

DATE: October 2, 1989

TITLE: THE DEVELOPMENT OF PRECIPITATED IRON CATALYSTS WITH IMPROVED STABILITY

AUTHORS: H. Abrevaya (Principal Investigator), W. M. Targos, M. J. Cohn

INSTITUTION: UOP Research Center
50 E. A. Monquin Road, Box 5016
Des Plaines, IL 60017-5016
(708) 391-2329

CONTRACT NO: DE-AC22-87PC79312

PERIOD OF PERFORMANCE: 9/16/87 - 9/16/91

OBJECTIVE: The objective of this program is to develop a precipitated iron Fischer-Tropsch catalyst that has improved stability, and is suitable for slurry reactors.

TECHNICAL APPROACH:

- (1) Upgrade the existing fixed-bed pilot plant so that it has slurry-bed reactor and Berty-reactor testing capabilities.
- (2) Establish the stability of a state-of-the-art reference-precipitated iron catalyst.
- (3) Construct an iron-catalyst preparation plant and develop a baseline iron catalyst.
- (4) Elucidate the deactivation chemistry for iron catalysts.
- (5) Modify the catalyst chemistry to improve the stability of the catalyst.

SIGNIFICANT ACCOMPLISHMENTS:

- (1) The existing fixed-bed pilot plant was upgraded so that it has slurry and Berty-reactor testing capabilities.
- (2) A reference-precipitated iron catalyst was acquired from Mobil Corporation for evaluation in the slurry reactor.
- (3) A pilot plant for preparing precipitated iron catalysts was constructed. A preparation procedure was developed for iron catalysts, and the screening of these catalysts in the slurry reactor has been initiated.

INTRODUCTION

Precipitated iron catalysts are expected to be used in next-generation slurry-bed reactors for the large-scale production of transportation fuels from synthesis gas. These reactors are expected to operate at higher temperatures and lower ratios of H_2 and CO relative to the Sasol Arge reactor. The utility of iron catalysts has been demonstrated under relatively mild Arge-type conditions but not under more-severe slurry conditions. A major improvement in catalytic stability will be needed to make iron catalysts suitable for slurry operation.

This program is aimed at identifying the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and using these chemical principles in the design of more-stable catalysts. The program has been divided into five major tasks to be conducted over a four-year period:

- Task 1: Upgrade the existing fixed-bed pilot plant so that it has slurry-bed reactor and Bertly-reactor testing capabilities.
- Task 2: Establish the stability of a state-of-the-art reference-precipitated iron catalyst.
- Task 3: Construct an iron-catalyst preparation plant and develop a baseline iron catalyst.
- Task 4: Elucidate the deactivation chemistry for iron catalysts.
- Task 5: Modify the catalyst chemistry to improve the stability of the catalyst.

EXPERIMENTAL

Catalyst Preparation Procedure

The schematic diagram for the iron-catalyst preparation plant is shown in Figure 1. Metal was not used as a material of construction for any wetted section in order to avoid catalyst contamination that may occur through dissolution of metallic components in contact with acidic solutions.

The iron-copper solution and the base solution are in two separate 15-gallon feed tanks. The weights of these solutions are continuously measured during the experiment. The feed solutions are pumped separately to a precipitation reactor. The precipitate slurry then flows to a 55-gallon tank that contains a large amount of water. This water acts as a quenching medium for the precipitation reactions. The precipitate slurry then is pumped to a centrifugal filter, where the catalyst is washed with a separate water-feed stream. The catalyst is finally dried, calcined and crushed to a 140-400 mesh-size range before being impregnated with potassium carbonate. Then the catalyst receives a final calcination and a reduction in situ in the Fischer-Tropsch synthesis reactor.

Catalyst Testing Procedure

For each test, 95 grams of calcined iron catalyst were loaded to a 1-liter autoclave along with 380 grams of C_{32} n-paraffin wax at 130°C. After the wax melted, the autoclave was sealed and pressure tested with N_2 at 25 atm. After a successful pressure test, the pressure was lowered to 11 atm, the stirring was initiated at 1,300 rpm, and the catalyst temperature was raised under N_2 to 280°C in 3 hours. A thermocouple inserted in a thermowell inside the slurry was used for temperature control. The temperature control point was 3 cm above the bottom of the autoclave. After 280°C was achieved, N_2 flow was cut out, and, synthesis gas with a molar ratio of 0.7 H_2 to 1 CO was introduced at $1.6 \times 10^{-1} \text{ Nm}^3/\text{hr}$. After a 12-hour reduction in situ, the temperature was lowered to 258°C in 2 hours, the pressure was raised to 14 atm, and the feed rate was decreased to $1.3 \times 10^{-1} \text{ Nm}^3/\text{hr}$. Each test then continued for a total of 40-200 hours.

Conversion and Selectivity Calculations

Argon, which was present in the synthesis gas feed at about the 6% (by mole) level, was used as an internal standard to determine conversions and light hydrocarbon selectivities according to the following formulas:

$$\text{CO Conversion, \%} = \frac{\left(\frac{\text{CO}}{\text{Ar}}\right)_{\text{feed}} - \left(\frac{\text{CO}}{\text{Ar}}\right)_{\text{product}}}{\left(\frac{\text{CO}}{\text{Ar}}\right)_{\text{feed}}} \times 100$$

(The $\text{CO} + \text{H}_2$ conversion was calculated in a similar manner to the CO conversion.)

$$C_n \text{ Selectivity, \%} = \frac{\left(\frac{C_n}{\text{Ar}}\right)_{\text{feed}} \times n}{\left(\frac{\text{CO}}{\text{Ar}}\right)_{\text{feed}} - \left(\frac{\text{CO}}{\text{Ar}}\right)_{\text{product}}} \times 100$$

In the latter equation, n is the number of carbon atoms in one molecule of hydrocarbon C_n . The calculation of selectivity of CO to CO_2 is similar to the calculation of selectivity to methane, for which $n = 1$.

RESULTS AND DISCUSSION

Task 1: Upgrade Catalyst Testing Plant

The existing fixed-bed-catalyst testing plant was upgraded so that it has slurry-bed and Berty-reactor testing capabilities. Although the initial catalyst screening work is being done in the slurry-bed reactor, fixed-bed and Berty reactors are going to be considered in the future for screening improved catalysts.

The schematic diagram of the integrated catalyst testing plant is shown in Figure 2. Two independent feed systems allow the fixed-bed reactor and the slurry-bed or Berty reactor to run simultaneously. The two reactor systems have their independent set of product collectors. During a simultaneous fixed-bed and slurry-bed run, the on-line gas chromatograms (GC's) alternate on an hourly basis between the two reactor systems. The first on-line GC is connected at the outlet of the first product collector, which is at 130°C and 14 atm. This GC analyzes paraffins, olefins, alcohols, and aldehydes in the C₁-C₂₀ carbon number range. The second on-line GC is connected at the outlet of the second collector, which is at 0°C and 4 atm. This second GC analyzes paraffins and olefins in the C₁-C₄ carbon-number range as well as CO, CO₂, H₂, and Ar. The third product collector is at -78°C and 1 atm.

For the slurry-bed reactor, various approaches for separating liquid products from catalyst are going to be considered. The current approach is to achieve this separation by means of a filter situated inside the slurry autoclave reactor (Figure 3). The filter is connected to the product exit line, which is 1/4 inches in diameter. The filter acts as a liquid-level controller, and its bottom edge is 6 1/2 inches from the bottom of the autoclave.

In Run 5, a filter that is 5/8 inch in diameter and 2 inches long was used. The filter has a nominal pore diameter of 0.15µm and an absolute pore diameter of 0.4µm. This filter plugged within 40 hours of testing an Fe-Cu-K catalyst.

In Run 6, another ceramic filter with a 0.7µm nominal and a 1.5µm absolute pore diameter was used. This filter also plugged within 40 hours of testing an iron-copper-potassium oxide (Fe-Cu-K) catalyst.

In Run 7, a stainless steel-filter with a 17µm nominal and a 45µm absolute pore diameter was used. This filter did not plug during 200 hours of operation. However, significant catalyst loss occurred across the filter. In Runs 8 and 9, a filter with a smaller pore size was used: 5µm nominal and 18µm absolute. However, catalyst loss still occurred.

Task 2: Establish Stability of a Reference Catalyst

A precipitated iron catalyst, MSCG-4, was acquired from Mobil Corporation. This catalyst is going to be evaluated in the slurry reactor to establish reference performance.

Task 3: Develop Baseline Catalyst

Catalyst Preparation

The preparation of iron catalyst is shown in Figure 4. The hydrolysis of ferric ion starts to occur at pH=1. A dinuclear Fe₂(OH)₂⁺⁴ and a trinuclear species Fe₃(OH)₄⁺⁵ are formed in solution (1). At pH's greater than 2.5, ferric ion precipitates, apparently in the form of iron hydroxide. The aging of the precipitate results in goethite (α-FeO(OH)) formation. Heating during calcination results in the formation of hematite (α-Fe₂O₃). During reduction, which can be accomplished in the presence of H₂ and/or CO, iron oxide typically undergoes several different forms, which include magnetite (Fe₃O₄), wustite (α-FeO) and metallic iron (α-Fe).

The precipitation of copper in the form of copper nitrate, requires a pH of at least 5. However, in the presence of iron, the precipitation of copper occurs at lower pH's (2).

Previous work conducted under this contract indicated that precipitation pH was one of the key variables that controlled the crystallite size of iron-copper oxide catalysts. The pilot plant which was constructed to prepare iron catalysts, is capable of precipitating iron and copper at any given pH level with a suitable choice of the feed rates for the iron-copper nitrate and sodium carbonate solutions, as described in the Experimental section.

The catalyst-preparation plant has operated for a maximum of 10 hours and makes about 1000 grams of catalyst in any given run. Because of the labor-intensive nature of the plant, operating the plant for much longer times is difficult. Several factors make the plant operation labor intensive. One of the factors is solids build up on the surface of the pH probe in the precipitation reactor. Solids build up causes erroneous pH readings. Currently, stream samples are being taken from the reactor every 15 minutes to measure pH off-line.

Another factor is the loss of catalyst through the centrifugal filter. A significant improvement in catalyst recovery was achieved when the pore size of the filter bag was lowered from 6 μ m to 0.5 μ m. However, the problem of catalyst loss across the filter was not eliminated with the fine-mesh filter bag. Currently, part of the slurry that passes through the bag is being recycled back to the centrifuge to help increase the catalyst recovery. The rest of the slurry is collected in a 55-gallon drum for catalyst separation at the end of the run.

Finally, the filter bag has a finite capacity of a few hundred grams of catalyst. Once the bag becomes essentially full, which occurs at the end of 2-3 hours, it is replaced with a new bag.

Catalyst Testing

The targets for the baseline catalyst have been set to at least 1 month's stable operation at 80% CO+H₂ conversion at 2.4 normal liters synthesis gas/gram iron hour with no more than 4% methane + ethane selectivity, based on the work done by Mobil Corporation under Contract DE-AC22-83PC60019. Other conditions are 258°C, 14 atm, 0.7 H₂:1 CO feed, 20% catalyst loading in slurry.

Because the design of the catalyst-wax separation system for the slurry-catalyst testing reactor has not been finalized, the screening of Fe-Cu-K catalyst can now only be done in short tests.

So far two different Fe-Cu-K catalysts were evaluated in the slurry-bed reactor. Catalyst A achieved 90% CO+H₂ conversion at 0.7 normal liters synthesis gas/gram iron-hour with 7.3% methane and ethane selectivity during the first 50 hours. Catalyst B achieved 72% CO+H₂ conversion at 1.6 normal liters synthesis gas/gram iron hour with 3.3% methane and ethane selectivity. The test with catalyst B indicates that although target catalytic selectivity was achieved, the catalytic activity needs to be increased. Longer-term testings will determine whether catalytic stability needs also to be improved.

FUTURE PLAN

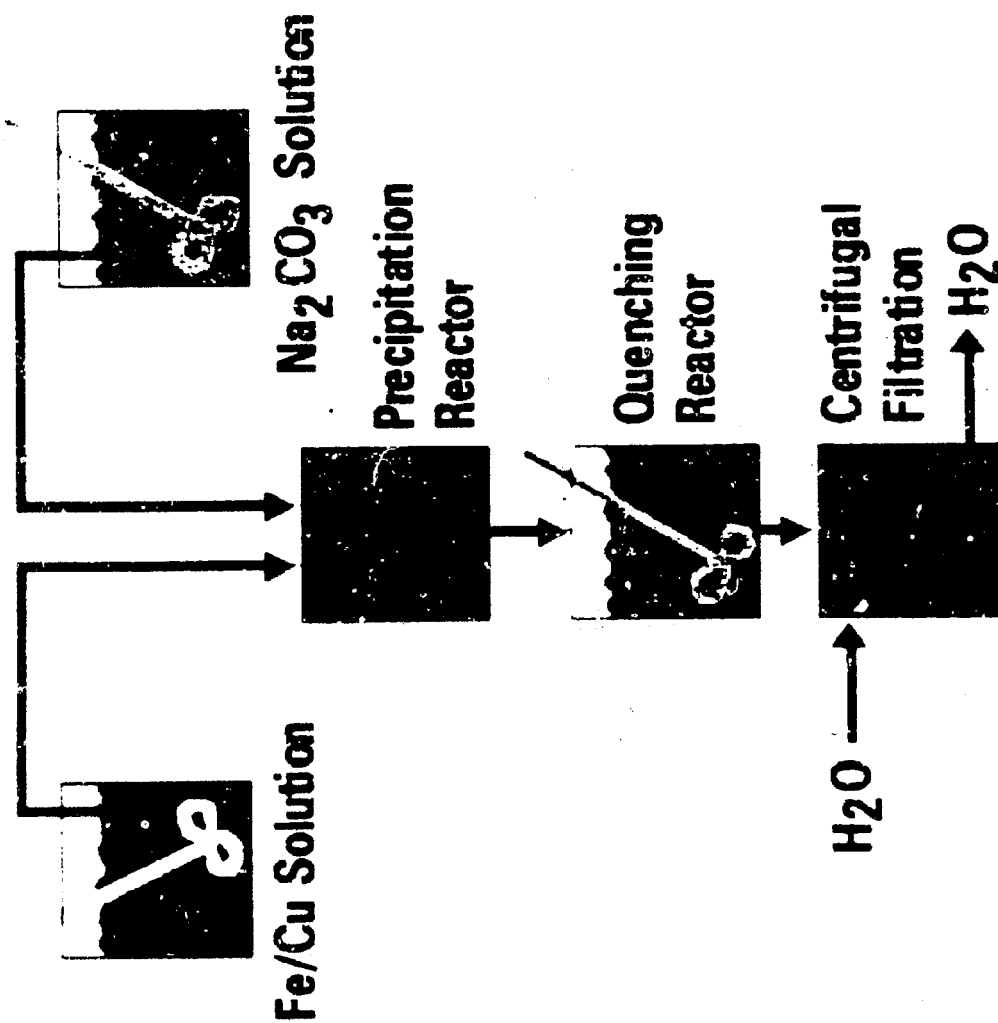
- Task 1: Filters with nominal pore diameters of between 0.7 μ m and 5 μ m will be utilized in the slurry-bed reactor.
- Task 2: After the design of the catalyst-wax separation system is finalized, the reference-precipitated iron catalyst from Mobil Corporation will be tested in the slurry autoclave in order to establish reference performance.
- Task 3: Various equipment and procedural modifications will be considered to decrease the man power requirements for running the catalyst preparation plant and to run the plant for periods exceeding 10 hours.
- Task 4: Various approaches will be considered for increasing the activity of the iron-copper-potassium oxide catalysts. These catalysts will be evaluated in longer tests to determine catalytic stability. A baseline catalyst will then be developed that matches the reported performance of Mobil catalyst.
- Task 5: The deactivation mechanism of the baseline catalyst will be determined.
- Task 6: Various approaches will be evaluated for improving the performance of the baseline catalyst.

REFERENCES

1. C. F. Bases and R. E. Mesmer, The Hydrolysis of Cations (New York City:) John Wiley & Sons, (1976).
2. H. Abrevaya, The Development of Precipitated Iron Catalysts with Improved Stability, Contract DE-AC22-87PC9812, Quarterly Technical Progress Report - Fourth Quarter 1987.

FIGURE

PILOT PLANT FOR PREPARATION OF IRON CATALYSTS



SB004-10

INTEGRATED FISCHER-TROPSCH PILOT PLANT

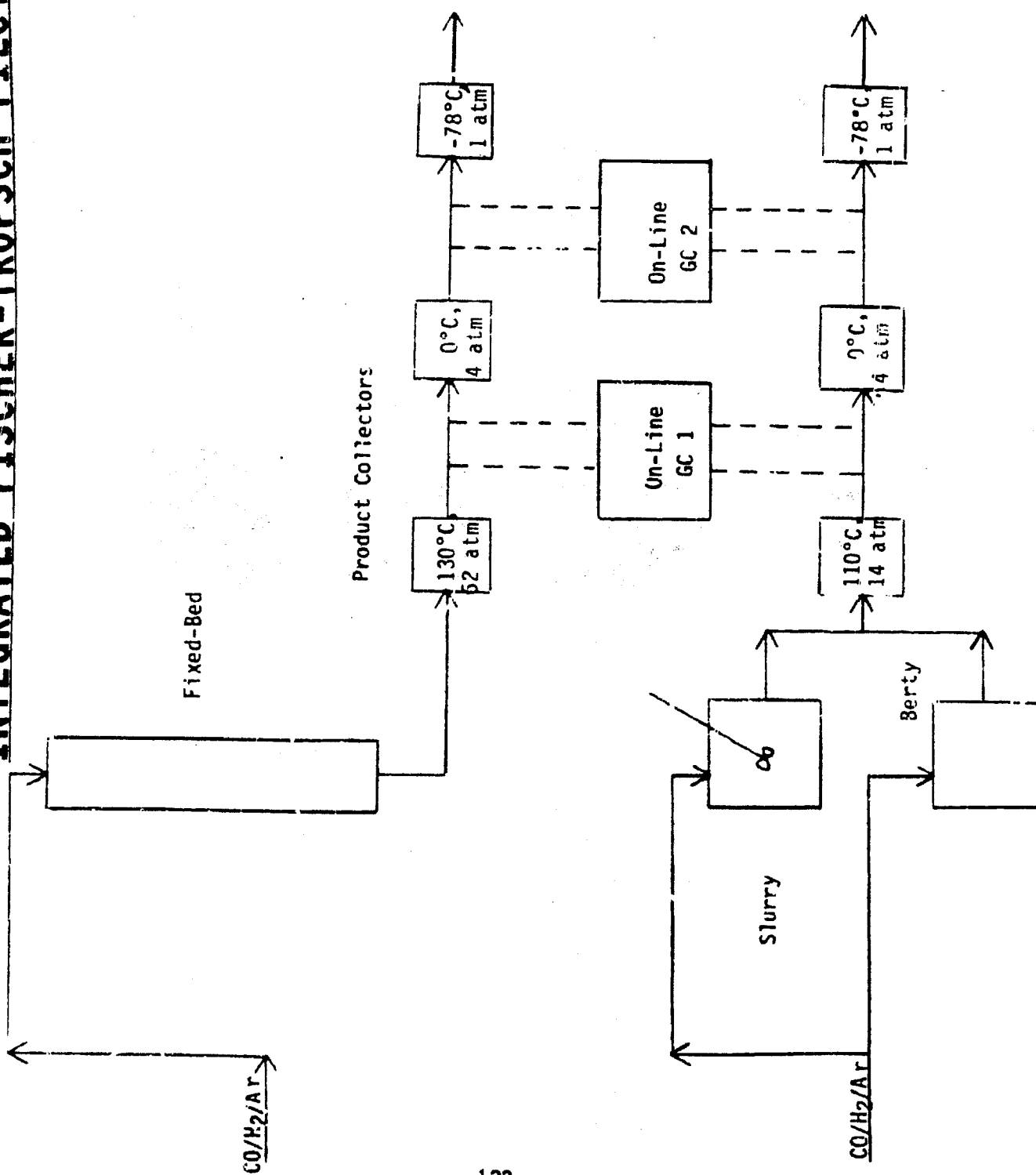


FIGURE 3

SLURRY AUTOCLAVE CONFIGURATION IN RUN 5, PLANT 700B

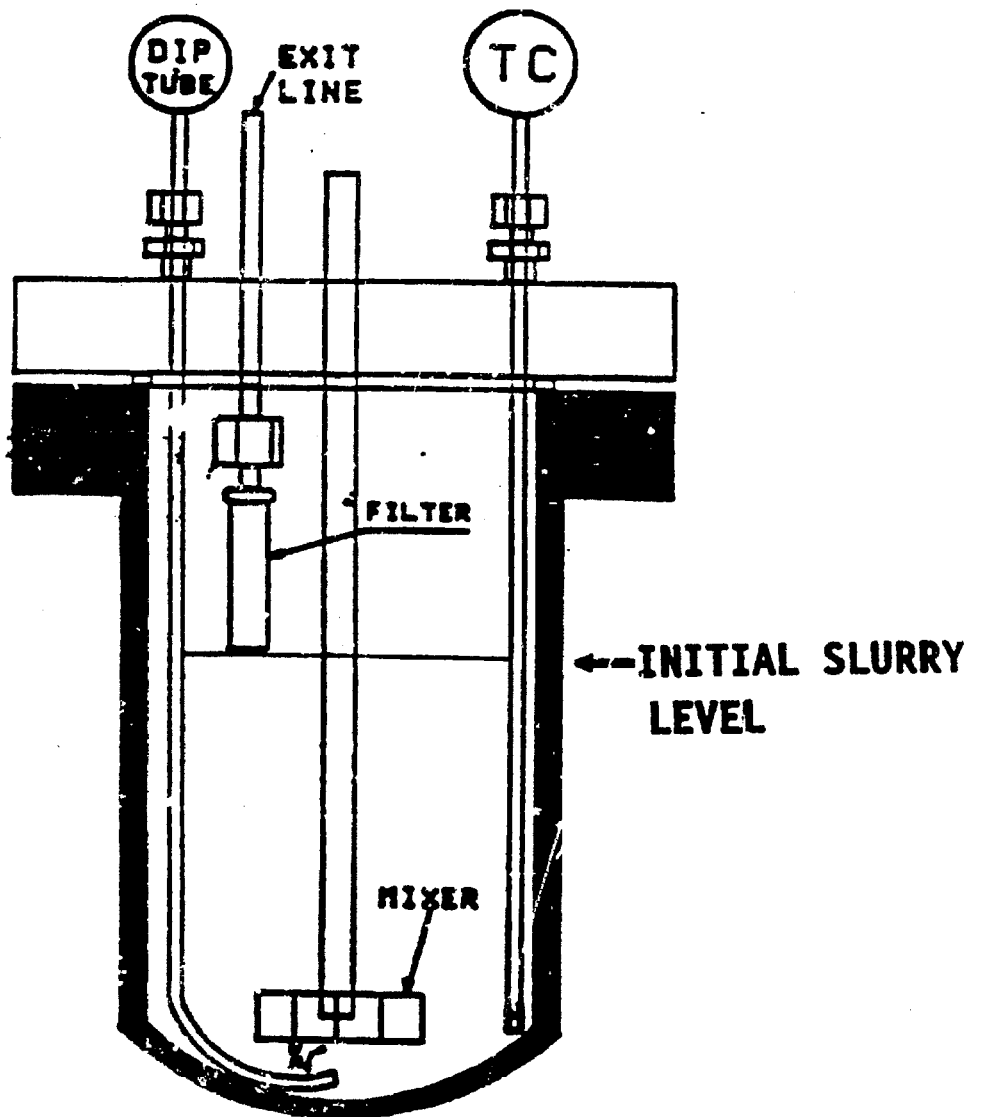
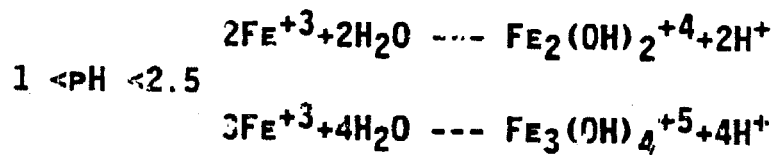


FIGURE 4

PREPARATION OF IRON CATALYST



PH >2.5

