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HYPOCHLORITE LEACHING OF GOLD ORE

By:

MOHAMAD ZA'IM BIN MOHAMAD ZAIDI

Supervisor: Dr. Norlia Baharun

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Hypochlorite leaching of gold ore". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

Name of Student: Mohamad Za'im bin Mohamad Zaidi   Signature:

Date :   25 June 2018

Witness by,

Supervisor :   Dr. Norlia Bharun   Signature:

Date: 25 June 2018

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PELARUT LESAPAN HIPOKLORIT SAMPEL BIJIH EMAS

ABSTRAK

Dalam penyelidikan ini, sampel bijih emas yang diterima dari Kuala Lipis, Pahang telah digunakan. Bijih emas mula-mula diayak untuk menentukan taburan partikal sampel bijih emas. Daripada analisis ayak menunjukkan bahawa hanya 11.20% sampel bijih emas adalah dibawah 75 μm. Sampel bijih emas terlebih dahulu menjalani pencirian dan kajian mineralogi. Kajian ini dilakukan untuk menentukan komposisi kimia, kehadiran fasa utama dan unsur-unsur yang bersekutu yang wujud bersama-sama dengan sampel bijih emas menggunakan XRF, XRD, SEM dan EDX. Daripada analisis XRF, XRD, SEM dan EDX, didapati bahawa taburan emas adalah sebahagiannya dalam arsenopirit (FeAsS) dan mineral quartza. Nilai gred emas untuk sampel bijih emas adalah 6.91 g/t yang diperoleh daripada kaedah cerakan api. Kaedah BLEG digunakan untuk menentukan emas terbebas iaitu 4.58 g/t. Daripada perbandingan peratusan emas yang terlarut lesap antara pembolehubah suhu pada 45 ° C dan 55 ° C dan kepekatan kalsium hipoklorit iaitu 0.25 M dan 0.75 M, keadaan terbaik untuk menjalankan pelarut lesapan hipoklorit adalah menggunakan 0.75 M kalsium hipoklorit pada suhu ambien, 27 ° C. Keadaan ini memperlihatkan peratusan emas tertinggi dengan 72.20%.

HYPOCHLORITE LEACHING OF GOLD ORE

ABSTRACT

In this research project, the bulk gold ore sample received from Kuala Lipis, Pahang was used. The gold ore was first sieved to determine the particle size distribution of the gold ore sample. Result from sieving shows that only 11.20 % of the gold ore sample is -75 µm. The bulk gold ore sample then was ground to obtain 80 % of the sample passing -75 µm. Before conducting the hypochlorite leaching with two different parameters which is the temperature and concentration of calcium hypochlorite [$Ca(OCl)_2$], the sample undergoes characterization and mineralogical study. The study was done to determine the chemical composition, major phases presence, and the elements that associated with the gold ore sample using XRF, XRD, SEM and EDX. From XRF, XRD, SEM and EDX analysis, it was found that distribution of gold is partly arsenopyrite (FeAsS) and quartz**.** The gold content in the gold ore sample is 6.91 g/t which was obtained from assaying method. BLEG method was used to determine the free milling gold which is 4.58 g/t. From the comparison of the percentage of gold leached between the variables which is temperature at 45 °C and 55 °C and the concentration of calcium hypochlorite which is 0.25 M and 0.75 M, the best condition to conduct hypochlorite leaching was using 0.75 M of calcium hypochlorite at ambient temperature, 27 °C. This condition gave the highest percentage of gold leached with 72.20%.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Cyanide is a lixiviant that is widely used in the gold industries. Cyanide leaching or also known as cyanidation was introduced by MacArthur and Forest in 1887. Since then, cyanide was used in the extraction of gold until today. Gold is well known because of it is insoluble in water and the main purpose of cyanidation process is to form a gold cyanide complex which is soluble in water so that gold can be extracted. Besides the complexing cyanide ions, oxidant is also needed to oxidize the gold ore. Oxygen and hydrogen peroxide are the two oxidants which is usually used in the process of extracting the gold ore. Bodlaender's equation, shown in Eq 1.1 and 1.2, shows the reaction of gold cyanide complex formed (Arslan, Ozdamar, & Muduroglu, 2003).

$$2Au + 4NaCN + 2H_2O + O_2 \rightarrow 2\ NaAu(CN)_2 + 2NaOH + H_2O_2 \qquad (1.1)$$

$$2Au + 4NaCN + H_2O_2 \rightarrow 2\ NaAu(CN)_2 + 2NaOH \qquad (1.2)$$
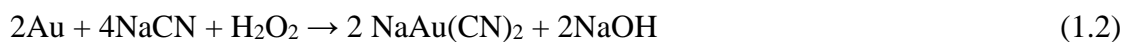
There are several drawbacks of cyanidation process, the main and biggest problem with cyanidation process or using cyanide to extract gold is that the toxicity that is affecting and damaging the environment and also bring health hazard to human. That is the main concern of the industries that is currently using the cyanidation method. Furthermore, cyanide also is not favorable to extract gold from refractory ores and also need longer leaching times (Hasab, Rashchi et al. 2013). Because of that, there are many research that have been done in order to find a new lixiviant that can replace cyanide on extracting gold that will minimise the percentage of polluting or damaging the

environment and at the same time will give the same amount of gold recovered as using cyanide. Finding shows that there are many alternative non-cyanide lixiviants which can give a high amount of recovery of gold the same as cyanide or maybe even better, such as thiourea, thiosulphate, chlorine and hypochlorite (Yen, Pindred et al. 1990).

This research project will be focusing on chlorine and hypochlorite as the lixiviant or reagent that will be used in leaching of gold. Not just because it does not harm the environment, the rate of dissolution of gold by chlorine is also much faster than cyanide (Yen, Pindred et al. 1990). The research will be conducted in order to study and discuss the leaching characteristics and the effect of some parameters on the recovery of gold using hypochlorite solution. The research will be focusing on the characterisation of gold and to investigate and study the effect of temperature and concentration of calcium hypochlorite on the performance of hypochlorite leaching and also the recovery of gold.

The dissolution of gold in hypochlorite solution does not only depend on the concentration of hypochlorite but also on other parameters such as the temperature during the leaching process, the initial pH and also the pH of the solution during leaching, type of oxidizing agent etc. Basically, the leaching process is much related to the gold pourbaix diagram. From the diagram mentioned, the reading of Eh and pH of the gold solution will provide the information regarding the type of oxidant presence and the gold ore complex formed. The most stable gold complex is in the form of $[AuCl_4]^-$. Theoretically, at pH more than 8, hypochlorite ion (ClO^-) is the dominant oxy-chloride species. However, at more acidic pHs which is between 3.5 to 7.5, hypochlorous acid forms according to the reaction shown in Eq 1.3;

$$H+ + ClO^- \rightarrow HClO \tag{1.3}$$

HClO is a stronger oxidant than ClO- which gives the reason for gold to leach faster. For pHs lower than 7.5, HClO becomes the dominant species. Leaching of gold with hypochlorous acid follows the following reaction shown in Eq 1.4;

$$2Au + 3HClO + 5Cl^- + 3H^+ \rightarrow 2[AuCl4]^- + 3H_2O \tag{1.4}$$
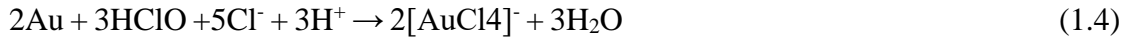
pH values lower than 3.5 will result in the formation of chlorine gas. Between all of the oxidant to oxidize gold ore, HClO is the best oxidant and will produce a more stable gold complex.

Gold is often associates with sulfide minerals such as pyrite and arsenopyrite. One of the advantages of using hypochlorite to extract gold is that it can recover this refractory gold ore. Eq 1.5 and 1.6 shows the reaction of hypochlorous acid (HClO) with pyrite, the most stable sulfide minerals (Hasab, Rashchi, & Raygan, 2014).

$$2\,FeS_2 + 15HOCl + 7H_2O \rightarrow 2Fe(OH)3 + 4SO_4^{2-} + 15Cl^- + 23H^+ \tag{1.5}$$

$$2\,Au + 3HOCl + 3H^+ + 5Cl^- \rightarrow 2[AuCl_4]^- + 3H_2O \tag{1.6}$$
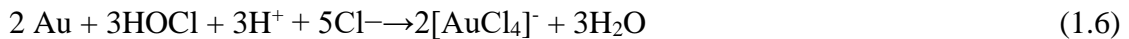
1.2 Problem Statement

Cyanidation is the best lixiviant to recover gold as its gives a high percentage or amount of recovery of gold. However, there are several issues regarding the usage of cyanide in the gold industry that lead to the ban of cyanide usage in some countries. The main problem with cyanidation is that it produce toxicity which can harm not only the environment but also human. Study shows that cyanide or HCN may cause some health hazard to the workers such as neurological, respiratory, cardiovascular and thyroid defects (Dhas, Chitra et al. 2011). This can also be proven with some of the cases which involves the loss of lives such as in Zimbabwe and South Africa this is due to the failure of

managing the usage of cyanide. Not only that, the eco-system, animals, environments also are largely affected by the usage of cyanide (Eisler & Wiemeyer, 2004). Some of the countries that had aware of the effect of using cyanide and had taken action to ban and against the usage of it are Greece, Turkey, Czech Republic, Argentina, Ecuador, and Costa Rica.

Studies shows that one of the reagent that can replace cyanide is hypochlorite. The main question raise with using hypochlorite to extract gold is that can hypochlorite gives high recovery of gold the same as cyanide or maybe even better? Until today, there are no or only a few test that are being done in a bigger scale. Most of the tests are being done only in lab scale. This will be proven in this research project whether or not hypochlorite can gives high recovery of gold. This research is to know the effect of two different variables which is, the concentration of calcium hypochlorite and temperature, on the performance of the leaching process and the recovery of gold. The recovery of gold from the variables will be compare and the best condition to perform hypochlorite leaching will be determined.

1.3 Objectives

This study aims:

i. To characterize the gold ore sample in terms of mineral presence using polish section of sample

ii. To investigate and study the effect of temperature and concentration of calcium hypochlorite used in the recovery of gold.

1.4 Scope of work

The quest of this project is to conduct hypochlorite leaching experiment and to determine the effect of temperature and the concentration of calcium hypochlorite on the recovery of gold and to determine the best condition to conduct the hypochlorite leaching. The sample weight, stirring speed, and the solid to liquid ratio were kept constant throughout the leaching process.

Firstly, the bulk powder gold ore sample was further ground to make sure that the gold ore particles pass -75 µm in order to liberate the gold particles from the gangue. Moreover, for an effective hydrometallurgical leaching process, it is necessary for the sample to be liberated at -75 µm. Next, sampling was done using two sampling methods which is cone and quartering method and John riffle box method to ensure the homogeneity and to obtain an amount of gold ore sample to be used in various processes.

For a better understanding of the gold ore sample, the characterization and mineralogical study is necessary. This is to gather the information about the major minerals presence, the associate minerals, and the phase presence in the gold ore sample. It was done using XRF analysis, XRD analysis, and SEM and EDX analysis. The information gathered is important for example to determine the chemicals used during the leaching process.

Another important method is the assaying method. This method is necessary to be conducted to determine the gold content of the gold ore sample. The assaying method involves fire assay and acid digestion. The gold content of the gold ore sample was determined using the assaying method. Bulk leach extractable gold (BLEG) test was used to determine the amount or concentration of the free milling gold in the gold ore sample. From this two results, the amount of interlock gold can also be determined.

The last stage of this research project is to investigate the effect of temperature and the concentration of calcium hypochlorite on the performance of hypochlorite leaching and the recovery of gold ore sample. The concentration of calcium hypochlorite are 0.25M and 0.75 M while the temperature was set at ambient temperature, 45°C and 55°C. Other variables were kept constant. The stirring speed was kept at 550 rpm, the solid to liquid ratio is 1:3, and the particle size of the gold ore sample. Each leaching process with different variables was conducted at different leaching time. Leaching process of concentration of calcium hypochlorite was conducted at 24 hours while leaching with different temperature was conducted for 6 hours. The pregnant solution from the leaching process will be collected and analysed using AAS and ICP to determine the amount of gold leached. The recovery of gold from different variables will be compare to determine the best condition to conduct a hypochlorite leaching process.

CHAPTER 2

LITERATURE REVIEW

2.1 Gold Formation

Gold is formed in the deepest portion of earth curst which letter transported to the earth curst by hydrothermal pressure. There some base metals that are usually associated with gold such as zinc, copper and iron. There are 2 type of deposits of gold which know as lode deposits or quartz vein deposit and placer deposit. Lode deposits consist of three class of deposits which is the hypothermal deposit, mesothermal deposit, and epithermal deposit.

2.1.1 Lode Gold Deposit

Lode deposit or also known as quartz vein deposit usually formed at the regions where intrusive igneous rocks are known to occur. This hydrothermal model with granitic intrusions providing the heat source or fluid source (D. Groves & Foster, 1991). The formation occurs at depth of 3-12 km and temperatures ranging from 200-400°C. The source of gold is said to be in the deepest of the earth crust. The golden rich source area are believed to be developed in the Archean crust. This melted gold which been transported by the hydrothermal fluid rises from the earth's crust to the earth's surface travel the path of the least resistance through fracture or fault of the rock. As gold travels, the change in temperature, pressure and also the chemical reaction with other minerals will lead to precipitation and deposition of gold. There are 3 class of lode gold which is the hypothermal, mesothermal and epithermal gold deposit (Arndt, Kesler, & Ganino, 2015). Table 2.1 shows the classification of ore which distinguished the deposits that

formed at different levels in the crust. Meanwhile, Figure 2.1 shows the type of hydrothermal ore deposits.

Table 2. 1: Lindgren's classification of ore deposits (Arndt et al., 2015)

	Depth	Temperature °C	Occurrence	Metals
Epithermal	Near surface to 1.5km	50 - 200	In sedimentary or igneous rocks; often in fault systems; simple veins or pipes and stockworks; little replacement phenomena	Pb, Zn, Au, Ag, Hg, Sb, Cu, Se, Bi, U
Mesothermal	1.2 – 4.5 km	200 - 300	Generally in or near intrusive igneous rocks; associated with regional faults; extensive replacement deposits or fracture fillings; tabular bodies, stockworks, pipes	Au, Ag, Cu, As, Pb, Zn, Ni, Co, W, Mo, U
Hypothermal	3 – 15 km	300 - 600	In or near deep-seated felsic plutonic rocks in deeply eroded areas. Fracture-filling and replacement bodies; tabular or irregular	Au, Sn, Mo, W, Cu, Pb, Zn, As
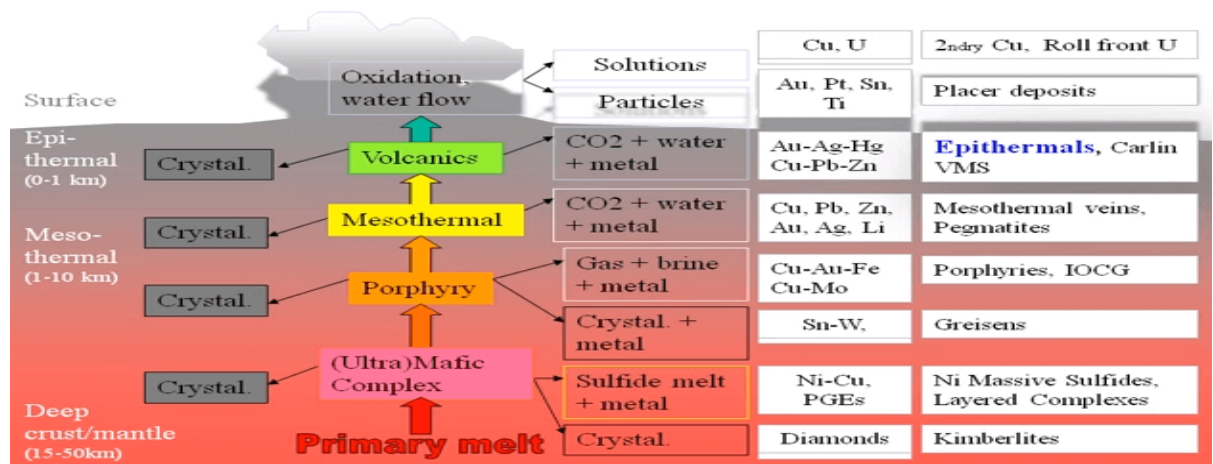
Figure 2. 1 Types of hydrothermal ore deposits

Epithermal gold deposit is the deposit of gold result from the intrusion of hydrothermal fluid on host rocks. It is said to be among the richest gold deposits in the world. It is refined with fluid inclusion data to indicate that epithermal ores form over the temperature range of <150°C to ~300°C, from the surface to as deep as 1 to 2 km. There are two different type of epithermal deposit which is the low sulphidation epithermal and high sulphidation epithermal. These two deposits are very much related to the amount or the degree of interaction between the magmatic fluid, groundwater, and host rock. Although these two deposits have the same alteration mineralogies, there are some ways to distinguish between these two for example the different in the characteristic of the deposits, texture, and gangue minerals present (White & Hedenquist, 1995).

The low sulphidation system is formed when the geothermal system in which the magmatic fluid is cool and diluted by the groundwater making the pH of the system to be neutralise or slightly alkaline. Low sulphidation often have high silica, mercury and arsenic content. The fluids that rise from great depth have equilibrated with their host rocks, and are reduced and have a near-neutral pH. Some of the places with low sulphide epithermal gold deposits are Emperor, Fiji, and Hishikari, Japan. In contrast, the high sulphidation system is formed in a geothermal system where the hot and acidic hydrothermal fluid from the intrusion remain undiluted by the groundwater. The HCl⁻ and

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SO$_2$-rich vapour may become absorbed by groundwater, resulting in a hot temperature range from 200-300°C and are highly acidic which the pH is between 0-2 and oxidized fluid that reacts extensively with and leaches the host rock at shallow depth (White & Hedenquist, 1995). Some of the places with high sulphidation system epithermal gold deposit are Goldfield, Nevada, USA, and El Indio, Chile (White & Hedenquist, 1995).

Another distinctive features is the characteristic between these two deposits. Most low sulphidation deposits consist of cavity-filling veins with sharp boundaries, or stockworks of small veins. Meanwhile, veins may be important in high sulphidation deposits, but the majority consist of disseminated ores that replace or impregnate leached country rock. One of the ways to differentiate these two deposits is from the textures. Low sulphidation deposits show a wide variety of textures, including banded, crustiform quartz and chalcedony veins, druse-lined cavities, and spectacular, multiple-episode vein breccias. High sulphidation deposits texture are very different with the low sulphidation deposits. The hot acid fluid with pH <2 rises and attack the host rock during the process to the surface. The host rock then progressively leached and altered so that the feldspars breakdown to clays and this clays are then removed leaving only the vuggy silica or also known as vuggy quartz. Most of the texture are massive bodies of vuggy quartz typical of Nansatsu-type deposits, though locally veins and breccias are important hosts to ore (White & Hedenquist, 1995).

Mesothermal gold deposits or also known as green lode gold deposits and orogenic gold deposits is another class of lode gold deposit. It is found that the gold-bearing quartz lode is originated in the late Archean and Mesozoic greenstone belts. Ores were formed during compressional to transpressional deformation processes at convergent plate margins in accretionary and collisional orogens (D. I. Groves, Goldfarb, Gebre-Mariam, Hagemann, & Robert, 1998). The gold that are deposited in the greenstone belts are high

grade of gold range from 7-10 g per tonne. The source of the gold comes from the deepest portion of the earth crust which is believed 20-30km below the surface. It is well developed in the Archean crust. Gold is known to be barely soluble in water and because of that, it form a chloride complex with chloride or fire complex with sulfa to transport the gold easier. The pre-existing faults or any available crack became the channel to the fluid to travel up the crust.

There are several ways to drop the gold or separate the gold from the fluid. One of the ways is by cooling the fluid. Naturally, as the fluid rises into the rocks, the change in temperature or mixing with groundwater will cool the fluid. Another method to separate the gold from the fluid is by dropping the pressure. As the pressure drop, the fluid will boil and will cause the gold to drop out of the solutions. However, this method are more suitable for epithermal type of deposits rather than the mesothermal type of deposits. This is due to the veins that are too deep and has higher pressure and temperature which will not allow boiling of the fluid from happening. The most effective method to get the gold for mesothermal type of deposit is by causing the fluids to break down and leave the gold with no passage to continue to the surface. Separated within a short distance, the wallrock alteration which is characterized by quartz-pyrite-muscovite assemblages adjacent to the veins. The veins of this type of deposits consist of gold, pyrite, arsenopyrite, quartz, and base metals.

2.1.2 Placer Deposits

Placer deposits is basically the naturally accumulation of valuable minerals such as gold in overburden, stream sediments or beach. Gold are one of the minerals that formed placer deposits. In fact, man most likely to first obtained gold from placer deposits, more than 6000 years ago and produced more than two-thirds of the total world gold supply. Gold artifacts survive from ancient civilizations and cultures such as the Egyptians and the Mesopotamians (Najafi, 2011). This deposits started with the process of mechanical and chemical weathering and disintegration of the primary minerals such as lode deposits or also known as gold-bearing quartz vein. Upon weathering and erosion, the gold from the primary minerals will then be transported via water, ice, and air. At a low current velocity, gold will settled down and concentrated while the lighter minerals will be wash away by the flowing water. When the velocity of the water slows, large minerals or minerals with a higher density are deposited. Heavy minerals like gold, diamond, Ti, Cr, Sn, and magnetite of the same size as a low density mineral like quartz will be deposited at a higher velocity than the quartz, thus the heavy minerals will be concentrated in areas where water current velocity is low (Harraz, 2013). Richness and size of a placer deposit depend on supply of source materials, and on conditions favourable for the concentration and preservation of the valuable minerals (Yeend Sharre, D. R., 1989). Minerals that form placer deposits have similar characterization such as high specific gravity, chemically resistant to weathering and durable. Some of the minerals that form placer deposits are gold, platinum, magnetite, ilmenite, and rutile. There are several type of placer deposits namely residual placer, alluvial placer, eluvial placer, and beach placer. Figure 2.2 illustrate the different position of the different type of placer.
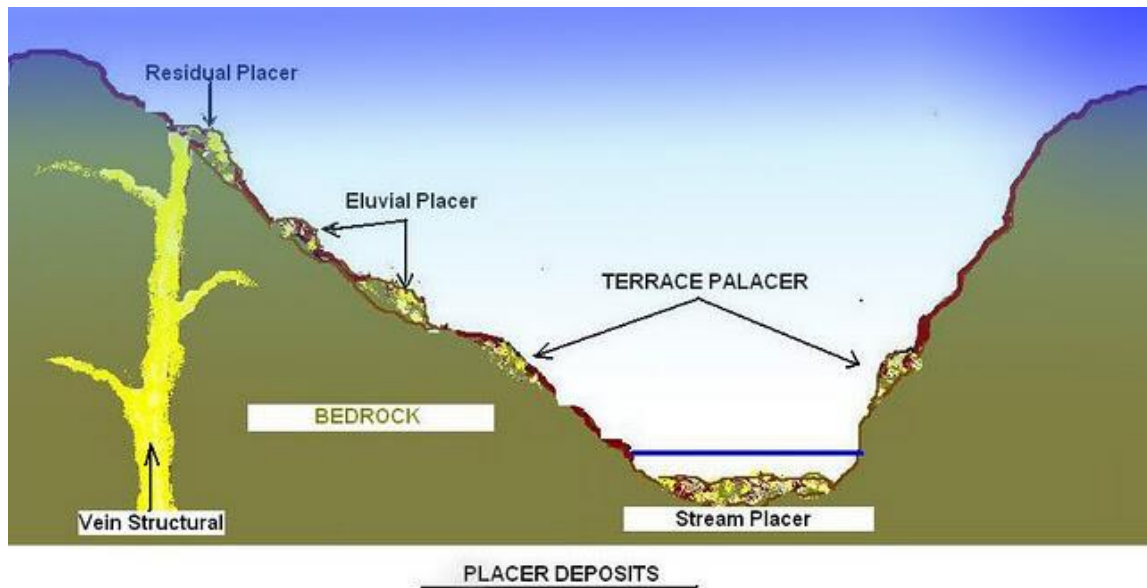
Figure 2. 2: Illustration of different type of placer deposits.

2.2 Gold Mineralization in Central Belt of Malaysia

Hydrothermal fluids is important in the formation of gold deposits in the geology of the Central Belt goldfield. Gold is dominant in the central belt of Malaysia. The Central "Gold" Belt is located at 20km wide, a major N-S trend of gold mining districts in Peninsular Malaysia, especially in the North Pahang and Kelantan area. Figure 3 shows the central mineral gold belt of Peninsular Malaysia with major gold bearing deposits. Pahang and Kelantan, two states which located in the central belt of Malaysia are the two main states that produce the majority of the gold production. The gold deposits that is mined in the central belt of Malaysia is usually from the quartz lode deposits and stockwork deposits which is correlate with accretionary prism along the terrain boundary that is known as the Raub – Bentong suture. It is reported that the mineralization of gold on the central belt occurred within a low grade Permo-Triassic island arc system mainly

composed of meta-sedimentary and volcanic rock followed by extensive deformation (brittle-ductile and shearing zone), metamorphism, and magmatic events which created the best environment for source and trap for the gold mineralization (Shah, 2012).

During the collision of the Sibumasu block underneath the East Malaya (Indochina) block through the Permian to late Triassic, low-grade meta-sedimentary-volcanic terrain was formed and it is where most of the gold mineralization occurs. Figure 2.3 show the crustal environment of orogenic gold deposits in term of depth of formation and structural setting within attracted terrain (Shah, 2012).

Gold mineralization within the central belt can be grouped into two groups which is the type 1 located at gold belt 2 and type 2 situated at gold belt 3 as shown in figure 2.4. Gold belt 2 have significantly large quartz reefs/lodes and parallel swarms of vein, traversing meta-sediments and granite.
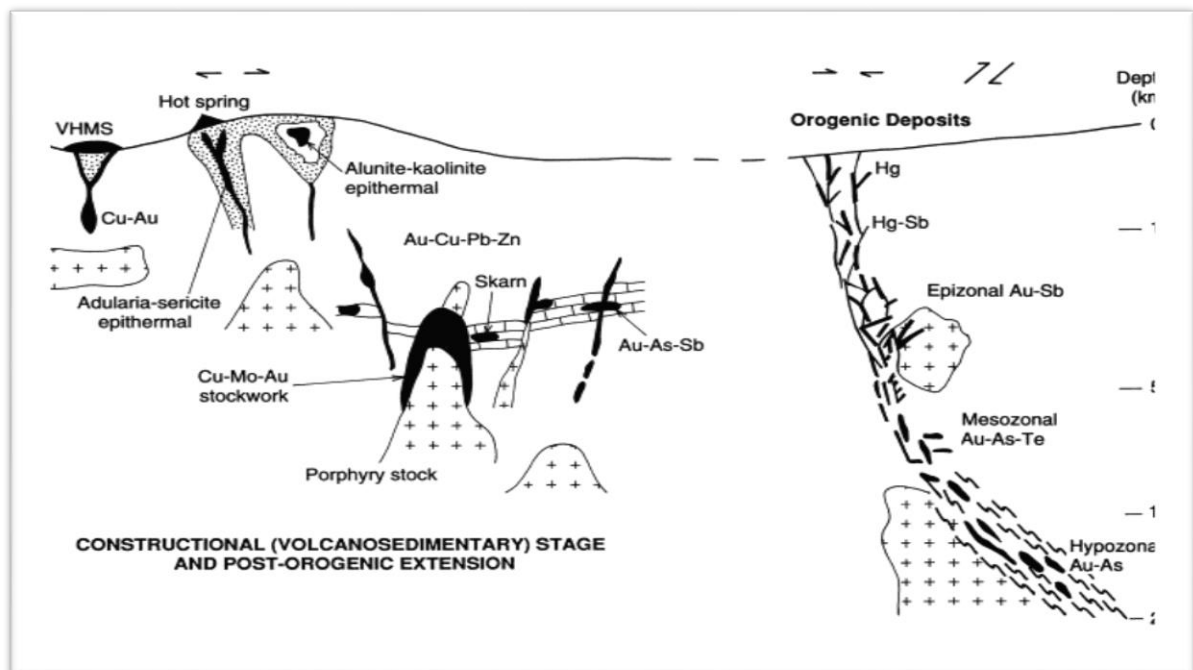
Figure 2. 3: Schematic representation of crustal environments of orogenic gold deposits in term of depth of formation and structural setting within accreted Terrance (Shah, 2012).

Beside gold mineralization of type 1, it is also known as gold geochemical zone and the brittle-ductile shear or brecciated zone are suspected to restraint the mineralization of the gold deposits. Buffalo Reef and Selinsing Gold Mine are the two major goldfields within the type 1 belt which is located at gold belt 2. Typical characteristic of the Buffalo Reef, Selinsing and Raub goldfields is the occurrences of stibnite and scheelite. Another type of gold mineralization is type 2 deposits which is situated to the east of the type 1 at gold belt 3, exhibits a broader variety of gold mineralization. Gold present in this area is scattered within a stockwork of quartz veins associated with intrusive bodies within a shear zone system (Ariffin & Hewson, 2007).
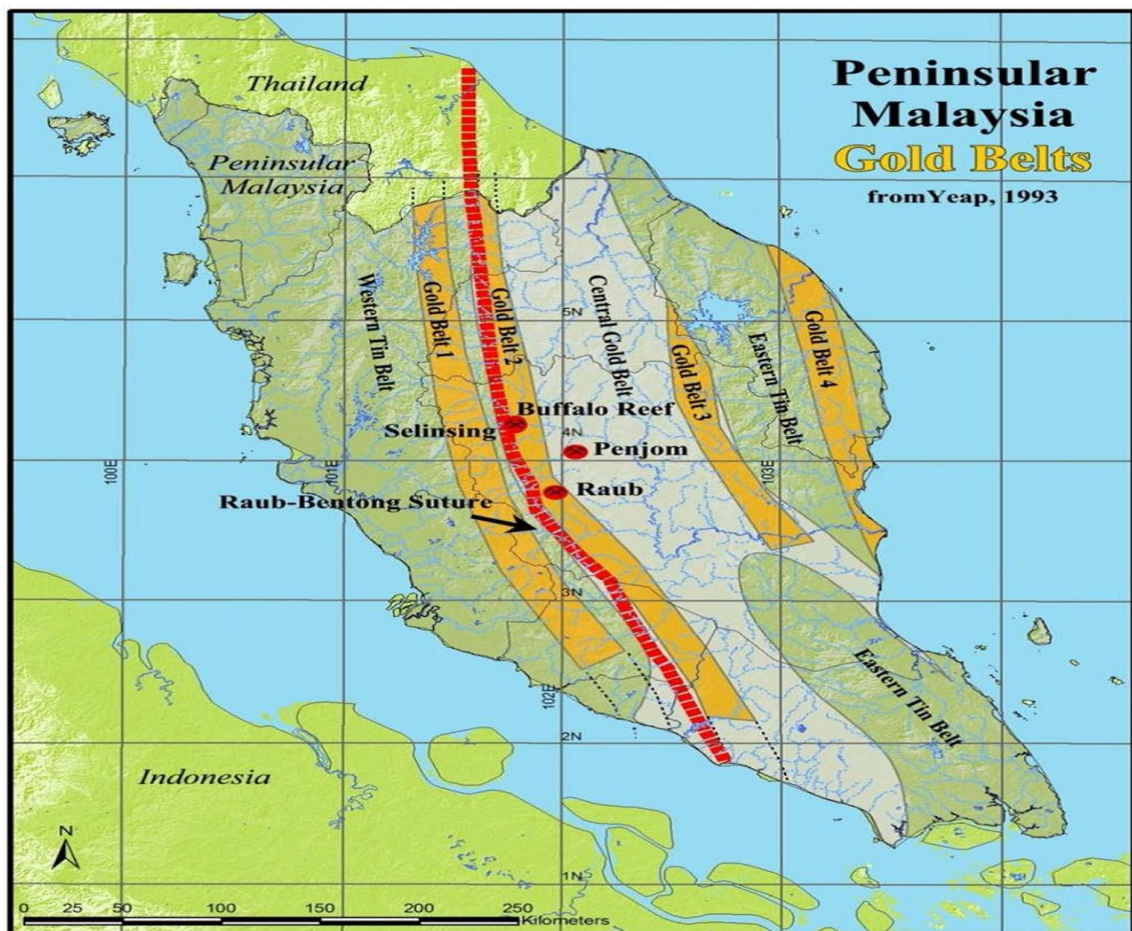
Figure 2. 4: Gold belts and occurences in central belt of Peninsular Malaysia

(Ariffin & Hewson, 2007)

2.3 Gold Characterization

Characterization is one of the most important part of this research project. Gold characterization is important as it will determine the information regarding the mineralogy and the chemical composition of the gold sample. The information of the composition of the gold sample is essential for the later stage of a suitable hydrometallurgical method for the extraction of gold.

2.3.1 Determination of Chemical Composition by X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) is an analytical method to determine the chemical composition in a sample. Fast, accurate, non-destructive, and usually requires minimum or no sample preparation and can be measure or tested in any shaped delivered are the advantages of using XRF (Cristea-Stan et al., 2012). XRF works by measuring the intensity of the x-rays emitted by the sample in the form of energy and wavelength. There are two main spectrometer system which is the energy dispersive system (EDXRF) which measure the intensity of the x-rays in the form of energy and the wavelength dispersive systems (WDXRF). XRF is a qualitative analysis because it involves identifying the elements present based on the energies or wavelength emitted by the sample.

Basically, XRF is a method which uses a source such as x-ray tube to produce x-rays to be exposed to the sample. The x-rays which has higher amount of energy level than the binding energy of the electron in the shell will tend to expel an electron from an atom and leave behind vacancies and this is call the initial vacancy. This result in making the atom to be unstable. To make the atom stable again, electron from outer shell with higher energy will be transferred to fill in the vacancies. The difference in energy between the shell with the vacancy and the shell at which the electron are transferred to fill the vacancy will produce or emit x-rays or commonly known as Fluorescence. Each element has its

own unique spacing between the orbital shells of an atom, it means that different atom of element such as iron, zinc, and gold has different spacing between its electron shells. On top of that, each of the atom also has its own specific energy level, thus the emitted x-rays is characteristics of that atom. The fluorescence produce from the direct contact with the x-rays from the source is called primary fluorescence. Meanwhile, fluorescence that are produced because of the primary fluorescence are called the secondary fluorescence (Brouwer, 2010). Figure 2.5 shows the primary and secondary fluorescence and the electron which expel from its orbit.
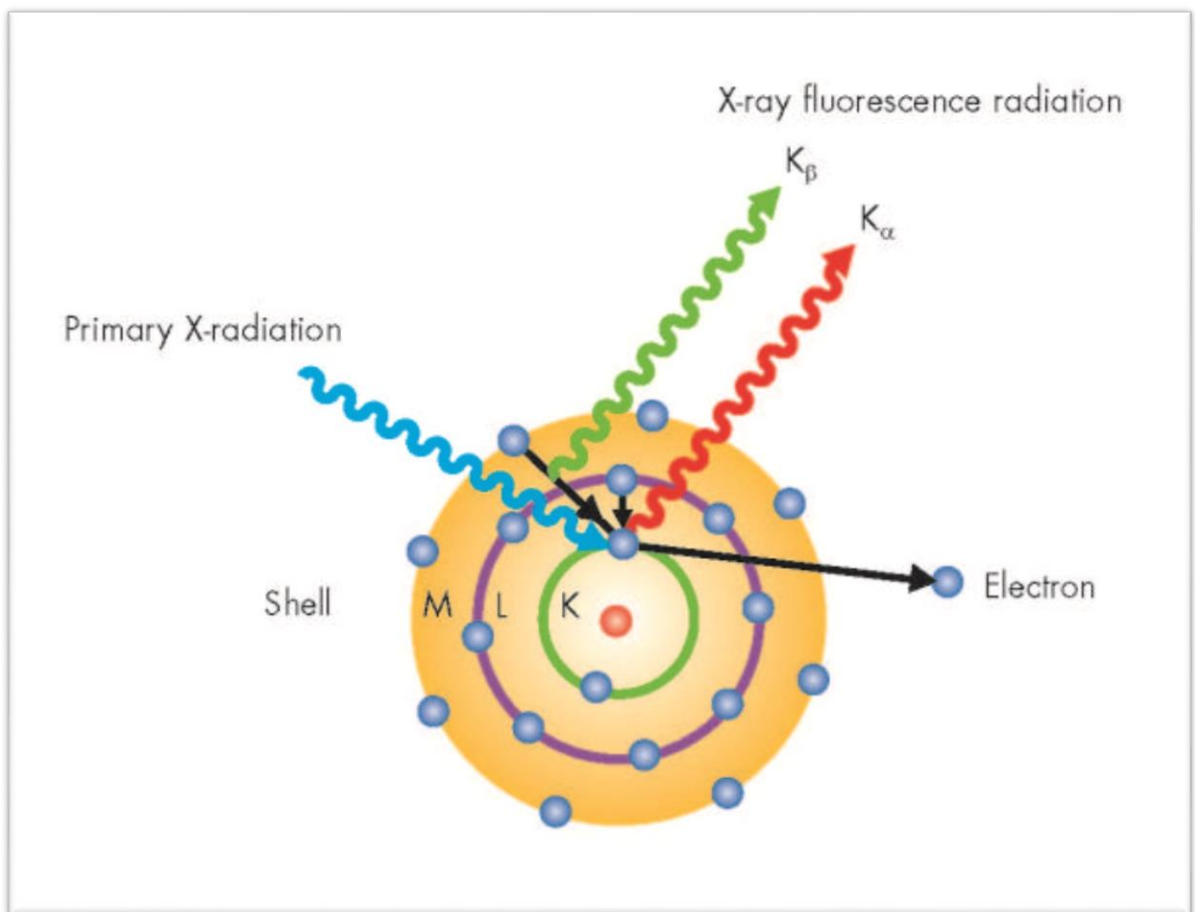
Figure 2. 5: Primary and secondary fluorescence and electron that expel from its orbit

2.3.2 Identification of Mineral Phases by x-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive analytical technique that are used widely to characterize a crystalline materials for example minerals with inorganic compound. Moreover it can also provide the information on the crystal structure, phases and properties of a material. The mechanism of this XRD technique is by irradiate a beam of monochromatic x-rays on a sample over different angle and phases. The monochromatic radiation is produced by x-rays which is generated by a cathode tube which then filtered. Constructive interference of a monochromatic beam of x-rays which scattered at specific angles from each set of lattice planes in a sample results in the production of x-ray diffraction peaks. The determination of the peak intensities is related with the distribution of atoms within the lattice. Constructive interference are produced when there is an interaction between the incident rays and the sample and the condition satisfy the Bragg's law in Eq 2.1;

$$n\lambda = 2dsin\emptyset \tag{2.1}$$

Where;

n = integer

λ = wavelength of the x-rays

d = interplanar spacing generating the diffraction

θ = diffraction angle

This law shows the relationship of the wavelength of the electromagnetic radiation with the diffraction angle and the lattice spacing in a crystalline sample. Electrons are produced in a cathode ray tube by heating a filament which will then generates x-rays.

Voltage then will be applied to the electrons to accelerate the electron towards the targeted material. Characteristics x-ray spectra are produced when there is sufficient energy to expel or dislodge the electrons from the inner shell of the target material. The intensity of the reflected x-rays is recorded (Bunaciu, Udriştioiu, & Aboul-Enein, 2015).

2.3.3 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) analysis

Scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX) are widely used in order to obtain the information about a sample's composition, surface topography and also its properties. SEM produce image of a sample in high resolution. The difference between this two techniques is that, the SEM detect the electrons from the sample while EDX detect the x-rays radiated from the sample (Valenzuela-muñiz, 2011).

SEM uses an electron beam with high energy on a sample which will results in variety signals at the surface of the sample. These generated signals carries different type of information about the sample. There are three type of signals that are detected which is the backscattered electrons (BE), secondary electrons (SE), and lastly the transmitted electrons. Each of the signals detected carries different information about the samples. The backscattered electron provide the information on the difference in atomic number, the topographic information is provided by the secondary electrons while the transmitted electrons describes the crystallography of the sample.

Beside electrons, x-rays that are emitted from the sample also can provide information about the sample. The high energy electron from the electron beam will

knocked-off the electrons in an atom leaving a hole which will later filled with an electron of higher energy from the outer shell of the atom. The difference of energy from the expelled electrons and the one that fill in the holes will produce or emit x-rays. Data from EDX which consist of spectra with peaks shows the chemical composition present in the sample (Sarecka-Hujar et al., 2017).

2.4 Gold Assaying Methods

Assaying method is define as the quantitative chemical analysis in which to determine the concentration or the grade of a specific interested metal in which this research project is gold (Corti, n.d.). Gold assaying method involve fire assay and acid digestion which will determine the concentration of gold generally in parts per million (ppm).

Before proceed with the gold analysis methods mention above, sample preparation is crucial and a step that need to be done. This is because the small amount of sample taken to be analyse represent the grade of the bulk sample. The sample size need to be - 75µm to increase the surface area which will be in contact with the lixiviant during the leaching process. The sample need to be crush or pulverise if 85% of the sample does not pass through 75µm (Abusah & Al-Hasan, 2013).

2.4.1 Bulk Leach Extractable Gold (BLEG) method

Cyanidation bottle roll leaching test also known as Bulk Leachable Extractable Gold (BLEG) assay method will determine the free gold which does not interlock with any other minerals. The free gold will directly leached with the cyanide. A specific weight of sample are taken and placed inside a poly-ethylene bottle which then will be mixed with sodium cyanide solution (NaCN) with 0.1% of its cyanide concentration. Lime

($CaCO_3$) will also added to the mixed solution to make the pH value of the solution to 11. For agitation process, the bottle then will be placed on a revolving bars for a period of time which is usually for 24 hours for a complete leaching process (Abusah & Al-Hasan, 2013).

The slurry or the pregnant solution from the bottle roll test will be filtered and the filtrate solution will be mixed with an organic solution, DIBK a process known as solvent extraction. The organic gold solution will then be analysed with AAS (Abusah & Al-Hasan, 2013). This method provides the concentration of free gold which can be directly leach using cyanidation process.

2.4.2 Fire Assay

Fire assay method is a well-known or the most accurate method and is widely used in gold industry to determine the concentration of the gold. Fire assay technique was first recorded being used in the Holy Roman Empire by an assayer name Erker. There is little difference between fire assay method today and the one that had been practiced before. The better quality of reagents and furnaces has help in improving the quality and efficiency of this method (Hoffman, Clark, & Yeager, 1998).

Fire assay is a method to determine the chemical present in an ore by which the interested metals are separated with its impurities with the aid of heat and dry reagents. There are two products from this process which is a complex liquid borosilicate which contain the impurities or the associate minerals. Another product contain the interested metal which is in the form of liquid lead phase.

The classical method involves three process in it which is the fusion, cupellation, and acid digestion processes. The procedure of this method starts with the fusion process which involves mixing the powdered sample with flux. Flux is typically the mixture of

soda ash (sodium carbonate), flour as reducing agent, litharge (PbO) as collector, silica (SiO_2), and borax (sodium borate). The mixture of sample and flux will be place inside a silica crucible which then will be inserted inside a maffle furnace at a temperature of 1000°C - 1200. The silica crucible are left inside the maffle furnace for 24 hours for a complete fusion process. Fusion process will results in the formation of metallic lead button which contain the noble metals and also the impurities in the form of slag (Hoffman et al., 1998).

The metallic lead button then will undergo the cupellation process. It is a process at which the lead button is placed on a 'cupel' and placed inside a maffle furnace and heat at 800°C - 850°C. Lead oxide from the lead button will be absorb by the 'cupel' leaving behind a bread of silver (Ag) and Pd bead or commonly known as 'prill'. The prill will be digested with nitric acid and hydrochloric acid before being analyse with AAS (Hoffman et al., 1998).

2.4.3 Acid Digestion

Acid digestion process is a process that digest or dissolve the 'prill' or the precious metals with nitric acid (HNO_3) and hydrochloric acid (HCl). The volumetric ratio of nitric acid to hydrochloric acid is 1:3. Each of the acids have difference task on dissolving the gold. Nitric acid, will form gold ions by dissolving the undetectable amount of gold. Meanwhile, the function of hydrochloric acid is to supply chloride ions which later will form chloroaurate anions ($AuCl_4^-$). The chemical reaction involve between nitric acid and hydrochloric acid with the gold sample can be define in the Eq 2.2:

$$Au0 + 4HCl + HNO3 \rightarrow HAuCl4 + NO + 2H_2O \qquad (2.2)$$

One of the precaution in acid digestion process is the nitric oxide (NO) gas, a yellow gas that evolves during the digestion process. The nitric gas (NO) gas can bring harmed and threat to the workers at the workplace. 70-80°C is the temperature needed to dissolve the gold in this process. The solution then will be filtered and diluted in a 50ml volumetric flask before being analyse using AAS. Fire assay method is applied to determine the head grade or the grade of the bulk sample.
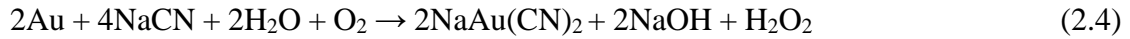
2.5 Cyanidation Process

Cyanidation process is a process at which gold is recovered using a lixiviant called cyanide. This process has been used since centuries to leach and recover gold. Some example of cyanide salts that is use in cyanide leaching is sodium cyanide (NaCN), potassium cyanide (KCN), and calcium cyanide [Ca (CN2)]. Free cyanide ions (CN^-) and metal cation are form when the cyanide salts dissolved in water. The dissolution of cyanide salts are presented in Eq 2.3 (Keskinen, 2013);

$$NaCN \rightarrow Na^+ + CN^-$$ (2.3)

The process is based on converting the gold which is insoluble in water to a water soluble gold cyanides. The process of mixing and dissolving gold and sodium cyanide which is a salt cyanide that is widely used in the gold industry will result in a water soluble gold cyanide. For the leaching process to be efficient, there must be sufficient amount of cyanide present to dissolve all the gold. To enhance the recovery of gold and oxidize the gold, oxidizing agents are added during the leaching process. Some oxidizing agents that usually being used in cyanidation process are oxygen (O_2) and hydrogen peroxide (H_2O_2). The rate of dissolution of gold is affected by the concentration of oxygen and cyanide. Moreover, pH and Eh of the slurry, particle size and temperature are the variables that will

also affect the dissolution of gold (Karimi et al., 2010). Bodlaender's equation shows the chemical reaction between the gold and the oxidants as shown in Eq 2.4 and 2.5 (Arslan, Ozdamar, & Muduroglu, 2003).

$$2Au + 4NaCN + 2H_2O + O_2 \rightarrow 2NaAu(CN)_2 + 2NaOH + H_2O_2 \qquad (2.4)$$

$$2Au + 4NaCN + H_2O_2 \rightarrow 2NaAu(CN)_2 + 2NaOH \qquad (2.5)$$

The cyanidation process is usually being done in a one litre beaker with fixed stirring speed using a mechanical agitator. pH will be adjust and kept constant at pH 10.5 by adding sodium hydroxide (NaOH). Oxygen or hydrogen peroxide will be use as the oxidizing agent and the silver nitrate titration will be carry out at the end of the experiment to determine the amount of aliquot consume. Gold will be analyse using fire assay method (Arslan et al., 2003).

2.6 Hypochlorite Leaching of Gold Ore

As mention earlier, cyanidation is a method that is widely used in the gold industry. The cyanidation method has high sensitivity, low operational cost and capable to extract gold up to 98% (Yanuar & Suprapto, 2015). However, discussions are made about the harm and the effect of using cyanide in the recovery of gold. This is because, the cyanidation process has some disadvantages such as high toxicity and also environmental pollutions (Eisler & Wiemeyer, 2004). This can be proven when there are several countries that have banned the usage of cyanide in the recovery of gold. For example, Czech Republic, Greece, Turkey, Germany, Hungary, Costa Rica, Argentina, Ecuador, and some states of the United States. To make it worse, there were also some cases that were recorded on the effect of cyanide towards human, animals, and also the environment. In January 2000, the released of cyanide had caused one of the Europe's largest ecological disasters when the toxic lixiviant eventually killed many organisms and damaged the food