According to Jackson (1986) and Habashi (1970), the bauxite ore typically contains gibbsite [$Al(OH)_3$], diaspore [$AlO(OH)$] or boehmite [$AlO(OH)$] with iron and silica oxides as the major impurities. These authors further reported that the Bayer process involves the selective solubilisation of the aluminium containing minerals in sodium hydroxide solution. The reaction between sodium hydroxide and alumina from bauxite occurs at high temperature (ranging from 120 - 200 °C) and pressure (ranging from 5 - 20 bar) with a retention time of 1 - 4 h.

According to Habashi (1970) and Warren and Hiner (1979b), both silica (SiO_2) and hematite (Fe_2O_3) remain undissolve during base leaching but silica that is associated with aluminium oxide (i.e. aluminium silicate) dissolves and forms sodium aluminium silicate. Habashi (1970), Warren and Hiner (1979b) and Helmboldt et al (2001) reported that the rate of dissolution of alumina depends heavily on the concentration of sodium hydroxide used. High concentrations of sodium hydroxide during bauxite ore digestion result in filtration problems. Such difficulties being alleviated by diluting the slurry. These authors also reported that impurities in the leach liquor solution have a detrimental effect on the aluminium extraction efficiency. The possible reactions that occur during the leaching step of the Bayer process are:

$$\underset{\text{gibbsite}}{Al(OH)_3} + NaOH \rightarrow \underset{\text{sodium aluminate}}{Na[Al(OH)_4]} \qquad (1.4)$$

$$\underset{\text{boehmite}}{AlO(OH)} + NaOH + H_2O \rightarrow \underset{\text{sodium aluminate}}{Na[Al(OH)_4]} \qquad (1.5)$$

Subsequent to the separation of sodium hydroxide insoluble material, the aluminium containing solution is processed further. The main advantage of the Bayer process is that sodium hydroxide can be recovered during the precipitation of gibbsite and recycled to the leaching step.

The precipitation of gibbsite will be discussed in more detail in Section 1.2.4.3.1.

1.2.2.2 Acid leaching process

The acid leaching process involves the solubilisation of minerals from the mineral-bearing ores in inorganic acid solutions such as sulphuric acid, nitric acid, phosphoric acid or hydrochloric acid. In this section acid-leaching process on the recovery of aluminium species, cobalt species and platinum species from the spent cobalt-containing catalyst will be discussed separately.

1.2.2.2.1 Acid leaching of aluminous (aluminium-bearing) material

According to Canon et al (1979), Burkin (1987) and Burnet et al (1984) mineral acids can be used to recover aluminium species from the aluminous material. These authors found that species of iron, nickel, barium, magnesium, titanium, cobalt and some trace elements present in the ore dissolve simultaneously with aluminium species when either sulphuric acid or nitric acid solutions are used in the acid leaching step. Trace amounts of silica are also soluble in acid during the leaching process. Unlike the alkaline leaching process discussed in Section 1.2.2.1 above, the acid leaching process is less selective to aluminium containing species. It was further argued that the leach liquor solution obtained after the filtration of the slurry from an acid leaching process should initially be purified by either solvent extraction or ion-exchange to produce pure aluminium-containing solution. This solution could possibly be used to produce metallurgical grade-alumina.

1.2.2.2.2 Acid leaching of platinum-containing material

Platinum does not dissolve readily in single mineral acids in the ordinary acid and is resistant to oxidation by oxygen. Warren and Hiner (1979a), Hartley

(1973), McDonald and Hunt (1983), Edward (1976), Habashi (1970), Renner (2001) and Bachmann and Renner (1984) clearly indicate that aqua regia (mixture of 3 parts hydrochloric acid and 1 part nitric acid) dissolves both platinum and palladium species, gold metals from platinum group metal (PGM) ore and leaves ruthenium, rhodium, osmium, iridium and silver species as an insoluble residue. Figure 1.4 summarises the procedures followed in order to separate platinum group metals from each other.

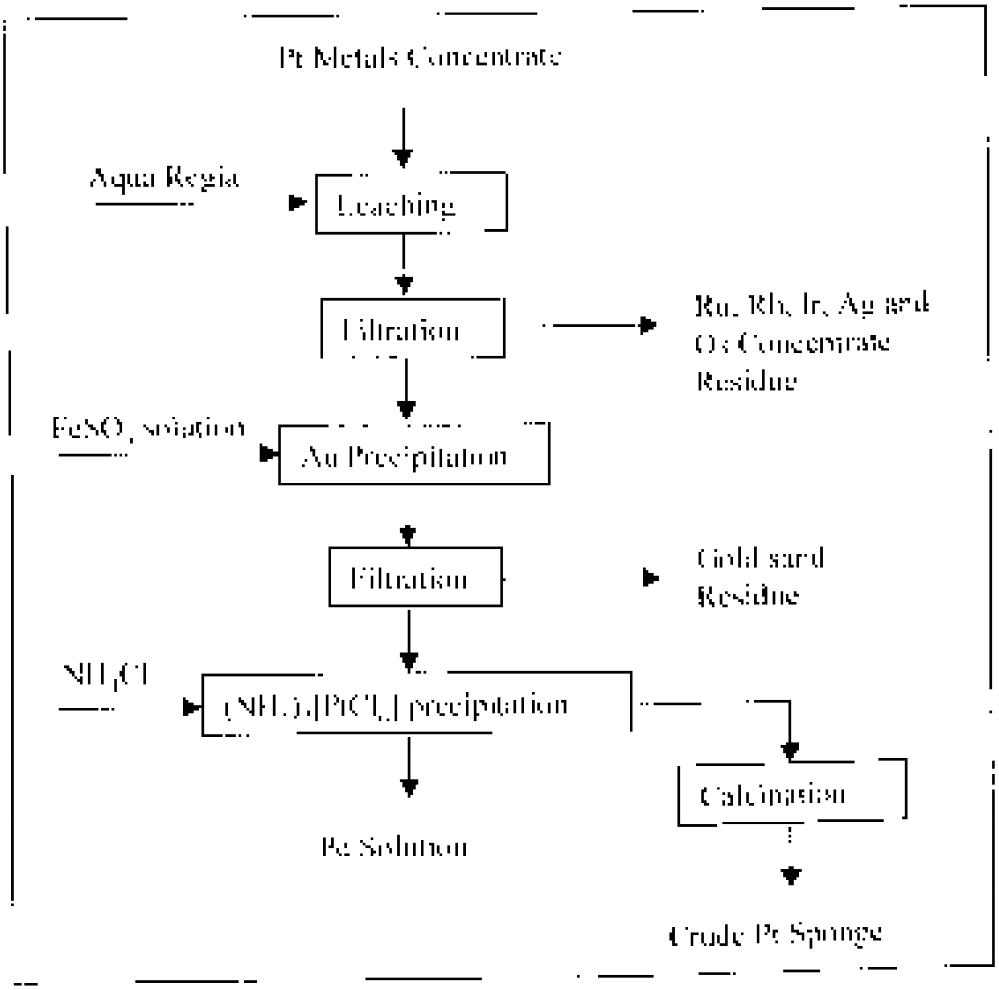

Figure 1.4: Process for treating platinum metals concentrate

During the dissolution process, aqua regia dissolves platinum with the formation of chloroplatinic acid, H_2PtCl_6, as shown in equation 1.6.

$$Pt + 2HNO_3 + 6HCl \rightarrow H_2PtCl_6 + NO + NO_2 + 3H_2O \qquad (1.6)$$

The residue obtained during treatment with aqua regia contains species of ruthenium, rhodium, osmium and iridium. The filtrate obtained in this manner typically contains platinum, palladium and gold.

Hahashi (1970) reported that ammonium chloride can be used as a precipitating agent to selectively precipitate platinum(II) ions from the filtrate. This resulting filtrate is further treated with ammonium hydroxide solution to precipitate palladium in the form of a tetraamine dichloro palladium(II) complex. Addition of hydrochloric acid to the insoluble tetraamine dichloro palladium(II) complex yields an insoluble diamine dichloro palladium(II) complex. The reactions of Pt and Pd during the precipitation steps described above are as follows:

$$PtCl_4 + 2NH_4Cl \rightarrow (NH_4)_2[PtCl_6] \qquad (1.7)$$

$$PdCl_2 + 4NH_3 \rightarrow [Pd(NH_3)_4]Cl_2 \qquad (1.8)$$

$$[Pd(NH_3)_4]Cl_2 + 2HCl \rightarrow Pd(NH_3)_2Cl_2 + 2NH_4Cl \qquad (1.9)$$

Hartley (1973), McDonald (1982), Edwards (1976) and Galan and Moreno (1992) have performed studies to identify and selectively separate Ru, Rh, Os and Ir from the aqua-regia insoluble residue. These studies will not be discussed at length in this dissertation as they do not form part of the current study.

1.2.3 Flocculation of the slurry

According to Adams et al (1986) and Burkert and Hartmann (2001), mineral industries currently utilise a flocculation process to separate aqueous ultra-fine mineral suspensions from leach liquor solutions and mine effluents. These slurries are colloidal in nature (i.e. contain ultra-fine solid particles which settle out of suspensions only very slowly) and the liquid-solid separation is problematic. These authors explicitly mentioned that the addition of flocculants to the slurry improves the settling rate of the ultra-fine solid particles and results in efficient separation of the solids from the aqueous suspending medium.

Adams et al (1986) and Burkert and Hartmann (2001) reported that flocculant manufacturers produce comprehensive ranges of non-ionic, anionic and cationic flocculants that can destabilise the suspensions and subsequently result in a rapid sedimentation. Anionic and non ionic organic flocculants are suitable for neutral suspensions that primarily contain inorganic ultra fine solids. However, cationic flocculants used for neutral suspensions that consist predominantly of organic ultra-fine solids. It was further stated that the performance of ionic flocculants depends mainly on the pH of the aqueous suspending medium during flocculation. Cationic flocculants are effective at pH < 7, while anionic flocculants operate at pH > 7. Non ionic flocculants work well only in highly acidic suspensions. Dosage rates of the flocculants play an important role during the flocculation process (Adams et al, 1986 and Burkert and Hartmann, 2001). A summary of the physical processes occurring during flocculation process, as proposed by Adams, et al (1986) is schematically shown in Figure 1.5.

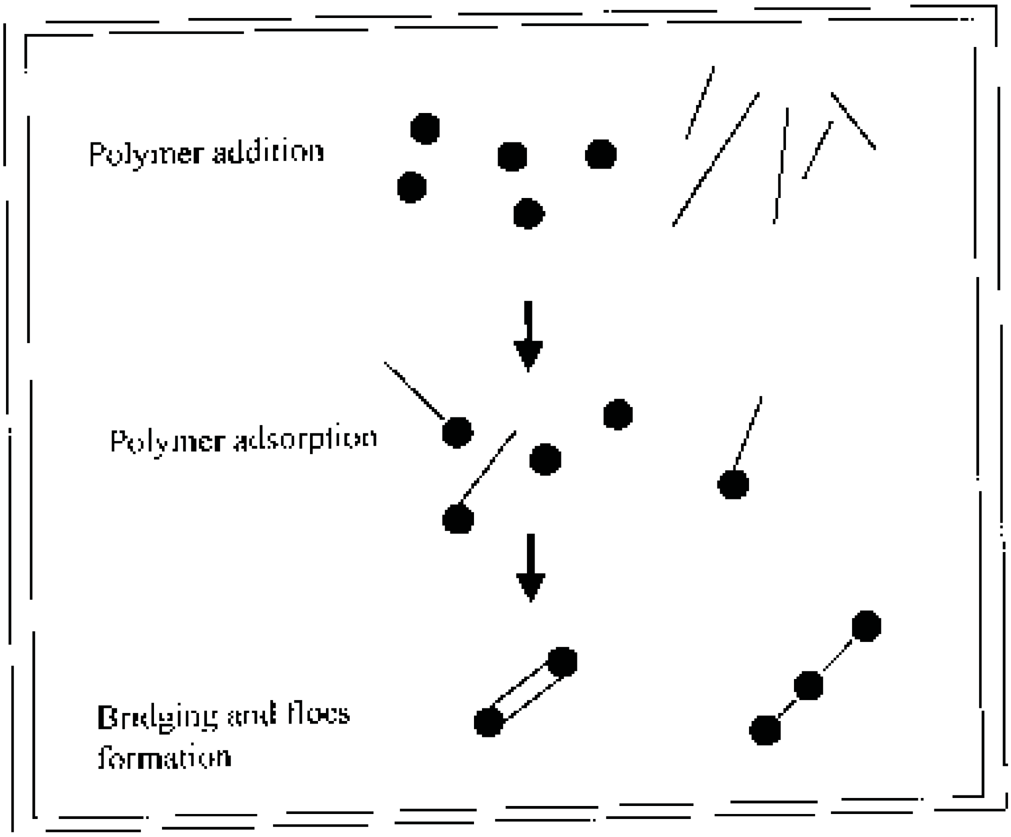

Figure 1.5: A flow diagram of the flocculation process

It can be seen from this Figure that the flocculation process involves two stages. In the first stage, the adsorption of polymer molecules onto individual suspended ultra-fine solid particles takes place. In the second stage the two polymer molecules containing the suspended solids contact each other and eventually result in formation of agglomerate (flocs) (Adams et al, 1986 and Van Heerden, 1989).

1.2.4 Purification of leach liquor solution

The leach liquor solution obtained after employing either acidic or alkaline leaching processes described in Section 1.2.2 above contains metal ions such as iron, cobalt, aluminium, platinum, magnesium and calcium. According to

Nathsarma (1987), Dreisinger and Cooper (1984), Habashi (1970), Jackson (1986), Charlot (1983), Sarma et al (1987) and Edwards (1976) purification methods such as selective precipitation, solvent extraction (SX), ion-exchange (IX) and crystallisation can be utilised to remove impurities such as iron and aluminium from the leach liquor solution prior to further treatment. In most cases, the various authors reported that purification methods such as SX, selective precipitation and crystallisation have the highest potential for the purification of aqueous leach liquor solutions containing aluminium(III) ions, cobalt(II) ions, iron(III) ions, nickel(II) ions and precious metal ions (Pt, Pd, Ru, Ir, Rh, Os).

Therefore, this dissertation deals specifically with:

- Selective precipitation of metal (Al and Fe) ions
- Solvent extraction
- Crystallisation of aluminium hydroxide, ammonium hexachloroplatinate and cobalt nitrate hydrate.

In the discussion of the theory of the above-mentioned common purification methods, their basic principles will be described in detail.

1.2.4.1 Selective precipitation

According to Jackson (1986) precipitation occurs when precipitating reagents are added to a solution of metal ions, resulting in the formation of solids. The precipitation processes had been used some years ago to separate either metals or metal ions or impurities from the leach liquor solution prior to its disposal. There are two types of precipitation reactions, namely, chemical precipitation and reductive precipitation (Jackson, 1986). During the chemical precipitation reaction, the precipitating reagent reacts with metal ions present in the aqueous solution to yield an insoluble precipitate (see equation 1.7). In the reductive precipitation a second metal precipitates the metal ions from the solution in the form of metal (e.g. $Cu^{2+} + Fe_{metal} \rightarrow Cu_{metal} + Fe^{2+}$).

Renner (2001), Hartley (1973), Bachmann and Rener (1984), Jackson (1986), Habashi (1970) and Warren and Hiner (1979a) mentioned that ammonium chloride can be used to precipitate platinum from the leach liquor solution in the form of ammonium hexachloroplatinate. The reaction between ammonium chloride and platinum *has already been discussed above (see equation 1.7).*

According to Jackson (1986), during the precipitation of metal hydroxides from the leach liquor solution, many metal ions prefer to hydrolyse resulting in the formation of sparingly soluble hydroxides. The general reaction is:

$$M^{n+} + n\,H_2O = M(OH)_n + n\,H^+ \qquad (1.10)$$

Where M^{n+} is a metal ion, and $M(OH)_n$ *is a metal hydroxide precipitate.*

It was also revealed that the selective precipitation of metal ions from the leach liquor solution using either sodium hydroxide or ammonium hydroxide depends substantially on the pH of the solution, solubility product value, temperature of solution as well as the oxidation *state of metal. It was also illustrated that* Co^{3+} can be precipitated from the leach liquor solution at pH 0 at 25 °C while Co^{2+} precipitates only at a pH between 8 and 10. The Fe^{3+} ion usually precipitates at a pH between 2.4 and 4. However, Fe^{2+} usually starts to precipitate at a pH of 6.5.

Charlot (1983) and Nathsarma (1987) also indicated that, when basic solutions containing either sodium hydroxide or potassium hydroxide are added to the iron-containing acidic leach liquor solution, Fe^{3+} *will start to selectively precipitate at* pH 2.5. The Al^{3+} starts to precipitate in the form of aluminium hydroxide at pH 3.5. Subsequent to the isolation of the precipitate of Al^{3+} and Fe^{3+} through filtration, the solution containing cobalt nitrate undergoes purification by solvent extraction. Relatively small amounts of the precipitate (containing Al^{3+} and Fe^{3+}) will be suitable *for disposal.*

Jackson (1986) indicated that selective precipitation can be used to recover valuable metals from the leach liquor solution. He argued that both concentration of the substance to be precipitated and the particle size of a precipitate play an important role during the precipitation. The relative supersaturation (σ) is expressed by:

$$\sigma = (C - C^*)/C^* \qquad (1.11)$$

where C is the concentration of the substance to precipitate.

C^* is its equilibrium solubility, and

σ Relative supersaturation.

Jackson (1986) also found that a relatively high supersaturation enhances the nucleation rate of metal ions and subsequently results in the formation of a precipitate of small particle size. This can cause the slurry obtained after the precipitation to be filtered with only difficulty and resulting in a poor solid-liquid separation. A relatively small supersaturation rate can be achieved by adding the precipitating agents very slowly to a hot, dilute solution of the leach liquor solution. This results in the formation of a crystalline precipitate of coarse particles that can be filtered only with ease. Accurate control of the nucleation rate is always required in order to improve the filterability of the precipitate from the slurry. It was also revealed that the metal hydroxide becomes positively charged under acidic conditions but negatively charged in alkaline media.

Skoog and West (1982) designed nucleation as a process whereby some number of ions or molecules unite to form a stable phase during the precipitation. It was also found that metal hydroxides such as aluminium hydroxide, ferric hydroxide and sulphides of heavy metals can be precipitated as colloids (gelatinous precipitate containing ultra-fine solid particles). These colloids can be coagulated/agglomerated by employing a flocculation process, as described in Section 1.2.3.

Genck (2000b) stated that rapid chemical reaction that occurs during the precipitation of metal ions from the leach liquor solution results in the formation of a precipitate with very small particle sizes ranging from 0,1 - 100 µm. A rapid chemical reaction can also cause high supersaturation resulting in the formation of ultra-fine particles during the precipitation. However, agglomeration of the precipitate containing ultra-fine particles can be caused by high speed of the agitator during precipitation. It was also found that particle size distribution is a function of the temperature of the leach liquor solution, the addition rate of reactants, mixing of the slurry and concentration of the reactants.

1.2.4.2 Solvent extraction (SX)

According to Ritcey and Ashbrook (1979) and Habashi (1970), the solvent extraction process involves a transfer of metal species (either desired or unwanted metal ions) from a solution of leach liquor into an organic phase after agitation of the two phases. Following the separation of these two phases, the loaded metal species are stripped with a solution of either acid or alkali from the loaded organic phase. The process in which the loaded metal species are removed from the loaded organic phase is termed stripping (back extraction). The stripped organic phase will undergo regeneration prior to recycling. However, the raffinate or aqueous phase is treated for the recovery of other metals and is also recycled to the solvent extraction circuit. The general flow diagram of solvent extraction circuit is shown schematically in Figure 1.6.

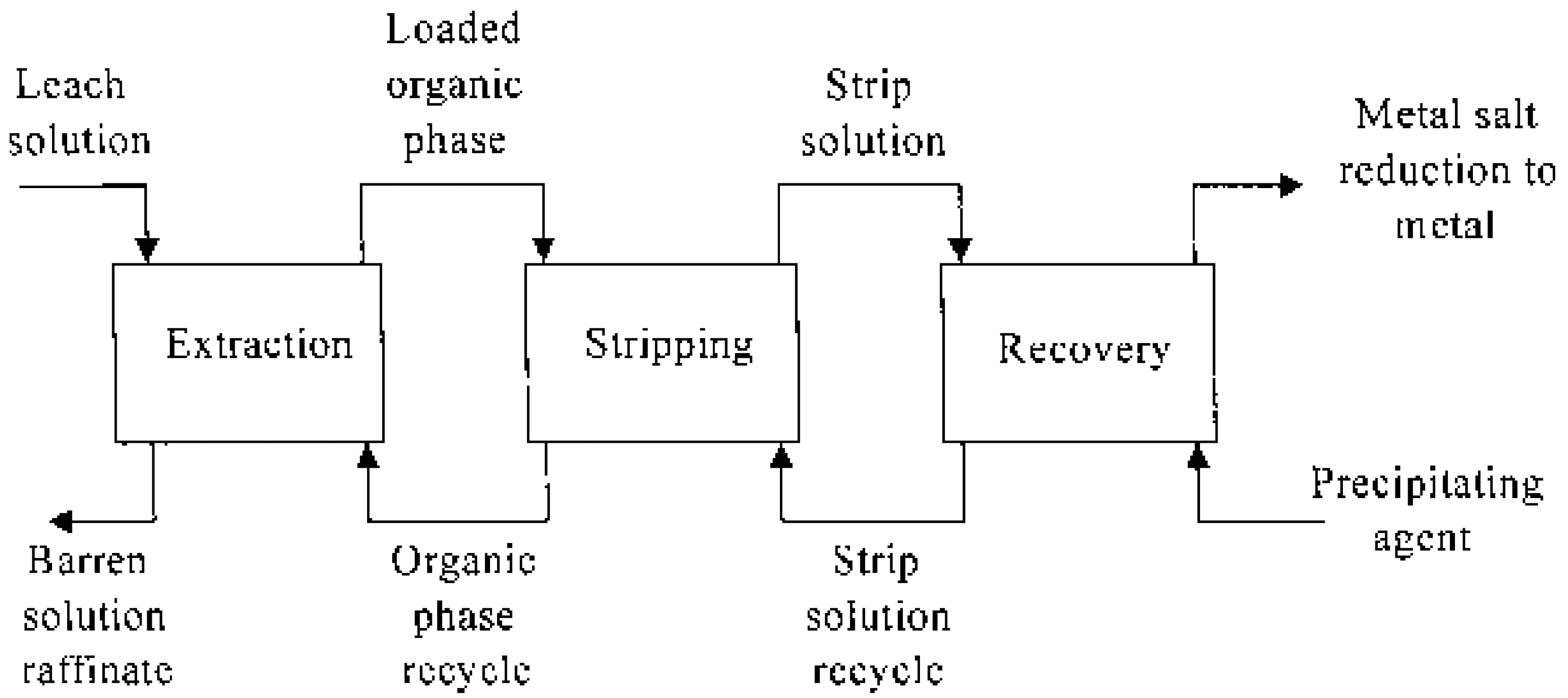

Figure 1.6: General Scheme in solvent extraction

Solvent extraction has been used since the beginning of the twentieth century in the petroleum industry and it is also used to purify leach liquor solution produced by mines and organic chemicals Habashi (1970). The reaction that takes place during the solvent extraction process when using di-(2 ethylhexyl) phosphoric acid (D2-EHPA) or salts of D2-EHPA as extractants is as follows:

$M^{n+} + nHA \Leftrightarrow MA_n + nH^+$ (1.12)

M^{n+} is a cationic metal species

nHA is an unionised extractant

MA_n is a compound or metal extractant complex

According to Ritcey and Ashbrook (1979), the use of the sodium salt of D2-EHPA as the extractant, in which cobalt(II) ions replace sodium ions at pH 5-6 during the solvent extraction results in sodium salt formation. These authors also reported that the formation of sodium salt does not affect the pH of the system because the hydrogen ions from the extractant in this case will not be released. This is then a metal-metal exchange rather than a metal-hydronium exchange process.

Solvent extraction process is used in commercial plants for the recovery of metals such as cobalt, nickel, uranium (Ritcey and Ashbrook, 1979, and Phillips and Wills, 1982). In this investigation, the effectiveness of solvent extraction in the recovery of cobalt containing species will be evaluated.

1.2.4.2.1 Organic phase

In this study, the organic phase which will be used in the solvent extraction practice is generally made up of the following organic reagents: an extractant, a diluent and if required, a modifier. In the following paragraphs more information is given about the extractant, diluent and modifier as well as the function of the stripping step.

1.2.4.2.2 Extractant

An extractant is the active organic part of the solvent primarily responsible for the extraction of metal species from the leach liquor solution. In this section, specifically di-2- ethylhexyl phosphoric acid (D2-EHPA) will be considered in the extraction of the cobalt(II) ions from the leach liquor solution, which was initially subjected to the precipitation method. In the precipitation method, impurities such as iron and aluminium will be selectively removed from the leach liquor solution, which then undergoes further treatment.

Habashi (1970) and Ritcey and Ashbrook (1979) stated that an ideal extractant should fulfil the following requirements:

- Selectivity
- High extraction capacity
- Easily stripped
- Separates easily from water, i.e. (a) density is appreciably different, (b) viscosity (c) high surface tension,
- Safe to handle i.e. (a) non-toxic (b) non-flammable (c) non-volatile
- Stable during storage or when in contact with acids or bases
- Must be locally available and inexpensive.

Habashi (1970) and Ritcey and Ashbrook (1984) revealed that the solubility of extractants, diluents and modifiers might vary greatly during the solvent extraction process. It was further stated that extractants like ethers, alcohols, aldehydes, ketones, oximes, phenols, esters, carboxylic acids and amines are partially soluble in either acidic or basic leach liquor solution. These authors generalised that the solubility of the extractants in the leach liquor solution during the solvent extraction process decreases with an increase in chain length while their extracting power increases with increasing chain length. Ritcey and Ashbrook (1984) also mentioned that the solubility of the extractants depends substantially on the temperature of the leach liquor solution as well as the concentration of acid or base present in the leach liquor solution. In this study esters (di-2-ethylhexylphosphoric acid) (D2-EHPA) and tributylphosphate (TBP) will be used to extract the cobalt(II) ions from the leach liquor solution. The solubility of these reagents will be described briefly.

Esters are formulated by the reaction of alcohols with inorganic acids (Habashi (1970) and Anil et al. (1970). For example, phosphoric acid is reacted with alcohols to form esters that can be used in extractive metallurgy. These esters are divided into acidic esters and neutral esters. It was found that the type of ester formed is determined by the molar ratio of the reactants, if the molar ratio of alcohol : P_2O_5 ratio is 2, then an alkyl pyrophosphoric acid is formed:

$$2ROH + P_2O_5 \rightarrow (RO)_2(PO)_2O(OH)_2 \qquad (1.13)$$

When a ratio of 3:1 is used, a mixture of mono and dialkyl orthophosphoric acid is obtained.

$$3ROH + P_2O_5 \rightarrow (RO)(HO)_2PO + (RO)_2(HO)PO \qquad (1.14)$$

Trialkyl phosphates can also be prepared by reacting three equivalents of alcohol with $POCl_3$ as shown in equation (1.15).

$$3ROH + POCl_3 \rightarrow (RO)_3PO + 3HCl \qquad (1.15)$$

The physical properties of tributylphosphate (TBP) formed after using equation 1.15 are summarised in Table 1.1 (Habashi, 1970).

Table 1.1: Physical properties of tributyl phosphate

Boiling point, °C	177-178 at 27 mm Hg
Flash Piont, °C	145
Viscosity at 20 °C, centipoise	3.41
Solubility in water, vol %	0.6
Solubility of water in TBP, vol %	7
Specific gravity	0, 973

The solubility of these alkyl phosphates (di-2-ethylhexylphosphoric) and tributylphosphate (TBP) will briefly be described. According to Ritcey and Ashbrook (1984) the solubility of alkyl phosphates (di-2-ethylhexylphosphoric) acid in an aqueous phase has not been extensively studied but the salts of this acidic ester such as ammonium di-2-ethylhexylphosphoric acid (D2-EHPA (NH_4)) and sodium di-2-ethylhexylphosphoric acid (D2-EHPA (Na)) depress the solubility of di-2-ethylhexylphosphoric acid (D2-EHPA) during the extraction of the cobalt(II) ions at pH 5-6 at 60 °C. The loss of this alkyl acid is found to be less than 50 ppm.

Ritcey and Ashbrook (1984) also mentioned clearly that the solubility study of TBP in various aqueous media was undertaken some years ago and it was eventually found that as the temperature of the leach liquor solution increases, the solubility of TBP decreases. It was further argued that the solubility of TBP in the aqueous phase increases with an increase in acid concentration. The TBP concentration also has a marked effect on the solubility of tributyl phosphate in acidic leach liquor solution.

According to Ritcey and Ashbrook (1984) and Habashi (1970) there is no substantial amount of information available on the solubility of various diluents in use or being studied in the solvent extraction circuits. The solubility of diluent is expected to be less than 2 ppm.

1.2.4.2.3 Diluents

Various authors defined the term diluent as an organic liquid, which dissolves both extractant and modifier, to form an organic solvent during the solvent extraction process. Ritcey and Ashbrook (1984) and Dreisinger and Cooper (1984) mentioned that the following criteria must be employed when selecting a suitable diluent, for the solvent extraction method:

- It should be locally available and inexpensive
- It must dissolve extractant and modifier
- It must not react with an extracted metal species
- It should have a low volatility and high flash point, thereby, decreasing losses due to volatility as well as fire hazards
- It should be insoluble in the aqueous phase
- It should have a low surface tension.

In the present study, illuminating paraffin produced by Sasol will be investigated for use in the preparation of the organic phase for the solvent extraction process. This illuminating paraffin conforms to the above-mentioned requirements of the diluent. Diluents act as carriers for the extractant and modifier and generally comprise the bulk of the organic phase. This organic solvent called diluent has no capacity of extracting metal ions from the aqueous phase, but will improve the physical properties of the extractant such as the density and viscosity. The diluent should be insoluble in water in order to prevent the loss of organic phase during the solvent extraction process. According to Habashi (1970) the diluent normally consists of hydrocarbons or substituted hydrocarbons.

1.2.4.2.4 Modifiers

A modifier is a reagent added to the organic phase in an attempt to prevent the formation of emulsions between the aqueous and organic phases during solvent extraction. A modifier will improve the solubility of the extractant in the diluent. The formation of a third phase (two organic phases) in solvent extraction systems poses many serious problems (Ritcey and Ashbrook, 1984).

According to Ritcey and Ashbrook (1984), isodecanol, tributylphosphate, ethylhexanol or p-nonylphenol must be added to the organic phase to prevent the formation of third phase (emulsion). The authors also indicated that a low temperature of the mixture, usage of aliphatic diluents and the extent of the solubility of the organic phase could result in the formation of the third phase in the aqueous phase during the solvent extraction process. The concentration of the modifier required during the solvent extraction ranges from 5 - 20 %vol. The modifier concentration depends largely on the concentration of extractant used during the solvent extraction step.

Furthermore, Ritcey and Ashbrook (1984), Dreisinger and Cooper (1984) reported details of studies undertaken in efforts to optimise the following parameters during the solvent extraction process:

- pH,
- Temperature cobalt(II) ions loading,
- Effect of diluent on the metal extraction with D2-EHPA,
- Effect of modifier on the extraction of cobalt(II) ions,
- Effect of modifier on phase separation,
- Effect of extractants on cobalt(II) ions loading and
- Properties of D2EHPA, TBP and illuminating paraffin (Kerosene).

In this dissertation, it is important to note that di-2-ethylhexylphosphoric acid, (extractant), illuminating paraffin and tributylphosphate (modifier) will be used in the preparation of the organic phase exclusively for the extraction of cobalt(II) ions from the leach liquor solution.

1.2.4.2.5 Stripping step

The stripping operation alternatively referred, as back extraction is the second step of the solvent extraction process. During the stripping step, the metal ions loaded in the organic phase are transferred into the aqueous phase. In this step the stripping agent such as basic or acidic solution is used to strip the loaded organic phase (Alguacil et al. 1987). The metal ions that are contained in the stripping liquor solution can be subjected to a variety of conventional processes like electrowinning, crystallisation and precipitation for the recovery of high value metals.

Basic stripping agents such as sodium hydroxide, ammonium hydroxide, potassium hydroxide, ammonium carbonate, ammonium chloride and sodium carbonate can be used to remove the extracted metal species from the loaded organic phase.

Acidic stripping agents such as hydrochloric acid, nitric acid and sulphuric acid can also be used to remove the extracted metal species from the loaded organic phase. In this dissertation, nitric acid will be used to strip the loaded organic phase. During the stripping step, the hydronium ions will exchange with the cation extracted in the organic phase. Finally the cobalt ions as well as the nitrate ions will move into the stripping liquor. This liquor solution or aqueous phase containing mostly cobalt nitrate salt can be subjected to other purification methods for metal recovery as stated earlier in this section. The stripped organic phase can be regenerated prior to recycling to the solvent extraction step.

1.2.4.3. Crystallisation of metal salts from the leach liquor solution

Hebashi (1980) indicated that crystallisation of metal ions from aqueous solution depends mainly on the temperature of the aqueous solution, organic solvents, complexing agents and fractional crystallisation. Genck (2003) demonstrated that macro-mixing (the overall circulation and the degree of solid suspension) and micro-mixing (contacting and mixing at the molecular level) as well as the crystallisation system hydrodynamics can affect the product parameters such as crystal size distribution (CSD), shape, purity, surface area and occurrence of polymorphs. Crystals with ultra-fine particles can potentially affect the filtration, drying and milling of the product obtained during crystallisation. Some of the factors that affect the crystallisation of metal ions from the aqueous solution as discussed by Habashi (1970) and Genck (2000a) will not be determined in this present study. Only three factors, namely, effect of temperature, effect of organic solvents and fractional crystallisation procedures that will affect the crystallisation of metal salts from the leach liquor solution will be addressed.

Regarding the effect of temperature, Habashi (1970) argued that the solubility of most metallic salts increases with increasing temperature up to approximately 100 °C, and finally the solubility starts to decrease until at about 250 °C and at which temperature crystals start to precipitate. However on evaporating the leach liquor solution, the metal ions present in the leach liquor solution will become concentrated and subsequently result in the formation of crystals. In contrast, aluminium nitrate will not undergo crystallisation after evaporating the leach liquor solution at high temperature (> 110 °C) because nitrate and free nitric acid that are suitable for the crystal formation will be completely decomposed. This implies that temperature of the leach liquor solution needs to be monitored carefully during the crystallisation step.

Gee et al (1947) and Vittorf (1924) found that the addition of ethanol to the sulphuric acid leach liquor solution results in efficient crystallisation of iron-free aluminium sulphate. The spent alcohol was recovered for further use in the process. Ethanol is also used in the production of ammonium sulphate in order to improve the crystallisation of the salt.

Habashi (1970) printed out that the fractional crystallisation is an old method and is currently being replaced by ion-exchange and solvent extraction procedures. Fractional crystallisation is time and energy consuming. In this process, the leach liquor solution can be evaporated until the crystals are formed and finally separated by filtration. The filtrate (leach liquor solution) can be evaporated until additional crystals are formed. These crystals will then be separated through filtration. The crystals obtained from the first step of evaporation will be redissolved in water and then evaporated until new crystals are formed and separated. Crystals from the second crystallisation step are combined with the least soluble fraction and evaporation carried out. The process is repeated several times until finally three fractions are obtained: one fraction contains the least soluble constituents, the second fraction contains the most soluble and the third contains constituents of intermediate solubility.

The crystallisation of metal salts from the leach liquor solution also depends on the concentration of cation (metal to be crystallised), concentration of anion and availability of water. To enhance the crystallisation rate of salts, seed crystals must be added to the leach liquor solution. According to the Bayer process concisely described in Section 1.2.2.1, gibbsite crystals are added to the supersaturated solution in order to speed up the rate of crystallisation (Habashi, 1970; Jackson, 1986; Helmboldt et al. 2001 and Warren and Hiner, 1979b).

Genck (2000a) also reported that the addition of the reactants to the leach liquor solution during crystallisation can form new nuclei or support the growth of the existing crystals. It was elaborated that excessive nucleation can result in too many small crystals with an unacceptable crystal size distribution. It was further mentioned that a wider crystal size distribution can also be obtained by increasing the percent solids thereby leading to a reduction of the tendency to high supersaturation levels.

In addition, seeding can be used, involving a process of adding crystals of a substance to be crystallised into a supersaturated solution of the same substance. On cooling, the crystallisation of the metal salts take place.

In this dissertation, the crystallisation steps of importance involve:

- The crystallisation of alumina trihydrate (ATH) from sodium aluminate solution
- Crystallisation of cobalt nitrate from the impure leach liquor solution
- Crystallisation of cobalt nitrate from the purified leach liquor solution
- And finally crystallisation of platinum salts such as ammonium hexachloroplatinate from chloroplatinic acid solution.

1.2.4.3.1 Crystallisation of alumina trihydrate (ATH)

Alumina trihydrate can be selectively separated from sodium aluminate solution produced by the Bayer process as illustrated earlier in Section 1.2.2.1. For this process, Habashi (1970) and Warren and Hiner (1979b) reported that more impurities such as silica, hematite, zinc and cobalt have a detrimental effect on the crystallisation of alumina from sodium aluminate solution. El-Katatny et al (2000), Helmboldt (2001) and Habashi (1970) mentioned that aluminium present in the sodium aluminate solution crystallises with three molecules of water to form a water insoluble alumina trihydrate, $Al_2O_3.3H_2O$. The crystalline phase present is termed gibbsite and is contaminated with trace amounts of iron, cobalt as well as zinc. It was also found that practically all the methods relating to the recovery of aluminium from aluminium containing ores are based on the crystallisation of an aluminium salt from the leach liquor solution. It was further stated that to produce a product of high purity, fractional recrystallization must be implemented. Aluminium trihydrate produced in this way, can be used in the production of pure alumina. This alumina is suitable for the production of aluminium metal. Aluminium hydroxide is normally used in the dyeing industry as a mordant to fix dyes (Warren and Hiner, 1979b and Helmboldt et al, 2001). Aluminium trihydrate can also be used in water treatment and the aluminium chemicals industry. The reaction occurring during the crystallisation of ATH from sodium aluminate solution is as follows:

$$2Na\,AlO\,(OH)_2 + 2H_2O \rightarrow Al_2O_3.3H_2O + 2NaOH \qquad (1.16)$$

Sodium hydroxide (NaOH) produced in the aforesaid reaction could be recycled to the sodium hydroxide make-up for further digestion of aluminium bearing-ores. The present study does not involve acid leaching of aluminium-containing-ore but Helmboldt et al (2001), Warren and Hiner (1979b), Phillips and Wills (1982) and Burkin (1987) reported that if the aluminium bearing substance contains substantial amount of silica, iron with low aluminium then this ore must be efficiently treated with sulphuric acid solution or nitric acid solution. The aluminium ions present in a leach liquor solution obtained after using sulphuric acid leaching will crystallise in the form of aluminium sulphate, $Al_2(SO_4)_3.18H_2O$. Aluminium(III) ions can also be crystallised from the leach liquor solution as ammonium aluminium sulphate by adding either ammonia or an ammonium sulphate solution (Helmboldt, 2001).

The chemical reactions for the formation of aluminium ammonium sulphate are as follows:

$$Al_2(SO_4)_3 + (NH_4)_2\,SO_4 + 40H_2O \rightarrow 2\,Al(NH_4)(SO_4)_2.20H_2O \qquad (1.17)$$

$$2NH_3 + Al_2(SO_4)_3 + H_2\,SO_4 + 40H_2O \rightarrow 2\,Al(NH_4)(SO_4)_2.20H_2O \qquad (1.18)$$

1.2.4.3.2 Crystallisation of cobalt nitrate

The leach liquor solution obtained during the leaching of the cobalt-containing residue with nitric acid solution needs to undergo crystallisation. In this study, crystallisation of impure and pure cobalt nitrate will be investigated. Precipitation of Al & Fe from the leach liquor solution as well as the solvent extraction process will be applied prior to the crystallisation to produce pure leach liquor containing mainly cobalt nitrate solution (Nathsarma and Bhaskara, 1987).

As stated in Section 1.2.4.3, the leach liquor solution will initially be concentrated by evaporation in order to obtain a supersaturated leach liquor solution that is adequate for crystallisation. Following the evaporation, a supersaturated leach liquor solution will be allowed to cool to room temperature. On cooling, cobalt(II) ions present in the solution will crystallise in the form of cobalt nitrate hydrate, $Co(NO_3)_2.6H_2O$. The pink crystals of the cobalt nitrate will lose the water of hydration when the temperature increases to 55 °C (Warren and Hiner, 1979a; Cotton and Wilkinson, 1980 and Donaldson, 2001). To produce chemically pure cobalt nitrate, fractional crystallisation or recrystallisation as discussed in Section 1.2.4.3. should be used. Cobalt nitrate produced in this manner, could, in future, be used in the production of fresh catalyst for Fischer-Tropsch synthesis reactions.

According to Culross (1999), cobalt nitrate supplies both catalytic metal (Co) and oxidant (nitrate) during the preparation of fresh catalyst for Fisher-Tropsch reactions for the industrial synthesis of certain hydrocarbons from carbon monoxide and hydrogen.

1.2.4.3.3 Crystallisation of hexachloroplatinate

The liquor solution obtained after leaching the residue from nitric acid leaching step with an aqua regia typically contains platinic acid. This dissertation will deal specifically with the precipitation crystallisation of ammonium hexachloroplatinate from the platinic acid. The production of platinum (tetra amine) di-nitrate complex will not be included in this study but its chemical reactions will briefly be described below. According to Renner (2001), Bachmann and Renner (1984) and Edwards (1976) it is quite possible to crystallise platinum(II) ions from the platinum containing leach liquor solution in the form of ammonium hexachloroplatinate. These authors indicated that the addition of a solution of ammonium chloride to the platinic acid would result in the precipitation crystallisation of hexachloroplatinate. The chemical reaction between NH_4Cl and Pt(II) ions is given in Section 1.2. It was mentioned that to further produce chemically pure ammonium hexachloroplatinate, recrystallisation method discussed in Section 1.2.4.3 must be applied. The platinum salts produced in this manner, could be used in the production of platinum metal. Ammonium hexachloroplatinate can also primarily be used to make catalysts by impregnating support materials (Renner, 2001).

1.3 Scope and objectives

The main objective of this study is to conduct theoretical and experimental investigation into the possibility of selectively recovering Co and Pt from a spent commercial catalyst prior to its disposal. Both platinum and cobalt are expensive and toxic. They pose health and environmental risk (Seiler and Sigel, 1988). The alumina support can be selectively dissolved by hydrothermally reacting the spent catalyst with a dilute NaOH solution (~25 % m/m) at 120-200 °C and pressures between 5 and 20 bar. Under such conditions, cobalt and platinum remain in the leached residue and can be separated by treating the residue with nitric acid to give cobalt nitrate and a Pt-containing residue. Further treatment of the latter with aqua regia (1 vol nitric acid: 3 vol hydrochloric acid) should yield chloroplatinic acid.

The sodium aluminate solution will be further treated to produce NaOH and aluminium hydroxide (gibbsite or aluminium trihydroxide) using a modified version of the Bayer method discussed in Section 1.2.2.1 above. The cobalt nitrate solution will be purified following the methods discussed in Section 1.2 above (i.e. solvent extraction, selective precipitation, flocculation and crystallisation). The recovered aluminium oxide could be sold to companies involved in the refractory business and aluminium chemicals industry, while Co and Pt could be re-used in FT catalyst preparation

1.4 Breakdown of the dissertation

In this Chapter the literature study of each step that will be used in the proposed process of recovering high value metal compounds from the spent catalyst is separately discussed. The proposed process comprises the following steps:

- Calcination of spent catalyst in the presence of air to oxidise the carbonaceous materials
- Sintering of the mixture of spent catalyst and sodium carbonate at a higher temperature to form water soluble sodium aluminate with prevention of the formation of cobalt aluminate spinel
- Selective base or acid leaching of the calcined spent catalyst
- Flocculation and filtration of the slurry
- Purification of the leach liquor solution
- Crystallisation of metal salts from the leach liquor solution obtained after base or acid leaching step.

The experimental part of this study is detailed in Chapter 2, and includes considerations of the chemical dissolution during occurring the leaching of the oxidised spent cobalt-based catalyst. The Chapter will commence with the calcination of the spent cobalt-based catalyst carried out in order to oxidise carbonaceous materials. Following the calcination step, the product, which will typically contain aluminium, cobalt, silicon and iron oxides, and some trace of platinum species, will be formed. This oxidised spent catalyst will first be used in the leaching step, where either inorganic acids like sulphuric acid, hydrochloric acid and nitric acid or a strong base like sodium hydroxide could be used to selectively dissolve aluminium from the oxidised spent cobalt-based catalyst. The parameters such as temperature of the slurry and concentration of sodium hydroxide will be optimised during the leaching step. The problems that may possibly be associated with the filtration of the slurry obtained after the leaching step will be identified and subsequently resolved through the flocculation method. In this experimental section, the purification method used to separate high value metal ions from the leach liquor solution will be discussed. The Chapter is concluded with an account of the precipitation and crystallisation of metal salts from the purified leach liquor solution and with subsequent characterisation of the product.

The results obtained after the experimental test work will be presented and discussed to a larger extent in Chapter 3. Conclusion drawn on the results and recommendations will be presented in Chapter 4. The recommendations may be implemented to further probe the catalytic behaviour of the products formed during the envisaged process of recovering high value metals from spent catalyst.

1.5 References

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