DIRECT COBALT RECOVERY FROM LOADED KELEX 100 BY REACTION WITH HYDROGEN

by

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To Sheri

A wish is a secret want
for something
very special --
it is kept in the heart
next to memories
and dreams,
and once in a while,
when the time
is just right,
you let someone special
know it's there.

Rebecca Thomas Shaw

ABSTRACT

Direct metal precipitation from loaded organic extractants by reaction with hydrogen gas may offer certain potential advantages over the conventional route of stripping, followed by a metal recovery stage.

In this work, the interaction of cobalt-loaded KELEX 100* with hydrogen has been studied. Rapid cobalt precipitation can be obtained with an appropriate combination of operating temperature (250 to 325 °C) and hydrogen pressure (1.38 to 3.45 MPa). Data are presented describing the effects of operating temperature, hydrogen pressure, stirring rate, and seeding on the kinetics of cobalt precipitation. The reaction rate is highly sensitive to the temperature and relatively insensitive to the hydrogen pressure and the stirring rate. Major increases in the precipitation rate can be achieved with seeding, particularly at the lower end of the temperature range studied.

The behaviour of the organic extractant under the experimental conditions was studied using gas-liquid chromatography and infrared spectroscopy. The extractant displayed excellent thermal and chemical stability and extensive recycling of the 'hydrogen-stripped' organic caused no organic decomposition.

The chemical and physical properties of the cobalt powder produced are also presented.

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*An alkylated 8-hydroxyquinoline extractant produced by Sherex Chemical Company.

RÉSUMÉ

Précipiter le métal directement de son agent extractant organique peut offrir certains avantages par rapport à la méthode conventionelle de ré-extraction suivie de la récupération du métal.

Ce projet porte sur l'interaction entre un KELEX 100* chargé de cobalt et l'hydrogène. On peut précipiter rapidement le métal, à des températures (250 à 325 °C) et pressions d'hydrogène (1.38 à 3.45 MPa) judicieusement choisies. On présente dans cet article des données décrivant l'effet de la température, pression d'hydrogène, degré d'agitation et de l'introduction de cobalt métallique en poudre sur la cinétique de précipitation. Le taux de réaction dépend beaucoup de la température, mais relativement peu de la pression d'hydrogène et du degré d'agitation. On peut, en introduisant dans la solution de la poudre de cobalt, augmenter considérablement le taux de précipitation, surtout entre 250 et 275 °C.

Le comportement de l'agent extractant utilisé a été étudié par chromatographie en phases liquide et gazeuse et par spectroscopie infra-rouge. L'agent a fait preuve d'une stabilité chimique et physique excellente, même lorsque recyclé plusiers fois.

On présente également les propriétés physiques et chimiques de la poudre de cobalt produite.

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*Un dérivé de la 8-hydroxyquinoléine de 'Sherex Chemical Company'.

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PREFACE

Conventional solvent extraction in hydrometallurgy is considered solely as a purification/concentration operation where the organic phase acts primarily as a transfer medium for the metal being extracted. However, there is also the possibility that chemical reactions may be conducted within the organic phase such that metal could be produced directly in a useful form. The aim of the present investigation is to determine whether or not cobalt can be precipitated from a cobalt-loaded chelating extractant (KELEX 100) by reaction with hydrogen under pressure.

The thesis begins with an introductory synopsis of the major hydrometallurgical processes. The advantages and disadvantages of several purification and concentration operations are given. The next chapter examines some of the previous work performed on the reduction of various metals from organic solutions, and in particular, on the reduction of metals from solvent extraction reagents. In the third chapter the experimental procedure used in the present investigation is outlined. A brief description of the experimental apparatus is included.

The fourth chapter deals with the chemical and thermal stability of KELEX 100 at elevated temperatures and pressures. For 'direct hydrogen stripping' to be technically and economically feasible, the organic solvent must be totally regenerated after reduction and show no loss in loading capacity. In the fifth chapter the various parameters which affect the kinetics of the cobalt precipitation process are given. In chapter six, several physical and chemical properties of the product powder are examined.

A brief evaluation of the reduction process is presented in chapter seven and the conclusions based on the present investigation are given. Areas which require further research are also outlined.

CHAPTER ONE

CONVENTIONAL HYDROMETALLURGY

SECTION 1.1 : ADVANTAGES AND DISADVANTAGES

As the reserves of sulphide nickel and cobalt ores are being depleted, worldwide attention is being focused on the treatment of oxide ores.[1] While several processes, both hydrometallurgical and pyrometallurgical, have been used in the past to process oxide ores, many factors make the hydrometallurgical process more attractive. The advantages that the hydrometallurgical approach has over the pyrometallurgical approach are summarized below:[2]

1) Hydrometallurgical processing is especially suited for the treatment of low-grade ores.
2) A hydrometallurgical process may start as a small-scale operation and expand as required. A pyrometallurgical process is designed on a large-scale, since it is more economical to build one large furnace than several smaller ones with the same total capacity.
3) The handling of leaching products is cheaper and easier than the handling of molten slags, mattes, and metals.
4) Corrosion problems are relatively mild in hydrometallurgy as compared to the inevitable deterioration of refractory linings in furnaces, and the subsequent need for periodic shutdowns and replacements.

5) The siliceous gangue in the ore is unaffected by most leaching agents. In the pyrometallurgical smelting process, this gangue must be slagged.
6) Hydrometallurgical plants usually do not pollute the environment to the extent that smelters do. This fact is important at present due to strict anti-air-pollution laws.

Some difficulties, however, may be encountered when processing an ore by hydrometallurgical methods. Hydrometallurgical processes are relatively slow, since they are carried out at low temperatures; the higher temperatures of pyrometallurgical operations allow for faster reactions. Also, the small particle size required for leaching may result in a slow solid-liquid separation.[2]

SECTION 1.2 : LEACHING

The various stages which comprise the complete hydrometallurgical process are shown in Figure 1.1. The feed to such a circuit is generally an oxide ore that has been crushed and ground, but other materials such as concentrates or mattes from a pyrometallurgical operation can be used. If the feed to the circuit is a sulphide concentrate, a chemical treatment stage (e.g. a roasting operation) may be necessary to render the material water soluble (e.g. a sulphate or an oxide).[3]

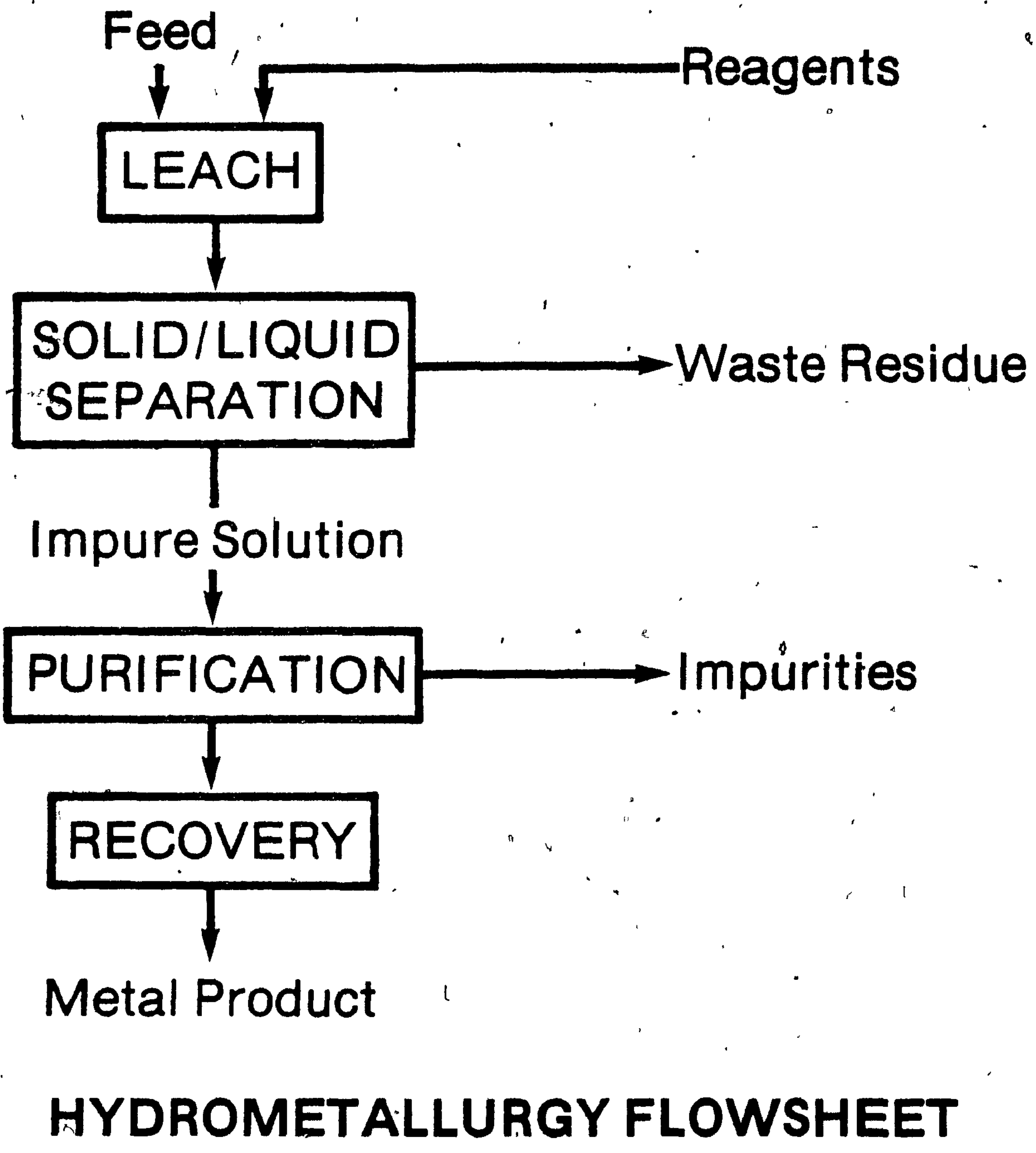


FIGURE 1.1 - CONVENTIONAL HYDROMETALLURGY FLOWSHEET

The first step in the hydrometallurgical process is leaching. Leaching is fundamentally a separation process. The object of leaching is to extract a soluble material from a heterogeneous solid by dissolution in a suitable liquid.[4] The choice of leaching agents depends upon many factors including cost, chemical and physical properties, and the type of minerals to be leached. Some common leaching agents are acids, bases, water, and aqueous salt solutions.

SECTION 1.3 : SOLID-LIQUID SEPARATION

After the desired constituent is leached from the feed material, it is necessary to remove the unreacted material in order to obtain a clear solution suitable for further processing. The solid-liquid separation is usually carried out in thickeners, followed by filtration.[5] The waste residue from the separation stage is disposed of, and the clear solution is forwarded to the purification stage (see Figure 1.1).

SECTION 1.4 : PURIFICATION AND CONCENTRATION

The pregnant liquor produced in the solid-liquid separation stage may require an additional purification step prior to the recovery of the desired metal(s). The object of the purification step is to treat the solution in order to remove unwanted impurities that were dissolved in the leaching stage.

Many purification processes are currently available. Selection of the appropriate one depends upon many factors, such as cost, the type of impurities to be removed, and the concentration of the metal in the leach solution. The three most common purification techniques are listed below:

1) neutralization;
2) ion exchange;
3) solvent extraction.

1.4.1 : NEUTRALIZATION

Neutralization is a very simple, but effective process for removing unwanted impurities, such as iron, from a leach solution. The ubiquitous iron can be removed by adjusting the pH with lime or soda ash, and by bubbling air through the solution to precipitate ferric hydroxide without removing valuable metals. Since the solubilities of hydroxides vary greatly (see Table 1.1), this procedure finds extensive application in hydrometallurgy.

It is also possible to precipitate other impurities by adding hydrogen sulphide gas to separate out insoluble sulphides (see Table 1.1). Although sulphide precipitation has limited application currently, it is a potentially useful technique.

METAL HYDROXIDE[6]	LOG K_{SP}	METAL SULPHIDE[7]	LOG K_{SP}
$Mg(OH)_2$	-9.2		
$Mn(OH)_2$	-12.8	MnS	-12.55
$Fe(OH)_2$	-14.0	FeS	-17.31
$Ni(OH)_2$	-14.7	NiS	-20.55
$Co(OH)_2$	-14.8	CoS	-21.64
$Zn(OH)_2$	-15.6	ZnS	-24.05
$Cu(OH)_2$	-18.8	CuS	-35.05
		Cu_2S	-47.70
$Fe(OH)_3$	-38.7		
		Co_2S_3	-125.9

TABLE 1.1 - SOLUBILITY PRODUCTS OF SOME METAL HYDROXIDES AND SULPHIDES AT 25°C

1.4.2 : ION EXCHANGE

Ion exchangers are materials which reversibly exchange ions which they contain, for ions in the leach solution.[8]

The phenomenon of ion exchange was first discovered in 1850 by H. S. Thompson and J. H. Way, who independently reported a systematic investigation of ion exchange in soils. They reported that, upon treating a soil with either ammonium sulphate or ammonium carbonate, most of the ammonia was absorbed and calcium was released into the solution.[9]

For fifty years, the ion exchange phenomenon remained solely of academic interest. At the turn of the century, the work of Gans with both natural and synthetic inorganic ion exchangers led to their first industrial use, namely the softening of water. Water softening was virtually the only industrial use of ion exchange until the development of synthetic organic extractants by Adams and Holmes in 1935.

As applied to the metallurgical industry, ion exchange is currently used to recover metals such as uranium and vanadium, and to separate closely related metals such as hafnium from zirconium.

Ion exchange consists of two distinct stages: sorption and elution.

In sorption, the leach solution is passed through a bed of resin, where the metal ions to be recovered leave the aqueous phase and enter the resin phase. The recovery of a cation from a leach solution can be expressed by the following equation:

$$2R^-Y^+_{(resin)} + A^{++}_{(aqueous)} \rightarrow R_2^-A^{++} + 2Y^+_{(aqueous)} \quad (1.1)$$

where:

A^{++} = cation to be recovered

Y^+ = counter ion (e.g. H^+, Na^+)

R^- = functional group (e.g. sulphonate).

If an anion is to be recovered, the sorption equation takes the following form:

$$2R^+X^-_{(resin)} + B^{--}_{(aqueous)} \rightarrow R_2^+B^{--} + 2X^-_{(aqueous)} \quad (1.2)$$

where:

B^{--} = anion to be recovered

X^- = counter ion (e.g. OH^-, Cl^-, NO_3^-)

R^+ = functional group (e.g. quaternary ammonium).

When the resin bed becomes saturated with the metal ion in the feed, the metal ion will appear in the effluent and the flow of feed is stopped.

In elution, a small volume of a suitable solution is added to the resin bed to remove the metal ions completely from the resin. In this way, a concentrated solution of pure metal is obtained and the resin is regenerated. The elution equations are simply the reverse of the sorption equations (Equations 1.1 and 1.2).

The first attempts to apply ion exchange to metal recovery were in connection with: (1) the recovery of copper from waste liquors of the brass industry, (2) silver from photographic film manufacturing wastes, and (3) chromium from electroplating wastes. Uranium was the first metal to be recovered from leach solutions using ion exchange on a large-scale. The vast amount of research involving uranium extraction gave rise to the possibility of using ion exchange for recovering other metals from leach solutions.

The ion exchange process is especially useful in the treatment of very dilute solutions, with metal ion concentrations of the order of 10 ppm or less. For solutions with metal ion concentrations above 1%, this method is generally not effective. Since ion exchange is essentially a batch operation, high metal concentrations will result in a rapid breakthrough and the feed to the exchanger will have to be stopped frequently. Consequently, many ion exchangers would have to be used and this could prove to be prohibitively expensive.

1.4.3 : SOLVENT EXTRACTION

The earliest record of an organic solvent being used to extract metal ions was by Péligot in 1842.[10] He observed that uranyl nitrate was appreciably soluble in diethyl ether, and this property was used for separating uranium from other constituents of pitchblende.

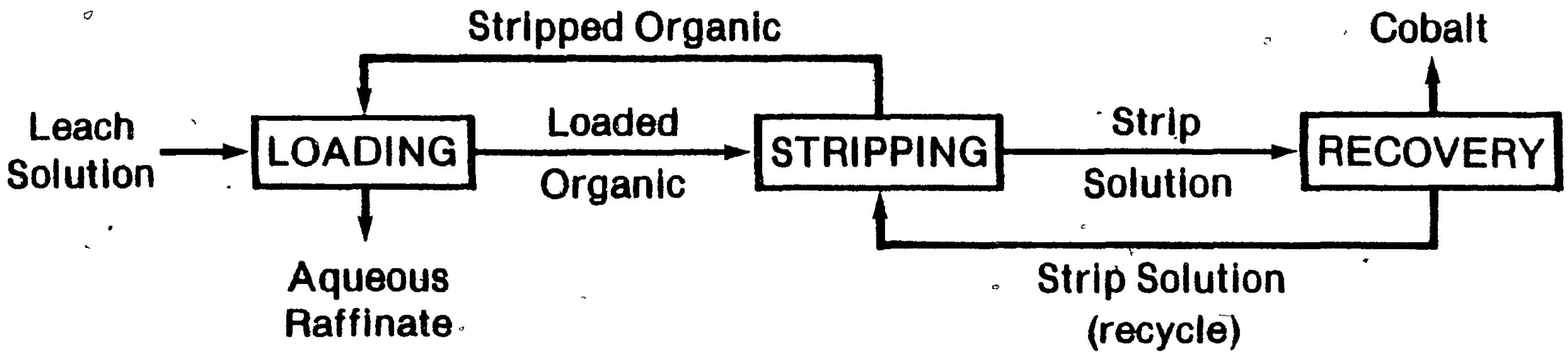
The first large-scale use of solvent extraction (or liquid-liquid extraction) in metallurgy was in connection with the preparation of uranium for the atomic energy program.

As a result of the large amount of research involving uranium extraction, particularly on reagents, solvent extraction is coming to play an integral part in the separation and recovery of a variety of nonferrous metals. Today, more than a dozen primary copper solvent extraction plants are in operation.[11] Other metals, such as nickel and cobalt, are beginning to be recovered using this technique.[12,13]

Conventional solvent extraction is comprised of two distinct steps: loading and stripping.

In loading, the metal values in the leach solution are extracted by agitation with an organic solvent immiscible in that phase. The two phases are then allowed to separate. The aqueous raffinate is either discarded or recycled to the leaching stage, and the loaded organic is sent to the stripping stage.

In the stripping stage, the metal values from the loaded organic are recovered by agitation with a small volume of a suitable solution. The stripped solvent is recycled to the loading stage and the 'strip' solution is sent to the metal recovery stage. The conventional solvent extraction circuit is shown in Figure 1.2.



CONVENTIONAL SOLVENT EXTRACTION FLOWSHEET

FIGURE 1.2 - SOLVENT EXTRACTION FLOWSHEET

A key element in the successful application of solvent extraction processing is the adoption of an organic extractant highly selective for the metal under consideration. In addition, good mass transfer and phase separation characteristics are essential. An ideal extractant should fulfill the following requirements:

1) high selectivity;
2) safety in handling (e.g. nonvolatile);
3) easily separable from water (e.g. low viscosity, different density than water, high surface tension);
4) high extraction capacity;
5) inexpensive.

In practice, however, it is not possible to find an extractant which fulfills all of the above requirements and a compromise must be made.

An extractant is seldom used in pure form. It is usually diluted with an inexpensive organic solvent in order to improve its physical properties (e.g. viscosity and density). In general, the organic solvent, called the diluent, is inert and has no capacity to extract metal ions from solution. The diluent must be insoluble in water and for this reason hydrocarbons and substituted hydrocarbons are the most commonly used diluents. Using diluents with high aromatic contents will result in a rapid disengagement of the organic and aqueous phases. Diluents with lower aromatic contents will increase the rates at which equilibrium conditions are approached.[14]

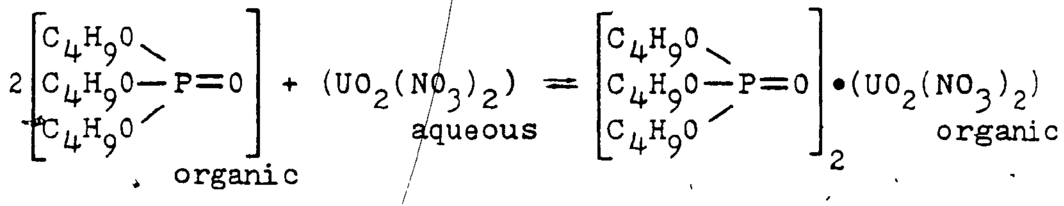
Some organic systems contain a third component, known as a modifier. Modifiers are used to suppress the formation of a third phase, and may also act to improve the solvent's physical properties. The phase separation during loading and stripping is therefore both improved and hastened. Modifiers are either aliphatic alcohols (e.g. isodecanol and 2-ethylhexanol) or aromatic alcohols (e.g. p-nonylphenol).

The various types of extractants used in the hydrometallurgical industry are summarized below:

SOLVATING EXTRACTANTS

In this category, extractants having an oxygen atom with a lone pair of electrons extract electrically neutral inorganic species by solvation. The inorganic metal-containing species are solvated either by (1) coordination of the oxygen bearing extractant molecules to the central metal ion or (2) by hydrogen bond formation between the proton in the extracted species and the oxygen in the solvent molecules.[15] Ethers, alcohols, esters, and ketones extract metals by this mechanism. Commercially available solvating extractants include tri-n-butyl phosphate (TBP), dibutyl carbitol (BUTEX), tri-n-octyl phosphine oxide (TOPO), and methyl isobutyl ketone (MIBK).

Two examples of metal extraction with solvating extractants are shown below:



COORDINATION TO THE CENTRAL METAL ION - TBP (1.3)

$$[(C_4H_9OCH_2CH_2)_2O]_{\text{organic}} + [HAuCl_4]_{\text{aqueous}} = [(C_4H_9OCH_2CH_2)_2O\text{---}HAuCl_4]_{\text{organic}}$$

SOLVATION DUE TO HYDROGEN BONDING - BUTEX (1.4)

Generally, stripping of the extracted inorganic species is accomplished by its contact with water. An exception is tri-n-octyl phosphine oxide, which bonds so tightly to the extracted species that alkaline solutions must be used in the stripping step.

ACIDIC EXTRACTANTS

Organic acids such as alkyl-phosphoric acids, carboxylic acids, and sulphonic acids belong to the acidic family of extractants. The extraction of metals by acidic extractants is via a cation-exchange mechanism in which the removeable hydrogen atom of the extractant is exchanged with the aqueous metal ion.[16] In its simplest form, the cation-exchange reaction is expressed as:

$$(M^{n+})_{\text{aqueous}} + n(HR)_{\text{organic}} = (MR_n)_{\text{organic}} + n(H^+)_{\text{aqueous}} \quad (1.5)$$

where M is the metal to be extracted and HR is the extractant.

Stripping of the loaded acidic extractant can be accomplished using either (1) strong acids in a direct reversal of the extraction process or (2) alkaline reagents which displace the metal from the organic salt and convert the remaining free acid to the alkaline salt.

One acidic extractant that has found extensive use in metallurgical solvent extraction processes is di-2-ethylhexyl phosphoric acid (D2EHPA). Among the commercial applications of D2EHPA are nickel-cobalt separation, rare earth separation, and uranium recovery from leach solution.

Other important acidic extractants are various tertiary mono-carboxylic acids marketed under the trade name 'Versatic Acids' which have been proposed for the extraction of transition metals.[17]

BASIC EXTRACTANTS

High molecular weight primary, secondary, and tertiary amines which are organophilic weak bases are used for solvent extraction of anionic species in acidic aqueous solutions. The quaternary ammonium halides are also considered to be basic extractants and are used to extract metal-anionic species from strong alkali leach liquors.[18]

The interaction of these extractants with the anionic metal species is due primarily to electrostatic forces which result in the formation of an ion-pair between the extractants and the metal species.

The primary, secondary, and tertiary amines form ion-pairs with anionic metal-bearing species only when protonated, which explains why the aqueous solution should be acidic for extraction to occur. This is not the case for the quaternary ammonium salts, since these latter extractants already have the required cation for ion-pair formation and therefore can be effective for metal extraction from alkaline solutions.

A typical example of metal extraction involving a basic extractant is that of uranium recovery from sulphate solutions using a tertiary amine (R_3N). First, the amine forms its corresponding ammonium salt:

$$\underset{\text{organic}}{2\left[R_3N\right]} + \underset{\text{aqueous}}{\left[2H^+ + SO_4^{2-}\right]} = \underset{\text{organic}}{\left[(R_3NH^+)_2SO_4^{2-}\right]} \qquad (1.6)$$

and subsequently, the anion-exchange reaction takes place:

$$\underset{\text{organic}}{2\left[(R_3NH)_2SO_4\right]} + \underset{\text{aqueous}}{\left[UO_2(SO_4)_3\right]^{4-}} = \underset{\text{organic}}{\left[(R_3NH)_4UO_2(SO_4)_3\right]} + \underset{\text{aqueous}}{2\left[SO_4^{2-}\right]} \qquad (1.7)$$

CHELATING EXTRACTANTS

The introduction of chelating extractants has been the most important solvent extraction development of the last two decades. Chelating extractants are superior to most alternatives due to their enhanced selectivity evidenced in many systems. Chelating reagents have long been known to play important roles in analytical chemistry, both as extraction and masking agents.[19]

Extraction of metals by this class of reagents is accomplished by chelate formation. Chelate extraction is a form of cation-exchange and can be expressed by the following chemical reaction:

$$\underset{\text{aqueous}}{(M^{n+})} + \underset{\text{organic}}{n(HL)} \rightleftharpoons \underset{\text{organic}}{(ML_n)} + \underset{\text{aqueous}}{(nH^+)} \qquad (1.8)$$

where HL is the chelating extractant.

In general, a metal complex is formed by association of a metal atom or ion and another species, known as the ligand, which is either an anion or a polar molecule. A simple description of the nature of the bond between a ligand and a metal shows the ligand to be an electron-pair donor and the metal, an electron-pair acceptor. In other words, the metal behaves like a Lewis acid and the ligand as a Lewis base. The donation of a pair of electrons from ligand to metal establishes a coordinate bond. For chelation to occur, the ligand must possess at least two donor atoms capable of bonding to the same metal atom. Elements which act as donors are usually electronegative (e.g. oxygen, nitrogen, or sulphur).

Donor atoms may form part of a basic or an acidic functional group. Some basic groups of importance to metallurgical solvent extraction include: (1) $-N=$ (tertiary acyclic or heterocyclic nitrogen), (2) $>C=O$ (carbonyl), and (3) $=S$. Examples of acidic groups are: (1) $-OH$ (enolic and phenolic), and (2) $-SH$ (thiolenolic and thiophenolic).

A chelating agent can have either two acidic groups, two basic groups, or one of each. From the standpoint of hydrometallurgy, chelating agents containing at least one acidic group are required to allow for exchange of a hydrogen atom with the metal ion. Chelating agents containing one acidic and one basic group are usually used since they give greater metal complex stability. The metal chelates formed are electrically neutral since both the oxidation and coordination numbers are satisfied.

The stability of metal chelates depends on a number of factors including: (1) the charge and electron structure of the metal ion, (2) the nature of the donor atoms in the reagent which are directly involved in complex formations, (3) the number of rings and their sizes, and (4) the presence of bulky constituents in the molecule which could cause steric effects.[20]

The most prominent chelating extractants currently available are the KELEX reagents produced by the Sherex Chemical Company, the LIX reagents produced by the Henkel Corporation, the P-5000 products of Acorga Limited, and SME 529 manufactured by the Shell Chemical Company.

SECTION 1.5 : METAL RECOVERY

After the purification stage (see Figure 1.1), the purified leach solution is ready for a metal recovery process. The three most important operations currently in use to recover metals from aqueous solutions are:

1) precipitation by metals;
2) electrowinning;
3) precipitation by gases.

1.5.1 : PRECIPITATION BY METALS

This process involves the precipitation of a metal from an aqueous solution by another metal. It is also known as cementation, because the precipitated metal is usually cemented onto the added metal. Cementation is the oldest metal recovery technique and was once described by the alchemists as 'transmutation', because when a piece of iron was dipped into a solution of copper sulphate, the iron emerged coated with a layer of metallic copper.

The process can be described by the following chemical equation:

$$M_1^o + M_2^{n+} \rightleftharpoons M_2^o + M_1^{n+} \tag{1.9}$$

The above process can be predicted in terms of electrode potentials. For any metal in solution, the reversible electrode potential can be described by the Nernst equation, given below for the half-reaction:[21]

$$E_M = E_M^o - \frac{RT}{nF} \ln \left[\frac{a_M}{a_{M^{n+}}} \right] \tag{1.10}$$

where:

R = gas constant (8.31 joules/g-mole/°K)

T = temperature °K

F = Faraday's constant (96,500 coulombs per gram equivalent weight)

n = valence of metal M

a_M = activity of metal M (assumed to be unity)

$a_{M^{n+}}$= activity of metal ion in solution

E^o = the normal electromotive force of the cell.

Equation 1.10 follows the Gibbs-Stockholm convention. The normal electrode potential (E^o) of a given electrode reaction is given a positive sign if the electrode is the positive terminal of a cell in which the counterelectrode is the normal hydrogen electrode.

In cementation, the metal with the less positive oxidation potential will pass into solution and displace the metal with the more positive potential.

Industrial applications of this technique include the addition of scrap steel to precipitate copper and the addition of zinc dust to precipitate cadmium out of solution.[22]

The main advantage of cementation is its simplicity. Virtually all of the metal value can be removed from solution in a short series of contact tanks or troughs. Against this simplicity must be weighed the fact that the metal produced is of low purity and the product requires further purification. For example, copper cemented on scrap steel contains 85-90% Cu, 0.2-2% Fe, 0.5% $SiO_2 + Al_2O_3$, and the remainder is oxygen.[22] The copper is usually purified by melting it in smelting furnaces or converters, from which it follows the standard anode-electrorefining route. Due to this extra refining step, only limited uses of cementation have been found in the metal producing industry.

1.5.2 : ELECTROWINNING

In electrowinning, the metal to be recovered is usually in solution in the electrolyte from which it is plated onto the cathode. The electrowinning cathodic reaction can be expressed as:

$$M^{n+} + ne^- \rightarrow M^0 \tag{1.11}$$

The anodic reaction in electrowinning primarily involves the evolution of oxygen. For an acidic solution, the overall reaction occurring at the anode can be expressed as:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1.12}$$

and for an alkaline solution, by:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{1.13}$$

In electrowinning, the anode is required to be inert so that (1) the electrolyte will not become contaminated during the operation, and (2) the anode will not require frequent replacement.

Since the reactions occurring at both electrodes are different, there is usually a considerable decomposition potential for the electrolytic process. The main contribution to this decomposition potential is from the difference between the reversible potentials for the anodic and cathodic reactions. The operating voltage of a cell is made up of additional terms which include the activation over-potential for the reactions at the appropriate current densities, the resistive potential of the electrolyte, and the contact potential at each electrode.[23]

Electrowinning is currently the most widely used procedure for recovering metal values from leach solutions. The advantages of this technique are: (1) the purity of the product is high, (2) the equipment required is simple, and (3) a large number of metals can be recovered. Its main disadvantage is the large amount of electrical energy required, which will be a definite concern as the cost of energy continues to rise.

1.5.3 : PRECIPITATION BY GASES

The first known application of precipitation by gases occurred in 1859 when Beketoff was able to reduce silver salts to metal using hydrogen gas under pressure.[24]

Little further research was done in this area until the 1950's when Schaufelberger successfully produced nickel metal using hydrogen to reduce nickel ammines dissolved in sulphate solutions.[25] He had encountered difficulties in nucleating the new phase, and unless powdered seed material was introduced, the metal was deposited on the walls of the reaction vessel. Schaufelberger's work was of obvious promise, and was immediately taken up by V. N. Mackiw of Sherritt Gordon Mines Limited. Mackiw later determined the chemistry of the reductions and made these reactions the basis of Sherritt Gordon's cobalt and nickel program.[26] The production of metal powders from aqueous solutions has developed rapidly in recent years as a result of the success of the Sherritt Gordon process and today, other companies are producing metal powders by similar hydrometallurgical routes.

Using hydrogen gas as an example, the overall reduction reaction can be expressed as:

$$\underset{\text{aqueous}}{M^{++}} + \underset{\text{gas}}{H_2} = M^{o} + \underset{\text{aqueous}}{2H^{+}} \qquad (1.14)$$

Gases such as carbon monoxide, sulphur dioxide, and methane may all be used as reducing agents but they act more slowly and are not of significant commercial interest.

Reaction 1.14 can be viewed as two opposing reactions:

$$M \rightarrow M^{++} + 2e^{-} \qquad (1.15)$$

and $$H_2 \rightarrow 2H^{+} + 2e^{-} \qquad (1.16)$$

Each of Reactions 1.15 and 1.16 has its own potential and clearly, if the metal potential exceeds the hydrogen potential, the metal reaction (1.15) will reverse direction and metal will be precipitated from solution.

The potential of the reversible metal-ion/metal electrode (Reaction 1.15) is:

$$E_M = E_M^{o} - \frac{RT}{2F} \ln\left[\frac{a_M}{a_{M^{2+}}}\right] \qquad (1.17)$$

A description of the symbols used in Equation 1.17 can be found on pages 19 and 20.

For the hydrogen half-reaction (Equation 1.16), the potential is governed by the concentration of hydrogen ions and hydrogen molecules in solution in contact with the electrode and is therefore a function of both pH and hydrogen fugacity:[27]

$$E_{H_2} = E^{o}_{H_2} - \frac{RT}{F} \ln\left[\frac{1}{a_{H^+}}\right] - \frac{RT}{2F} \ln\left[P^{*}_{H_2}\right] \qquad (1.18)$$

where:

$P^{*}_{H_2}$ = fugacity of the hydrogen gas

a_{H^+} = activity of the hydrogen ions.

To simplify the above equation, the hydrogen fugacity can be replaced by its partial pressure. This is a reasonable assumption because at 100 atmospheres (10.1 MPa) of hydrogen pressure, the fugacity is 106.1, and this alters the last term of Equation 1.18 by one percent.[28] Also, since pH is defined as $-\log_{10}(a_{H^+})$, and $E^{o}_{H_2}$ is defined to be zero, the hydrogen potential simplifies to:

$$E_{H_2} = \left[\frac{-2.303\ RT}{F}\right] pH - \frac{2.303\ RT}{2F} \log_{10}\left[P_{H_2}\right] \qquad (1.19)$$

where P_{H_2} is the partial pressure of hydrogen expressed in atmospheres.

Equations 1.17 and 1.19 have been plotted in Figure 1.3 for various metals. The metal potentials are plotted against metal ion activity on the top scale, and the hydrogen potential is plotted against pH on the bottom scale. This diagram is only appropriate for simple ionized metal salt solutions, such as sulphates and chlorides at 25 °C.[29]

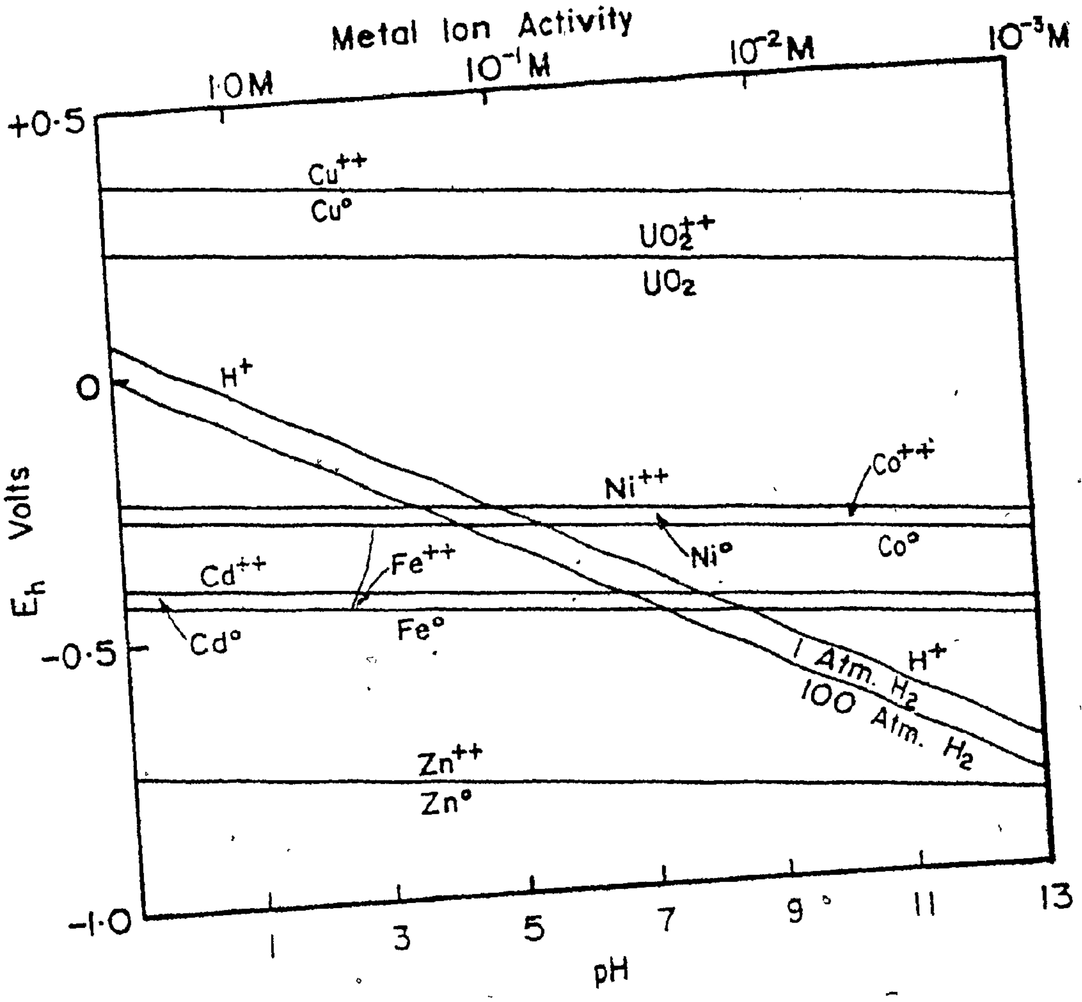


FIGURE 1.3 - THERMODYNAMICS OF HYDROGEN REDUCTION FROM AQUEOUS SOLUTIONS

Figure 1.3 clarifies the following points:

1) The hydrogen potential at 1 atmosphere is sufficiently reducing to reduce cupric ions to copper metal at all pH values and throughout the metal concentration range shown.
2) The reduction of Zn(II) to metal by hydrogen is not possible at any pH and at any realistic hydrogen pressure.
3) Nickel and cobalt can be reduced to metal only at high pH values. For example, nickel(II) will be reduced by 100 atmospheres of hydrogen pressure from a 10^{-3}M solution activity at pH values above 5.

The critical pH value can be obtained from the intersection of a horizontal line through the metal line at an appropriate concentration with the corresponding hydrogen line.

From Figure 1.3, it is evident that the driving force for reduction increases as the pH increases and the conditions for reduction become more favourable as the solution becomes more alkaline. However, at high pH values, the metal ions may react with the hydroxyl ions and precipitate out of solution as a metal hydroxide, or basic salt. Therefore, a limit is set to the pH range which may be used with any given metal.

The maximum pH for a simple dissolved ion can be increased by forming complex ions. Ammonia is a common complexing agent. The formation of complexes stabilizes the metal ions not only against hydrolysis at high pH, but also against reduction to metal, since the complexing agent must be detached from the ion before metal will precipitate.

Using cobalt as an example, the ammine complexes are formed according to the following reactions:

$$\left\{\begin{array}{rcll} Co^{++} + NH_3 & = & \left[Co(NH_3)\right]^{++} & \text{cobalt monammine} \\ \left[Co(NH_3)\right]^{++} + NH_3 & = & \left[Co(NH_3)_2\right]^{++} & \text{cobalt diammine} \\ \vdots & & \vdots & \quad\vdots \\ \left[Co(NH_3)_5\right]^{++} + NH_3 & = & \left[Co(NH_3)_6\right]^{++} & \text{cobalt hexammine} \end{array}\right\} \quad (1.20)$$

The type of ammine formed will be governed by the Co/NH_3 ratio in the solution. For any given ammine, $\left[Co(NH_3)_x\right]^{++}$, the reduction reaction can now be expressed as:

$$\left[Co(NH_3)_x\right]^{++} + H_2 \rightarrow Co + xNH_3 + 2H^+ \qquad (1.21)$$

This reaction can be expressed by the sum of the following sub-reactions:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (1.22)$$

$$Co^{++} + 2e^- \rightarrow Co \qquad (1.23)$$

$$\left[Co(NH_3)_x\right]^{++} \rightarrow Co^{++} + xNH_3 \qquad (1.24)$$

For the reduction of any cobalt ammine:[28]

$$\left[Co(NH_3)_x\right]^{++} + 2e^- \rightarrow Co + xNH_3 \qquad (1.25)$$

the ammine potential can be expressed by:

$$E_M = E_M^o + E^o_{\substack{\text{ammine}\\ \text{complex}}} + \frac{RT}{2F} \ln\left[\frac{a_{\left[Co(NH_3)_x\right]^{++}}}{(a_{NH_3})^x}\right] \qquad (1.26)$$

As before, the hydrogen potential (Equation 1.19) must be less than the cobalt metal potential (Equation 1.26) for precipitation to occur.

While thermodynamics is important in determining whether or not a specific reaction is possible, kinetic considerations are important in determining whether or not a certain process is economically feasible. In practice, the solubility of gases in water is quite low at atmospheric pressure and room temperature. Hydrogen pressures up to 500 p.s.i. (3.45 MPa) may be required to achieve reasonable reaction rates. Also, the solubility of gases in water decreases with increasing temperature up to 100 °C, then markedly increases with a further increase in temperature. In industry, temperatures up to 250 °C are not uncommon. At 250 °C, the vapour pressure of water is approximately 575 p.s.i. (3.96 MPa),[29] and this is a significant proportion of the total working pressure. Pressures such as these indicate that thick, and hence, expensive autoclave equipment is required to safely carry out the reduction reactions. Other disadvantages are inherent in an aqueous system. With such a system, there is always the possibility of corrosion of the reaction vessel, especially at high operating temperatures. Furthermore, there is the need for a high solution pH due to thermodynamic considerations when reducing nickel and/or cobalt solutions. Although the problem of hydrolysis can essentially be solved using complexing agents such as ammonia, some hydrolysis might still occur if a significant amount of ammonia is transferred into the vapour phase due to evaporation.

CHAPTER TWO

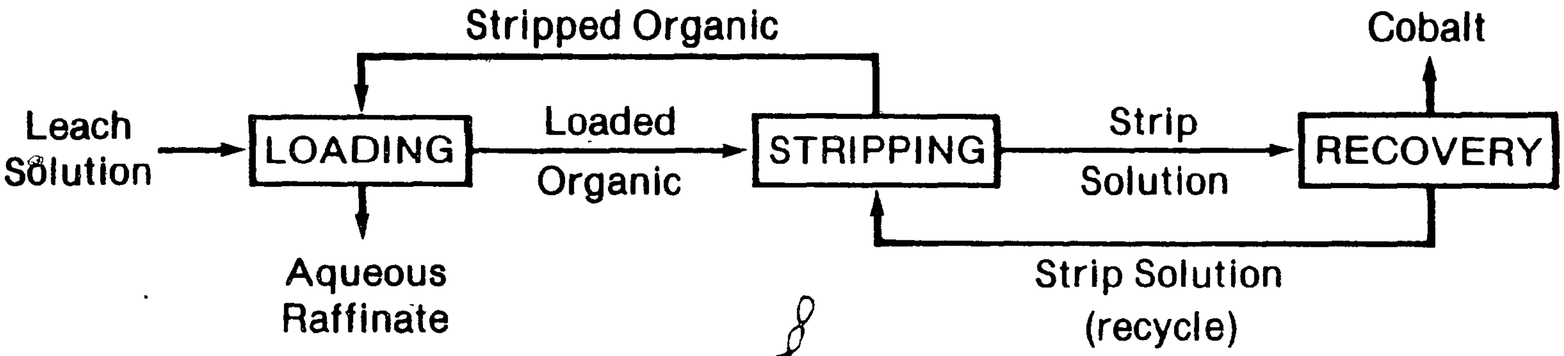
DIRECT REDUCTION OF ORGANIC SOLVENTS

SECTION 2.1 : DIRECT HYDROGEN REDUCTION

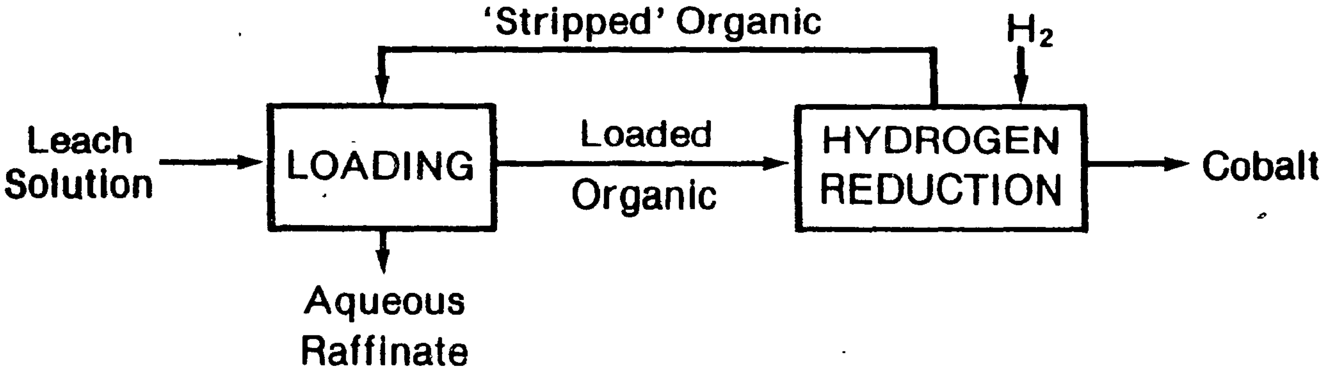
As mentioned in the previous chapter, conventional solvent extraction is treated solely as a purification/ concentration operation. The organic phase acts primarily as a transfer medium for the metal being extracted. The metal is then stripped from the loaded organic phase and is recovered in a separate recovery stage (see Figure 1.2).

However, in addition to considering the organic phase solely as a transfer medium, there is the potential for conducting chemical reactions within this phase such that metal could be produced directly in a useful form. A schematic diagram outlining the proposed flowsheet for the direct recovery of cobalt from a loaded organic extractant is shown in Figure 2.1. This procedure can, in some systems, have a theoretical advantage over the conventional use of reduction from aqueous solutions of metal salts, and these advantages are given below:

1) In aqueous solutions, the maximum thermodynamic activity which the metal ions can reach is determined by the pH and the solubility product of the metal hydroxide. This limitation does not apply when water is not the solvent.



CONVENTIONAL SOLVENT EXTRACTION FLOWSHEET



PROPOSED FLOWSHEET

FIGURE 2.1 - CONVENTIONAL AND PROPOSED SOLVENT EXTRACTION FLOWSHEETS

2) The vapour pressure of water at an operating temperature of 250 °C is 575 p.s.i. (3.96 MPa). At this temperature, the vapour pressure using a KELEX 100-kerosene-decanol organic system is only 60 p.s.i. (0.41 MPa). This implies that a thinner, hence less expensive, reaction vessel could be used.
3) The process flowsheet is simplified as the stripping and reducing operations are combined into one step, termed 'pressure hydrogen stripping'.[11]
4) The heating cost for the organic solvent would be much lower than that for an aqueous solution. The specific heat of water is approximately 1.0 cal/gm/°C, whereas the specific heat for aliphatic hydrocarbons is only 0.5 cal/gm/°C.[29]
5) No corrosion of the reaction vessel is expected to occur using an organic solvent, in contrast to the difficulties encountered using an aqueous system.
6) When cobalt is loaded using KELEX 100 it oxidizes very rapidly to the stable cobaltic form, making acid stripping very difficult.[30] Using pressure hydrogen stripping, this difficulty could be overcome.
7) KELEX 100 has been found to be an excellent extractant for copper, nickel, and cobalt.[31] However, KELEX 100, when stripped with acid, suffers from acid 'carry-over' in the form of protonated quinoline molecules. This high acid pick-up characteristic, which greatly inhibits its commercial use, can

be avoided using pressure hydrogen
stripping of the loaded organic.

SECTION 2.2 : EARLY WORK

The concept of reducing metals in organic solvents using hydrogen gas is not new. Various studies conducted as early as 1938 have involved hydrogen reduction of copper(II), silver(I), and mercury(II) in organic solvents.[32] However, this work was carried out in order to investigate the homogeneous catalytic activation of molecular hydrogen, and it was not reported whether or not metal was formed.

In 1956, it was reported that the reaction between hydrogen and silver acetate in pyridine forms a hydrogen-carrying intermediate, the principal mechanism being the irreversible reaction with silver ions to form metallic silver.[33]

Calvin[34] showed that quinoline solutions of cupric acetate and cupric-salicylaldehyde complexes could be reduced homogeneously by hydrogen at 100 °C with a hydrogen pressure of 7.6 p.s.i. (0.052 MPa). Two distinct stages were apparent from the reaction curves: (1) an autocatalytic step of copper(II) reduction to copper(I) with cuprous copper as the catalytic species, and (2) a second slower step with copper(I) being reduced to metallic copper. Under the experimental conditions applied, no catalytic activity was detected for the cupric salts.

The reduction of cupric heptanoate dissolved in heptanoic acid, biphenol, and octadecane has also been studied, using hydrogen pressures up to 14.7 p.s.i. (0.10 MPa) and temperatures up to 145 °C.[35] The reduction kinetics were studied in detail and it was observed that the reduction from the cuprous state to pure metal was much slower than the cupric to cuprous reduction. It was also reported that the heptanoates of iron(III), nickel(II), cobalt(II), and cadmium(II) did not react appreciably at temperatures up to 150 °C.

SECTION 2.3 : PRESSURE HYDROGEN STRIPPING

A radical departure from the conventional solvent extraction scheme used in hydrometallurgy was put forth a decade ago by Burkin.[36] He proposed the replacement of the conventional stripping and subsequent recovery stages by one process. This process involves the direct precipitation of metal powders from the loaded organic phase using hydrogen under pressure.

Burkin and Burgess[37] performed a number of screening tests on various classes of extractants. These tests were carried out using copper, iron, nickel, and cobalt at 200 °C with 350 p.s.i. (2.41 MPa) of hydrogen. It was reported that most of the tested extractants decomposed, producing ill-defined solid products. This was the case for:

1) tri-n-butyl phosphate in Shellsol T;
2) alkyl methyl sulphonium chloride in 1,2 dichloroethane;
3) Alamine 336 (a tertiary amine) in Shellsol T;
4) Aliquat 336 (a quaternary amine) in Shellsol T;
5) LIX 63 (an aliphatic α-hydroxy oxime);
6) LIX 64 (a compounded mixture of β-hydroxy benzophenone oxime with LIX 63).

In contrast to the above systems, encouraging results were obtained using Versatic extractants (aliphatic carboxylic acids) at 200 °C, and using di-2-ethyl-hexyl phosphoric acid (D2EHPA) at lower temperatures (<180 °C).

In the case of cupric salts of Versatic 911, homogeneous reduction to the cuprous state occured first, followed by metal formation. The initial rate of reduction of the cupric salt was slow, but the reaction was very strongly autocatalytic. The metal produced was in colloidal form, and the addition of copper powder before reduction did not alter the form of the product. However, when colloidal carbon was used as a seed material, the result was the formation of a heavy deposit of metal powder which was easily filtered.

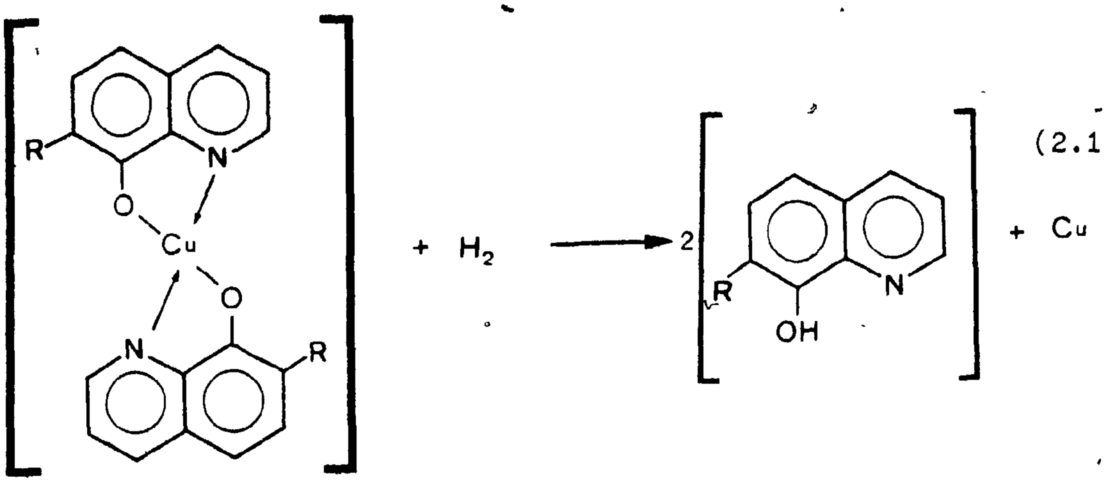
The presence of catalytically active solids was necessary to precipitate nickel and cobalt from their Versatic 911 salts. Temperatures between 180-200 °C and a hydrogen pressure of 300 p.s.i. (2.07 MPa) were used. Evidence for reduction to the univalent state was observed for nickel but not for cobalt. In D2EHPA, nickel and cobalt were found to behave differently, enabling the separation of the two metals. At 140 °C and 300 p.s.i. (2.07 MPa) of hydrogen, nickel was found to precipitate readily in the presence of nickel powder as seed, while cobalt reduction was very slow under the same conditions.

In the case of iron reduction from its Versatic 911 salt, the presence of ammonia was essential for the neutralization of the free organic acid that was liberated. Burkin reported that the iron precipitation reaction proceeded via the initial reduction of iron(III) to iron(II).

Van der Zeeuw and Gandon[38] carried out a fundamental study of the hydrogenation of the Versatic acid salts of copper, nickel, and cobalt using 14.7 p.s.i. (0.10 MPa) of hydrogen at 140 °C. They confirmed the observation that copper(II) was reduced to copper(I) prior to metal formation. The copper reduction was autocatalytic, with the cuprous species being the homogeneous catalyst. The mechanism proposed by these investigators involves the heterolytic splitting of hydrogen molecules by the cupric salt and homolytic splitting by the cuprous salt of the Versatic acid. In addition, the presence of nickel salts of Versatic acid was found to accelerate the copper reduction. The catalytic activity of nickel salts was attributed to partial reduction to univalent nickel. In contrast, the cobalt salts did not catalyze cupric reduction, since no intermediate cobalt species was formed.

The next major work using direct organic reduction techniques was by Demopoulos[11] using copper-loaded KELEX 100 (an alkylated 8-hydroxyquinoline). He found that KELEX 100 exhibited excellent thermal and chemical stability up to 300 °C and 400 p.s.i. (2.76 MPa) of hydrogen pressure. The chemical stability of KELEX 100 was somewhat reduced when loaded with copper. In the presence of copper, limited hydrogenation of the quinoline nucleus of the extractant occurred. Occasionally, similar hydrogenation was observed in some of the impurities (e.g. furoquinoline) of KELEX 100. The chemical stability of the extractant was found to be enhanced when at least 0.52M of decanol was added to the organic solvent (0.4M KELEX 100 in kerosene).

Demopoulos[11] reported that copper in powder form was found to precipitate rapidly from loaded KELEX 100-decanol-kerosene solvents by reaction with hydrogen at pressures between 75-580 p.s.i. (0.52-4.00 MPa) and temperatures from 170 to 215 °C. The overall process displayed heterogeneous characteristics. Nuclei were provided through slow thermal dissociation of the copper chelate. The freshly produced metallic copper, acting autocatalytically, accelerated the precipitation kinetics. Reduction of the copper(II) chelate to the copper(I) complex appeared to be the rate controlling step. In its simplest form, the overall reaction by which copper-loaded KELEX 100 is reduced to metal is given by:



(2.1)

Demopoulos[11] reported that the operating temperature, hydrogen pressure, copper concentration, ligand concentration, and copper chelate age all affect the overall reduction rate.

It is of interest to note that Burkin[39] expressed doubt as to the suitability of a quinoline-based extractant for ~~the~~ direct reduction of organic liquids. He predicted that hydrogenation of the aromatic ring would make KELEX 100 ineffective for this purpose. This opinion was presumably based on his experience with LIX 64, which decomposed in the presence of hydrogen at 200 °C. However, as previously noted, LIX 64 contains LIX 63, which is known to be unstable at temperatures above 40 °C.[40]

Li[41] performed tests using a nickel-loaded KELEX 100-decanol-kerosene system. He reported that rapid nickel precipitation is possible using an operating temperature range of 200-300 °C and a hydrogen pressure range of 150 to 550 p.s.i. (1.03 to 3.79 MPa). Li reported that an increase in the operating temperature and/or hydrogen pressure would result in an increase in the reduction rate. Also, the presence of a seeding material such as nickel carbonyl powder would greatly accelerate the reaction rate.

In the area of metal-stripping from loaded organic phases using pressure techniques, the work of Monhemius and Thorsen[42] should also be included. Their technique, termed 'hydrolytic stripping', involves precipitation of metal oxides by heating metal-loaded carboxylic acid solutions with water at 150-200 °C. The metals under investigation were iron(III), nickel(II), and copper(II).

The most recent work carried out on 'direct hydrogen stripping' is the precipitation of copper from loaded LIX 34 (8-alkarylsulphonamido quinoline) and LIX 65 (2-hydroxy-5-nonyl benzophenone oxime).[43] Preliminary results indicate that the LIX 34 extractant decomposes at temperatures above 180 °C yielding hydrogen sulphide and copper sulphide products. The results based on a LIX 65 system were more encouraging. Temperatures up to 265 °C have been reached with no apparent organic decomposition.

CHAPTER THREE

EXPERIMENTAL PROCEDURE

SECTION 3.1 : EXPERIMENTAL PROGRAM

The main objective of this work was to investigate the suitability of a commercially available chelating extractant, namely KELEX 100, for direct hydrogen stripping of cobalt at high temperatures and pressures. The tests performed were aimed at studying various aspects of hydrogen stripping as follows:

1) The study of the chemical and thermal properties of the organic liquid during the reduction experiments. Direct hydrogen stripping would not be technically feasible unless the organic extractant was regenerated after the reduction experiment, and could then be recycled to the loading stage.
2) The study of the parameters which affect the kinetics of hydrogen stripping of cobalt-loaded KELEX 100.
3) The examination of the physical and chemical properties of the cobalt powder produced. For the process to be economically feasible, the cobalt produced must be readily filterable and of satisfactory purity.

In this chapter, the experimental procedure used to perform the experiments and to analyze the products, will be presented.

SECTION 3.2 : THE ORGANIC LIQUID

The organic phase used throughout this work was made by dissolving fifteen volume percent KELEX 100 in a low vapour pressure kerosene (aromatic content <1%). For all experiments, ten volume percent of decanol was added as a modifier since this addition was found to enhance the chemical stability of the extractant in a parallel system using copper.[11] Some of the more important properties of the three constituents of the organic phase are summarized in Table 3.1.

	KELEX 100[11]	KEROSENE		DECANOL
SUPPLIER	SHEREX CHEMICAL COMPANY	FISHER SCIENTIFIC COMPANY		EASTMAN KODAK COMPANY
SPECIFIC GRAVITY	0.976	0.774		0.83
BOILING POINT (°C)	260 AT 760 mm Hg	DISTILLATION	RANGE	229 AT 760 mm Hg
		I B.P.	190	
		10%	202	
		50%	214	
		90%	240	
		D.P.	255	

TABLE 3.1 - PHYSICAL PROPERTIES OF THE THREE CONSTITUENTS OF THE ORGANIC PHASE

The 'as-received' KELEX 100 was subjected to a purification step prior to any investigation. One litre of the organic phase, consisting of extractant, modifier and diluent, was washed using 500 mls. of a ten volume percent sulphuric acid (H_2SO_4) solution. The aqueous phase was allowed to settle and was then removed and discarded. The organic phase was washed twice using distilled water. Any impurities in the original organic liquid which were water soluble were removed and discarded with the aqueous raffinate.[44]

SECTION 3.3 : LOADING

The aqueous phase used for the organic loading consisted of analytical reagent grade cobaltous sulphate dissolved in distilled water. The cobaltous sulphate was purchased from Fisher Scientific Company (Catalogue C-386, Lot 793572) and contained less than 0.065 weight percent of nickel, copper, and iron combined. The aqueous solution was adjusted to contain 20 grams per litre (g.p.l.) of cobalt (pH ~4.4).

To carry out a hydrogen stripping experiment, one litre of the organic liquid was placed in a two litre separatory funnel. One litre of the 20 g.p.l. cobalt solution was then added to the funnel. The separatory funnel was shaken manually for approximately forty minutes. To produce an equilibrium pH in the raffinate of approximately 5.0, 20 mls. of ammonium hydroxide (Fisher Scientific Company-Catalogue A669) was added to the separatory funnel during the shaking procedure.

The contents of the separatory funnel were allowed to settle overnight (24 ± 2 hours). The raffinate was removed and the loaded organic solvent was poured into the glass liner of the autoclave.

A 3.5 ± 0.1 g.p.l. cobalt organic solution was prepared using this technique.

SECTION 3.4 : THE AUTOCLAVE ASSEMBLY

All reduction experiments were conducted inside a two litre Parr autoclave. The main features of the autoclave are shown in Figure 3.1. The bomb cylinder is made of titanium and the glass liner used to hold the organic liquid is made of pyrex.

3.4.1 : HEATING AND TEMPERATURE CONTROL

The autoclave was heated by a sealed 1500 watt element built into an insulated stainless steel shell surrounding the bomb cylinder. During the initial stage of this work, automatic temperature control was obtained using the standard temperature controller supplied with all Parr reactors. The temperature controller consisted of a solid-state potentiometric system operating in conjunction with an iron-constantan thermocouple inserted into the bomb thermowell. While this temperature control system is considered to be satisfactory for aqueous solutions, it

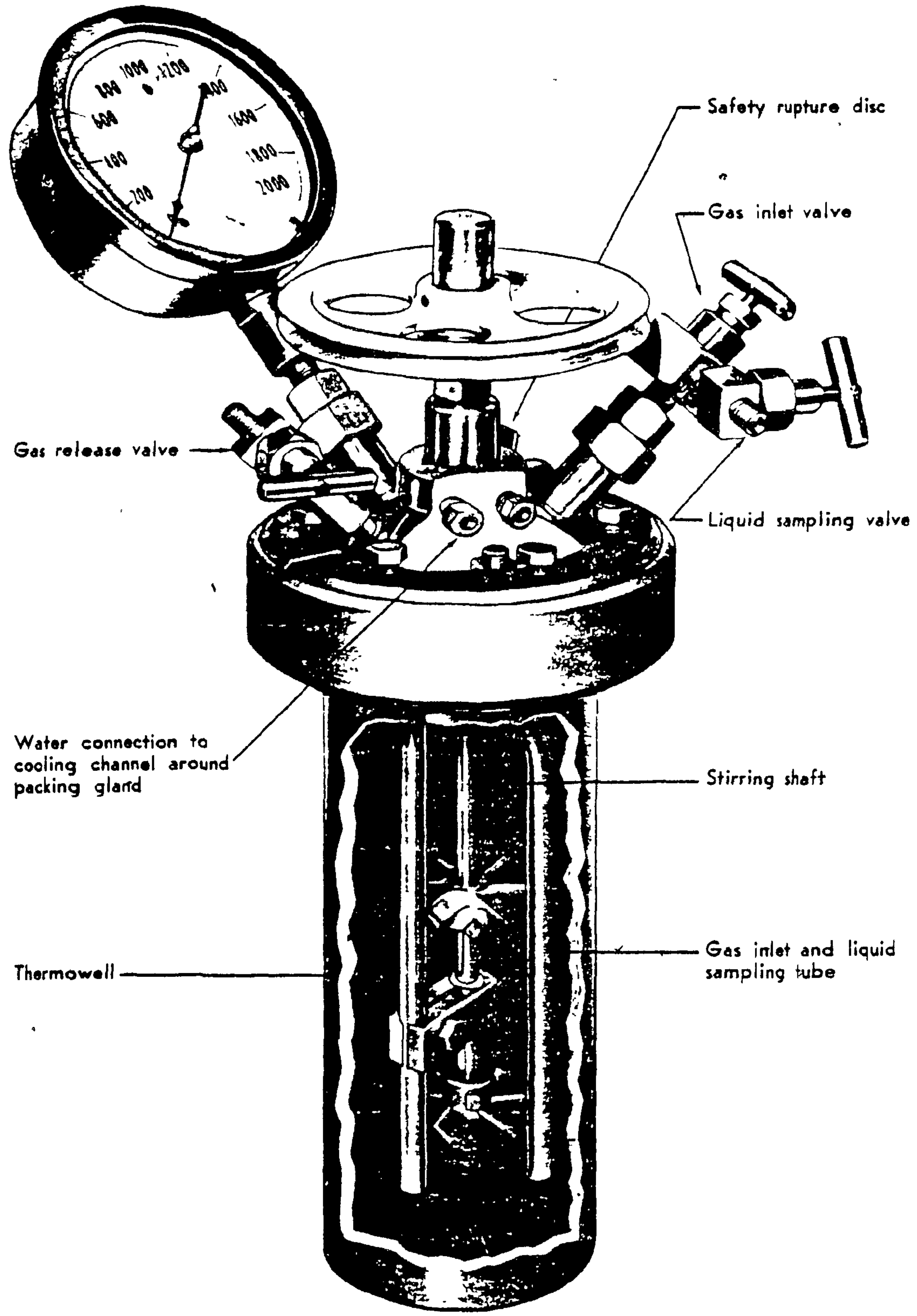


FIGURE 3.1 - SECTIONED VIEW OF THE AUTOCLAVE ASSEMBLY

was found to be inadequate for the present work due to the low specific heat of the kerosene solvent used (~0.5 cal/gm/°C). Specifically, a large temperature overshoot was observed at the end of the initial heating period (above 100 °C when the set temperature was 300 °C). In addition, an unacceptably large deviation of ± 5 °C from the desired set temperature occurred.

A new temperature control system was selected to overcome the aforementioned problems. The new system, supplied by Leeds and Northrup Limited, was a Current Adjusting Type (Soft) 'Electromax 3' controller which provides a 0-5 mA DC output, and whose magnitude varies with the deviation of input signal from the set point. This controller works in conjunction with a Zero-Voltage-Firing solid-state power package. The latter supplies power to the heating element of the autoclave with an infinite power resolution. It is superior to discrete-step conventional units because it allows control of the process up to the sensitivity of the controller.

The 'Electromax 3' unit is equipped with the following controls: (1) Proportional Action, (2) Reset Action, (3) Rate Action, and (4) Approach Action. The first three controls minimize the fluctuation of temperature around the set point, while the fourth control minimizes the overshoot during start-up. The accuracy obtained with the new controller was better than ± 1 °C and the initial overshoot was less than

10 °C at 300 °C. For a more accurate reading of the temperature, a digital thermometer with a one degree resolution was used.

3.4.2 : PRESSURE CONTROL

Hydrogen gas was supplied at constant pressure via a high pressure delivery regulator. The hydrogen gas was purchased from Union Carbide Canada Limited and contained less than 5 parts per million of oxygen (Ultra High Purity-99.999% H_2).

Pressure release was achieved by means of a needle valve in the autoclave head. Release of pressure was accomplished via tygon tubing immersed in a kerosene solution. The pressure in the reaction compartment of the autoclave was indicated by a 0-1000 p.s.i. gauge. Protection against equipment damage in case of accidental overpressure was provided for by a 1000 p.s.i. gold-plated rupture disc installed in the head of the reactor.

3.4.3 : AGITATION

The organic liquid, along with any cobalt powder produced in the autoclave, was agitated by a belt-driven stirring shaft fitted with two 6-pitched-blade titanium turbine impellers. The two impellers were vertically adjustable on the shaft, and were positioned approximately 3 cm. from the bottom of the reactor and 3 cm. below the liquid level respectively (see Figure 3.2). With this arrangement, all solid materials were kept in suspension and good gas distribution was achieved. The stirring speed could be varied from 0-1000 RPM by means of an adjustable speed motor.

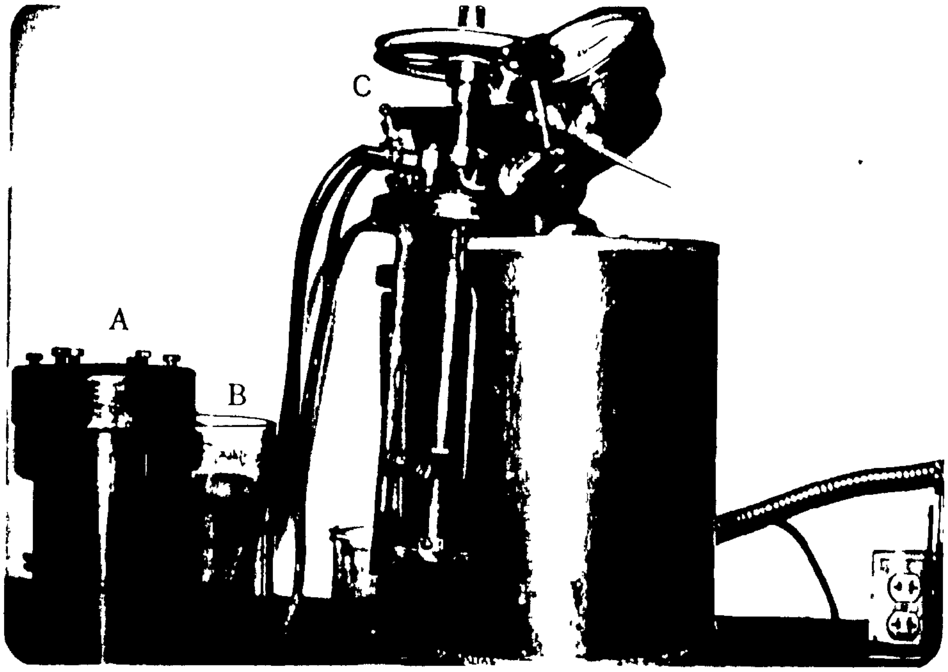


FIGURE 3.2 - VIEW OF THE AUTOCLAVE ASSEMBLY

A - THERMOWELL
B - PYREX LINING
C - BELT-DRIVEN STIRRING DEVICE

3.4.4 : SAMPLE WITHDRAWAL

Liquid samples could be withdrawn via a sampling valve attached to the head of the autoclave whenever the bomb was pressurized (Figure 3.3). Through the same sampling dip tube, hydrogen gas was introduced under the liquid level.

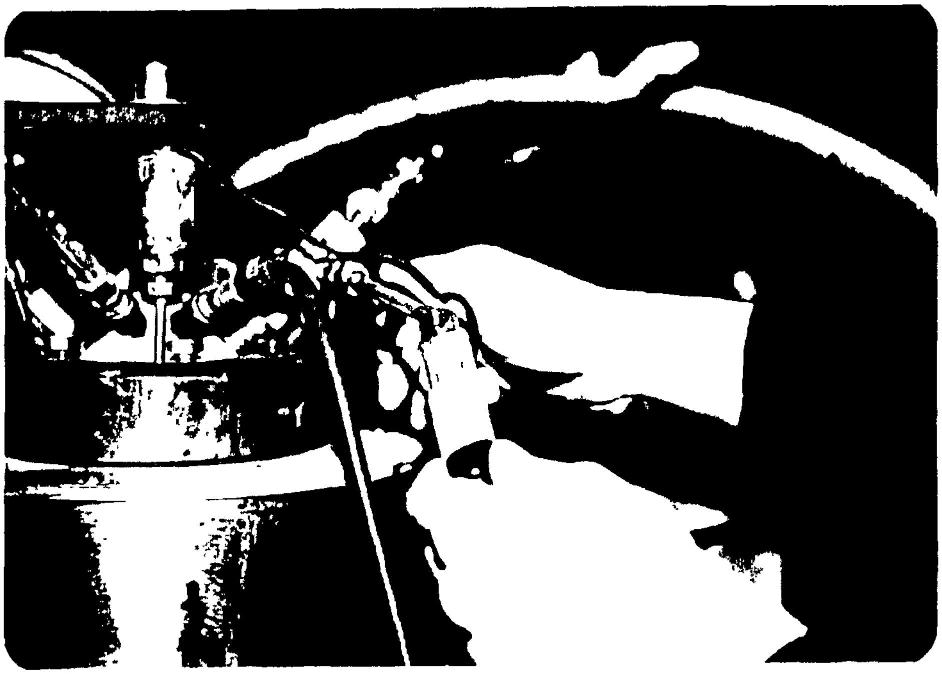


FIGURE 3.3 - SAMPLE WITHDRAWAL DURING A REDUCTION EXPERIMENT

SECTION 3.5 : REDUCTION EXPERIMENTS

One litre of loaded organic, containing approximately 3.5 g.p.l. of cobalt, was poured into the glass liner of the autoclave. The glass liner was inserted into the autoclave and the bolts were tightened. The loaded autoclave was purged with prepurified nitrogen gas (Union Carbide Canada Limited-<3 ppm O_2) to remove the enclosed air.

Purging with nitrogen was carried out for ten minutes using 200 p.s.i. (1.38 MPa) pressure, with simultaneous agitation of the liquid.

When the purging operation was completed, the organic solution was heated to the desired temperature with the stirrer operating at 700 RPM.

When thermal equilibrium was reached (the heating time was usually two hours), a sample of liquid was collected to determine the initial cobalt concentration. Hydrogen gas was then introduced into the autoclave and the pressure was adjusted using the delivery regulator. Introduction of the gas resulted in a 3-5 °C temperature drop, apparently due to the cool hydrogen mass. This temperature drop did not significantly alter the reaction kinetics, since within 5-10 minutes the controller re-established thermal equilibrium at the desired temperature.

At selected time intervals (every 30-60 minutes), liquid samples (15 mls.) were withdrawn. Prior to sample taking, the sampling tube was flushed with approximately 5 mls. of organic solution, which was then discarded.

When the hydrogen stripping experiment was completed, the heater was turned off and the autoclave was left pressurized overnight in order to cool.

The stripped organic liquid was filtered through a 350 mls. Buchner funnel (fine porosity) having a fritted disc. A water tap vacuum pump was used to accelerate filtration. The powder retained in the filter was thoroughly washed with acetone and stored for future physical and chemical analyses. The filtered organic liquid, replenished with fresh liquid to compensate for sampling losses, was recycled several times.

After some reduction tests, cobalt plated onto both the immersed metallic surfaces of the autoclave and the glass liner. After washing with acetone, the plated surfaces were immersed in a fifty volume percent nitric acid solution and allowed to stand for 15 minutes. Finally, after washing with water and drying, the autoclave was ready for the next experiment.

SECTION 3.6 : ANALYSIS

Three groups of analytical methods were used during the course of the present investigation:

1) Qualitative and quantitative structural analyses of the organic liquid using ultraviolet spectroscopy, gas-liquid chromatography, and infrared spectroscopy.
2) Analysis of the liquid samples taken during the reduction experiments using atomic absorption in order to determine the amount of cobalt which had been precipitated.
3) Examination of some of the chemical and physical properties of the cobalt powder produced using X-ray diffraction, chemical analysis, scanning electron microscopy,

and particle size distribution.

3.6.1 : ORGANIC STRUCTURE ANALYSIS

Gas-liquid chromatography could not be applied to the KELEX 100 samples without special pretreatment because the material is insufficiently volatile to pass through the chromatographic column. Silylation, which is the substitution of the trimethylsilyl group ($-Si(CH_3)_3$) for active hydrogen in a compound, is a common derivatization method used in the event that gas chromatography has to be carried out on organic compounds of low volatility.[45]

5

The KELEX 100 samples were silylated by treating 0.25 mls. with 0.5 mls. of bis-silyltrifluoroacetamide (BSTFA-Pierce Chemical Company) and heating the mixture for 45 minutes at 100 °C.

Two OV type (0.32 cm.) chromatography columns (sensing and reference) were used. Each column was 244 cm. long with 3% liquid phase on a 90-100 'Gas Chrom. Q.' mesh. The analysis was carried out using a Perkin-Elmer Model 881 gas chromatograph connected to a highly accurate strip-chart recorder (Hewlett Packard 7101B). A flame ionization detector was used, while the gas-liquid chromatograph was programmed at 6 °C/min. from 180-300 °C and held for 2 minutes at 300 °C. The carrier gas used was helium.

The infrared spectra of KELEX 100 were recorded in the 600-4000 cm^{-1} range using a Perkin-Elmer Model 457 grating infrared spectrophotometer (± 2 cm^{-1} resolution).

The KELEX 100 samples were diluted in kerosene and decanol (15 volume percent KELEX 100, 10 volume percent decanol, and 75 volume percent kerosene) and analyzed. The reference solution consisted of decanol dissolved in kerosene.

Gas-liquid chromatography and infrared spectroscopy were performed in order to determine whether or not the organic liquid had decomposed during the reduction experiments.

In order to determine the structure of the cobalt-KELEX molecule, samples of loaded organic were analyzed using a Perkin-Elmer 124D Double Beam Spectrophotometer. Measurements were made in the 300-500 nm. wavelength range and the results were printed by a Perkin-Elmer 165 chart recorder. Kerosene was used as the reference liquid.

3.6.2 : DISSOLVED COBALT CONCENTRATION

The samples taken during the reduction experiments were analyzed directly using a Perkin-Elmer Model 306 Double Beam Atomic Absorption Spectrophotometer. For some samples, a Pye Unicam SP190 Atomic Absorption Spectrophotometer was used.

Since cobalt oxidizes to form a very stable cobaltic-KELEX complex, it was not possible to acid-strip the samples and to then analyze the aqueous solutions using conventional atomic absorption techniques.

Direct analysis of the organic solutions was possible, and the sensitivity of the instrument was found to be twice that for an aqueous solution. The samples had to be diluted below 8 ppm cobalt as the calibration curve was linear only up to this concentration level. The samples were diluted using kerosene, and therefore kerosene was used as the reference solution. The flame was adjusted to allow for the flammable diluent by reducing the acetylene flow rate.

Organic standards were prepared by diluting a KELEX 100 sample containing a known amount of cobalt. The amount of cobalt in the organic phase was carefully determined by the difference between cobalt levels in the aqueous feed and raffinate. Four standards were prepared in the 2-8 ppm range.

3.6.3 : COBALT POWDER ANALYSIS

Oxygen, hydrogen, and carbon levels of the cobalt powder products were measured independently by Technitrol Canada Limited.

X-ray powder diffraction was performed on several samples using a Phillips Diffractometer. The operating conditions were: 40 kV voltage, 20 mA tube current, FeK_{α} radiation, Mn filter, and 6 hours of exposure time.

Particle size analysis of the cobalt powder was performed using a Warman Cyclosizer (Model M4).

Scanning electron microscopy was performed using a JEOL-JSM-35S instrument located in the McGill Department of Epidemiology. The operating conditions were 10 kV voltage and a 39 mm. working distance. The samples were mounted on aluminum stubs with epoxy.

CHAPTER FOUR

DISCUSSION OF RESULTS:
CHEMICAL AND THERMAL STABILITY OF KELEX 100

SECTION 4.1 : OBJECTIVES OF THE EXPERIMENTAL PROGRAM

The main objective of this work was to investigate the possibility of precipitating metal directly from cobalt-loaded KELEX 100 using hydrogen under pressure.

The discussion of the experimental results will be divided into three parts:

1) The study of the chemical and thermal stability of the organic liquid during the reduction experiments. In order for this process to be economically feasible, the organic liquid must be totally regenerated after reduction, and show no signs of organic degradation and no loss in loading capacity.
2) The study of the parameters which affect the kinetics of the stripping process. This is dealt with in Chapter five.
3) The examination of some of the chemical and physical properties of the cobalt powder produced. These results are presented in Chapter six.

Since potential application of this process on a commercial scale is envisaged, commercial grade KELEX 100 was used in the present investigation to allow for a more relevant evaluation.

SECTION 4.2 : PROPERTIES OF KELEX 100

4.2.1 : HISTORY OF KELEX 100

Ashland Chemical Company [now Sherex Chemical Company] developed KELEX 100 in 1968 as an extractant for copper from both dilute and relatively concentrated leach solutions.[46]

KELEX 100 is a derivative compound of the analytical chemical reagent 8-hydroxyquinoline [often referred to as 8-quinolinol or oxine]. 8-Hydroxyquinoline has a hydrogen atom that is replaceable by a metal ion, and a heterocyclic nitrogen atom as shown below:

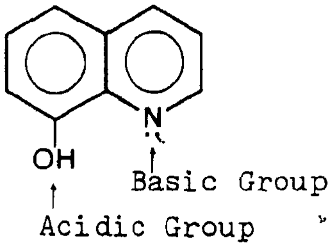
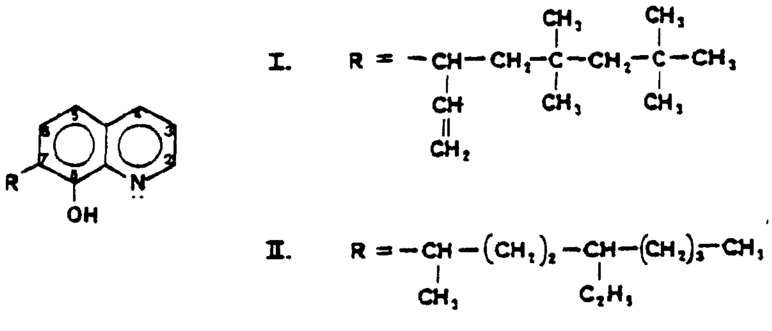


FIGURE 4.1 - CHEMICAL STRUCTURE OF 8-HYDROXYQUINOLINE

Preparation of KELEX 100 involves the reaction of an alkenyl or alkyl chloride with 8-hydroxyquinoline.[47] The active component of this commercial extractant was previously 7-[3-(5,5,7,7-tetramethyl-1-octenyl)]-8-hydroxyquinoline (see Figure 4.2 I), but its production was discontinued in 1976. Presently, the active component of KELEX 100 is 7-[2-(5-ethyl-nonyl)]-8-hydroxyquinoline (see Figure 4.2 II).



$$\text{I.}\quad R = -CH(CH{=}CH_2)-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-CH_3$$

$$\text{II.}\quad R = -CH(CH_3)-(CH_2)_2-CH(C_2H_5)-(CH_2)_3-CH_3$$

FIGURE 4.2 - THE ACTIVE COMPONENT OF KELEX 100

Theoretically, the hydrocarbyl 'R' group can be attached to carbon ring atoms in the 2nd, 3rd, 4th, 5th, 6th, or 7th positions. However, Budde[47] claimed that for optimum extraction the 'R' group should be attached at the 7th position as shown in Figure 4.2.

The active component of KELEX 100 accounts for approximately 78 weight percent, while the balance is made up of various by-products of the alkylation process.[48] These impurities are analyzed in the next section.

4.2.2 : GAS-LIQUID CHROMATOGRAPHY

In gas-liquid chromatography, the components of a vapourized sample are fractionated as a consequence of partition between a mobile gas phase and a stationary liquid phase contained in a column.[49]

A sample containing the solutes is injected into a heating block where it is immediately vapourized and swept as a plug of vapour by the carrier gas stream into the column inlet. The solutes are absorbed at the head of the column by the stationary phase and then desorbed by fresh carrier gas. This partitioning process occurs repeatedly as the sample is moved toward the outlet by the carrier gas. Each solute travels at its own rate through the column, and consequently, a band corresponding to each solute will appear. The degree to which the bands separate is determined by the partition ratios of the solutes and the extent of band spreading. The solutes are eluted, one after another, in increasing order of their partition ratios, and enter a detector attached to the column exit. The time of emergence of a peak identifies the component, and the peak area reveals the relative concentration of the component in the original sample mixture.

Figure 4.3 shows a gas-liquid chromatogram of a typical KELEX 100 sample of post-1976 manufacture. The specific conditions for the gas-liquid chromatographic analysis are given in the Experimental Chapter.

The attenuator setting for all peaks, with the exception of peak 4, was X500. The setting for peak 4 was X1000, indicating that this peak should be twice as big as it appears in Figure 4.3.

The various components of KELEX 100 were analyzed using mass spectrometry by Dr. O. Mamer of the McGill Biomedical Mass Spectrometry Unit. The mass spectrometric conditions were as follows: 70 eV ionizing energy, ion source temperature of 290 °C, and a scan rate (M/Z) of 10 to 500 in four seconds.

In Table 4.1 the molecular weights and the chemical structures of the various components, when known, are summarized.

The composition of the sample was determined by estimating the area under each peak, and the results are also shown in Table 4.1. The active component was found to be approximately 77.1% which is in accordance with the value obtained by Ashbrook.[48]

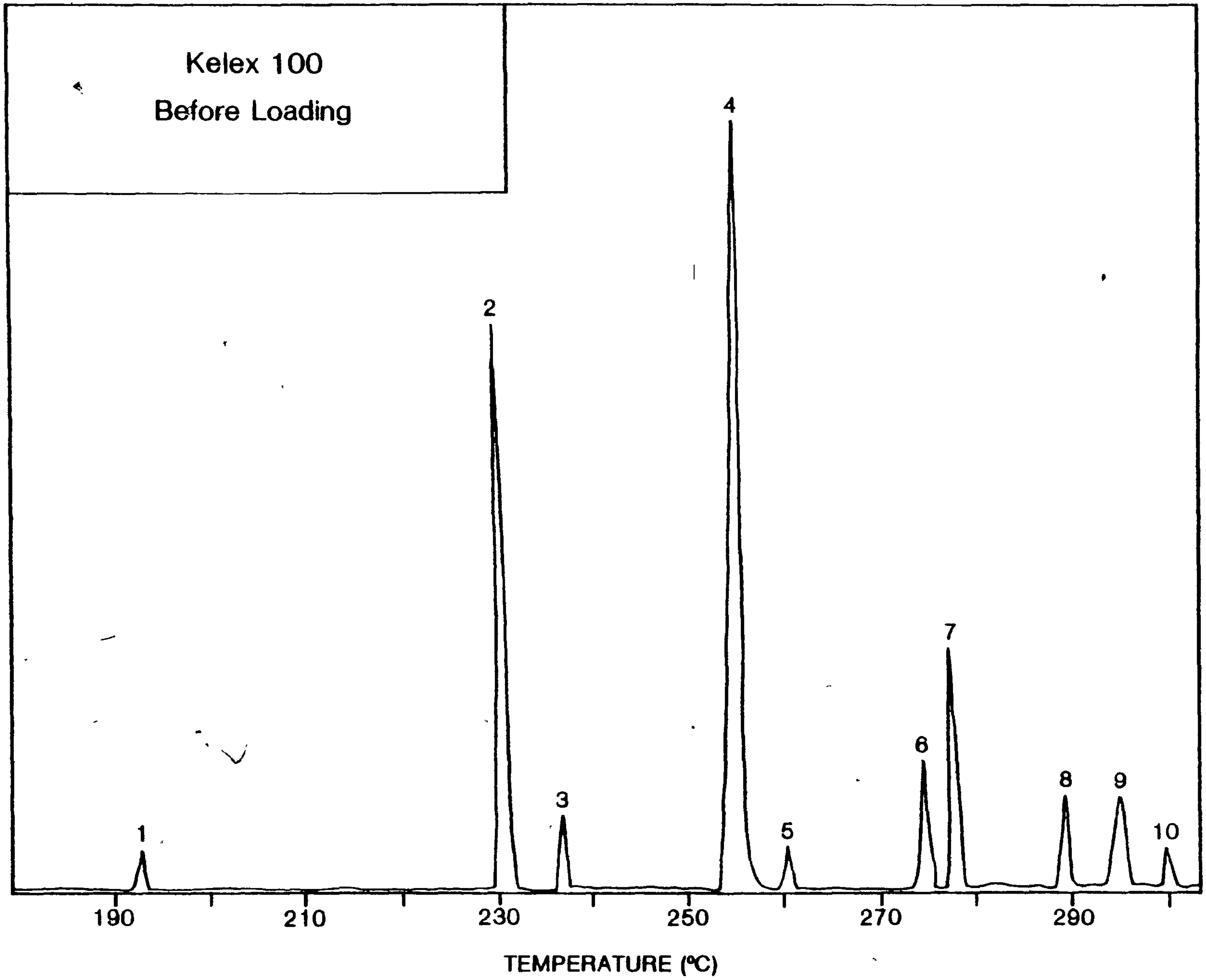


FIGURE 4.3 - GAS-LIQUID CHROMATOGRAM OF KELEX 100 BEFORE LOADING

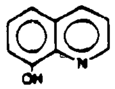
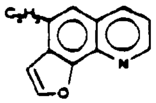
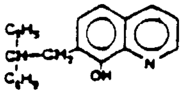
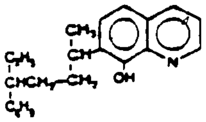
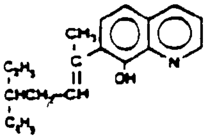
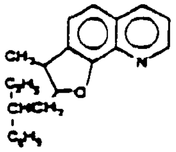
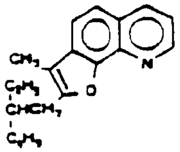
PEAK #	MOLECULAR WEIGHT	WEIGHT %	MOLECULAR STRUCTURE
1	145	0.6	
2	197	11.0	
3	257	1.2	
4	299	77.1	
5	297	0.8	
6	297 (probably)	2.1	
7	295	4.1	
8	453	1.0	?
9	?	1.6	?
10	?	0.5	?

TABLE 4.1 - VARIOUS COMPONENTS OF KELEX 100

4.2.3 : INFRARED SPECTROSCOPY

Infrared spectroscopy involves the twisting, bending, rotating, and vibrating motions of atoms in a molecule.[50] Upon interaction with infrared radiation, portions of the incident radiation are absorbed at specific wavelengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is uniquely characteristic of both the functional groups comprising the molecule and the overall configuration of the atoms.

For infrared absorption to occur, two major conditions must be satisfied. First, the energy of the radiation must coincide with the energy difference between the excited and ground states of the molecule. Radiant energy will then be absorbed by the molecule, increasing its natural vibration. Second, vibration must entail a change in the electrical dipole moment, a restriction which distinguishes infrared from Raman spectroscopy.

The infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwaves. This region includes radiation at wavelengths between 0.7 and 500 μm or, in wavenumbers, between 14,000 and 20 cm^{-1}. The spectral range of greatest use is the mid-infrared region, that is, the region between 4000-600 cm^{-1}.

The infrared spectrum of the unloaded KELEX 100 sample is shown in Figure 4.4.

Harrison et al.[51] have reported some characteristic

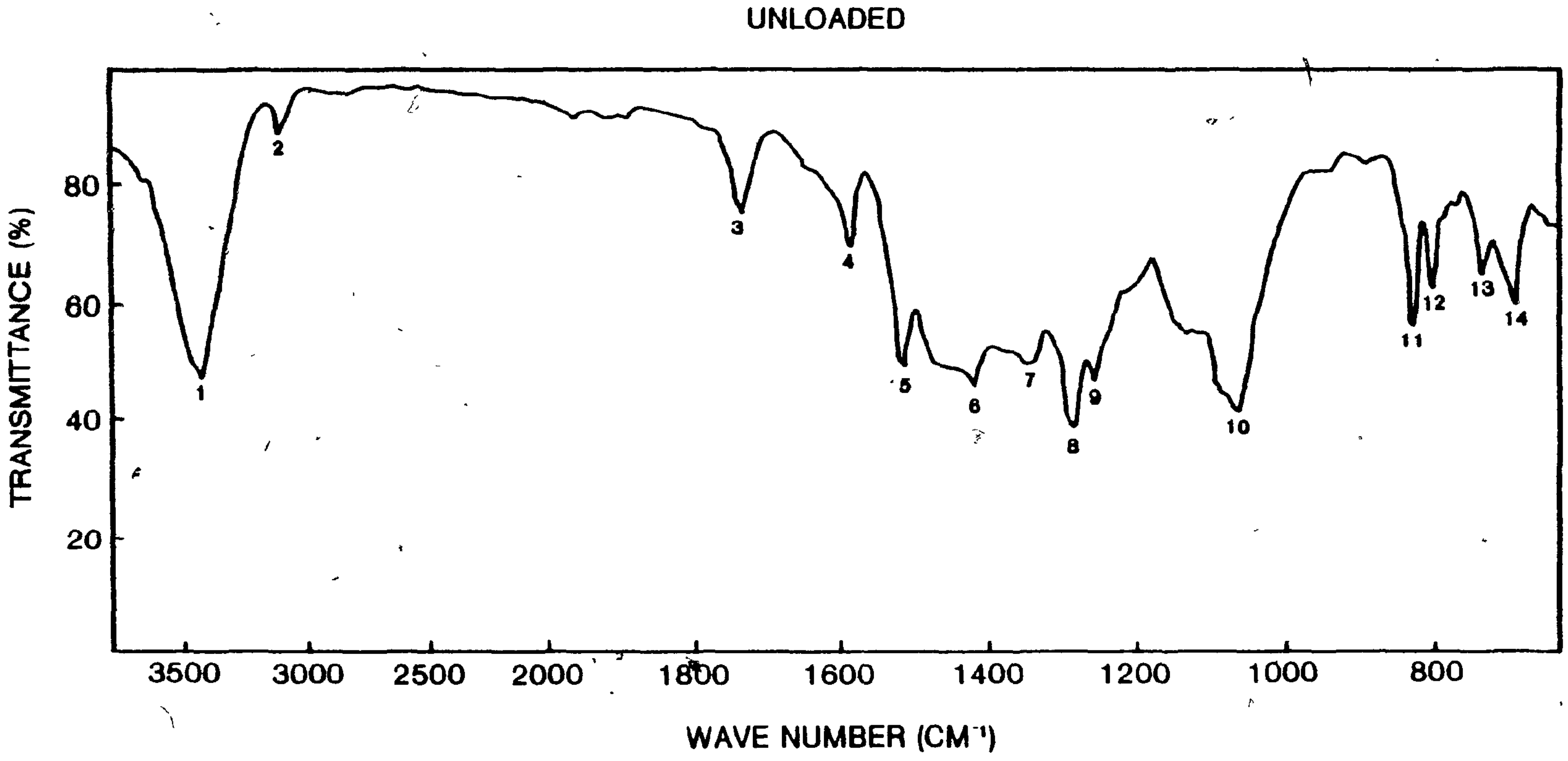


FIGURE 4.4 - INFRARED SPECTRUM OF UNLOADED KELEX 100 SAMPLE

frequencies of the infrared spectrum of KELEX 100. For instance, the OH-phenolic stretching frequency was measured at 3400 cm^{-1}, the C-N stretching frequency at 1280 cm^{-1}, the C-N bending frequency at 720 cm^{-1}, and the C-O stretching frequency at 1090 cm^{-1}.

Ashbrook[52] maintained that the phenolic hydroxyl group in KELEX 100 is involved in intramolecular hydrogen bonding. This was deduced from the presence of an absorption peak around 3400 cm^{-1}, which was in evidence down to a concentration of 0.0025M in carbon tetrachloride. This is similar to a peak present in the spectrum of 8-hydroxyquinoline at 3410 cm^{-1}, which has also been associated with hydrogen bonding.

The infrared spectra of the parent compound of KELEX 100, 8-hydroxyquinoline and its metal chelates, have been studied in much greater detail than the infrared spectra of KELEX 100 itself.[53,54] In most studies thus far, solid samples of 8-hydroxyquinoline and its chelates were used. In the present investigation, only liquid samples of KELEX 100 were analyzed.

SECTION 4.3 : COBALT-LOADED KELEX 100

4.3.1 : OXIDATION OF COBALT CHELATES

The oxidation of cobalt chelates during solvent extraction is a very frequent phenomenon that occurs with most extractants of industrial or analytical interest. The cobalt(III) complex resulting from this oxidation is highly stable and is very difficult to strip using dilute acid solutions.[55]

In studies designed to extend the scope of application of KELEX 100, Ritcey and Lucas[31,44] examined the extraction of several metals, including cobalt, from aqueous solutions. They found that the cobalt tended to become 'fixed' in the organic phase and only 20% of the cobalt could be stripped using a 10% sulphuric acid solution. They concluded that once cobalt(II) is extracted, it must be stripped in a relatively short time because prolonged exposure to air oxidizes the cobalt(II) to cobalt(III).

In a more fundamental study, Lakshmanan and Lawson[56] examined the extraction of cobalt by KELEX 100 and KELEX 100/ Versatic 911 mixtures. They concluded from slope analysis of graphical plots of their experimental data that KELEX 100 (HL) forms a complex with cobalt of the type $CoL_2 \cdot 2HL$. They also found that the cobalt could not be stripped from the organic phase. They did not consider that the cobalt was being oxidized to the trivalent state, but rather claimed that the cobalt(II) chelate complex was extremely stable and hence difficult to strip. It is interesting to note that the $CoL_2 \cdot 2HL$ stoichiometry of the extracted complex agrees with that given by Starý[57] for cobalt-8-quinolinate. Starý conducted a systematic study of the formation and extraction of over thirty metal-8-quinolinates and, like Lakshmanan and Lawson, made no mention of possible cobalt oxidation.

Flett et al.[58] showed that it can be misleading to draw conclusions about stoichiometry based on slope analysis data alone. They showed that an equation can be written which provides a log(distribution) versus pH graph with a slope of 2, normally indicating the presence of a cobalt(II) complex, but yielding, in fact, a cobalt(III) complex:

$$Co^{++} + 3HL_{organic} + 1/4\ O_2 \rightleftharpoons CoL_{3\,organic} + 2H^{+} + 1/2\ H_2O \quad (4.1)$$

Equation 4.1 could be the sum of consecutive extraction and oxidation reactions as follows:

$$Co^{++} + 4HL_{organic} \rightleftharpoons CoL_2 \cdot 2HL_{organic} + 2H^{+} \quad (4.2)$$

$$CoL_2 \cdot 2HL_{organic} + 1/4\ O_2 \rightleftharpoons 1/2\ H_2O + \{CoL_3 + HL\}_{organic} \quad (4.3)$$

Guesnet et al.[30] cleared up some of the controversy surrounding cobalt oxidation by performing visible and ultraviolet absorption spectrophotometry on samples of 8-hydroxyquinoline and KELEX 100.

They reported that after separation from the aqueous phase and dilution, the organic phase showed an absorption maximum around 375 nm in nonbasic solvents such as kerosene or toluene. This absorption maximum decreased with time and a new maximum progressively appeared at 420 nm. They claimed that this phenomenon was due to the oxidation of the extracted cobalt(II) 8-hydroxyquinoline complex [absorption maximum at 375 nm] to the cobalt(III) complex [absorption maximum at 420 nm]. Complete oxidation took approximately 200 minutes.

When the extraction was performed using KELEX 100 instead of 8-hydroxyquinoline, the organic phase showed an absorption maximum at 440 nm in nonbasic solvents. The position of this band did not change with time and stripping was impossible with dilute acids. These facts suggest that when cobalt is extracted with KELEX 100 the oxidation is as fast as the extraction.

This phenomenon was verified in the present work and the UV absorption spectrum is shown in Figure 4.5. The equipment used for this analysis is described in the Experimental Chapter.

The KELEX 100 sample was analyzed two minutes after it was loaded, and an absorption maximum appeared at 440 nm indicating the presence of a cobalt(III) complex. The loaded organic was again analyzed after a period of 12 hours and there was no detectable change in peak height or position.

Guesnet et al.[30] reported that compounds that can donate electrons through an oxygen atom, such as tributylphosphate, to the organic phase, decrease the cobalt oxidation rate. The addition of these oxo-donor compounds produces a shift of the absorption maximum of the cobalt(II) complex to longer wavelengths, whereas the absorption band of the cobalt(III) complex is unaltered. The cobalt(II) shift indicates a change in the structure of the complex, which can be explained by the acid-base properties of the cobalt(II) ion and oxo-donor compounds. Since the cobalt ion is an electron acceptor, bonds between the donor compound and the cobalt ion are formed. These bonds increase the stability of the cobalt(II) complex, and hence the complex is rendered less oxidizable.

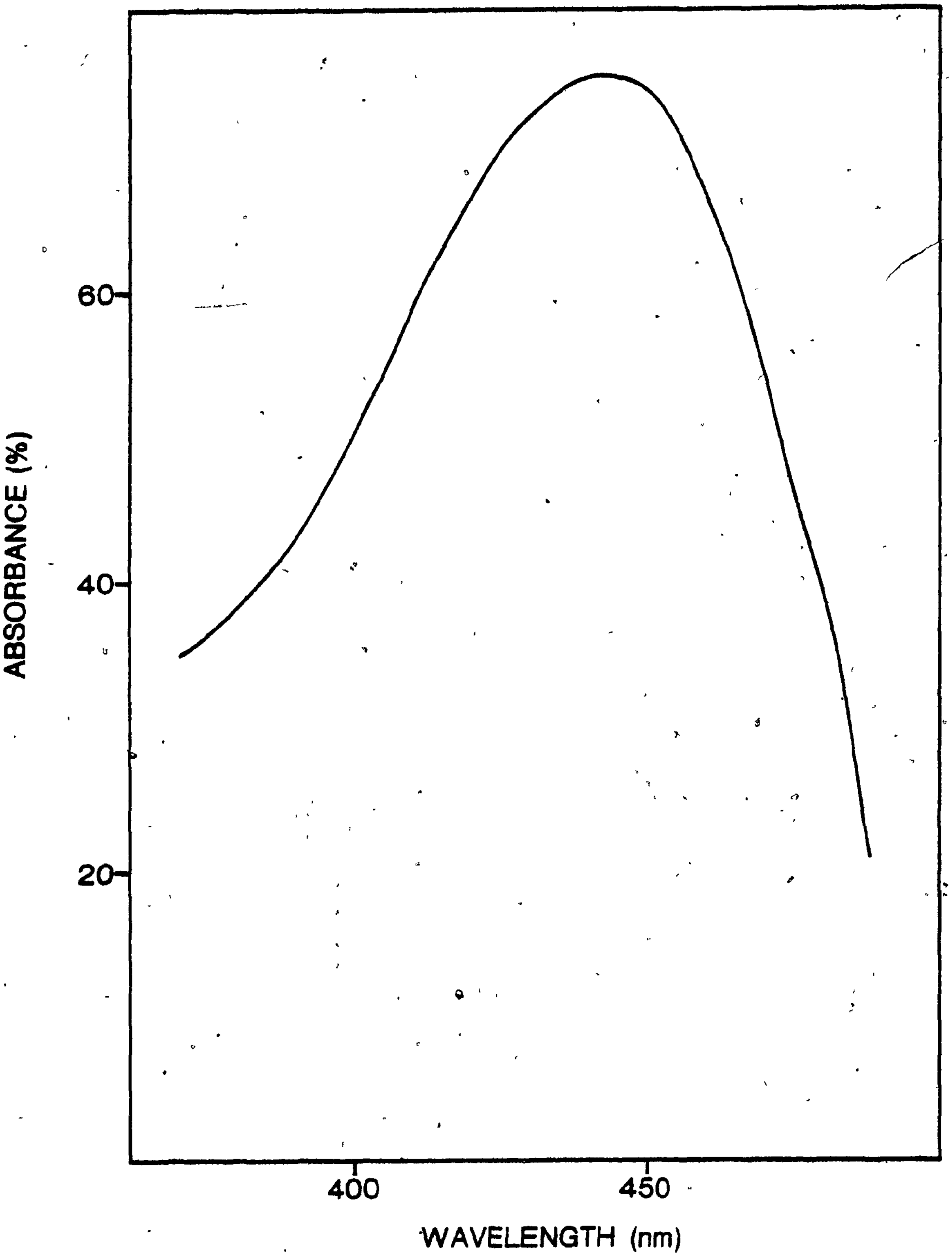


FIGURE 4.5 - ABSORPTION SPECTRUM OF COBALT-LOADED KELEX 100

The addition of various amounts of acidic compounds, such as Versatic 10 acids, to the organic phase, also decreases the cobalt oxidation rate. These compounds shift the absorption maximum of the cobalt(II) complex towards lower wavelengths. The addition of acidic compounds (HR) leads to the equilibrium:

$$HL + HR \rightleftharpoons (H_2L^+ \ , \ R^-) \tag{4.4}$$

which is termed protonation of the KELEX molecule. The increase in the R^- concentration promotes the formation of poorly oxidizable cobalt(II) complexes such as $(CoL \bullet 2HL)^+, R^-$.

4.3.2 : STRUCTURAL CHANGES AFTER LOADING

After loading with cobalt, the organic liquid was once again analyzed using gas-liquid chromatography and infrared spectroscopy. These results are presented in Figures 4.6 and 4.7. Comparing the chromatogram of the unloaded extractant (Figure 4.3) to that of the loaded extractant (Figure 4.6), it can be seen that peaks 1, 3, 6, 8, 9, and 10 disappear. This implies that the compounds corresponding to these peaks probably take part in the loading reaction. Peak 4, which represents the unloaded C_{11}-alkylate of 8-hydroxyquinoline and is hence the main active component of KELEX 100, is much smaller than the corresponding peak in the unloaded chromatogram (Figure 4.3). This indicates that the extractant is being loaded with cobalt. Peaks 2, 5, and 7 remain essentially unchanged before and after loading, indicating that these compounds do not take part in the loading reaction.

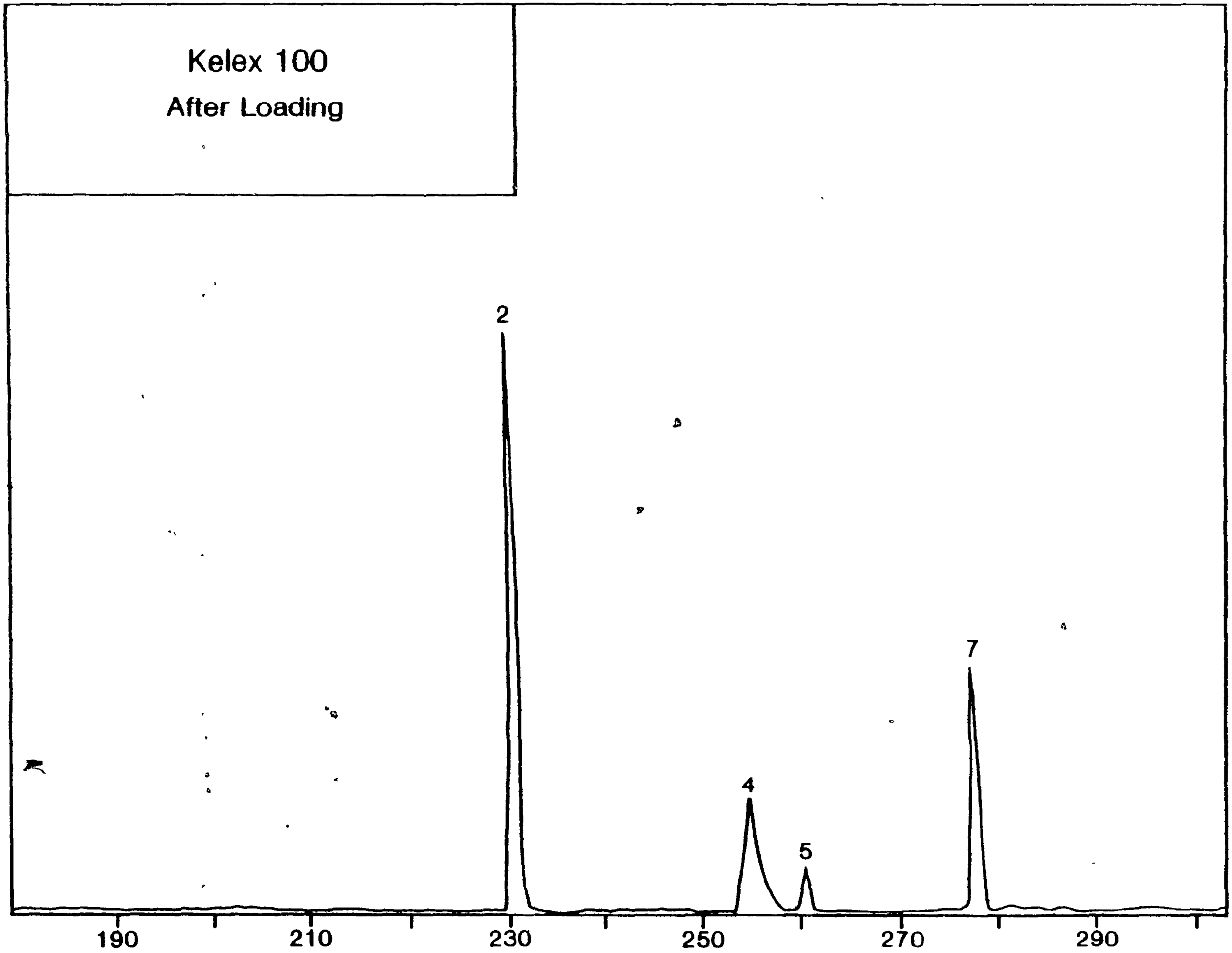


FIGURE 4.6 - GAS-LIQUID CHROMATOGRAM OF KELEX 100 AFTER LOADING WITH COBALT

The infrared spectrum of the loaded organic sample is shown in Figure 4.7. The changes that occur in the various peaks are indicated by arrows, and can be seen by comparison with Figure 4.4.

As expected, the peak at 3400 cm^{-1} (the OH-phenolic stretching involved in intramolecular bonding) is smaller after loading because this site is actively involved in the loading reaction. There is a corresponding change in peak 8 which is associated with the OH-phenolic bending frequency. There is also a noticeable increase in peaks 4 and 6, which are associated with hetero-ring stretching and aromatic-ring stretching respectively.[11] The increase in frequency in peak 13 seems to be due to changes in the frequency of C-N bending. The increase in size of peak 11 may be due to changes in out-of-plane CH-deformation before and after loading.[59] The shift in peak 9 from 1280 to 1140 cm^{-1} appears to be due to changes in the C-N stretching frequency. It was not possible to determine exactly what structural shifts occurred in the organic sample to cause changes in peaks 5 and 7.

All of the infrared studies were performed in the mid-infrared range (4000-600 cm^{-1}) where vibrations due to the 8-hydroxyquinoline ligand can be detected. Direct information about the structure of the cobalt complexes and the strength of the metal-ligand bonds could not be obtained with the apparatus used as these appear in the far-infrared region (600-10 cm^{-1}).

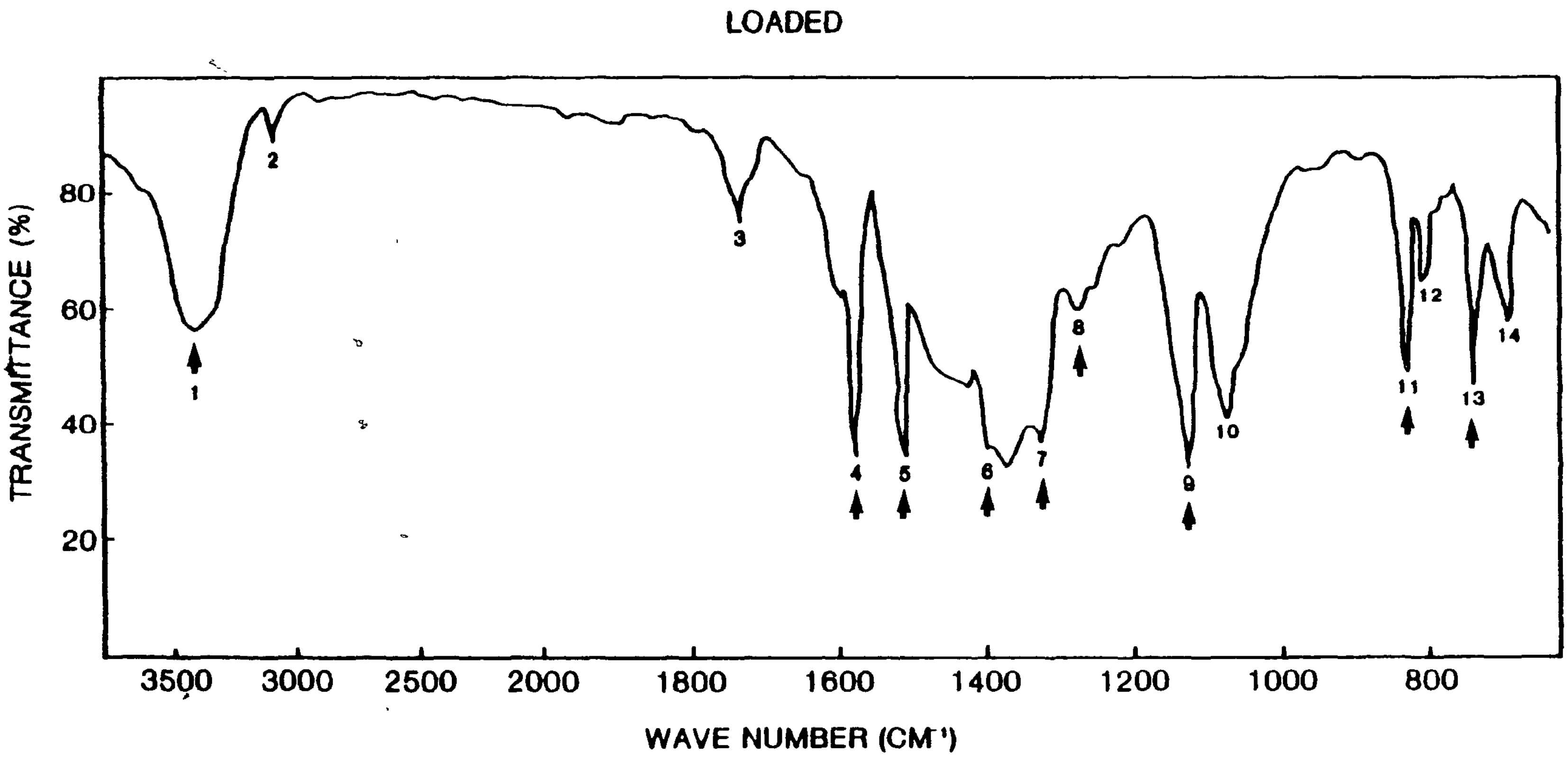


FIGURE 4.7 - INFRARED SPECTRUM OF COBALT-LOADED KELEX 100

A comprehensive study of the far-infrared frequency spectra of various metal-8-hydroxyquinolinates has been conducted by Ohkaku and Nakamoto.[60] They claimed that the cobalt complex exhibits two bands in the 420-370 cm^{-1} region and three bands in the 280-200 cm^{-1} region. They assigned the two strong bands at 278 and 263 cm^{-1} to the asymmetric and symmetric Co-O stretching modes, respectively. The Co-N stretching modes were identified at approximately 228 cm^{-1} where a very strong band was observed. They claimed that since the spectral pattern for cobalt is very similar to those for nickel and zinc complexes, the structure of cobalt-8-hydroxyquinolinate is likely to be tetrahedral.

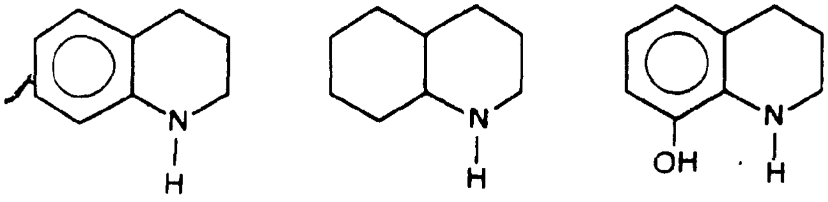
SECTION 4.4 : ORGANIC REGENERATION AFTER REDUCTION

4.4.1 : HYDROGENATION OF QUINOLINE COMPOUNDS

Evaluation of an extractant for conventional hydrometallurgical solvent extraction involves consideration of thermal stability up to 50-60 °C. However, for the hydrogen stripping of cobalt from loaded KELEX 100, thermal stability up to 325 °C is required. Studies specifically designed to determine the thermal characteristics of 8-hydroxyquinoline and its derivatives are not readily available in the literature. It should be noted that during manufacture, KELEX 100 is subjected to temperatures up to 260 °C in a reducing atmosphere (0.10 MPa H_2) and there are no signs of organic decomposition.[11] However, heating in the presence of air greatly accelerates decomposition of the extractant. This suggests that KELEX 100 can withstand the high temperatures of hydrogen stripping as long as air is evacuated from the system.

The reactivity of KELEX 100 with hydrogen, or instability under high temperature and pressure conditions, could prevent the use of hydrogen stripping. Interaction of KELEX 100 with hydrogen could lead either to hydrogenation of the aromatic rings or, under more drastic conditions, to decomposition due to breakage of the rings. In addition, high temperature could, in itself, lead to ring breakage (pyrolysis).

In the literature, a number of references describe the catalytic and destructive hydrogenation of quinoline under a variety of temperatures, hydrogen pressures, and catalyst environments. Quinolines are usually reduced preferentially in the hetero-ring, regardless of catalyst, producing 1,2,3,4-tetrahydroquinoline (Figure 4.8 I).[61] Under stronger hydrogenation conditions (>10 MPa), decahydroquinoline is produced (Figure 4.8 II), while under extreme conditions (>15 MPa), the ring system breaks down yielding ammonia, amines, and hydrocarbons.[62]



(I) (II) (III)

FIGURE 4.8 - POSSIBLE HYDROGENATION PRODUCTS

8-Hydroxyquinoline exhibits the same behavioural pattern as quinoline when catalytic hydrogenation is carried out. The 1,2,3,4-tetrahydroquinolinol compound (Figure 4.8 III) was the reported hydrogenation product by Cavallito and Haskell.[63] The reduction was carried out at 55 °C and 3 atm. (0.30 MPa) of hydrogen using a palladium catalyst. The presence of a methyl group, as in 2-methyl-4-hydroxyquinoline, prevented reduction.

4.4.2 : COPPER-KELEX 100 SYSTEM

Demopoulos[11] was the first to investigate the thermal and chemical stability of KELEX 100. His experiments showed that KELEX 100 exhibits excellent chemical stability up to 300 °C and 400 p.s.i. (2.76 MPa) of hydrogen pressure. Gas-liquid chromatograms and infrared and proton n.m.r. spectra showed no signs of hydrogenation of the quinoline rings. However, when Demopoulos loaded the extractant with copper, he occasionally observed extensive degradation of the extractant, even at temperatures as low as 200 °C. Using gas-liquid chromatography, he was able to conclude that the degradation was due to the hydrogenation of the 5-membered aromatic ring of furoquinoline (Table 4.1 - peak 7) which yielded dihydrofuroquinoline (Table 4.1 - peak 6). The alkylated 8-hydroxyquinoline (Table 4.1 - peak 4) was hydrogenated in only a few cases. However, Demopoulos reported that when decanol was used as a modifier, no degradation was observed. He assumed that the prevention of hydrogenation of the extractant was due to hydrogen bonding between the decanol molecules amd those groups most vulnerable to hydrogenation [e.g. >O (furan ring) and ≥N (quinoline ring)]. After reduction of the metal chelate and exposure of ≥N to hydrogen attack, the decanol forms a protective hydrogen bond with the nitrogen hetero-atom (or with the oxygen hetero-atom) and degradation is prevented.

It is also possible that decanol prevents hydrogenation by lowering the catalytic activity of the metallic copper produced during the reduction experiments.[11] The electronegative oxygen atom of the alcoholic OH group may be adsorbed on the surface of the electropositive metallic copper, forming weak electrostatic bonds. Due to this adsorption, the catalytic activity of copper is lowered such that the hydrogen is sufficiently active to reduce the copper-KELEX 100 complex, but is not sufficiently active to promote hydrogenation of the less reactive quinoline ring.

4.4.3 : COBALT-KELEX 100 SYSTEM

After loading with cobalt and reduction with hydrogen, the remaining organic liquid was once again analyzed using gas-liquid chromatography and infrared spectroscopy. The results are presented in Figures 4.9 and 4.10. For all reduction tests, the organic phase consisted of 15% KELEX 100, 75% kerosene, and 10% decanol by volume.

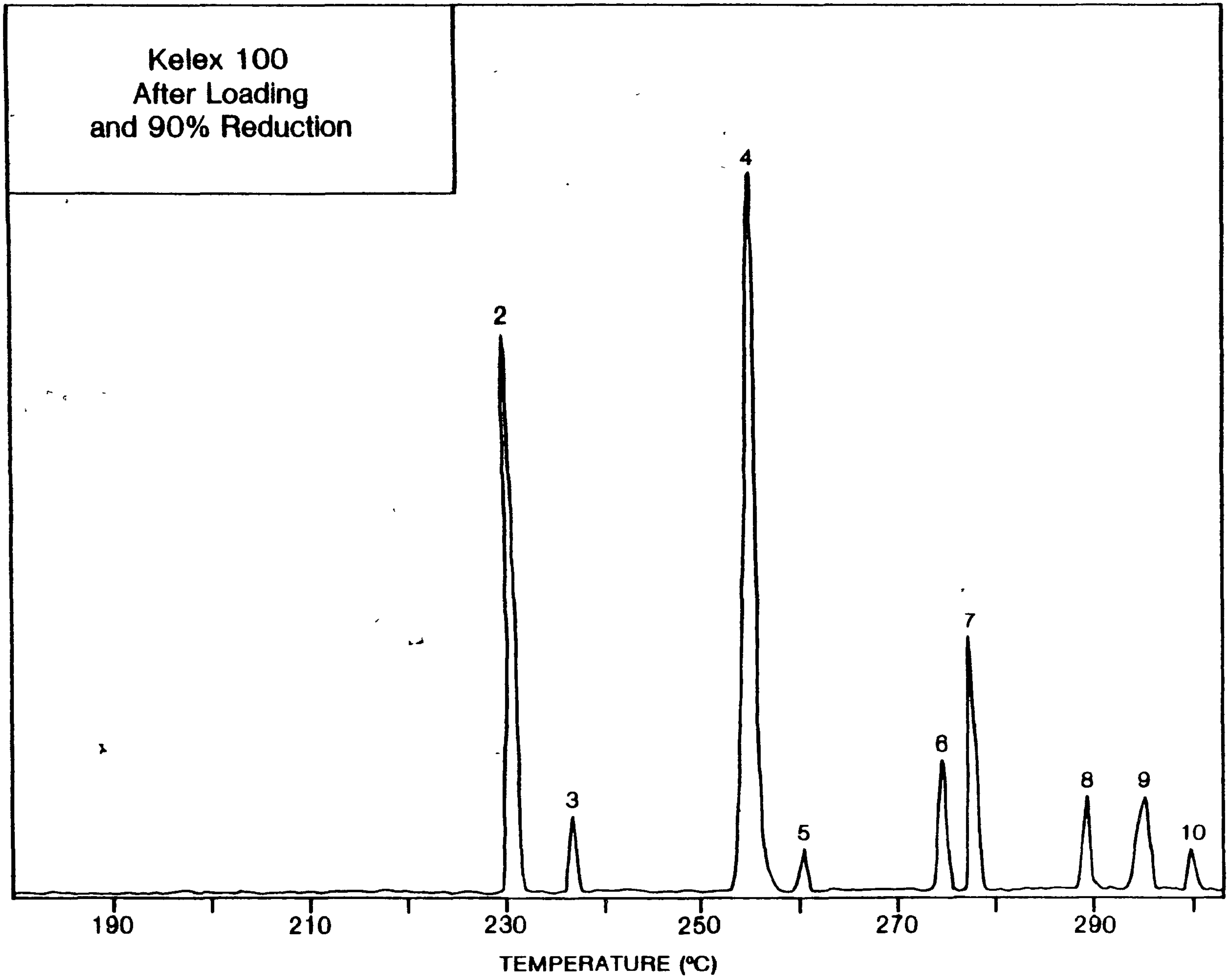


FIGURE 4.9 - GAS-LIQUID CHROMATOGRAM OF KELEX 100 AFTER 90% REDUCTION

A comparison of Figures 4.3 and 4.9 reveals that all of the original peaks, with the exception of peak 1, have reappeared. The parent compound, 8-hydroxyquinoline (peak 1), is slightly soluble in water and probably enters the raffinate during loading. Peak 4 returns to approximately 90% of its original height, and this is to be expected as only 90% reduction occurred with this sample (Appendix - R5). The missing 10% is in the form of a cobalt chelate complex and is not shown in the chromatogram. Since no new peaks were formed, it appears that no significant changes took place and thus the organic extractant showed resistance to hydrogenation.

A comparison of Figures 4.4 and 4.10 also reveals that the major peaks have returned to approximately their original heights and positions. Peaks 1 and 8, corresponding to OH-phenolic stretching and bending respectively, have essentially returned to 90% of their original heights. From the appearance of these peaks, it is apparent that hydrogen exchange took place between the cobalt-loaded extractant and hydrogen gas. Peak 9, which shifted from 1280 to 1140 cm^{-1} after loading, appears to have shifted back to its original position. As with the gas-liquid chromatograms, no significant changes occurred between the spectra of the unloaded and reduced KELEX 100 samples. This, in conjunction with the fact that no detectable loss in loading capacity was observed when the organic liquid was recycled, indicates that hydrogenation did not occur and that KELEX 100 is a suitable extractant for

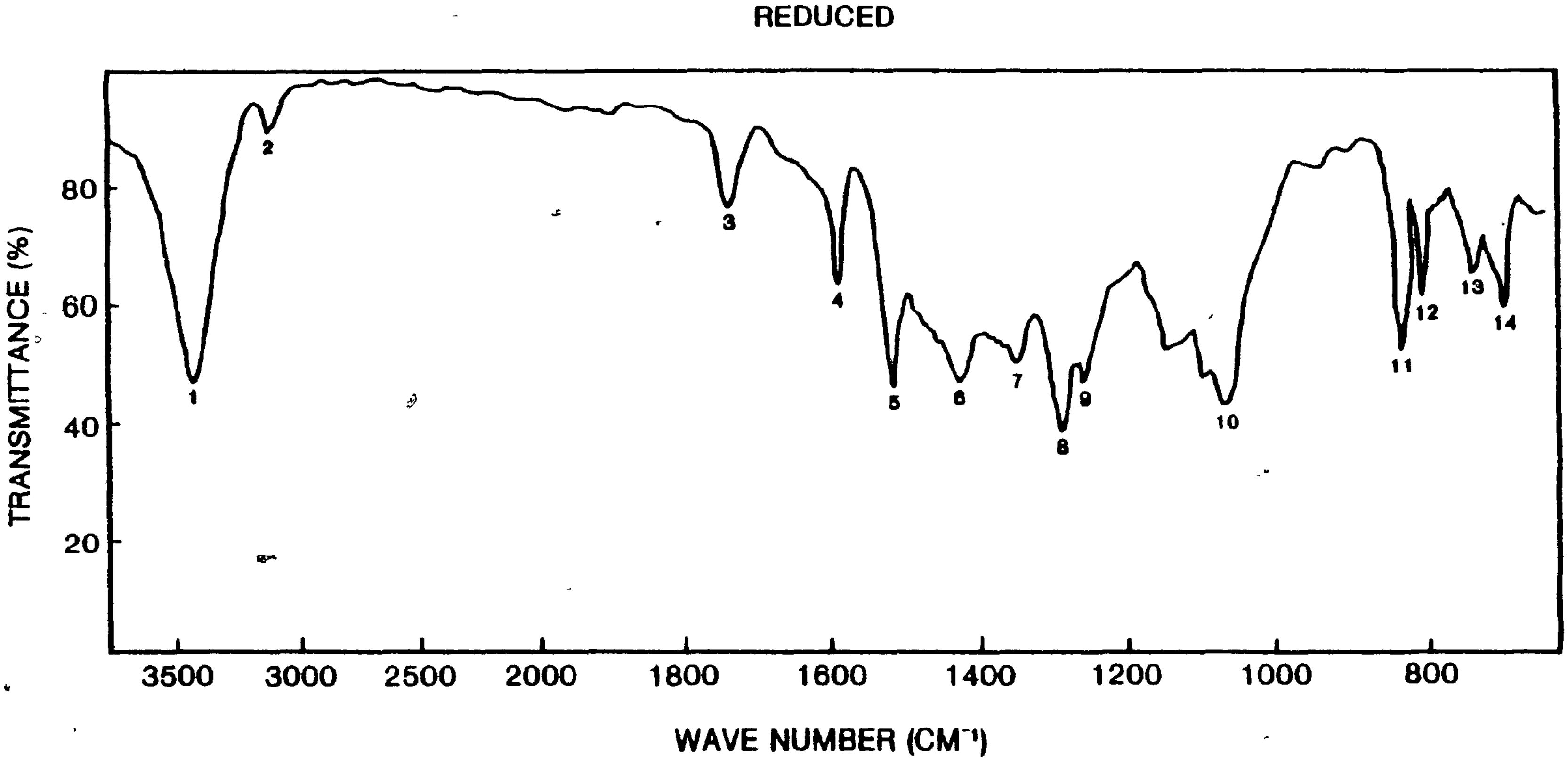

REDUCED

FIGURE 4.10 - INFRARED SPECTRUM OF KELEX 100 AFTER REDUCTION

pressure hydrogen stripping.

In the laboratory, the organic liquid was recycled 8-10 times and then a fresh sample of KELEX 100 was used. Before this process is ready to be used commercially, more work must be directed at determining whether or not there are any deleterious effects of recycling over longer periods.

SECTION 4.5 : THERMAL STABILITY OF KELEX 100

As has been described in the Experimental Chapter, the standard procedure for a hydrogen stripping test was to heat the loaded organic extractant under nitrogen until the operating temperature was reached. There exists the possibility that heating the loaded extractant under nitrogen could result in cobalt precipitation, while at the same time partially regenerating the organic solvent. This phenomenon is termed 'thermal precipitation' and is discussed below.

Charles et al.[64] have perhaps carried out the most extensive investigation on pyrolysis of 8-hydroxyquinoline chelates. In their investigation, various metal chelates (Cu, Ni, Co, Mn, Zn, Pb, and Cd) were prepared in solid form and were then heated in air, in vacuo, or in inert atmospheres. The methods used to study the thermal properties of the metal chelates were TGA (thermal gravimetric analysis), TMA (thermal-manometric analysis), and DTA (differential thermal analysis).

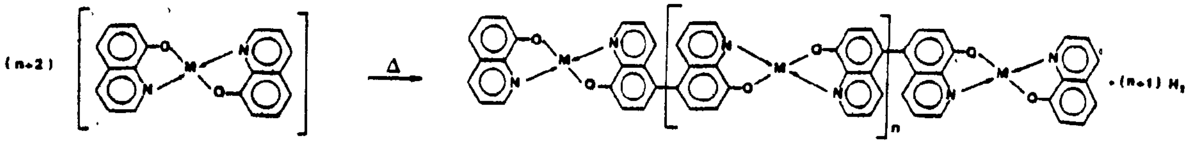
The 8-hydroxyquinoline chelates of copper(II), nickel(II), cobalt(II), cadmium(II), and lead(II) gave free metals in the dissociation residues, whereas manganese(II) and zinc(II) yielded metal oxides. Hydrogen gas was the main volatile product in all cases. The temperatures at which decomposition of the oxinates first became detectable are shown below for a few metals:

METAL	TEMPERATURE (°C)
Cu	275
Pb	310
Ni	400
Co	420
Cd	460

TABLE 4.2 - OXINATE DECOMPOSITION TEMPERATURE (HEATING UNDER ARGON)

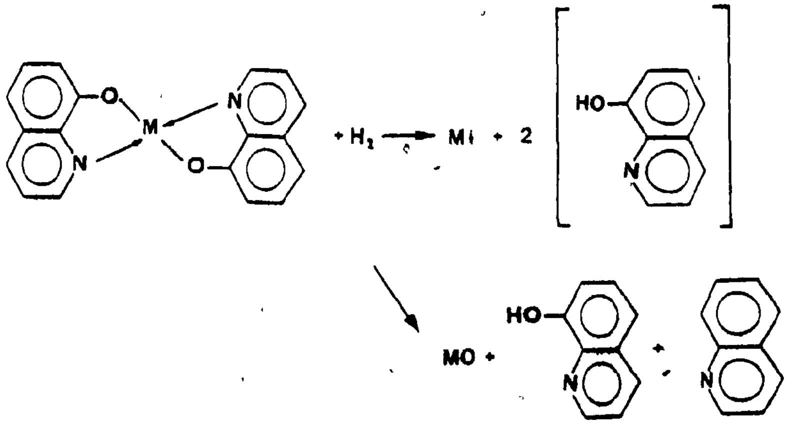
Charles et al. proposed a reaction mechanism to account for the pyrolysis phenomenon. This mechanism consists of two reactions:

1) Intermolecular dehydrogenation between chelate molecules giving a polymeric structure in which the ring system is retained.



(4.5)

2) The hydrogen released may be evolved as a free gas or it may react according to:



(4.6 I)
METAL

(4.6 II)
OXIDE

Equations 4.6 I and 4.6 II are approximations of what is actually occurring and only apply to temperatures close to the decomposition temperature. At higher pyrolysis temperatures, dehydrogenation is accompanied by partial disruption of the ring systems, while above 700 °C even the quinoline nucleus is disrupted to some extent.[64]

Using solid 8-hydroxyquinoline samples, Charles et al. found that the cobalt complex decomposed at 420 °C (see Table 4.2). Since the present work was performed using liquid KELEX 100, it was necessary to determine whether or not thermal precipitation occurs at operating temperatures around 300 °C. It is known that copper is thermally precipitated at temperatures below 275 °C (see Table 4.2) when KELEX 100 is used. Demopoulos[11] found that at temperatures as low as 200 °C, approximately 15% of the copper initially in the loaded organic had precipitated out of solution after a heating period of 12 hours. A plot of heating time versus metal concentration is shown in Figure 4.11.

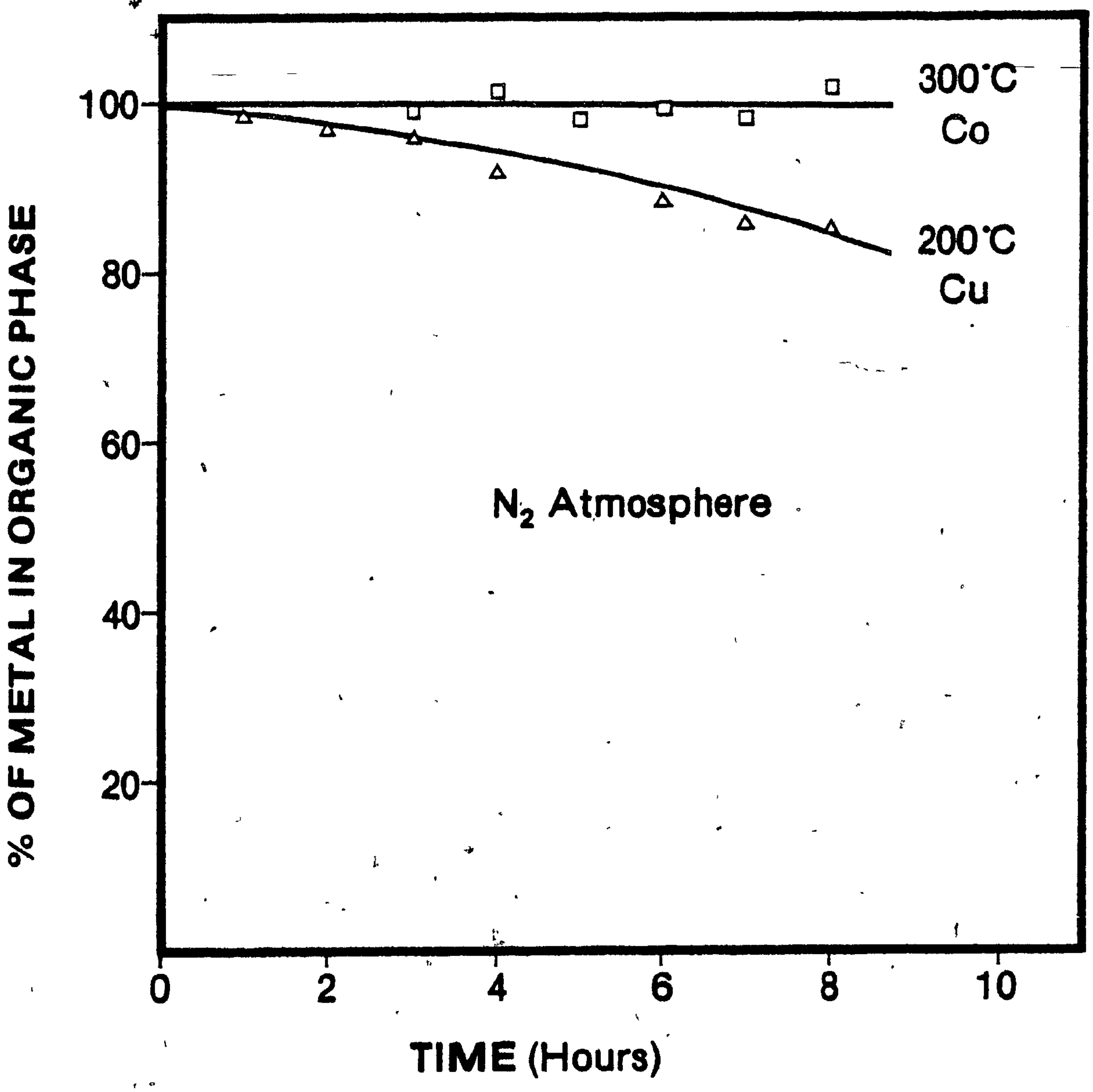


FIGURE 4.11 - THERMAL PRECIPITATION OF COPPER AND COBALT WHILE HEATING UNDER NITROGEN

The initial copper concentration was approximately 10 gpl and this corresponds to 100% at time zero. Using X-ray techniques, Demopoulos determined that the precipitate was metallic copper powder. Demopoulos reported that "the slow thermal dissociation observed was ... beneficial since it produced the first nuclei for further copper precipitation during hydrogen stripping."[11]

When cobalt-loaded KELEX 100 was heated under nitrogen, no thermally precipitated powder was produced. Atomic absorption did not reveal any change in cobalt concentration in the organic liquid. The results from heating at 300 °C under nitrogen are included in Figure 4.11. The initial cobalt concentration was approximately 3.5 gpl and this corresponds to 100% at time zero for the cobalt curve.

Thermal precipitation does not occur using a cobalt-KELEX 100 system at temperatures below 300 °C. According to Table 4.2, temperatures closer to 400 °C may be required before any cobalt would be produced via a thermal precipitation mechanism.

CHAPTER FIVE

DISCUSSION OF RESULTS: THE KINETICS OF COBALT PRECIPITATION

SECTION 5.1 : KINETIC STUDIES

The kinetic investigation of cobalt precipitation from loaded KELEX 100 involved the study of several parameters affecting the reaction rate. The particular parameters studied were operating temperature, hydrogen partial pressure, agitation, cobalt chelate age, cobalt chelate concentration, and seeding.

5.1.1 : OPERATING TEMPERATURE

Hydrogen stripping of cobalt-loaded KELEX 100 was investigated in the 250-325 °C temperature range and the results are summarized in Figure 5.1.

The abscissa refers to the reduction time in hours. Time zero corresponds to the time at which the operating temperature was reached, that is, the point at which the hydrogen was admitted to the autoclave. The ordinate represents the percent cobalt remaining in the organic phase. At time zero, 100 percent corresponds to the initial cobalt concentration in the organic phase (3.5 ± 0.1 g.p.l.). A comprehensive list of all the reduction tests carried out at these temperatures is given in the Appendix.

As Figure 5.1 shows, the reaction rate was found to be

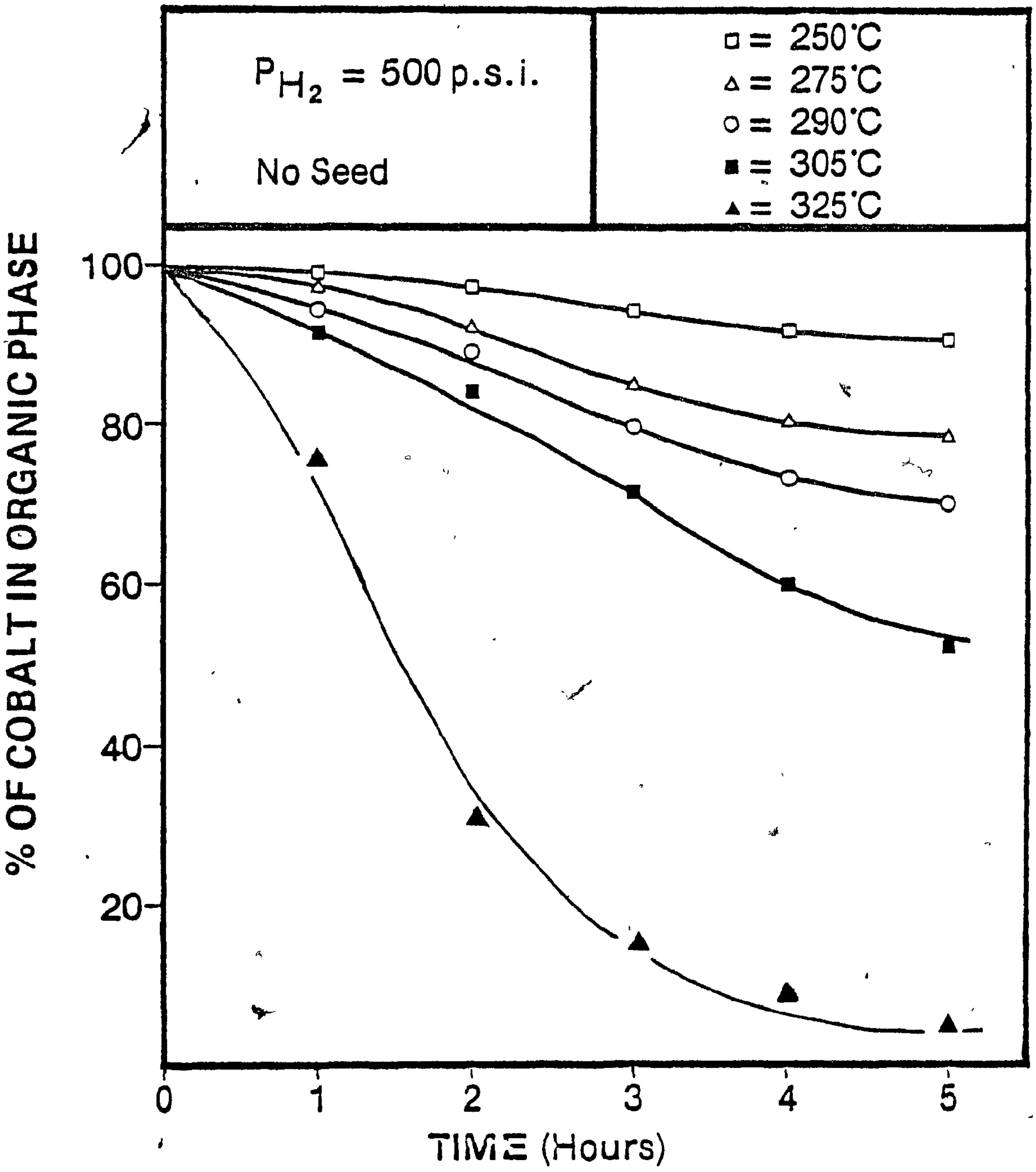


FIGURE 5.1 - EFFECT OF OPERATING TEMPERATURE ON REACTION RATES (500 p.s.i. and no seed)

strongly dependent on the operating temperature. For example, at a hydrogen pressure of 500 p.s.i. (3.45 MPa), the precipitation kinetics becomes unacceptably slow at temperatures around 250 °C. Even after a period of 5 hours under these conditions, the total reduction amounts to only 10% of the initial cobalt in the loaded organic.

At a higher temperature of 325 °C, there is approximately 70% reduction within 2 hours, and almost complete reduction within 4 hours.

The cobalt produced during these reduction experiments was found to be plated onto the impeller and all metallic surfaces immersed in the organic liquid. The plated cobalt was extremely difficult to remove manually and had to be dissolved using a concentrated acid solution. The washing procedure is described in greater detail in the Experimental section.

5.1.2 : HYDROGEN PARTIAL PRESSURE

The effect of hydrogen partial pressure on the reaction kinetics is illustrated in Figure 5.2, where typical results from tests conducted at 325 °C and various hydrogen pressures are given.

Figure 5.2 clearly shows that an increase in hydrogen pressure significantly favours the overall precipitation kinetics.

When thermal equilibrium had been reached and the hydrogen

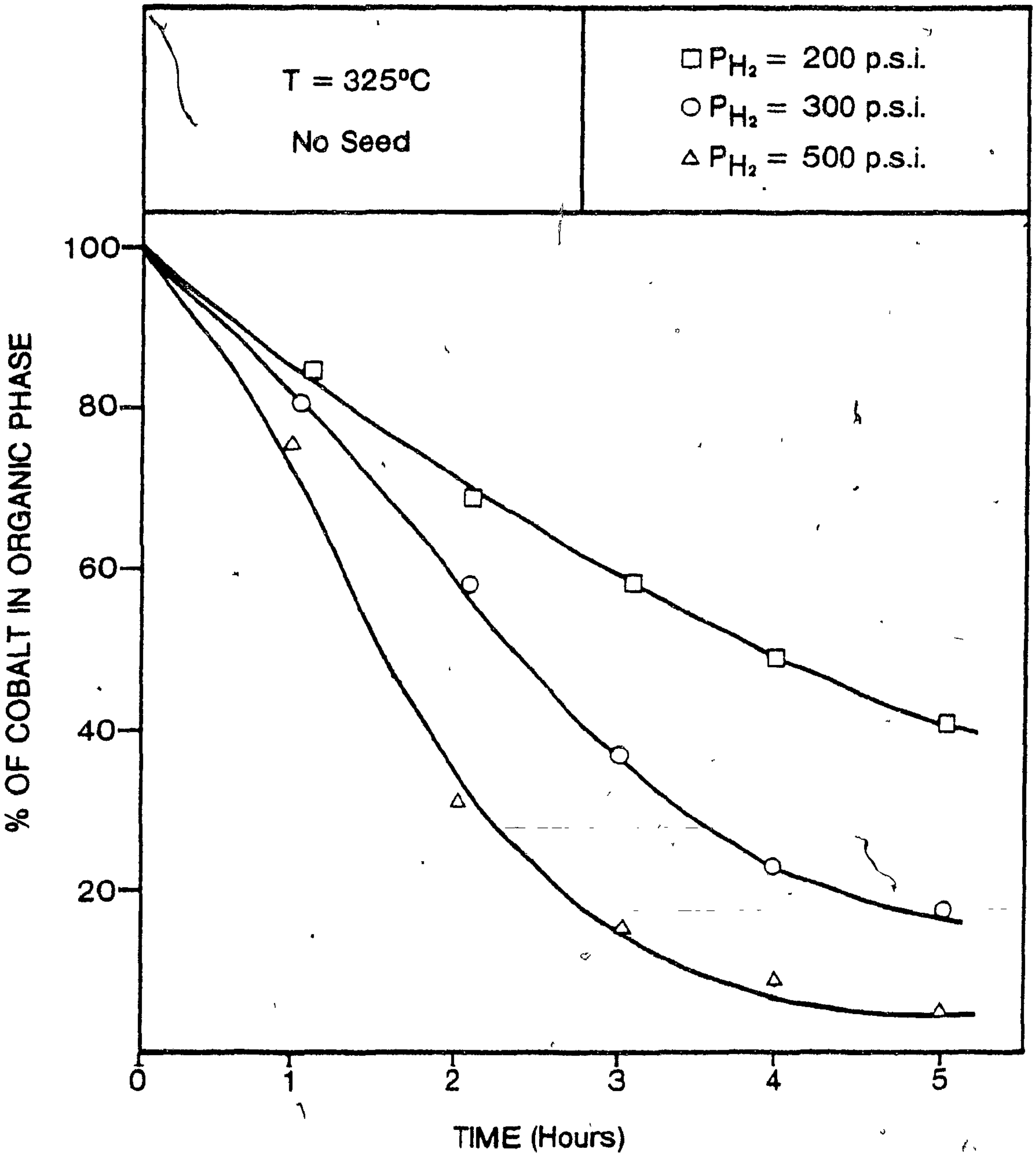


FIGURE 5.2 - EFFECT OF HYDROGEN PRESSURE ON REACTION RATES (325 °C and no seed)

gas was admitted to the system, there was a 5-10 p.s.i. (0.035-0.070 MPa) drop in the total pressure. It is believed that this drop was due to hydrogen dissolution in the organic liquid rather than to a chemical reaction taking place since this drop was also observed in cases where no cobalt powder was produced.

The vapour pressure of the organic liquid ranged from 30-100 p.s.i. (0.21-0.69 MPa) in the 250-325 °C temperature region investigated. The pressures referred to in Figure 5.2 represent only the hydrogen partial pressures. The total pressure in the autoclave consisted of the organic vapour pressure plus the hydrogen partial pressure.

According to Mackiw et al.[65], a measure of the rate at which a reaction takes place can be given by $(100/t_{50})$ where t_{50} is the time required for reduction of 50% of the metal in solution. According to these authors, a kinetic law can be derived that gives a linear relationship between $\ln(100/t_{50})$ and $\ln(P_{H_2})$. Using the results of Figure 5.2, at 200, 300, and 500 p.s.i., the t_{50} values are 4.0, 2.4, and 1.6 hours respectively. Using linear regression, the slope of a $\ln(100/t_{50})$ versus $\ln(P_{H_2})$ graph would be 0.995 with a correlation coefficient of 0.992. In other words, the rate of reduction is almost directly proportional to the partial pressure of hydrogen in the pressure range investigated. Similar dependency of the reduction rate on hydrogen pressure was observed in: (1) the heterogeneous system of nickel precipitation from aqueous ammoniacal sulphate solutions,[65] (2) the reduction of cobalt from aqueous ammine ammonium sulphate solutions,[66] and (3) the reduction of copper from loaded KELEX 100[11].

5.1.3 : EFFECT OF AGITATION

The reduction of cobalt from loaded KELEX 100 involves gas, liquid and solid phases. Agitation of the loaded organic solvent is required for two reasons: (1) good gas dispersion, and (2) suspension of precipitated solids to allow for complete exposure of metallic surfaces to the solution.

To study the effect of agitation on the reaction kinetics, three stirring rates were selected in the 450-900 RPM range. The results are plotted in Figure 5.3. The tests were carried out at 305 °C with a hydrogen pressure of 500 p.s.i. (3.45 MPa).

As Figure 5.3 shows, no significant effect was observed. The independence of reaction rate on stirring rate suggests that the overall precipitation process is not diffusion controlled. Burkin[67], in his report on the physical chemistry of metal precipitation from loaded carboxylic acids with hydrogen, suggested that in his system the rate controlling step was the transfer of hydrogen from the gas phase into solution. In Burkin's work, however, hydrogen was introduced above the liquid phase, while in the present investigation hydrogen gas was drawn down and dispersed as small bubbles below the liquid surface by the action of the impeller. Therefore, under the present experimental conditions, a

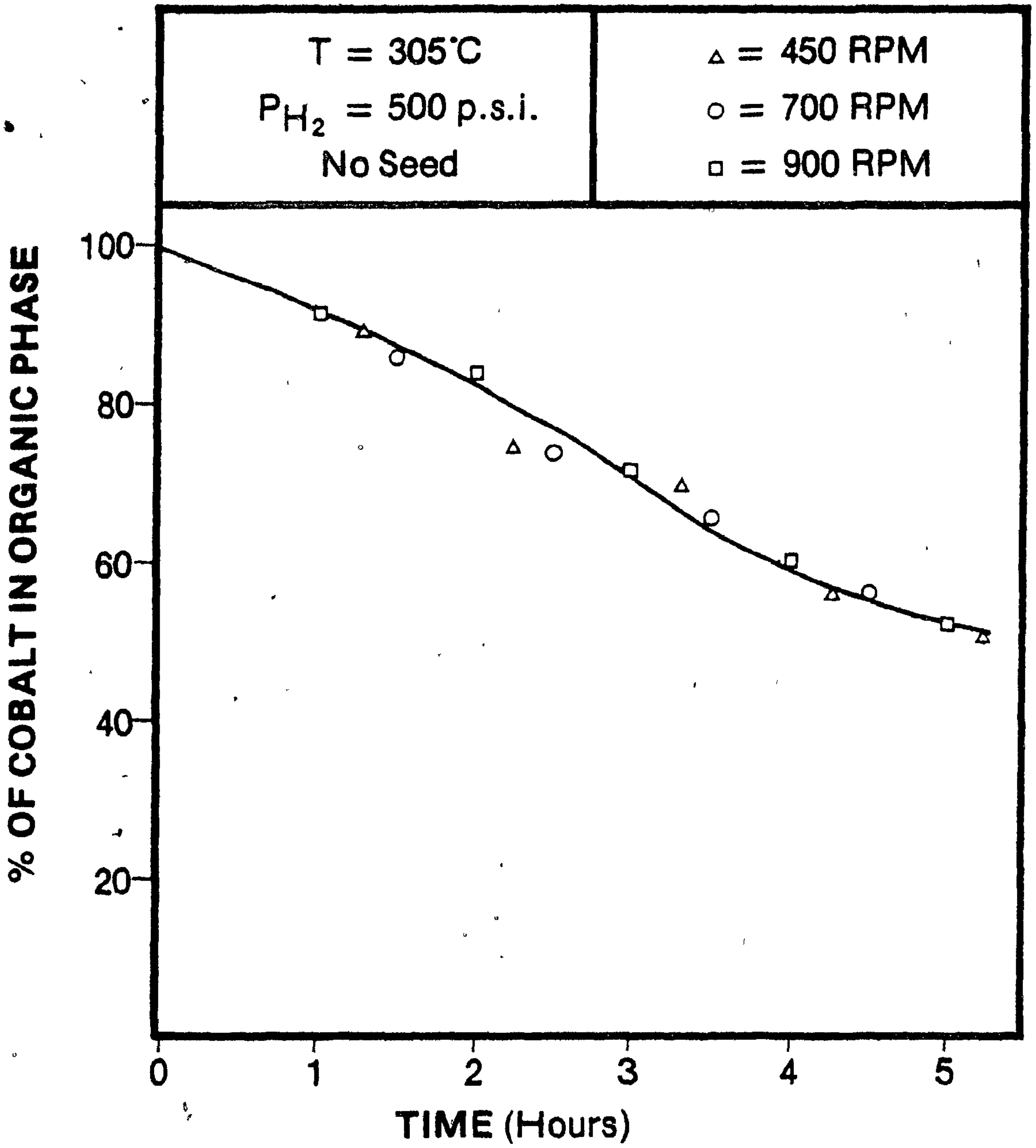


FIGURE 5.3 - EFFECT OF AGITATION ON REACTION RATES
(305 °C, 500 p.s.i. and no seed)

chemical reaction appears to be the rate controlling step for the overall reduction process.

5.1.4 : COBALT CHELATE AGE

Previous experience[11] with the copper-KELEX 100 system suggested that precipitation kinetics in the present work may be affected by chelate age. A number of experiments were performed using organic solutions of different ages to determine the effect of chelate age.

The standard procedure for the preparation of the loaded organic extractant was to dilute KELEX 100 and modifier in kerosene and then to immediately load with cobalt. The phases were allowed to separate overnight and the solvent age for a typical experiment was 24 ± 2 hours. Other tests were performed using loaded organic solvents aged anywhere from 12 hours to 10 days and the results from these experiments are presented in Figure 5.4. While no significant effect was observed up to 1 day, loaded organic solvents with greater ages gave much slower reaction rates as can be seen from Figure 5.4.

This strong ageing effect suggests that the cobalt-bearing KELEX molecules form polymeric associates which have a suppressing effect on the hydrogen stripping kinetics. Difficulty of reduction increases with age.

Such effects have not, however, been reported in conventional acid stripping kinetics where KELEX 100 was used as

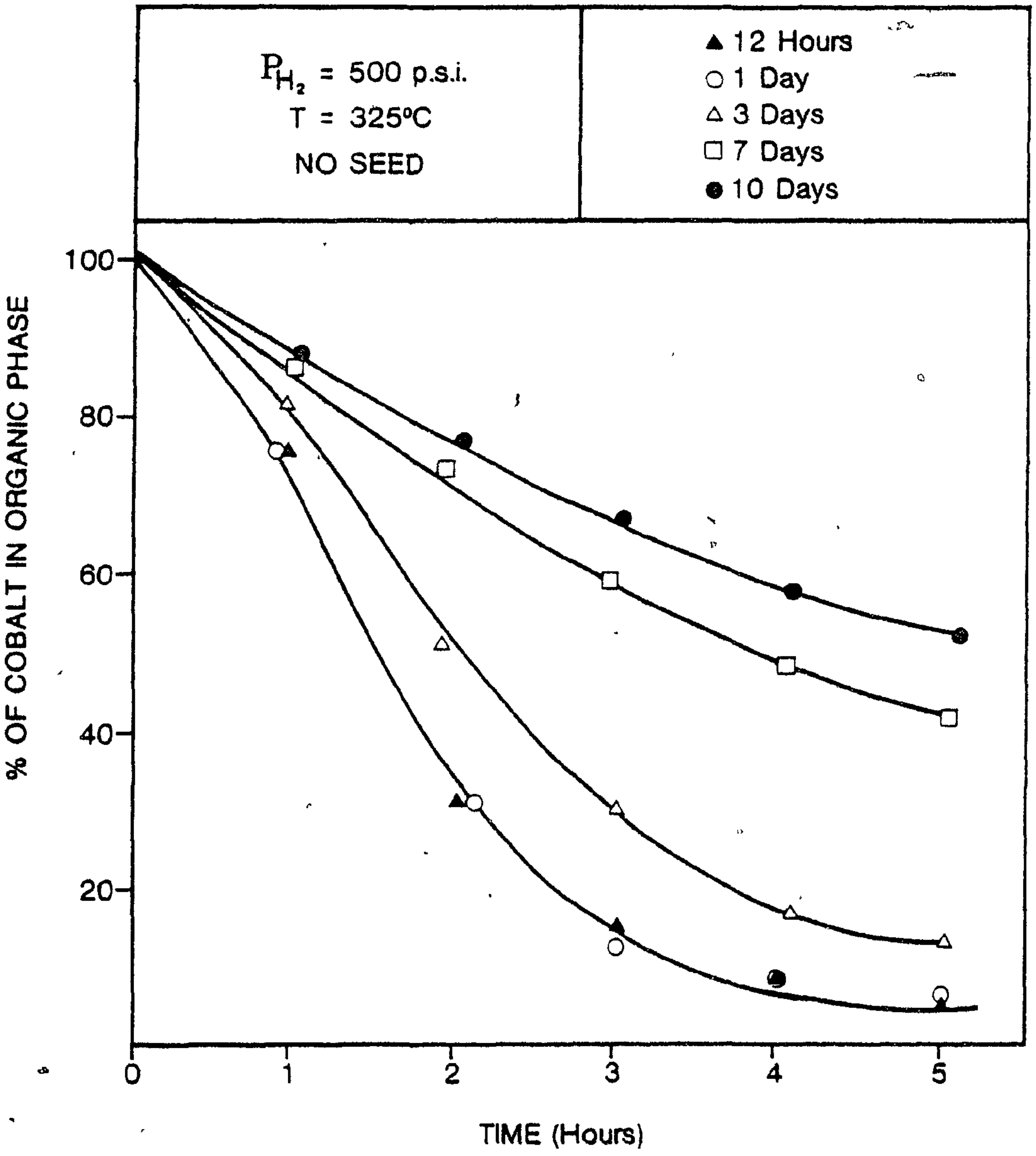


FIGURE 5.4 - EFFECT OF COBALT CHELATE AGE ON REACTION RATES (325 °C, 500 p.s.i. and no seed)

the metal extractant. It should be noted that kinetic studies related to conventional solvent extraction deal primarily with the extraction stage of the process, and only on occasion is reference made to the stripping kinetics. The latter is very fast, and if any ageing effect exists, it would be too insignificant to have been noted in the literature.

In industrial practice, the loaded organic would probably be reduced shortly after it was loaded and no significant ageing effect should be encountered.

5.1.5 : EFFECT OF INITIAL COBALT CHELATE CONCENTRATION

All of the previous experiments in this chapter were conducted using a 15 volume percent solution of KELEX 100 diluted in kerosene and decanol. Higher concentrations of KELEX 100 were not used since handling of the solution would be too difficult due to its high viscosity. Non-aqueous titration of the 15 volume percent KELEX 100 solution with perchloric acid indicated a 0.4M ligand (HL) concentration. Assuming a CoL_3 complex, this corresponds to a theoretical 7.9 g.p.l. cobalt loading capacity. Preparation of the loaded organic solution according to the extraction procedure described in Chapter three yielded an organic solution containing 3.5 g.p.l. cobalt. Theoretically, it would have been possible to extract more cobalt by adding more ammonium hydroxide to raise the pH of the aqueous solution. This practice was rejected because when large quantities of ammonium hydroxide are used, some becomes entrapped in the loaded organic and substantially raises the vapour pressure of the liquid when heated.

The effect of lowering the initial cobalt concentration in the organic phase is shown in Figure 5.5. Clearly, a decrease in the initial cobalt chelate concentration results in slower reaction rates. For example, the time required for 50% reduction was 1.6 hours for the 3.5 g.p.l. solution and over 4 hours for the 1.9 g.p.l. solution. The slower reaction rate is probably due to a decrease in the cobalt concentration but it may also be due to an increase in the free ligand (HL) concentration. Assuming a ligand concentration of 0.4M before loading and a CoL_3 complex after loading, an organic solution containing 3.5 g.p.l. cobalt implies that the free ligand concentration is 0.22M. With an organic solution containing 1.9 g.p.l. cobalt, the free ligand concentration is 0.3M. This increase in free ligand concentration may result in the formation of 'adduct complexes' between the cobalt chelate complex and molecules of free ligand, and the precipitation rate may be hindered. This same phenomenon was observed in a parallel system using copper.[11]

This hindrance due to the increase in free ligand concentration may also be related to the ageing effect observed with KELEX 100 where polymeric associates have a suppressing effect on the hydrogen stripping kinetics. No attempts were made to determine the structure of these presumed 'adduct complexes'.

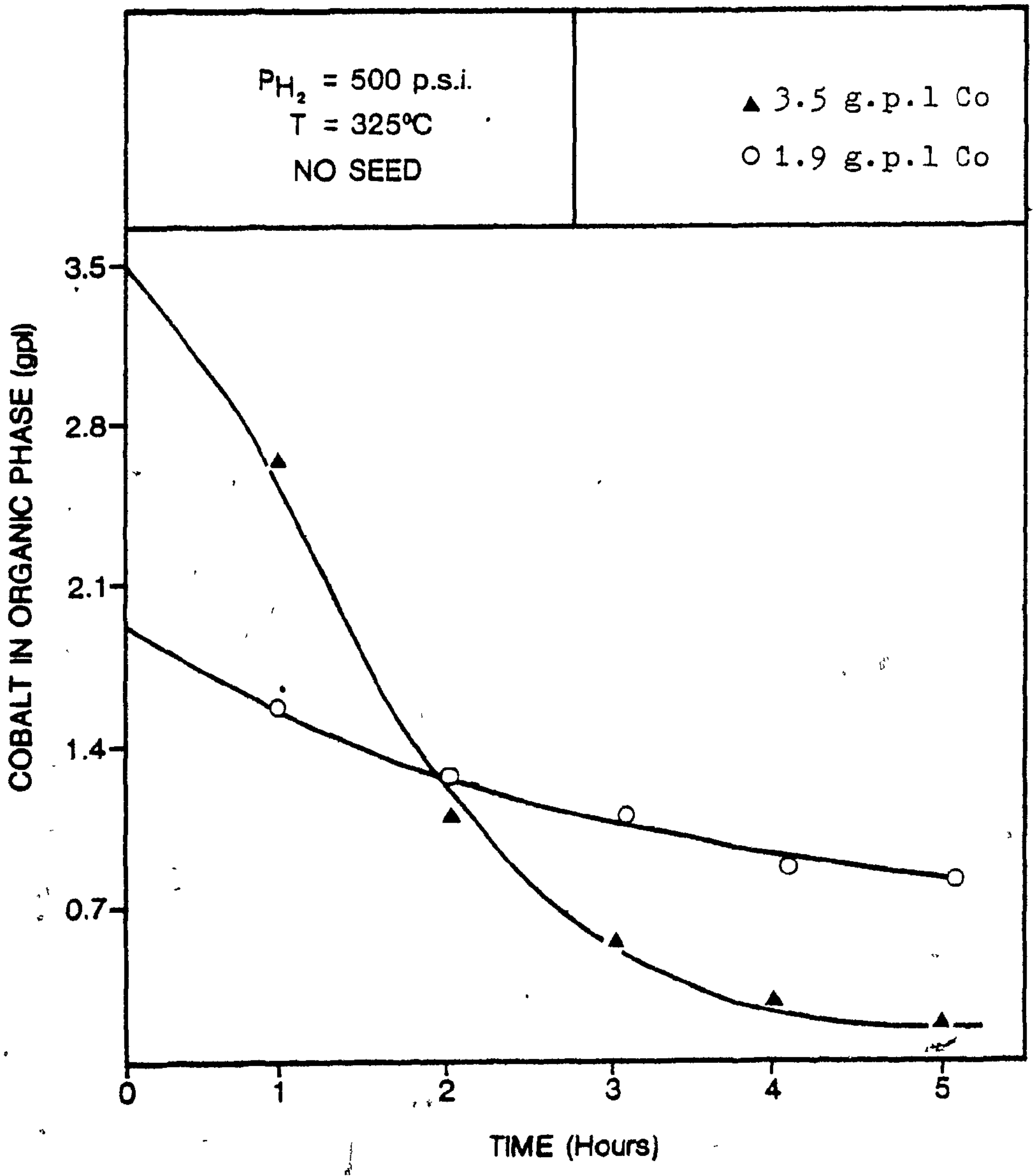


FIGURE 5.5 - EFFECT OF INITIAL COBALT CHELATE CONCENTRATION ON REACTION RATES (325 °C, 500 p.s.i. and no seed)

SECTION 5.2 : SEEDING

Although seeding was not necessary to initiate metal precipitation, a decision was made to add an external seeding agent in order to see whether or not the precipitation kinetics could be increased.

In the first seeding experiment, 0.5 grams of activated carbon powder (Darco G-60 : Fisher Scientific Company) was added to the loaded organic before it was placed in the autoclave. The effect of adding the carbon powder is shown in Figure 5.6. The curve obtained in the absence of an external seed is also shown in Figure 5.6. After a period of 5 hours, the amount of cobalt reduced using carbon powder was greater than 60%. Without a seeding agent, the amount of cobalt reduced was approximately 20%.

It was also noticed that no plating occurred during the carbon seeding experiment. It appears that the carbon powder provided the initial nuclei for reduction to occur, and then once the carbon was covered with cobalt, the metal surface enabled the reaction to continue. Unfortunately, when the organic liquid was filtered, a black sludge formed on the bottom of the filter disc and it took over 6 hours to filter 1 litre of the organic solution. Carbon powder may be acceptable as a seeding agent from an academic viewpoin[illegible] however it is unacceptable for commercial use.

Another seeding agent used was cobalt powder (Certified Cobalt Metal Powder : Fisher Scientific Company). The graph

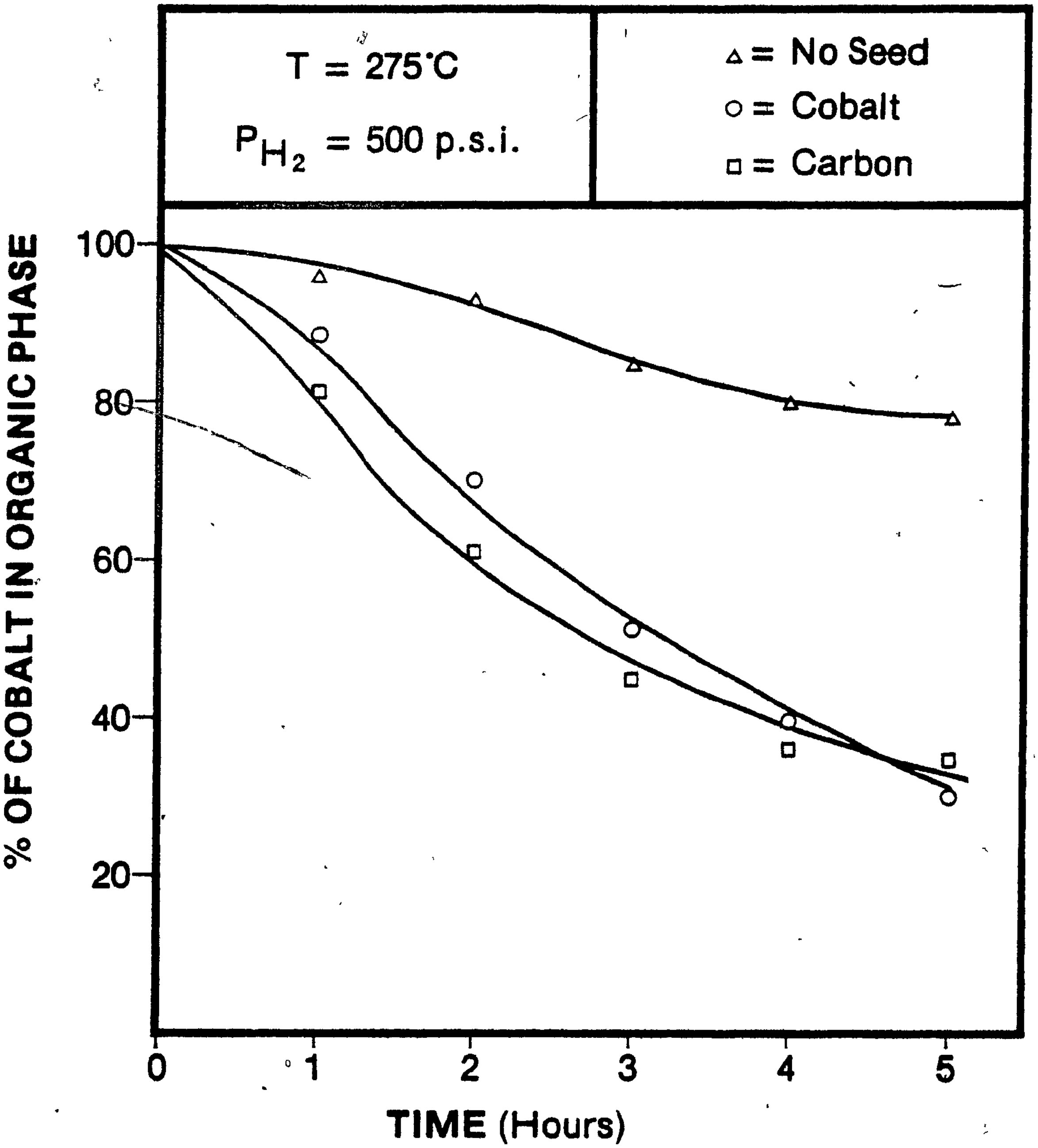


FIGURE 5.6 - EFFECT OF SEEDING WITH ACTIVATED CARBON POWDER AND COBALT POWDER (275 °C and 500 p.s.i.)

obtained using 0.5 grams of cobalt powder is superimposed on Figure 5.6.

The carbon powder allowed for faster precipitation at the beginning of the reaction. The reasons for this occurrence will be discussed in Section 5.4. However, at the end of 5 hours, the reduction using cobalt powder and the reduction using carbon powder were approximately equal.

When a cobalt seed was used no product was firmly plated onto the stirrer assembly. The product from the cobalt seed experiment was much easier to filter than that from the carbon seed experiment. It took approximately 1 hour to filter 1 litre of the organic liquid.

The effect of adding cobalt powder was also examined at another temperature and the results are plotted in Figure 5.7. The effect is even more significant. At 250 °C, there is approximately 10% reduction without a seed after 5 hours, and almost 40% reduction after the same period of time in the presence of an external seed.

SECTION 5.3 : EXPERIMENTAL REPRODUCIBILITY

After having standardized the experimental reduction and cleaning procedures, two replicate runs were conducted under typical reducing conditions. The results are illustrated in Figure 5.8. In addition to the replicate runs of Figure 5.8, a further indication of the experimental reproducibility obtained is given by the reaction curves in Figure 5.3. The

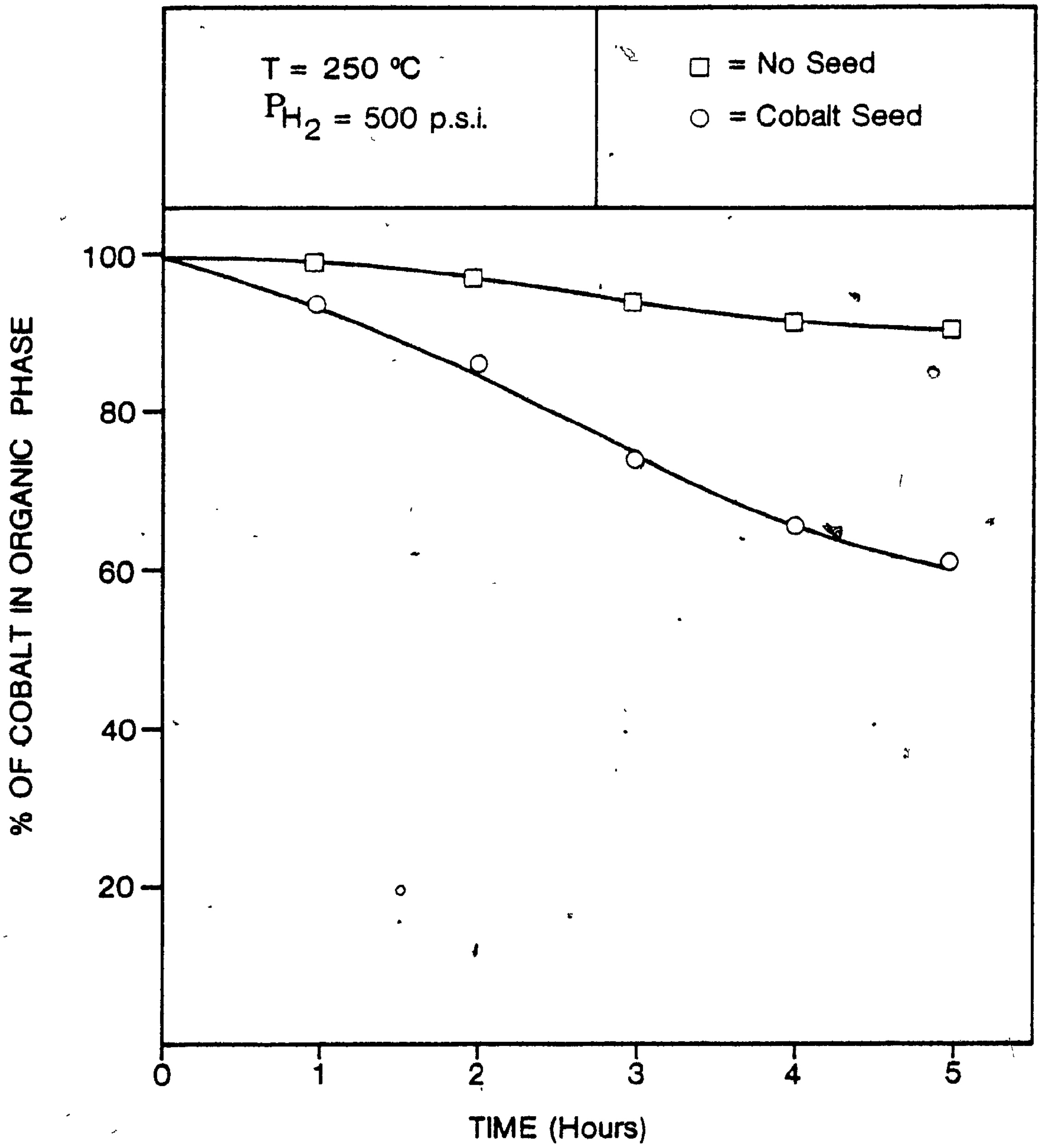


FIGURE 5.7 - EFFECT OF SEEDING WITH COBALT POWDER (250 °C and 500 p.s.i.)

results in Figure 5.3 are not strictly true replicates since they represent runs with different stirring rates. However, since the stirring rate was considered to have no effect on the reduction kinetics, these tests can be regarded as replicates.

From Figures 5.3 and 5.8, the observed variations in reaction rates for replicate runs were estimated to be better than ±10%. The observed variations can be attributed to difficulties in precisely controlling the following parameters:

1) Initial cobalt concentration (3.5 ± 0.1 g.p.l.).
2) Temperature. Although the temperature controller kept the temperature within ±1 °C, Figure 5.1 reveals that the precipitation rate is highly sensitive to the operating temperature. Even a slight increase in temperature could result in a large increase in precipitation rate.

Errors could also arise due to inaccuracies in analyzing the organic liquid samples as, for example, in dilution before atomic absorption.

Considering these possible sources of error, ±10% is deemed acceptable.

SECTION 5.4 : NUCLEATION

Metal precipitation by reduction of KELEX 100 with hydrogen is composed of nucleation, followed by growth. Nucleation of a new solid phase can be homogeneous, heterogeneous, or both mechanisms can occur simultaneously. The present system is apparently characteristic of heterogeneous nucleation.

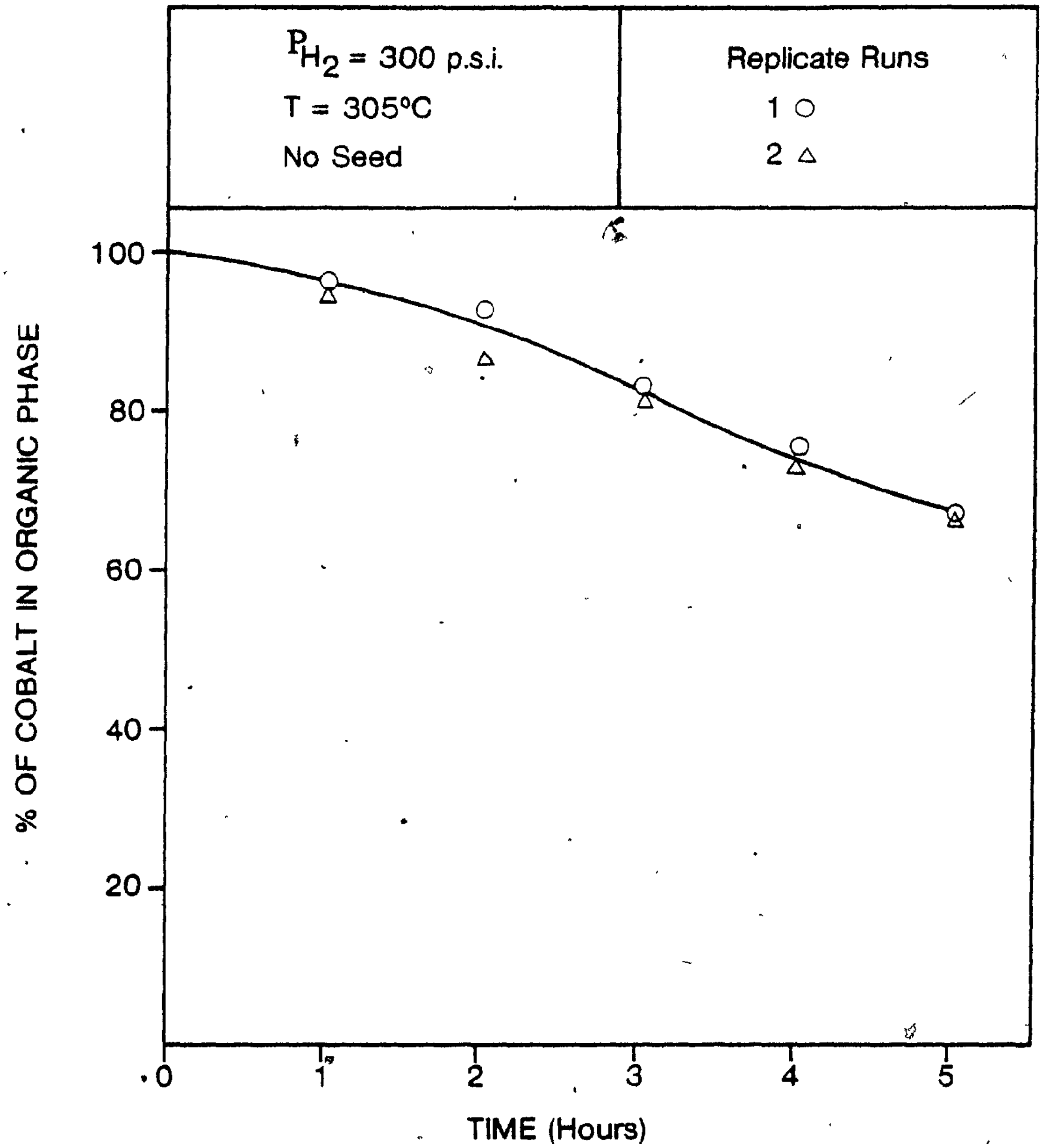


FIGURE 5.8 - REPLICATE RUNS CARRIED OUT UNDER THE SAME EXPERIMENTAL CONDITIONS (305 °C, 300 p.s.i. and no seed)

5.4.1 : HOMOGENEOUS NUCLEATION

It seems improbable that homogeneous nucleation would take place in the system under investigation. From nucleation theory, it is known that there are two requirements in order for homogeneous nucleation to occur:[68]

1) A high concentration of the reacting species (preferably uncomplexed) to the point of supersaturation.
2) A sufficiently high temperature to provide the high activation energy of nucleation.

Although a decrease in initial cobalt chelate concentration yielded a slower reaction rate (see Figure 5.5), this was probably due to the retarding effect of high concentrations of free HL molecules rather than to slower homogeneous nucleation because of decreased cobalt chelate levels. In addition, an increase in temperature did not result in noticeable reduction of the plating problem, which would be expected if homogeneous nucleation was in fact the dominating mechanism. Moreover, the strong accelerating effect of seed addition observed with the tests illustrated in Figures 5.6 and 5.7 supports the idea of a heterogeneous nucleation mechanism.

5.4.2 : HETEROGENEOUS NUCLEATION

To initiate cobalt precipitation an external seed was not required, although in its absence, most of the cobalt produced was plated onto the titanium impeller and stirrer shaft.

During a hydrogen stripping test without seed, the immersed titanium surfaces of the autoclave were the only metallic surfaces that could activate hydrogen. The surprisingly strong catalytic effect observed here requires further elaboration.

In aqueous systems, titanium is known to perform well under oxidizing conditions but not under reducing conditions. Therefore titanium is not suitable for autoclave construction in the latter case. Titanium under reducing conditions is embrittled by hydrogen picked up either from hydrogen gas present in a process stream or produced as a corrosion product. For embrittlement to occur, hydrogen must be in the metal at concentrations such that a separate localized hydride phase can form.[69] When hydrogen comes in contact with titanium, molecular hydrogen dissociates and ionizes to some extent due to the potential field of the metal.[70] In this condition, the titanium surface would be expected to be catalytically very active.

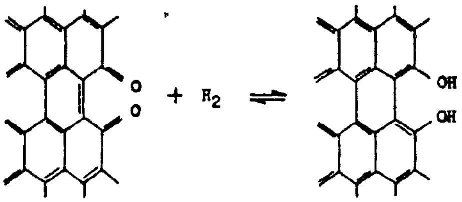
It is also believed that during cleaning of the stirrer assembly, titanium adsorbs hydrogen which is produced during dissolution of plated cobalt with nitric acid as shown below:

$$\mathrm{Co} + 2\mathrm{HNO_3} \rightarrow \mathrm{Co^{++}} + 2\mathrm{NO_3^-} + \mathrm{H_2} \qquad (5.1)$$

For this reason a standardized cleaning program, including acid strength and contact time, is extremely important if good experimental reproducibility is desired.

In addition to the above mechanism, it is presumed that hydrogen is also adsorbed during the reduction experiment, thus enhancing the catalytic activity of the metallic surfaces.

When activated carbon is used as a seed material, it is believed that hydrogen adsorbs on the surface of the carbon by the following reversible reaction:[71]



(5.2)

SPECIES I SPECIES II

The quinoid form (Equation 5.2, SPECIES I) of the carbon structure possesses fixed olefinic bonds which produce surface strain. This strain is relieved by the resonance shift associated with the adsorption of hydrogen resulting in a phenolic form (Equation 5.2, SPECIES II).[71]

When cobalt powder is used as a seed material, it is believed that hydrogen is chemisorbed on the metal surface by the following mechanism:[72]

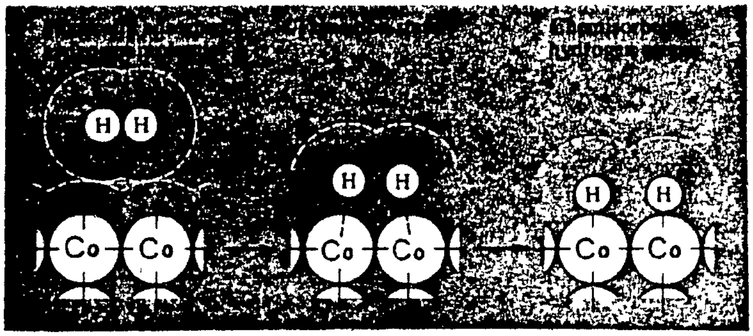


FIGURE 5.9 - CHEMISORPTION OF A HYDROGEN MOLECULE

According to a valence bond model of metallic bonding[72], the formation of a chemical bond to a surface metal atom can be visualized as involving 'dangling orbitals' of the surface metal atoms. The metal atoms on the surface are assumed to have the same arrangement of orbitals as those in the bulk, although not possessing their full complement of nearest neighbour atoms. The orbital of the adsorbing species (1s for a hydrogen atom) and the unfilled orbital of the surface metal atom overlap and form a chemical bond.[68]

As Figure 5.6 illustrates, cobalt precipitation is initially faster when carbon is used than when cobalt powder is used. This is probably due to the nature of activated carbon which contains many pores or active sites (greater surface area per unit weight). After a period of 5 hours, the amount of cobalt precipitated is approximately the same using either powder. A possible explanation is that the carbon powder becomes covered with cobalt metal and the two seeding agents then behave similarly.

As mentioned in Section 5.2, no plating on the metallic stirrer occurred when a seeding agent was added. This suggests that the hydrogen chemically adsorbed on the seeding powder is more active than the hydrogen on the titanium surfaces.

An interesting phenomenon occurred when seeding with either cobalt or carbon powder. When the glass liner was removed from the autoclave, it appeared that some of the cobalt had plated onto the liner producing a mirror-like surface. The amount of cobalt plated onto the liner was determined by dissolving the cobalt into a known volume of acid and then using atomic absorption to analyze the liquid. The cobalt plated was always less than 2% of the initial cobalt in the loaded organic. It is believed that the cobalt was not actually nucleated on the glass liner, but rather it seemed that the seeding agent was forced to the liner wall by the centrifuging action of the impeller. Evidence for this hypothesis comes from the fact that no cobalt plated onto the glass liner when no seed was added. This phenomenon illustrates the need for proper baffling if a seed is to be added.

It is known that when the loaded organic is placed in the autoclave, the cobalt is present as a cobalt(III) chelate complex. It is also believed that during the reduction experiments hydrogen gas adsorbs onto the carbon or cobalt powder and becomes catalytically active. However, it is not known by what means the CoL_3 complex is reduced to pure cobalt metal. Further studies should be carried out using analytical chemical techniques to determine if the cobaltic complex is reduced directly to metal or if it becomes reduced via a cobaltous intermediate complex.

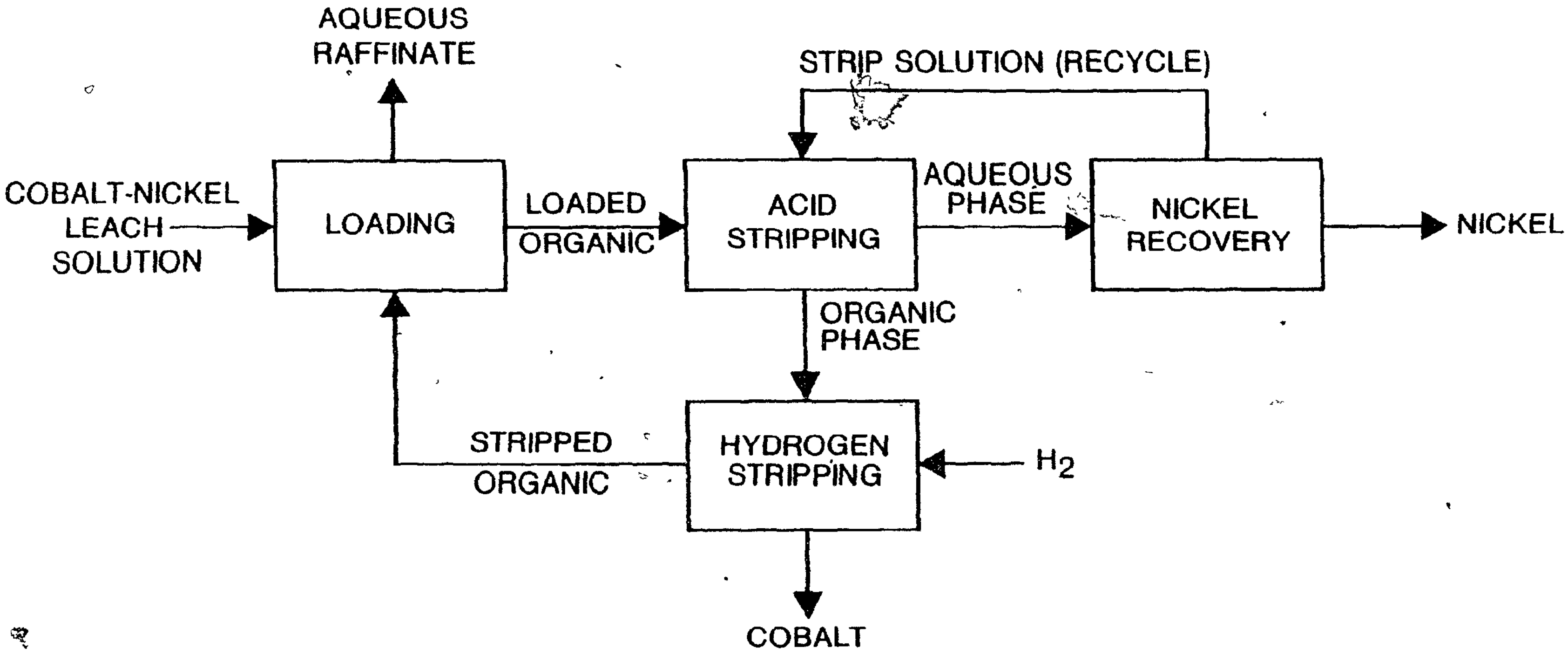
SECTION 5.5 : COBALT-NICKEL SEPARATION

Nickel and cobalt metals are very similar in their physical and chemical properties. The same is true of their salts and naturally occurring minerals. Moreover, minerals of both generally occur together in natural deposits and usually cannot be separated by ordinary mineral dressing practices. For these reasons, both metals are generally present in varying amounts in any solution resulting from any type of leaching of materials containing cobalt and nickel.

Nickel and cobalt are both readily loaded from leach solutions using KELEX 100.[44] However, there is one property in which cobalt and nickel differ. While nickel is readily stripped by various acids, cobalt is extremely difficult to strip since it oxidizes to the stable cobaltic form. Using these facts, it may be possible to separate cobalt from nickel using a scheme as shown in Figure 5.10.

In the first stage, the cobalt-nickel leach solution is loaded by KELEX 100. The loaded organic would then be stripped with acid. The organic phase, containing cobalt but not nickel, would be sent to the hydrogen stripping plant. The aqueous phase, containing the nickel, would be sent to the nickel recovery stage (e.g. electrowinning, etc.). An alternative approach may be to reload the nickel solution and then send the loaded organic to a separate hydrogen stripping plant, although the highly acidic strip solution would require neutralization.

To see if this scheme is feasible, an experiment was conducted using a synthetic feed solution. The organic feed consisted of 200 mls. of a 8.0 g.p.l. nickel solution and



PROPOSED FLOWSHEET FOR
NICKEL — COBALT SEPARATION

FIGURE 5.10 - NICKEL-COBALT SEPARATION FLOWSHEET

800 mls. of a 3.5 g.p.l. cobalt solution. When mixed, this resulted in an organic feed solution containing 1.6 g.p.l. nickel and 2.8 g.p.l. cobalt. The loaded organic was then stripped using 150 mls. of a 15 volume percent sulphuric acid solution. The phases were allowed to separate and the aqueous phase was removed. The organic phase was then stripped using 200 mls. of a 10% sulphuric acid solution. After phase separation, the aqueous phase was once again removed.

The loaded organic was then placed inside the autoclave for a standard hydrogen reduction experiment. The operating temperature for this test was 325 °C and the hydrogen pressure was maintained at 500 p.s.i. (3.45 MPa). No external seed was added.

After 5 hours the experiment was stopped and the autoclave was allowed to cool.

A sample of organic liquid was analyzed after the experiment and the results revealed that over 90% of the cobalt initially present had been reduced to metal.

The aqueous phases were also analyzed using atomic absorption and these results revealed that less than 3% of the cobalt initially in the organic phase had been stripped by the acid solutions.

The cobalt metal produced during the reduction experiment was sent to Technitrol Canada Limited for chemical analyses. The results are shown in Table 5.1.

ELEMENT	WEIGHT (%)
CARBON	0.08
HYDROGEN	0.006
OXYGEN	0.10
NICKEL	0.17

TABLE 5.1 - CHEMICAL ANALYSIS OF COBALT-NICKEL POWDER

The carbon, hydrogen, and oxygen impurity levels will be discussed in the next chapter. The nickel level can be considered to be acceptably low. Cathodic cobalt produced electrolytically from Union Minièra in Katanga averages 0.15-0.25 weight percent nickel.[73] Cobalt produced hydrometallurgically via the 'Sherritt Gordon Soluble Ammine Process' averages 0.12 weight percent nickel.[74]

This preliminary experiment has shown that a scheme as illustrated in Figure 5.10 may be used to separate cobalt from nickel. Further testing must be carried out using different experimental conditions and different feed solutions before the merit of this scheme can be established more positively.

CHAPTER SIX

DISCUSSION OF RESULTS: POWDER PRODUCT PROPERTIES

SECTION 6.1 : CHEMICAL ANALYSIS

Several samples of cobalt powder were sent to Technitrol Canada Limited for a chemical analysis. Only samples from experiments in which no seed was added were sent, as the presence of seed material would have confounded the interpretation of the results. The seed material was only of technical grade (Fisher Scientific Company - 99.5% Co) and it would have been difficult to discern whether the impurities were from the seed or from the reduction experiments.

The powder product samples were analyzed for carbon, hydrogen, and oxygen and the results are summarized in Table 6.1:

ELEMENT	WEIGHT (%)
CARBON	0.08 - 0.18
HYDROGEN	0.003 - 0.009
OXYGEN	0.065 - 0.100

TABLE 6.1 - CHEMICAL ANALYSIS OF COBALT POWDER

The carbon and hydrogen impurities can originate from two possible sources: (1) organic degradation of KELEX 100 during the reduction experiments, or (2) organic entrainment during filtration.

It is not believed that the carbon and hydrogen impurities originated from organic degradation. The results using infrared spectroscopy and gas-liquid chromatography indicate that after reduction, the organic extractant was regenerated with no detectable signs of degradation (see Chapter four). Rather, these impurities are believed to be due to organic entrainment during filtration. After filtration, the cobalt powder was washed with acetone but since KELEX 100 is extremely viscous, it is possible that traces of organic liquid became entrained in the powder. It is interesting to note that cobalt powder purchased from Fisher Scientific Company is easily wetted by water. Samples of powder after reduction were not easily wetted, and appeared as though they were coated by a thin layer of organic material.

The oxygen contaminant was apparently due to surface oxidation of the fine cobalt particles, since no protective measures to prevent this were adopted during the filtration and subsequent handling of the powder. The autoclave was flushed using nitrogen so it was not likely that oxidation occurred inside the apparatus. Also, the aqueous and organic phases were allowed to separate for 24 hours after loading, making it unlikely that entrapped water caused hydrolysis of the cobalt chelate complex during the heat-up period, and thereby avoiding the precipitation of a cobalt compound.

Metal impurities were not present in the product since a synthetic cobalt sulphate leach solution was used to load the organic extractant. However, as shown in the previous chapter, hydrogen stripping may be a viable means for separating cobalt from nickel from a leach solution containing both metals.

The impurity levels found in the cobalt product were similar to those found in cobalt powder produced from industrial aqueous solutions. In the Sherritt Gordon operation (Fort Saskatchewan Plant)[75] cobalt is produced in a cycle comprising one 'nucleation' reduction with a Na_2S-NaCN catalyst and 30-50 'densification' reductions, in which the produced cobalt powder is used as a catalyst. Cobalt precipitated by hydrogen from this aqueous ammonium sulphate system contains: 0.05% carbon, 0.03% sulphur, 0.1% nickel, 0.01% iron, and approximately 99.8% cobalt. The levels of nickel and iron impurities are dependent upon the efficiency of the purification steps preceeding the reduction. The catalysts and surface active reagents added to the reduction solution are the main sources of the sulphur and carbon impurities.

The powder produced using direct hydrogen reduction of the organic phase also analyzes approximately 99.8% cobalt. It is important to note that impurities such as carbon can be easily removed by treatment with hydrogen at temperatures above 800 °C, and thus the impurity levels can be lowered.[75]

SECTION 6.2 : X-RAY DIFFRACTION

Every atom in a crystal scatters an X-ray beam incident upon it in every direction. Even the smallest crystal contains a very large number of atoms, and therefore the chance that these scattered waves would constructively interfere would be approximately zero, except for the fact that the atoms in crystals are arranged in a regular, repetitive manner.[76] Atoms located exactly on the crystal planes contribute maximally to the intensity of the diffracted beam. Atoms exactly halfway between the planes exert maximum destructive interference. Those at some intermediate location interfere constructively or destructively, depending upon their exact location, but with less than maximum effect. Furthermore, the scattering power of an atom for X-rays depends upon the number of electrons it possesses. Thus, the position of the diffraction beams from a crystal depends only upon the size and shape of the repetitive unit of the crystal and the wavelength of the incident X-ray. The intensities of the diffracted beams depend upon the type of atoms in the crystal and the location of the atoms in the unit cell. No two substances have absolutely identical diffraction patterns when one considers both the direction and intensity of all diffracted beams. The diffraction pattern is thus a 'fingerprint' of a crystalline compound and the crystalline components of a mixture can be identified individually. The diffraction pattern of an unknown sample is compared with the patterns of known substances until a match is obtained and positive identification established.

A sample of cobalt powder produced from Experiment R-5 (325 °C, 500 p.s.i. H_2, no seed, 5 hours) was analyzed using X-ray diffraction and the results are compared with cobalt patterns from the ASTM powder diffraction file in Table 6.2. The operating conditions for the X-ray analysis are given in Section 3.6.

α-COBALT ASTM FILE 5-0727 'd' (Å)	I/I₀	LINE #	β-COBALT ASTM FILE 15-806 'd' (Å)	I/I₀
2.165	20	1	2.0467	100
2.023	60	2	1.7723	40
1.910	100	3	1.2532	25
1.252	80	4	1.0688	30
1.149	80	5	1.0233	12
1.083	20	6		
1.066	80	7		
1.047	60	8		
1.015	20	9		

'd' (Å)	EXPERIMENTALLY DETERMINED IDENTIFICATION
2.169	α-1 line
2.022	α-2 line
1.913	α-3 line
1.250	α-4 or β-3 lines
1.144	α-5 line
1.067	α-7 or β-4 lines
1.048	α-8 line
2.047	β-1 line
1.770	β-2 line

TABLE 6.2 - EXPERIMENTAL X-RAY DIFFRACTION PATTERN (BOTTOM) COMPARED TO ASTM STANDARDS (TOP)

It appears that the powder sample is a combination of both α- and β-cobalt. All of the α and β cobalt lines with relative intensities (I/I_o) of 20 or more were detected, although 2 of these lines could be due to either allotrope. There were no lines that could not be attributed to either α or β cobalt.

Hull[77] was the first investigator to report that cobalt can exist in two forms - hexagonal close-packed (α, low temperature form) and face-centered cubic (β, high temperature form). There is, however, no general agreement as to the transformation temperature, and X-ray evidence has shown that the two phases often coexist in the same specimen over a wide range of temperatures.[78,79] There should be, of course, a definite temperature at which one form transforms into the other, but with cobalt the transformation temperature appears to be affected by the grain-size of the sample.[79] One possible explanation is that the changes in surface area may become comparable with the energy of the transformation for small grains.[80] For large grains, the transformation occurs at temperatures close to 400 °C, while for smaller grains, the transformation can occur at temperatures as low as 320 °C.[78] Even when cooled to room temperature, the samples contained a mixture of both allotropes.

In the present system when no seed was added, cobalt was precipitated onto the immersed titanium stirrer and the first cobalt particles to grow were sub-micron in size.

Therefore, it is possible that the cobalt powder produced using hydrogen reduction could be a combination of both forms even at reduction temperatures well below 400 °C.

SECTION 6.3 : PARTICLE SIZE DISTRIBUTION

The particle size distribution of the cobalt powder was determined using a Warman Cyclosizer. The cyclosizer unit consists of five hydrocyclones arranged in series such that the overflow of one unit is the feed to the next unit.[81]

The individual units are inverted in relation to conventional cyclone arrangements, and at the apex of each, a chamber is situated so that the discharge is effectively closed. Water is pumped through the units at a controlled rate, and a weighed sample of solids is introduced ahead of the cyclones.

The tangential entry into the cyclone induces the liquid to spin, causing a portion of the liquid, together with the faster-settling particles, to leave via the apex opening. The remainder of the liquid, together with the slower-settling particles, is discharged through the vortex outlet and reports to the next cyclone in the series. There is a successive decrease in the inlet area and vortex outlet diameter of each cyclone in the direction of the flow, resulting in a corresponding increase in both the inlet velocity and the centrifugal forces within the cyclone. This results in a successive decrease in the limiting particle-separation size of the cyclones.

Complete elutriation normally takes place within 20 minutes, after which the sized fractions are collected by discharging the contents of each apex chamber into separate beakers. The water is removed, and the solids are allowed to dry prior to weighing.

Particle size distributions were performed on the cobalt seed (Fisher Scientific Company - C363) and on the product after three 'densification' runs. The results are given in Table 6.3:

SIZE CLASS (μm)	SEED (%)	3 'DENSIFICATION' RUNS (%)
- 7.0	23.5	10.0
+ 7.0 - 8.9	17.9	13.0
+ 8.9 - 13.0	33.4	19.1
+ 13.0 - 17.4	18.6	35.4
+ 17.4 - 22.9	3.0	16.4
+ 22.9	3.6	6.1

TABLE 6.3 - PARTICLE SIZE DISTRIBUTIONS

As Table 6.3 clearly shows, there is definite growth in the cobalt particles after three 'densification' runs. In particular, there is significant growth in the largest three size classes.

This approach is similar to the 'densification' procedure employed by Sherritt Gordon Mines Limited.[75] In their plant, the cobalt powder is essentially less than 5 μm after one 'nucleation' run. After one 'densification' run, half of the powder is greater than 15 μm and after fifteen runs, half of the product is greater than 44 μm. Although only three 'densification' runs were attempted in the present investigation, it is expected that the particles would have grown in a similar manner with more 'densification' runs. The number of 'densification' runs, and hence the final particle size, is determined by the future application of the powder.

A particle size analysis of the product was not possible when no seed was added as the cobalt produced plated onto the titanium stirrer.

SECTION 6.4 : SCANNING ELECTRON MICROSCOPY

Unlike the optical or the transmission electron microscope, the scanning electron microscope has only one lens (a condenser lens), which focuses electrons emitted from the electron gun to a fine spot on the surface of the specimen being examined.[82] As its name implies, the primary electron beam is scanned, or deflected, in a raster on the surface of the sample. This is accomplished by X-Y deflection plates which are placed on opposite sides of the beam.

When the primary electron beam strikes the surface of the sample, its energy is converted into many different forms.

A portion of this energy is converted into secondary electrons. Secondary electrons are electrons which are excited within the specimen by the higher primary ones. These electrons have extremely low energies (<30 eV) and therefore have rather limited ranges within the specimen. Because of their limited ranges, those which leave the sample without being absorbed are only from the top 5-50 Å thickness layer, depending on the material being analyzed. Due to the low energies of these elctrons, they are easily attracted by a detector mesh which incorporates a potential of approximately 200 volts. The attracted electrons are processed, and a visual image of the specimen is presented on a cathode ray tube.

The scanning electron microscope (JEOL-JSM-35S) located in the McGill Department of Epidemiology was used to examine three different samples:

1) cobalt produced when no external seed was added (Figure 6.1)
2) cobalt powder purchased from Fisher Scientific Company (Figure 6.2)
3) cobalt powder after three 'densification' runs using cobalt purchased from Fisher Scientific Company as the initial seed (Figure 6.3).

The scanning electron microscope revealed that the surface of the 'cobalt foil' (Figure 6.1) takes on a definite crystallographic facetted appearance. Most of the individual grains are sub-micron in size. The 1 μm bar is shown in the bottom right-hand corner of the photograph. The foil appears to be only several microns thick.

A photograph of a typical sample of cobalt powder purchased from Fisher Scientific Company is shown in Figure 6.2. Most of the particles were found to be less than 20 μm in size, which is in agreement with the results obtained using the Warman Cyclosizer (Section 6.3). The surface of each of the particles appears to be extremely smooth and irregular in shape.

A photograph of a sample taken after three 'densification' runs using cobalt powder as an initial seeding agent is shown in Figure 6.3. In contrast to Figure 6.2, the surface of the particles are extremely rough. It appears as though cobalt metal has precipitated onto the seed. This would result in a coarsening of the individual particles, which is again in agreement with the results of Section 6.3.

FIGURE 6.1 - ELECTRON MICROGRAPH OF COBALT PRODUCED IN THE ABSENCE OF A SEED

FIGURE 6.2 - ELECTRON MICROGRAPH OF COBALT USED AS INITIAL SEED

FIGURE 6.3 - ELECTRON MICROGRAPH OF COBALT AFTER THREE 'DENSIFICATION' RUNS

CHAPTER SEVEN

CONCLUSIONS

SECTION 7.1 : PROCESS EVALUATION

The present investigation has shown that high purity cobalt powder can be produced by reacting cobalt-loaded KELEX 100 with hydrogen at temperatures between 250 and 325 °C. There are numerous advantages that this system has over a conventional acid stripping system and these are outlined in Section 2.1. In particular, hydrogen stripping could solve the problems encountered when cobalt is acid stripped from loaded KELEX 100. Under acid stripping conditions, dissolved cobalt is oxidized to the cobaltic state, which results in the formation of a highly stable chelate complex.

The behaviour of the extractant during the reduction experiments was followed using infrared spectroscopy and gas-liquid chromatography. It was shown in Chapter four that the organic extractant was regenerated after reduction and no signs of organic degradation were detected. Furthermore, the extractant was recycled 8-10 times with no loss of loading capacity. However, it would be necessary to run a continuous pilot-plant operation for an extended period to evaluate the long term stability of the extractant in the present application.

The major impurities found in the product were carbon, hydrogen, and oxygen. As compared to reduction from aqueous solutions, the impurity levels were found to be quite acceptable.

When no seed was added to the system, the cobalt product plated onto the immersed metallic surfaces of the autoclave. When activated carbon or cobalt powder was added to the system prior to reduction, the plating phenomenon was prevented and the cobalt deposited onto the seed material. By recycling the powder, considerable particle coarsening was achieved. The cobalt powder produced by hydrogen stripping techniques can be used in three main areas: (1) in the manufacture of chemicals, (2) in alloying, and (3) in the production of fabricated articles by powder-metallurgy techniques.

The temperature at which reduction occurs in the KELEX 100 system (250-325 °C) is higher than the temperature at which reduction occurs in an aqueous system (120-180 °C).[83] This is probably due to relatively weak ammine formation in the aqueous system, in contrast to strong chelate formation in the organic system. It should be noted that the specific heat of water (~1.0 cal/gm/°C) is twice that of aliphatic hydrocarbons (~0.5 cal/gm/°C) so the heating costs for the two solutions should be comparable.

The hydrogen pressure range (1.38-3.45 MPa) examined in the present investigation is the same as that in an aqueous system.[83]

Since the cobalt concentration in the present study (3.5 g.p.l.) and in the aqueous system (>25 g.p.l.) are so dissimilar, it would be meaningless to compare the time taken to precipitate all of the cobalt from solution.

Separation of the metal powder from the bulk of the organic phase is expected to be quite easy, although it is difficult to remove the viscous film of organic that remains attached to the particles. The solids could be recovered by conventional filtration or by an innovative technique known as 'High Gradient Magnetic Separation'.

A high gradient magnetic separator consists of an iron-clad solenoid surrounding a matrix of ferromagnetic steel wool.[84] The matrix perturbs the field creating large field gradients and consequently large magnetic forces. The magnetic particles in the wet feed are trapped by the matrix and these particles are subsequently flushed out after removing the field. The flow rate of organic solution through the magnet could be adjusted to recover all particles above a given size. All particles below this size would exit from the magnet with the liquid and hence be recycled for a further reduction run. The particles trapped in the magnet could be flushed out with a suitable liquid, such as acetone, to remove any organic liquid entrained in the particles.

This study has shown that it is technically feasible to precipitate cobalt directly from loaded KELEX 100 solutions by reaction with hydrogen. At present, no cost analysis has been performed to determine whether or not this process is economically feasible.

SECTION 7.2 : SPECIFIC FINDINGS

The study of direct cobalt precipitation from loaded KELEX 100 using hydrogen under pressure has allowed a number of conclusions to be drawn pertaining to the technical feasibility of this process. These conclusions are presented below:

1) A novel technique has been developed for direct cobalt recovery with hydrogen from a loaded organic phase containing a commercial chelating extractant. KELEX 100, an alkylated 8-hydroxyquinoline extractant, was shown to satisfy the requirements of chemical stability, thermal stability, and organic regeneration after reduction.
2) Cobalt was precipitated from solution at temperatures between 250-325 °C and hydrogen pressures between 200-500 p.s.i. (1.38-3.45 MPa). An increase in operating temperature and/or hydrogen pressure accelerates the reaction kinetics.
3) External seed was not required to initiate the reaction, however seed is desirable since it accelerates the precipitation kinetics and prevents the plating of cobalt on the immersed metallic parts of the autoclave.
4) An increase in cobalt chelate age or a decrease in cobalt chelate concentration retards the reaction kinetics.
5) The stirring speed did not have any affect on the kinetics within the range of experimentation.
6) The cobalt powder produced was a combination

of two allotropes of the metal: hexagonal close-packed (α) and face-centered cubic (β).

7) The major impurities in the cobalt powder were found to be carbon (0.08-0.18 weight %), hydrogen (0.003-0.009 weight %), and oxygen (0.065-0.100 weight %). The carbon and hydrogen impurities originated from organic entrainment during filtration. The oxygen impurity was due to surface oxidation of the cobalt particles.
8) Precipitate coarsening can be accomplished through a series of 'densification' runs. During the reduction experiments, cobalt precipitated onto the seed added to the system.
9) This process may offer a means by which cobalt can be separated from nickel from a leach solution containing both metals.

SECTION 7.3 : FURTHER INVESTIGATIONS

The findings of the present work provide an extra degree of flexibility to the hydrometallurgist who considers the application of solvent extraction in the metal producing industry. However, a great amount of research has yet to be performed in the following areas before an attempt is made to scale up this process to production level:

1) An extensive recycling of the organic solution should be carried out to allow for a more precise determination of the extractant losses.
2) Industrial leach solutions must be used in order to determine the amount of impurities

transferred to the final metal product.

3) The apparent 'polymerization' of loaded KELEX 100 during ageing should be clarified through specially designed spectroscopic studies.
4) Academic studies using analytical chemical techniques should be carried out to determine whether the cobalt(III) complex is reduced via a cobalt(II) intermediate complex or directly to metal.

SECTION 7.4 : CLAIM TO ORIGINALITY

Many aspects of this work constitute contributions to original knowledge. The following contributions are, in the author's opinion, the most important:

1) This is the first time that a successful attempt has been made to precipitate cobalt directly from KELEX 100 using hydrogen under pressure.
2) This is the first time that a successful attempt has been made to separate cobalt from nickel using direct hydrogen stripping of KELEX 100. The nickel was removed using conventional acid stripping and the cobalt was recovered using direct hydrogen stripping.

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APPENDIX

EXPERIMENTAL DATA AND CONDITIONS

EXPERIMENT # R-1

CONDITIONS: 250 °C, 500 p.s.i., 900 RPM, No Seed

COMMENTS: Temperature Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	3.47	3.43	3.29	3.26	3.19
% REMAINING IN ORGANIC PHASE	100	99	98	94	93	91

EXPERIMENT # R-2

CONDITIONS: 275 °C, 500 p.s.i, 900 RPM, No Seed

COMMENTS: Temperature Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.49	3.39	3.21	3.04	2.90	2.72
% REMAINING IN ORGANIC PHASE	100	97	92	87	83	78

EXPERIMENT # R-3

CONDITIONS: 290 °C, 500 p.s.i., 900 RPM, No Seed

COMMENTS: Temperature Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	3.36	3.12	2.80	2.59	2.45
% REMAINING IN ORGANIC PHASE	100	96	89	80	74	70

EXPERIMENT #

R-4

CONDITIONS: 305 °C, 500 p.s.i., 900 RPM, No Seed

COMMENTS: Temperature Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.51	3.30	3.02	2.56	2.11	1.83
% REMAINING IN ORGANIC PHASE	100	94	86	73	60	52

EXPERIMENT #

R-5

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, No Seed

COMMENTS: Temperature Survey (4 hour sample used for infrared spectroscopy and G.L.C)

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	2.70	1.12	0.56	0.35	0.14
% REMAINING IN ORGANIC PHASE	100	77	32	16	10	04

EXPERIMENT #

R-6

CONDITIONS: 325 °C, 300 p.s.i., 900 RPM, No Seed

COMMENTS: Pressure Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.48	2.78	2.02	1.25	0.80	0.59
% REMAINING IN ORGANIC PHASE	100	80	58	36	23	17

EXPERIMENT # R-7

CONDITIONS: 325 °C, 200 p.s.i., 900 RPM, No Seed

COMMENTS: Pressure Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.52	2.96	2.46	2.08	1.69	1.44
% REMAINING IN ORGANIC PHASE	100	84	70	59	48	41

EXPERIMENT # R-8

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, 12 Hours

COMMENTS: Age of Cobalt Chelate Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	2.70	1.12	0.60	0.35	0.11
% REMAINING IN ORGANIC PHASE	100	77	32	17	10	03

EXPERIMENT # R-9

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, 3 Days

COMMENTS: Age of Cobalt Chelate Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	2.84	1.89	1.09	0.67	0.53
% REMAINING IN ORGANIC PHASE	100	81	54	31	19	15

EXPERIMENT #

R-10

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, 7 Days

COMMENTS: Age of Cobalt Chelate Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	3.01	2.56	2.10	1.75	1.51
% REMAINING IN ORGANIC PHASE	100	86	73	60	50	43

EXPERIMENT #

R-11

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, 10 Days

COMMENTS: Age of Cobalt Chelate Survey

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.51	3.12	2.74	2.39	2.14	1.97
% REMAINING IN ORGANIC PHASE	100	89	78	68	61	56

EXPERIMENT #

R-12

CONDITIONS: 325 °C, 500 p.s.i., 900 RPM, No Seed

COMMENTS: Initial Cobalt Chelate Concentration

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	1.9	1.6	1.3	1.1	0.9	0.8
% REMAINING IN ORGANIC PHASE	100	84	68	58	47	42

EXPERIMENT #
R-13

CONDITIONS: 305 °C, 500 p.s.i., 450 RPM, No Seed

COMMENTS: Stirring Rate Survey

TIME (HR)	0	1.2	2.2	3.2	4.2	5.2
g.p.l. Co	3.53	3.18	2.68	2.47	2.05	1.91
% REMAINING IN ORGANIC PHASE	100	90	76	70	58	54

EXPERIMENT #
R-14

CONDITIONS: 305 °C, 500 p.s.i., 700 RPM, No Seed

COMMENTS: Stirring Rate Survey

TIME (HR)	0	1.4	2.4	3.4	4.4
g.p.l. Co	3.54	2.97	2.69	2.27	2.05
% REMAINING IN ORGANIC PHASE	100	84	76	64	58

EXPERIMENT #
R-15

CONDITIONS: 275 °C, 500 p.s.i., 900 RPM, Co Seed

COMMENTS: Seeding With Cobalt Powder

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.45	3.07	2.42	1.76	1.38	1.04
% REMAINING IN ORGANIC PHASE	100	89	70	51	40	30

EXPERIMENT #
R-16

CONDITIONS: 275 °C, 500 p.s.i., 900 RPM, C Seed

COMMENTS: Seeding With Carbon Powder

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.48	2.85	2.12	1.57	1.25	1.22
% REMAINING IN ORGANIC PHASE	100	82	61	45	36	35

EXPERIMENT #
R-17

CONDITIONS: 250 °C, 500 p.s.i., 900 RPM, Co Seed

COMMENTS: Seeding With Cobalt Powder

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.50	3.33	3.08	2.66	2.24	2.14
% REMAINING IN ORGANIC PHASE	100	95	88	76	64	61

EXPERIMENT #
R-18

CONDITIONS: 305 °C, 300 p.s.i., 900 RPM; No Seed

COMMENTS: Experimental Reproducibility (#1)

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.51	3.40	3.33	2.91	2.63	2.39
% REMAINING IN ORGANIC PHASE	100	97	95	83	75	68

EXPERIMENT #
R-19

CONDITIONS: 305 °C, 300 p.s.i., 900 RPM, No Seed

COMMENTS: Experimental Reproducibility (#2)

TIME (HR)	0	1	2	3	4	5
g.p.l. Co	3.53	3.39	3.04	2.86	2.61	2.40
% REMAINING IN ORGANIC PHASE	100	96	86	81	74	68

EXPERIMENT #
R-20

CONDITIONS: 300 °C, 50 p.s.i. N_2

COMMENTS: Thermal Stability of KELEX 100

TIME (HR)	0	3	4	5	6	7	8
g.p.l. Co	3.50	3.50	3.51	3.47	3.50	3.43	3.51
% REMAINING IN ORGANIC PHASE	100	100	101	99	100	98	101

EXPERIMENT #
R-21

CONDITIONS: 200 °C, 50 p.s.i N_2 - Copper System

COMMENTS: See Reference #11

TIME (HR)

g.p.l. Cu

% REMAINING
IN ORGANIC
PHASE

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