ELECTROGENERATIVE REMOVAL OF COBALT IONS FROM CHLORIDE MEDIA USING A BATCH CELL

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by

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A	electrode surface area, m^2
A_e	specific surface area of cathode, m^{-1}
C	analyte concentration, mol cm^{-3}
C_o	initial metal concentration, mol cm^{-3}
C_t	metal concentration at time t, mol cm^{-3}
D	diffusion coefficient, m^2 s^{-1}
E^0	standard reduction potential, V
E^0_{cell}	overall cell potential, V
E_c	overcrossing potential
E_n	nucleation potential
F	Faraday's constant, 96485.309 C mol^{-1}
ΔG^0	standard Gibb's free energy, kJ mol^{-1}
ΔH^0	standard enthalpy change, kJ mol^{-1}
i_p	peak current, A
j	current density, mA cm^{-2}
k	rate of cobalt deposition reaction, s^{-1}
k_m	mass transport coefficient, m s^{-1}
K	equilibrium constant
n	number of electrons per mole of reactant
R	universal gas constant, 8.31451 J K^{-1} mol^{-1}
ΔS^0	standard entropy change, kJ mol^{-1}
t	time, s
$t_{1/2}$	half life, min^{-1}
T	absolute temperature, K

v	potential scan rate, V s^{-1}
V_e	cathode volume, m^3
V_R	volume of electrolyte, m^3

LIST OF ABBREVIATIONS

3D	Three dimensional
AAS	Atomic absorption spectrometer
CP	Cell performance
USEPA	United States Environmental Protection Agency
EDX	Energy dispertive X-ray
FAO	*Food and Agriculture Organisation of the United Nations*
HER	Hydrogen evolution reaction
ISO	International Organisation for Standardisation
PG	Porous graphite
ppi	Pores per inch
RVC	Reticulated vitreous carbon
SCE	Saturated calomel electrode
SHE	Standard hydrogen electrode
SEM	Scanning electron microscopy
WHO	World Health Organisation (WHO)
XRD	X-ray diffraction

PENYINGKIRAN KOBALT ION DARIPADA MEDIUM KLORIDA SECARA ELEKTROGENERATIF DENGAN MENGGUNAKAN SEL BERKELOMPOK

ABSTRAK

Kobalt dipulihkan secara elektrogeneratif dengan menggunakan sel berkelompok. Dalam sistem ini, tindak balas kimia secara spontan akan berlaku di mana kobalt akan diturunkan di katod manakala zink akan dioksidakan untuk menghasilkan tenaga elektrik. Prestasi karbon kekaca berongga (RVC) dan grafit berliang (PG) sebagai katod dinilai berdasarkan masa dan peratusan penyingkiran di dalam reaktor berkelompok. Peratusan pemulihan untuk RVC adalah 99.9% dalam masa 120 min berbanding dengan 210 min untuk PG. Keunggulan RVC katod adalah dijangkakan kerana berupaya mencapai puncak penurunan ketumpatan arus tertinggi, iaitu 8.60 mA cm^{-2} berbanding dengan 6.42 mA cm^{-2} bagi PG dalam kajian pengelektroenapan kobalt melalui teknik voltammetri kitaran. Sistem elektrogeneratif juga kelihatan kurang dipolarisasikan apabila RVC digunakan sebagai katod.

Selain itu, beberapa eksperimen telah dijalankan untuk menentukan medium yang paling sesuai untuk memulihkan kobalt secara elektrogeneratif. Penggunaan medium klorida dan RVC katod dalam sistem elektrogeneratif telah menunjukkan prestasi yang baik dengan nilai tenaga bebas yang paling tinggi, iaitu 389.8 kJ mol^{-1} berbanding dengan medium sulfat dan nitrat. Data daripada kajian voltammetri kitaran yang dijalankan terhadap ketiga-tiga medium juga menyokong bahawa medium klorida adalah medium yang lebih sesuai di mana ia dapat memangkinkan pengenapan kobalt. Hal ini disebabkan medium klorida dapat menghasilkan puncak penurunan ketumpatan arus yang tertinggi untuk semua kepekatan kobalt. Polarisasi elektrogeneratif sistem yang menggunakan medium klorida juga adalah paling kurang berbanding dengan medium lain. Apabila digunakan untuk memulihkan 200 mg L^{-1} Co^{2+}, kadar untuk tindak balas penurunan kobalt meningkat mengikut susunan $NO_3^{-} < SO_4^{2-} < Cl^{-}$.

Akhir sekali, pengoptimuman sistem dijalankan dengan mempelbagaikan kepekatan awal kobalt dan kepekatan natrium klorida. Kajian ini menunjukkan bahawa lebih kurang 100% pemulihan dapat dicapai dalam masa satu hingga empat jam sepanjang proses pemulihan. Pengaruh pH dikaji di mana sistem elektrogeneratif menunjukkan prestasi terbaik antara pH 5.0 hingga pH 7.0. Prestasi sel (CP) maksimum adalah 83% dan penyingkiran kobalt sebanyak 99% dapat dicapai dalam masa 90 min apabila 100 mg L^{-1} Co^{2+} dalam 0.5 M NaCl digunakan sebagai katolit. Nilai ΔH and ΔS bagi sistem elektrogeneratif ini adalah masing-masing 33.41 kJ mol^{-1} dan 0.13 kJ mol^{-1}. Mekanisma pengenapan kobalt telah dicadangkan berdasarkan analisis data voltammetri kitaran dan analisis pembelauan sinar-X (XRD) bagi kobalt yang telah dienapkan.

ELECTROGENERATIVE REMOVAL OF COBALT IONS FROM CHLORIDE MEDIA USING A BATCH CELL

ABSTRACT

Cobalt was recovered electrogeneratively by using a batch cell. In this system, a spontaneous chemical reaction occurred where cobalt is reduced at the cathode and zinc is oxidized to produce a free flow of electrical energy. The performances of reticulated vitreous carbon (RVC) and porous graphite (PG) as cathodes were evaluated based on the time and percentage of removal in an electrogenerative cell. RVC was able to recover 99.9% of cobalt in 120 min compared to 210 min for PG. The superiority of RVC cathode was expected as it obtained the highest reductive peak current density of 8.60 mA cm^{-2} compared to 6.42 mA cm^{-2} of PG in the electrodeposition of cobalt by means of cyclic voltammetry. The electrogenerative system also appeared to be less polarised with RVC as cathode.

Besides that, a series of experiments were carried out to determine the best medium for the recovery of cobalt by means of an electrogenerative system. Use of the electrogenerative system with a chloride medium and RVC cathode had shown promising performance with the highest free energy of -389.8 kJ mol^{-1} compared to that with sulfate and nitrate media. Cyclic voltammetric data obtained with the three media also supported that chloride medium was the better medium which catalysed the cobalt deposition since it generated the highest reductive peak current densities at all concentrations of cobalt. The electrogenerative system with chloride medium was also the least polarised among the other mediums. When used in the recovery of 200 mg L^{-1} of Co^{2+}, the rate of cobalt reduction reaction increased in order of $NO_3^- <$

$SO_4^{2-} < Cl^-$.

Lastly, optimisation of the system was performed by varying the initial cobalt concentration and sodium chloride concentration. The results showed that almost 100% recovery was attained within one to four hours of the recovery process. Influence of pH was investigated where the electrogenerative system performed best between pH 5.0 to 7.0. A maximum cell performance (CP) of 83% with 99% cobalt removal was obtained at 90 min when 100 mg L^{-1} of Co^{2+} in 0.5 M NaCl was used as the catholyte solution. The values of ΔH and ΔS of the process were evaluated as 33.41 kJ mol^{-1} and 0.13 kJ mol^{-1} respectively. The cobalt deposition mechanism was also proposed through analysis of cyclic voltammetric data and X-ray diffraction (XRD) analysis of the deposited cobalt.

CHAPTER 1 INTRODUCTION

1.1 Cobalt

Cobalt is a hard lustrous gray metal with atomic number 27. It ranks 33 in abundance and is widely scattered in the earth crust. Metallic cobalt bears a standard atomic weight of 58.93. As a transition metal, it is located in group 9 and period 4 of the periodic table with electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ that leads to its most common valency, which is Co^{2+} (Housecroft and Sharpe, 2008). Potential applications of cobalt in both scientific and technological fields have made cobalt one of the most sought after heavy metals on earth. The demand for cobalt in recent years has increased significantly due to the rise in manufacturing of electric vehicles and digital components (Bhuiyan et al., 2008). With the public awareness on green technology especially on reducing the usage of natural resources such as petroleum, much research have been focused on producing the next generation of vehicles which rely on electricity to operate. Thus, cobalt has been proven to be most valuable since it is the key element used in designing transformers, motors and generators for electric vehicles. The development of tablet computers and smart phones in recent years also hinges on the increasing usage of cobalt especially in mass production of digital components (Rios-Reyes et al., 2009). One of its prominent uses is in the Li-ion batteries or more commonly known as rechargeable batteries. Unique characteristics such as high energy density, low auto-discharge and high potential difference make cobalt desirable in the electronic fields.

Besides that, cobalt and cobalt alloys exhibit special properties such as high corrosion resistance, high thermal and electrical conductivities (Chi et al., 2005). These special properties have been utilized in the manufacture of super alloys used in turbine blades for aircraft jet engines and gas turbines for pipelines compressors. Moreover, combined with tungsten and carbon atoms, the cobalt-tungsten carbide demonstrates tremendous hardness and brittleness as well as wear resistance. The fact that it possesses a high melting point shows that cobalt carbide is temperature resilient. These properties fulfill all the requirements of a high grade cutting tool and rock drill in the mining and metal forming industries (Zhao et al., 2012). Perhaps one of the oldest uses for cobalt is as colouring agent which is dated back to the Egyptians and Persians. As a transition metal with various oxidation states, cobalt imparts a distinctive blue tint to glass, porcelain, ceramics and paints. The most common usage nowadays is as a catalyst especially in the petrochemical and plastic industries. Abilities of cobalt to form complexes and demonstrate several valencies attributed to its applications as both heterogeneous and homogeneous catalysts.

In addition to its various industrial applications, advances in modern medicine also deploy the use of cobalt-base alloys in the cast of dental implants. The rationale behind this material choice is its excellent resistance to degradation in the oral environment (Marti, 2000). The cobalt-chromium alloy also exhibits optimum flexibility that allows it to clasp firmly and obtain retention from teeth. (Teigen and Jokstad, 2012). Furthermore, it is more cost effective than the gold alloy dental prostheses (Hassan et al., 2005). The use of cobalt alloys for surgical applications is generally associated to orthopaedic prostheses for the knee, shoulder and hip as well as fracture fixation devices. The solid-solution-strengthening effect of chromium and molybdenum, the formation of extremely hard carbides and the corrosion resistance imparted by chromium are among the attractive characteristics of the cobalt-chromium-molybdenum alloy that is suitable as orthopaedic prostheses (Marti, 2000).

Lastly, the most common radioactive isotope of cobalt is *cobalt-60.* It is used medically in radiation therapy and for the sterilization of medical equipments.

1.2 Global Demand and Supply

Owing to its vital role in the rechargeable battery sector, the growing importance of cobalt in the future energy economy is undeniable. As reported by the Global Cobalt Corporation, a multinational cobalt exploration and development company with world-class assets in Russia, Mongolia and Canada, the growing middle class in developing nations are feeding the demand for electronics powered by cobalt batteries which accounts for nearly 30% of worldwide cobalt demand in 2011 (The Cobalt Development Institute, 2011). This is followed by the increasing demand of super alloys by the automotive and aerospace technologies which constitute about 19% of the worldwide cobalt demand. The worldwide demand of cobalt in various industries by 2011 is illustrated in Fig. 1.1.

Generally, cobalt is produced as by-products in the metallurgical processes of copper and nickel deposits. With the majority of the global cobalt supply chain being derived from the politically and socio-economically unstable West African countries of the Democratic Republic of Congo (DRC) and Zambia, the United States, the European Union, Netherlands and Japan have all declared cobalt a strategic metal that requires stockpiling. Moreover, a legislation called Dodd-Frank Act has been passed by the United States Government and European Union to protect the chain of custody of a group of minerals defined as “Conflict Minerals”. Henceforth, all electronics that contain metals sourced from areas of conflict are required to be labeled in order to secure the domestic source of cobalt.

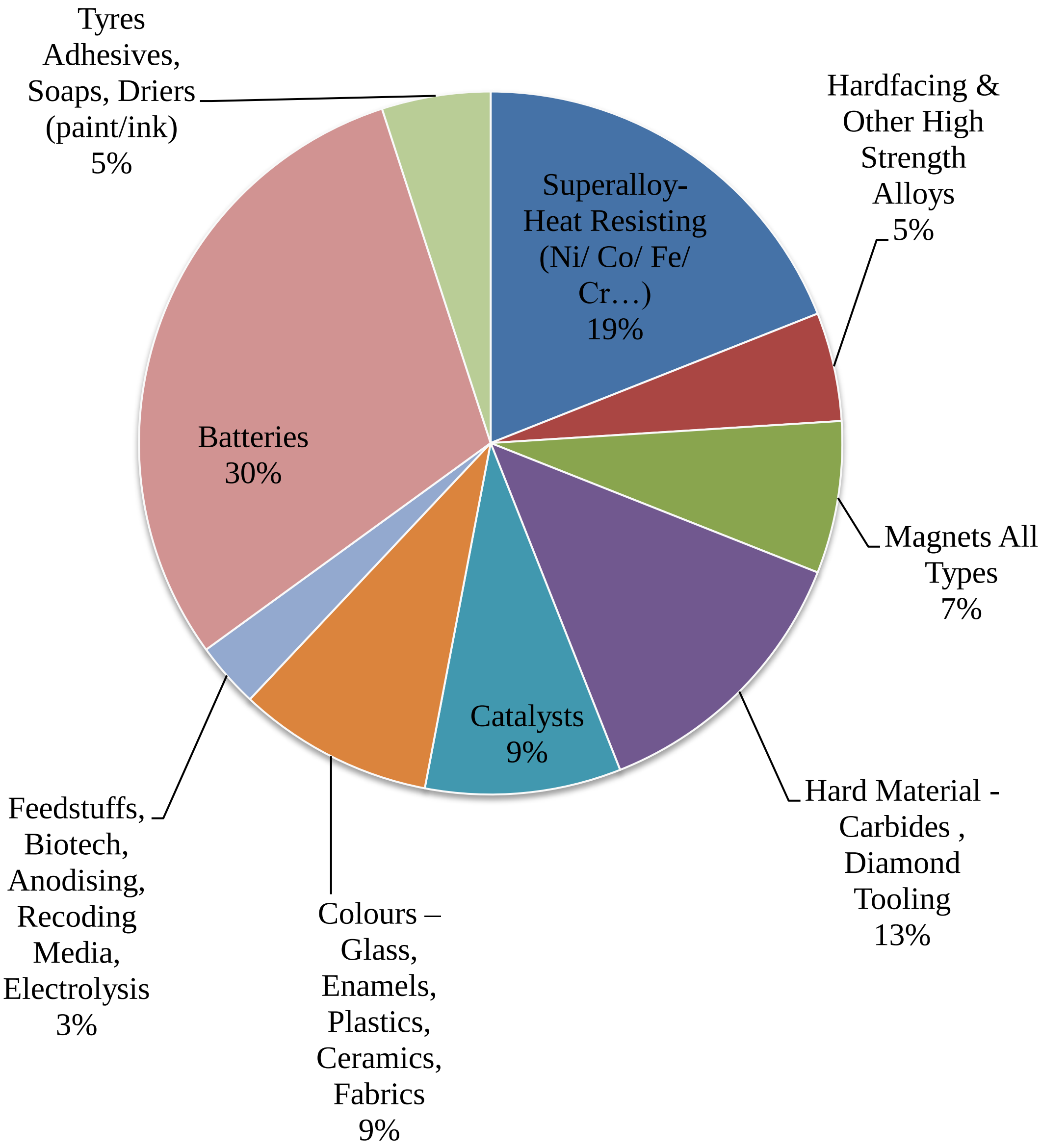

Figure 1.1 The worldwide demand of cobalt in various industries by 2011 (adapted from The Cobalt Development Institute, 2011).

Despite this, the cobalt market maintained its resilience as the global cobalt supply in 2011 grew around 72 % to 82,247 tonnes from 23,207 tonnes in 1995 (Kapusta, 2006; The Cobalt Development Institute, 2012). This is also caused by the shift of the cobalt dynamic demands over the past 15 years. The first shift is the transition of demand from the United States and Western Europe to Asia particularly China where its cobalt industry relies heavily on imported cobalt ores and intermediates (Global Cobalt Corporation, 2011). The second shift is the increasing application of cobalt in the batteries and catalysts industries. In addition, the supply of cobalt is supported by other important cobalt producers such as Australia, Brazil, Cuba, Russia and China.

1.3 Health Concerns, Regulations and Advisories

As the crucial element powering the global green agenda, the continuous exploitation of the supply of cobalt will have adverse impacts on the environment. The large amount of industrial effluents containing the non-biodegradable and toxic cobalt released each year has posed significant threats to the environment in the form of water and air pollutions. Inhalation exposures to elemental cobalt powders, salts, oxides and mixed metal-cobalt compounds are related with varying toxic manifestations that affects the respiratory system such as asthma and cystic fibrosis to lung cancer (United States Department of Health and Human Services, 2004a). Dermal exposures have been reported to cause allergic reactions (Lison et al., 2001). The proven genotoxic and carcinogenic effects of cobalt on experimental rodents in various studies also clarify the potential health hazard of cobalt exposure in humans. (Browning, 1969; De Boeck et al., 2003; Beyersmann and Hartwig, 2008). In all cases, cobalt compounds were reported to induce DNA damage, DNA protein cross links, gene mutations, aneuploidy, and sister chormatid exchanges in the rodent cells.

Concern over the damaging effects of cobalt on humans and the environment has long captured the attention of several international organisations such as World Health Organisation (WHO), *Food and Agriculture Organisation of the United Nations* (FAO) and International Organisation for Standardisation (ISO). Legal constraints have been imposed on the permissible level of cobalt concentration in industrial effluents and drinking water. The maximum acceptable concentration of cobalt in drinking water permitted by international regulations is 10 μg L^{-1} (World Health Organization, 1993; Tuzen and Soylak, 2006). Meanwhile, the amount of cobalt in sewage effluents regulated by the United States Environmental Protection Agency (EPA) is limited at 500 μg L^{-1} (United States Department of Health and Human Services, 2004b). According to the Canadian Water Quality Guidelines provided by Canada Environmental Bureau of Investigation, the permissible limit of cobalt in irrigation water and livestock waste are 0.05 and 1.0 mg L^{-1} (Rengaraj and Moon, 2002). As for Malaysia, there has been no regulations being laid down yet by the Malaysian Department of Environment regarding the permissible level of cobalt in wastewater.

1.4 Recovery and Recycling Technologies

The world current cobalt reserve is estimated to be 7,500,000 tonnes by 2011 (United States Geological Survey, 2012). With increasing consumption of cobalt every year, the reserve is expected to be reduced. Though the growth of cobalt demand is relatively strong over the years, the supply side remains unstable as cobalt is mined predominantly in the politically unstable African countries. The scarcity of cobalt is also demonstrated by its role as the substantial technology-enabling metal with various applications. It is mined and used extensively in high-tech products and technologies, along with other important uses. With growing environmental awareness and regulations enforced on discharge of effluents, treatment and recovery processes for industrial effluents are essential to ensure the sustainable development of the cobalt industry as well as to maximize the cobalt resources.

In light of the above, various techniques have been developed and they are summarized into two categories, abiotic and biotic methods (Dhankhar and Hooda, 2011). By far the most widely used methods are the abiotic methods which usually comprise of precipitation, adsorption, ion exchange, membrane and electrochemical technologies and solvent extraction. One of the oldest methods used for recovery of heavy metals from industrial solutions is that of chemical precipitation. During the process, the dissolved metal is converted into its insoluble form by chemical reaction between the soluble metal compound and the precipitating reagent. The insoluble precipitates are then removed from the solutions by filtration or other separation techniques (Szabadvary, 1992). For example, Co(II) was oxidized to the Co(III) state which precipitated out of the Zn-Cd-Co-Ni sulphate solution as an insoluble cobaltic hydroxide, $Co(OH)_3$. In this oxidation-precipitation reaction done by Owusu (1998), the precipitating reagent was a power oxidant called Caro’s acid, a mixture of hydrogen peroxide and concentrated sulphuric acid. However, there are several disadvantages in the precipitation treatment. It is not efficient for selective recovery of metals due to coprecipitation of more concentrated metals or any iron present in the effluent resulting in large volumes of solid sludge being generated for disposal (Eccles, 1995; Suzuki et al., 2012). It is also time consuming where pH adjustment was required in separate tanks with extensive set ups (Parga et al., 2005).

Another common treatment for industrial waste is solvent extraction. The extraction process basically involves a two phase system. An organic solution containing an extracting reagent is used to transport the respective metal from one aqueous solution to another, leaving behind other metals and impurities in the aqueous solution. The extractant is run counter current to the aqueous solutions at a temperature slightly higher above the ambient temperature to improve the exchange kinetics and assist the phase separation process (Peters et al., 1985). Extraction of cobalt has been carried out from sulphate solution containing phosphoric, phosphonic and phosphinic acids. For instance, Luo et al. (2006) and Swain et al. (2007) had reported using 2-ethyl hexyl phosphonic acid combined with mono 2-ethyl hexyl ester (PC88A) and bis(2,4,4 trimethylpentyl) phosphonic acid (Cyanex 272) as extractants to recover cobalt from nickel-cobalt waste and lithium ion battery respectively. Nonetheless, several potential operational challenges in solvent extraction must be addressed. Among them is the use of flammable organic liquids, degradation and poisoning of the extractant and possibility of formation of a third phase, hereby increasing the risk of environmental pollution and operating costs (Peek et al., 2009).

Next is the ion exchange treatment process. It is a reversible chemical process where the removal of heavy metals is achieved by the exchange of ions on the resin in the wastewater (Peek et al., 2009). There are a variety of resins for specific applications with various metals but polymeric resins are usually employed for almost any separation process because of their ability to provide a more specific and straightforward purification compared with solvent extraction or precipitation (Mendes and Martins, 2005). In cobalt removal, a cation exchanger resin is used for adsorption of cobalt ions from aqueous solutions. Rengaraj et al. (2002) and Kang et al. (2004) had employed the use of Amberlite IRN-77 cation exchange resin to remove cobalt from a synthetic waste water consisting of nickel, chromium and cobalt. Even though ion exchange is easy and inexpensive to implement on a production scale, large quantities of chemicals and water are required to regenerate the resins after exhaustion (Thang et al., 2010). Other problems typically faced by ion exchange treatment process include susceptibility to fouling by organic substances and metals present in the wastewater along with generation of waste as a result of ion exchanger regeneration.

Adsorptive removal of heavy metals from aqueous effluents involves the physical adherence or bonding of ions and molecules on to the surface of another molecule known as adsorbents (Dhankhar and Hooda, 2011). After adsorption, the accumulated adsorbates are then eluted from the adsorbents through a stripping process. Adsorptive removal of heavy metals is usually achieved using activated alumina such as bentonite and zeolite. They are chosen because they are abundant in nature which contributed to their low mining cost and high resistance to alteration (Manohar et al., 2006; Al-Dwairi and Al-Rawajfeh, 2012). The major drawbacks of the adsorption process are the recovery of the adsorption column and the further treatment of the backwash water (Gao et al., 2005). Apart from physical adsorption, biotic methods such as biosorption for the removal of heavy metals from industrial effluents have gained significant momentum in recent years and are poised for commercial exploitation. Biosorption is defined as the passive uptake of toxicants by dead or inactive biological materials or by materials derived from biological sources (Vijayaraghavan and Yun, 2008). Biosorbents for removal of metals are usually divided into the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials. Examples of biosorbents that have demonstrated good adsorption capacities toward cobalt are crab shell particles (Vijayaraghavan et al., 2006), lemon peel waste (Bhatnagar et al., 2010), biomass of moss *Rhytidiadelphus squarrosus* (Marešová et al., 2011) and freshwater cynobacterial biomass of *Nostoc linckia* (Mona et al., 2011). The downside aspects of biosorption are early saturation and the lengthy pretreatment of the biosorbents which normally ranges from 24 hours to 6 days (Ahluwalia and Goyal, 2007).

In search of treatment technologies that are both efficient and environmental friendly, electrochemical methods emerged as the frontiers with promising prospects for the future. Generally, the electrochemical methods are divided into electrolytic and galvanic processes where both differ by their power consumption in which the latter does not require any of it. The principles and techniques of the electrochemical methods have been described in various literatures (Moskalyk and Alfantazi, 2000; Walsh, 2001). The theory of operation basically involves a redox reaction where electrons are provided by an electrical source, either through external power voltage or spontaneous chemical energy to reduce the metal ions in the electrolyte to form elemental metal at the cathode surface (Peters et al., 1985). Electrolytic metal recovery has been used for many years in electrowinning and electrorefining of cobalt from sulphide ores and sulphate electrolytes (Das and Subbaiah, 1984; Jeffrey et al., 2000; Kongstein, et al., 2007a). In the electrolytic recovery of metal, external power supply is used to pass the current directly through the electrolyte between the cathode plates and insoluble anodes. Even though the sludge of the waste generated by electrolytic recovery route is considerably lesser compared to other recovery methods, the process is highly energy dependent and labour intensive (Peters et al., 1985) especially when dealing with very dilute solutions. The capital cost is extremely high with low current and removal efficiency.

Electrodialysis is introduced as an electrochemical separation process that uses cationic or anionic membranes to remove ions from the solution. Just like electrolytic metal recovery, the driving force for separation in eletrodialysis is the current that is applied across the membranes. Electrodialysis consists of three different compartments: a feed or diluate compartments where ions are removed, a concentrate compartment where ions are transported to and a rinse compartment where electrodes are cleaned and chemicals are prevented from accumulating and corroding the electrodes (Thang et al., 2010). The use of membranes in electrodialysis reduce the amount of chemicals and water used in the separation process but selectivity of the process is limited to charged mobile ions with low molecular weight. Another method that evolved from the electrodialyis method is the electrodeionisation separation process. It combines the selective removal of ion exchange resin with the continuous processing of electrodialysis. The ion exchange resins are packed between the cation and anion exchange membranes in the diluate compartment to enhance the transport of ions across the membrane. With ion exchange resins functioning as the ionic bridge, the overall conductivity of the diluate compartment is increased, the concentration polarisation phenomena is minimized and a high removal efficiency of hardness material can be obtained (Erwan and Wenten, 2002). However, electrodeionisation faces the disadvantage of scale formation on the surface of resins and membranes when the pH of the solution becomes basic (Lee et al., 2012). The presence of resins in the diluate compartment also causes uneven flow distribution where more direct current is needed to assist the ion migration process.

Cementation is a galvanic process that has long been used in the extractive metallurgy to recover valuable metals. In cobalt cementation, the cobalt is extracted by using zinc dust. The less noble metal which is zinc will displace the ion of the more noble metal, cobalt from the electrolyte when placed in contact with it (Nelson el al., 2000a). The mechanism of the process is summarised as below:

Anodic reaction : $\mathrm{Zn^0 \rightarrow Zn^{2+} + 2e^-}$ (1.1)

Cathodic reaction : $\mathrm{Co^{2+} + 2e^- \rightarrow Co^0}$ (1.2)

Overall reaction : $\mathrm{Zn^0 + Co^{2+} \rightarrow Zn^{2+} + Co^0}$ (1.3)

However, this method faces several limitations such as slow reaction rates and low removal efficiency. High temperatures are essential to activate the reaction which results in high operating costs. The introduction of additives to improve the cementation rate poses the risk of introducing hazardous waste to the environment.

The electrogenerative metal recovery process is an innovative technology that is inspired from the cementation process. This technology was pioneered by Kumar and Vasu (1972) which was known as galvanic cementation at that time to recover copper metal from chalcopyrite leach liquors using scrap iron as the sacrificial anode. Langer and Anderson (1976) used the same method to recover copper metal from acidic Cu(II) solutions. Hor and Mohamed (2003, 2005), Yap and Mohamed (2007), Karoonian et al. (2012a) and Ramalan et al. (2012) then applied this technology to recover copper, gold and lead. This method of treatment offers an efficient and clean way of recycling and recovering both metal and water. It is also an attractive alternative treatment process compared to the conventional method of electrolysis because its driving mechanism is a spontaneous electrochemical reaction which does not require an external energy supply. Electrogenerative recovery of cobalt using a batch cell was first introduced by Tan and Mohamed (2011). This process was carried out in a sulphate medium where recovery of 200 mg L^{-1} cobalt was almost 100% after 10 hours of operation. The long period of recovery for cobalt in sulphate medium prompted the possible replacement of the conventional sulphate bath with a chloride bath. According to Kongstein et al. (2007a, 2007b), use of the chloride medium in the electrolytic system offers better electrical conductivity, greater depolarising effect, lower overpotential and higher cathodic current efficiency. Moreover, higher activity coefficients of the cobalt chloride solutions and better solubility of the cobalt chloride salts enable higher concentrations of cobalt to be used in the system (Åkre, 2008). Thus, the purpose of this work is to study the feasibility of the chloride medium in cobalt recovery at RVC cathodes using an electrogenerative process.

1.5 Medium of Metal Bearing Waste

Perusal of reviews on methods of metal recovery shows that most of the studies focused on the design of reactors, the performance of the electrodes and mass transport correlations. Carreño et al. (1999) have reported the influence of solutions (nitrate, chloride, and sulphate) on the electrolytic removal of Pb(II) ions using a vitreous carbon electrode. The experiment was conducted in a membrane cell in a flow by mode. They have established that complications arose while attempting to remove Pb(II) from nitrate and sulphate medium. Higher removal efficiency was achieved with chloride containing electrolyte. The total charge consumption increased in order of $Cl^- < NO_3^- < SO_4^{2-}$. Further study on cyclic voltammetry also showed that the Pb(II) dissolution peaks differed according to the medium used with the chloride medium having the highest charge. Based on this observation, Carreño et al. (1999) deduced that chloride medium is a good complexing agent that adsorbs on the electrode surface to catalyse the lead deposition whereas nitrate is a non complexing agent without the ability to adsorb on the electrode surface. The reduction of lead from sulphate was only possible at very negative potentials. The medium used also affected the surface morphology of the Pb deposits on electrode. Atomic force microscopy (AFM) visualization of the Pb deposits revealed that the deposits formed from sulphate and chloride appeared to be slightly rougher than nitrate electrolyte. In chloride and nitrate medium, the Pb deposits appeared as ellipsoidal grains with small round shape cluster whereas the Pb deposits cluster in sulphate medium was distributed randomly on the electrode surface.

Electrochemical coagulation of cadmium from different mediums was conducted by Huang et al. (2009). They have reported that the performance of the electrocoagulation process was found to be strongly affected by the presence of anions in the solutions. The removal of cadmium is focused on the dissolution of aluminium which was used as anode in the process. At the same time, the current provided was used to dissociate water molecules on the cathode and increased pH in the solution. The OH^- ions then reacted with Cd^{2+} ions to form $Cd(OH)_2$ coagulants.

Under these circumstances, the $Cd(OH)_2$ formed was removed from the solution by adsorption on the electrode as charged colloidal particle. Solutions of nitrate, sulphate and chloride were added to comprehend their effect on cadmium removal. The removal percentage increased in order of $SO_4^{2-} < NO_3^{-} < Cl^{-}$. In the chloride solutions, the presence of chloride ions provided electrolytic conductivity to maintain a current flow in cell. The sustainable current ensured the dissolution of aluminium, generation of hydroxyl group, production of coagulant and removal of cadmium from solution. Although nitrate ions were able to sustain a healthy current in the cell, no coagulant was observed due to excessive OH^- generation. $Al(OH)_3$ was further reduced to form $Al(OH)_4^-$, therefore no coagulant was observed. In the case of sulphate medium, an inert film was formed on the aluminium anode that prevented the current from passing through the cell. Thus, no reaction was observed.

Hexavalent chromium, Cr(VI) is a heavy metal pollutant frequently found in wastewater produced from dye and electroplating industries. Han et al. (2008) have studied the use of microalgal isolate, *Chlorella miniata* to remove chromium from wastewater by means of biosorption and bioreduction in the presence of different anion systems such as SO_4^{2-}, NO_3^- and Cl^-. The studies proved that anions had inhibitory effects on the Cr(VI) removal by C. *miniata* with NO_3^- having the highest inhibitory effect followed by Cl^- and SO_4^{2-} respectively. The presence of anions tend to compete with Cr(VI) for the adsorption sites of the algae where the affinity of anions to biomass was $NO_3^- > Cl^- > SO_4^{2-}$. Thus, the biosorption of Cr(VI) was least affected by sulphate. This is because in the sulphate system, besides the dominant species, $HCrO_4^-$, the existence of another species with two negative charges, $CrO_3SO_4^{2-}$ made it easier to be adsorbed on the biomass rather than solely $HCrO_4^-$ in the chloride and nitrate system. Moreover, the hydration energy of the anions in the solution differed among each other in the order of $\Delta G_{\text{sulphate}}\,(-1103\ \text{kJmol}^{-1})>$ $\Delta G_{\text{chloride}}(-338\ \text{kJmol}^{-1})$ > $\Delta G_{\text{nitrate}}(-314\ \text{kJmol}^{-1})$. Anion with low ΔG such as nitrate was easily absorbed on the sorbents.

Grujicic and Pesic (2005) had investigated the iron nucleation mechanisms from chloride and sulphate solutions on vitreous carbon electrode by using the cyclic voltammetry and chronoamperometry methods coupled with atomic force microscopy under pH 2 and 5. According to them, the iron nucleation was less inhibited in the chloride medium resulting in higher current efficiency. This was because in the cyclic voltammogrammes, the cathodic peak, I_c in the chloride medium was less obscured by hydrogen reduction current since the hydrogen reduction reaction was shifted in a more negative direction. Consequently, the cathodic currents at the vertex potential in the chloride system (-1300 mV) was lower than in sulphate medium (-1200 mV). Hence, it was apparent that the hydrogen evolution reaction was prevalent in the sulphate system with the hydrogen gas bubbles readily observed visually especially at pH 2. Furthermore, the onset of iron deposition was less negative in the chloride solutions compared to the sulphate solutions. Despite this, the extent of hydrogen reduction was larger at pH 2 than at pH 5 in both systems. Based on their chronoamperometry studies, the iron deposition at pH 2 involved the direct deposition of Fe^{2+} ions whereas at pH 5, the deposition proceeded through the formation of iron hydroxide or iron hydroxyl chloride. The morphology of iron deposited from both chloride and sulphate system was similar even though the nuclei of chloride system were larger with sharper defined contours.

Reactive deposition of cobalt under the influence of anions was carried out by Jiang and Tseung (1990b) by employing the rotating ring-disk electrode (RRDE) technique with standard calomel electrode (SCE) as reference electrode. The electrode consisted of a nickel disk electrode with a concentric gold ring electrode. The electrochemical activities of the electrodes were evaluated by measuring the anodic peak current density by linear potential sweep and were found to decrease in the order of $Cl^- > SO_4^{2-} > CH_3COO^- > NO_3^-$. The current density was lowest in nitrate solutions because the deposition reaction was depressed by nitrate reduction. Further investigation by cyclic voltammetry showed that the chloride had the most distinct cathodic peak compared with other anions. The voltammetry curve of the chloride medium was also characterized by two anodic peaks where the first peak was associated with the dissolution of cobalt metal and second peak was due to dissolution of the nickel disk electrode. Meanwhile, sulphate and acetate mediums portrayed similar voltammetry characteristic where their cathodic parts were characterized by gradual increase of the cathodic current and there was only one anodic peak. The disparity between the two mediums was the cathodic current of the acetate medium started to rise at a more positive potential and the electrodeposition of Co^{2+} occurred at more cathodic potential. Based on the finding in cyclic voltammetry, Jiang and Tseung (1990b) concluded that the oxygen reduction has profound effect on the cobalt deposition with SO_4^{2-} and CH_3COO^- ions being the most affected. The scanning electron micrographs of the cobalt deposits in the presence of Cl^- ions showed the porous structure of the deposits characterised by coarse pores (~1 µm) and fine pores (~0.2 µm) whereas the cobalt grains appeared to be deposited in bamboo shape in the presence of SO_4^{2-}. In the cases of CH_3COO^- and NO_3^- ions, the cobalt deposits appeared in the form of a dense cobalt deposit layer.

The electrogenerative recovery of gold from cyanide and chloride systems was carried out by Yap and Mohamed (2007) and Karoonian et al. (2012b) respectively using a batch reactor. Both studies employed the use of zinc as sacrificial anode and reticulated vitreous carbon (RVC) as cathode to recover 500 mg L^{-1} of simulated gold waste. The spontaneity of both systems was given by their positive overall cell potentials which were 0.65 V and 1.74 V for cyanide and sulphate system respectively. According to Yap and Mohamed (2007), the cyanide system required 42 min to achieve 90 % of gold recovery with the rate of 0.046 min^{-1} whereas in chloride system, 99 % of gold was recovered in 90 min with the rate of 0.056 min^{-1} (Karoonian et al., 2012b). The mass transport coefficients (k_mA_e) for cyanide and chloride systems were similar in which cyanide obtained a value of 0.027 s^{-1} and the latter 0.023 s^{-1}. Kinetically, the chloride system performed better than cyanide system as proven by its higher rate of recovery. Furthermore, the chloride system was able to accomplish a maximum current density of 3.78 mA cm^{-2} compared to the 0.67 mA cm^{-2} of cyanide system during the polarisation study. The surface morphology of the gold deposited on the RVC cathode determined by scanning electron microscopy (SEM) revealed that the gold deposits appeared in small nodular structure with an average grain size of 150 nm in cyanide medium whereas in chloride medium, the deposited particles were spherical, granular and more homogenous with average size between 60 to 300 nm.

In conclusion, Winand (1991) had reported the use of chloride medium in extraction of metals offered several advantages over the conventional sulphate medium. Most of the metal chloride compounds are highly soluble in water. The sulfide complex from the ores can be easily removed in a concentrated chloride solution. Moreover, the chloride medium has better electrical conductivity and current efficiency. Lastly, the electrocystallisation of cobalt from aqueous chloride solutions produced cobalt deposits of better quality without the use of additives.

1.6 Objectives of Research

This work describes an easy means to recover cobalt electrogeneratively from the chloride bath as an alternative to the more expensive and complicated electrolytic recovery process. The performance of the batch cell system was evaluated based on the medium used, initial cobalt(II) concentration, concentration of sodium chloride as supporting electrolyte, addition of other metals, influence of pH and temperature. The thermodynamic, kinetic and mass transport characteristics of the chloride systems were further explored in order to optimise the cobalt recovery process. This investigation will concentrate on the use of reticulated vitreous carbon (RVC) as cathode material and chloride as the electrolyte to recover cobalt. Performances of the chloride, sulphate and nitrate system were also compared. Scanning electron microscope coupled with energy dispersive X-ray spectroscopy and X-ray diffraction were used to characterise the deposited cobalt.

The overall objectives of this research are summarised as the following:

i. To evaluate the performance of reticulated vitreous carbon and porous graphite as cathodes in the electrogenerative removal system.

ii. To investigate the use of chloride, sulphate and nitrate medium in the electrogenerative removal system.

iii. To optimise the cobalt recovery process using RVC cathode and chloride medium.

CHAPTER 2 THE ELECTROGENERATIVE SYSTEM

2.1 The Spontaneity of the Electrogenerative Process

The focus of this research is on recovery of cobalt using an electrogenerative system. The driving mechanism for this cell is a spontaneous chemical reaction that produces electrical energy as opposed to an electrolytic cell that requires high electrical energy. The reaction occurs in a divided cell where a more noble metal is reduced at the cathode whereas the less noble metal is oxidized at the anode. The thermodynamics of a galvanic cell can be described by the Gibb's free energy:

$$\Delta G^0 = -nFE^0_{cell} \tag{2.1}$$

where n is the number of electrons per mole of reactant, F is Faraday's constant and E^0_{cell} is the overall cell potential. For a spontaneous chemical reaction in an electrogenerative process, the value of Gibb's free energy is always negative.

In the case of electrogenerative recovery of cobalt using a reticulated vitreous carbon (RVC) as cathode and zinc as anode under the influence of sulphate medium, Tan et al. (2012) had established the spontaneity of the redox process experimentally by constructing an electrochemical cell with a configuration of Zn|$ZnSO_4$ (1.0 M)||$CoSO_4$ (1.0 M)|RVC to operate at room temperature and solution of pH 5. Taking into account the Pourbaix's diagram for zinc (Pourbaix, 1966; Beverskog and Puigdomenech, 1997) and reports by previous studies (Nelson et al., 2000b; Ku et al., 2002; Ramalan et al., 2012), the standard oxidation potential of Zn^{2+}/ Zn couple in the presence of 1.0 M Zn^{2+} is 0.763 V with respect to the standard hydrogen electrode (SHE). According to Tan et al. (2012), when the Zn anode was coupled with a RVC cathode in the electrochemical cell, an overall cell potential of 1.421 V was generated. In other words, a reduction potential of 0.658 V versus SHE was triggered when Co^{2+} was reduced to Co^0 on the RVC surface. Consequently, a negative free energy of ΔG = -274.0 kJ mol^{-1} was obtained indicating the spontaneity of the cobalt recovery process. The electrode processes have been described as in following equations:

Anode : $\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{2+} + 2\mathrm{e}^-$ $\qquad \mathrm{E}^0 = 0.763\ \mathrm{V}$ (2.2)

Cathode : $\mathrm{Co}^{2+}/\mathrm{RVC} + 2\mathrm{e}^- \rightleftharpoons \mathrm{Co}/\mathrm{RVC}$ $\qquad \mathrm{E}^0 = 0.658\ \mathrm{V}$ (2.3)

Overall : $\mathrm{Zn} + \mathrm{Co}^{2+} \rightarrow \mathrm{Zn}^{2+} \rightleftharpoons \mathrm{Co}$ $\qquad \mathrm{E}^0_{\mathrm{cell}} = 1.421\ \mathrm{V}$ (2.4)

2.2 Three Dimensional Electrodes

The merit of the electrogenerative system lies on the spontaneity of the process. In the case of this work, three dimensional (3D) porous carbon electrodes were used as cathode materials and zinc as the sacrificial anode. According to Friedrich et al. (2004), three dimensional electrodes are used to counteract the limitation of low space-time yield and low normalised space velocity faced by two dimensional electrodes. Moreover, three dimensional carbon electrodes exhibit advantages such as large specific area, chemical inertness, good electrical conductivity, good fluid permeability and good mechanical resistance especially when treating dilute aqueous solutions. The porous structure of the electrode also ensures the ability of the electrode to hold the infused materials within controlled pore sizes. Examples of 3D electrodes are porous graphite, packed bed electrodes, carbon felt and reticulated vitreous carbon (RVC). However, the focus of this research will be on the performance of the electrogenerative system using RVC.

2.3 The Membrane

The electrogenerative recovery process employed the use of anion exchange membrane in the system. The application of an anion exchange membrane offers several advantages over the conventional method of cementation. Firstly, it only allows the anions to diffuse from the anode compartment to the cathode compartment or vice versa. It is stationed in between the anode and cathode compartments where it serves as a separator to prevent the mixing of both electrolytes. This arrangement will improve the selectivity and reduction of cobalt ions on the cathode. Moreover, the products of oxidation and reduction are well separated. The Neosepta anion exchange membrane used in this work also exhibits desirable characteristics such as low electric resistance, low diffusion coefficient, high mechanical strength, high chemical stability and high dimensional stability (ASTOM Corp., 2004). Furthermore, Karoonian et al. (2012b) compared the use of Neosepta and Mega Ralex anion exchange membrane in the electrogenerative recovery of gold from chloride medium and discovered that the Neosepta membrane resulted in higher gold recovery. This is because Neosepta anion exchange membrane is thinner and less resistant than the Mega membrane.

2.4 Cell Performance

The electrogenerative removal of cobalt emphasizes on the spontaneity of the process where the spontaneous discharge of Zn^{2+} provides the current to reduce the Co^{2+} species. During the course of the process, the current generated might also be used to facilitate potential side reactions such as hydrogen and oxygen reductions. Thus, the total charge generated is proportional to the amount of zinc oxidised and to the amount o f cobalt deposited. Details of the concentration profiles of zinc and cobalt have been discussed amply by Tan et al. (2012) and Ramalan et al. (2012).

The cell performance (CP) is evaluated according to the following equation:

$$\mathrm{CP} = \frac{\text{number of moles of Co(II)deposited on the RVC cathode}}{\text{number of moles of Zn(II)discharged at the anode}} \times 100\% \qquad (2.5)$$

CP expresses the efficiency of the reactor at a fixed time with reference to the reaction in Eq. 2.4. It was also important to evaluate the kinetic constants for the electrode process to explain the influence of concentration on Co^{2+} removal at the RVC surface. Reduction of metal ions in an electrochemical cell involves two major transport processes, mass transport and charge transfer. The relationship between the concentration and time for a 3D electrode under mass transport control can be expressed by Eq. 2.6 (Pletcher et al., 1991):

$$\ln\left(\frac{C_t}{C_o}\right) = -kt \qquad (2.6)$$

where, $k = \frac{V_e k_m A_e}{V_R}$, C_t is the metal ion concentration at time t, C_o is the initial metal ion concentration, k_m is the mass transport coefficient, A_e is the specific surface area, V_e is the cathode volume and V_R is the volume of the electrolyte within the reactor. The product of k_mA_e represents the volumetric mass transport coefficient used for a 3D electrode system (Bertazzoli et al., 2008). The transport processes in an electrogenerative cell are visualized in the Fig. 2.1.

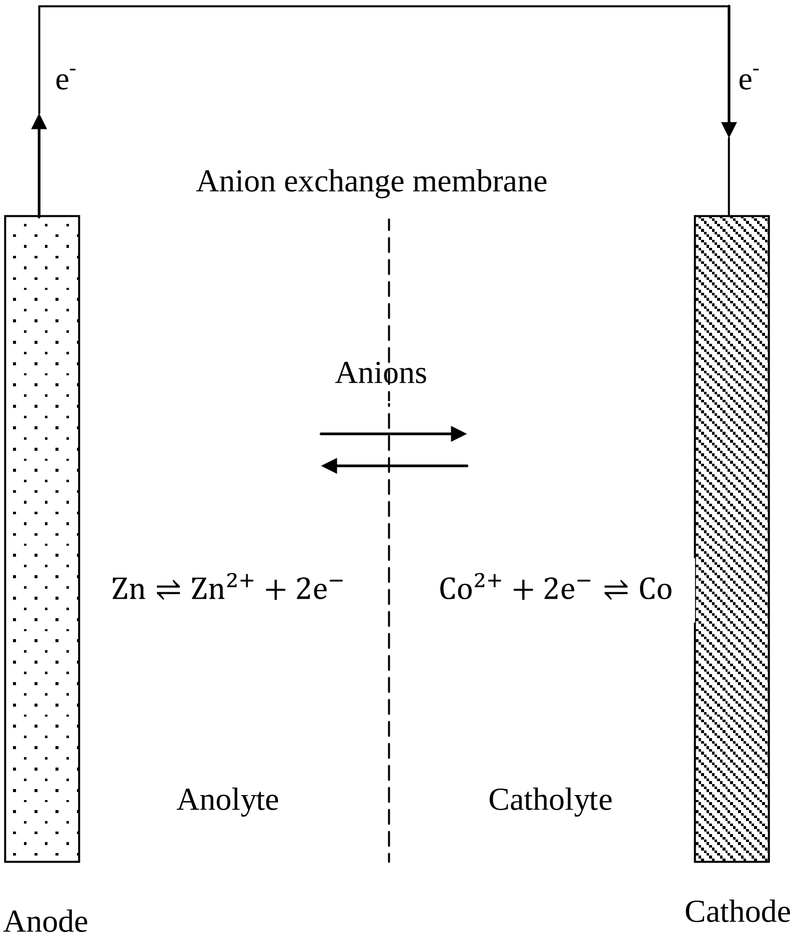

Figure 2.1 Charge transfer and ion transport in an electrogenerative reactor with an anion exchange membrane (adapted from Tan 2010).