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REDUCTION OF CUPRIC AND NICKELOUS IONS FROM
AQUEOUS COPPER AND NICKEL SULFATE SOLUTIONS
BY HYDROGEN.

The University of Oklahoma, Ph.D., 1973
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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

REDUCTION OF CUPRIC AND NICKELOUS IONS FROM AQUEOUS COPPER
AND NICKEL SULFATE SOLUTIONS BY HYDROGEN

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

OLMEDO KIESWETTER, JR.

Norman, Oklahoma

1973

REDUCTION OF CUPRIC AND NICKELOUS IONS FROM AQUEOUS COPPER
AND NICKEL SULFATE SOLUTIONS BY HYDROGEN

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ABSTRACT

Reduction of cupric ion, Cu(II) , and nickelous ion, Ni(II) , by hydrogen in aqueous sulfate solutions was studied in reactor tubes to complement the research at the University of Oklahoma in the general field of hydrometallurgy as related to the reduction of metal ions in aqueous solutions by hydrogen.

A special rocking mechanism was designed and built to produce agitation in the reactor tubes which were immersed in a hot oil bath. The extent of the reaction was followed by measuring the hydrogen pressure in the reactors.

Reduction of Cu(II) from aqueous 0.5 molar copper sulfate solutions was studied in the hydrogen partial pressure range from 27 atmospheres (400 psig) to 41 atmospheres (600 psig), and a temperature range from 140°C to 170°C . Experimental results indicate that Cu(II) reduction is favored by higher hydrogen partial pressure and higher temperature. An apparent activation energy of 26.65 kilocalories was determined for the hydrogen reduction of Cu(II) .

Reduction of Cu(II) from ammoniacal copper sulfate solutions at 150°C and 31 atmospheres (450 psig) hydrogen partial pressure showed that the initial rate of Cu(II)

reduction varies with the initial $\text{NH}_3/\text{Cu(II)}$ molar ratio. For initial $\text{NH}_3/\text{Cu(II)}$ molar ratios of 0, 1, 2 and 4, the initial rate decreased with $\text{NH}_3/\text{Cu(II)}$ molar ratio in the order $0 > 1 > 4 > 2$. However, reduction of Cu(II) in the absence of NH_3 could not be carried to completion (100 percent). On the other hand, high initial $\text{NH}_3/\text{Cu(II)}$ molar ratios had an adverse effect on the purity of the copper powder produced.

The effect of adding sulfuric acid to an ammoniacal copper sulfate solution with initial $\text{NH}_3/\text{Cu(II)}$ molar ratio of 4 was studied at 150°C and 31 atmospheres (450 psig) initial hydrogen partial pressure. Small acid additions had an adverse effect on the rate of Cu(II) reduction, but large acid additions (up to $\text{H}_2\text{SO}_4/\text{Cu(II)}$ molar ratio of about two) improved the rate of Cu(II) reduction.

Hydrogen reduction of Ni(II) catalyzed by ferrous ion, Fe(II) , was studied in aqueous ammoniacal nickel sulfate solutions. The temperature range was from 125°C to 150°C . The hydrogen partial pressure range was from 20 atmospheres (300 psig) to 24 atmospheres (500 psig), and the $\text{NH}_3/\text{Ni(II)}$ molar ratios ranged from one to six. At 150°C , it was found that for a fast rate of Ni(II) reduction the best $\text{NH}_3/\text{Ni(II)}$ initial molar ratio was two. In solutions with initial $\text{NH}_3/\text{Ni(II)}$ molar ratio of two, the concentration of Fe(II) was found to have a marked effect on rate of Ni(II) reduction. In solutions with an initial $\text{NH}_3/\text{Ni(II)}$ molar ratio of six, an apparent activation energy of 11.27 kilocalories was determined

for the reduction of Ni(II) by hydrogen in the temperature range from 125°C to 150°C.

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CHAPTER I

INTRODUCTION

This work complemented the research and development effort being carried out at the University of Oklahoma to develop a continuous hydrometallurgical process for the chemical reduction of metal ions by hydrogen in aqueous solutions. Details of the continuous reduction process are given by Sliepcevich and Brown (37), and Neskora (22) has given a detailed description of the continuous reduction equipment along with preliminary experimental results.

Hydrogen Reduction of Metal Ions in Aqueous Solutions, State of the Art

Habashi (11) briefly outlines historical developments on the reduction of metal ions by hydrogen in aqueous solutions. In 1859, Beketoff precipitated silver and mercury from aqueous solutions. Later, between 1901 and 1931, Ipatieff and coworkers precipitated copper, nickel, cobalt, lead, bismuth, arsenic, antimony, platinum and iridium from aqueous solutions. Between 1937 and 1959, Tronev and coworkers precipitated copper, nickel and cobalt from aqueous solutions of their complex salts. They showed that the

platinum metals could be separated from one another by selective precipitation with hydrogen.

In recent years, hydrogen reduction of non-ferrous metals (notably copper, nickel and cobalt) has attracted the attention of several workers. Table I lists some of the work published on the reduction of copper and nickel ions by hydrogen in aqueous solutions.

Even though a substantial amount of work has been done on the reduction by hydrogen of metal ions in aqueous solutions (as attested by Table I), very little of this technology has found its way into the commercial scale. Where hydrogen reduction is practiced commercially, it is done in batch autoclaves. To date no continuous operation has been reported.

Evans (8) indicates that until 1970 only six commercial installations, incorporating hydrogen reduction had been built; of these, two had been shut down for lack of feed, and a third had been abandoned when operating problems could not be overcome.

Of the three commercial plants presently in operation, that of Sherritt Gordon Mines in Canada is by far the largest and most innovative. Sherritt Gordon processes sulfide ore-concentrate with copper, nickel and cobalt as metal values. The finely ground mineral is leached with aqueous ammonia in a batch autoclave at 200°F and 115 pounds per square inch gauge (psig) air pressure. The leaching step extracts the

TABLE I

RECENT PUBLICATIONS ON REDUCTION OF Cu(II) AND Ni(II)
BY HYDROGEN FROM AQUEOUS SOLUTIONS

Author	Metal	Ref. #
1. Schaufelberger, R. A.	Cu, Ni	33
2. Sircar, S. C., and Wiles, D. R.	Ni	36
3. Mackiw, V. N.; Lin, W. C.; and Kunda, W.	Ni	18
4. Kunda, W.; Evans, D. J. I.; and Mackiw, V. N.	Ni	15
5. Meddings, B.; Kunda, W.; and Mackiw, V. N.	Ni	19
6. Evans, D. J. I.	Ni, Cu	8
7. Schaufelberger, F. A., and McCormick, W. R.	Ni	34
8. von Hahn, E. A., and Peters, E.	Cu	38
9. Dunning, W. J., and Potter, P. E.	Cu	7
10. MacGregor, E. R., and Halpern, J.	Cu	17
11. Kunda, W. and Evans, D. J. I.	Cu	14
12. Roberts, E. S.	Cu	29
13. Evans, D. J. I.; Romanchuk, S.; and Mackiw, V. N.	Cu	9
14. Evans, D. J. I.; Romanchuk, S.; and Mackiw, V. N.	Cu	10
15. Courtney, W. G., and Schaufelberger, F. A.	Ni	6
16. Meddings, B., and Mackiw, V. N.	Ni	20
17. Conner, H. S.	Cu	5
18. Brown, R. L.	Cu	4
19. Kothari, R. H.	Ni	13
20. Peters, E., and von Hahn, E.	Cu	25
21. Nasher, S., and Schaufelberger, F. A.	Cu, Ni	21
22. Schaufelberger, F. A.	Cu, Ni	32
23. Peters, E., and Halpern, J.	Cu	23
24. Peters, E., and Halpern, J.	Cu	24

metal values from the ore as soluble metal ammines. Subsequently, the metal-rich solution is purified by distilling excess ammonia and oxidizing the sulfide impurities to sulfates. Next, the solution is clarified, and from the clear solution copper is precipitated as copper-sulfide by bubbling hydrogen sulfide (H_2S) into the solution under controlled conditions. The copper-free solution is next stripped of nickel by a hydrogen reduction step. After nickel removal, the solution composition is adjusted so that cobalt can be precipitated as the sulfide with H_2S . The metal-free solution is then returned to the leaching step. Cobalt sulfide precipitated with H_2S is dissolved in acid, and cobalt is reprecipitated as the metal by reducing the metal ion with hydrogen.

The Bagdad Copper Corporation operation in Bagdad, Arizona, is a simpler operation than that of Sherritt Gordon. Bagdad buys cement-copper about 77 percent to 85 percent copper and leaches it with a sulfuric acid solution. After purifying and clarifying the pregnant solution, copper is precipitated from it by hydrogen reduction. The spent solution is then recycled to the cement-copper leaching step.

Universal Minerals and Metals of Kansas City, Missouri, recovers copper from scrap by a process similar to that of Bagdad, but Universal must pay close attention to leach solution purification and clarification because the many impurities liberated from the scrap.

Future Significance of Metal Ions Reduction by Hydrogen
in Aqueous Solutions

The potential of reducing metal ions from aqueous solutions by hydrogen is bound to have considerable impact in the next few years because:

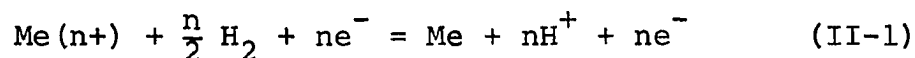
1. Industry is being forced to recover metals from ores by "chemical mining" with aqueous solutions as opposed to traditional smelting methods. Departure from smelting or pyrometallurgy is being forced by government regulation to reduce air pollution (Rohrman and Ludwig (30) point out that 12.2 percent of the total sulfur dioxide emitted over the United States in 1966 was produced by metallic ore smelters).
2. The "coming of age" of hydrometallurgy and the realization by the metal industry of its potentials: extraction of metals with aqueous solutions for example does not require expensive furnaces. In addition, aqueous leaching is often selective and leaves the bulk of the gangue materials unaffected.
3. In future years, the use of nuclear devices and hydraulic fracturing to fracture ore formations in order to allow percolation of leach solutions will remove the need for environmental destruction caused by surface mining.
4. There exists an increased need to recover metal values from "secondary ores" (solid waste) which are not practically recovered by traditional ore processing.

5. The possibility of recovering certain metals from leach solutions of sea-bottom manganese nodules exists. Present plans to recover metals from these nodules involve first making metal-chlorides by hydrochlorinating the metals at high temperature. The metal chlorides are then dissolved in water, and the metals are deposited electrolytically from the aqueous solution. In the electrolytic process, chlorine is generated which has to be converted to HCl for recycling to the hydrochlorinating step. By using hydrogen reduction of the metal chloride, HCl would be a by-product of the metal reducing step and could be easily recycled.
6. Biological leaching is receiving increased attention. In this type of leaching, the end solution would provide an excellent feed from which metals could be recovered by hydrogen reduction.

CHAPTER II

HYDROGEN REDUCTION OF METAL IONS IN AQUEOUS SOLUTIONS, THERMODYNAMIC CONSIDERATIONS

The chemical reduction of a metal ion $[\text{Me}(n+)]$ by hydrogen in an aqueous solution can be represented by



where Me is the metal produced by the hydrogen reduction of the metal ion $\text{Me}(n+)$. n is the oxidation number of the metal ion. ne^- are the electrons transferred in the reaction. For future reference, bear in mind that Equation II-1 can be represented by the two half-cell reactions



The chemical potential (μ_i) of the species involved in the reaction represented by Equation II-1 is defined as

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (\text{II-4})$$

where a_i is the activity of the species in solution, R is the universal gas constant, T the absolute temperature and

μ_i° the chemical potential of the species at a reference state of unit activity chosen as follows:

1. For gases, the ideal gaseous state at 1 atmosphere pressure.
2. For solids, the pure solid at one atmosphere pressure.
3. For aqueous solutions, the hypothetical ideal 1.0 molal solution in which the activity of the solute is one.

The condition for reaction-chemical-equilibrium requires that at constant temperature and pressure, the chemical potentials (or molal free-energies) of the products equals those of the reactants; or,

$$\sum_{i=1}^N \gamma_i \mu_i = 0 \quad (\text{II-5})$$

where the summation is taken over all species involved in the reaction and γ_i 's are the stoichiometric coefficients of the reaction as written.

Applying the condition for chemical equilibrium (Equation II-5) to the reaction represented by Equation II-1 and then substituting for chemical potentials the definition given by II-4,

$$\mu_{\text{Me}(n+)}^\circ + \frac{n}{2} \mu_{\text{H}_2}^\circ - n\mu_{\text{H}^+}^\circ - \mu_{\text{Me}}^\circ + RT \ln \frac{a_{\text{Me}(n+)} a_{\text{H}_2}^{n/2}}{a_{\text{H}^+}^n a_{\text{Me}}} = 0 \quad (\text{II-6})$$

If the oxidation number of the metal ion n is +2,

$$\mu_{\text{Me}(2+)}^\circ + \mu_{\text{H}_2}^\circ - 2\mu_{\text{H}^+}^\circ - \mu_{\text{Me}}^\circ + RT \ln \frac{a_{\text{Me}(2+)} a_{\text{H}_2}}{a_{\text{H}^+}^2 a_{\text{Me}}} = 0 \quad (\text{II-7})$$

Defining the chemical equilibrium constant K_a as

$$K_a = \frac{a_{\text{Me}(2+)} a_{\text{H}_2}}{a_{\text{H}+}^2 a_{\text{Me}}} \quad (\text{II-8})$$

and combining the standard free energies of formation, Equation II-7 yields

$$\Delta G^\circ = -RT \ln K_a \quad (\text{II-9})$$

where ΔG° is the free energy change for the reaction when each product and each reactant is in its standard or reference state. Equation II-9, then, allows calculation of the chemical equilibrium constant from a knowledge of chemical potentials.

Equation II-7 can also be rearranged to

$$[\mu_{\text{H}_2}^\circ - 2\mu_{\text{H}+}^\circ + RT \ln \frac{a_{\text{H}_2}}{a_{\text{H}+}^2}] - [\mu_{\text{Me}}^\circ - \mu_{\text{Me}(2+)}^\circ + RT \ln \frac{a_{\text{Me}}}{a_{\text{Me}(2+)}}] = 0 \quad (\text{II-10})$$

where the first portion in the left side of Equation II-10 represents Equation II-3 and the second portion Equation II-2. Combining reference-state chemical potentials in II-10,

$$[\Delta G_{(\text{II-3})}^\circ + RT \ln \frac{a_{\text{H}_2}}{a_{\text{H}+}^2}] - [\Delta G_{(\text{II-2})}^\circ + RT \ln \frac{a_{\text{Me}}}{a_{\text{Me}(2+)}}] = 0 \quad (\text{II-11})$$

or,

$$\Delta G_{(\text{II-3})} - \Delta G_{(\text{II-2})} = 0 \quad (\text{II-12})$$

where $\Delta G_{(II-3)}$ and $\Delta G_{(II-2)}$ are the free energy changes at reaction conditions associated with the reactions represented by Equations II-3 and II-2. $\Delta G^\circ_{(II-3)}$ and $\Delta G^\circ_{(II-2)}$ are the free energy changes associated with the reactions represented by Equations II-2 and II-3 if the reactions are carried out at the reference or standard conditions.

Electrochemistry teaches that one way to determine the quantities $\Delta G_{(II-3)}$ and $\Delta G_{(II-2)}$ is by measuring the electromotive force (emf) E of a reservible cell where in one-half-cell, the reaction in question is occurring, and in the other half-cell a reference reaction takes place. From electrochemistry,

$$\Delta G = -|n| FE \quad (II-13)$$

where F is the Faraday equivalent of electric charge necessary to convert one gram-equivalent of reactants to products.

Substituting Equation II-13 into Equation II-12 and simplifying

$$E_{(II-3)} - E_{(II-2)} = 0, \text{ or } E_{\text{Me/Me}(2+)} - E_{\text{H}_2/\text{H}^+} = 0 \quad (II-14)$$

Further, from Equation II-11 remembering that we are considering a metal ion with an oxidation number of +2,

$$\begin{aligned} [E^\circ_{\text{Me/Me}(2+)} + \frac{RT}{2F} \ln \frac{a_{\text{Me}}}{a_{\text{Me}(2+)}}] - [E^\circ_{\text{H}_2/\text{H}^+} + \frac{RT}{2F} \ln a_{\text{H}_2} \\ - \frac{RT}{F} \ln a_{\text{H}^+}] = 0 \end{aligned} \quad (II-15)$$

where E° refers to electromotive forces measured with respect to some reference half-cell, normally the hydrogen half cell reaction (represented by Equation II-3) at 25°C with hydrogen ions at unit activity and hydrogen gas at unit fugacity, in which case E° is referred to as the standard electrode potential.

Equations II-14 and II-15 are exactly analogous, but studied together they help to understand the thermodynamics of the reduction by hydrogen of metal ions.

Under reaction conditions, if $E_{H_2/H^+} > E_{Me/Me(2+)}$, the equilibrium condition of Equation II-14 will not be met, and a change must take place in the system to cancel the inequality in electric potentials. If $E_{Me/Me(2+)}$ is to increase at constant temperature and pressure, from the first portion of the left side in Equation II-15 it can be seen that this requirement is only possible if $a_{Me(2+)}$ decreases (since a_{Me} is fixed by the requirement of phase equilibrium between the liquid solution and the solid metal); that is, if the concentration of metal ion in solution (ideal solution at least) decreases due to the formation of metal. Clearly then, it follows that in order to reduce a metal ion by hydrogen from an aqueous solution at constant temperature and pressure, it is required that $E_{H_2/H^+} > E_{Me/Me(n+)}$.

In theory, all those metal ions in an aqueous solution whose electrode potentials satisfy the inequality $E_{Me/Me(n+)} <$

E_{H_2/H^+} can be reduced by hydrogen. For example, cupric ion $Cu(II)$, whose standard electrode potential $E_{Cu/Cu(II)}^\circ$ is -0.337 volts should be reduced by hydrogen at 25°C and one atmosphere hydrogen pressure. However, in practice the rate of $Cu(II)$ reduction by hydrogen at these conditions is negligible. More stringent conditions must be imposed to accomplish a measurable rate of reduction.

When $E_{Me/Me(n+)} > E_{H_2/H^+}$, hydrogen cannot reduce the metal ion; thus, means must be devised to reverse the inequality. Nickelous ion $Ni(II)$ for example, whose $E_{Ni/Ni(II)}^\circ$ is +0.25 cannot be reduced by hydrogen at 25°C and one atmosphere hydrogen pressure; instead, at these conditions, nickel metal should liberate hydrogen from water and go into solution as the nickelous ion. It follows then that in order to reduce $Ni(II)$ in an aqueous solution with hydrogen, conditions must be found at which $E_{H_2/H^+} > E_{Ni/Ni(II)}$.

Variations of E_{H_2/H^+} and $E_{Me/Me(2+)}$

From the left side of Equations II-14 and II-15,

$$E_{Me/Me(2+)} = E_{Me/Me(2+)}^\circ + \frac{RT}{2F} \ln \frac{a_{Me}}{a_{Me(2+)}} \quad (II-16)$$

$$E_{H_2/H^+} = E_{H_2/H^+}^\circ - \frac{RT}{F} \ln a_{H^+} + \frac{RT}{2F} \ln a_{H_2} \quad (II-17)$$

where $E_{Me/Me(2+)}^\circ$ is fixed by the reference standard state, and E_{H_2/H^+}° is specifically set equal to zero.

At constant temperature, $E_{\text{Me/Me}(2+)}$ can vary only by varying $a_{\text{Me}(2+)}$, since a_{Me} is fixed by the condition of phase equilibrium and can be set equal to unity while introducing little error. Figure 1 shows values of $E_{\text{Ni/Ni(II)}}$ and $E_{\text{Cu/Cu(II)}}$ for nickel and copper in equilibrium with their sulfate solutions; these values were calculated using Equation II-16 and data on activities obtained from Latimer (16) (Latimer actually gives molal concentrations and activity coefficient (γ_i) data which were used to compute activities from the relation $a_i = \gamma_i m_i$.)

At constant temperature $E_{\text{H}_2/\text{H}^+}$ can vary only by varying a_{H^+} or a_{H_2} ; however, these activities are commonly expressed by the more easily measurable quantities given by the relations

$$\text{pH} = -\log a_{\text{H}^+} = -\frac{\ln a_{\text{H}^+}}{2.303} \quad (\text{II-18})$$

$$a_{\text{H}_2} = \bar{f}_{\text{H}_2} = \bar{P}_{\text{H}_2} \quad (\text{II-19})$$

where pH is defined by Equation II-18. $\bar{f}_{\text{H}_2}$ is the fugacity of the hydrogen gas in equilibrium with the gas in solution. $\bar{P}_{\text{H}_2}$ is the hydrogen partial pressure obtained by assuming that hydrogen behaves as an ideal gas.

Substituting the relations II-18 and II-19 into Equation II-17, and introducing values for R and F, at 25°C we have

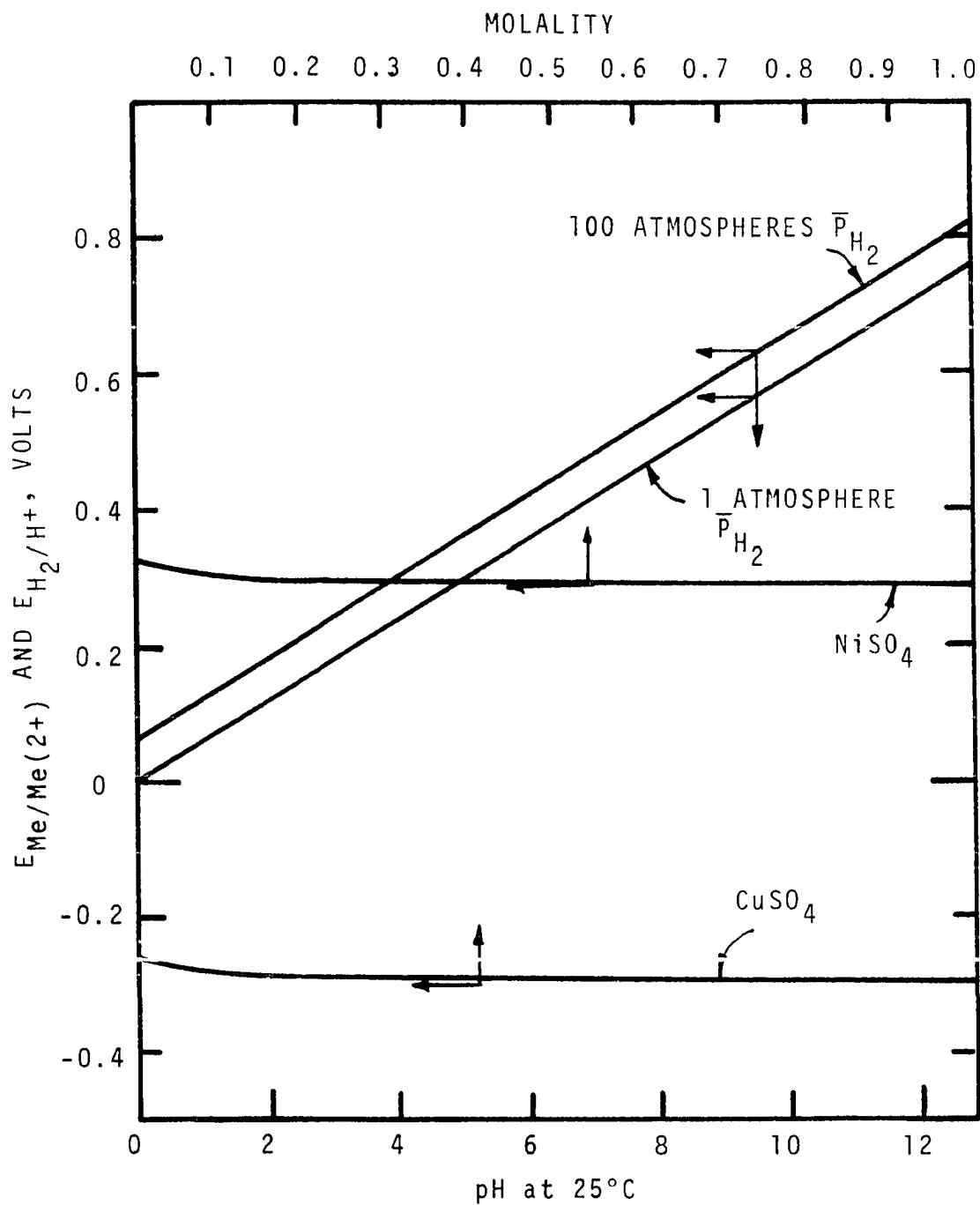


Figure 1. Hydrogen and Metal Electrode Potentials at 25°C.

$$E_{\text{H}_2/\text{H}^+} = 0.05916 \text{ pH} + 0.02958 \log \bar{P}_{\text{H}_2} \quad (\text{II-20})$$

from which it follows that at constant temperature $E_{\text{H}_2/\text{H}^+}$ can vary with pH or with $\bar{P}_{\text{H}_2}$. From the right hand side of Equation II-20, it is evident that $E_{\text{H}_2/\text{H}^+}$ is more sensitive to variations in pH than to variations of $\bar{P}_{\text{H}_2}$, since the coefficient of the pH term is twice the coefficient of the $\log \bar{P}_{\text{H}_2}$ term. Variation of $E_{\text{H}_2/\text{H}^+}$ with pH and $\bar{P}_{\text{H}_2}$ at 25°C is shown in Figure 1.

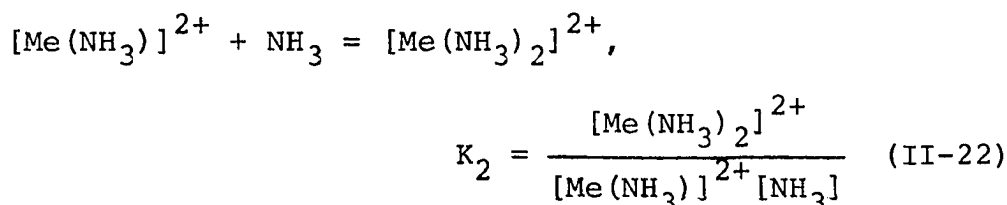
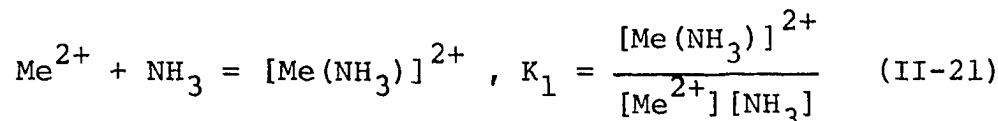
Figure 1 shows the greater sensitivity of $E_{\text{H}_2/\text{H}^+}$ to pH than to $\bar{P}_{\text{H}_2}$; the figure also gives an indication of the conditions required to reduce Cu(II) and Ni(II) with hydrogen in their sulfate solutions. Cu(II) for example, at 25°C should be reduced by hydrogen over the whole range of pH shown and at all hydrogen partial pressures. Ni(II), on the other hand, in a one molal NiSO_4 solution can only be reduced by hydrogen at a pH above 5 if $\bar{P}_{\text{H}_2}$ is one atmosphere, or above pH or 4 if $\bar{P}_{\text{H}_2}$ is 100 atmospheres.

Effect of NH_3

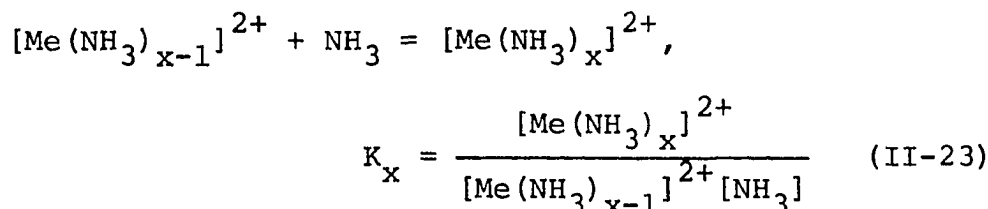
From Figure 1 it appears that the driving force for reduction of Ni(II) and Cu(II) increases with pH (since $E_{\text{H}_2/\text{H}^+}$ increases), that is, as the solution becomes more alkaline. In commercial practice, economics would dictate that a cheap reagent such as ammonia (NH_3) be used to raise the pH of the solution. Ammonia, however, forms complexes with metal cations

in solution which raise the potential of the metal ion.

Bjerrum (2) describes the metal-complex formation mechanism,



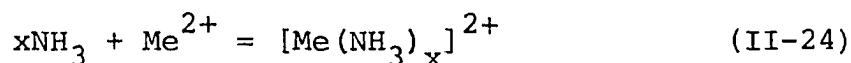
⋮



where the metal complex ions are formed stepwise up to $x = Z$, Z being Bjerrum's "characteristic coordination number" (number of first firmly and uniformly bound ligands) of the metal cation ($Z = 4$ for $\text{Cu}(\text{II})$ and $Z = 6$ for $\text{Ni}(\text{II})$). $K_1, K_2 \dots K_x$ are the activity equilibrium constants (Bjerrum's consecutive association constants) of the reactions.

It follows then that in ammoniacal solutions $E_{\text{Me}/\text{Me}^{2+}}$ represented by Equation II-16 has little significance. Instead, a metal electrode potential which accounts for the complexing action of NH_3 must be considered. For a given complex, the metal potential ($E_{\text{Me}/[\text{Me}(\text{NH}_3)_x]^{2+}}$) is given by the sum of the

two electrode potentials of the two stages



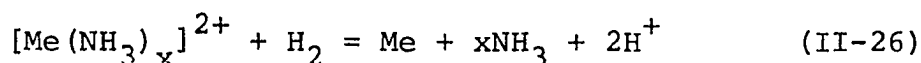
where the first stage is merely the electrode potential for the metal while the other is the electrode potential of the complex $[\text{Me}(\text{NH}_3)_x]^{2+}$. Bjerrum (3) and Meddings and Mackiw (20) note that $E_{\text{Me}/[\text{Me}(\text{NH}_3)_x]^{2+}}$ can be determined from the relation

$$nFE_{\text{Me}/[\text{Me}(\text{NH}_3)_x]^{2+}} = RT \ln K_x \quad (\text{II-25})$$

if K_x can be determined from measurements of activities.

The latter authors further point out that for any given ammoniacal metal salt solution, in which all the metal-ammine species are necessarily in equilibrium, there will be only one metal-ammine potential. The absolute value of the potential will depend upon both the absolute metal concentration and the ratio of ammonia to metal present in the solution.

Further complications to the thermodynamic treatment of metal ions reduction by hydrogen in ammoniacal solutions arise from the fact that depending upon the initial $\text{NH}_3/\text{Me(II)}$ molar ratio, the complex-ion composition in the reaction system changes as reduction proceeds. In general, reduction of the complex-ion by hydrogen can be represented by



where, depending upon the value of x , three situations can arise:

1. If $x = 2$, the acid generated by the reduction (H^+) should combine with NH_3 liberated from the metal complex and the pH will remain essentially constant (and therefore so will $E_{\text{H}_2/\text{H}^+}$).
2. If $x < 2$, as the reduction proceeds towards completion, H^+ will be generated for which no NH_3 will be available for neutralization; in this case the pH will decrease and so will $E_{\text{H}_2/\text{H}^+}$ down to a point where the reaction could stop because $E_{\text{H}_2/\text{H}^+}$ has become smaller than $E_{\text{Me}/\text{Me}^{2+}}$.
3. If $x > 2$, as the reduction proceeds, more NH_3 than H^+ will be generated and the pH of the solution will increase (and therefore so will $E_{\text{H}_2/\text{H}^+}$).

It should be noted that if $x \neq 2$, as the reaction proceeds, the $\text{NH}_3/\text{Me}^{2+}$ molar ratio is also changing which causes variations in the composition of the metal ammine complexes and their potentials.

The reader should bear in mind that the treatment presented above applies only to homogeneous solutions, and will not apply to the bulk of the work presented later, where ammonia addition causes formation of basic salts that precipitate as a solid phase.

CHAPTER III

REVIEW OF PREVIOUS WORK

Table I on page 3 lists much of the work published on reduction of copper and nickel ions by hydrogen in aqueous solutions. Although the scope of the subjects covered by the publications listed in Table I is vast, this chapter of this text will be limited to review of previous work done which closely relates to the subject of this investigation, that is, reduction by hydrogen of copper ion in aqueous copper sulfate solutions and nickel ion in aqueous nickel sulfate solutions.

Before passing to review previous work on reduction of Cu(II) and Ni(II) in their sulfate solutions by hydrogen, a general comment should be made about the mechanism of copper and nickel metal particles formation when the metal ion is reduced in aqueous solutions.

Courtney and Schaufelberger (6) outline two different mechanisms by which metal nuclei can be formed in aqueous solutions. In homonucleation, the metal nucleus is formed directly from metal atoms produced by chemical reduction in the bulk solution. On the other hand, in heteronucleation, the initial

deposition of metal takes place on the surface of a foreign catalytic particle.

Cu(II) solutions homonucleate readily when H_2 is used as the reducing agent, and it is relatively easy to produce metallic copper powder from Cu(II) solutions. On the other hand, Ni(II) solutions are hard to homonucleate with H_2 , and a nucleating catalyst must be added to the solution to start Ni(II) reduction by H_2 . Once nickel metal nuclei are formed by the nucleating agent, Ni(II) reduction by hydrogen proceeds smoothly on the nuclei surface by a heterogeneous reduction mechanism.

After the nuclei are formed, they can grow to microscopic metal particles through atom by atom deposition of metal onto the metal nuclei. Also, metal nuclei or metal particles can agglomerate to form large multiparticle agglomerates.

Precipitation of Copper by Hydrogen from Aqueous Copper Sulfate Solutions

Schaufelberger (33) using batch autoclaves studied the reduction by hydrogen of copper in weak (about 0.16 molar) copper sulfate aqueous solutions. The solution contained about 0.09 molar ferrous sulfate; also, 80 grams per liter of copper metal powder were loaded to the autoclaves with the feed solution. Among the variables and their ranges studied by Schaufelberger in this investigation were

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temperatures from 177°C to 232°C, hydrogen partial pressure from 50 psig to 600 psig, initial sulfuric acid concentration from 0.04 molar to 1.4 molar, and initial ammonium sulfate concentration from 0 molar to 1.5 molar. Some of Schaufelberger's findings from this work were:

1. An increase in hydrogen partial pressure increased the rate of copper reduction. At low hydrogen partial pressures the reaction was apparently controlled by the rate of dissolving hydrogen (that is, the reaction was mass-transfer limited).
2. As would be expected, the rate of copper reduction increased considerably with temperature.
3. Increase in initial sulfuric acid concentration (H_2SO_4) adversely affected the reaction equilibrium. Other variables held constant, the extent to which copper could be reduced from the solution decreased as the solution acidity increased.
4. The rate of copper reduction increased with increased ammonium sulfate concentration.

MacGregor and Halpern (17) studied reduction of Cu(II) by hydrogen in acidic CuSO_4 solutions. Their experiments were carried out in a one gallon titanium-lined autoclave. Experimental solutions were 0.1 molar CuSO_4 with H_2SO_4 concentrations varied from 0.05 molar to 0.3 molar. Temperature was varied between 150°C and 175°C, and H_2 partial pressure was set at

either 10 or 20 atmospheres. In addition, they ran some experiments with 0.1 or 0.2 molar Na_2SO_4 added to the acidic CuSO_4 solution.

MacGregor and Halpern (17) results were qualitatively the same as those obtained by Schaufelberger (33). Their work, however, clarified the effect of sulfate ion (SO_4^{--}) concentration on rate of Cu(II) reduction. They found that the efficiency of Cu(II) reduction increased with addition to the solution of an inert sulfate salt (Na_2SO_4). Addition of Na_2SO_4 in an amount at least as great as the initial CuSO_4 concentration allowed complete Cu(II) reduction because the H^+ generated in reducing Cu(II) was tied up by SO_4^{--} as the hydrogen sulfate anion (HSO_4^-)

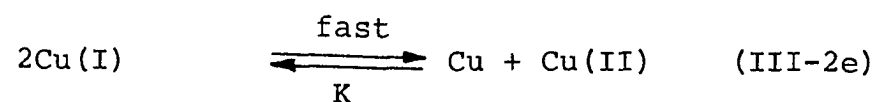
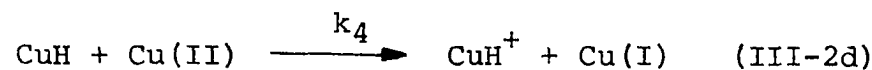
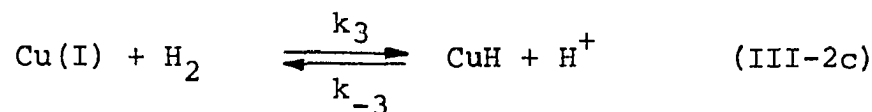
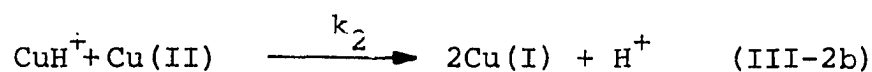
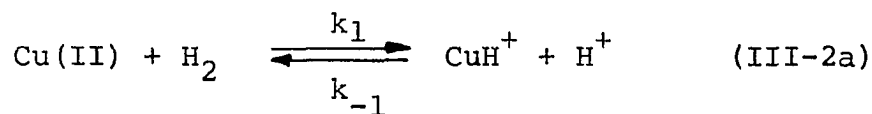


which effectively prevented increase in acidity of the solution. In addition, Na_2SO_4 was found to increase the initial rate of Cu(II) reduction by increasing the concentration of undissociated CuSO_4 in solution. Undissociated CuSO_4 in solution has been shown by Peters and Halpern (24) to activate hydrogen about six times faster than Cu(II) . MacGregor and Halpern also found that addition of metallic-copper-powder to the solution did not affect the rate of reduction suggesting that the rate of Cu(II) reduction in acidic CuSO_4 solutions is homogeneously determined.

Peters and coworkers (23, 24, 25, 38) probably have done the largest amount of work in the study of Cu(II) reduction by hydrogen in cupric-salt aqueous solutions.

von Hahn and Peters (38) studied Cu(II) reduction by H_2 in acidic, aqueous $CuSO_4$ solutions. Their experimental equipment consisted of a 2 liter titanium-lined autoclave fitted with a special sampling system which allowed determination of Cu(I) and Cu(II) concentrations at the reaction temperature. Experimental conditions were 160°C, 5 atmospheres H_2 partial pressure, 0.15 molar $CuSO_4$, and a total SO_4^{--} concentration of 1 molar (from H_2SO_4 and the inert salt $MgSO_4$).

To describe the reduction kinetics of Cu(II) in aqueous $CuSO_4$ solutions, von Hahn and Peters adapted the following mechanism which had been proposed earlier by Dunning and Potter (7)



where CuH^+ and CuH are reactive intermediates. From the above mechanism they obtained the rate equation

$$\frac{-d[\text{H}_2]}{dt} = \frac{k_1 [\text{Cu(II)}]^2 [\text{H}_2]}{\frac{k_{-1}}{k_2} [\text{H}^+] + [\text{Cu(II)}]} \quad (\text{III-3})$$

$$+ \frac{k_3 [\text{Cu(I)}] [\text{Cu(II)}]^2 [\text{H}_2]}{\left(\frac{k_{-1}}{k_2} [\text{H}^+] + [\text{Cu(II)}] \right) \left(\frac{k_{-3}}{k_4} [\text{H}^+] + [\text{Cu(II)}] \right)}$$

or

$$- \frac{d[\text{H}_2]}{dt} = R_{\text{Cu(II)}} + R_{\text{Cu(I)}} \quad (\text{III-4})$$

where $R_{\text{Cu(II)}}$ and $R_{\text{Cu(I)}}$ correspond to the reduction rates due to the activation of hydrogen by cupric and cuprous ions respectively. von Hahn and Peters also concluded:

1. "Rate of reduction of aqueous cupric sulfate by hydrogen depends, in part, on a strong first order catalytic effect of cuprous ions."
2. "In this reaction the activation of hydrogen by both the cupric and cuprous ions occurs by heterolytic splitting of the H_2 molecule."
3. Cuprous ion appears to be 20 times more active towards H_2 than cupric ion (Dunning and Potter (7) estimated cuprous ion activity towards H_2 to be about 100 times larger than that of cupric ion).
4. Acidity has an adverse effect on both cuprous and cupric-activated reduction rates.

Evans, Romanchuk and Mackiw (9) developed and piloted a process to produce copper-powder from sulfide copper-ore-concentrates. The process includes ammoniacal leach of the ore to extract metal values and hydrogen reduction to recover metallic-copper-powder. Feed to the hydrogen reduction batch autoclave consists of a slurry of basic cupric sulfates of the general formula $(\text{CuSO}_4)_m\text{Cu}(\text{OH})_2$ (where m lies between 2 and 3) in an aqueous solution of copper triammine sulfate. During the reduction, numerous solid phases (including basic cupric sulfate, various cuprous sulfates, cupric oxide and cuprous oxide) may be identified in this system.

In their work Evans and coworkers studied H_2 reduction of $\text{Cu}(\text{II})$ in a slurry with 50 grams per liter (gpl) $\text{Cu}(\text{II})$ (about 0.785 molar $\text{Cu}(\text{II})$). Variables studied included temperature (350°F to 450°F), hydrogen partial pressure (100 psig to 500 psig), initial $\text{NH}_3/\text{Cu}(\text{II})$ molar ratio (1.6 to 3.0), initial $(\text{NH}_4)_2\text{SO}_4$ concentration (0 gpl to 450 gpl), and addition of organic agents (ammonium polyacrylate). Some of their more important experimental findings were

1. The rate of $\text{Cu}(\text{II})$ reduction decreases with increasing initial $\text{NH}_3/\text{Cu}(\text{II})$ molar ratio.
2. $\text{Cu}(\text{II})$ reduction rate curves indicates that, apart from the initial 10 minutes of the reduction, the reaction is zero order with respect to unreduced $\text{Cu}(\text{II})$.
3. Rate of $\text{Cu}(\text{II})$ reduction increases with increasing initial $(\text{NH}_4)_2\text{SO}_4$ concentration.

4. Higher temperatures and higher hydrogen partial pressures favored the rate of Cu(II) reduction.
5. Addition of ammonium polyacrylate to the reduction charge improved the rate of Cu(II) reduction and prevented plastering and plating of copper on the walls of the reduction autoclave. Ammonium polyacrylate also controlled the growth pattern of copper powder particles and inhibited their agglomeration during densification (reduction of fresh slurry in presence of copper particles produced in a previous charge, so that in effect, old particles grow and densify).

Precipitation of Nickel by Hydrogen from Aqueous Nickel Sulfate Solutions

Solutions of NiSO_4 do not homonucleate readily, and when they homonucleate, Ni(II) reduction does not proceed to a considerable extent because H^+ generated in reducing Ni(II) stops the reaction. Schaufelberger (33), for example, showed that only 10 percent of the Ni(II) in NiSO_4 solutions could be reduced by hydrogen before the solution became too acid (at a pH of about 2.0) and Ni(II) reduction stopped.

Although Ni(II) does not homonucleate readily in NiSO_4 solutions, the rate of Ni(II) reduction can be increased if nickel metal "seeds" are added to the solution. However, the metal seeds do not solve the problem of the reaction stopping when a critical acid concentration (pH) is reached due

to acid formation as Ni(II) is reduced. To solve the acidity problem, either neutralizing or buffering agents must be added to the solution.

Schaufelberger (32) found that addition of H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$, or a combination of both to NiSO_4 solutions seeded with nickel metal allowed reduction of Ni(II) at higher acidities (lower pH) than was possible when H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ was absent. Schaufelberger's explanation for this behavior was that in the presence of sulfate ion, an anionic complex of nickel is formed which permits the reduction to continue at lower pH.

As mentioned above, to achieve complete Ni(II) reduction in NiSO_4 solutions either a neutralizing or a buffering agent must be added to stop acid formation. Schaufelberger (33) and Kothari (13) using ammonium acetate as buffer could reduce all the Ni(II) in NiSO_4 solutions. However, Kothari reports that the bulk of the nickel product was sheet metal that adhered to the reactor walls and was difficult to remove.

When Ni(II) is reduced in an ammoniacal solution with initial $\text{NH}_3/\text{Ni(II)}$ molar ratio greater than 2.0, the acid generated in reducing Ni(II) presents no problem because the H^+ is neutralized immediately.

Most of the work on reduction of Ni(II) by hydrogen in ammoniacal solutions has come from workers (Schaufelberger, Mackiw, Lin, Kunda and Courtney) who were involved in development of the Sherritt Gordon Mines process. At Sherritt Gordon

sulfide ore concentrate is leached with an ammoniacal solution, and the Ni(II) is then reduced with H_2 in the ammoniacal solution.

Courtney and Schaufelberger (6), using a 3 liter titanium-lined autoclave, studied nucleation of Ni(II) by nucleating catalysts in heavily buffered, ammoniacal $NiSO_4$ solutions. These workers also studied Ni(II) reduction in solutions seeded with Ni metal. To study nucleation of the Ni(II) - H_2 reduction, they used a solution containing (gpl) 22 $NiSO_4$, 110 $(NH_4)_2SO_4$, and 6.1 NH_3 . Hydrogen partial pressure was 600 psig and the temperature range was between 150°C and 200°C. Their work showed that for $FeSO_4$, Na_2S and $CrSO_4$ the catalytic effectiveness in nucleating the Ni(II) - H_2 reduction decreased from $CrSO_4$ to Na_2S to $FeSO_4$. Although reproducibility of their work was limited to 50 percent, they made the following conclusions:

1. Efficient nucleation required a very high level of agitation in the liquid.
2. "Nucleation of the Ni(II) - H_2 reaction usually seems to involve a mixed salt of Ni(II) and the reducing agent with only transient effectiveness, and the elucidation of the nucleating mechanism will be difficult."
3. When $FeSO_4$ is used as nucleating catalyst, apparently a Fe(II) - Ni(II) hydroxide or sulfate is involved in nucleating the Ni(II) - H_2 reaction.

4. Nucleation was drastically affected by how the sequence of events (time of catalyst addition and hydrogen injection, heating, agitation) were varied before the final reaction conditions were attained.

In their work on Ni(II) reduction using nickel metal seed, Courtney and Schaufelberger (6) used solutions of 0.14 molar nickel sulfate with $\text{NH}_3/\text{Ni(II)}$ initial molar ratios between 2 and 9, $(\text{NH}_4)_2\text{SO}_4$ concentrations from 0.6 molar to 1.8 molar and granular nickel seed of either 50 or 100 grams per liter. The temperature range was between 150°C and 175°C , and the hydrogen partial pressure range was between 50 psig and 600 psig. In this work they arrived at the rate expression

$$R_O = A \cdot f(\text{NH}_3) \cdot \frac{\bar{P}_{\text{H}_2}^{1/2}}{[(\text{NH}_4)_2\text{SO}_4]} \quad (\text{III-5})$$

for the initial rate of Ni(II) reduction, where A is a temperature dependent constant which includes kinetic and thermodynamic factors, $f(\text{NH}_3)$ is an undetermined function of the NH_3 concentration and the $\text{NH}_3/\text{Ni(II)}$ molar ratio, $[(\text{NH}_4)_2\text{SO}_4]$ is the ammonium sulfate concentration, and $\bar{P}_{\text{H}_2}$ is the hydrogen partial pressure.

Some of Schaufelberger (32) findings on reducing Ni(II) from ammoniacal NiSO_4 solutions buffered with $(\text{NH}_4)_2\text{SO}_4$ and using nickel metal as seed were:

1. The presence of some $(\text{NH}_4)_2\text{SO}_4$ is helpful and prevents the formation of solid nickel hydroxide.

2. Optimum rate of reduction is obtained for solutions having an initial $\text{NH}_3/\text{Ni(II)}$ molar ratio of two; further, a dense nickel powder is produced.
3. At high initial $\text{NH}_3/\text{Ni(II)}$ molar ratios (4 or more) or high concentrations of $(\text{NH}_4)_2\text{SO}_4$ (2 molar), the reduced nickel had a tendency to plate on the autoclave walls.

Mackiw, Lin and Kunda (18) using a one gallon autoclave did experimental work on the Sheritt Gordon process to recover nickel from ammoniacal NiSO_4 solutions. In this process, ferrous sulfate is used as a nucleating catalyst in the first batch of a seven batch cycle; subsequent batches of solution feed are reduced using as seed the nickel produced in the previous batch. Among Mackiw, Lin, and Kunda findings were:

1. Addition of FeSO_4 to an ammoniacal ($\text{NH}_3/\text{Ni(II)}$ molar ratio of two) NiSO_4 solution not only catalyzed the reduction of nickel by hydrogen, but it also resulted in the production of a very fine and active (as seed for reducing following batches) powder.
2. Using FeSO_4 as catalyst, the apparent activation energy for reducing Ni(II) from ammoniacal solutions ($\text{NH}_3/\text{Ni(II)}$ molar ratio of 2.0) varied between 13.7 kcal at 300°F to 350°F to 6.5 kcal at 350°F to 400°F .
3. Addition of $(\text{NH}_4)_2\text{SO}_4$ to a reaction batch using FeSO_4 as catalyst was found to retard the reaction.

4. Reduction of Ni(II) proceeds to completion only when the $\text{NH}_3/\text{Ni(II)}$ molar ratio is in the range of about 1.5 to 2.5.

CHAPTER IV

EXPERIMENTAL EQUIPMENT

The basic experimental equipment consisted of a hot oil bath with a rocking mechanism for "reactor-tubes." Following is a description of the equipment which is somewhat unique to the purpose of this investigation.

Reactors

Figure 2 shows a schematic drawing of the "tube-reactors" used to perform the experiments. Reactor parts are listed in Table II (Appendix A). The reactor "valve-heads" were manufactured to specification by Autoclave Engineers, Inc., Erie, Pennsylvania. Bottom-caps, nuts and ferrules were standard parts manufactured by Crawford Fitting Company, Solon, Ohio.

Reactor bodies were cut from standard 316 stainless steel tubing 3/4" outside diameter by 0.049" wall thickness. The length of the reactor bodies was determined experimentally. Prior to the start of the experimental work, visual inspection of mixing patterns in transparent prototype reactors indicated that for a given reactor liquid load (liquid load, as a percentage of the reactor volume), a minimum reactor length

was required to accomplish good mixing of the gas and liquid phases. The poor mixing observed in the transparent prototype reactors was later confirmed experimentally, as it was found that for set experimental conditions, the rate of reaction increased with reactor-body length up to a point where further increase in reactor-body length yielded no improvement in rate of reaction (that is, the reaction was no longer mass transfer limited).

Hot Oil Bath

Figure 3 shows a schematic drawing of the hot oil bath and its related equipment. The oil-holding tank itself, was a circular steel tank 32" inside diameter and 24" deep. The tank was insulated with 2" of calcium silicate insulation. Heating oil was Terrestic 85, a heat transfer oil provided by Esso Research and Engineering, Bayton, Texas. Heat was supplied by two electric-resistance cable heaters rated at 3,700 watts and manufactured by Emerson Electric Company, Pittsburgh, Pennsylvania. Temperature could be controlled within $\pm 1^{\circ}\text{C}$ by a Pyro-vane temperature indicator-controller (TIC) manufactured by the Honeywell corporation, Minneapolis, Minnesota.

Rocking Mechanism

To "rock" the reactors, a rocking mechanism was installed in the oil bath. Power to the rocking mechanism was provided by a 3/4 horsepower electric gear-motor with

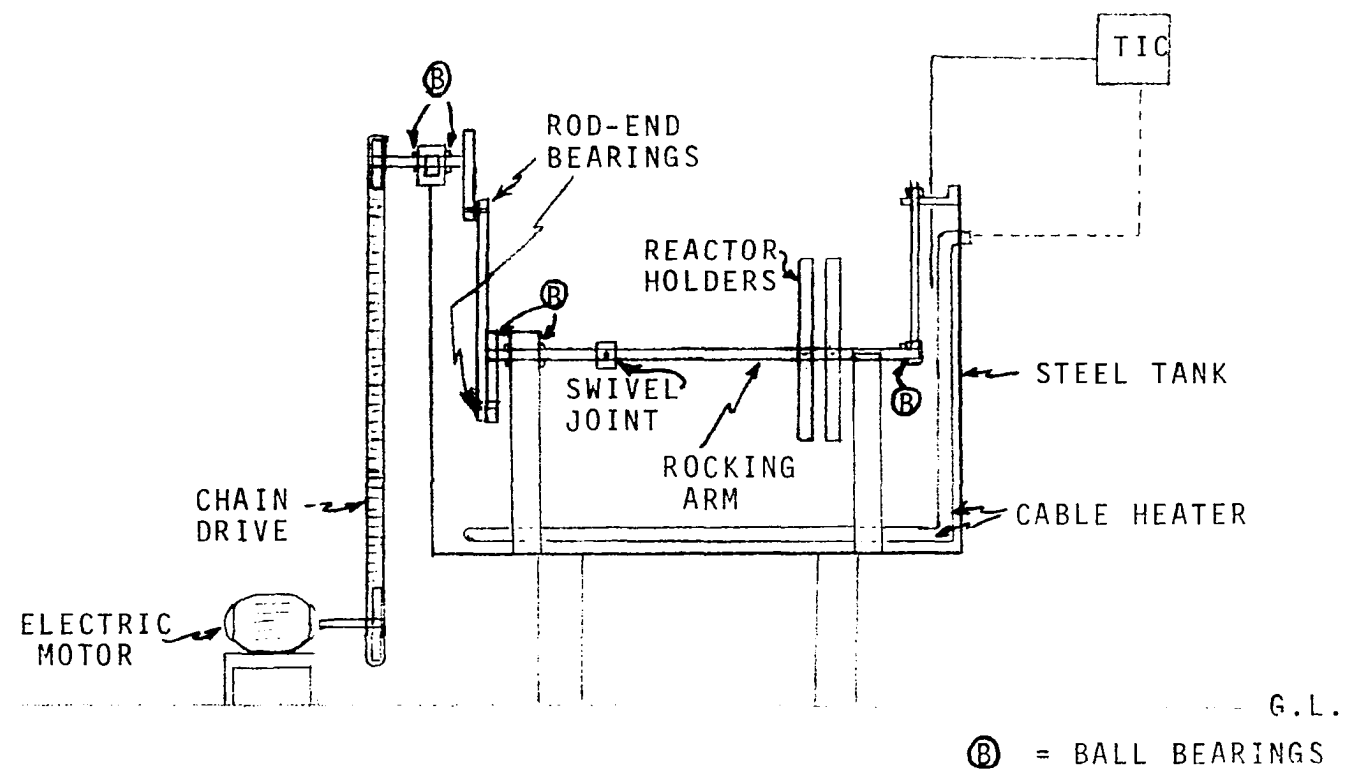


Figure 3. Hot Oil Bath.

drive-shaft speed of 60 revolutions per minute. The electric motor's drive-shaft was coupled to a secondary drive-shaft by a drive-chain and reducing gears that set the speed of the secondary drive-shaft at 30 revolutions per minute. The secondary drive-shaft was in turn connected to the mechanism's rocking arm by a one-half inch steel rod which had rod-end bearings at each end. The rod-end bearings at each end of the steel rod permitted connecting the rod to the secondary drive-shaft and to the rocking arm. This arrangement allowed the secondary drive shaft end of the connecting rod to rotate through 360 degrees, while the rocking arm end made a forward and a backward motion through a 150 degree arc. In effect then, the reactors were rocked 60 times per minute.

The rocking arm of the mechanism had a swivel-joint which allowed inserting or removing the reactor-holders out of the hot oil as desired. Compression-clamps were used to attach the reactors to the reactor holders.

The hot oil bath was enclosed in a metal hood. Fumes given off by the hot oil were exhausted from the hood by a fan driven by an explosion-proof electric motor.

Auxiliary Equipment

Figure 4 shows a schematic drawing of some of the auxiliary equipment. Auxiliary equipment included hydrogen and nitrogen cylinders, pressure regulators, a calibrated pressure gauge, and a circuit of 1/8" 316 stainless steel

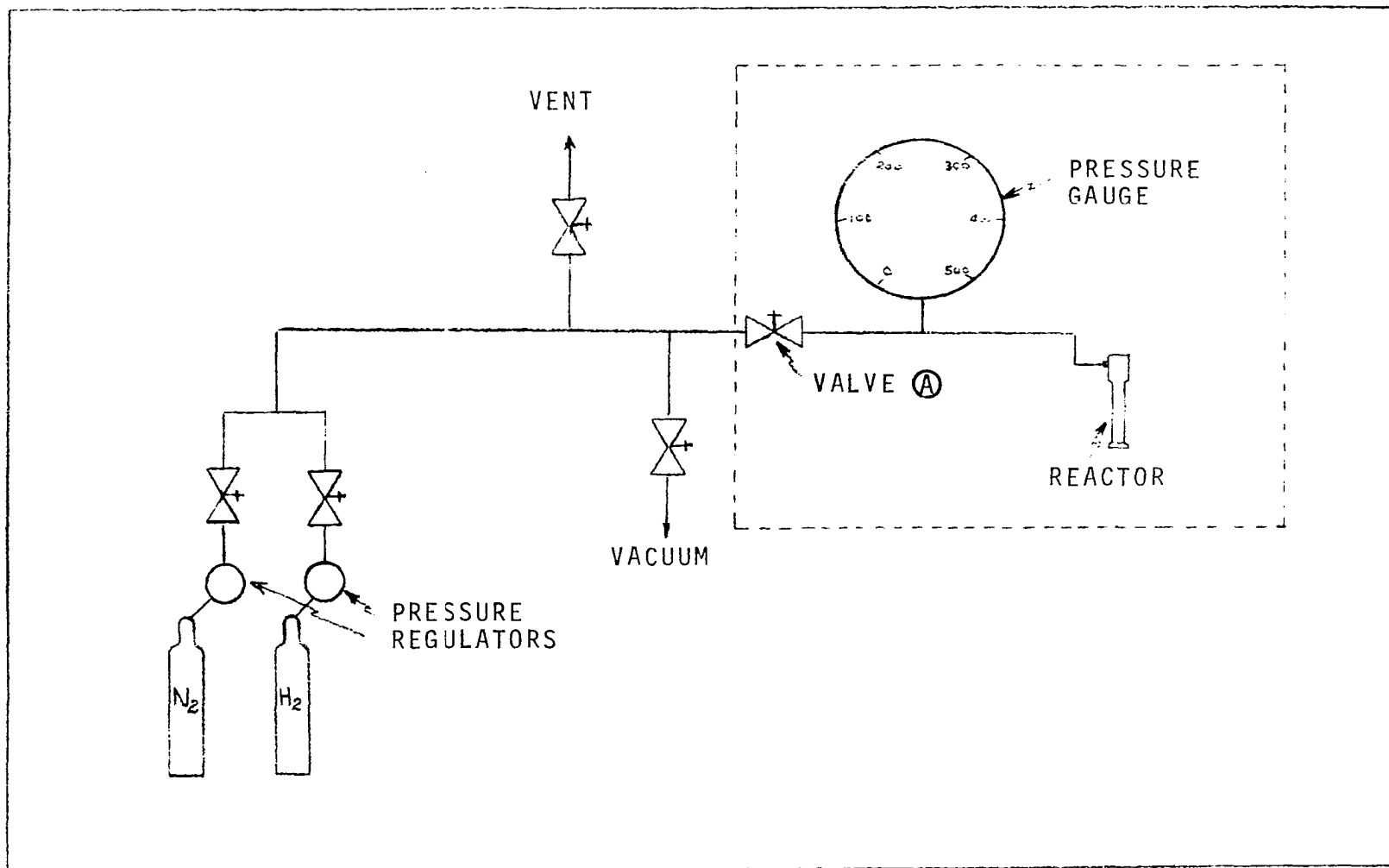


Figure 4. Auxiliary Equipment.

tubing and valves that allowed loading hydrogen to the reactors.

In Figure 4 the portion of the hydrogen loading circuit that is enclosed by the dashed lines was used to discharge hydrogen from the reactors at the end of an experiment. The internal volume of this portion of the circuit was known. It included the internal volume of the pressure gauge's Bourdon tube, the internal volume of the 1/8" tubing leading from the pressure gauge to valve A and to the reactor, and the internal volume of the reactor-head-valve from the 1/8" tubing connection to the valve's stem-seat. See Appendix B for details on internal volume calibration procedure and for internal volume calibration curve. Knowledge of the internal volume of this portion of the circuit allowed back-calculation of the pressure inside the reactor before it was opened.

Additional equipment consisted of laboratory glassware, reagent grade chemicals and analytical equipment.

CHAPTER V

EXPERIMENTAL PROCEDURE

Basically, the experimental procedure consisted of four steps:

1. Loading liquids to reactors.
2. Loading hydrogen.
3. Immersion of reactors in the hot oil bath for the desired length of reaction.
4. Unloading reactors and product analysis.

Preparing Feed for the Reactors

To load liquid solutions into the reactors, the "valve-heads" were closed and the bottom-caps removed. The reactors were turned up-side-down and solutions loaded through the bottom opening. After the liquids were loaded the bottom opening was closed by replacing the bottom-cap.

Loading solutions of NiSO_4 or CuSO_4 presented no problem and the solutions were merely pipeted into the reactors.

Loading charges that contained several solutes (metal-salt and ammonia, for example) required more attention. Certain combinations of ammonia and the metal salts formed solid

basic-salts which precipitated out of solution. In this case, homogeneous solutions of one or more solute were charged independently into the reactors to make up the final charge. When the final charge was made up with more than one solution, they were well shaken after closing the reactors to insure good mixing and were then allowed to reach room temperature.

In most cases the final volume of the liquid charge was 25 milliliters (except the runs of copper with ammonia when the liquid charge was 30 milliliters) at room temperature. The homogeneous solutions were prepared so that when they were mixed in the reactors, the combined solutions would meet the experimental requirements as to relative and absolute solute concentrations.

Loading CuSO_4 , NH_3 and H_2SO_4

Charges which contained NH_3 and CuSO_4 were prepared by two different procedures. When the initial $\text{NH}_3/\text{CuSO}_4$ molar ratio in the charge was four or more, a standard aqueous solution of NH_3 and CuSO_4 was loaded since aqueous solutions of NH_3 and CuSO_4 with $\text{NH}_3/\text{CuSO}_4$ molar ratio of four or more are homogeneous and no basic salts precipitate out of them. However, if the initial $\text{NH}_3/\text{CuSO}_4$ molar ratio of the charge was less than four, the charge was made up with two different solutions: one, an NH_3 solution, and the other a CuSO_4 solution.

For charges that contained H_2SO_4 in addition to CuSO_4 and NH_3 , the acid was loaded last after NH_3 and CuSO_4 had been loaded by the procedure described above.

Loading NiSO_4 , NH_3 and FeSO_4

Charges of experiments with NiSO_4 were prepared from two homogeneous solutions. One solution contained NiSO_4 and FeSO_4 as solutes, and the other was an NH_3 solution.

Loading Hydrogen

Hydrogen was added after the liquids were loaded. To add hydrogen, the reactors were first purged with H_2 by pressurizing to 100 psig and then releasing the pressure. Next, the reactors were loaded with H_2 to a pressure which had been calculated to give the initial hydrogen partial pressure at the reaction temperature. In calculating the required hydrogen loading pressures, account was taken of gas phase compression due to expansion of the liquid phase (water expansion data from Perry's (1)) caused by heating the solution from ambient temperature to reaction temperature. Appendix C shows the procedure used to determine hydrogen loading pressures.

Operating the Oil Bath

When the oil bath had attained the desired reaction temperature, the reactors were placed on the rocking mechanism and immersed in the hot oil. The rocking motion was started

within five seconds after immersion. Five seconds before the desired time of immersion had lapsed, the rocking mechanism was stopped, the reactors were removed from the oil bath and were quickly immersed in ice water to stop the reaction. After 2 to 5 minutes, the reactors were taken out of the ice water and allowed to reach room temperature before opening.

Figure 5 shows typical temperature curves for reactor heat-up when reactors were immersed in the hot oil bath, and reactor cool-down curves when the reactors were immersed in ice water. Curves in Figure 5 were obtained by inserting a bayonet thermocouple in the center of a reactor and simulating the experimental procedure. Temperature curves show that it took approximately 2 minutes for the reactors to heat up from room temperature to reaction temperature and approximately the same time to cool-down from reaction temperature to room temperature.

Analyzing Reactor Charge

After taking them out of the cool bath, the reactors were allowed to reach room temperature. When the reactors had reached room temperature, they were connected to the H₂ unloading circuit enclosed by the dashed lines in Figure 4. Next, the reactors were opened to measure final reactor pressure. Final reactor pressure and ambient temperature were recorded to determine the amount of hydrogen left in the reactors. After releasing the reactor pressure, the reactors

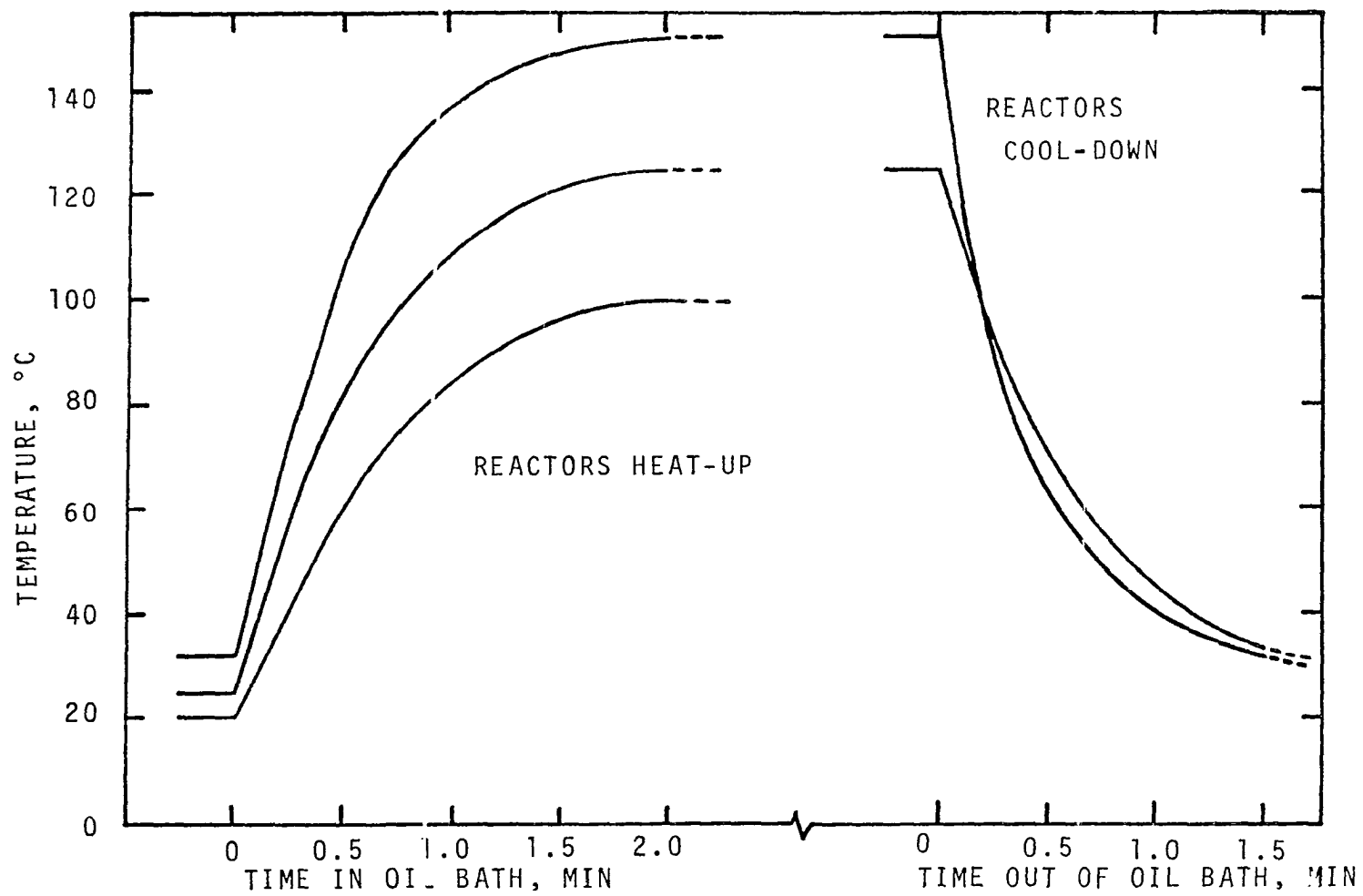


Figure 5. Heat-Up and Cool-Down Curves of Reactors.

were disconnected from the H_2 unloading circuit and the bottom cap was removed in order to collect the reaction products. Reactor products were collected in sample bottles for wet methods of analysis. In most cases the solid and liquid phases of the products were separated immediately by filtering the products out of the reactor.

Determining Hydrogen Consumed

The hydrogen consumed in a reactor proved the most reliable procedure for determining the amount of metal ion in the charge that had been reduced. Of necessity, this procedure required the assumption that all hydrogen consumed had been used in reducing the metal ion from its divalent state to the elemental state. Data used to determine hydrogen consumption included calibrated volumes of the pressure gauge, connections and reactors (see Appendix B), metal ion concentration and volume of the liquid load, and the initial and final reactor pressures with their corresponding room temperatures.

Appendix D gives details of how the amount of metal ion reduced was determined by calculating the hydrogen consumption in a reactor. Several comments must be made about assumptions made in the computer program (shown in Appendix D) used to calculate the hydrogen consumption in a reactor:

1. The vapor pressure of the liquid load was always assumed to be equal to the vapor pressure of water. This assumption was necessary because vapor pressure data for the

aqueous solutions was not available. This assumption should not introduce grave error in calculations of ammonia-free solutions. However, in the cases where NH_3 was present, it can be expected that a larger error is introduced; nevertheless, ammonia and the metal ions formed solid basic salts which should not increase the vapor pressure of water. The NH_3 which did not precipitate as a basic salt was tied up by the metal ions in solution in the form of ammine complexes, so that little NH_3 was free in solution to elevate considerably the vapor pressure of the solution. Bjerrum (3) has shown that 1 molar aqueous Ni(II) solutions with $\text{NH}_3/\text{Ni(II)}$ molar ratio of 4 contain only 0.10 molar free ammonia. For a 0.1 molar NH_3 aqueous solution, the data of Scatchard and coworkers (31) shows that at 150°C the vapor pressure of the solution is about 82 psia, while that of water at 150°C is 69 psia. This 13 pound per inch square difference in vapor pressure of the solution would only introduce a 6.5 percent error in determining the partial pressure of hydrogen, if the partial pressure of hydrogen is around 200 psi. To justify this assumption further, it should be mentioned that Bjerrum's (3) measurements were made in heavily buffered solutions which prevented precipitation of solid basic salts; consequently higher free NH_3 concentrations were present than in this work where solid basic salts precipitated out of solution, thereby lowering

the concentration of free ammonia in solution.

2. The computer program output gives two figures for percent metal ion conversion: one (H2CONV) is based on the hydrogen consumed as calculated from raw data; the other (ADH2CONV) takes account of hydrogen which would be in the liquid solution at 75°C (data of hydrogen solubility in water of Pray and coworkers (27)). Although ADH2CONV was calculated, in the treatment of data in Chapter VI H2CONV was used to discuss the results because this figure was found to agree better with the results obtained by wet methods of analysis (see Appendix E).

Analysis by Wet Methods

Wet methods of analysis were used during the initial stages of this work. However, wet methods of analysis were abandoned (and instead the hydrogen consumption determination described above was used to determine the amount of non-reduced metal in the charge) when work in reducing the metal ions from ammoniacal solutions was started. Addition of ammonia to the metal-salt solutions formed ammine complexes in solution, and basic-salts which precipitated out of the solution, so that the charge would become a slurry, and the solution no longer represented the non-reduced metal in the charge. Further, when ammonia was present in the charge, it was impossible to obtain a meaningful sample (by agitating the products before sampling) of the slurry products because the sample

would contain solid basic salts and reduced metal which would be determined as non-reduced metal by the wet analysis methods.

The wet methods of analysis used on various occasions (to check hydrogen consumption calculations, and purity of solid products) were:

1. Iodometric titration to analyze for copper.
2. Precipitation with dimethylglyoxime, and titration with EDTA (ethylene diamine tetra-acetic acid) to analyze for nickel.

Details of the wet methods of analysis are given in Appendix F.

Analysis of Solids

Solids were analyzed by x-ray diffraction in the Norelco x-ray machine of the School of Geology. See Appendix F for details.

Cleaning The Reactors

After the charge was removed from the reactors, the reactors were filled with nitric acid and were left overnight to remove all traces of metal (nickel or copper). After the acid leach, the reactors were scrubbed with a detergent solution, rinsed well and dried. This careful cleaning procedure was necessary to avoid reaction inhibition or catalysis by foreign matter which could have gotten into the reactors.

CHAPTER VI

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results for the reduction of copper from copper sulfate solutions both in the presence and absence of ammonia and the iron catalyzed reduction of nickel from ammoniacal nickel sulfate solutions will be presented in this chapter.

Reduction of Cu(II) from Aqueous Copper Sulfate Solutions

Reduction of Cu(II) from CuSO_4 solutions is of interest because CuSO_4 solutions result when copper oxide ores are leached with sulfuric acid.

Figure 6 shows the effect of initial hydrogen partial pressure in reducing Cu(II) from a 0.5 molar CuSO_4 solution at 150.0°C ; it also shows how the hydrogen partial pressure in the reactors vary with time as Cu(II) is reduced. Two observations can be made from the Cu(II) reduction curves of Figure 6:

1. At the beginning of the reaction there appears to be an induction period before the reaction starts. This induction period can probably be attributed to two factors: one, the time required for the reactors to reach reaction

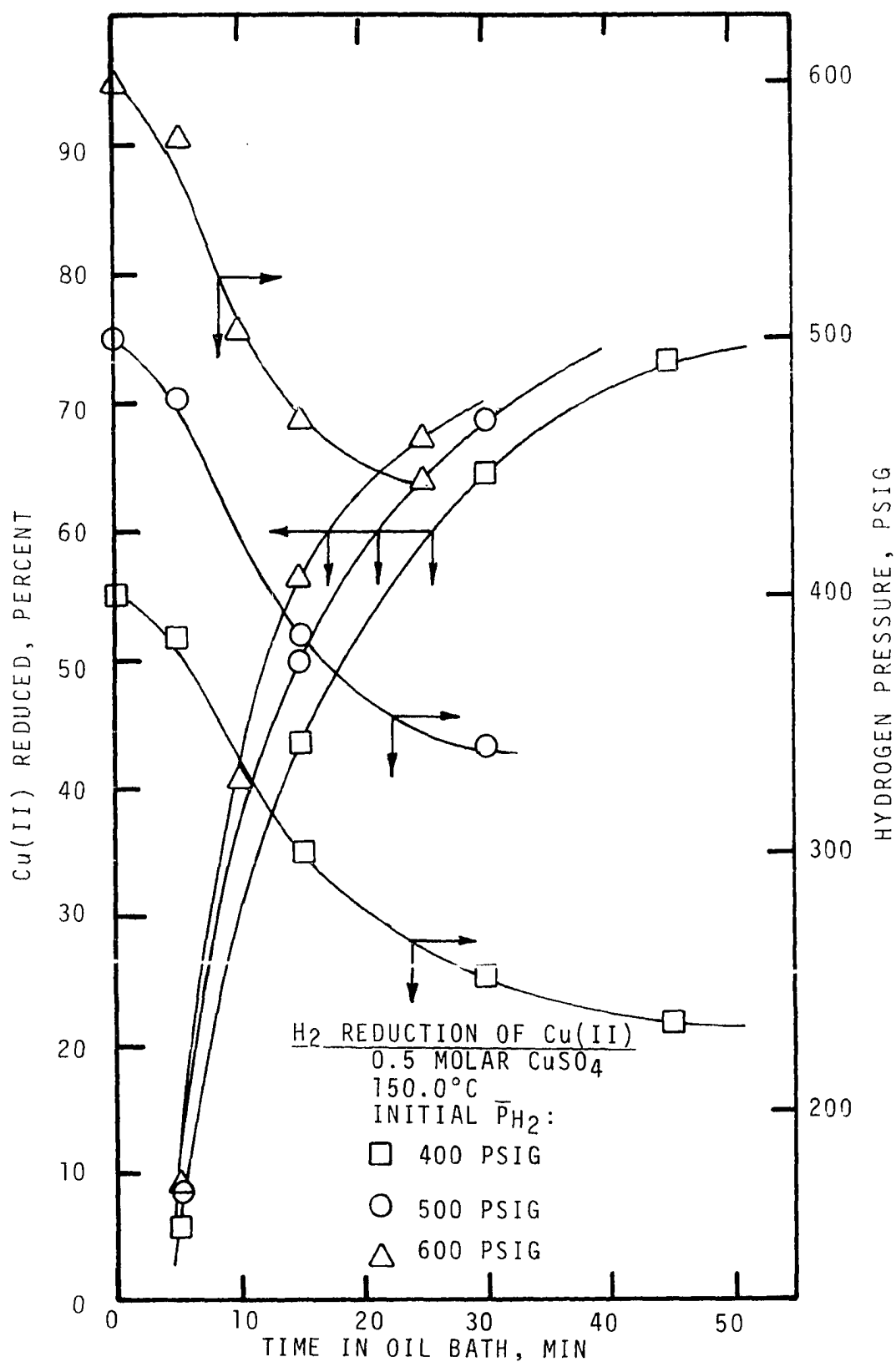


Figure 6. Effect of Initial Partial Pressure of Hydrogen on Reduction of Cu(II) in CuSO₄ Solutions.

temperature; the other, the time required for hydrogen to go into solution. However, a similar induction period was noted in the work of Dunning and Potter (7).

2. Hydrogen partial pressure has a definite effect on the rate of Cu(II) reduction by affecting the H_2 solubility in the liquid solution.

Figure 7 was obtained from the data shown in Figure 6. The data for each Cu(II) reduction curve in Figure 6 was fitted with a fourth degree polynomial (see least squares program in Appendix G). The resulting polynomials were then solved for $t_{1/2}$, the time required for 50 percent Cu(II) reduction. The reciprocals of $t_{1/2}$ times 100 (represented by $K_{t_{1/2}}$) were taken as a measure of the rate constants and used to plot the lines of Figure 7. Figure 7 shows that the rate of Cu(II) reduction varied with pressure to approximately the 0.88 power of the initial hydrogen partial pressure and a slightly lower power of the hydrogen partial pressure at $t_{1/2}$. The value for the dependency of Cu(II) reduction (to approximately the 0.9 power of $\bar{P}_{H_2}$) obtained in this work is lower than the value of 1.0 obtained by Peters and Halpern (23) in the cupric perchlorate system, which has become the accepted value. This discrepancy on pressure dependency can be attributed to two factors:

1. In the present work, $\bar{P}_{H_2}$ fell as the reaction proceeded thereby slowing the rate of Cu(II) reduction by lowering the amount of hydrogen in solution. Peters and Halpern

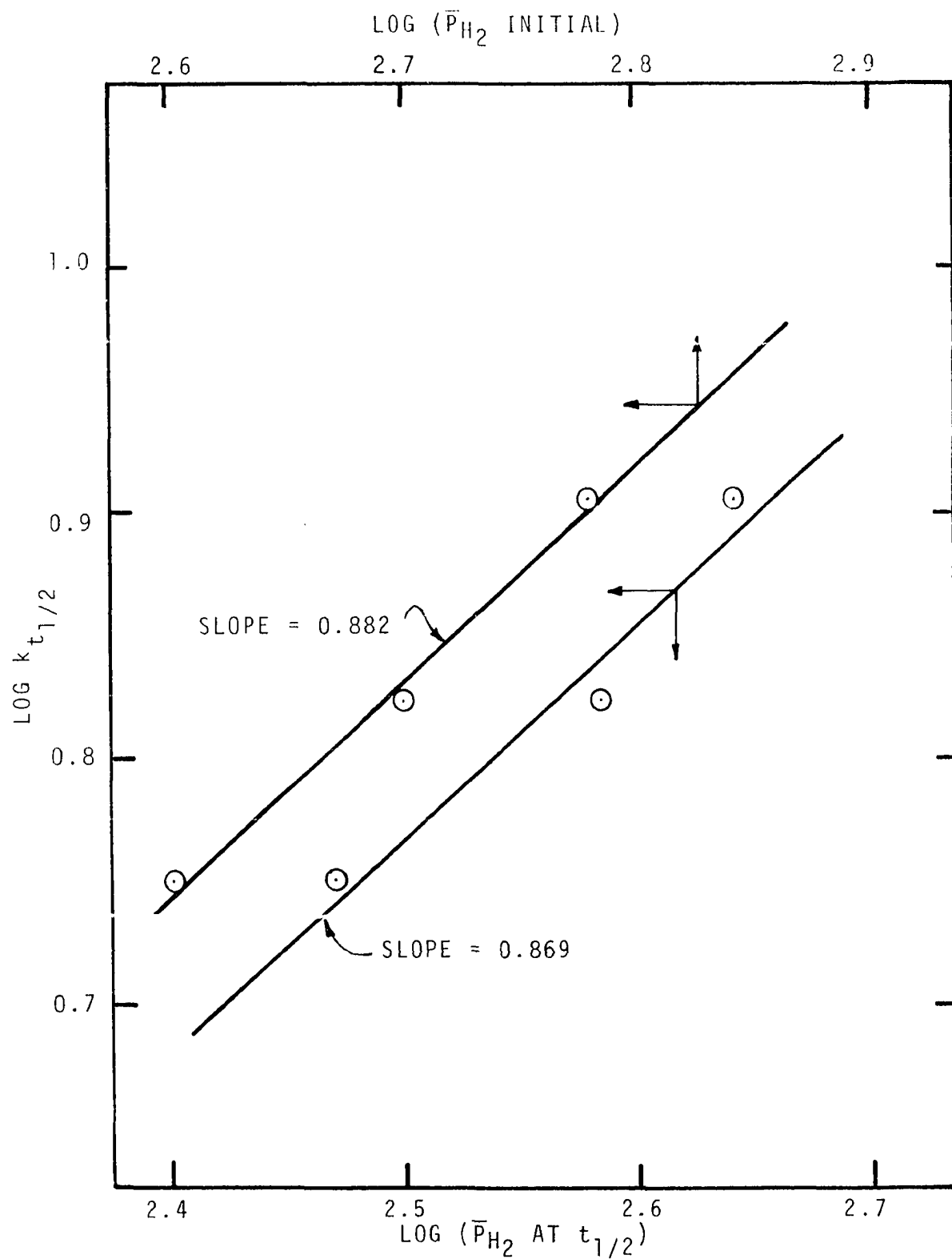


Figure 7. Dependence of Rate of Cu(II) Reduction on Partial Pressure of Hydrogen.

(23) on the other hand, could maintain constant $\bar{P}_{H_2}$ in their autoclave and therefore also a constant hydrogen concentration in solution.

2. Probably more important is the fact that Peters and Halpern worked with dilute solutions (0.1 molar cupric perchlorate) whose acidity did not increase significantly as reduction proceeded, while in this work the acidity of the solution increased rapidly to a limiting value where reduction of Cu(II) could no longer continue. The variation of pH with time in this work is shown in Figure 8 to illustrate this point.

Figure 9 shows the effect of temperature on the hydrogen reduction of Cu(II) from 0.5 molar $CuSO_4$ under 500 psig initial hydrogen partial pressure. Figure 10 is an Arrhenius plot obtained from half time ($t_{1/2}$) measurements from the Cu(II) reduction curves of Figure 9.

The activation energy of 26.65 kilocalories for the activation of H_2 by Cu(II) obtained in this work is larger than the value of 22.4 kilocalories obtained by von Hahn and Peters (38) and the 24 kilocalories measured by Dunning and Potter (7). This discrepancy is probably due to the ability of these workers to measure Cu(II) concentrations at reaction temperatures. As noted in Chapter III, the experimental autoclave of von Hahn and Peters had a special sampling device which allowed taking samples at reaction temperature and determining Cu(II) and Cu(I) concentrations. Dunning and Potter (7) on the other hand carried their experiments in glass

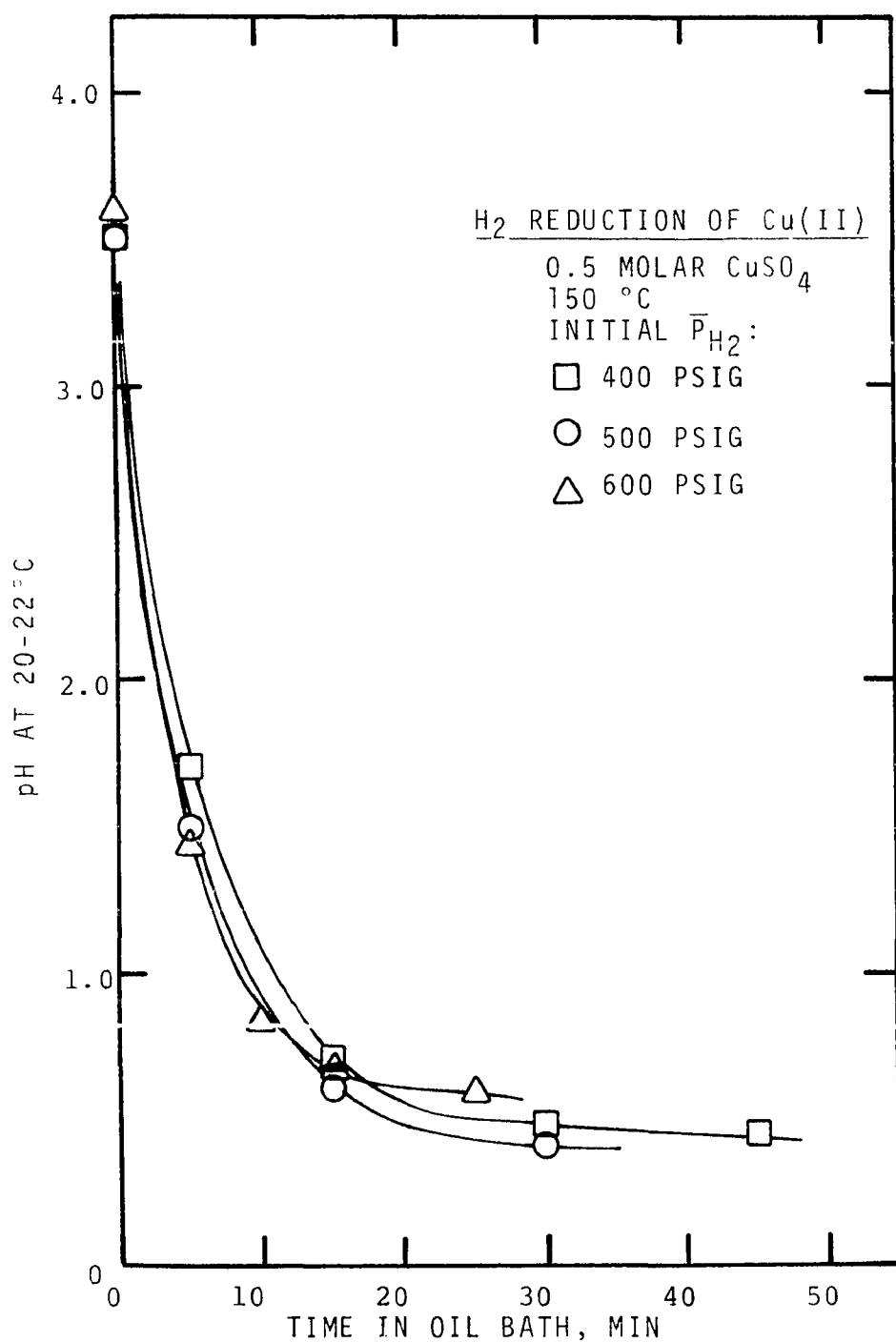


Figure 8. pH of Reactor Charge in Reduction of Cu(II) from Aqueous CuSO_4 Solutions.

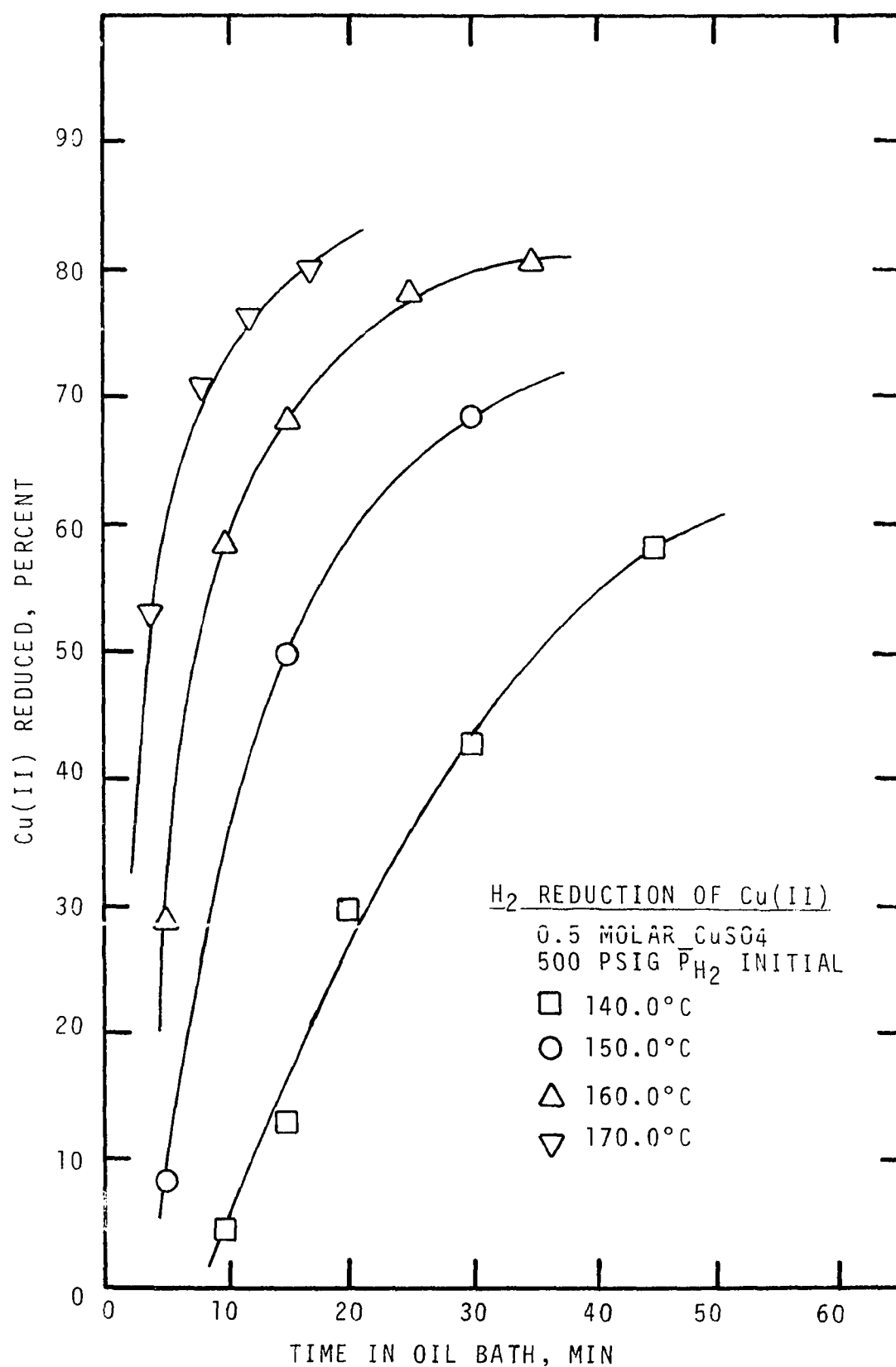


Figure 9. Effect of Temperature on Cu(II) Reduction from CuSO₄ Solutions.

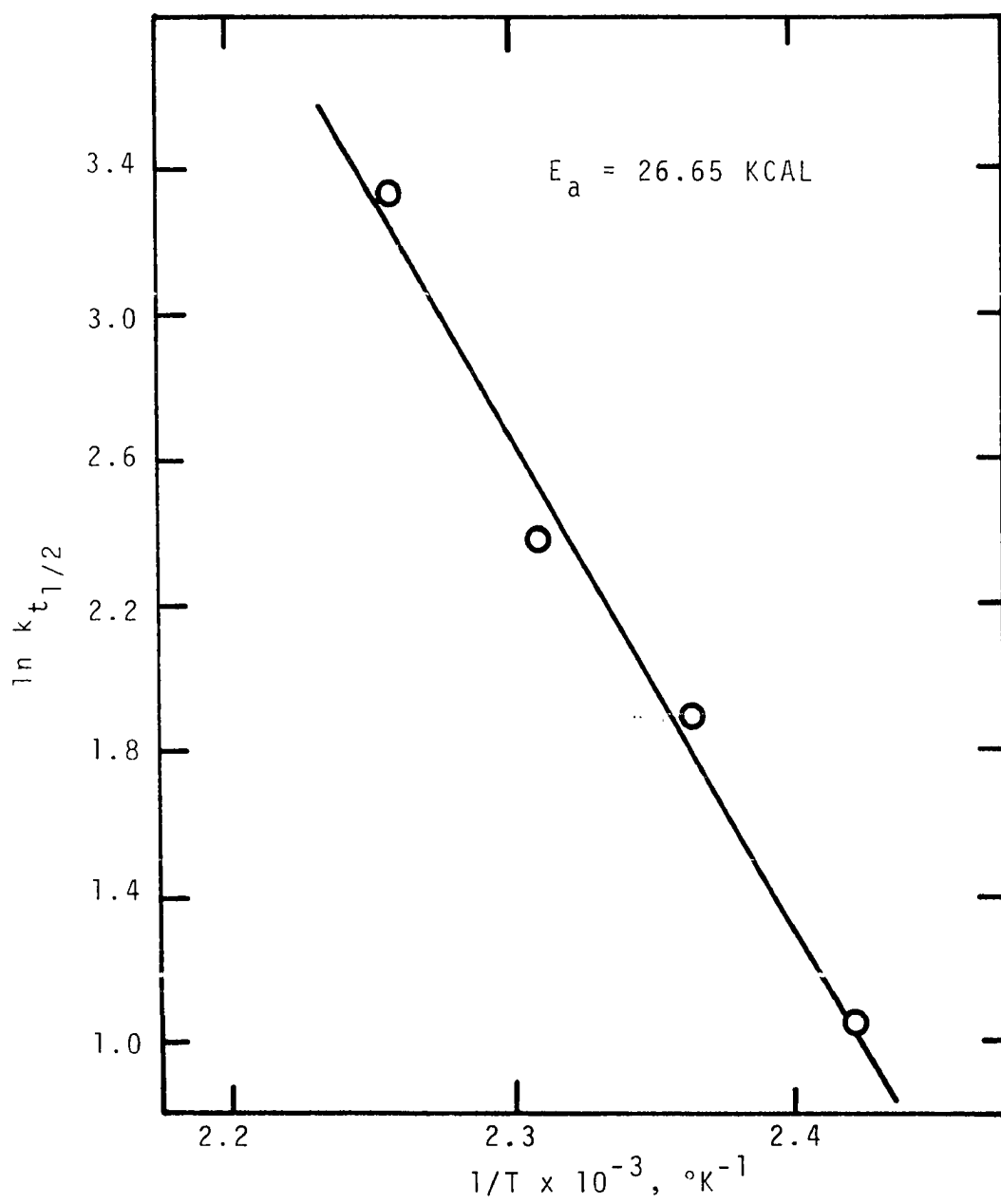


Figure 10. Arrhenius Plot for Cu(II) Reduction in CuSO_4 Solutions.

tubes which permitted measuring the Cu(II) concentration at reaction temperature with a spectrophotometer. In this work, however, the reactors had to be cooled down before Cu(II) concentrations could be measured, because at reaction temperature while the reactors were "capped" and immersed in the oil bath, it was not possible to obtain a sample of the liquid phase. The above explanation for the difference in energy of activations measured is somewhat supported by the work of Peters and Halpern (23) who obtained an activation energy of 26.6 kilocalories for the activation of hydrogen by Cu(II) in perchlorate solutions by measuring Cu(II) concentrations at room temperature.

The effect of increased acidity on Cu(II) reduction from CuSO_4 solutions was not studied because it seemed unimportant for the purpose of this work. Thermodynamic considerations in Chapter II indicate that metal ion reduction is favored by low acidities; in addition, the corrosivity of acidic media dictate that acid concentrations should be kept low. Similarly, the effect of Cu(II) concentrations was not studied because in industrial applications, Cu(II) concentrations are somewhat fixed by the leaching conditions.

Reduction of Cu(II) in Ammoniacal CuSO_4 Solutions

Since leaching copper sulfide ores with ammoniacal solutions (and as noted in Chapter I is practiced by Sherritt Gordon Mines to provide feed solution for their hydrogen

reduction autoclaves) offers certain advantages (negligible corrosion problems and selectivity, since iron oxide ores are not leached), an important aspect of this program was to investigate what effect different amounts of NH_3 (as NH_4OH) have in the reduction by hydrogen of metal ions in ammoniacal solutions.

Figure 11 shows that the rate of Cu(II) reduction (as represented by the slope of the curves shown in Figure 11) varies with initial $\text{NH}_3/\text{Cu(II)}$ molar ratio; it also shows that NH_3 slows down the rate of Cu(II) reduction, since at all initial $\text{NH}_3/\text{Cu(II)}$ molar ratios shown, the rate of Cu(II) reduction (slope of the curves) is lower when NH_3 is present than when NH_3 is absent.

From Figure 11 three observations can be made:

1. The initial rate of Cu(II) reduction for NH_3 -free solutions is considerably faster than when ammonia is present.
2. The adverse effect of ammonia is not straightforward since the $\text{NH}_3/\text{CuSO}_4$ molar ratio of 2 gives a slower rate than the $\text{NH}_3/\text{CuSO}_4$ molar ratios of 1 and 4. This behavior is probably due to the formation of basic salts when ammonia is added to the CuSO_4 solution. As NH_3 is added to make the solution with $\text{NH}_3/\text{Cu(II)}$ molar ratio of 1, basic salts start to precipitate. Further addition of NH_3 to $\text{NH}_3/\text{Cu(II)}$ molar ratio of 2 increases the amount of basic salts formed. As more ammonia is added (above $\text{NH}_3/\text{Cu(II)}$ molar ratio of 2), the amount of basic salts

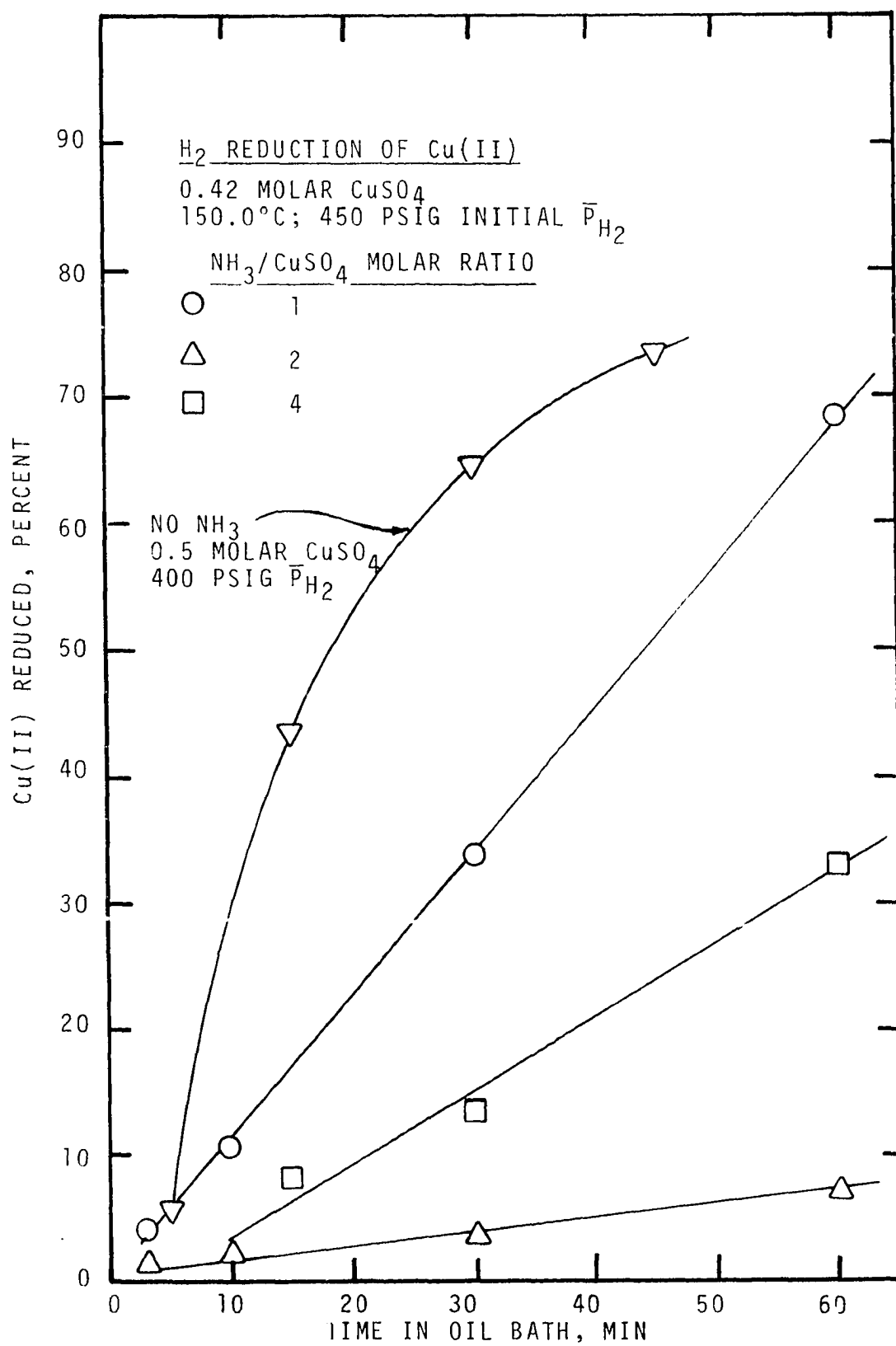


Figure 11. Effect of NH₃/Cu(II) Molar Ratio on Cu(II) Reduction.

starts to decrease by going into solution until, at $\text{NH}_3/\text{Cu(II)}$ molar ratio of 4 almost all solids have gone back into solution.

3. Addition of NH_3 appears to change the reduction mechanism. Note in Figure 11 that when NH_3 is absent, the rate of reduction varies and is dependent on the Cu(II) in solution, while when NH_3 is present the rate of reduction is constant and independent of the concentration of unreduced Cu(II) in the charge. The change in reduction mechanism is probably due to a combination of basic solids formation and Cu(II) ammine complexes formation when NH_3 is added. Peters and Halpern (24) have shown that reduction of Cu(II) complexed with nitrogen containing compounds is slower than reduction of uncomplexed Cu(II) . The data compiled by Sillén and Martell (35) also show that the solubility product constant of some of the basic salts formed by NH_3 addition (brochantite and cupric hydroxide) is of the order of 10^{-17} to 10^{-20} at 25°C . By combining these two results with the results shown in Figure 11, it can be suggested that in presence of NH_3 , the rate of Cu(II) reduction is determined by the concentration of uncomplexed Cu(II) in solution, and that in turn the concentration of uncomplexed Cu(II) in solution is maintained essentially constant at a value determined by the solubility of the basic salts and the dissociation of the Cu(II) ammine complexes.

Figure 12 shows pH curves for the same reduction curves of Figure 11. As can be seen in Figure 12, the pH of the NH_3 -free solution decreases rapidly (in turn slowing up the rate of Cu(II) reduction due to acid formation) to a limiting value, while the pH of solutions containing NH_3 decrease slowly except for the $\text{NH}_3/\text{Cu(II)}$ molar ratio of 1. This figure shows that the slow rate of Cu(II) reduction in the presence of NH_3 is not due to high acid concentrations, but rather due to the formation of the solids and complexes mentioned above.

The implications of Figures 11 and 12 for the development of a tubular reactor to reduce Cu(II) continuously are obvious; it would be desirable to take advantage of the high initial reduction rate of NH_3 -free solutions (as indicated by the slope of the NH_3 -free curve of Figure 11 at low residence times), but, at some point in the reactor, NH_3 should be added (assuming the flow in the reactor is upwards-plug-flow, at that point in the reactor where the acid generated by reducing Cu(II) in the lower portions of the reactor has caused the rate of Cu(II) reduction to slow down) to neutralize the acid generated in the lower portion of the reactor and maintain an appropriate pH and therefore a high reduction rate throughout the reactor.

Figure 13 shows how the rate of Cu(II) reduction ($d\text{Cu(II)}/dt$, from measurement of curve slope) for the NH_3 -free curve of Figure 11 varies with the pH of the reactor

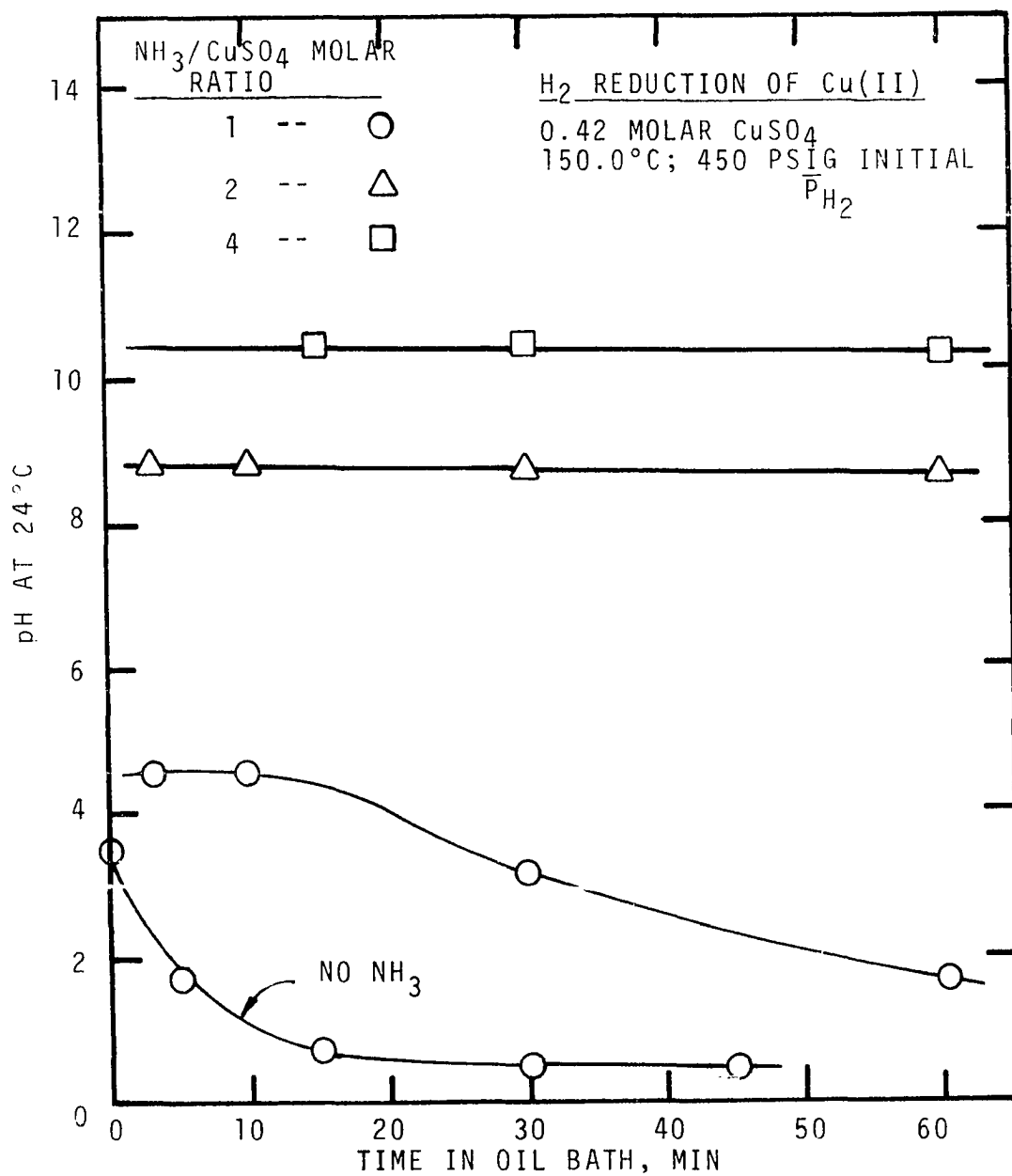


Figure 12. pH of Reactor Charge in Reduction of Cu(II) from Ammoniacal Aqueous CuSO₄ Solutions.

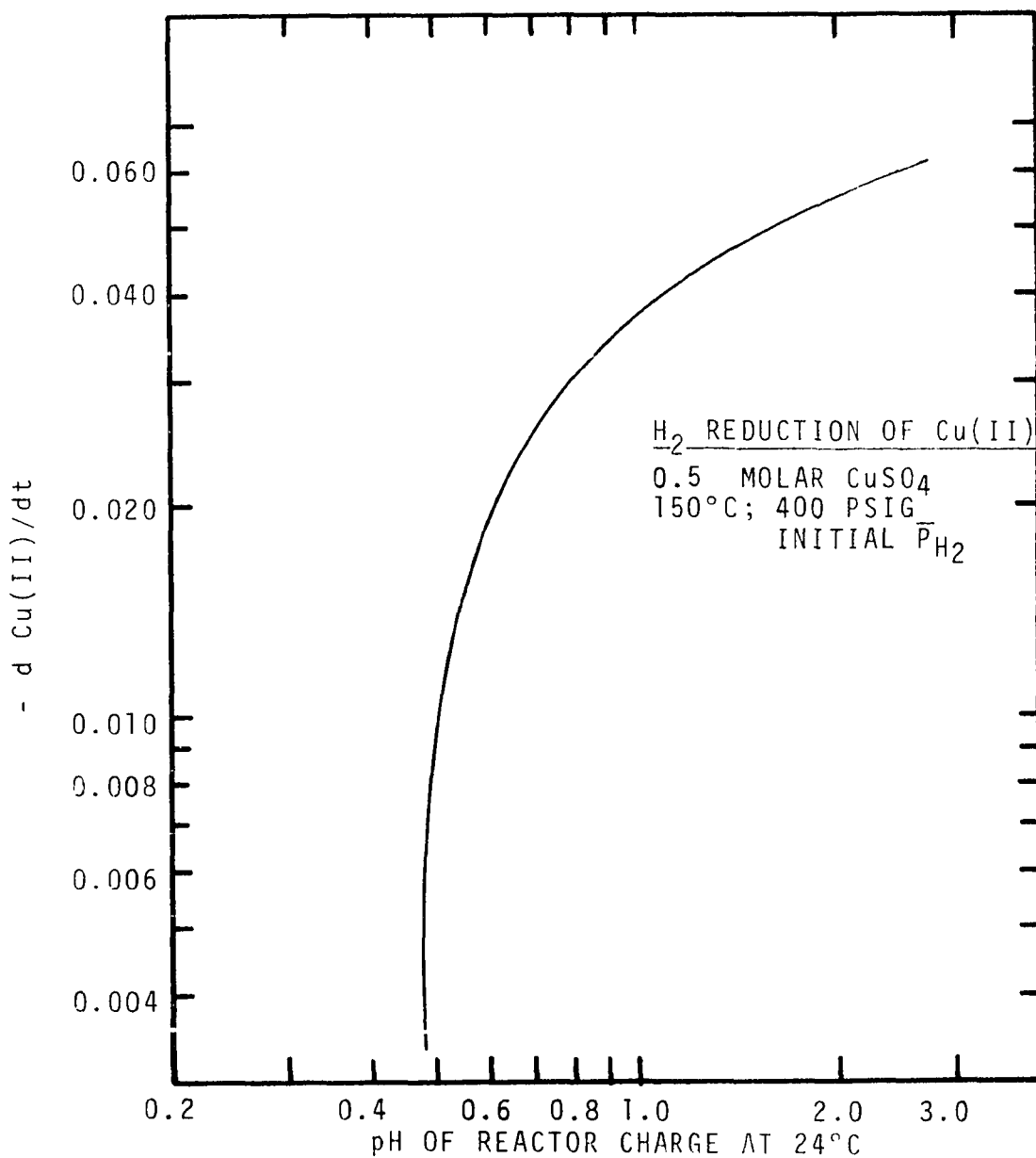


Figure 13. Effect of Reactor Charge pH on Rate of $Cu(II)$ Reduction in Aqueous $CuSO_4$ Solution.

charge. Figure 13 shows that in NH_3 -free solutions, the rate of Cu(II) reduction falls rapidly when the pH of the reactor charge is below 0.6. This result should indicate that to reduce Cu(II) from CuSO_4 solutions in a continuous tubular reactor, NH_3 should be added at that point in the tubular reactor where the pH has fallen to about 0.6 due to the acid generated by Cu(II) reduction in the upstream portion of the reactor.

Figure 14 shows the effect of NH_3 on the rate of Cu(II) reduction. The value of the rate of Cu(II) reduction ($d\text{Cu(II)}/dt$) shown in Figure 14 for Cu(II) reduction in the presence of NH_3 , is the value of the slope of the straight lines shown in Figure 11. The value of $d\text{Cu(II)}/dt$ shown in Figure 14 for the rate of Cu(II) reduction in NH_3 -free solutions is the value of $d\text{Cu(II)}/dt$ given at $t_{1/4}$ (25 percent Cu(II) reduced) by a fourth order polynomial that fits the data for the NH_3 -free curve shown in Figure 11. Figure 14 shows the magnitude of the decrease in initial rate of Cu(II) reduction (where the rate at $t_{1/4}$ is taken to represent the initial rate in NH_3 -free solutions) caused by NH_3 additions, and shows that in the continuous tubular reactor it would be advantageous to start Cu(II) reduction in NH_3 -free solutions.

Effect of Adding H_2SO_4 to Ammoniacal CuSO_4 Solutions

While operating the continuous reduction process, using ammoniacal copper sulfate feed, D. R. Neskora (22) found

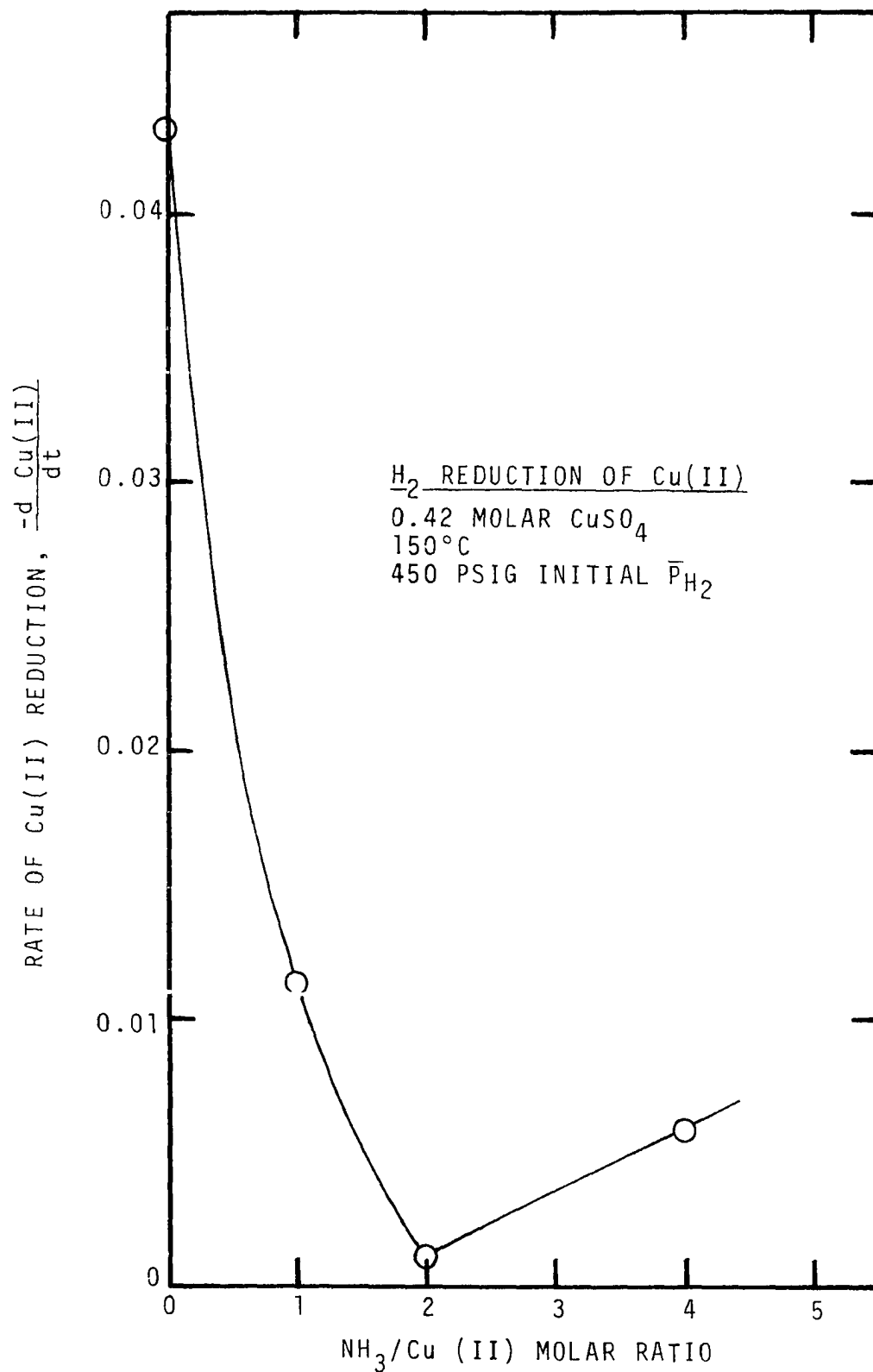


Figure 14. Effect of NH_3 on Rate of Cu (II) Reduction.

that additions of H_2SO_4 to the ammoniacal feed solution reduced reactor plugging problems and improved product quality. These results directed this work to an investigation of the effect on Cu(II) reduction of H_2SO_4 additions to ammoniacal solutions.

Figure 15 shows the effect of adding H_2SO_4 to an ammoniacal copper sulfate solution. Reaction conditions were 150°C , 450 psig initial H_2 partial pressure and a standard solution of NH_3 and CuSO_4 with an $\text{NH}_3/\text{CuSO}_4$ molar ratio of 4 to which different amounts of sulfuric acid were added. From Figure 15 it can be seen that small additions of H_2SO_4 (up to about 0.5 M/l) have an adverse effect on the rate of Cu(II) reduction, but further increases in H_2SO_4 concentration (up to about 1.0 M/l H_2SO_4) increases the rate of Cu(II) reduction. Finally, the rate of Cu(II) reduction falls again as the H_2SO_4 concentration is increased further. The dashed curve in Figure 15 represents conditions where the amount of H_2SO_4 added would just neutralize the NH_3 initially in the $\text{CuSO}_4 - \text{NH}_3$ feed solution) and theoretically the molar ratio of $\text{NH}_3/\text{CuSO}_4$ would be zero); this dashed line was obtained by interpolating between the curves of 0.74 and 0.95 M/l H_2SO_4 .

From the present work no explanation can be given for the decrease in rate of Cu(II) reduction with small H_2SO_4 additions (up to 0.53 M/l). At higher acid additions, the rate of Cu(II) reduction increases because the Cu(II) ammine

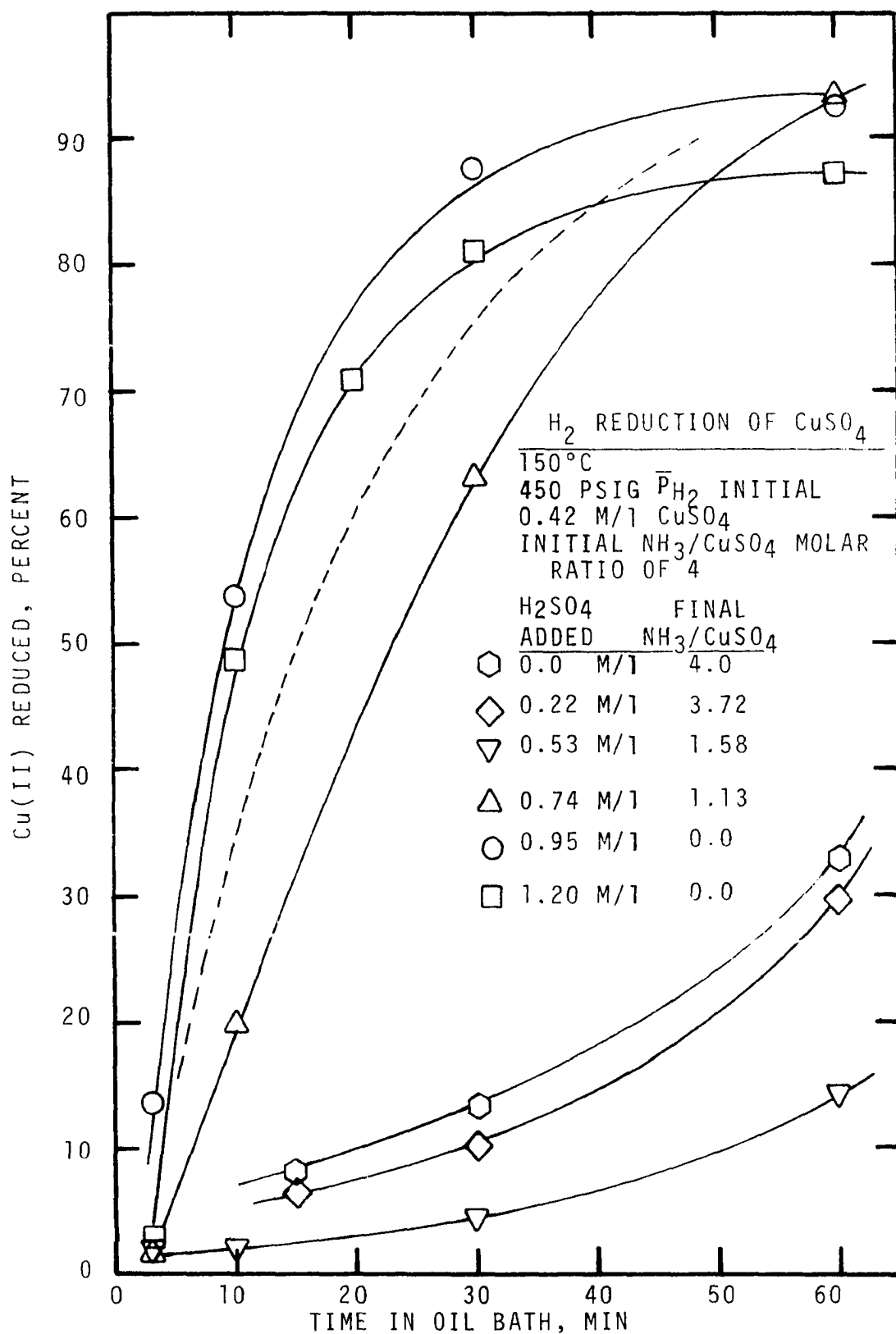


Figure 15. Effect of H₂SO₄ Additions on Reduction of Cu(II) from Ammoniacal CuSO₄ Solutions.

complexes are broken up by the acid so that NH_3 -free Cu(II) that can be readily reduced exist in the solution. However, when the acid additions are high (above say, that required for complete NH_3 neutralization) as reduction proceeds, the rate of reduction slows down because of increased acidity as is evident from the pH curves of Figure 16.

Figure 17 compares the dashed line obtained from Figure 15 with the curve for reduction of Cu(II) in NH_3 -free CuSO_4 solutions of Figure 11. As the dashed line of Figure 17 indicates, the presence of NH_3 and H_2SO_4 in the neutral charge enhanced the rate of Cu(II) reduction and allowed the reduction of a higher percentage of Cu(II) than when NH_3 and H_2SO_4 were absent. This behavior can be explained if it is accepted that NH_3 and H_2SO_4 formed $(\text{NH}_4)_2\text{SO}_4$, which has been shown by Evans and co-workers (9) to enhance the rate of Cu(II) reduction from ammoniacal solutions.

The implication of these results (and particularly those of Figure 17) in the development of a tubular reactor for continuously reducing Cu(II) from ammoniacal CuSO_4 solutions, is that the ammoniacal solution should be neutralized with H_2SO_4 up to a level where the molar ratio of $\text{NH}_3/\text{CuSO}_4$ is around zero.

Figure 18 shows the effect of reaction temperature on the rate of Cu(II) reduction from ammoniacal CuSO_4 solutions which had been neutralized with H_2SO_4 to a final $\text{NH}_3/\text{CuSO}_4$ molar ratio of 1 (dashed lines) and 0 (solid lines).

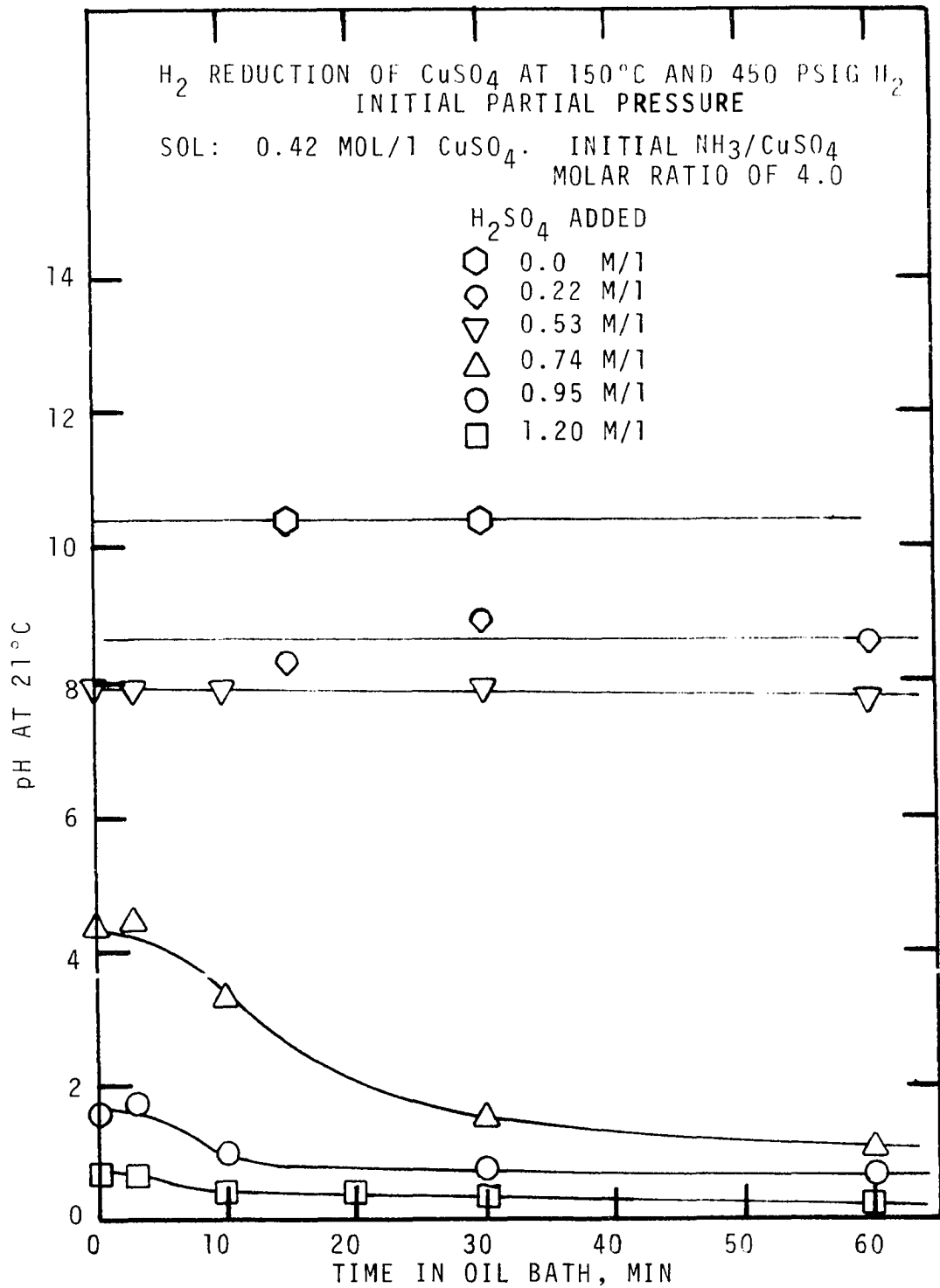


Figure 16. pH of Reactor Charge of Ammoniacal CuSO_4 Solutions Treated with H_2SO_4 .

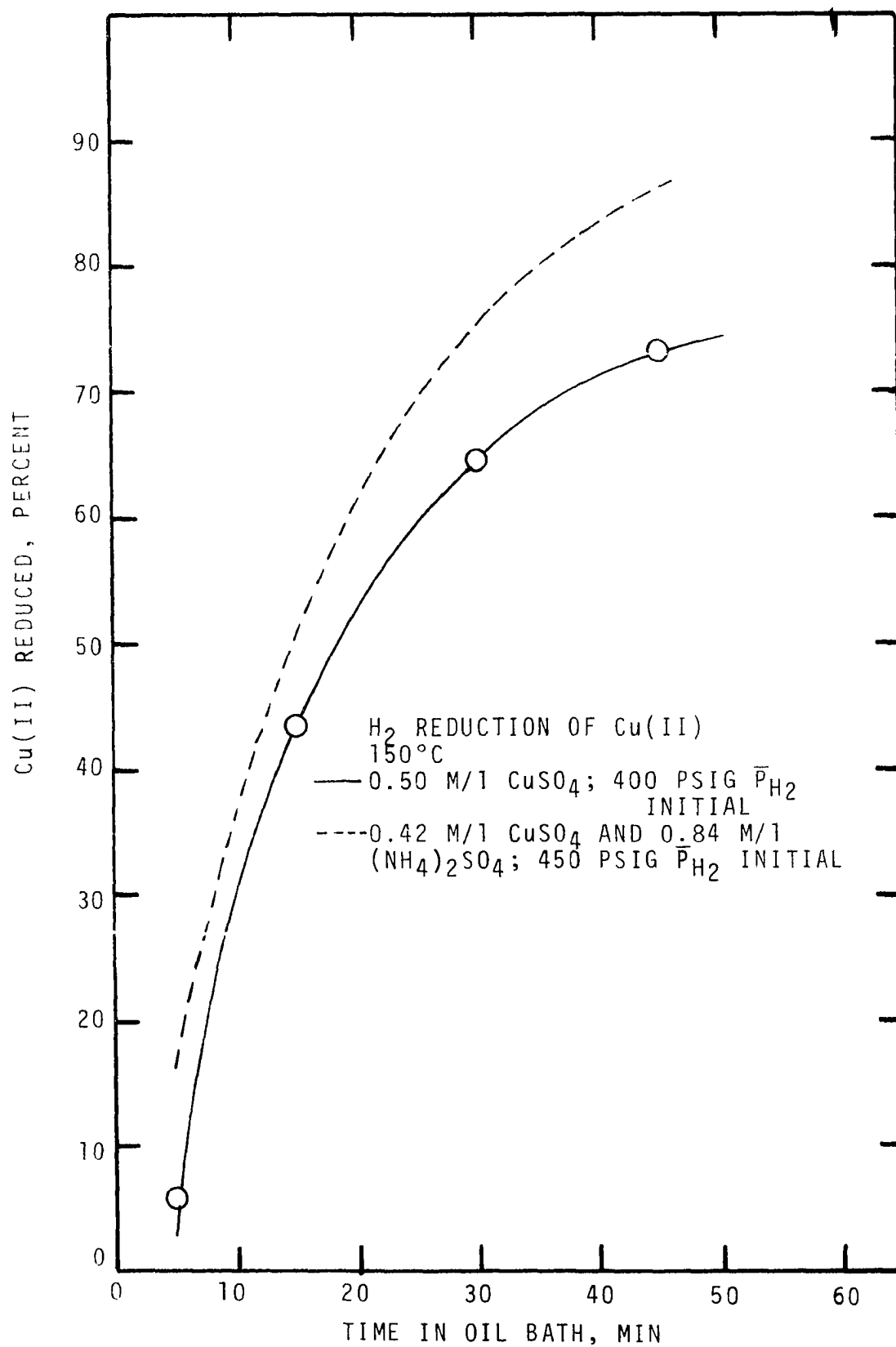


Figure 17. Effect of (NH₄)₂SO₄ on Cu(II) Reduction from CuSO₄ Solutions.

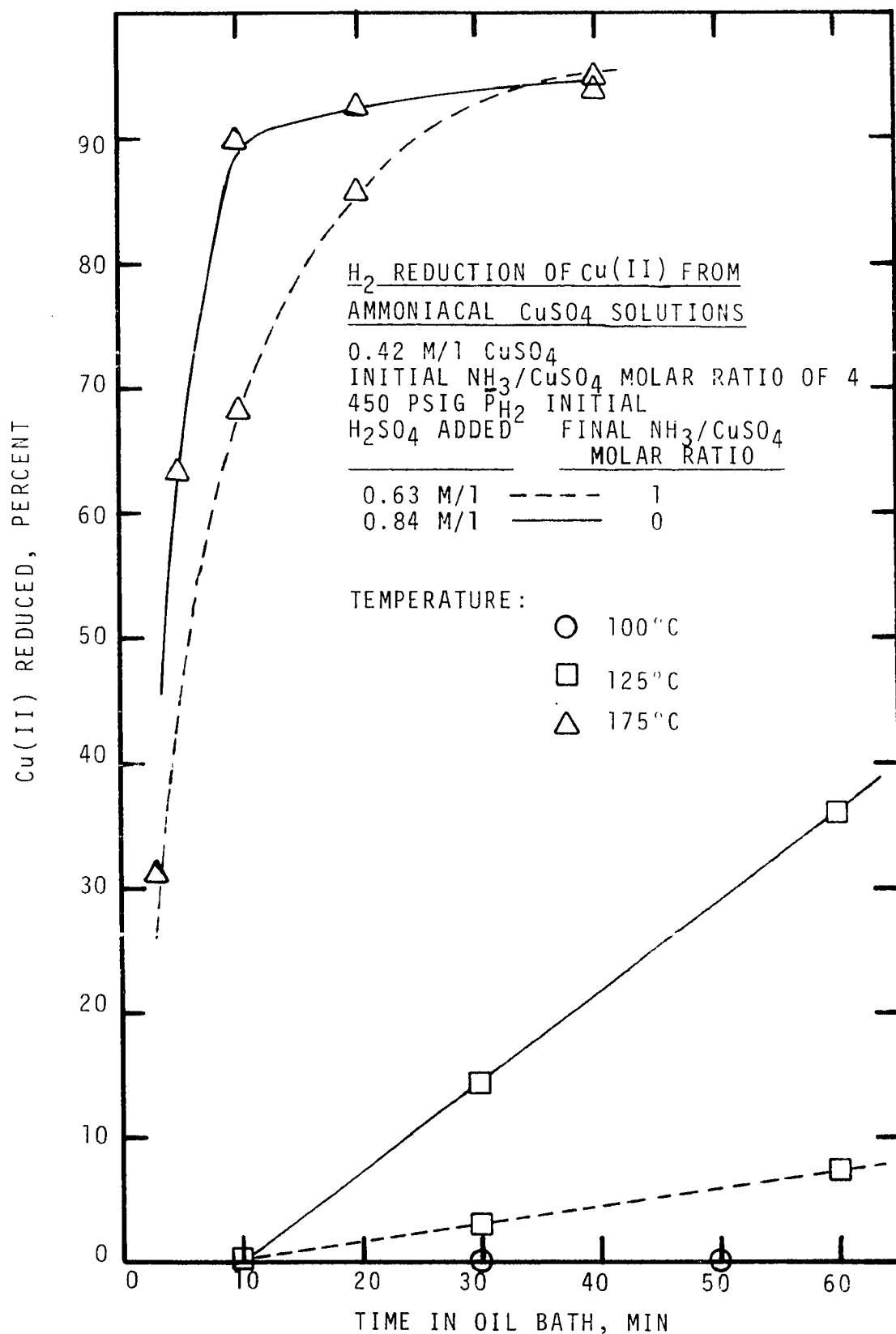


Figure 18. Effect of Temperature and H₂SO₄ Additions on Reduction of Cu(II) from Ammoniacal CuSO₄ Solutions.

Figure 18 illustrates the necessity to neutralize the NH_3 completely in the ammoniacal solution in order to take advantage of the kinetics. At 175°C for 90 percent Cu(II) reduction in the reactor, complete neutralization of NH_3 , as opposed to only partial neutralization to an $\text{NH}_3/\text{CuSO}_4$ molar ratio of 1, would mean over 100 percent increase in reactor throughput. The advantage of complete neutralization is greater at lower temperatures as indicated by the curves at 125°C . Note that at 100°C no reduction is evident as indicated by the circles in the abscissa.

Iron Catalyzed Reduction of Ni(II) by Hydrogen in Ammoniacal Nickel Sulfate Solutions

Attempts were made to reduce Ni(II) from NiSO_4 solutions with little success. Use of ammonium acetate and ammonia to buffer the reaction helped the kinetics slightly, but the product obtained was mostly nickel sheet that adhered to the reactor walls and was difficult to remove. The slow kinetics (4-1/2 hours to reduce about 90 percent of the Ni(II) in a 0.45 molar NiSO_4 solution at 150°C and about 300 psig $\bar{P}_{\text{H}_2}$ initial) and the kind of product formed indicated that this type of solution feed would not be amenable to continuous reduction.

Discussion with D. R. Neskora (22) about the nucleating catalyst that should be used to reduce Ni(II) led to a trial run using ferrous sulfate as the nucleating catalyst (the same catalyst used by Sherritt Gordon Mines in their

commercial operation to reduce Ni(II) from ammoniacal leach solutions and also used by Kothari (13) in some exploratory experiments). The nickel product from this run was a spherical, free-flowing nickel powder which did not adhere to the reactor walls. With this result, it was decided to obtain more information on recovering nickel from ammoniacal NiSO_4 solutions using FeSO_4 as the nucleating catalyst.

Effect of Initial $\text{NH}_3/\text{NiSO}_4$ Molar Ratio

Figure 19 shows the effect of initial $\text{NH}_3/\text{NiSO}_4$ molar ratio on rate of Ni(II) reduction when 0.5 grams per liter Fe(II) (from FeSO_4) is used as the nucleating catalyst.

From Figure 19, it is evident that at low (one) initial $\text{NH}_3/\text{NiSO}_4$ molar ratios, the rate of Ni(II) reduction by hydrogen is negligible. As the initial $\text{NH}_3/\text{Ni(II)}$ molar ratio is increased to two, the rate of reduction becomes very fast, but as the initial $\text{NH}_3/\text{Ni(II)}$ molar ratio is further increased, the rate of reduction decreases. The effect of ammonia in this system is difficult to explain, because in addition to ammine complex and solid basic salt formation the role of Fe(II) as nucleating catalyst must be accounted for. However, a possible explanation for the high rates of Ni(II) reduction at $\text{NH}_3/\text{Ni(II)}$ initial molar ratio of two can be borrowed from Meddings and Mackiw (19) who show that in homogeneous ammoniacal nickel solutions, the greatest driving force ($E_{\text{H}_2/\text{H}^+} - E_{\text{Ni}/\text{Ni}^{++}\text{ammine}}$) for Ni(II) reduction by hydrogen exists at $\text{NH}_3/\text{Ni(II)}$ molar ratio of two.

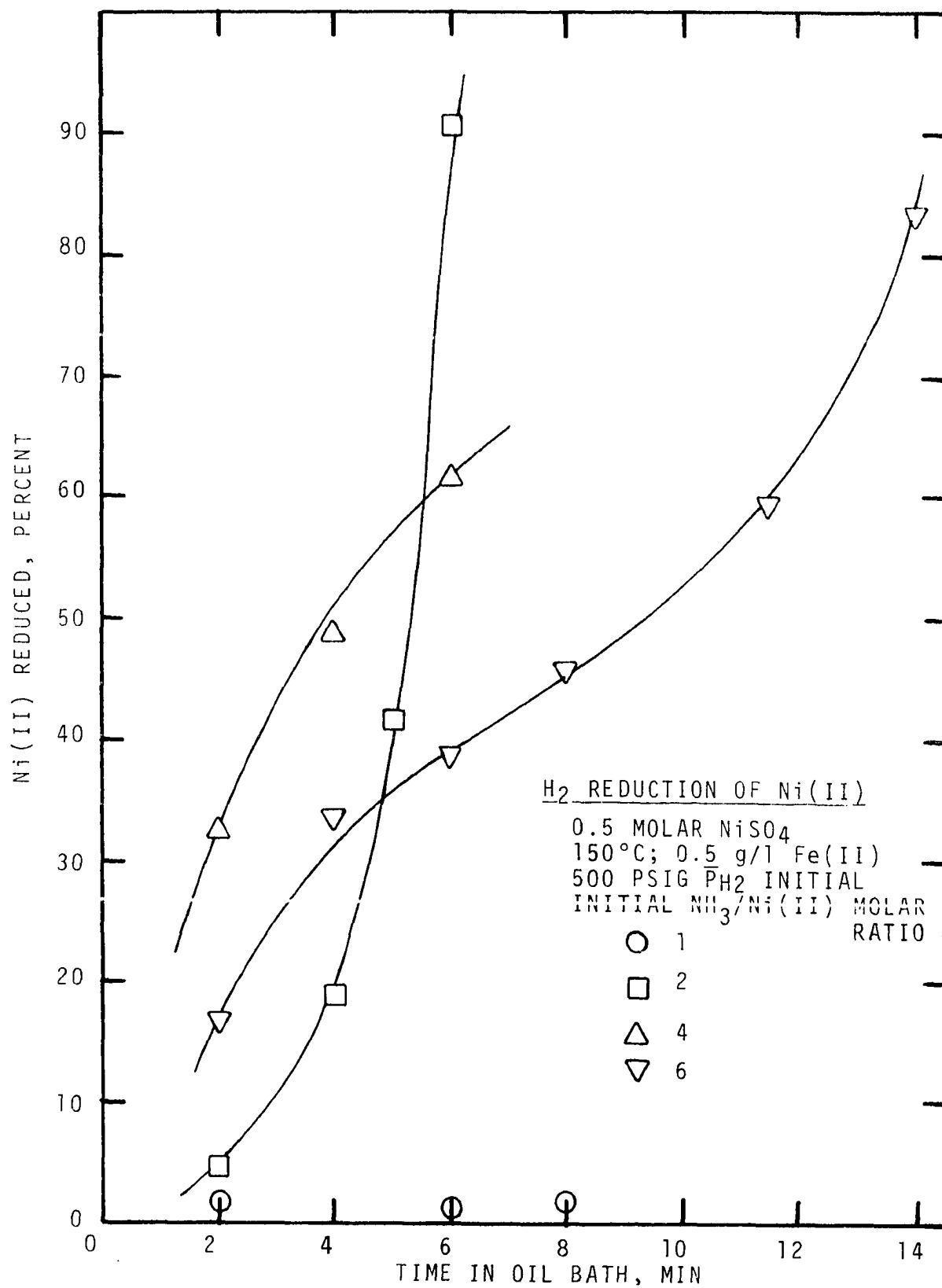


Figure 19. Effect of NH₃/NiSO₄ Molar Ratio on Reduction of Ni(II) from Ammoniacal NiSO₄ Solutions.

The results of Figure 19 indicate that to reduce Ni(II) from ammoniacal solutions, using iron as the catalyst, in a continuous reactor, the $\text{NH}_3/\text{Ni(II)}$ initial molar ratio should be maintained around two.

Effect of Fe(II) Concentration on Ni(II) Reduction

Figure 20 shows the effect on Ni(II) reduction of varying the Fe(II) concentration in the reactor charge. The reactor charge was 0.5 molar NiSO_4 with an initial $\text{NH}_3/\text{NiSO}_4$ molar ratio of two. The initial hydrogen partial pressure was 500 psig and the temperature was 150°C . Figure 20 shows that the Fe(II) concentration has a marked effect on the rate of Ni(II) reduction; further, it shows that under the conditions of the experiments, there is a critical Fe(II) concentration (between 0.25 gpl and 0.5 gpl) below which the rate of Ni(II) reduction would be too slow for commercial practice. It also appears that the relative concentrations of Fe(II) and Ni(II) in the charge play an important role on how fast Ni(II) can be reduced. Mackiw and coworkers (18) operating at similar conditions to the experiments outlined above, but with a Ni(II) concentration of 1.9 molar, did not get an appreciable rate of Ni(II) reduction until after about 80 minutes at reduction temperature even though their Fe(II) concentration was 0.5 gpl. Further, during the present work an experiment was conducted with somewhat similar conditions as above ($\text{NH}_3/\text{Ni(II)}$ molar ratio of 6, but remember from

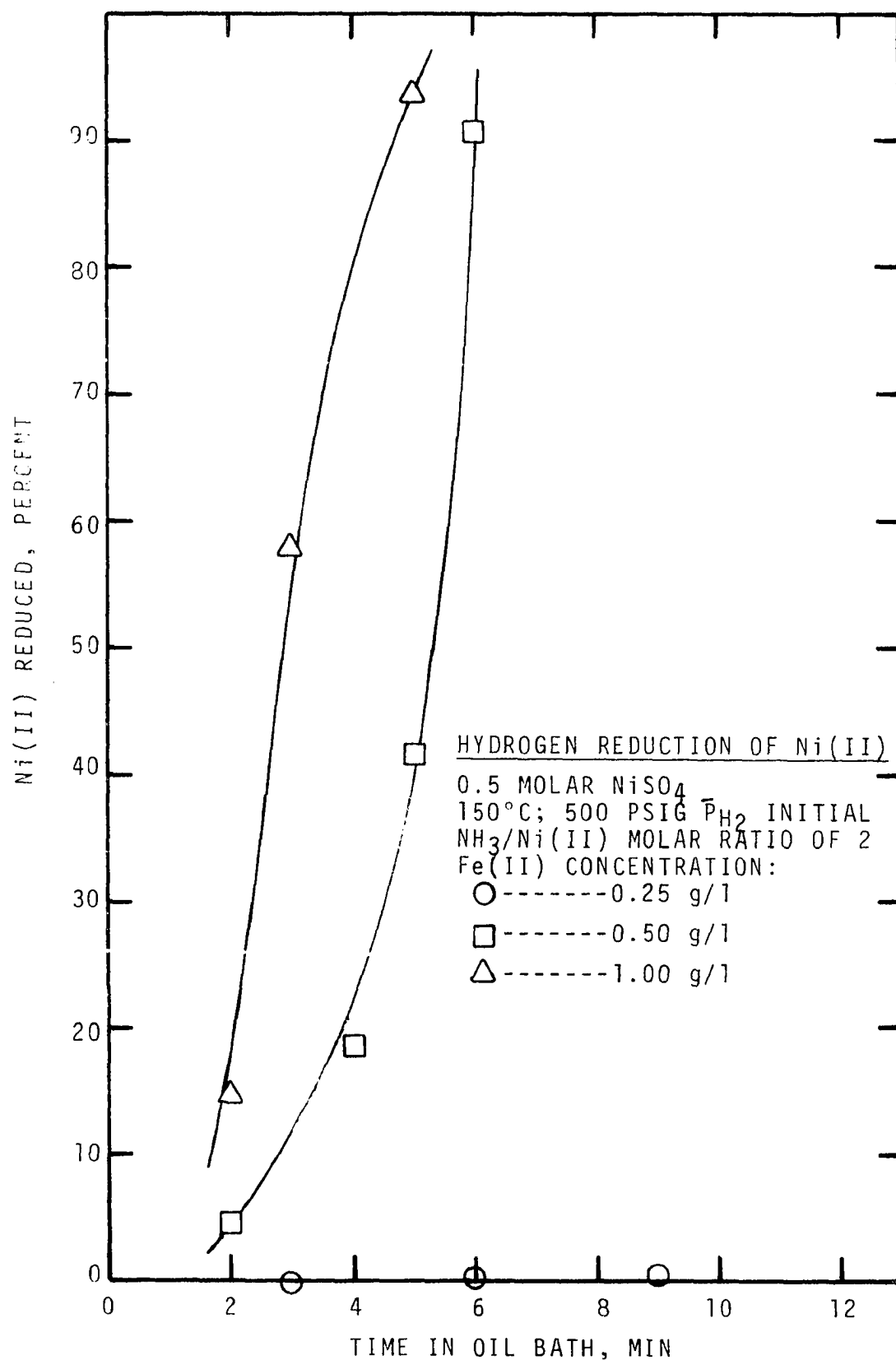


Figure 20. Effect of Fe(II) on Rate of Ni(II) Reduction from Ammoniacal NiSO_4 Solutions.

Figure 19 this high $\text{NH}_3/\text{Ni(II)}$ molar ratio should retard the rate of Ni(II) reduction) but with a Ni(II) concentration of 0.2 molar; in this case, 0.2 gpl Fe(II) yielded a substantial rate of reduction after 5 minutes.

Effect of Temperature

Figure 21 shows the effect of temperature on the iron catalyzed reduction of Ni(II) by hydrogen in an ammoniacal solution. Initially, the reactor charge was 0.5 molar NiSO_4 , 0.5 gram per liter Fe(II) and $\text{NH}_3/\text{NiSO}_4$ molar ratio of six. Initial hydrogen partial pressure was 400 psig.

Figure 22 shows an Arrhenius plot obtained from half-time measurements of the curves in Figure 21. At these conditions, an apparent activation energy of 11.3 kilocalories was obtained for the reduction of Ni(II) by hydrogen in the temperature range from 125°C to 150°C . No previous report for the activation energy of Ni(II) reduction from ammoniacal solutions with $\text{NH}_3/\text{Ni(II)}$ molar ratio of 6 has been made; however, the value of 11.3 kilocalories obtained in the present work is close to the value of 13.7 kcal obtained by Mackiw and coworkers (18) for the reduction of Ni(II) from ammoniacal solutions with $\text{NH}_3/\text{Ni(II)}$ molar ratio of 2.0 in the temperature range from 200°F (149°C) to 350°F (177°C).

Effect of Initial Hydrogen Partial Pressure

Figure 23 shows the effect of initial H_2 partial pressure on the rate of Ni(II) reduction. Experimental conditions

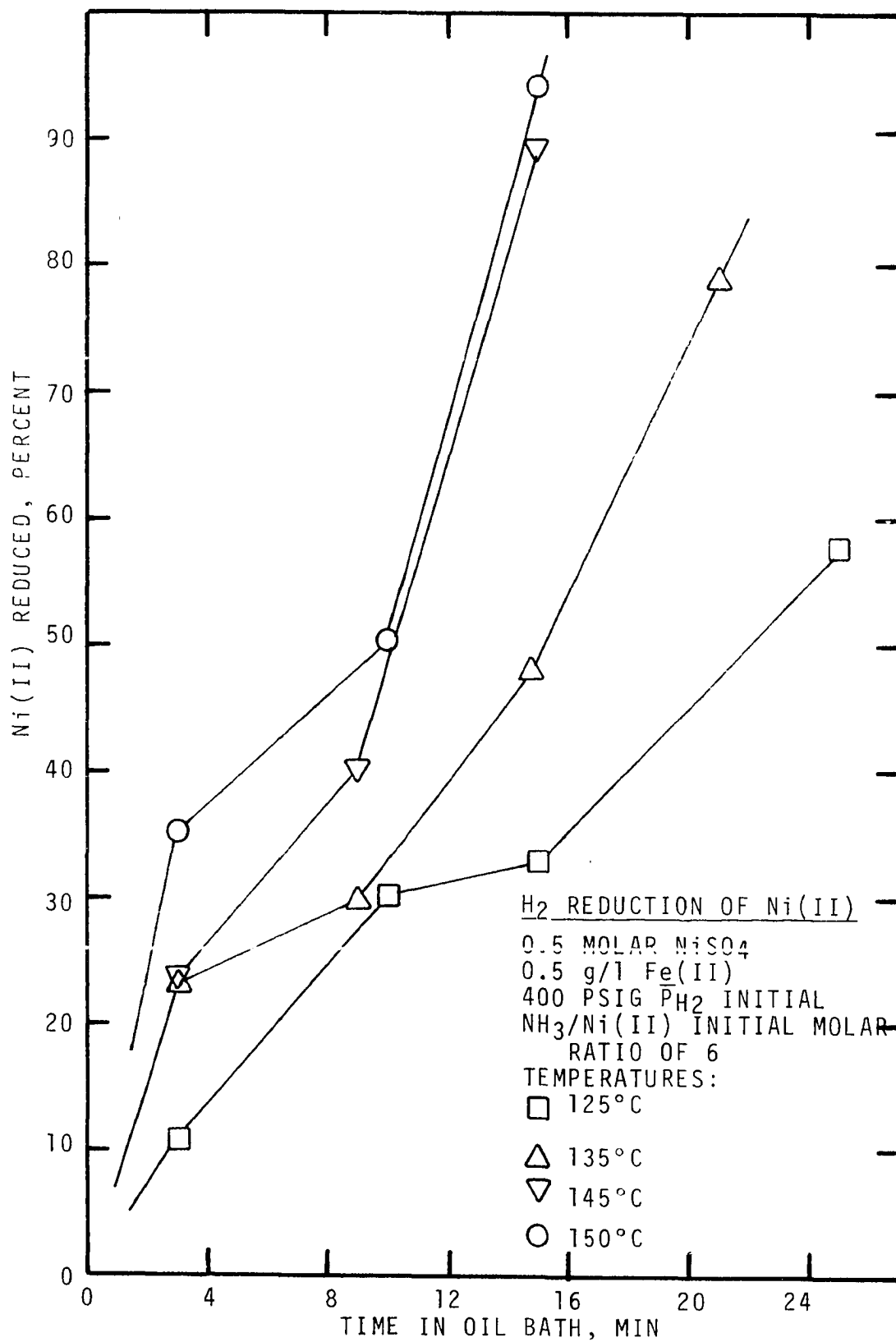


Figure 21. Effect of Temperature on Ni(II) Reduction from Ammoniacal NiSO₄ Solutions.

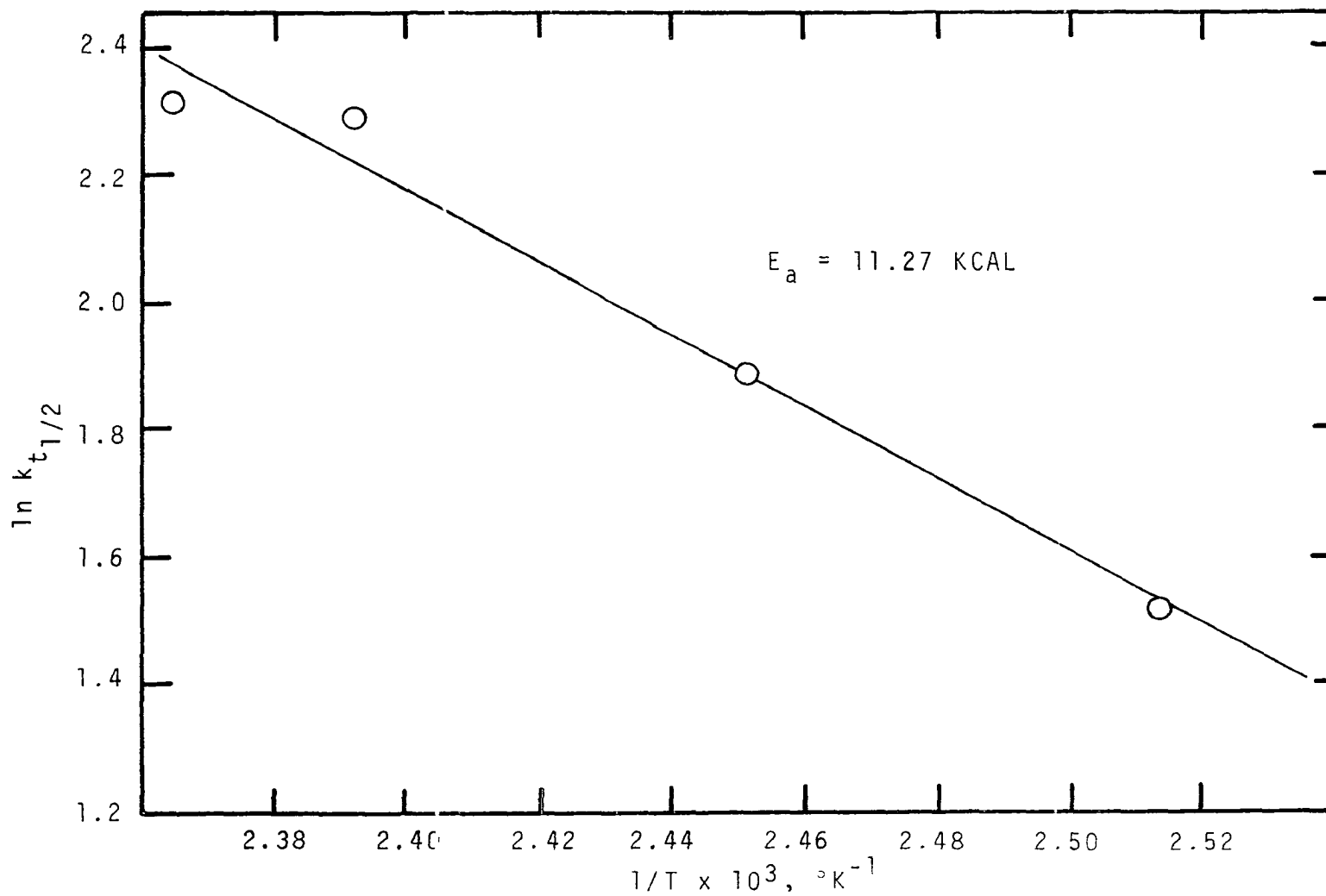


Figure 22. Arrhenius Plot for Ni(II) Reduction from Ammoniacal Solutions with $\text{NH}_3/\text{Ni(II)}$ Initial Molar Ratio of Six.

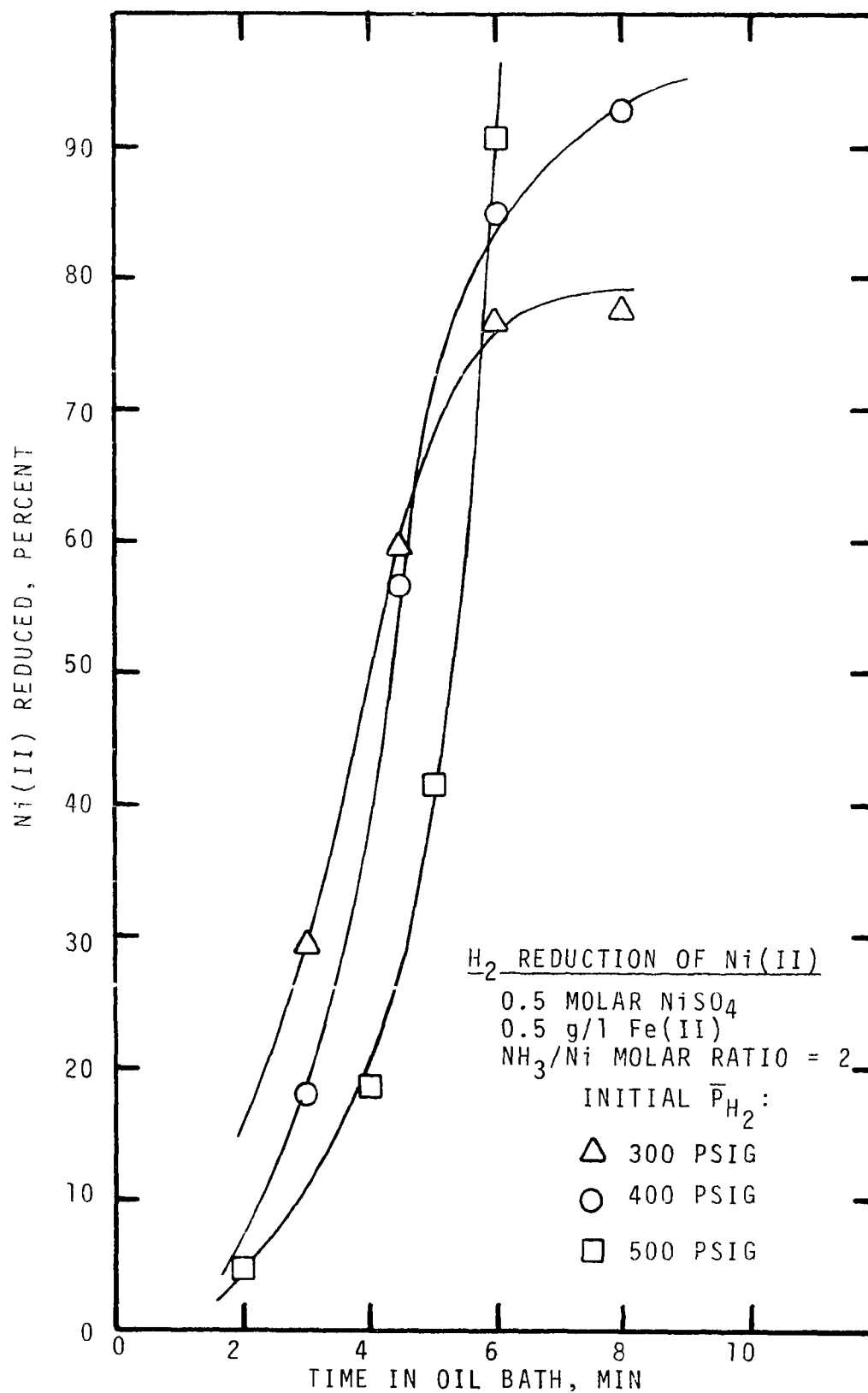


Figure 23. Effect of Hydrogen Partial Pressure on $Ni(II)$ Reduction from Ammoniacal $NiSO_4$ Solutions.

were a solution of 0.5 molar NiSO_4 with 0.5 gpl Fe(II) , 150°C and an $\text{NH}_3/\text{Ni(II)}$ molar ratio of two. Initial hydrogen partial pressure varied between 300 psig and 500 psig.

The way in which the rate of Ni(II) reduction varies with H_2 partial pressure is puzzling. Figure 23 shows that low $\bar{P}_{\text{H}_2}$ favor high initial rate of Ni(II) reduction; however, this high initial rate could not be maintained probably because the hydrogen partial pressure (in the reactors with lower initial hydrogen partial pressures) drops to a level where the reaction becomes mass transfer limited (see Figure 24 for hydrogen partial pressures). The results of Figure 23 indicate that apparently the hydrogen partial pressure has a definite effect on the $\text{Fe(II)} - \text{Ni(II)}$ complex which Courtney and Schaufelberger (6) hypothesized as being responsible for nucleating the $\text{Ni} - \text{H}_2$ reaction.

Figure 25 shows the dependency of the "initial rate" of Ni(II) reduction (represented here by $t_{1/4}$) on the initial hydrogen partial pressure; a similar dependence is obtained on $\bar{P}_{\text{H}_2}$ at $t_{1/4}$. The result presented here for the hydrogen partial pressure effect ($\text{Rate} \approx \bar{P}_{\text{H}_2}^{-0.9}$) is different from that presented by other workers, notably Mackiw and coworkers (17) and Meddings and Mackiw (19) who found that the rate of reduction varied linearly with pressure. However, neither of these authors studied the effect of $\bar{P}_{\text{H}_2}$ when Fe(II) was used as the nucleating catalyst. Instead, they used nickel metal powder to catalyze the Ni(II) reduction.

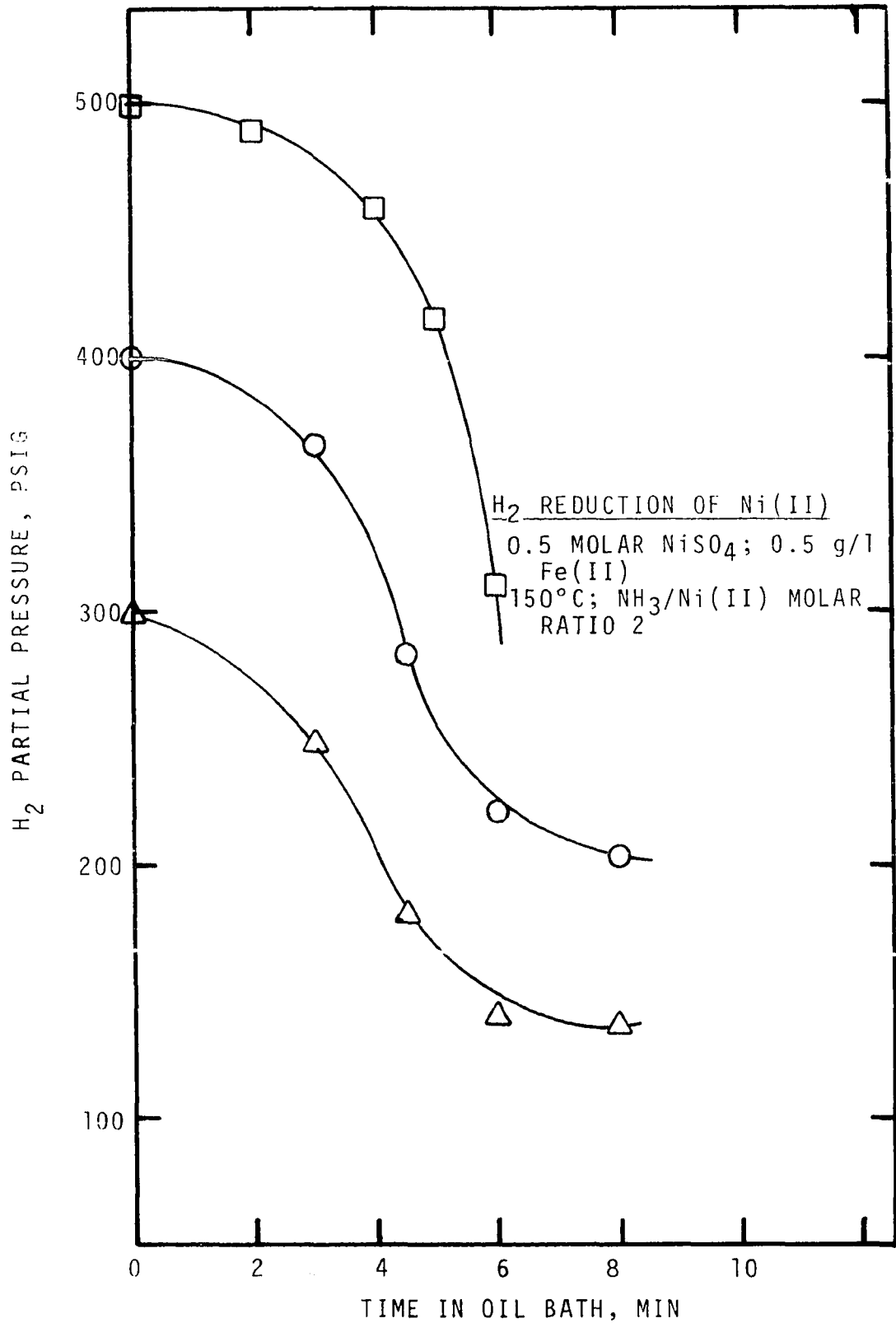


Figure 24. Hydrogen Partial Pressures in $Ni(II)$ Reduction from Ammoniacal $NiSO_4$ Solutions.

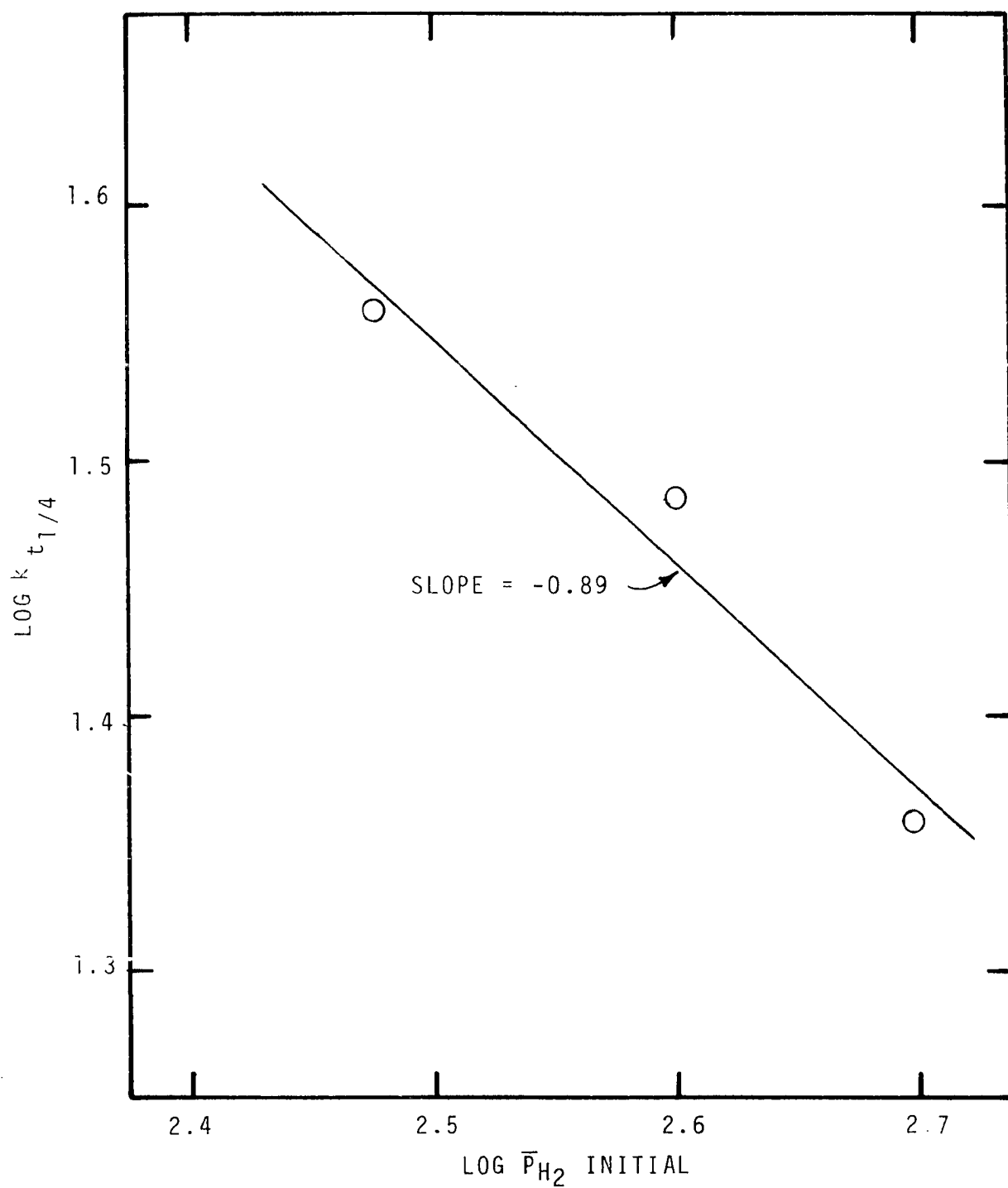


Figure 25. Dependence of Initial Rate of Ni(II) Reduction from Ammoniacal NiSO_4 Solutions on $\bar{P}_{\text{H}_2}$.

To operate a continuous tubular reactor, the results for Ni(II) reduction presented in the previous pages suggest the following:

1. The temperature should be maintained at the highest practical value.
2. A minimum Fe(II) concentration is required to maintain rapid rates of Ni(II) reduction.
3. A compromise must be reached between the low hydrogen partial pressures at which the reaction would be mass-transfer limited and a $\bar{P}_{H_2}$ at which the initial rate of Ni(II) reduction would be too slow.
4. Optimization of these parameters should be determined by actual runs using a continuous tubular reactor and economic considerations.

Nature of the Metal Produced

In all cases, the metal produced in this work was (Cu or Ni) metal powder. Below is given a short discussion of the nature of the powders produced.

Powders from Reduction of Cu(II) in CuSO₄ Solutions

The purity of the copper powders produced varied markedly with the pH of the reactor charge. Highly pure powders (at least three mines) could be obtained from solutions of CuSO₄ alone and from ammoniacal CuSO₄ solutions to which enough sulfuric acid had been added to neutralize essentially all the NH₃. These powders however, were prone to air

oxidation and care had to be exercised in washing and drying them to prevent oxidation.

As the pH of the charge increased (above a pH of about 4), copper oxides coprecipitated with copper metal. First, at pH's immediately above 4, Cu_2O would coprecipitate as an impurity; as the pH was further increased, the amount of Cu_2O precipitated increased, and in addition CuO appeared as an impurity. Finally, if the pH was high enough (about 8), essentially only CuO precipitated.

Figures 26 and 27 show typical copper powder precipitated from acidic solutions. Figure 26 shows the particles present in the reactors after 15 minutes in the hot oil bath and Figure 27 shows the particles present in the reactor after 30 minutes in the hot oil bath. Comparison of the size of the particles shown in Figures 26 and 27 show that the particles increased in size with time. This increase in particle size is probably due to agglomeration of the particles caused by the dynamics of the rocking mechanism. It was found that if the particles were left rocking in the oil bath, less and less "particles" would be left in the reactor until, after a few hours, only a big spherical particle was left.

Powders from Reduction of Ni(II) in NiSO_4 Solutions

The purity of the nickel powders produced varied with the length of reaction (and extent of total Ni(II) reduced). For lengths of reaction for which less than

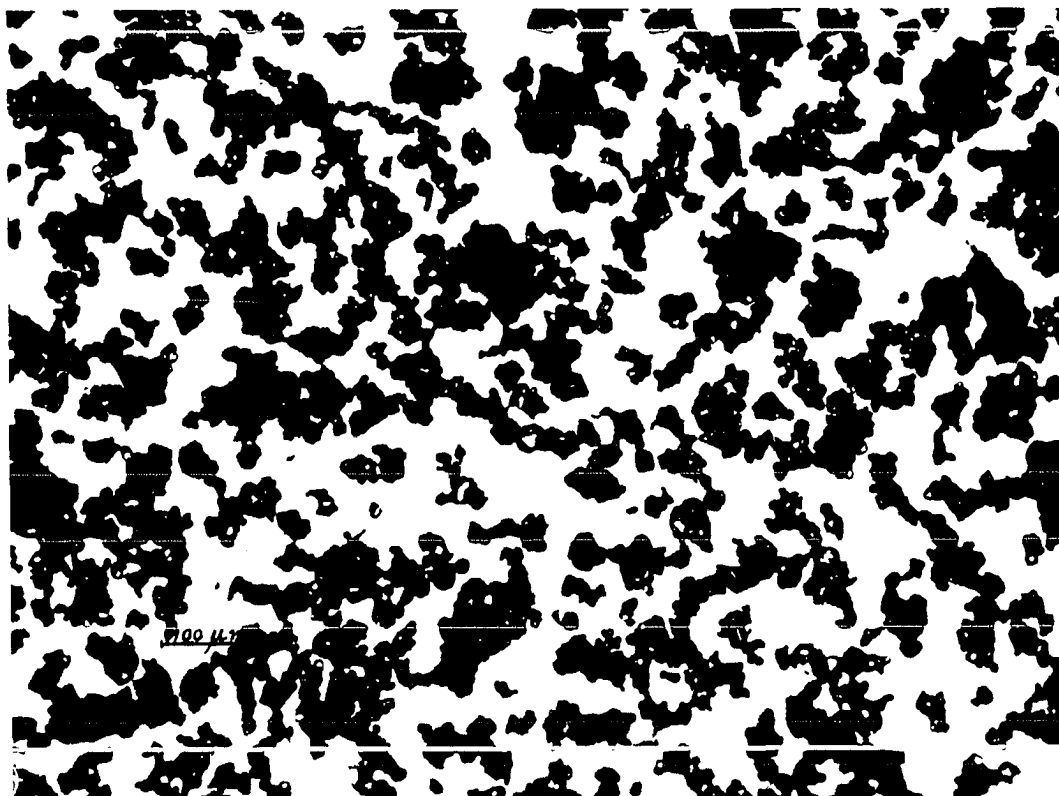


Figure 26. Typical Copper Powder from 0.5 Molar CuSO_4 Solution After 15 Minutes at 150°C and 400 psig Initial $\bar{P}_{\text{H}_2}$. Magnification 200 x.

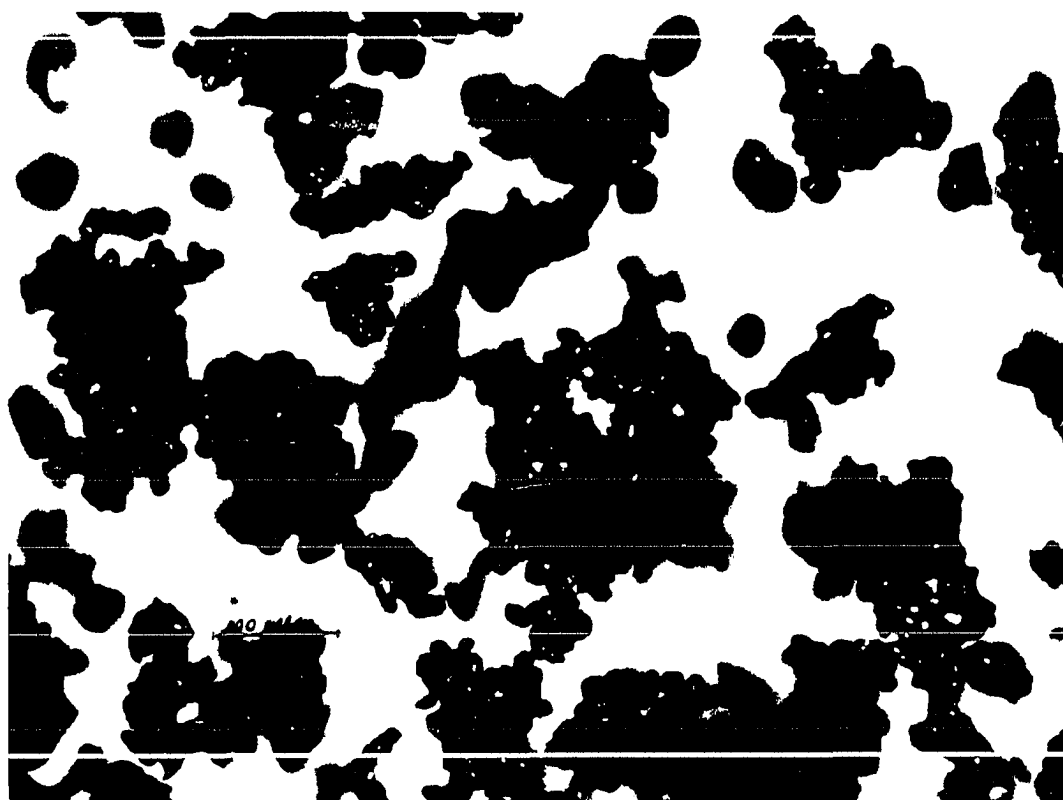


Figure 27. Typical Copper Powder from 0.5 Molar CuSO_4 Solution After 30 Minutes at 150.0°C and 400 psig Initial $\bar{P}_{\text{H}_2}$. Magnification 200 x.

approximately 70 percent of the Ni(II) in the charge had been reduced, a fine (see Figure 28) nickel-looking powder would be obtained. This fine powder would test 100 percent nickel by x-ray diffraction, but would show impurities (apparently amorphous) by wet methods of analysis. When more than about 85 percent of the Ni(II) in the reactor charge had been reduced, the powder had attained a fairly spherical shape and was quite uniform in size (see Figure 29). In addition, this spherical powder was highly pure (more than two nines nickel), and contrary to the behavior of copper, nickel powders would not agglomerate into a single mass with extended periods of agitation.

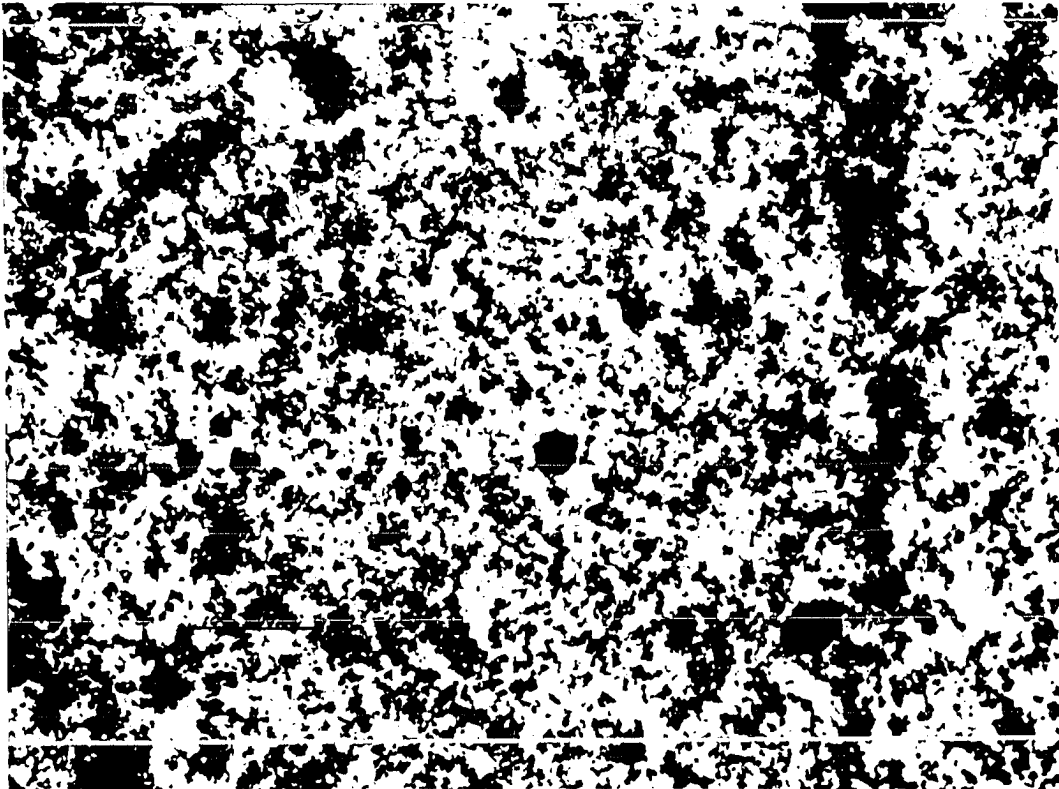


Figure 28. Typical Nickel powder from Ammoniacal 0.5 Molar NiSO_4 Solution After 9 Minutes at 145.0°C and 400 psig Initial $\bar{P}_{\text{H}_2}$. Magnification 200 x.



Figure 29. Typical Nickel Powder from Ammoniacal 0.5 Molar NiSO_4 Solution After 15 Minutes at 145.0°C and 400.0 psig Initial P_{H_2} . Magnification 200 x.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Several conclusions and recommendations can be drawn from this work.

Conclusions

1. The experimental equipment used in this work proved to be versatile and practical to obtain data in exploratory-developmental work. However, to make fundamental mechanistic studies the reactors have the disadvantage that they cannot be sampled at reaction temperatures, and the pressure cannot be kept constant throughout the reaction period.
2. In general agreement with previous work, it was found that ammonia retards the initial rate of Cu(II) reduction in aqueous copper sulfate solutions; however, ammonia is required to carry the reduction to completion.
3. Neutralization of ammoniacal copper sulfate solutions with sulfuric acid improved both, the rate of Cu(II) reduction and product quality. Best results were obtained when approximately all NH_3 had been neutralized.

4. Addition of ammonia to CuSO_4 solutions appears to shift the Cu(II) reduction mechanism from one being kinetically limited to a mechanism being mass transfer limited.
5. Reduction of Ni(II) catalyzed by Fe(II) from ammoniacal NiSO_4 solutions was best in solutions with $\text{NH}_3/\text{Ni(II)}$ molar ratios of two. For Ni(II) reduction in solutions with $\text{NH}_3/\text{Ni(II)}$ molar ratio of two, there appears to be a critical Fe(II) concentration below which no Ni(II) reduction occurs.
6. Very uniform (spherical) and highly pure (> 99 percent) nickel powders can be obtained by reducing Ni(II) with hydrogen from ammoniacal NiSO_4 solutions using Fe(II) as catalyst. However, to obtain the highly pure powders it is required that at least 85 percent of the Ni(II) in the charge be reduced.

Recommendations

1. For optimum continuous reduction of acidic CuSO_4 leach solutions, reduction should be started with the raw solution provided it is not very acidic; and then, at some point in the reactor, NH_3 should be added to maintain the high reduction rates. An experimental program using a continuous tubular reactor is needed to verify this recommendation.
2. For continuous reduction of ammoniacal CuSO_4 solutions, the ammoniacal solutions should be neutralized with H_2SO_4 before feeding them to the reactor.

3. Nickel reduction from ammoniacal solutions in the continuous reactor should be carried out at $\text{NH}_3/\text{Ni(II)}$ molar ratio of two. In order to produce a uniform and highly pure nickel powder an experimental program using the continuous reactor should be started to determine the residence times required in the continuous reactor to obtain the high quality product and to determine the lowest Fe(II) concentration which will give an economic rate of reduction.
4. The mechanism of Fe(II) in nucleating the $\text{Ni(II)} - \text{H}_2$ reaction is of interest. To study the mechanism, an experimental set-up similar to Dunning and Potter's (7) is recommended. The reaction would be followed with a spectrophotometer and carried out in thick-wall glass tubes (which would limit the $\bar{P}_{\text{H}_2}$ to about fifty psig) to which Fe(II) could be injected from an attached reservoir.

NOMENCLATURE

a	chemical activity
Cu(II)	cupric ion in solution
e^-	electron
E	electromotive force or electrode potential of a reversible cell
$\bar{f}$	partial fugacity
F	Faraday equivalent of electric charge necessary to convert one gram-equivalent of reactants to products (96,496 coulombs)
G	molal free energy
H^+	hydrogen ion in solution
H_2	hydrogen as a gas or in solution
k	rate constant
K	equilibrium constant in term of activities
Me	metal in its elemental solid state
Me _(n+)	metal ion in solution with an oxidation number n+
Ni(II)	nickelous ion in solution
$\bar{P}$	partial pressure
R	universal gas constant, 1.987 calories/gr-mole-°K
T	absolute temperature

Greek Letters

γ	activity coefficient
Δ	change or finite differential
μ	chemical potential
ν	stoichiometric coefficient in a reaction

Subscripts

i	any of the chemical species involved in a reaction
H_2/H^+	refers to the half-cell reaction $H_2 = 2H^+ + 2e^-$
$Me/Me(2+)$	refers to the half-cell reaction $Me = 2Me^+ + 2e^-$
$t_{1/2}$	time required to reduce 50 percent of the metal ion in solution, minutes
$t_{1/4}$	time required to reduce 25 percent of the metal ion in solution, minutes

Superscripts

$^\circ$	refers to some standard or reference state
----------	--

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APPENDICES

APPENDIX A

PARTS LIST FOR REACTORS

TABLE II
PARTS LIST FOR REACTORS

Item No.	Description	Material
1	Valve body	316 stainless steel
2	Bottom washer	304 stainless steel
3	Packing	asbestos-graphite
4	Spacer	416 stainless steel
5	Insert	AMPCO (bronze-aluminum alloy)
6	Gland nut	416 stainless steel
7	Stem assembly	316 stainless steel
8	Handle	aluminum
9	Set screw	steel
10	Front ferrule	316 stainless steel
11	Back ferrule	316 stainless steel
12	Universa-Lok nut	316 stainless steel
13	Reactor body	316 stainless steel
14	Bottom cap	316 stainless steel
15	Pipe to tubing adapter (1/4")	316 stainless steel

APPENDIX B

CALIBRATION OF VOLUME OF PRESSURE GAUGE AND CONNECTIONS

The volume of the Bourdon tube of the pressure gauge and of the tubing connecting the gauge to the reactors was calibrated as follows:

1. A reactor with a known volume of 55.90 cubic centimeters was connected to the tubing and gauge (see Figure 4).
2. The system was pressurized with hydrogen and the reactor closed. At this point the pressure in the reactor and the ambient temperature was known.
3. The pressure was released from the system (except pressure from the reactor). Pressure gauge read 0 psig at this point.
4. The hydrogen unloading system was isolated (by closing valve A in Figure 4) and the reactor opened. Next, the final reactor pressure and ambient temperature were recorded to calculate the gauge and connections volume shown in Figure 30.
5. Raw data at 21.8°C:
Reactor with 86 psig; upon opening, gauge read 59.0 psig.

Reactor with 300 psig; upon opening, gauge read 205.0 psig.

Reactor with 500 psig; upon opening, gauge read 340.0 psig.

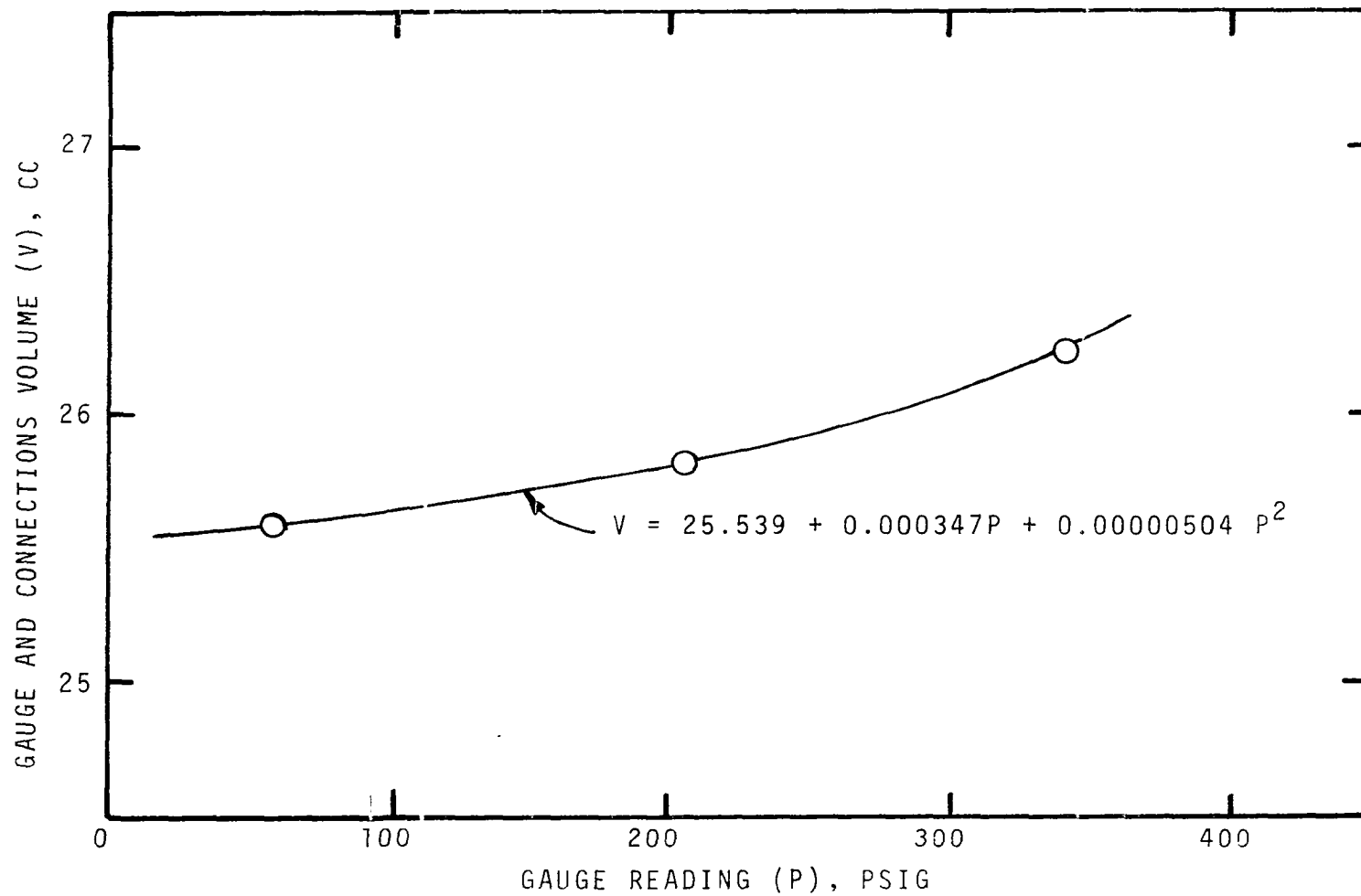


Figure 30. Volume of Pressure Gauge and Connections.

APPENDIX C

PROCEDURE TO DETERMINE HYDROGEN LOADING PRESSURES

To determine the hydrogen pressure (denoted as $APL(I)$ in the computer program that follows) required in each reactor at ambient temperature to obtain the desired hydrogen partial pressure at the run temperature, the following information was required:

1. Estimate of the ambient temperature.
2. Hot oil temperature (TRUN).
3. Initial H_2 partial pressure desired (H2PP).
4. Volume of the reactors (RXTRV(I)).
5. Volume of liquid load (LOAD).
6. Coefficient for expansion of water (EXFAC) from TLOAD to TRUN. See Figure 31 for sample determination of EXFAC.
7. Base temperature (TBASE) for determining EXFAC. See Figure 31.
8. Vapor pressure of water (VP) at TRUN.

The above information was input as data to the computer program shown on page 106. The computer output listed the hydrogen pressure required by each reactor at different ambient temperatures to obtain the desired operating H_2

pressure at TRUN. A partial sample of the computer output is shown on page 107.

```

$JOB          478641964,KP=29,TIME=50
C      APL(I)=REQUIRED H2 LOADING PRESSURE IN REACTOR I
C      EXFAC=COEFFICIENT FOR EXPANSION OF WATER DUE TO HEATING
C      H2PP=DESIRED INITIAL H2 PARTIAL PRESSURE
C      LOAD=VOLUME OF LIQUID LOAD IN REACTOR
C      RXTRV(I)=TOTAL VOLUME OF REACTOR I
C      TBASE=BASE TEMPERATURE USED TO CALCULATE EXFAC
C      TRUN=RUN TEMPERATURE
C      VP=VAPOR PRESSURE OF WATER AT TRUN
1      REAL LOAD
2      DIMENSION RXTRV(10),APL(10)
3      READ(5,10) TRUN,H2PP,VP
4      10 FORMAT(3(F10.4))
5      WRITE(6,20)TRUN
6      20 FORMAT(1H1,' H2 LOADING PRESSURES (PSIG) FOR RUNS AT',F5.1,
7          1 ' DEGREES CENTIGRADE')
8      WRITE(6,21)H2PP
9      21 FORMAT(' AND',F6.1,' PSIG HYDROGEN PARTIAL PRESSURES ')
10     30 FORMAT(' CALCULATIONS ACCOUNT FOR VARIATION OF WATER DENSITY
11         1 WITH TEMPERATURE',/)
12     40 READ(5,40)(RXTRV(I),I=1,10)
13     40 FORMAT(F10.2)
14     LOAD=25.0
15     TBASE=20.0
16     TLOAD=TBASE
17     DELT=0.0
18     DO 100 J=1,75
19     TLOAD=TLOAD+DELT
20     47 IF (TRUN-150.0)48,49,48
21     48 WRITE (6,99)
22     99 FORMAT (' SOMETHING SCREWED ')
23     49 EXFAC=8.86-0.03283*(TLOAD-TBASE)
24     50 DO 52 I=1,10
25     52 APL(I)= ((TLOAD+273.16)*(RXTRV(I)-LOAD*(1.0+0.01*EXFAC))
26         1 *(VP+H2PP))/(((TRUN+273.16)*(RXTRV(I)-LOAD))-14.696
27         IF(J-1)30,60,80
28     60 WRITE(6,70)
29     70 FORMAT(1X,'TLOAD',2X,'REACTOR1',1X,'REACTOR2',1X,'REACTOR3',1X,'
30         1REACTOR4',1X,'REACTOR5',1X,'REACTOR6',1X,'REACTOR7',1X,'REACTOR8'
31         2 ,1X,'REACTOR9',1X,'REACTOR10',/)
32     80 WRITE(6,90)TLOAD,(APL(I),I=1,10)
33     90 FORMAT(F6.2,1X,10(3X,F6.2))
34     DELT=0.2
35     100 CONTINUE
36     STOP
37     END
$EXEC

```

H₂ LOADING PRESSURES (PSIG) FOR RUNS AT 150.0 DEGREES CENTIGRADE
AND 500.0 PSIG HYDROGEN PARTIAL PRESSURES
CALCULATIONS ACCOUNT FOR VARIATION OF WATER DENSITY WITH TEMPERATURE

TLOAD	REACTOR1	REACTOR2	REACTOR3	REACTOR4	REACTOR5	REACTOR6	REACTOR7	REACTOR8	REACTOR9	REACTOR10
20.00	351.45	351.41	351.41	351.27	351.54	351.59	351.45	351.54	351.52	351.50
20.20	351.72	351.68	351.68	351.54	351.81	351.96	351.72	351.81	351.79	351.77
20.40	351.97	351.75	351.95	351.81	352.04	352.13	351.99	352.03	352.06	352.04
20.60	352.26	352.22	352.22	352.08	352.35	352.40	352.26	352.35	352.34	352.31
20.80	352.53	352.49	352.49	352.35	352.62	352.67	352.53	352.62	352.61	352.53
21.00	352.81	352.76	352.76	352.62	352.89	352.94	352.80	352.89	352.89	352.85
21.20	353.03	353.03	353.03	352.99	353.17	353.21	353.08	353.17	353.15	353.12
21.40	353.35	353.30	353.30	353.17	353.44	353.49	353.35	353.44	353.42	353.39
21.60	353.62	353.57	353.57	353.44	353.71	353.75	353.62	353.71	353.69	353.66
21.80	353.91	353.94	353.84	353.71	353.98	354.02	353.89	353.79	353.96	353.93
22.00	354.16	354.11	354.11	353.98	354.25	354.29	354.16	354.25	354.23	354.20
22.20	354.43	354.39	354.39	354.25	354.52	354.56	354.43	354.52	354.50	354.47
22.40	354.70	354.66	354.66	354.52	354.79	354.84	354.70	354.79	354.77	354.75
22.60	354.97	354.93	354.93	354.79	355.06	355.11	354.97	355.06	355.04	355.02
22.80	355.24	355.20	355.20	355.06	355.33	355.38	355.24	355.33	355.31	355.29
23.00	355.51	355.47	355.47	355.33	355.60	355.65	355.51	355.60	355.59	355.56
23.20	355.73	355.74	355.74	355.60	355.87	355.92	355.79	355.87	355.86	355.83
23.40	356.06	356.01	356.01	355.87	356.15	356.17	356.06	356.15	356.13	356.10
23.60	356.33	356.28	356.28	356.15	356.42	356.46	356.33	356.42	356.40	356.37
23.80	356.60	356.55	356.55	356.42	356.69	356.73	356.60	356.69	356.67	356.64
24.00	356.87	356.82	356.82	356.69	356.96	357.00	356.87	356.96	356.94	356.91
24.20	357.14	357.09	357.09	356.96	357.23	357.27	357.14	357.23	357.21	357.19
24.40	357.41	357.37	357.37	357.23	357.50	357.55	357.41	357.50	357.48	357.46
24.60	357.69	357.64	357.64	357.50	357.77	357.82	357.68	357.77	357.75	357.73
24.80	357.95	357.91	357.91	357.77	358.04	358.09	357.95	358.04	358.03	358.00
25.00	358.23	358.18	358.18	358.04	358.32	358.36	358.23	358.32	358.30	358.27
25.20	358.50	358.45	358.45	358.32	358.59	358.63	358.50	358.59	358.57	358.54
25.40	358.77	358.72	358.72	358.59	358.86	358.90	358.77	358.86	358.84	358.81
25.60	359.04	359.99	358.99	358.86	359.13	359.17	359.04	359.13	359.11	359.08
25.80	359.31	359.27	359.27	359.13	359.40	359.45	359.31	359.40	359.38	359.36
26.00	359.58	359.54	359.54	359.40	359.67	359.72	359.58	359.67	359.65	359.63
26.20	359.85	359.81	359.81	359.67	359.94	359.97	359.85	359.94	359.93	359.90
26.40	360.13	360.08	360.08	359.94	360.22	360.26	360.13	360.22	360.20	360.17
26.60	360.40	360.35	360.35	360.22	360.49	360.53	360.40	360.49	360.47	360.44
26.80	360.67	360.62	360.62	360.49	360.76	360.80	360.67	360.76	360.74	360.71
27.00	360.94	360.89	360.89	360.76	361.03	361.07	360.94	361.03	361.01	360.99
27.20	361.21	361.17	361.17	361.03	361.30	361.35	361.21	361.30	361.28	361.26
27.40	361.49	361.44	361.44	361.30	361.57	361.62	361.48	361.57	361.55	361.53
27.60	361.75	361.71	361.71	361.57	361.84	361.89	361.75	361.84	361.83	361.80
27.80	362.03	361.98	361.98	361.84	362.12	362.16	362.03	362.12	362.10	362.07
28.00	362.30	362.25	362.25	362.12	362.39	362.43	362.30	362.39	362.37	362.34
28.20	362.57	362.52	362.52	362.39	362.66	362.70	362.57	362.66	362.64	362.61
28.40	362.84	362.80	362.80	362.66	362.93	362.98	362.84	362.93	362.91	362.89
28.60	363.11	363.07	363.07	362.93	363.20	363.25	363.11	363.20	363.19	363.16
28.80	363.39	363.34	363.34	363.20	363.48	363.52	363.39	363.48	363.46	363.43
29.00	363.65	363.61	363.61	363.48	363.75	363.79	363.66	363.75	363.73	363.70
29.20	363.93	363.88	363.88	363.75	364.02	364.06	363.93	364.02	364.00	363.97
29.40	364.21	364.16	364.16	364.02	364.29	364.34	364.20	364.29	364.27	364.25
29.60	364.47	364.43	364.43	364.29	364.56	364.61	364.47	364.56	364.54	364.52
29.80	364.75	364.70	364.70	364.56	364.83	364.88	364.75	364.83	364.82	364.79
30.00	365.02	364.97	364.97	364.84	365.11	365.15	365.02	365.11	365.09	365.06
30.20	365.29	365.24	365.24	365.11	365.38	365.42	365.29	365.38	365.36	365.33
30.40	365.56	365.52	365.52	365.38	365.65	365.70	365.56	365.65	365.63	365.61
30.60	365.83	365.79	365.79	365.65	365.92	365.97	365.83	365.92	365.90	365.88

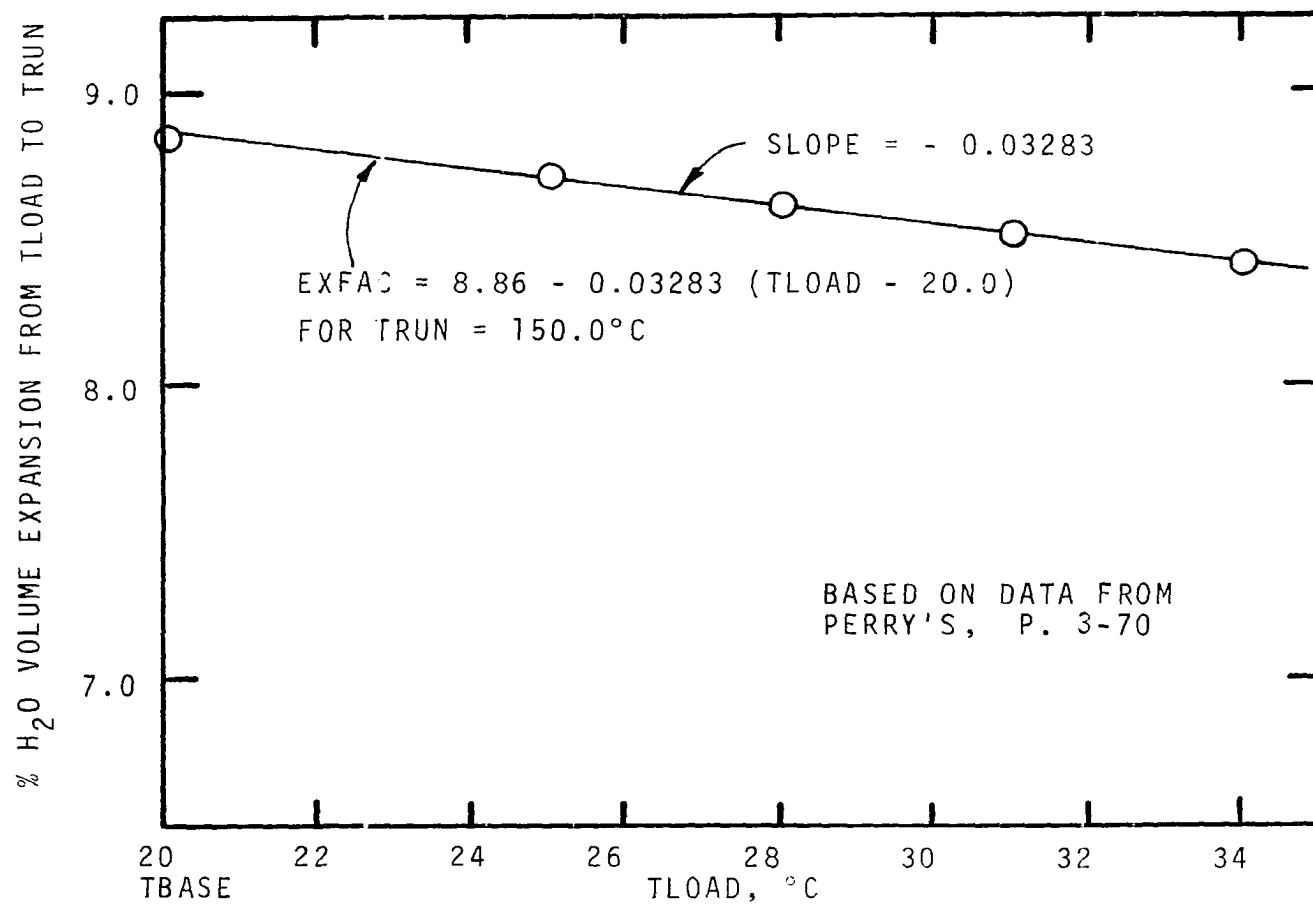


Figure 31. Increase in H₂O Volume on Heating from TLOAD to 150.0°C.

APPENDIX D

DETERMINATION OF METAL ION REDUCED BY CALCULATING HYDROGEN CONSUMPTION

To determine the hydrogen consumed in a reactor, and in turn the amount of metal ion that had been reduced, the following information was required:

1. Reactors loading pressure and temperature (ambient).
2. Expansion coefficient of water in heating from loading temperature to run temperature. See Appendix E.
3. Reactors final pressure and temperature (ambient).
4. Volume of liquid load.
5. Molar concentration of metal ion in reactor charge.
6. Total volume of reactors.
7. Run temperature.
8. Vapor pressure of water at run temperature.
9. Volume of Bourdon tube and connections. See Appendix B.

The above information was supplied as data to the computer program that follows below. A short sample of the computer calculations output is shown on pages 113 and 114.

```
SJN8      748641964,KP=29,TIME=300  
CCCCCCCCCC CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
C    ADOX=METAL ION REDUCED ACCOUNTING FOR H2 IN SOLUTION  
C    ALQAP AND ATEMP=LOADING PRESSURES AND TEMPERATURES  
C    APP=H2 PARTIAL PRESSURE AT END OF REACTION  
C    APIN=H2 PARTIAL PRESSURE AT BEGINNING OF REACTION  
C    COEFF,X,M,RDCTR,RDOTI,IER=ARGUMENTS NEEDED TO USE POLRT SUBROUTINE  
C    COEFF(1) TO COEFF(4)=COEFFICIENTS IN REDLICH-KWONG EQUATION OF  
C    STATE IN FORM Z**3,O-Z**2,O*(A**2.O*B)*Z-(B*A)*Z*.O-(B*A)**2.O  
C    CONV=METAL ION REDUCED NOT ACCOUNTING FOR H2 IN SOLUTION  
C    EXFAC(I)=COEFFICIENT FOR EXPANSION OF WATER IN REACTOR I  
C    FLDAP AND FTMP=FINAL REACTOR PRESSURES AND TEMPERATURES  
C    I=NUMBER OF REACTOR BEING ANALYSED  
C    LAST=NUMBER OF REACTORS IN RUN  
C    LDATE=DATE OF RJN  
C    LOAD=VOLUME OF LIQUID LOAD,MILLILITERS  
C    LRUN=RUN NUMBER  
C    MOLES=MOLAR CONCENTRATION OF METAL ION IN LIQUID LOAD  
C    NRUNS=NUMBER OF RUNS FOR WHICH COMPUTATIONS ARE BEING MADE  
C    PC AND TC=HYDROGEN'S CRITICAL PRESSURE (PSI) AND TEMPERATURE (K)  
C    PLRTE-SUBROUTINE IN IBM SCIENTIFIC SUBROUTINE PACKAGE.  
C    SEE IBM PUBLICATION NUMBER GH20-0205-4  
C    RXTRV(I)=TOTAL VOLUME OF REACTOR I,MILLILITERS  
C    SOLH2=IS H2 DISSOLVED IN LOAD AT 75 °F  
C    THASE=BASE TEMPERATURE TO CALCULATE EXFAC  
C    TIME=TIME OF REACTOR IN OIL BATH  
C    TOUN=RUN TEMPERATURE  
C    VP=VAPOUR PRESSURE OF WATER AT TRUN  
CCCCCCCCCC CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC  
  
1   REAL LOAD,MOLFS  
2   DIMENSION RXTRV(1),ALQAV(1),ALQAP(1),ATEM(1),FLDAP(1),  
3       1 FTMP(1),EXFAC(1),COEFF(4),X(4),RDCTR(3),RDOTI(3)  
4       5 READ(5,A,NRNS  
5       6 FORMAT(12)  
6       D) 400 K=L,NPUNS  
7       WRITE(6,15)  
8       15 FORMAT(/,'XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX     CALCULATIONS FROM  
9           IM HYDR-HEN PRESSURE MEASUREMENTS XXXXXXXXXXXXXXXXXXXXX',//)  
10      READ(5,10)LRUN,LDATE,LAST,TRUN,VP,MOLES,LOAD  
11      10 FORMAT(12,16,12,4F10.4)  
12      WRITE(6,20)LRUN,LDATE,LAST,TRUN  
13      20 FORMAT('  RUNNUMBER ',12 , ' DATE ', 16 ' LAST=',12,  
14          1 5X,' RUN TEMPERATURE=' ,F8.3)  
15      WRITE(6,19)LOAD,MOLFS  
16      19 FORMAT(3X,'LOAD=' ,F6.2,' MLS OF' ,F8.4,' MOL PER LITER',//)  
17      RXTRV(1)=56.10  
18      RXTRV(2)=56.15  
19      RXTRV(3)=56.05  
20      RXTRV(4)=55.90  
21      RXTRV(5)=56.20  
22      RXTRV(6)=56.25  
23      RXTRV(7)=56.10  
24      RXTRV(8)=56.20  
25      RXTRV(9)=56.18  
26      RXTRV(10)=56.15  
27      THASE=20.0  
28      WRITE(6,40)  
29      40 FORMAT(' RXTRV ',3X,' H2N ', 6X,' H2END',7X,' SOLH2',5X,' LPPI',4X,  
30          1  ' H2PPI INITIAL ',4X,' H2CINV ',3X,' ADH2C INV ',3X,' RXTN MIN ',//)  
31      D) 300 L=1, LAST
```

```

28      READ(5,50) I, TIME
29      50 FORMAT(12,F9.2)
30      READ(5,100) ALQAP(I), ATEMP(I), FLOAP(I), FTEMP(I)
31      100 FORMAT(4F10.3)
32      ALQAP(I) = ALQAP(I) + 14.696
33      FLOAP(I) = FLOAP(I) + 14.696
34      109 IF (TRUN-150.0) 110, 112, 110
35      110 WRITE(6,111)
36      111 FORMAT('SOMETHING SCREW(')
37      112 EXFAC(I) = 8.6765 - 0.03293*(ATEMP(I) - TBASE)
38      133 N=0
39      M=3
40      PC=138.1089
41      TC=33.3
42      T=ATEMP(I)+273.16
43      P=ALQAP(I)+14.696
44      134 A=((0.4278*TC**2.5)/(PC*T**2.5))**0.5
45      B=(0.0867*TC)/(PC*T)
46      COEFF(1)=-B*P**2.0*A**2.0
47      COEFF(2)=A**2.0*P-(B*P)**2.0-H*P
48      COEFF(3)=-1.0
49      COEFF(4)=1.0
50      CALL POLRT(COEFF,W,M,ROOTR,ROOTI,IER)
51      599 IF(IER-1) 900,600,700
52      600 WRITE(6,650)
53      650 FORMAT(/, ' SOMETHING SCREW(')
54      700 IF(IER-3) 750,800,780
55      750 WRITE(6,650)
56      780 WRITE(6,650)
57      800 WRITE(6,850)
58      850 FORMAT(/, ' UNABLE TO DETERMINE ROOT, THOSE ALREADY FOUND ARE ')
59      900 WRITE(6,950)
60      950 FORMAT(/, 5X, 9HREAL ROOT, 6X, 12HCOMPLEX ROOT/ )
61      DO 960 J=1,M
62      951 IF(ROOTI(J)) 960,952,960
63      952 IF(ROOTR(J)-1.1) 953,960,960
64      953 IF(ROOTR(J)-0.9) 960,960,955
65      955 IF(N) 957,956,957
66      956 Z1=ROOTR(J)
67      GO TO 960
68      957 Z2=ROOTR(J)
69      960 WRITE(6,970) ROOTR(J), ROOTI(J)
70      970 FORMAT(2E16.7)
71      145 IF(N) 148,146,148
72      146 WRITE(6,147) Z1
73      147 FORMAT(6X, ' Z= ', E11.4)
74      GO TO 149
75      148 WRITE(6,147) Z2
76      149 IF(N-1) 150,159,110
77      150 H2IN = (ALQAP(I)/14.696)*((RXTRV(I)-LOAD )/1000.01)/
       1 (0.03295*(ATEMP(I)+273.16)**2)
C      CALCULATION NEGLECTS VAPOR PRESSURE OF WATER AT ATEMP
78      151 IF(N-1) 152,110,110
79      152 N=1
80      T=FTEMP(I)+273.16
81      P=FLOAP(I)+14.696
82      GO TO 134
83      159 GAGEV=25.539+0.000347*FLOAP(I)+0.00000504*((FLOAP(I))**2.0)
84      160 H2END= ((FLOAP(I)/14.696)*((RXTRV(I)-LOAD+GAGEV)/1000.01)/(0.08205
       1 *(FTEMP(I)+273.16)**2)-GAGEV/(82.05*(FTEMP(I)+273.16))

```

```

      C      H2END IS H2 GAS LEFT AT END OF REACTIO,NEGLECTS H2 GAS IN SOLUTION
85      APP=(Z2*H2END*0.08205*(TRUN+273.16))/((RXTRV(1)-LOAD*(1.0+
      1 0.01*EXFAC(1)))/1000.0)*14.696-VP
86      SOLH2=(0.001199*APP*LOAD)/22414.0
87      ADJH2=H2END+SOLH2
88      ADCON=(H2IN-ADJH2)/(MOLES*LOAD/1000.0)
89      CONV=(H2IN-H2END)/(MOLES*LOAD/1000.0)
90      APPIN=(Z1*H2IN*0.08205*(TRUN+273.16))/((RXTRV(1)-LOAD*(1.0+
      1 0.01*EXFAC(1)))/1000.0)*14.696-VP
91      WRITE(6,99)I,H2IN,H2END,SOLH2,APP,APPIN,CONV,ADCON,TIME
92      99 FORMAT(2X,I2,7(2X,F10.5),2X,F8.2)
93      300 CONTINUE
94      400 CONTINUE
95      STOP
96      END

```

SEXEC

```

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
RUNNUMBER 22 DATE 60872 LAST= 4
RUN TEMPERATURE= 150.000
LOAD= 30.00 MLS OF 0.4300 MOLES PER LITER
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

PXR# H2IN H2END SOLH2 H2PP H2PP INITIAL H2CONV ACH2CONV RXTN MIN
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

REAL ROOT COMPLEX ROOT
-0.7191421E-02 -0.1733653E-02
-0.7191421E-02 0.1733653E-02
0.1014362E 01 0.0000000E 00
Z= 0.1014E 01

REAL ROOT COMPLEX ROOT
-0.3761744E-02 -0.7955337E-03
-0.3761744E-02 0.7955337E-03
0.1007523E 01 0.0000000E 00
Z= 0.1008E 01
6 0.02327 0.02231 0.00067 414.68160 439.94970 0.07451 0.02292 3.00

REAL ROOT COMPLEX ROOT
-0.7196392E-02 -0.1736142E-02
-0.7196392E-02 0.1736142E-02
0.1014392E 01 0.0000000E 00
Z= 0.1014E 01

REAL ROOT COMPLEX ROOT
-0.3148654E-02 -0.6598109E-03
-0.3148654E-02 0.6598109E-03
0.1005297E 01 0.0000000E 00
Z= 0.1006E 01
7 0.02319 0.02113 0.00052 376.16670 440.35910 0.39170 0.35112 1.00

REAL ROOT COMPLEX ROOT

```

-0.7176440E-02 -0.1699018E-02
 -0.7176440E-02 0.1699018E-02
 0.1014353E 01 0.0000000E 00
 Z= 0.1014E 01

REAL ROOT COMPLEX ROOT

-0.2345703E-02 -0.5171994E-03
 -0.2345703E-02 0.5171994E-03
 0.1004691E 01 0.0000000E 00
 Z= 0.1005E 01

8 0.02320 0.01277 0.00033 207.69600 439.48120 0.80847 0.78263 30.00

REAL ROOT COMPLEX ROOT

-0.7169805E-02 -0.1652031E-02
 -0.7169805E-02 0.1652031E-02
 0.1014339E 01 0.0000000E 00
 Z= 0.1014E 01

REAL ROOT COMPLEX ROOT

-0.2144476E-02 -0.4706595E-03
 -0.2144476E-02 0.4706595E-03
 0.1004289E 01 0.0000000E 00
 Z= 0.1004E 01

9 0.02315 0.01141 0.00029 178.29250 437.76090 0.91017 0.89799 60.00

APPENDIX E

COMPARISON OF RESULTS BY WET METHODS OF ANALYSIS WITH RESULTS FROM HYDROGEN CONSUMPTION CALCULATIONS

Figure 32 shows a comparison of analytical results from wet methods of analysis and from the hydrogen consumption determinations described in Appendix D.

Of the two hydrogen consumption figures (H2CONV and ADH2CONV) calculated by the computer program, in general, H2CONV (hydrogen consumed without adjustment for H_2 dissolved in the liquid solution at the end of the run) gave better agreement with the results from wet methods of analysis.

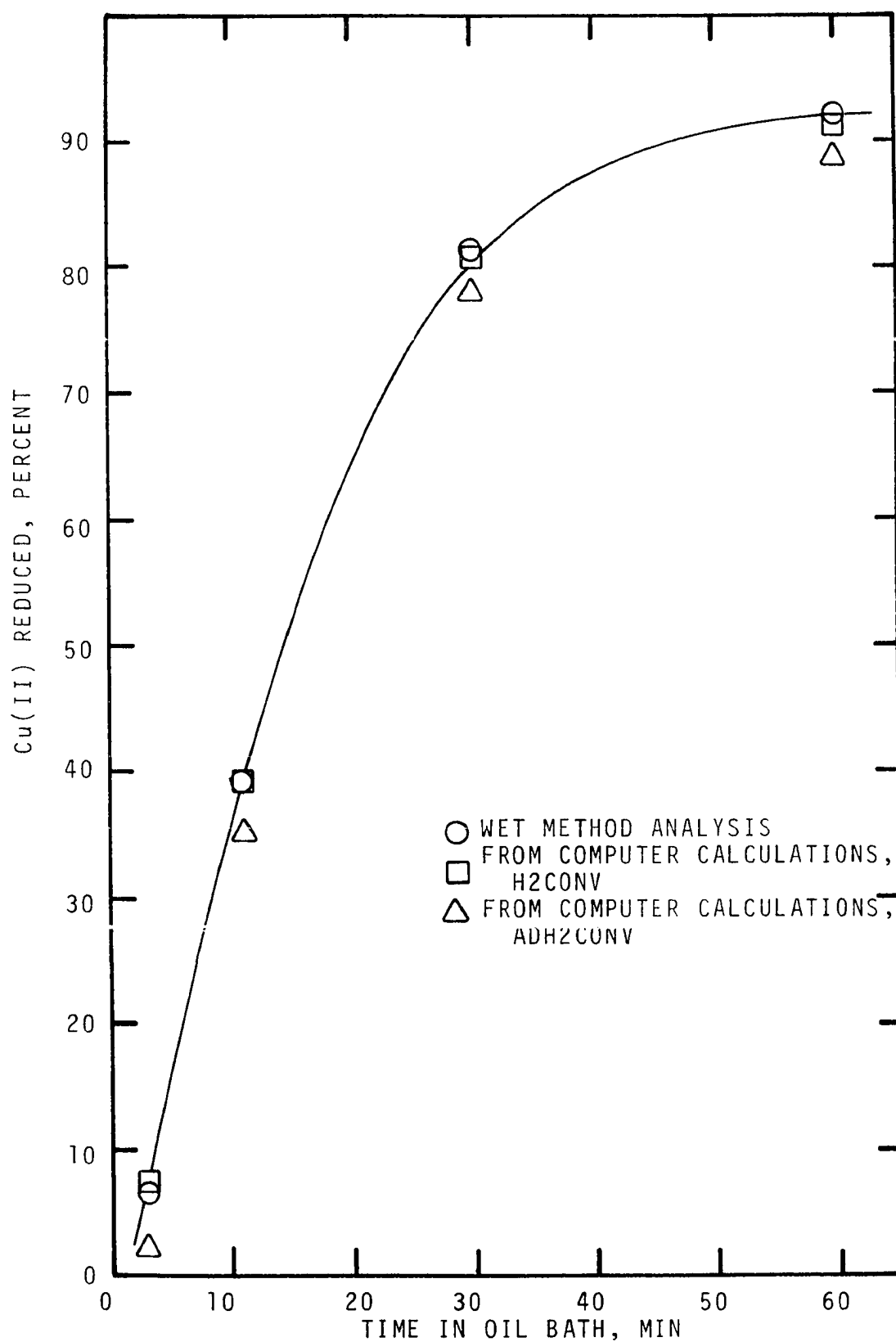


Figure 32. Comparison of Conversions by Wet Methods of Analysis and by Hydrogen Consumption Calculations.

APPENDIX F

ANALYSIS BY WET METHODS AND BY X-RAY DIFFRACTION

This appendix presents an abbreviated description of the procedures used in the wet methods of analysis and in the analysis of solids by x-ray diffraction.

Copper Determination Procedure

The following procedure to determine Cu(II) in solution was used (recommended by Pierce, Sawyer and Haenisch (26)):

1. A sample (5 to 10 ml) was taken of the solution whose Cu(II) content was to be determined. When solids were analyzed, a weighed sample of the solid was first dissolved in nitric acid, and the whole sample used in the Cu(II) determination.
2. When analyzing a solid sample, a small amount of urea (about 1 gm) was added and the sample boiled for about 1 minute and then cooled.
3. Ammonia was added until the solution showed a deep blue color.
4. Acetic acid was added (about 5 ml) to buffer the solution.

5. Potassium iodide (about 5 gm) was added and the sample allowed to stand for a couple of minutes.
6. The sample was titrated with a standard solution of sodium thiosulfate until the iodine color began to fade. Starch was added as an indicator, and then the titration with sodium thiosulfate was continued to the starch end point.

Determination of Nickel with Dimethylglyoxime

One of the procedures to determine Ni(II) (recommended by Pierce, Sawyer and Haenisch (26)) was as follows:

1. Samples were taken of the solution (to contain about 20-30 mg of Ni(II)) or solid (which was dissolved in nitric acid) that was being analyzed.
2. Tartaric acid was added (10 ml of a solution of 20 gm tartaric acid per 100 ml of water).
3. The sample was diluted to 200 ml and neutralized with NH_3 .
4. The sample was just acidified with HCl and warmed to about 70°C . Then, enough dimethylglyoxime was added to precipitate (as the nickel-dimethylglyoxime complex) all the nickel in the sample.
5. The sample was neutralized with NH_3 and digested in a steam bath for about one hour.
6. The sample was cooled and the nickel-dimethylglyoxime solid complex filtered in filtering crucibles. The crucibles were then dried in an oven at about 125°C for two hours before weighing.

Determination of Nickel with EDTA

The following procedure to determine nickel with EDTA (ethylene diamine tetraacetic acid) was described by Homer (12):

1. Same as step 1 above.
2. Adjust the sample pH to 9 with NH_3 .
3. Add murexide (purpuric acid) as indicator.
4. Titrate with EDTA to the murexide end point.

Analysis of Solids by X-Ray Diffraction

To analyze solids by x-ray diffraction the following procedure was used:

1. The solid samples were dried in an oven at about 125°C for about 2 hours.
2. The solid samples were ground to a fine powder with a mortar and pestle.
3. A small portion of the solid sample was mounted in a sample-support, and the sample exposed to x-rays from the Norelco x-ray unit located in the School of Geology.
4. The x-ray pattern obtained from the x-ray unit was then compared with cards from the Alphabetical and Grouped Numerical Index of X-Ray Diffraction Data published by the American Society of Testing Materials.

APPENDIX G

COMPUTER PROGRAM USED IN FITTING DATA TO CURVES

To fit the experimental data to curves the computer program shown on the next page was used. The program is written in "FOCAL" computer language, and the PDP-8-E computer of the School of Chemical Engineering and Materials Science was used to make the computations.

C-FOCAL, 1969

01.05 A NP;F I=1,NP;D 2.0

01.10 G 5.01

02.05 A CU,T;S X=FADC(I,CU);S X=FADC(50+I,T)

05.01 A N;T "INITIAL VALUES",!;F I=1,N;A X(I)

05.03 F I=1,N;S D(I)=.11*X(I)

05.04 S G=0

05.05 S A=1;D 10.0;S R=D;F I=1,N;S Z(I)=0

05.10 S C=0;F I=1,N;D 6.0

05.15 I (A+C-1)5.20,5.45,5.25

05.20 S A=1;F I=1,N;S X(I)=X(I)-Z(I)*D(I);S Z(I)=0

05.22 G 5.10

05.25 F I=1,N;S X(I)=X(I)+Z(I)*D(I)

05.30 D 10.0;I (R-D)5.35,5.40,5.40

05.35 S A=2;S R=D;G 5.10

05.40 S A=0;G 5.10

05.45 S A=1;S G=G+1;F I=1,N;S D(I)=D(I)/2

05.47 T "S"

05.50 I (G-12)5.10;F I=1,N;T Z,X(I)

05.53 T !,!, "FIT",R,!

05.55 F J=1,NP;D 11.0;T FADC(J),R,FADC(J)-R,!

05.60 0

06.01 S X(I)=X(I)+D(I);D 10.0;I (R-D)6.05,6.10,6.10

06.05 S R=D;S C=4;S Z(I)=Z(I)+1;R

06.10 S X(I)=X(I)-2*D(I);D 10.0;I (R-D)6.15,6.20,6.20

06.15 S R=D;S C=4;S Z(I)=Z(I)-1;R

06.20 S X(I)=X(I)+D(I)

10.05 S D=0;F J=1,NP;D 11.0

10.10 S D=-D

11.05 S W=X(1)+X(2)*((FADC(J+50))+X(3)*((FADC(J+50))+2.0)

11.06 S T=X(4)*((FADC(J+50))+3.0)

11.07 S P=W+T

11.15 S D=D+(FADC(J)-R)+2

APPENDIX H

EXPERIMENTAL DATA

Raw experimental data are given in the following tables. More details (observations made while runs were in progress) and comments are given in University of Oklahoma Research Institute Data Books Numbers 1976-DB-3 and 1796-DB-4. available in the extractive metallurgy laboratory.

Significance of the abbreviations used in the following tables are:

Run #	run number as listed in the data books
t	time reactor was in oil bath, minutes
T_i	ambient temperature when H_2 was loaded, °C
T_f	ambient temperature when residual H_2 was unloaded, °C
P_i	H_2 pressure in reactor when H_2 was loaded at T_i , psig
P_f	H_2 pressure in reactor, gauge and connections when H_2 was unloaded at T_f , psig
pH	$-\log a_{H_2}$ at temperature at which it was measured (T_{pH})
T_{pH}	temperature at which pH was measured, °C
$CuSO_4$	initial (feed) $CuSO_4$ concentration, moles/liter
T_R	run temperature, °C
P_{H_2}	desired initial H_2 partial pressure, psig

NiSO_4	initial (feed) NiSO_4 concentration, moles/liter
NH_3	initial (feed) NH_3 concentration, moles/liter
H_2SO_4	initial (feed) H_2SO_4 concentration, moles/liter

TABLE III
DATA FOR REDUCTION OF Cu(II) IN AMMONIACAL AQUEOUS CuSO₄ SOLUTIONS

Run #	CuSO ₄	H ₂ SO ₄	T _R	$\bar{P}_{H_2}$	t	T _i	P _i	T _f	P _f	pH	TpH
17	0.42 and 1.7 m/l NH ₃	0.74	150.0	450.0	0					4.31	21.0
					3.0	24.2	310.0	31.2	157.5	4.45	
					10.0	25.4	309.5	31.8	140.0	3.31	
					30.0	26.0	309.6	32.2	100.0	1.53	
					60.0	26.7	310.0	32.4	73.8	1.10	
18	0.42 and 0.42 m/l NH ₃	0.0	150.0	450.0	0					4.42	21.0
					3.0	27.2	310.0	31.2	154.0	4.57	
					10.0	27.6	309.8	31.4	147.4	4.47	
					30.0	27.9	310.0	32.3	127.1	3.15	
					60.0	28.3	310.0	32.4	95.7	1.71	
19	0.43 and 1.7 m/l NH ₃	0.53	150.0	450.0	0					7.92	21.0
					3.0	23.4	310.0	32.1	158.1	7.90	
					10.0	23.4	310.0	31.9	158.0	7.86	
					30.0	24.1	310.0	31.7	155.0	7.91	
					60.0	23.9	310.0	31.5	145.0	7.72	
20	0.42 and 1.7 m/l NH ₃	0.95	150.0	450.0	0					1.58	21.0
					3.0	24.4	310.0	32.2	147.0	1.75	
					10.0	24.6	310.0	32.1	110.0	0.98	
					30.0	25.2	310.0	31.6	79.4	0.76	
					60.0	25.0	310.0	31.6	74.8	0.70	
26	0.43 and 1.7 m/l NH ₃	0.22	150.0	450.0	0						24.0
					15.0	23.2	310.0	27.4	151.8	8.30	
					30.0	23.4	310.0	27.6	148.0	8.91	
					60.0	23.7	310.0	27.9	130.2	8.62	

TABLE III--Continued

Run #	CuSO ₄	H ₂ SO ₄	T _R	P _{H2}	t	T _i	P _i	T _f	P _f	pH	TpH
27	0.44 and 0.88 m/l NH ₃	0.0	150.0	450.0	0 3.0 10.0 30.0 60.0	24.0 24.6 24.15 24.3	310.0 310.0 309.9 310.0	28.3 28.2 27.7 27.5	156.1 155.0 153.0 150.5	8.83 8.80 8.70 8.71	24.0
29	0.43 and 1.7 m/l NH ₃	0.63	100.0	450.0	0 3.0 10.0 30.0 50.0	23.6 23.8 24.1 24.25	325.0 325.0 325.0 325.0	28.05 28.0 28.3 28.25	165.5 165.0 164.8 165.0	4.61 4.60 4.78 4.73	24.0
30	0.43 and 1.7 m/l NH ₃	0.84	100.0	450.0	0 3.0 10.0 30.0 50.0	24.45 24.6 24.9 25.2	325.3 325.3 325.0 325.2	28.0 28.05 28.20 28.20	165.3 166.0 166.0 163.5	4.10 4.11 3.40	24.0
31	0.43 and 1.7 m/l NH ₃	0.63	125.0	450.0	0 3.0 10.0 30.0 60.0	25.4 25.7 26.2 26.25	317.0 317.0 317.6 318.3	31.8 32.0 32.0 32.1	162.6 161.8 158.8 156.3	4.60 4.61 4.52 4.51	24.0
32	0.43 and 1/7 m/l NH ₃	0.84	125.0	450.0	0 3.0 10.0 30.0 60.0	27.3 27.9 28.0 28.25	318.2 318.0 318.5 318.3	31.8 32.0 32.05 32.1	164.0 161.3 149.0 129.2	4.34 2.70 1.61 1.16	24.0

TABLE III-Continued

Run #	CuSO ₄	H ₂ SO ₄	T _R	$\bar{P}_{H_2}$	t	T _i	P _i	T _f	P _f	pH	TpH
33	0.43 and 1.7 m/l NH ₃	0.63	175.0	450.0	0						24.0
					3.0	24.05	365.0	29.2	157.0	3.04	
					10.0	24.40	365.0	29.65	123.2	1.52	
					20.0	24.80	364.7	29.75	106.2	1.26	
					40.0	25.15	365.0	30.05	99.5	1.08	
34	0.43 and 1.7 m/l NH ₃	0.84	175.0	450.0	0						24.0
					3.0	25.40	365.0	29.3	129.0	0.92	
					10.0	25.60	366.0	29.45	105.0	0.70	
					20.0	25.80	366.0	29.90	103.0	0.68	
					40.0	26.60	365.9	30.05	101.3	0.62	
35	0.41 and 1.7 m/l NH ₃	1.20	150.0	450.0	0						24.0
					3.0	26.5	314.0	33.9	157.5	0.60	
					10.0	27.0	313.0	34.65	117.0	0.36	
					30.0	27.3	314.0	35.0	90.0	0.30	
					60.0	27.6	315.0	35.20	84.4	0.21	

TABLE IV
DATA FOR REDUCTION OF Cu(II) IN AQUEOUS CuSO₄ SOLUTIONS

Run #	CuSO ₄	T _R	$\bar{P}_{H_2}$	t	T _i	P _i	T _f	P _f	pH	TpH
74	0.5	150.0	400.0	0					3.50	22.0
				5.0	22.70	290.0	22.30	153.0	1.70	
				15.0	22.60	290.0	22.20	123.0	0.71	
				30.0	22.60	290.0	22.40	106.0	0.48	
				45.0	22.60	290.0	22.50	100.0	0.45	
75	0.5	150.0	500.0	0					3.50	22.0
				5.0	22.20	354.0	22.10	185.8	1.50	
				15.0	22.10	354.0	22.10	153.0	0.60	
				30.0	22.00	354.0	22.40	138.4	0.42	
76	0.5	160.0	500.0	0					3.61	15.0
				5	23.70	356.0	20.4	167.8	0.99	
				10	23.10	355.0	20.35	144.6	0.67	
				15	24.40	356.0	20.0	136.0	0.60	
				25	23.40	356.0	18.8	129.2	0.55	
				35	24.00	356.0	18.3	127.0	0.55	
				45	24.00	356.0	17.4	126.5	0.52	
78	0.5	140.0	500.0	0					3.40	20.0
				10	20.5	354.8	19.0	188.0	1.58	
				15	20.5	353.6	18.6	180.5	1.23	
				20	20.8	355.3	18.5	168.0	0.91	
				30	20.0	352.9	18.8	156.5	0.78	
				45	20.0	352.1	20.6	146.0	0.69	

TABLE IV--Continued

Run #	CuSO ₄	T _R	$\bar{P}_{H_2}$	t	T _i	P _i	T _f	P _f	pH	TpH
79	0.5	150.0	600.0	0					3.60	20.0
				5.0	18.8	414.7	20.80	219.7	1.45	
				10.0	19.1	414.6	20.45	193.4	0.84	
				15.0	19.0	414.7	20.10	181.5	0.67	
				25.0	18.7	414.6	19.90	173.0	0.60	
80	0.5	170.0	500.0	0					3.60	20.0
				4.0	20.0	354.9	19.65	151.0	0.70	
				8.0	20.5	355.5	19.45	137.0	0.58	
				12.0	20.4	356.0	19.25	132.5	0.58	
				17.0	20.1	355.0	19.10	128.5	0.52	

TABLE V
DATA FOR REDUCTION OF Ni(II) IN AMMONIACAL AQUEOUS NiSO₄ SOLUTIONS

Run #	NiSO ₄	NH ₃	T _R	P _{H2}	t	T _i	P _i	T _f	P _f	pH	TpH
42	0.5 and 0.5 g/l Fe(II)	3.0	150.0	400.0	0					10.98	30.0
					3.0	29.4	324.0	33.6	150.0	10.20	
					10.0	29.5	324.0	33.4	137.2	10.17	
					15.0	29.8	324.0	33.4	101.4	10.13	
44	0.5 and 0.5 g/l Fe(II)	3.0	125.0	400.0	0					11.01	32.5
					3.0	28.0	327.5	31.6	171.8	10.36	
					10.0	28.2	327.9	32.30	156.0	10.23	
					15.0	28.6	328.1	32.40	154.0	10.23	
					25.0	28.8	328.2	32.40	134.0	10.20	
59	0.5 and 0.5 g/l Fe(II)	2.0	150.0	500.0	0					10.0	30.0
					2.0	25.5	368.0	29.1	176.0	9.77	
					4.0	25.8	368.0	29.8	163.0	9.81	
					6.0	25.9	368.0	29.9	152.0	9.86	
60	0.5 and 0.5 g/l Fe(II)	1.0	150.0	500.0	0					8.60	30.09
					2.0	26.6	369.1	29.2	198.8	8.40	
					4.0	26.6	369.0	29.6	187.2	8.32	
					5.0	25.2	367.0	28.8	166.0	8.20	
					6.0	26.9	370.0	29.5	130.0	7.93	
61	0.5 and 0.5 g/l Fe(II)	3.0	150.0	500.0	0					11.09	31.0
					2.0	26.0	386.0	29.3	198.3	10.41	
					4.0	26.2	386.0	30.5	185.0	10.32	
					6.0	26.4	386.1	30.0	180.0	--	
					8.0	26.6	387.0	30.35	176.0	10.29	
					11.5	25.6	385.0	28.80	164.0	10.31	
					14.0	25.8	385.0	28.9	144.4	10.30	

TABLE V--Continued

Run #	NiSO ₄	NH ₃	T _R	P _{H2}	t	T _i	P _i	T _f	P _f	pH	T _{pH}
62	0.5 and 0.5 g/l Fe(II)	0.5	150.0	500.0	0						
					2.0	27.3	366.0	29.6	199.1		
					4.0	27.5	366.0	30.8	201.0		
					6.0	27.6	366.0	29.7	199.2		
					8.0	27.75	366.2	30.0	199.0		
63	0.5 and 1 g/l Fe(II)	1.0	150.0	500.0	0					8.50	29.0
					2.0	23.8	365.0	28.4	189.1	8.31	
					3.0	24.0	365.0	28.45	154.0	8.11	
					5.0	24.2	366.0	28.80	125.0	7.48	
64	0.5 and 0.25 g/l Fe(II)	1.0	150.0	500.0	0					8.69	29.0
					3.0	23.4	365.0	27.70	203.5	8.50	
					6.0	23.5	365.0	27.80	202.4	8.49	
					9.0	23.6	365.0	28.00	201.5	8.47	
					12.0	23.75	365.0	27.90	202.3	8.47	
66	0.5 and 0.5 g/l Fe(II)	3.0	135.0	400.0	0					11.30	25.0
					3.0	23.6	311.0	25.35	151.0	10.54	
					9.0	23.6	311.0	25.20	146.0	10.52	
					15.0	23.65	311.0	25.20	131.0	10.50	
					21.0	23.70	311.0	25.20	107.2	10.48	
67	0.5 and 0.5 g/l Fe(II)	3.0	145.0	400.0	0					11.30	25.0
					3.0	23.80	315.0	25.20	153.5	10.56	
					9.0	23.80	315.0	25.20	140.0	10.50	
					15.0	23.80	315.0	25.20	101.0	10.47	

TABLE V--Continued

Run #	NiSO ₄	NH ₃	T _R	$\bar{P}_{H_2}$	T	T _i	P _i	T _f	P _f	pH	TpH
69	0.5 and 0.5 g/l Fe(II)	1.0	150.0	400.0	0					8.87	30.0
					3.0	25.60	302.2	28.80	152.0	8.76	
					4.5	25.80	302.0	29.60	120.5	8.62	
					6.0	25.80	302.0	28.90	97.6	8.53	
					8.0	26.00	302.0	29.00	91.1	8.41	
70	0.5 and 0.5 g/l Fe(II)	1.0	150.0	300.0	0					8.59	30.0
					3.0	26.80	238.0	30.1	107.5	8.31	
					4.5	26.90	238.0	30.1	82.5	8.20	
					6.0	26.90	238.0	30.2	68.1	8.12	
					8.0	27.00	238.0	30.2	68.3	8.13	