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February 21, 1981

MEMORANDUM

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TO: H. D. HARMON

FROM: D. G. KARRAKER DGKarraker

Cu(II) - CATALYZED HYDRAZINE REDUCTION OF FERROUS NITRATE

INTRODUCTION

Hydrazine, as hydrazine nitrate solution, is used in 200 Area processing as a holding reductant to prevent the oxidation of reduced ions, such as Fe^{+2}, Np^{+4}, and Pu^{+3} during processing. As a holding reductant, hydrazine destroys the radiolytically-produced or chemically-produced nitrous acid kinetically necessary for oxidation by nitric acid. At room temperature, hydrazine destroys nitrous acid more than twice as fast as the sulfamate ion, the common holding reducant in process use.[1]

Ferrous sulfamate solution is a combination reducing agent and holding reductant that is in general use in 200 Area processes. The penalty for its use is the eventual decomposition of the sulfamate ion to sulfate. Sulfate is considered responsible for increased waste evaporator corrosion, and in some processes sulfate complexing of +4 ions (Np, Pu) affects process operation. A major drawback of sulfate is its deleterious effect on the quality of glass produced in proposed Defense Waste Process Facility. It is estimated that a 60-fold reduction in sulfate would be necessary to have a satisfactory process for incorporation of acid-evaporated waste solids in borosilicate glass.[2]

Ferrous nitrate-hydrazine (FeNH) solution is an effective reducing agent-holding reductant, and could be substituted for ferrous sulfamate in 200 Area processes. Laboratory tests have shown satisfactory Purex 1B-bank partitioning of plutonium and uranium with ferrous nitrate-hydrazine as a reductant.[3] U(IV) nitrate-hydrazine is under development as a replacement for ferrous sulfamate, but U(IV) interferes with anion exchange processes, and its use in enriched uranium processing may be complicated by requiring the same uranium isotopic composition for U(IV) and the enriched uranium in process. FeNH has neither disadvantage. The use of FeNH avoids the sulfate problem in waste, although there are objections to hydrazine because of its listing by OSHA as a carcinogen, and because of the formation of hydrazoic acid in some reactions. The hazards of HN_3 have been dealt with in previous laboratory studies.[4]

SUMMARY

Ferrous nitrate-hydrazine solution was produced by reducing ferric nitrate solution with hydrazine with 0.05-0.08M Cu(II) as a catalyst. Solutions of 1.1-1.2M Fe(II) are produced in 1.5 hours at 40°C, 6 hours at 30°C, and ~30 hours at 23.5°C. The solutions are stable for 1 to 2 weeks. A reaction between nitrate ion (or nitric acid) and hydrazine produces HN_3 in substantial quantities (~0.25M) during the preparation. HN_3 can be removed from solution by sparging with nitrogen. In large scale preparations, vessel off-gas should be routed through a sodium nitrite (solution) scrubber.

Hydrazine Reactions

Hydrazine is a strong reducing agent, although its reactions are often slow at room temperature. The oxidation of hydrazine involves free radical reactions, and depends upon the oxidizing agent. In general, one-electron oxidizing agents produce NH_3 on reaction with hydrazine, and two-electron oxidizing agents produce both NH_3 and HN_3 (hydrazoic acid).[5] The kinetics of hydrazine oxidation can be explained[6,7] by the following mechanisms (acid hydrogen ions omitted in formulae below):

A. For one-electrons oxidants, e.g., Fe(III)

(1) Hydrazyl radical formation

$N_2H_4 + Fe(III) \rightarrow N_2H_3 + Fe(II)$

(2) Back-reaction

$N_2H_3 + Fe(II) \rightarrow N_2H_4 + Fe(III)$

(3) N_2H_3 dimerization

$2N_2H_3 \rightarrow [N_4H_6] \rightarrow 2\ NH_3 + N_2$

(4) N_2H_3 disproportionation

$2N_2H_3 \rightarrow N_2H_4 + N_2H_2$

(5) Diazene radical (N_2H_2) oxidation

$N_2H_2 + 2\ Fe(III) \rightarrow N_2 + 2\ Fe(II)$

(6) N_2H_3 oxidation

$N_2H_3 + Fe(III) \rightarrow N_2H_2 + Fe(II)$

B. For two electron oxidants, e.g., HNO_2

(7) Diazene radical formation

$N_2H_4 + HNO_2 \rightarrow N_2H_2 + 3/2\ H_2O + 1/2\ N_2O$

(8) N_2H_2 dimerization

$2\ N_2H_2 \rightarrow [N_4H_4] \rightarrow NH_3 + HN_3$

(9) N_2H_2 oxidation

$N_2H_2 + 2\ HNO_2 \rightarrow 2\ N_2 + 2\ H_2O$

(10) With excess HNO_2

$HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O$

Previous workers have found that the rate of hydrazine oxidation is increased at 40 to 80°C, and that under some conditions hydrazine reactions are catalyzed by metal ions, principally Cu(II) and Fe(III). This work reported here applies these findings to systems that are useful in 200 Area processes.

Ferrous Nitrate Production

Three methods for producing FeNH have been explored, electrolysis of ferric nitrate-hydrazine solution, dissolving iron metal in nitric acid-hydrazine solution and Cu(II)-catalyzed reduction of ferric nitrate by hydrazine. Electrolysis requires expensive electrolytic equipment not currently available; iron metal must be dissolved under carefully controlled conditions to avoid oxidation. The reduction of ferric nitrate by hydrazine aided by heating and Cu(II) catalysis was seen as a less expensive alternative.

Experimental

Ferric nitrate stock solutions were prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ (40 g, 0.1 mole) in 1M HNO_3 (25 ml). The final volume of the solution is about 50 ml, so its concentration is about 2M $Fe(NO_3)_3$ - 0.5M HNO_3. Solubility tests found that at room temperature, the solutions of the same ferric concentration could be prepared with HNO_3 concentations only up to 3M HNO_3; in higher acid, the solubility of $Fe(NO_3)_3 \cdot 9H_2O$ was decreased.

Hydrazine nitrate stock solutions of about 6M concentration were prepared by adding 85% $N_2H_4 \cdot H_2O$ drop-wise, with stirring, to concentrated HNO_3 cooled in an ice bath. Hydrazine concentrations were determined by the iodate method.

Cupric nitrate solution was prepared by dissolving a weighed amount of $Cu(NO_3)_2 \cdot 3H_2O$ in distilled water.

Solution were made up by pipette in vented vials, and immersed in a thermostated water bath for tests. Samples were withdrawn from the samples at appropriate times, and immediately analyzed for ferrous ion by titration with Ce^{+4} in a 2.4M HCl-0.01M $Fe_2(SO_4)_3$ solution with ferroin indicator. Tests showed that neither hydrazine nor hydrazoic acid reacted significantly with Ce^{+4} during the period required for the titration. Azide ion was determined spectrophotometrically by measurement of the absorbance of the ferric azide complex.[8]

Results

Preliminary experiments at room temperature explored the effect of Cu(II) catalysis on solutions 1.2M Fe(III), 0.90M HNO_3 and 0.33M $N_2H_4 \cdot HNO_3$, approximately a stoichiometric ratio of Fe(III) to N_2H_4, assuming the net reaction

$$4\ Fe(III) + N_2H_4 \rightarrow 4\ Fe(II) + N_2 + 4\ H^+.$$

The results (Figure 1) showed that Cu(II) had a catalytic effect up to about 0.06M Cu(II). Adding 0.09M Cu(II) increased the yield of Fe(II) only 3 to 5% over 0.06M Cu(II) after 72 hours. No further increase in Fe(II) yield was observed up to 144 hours.

A more rapid reduction of Fe(III) was observed when the temperature was increased to 40°-50°C and the hydrazine concentration increased to 0.79M, a Fe(III)/N_2H_4 ratio of 1.9. The reaction at 40° showed the catalytic effect of Cu(II) (Figure 2) and a greatly increased reaction rate, compared to 25°C experiments. The reaction was sensibly complete in 1.5 hours, with a 66% conversion of Fe(III) to Fe(II) with 0.069M Cu(II) as a catalyst. At 50°C, and with the same concentrations (Figure 2), the reaction was complete in less than one hour (no data taken before one hour), with a 80% conversion of Fe(III) to Fe(II).

The dependence of the reaction on Fe(III)/N_2H_4 ratio was investigated at 40°C. The results (Figure 3) showed 91% conversion for an Fe(III)/N_2H_4 ratio of 0.9 in 1.5 hours. 100% conversion of Fe(III) to Fe(II) was observed after 4 hours. Increasing the temperature to 50°C resulted in 100% reduction of Fe(III) to Fe(II) in 45 minutes.

The effect of acid concentration on the reduction of ferric ion was explored with solutions 1.6M Fe(III)-0.05M Cu(II)-1.1M N_2H_4-0.4 to 2.4M HNO_3 at 50°. The results (Figure 4) showed that the highest concentration of Fe(II) was reached in about 45 minutes in 0.4M HNO_3 solution. Heating more than 45 minutes destroyed Fe(II), most markedly in the 2.4M HNO_3 solution. Only 60% of the Fe(III) was reduced in the 0.4M HNO_3 since these tests were run at an initial Fe(III)/N_2H_4 ratio of 1.5, less than necessary for complete reduction. However, solutions containing the minimum acid to prevent Fe(III) hydrolysis (0.3-0.5M) were used in the remainder of this study.

The reduction of Fe(III) by hydrazine was investigated at lower temperatures, and at Fe(III)/N_2H_4 ratios of 0.94 and 0.73, with the aim of developing a convenient procedure for large-scale production. The results are shown in Table I. In general, Fe(II) solutions of 1.1 to 1.2M were produced in 1.25 hours at 40°C, about 6 hours at 30°C, and ~30 hours at 23.5°C (room temperature). Further standing of these solutions at room temperature led to a further small increase in Fe(II) concentration for 1 to 2 days; the solutions were stable for 4 to 5 days. A slow decrease in Fe(II) concentration begins after a week - of the order of 5% per day. The solutions with the highest N_2H_4 concentrations were more stable, suggesting that a reaction between nitric acid and hydrazine is occurring, and as the hydrazine concentration decreases, Fe(II) is more susceptible to oxidation by nitric acid.

TABLE I

Preparation of Ferrous Nitrate

Initial Concentration*	Temp., °C	Final Fe(II) Concentration M	Time, hrs
1.3M Fe(III)	40	1.07	1.25
1.4M N_2H_4			
0.05M Cu(II)	30	1.04	6**
0.35M HNO_3			
	23.5	1.04	30
1.3M Fe(III)	40	1.14	1.25
1.4M N_2H_4			
0.08M Cu(II)	30	1.10	6**
0.35M HNO_3			
	23.5	1.26	30
1.3M Fe(III)	40	1.11	1.25
1.7M N_2H_4			
0.05 M Cu(II)	30	1.10	6**
0.35M HNO_3			
	23.5	1.18	30
1.2M Fe(III)	40	1.20	1.25
1.7M N_2H_4			
0.08M Cu(II)	30	1.20	6**
0.35M HNO_3			
	23.5	1.30	30

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* Fe(III) Concentrations estimated from makeup.

** Extrapolated.

The solutions prepared by this reaction are red-brown in color from the ferric azide complex ion. Hydrazoic acid concentrations as high as 0.25M were found by analyses, but did not show any correlation with temperature, hydrazine concentration, cupric ion concentration, or time elapsed from preparation. As the reaction tubes were vented to allow escape of nitrogen, it is presumed that some HN_3 escaped with the nitrogen. (The vapor pressure of HN_3 is 509 mm at 24.7°C.[9]) In several tests, a 10- to 15-minute nitrogen sparging of the Fe(II) solutions removed all the HN_3, as evidenced by the change in solution color from red-brown to green. A slow color change indicated the slow growth of HN_3 in the solution over the next 24 hours. Large-scale preparation of ferrous nitrate-hydrazine solutions (by this or any other method) should consider nitrogen-sparging of the storage tank, and aqueous sodium nitrite scrubbing of the tank off-gas to destroy HN_3.

Discussion

The effect of Cu(II) on the reduction of Fe(III) by hydrazine is believed[5] to be the result of decreasing the back-reaction (Equation 2), which in an uncatalyzed system acts to prevent complete reduction of Fe(III). As the Fe(II) concentration increases,

$$(2)\ N_2H_3 + Fe(II) \rightarrow Fe(III) + N_2H_4$$

the concentration of the N_2H_3 radical is decreased by reaction (2); as the Fe(III) concentration is also decreased, the reaction is stopped before complete reduction occurs.

With Cu(II) present, the concentration of N_2H_3 is reduced by

$$(12)\ N_2H_3 + Cu(II) \rightarrow N_2H_2 + Cu(I)$$

followed by

$$(13)\ Cu(I) + Fe(III) \rightarrow Fe(II) + Cu(II)$$

and reaction (5), diazene radical oxidation. To achieve complete reduction, a lower ratio of $Fe(III)/N_2H_4$ is desirable to maintain the production of hydrazyl (N_2H_3) radicals, so far as possible, as Fe(III) is depleted. Elevated temperatures presumably also increase the rate of free radical production.

Previous workers [5,6,7] report that little, if any, HN_3 is formed by the Fe(III)-hydrazine reaction, but all carried out their experiments in sulfuric acid solutions. From the present work, it is apparent that there is a substantial reaction between hydrazine and nitrate ion (or nitric acid) to produce HN_3 during both the reduction of Fe(III) and during storage at room temperature. Color changes indicative of HN_3 production have also been observed in Fe(II)-hydrazine solutions produced by dissolving iron metal in HNO_3-N_2H_4 solutions. The storage of any Fe(II)-hydrazine-nitric acid solution would be accompanied by accumulation of HN_3.

Recommended Conditions for Large-Scale Preparation

The recommended conditions for preparation of ferrous nitrate - hydrazine nitrate solution are heating a 1.3M Fe(II) - 1.7M $N_2H_4 \cdot HNO_3$ - 0.35M HNO_3 - 0.08M Cu(II) solution for 1.5 hours at 40°C in a tank equipped with an off-gas scrubber. The tank off-gas should be scrubbed with $NaNO_2$ solution, and after cooling to room temperature, a nitrogen sparge should be continued to remove HN_3 as formed. Despite the complication of the storage conditions, the product solution is an effective reducing agent that can be substituted for ferrous sulfamate solution in any 200 Area process.

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FIGURE 1 Cu(II) - Catalyzed Hydrazine Reduction of Fe(III) at 25°C

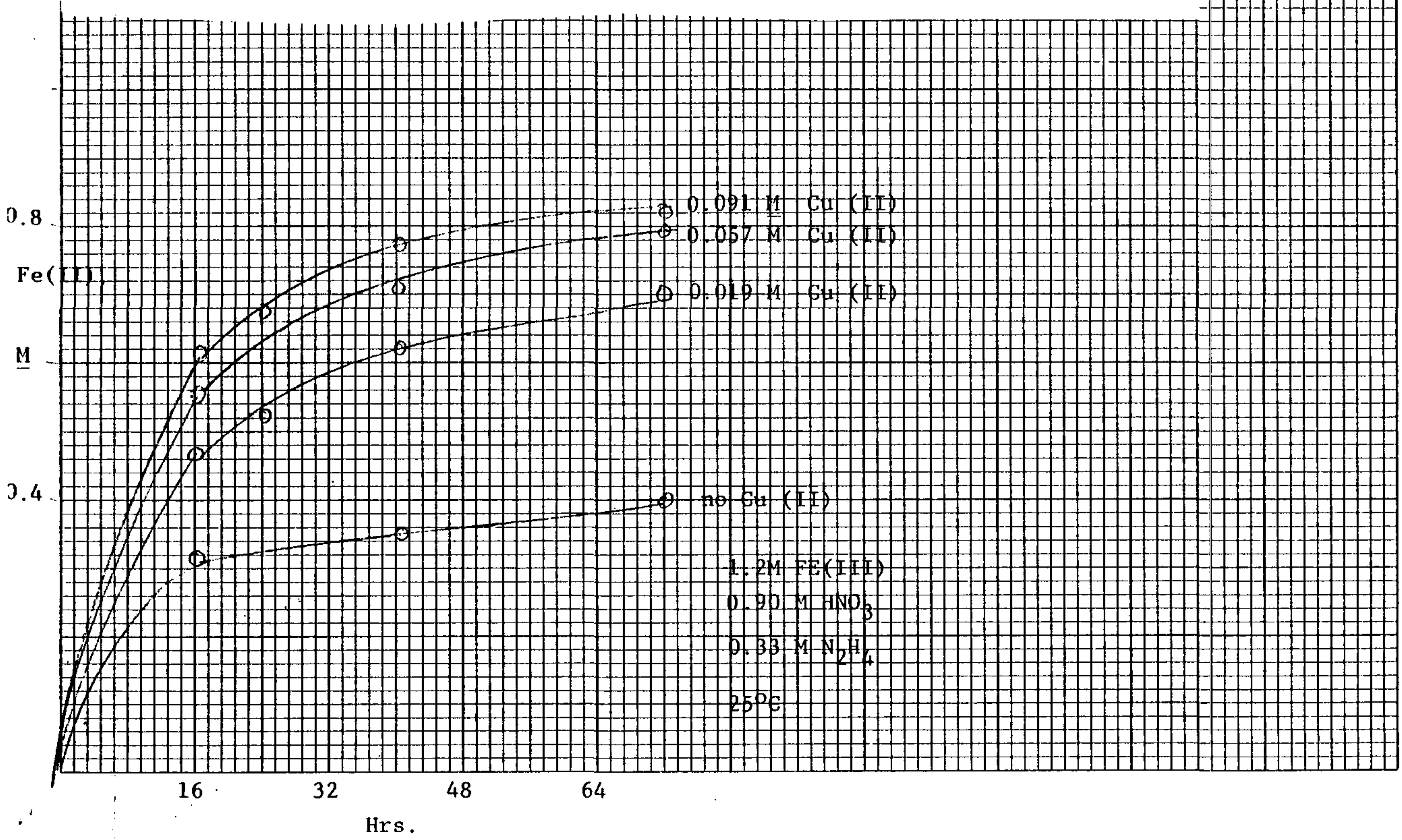
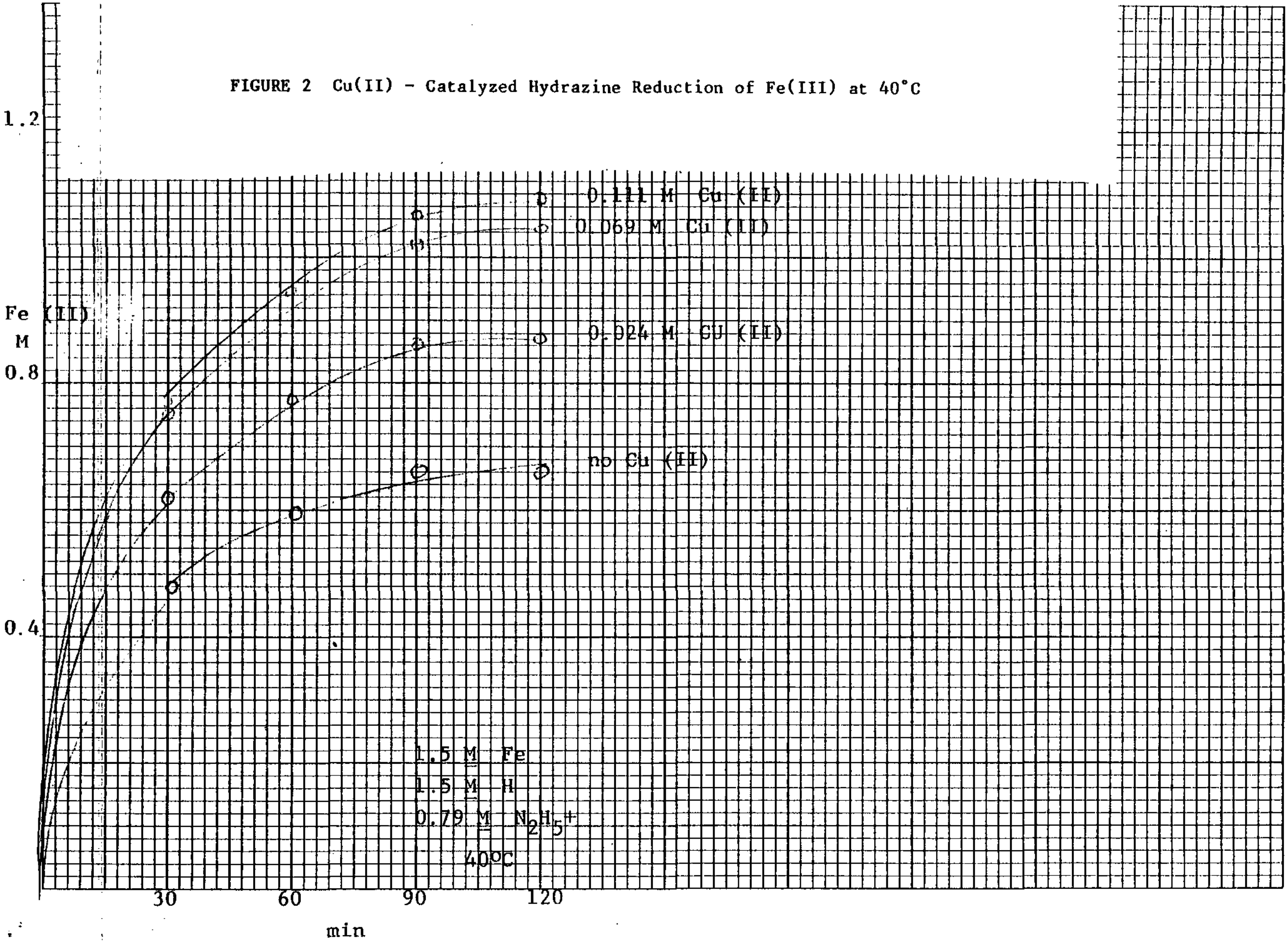


FIGURE 2 Cu(II) - Catalyzed Hydrazine Reduction of Fe(III) at 40°C



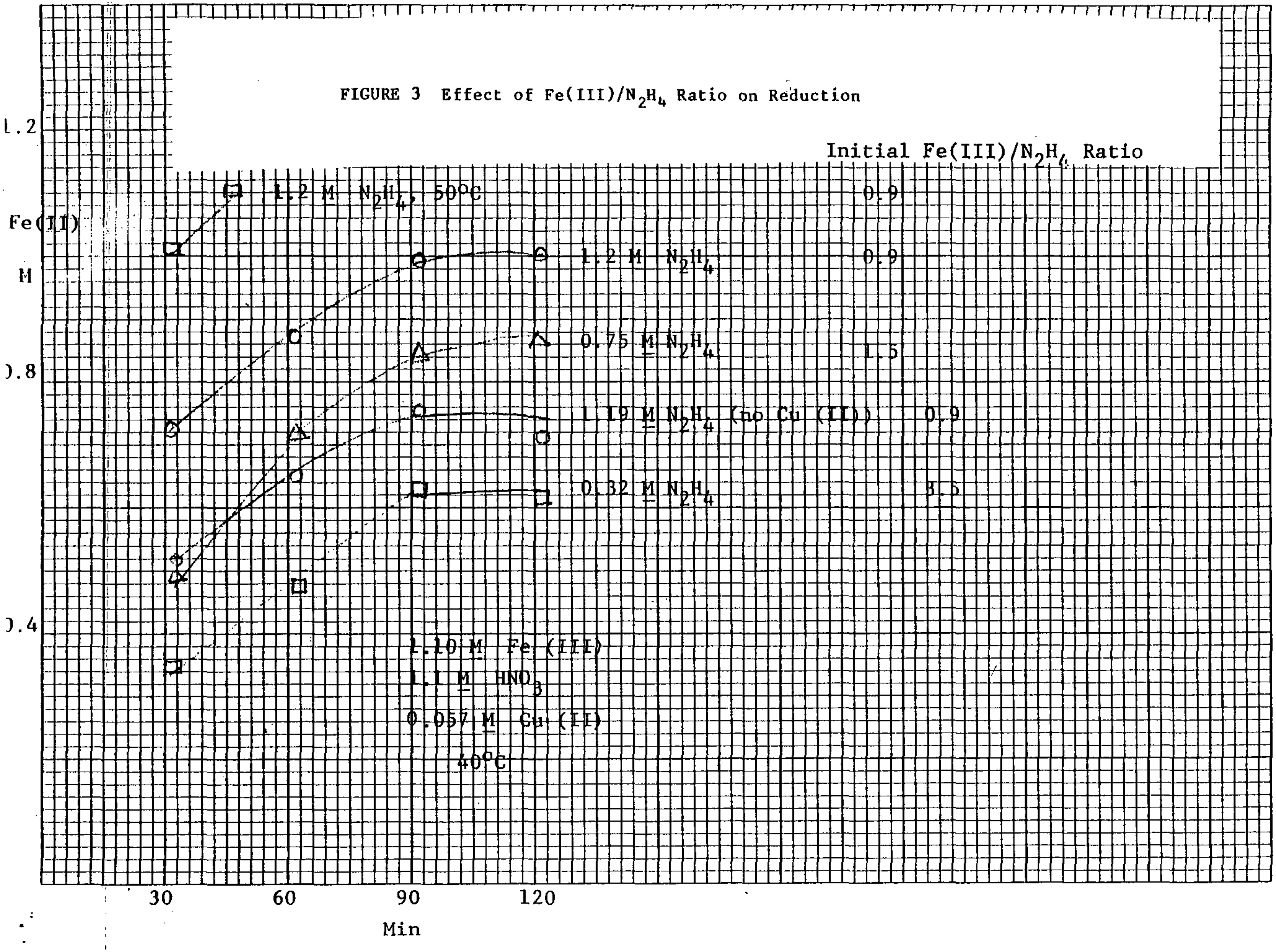


FIGURE 3 Effect of Fe(III)/N_2H_4 Ratio on Reduction

Figure 4 Effect of HNO_3 on Fe(II) Preparation