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**The extraction of metals from metal containing catalysts by
supercritical fluids**

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University of Nevada, Reno, 1989

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The Extraction of Metals from Metal Containing
Catalysts by Supercritical Fluids

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science
in Metallurgical Engineering

by

Jack Stuart McPartland

May, 1989

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ABSTRACT

Experiments were conducted to determine the feasibility of leaching cobalt from a hydrotreating catalyst material using supercritical aqueous ammonia solvents. Supercritical phase leaching conditions were attained using a modified Autoclave Engineers Supercritical Screening System. The effects on cobalt extraction caused by variations in solvent composition, pressure and temperature, including subcritical conditions, were investigated. Four series of experiments, each using various solvent compositions ranging from 0 to 30 percent ammonia at one temperature - pressure condition, were conducted.

Cobalt in the catalyst material was leachable at supercritical and subcritical solvent phase conditions. Cobalt extraction at supercritical phase conditions was generally higher than extraction obtained at any of the other pressure - temperature conditions tested. Leaching enhancement at supercritical conditions was determined not to be solely the result of simple pressure or temperature effects. Rather, leaching enhancement is probably caused by the improved transport properties exhibited by supercritical fluid solvents. Cobalt extraction at supercritical conditions was enhanced by an average of 14.2 percent over extraction at supercritical pressure - elevated temperature conditions, 6.8 percent over extraction at low pressure -

low temperature conditions, and 4.0 percent over extraction at supercritical pressure - low temperature conditions. Cobalt extraction generally increased with increasing ammonia concentration at all four temperature - pressure conditions tested.

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I. INTRODUCTION

There has been increasing interest in the use of supercritical fluids as solvents. Supercritical fluid (SCF) extraction processes have been shown to have advantages, including lower energy requirements, utilization of less toxic more environmentally acceptable solvents, and the ability to meet process requirements which traditional extraction processes cannot meet (1). There have been many books and papers published which review SCF technology (1-9,18).

Unique physiochemical properties shown by fluids in the supercritical phase region are what account for the advantages gained by using SCF processes. In the supercritical phase region, fluids have very high, liquid-like densities (1,7,10,11-15), which give rise to correspondingly high capacity for solutes. Fluid density in this phase region is also extremely sensitive to changes in pressure. This may allow desired solubility to be realized by setting pressure and temperature operating conditions in SCF processes. In addition to the density behavior, SCFs demonstrate gas-like transport properties (1, 6, 7, 10, 11, 13, 14, 16, 17). The viscosity of SCFs is nearly as low as that of gases, and the diffusivity of SCFs is 1-2 orders of magnitude higher than that of liquids. SCFs also have zero surface tension (1). This property makes SCFs an ideal class of solvents for the

leaching of solutes from microporous materials.

Previous development of processes using SCF's has been concentrated in applications which utilize the unique solubility characteristics of SCFs. Most of these processes have been concerned with the extraction of organic solutes in the areas of food processing (2, 5, 6) petrochemical processing (2, 5), and supercritical chromatography (3, 18). There is no literature available on previous work done on the extraction of inorganic solutes, using SCF processes.

An inorganic solute extraction application which could potentially benefit from the use of SCF solvents is the recovery of metals from spent metal containing catalysts. The transport properties of SCFs should facilitate this type of process, allowing easy penetration of the solvent into the catalyst material.

Currently, spent catalysts containing metals of comparatively low value are usually placed in a land fill, without recovering the metals still present in the catalyst. An example of this is the land filling of spent hydro-treating catalysts used in the petrochemical industry. Other catalysts, containing metals of higher values, are sometimes processed for recovery of these metals. However, these processes often involve undesirable solvents, or are energy intensive. Examples of this are the recovery of

platinum group metals from spent automotive catalytic converters using aqua regia solvent, or using support dissolution processes (19,20,21,22). This study investigates the leaching of metals from two different catalyst materials using supercritical solvents. Cobalt was leached from a hydrotreating catalyst over a range of pressure, temperature, and leaching solution composition. Experimental parameters were varied to determine the advantages of leaching in the supercritical region. Attempts were made to leach platinum group metals from spent automotive catalytic converters, using a supercritical fluid solvent. Attempts were also made to leach platinum from a platinum wire using a supercritical fluid solvent.

II. LITERATURE REVIEW

The critical state of a fluid is the point on the pressure-volume-temperature surface where the volumes of the gas and liquid phase become identical. The requirements of thermodynamic stability lead to some powerful inequalities between the rates at which different thermodynamic properties ($V_g - V_l$, P/V , C_p , etc.) become zero as the critical point is approached. This is discussed in depth by Rowlinson (13,23). Precise equilibrium measurements of critical constants are made difficult by the highly unusual mechanical, thermal and optical properties of fluids in this region. As the volumes of the liquid and gas approach each other the dividing meniscus becomes very faint and hazy. Observation of the system is further complicated by the strong scattering of light (critical opalescence) which can cause complete opacity at the critical point.

A supercritical fluid is one which has been compressed and heated beyond its critical point. The supercritical region for a typical pure solvent is qualitatively shown on a P-T diagram in Figure 1. Increasing the temperature or pressure beyond the critical point takes the solvent into its supercritical phase region. Critical temperatures and pressures for some potential critical solvents are shown in Table 1. The relatively extreme temperature and pressure shown by some of the solvents in Table 1 may be attributed to polarity, or to hydrogen bonding (23).

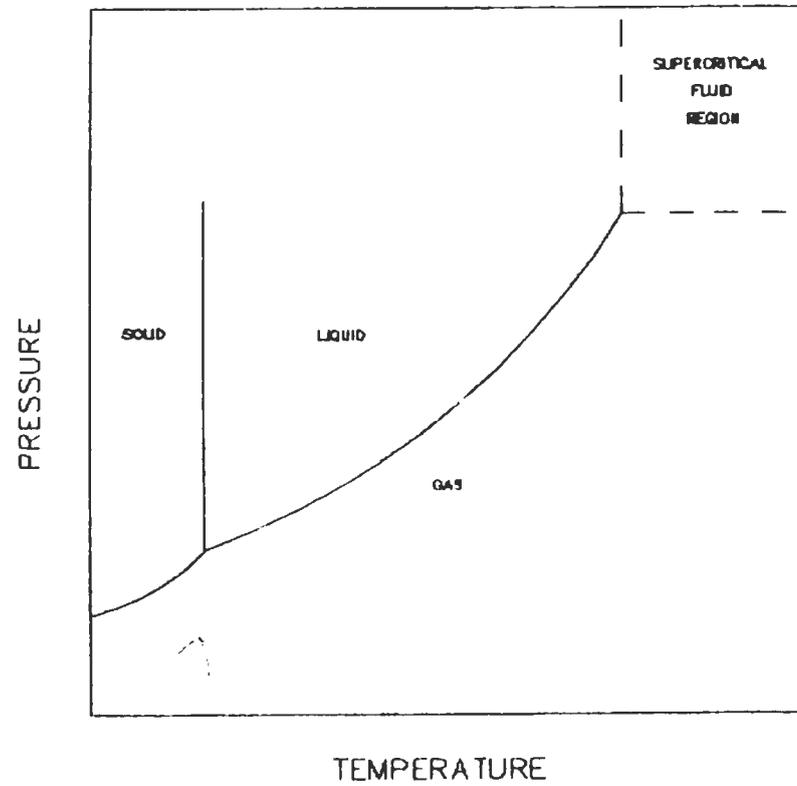


Figure 1., Pressure Temperature Phase Diagram,
Single Component System

Table 1. - Critical Conditions for Various Supercritical Solvents

Solvents	Critical Temperature (C)	Critical Pressure KPa x 10 ⁻³
Carbon dioxide	31.1	7.28
Ethylene	9.3	5.04
Propane	96.7	4.25
Ammonia	132.5	11.28
Water	374.2	22.05

The existence of the critical point of elements has been known of as far back as the early 19th century. In 1822, Baron Cagniard de la Tour discovered the critical point of a substance, using a sealed piece of rifled cannon for his high pressure investigations (1). Later in the 19th century, Dr. T. Andrews carried out extensive investigations of the critical properties of CO₂ reporting critical point values which are very close to the values accepted today (1). The concept of supercritical fluid extraction was first utilized over one hundred years ago, when potassium iodide was dissolved in, and precipitated from supercritical ethanol (1).

The anomalous solvating power of supercritical solvents has been well documented (1,7,8,10-13,15). A summary of supercritical solubility studies has been written by Reid (18). The thermodynamics applicable to equilibrium solubility in supercritical fluids have been treated by Prausnitz (24) and discussed later by Reid (18). Available data suggest that to a first approximation, the high solvent

power of supercritical fluids can be related to their high densities (1,7). This is further evidenced by the existence of a temperature maximum in solubility, which most crystalline solid-supercritical fluid systems demonstrate. The maximum is the result of two competing effects (7). As the temperature of a supercritical solvent is increased above its critical point, the solvent's density decreases, causing its solvating power to decrease. The same increase in temperature, however, causes an increase in sublimation pressure of the crystalline solid, which in turn causes an increase in the solubility of the solute in the SCF. Therefore, the solubility of the solute will have a maximum value at a temperature which represents a compromise between these two competing effects. It has also been demonstrated that the solvating power of SCFs cannot be attributed to a simple hydrostatic pressure effect (1).

To fully understand and utilize supercritical solubility, it is important to know the behavior of the partial molar volume and enthalpy of the solute (8). The effect of pressure on supercritical solubility has been studied by Kim and Johnson (25). They showed that the pressure effect on solubility can be described by the partial molar volume of the solute. They used classical critical theory to show that this pressure is at a maximum at the same point where the partial molar volume of the solute is at a minimum and the isothermal compressibility of the solvent is at a

maximum. Christensen and co-workers (10) studied the excess enthalpy versus composition curves for a number of supercritical binary systems. Using thermodynamic stability considerations, the Gibbs - Konowalow rule and properties of near critical mixtures, they determined that knowledge of the supercritical enthalpy is essential for an understanding of supercritical solubility. Lattice gas models have been used successfully to qualitatively model solubility behavior in SCFs, and with limited success to quantitatively model SCFs (15).

The anomalous transport properties of SCFs have been studied, but to a lesser extent than the solubility behavior (1,11,16,17,26). The gas-like transport properties exhibited by SCFs are favorable for solute extraction in terms of mass transfer characteristics. Using dimensionless numbers, Debenedetti and Reid (16) have shown that under diffusive mass transfer conditions, the relative importance of natural convection to mass transfer is inversely proportional to the square of the kinematic viscosity of the fluid in question. They used this relationship to explain the large gas-like diffusion coefficients which they determined experimentally for some binary supercritical systems. These results led them to conclude that in systems where the controlling resistance to mass transfer is in the supercritical phase, significant rate enhancement can be expected from using SCFs as solvents. Rate enhancement is not

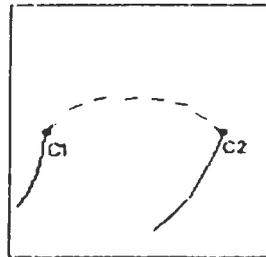
expected when controlling resistance to mass transfer is in a second phase, either solid or liquid. Rice and co-workers (17) presented empirical correlations of mass transfer rates using dimensionless numbers for some solid - SCF and liquid - SCF systems.

Reaction rate enhancement has been demonstrated for reactions taking place in SCFs (26,27). This is usually explained in terms of the transition-state analysis and the known anomalous partial molar volume behavior of solutes solubilized in SCF solvents. Successful modeling of the dynamic behavior of SCF leaching systems has been presented for a CSTR type reactor (17), and for a packed bed type reactor (28).

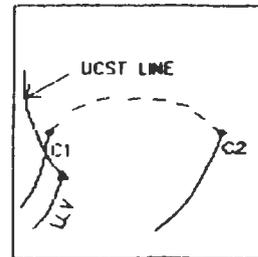
In order to understand fully data obtained from experiments conducted in the near-critical to supercritical region, it is necessary to understand the phase behavior of the SCF system. This behavior can be very complex, even for simple binary systems. Typically, the complex pressure - temperature - composition phase diagrams of binary systems in the critical region are projected onto a pressure-temperature (P-T) surface. The use of these field variables results in a simplification of the data. Resulting P-T diagrams have been classified into five basic types which have been observed experimentally. These five types are shown in Figure 2. (1). Here, critical mixture curves and

three phase lines are shown, and phase boundaries at lower temperatures are omitted. Abbreviations that appear in Figure 2 and in the following discussion of Figure 2 are defined as follows (1):

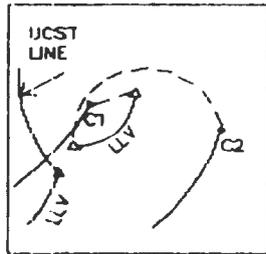
- LCST is the lower critical solution temperature. This is the temperature at which two liquids critically merge to form a single liquid phase as the system temperature is lowered.
- UCST is the upper critical solution temperature. This is the temperature at which two liquids critically merge to form a single liquid phase as the system temperature is raised.
- UCEP is the upper critical end point. This is the point at which the higher temperature branch of the solid - liquid - gas line intersects the critical mixture curve.
- LCEP is the lower critical end point. This is the point where the low temperature branch of the solid - liquid - gas line intersects the critical mixture curve.



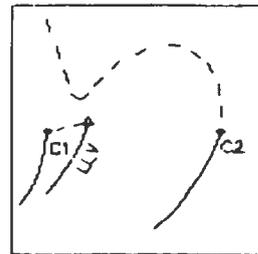
TYPE I



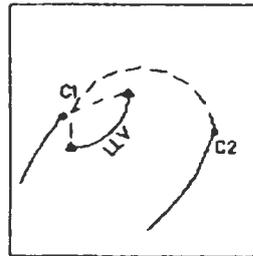
TYPE II



TYPE III



TYPE IV



TYPE V

Figure 2., Five Classes of Binary Phase Diagrams

The simplest binary system is type I. In this system, the two liquids are miscible in all proportions. The critical curve is continuous from the critical point of pure component 1 (the more volatile component) to the critical point of pure component 2.

In type II phase behavior, the liquids are no longer completely miscible in all proportions. A liquid - liquid - vapor (LLV) phase boundary line is shown, and ends at the UCEP. The critical curve is still continuous between the pure component critical points.

Type III phase behavior shows a region of liquid - liquid immiscibility like type II. Here, however, the branch of the critical curve starting at the higher temperature, pure component critical point (C2) intersects the region of liquid - liquid immiscibility at the LCST. The branch of the critical curve starting at the lower temperature pure component critical point (C1) intersects the regions of liquid - liquid immiscibility at an UCEP. Because of the typical proximity of the LLV line to the critical point of the more volatile components, type III systems may be especially amenable to supercritical fluid processing. Separation of reactants from products may be facilitated by operation close to the LLV line in these systems (8).

When the system has lower mutual miscibility, type IV phase behavior is obtained. Here, the critical mixture curve has two branches. The branch starting at the critical point of the less volatile component can either go to lower temperatures and higher pressures as shown, or it can go back and assume a positive slope at high pressures. This branch does not intersect a LLV line as in type III. The branch starting at the critical point of the more volatile component, is similar to that of the type III phase behavior.

When still lower mutual miscibility of components is present, type V phase behavior is obtained. This behavior is similar to type III phase behavior, except that there is no region of liquid immiscibility below the LCST. McHugh and Krukonis (1) have reviewed experimental techniques for determining both phase border curves in supercritical systems, and solubilities in supercritical fluids.

The thermophysical properties of supercritical water have been reviewed extensively (29,30,31). Supercritical water has been shown to be very a dense solvent (29,30), and to demonstrate high levels of miscibility with non-polar fluid partners which are only sparingly soluble in liquid water (30). Diffusion coefficients are very difficult to measure directly at the high pressures and temperatures of supercritical water. They have, however, been estimated

using viscosity data (Einstein-Stokes relation) (29). These results show supercritical water to have almost gas-like diffusion coefficients, and ion mobilities. At high temperatures and very high densities, water approaches a fully ionized fluid (fused salt), which is "non-aqueous" behavior, typical of such non-aqueous liquids as methanol, ammonia, and sulfur dioxide (30). Small additions of soluble salts added as a third component to binary aqueous systems can shift the critical phase boundaries to higher temperatures by 100 degrees centigrade or more (30).

There are little data on the critical phase behavior of binary polar inorganic systems. Until recently, critical phase behavior data on the ammonia - water system (the solvent system used in this study) were very limited. However, in 1985, Rizvi published a thesis (32) which presented a comprehensive phase behavior study of the ammonia - water system. The study included vapor - liquid equilibria over the composition range from pure ammonia to pure water, and over the pressure - temperature range from ambient conditions to the supercritical phase region. Figure 3 shows the ammonia - water critical locus, on a pressure - composition diagram, from pure water to 30 mole percent ammonia, as reproduced from Rizvi's thesis. This locus starts at the critical point of pure water, and passes through the maxima of the two isothermal phase envelopes which are also shown in Figure 3. Thirty mole percent is

the approximate solubility limit of ammonia in water at ambient conditions, making it the practical concentration limit for aqueous ammonia solvents used in the present study.

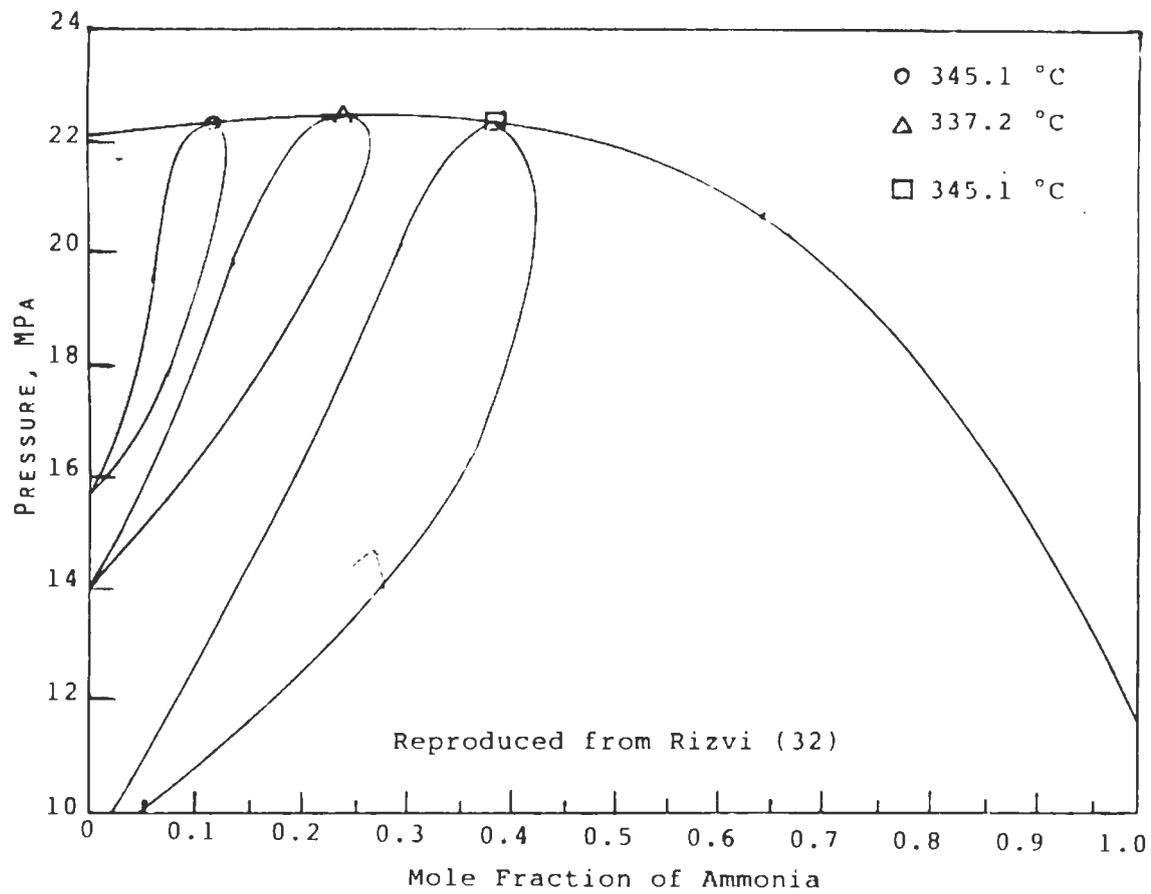


FIGURE 3., HIGH PRESSURE DIAGRAM FOR AMMONIA-WATER

There is no information in the literature on the recovery of cobalt from spent catalyst using ammonia, or any other solvent. The simple cobalt ion is most stable in the bivalent state (33). In most cobalt complexes, including amines, cobalt is most stable in the trivalent form (33). In an aqueous solution of ammonia, the cobaltic ion readily forms the six-coordinate, octahedral hexamminecobalt (III) ion $(\text{Co}[\text{NH}_3]_6)^{3+}$ (34).

Commercially, ammonia is used in a pressure leach process to extract cobalt from high grade nickel concentrate at the Sherrit Gordon Mines, Fort Saskatchewan, Alberta (31). Ammonia leaching takes place at 862 KPa and 150 °F to 220 °F, well below supercritical conditions. The rate of leaching and ultimate extraction of cobalt in this process were both found to increase with increasing temperature and with increasing ammonia concentration. The rate of leaching of cobalt was also found to increase with increasing oxygen partial pressure.

Laboratory studies on the leaching of cobalt from cobalt metal powder by ammonia solutions have been conducted by Han and Vu (35-39). They reported the overall reaction mechanism at near ambient conditions as follows:



Han and Vu proposed that in this reaction, the oxygen atoms are first adsorbed to the catalyst surface at a site containing cobalt metal to form an intermediate $\text{Co}\dots\text{O}$.



The intermediate acts as a cobaltous oxide (CoO) and reacts with ammonium ions to produce a cobaltous ammine complex $\text{Co}(\text{NH}_3)_6^{2+}$.



This cobaltous ammine complex is then oxidized to form a cobaltic hexamine complex.



Mass transfer of the oxygen to the solid - liquid interface was determined to be the rate limiting step. The surface reaction is fast and irreversible. An activation energy of 12.54 Kcal/mole was obtained. This indicates a diffusion controlled mechanism.

III. THEORY

No data are available on the reaction mechanism for the leaching of cobalt from a hydrotreating catalyst by aqueous ammonia solvent at supercritical conditions. It will be assumed in this study that the mechanism is the same as that determined by Han and Vu (Equations (1) through (4)).

In changing from the pure cobalt metal powder, leached by Han and Vu, to the cobalt containing catalyst material leached in this study, we will be introducing more mass transfer resistance to the system. By leaching at the much higher SC temperature, we should be increasing reaction rate and mass transfer coefficients. But, because the activation energy of the reaction is larger than that of the mass transfer, reaction rate coefficient will be enhanced more than the mass transfer coefficient. This being the case, the degree of leaching enhancement gained by using SCF solvent, will depend upon the improved mass transfer of the limiting reactant (oxygen) to the cobalt sites on the surface of the porous catalyst material. To qualitatively show the leaching enhancement expected to be gained by using SCF solvent, a mass balance is taken for differential volume of an idealized spherical catalyst pellet (Figure 4), using the shell balance method (38).

$$4r^2N|_r - 4\pi(r+\Delta r)^2N|_{r+\Delta r} + 4\pi r^2\Delta rkaC = 0 \quad (5)$$

Here $N|_r$ is the molar flux of O_2 in the r direction, at a distance r from the center of the sphere. $N|_{r+\Delta r}$ is the molar flux of O_2 in the r direction at a distance $r+\Delta r$ from the center of the sphere.

k is the reaction rate constant for the reaction of O_2 .

a is the surface area per unit volume of the catalyst material.

C is the concentration of O_2 . The first term in Equation (5) represents the molar rate of transfer of O_2 into the differential volume in the r direction. The second term in Equation (5) represents the molar rate of transfer of O_2 from the differential volume in the r direction. The third term in Equation (5) represents the rate of reaction of O_2 within the differential volume.

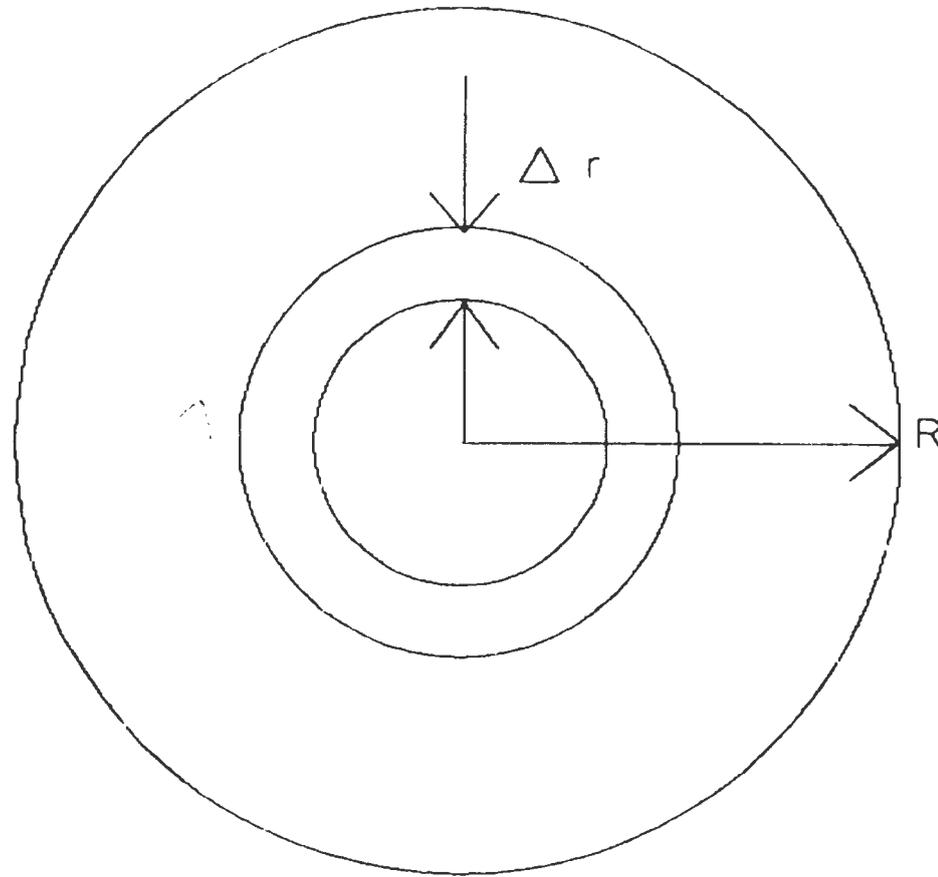


Figure 4., Idealized Spherical Catalyst Pellet

The mass balance assumes that the chemical reaction can be described as being distributed homogeneously throughout the particle, because the catalyst material has a large internal surface area. This assumption accounts for the reaction term appearing in the shell balance, rather than in the boundary conditions. To further simplify this model, the balance assumes that the chemical reaction is pseudo-first order with respect to the limiting reactant (oxygen). This assumption accounts for the form of the reaction term. Dividing Equation (5) by $4\pi r$, and shrinking the differential element to zero gives:

$$-d/dr(r^2N) + r^2kaC = 0 \quad (6)$$

The molar flux of oxygen may be expressed using Fick's law as:

$$N = -D_e dC/dr \quad (7)$$

where D_e is the effective diffusivity of oxygen in the SCF.

Combining Equations (6) and (7) gives the differential equation that describes diffusion of oxygen in the sphere, accompanied by the homogeneous chemical reaction.

$$D_e \frac{1}{r^2} \frac{d}{dr}(r^2 dC/dr) = kaC \quad (8)$$

The boundary conditions for Equation (8) are obtained by first considering the concentration symmetry of the pellet in the r direction:

$$dC/dr = 0 \text{ at } r = 0 \quad (9)$$

and then by specifying the oxygen concentration at the surface of the sphere to be C_s :

$$C = C_s \text{ at } r = R \quad (10)$$

In order to solve Equation (8), the transformation $f(r) = rC$ is introduced. Thus, Equation (8) becomes:

$$d^2f/dr^2 - (ka/D_e f) = 0 \quad (11)$$

The solution for Equation (11) involving a second order, linear, homogeneous, differential equation is:

$$C = K_1/r [\cosh([ka/D_e]^{1/2}r)] + K_2/r [\sinh([ka/D_e]^{1/2}r)] \quad (12)$$

where K_1 and K_2 are constants of integration. Applying the boundary conditions (Equations (9) and (10)), Equation (12) become:

$$\frac{C}{C_s} = \frac{R}{r} \frac{\sinh([ka/D_e]^{1/2}r)}{\sinh([ka/D_e]^{1/2}R)} \quad (13)$$

The extent to which diffusion effects are important can be expressed by the magnitude of a modified Thiele modulus (ϕ), defined for a sphere as (39):

$$\phi = \frac{R}{3} (K_a/D_e)^{1/2} \quad (14)$$

where $R/3$ is the characteristic length of a sphere.

Combining Equations (13) and (14) to express the concentration profile in terms of the Thiele modulus gives:

$$\frac{C}{C_a} = \frac{R \sinh(3\phi r/R)}{r \sinh(3\phi)} \quad (15)$$

Equation (12) shows that as the Thiele modulus increases (increasing diffusional resistance), a concentration profile develops in the pellet since oxygen cannot diffuse in from the bulk fluid sufficiently rapidly, since the reaction rate at any point in a pore is equal to $k_a C$. The effectiveness factor (η) is a parameter that can be used to describe mass transfer and chemical reaction in a porous catalyst (39). The effectiveness factor is defined as the ratio of the rate of reaction with pore diffusion resistance to the rate of reaction with only the surface resistance. For the spherical catalyst pellet this is:

$$\eta = \frac{\int_0^R k_a \frac{4}{R} \pi r^2 C(r) dr}{k_a C_a \int_0^R 4 \pi r^2 dr} \quad (16)$$

Evaluating the integral, we obtain:

$$\eta = 1/3\phi^2(3\phi \coth[3\phi] - 1) \quad (17)$$

Aris (40) presented η versus ϕ data for various catalyst geometries and found that these curves could be practically superimposed. For all the geometries studied (slab, cylinder, and sphere), η tended to 1.0 as ϕ tended to zero. Recalling the definition of ϕ (Equation 11), the relation between diffusivity and the effectiveness factor can be defined by:

$$\phi = \frac{R}{3} \frac{ka}{De} \quad (11)$$

As the diffusivity values becomes very large, which would be expected in SCFs, ϕ tends to zero, and η tends to 1.0. As η tends to 1.0, the chemical reaction becomes the rate limiting step, which increases the overall rate. Increasing the overall rate will lead to improved cobalt extractions at given leaching flow rate conditions.

Cobalt extractions were determined in this study by analyzing leached catalyst material after each experiment for residual cobalt content. The amount of residual cobalt in the catalyst material was then compared to the amount of cobalt present in samples of the catalyst material before leaching to determine the extent of reaction. The extent of

reaction is defined as:

$$e = 1 - \frac{\text{wt. \% residual Co in leached catalyst}}{\text{wt. \% Co in non-leached catalyst}} \quad (18)$$

Assuming mass transfer of oxygen to the solid fluid interface to be the rate limiting step, the dissolution of cobalt by supercritical aqueous ammonia should be more effective than dissolution by liquid aqueous ammonia. The much higher diffusivities associated with supercritical fluids should produce a correspondingly small diffusional resistance (small ϕ), and therefore a chemical reaction rate limiting step ($n \rightarrow 1.0$).

In the present study, cobalt extraction from a catalyst material using supercritical aqueous ammonia solvent was compared to cobalt extraction using similar experimental parameters with subcritical aqueous ammonia solvent to determine the extent of leaching enhancement gained by leaching at supercritical conditions.

IV. EXPERIMENTAL

A. Experimental Apparatus

The apparatus used in this study was designed to measure the extent of reaction attained in catalyst material - solvent systems, under conditions ranging from ambient to supercritical. The apparatus consisted of three main components: a solvent delivery unit, an extraction and sampling unit, and a pressure and temperature control unit. A schematic diagram of the experimental apparatus is shown in Figure 5. A detailed description of each system follows. Except as otherwise noted, the material of construction for all tubing and wetted parts of the apparatus is 316 stainless steel. The maximum pressure rating of the tubing and fittings used was 79.3×10^2 KPa, except as otherwise noted.

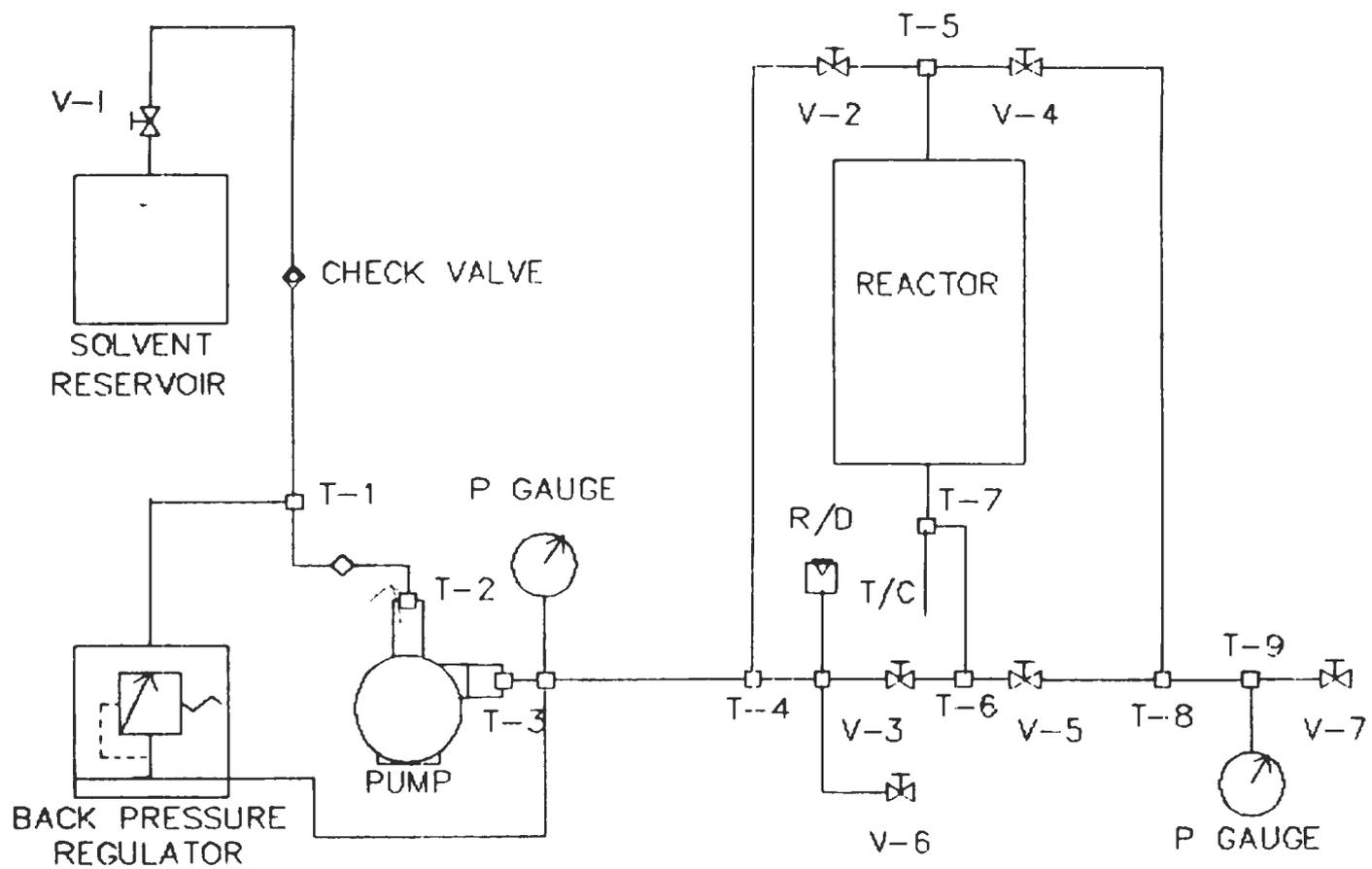


Figure 5., Experimental Apparatus

1. Solvent Delivery Unit

Solvent to be used in each experiment was stored, at room temperature, in a pressurized autoclave (Autoclave Engineers, Inc. Model #83-07200-00). The autoclave was a bottle closure type vessel and was pressurized with bottled nitrogen fed through an opening in the top of the vessel. The vessel was fitted internally with a glass sleeve, giving it a solvent capacity of approximately 600 ml. The vessel was connected by tubing (0.062" x O.D. x 0.031" I.D.) to a shut off valve (V-1). Valve (V-1) was connected by tubing (0.025" O.D. x 0.125" I.D.) to an O-ring check valve (Autoclave Engineers, Inc. Part #SWO 04400). The check valve consisted of a gland (constructed of type 17-4 PH stainless steel), a spring (type 18-8 stainless steel) and an o-ring (Viton). The check valve was connected to a tee (T-1), which was connected to a filter (Autoclave Engineers, Inc. Part #SLF 440), both by tubing (0.025" O.D. x 0.125" I.D.). The filter was a dual-disk line filter, with upstream and downstream filter element sizes of 5 and 10 microns, respectively. The filter was connected by tubing (0.250" O.D. x 0.125" I.D.) to a tee (T-2) which was connected by two lengths of tubing (0.125" O.D. x 0.062" I.D.) to the two inlet ports of a high pressure liquid pump.

The pump (Milton Roy, Part #2396-89) was a reciprocating plunger, positive displacement type pump, with two pump bodies mounted on either side of the drive motor. Pump flow

rate was controlled by adjusting manual micrometer dials which regulated the stroke length of the pump. Pump flow rate capacity was 460ml per hour. Table 2 lists the materials of construction of the wetted pump parts.

The pump was connected by two lengths of tubing (0.062" O.D. x 0.031" I.D.) to a tee, (T-3) which was connected by tubing (0.250" O.D. x 0.125" I.D.) to a cross. The cross was connected by three lengths of tubing (0.250" O.D. x 0.125" I.D.), one each to a back pressure regulator, a pressure gauge, and a tee (T-4).

The back pressure regulator (Tescom Series 26-1700) was a manually adjusted, spring loaded, piston sensing regulator. The materials of construction of this regulator are listed in Table 3. When the system pressure exceeded the regulator set point the regulator would bleed solvent from the cross downstream of the pump to the tee upstream of the pump (T-1), via tubing (0.250" O.D. x 0.125" I.D.).

Table 2. - Wetted Surfaces Material

<u>Component</u>	<u>Materials</u>
Pressure Regulator	316 Stainless Steel
Pressure Regulator	Kel-F
Pressure Regulator	Teflon
Pressure Regulator	Buna N
Pump	316 Stainless Steel
Pump	Single Crystal Sapphire
Pump	Single Crystal Ruby
Pump	Teflon (FEP)
Pump	Carbon Graphite - filled Teflon (PTFE)
Pump	Rulon (proprietary filled Teflon)
Pump	Hastelloy C
Pump	Ceramic

2. Extraction and Sampling Unit

Tee (T-4) was connected by two lengths of tubing (0.250" O.D. x 0.125" I.D.), one each to a valve (V-2) and to a cross.

Valve (V-2) was a shut off valve used to deliver solvent to the top of the extraction vessel, and was connected to a tee (T-5) which was in turn connected to the top of the extraction vessel by tubing (0.250" O.D. x 0.125" I.D.), and to a valve (V-4).

The cross connected to tee (T-3) was also connected by three lengths of tubing (0.250" O.D. x 0.125" I.D.), one each, to a valve (V-6), a rupture disk assembly, and a second valve (V-3). Valve (V-6) was a shut-off valve used to bleed gas from the system before each experiment. The rupture disk assembly was a safety feature installed in case of excessive system pressure surges. The assembly (Autoclave Engineers, Inc. Part #SS-4600-1A) features a non-rotating double-cone plug, with an angled rupture disk (Autoclave Engineers, Inc. Part #P-734) constructed of Inconel. The disk has a nominal rupture pressure rating of 10,000 psi. Valve (V-3) was shut-off valve used to deliver solvent to the bottom of the extraction vessel and was connected to a tee (T-6) which was in turn connected to the bottom of the extraction vessel and to a valve (V-5) by tubing (0.250" O.D. x 0.125" I.D.).

The extraction vessel (Autoclave Engineers, Inc. Part #CNLX16012) was a vertically mounted, coned and threaded length of tubing connected directly to a collar and gland on both ends. Connected directly to each of the two glands was a reducer coupling, which in turn were connected directly to male/female adapters. The adapter on the top end of the extraction vessel was connected to the tee (T-5) by tubing (0.250" O.D. x 0.125" I.D.) which led to the top inlet and outlet valves (V-2 and V-4, respectively). The adapter on the bottom of the extraction vessel was connected by tubing (0.250" O.D. x 0.125" I.D.) to a tee (T-7). Tee (T-7) was connected by tubing (0.250" O.D. x 0.125" I.D.) to tee (T-6), and was also connected directly to a thermocouple assembly. Tee (T-6) was connected to the bottom inlet and outlet valves (V-3 and V-5, respectively). Stainless steel screens (60 mesh) were placed inside both the top and bottom couplings to hold the catalyst material inside the extraction vessel during experiments. Extraction vessel assembly had a maximum pressure rating of 20,000 psi.

Top and bottom exit valves (V-4 and V-5, respectively) were each connected by tubing (0.250" O.D. x 0.125" I.D.) to the same tee (T-8). Tee (T-8) was in turn connected by tubing (0.250" O.D. x 0.125" I.D.) to another Tee (T-9). The tee (T-9) was connected by two lengths of tubing (0.250" O.D. x 0.125" I.D.), one each to a pressure gauge and a shut off valve (V-7).

Valve (V-7) was used to take samples of the pregnant leaching solution, and to control the flow rate of solution from the system.

3. Pressure and Temperature Control Unit

The pressure of the solvent in the autoclave reservoir was maintained by the pressure of the bottled nitrogen which was fed to the autoclave. Nitrogen pressure was controlled by a regulator on the nitrogen bottle. The autoclave pressure was maintained at approximately 690 KPa during the experiments. This was sufficient pressure to deliver the solvent past the check valve to the pump.

The pump was used to adjust the system pressure to the desired reaction pressure, and to maintain the desired system pressure and solvent flow rate. System pressure was measured by the two pressure gauges, one each upstream and downstream from the extraction vessel. System pressure was controlled by the back pressure regulator, as described previously in the "Solvent Delivery Unit" section. The rupture disk, also previously described, was vented to a hood.

The solvents and catalyst material were heated to the desired reaction conditions inside the extraction vessel, using two ceramic band resistance type heating mantles. The mantles were mounted around the length of tubing that was

the body of the extraction vessel. Power to these heating mantles determined the temperature of the mantles, and thereby the temperature of the extraction vessel. The temperature was controlled by a percentage type temperature controller. The controller provided a manually adjustable control of the average heating mantle power by varying the proportion of on and off time of the heating mantles. The system temperature was measured by a type J thermocouple inserted into the bottom of the extraction vessel. The thermocouple was surrounded by a sheath (constructed of 304 stainless steel), and was secured in the bottom of the extraction vessel by the gland and sleeve which were connected to the tee (T-7) at the bottom of the extraction vessel.

B. Experimental Procedure

The effects on cobalt extraction caused by variations in solvent composition, pressure and temperature were investigated in this study. Four series of experiments were conducted in order to determine the enhancement gained by leaching cobalt from a hydrotreating catalyst material at supercritical conditions. Each series consisted of experiments conducted at a particular pressure - temperature condition, while varying leaching solution composition from experiment to experiment. Pressure - temperature conditions of the four series of experiments were as follows: super-

critical phase, ambient temperature - low pressure, ambient temperature - supercritical pressure and elevated temperature supercritical pressure. Five grams of catalyst material was leached with 600 ml of aqueous ammonia solvent during each of the experiments.

Supercritical phase leaching experiments were carried out first, as these experiments dictated the dynamic experimental parameters used during the other three series of experiments. During supercritical phase leaching experiments, the system was initially pressurized to a pressure that was greater than the critical pressure for the solvent composition being used. This took approximately 30 seconds, during which time no leaching solution was allowed to exit the system. The extraction vessel was then heated isobarically to supercritical conditions. Time required for this isobaric heating varied between experiments from 30 to 51 minutes, during which time the pressure would fluctuate by as much as 3.45×10^3 KPa. Leaching solution exit flow rate during this phase of the experiment differed between experiments from 1.18 to 3.33 ml/min. The system was maintained at supercritical conditions until the leaching solution supply was exhausted. Time of and solvent flow rates during this phase of the experiments varied between experiments from 5 to 17 minutes and from 4.67 to 6.00 ml/min, respectively.

Ambient temperature - low pressure leaching experiments were conducted at room temperature and at the minimum pressure required to deliver the solvent past the check valve. This was 690 to 1,379 KPa. During these experiments, neither the heating elements nor the pump were used. Experimental flow rates and times that best approximated those used during the corresponding supercritical phase experiments were used. Flow rates through the apparatus were maintained by the pressurization of the fluid reservoir (autoclave).

Ambient temperature - supercritical pressure leaching experiments were conducted at room temperature and at pressures greater than the critical pressure of the solvent being used. Initially the system was pressurized in the same manner as in the supercritical phase experiments. Heating elements were not used during these experiments. While the system pressure was maintained, the solvent was allowed to exit the system at flow rates and for times which best approximated those used during the corresponding supercritical phase experiments.

High temperature - supercritical pressure leaching experiments were run at reduced temperature (T_r) of approximately 0.75, and at a pressure greater than the critical pressure, for the solvent composition used. Solvent flow rates and experimental times were adjusted to

best approximate those used during the corresponding supercritical phase experiments.

The detailed operating procedure was as follows:

1. The extraction vessel was removed from the apparatus and disassembled at the top gland - reducer coupling connection. A 5 gram charge of catalyst was placed into the extraction vessel, supported on the bottom screen. The extraction vessel was reassembled and replaced into the apparatus, with the bottom tee reconnected to the tubing and the top adapter still disconnected from the tubing.

2. The fluid reservoir (autoclave) was filled with solvent and was pressurized to 1,034 KPa with bottled nitrogen. Valve V-1 was opened, allowing solvent to flow through the pump, and to valves V-2 and V-3, which were closed. Gases were then bled from the system by slowly opening valve V-6 and allowing solvent to flow from the system until no more gases were observed in the solution. At this time, V-6 was closed. This procedure required approximately 50 ml of solvent.

3. The extraction vessel was filled with solvent by slowly opening valve V-3, and leaving it partially open until solvent was observed at the extraction vessel top adapter. This adapter was still disconnected from the

tubing. Valve V-3 was then closed. Valve V-2 was slowly opened and remained open until solvent was observed at the disconnected tubing connection. Valve V-2 was then closed. Tubing then reconnected to the extraction vessel top adapter.

4. To facilitate a top down flow scheme through the extraction vessel, valves V-2 and V-5 were opened while V-3 and V-4 remained closed. Any remaining gases were bled from the system by slowly opening the sampling valve (V-7) until no more gases were observed in the solvent. Valve V-7 was then closed.

5. The unit was then pumped to the desired reaction pressure, with the exception of the ambient temperature - low pressure experiments. Desired pressure for this series of experiments was attained when the system was charged with solvent. During the other experiments, the pump was operated at 90 percent of its rated flow capacity of 7 ml/hr. Throughout the experiments, the system pressure was automatically controlled by the back pressure regulator. The regulator was set at the desired pressure when the system was being pressurized initially.

6. Exit flow rate from the system determined the flow rate through the extraction vessel and was controlled by manipulating valve V-7. Solvent flow was maintained at a

nearly constant rate by adjusting valve V-7. Flow rate was maintained at a low rate during this portion of the experiment (including heating, Step 7) so that the solvent could be conserved for use after the system was at the desired reaction conditions.

7. The extraction vessel was heated to the desired reaction conditions, with the exception of the ambient temperature experiments. The vessel was heated by supplying power to the heating elements from the variac temperature controller. During the experiments, the controller was adjusted so as to incrementally increase the amount of power supplied to the heating elements until the desired extraction vessel temperature was reached.

8. Once the desired reaction temperature was reached, the exit flow rate was increased by further opening valve V-7. During the supercritical experiments, the flow rate was increased by as much as was possible without significantly changing the system pressure and temperature. These conditions were maintained until the solvent supply was exhausted.

9. The pump and temperature controller were turned off. The system was depressurized by slowly venting gas through valve V-7. The system was allowed to cool for about 1 hour. The extraction vessel was removed and disassembled.

Catalyst material was recovered from the extraction vessel for cobalt analysis. The wetted surfaces of the experimental system were rinsed by charging distilled, deionized water through the apparatus. Water samples were taken to be analyzed for residual cobalt.

C. Cobalt Analysis

The cobalt catalyst material used in this study was a hydrotreating catalyst containing both cobalt and molybdenum. The chemical composition and physical properties of the catalyst material are provided in Table 3.

Table 3. - Chemical Composition and Physical Properties of Cobalt Hydrotreating Catalyst Material

<u>Chemical Composition</u>	
CoO	4.0-6.0 weight pct.
MoO ₃	19.0-21.0 weight pct.
Al ₂ O ₃	73.0-78.0 weight pct.
Na	<0.05 weight pct.
Other Heavy Metals	<0.20 weight pct.
<u>Physical Properties</u>	
1/8 Extrusions	
Bulk Density, lb/ft ³	47-53
Surface Area, m ² /g	150-200
Pore Volume, cm ³ /g	0.45-0.55

The amount of cobalt leached from the hydrotreating catalyst was determined by analyzing the catalyst material for cobalt after the leaching experiments and comparing these results to the analytical results on the non-leached catalyst. The analysis for cobalt was carried out as follows:

1. The catalyst material was ground to minus 60 mesh and dried.
2. Approximately 0.25 grams of the catalyst was weighed and placed into a porcelain crucible.
3. Approximately 5 grams of potassium pyrosulfate were added to the crucible, and mixed with the catalyst sample.
4. The mixture was then fused over an open flame until a clear melt was produced.
5. The melt was allowed to cool, and then transferred to a beaker containing distilled, deionized water. The beaker was heated until the melt dissolved in the water.
6. Five grams of sodium fluoride was added to the solution to mask alumina, calcium, iron, and magnesium. This prevented them from interfering with the subsequent titration.
7. Solution pH was adjusted to between 9.0 and 10.0 by adding 15 mole percent solution of ammonium hydroxide.

8. Murexide indicator was added to the solution. The solution was titrated with ethylenediaminetetraacetic acid (EDTA) until the color of the solution changed from yellow to a violet end point.

D. Platinum Group Metals Analyses

The amount of platinum leached from the spent automotive catalysts and from the platinum wire was determined by analyzing the solvent taken from the sample valve (V-7) during the experiments. These solvents were analyzed for platinum with a Perkin Elmer, Model #2380 atomic absorption spectrophotometer, using a hollow cathode platinum lamp at a wavelength of 265.9nm. The amount of palladium leached was determined in similar manner, using a hollow cathode palladium lamp at a wavelength of 244.8nm.

V. RESULTS

A. Cobalt Hydrotreating Catalyst

The experimental system as described was capable of attaining supercritical conditions, using the procedures detailed in the Experimental section. There were no optical means available for determining the presence of the supercritical phase in the reactor. However, during the supercritical phase condition experiments, there were very rapid increases of 1,000 to 1,500 psi in the system pressure as critical temperatures were approached isobarically at supercritical pressures. Pressure increases as the liquid - supercritical phase transition was approached were expected due to the much lower density of the supercritical phase. Critical temperatures and pressures for the binary ammonia water system, at the various concentrations used in this study, are given in Table 4. Data from cobalt analyses of leached and non-leached catalyst material samples are provided in Table 5.

Table 4. - Ammonia-Water Critical Conditions

<u>Composition</u> <u>mole % NH₃</u>	<u>Critical Temperature</u> <u>C</u>	<u>Critical Pressure</u> <u>KPa x 10⁻³</u>
0	374	22.07
5	361	22.18
10	350	22.18
15	345	22.37
20	340	22.48
25	335	22.50
30	325	22.48

Table 5. - Cobalt Analysis Data,
Hydrotreating Catalyst Material

Experiment Number	Catalyst Weight, grams	EDTA Solution Volume, ml	Cobalt Content, weight percent
S-1	0.2560	5.90	2.72
S-2	0.2539	6.40	2.97
S-19	0.2499	6.20	2.92
S-3	0.2559	6.25	2.89
S-4	0.2528	4.20	1.95
S-5	0.2492	4.20	1.98
S-20	0.2506	5.35	2.51
S-6	0.2507	4.00	1.88
S-7	0.2556	3.95	1.82
S-8	0.2542	3.50	1.62
S-21	0.2589	4.45	2.02
S-9	0.2504	3.65	1.73
S-18	0.2528	3.65	1.70
S-17	0.2561	3.50	1.61
S-22	0.2511	3.70	1.74
S-10	0.2488	3.10	1.48
S-16	0.2539	3.90	1.80
S-15	0.2531	3.40	1.59
S-23	0.2526	3.75	1.74
S-11	0.2613	2.95	1.33
S-14	0.2511	2.90	1.36
S-13	0.2539	3.10	1.45
S-24	0.2544	3.50	1.62
S-12	0.2516	1.55	1.30
Non-Leached Catalyst	0.2518	6.25	2.92
Non-leached Catalyst	0.2663	6.45	2.85
Non-leached Catalyst	0.2602	4.90	2.22

The extent of reaction for the extraction of cobalt from hydrotreating catalyst material at the various aqueous ammonia solvent compositions tested are given for the four reactions conditions in tested Table 6. The supercritical phase (super critical pressure - supercritical temperature) experiments had, in general, the highest extent of reaction. They were followed in order of decreasing extent of reaction

generally by the supercritical pressure - low temperature experiments, low pressure - low temperature experiments and the supercritical pressure - elevated temperature experiments.

Table 6. - Extent of Reaction, Cobalt Extraction from Hydrotreating Catalyst Material

Solvent Composition mole % NH ₃	Extent of Reaction (e), percent			
	Low	S.C.	S.C.	S.C.
	Pressure Low Temp.	Pressure Low Temp.	Pressure Elvtd. Temp.	Pressure S.C. Temp.
5	0	0	0	0
10	26.7	25.6	5.6	29.3
15	31.6	39.1	24.1	35.0
20	36.1	39.5	35.0	44.3
25	32.3	40.2	35.0	50.0
30	48.9	45.3	39.1	51.1

Extent of reaction results, grouped according to the desired reaction conditions, are presented in Tables 7 through 10, and shown graphically in Figures 6 through 9.

Table 7. - Extent of Reaction (e) at Low Pressure Low Temperature Conditions

Experiment No.	Solvent		Pressure - KPa x 10 ⁻³ (Pr)	e (%)
	Composition mole % NH ₃	Temperature C (Tr)		
S-1	5	21(0.46)	1.38(0.062)	0
S-4	10	21(0.47)	1.24(0.056)	26.7
S-7	15	23(0.48)	1.03(0.061)	31.6
S-18	20	21(0.48)	1.38(0.061)	36.1
S-16	25	23(0.48)	1.03(0.046)	32.3
S-14	30	24(0.50)	0.69(0.031)	48.9

Table 8. - Extent of Reaction (e) at Supercritical Pressure-Low Temperature Conditions

Solvent				
Experiment No.	Composition mole % NH ₃	Temperature C (Tr)	Pressure KPa x 10 ⁻³ (Pr)	e (%)
S-2	5	21(0.46)	22.41(1.01)	0
S-5	10	22(0.47)	22.41(1.01)	25.6
S-8	15	20(0.47)	22.41(1.03)	39.1
S-17	20	21(0.48)	23.44(1.04)	39.5
S-15	25	26(0.49)	24.13(1.07)	40.2
S-13	30	23(0.49)	25.51(1.13)	45.3

Table 9. - Extent of Reaction (e) at Supercritical Pressure - Elevated Temperature Conditions

Solvent				
Experiment No.	Composition mole % NH ₃	Temperature C (Tr)	Pressure KPa x 10 ⁻³ (Pr)	e (%)
S-19	5	210(0.76)	24.13(1.09)	0
S-20	10	200(0.76)	24.13(1.09)	5.6
S-21	15	192(0.75)	25.86(1.16)	24.1
S-22	20	195(0.76)	24.82(1.10)	35.0
S-23	25	192(0.76)	24.82(1.10)	35.0
S-24	30	188(0.77)	24.13(1.07)	39.1

Table 10. - Extent of Reaction (e) at Supercritical Pressure - Supercritical Temperature Conditions

Solvent				
Experiment No.	Composition mole % NH ₃	Temperature C (Tr)	Pressure KPa x 10 ⁻³ (Pr)	e (%)
S-3	5	373(1.02)	22.75(1.03)	0
S-6	10	361(1.02)	23.10(1.04)	29.5
S-9	15	364(1.03)	24.59(1.10)	35.0
S-10	20	370(1.05)	22.93(1.02)	44.3
S-11	25	360(1.04)	24.24(1.08)	50.0
S-12	30	334(1.02)	24.18(1.07)	51.1

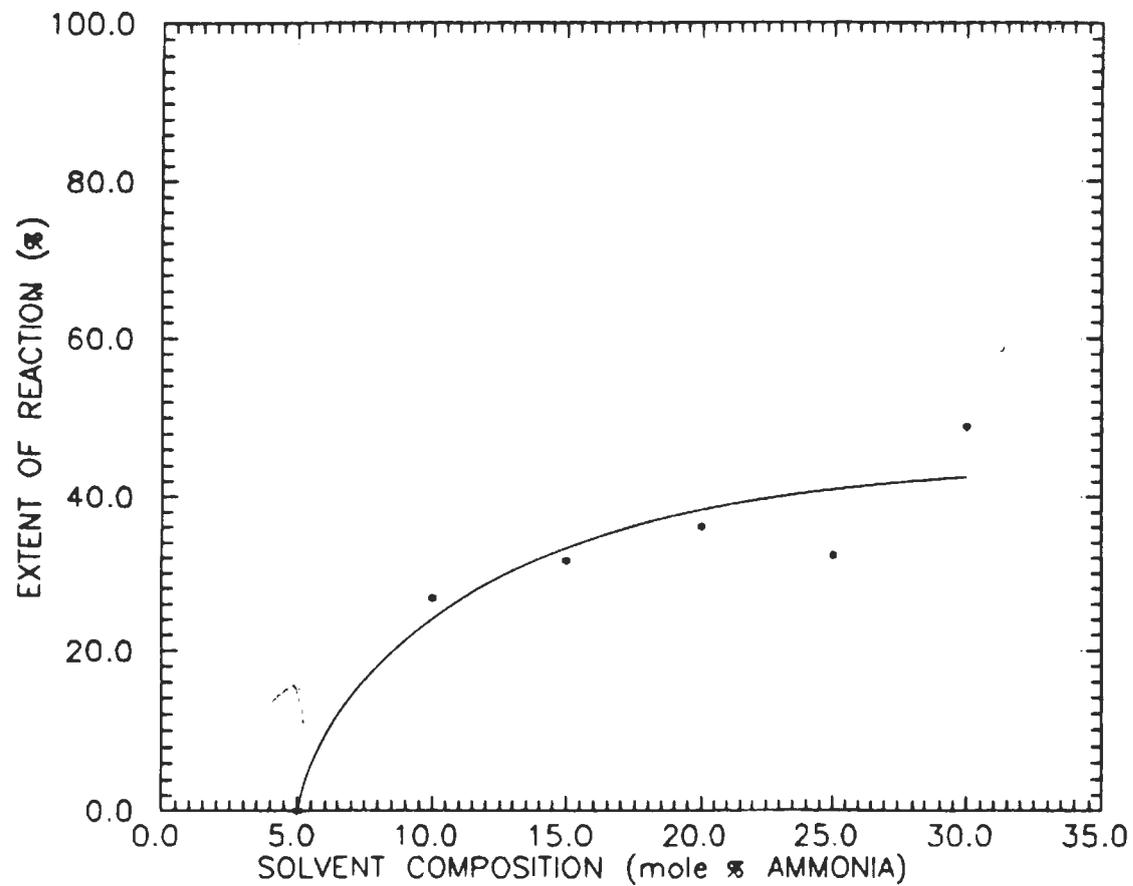


FIGURE 6., COBALT EXTRACTION AT LOW PRESSURE -
LOW TEMPERATURE CONDITIONS

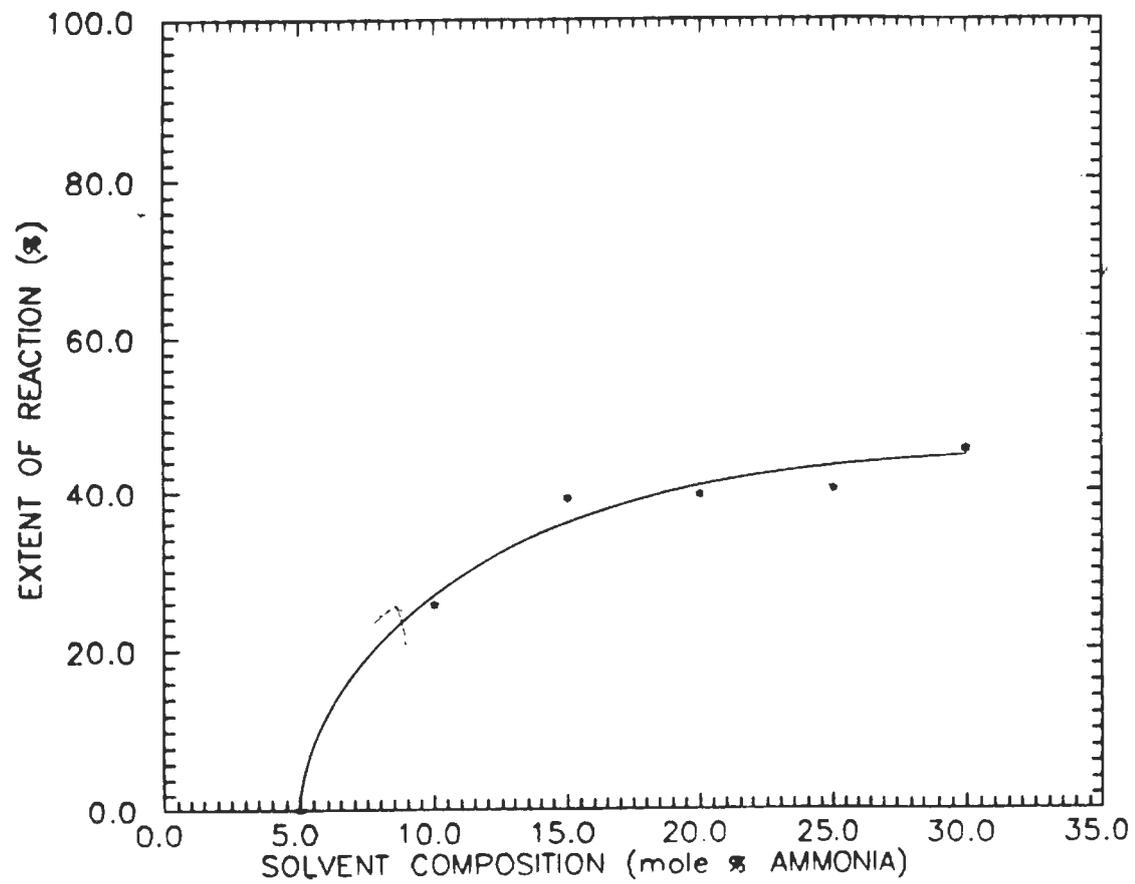


FIGURE 7., COBALT EXTRACTION AT SUPERCRITICAL PRESSURE -
LOW TEMPERATURE CONDITIONS

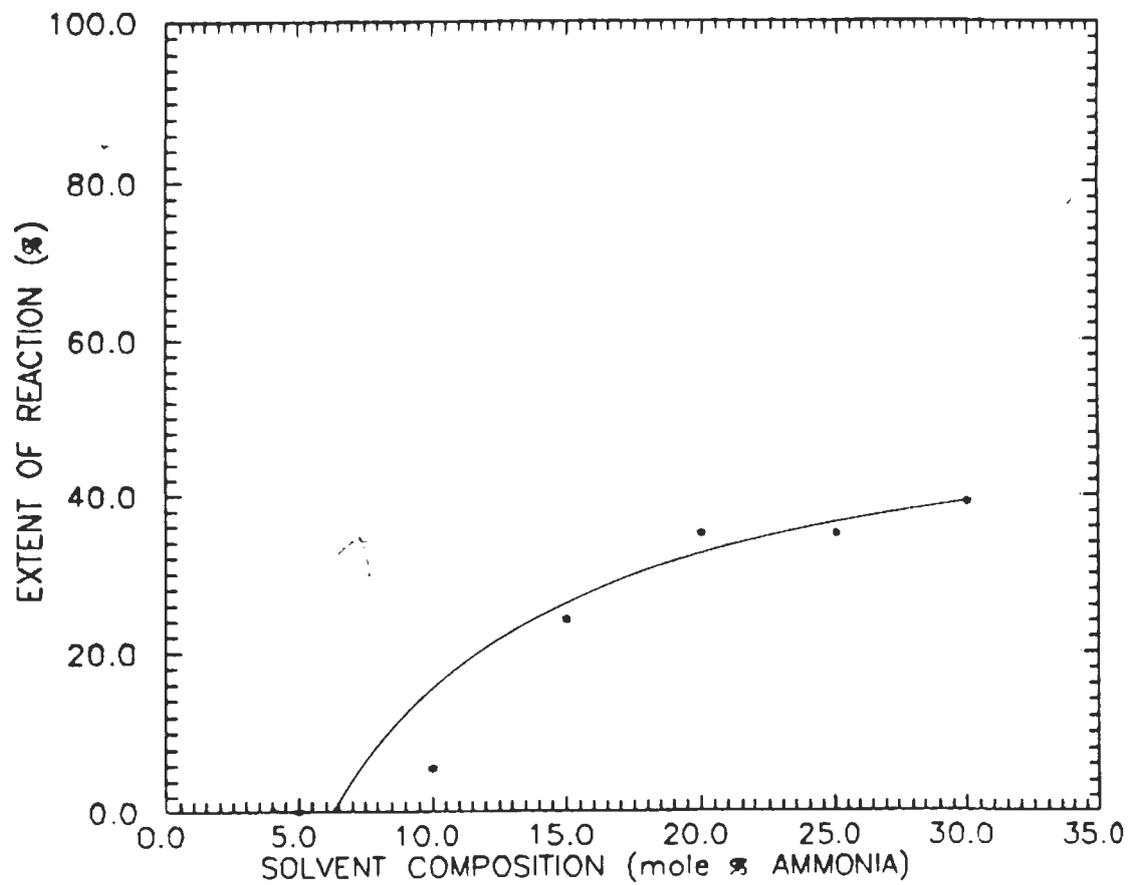


FIGURE 8., COBALT EXTRACTION AT SUPERCRITICAL PRESSURE - ELEVATED TEMPERATURE CONDITIONS

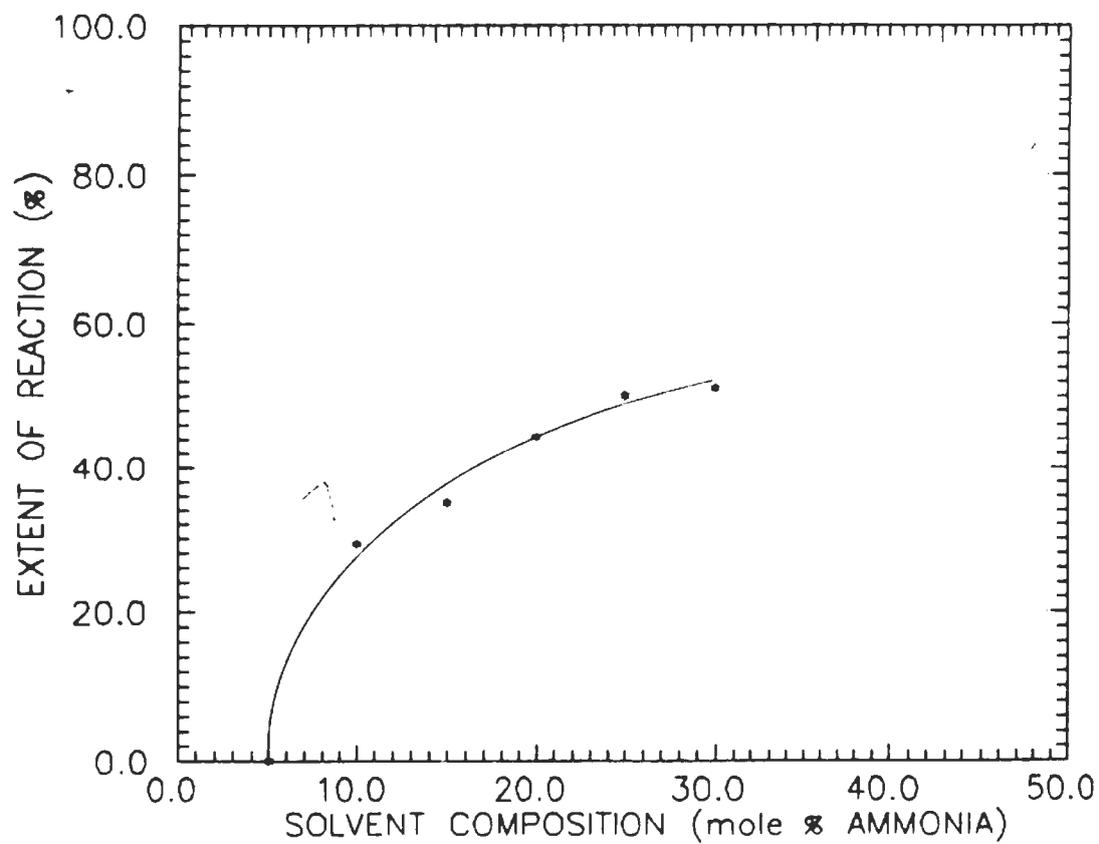


FIGURE 9., COBALT EXTRACTION AT SUPERCRITICAL PRESSURE - SUPERCRITICAL TEMPERATURE CONDITIONS

Extent of reaction (e), for various solvent ammonia concentrations, at low temperature - low pressure conditions is shown in Table 7. Reaction conditions that were attained are given as both actual temperature and pressure, and reduced temperature and pressure (T_r , P_r). Extent of reaction (e) results is shown graphically in Figure 6. Results show that the catalyst material was leachable with aqueous ammonia solvent at the low temperature - low pressure conditions tested. Extent of reaction ranged from 0 to 48.9 percent. The general trend of the data is shown in Figure 6 by a hand drawn curve.

Extent of reaction results (e), for various solvent ammonia concentrations, at supercritical pressure - low temperature conditions are shown in Table 8. Results are shown graphically in Figure 7. Results show that the catalyst material was leachable with aqueous ammonia at the supercritical pressure - low temperature conditions tested. Extent of reaction (e) ranged from 0 to 45.3 percent. The trend of the data is shown by the hand drawn curve in Figure 7.

Extent of reaction results (e), for various solvent ammonia concentrations, at supercritical pressure - elevated temperature conditions are shown in Table 9. Extent of reaction (e) results are shown graphically in Figure 8. Results show that the catalyst material was leachable with

aqueous ammonia at the supercritical - pressure - elevated temperature conditions tested. Extent of reaction (e) ranged from 0 to 39.1 percent. The general trend of the data is shown by the hand drawn curve in Figure 8.

Extent of reaction (e), for various solvent ammonia concentrations, at supercritical pressure - supercritical temperature conditions are shown in Table 10. Extent of reaction results are shown graphically in Figure 9. Results show that the catalyst material was leachable with aqueous ammonia at the supercritical -conditions tested. Extent of reaction (e) ranged from 0 to 51.1 percent. The trend of the data is shown by the hand drawn curve in Figure 9.

Extent of reaction for all four reaction conditions (presented in Table 4) are shown graphically in Figure 10 for comparison.

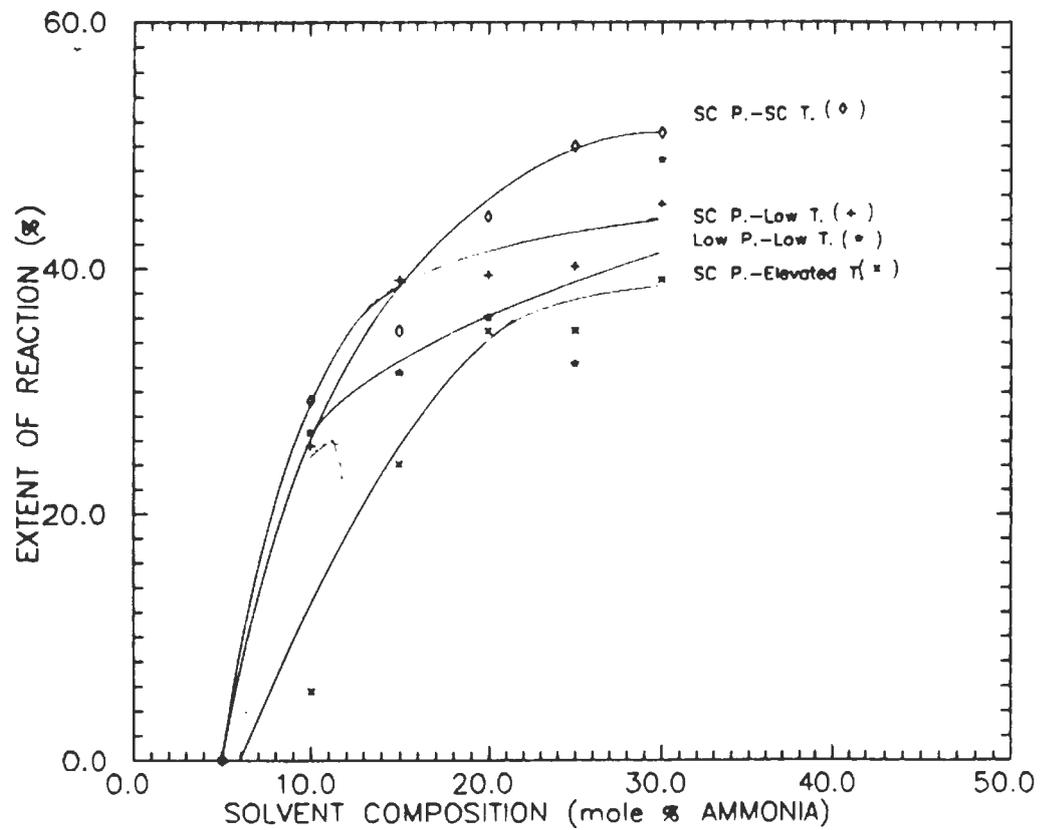


FIGURE 10., COBALT EXTRACTION VERSUS AMMONIA CONCENTRATION

The supercritical pressure - supercritical temperature experiments had, in general, the highest extent of reaction. They were followed generally in order of decreasing extent of reaction, by the supercritical pressure - low temperature experiments, low pressure - low temperature experiments and the supercritical pressure elevated temperature experiments.

In all four series of experiments, there was no significant leaching of cobalt at the 5 mole percent ammonia solvent composition. A possible explanation for this is that leaching of cobalt was taking place, but to an extent that was negligible in comparison to experimental errors. A more likely explanation is the available ammonia in the solvent reacted with other constituents of the catalyst material, particularly molybdenum. Molybdenum is present in the catalyst material in concentrations approximately 3.4 times that of cobalt. However, assuming the catalyst material was exposed to the amount of solvent delivered to the system during experiments, ammonia available, even at 5 mole percent ammonia solvent composition, would be sufficient for an excess of ammonia to be available to react with both cobalt and molybdenum. Cobalt leaching was significantly enhanced during the supercritical pressure - supercritical temperature experiments at solvent compositions greater than 5 percent ammonia. The one exception to the supercritical enhancement was at the 15 mole percent ammonia solvent composition. Here, the extent of reaction

was 35.0 percent at supercritical conditions, and 39.1 at supercritical pressure - low temperature conditions.

The average increase in (e) from the supercritical pressure - low temperature experiments to the supercritical pressure - supercritical temperature experiments (with the exception of the 5 mole percent and NH_3 experiments) was 4.0 percent. Average increase in (e) from the low pressure - low temperature experiments to the supercritical pressure - supercritical temperature experiments (with the exception of the 5 mole percent NH_3 experiments), was 6.8 percent. Average increase in (e) from the supercritical pressure - elevated temperature experiments to the supercritical pressure - supercritical temperature experiments (with the exception of the 5 mole percent NH_3 experiments), was 14.2 percent.

Extent of reaction (e) results from the supercritical pressure - low temperature experiments was generally slightly higher than those for the low pressure - low temperature experiments. However, the differences were small.

The supercritical pressure - elevated temperature extent of reaction (e) results were significantly lower than those from the other three reaction conditions. This could be caused by a lower rate of adsorption of oxygen onto the

catalyst surface at increased temperatures. The oxygen molecules may also desorb from the catalyst surface at an accelerated rate as the system temperature is increased. Either one, or a combination of both of these effects, would lower the probability of an oxygen - cobalt reaction on the surface of the catalyst.

The enhancement of cobalt extraction at supercritical conditions appears to be the result of the enhanced transport properties of supercritical solvents. The gas-like diffusion coefficients shown by SCFs lowers diffusional resistance to mass transfer, causing the effectiveness factor to tend to 1.0. Enhancement of cobalt extraction gained by pressure or temperature effects not associated with critical phenomena would have been observed in results from experiments conducted at subcritical phase conditions. Although increase in extent of reaction were observed during supercritical pressure - low temperature experiments, the lowest (η) values were almost always obtained from the supercritical pressure - elevated temperature experiments, even though temperature and pressure conditions for these 2 series of experiments were most nearly the same. This indicates that the enhancement is the result of the critical phenomena, most likely the mass transfer enhancement discussed in preceding sections.

B. Error Analysis

The main errors encountered during these experiments were caused by the difficulties in maintaining constant dynamic experimental parameters (flow rates and leach time) for the supercritical experiments at various solvent compositions. However, the main purpose of the experiments was to determine enhancement of leaching at supercritical conditions over subcritical conditions at various solvent compositions. Dynamic parameters of subcritical experiments were closely matched to parameters from the corresponding supercritical experiments. The main source of error was therefore introduced in the analytical procedures. This error is estimated as follows: Extent of reaction (e) was defined by equation (18). We first consider the term in the numerator of the right hand side of equation (18). The potential error in the residual Co content of the leached catalyst material is found by considering the equation used for calculating this content.

$$C_o = \frac{(1.179 \times 10^{-3} \text{ gCo/ml EDTA})(\text{ml EDTA})100}{\text{sample weight (g)}} \quad (19)$$

An equation for the approximate potential error in this equation can be written as:

$$\Delta C = \frac{\delta C}{\delta V} \Delta V + \frac{\delta C}{\delta W} \Delta W \quad (20)$$

where C = cobalt concentration (percent), V = volume titrate (ml EDTA), W = sample weight (g).

The partial derivatives in this equation are determined from Equation (19).

$$\frac{\delta C}{\delta V} = \frac{0.1179}{W} \quad (21)$$

$$\frac{\Delta C}{W} = \frac{-0.1179V}{W^2} \quad (22)$$

The most probable values and maximum estimated errors for the ml EDTA and sample weight are V = 5.0ml, $\delta V = 0.025$ ml, W = 0.2500g, $\delta W = -0.001$ g. Combining equations (20), (21) and (22) and substituting the estimated values gives:

$$C = \frac{0.1179}{0.2500} (0.025) - \frac{0.1179(5.0)}{(0.2500)^2} (-0.001)$$

$$C = 0.02 \text{ weight percent}$$

The magnitude of potential error in the denominator of the right hand side of equation (18) is evaluated by calculating the standard deviation of the 3 measurements of cobalt concentration in the non-leached catalyst material.

Standard deviation is defined as:

$$\sigma = \left(\frac{\sum x^2 - (\sum x)^2/n}{n} \right)^{1/2} \quad (23)$$

Therefore for x equal to the cobalt concentration in the non-leached catalyst material, the values of which are provided in Table 4, $\sigma = 0.31$.

The overall maximum error in (e) can now be calculated in the same manner as the error in residual cobalt content of leached catalyst material was calculated. From Equation (18).

$$\Delta e = \frac{\delta e}{\delta C_1} \Delta C_1 + \frac{\delta e}{\delta C_F} \Delta C_F \quad (24)$$

where C_1 is the cobalt concentration of the non-leached catalyst material and C_F is the cobalt concentration of the leached catalyst material.

$$\frac{\delta e}{\delta C_1} = - \frac{1}{C_F} \quad (25)$$

$$\frac{\delta e}{\delta C_F} = \frac{C_1}{C_F^2} \quad (26)$$

The most probable values and previously estimated errors for cobalt concentration in the catalyst material before and after leaching are $C_1 = 2.62$, $\Delta C_1 = -0.31$, $C_F = 1.90$, and $\Delta C_F = 0.02$. Combining Equations (24), (25) and

(26), and substituting the appropriate values gives:

$$e = - \frac{1}{1.90} (-0.31) + \frac{2.62}{(1.90)^2} (0.02)$$

$$e = 0.18$$

The main source of this error is the standard deviation of the measurements of cobalt concentration in the unleached catalyst material. This deviation is large because of the apparently anomalous cobalt concentration measurement of 2.22 weight percent cobalt.

The maximum estimated error in e introduced during the analytical procedure is 18 percent. The average increases in extraction of cobalt observed at supercritical conditions ranged from 4.0 to 14.2 percent. While enhancement falls within the ranged of estimated maximum experimental error, actual experimental error was probably lower than 18 percent. This is supported by the consistency of the leaching enhancement observed at supercritical conditions.

C. Platinum Automotive Catalyst

Two experiments were also conducted to determine the leachability of platinum group metals from spent automotive catalytic converters, using supercritical aqueous ammonia solvent. Samples of catalyst material from automotive

catalytic converters were leached with supercritical aqueous ammonia, at 15 and 30 mole percent ammonia. The solvents from either of the two experiments were analyzed for trace amounts of platinum group metals present in the solvents from either of the two experiments. No detectable platinum group metals were present in the solvents from either of the two experiments.

Three experiments were also conducted to determine the leachability of platinum from platinum wire. The first of these experiments was conducted using the same procedures with supercritical, 5 mole percent ammonia solvent. The other two experiments were conducted in a batch mode using supercritical, 5 and 10 mole percent ammonia solvents. The solvents were analyzed for the amounts of platinum (Pt and Pd for experiments leaching catalytic converters) after leaching. There was no platinum (nor palladium) detected in the solvents from the three experiments conducted.

VI. CONCLUSIONS AND DISCUSSION

Leaching cobalt from a hydrotreating catalyst material using supercritical aqueous ammonia conditions results in a significant increase in cobalt extraction (extent of reaction) over that obtained by leaching at any of the variety of subcritical conditions tested. Leaching of cobalt at supercritical conditions was enhanced in comparison to leaching at supercritical pressure - elevated temperature, low pressure - low temperature and supercritical pressure - low temperature conditions by an average of 14.2, 6.8, and 4.0 percent respectively. Leaching enhancement at supercritical conditions is made more significant by the low solvent flow rates used in this study. Only 50 to 100 milliliters of solvent at supercritical conditions was introduced into the reactor during the supercritical experiments. The supercritical leaching enhancement is not the results of simple pressure or temperature effects, but is probably caused by the improved mass transfer characteristics of supercritical fluids. These characteristics decrease diffusional resistance to mass transfer ($\phi \rightarrow 0$) and make the process more nearly chemical reaction rate controlled ($\eta \rightarrow 1.0$).

Attempts to extract platinum group metals from spent automotive catalytic converters and from platinum wire using supercritical aqueous ammonia solvent were unsuccessful.

Platinum is inert, and will not react with the aqueous ammonia regardless of the enhanced mass transfer characteristics of the supercritical solvent.

Additional experimental work is needed for more definitive results on the potential advantages supercritical solvents offer for metals extraction. A more simple experimental system operated in a batch mode would allow extraction results to be based upon calculated head grades, rather than being based upon leached versus non-leached head grades. This system would also eliminate flow variable and the corresponding errors.

Analysis of solvents could be used for calculating metal concentrations in the non-leached samples which would significantly reduce the analytical errors. In addition, experiments should be conducted to determine the transport properties of the solvents being used. These data could be used to quantitatively compare the leaching enhancement gained by leaching at supercritical conditions to that predicted by theory.

Potential future applications for supercritical fluids in extractive metallurgy include leaching metals from materials where mass transfer is the rate limiting step. Extracted metals would have to be of relative high value because of high capital costs associated with supercritical

fluid extraction. Removal of toxic metals from waste material is another potential future application for SCF in extractive metallurgy.

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