0.0304	Significant
Residual	12.85	13	0.99			
Lack of Fit	7.16	8	0.90	0.79	0.6377	
Pure Error	5.69	5	1.14			
Correlation Total	33.05	19				

Table 9. Analysis of variance results for molybdenum extraction by Aliquat336 ($R^2 = 0.99$)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	11687.50	9	1298.61	178.03	< 0.0001	significant
Residual	72.94	10	7.29			
Lack of Fit	72.89	5	14.58	1508.17	< 0.0001	
Pure Error	0.048	5	9.667E-003			
Cor Total	11760.45	19				

6.3.6.   Optimization

Optimization was conducted using the Design Expert software. Optimum conditions for the metal extractions using Alamine308 were determined using the optimization tool of Design Expert software. The strategy of the programme is to optimize multiple responses, so the desirability function between 0 and 1 can be maximized. The minimum concentrations of Aliquat336, O/A ratios, and stirring times were targeted, due to cost considerations, and all hazardous metal extractions were considered to appear in the maximum values. The optimum point for all these goals to happen was generated with the desirability of 0.823. For the optimum point, the Aliquat336 concentration is 0.24M, the O/A ratio is 0.50 and the stirring time is 10 min. The result would be predicted to be 99%, 52%, and 78% for cobalt, nickel and molybdenum extractions, respectively.

6.4. Effect of Alamine308 on hazardous metals removal

6.4.1 Effect of contact time

The effect of stirring time was measured for different metals and except for molybdenum, maximum efficiency can be reached after only 10 minutes. For cobalt, the extraction is the same and nickel extraction starts dropping drastically after the 10th minute, which suggests that for optimal nickel extraction, a 10 minute stirring time is sufficient. Molybdenum extraction becomes slightly increased over time and the maximum extraction occurs at the end of the extraction time considered in this study (120 minutes). The general pattern for all metal extraction versus the contact time for Alamine308, as shown in Figure 15, is similar to what was observed with Aliquat336.
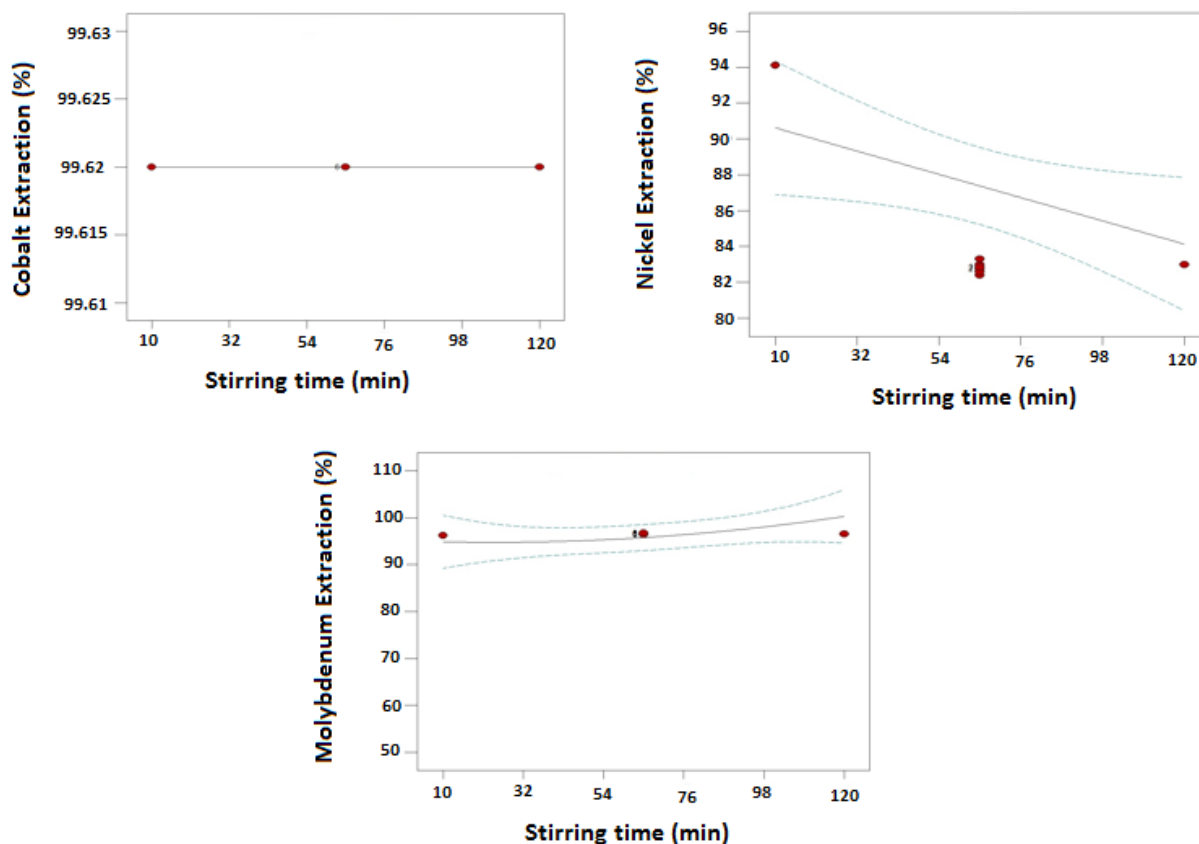
Figure 15. Metal extractions vs. time of stirring for (*left*) cobalt, (*right*) nickel and (*center*) molybdenum (Alamine308 conc.: 0.305 M and O/A ratio: 1.75 ml/ml)

6.4.2 Effect of reagent concentration

Figure 16 illustrates the changes of extraction efficiencies for all of the targeted metals versus the concentration of Alamine308 in toluene. Maximum cobalt and nickel extraction can be achieved using an ultra-low concentration of Alamine308 in toluene, and with more concentrated solutions, nickel extraction efficiency decreases drastically. Low concentrations of Alamine308 are not capable of removing all of molybdenum as with increasing the concentration, the efficiency increases to a certain point, and then starts decreasing. As the trends for nickel and molybdenum are completely different with the change of Alamine308 concentrations, an optimum point should be determined to achieve acceptable extraction efficiencies for both of these metals. The overall pattern of metal extractions versus the Alamine308 concentrations is similar to Aliquat336.
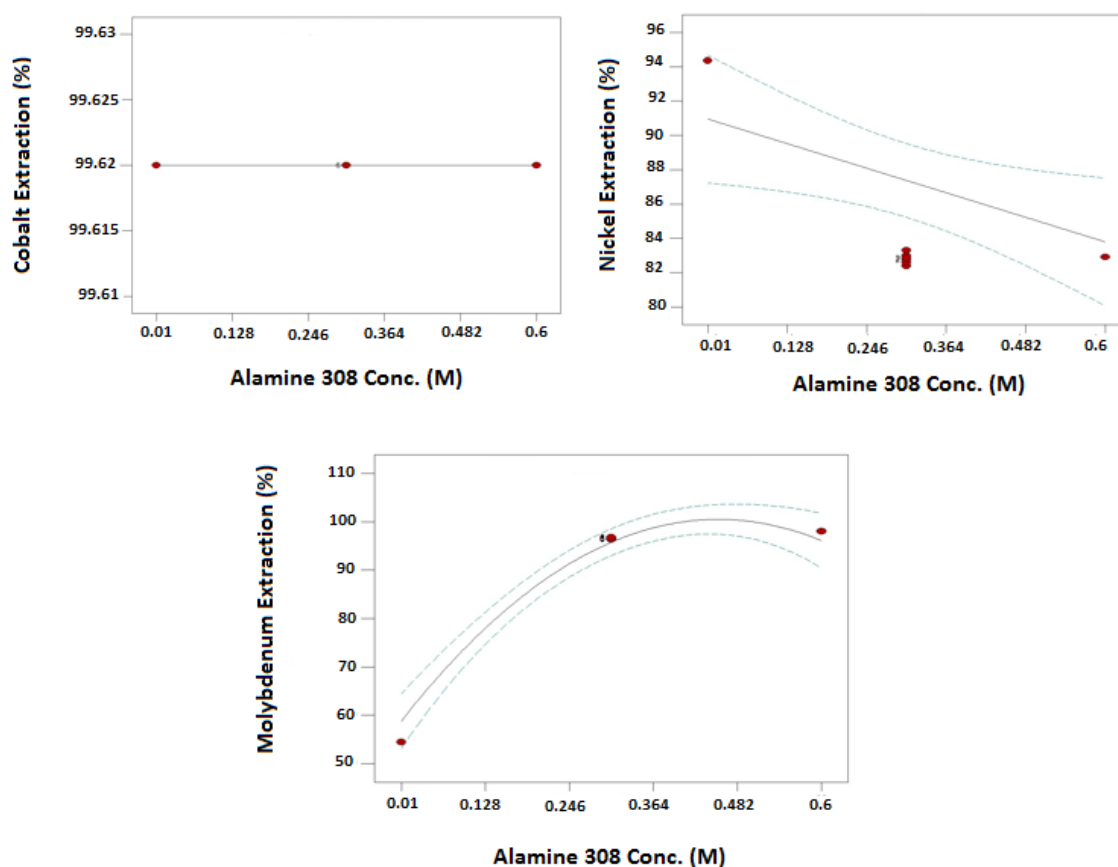
Figure 16. Changes of extraction efficiency for different metals with the changes in Alamine308 concentrations (O/A ratio: 1.75 ml/ml and stirring time: 65 min)

6.4.3 Effect of organic/aqueous ratio

Unlike the last two parameters, the behaviour of Alamine308 for different metal extractions using the different organic/aqueous ratios is not completely similar to that in Aliquat336. Figure 17 shows that although the cobalt does not change and molybdenum extraction slightly increases with more O/A ratios, nickel extraction efficiency decreases drastically and the maximum amount can be obtained at the 1:1 ratio. Due to dissimilar trends for nickel and molybdenum, an optimum point should be determined in between, for proper efficiencies for both metals.
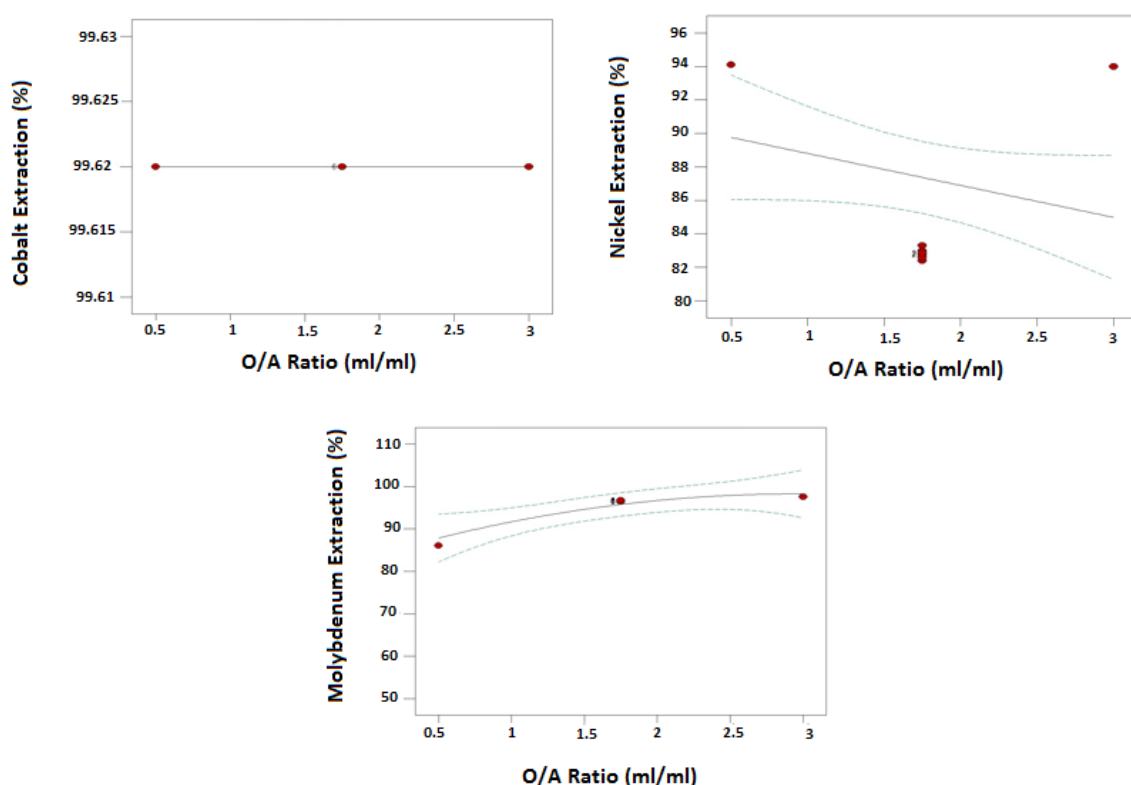
Figure 17. Effect of O/A ratio on various metal extractions
(Alamine308 conc.: 0.305 M and stirring time: 65 min)

6.4.4 Statistical modeling

Design Expert software was employed to develop a statistical model to predict the behaviour of the hazardous metals removal using Alamine308. These fitted models are good

sources to predict the process with the parameter levels outside of our considered limits, and to determine the scale of importance of each parameter on the extraction efficiencies. A bigger coefficient in these models represents a more significant effect of such a parameter. Plus and minus signs represent negative and positive impacts of parameters on the extraction efficiency.

For Alamine308, a mean model was suggested for cobalt extraction as it could be completely extracted using very dilute solutions in only 10 minutes. For nickel and molybdenum, linear and quadratic models were developed, and the r-squared was calculated to be 0.47 and 0.98 respectively. It can be implied that the most reliable and accurate model is the one developed for molybdenum extraction. All these fitted models for metal removal by Alamine308 can be seen below, as equations 6 and 7.

$$\text{Ni E\%} = [87.37 + (-3.58 \times A) + (-2.39 \times B) + (-3.24 \times C)] \qquad \text{Eq. 6}$$

$$\text{Mo E\%} = [95.75 + (18.63 \times A) + (5.20 \times B) + (2.70 \times C) + (-3.55 \times AB) + (-2.40 \times AC) + (2.29 \times BC) + (-18.30 \times A^2) + (-2.70 \times B^2) + (1.81 \times C^2)] \qquad \text{Eq. 7}$$

6.4.5 ANOVA results

Similar to the analysis for Aliquat336, a least-squares fit procedure was applied to estimate the coefficients of the polynomial for metal extraction, and then based on the fitted surface response, analysis was performed. The generated models developed by Design Expert software and their statistical importance were evaluated by the Fisher test (F-test) which is calculated by dividing the Model Mean Square by its Residual Mean Square for the analysis of variance (ANOVA).

Tables 10 and 11 list the ANOVA results for the nickel and molybdenum extraction efficiency models, respectively. For these two, a very low probability value imply that these models are significant for the 95% confidence interval as the P-value less than 0.05 indicates significance. As the P-value decreases, it becomes less likely the effect is due to change, and more likely that there was a real cause. There is only 1.54% and 0.01% chance that a "Model F-

value" having the same great magnitude could occur due to noise. As it was concluded by r-squared values, a most accurate model was developed for molybdenum extraction. The same procedure was observed for Aliquat336 too.

Table 10. Analysis of variance results for nickel extraction by Alamine308 ($R^2 = 0.47$)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	290.31	3	96.77	4.70	0.0154	significant
Residual	329.15	16	20.57			
Lack of Fit	328.66	11	29.88	304.83	< 0.0001	
Pure Error	0.49	5	0.098			
Cor Total	619.45	19				

Table 11. Analysis of variance results for molybdenum extraction by Alamine308 ($R^2 = 0.98$)

| Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	5798.04	9	644.23	49.25	< 0.0001	Significant
Residual	130.80	10	13.08			
Lack of Fit	130.72	5	26.14	1580.96	< 0.0001	
Pure Error	0.083	5	0.017			
Cor Total	5928.84	19				

6.4.6 Optimization

Optimum conditions for the metal extraction using Alamine308 were determined using the optimization tool of Design Expert software. The strategy of the programme is to optimize multiple responses, so the desirability function between 0 and 1 can be maximized. The minimum concentrations of Alamine308, O/A ratios, and stirring times were targeted, due to cost

considerations, and all targeted metal extractions were considered to appear in the maximum values. For the optimum point, the Alamine308 concentration is 0.23M, the O/A ratio is 0.50 and the stirring time is 10 min. The results would be predicted to be 99%, 94%, and 82% for cobalt, nickel and molybdenum extractions, respectively. A comparison between these results and the ones for Aliquat336 shows that Alamine308 is a better extractant, as it can remove all the three targeted metals in 10 minutes with much less diluted solutions than Aliquat336. Aliquat336 showed a little weakness in extracting nickel alongside cobalt and molybdenum.

6.5 Effect of Alamine336 on hazardous metal removal

6.5.1 Effect of contact time

The effects of stirring time on different metal extraction efficiencies by Alamine336 have been determined and illustrated in Figure 18. All the three targeted metal extraction efficiencies increase with increasing the contact time, and unlike the other two extractants, 10 minutes are not sufficient to achieve maximum efficiency for cobalt, nickel, and molybdenum extraction. This suggests that the extraction time required for metal extraction using Alamine336 is more than the time required for equal extraction by Aliquat336 and Alamine308. This should be considered a big disadvantage for Alamine336 applicability to remove hazardous metals from spent HPCs.
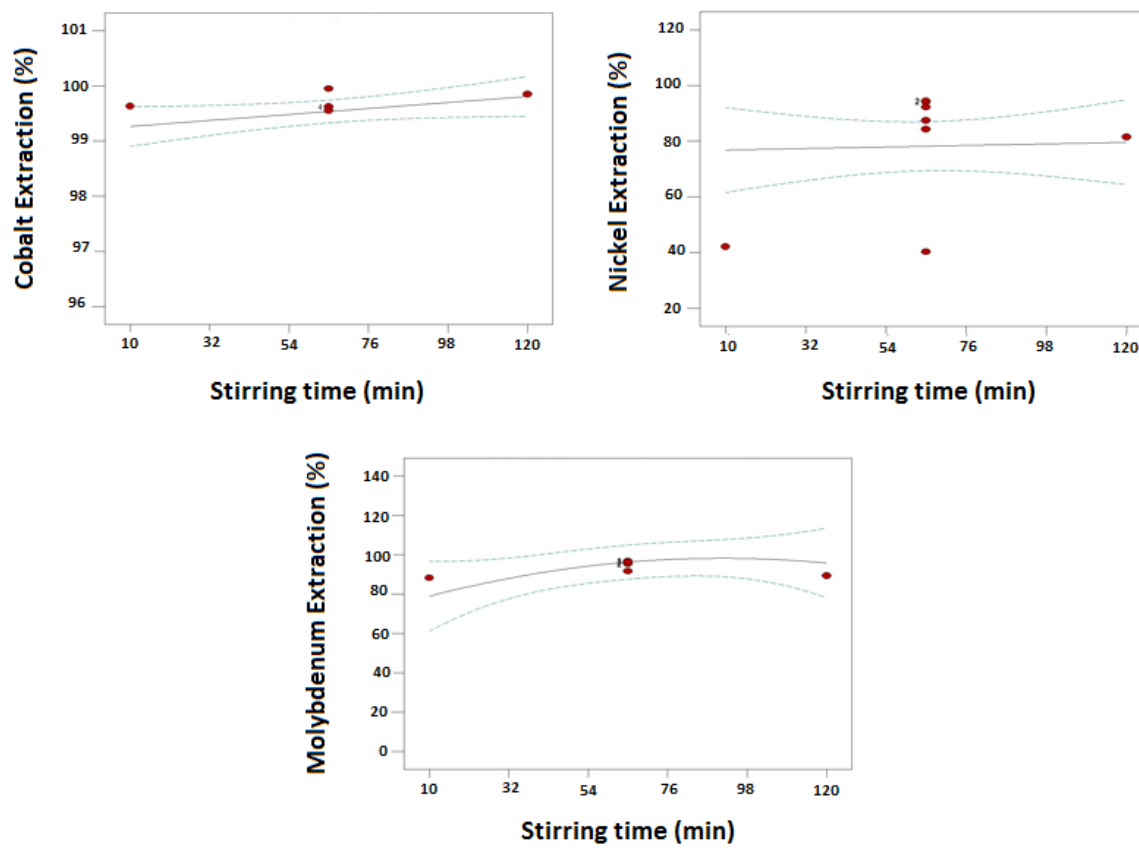
Figure 18. Metal extractions vs. time of stirring for (*left*) cobalt, (*right*) nickel and (*center*) molybdenum (Alamine336 conc.: 0.305 M and O/A ratio: 1.75 ml/ml)

6.5.2 Effect of reagent concentration

The effects of Alamine336 concentration in toluene on different metal extraction efficiencies are illustrated in Figure 19. Cobalt and molybdenum extraction follow a similar trend with increasing the concentration; however, nickel extraction decreases by having a more concentrated organic solution. Therefore, an optimum point of Alamine336 concentration should be determined for the most suitable extraction of all three metals.
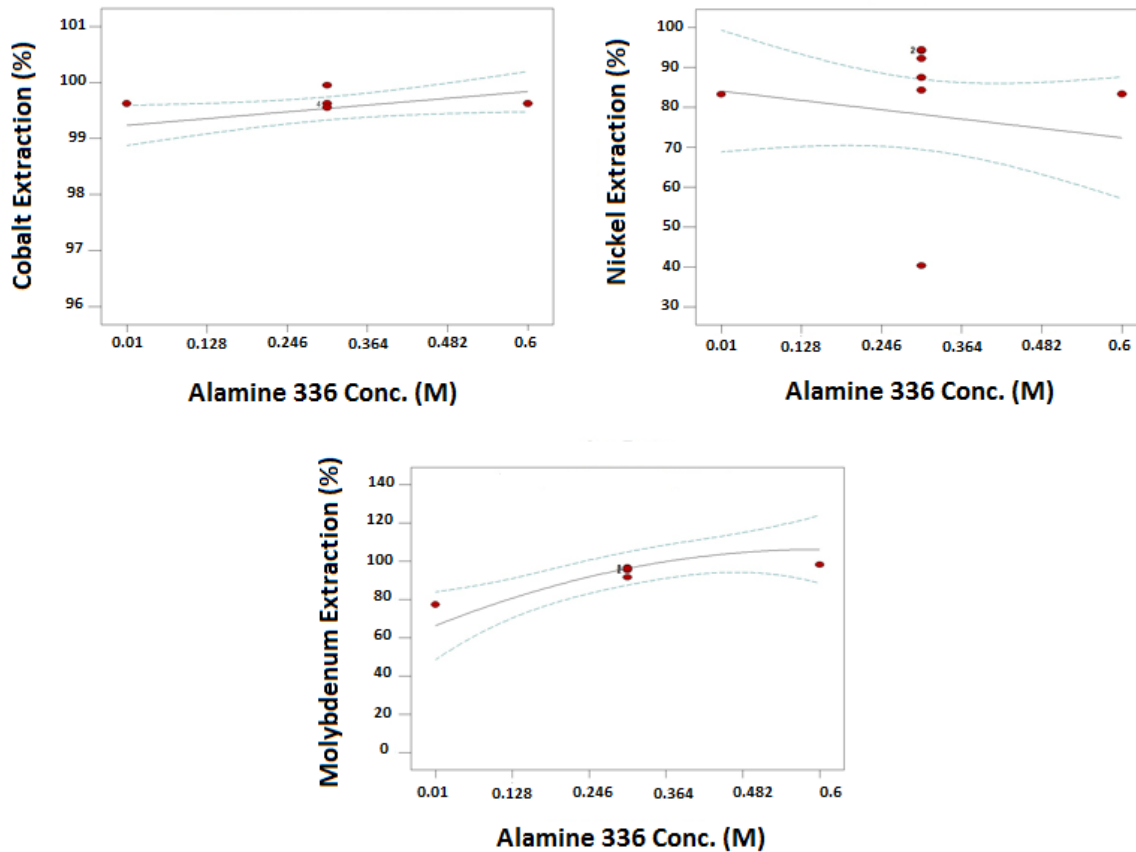
Figure 19. Changes of extraction efficiencies for different metals with the changes in Alamine336 concentrations (O/A ratio: 1.75 ml/ml and stirring time: 65 min)

6.5.3 Effect of organic/aqueous ratio

Figure 20 shows the effects of different O/A ratios on all three metal extraction efficiencies. Although both cobalt and molybdenum extractions increase with more O/A ratios, the slope value of cobalt is higher, which suggest that the effect of the O/A ratio is more significant for cobalt extraction. Nickel extraction decreases with increasing the O/A ratio, which is the similar pattern to both Alamine308 and Aliquat336.
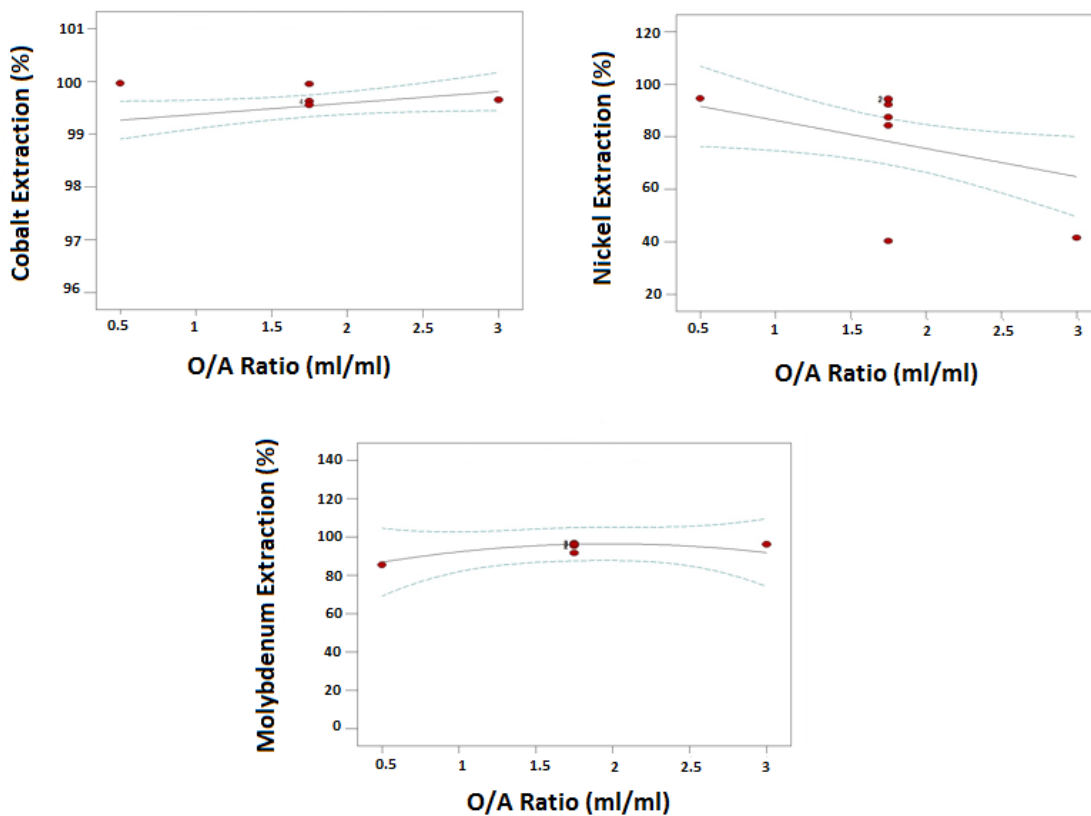
Figure 20. Effect of O/A ratio for various metal extractions

(Alamine336 conc.: 0.305 M and stirring time: 65 min)

6.5.4 Statistical modeling

As with the other two extractants, Design Expert software was employed to develop a statistical model to predict the behaviour of hazardous metal removal using Alamine308. These fitted models are good sources to predict the process with the parameter levels outside of our considered limits, and to determine the scale of importance of each parameter on the extraction efficiencies. A bigger coefficient in these models represents a more significant effect of such a parameter. Plus and minus signs represent negative and positive impacts of a parameter on the extraction efficiency.

For Alamine336, a two factor interaction (2FI) model was developed with a 0.70 value for r-squared. Similar to Alamine308, linear and quadratic models were suggested for nickel and

molybdenum with r-squared values of 0.28 and 0.86 respectively. Although the reliability for nickel is pretty low, the accuracy of molybdenum extraction efficiency model is higher than both cobalt and nickel. All these fitted models for metal removal by Alamine336 can be seen as equations 8-10:

Co E% = [99.54 + (0.30×A) + (0.27×B) + (0.27×C) + (-0.32×AB) + (-0.38×AC) + (-0.38×BC)] Eq. 8

Ni E% = [78.20 + (-5.84×A) + (-13.40×B) + (1.38×C)] Eq. 9

Mo E% = [96.18 + (19.95×A) + (2.49×B) + (8.44×C) + (5.25×AB) + (-6.86×AC) + (6.72×BC) + (-9.95×A^2) + (-6.88×B^2) + (-8.92×C^2)] Eq. 10

6.5.5 ANOVA results

A similar approach to Aliquat336 and Alamine308 was followed for process optimization for Alamine336. A least-squares fit procedure was applied to estimate the coefficients of the polynomial for metal extraction, and then based on the fitted surface response, analysis was performed. The generated models developed by Design Expert software and their statistical importance were evaluated by the Fisher test (F-test) which is calculated by dividing the Model Mean Square by its Residual Mean Square for the analysis of variance (ANOVA).

ANOVA results for the cobalt, nickel and molybdenum extraction efficiency models are listed in Tables 12, 13, and 14, respectively. For cobalt and molybdenum, a very low probability value imply that these models are significant for the 95% confidence interval as the P-value less than 0.05 indicates significance. As the P-value decreases, it becomes less likely the effect is due to change, and more likely that there was a real cause. There is only a 0.74 and 0.26% chance that a "Model F-value" having the same great magnitude could occur due to noise. As it was concluded by r-squared values, among all the three metal extraction processes, the most accurate model was developed for molybdenum extraction. The same procedure was observed for

Aliquat336 too. The developed model for nickel extraction has a P-value of 0.1431, which is higher than the previous values for nickel extraction by other two extractants (Aliquat336 and Alamine308) and shows that this model is not as significant; however, this model was the best fit among possible models for nickel extraction for Alamine336.

Table 12. Analysis of variance results for cobalt extraction by Alamine336 ($R^2 = 0.70$)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	5.50	6	0.92	4.98	0.0074	Significant
Residual	2.39	13	0.18			
Lack of Fit	2.29	8	0.29	13.95	0.0050	
Pure Error	0.10	5	0.021			
Cor Total	7.89	19				

Table 13. . Analysis of variance results for nickel extraction by Alamine336 ($R^2 = 0.28$)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	2154.88	3	718.29	2.08	0.1431	not significant
Residual	5523.42	16	345.21			
Lack of Fit	3346.34	11	304.21	0.70	0.7125	
Pure Error	2177.08	5	435.42			
Cor Total	7678.31	19				

Table 14. Analysis of variance results for molybdenum extraction by Alamine336 (R^2 = 0.86)

Source	Sum of Squares		Mean Square	F-value	p-value Prob > F	
Model	8151.96	9	905.77	7.06	0.0026	Significant
Residual	1282.12	10	128.21			
Lack of Fit	1264.93	5	252.99	73.59	0.0001	
Pure Error	17.19	5	3.44			
Cor Total	9434.08	19				

6.5.6 Optimization

Optimum conditions for the metal extraction using Alamine336 were determined using the optimization tool of Design Expert software. The strategy of the programme is to optimize multiple responses, so the desirability function between 0 and 1 can be maximized. The minimum concentrations of Alamine336, O/A ratios, and stirring times were targeted, due to cost considerations, and all hazardous metal extractions were considered to appear in the maximum values. For the optimum point, the Alamine336 concentration is 0.20M, the O/A ratio is 0.50 and the stirring time is 37.55 min. The result would be predicted 98.64%, 93.05 %, and 81.46% for cobalt, nickel and molybdenum extractions, respectively. A comparison between these results and the ones for Aliquat336 shows that Alamine308 is a better extractant, as it can remove all the three targeted metals in 10 minutes with much less diluted solutions than Aliquat336. Aliquat336 showed less efficiency in extracting nickel alongside cobalt and molybdenum.

7.   Recommendations and future trends

All of our considered extractants showed excellent capability to remove the target hazardous metals from the spent HPCs with very dilute solutions in short periods of time. As these results are from laboratory scale experiments, it is strongly recommended that the possibility of a plant scale-up be investigated to gain a more practical understanding of how

hydrometallurgical methods can be applied in solid waste management. Different reliable software can be employed for this purpose.

Furthermore, all these experiments have been conducted in batch conditions. To achieve a complete understanding of how these results can be implemented in the industrial world, it is also necessary to conduct similar experiments in continuous conditions, for which, specific columns must be designed and tested.

Solvent recovery is another aspect of future work, as it was not covered in this study. If solvents can be regenerated by an easy-to-implement and cost-effective process, it can minimize the cost of the whole process. Stripping of the metals available in organic phase can be investigated too, and in that case, it is also required to observe how the stripping agent can be recovered to reduce the operating costs.

Another improvement to the process can be the use of novel biosorbents for metal removal. Although using our amine-based extractants in very dilute solutions may not be harmful, the use of biosorption processes can improve the environmentally-friendliness of such processes. Besides, biosorbents can be derived from different cheap biomaterials which can improve the cost-effectiveness of the whole process.

8.   Conclusions

This study showed that all three investigated extractants have excellent potentials to extract the hazardous metals cobalt, molybdenum, and nickel from the spent hydroprocessing catalyst, especially for cobalt and molybdenum. All extractants were capable of separating the metals from their aqueous (acidic) phase and transporting them into the extractant-rich organic phase; however, Alamine308 can be considered to be the most effective and suitable extractant for spent HPCs. Alamine308 is capable of removing all three metals to the maximum amounts, for which Aliquat336 is not as effective, especially for nickel extraction. On the other hand, it is able to separate all of these metals in the first 10 minutes, unlike the Alamine336 which requires more than 35 minutes to do so. Modeling and optimization experiments were conducted using a central composite design and the optimized conditions were calculated using the Design Expert software.

The followings are a summary of the results obtained through this study:

- Spent HPCs are classified as hazardous wastes produced in petrochemical industries according to the USEPA.

- Disposal and/or landfilling of spent HPCs without proper treatment(s) is strongly prohibited due to their leachate toxicity to humans, plants, and animals.

- Hydrometallurgical methods to remove hazardous metals from spent catalysts have been studied as easy-to-implement, feasible, cost-effective, and environmentally-friendly processes such as solvent extraction (SX), ion exchange, and membrane separations.

- Among the extractants employed for our solvent extraction processes, Alamine308 is the most suitable extractant for metal removal from spent HPCs due to very short extraction time, low required organic to aqueous ratio, and high efficiencies toward all three targeted metals.

- Aliquat336 showed excellent potential to remove cobalt and molybdenum in 10 minutes, but was unable to remove all nickel from our solid catalyst waste.

- Alamine336 was capable of removing all the three targeted metals only after the 37 minutes which is the highest required extraction time among our three investigated extractants.

- Most developed statistical models showed excellent accuracy and are great sources to determine the effects of different parameters and predict the extraction behaviour in different extraction conditions.

- Models developed for molybdenum have been proven to be the most reliable and accurate models among all three targeted metals.

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10. Appendix

10.1. Poster Presentation in the International Conference of Environmental Protection and Remediation (ICEPR 2015), Barcelona, Spain, 15 – 17 July 2015.

Hazardous Metal Removal from Spent Hydroprocessing Catalysts

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Extended Abstract

Hydroprocessing catalysts (HPCs) are widely used in petrochemical industries, mostly to purify the hydrocarbon processing streams. These catalysts are mainly employed to enhance the efficiency of the process, remove sulphur from the stream, and to break the heavier hydrocarbons to short-chain sulphur-free hydrocarbons (Ancheyta. J., Speight. J. G., 2007). Spent HPCs are classified as hazardous solid wastes produced in petrochemical industries according to the United States Environmental Protection Agency (USEPA, 2003) and cannot be disposed into the environment, or landfilled without a proper treatment due to the presence of hazardous materials including, but are not limited to, the heavy metals, metal oxides, and metal sulphides.

In this research, a hydrometallurgical process has been developed for metal recovery from spent HPCs. After analysing our catalyst using ICP and SEM analysis, preliminary experiments showed that aqua regia is a more effective leaching agent to dissolve metals from our spent catalyst samples than hydrochloric and nitric acids. Two amine-based extractants (Alamine308 & Alamine336), and one quaternary ammonium salt (Aliquat336) were diluted in toluene and were tested for cobalt, nickel, and molybdenum extraction from leached catalysts in aqua regia. A face-centered central composite design (CCD) was employed for our experimental design, and the alamine 308 was selected as the best extractant, based on the ICP analysis on the efficiency, concentration requirement (cost-effectiveness), and required contact time for optimum metal removal. The effects of significant parameters on the extraction processes have been measured, and statistical models were developed using the Design Expert software. ANOVA results were also studied to measure the accuracy and significance of the fitted models. Optimization of each solvent extraction process was completed and optimum points were determined for maximum metal removal from spent HPCs.

Hazardous Metal Removal from Spent Hydroprocessing Catalysts

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AIM OF THE STUDY:

OPTIMIZATION OF A HYDROMETALLURGICAL PROCESS TO REMOVE HAZARDOUS METALS FROM SPENT CATALYSTS

BACKGROUND

➤ Hydroprocessing catalysts are widely used in Hydrodesulphurization (HDS), Hydrogenation (HYD), and Hydrocracking (breaking C-C bonds) processes to remove sulphur from the streams and to break the heavier hydrocarbons and convert them into more valuable light and short-chain hydrocarbons

➤ Spent Hydroprocessing catalysts are considered hazardous wastes by the United States environmental protection agency (EPA) and Canadian Environmental Protection Agency (CEPA) due to the presence of hazardous substances and toxic metal compounds

➤ The landfilling and/or disposal of these wastes are prohibited and appropriate treatment processes should be implemented

➤ Hydrometallurgical processes are considered efficient, cost-effective and low energy using methods, and have widely been employed for different metal uptake from aqueous leachates of secondary materials

RESEARCH METHODOLOGY

➤ Leaching of spent hydroprocessing catalysts were completed in aqua regia:

$$HNO_{3\,(aq)} + 3HCl_{(aq)} \rightarrow NOCl_{(g)} + Cl_{2\,(g)} + 2H_2O_{(l)}$$
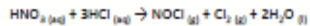
➤ Solvent extraction experiments were conducted by Alamine308, Alamine 336, and Aliquat336

➤ The effects of extractant concentration, contact time, and organic/aqueous ratio were investigated

Fig. 1 - Spent Hydroprocessing catalysts in aqua regia

RESULTS AND DISCUSSION

➤ SEM image of powdered spent catalyst showed coke and metal deposition on active surface of HPC sample used in this study

➤ Most of the active sites of the catalyst are covered with mostly coke and metal complexes which are the main causes of catalyst deactivation

➤ Aqua regia was very efficient in leaching the spent catalysts
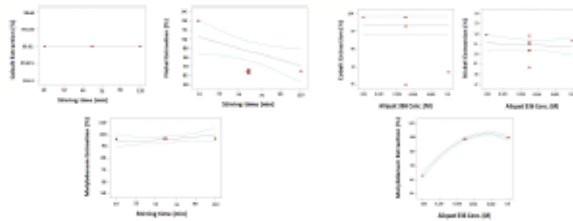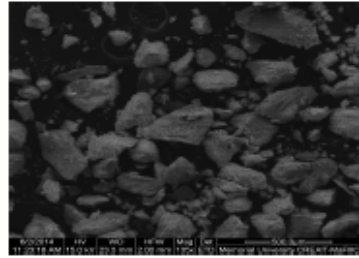

Fig. 2 - Metal extractions vs. time of stirring for (left) cobalt, (right) nickel and (center) molybdenum (Alamine308 conc.: 0.305 M and O/A ratio: 1.75 ml/ml)

Fig. 3 - Changes of extraction efficiencies for different metals with the changes in Aliquat concentrations (O/A ratio 1.75 and stirring time 65 min)

CONCLUSIONS

❑ Aqua regia was selected as the best leaching agent for spent Hydroprocessing catalysts

❑ Alamine308 can be considered to be the most effective and suitable extractant for spent Hydroprocessing catalysts, capable of removing all three metals to the maximum amounts, for which Aliquat336 is not as effective, especially for nickel extraction

❑ Alamine308 is able to separate all of targeted metals in the first 10 minutes, unlike the Alamine336 which requires more than 35 minutes

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OBSERVATIONS ON TOXIC METAL REMOVAL FROM SPENT HYDROPROCESSING CATALYSTS FOR ALIQUAT 336

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ABSTRACT

Data are presented on the extractant behaviour on toxic metal removal from spent hydroprocessing catalyst, produced at the North Atlantic Refinery plant in Newfoundland and Labrador. Aliquat 336 was selected due to its potential capabilities for the separation of cobalt, molybdenum and nickel from the leachate extractant produced by aqua regia. The solvent extraction process was statistically modeled using central composite design (CCD), and the numerical optimization was conducted to achieve the optimum point for toxic metal recovery for the extractant.

KEYWORDS

Toxic metals, Solvent extraction modeling, Spent Hydroprocessing Catalyst, Central Composite Design (CCD), Optimization, Aliquat 336

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Hydrometallurgical Removal of Cobalt, Molybdenum, and Nickel from Spent Hydroprocessing Catalysts

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Abstract

A solvent extraction process is developed for removal of hazardous metals from spent hydroprocessing catalysts. Three extractants were experimentally tested including Aliquat336, Alamine308, and Alamine336. The concentration of extractants, stirring time, and organic/aqueous ratio were considered as the most significant parameters, and Alamine308 was selected as the most efficient extractant due to its capability to remove nickel, molybdenum, and cobalt completely in only 10 minutes with diluted solutions. Statistical modeling was also conducted using the central composite design (CCD) in Design Expert® software and ANOVA results are presented.