HYDROGEN REDUCTION OF LEAD FROM
KELEX 100

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Masters of Engineering.

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March, 1987
Montreal, Quebec
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ISBN 0-315-38140-X

ABSTACT

In this study the possibility of producing lead metal by loading lead into KELEX 100 (an alkylated 8-hydroxyquinoline commercial extractant produced by Sherex Chemical Company) from an aqueous acetate solution and then reacting the loaded organic with hydrogen was investigated.

Prior to hydrogen reduction, the extraction of lead by KELEX 100 was studied, along with the stripping abilities of both nitric and acetic acid for removing lead from loaded KELEX 100. Lead was found, by the method of slope analysis, to be extracted as a 2 to 1 organic ligand to metal species (i.e. as PbR_2), and could easily be stripped from KELEX 100 by either nitric or acetic acid to produce supersaturated lead aqueous solutions.

The thermal and chemical stability of the extractant was investigated using gas-liquid chromatography and infrared spectroscopy and found to exhibit excellent stability within the temperature and pressure range used to study the kinetics of reduction (493-533 K and 1.38-4.14 MPa H_2). However, pressure hydrogen stripping above the melting point of lead resulted in decomposition of the organic molecule.

The kinetics of lead reduction was studied with respect to the effects of temperature, hydrogen partial pressure, seed addition, agitation, and chelate age on the reaction rate. Only temperature, pressure, and seed addition influenced the

reaction rate, and the effects of seeding suggest a heterogeneous nucleation mechanism.

The characteristics of the lead metal produced by hydrogen reduction were also investigated.

RESUME

Cette étude évalue la possibilité de produire du plomb métallique par réduction directe d'un agent d'extraction chargé dans une autoclave sous atmosphere d'hydrogène. L'agent d'extraction est le KELEX 100. Ce produit est un agent d'extraction commercial fabriqué par la compagnie Sherex Chemical Co., il est chargé à partir d'une solution aqueuse d'acétate de plomb.

En préalable à la reduction par l'hydrogène, l'extraction du plomb par KELEX 100 est étudié ainsi que les capacités des acides nitrique et acétiques de re-extraire le plomb à partir des solutions de KELEX 100. Nous avons mis en évidence par la mèthode d'analyse de pente que le plomb est extrait sous forme de chélate avec un rapport ligand/plomb de 2 à 1 (comme par exemple PbR_2). Le plomb peut être facilement extrait du KELEX 100 par l'acide nitrique ou acétique, produisant des solutions aqueuses supersaturées.

La stabilité thermique et chimique de l'agent d'extraction est etudieé par chromatographie en phase liquide et gazeuse et par spectroscopie infra-rouge. L'agent possède une stabilité chimique et physique excellente pour des températures comprises entre 493 a 533 K et des pression d'hydrogène allant de 1.38 et 4.14 MPa. Par contre, on a montré que l'utilisation de température plus élevée que le point de fusion du plomb provoque la décomposition de la phase organique.

Ce travail presente des données décrivant les effets de la température, de la pression d'hydrogène, de l'introduction du plomb métallique en poudre comme germes, du degré d'agitation et du vieillissement du chélate de plomb sur la cinétique de précipitation. Ces résultats démontrent que la vitesse réactionelle ne dépend que de la température, de la pression et de la présence de germes. Ce dernier facteur suggère un mécanisme de nucléation hètèrogene.

Les caractéristiques du plomb métalliques produit par reduction suos hydrogène fuent aussi étudiées.

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CHAPTER 1

INTRODUCTION

Solvent extraction is presently being used commercially in the hydrometallurgical industry as a unit process to purify and concentrate metal values from very dilute leach liquors.[1] This is accomplished by transferring the metal into and out of immiscible aqueous and organic solvents. The organic phase in this process is used solely as a transfer medium for the metal. But, investigations have been performed whereby chemical reactions are conducted directly in the organic phase to produce metal.[2]

Burkin [3] was the first to suggest that metals could be reduced in organic solutions with the use of hydrogen gas to produce high purity metal powders and regenerate the organic extractant. Recent attention on the study of such a process has focused on the KELEX 100/decanol/kerosene system. [2] This system has been shown to have good chemical (resistant to hydrogenation) and thermal (resistant to pyrolysis) stability [4], and was therefore chosen as the organic phase for this investigation.

Since the extractant used was designed for the extraction of copper from sulphate solutions [5], its extraction characteristics for lead were not known. Therefore, it was necessary to determine under what conditions it was possible to extract lead, and what species is extracted.

Research in the hydrometallurgical processing of lead and other base metal sulphides has concentrated on chloride media as the lixiviant.[6,7,8,9] But none of these processes has yet to see commercial application. On the other hand, the use of acetate media has been applied for the leaching of lead from copper refinery anode slimes with two processes in commercial operation.[10,11] Extraction of lead with KELEX 100 from an acetate solution followed by hydrogen reduction may provide a suitable means for producing lead metal.

Successful application of pressure hydrogen stripping requires that the extractant molecule exhibit good chemical and thermal stability under the experimental conditions required to produce acceptable kinetics and good metal product characteristics. Therefore, the chemical and thermal stability of lead loaded KELEX 100 during the reduction of lead with hydrogen at high temperature and pressures was investigated. The effects of temperature, pressure, agitation, seeding, and lead-KELEX 100 chelate age on the kinetics of reduction, along with the lead metal product characteristics, were examined.

CHAPTER 2

LITERATURE SURVEY

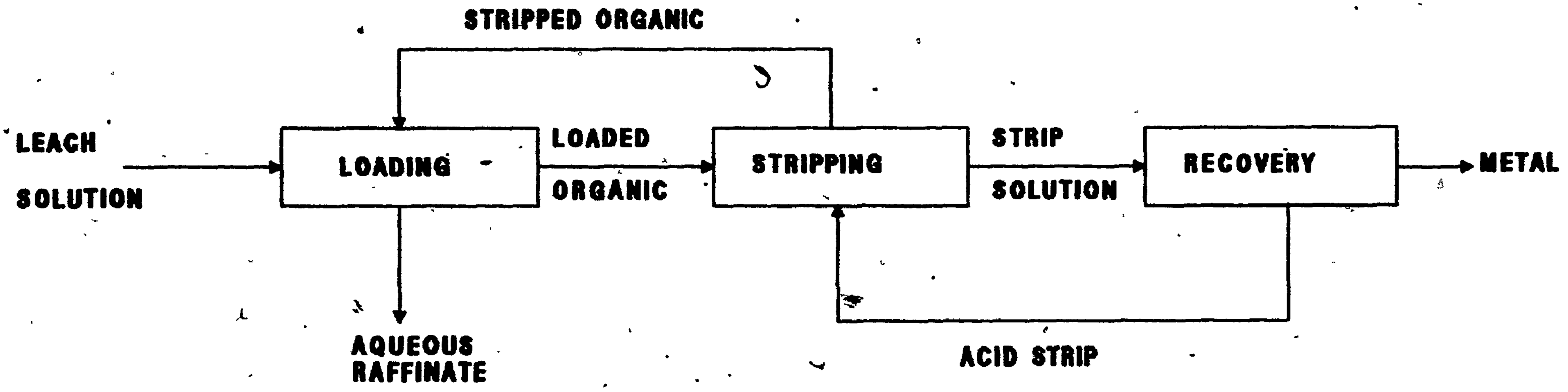
2.1 SOLVENT EXTRACTION IN HYDROMETALLURGY

In this chapter the generalized hydrometallurgical flowsheet will be briefly reviewed with emphasis on solvent extraction. Recent advances in the hydrometallurgical processing of lead materials will also be presented with emphasis on the extraction of lead from galena (PbS). A detailed description of the use of ammonium acetate leaching processes for the removal of lead from copper anode slimes will then be given. The final section of the chapter deals with previous work on the reduction of metals from aqueous and organic solutions with hydrogen.

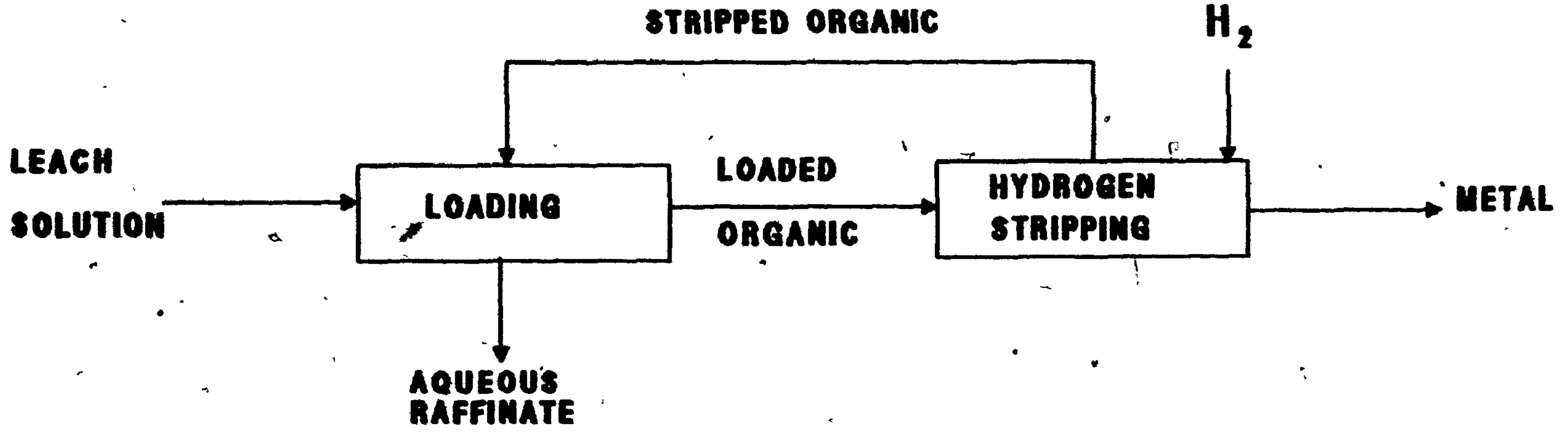
2.1.1 CONVENTIONAL SOLVENT EXTRACTION

Solvent extraction is now a well established process in hydrometallurgy. Its first application was to the recovery of nuclear materials.[12] But, solvent extraction sees its greatest application in the extraction of copper. It has been ranked, by some, as the most important development in separations since the introduction of selective flotation reagents in the early 1920's.[13]

A generalized flowsheet using solvent extraction to purify and concentrate metal values prior to metal recovery is shown in Figure 2.1 (a), and compared to a novel flowsheet proposed



a) CONVENTIONAL SOLVENT EXTRACTION



b) SOLVENT EXTRACTION WITH HYDROGEN STRIPPING

Figure 2.1 Flow diagrams of a) conventional solvent extraction and b) solvent extraction with hydrogen stripping.

for the recovery of metals from loaded organic extractants using hydrogen.

There are two main stages in conventional solvent extraction, namely loading and stripping. In the loading stage the leach solution is brought into contact with an immiscible organic phase into which the metal value is transferred. The aqueous raffinate from loading is then recycled to leaching. The loaded organic moves on to stripping where the metal is transferred to an aqueous strip solution. The stripped organic is recycled to the loading stage and the metal is recovered from the strip solution, regenerating it to be reused for stripping.

The best example of this type of operation in commercial use is the sulphuric acid dump or heap leaching of low grade (2 to 3 percent) copper oxide ores followed by solvent extraction and subsequent electrowinning of copper.[14,15] Leach solutions contain between 1 and 2 grams per liter (gpl) copper and a greater concentration of iron at a pH lying between 1 and 2. The copper is selectively extracted into the organic phase and then stripped by spent electrolyte (100-120 gpl H_2SO_4), upgrading it from about 25 to 30 gpl copper.

A novel process for producing copper directly from chelating type extractants by hydrogen reduction has been proposed.[16] In this process the organic phase is stripped of the copper to produce fine copper powder and regenerate the extractant by reaction with hydrogen gas at high temperatures and pressures (known as pressure hydrogen stripping). This combines the stripping and metal recovery step in conventional solvent extraction into one stage. A more detailed description of the chemistry of hydrogen reduction of metals from organic solvents will be given later in the chapter.(Section 2,3.2)

2.1.2 COMPONENTS IN THE ORGANIC PHASE

The successful application of solvent extraction to hydrometallurgy has been due to the production and use of extractants highly selective for the required metal. It is usual to put the extractant in a diluent to enhance various aspects of the extraction and stripping process. A diluent is used to decrease the viscosity of the extractant, since most extractants used in commercial solvent extraction are viscous and cannot be used in the as-received form. Other reasons for using a diluent are to provide a suitable concentration of the extractant as required for a particular purpose, to decrease emulsion-forming tendencies of the extractant, and to improve dispersion and coalesence properties of the solvent. Both aromatic and aliphatic materials are available for use as diluents in solvent extraction processes and are fractions of crude oil,[6] which makes them available in bulk and relatively cheap.

Modifiers are commonly used to overcome third phase and emulsion tendencies in a solvent system. The four most used reagents are isodecanol, 2-ethylhexanol, p-nonylphenol and tributylphosphate. Researchers have found that diluents and modifiers play a substantial role in determining the characteristics of an extraction system [17,18,19].

There are several ways of classifying extractants. In a recently published authoritative book on solvent extraction in hydrometallurgy the authors classify the ~~various~~-extractants according to the following classes:[20]

(1) those which involve solvation of the metal ion

(2) those which involve ion association

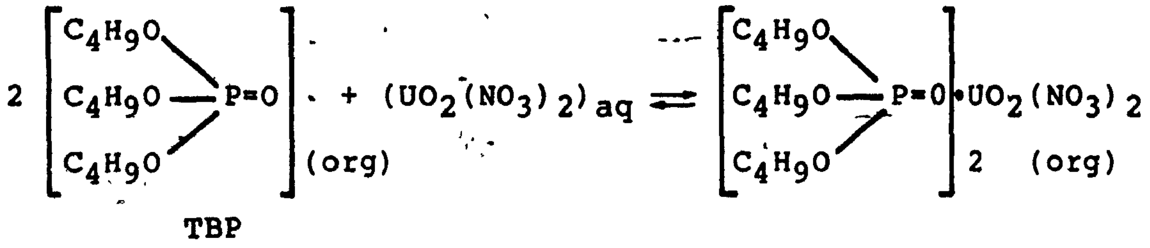
(3) those which involve compound formation

2.1.3 EXTRACTANTS INVOLVING SOLVATION

Extractants in this group have an oxygen atom with a lone pair of electrons which extract electrically neutral inorganic species by solvation. Solvation of the inorganic metal containing species may occur either by coordination of the oxygen bearing extractant molecules to the central metal ion or by hydrogen bonding between the proton in the extracted species and the oxygen in the solvent molecules [21].

Ritcey and Ashbrook [20] place this type of extractant into two main groups. Those organic reagents containing oxygen bonded to carbon, such as ethers, esters, alcohols and ketones, and those containing oxygen or sulphur bonded to phosphorus, as in alkylphosphates or alkythiophosphates. Examples of commercially available extractants of this type are tri-n-butyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), methyl isobutyl ketone (MIBK), and dibutyl carbitol (BUTEX).

Examples of metal extraction by solvating reagents are shown below:



Solvation due to coordination to the central metal ion (2.1)

$$\underset{(org)}{[(C_4H_9OCH_2CH_2)_2O]} + \underset{(aq)}{[HAuCl_4]} \rightleftharpoons \underset{(org)}{[(C_4H_9OCH_2CH_2)_2O{-}{-}{-}[HAuCl_4]}$$

Solvation due to hydrogen bonding-BUTEX (2.2)

2.1.4 EXTRACTANTS INVOLVING ION ASSOCIATION [20,22]

This type of extractant comprises amines and quarternary ammonium halides. High molecular weight primary (RNH_2) secondary (R_2NH) and tertiary (R_3N) amines that are organophilic weak bases are used for solvent extraction of anionic species from acidic solution. While the simple amines are ineffective at high pH, quarternary ammonium halides (R_4N) extract metal-anionic species from strong alkali solutions.

In order for primary, secondary, and tertiary amines to form ion-pairs with anionic metal species in solution they must first be converted to the appropriate amine salts to provide an anion to exchange with the metal species. The general reactions for the extraction of an anionic species with an amine is shown below:

1. Formation of ammonium salt

$$[R_3N]org + [HX]aq \rightleftharpoons \underset{\underline{\text{ion-pair}}}{[R_3NH^+X^-]org} \quad (2.3)$$

2. Anion-exchange process

$$[R_3NH^+X^-]org + [MY^-]aq \rightleftharpoons [R_3NH^+MY^-]org + [X^-]aq \quad (2.4)$$

Basic extractants have been used widely for a variety of applications in the extraction of U,V,W, and Co [23]. For the case of uranium extraction from sulphate media with a tertiary ammine, the following extraction mechanism has been shown to operate:

First, the amine forms its corresponding ammonium salt,

$$2\ [R_3N]org + [H_2SO_4]aq \rightleftharpoons [(R_3NH^+)_2SO_4{}^{-2}]org \quad (2.5)$$

and then the anion exchange reaction takes place

$$\underset{(org)}{2[(R_3NH)_2SO_4]} + \underset{(aq)}{[UO_2(SO_4)_3]^{-4}} \rightleftharpoons \underset{(org)}{[(R_3NH)_4UO_2(SO_4)_3]} + \underset{(aq)}{2[SO_4{}^{-2}]} \quad (2.6)$$

2.1.5 EXTRACTANTS INVOLVING COMPOUND FORMATION

Extraction involving compound formation occurs when using acidic and chelating extractants. Acidic extractants are cationic liquid ion exchangers and extract metals by a cation exchange mechanism.[24] In its simple form it is expressed by the following equation:

$$M^{n+}(aq) + nHR(org) \rightleftharpoons MR_n(org) + nH^+(aq) \qquad (2.7)$$

One organic reagent of this type used extensively in the metallurgical industry is di-(2-ethyhexyl) phosphoric acid (D2EHPA). D2EHPA sees applications in uranium recovery,nickel-cobalt separation, and europium extraction.[25,26] The virtues of this extractant in solvent extraction processing are its chemical stability, generally good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase, versatility in extraction, and availability. Also included in this class of extractants are the synthetically produced 'Versatic' carboxylic acids (Shell Chemical Co.).

In terms of tonnages of metal produced and reagent use, chelating type extractants are the most intensively used. It is the development of copper-specific reagents which has made copper solvent extraction a commercial reality, and many plants have been built.[27] To date, most of these plants treat dilute leach liquors from the sulphuric acid leaching of low grade oxide ores. Copper production in this manner accounts for about 15 percent of the world's primary copper metal production.[1]

Chelating type reagents for use in copper solvent extraction were first developed in the sixties and their development has continued, such that today there exists a wide variety for use in copper extraction as well as for the extraction of other metals. A summary of the most widely available chelating type extractants is given in Table 2.1[23].

KELEX 100 was developed in 1968 as an extractant for copper [5]. The application of this reagent to commercial operation has not been as successful as the LIX or ACORGA reagents, but it has received extensive investigations up to the pilot plant stage [28,29,30]. A combination of 20 v/o KELEX 100 in p-nonyl phenol is also available by the brand name of KELEX 120. This mixture was formulated to improve the

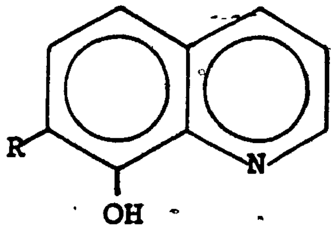
Table 2.1 Some solvent extraction reagents for hydrometallurgy.

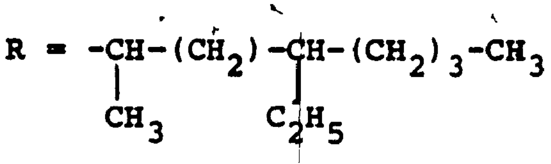
Type	Trade Name	Manufacturers	Commercial Uses
Hydroxyoximes	LIX63, LIX64N, LIX65N, LIX70, LIX71, LIX73	Henkel Corp.	Cu extraction & Ni extraction (LIX65N). Pd extraction.
	SME 529	Shell Chemical Co.	Cu extraction
	P5000 series	Acorga Ltd.	Cu extraction
Oxine derivatives	KELEX 100 & KELEX 120	Sherex Chemical Co.	Proposed for Cu extraction
Diketones	LIX54	Henkel Corp.	Proposed for Cu extraction

physical characteristics of extraction, compared to KELEX 100.[31]

Initial investigations of KELEX 100 for copper extraction from both dilute and concentrated solutions were encouraging, with KELEX 100 reported as having superior extraction kinetics and a greater extraction power when compared to extractants available at the time.[31,32] Discrimination of KELEX 100 for copper over iron, attributed to kinetic factors, was also reported as very good.[33]

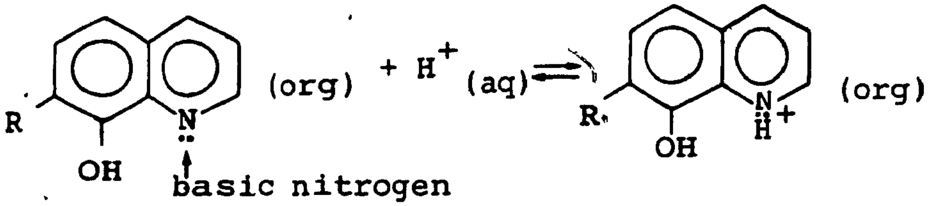
KELEX 100 is an alkyl derivative of a very commonly used analytical reagent 8-hydroxyqinoline (also known as oxine or 8-quinolinol). The main active component of KELEX 100 used to be 7-(1-vinyl-3,3,5,5,-tetramethylhexyl)-8-hydroxyquinoline. [34, 35] In 1976, the manufacturing process was changed such that the active component is now 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline and its structure is shown below.





$R = -\underset{\displaystyle CH_3}{CH}-(CH_2)-\underset{\displaystyle C_2H_5}{CH}-(CH_2)_3-CH_3$

The problem with KELEX 100, which has prevented it from being applied commercially for the recovery of copper, is its ability to form salts with acids. This is due to the fact that the tertiary nitrogen on the molecule behaves as a base and can pick up acid during stripping, which must be removed before recycling to the extraction stage. Protonation of the KELEX 100 molecule is shown below.



(2.8)

This problem is eliminated if hydrogen stripping is used.

2.2 HYDROMETALLURGICAL PROCESSING OF LEAD

The past twenty-five years has seen a boom in the development of hydrometallurgical techniques for the winning of lead and other base metals (Cu and Zn) from both primary and secondary sources [36]. The impetus has come from the need to find a more environmentally acceptable alternative to smelting, and the desire to exploit complex materials for which hydrometallurgical techniques are particularly suited.

2.2.1 HYDROMETALLURGICAL PROCESSES FOR PRODUCING LEAD

Focus on the extraction of lead from primary sources has been centered on the processing of PbS concentrates, bulk complex sulphide concentrates, and the so-called 'dirty' PbS concentrates obtained from the differential flotation of complex sulphides. Bulk concentrates are produced from the flotation of fine-grained, intimate associations of chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and galena (PbS) freely disseminated in a pyrite (FeS_2) or pyrrhotite ($Fe_{1-x}S$) matrix which sometimes contains valuable amounts of precious metals [37]. Many processes have been developed, and exploitation strategies proposed, for the treatment of complex sulphides [8,9]..Of the leaching media investigated chloride-based systems are the most extensively studied [6,7].

The MINIMET RECHERCHE [38] and U.S.B.M. [39] processes have been developed dedicated solely to the hydrometallurgical treatment of PbS concentrates capable of directly producing commercial lead. Both processes have similar flowsheets and use a chloride leach followed by a purification step and then electrowinning. Table 2.2 shows relevant information for the different unit processes.

Problems encountered with the operation of the molten salt electrolytic cell used in the U.S.B.M. process, and the desire to produce a lead deposit in a compact form from aqueous chloride media has spurred on investigations into the electrowinning of lead from various aqueous solutions.

Investigators have reported that deposits obtained from the electrowinning of lead from aqueous chloride media are characteristically dendritic and non-compact [40]. The electrodeposition of lead from buffered electrolytes containing ammonium acetate and acetic acid has been studied with the researchers reporting that lead had been deposited, in a smooth and compact form, on lead and copper electrodes [41]. The high solubility of $PbCl_2$ crystals in acetate media makes this process attractive as an alternative to molten salt electrolysis.

Table 2.2 Relevant information on the hydrometallurgical production of lead from PbS by the MINIMET RECHERCHE and U.S.B.M. Processes.

PROCESS	LEACHING	PURIFICATION	ELECTROWINNING
MINIMET RECHERCHE[a]	$FeCl_3$(+NaCl) brine leach of PbS concentrate	2 stage solution purification: 1. Coarse Purification: Cu,Ag,Bi cementation 2. Fine Purification: Ion exchange of Cu^+ and Ag^+	Pb electrowon from clear chloride solution in a special cell (Ti cathode and C anode) producing fine Pb powder
U.S.B.M.[b]	$FeCl_3$(+NaCl) brine leach of PbS concentrate	Crystallization of $PbCl_2$ from leach liquor by cooling	Electrolysis of $PbCl_2$ in $LiCl-KCl-PbCl_2$ fused salt electrolyte

a- developed to treat PbS concentrates from mixed sulphide ores

b- developed to treat PbS concentrates

The use of acetate media has also been investigated to process PbS concentrates. A study of the kinetics of oxidation of PbS in ammonium acetate solution and oxygen under pressure has shown that the reaction products are lead acetate in solution and elemental sulphur, the latter forming a nonpermeable film on the PbS crystal making this process unsuccessful [42]. But a successful attempt to use acetate electrolyte for direct electrowinning of lead from PbS concentrate compact anodes has recently been reported [43].

2.2.2 REMOVAL OF LEAD FROM COPPER ANODE SLIMES

Use of acetate media has been applied successfully to the treatment of copper anode slimes previously unsuitable for treatment by conventional means because of high lead content [5]. This patent describes a process for the removal of lead content in anode slimes by primary and secondary leaches in ammonium acetate solution at a temperature not exceeding 353 K. Lead dissolution is maximized, with minimal coextraction of other metals. The leach solution is then separated from the undissolved slime residue, while lead is crystallized and recovered from the separated leach solution as lead acetate.(See Figure 2.2)

A similar process has been developed by Kidd Creek Mines Ltd,, of Timmins, Ontario, Canada, in which an acetic acid pressure leach is used to remove the lead from their anode slimes. The lead is recovered as lead acetate crystals and sold as a marketable product. Details of the process are not well known since a patent search is ongoing [11].

Whereas the above patents call for the residue from leaching to be treated for recovery of precious metals and other metal values by conventional means, the INER Process [10] is a totally hydrometallurgical process which recovers

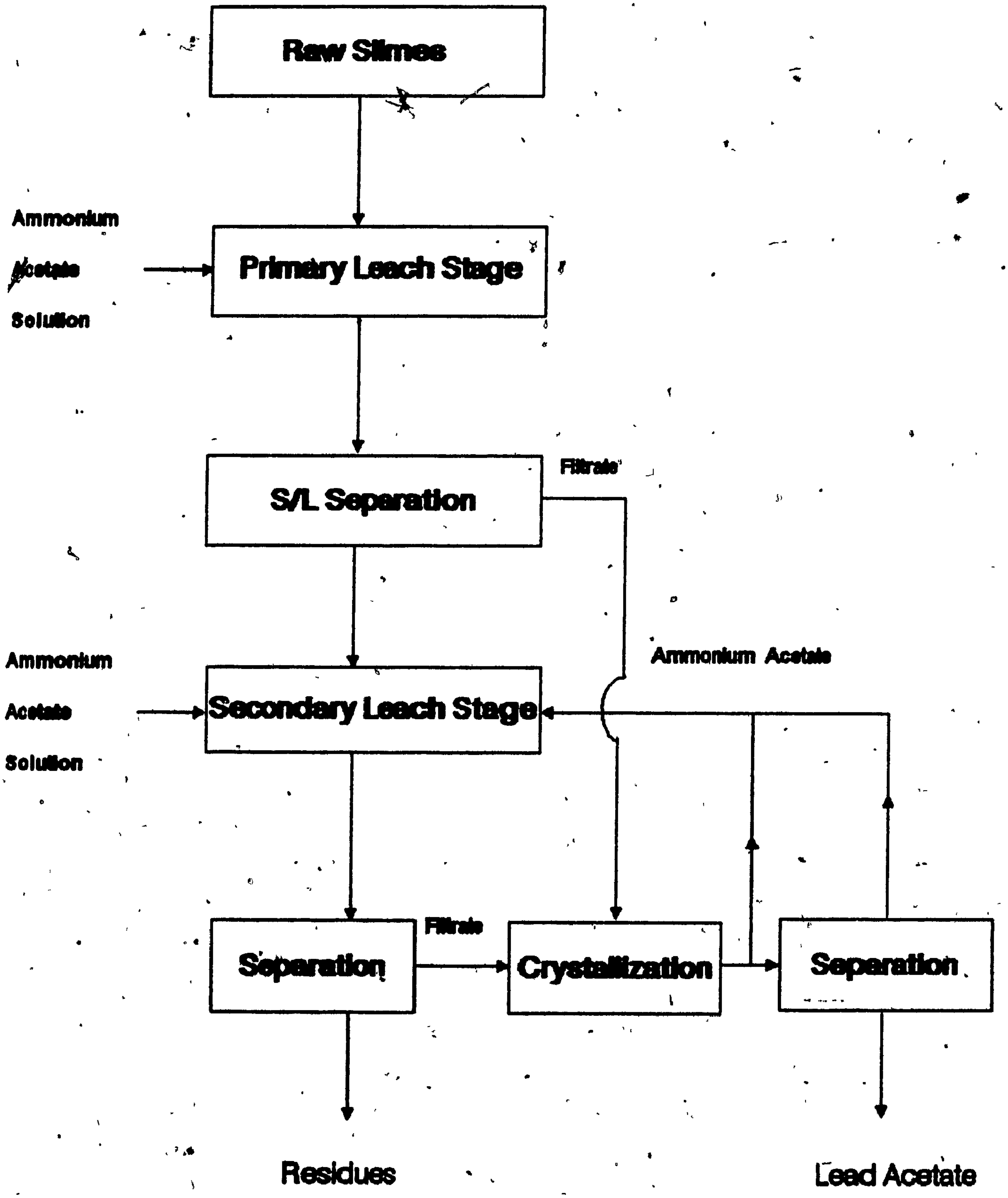


Figure 2.2 Removal of lead from copper anode slimes by leaching with ammonium acetate.

all metal values (including Au,Ag,Te,Se and Sn) from copper anode slimes. This process has been tested successfully in a pilot plant, and based on those results a production plant with a capacity of 300 tonnes of anode slime per year has been constructed. Figure 2.3 shows that part of the process which involves removal of lead. Five to seven normal acetate solution is used as the leaching reagent. The partially decopperized slimes are leached at a temperature ranging from 273 K to 343K. After 2 to 3 hours, 95% of the lead content is dissolved along with a small amount of copper. The lead and copper are co-extracted and selectively stripped using LIX 34 [44] or LIX 64N [45].

As evidenced from above, future hydrometallurgical techniques developed to treat anode slimes containing appreciable amounts of lead will focus some attention on the processing of lead from acetate solutions.

2.3 HYDROGEN REDUCTION OF METALS

2.3.1 HYDROGEN REDUCTION OF METALS FROM AQUEOUS SOLUTIONS

Many laboratory studies have been conducted on the reduction of metals in aqueous solutions by hydrogen, [46,47,48,49] and commercial application of this process has been realized [50,51]. Pressure hydrometallurgy is used by companies, such as Sherritt Gordon Mines Ltd., for both leaching and hydrogen reduction to produce nickel and cobalt powders as well as small amounts of copper powder for special

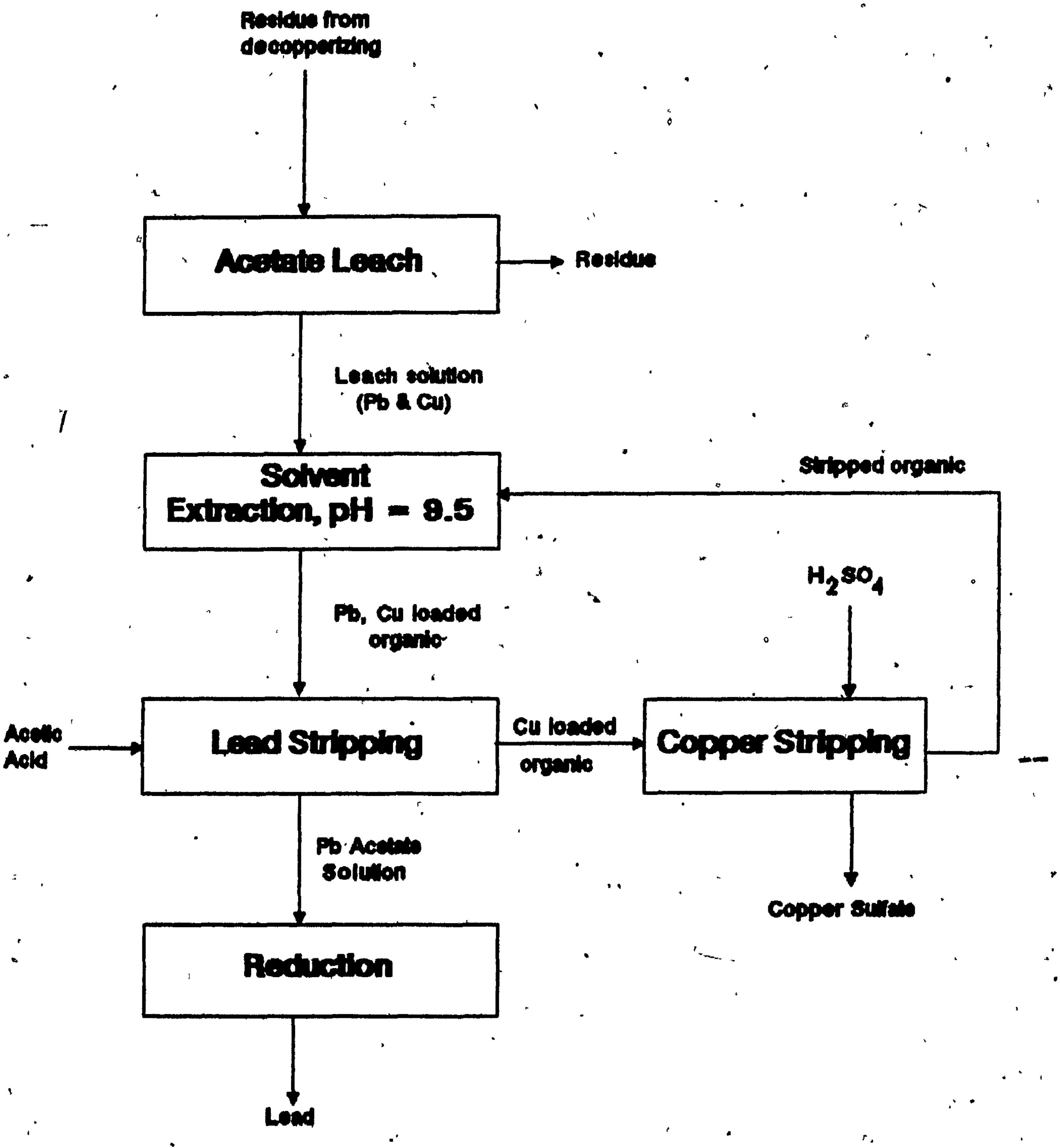


Figure 2.3 Lead removal in the INER process.

purposes.

The overall reaction for the reduction of metals in aqueous solution by hydrogen gas is shown below.

$$M^{n+}\ (aq) + nH_2\ (g) \rightleftharpoons M^{\circ}(s) + nH^{+}\ (aq) \qquad (2.9)$$

The thermodynamics of this reaction can be explained using the electrode potentials, E , of the following opposing half-reactions

$$M^{n+} + ne^{-} \longrightarrow M \qquad (2.10)$$

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (2.11)$$

The Nernst potentials for the above reactions at 298 K are given by

$$E_M = E_M{}^{o} + \frac{0.0592}{n} \ln [a_M{}^{n+}] \qquad (2.12)$$

for reaction 2.10, and

$$E_{H_2} = -0.0592\ pH - 0.0296 \log P_{H_2} \qquad (2.13)$$

for reaction 2.11, where

$E_M{}^{o}$ = standard Nernst reduction potential

n = number of electrons per ion

$a_M{}^{n+}$ = metal ion activity

P_{H_2} = hydrogen pressure

The total potential, E_T, for reaction 2.9 is given by the sum of potentials of the opposing half-reactions $\{E_T = E_M + (E_{H_2})\}$. For reduction to occur, the free energy change, ΔG, of the overall reaction must be negative. The free energy change of reaction 2.9 is given by

$$\Delta G = -nFE_T \tag{2.14}$$

where F = Faraday.

In Figure 2.4 the potential, E_M, of equation 2.12 is plotted as a function of metal ion activity for various metals. Superimposed on this is a plot of the potential, E_{H_2}, given by equation 2.13 as a function of pH at various constant P_{H_2} values. In Figure 2.4 the requirement for metal reduction is satisfied when the line representing the potential of the metal is above that representing the potential of hydrogen.

For an uncomplexed metal ion in solution the thermodynamic driving force for reduction is increased by increasing pH.[47] The increase in pH is limited by hydrolysis and precipitation of the metal salt. In commercial operations, the operating pH is maximized by the use of complexing agents such as ammonia. Complex formation of the metal prevents hydrolysis. In turn, complex formation makes hydrogen reduction more difficult since hydrogen must overcome the affinity of the metal for the complexing ligand instead of just displacing the water of hydrolysis. In determining the thermodynamics of hydrogen reduction when the metal is complexed, the electrode potential

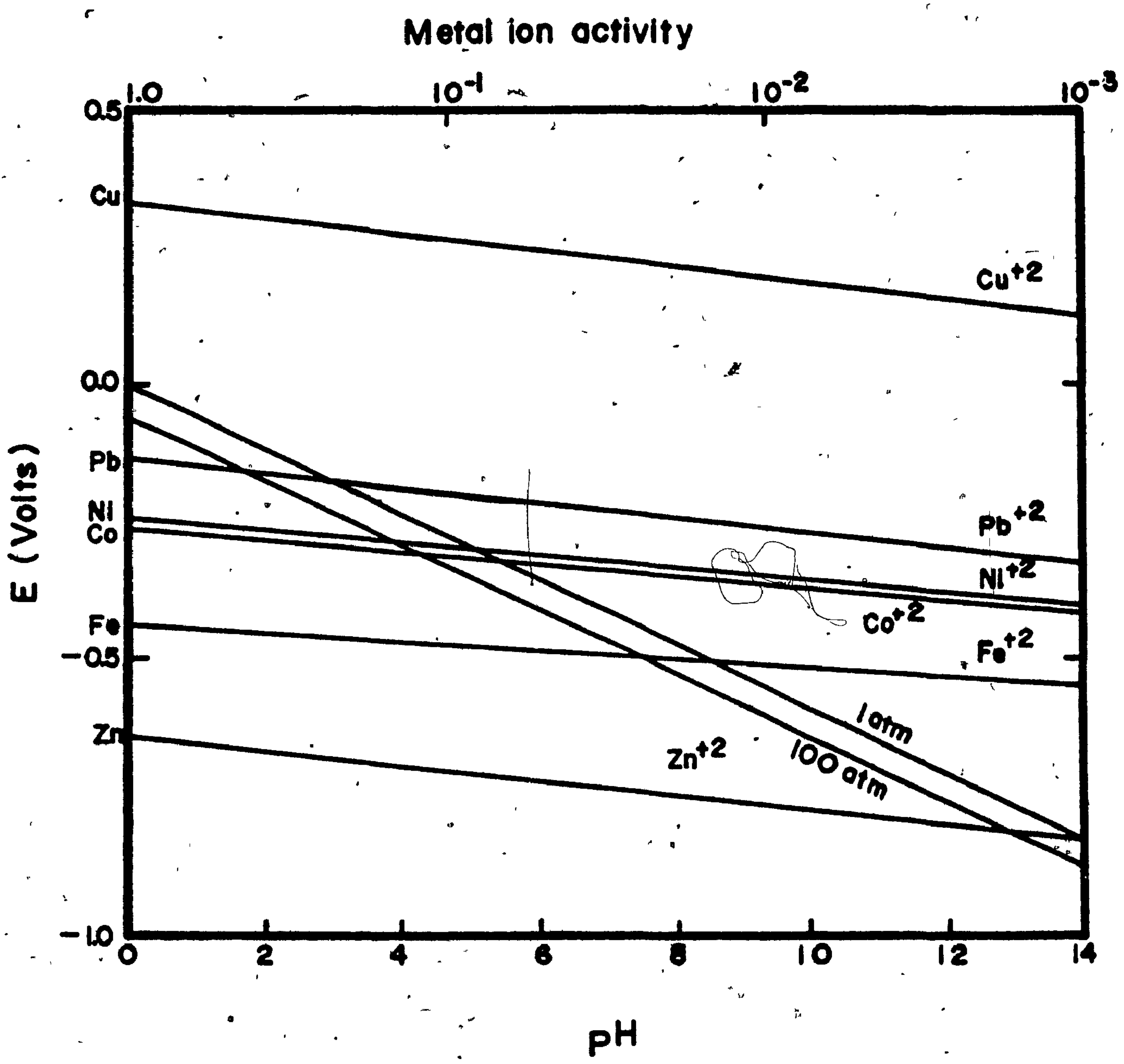


Figure 2.4 Variation of reduction potential, E, for various metals at different metal ion activities, and for different hydrogen pressures and pH.

of the complexed metal cation must be used [52].

Both homogeneous and heterogeneous catalysis have been observed in the kinetics of hydrogen reduction of metals from aqueous solutions. For systems where heterogeneous catalysis is in operation, a seed such as nickel, cobalt, or palladium is added to avoid plating of the pressure vessel's internal parts, which may act as a catalysing surface in the absence of seed material. Metal ions in solution such as Cu^{+2}, Cu^{+}, and Ag^{+} act as homogeneous catalysts. Autocatalytic kinetics have also been observed, whereby no external solid catalyst is required for the reaction to start, but freshly deposited metal accelerates the process [53].

Particle growth during metal reduction by hydrogen occurs not only by precipitation at metal surfaces, but also by agglomeration. Agglomeration results in nonuniform particles which tend to become plastered on the walls of the reduction vessel. Plastering is defined as the bonding of discrete finite particles to the walls, whereas plating is the catalytic precipitation of metal to form a continuous phase. Organic additives such as ammonium polyacrylate and lignid are added in order to prevent plastering [54]. In order to obtain more uniform deposits organic additives such as anthraquinone may also be added [54].

2.3.2 HYDROGEN REDUCTION OF METALS FROM ORGANIC SOLUTIONS

Hydrogen stripping of base metals from commercial extractants was first applied successfully to 'Versatic' (carboxylic) acid and organophosphoric acid extractants [3,55]. This concept was extended to the more widely used chelating extractants, especially KELEX 100 [16].

Research in the hydrogen stripping of metals from organic solutions involves three types of experiments. Experiments are conducted to examine the stability of the organic structure, to study the kinetics of reduction, and to determine the characteristics of the solid products of reduction (e.g. metal powders, metal salts).

For hydrogen stripping to be successful, the metal must be recovered in a manner that regenerates unloaded organic without attacking the extractant molecule either by hydrogenation or thermal decomposition. The stability behavior of extractants tested for hydrogen stripping are shown in Table 2.3 [2].

As might be deduced from Table 2.3, successful pressure hydrogen stripping, which yields metal and regenerated extractant, follows one of two reaction paths. For chelating and acidic extractants the reduction reaction may be represented, for example, as follows.

$$CuR_2\ (org) + H_2\ (g) \longrightarrow Cu\ (s) + 2\ HR\ (org) \qquad (2.15)$$

For the solvating extractant 'Butex', the reduction reaction may be represented as follows [56].

Table 2.3 Available stability data for extractants tested for pressure hydrogen stripping. [2]

Extractant			Conditions Tested		
Type	Trade Name^{a-e}	Chemical Name	Max T (K)	Max P_{H_2} (MPa)	Remarks
Chelating (in kerosene + decanol)	KELEX 100	7-alkylated 8-hydroxiquinoline	598	4.14	No degradation after 40 recycles at various T and P_{H_2}
	LIX34	8-alkarylsulphonamido quinoline	453	2.76	Substantial degradation above 453 K-H_2S forms
	LIX64N	LIX63 in LIX65N (see below)	473^f	2.41^f	Very unstable
	LIX63	aliphatic α-hydroxyoxime	473^f	2.41^f	Very unstable
	LIX65N	2-hydroxy-5-nonyl benzophenone oxime	473	2.76	No degradation after 9 recycles at 473 K
	SME 529	2-hydroxy-5-nonyl acetophenone oxime	473	2.76	Gradual degradation during recycling at 473 K
	Acorga P-5100	5-nonyl salicylaldoxime in 4-nonylphenol	373	2.41	Substantial degradation at 373 K-NH_3
ACIDIC (in Shellsol T or kerosene)	Versatic 911	Tertiary carboxylic acid	573	6.90	Very stable
	________	Di-2-ethylhexyl phosphoric acid (D2EHPA)	453	2.76	Stable below 453 K Substantail degradation at 373 K-greenish solid forms
SOLVATING	Butex	Diethylene glycol dibutyl ether (Dibutyl carbitol)	403	2.76	No degradation after 10 recycles
(in Shellsol T)	________	Tributyl phosphate (TBP)	473^f	2.41^f	Very unstable
BASIC (in Shellsol T)	Alamine 336	Tertiary amine	473^f	2.41^f	Non-metallic product formed
	Aliquat 336	Quarternary amine	473^f	2.41^f	Non-metallic product formed

a-KELEX 100	Sherex Chemical Co.
b-LIX reagents Alamine 336, Aliquat 336	Henkel Corp.
c-SME-529, Versatic 911 Shellsol T	Shell Chemical Co. Ltd.
d-Acorga P-5100	Acorga Ltd.
e-Butex	Ansul Co. Ltd.
f-the only coditions reported.	

$$2DBC\ HAuCl_4(org) + 3H_2(g) \longrightarrow 2Au(s) + 2DBC(org) + 8HCl(aq) \quad (2.16)$$

In this system, a small amount of dilute hydrochloric acid solution is added to the organic phase to dissolve the hydrogen chloride gas generated.

Pressure hydrogen stripping kinetics have been demonstrated to follow one of the two paths,homogeneous or hetergeneous metal nucleation. In homogeneous nucleation the metal is easily reduced requiring no catalyst. Minor amounts or no metal plating is observed on wetted autoclave surfaces.

Heterogeneous nucleation prevails when base metals are hydrogen reduced. In general, heterogeneous nucleation requires higher reduction temperatures than homogeneous nucleation, and seed addition is necessary to prevent deposition on reactor surfaces. Seed addition is also seen to increase reduction rates. Table 2.4 shows a summary of the kinetics of the metal organic reduction systems already studied.[2]

Most of the hydrogen reduction studies involving organic solvents have been conducted on organic phases loaded from pure aqueous solutions as opposed to real leach solutions. Therefore, the main impurities in the very fine metal powder products have been carbon, hydrogen, and oxygen. Carbon and hydrogen contamination is thought to be a result of organic entrainment during filtration. Oxygen contamination is

Table 2.4 Summary of metal organic reduction systems. [2]

System			Reduction Conditions		Characteristics		
Extractant	**Metal**	**Complex**	**T(K)**	**P(MPa H_2)**	**Nucleation**	**Kinetics**	**Remarks**
KELEX 100	Au	$AuCl_4^- \cdot H_2L^+$	298-373	0.35-0.69	Homogeneous	Under study	Minor plating occurred
	Pd	PdL_2 chelate	373-423	0.69-2.78	Homogeneous	Under study	No plating
	Cu	CuL_2 chelate	443-488	0.52-4.14	Heterogeneous	Autocatalytic	Seed needed to aviod plating
	Pb	PbL_2 chelate	473-518	2.76	Under study		
	Ni	NiL_2 chelate	523-598	1.03-3.79	Heterogeneous	Weakly Autocatalytic	Seed needed to avoid plating
	Co	CoL_3 chelate	523-598	1.38-3.45	Heterogeneous	Weakly Autocatalytic	As above
	Fe	FeL_3 chelate	473-598	2.76	No metal formed	Very slow	Fe(II) formed. Catalyst needed.
LIX 65N	Cu	CuL_2 chelate	433-473	0.69-2.76	Heterogeneous	Weakly Autocatalytic	Seed needed to aviod plating
Versatic 911	Cu	CuA_2 salt	393-473	0.10-6.90	Homogeneous	Autocatalytic	
	Ni	NiA_2 salt	433-473	0.10-6.90	Heterogeneous	Fast	NH_3 addition facilitates reduction and prevents colloid formation
	Co	CoA_2 salt	433-473	0.10-6.90	Heterogeneous	Fast	
	Fe	FeA_3 salt	573	6.90	Heterogeneous	Very slow	Reduction to Fe(II). Metal formed only when NH_3 added.
D2EHPA	Ni	NiA_2 salt	413	2.07	Heterogeneous	Very fast	Co/Ni separation possible
	Co	CoA_2 salt	413	2.07	Heterogeneous	Very slow	
	Fe	FeA_3 salt	398	2.76	No metal formed	Fast	Fe(II) formed. Catalyst needed
Butex	Au	$DBC \cdot HAuCl_4$	353-403	0.34-2.76	Homogeneous	First order in Au	No plating

considered to be probably caused by surface oxidation of the highly active metal powders.

In general, when precipitation occurs through homogeneous nucleation, the particles are fine, and no coarsening is observed if seed is added. If heterogeneous nucleation occurs, seed is added to prevent plating and a coarsening effect of the seed, onto which fresh metal deposits, is observed.

CHAPTER 3

EXPERIMENTAL

3.1 SUMMARY OF EXPERIMENTAL

Mixing of the two phases during the shake-out tests was performed in separatory funnels by mechanical shaking. Loading of the organic for reduction was achieved by mixing in a separatory funnel with the addition of concentrated ammonium hydroxide for pH control. Hydrogen reduction at high temperatures and pressures was carried out in an autoclave. Measurement of lead concentration was accomplished by Atomic Absorption Spectroscopy (AAS). Organic structure analysis was performed using Infrared Spectroscopy (IRS), Ultra-Violet Spectroscopy (UVS) and Gas Liquid Chromatography (GLC).

3.2 CHEMICAL REAGENTS

3.2.1 ORGANIC PHASE COMPOSITION

The organic phase used in this work consisted of KELEX 100 dissolved in a low aromatic (< 1%) kerosene diluent and a decanol modifier. The mixture contained 15 volume percent (v/o) KELEX 100 (Sherex Chemical Company), 10 volume percent decanol (Eastman Kodak Chemicals), and 75 volume percent kerosene (Fisher Scientific). The physical properties of the three components of the organic phase are presented in Table 3.1. Decanol was added as a modifier because it has been shown to enhance the chemical stability of the extractants in similar systems using copper nickel [56], copper [57], and cobalt [58].

Table 3.1 Physical properties of components in the organic phase.

Component	Physical Property	
	Specific Gravity	Boiling Point (K)
KELEX 100	.976	533 at 760 mm Hg
Kerosene	.774	Distillation Range 10% 475 50% 487 90% 513
Decanol	.83	502 at 760 mm Hg

Prior to use the organic liquid was "purified" by acid washing [29]. Any water soluble impurities in the as-received organic were removed by washing, at an organic to aqueous ratio of 2 to 1, with a 10 v/o H_2SO_4 solution. The colored raffinate was discarded, and the organic scrubbed with distilled water to remove any extracted acid.

3.2.2 **AQUEOUS PHASE COMPOSITION**

The aqueous phase used in this work consisted of a lead acetate solution prepared by the dissolution of reagent grade lead acetate trihydrate (Anachemia Ltd.) in distilled water with glacial acetic acid (Fisher Scientific Ltd.) added as backing electrolyte. Ammonium hydroxide (Fisher Scientific Ltd.) was added as base to increase the pH.

3.2.3 REDUCTION GASES

Gases were supplied to the reaction vessel via high pressure cylinders. Prepurified grade hydrogen and nitrogen gas, produced by Union Carbide Ltd. and distributed by Welding Products Ltd., were used. The purity, moisture content, and oxygen content are listed in Table 3.2.

Table 3.2 Quality of hydrogen and nitrogen gases used in the reduction experiments.

	Hydrogen	Nitrogen
Minimum Purity	99.99%	99.998%
Maximum Moisture	5 ppm	5 ppm
Maximum Oxygen	3 ppm	3 ppm

3.3 AUTOCLAVE ASSEMBLY

The reduction experiments were conducted in a two litre autoclave manufactured by Parr Instrument Company. Two main components comprise the autoclave assembly; a reaction vessel and a heating circuit.

3.3.1 REACTION VESSEL

Figure 3.1 shows the main features of the stirrer assembly.

and bomb which were constructed of titanium. The glass liner used to hold the organic liquid was made of Pyrex.

Agitation of the organic liquid and lead powder seed was provided by a belt-driven stirring shaft fitted with two, 6 pitched-blade, turbine impellers. The impellers were adjusted vertically on the shaft resulting in a positioning of the impellers 3 cm from the bottom of the reactor and 3 cm below the liquid level. Stirring speed could be adjusted from 0 to 1000 rpm by means of a variable speed motor.

Liquid could be withdrawn from the autoclave for sampling through the dip tube by opening of a sampling valve attached to the head of the autoclave while the autoclave was pressurized. Gas was introduced through this same dip tube under the liquid level via the gas inlet valve, also attached to the head of the autoclave. Care was taken to close the gas inlet valve during sample withdrawal to ensure that the gas lines from the pressure cylinders were not contaminated with organic liquid.

Removal of gases from the reaction vessel was achieved by means of a needle valve in the autoclave head, which released gas into a kerosene trap via a Tygon tube. Gas pressure was measured by a bourbon-tube pressure gauge having a pressure range from 0 to 6.9 MPa. Safety from overpressure was provided by a 6.9 MPa gold-plated rupture disc installed in the head of the reactor.

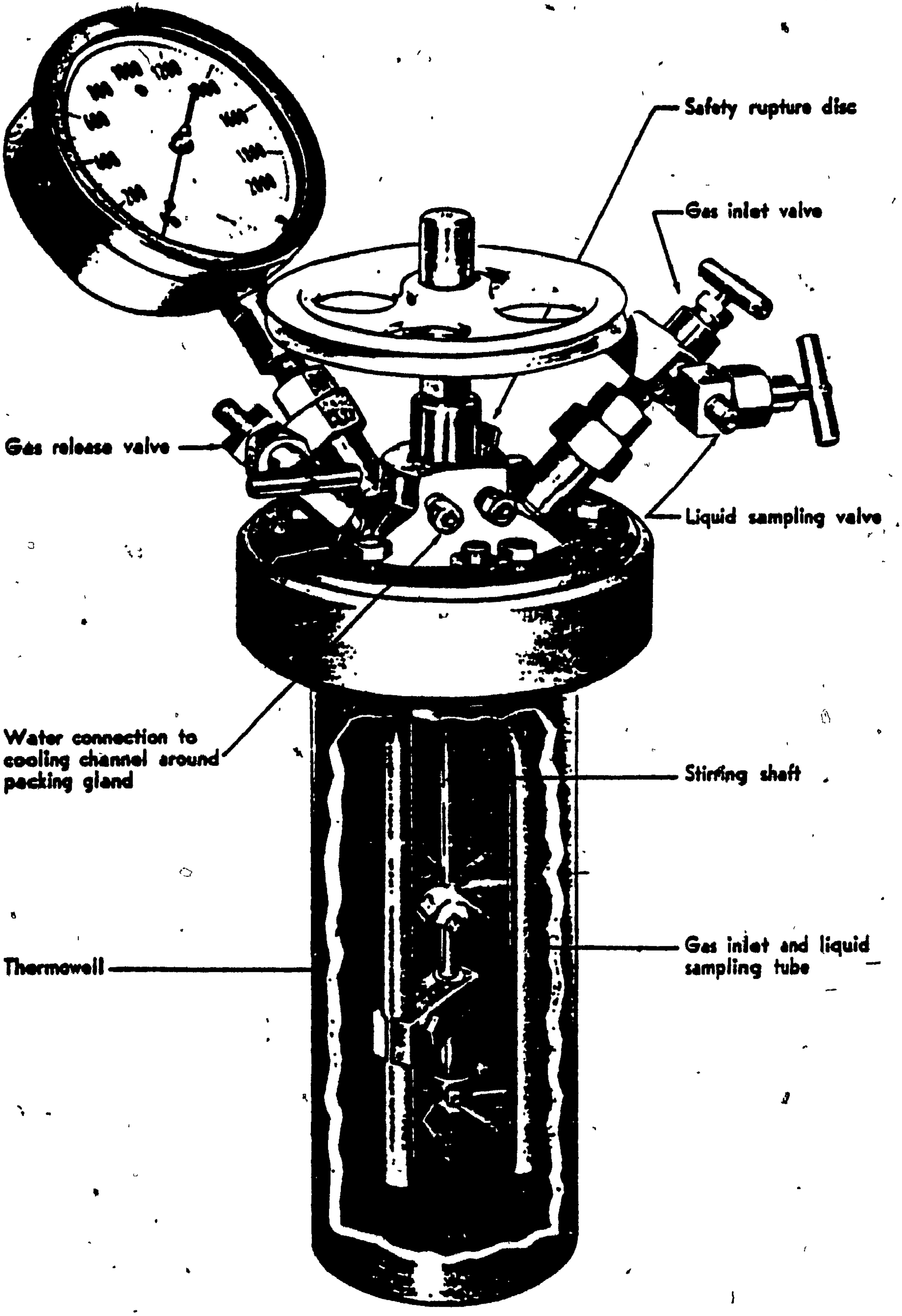


Figure 3.1 Sectioned view of the autoclave assembly reactor vessel.

3.3.2 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 initial stages of the work , [16], the standard Proportional Control Type automatic temperature controller supplied with the autoclave by the manufacturer proved to be inadequate for achieving and maintaining the required set point temperature for the process. A large overshoot was observed during the initial heating period, followed by an unacceptably large deviation. It was surmised that although this temperature control system was considered adequate for aqueous solutions it was unsatisfactory for the present work due to the low specific heat of the kerosene solvent used (~0.5 cal/gm/°C).

Temperature control was achieved with the use of a Proportional Integral Derivative action controller. The new system, manufactured by Leeds and Northrop 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 from the set point. Power was supplied to the heating element via a Zero-Voltage-Firing solid-state power package. The accuracy obtained from this temperature control system was within ± 1 K of the set point temperature. Accurate reading of the temperature was obtained by the use of a digital thermometer, having one degree of resolution, measuring the output of an iron-constantan (J-type) thermocouple inserted into the bomb thermowell.(see Figure 3.2)

3.4 EXPERIMENTAL PROCEDURE

3.4.1 SHAKE OUT TESTS

The shake-out tests were conducted using a 'Wrist Action' Model 75 (Burrell Corporation) mechanical shaker. The aqueous and organic phases were placed into 125-ml Nalgene brand polypropylene separatory funnels and shaken at room temperature. To determine the extraction of lead by KELEX 100 as a function of pH, 10 ml aliquots of an aqueous solution, with 3 gpl initial lead concentration and pH=5.05, and an organic phase were shaken mechanically for 5 minutes and the phases allowed to separate. The pH of the aqueous phase was measured and adjusted, if necessary, by the addition of NH_4OH. Then, the phases were re-equilibrated. The above procedure was repeated until the desired pH values were obtained. After shaking, the aqueous phase was filtered through WHATMAN 1 type filter paper and analyzed for lead. The appropriate mass balance calculation was then performed to determine the amount of lead in the organic phase. The slight volume change caused by the addition of NH_4OH was considered negligible and an aqueous to organic phase ratio (A/O) of one was used in the extraction calculations.

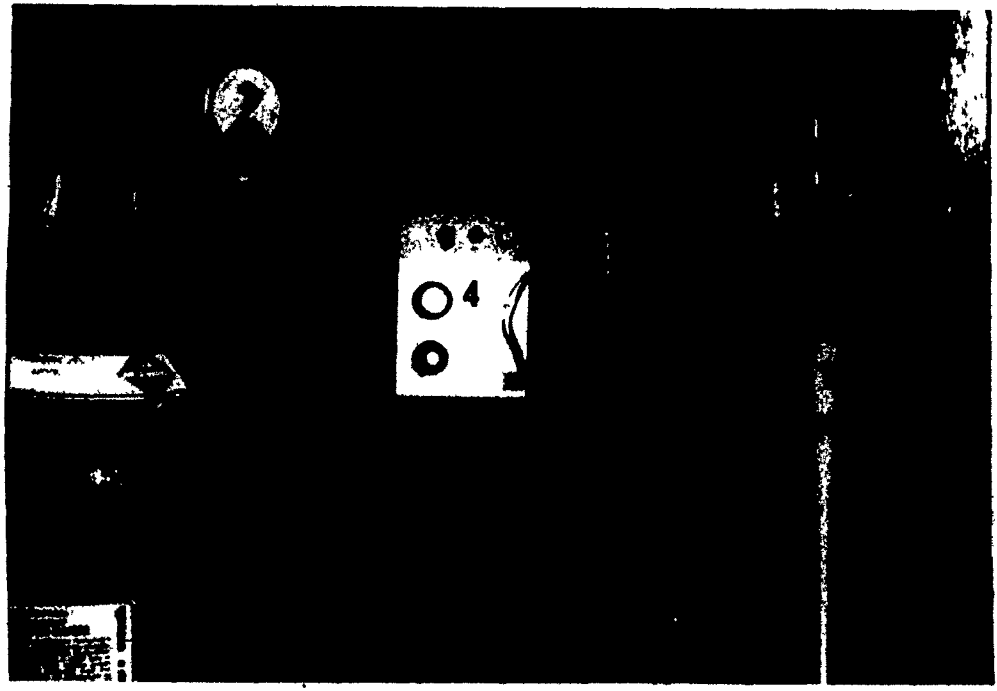


Figure 3.2 Components of the apparatus for reduction: (1) autoclave (2) temperature controller (3) power pack (4) stirrer controller (5) reduction gas.

3.4.2 LOADING THE ORGANIC PHASE FOR REDUCTION

Lead was loaded into the organic phase prior to reduction by contact with an aqueous phase analyzed to contain 20.18 ± .64 gpl lead and initial pH of 4.95.

The aqueous and organic phases were mixed at an initial A/O of 1 in a 'Pyrex' glass separatory funnel into which a teflon stirrer had been inserted. A total of 15 ml of concentrated NH_4OH was added to the aqueous phase in increments of 5 ml by periodically stopping the stirring and separating the phases at 15 minute intervals. After the final addition of NH_4OH, the phases were stirred for one hour to ensure equilibrium. This resulted in a raffinate having an equilibrium pH of 5.90 and an organic phase of 19.54 ± .86 gpl lead.

After phase disengagement and separation, the loaded organic phase was filtered through WHATMAN 1PS filter paper to ensure that no water was transferred into the autoclave. It was necessary to ensure that no water was transferred into the autoclave in order to avoid the possibility of hydrolytic stripping and for reasons of safety. The vapor pressure of water is much higher than that of kerosene, at the operating temperatures used.

3.4.3 HYDROGEN REDUCTION

One litre of the loaded organic was poured into a glass liner which was placed into the autoclave bomb and the stirrer assembly fastened. Twenty grams of fine lead powder (~200 mesh, Fisher Catalog #L-29) was also added with the loaded organic as a seed material when experimental conditions warranted. The bomb assembly was then inserted into the heating jacket and the cooling water, thermocouple, and stirrer pulley attached.

Entrapped air was removed from the autoclave by purging for 15 minutes at a pressure of 1.04 MPa with N_2 gas while stirring at 800 rpm. After purging, the loaded organic was heated to the set temperature under an inert nitrogen atmosphere while stirring continued.

Once the temperature had stabilized a sample was withdrawn to be analyzed and taken as the initial lead concentration. All samples were taken by stopping the stirrer for sixty seconds, in order to allow settling of most of the lead powder suspended in the organic, flushing out of the sampling tube with 5 ml of solution, and collecting 10 mls for metal analysis.

After the first sample was taken, hydrogen was introduced into the autoclave and the pressure adjusted. Upon initial introduction of the hydrogen gas into the autoclave a slight drop in temperature was observed, attributed to the cool hydrogen mass. Thermal equilibrium was established quickly, however. After final sample withdrawal, heating was turned off and the hydrogen pressure reduced by opening the gas outlet valve. The autoclave was then purged with nitrogen for 15 minutes at 1.40 MPa and allowed to cool overnight while being stirred.

The autoclave was dismantled the following morning and its contents filtered through a 350 ml Buchner funnel having a fritted disc of fine porosity. Filtration was aided by the use of vacuum. The organic was acid stripped using 50 gpl HNO_3 of any remanining lead and recycled. The organic loss due to sampling and handling was replaced by fresh organic. The residue of filtration was washed thoroughly with acetone, allowed to dry at room temperature, collected, and stored.

After reduction, the impeller assembly had a very thin lead coating and small amounts of agglomerated lead chunks adhered to its surfaces. The surfaces were cleaned by scraping them with a small brush, and washing with acetone. Any lead metal remaining adhered to the stirrer assembly was removed by soaking in a 50 v/o HNO_3 solution for one hour. After rinsing with distilled water and drying, the autoclave was ready for the next experiment.

3.5 CHEMICAL ANALYSIS

3.5.1 DETERMINATION OF LEAD CONCENTRATION

Direct determination of lead concentration in the organic phase was not peformed. Lead concentration in the organic phase for the extraction tests was determined by analysis of the aqueous phase and calculation of the mass balance.

Lead concentration of the organic samples taken during the reduction experiments was determined by acid stripping of the lead. To find an appropriate stripping medium, stripping isotherms were determined for various concentrations of acetic and nitric acid solutions.

The stripping isotherms were constructed by shaking varying amounts of aqueous and organic phases and determining the lead distribution between the two phases. The organic phases used in these experiments had been loaded prior to stripping from a lead acetate solution. Samples were equilibrated for 30 minutes in separatory funnels after which the strip solution was analyzed for lead, and a mass balance performed. The aqueous to organic phase ratio was varied from an A/O of 1/5 to 5/1.

In order to ensure that 30 minutes of shaking was sufficient to strip all the lead from the organic, the kinetics of lead stripping by 50 gpl HNO_3 was studied. Separatory funnels containing 10 ml of acid and 5 ml of loaded organic were shaken for time intervals of 30 seconds, 1, 5, 15 and 30 minutes, the phases separated and the strip solution analysed for lead.

Lead concentration of the organic samples taken during the reduction experiments was determined by stripping 5 ml of sample with 10 ml of 50 gpl HNO_3. Prior to stripping, the organic samples were centrifuged for 15 minutes at 1500 rpm in order to settle out the lead powder product that was taken when sampling. These samples were then filtered through WHATMAN 1PS filter paper. The organic and aqueous phases were mechanically shaken for 30 minutes and the phases separated. The strip solution was then diluted and analysed for lead using atomic absorption spectroscopy on an Instrumental Laboratory 357 Spectrophotometer.

3.5.2 ORGANIC STRUCTURE ANALYSIS

The infrared spectra of KELEX 100 were recorded in the wavenumber range of 400 to 4000 cm^{-1} using a Perkin-Elmer 467 Grating Infrared Spectrophotometer. The KELEX 100 solution was injected into a liquid sample cell made up of two NaCl crystals with a spacer of .125 mm. The reference solution used was 10 v/o decanol, 90 v/o kerosene.

A UV wavelength scan from 201 to 900 nm was performed with an LKB-BIOCHROM Ultraspec 4050 Spectrophotometer. The samples and reference solution were held in 1 cm 'Spectrosil' cells.

Pretreatment of the KELEX 100 samples was necessary prior to analysis by gas-liquid chromatography. The KELEX 100 mixture is insufficiently volatile to pass through the chromatographic column. Silylation is a common derivation method used in carrying out gas chromatography on organic compounds of low volatility. In this process, the trimethysilyl group ($-Si(CH_3)_3$) is substituted for active hydrogen in a compound. Small aliquots of KELEX 100 samples were converted to the trimethysilyl derivatives with bissilyltrifluoroacetamide (BSTDFA - Pierce Chemical Company) and heated at 333 K for 20 minutes. A small aliquot of the reaction mixture was injected into a GC-MS chromatograph, having a 183 cm column coated with 6% OV-101, and temperature programmed from 423 K at 16 K per minute. Mass spectrometer scans were made from 40 to 600 atomic mass units every 3 seconds.

CHAPTER 4

RESULTS AND DISCUSSION:

PRELIMINARY EVALUATION OF THE LEAD-KELEX 100 SYSTEM

4.1 EXTRACTION AND STRIPPING OF LEAD

4.1.1 EFFECT OF pH ON EXTRACTION

The effect of pH on the extraction of lead by KELEX 100 is shown in Figure 4.1. As the equilibrium pH of the aqueous acetate solution was increased the amount of lead extracted also increased. This can be explained by examining the equilibrium of the reaction which describes the extraction of a metal cation by a chelating extractant.

$$M^{n+}\ (aq) + nRH\ (org) \rightleftharpoons MR_n\ (org) + nH^+\ (aq) \qquad (2.7)$$

As can be seen from the above, the equilibrium position of this reaction favors the formation of the products (extraction of lead) with an increase in equilibrium pH.

The effect of pH on the logarithm of the distribution coefficient, log D, for the data in Figure 4.1 is shown in Figure 4.2. The data in Figure 4.2 can be seen to comprise two distinct regions; a non-linear portion at pH's below 4.5 and a linear portion above pH 4.5. The linear portion of Figure 4.2 can be used to provide useful information on the stoichiometry of the extracted species by the method of slope analysis. The conditions required for the use of slope analysis have been met, in that the extraction was conducted in large excess of

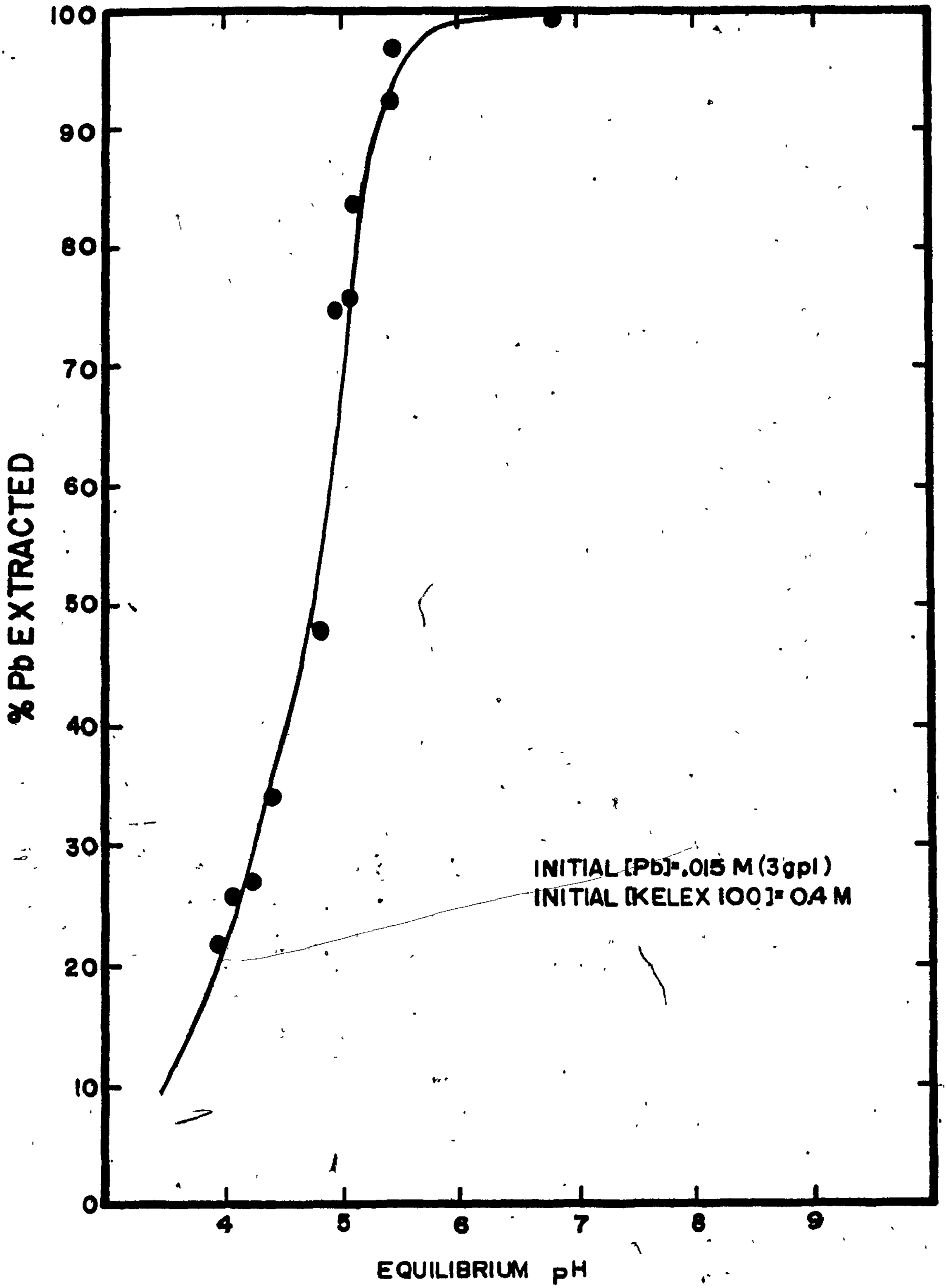


Figure 4.1 Effect of equilibrium pH on the extraction of lead by KELEX 100.

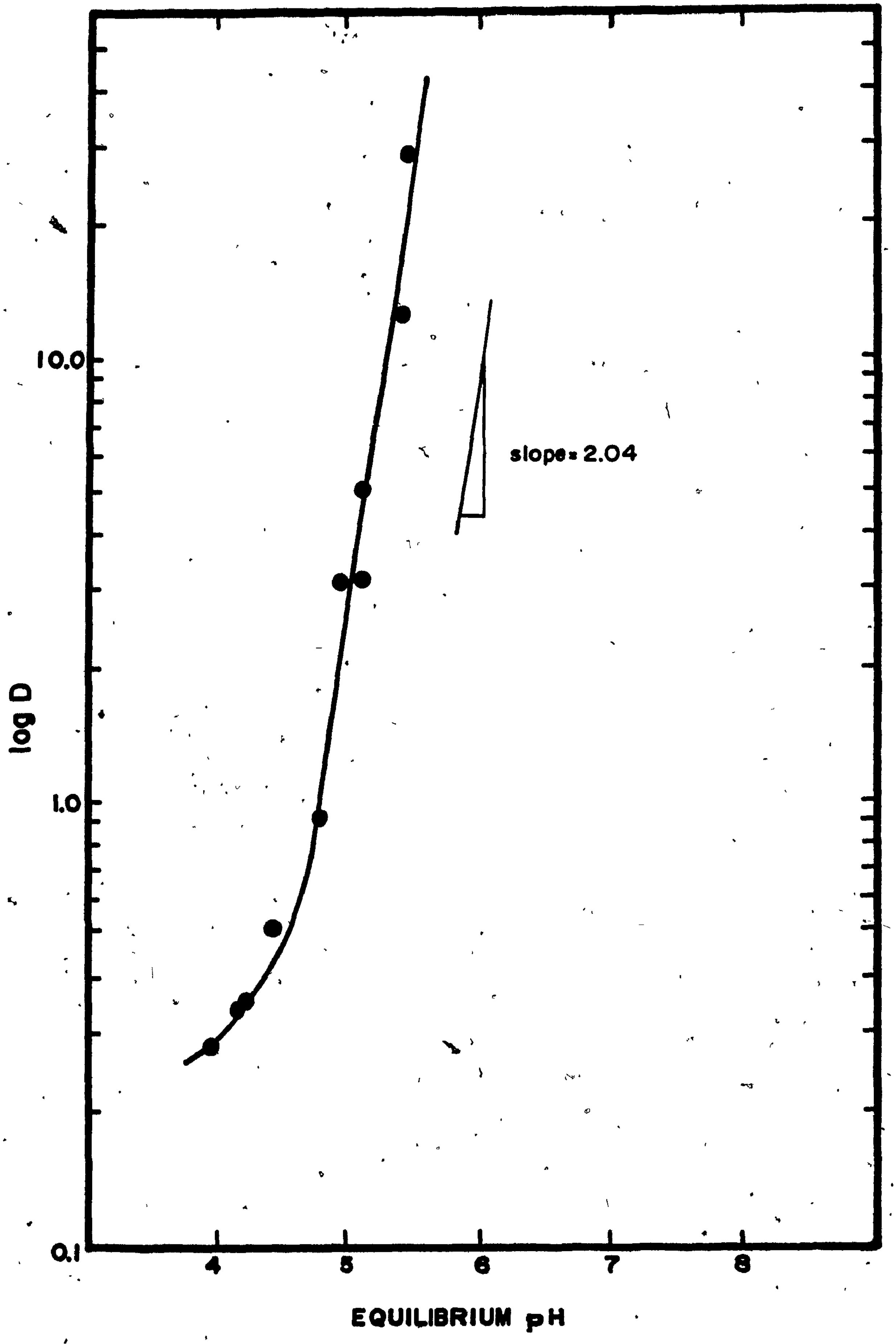


Figure 4.2 Variation of the logarithm of the distribution coefficient, log D , with equilibrium pH.

KELEX 100 compared to lead concentration, allowing us to assume constant extractant concentration. Also, the use of a large excess of acetic acid as a backing electrolyte and low metal concentration allows for the use of concentrations to approximate activities. The applicability of slope analysis to this system is based on the following simplifying assumptions [59].

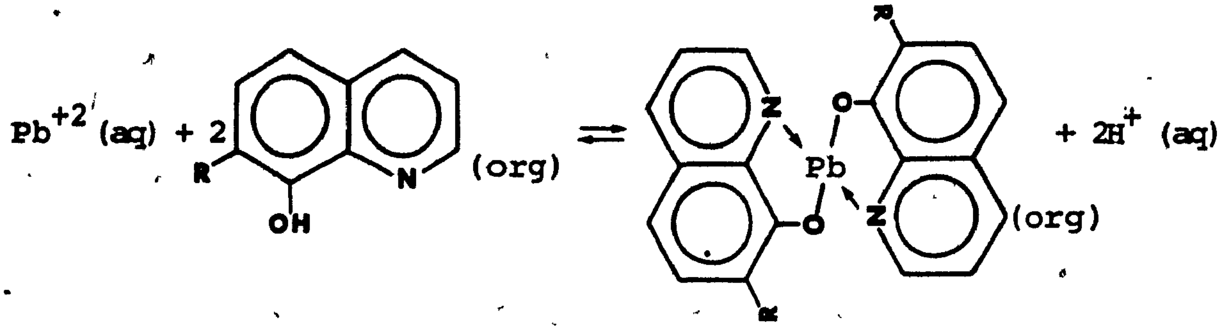
1. No polymeric species are formed in either phase.
2. Only uncharged species are extracted.
3. The formation of intermediate non-extractable complexes can be neglected.
4. No adduct formation between complexes and undissociated extractant molecules or the organic diluent or modifier takes place.
5. All hydrolysis reactions are insignificant.

For the range corresponding to $.90 < \log D < 30$ in Figure 4.2 linear regression yields a slope of 2.04 ± .28 with a regression coefficient, r, of 0.97 and a $pH_{.5}$ of 4.79. The relatively large deviation in slope (±14%) may be due to the non-water soluble impurities present in KELEX 100 which cannot be removed by acid washing. Present in minor amounts, some possess chelating abilities of their own.

Thus, the extraction reaction for lead by KELEX 100 for the system under investigation at pH values above 4.5 can be written as the following.

$$Pb^{+2}(aq) + 2[KELEX\ 100](org) \rightleftharpoons Pb[KELEX\ 100]_2(org) + 2H^+(aq) \qquad (4.1)$$

In its structural form, it may be represented as the following.



The determination of a stoichiometry of 2 to 1 for KELEX 100 and lead is consistent with the species reported by other researchers who have studied the extraction of lead with KELEX 100 and other chelating type extractants. Hoh and co-workers [44,45] have assumed the structure of the extracted species from acetate solution with LIX 34 and LIX 64N as being the same as determined in this work. In addition, organic ligand to lead stoichiometry of 2 has been reported for the extraction of lead from chloride media [60] by LIX 34, LIX 54, LIX 70 and KELEX 100, and from highly alkaline media by KELEX 100 [61,62]. At pH values below 4.5 a different extraction mechanism than that described by equation 4.1 seems to be in operation. Gradients for log D versus pH in this region are less than 2, which is probably due to mixed species being extracted into the organic phase. Lead forms several stable acetate species in aqueous solution [63], and it is possible that aceto-lead-KELEX 100 species may be extracted in this region. This is only speculation , and more detailed study of the extracted species formed in this region is required. For the purposes of this investigation it is sufficient to determine the structure of the extracted species under the conditions of loading used (pH > 4.5) prior to pressure hydrogen stripping.

4.1.2 STRIPPING OF LEAD FROM KELEX 100

A study of the stripping characteristics of lead loaded KELEX 100 was undertaken to determine the suitability of using solutions of HNO_3 or HOAc for lead concentration determination of the organic samples from pressure hydrogen stripping. Results obtained for the stripping of lead from KELEX 100 by HNO_3 and HOAC under the experimental conditions described in the previous chapter (Section 3.5.1) are shown in Figure 4.3 and 4.4.

The shape of these curves is not indicative of stripping isotherms under equilibrium conditions. The aqueous samples from these tests were analyzed directly after stripping and none of the samples contained visible precipitates. But, over a period of time precipitates were formed in most of the solutions. Stripping of lead from LIX 34 with 1 v/o HOAc was not reported to have had the same problem with precipitation.[44,45] However, Kordosky et al [64] did report that $Pb(NO_3)_2$ was precipitated after stripping 14 v/o LIX 34 in

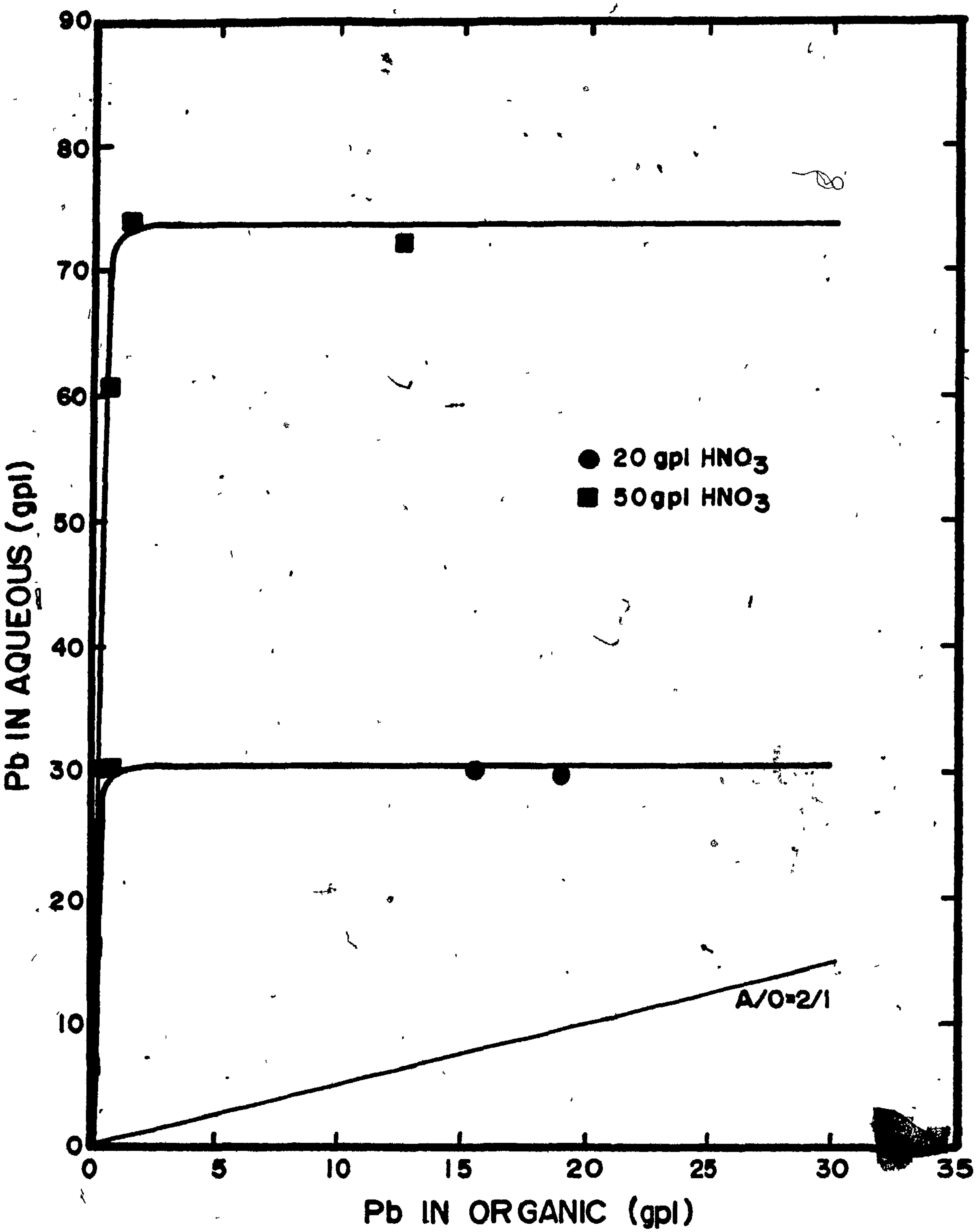


Figure 4.3 Stripping of lead from KELEX 100 with 20 and 50 gpl nitric acid.

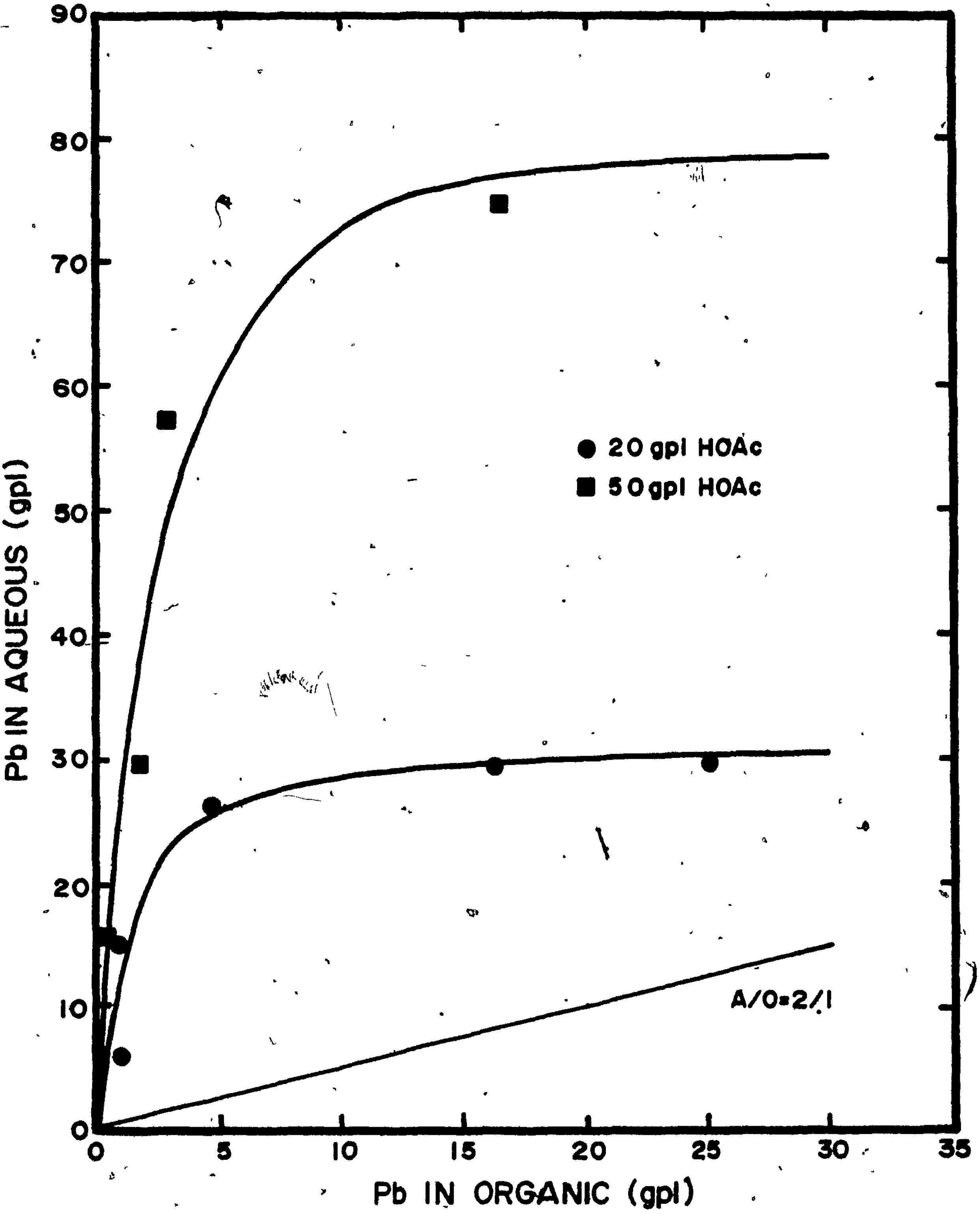


Figure 4.4 Stripping of lead from KELEX 100 with 20 and 50 gpl acetic acid.

Napoleum 470B, loaded to 9.56 gpl lead, at a stripping O/A of 6/1 with 150 gpl HNO_3.

The delayed precipitation observed in this investigation is thought to be due to supersaturation of the aqueous phase under the stripping conditions used. The stripping lines reach a constant maximum lead concentration in the aqueous phase. This is thought to represent the supersaturation point of the strip solution. This is more clearly seen when HNO_3 is used as the stripping medium. From Figure 4.3 we see that the maximum lead concentration for 20 gpl HNO_3 is about 30 gpl lead, and for 50 gpl HNO_3 it is about 72 gpl lead.

A comparison of the stripping curves in Figures 4.3 and 4.4 shows that at an A/O of 2 all of the lead has been stripped from the organic phase containing 20 gpl lead in one stage with either 20 gpl HNO_3 or 50 gpl HNO_3. In contrast 2 stages of stripping are required to strip 20 gpl lead with either 20 or 50 gpl HOAc at A/O of 2. Therefore the use of nitric acid media would facilitate chemical analysis.

It is important to note that since the analysis of supersaturated solutions of lead were used to construct Figures 4.3 and 4.4, they do not represent equilibrium stripping isotherms. Nevertheless, the information obtained from these tests can still be used to produce an effective analytical method for determining the lead concentration in the organic phase. This is accomplished by exploiting the kinetic requirements of lead precipitation from solution. Defined, supersaturation is an effect resulting from the appreciable time lag required for the condensation of ions upon invisible nuclei to form particles large enough to precipitate, even though the solubility product (K_{sp}) has been exceeded.[65] By analysing the aqueous samples quickly enough after stripping to ensure that precipitation has not begun, accurate measurement can be achieved.

Apart from the kinetics of precipitation in the strip solution, the kinetics of stripping are also important in assuring that the lead concentration measured in the strip solution can be used to measure accurately the lead concentration in the organic phase. Figure 4.5 shows the kinetics of stripping an organic phase with 50 gpl HNO_3 at an A/O of 2/1. As can be seen, the stripping kinetics are very fast with almost all the lead being stripped after 30 seconds.

From the above information, it can be said that stripping with 50 gpl HNO_3 at an A/O of 2 for 30 minutes followed by immediate analysis of the aqueous phase for lead gives an accurate measurement of the lead concentration in the organic samples from pressure hydrogen stripping. It should also be noted that, in addition to application as an analytical technique, nitric and acetic acid stripping could be considered as suitable stripping media in a practical process involving lead solvent extraction.

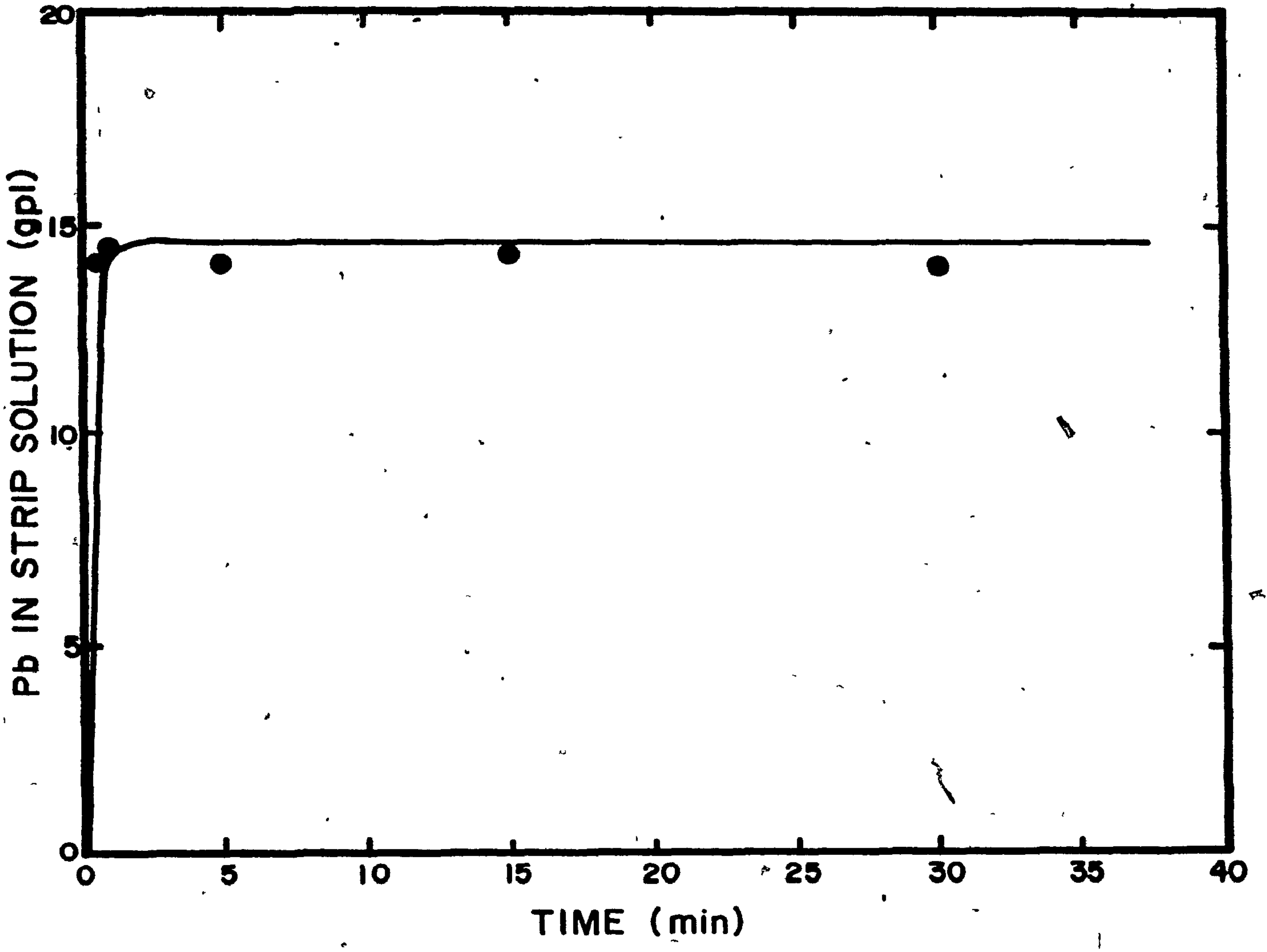


Figure 4.5 Kinetics of stripping of lead from KELEX 100 with 50 gpl nitric acid.

4.2 CHEMICAL AND THERMAL STABILITY

Reaction of KELEX 100 with hydrogen at elevated temperatures and pressures could lead either to hydrogenation of the aromatic rings or, under more drastic conditions, to decomposition due to breakage of the rings (hydrogenolysis). The effect of high temperatures could in itself lead to ring breakage (pyrolysis). Any of these conditions would make KELEX 100 unsuitable for pressure hydrogen stripping since organic regeneration and recycling is essential for the process.

Evaluation of an extractant for conventional hydrometallurgical solvent extraction involves consideration of thermal stability up to 323-333 K. However, for the hydrogen stripping of lead from loaded KELEX 100, thermal stability at much higher temperatures is required. It should be noted that during manufacturing KELEX 100 is subjected to temperatures up to 533 K in a reducing atmosphere (0.10 MPa H_2) with no signs of organic decomposition [16]. However, heating in the presence of air greatly accelerates decomposition of the extractant. This suggests that reactions with KELEX 100 at high temperatures cannot be conducted in the presence of air.

In order to determine the chemical and thermal stability of the lead-loaded organic phase, the structure of KELEX 100 was compared, using gas liquid chromatography and infrared spectroscopy, before and after reaction with hydrogen.

4.2.1 GAS-LIQUID CHROMATOGRAPHY

The gas-liquid chromatogram of the unreduced, acid 'purified', KELEX 100 used in this investigation is shown in Figure 4.6. The sample displayed a prominent peak at slightly over 8 minutes retention time. The molecular weight of the compound represented by this peak was found, using mass spectroscopy, to be 299.

Detailed analysis of the different components in the organic phase is not possible using this chromatogram, but much information has been published on the composition and structure of the various components of KElEX 100.[4,66]

A typical gas-liquid chromatogram of the same batch of KELEX 100 (Lot No. 8313R) that was used in this investigation with major peaks numbered is shown in Figure 4.7.[58] In addition to the main active component the commercial extractant also contains several by products of the manufacturing process. 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. Molecular weights of the components, as identified by mass spectrometry, along with their assigned structures are shown in Table 4.1.[66] Also shown in this table is the weight percent of each component present which was estimated by measuring the areas enclosed by the respective peaks in the chromatogram of KELEX 100.

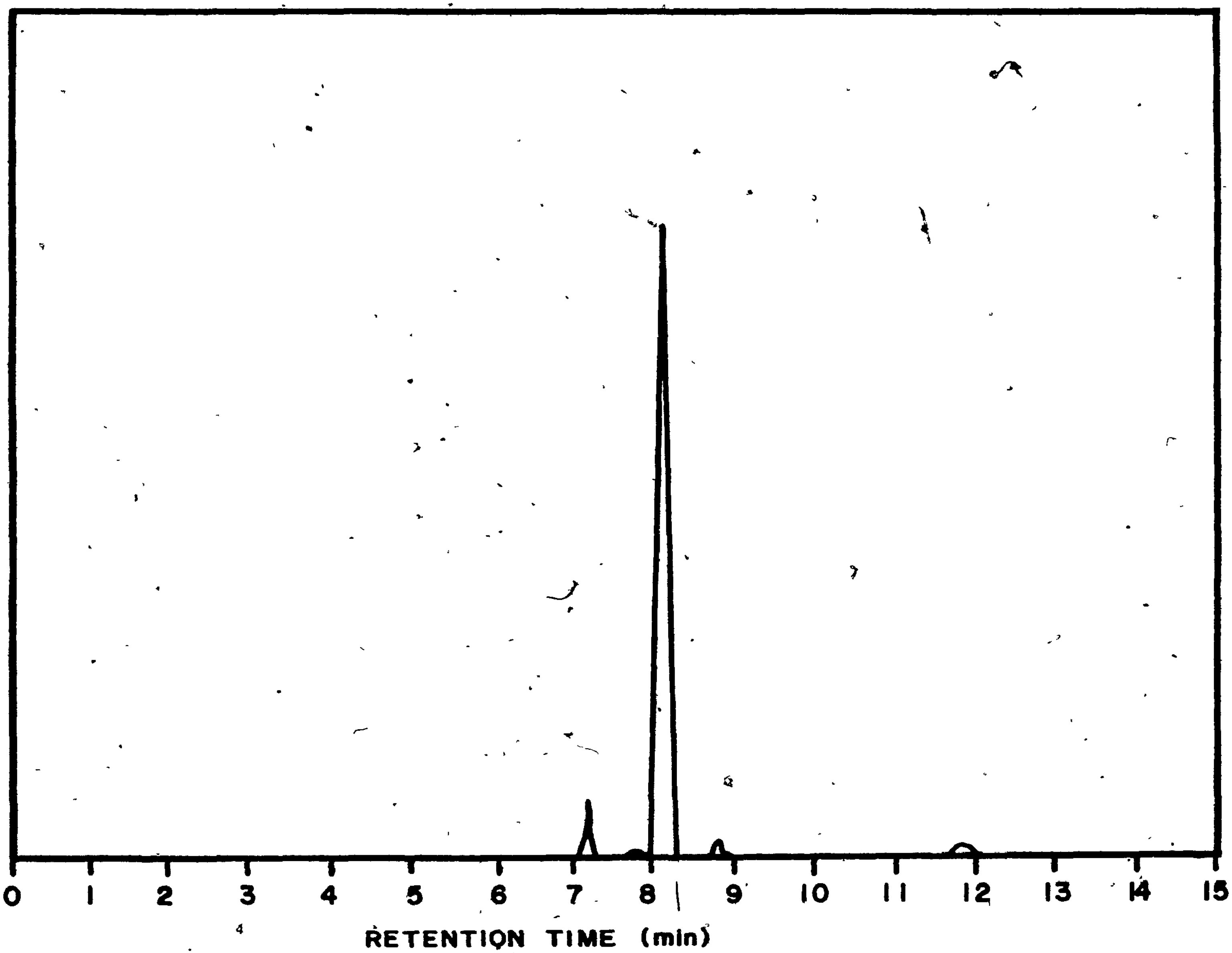


Figure 4.6 Gas-liquid chromatogram of unloaded, unreduced KELEX 100.

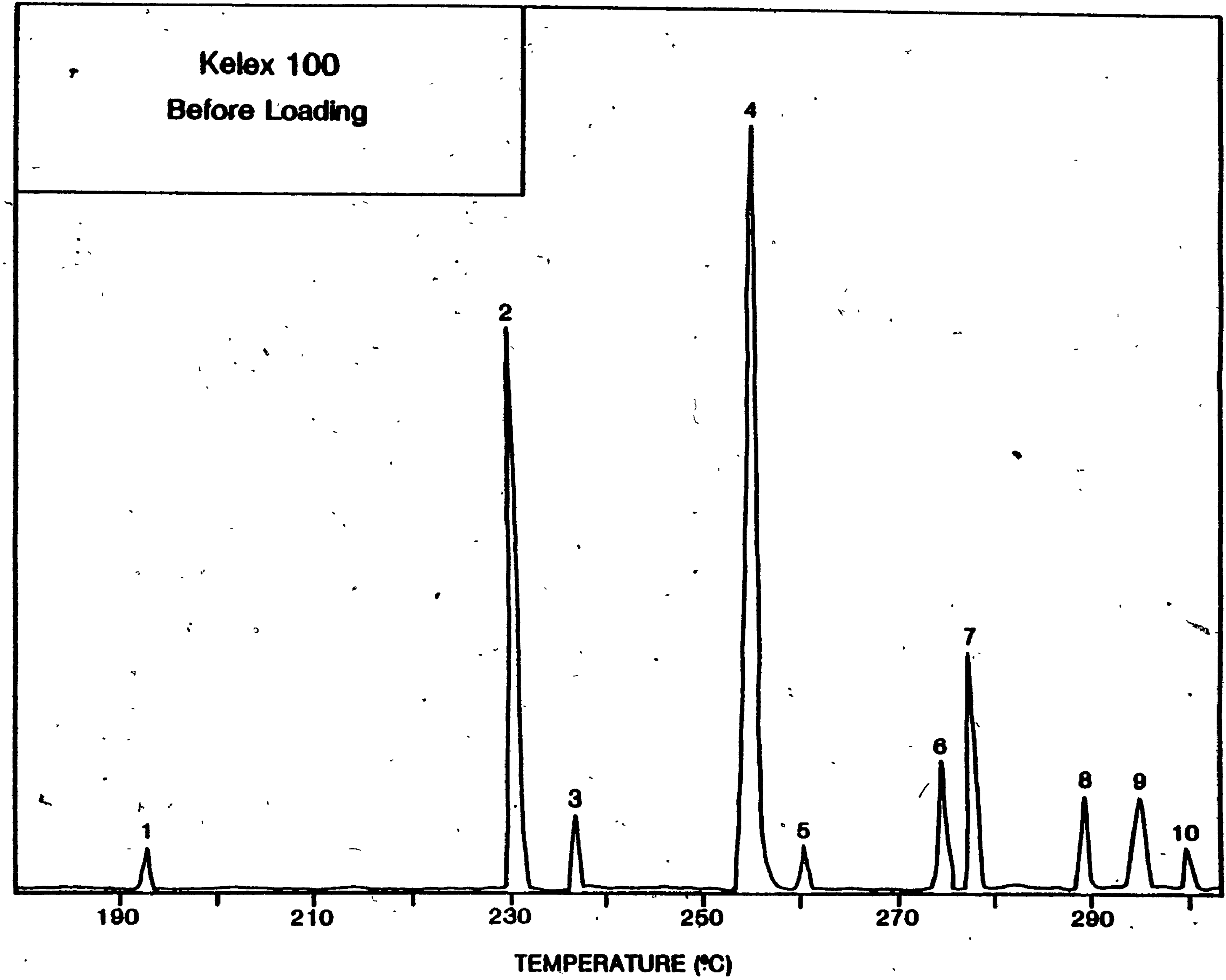
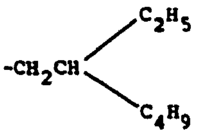
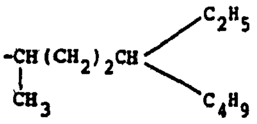
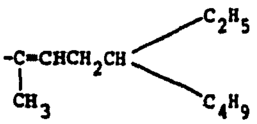
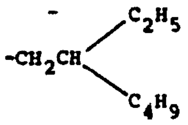
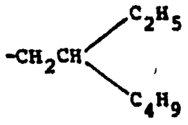
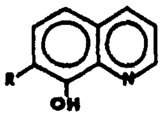


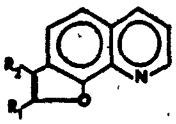
Figure 4.7 Detailed gas-liquid chromatogram of unloaded, unreduced KELEX 100 showing peaks of the major components.

Table 4.1 Components of KELEX 100 determined by gas-liquid chromatography and mass spectroscopy. [66]

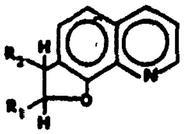
Peak	Molecular weight	Wt. %	Molecular structure
1	145	0.5	a, $R = H$
2	197	8.0	b, $R_1 = H$ $R_2 = C_2H_5$
3	257	1.0	a, R =  $-CH_2CH(C_2H_5)(C_4H_9)$
4	299	82.0	a, R =  $-CH(CH_3)(CH_2)_2CH(C_2H_5)(C_4H_9)$
5	297	0.5	a, R =  $-C(CH_3){=}CHCH_2CH(C_2H_5)(C_4H_9)$
6	297	0.5	c, R_1 =  $-CH_2CH(C_2H_5)(C_4H_9)$ $R_2 = CH_3$
7	295	4.5	b, R_1 =  $-CH_2CH(C_2H_5)(C_4H_9)$ $R_2 = CH_3$
8	453	3.0	?



structure a



structure b



structure c

Two types of organic structures were reported to be present, those based on 8-hydroxyquinoline (structure a) and furoquinoline derivatives (structures b and c). Those components based on 8-hydroxyquinoline contain the exchangeable hydrogen that takes part in the loading reaction but the furoquinolines do not have complexing properties.

The main active component (peak 4) was reported to comprise 82 weight percent with a molecular weight of 299. Therefore the peak found by gas-liquid chromatography in this investigation is that of the main component in KELEX 100, and comparison of this peak before and after hydrogen reduction of lead loaded KELEX 100 will determine the chemical and thermal stability of the organic phase. The lack of detailed information displayed in the gas-liquid chromatogram of Figure 4.6, compared to previous work[16,58], is thought to be due to the different procedures and equipment used to generate the gas-liquid chromatograms. Differences in starting temperature, adsorption columns, heating rates, attenuator settings, and gas flow rate, all affect the gas-liquid chromatogram generated [67].

The gas-liquid chromatogram of a sample of lead-loaded KELEX 100 which had been reacted with hydrogen is shown in Figure 4.8. An organic phase, analysed to contain 26.90 gpl lead, was reacted at 2.76 MPa H_2 and 475 K for six hours. Any remaining lead was stripped, and the sample analysed. A

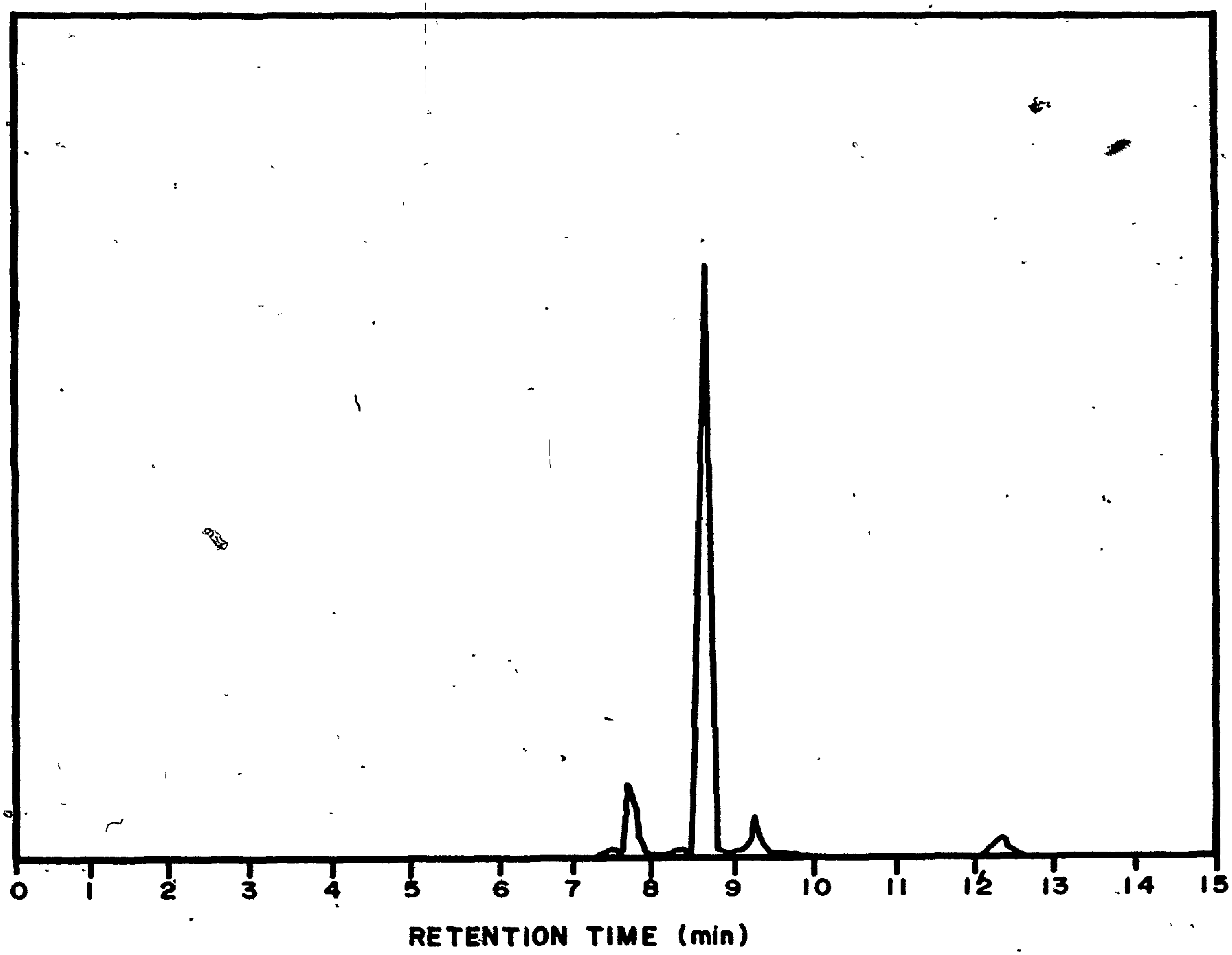


Figure 4.8 Gas-liquid chromatogram of unloaded KELEX 100 after reduction at 475 K and 2.76 MPa H_2 for six hours.

dominent peak is again eluted at just over 8 minutes retention time and was found to have a molecular weight of 299, the same as was found for the organic prior to hydrogen stripping. Nonidentical retention times are the result of the difficulty of matching starting temperatures in the program mode.

Reappearance of the peak for the major component of KELEX 100 (peak 4) after pressure hydrogen stripping suggests good chemical stability of lead loaded KELEX 100. Further evidence will be presented in a study of the infrared spectra.

4.2.2 INFRARED SPECTROSCOPY

The structural changes which KELEX 100 undergoes during the loading of lead, and hydrogen stripping, are better shown using infrared spectroscopy. Figure 4.9 shows the spectra of unreduced, unloaded KELEX 100 in the wavenumber range between 4000 and 400 cm^{-1}. Harrison et al [68] have reported some characteristic 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 [69] 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

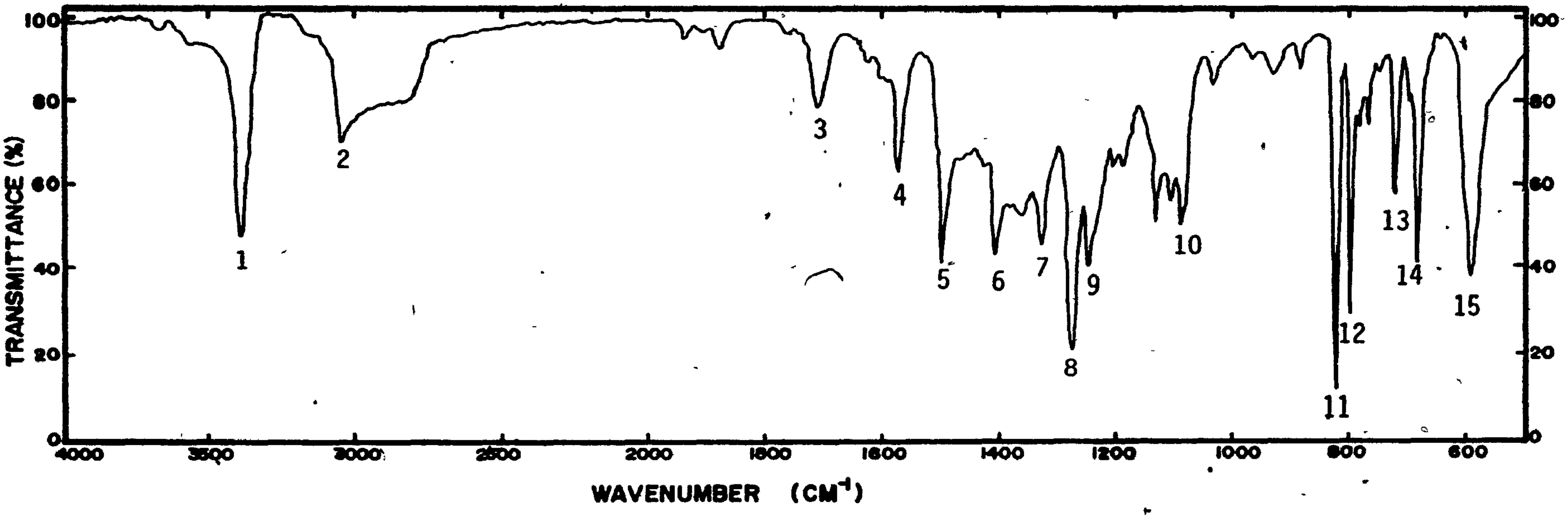


Figure 4.9 Infrared spectra of unreduced, unloaded KELEX 100.

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-hydroyquinoline and its metal chelates, have been studied in much greater detail than the infrared spectra of KELEX 100.[70, 71] 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 analysed.

Structural changes undergone by the molecule of the active component of KELEX 100 when loaded with lead can be shown by examining the spectra of the loaded extractant shown in Figure 4.10. Changes in both transmittance and frequencies of the peaks is expected when comparing loaded and unloaded KELEX 100 due to the effects of the lead on both bending and stretching vibrational modes of the various functional groups of the molecules. Darkened arrows in Figure 4.10 indicate those peaks for which changes are considerable. (shift > ± 5 cm^{-1}).

The peaks at 3400 cm^{-1} (peak 1) and 1330 cm^{-1} (peak 7) have been attributed to represent the stretching and bending, respectively, of the phenolic-hydroxyl group on the KELEX 100 molecule. [35,68] Their drastic reduction in the spectra of loaded KELEX 100 signifies the replacement of hydrogen by lead. Shifting of peak 4 from 1572 cm^{-1} to 1550 cm^{-1} and peak 6 from 1405 cm^{-1} to 1420 cm^{-1} is attributed to the effects of lead on hetero-ring stretching and aromatic ring stretching

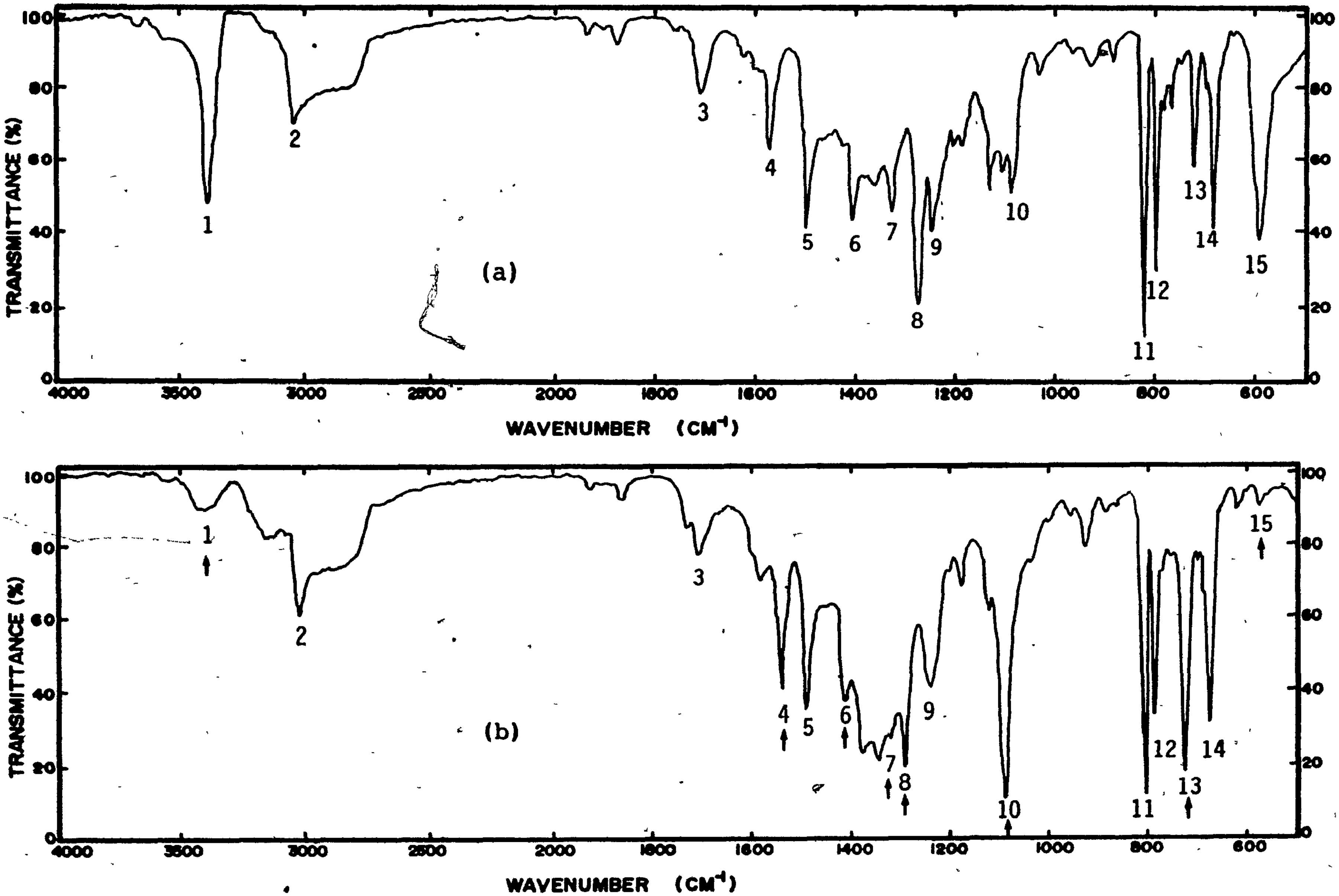


Figure 4.10 Infrared spectra of (a) unreduced, unloaded KELEX 100 and (b) loaded, unreduced KELEX 100.

respectively [66]. Similarly, C-N stretching is thought to be represented by the shift of peak 8 from 1272 cm^{-1} to 1250 cm^{-1} [68], while C-O stretching has been assigned to the shift of peak 10 from 1090 cm^{-1} to 1100 cm^{-1}. [72] The shift in peak 13 from 720 cm^{-1} to 735 cm^{-1} is attributed to C-N bending.[68]

Figure 4.11 compares the infrared spectra of KELEX 100 before and after hydrogen reduction. The spectra in Figure 4.11(b) is of KELEX 100 which has been subjected to three recycles of loading and hydrogen stripping under various conditions of temperature and pressure used in the study of the kinetics of reductions (493K to 533K and 1.38 to 4.14 MPa H_2). The lead which had not been removed by hydrogen reduction was stripped from the organic with nitric acid prior to infrared analysis.

A comparison of Figure 4.11(a) and (b) reveals that the major peaks have returned to their original heights and positions. The only exception is with peak 3 (1720 cm^{-1}), discussion of which will be taken up in the section dealing with thermal dissociation under nitrogen (Section 4.2.4). Peaks 1 and 7, corresponding to OH-phenolic stretching and bending respectively, have returned to their original heights. From the changes of these peaks, it is apparent that hydrogen exchange took place between the lead loaded extractant and hydrogen.

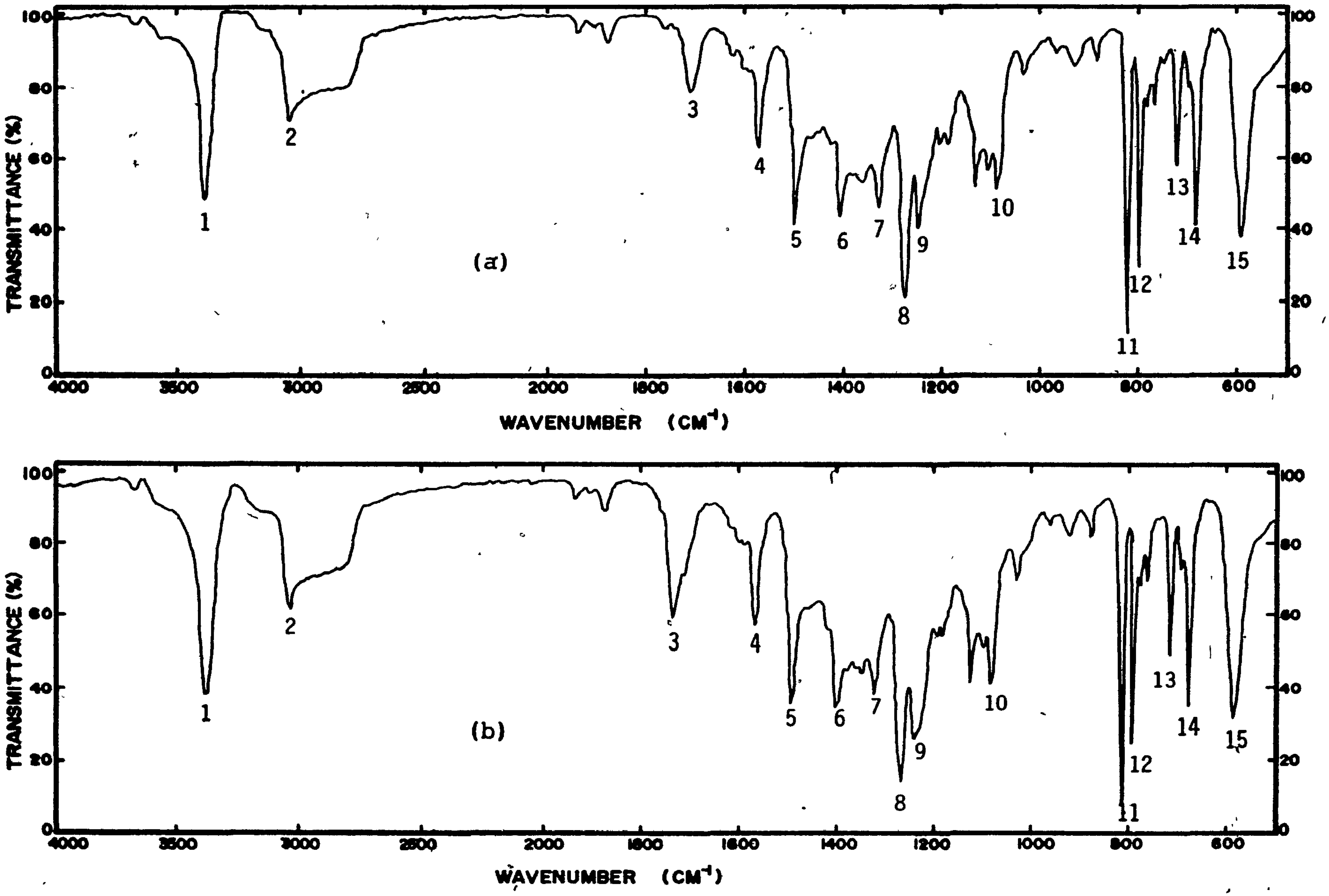
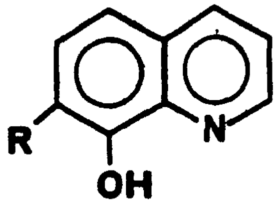
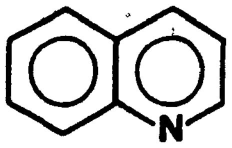


Figure 4.11 Infrared spectra of (a) unreduced, unloaded KELEX 100 and (b) unloaded KELEX 100 recycled three times.

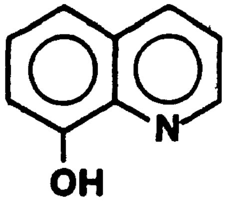
KELEX 100 (stucture I), being a C11 alkylate of 8-hydroxyquinoline, has structural similarities to quinoline (structure II) and 8-hydroxyquinoline (structure III). Because of this, an insight into the possible hydrogenation and/or pyrolysis of KELEX 100 can be obtained from information about hydrogenation and pyrolysis of these compounds.



I



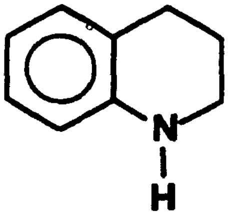
II



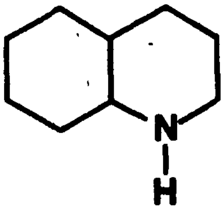
III

In the literature, a number of references describe the catalytic hydrogenation of quinoline under a variety of temperatures, hydrogen pressures, and catalyst environments. [73,74,75,76] Quinolines are usually reduced preferentially in the hetero-ring, regardless of catalyst, producing 1,2,3,4 tetrahydroquinoline (structure IV).[74] Under stronger hydrogenation conditions (>10 MPa H_2), decahydroquinoline is produced (structure V), while under extreme conditions (>15 MPa H_2), the ring system breaks down yielding ammonia, amines, and hydrocarbons. [77]

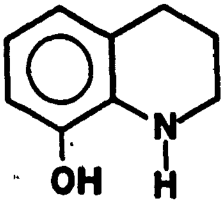
8-Hydroxyquinoline exhibits the same behavioral pattern as quinoline when catalytic hydrogenation is carried out. The 1,2,3,4-tetrahydroquinolinol compound (structure VI) was the reported hydrogenation product. [74]



IV



V



VI

Catalytic hydrogenation of the KELEX 100 molecule has been reported for the pressure hydrogen stripping of copper when decanol was not present, and was attributed to hydrogenation of the hetero-ring of the active component of KELEX 100 [16]. In addition to the active component of the extractant, some impurities in the as-received reagent were also found to be unstable in the absence of decanol. These impurities were identified as dihydrofuroquinoline (peak 6, Table 4.1) and duroquinoline (peak 7, Table 4.1).

Resistance to hydrogenation for the lead-KELEX 100 system under the pressure and temperature conditions employed in the present work may be explained by taking into account the inactivity of lead metal as an hydrogenation catalyst because of its inability to chemisorb hydrogen gas [78].

Further experimental evidence of the resistance to hydrogenation of KELEX 100 is that in parallel systems of nickel [56], copper [57] and cobalt [58] precipitation, no problems of degradation due to extractant hydrogenation were encountered at higher temperatures and pressures than used in this investigation in the presence of these well-known hydrogenation catalysts [79,80].

Reappearance of the major peaks for both the gas-liquid chromatogram and infrared spectra, in conjunction with the fact that no detectable loss in loading efficiency was observed when the organic liquid was recycled, indicates that hydrogenation did not occur and that KELEX 100 is a suitable extractant for pressure hydrogen stripping of lead.

4.2.3 ULTRAVIOLET SPECTROSCOPY

A wavelength scan was performed from 201 nm to 900 nm of lead loaded KELEX 100 versus both a 10v/o decanol, 90v/o kerosene blank, and a 15v/o KELEX 100, 10 v/o decanol, 75v/o kerosene blank. Both the sample and the reference solutions were diluted the same amount with kerosene. The peaks observed for a sample containing 38.4 ppm lead are shown in Figure 4.12. Only the wavelength region from 325 nm to 500 nm provided useful information and is shown in Figure 4.12.

In the absence of KELEX 100 from the reference solution, two peaks are observed, at 337 nm and 425 nm. When KELEX 100 is included in the reference solution only the peak at 425 nm appears. Therefore, it is surmized that the peak at 337 nm is due to KELEX 100 and the lead-KELEX 100 chelate absorbs at 425 nm.

The absorption of KELEX 100 at 337 nm is similar to one of the peaks reported by Cote and Bauer [81] at 330 nm of pre-1976 manufacture KELEX 100 in pure hexane. Attempts to use ultraviolet spectroscopy for quantitative analysis were

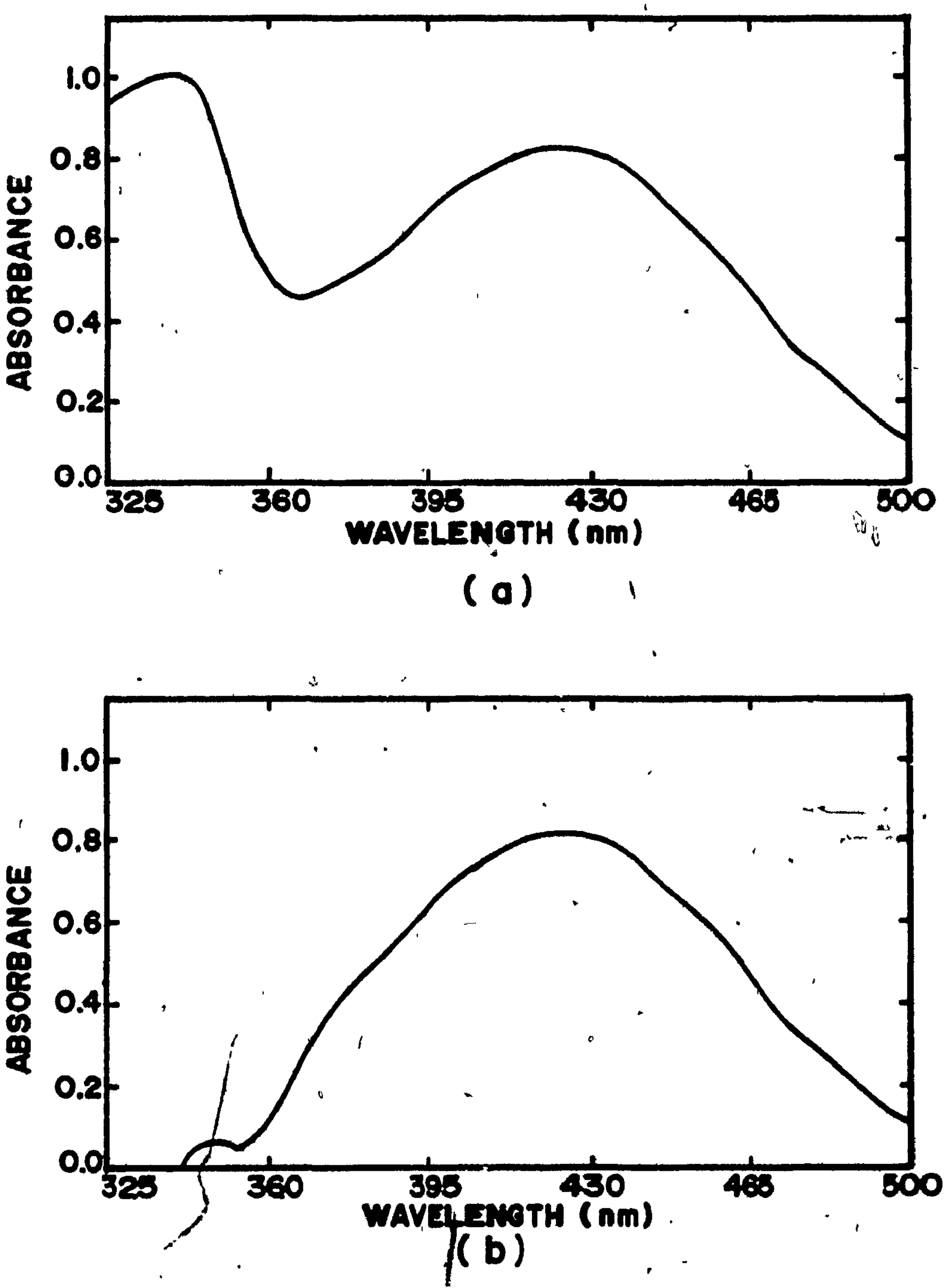


Figure 4.12 Ultraviolet spectra of the lead-KELEX 100 chelate versus (a) 90 v/o kerosene-10 v/o decanol blank, and (b) KELEX 100 blank.

unsuccessful because Beer's law was not satisfied, even at very dilute concentrations of the metal chelate.

4.2.4 THERMAL DISSOCIATION UNDER NITROGEN

As mentioned in the experimental section of the thesis, the initial heat-up period to the experimental temperature was conducted under a chemically inert atmosphere of nitrogen gas until the reaction temperature was established (standardized to 2 hrs).

During the initial hydrogen reduction experiment it was noticed, after chemical analysis, that the lead concentration of the sample at time equals zero was different from the lead concentration of the organic phase before heat up. Also, lead powder was observed to be part of the initial sample. It was therefore speculated that lead was precipitating during the initial heating period. The extent of this phenomenon can be seen from Figure 4.13 where at 518 K, under a nitrogen atmosphere, about 5 percent of the lead had precipitated after 6 hours.

This phenomenon, of metal precipitation under an inert atmosphere, was also reported by Demopoulos [16] in his investigation of a parallel system with copper. A comparison of reaction curves for the two systems under similar conditions of temperature (as shown in Figure 4.13) indicates that the copper chelate is more susceptible to thermal precipitation than is lead.

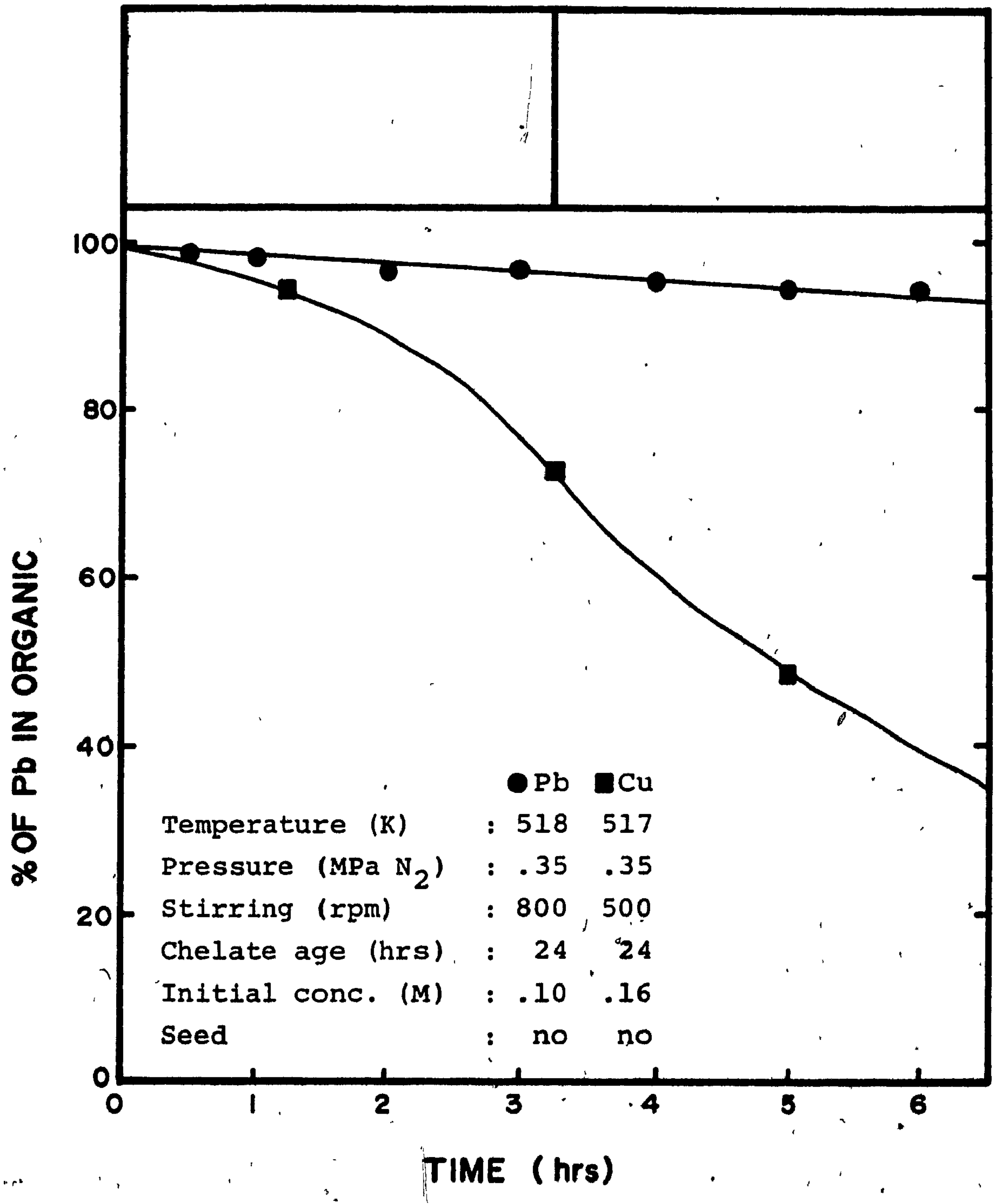


Figure 4.13 Comparison between the thermal precipitation of lead and copper under nitrogen.

Similarly as observed in this investigation, Demopoulos [4] reported regeneration of the organic solvent after pressure hydrogen stripping of copper. However, infra-red spectroscopy revealed some changes due to thermal precipitation of copper during heating under a nitrogen atmosphere. Notably the peak at 3400 cm^{-1} was slightly reduced while a relatively strong peak at 1720 cm^{-1} was observed.

Some speculation concerning a plausible pyrolysis mechanism prevailing during the thermal dissociation of the copper chelate when heated under nitrogen was put forward and is shown in Figure 4.14.

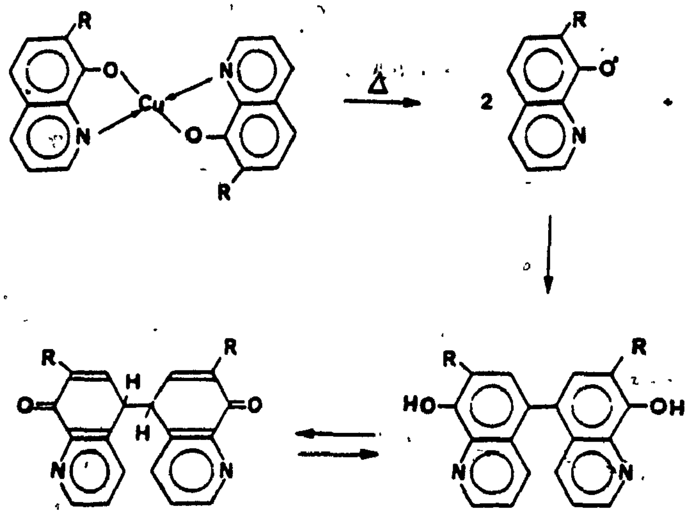


Figure 4.14 Proposed mechanism for the thermal dissociation of the copper-KELEX 100 chelate.[4]

Adoption of this mechanism explains the differences in the infrared spectra of KELEX 100 before and after pressure hydrogen stripping of lead. Heat-up and cool-down periods under nitrogen resulted in production of polymeric species of the KELEX 100 molecule. The decreased peak at 3400 cm^{-1} associated with KELEX 100 after reduction (representing the stretching frequency of OH) and the strong peak at 1720 cm^{-1} (representing the keto group $>$C=O) are indicative of the assumed tautomerism.

Build-up of these polymeric species would affect loading and stripping performance in a practical operation involving extractant recycling, but could be avoided if the entire process (including heat-up and cool-down) were conducted under hydrogen. Because the reproducibility of loading upon recycle of the organic phase was high (20.18 ± .64 gpl lead) polymerization is not considered to be a significant problem in the study of the kinetics of hydrogen stripping of lead.

The pyrolytic behavior, in an inert atmosphere (argon), of a series of divalent metal chelates derived from 8-hydroxyquinoline has been studied by Charles et al. [82] The order of decreasing heat stability of the solid chelates was reported as being Ca>Mg>Sr$\sim$Mn>Ba>Co>Ni>Zn>Pb>Cu. Principal products of decomposition include hydrogen, 8-hydroxyquinoline, the free metal or metal oxide, and carbonaceous materials in which a portion of the metal chelate ring systems is retained.

The order of thermal stability found by these researchers correlates well with observations of thermal precipitation reported in the various studies with different metals and KELEX 100. Thermal precipitation was reported not to occur in the nickel [56] or cobalt [58]-KELEX 100 systems at temperatures below 573 K (the maximum temperature studied). While, as shown in Figure 4.13, copper is more susceptible to thermal precipitation than lead.

Charles [82] also reported the decomposition of the lead chelate of 8-hydroxyquinoline to occur at temperatures above 583 K. Assuming similar thermal characterisitcs for KELEX 100, decomposition of the lead-KELEX 100 chelate might be expected to occur near, at or above 583 K .

A reduction test run at above the melting point of lead (600.5 K) was conducted to see if reduction was possible of a metal in molten form. The experimental conditions were 611 K , 2.76 MPa H_2, 20.0 grams of lead seed, 800 rpm agitation and 24-hour chelate age. Upon opening of the autoclave after reduction it was apparent from the foul smell of the organic phase that decomposition had occurred. Infrared specroscopy confirmed this observation and a comparison of the infrared spectra before and after reduction is shown in Figure 4.15. A drastic reduction in transmittance is observed for peak 1, suggesting destruction of the OH-phenolic group on the KELEX 100 molecule.

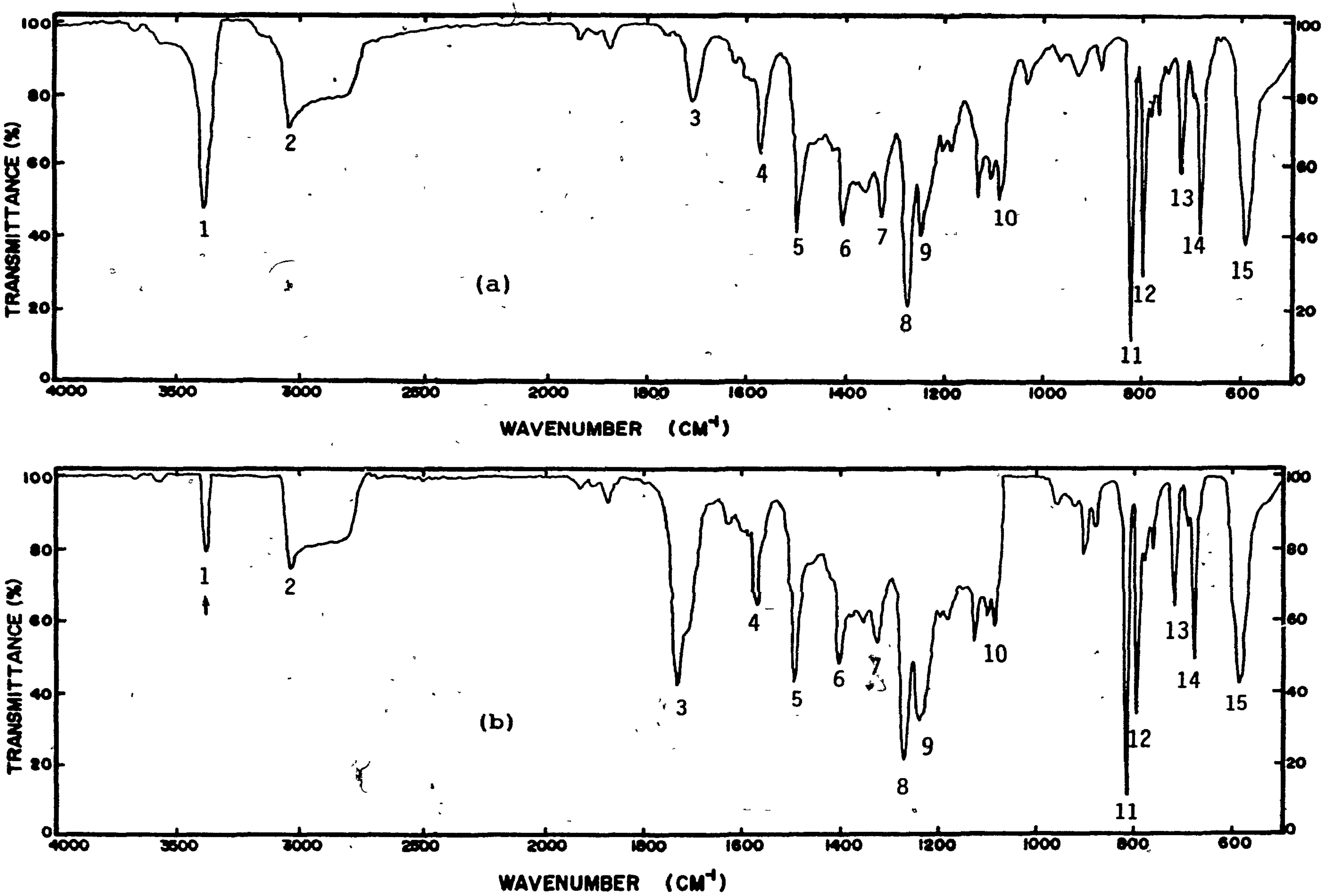


Figure 4.15 Infrared spectra of (a) unreduced, unloaded KELEX 100 and (b) decomposed KELEX 100 after reduction above the melting point of lead (611 K).

CHAPTER 5

RESULTS AND DISCUSSION:

PRESSURE HYDROGEN STRIPPING

5.1 KINETICS

The effects on the rate of lead precipitation from loaded KELEX 100 using hydrogen was investigated with respect to several process parameters. The parameters studied were seed addition, and its effect on plating, agitation, lead chelate age, temperature, and hydrogen partial pressure.

5.1.1 SEEDING AND PLATING

In a chemical precipitation system where a solid phase is produced from a solution, it is important to clarify if the nucleation taking place is homogeneous, heterogeneous or if both mechanisms are occurring. The effects of the presence of external seed and immersed metallic surfaces on the reaction rates of lead precipitation will give an indication of the nucleation mechanism.

Reaction rates are presented as percent lead in the organic phase versus time. Time zero corresponds to the time at which the operating temperature was reached and the hydrogen gas was introduced into the autoclave. One hundred percent lead in the organic represents the initial lead concentration at time zero.

The effect of adding 20 grams of fine lead powder as seed on lead precipitation rates is shown in Figure 5.1. Although

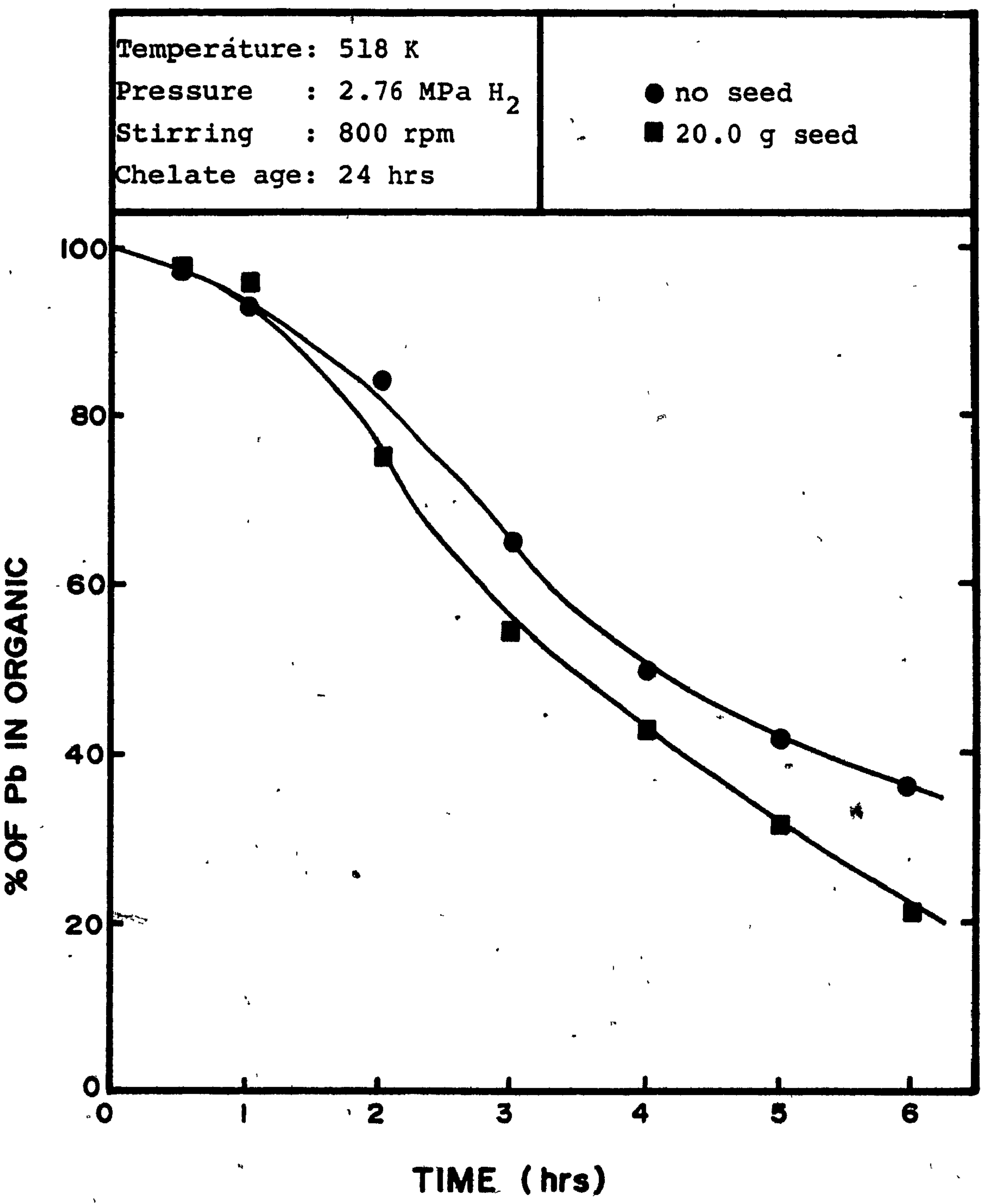


Figure 5.1 Effect of seeding on reaction rate.

external seed addition is not necessary to precipitate lead, the rate is increased if fine lead powder is added. The effect of seed addition is not very great, yet observable. At six hours reaction time the amount of lead in the organic phase has been reduced to 21 percent of the initial concentration when seed is present compared to about 36 percent when seed is not present. This enhanced reaction rate when seed is added indicates that the nucleation kinetics are hetergeneous. It is unlikely that homogeneous nucleation is important in the present system because of the requirements for homogeneous nucleation. From nucleation theory, it is known that there are two requirements in order for homogeneous nucleation to occur [83]:

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.

The submerged titanium surfaces of the impeller assembly, thermowell, and sampling tube may also act as nucleation sites, and it was observed that a fine coating of lead always adhered to the surface of the submerged surfaces.

When hydrogen comes in contact with titanium, molecular hydrogen dissociates and ionizes to some extent due to the potential field of the metal [84]. 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 lead with nitric acid as shown below:

$$Pb + 2HNO_3 \rightleftharpoons Pb^{+2} + 2NO_3^- + H_2 \qquad (5.1)$$

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

Massive plating of the stirrer assembly was not observed in this sytem as was reported for copper [16] and cobalt [85] in the absence of catalytic seed. This is believed to be due to the much greater catalytic activities of cobalt and copper for the chemisorption of hydrogen on their surfaces than lead [78]. Once the submerged surfaces have been coated with lead, the catalytic activity of these surfaces becomes greatly reduced and further plating occurs very slowly.

The effect of adding seed may have been better studied if nickel or copper powder had been added. However, the lead product would have been impure. It is probable that an increased reaction rate would be observed in the initial stages of reduction if nickel or copper seed were added. Up to that point where the seed particles become covered with lead and effectively begin to behave chemically similar to lead seed.

Although plating of the stirrer assembly was not severe, agglomeration of seed and newly precipitated lead powder was severe. This is thought to be enhanced by the high temperatures (very close to the melting point of lead of 600 K) and pressures required for the hydrogen stripping of lead. Because the evidence suggests that precipitation is heterogeneous in nature a quantitative study of the kinetics is not possible due to the varying surface area caused by agglomeration. Thus, only a qualitative study is presented in this report.

As was observed in the rest of the reduction tests and as is shown in Figure 5.1, the reaction curves are generally S-shaped with an initially slow rate followed by fairly constant reduction, ending in a slowing down of the rate of reduction. It is proposed that in the initial stages the temperature decrease observed (of about 5 K for the first 5 minutes) when the hydrogen gas is first introduced into the autoclave lowers the reaction rate. Once temperature equilibrium has been established the reaction assumes a fairly constant rate, as is observed. Depression of the reaction rate as the reaction progresses is thought to be due to the decrease in specific surface area resulting from increased agglomeration of the seed material and freshly deposited lead. That is to say, it is expected that agglomeration increases with time, at constant temperature and pressure, resulting in less exposed surface available for reaction.

The rate of hydrogen dissolution into the organic phase is not considered to have any effect on the reaction rate of lead reduction because of experimental evidence showing that hydrogen gas dissolves rapidly in the KELEX 100/decanol/kerosene system. The apparent solubility of hydrogen in the unloaded organic solvent has been previously determined [4]. Under similar conditions of temperature and pressure, as were used in this investigation, the pressure was found to stabilize within 1 to 2 minutes resulting in a hydrogen saturated solution very early. Thus initial hydrogen starvation is considered to have only an insignificant influence on the slow reaction rate observed at the beginning of reduction. The reaction is considered to proceed under conditions of apparent hydrogen saturation because copper and nickel are precipitated much more rapidly than lead, and calculations show that they react under conditions of apparent hydrogen saturation. Thus, lead is considered to be reduced under conditions of hydrogen saturation.

5.1.2 EFFECT OF AGITATION

The reduction of lead from loaded KELEX 100 involves gas, liquid, and solid phases. Agitation of the loaded organic solvent is required for two reasons: good gas dispersion, and suspension of precipitated solids to allow for complete exposure of metallic surfaces to the solution. Figure 5.2 shows the reaction curves obtained for stirring rates of 600 and 800

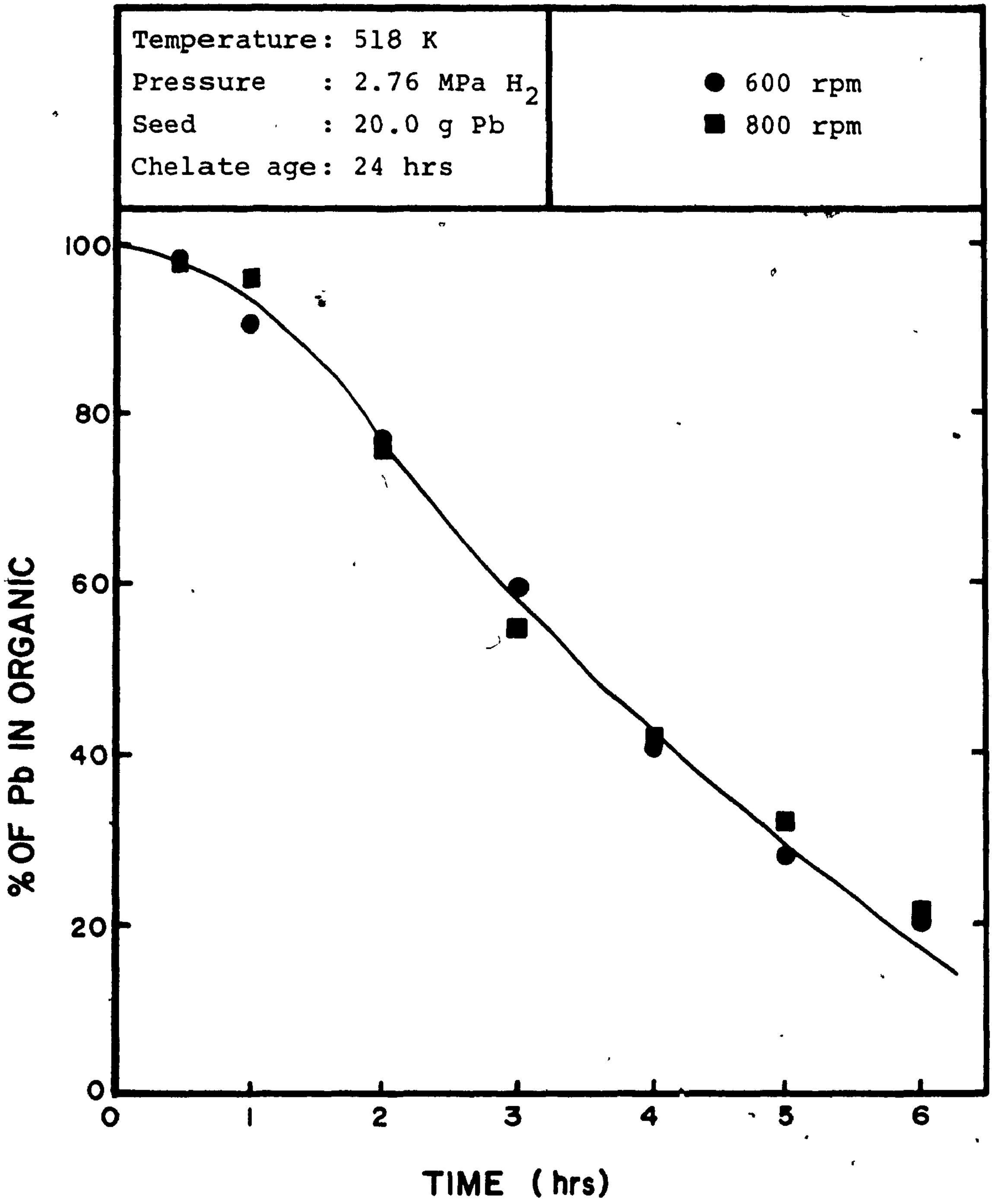


Figure 5.2 Effect of agitation on reaction rate.

rpm at a temperature of 518 K and 2.76 MPa H_2.

It appears that the reaction rate is not effected by increasing the stirring rate from 600 to 800 rpm. The independence of reaction rate on stirring suggests that the overall precipitation process is not diffusion controlled.

Burkin [86], in his report on the physical chemistry of metal precipitation from loaded carboxylic acids with hydrogen, reported that in his system the rate controlling step was the transfer of hydrogen from the gas phase into solution. But in Burkin's work 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 chemical reaction appears to be the rate controlling step for the overall reduction process.

5.1.3 LEAD CHELATE AGE

Previous experience with the copper-KELEX 100 [16] and cobalt-KELEX 100 [85] systems suggests that precipitation kinetics in the present case may be affected by chelate age. Strong aging effects in these former systems have been attributed to the metal-bearing KELEX 100 molecules forming polymeric associations, which have a suppressing effect on the hydrogen stripping kinetics. Difficulty in reduction increases with age.

The effect of lead-KELEX 100 chelate age on the kinetics of reduction at 518 K and 2.76 MPa H_2 following storage for 24 and 72 hours is shown in Figure 5.3. The reaction curve for both the 24-hour old chelate and 72-hour chelate is similar, and there seems to be no change in reaction rate due to aging within this time period.

5.1.4 TEMPERATURE EFFECT

It is expected that as the temperature is increased, lead precipitation rates will also increase. The reaction curves obtained by varying the temperature between 493 K and 533 K are shown in Figure 5.4. At 493 K the reaction rate is very slow and about 85 percent of the initial lead remains in the organic phase after 6 hours. However, reaction rates seem to be enhanced greatly by an increase in temperature beyond 493 K. An increase of 25 degrees, to 518 K, results in only about 20 percent of the initial lead remaining dissolved after 6 hours, while a further increase of 15 degrees, to 533 K, reduces the 6-hour dissolved lead level to about 10 percent of the initial concentration.

5.1.5 HYDROGEN PARTIAL PRESSURE

Changes in hydrogen partial pressure are also expected to affect lead reduction rates. Figure 5.5 shows the effects on the reaction rate of increasing the hydrogen partial pressure from 1.38 MPa to 4.14 MPa H_2. As the hydrogen partial pressure increases so does the rate of reduction. After 6 hours

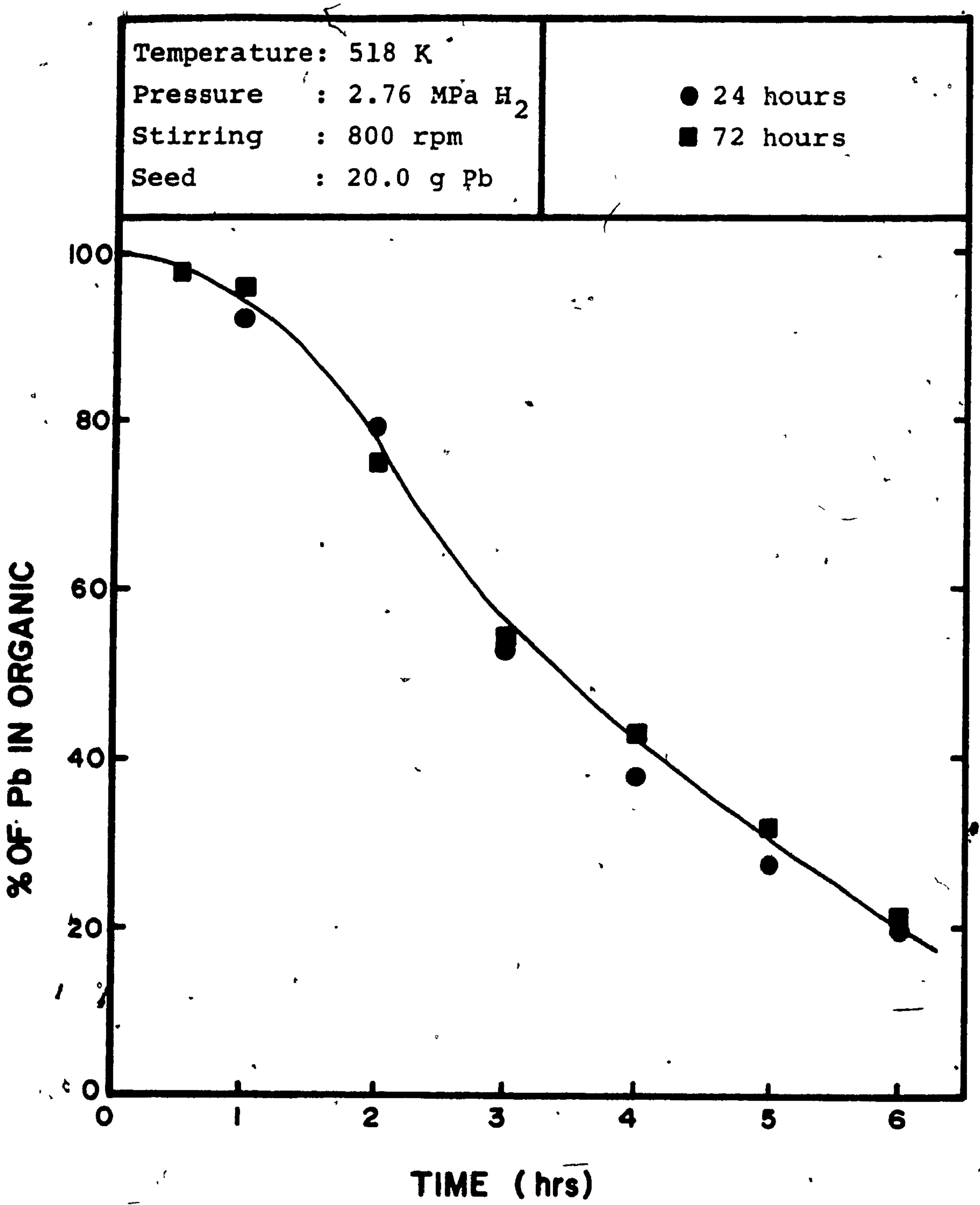


Figure 5.3 Effect of chelate age on reaction rate.

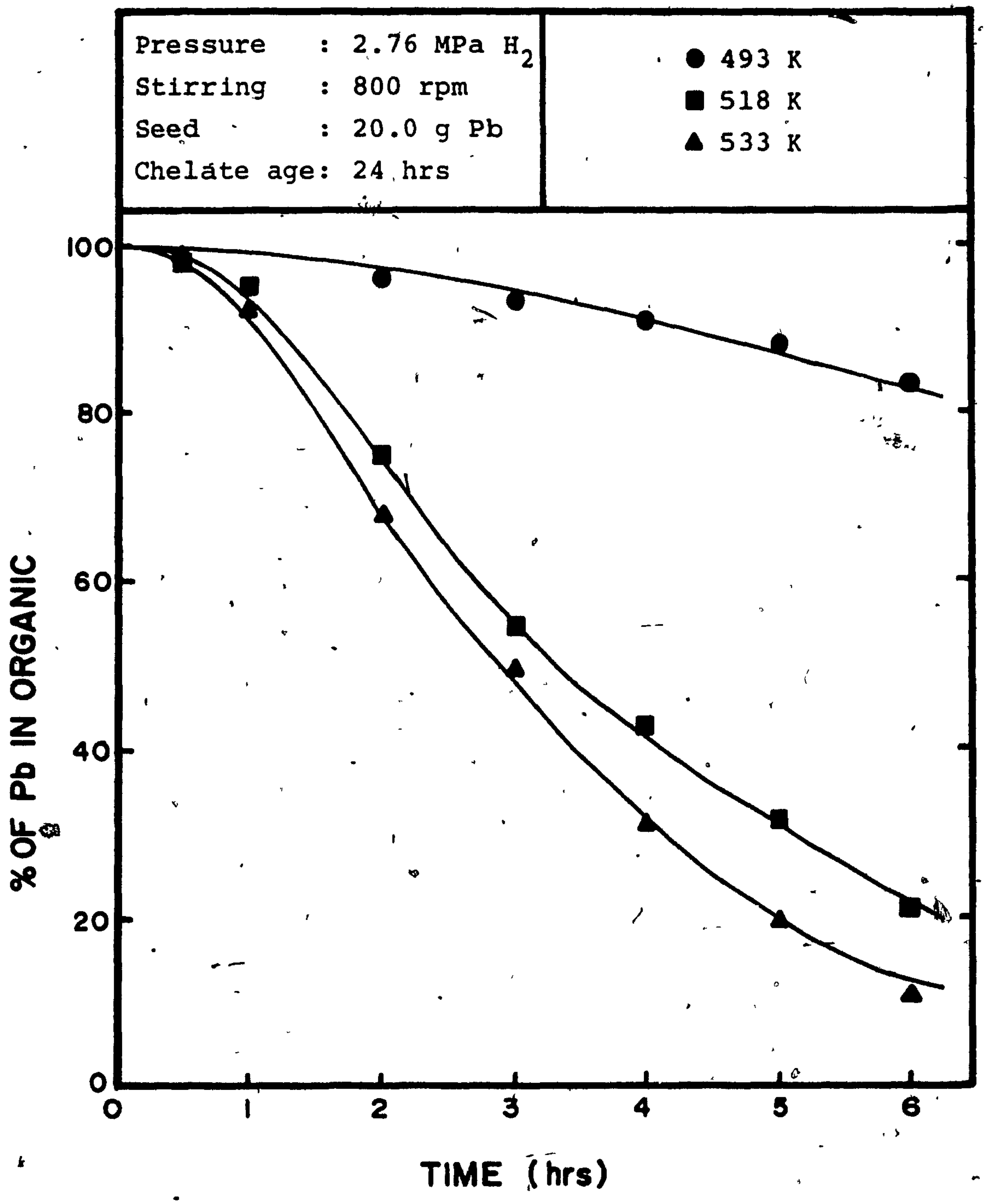


Figure 5.4 Effect of temperature on reaction rate.

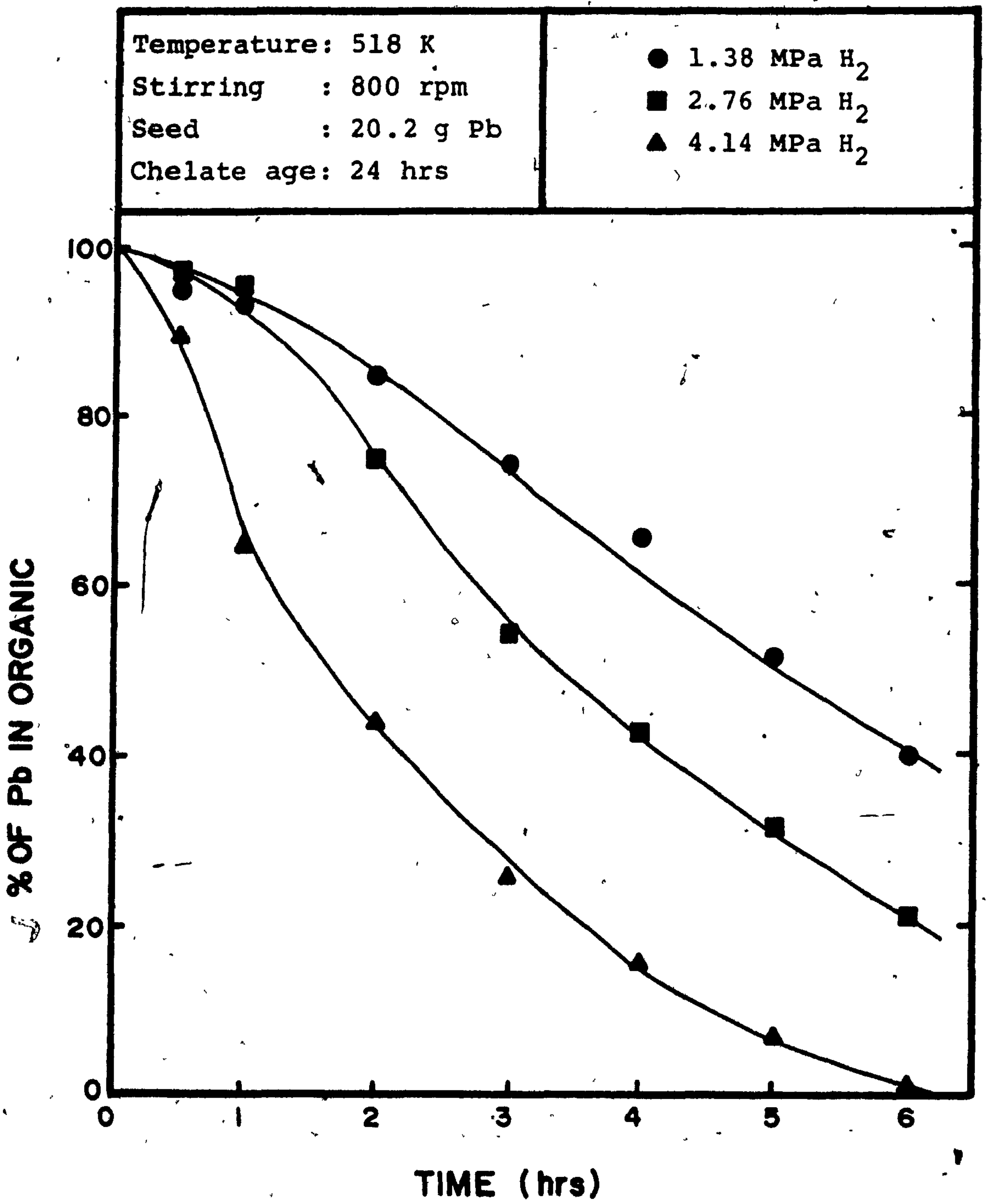


Figure 5.5 Effect of hydrogen partial pressure on reaction rate.

reaction, about 40 percent of the lead remains in solution at 1.38 MPa H_2, about 21 percent at 2.76 MPa H_2 and about 1 percent at 4.14 MPa H_2. Again the S-shaped nature of the curve is observed.

According to Mackiw et al [87], 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 percent of the metal in solution. It was empirically observed that a linear relationship exists between $\ln(100/t_{50})$ and $\ln(P_{H_2})$. Using the results in Figure 5.5, at 1.38 MPa, 2.76 MPa, and 4.14 MPa H_2 t_{50} equals 5.35, 3.45, and 1.75 hours respectively. Using linear regression the slope of $\ln(100/t_{50})$ versus $\ln(P_{H_2})$ is 0.98 with a correlation coefficient of 0.96. 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 partial pressure was observed in the heterogeneous systems of nickel precipitation from aqueous ammoniacal sulphate solutions, [87] the reduction of cobalt from aqueous ammine sulphate solutions [88], and the reduction of copper [16] and cobalt [85] from loaded KELEX 100.

5.1.6 REPRODUCIBILITY AND ORGANIC RECYCLING

Replicate experiments were conducted at 518 K, 2.76 MPa H_2, 800 rpm agitation, 24 hour chelate age, and 20.0 grams of seed in order to determine the reproducibility of the

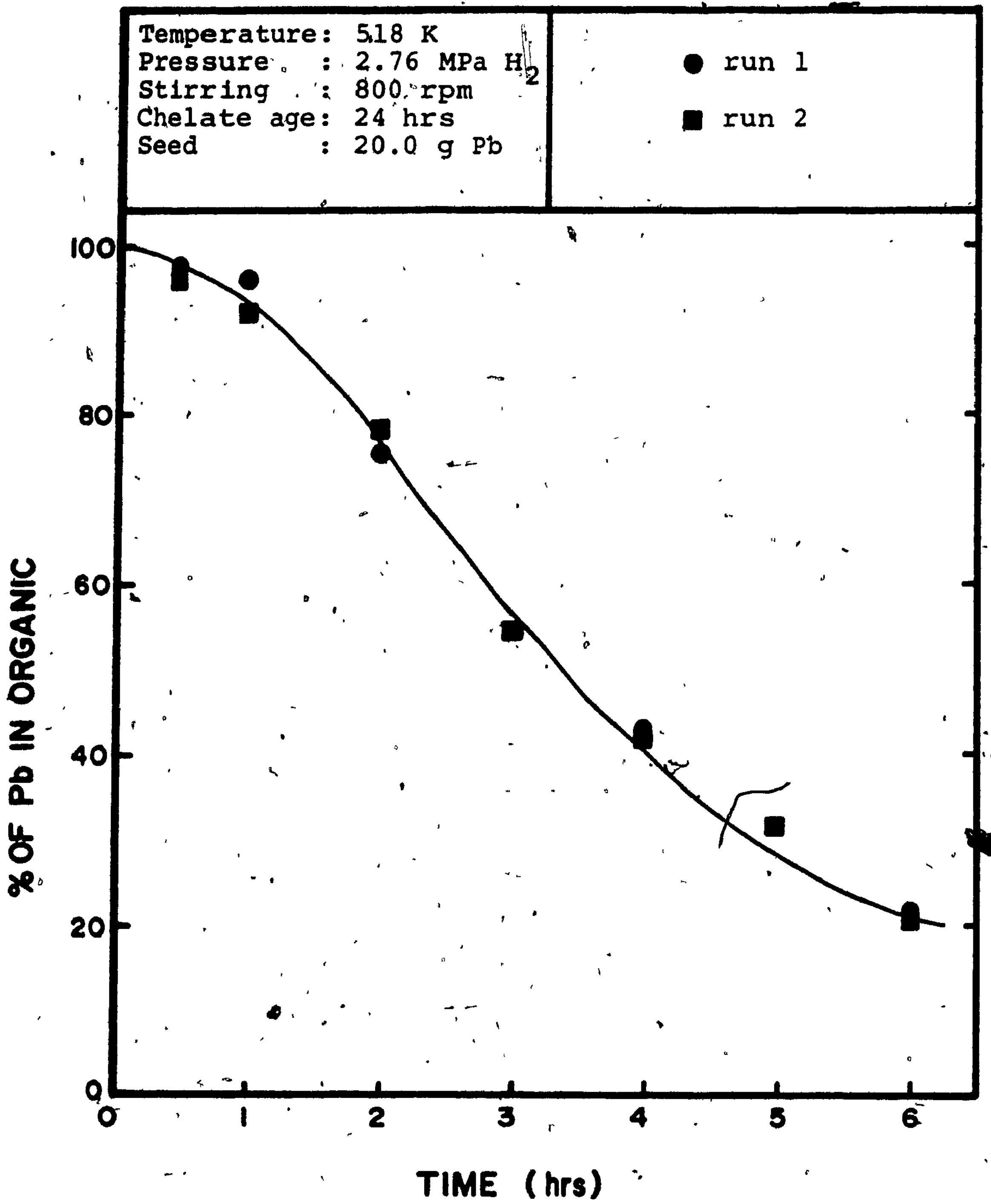


Figure 5.6. Reproducibility and recycle of the organic solution for reduction.

experimental procedure. As can be seen from Figure 5.6 excellent experimental reproducibility was obtained.

The effects of organic recycling are also shown in Figure 5.6, since the second experimental run was conducted with recycled organic, as were most of the reduction experiments. It is apparent that recycling does not adversely affect the organic phase. Good recyclability of the extractant is also evidenced in the reproducibility of loading after reduction which resulted, after loading, of solutions of 20.18 ± .64 gpl lead (a deviation of only 3.2 percent).

5.2 METAL PRODUCT CHARACTERISTICS

The lead produced by pressure hydrogen stripping, regardless of whether seed was added or not, consisted of large and small agglomerated chunks of metal mixed with fine lead powder. A photograph of the lead product recovered after filtration is shown in Figure 5.7. The largest portion of the agglomerated chunks of lead metal was characterized by a rough porous upper face and a smooth porous opposite side with an imprint of the bottom of the glass liner. It is believed that this large chunk of metal forms at the vortex which occurs directly under the bottom impellor due to rotation. A cross-section of this chunk of metal, shown in Figure 5.8, reveals that the porosity is found throughout the particle. This massive agglomeration of metal is thought to be due to the dual actions of sintering and intergrowth of particles caused by

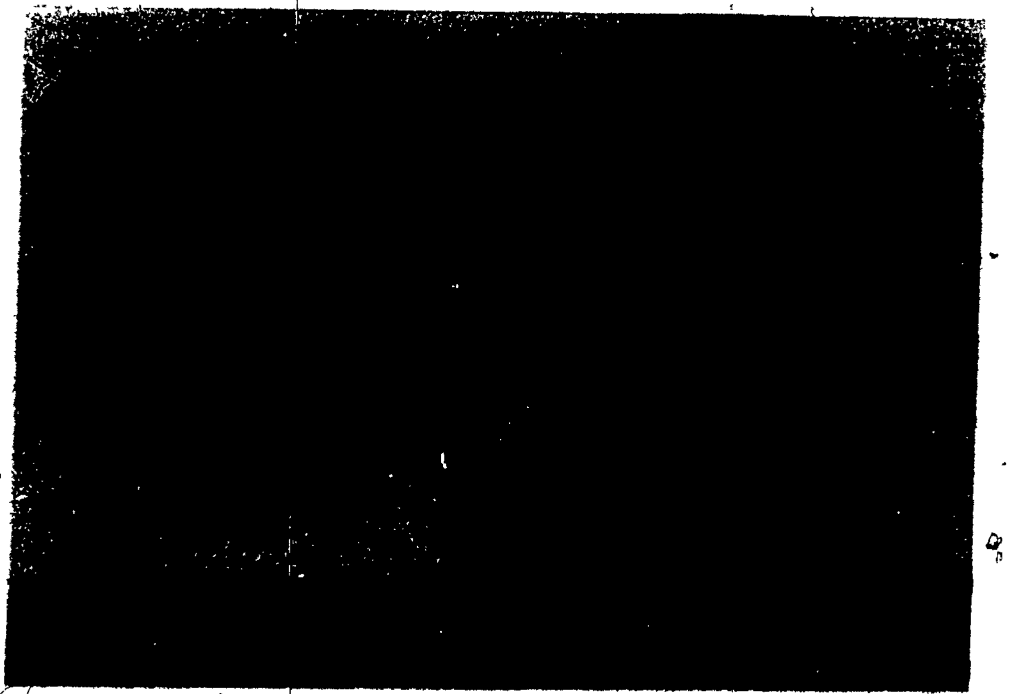


Figure 5.7 Reduction product produced at 518 K and 2.76 MPa H2 (a) without seed addition, and (b) with seeding.

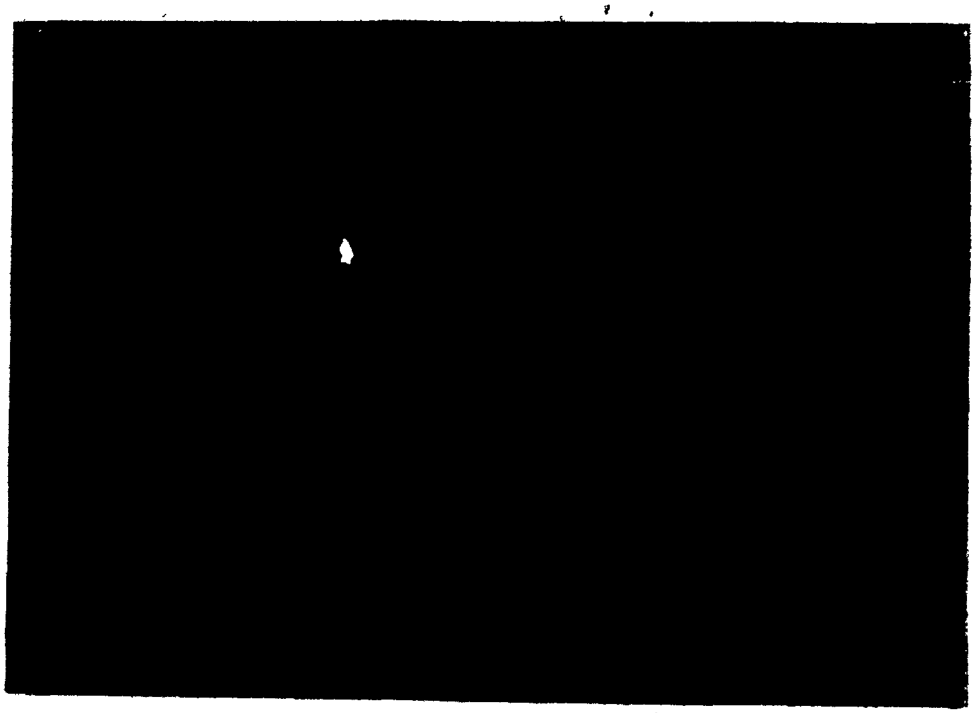


Figure 5.8 Cross section of the massive agglomerated particle produced by hydrogen reduction at 518 K and 2.76 MPa H_2.

metallic deposition and growth. The large chunks of metal are very friable and can easily be broken by hand.

Figures 5.9, 5.10, and 5.11 are micrographs of the original seed material and the powdered portions of the lead product produced with and without seed addition at 518K with 2.76 MPa H_2. The original seed material (Figure 5.9) consists of uniform sized distinct particles. The morphology of the fine lead powder produced when no seed is added consists of porous spongy particles. The powdered product produced when seed is added is observed to be a combination of the product produced without seed as well as agglomerated particles of seed material.

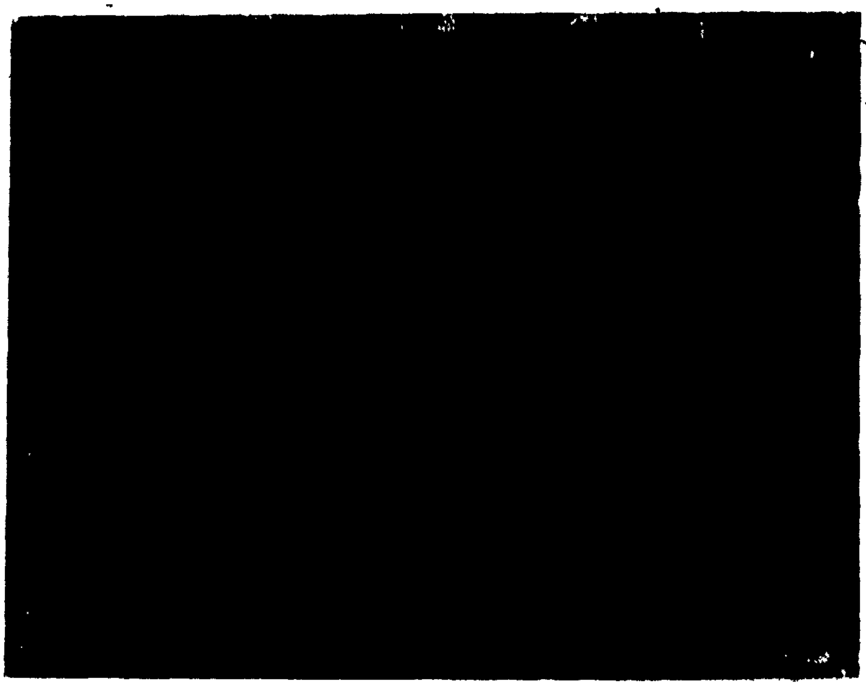


Figure 5.9 Micrograph of the original fine lead powder seed. (x125)

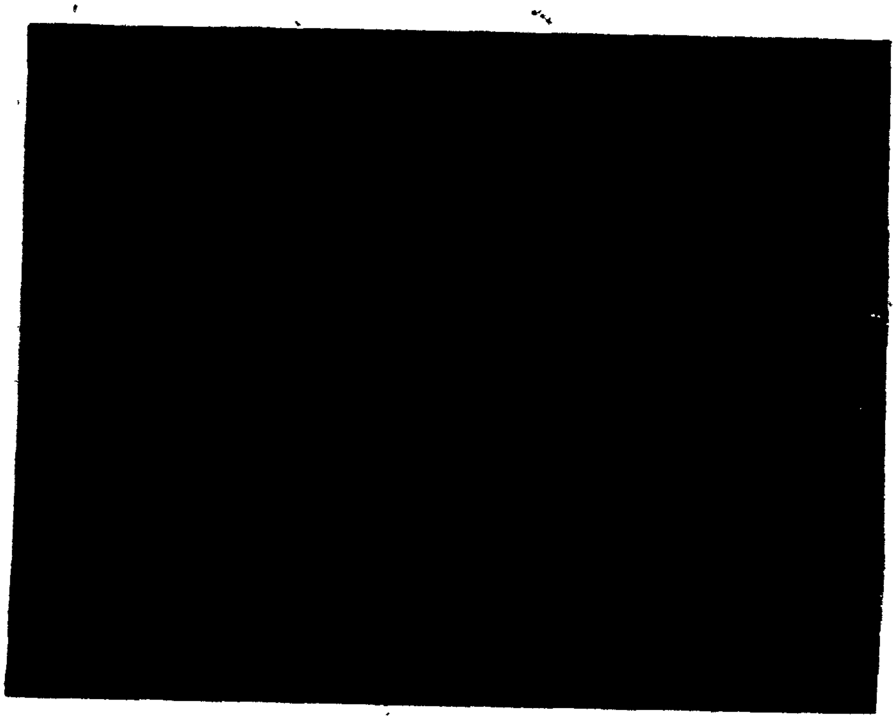


Figure 5.10 Micrograph of the powdered portion of the lead product produced at 518 K and 2.76 MPa H_2, without seed.(x125)

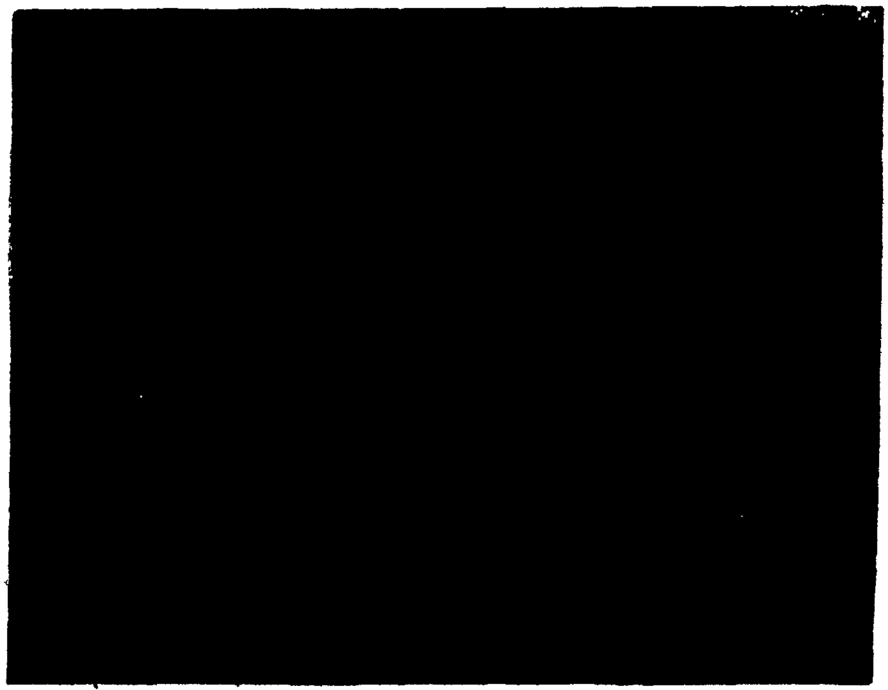


Figure 5.11 Micrograph of the powdered portion of the lead product produced at 518 K and 2.76 MPa H_2, with seed.(x125)

CHAPTER 6

CONCLUSIONS

6.1 FINDINGS

The experiments conducted in this investigation permit the following conclusions:

1) The method of slope analysis revealed that lead is extracted from acetate solutions as a 2 to 1 organic molecule to lead chelate species.

2) Lead can be efficiently and rapidly stripped from KELEX 100 with both 20 and 50 gpl solutions of either acetic or nitric acid to produce supersaturated lead aqueous strip solutions. Rapid analysis of these strip solutions provides a good method to determine the lead concentration in the organic phase.

3) Lead loaded KELEX 100, which has been pressure hydrogen stripped at temperatures between 493 K and 533 K with hydrogen partial pressure between 1.38 MPa and 4.14 MPa H_2, shows excellent chemical and thermal stability resulting in regeneration of the organic molecule for recycle. However, pressure hydrogen stripping at above the melting point of lead resulted in decomposition of the organic molecule.

4) Fine lead powder has been observed to precipitate from loaded KELEX 100 when heated to high

temperatures in an inert atmosphere of nitrogen gas. It is proposed that this may be due to the formation of polymeric species of KELEX 100.

5) A wavelength scan in the ultra violet region of the spectrum between 201 nm and 900 nm revealed an absorbance peak for KELEX 100 at 337 nm and 425 nm for the lead chelate.

6) A study of the effects of various parameters on the rate of lead reduction revealed that the addition of fine lead powder as seed increases the rate of lead precipitation slightly. An increase in operating temperature and/or hydrogen pressure accelerates the reaction rate in the temperature and pressure range investigated. There was no observable effect on the rate by varying the chelate age between 24 and 72 hours, or the agitation speed from 600 rpm to 800 rpm.

7) The lead metal product produced in both the presence and absence of seed consisted of large and small agglomerated chunks of metal mixed with fine powder.

6.2 FURTHER INVESTIGATIONS

Although much knowledge has been gained in the investigation of pressure hydrogen stripping of lead from loaded KELEX 100, the following points are suggestions as to where more knowledge could be gained in further study of this system:

1) Owing to the low catalytic activity of lead and the agglomerating properties of the reduction product, a nucleation model or reaction mechanism was not determined in this investigation. Further work should be conducted to clarify the reaction chemistry.

2) Heat up and cool down cycles of the loaded organic solution should be conducted under a hydrogen instead of a nitrogen atmosphere in order to determine if the changes revealed by infrared spectroscopy are indeed due to the assumed tautomerism.

3) The addition of various organic reagents known to affect the physical properties of metals produced by hydrogen reduction in aqueous solutions should be investigated in an attempt to improve the physical characteristics of the reduced lead product. A high purity, uniform sized, non-porous metal product is the most desirable, especially for powder metallurgy applications.

6.3 CLAIM TO ORIGINALITY

Original aspects of this work are thought to be, in author's opinion, the following.

1) It is the first time that the stochiometry of the

lead-KELEX 100 chelate has been determined when lead is extracted from an acetate solution.

2) It is the first time that lead has been successfully reduced from loaded KELEX 100 with hydrogen under pressure.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the helpful comments and assistance received from his thesis supervisor Dr. P. A. Distin. Also, the author wishes to thank Dr. G. P. Demopoulos, and fellow graduate students, P. Kondos and V. Papangelakis for the discussions held during the course of this work.

Thanks are also due to technicians M. Riendeau and M. Leroux for their technical assistance during the experimental portion of this investigation.

APPENDIX

EXPERIMENTAL DATA

I. EXTRACTION AND STRIPPING

1. Effect of pH on extraction: Figures 4.1 and 4.2

pH	$[Pb]_o$ (gpl)	$[Pb]_a$ (gpl)	D	log D	% Pb EXTRACTED
3.95	.63	2.26	.28	-.553	21.8
4.18	.74	2.15	.34	-.469	25.6
4.26	.75	2.14	.35	-.456	26.0
4.42	.99	1.91	.52	-.284	34.1
4.81	1.39	1.51	.92	-.036	47.9
4.95	2.22	.72	3.08	.489	75.5
5.09	2.19	.70	3.18	.502	75.8
5.12	2.46	.48	5.13	.710	83.7
5.40	2.68	.22	12.18	1.09	92.4
5.43	2.84	.10	28.40	1.45	96.6
6.80	2.92	.02	146.0	2.16	99.3

2. Stripping with 20 and 50 gpl nitric acid: Figure 4.3

20 gpl HNO_3		50 gpl HNO_3	
$[Pb]_a$ (gpl)	$[Pb]_o$ (gpl)	$[Pb]_a$ (gpl)	$[Pb]_o$ (gpl)
6.36	N.D.	6.36	N.D.
15.40	N.D.	15.30	N.D.
30.10	.46	29.81	0.74
30.0	15.56	60.41	0.35
29.61	19.00	72.33	12.47
		73.52	1.14

3. Stripping with 20 and 50 gpl acetic acid: Figure 4.4

20 gpl HOAc		50 gpl HOAc	
$[Pb]_a$ (gpl)	$[Pb]_o$ (gpl)	$[Pb]_a$ (gpl)	$[Pb]_o$ (gpl)
5.96	1.14	6.56	N.D.*
15.0	0.94	15.7	0.05
26.33	4.61	29.61	1.84
29.11	16.39	57.23	2.84
29.51	25.04	74.71	16.51

* not detected

4. Kinetics of stripping with 50 gpl nitric acid: Figure 4.5

TIME (min)	$[Pb]_a$ (gpl)
0.5	14.03
1.0	14.37
5.0	14.03
15.0	14.26
30.0	13.92

II. INFRARED SPECTRA

1. Unloaded, unreduced KELEX 100: Figures 4.9, 4.10, 4.11 and 4.15

Peak number:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wavenumber (cm^{-1}):	3395	3050	1710	1572	1500	1405	1330	1272	1245	1090	820	800	720	685	592

2. Loaded, unreduced KELEX 100: Figure 4.10

Peak number :	1	2	3	4	5	6
Wavenumber (cm^{-1}) :	3400	3050	1715	1550	1500	1420

7	8	9	10	11	12	13	14	15
N.D.	1300	1250	1100	815	797	735	685	589

3. Unloaded, KELEX 100 recyled 3 times: Figure 4.11

Peak number :	1	2	3	4	5	6
Wavenumber (cm^{-1}) :	3395	3050	1740	1572	1500	1405

7	8	9	10	11	12	13	14	15
1328	1272	1245	1090	820	800	720	685	590

III. HYDROGEN REDUCTION

EXPERIMENT 1

CONDITIONS : 518 K, 2.76 MPa H_2, 0.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Effect of seeding

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	20.6	20.2	19.3	17.4	13.5	10.3	8.6	7.5
% Pb IN THE ORGANIC :	100	98.2	93.4	84.2	65.5	49.8	41.9	6.2

EXPERIMENT 2

CONDITIONS : 518 K, 2.76 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Effect of seeding, temperature, and pressure

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	21.2	20.8	20.4	15.3	11.6	9.1	6.7	4.5
% Pb IN THE ORGANIC :	100	98.3	96.2	75.2	54.6	42.9	31.9	21.2

EXPERIMENT 3

CONDITIONS : 518 K, 2.76 MPa H_2, 0.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Thermal dissociation under nitrogen

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl):	19.7	19.5	19.5	19.1	19.1	18.9	18.7	18.7
% Pb IN THE: ORGANIC	100	98.3	96.2	75.2	54.6	42.9	31.9	21.2

EXPERIMENT 4

CONDITIONS : 518 K, 2.76 MPa H_2, 20.0 g seed, 800 rpm, 72 hr chelate age

COMMENTS : Chelate age effect

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl):	18.3	17.9	16.9	14.6	11.5	7.0	5.0	3.5
% Pb IN THE: ORGANIC	100	98.0	92.4	79.9	62.7	38.2	27.3	19.3

EXPERIMENT 5

CONDITIONS : 518 K, 2.76 MPa H_2, 20.0 g seed, 600 rpm, 24 hr chelate age

COMMENTS : Effect of agitation

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl):	18.8	18.5	17.1	14.5	11.1	7.6	5.2	3.7
% Pb IN THE: ORGANIC	100	98.5	90.7	77.3	59.2	40.4	27.6	19.7

EXPERIMENT 6

CONDITIONS : 518 K, 1.38 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Pressure Effect

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl):	22.4	21.3	21.0	19.1	16.7	15.4	12.1	9.4
% Pb IN THE: ORGANIC	100	95.2	94.1	85.6	74.6	65.7	51.7	40.0

EXPERIMENT 7

CONDITIONS : 518 K, 4.14 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Pressure Effect

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	18.8	17.0	12.3	8.6	5.0	3.1	1.4	0.3
% Pb IN THE: ORGANIC	100	90.3	64.9	45.1	25.9	15.8	6.8	1.4

EXPERIMENT 8

CONDITIONS : 493 K, 2.76 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Temperature Effect

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	18.3	18.1	17.5	17.7	17.1	16.8	16.3	15.4
% Pb IN THE: ORGANIC	100	98.9	95.9	96.7	93.7	91.8	89.2	83.9

EXPERIMENT 9

CONDITIONS : 533 K, 2.76 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Temperature Effect

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	16.6	16.6	15.4	11.3	8.3	5.3	3.2	1.8
% Pb IN THE: ORGANIC	100	99.6	92.5	68.2	49.9	31.9	19.3	10.8

EXPERIMENT 10

CONDITIONS : 518 K, 2.76 MPa H_2, 20.0 g seed, 800 rpm, 24 hr chelate age

COMMENTS : Organic recycling

TIME (hrs) :	0	.5	1	2	3	4	5	6
[Pb]o (gpl) :	20.8	20.1	19.2	16.4	11.4	8.7	6.5	4.3
% Pb IN THE: ORGANIC	100	96.5	92.3	78.8	54.7	42.1	31.4	20.6

EXPERIMENT CONDITIONS : 517 K, 0.0 MPa H_2, 0.0 g seed, 500 rpm, 24 hr chelate age

Thermal dissociation of Cu

COMMENTS : Comparison with thermal dissociation of Pb

TIME (hrs) :	0	1.25	3.25	5
[Cu]o (gpl):	9.55	9.05	7.00	4.025
% Cu IN THE: ORGANIC	100	95.0	73.0	48.5

Source: Reference No. 16 p. 222

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