DECOMPOSITION OF HYDRAZINE IN PRESERVED BOILERS[1]

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ABSTRACT

A detailed study was carried out in the R&D Center laboratory at Al Jubail using bench top experimental set up to investigate the decomposition of hydrazine in preserved boilers. Effects of temperature and the presence of trace concentrations of metal oxides on the decomposition of hydrazine were determined by monitoring hydrazine and ammonia concentrations in hydrazine solutions kept in contact with trace metals for periods of l-60 days. This report describes the details of the study, discusses the results and proposes some recommendation for consideration during boiler preservation.

INTRODUCTION

Hydrazine and sodium sulfite are the most widely used chemical oxygen scavengers for boiler feed water. Though sodium sulfite reacts with dissolved oxygen at a faster rate even at low temperatures it increases the dissolved solids in boiler water and causes loss of thermal energy due to the requirement of increased frequency of blow downs to reduce the solid contents. Decomposition of sodium sulfite also becomes significant at boiler pressures above 950 psig and hence not used in high pressure boilers. In comparison hydrazine does not contribute to the dissolved salt contents of the boiler water. Hydrazine is slightly volatile but starts to decompose to ammonia at

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high temperatures reducing its efficiency as oxygen scavenger. In comparison with sodium sulfite hydrazine reacts with oxygen slowly and the kinetics of reaction increases as temperature increases.

Hydrazine may be lost from the boiler water by a variety of reactions as shown below:

(a) In the presence of oxygen,

$$N_2H_4 + O_2 \longrightarrow 2H_2O + N_2 \qquad (1)$$

(b) At high temperature or in the presence of catalysts:

$$3N_2H_4 \dashrightarrow N_2 + 4NH_3 \qquad (2)$$

Or

$$2N_2H_4 \dashrightarrow N_2 + 2NH_3 + H_2 \qquad (3)$$

(c) In the presence of metal oxides,

$$N_2H_4 + 6Fe_2O_3 \longrightarrow 4Fe_3O_4 + 2H_2O + N_2 \qquad (4)$$

$$N_2H_4 + 4CuO \dashrightarrow 2Cu_2O + 2H_2O + N_2 \qquad (5)$$

Considering some of the disadvantages of sodium sulfite and hydrazine as noted above various all volatile amines such as diethyl hydroxylamine, cyclohexylamine, morpholine and some filming amines such as octadecylamine have been successfully used for high pressure boiler water treatments.

Since 1982 in all boilers under operation in the Phase-II of SWCC Desal/Power plants in Al Jubail, hydrazine has been successfully used as oxygen scavenger with coordinated phosphate treatment to control pH and scale formation. Phase-II A and B areas have 5 BTG units each and two spare boilers, one on each area. The spare boilers are usually kept under long term preservation under wet storage condition. The boiler parts are filled with DM water containing 300-500 ppm hydrazine and a nitrogen atmosphere is maintained above the water level. Hydrazine concentration is monitored periodically and maintained at the required concentration by topping up when needed.

During a prolonged period of Jan. 89 to June, 92, boilers #66 and 86 in Phase-II A and B, respectively, were under long term preservation. Periodic analysis of the boiler water revealed a dramatic drops in hydrazine concentrations. Frequent addition of hydrazine was required to maintain its concentration at the required level. Fig. 1 indicates the variation of hydrazine level in boiler #66 during this period. Despite frequent topping up with fresh addition of hydrazine (indicated by arrows in Fig. 1. loss of hydrazine continued to occur. Analysis revealed the presence of ammonia in substantial quantities in the boiler water.

The incidence caused serious concern as hydrazine is not expected to show such rapid decomposition at low temperatures unless an active surface or ionic impurities that can catalyze the decomposition reaction is present. Traces of copper and iron, normally found in the solution at less than 10 PPb, are not considered to be sufficient to cause decomposition of such large amounts of N_2H_4 Source of Cu is from the corrosion of Cu/Ni heat exchanger tubes used in H.P. heaters as well as the brine heaters of the SW desalination plants. To overcome the problem efforts were made to find an alternative chemical for long term preservation. Several proprietary chemicals, claimed to be “hydrazine alternatives”, were evaluated based on informations from the suppliers. A chemical with the trade name “Betz Layup-1”, manufactured by Betz, USA was tested in boiler #66. For a period of 4 months (Aug-Dec. 1991, see Fig. 1. the boiler was preserved with 2000-3000 ppm of Betz Layup-l and nitrogen blanketing. Two corrosion coupons (one mild steel and one copper) were installed in the steam drum. Periodic analysis of DO, iron and copper in the drum water was carried out during this period. After 4 months the boiler was drained and the steam drum was inspected, The condition of the drum was found to be good and coated with a black film of magnetite. The corrosion rates determined with test coupons were very low (< 0.1 mpy).

After draining Betz Layup-l the boiler was subsequently preserved in hydrazine (<300 ppm). An interesting observation was subsequently noted - after the Betz Layup-l treatment, hydrazine concentration in the boiler water did not show significant reductions, as was the case before the treatment. However, copper contents in the preservation water showed significant increases (Fig. 1).

The incident was reported to the SWCC O&M Seminar conducted at Al-Jubail in April 1992 by Mr. Ghazzai Al Mutairi, Plant Chemist, Al Jubail Plant and a co-author of this report. The report generated considerable interest and the Engineering Department, SWCC (EP) suggested in their letter dated 5 July, 1992 that the R&D Center conduct further studies to confirm the findings and suggest possible alternative measures. R&D Center has subsequently conducted a series of tests using bench top experimental set up. The details of the tests and the results are described below:

EXPERIMENTAL

Degradation of hydrazine at various conditions, expected to be present in Al-Jubail desal power plant boilers, were studied in the R&D laboratory.

(a) Test Procedures

300 ml volumes of hydrazine solution at initial concentrations of about 300 ppm prepared in ultrapure demineralized water were used during the studies. Amber colored bottles, tilled with the solution without leaving voids on the top, were maintained at the experimental temperatures in an incubator for various contact periods. Hydrazine, ammonia and pH were monitored after frixed contact times under the following conditions:

(1) Hydrazine kept at 45^{o} C for 1 - 60 days to obtain reference data. 45^{o} C was chosen for all experiments so as to bring the temperature closer to the steam drum condition that may be prevalent in summer.

(2) Hydrazine containing 100 ppb Fe^{+++} ions as ferric chloride. Temp = 45^{o}C, contact time = 1 - 60 days.

(3) Same as above, but with 100 ppb Cu^{+} ions, as cupric chloride, in place of Fe^{+++} ions.

(4) As above, but the solution was kept in contact with about 10 gr of carbon steel turnings which was allowed to corrode for 3 - 4 days in the open air before the experiment.

(5) Same as in 4. But precorroded Cu/Ni 70/30 turnings were used instead of iron turnings.

(6) Experiments described in 4 & 5 above were repeated at 20, 30 and 45^{o} C, and at 14 days contact time to study the effect of temperature on the decomposition rate.

(7) 50x25x2 mm specimens of carbon steel and Cu/Ni alloy, precorroded, were immersed in 1000 ppm Betz Layup-l for one week. The specimens were removed, rinsed with DM water and kept in contact with 300 ppm hydrazine in separate bottles for one week. Hydrazine decomposition, and Cu , Ni and Fe and Fe ions in the solutions were determined.

(b) Analytical Procedures

Hydrazine was estimated iodometrically by titrating the sample against standard sodium thiosulfate using starch as indicator [Ref.l]. The titration was carried out after buffering the sample to pH 7.0-7.2 by the addition of sodium bicarbonate.

Ammmonia in hydrazine was estimated by nesslerization method after oxidizing hydrazine completely by hydrogen peroxide in boiling acid solution with iodine as catalyst [Ref.2]. The nesslerized sample was analyzed at 410nm using a Shimadzu UV-2100S UV- visible spectrophotometer.

Metal ions were determined by Graphite Furnace AA spectrometry, after making appropriate dilutions wherever necessary.

RESULTS AND DISCUSSIONS

Degradation of pure hydrazine at 45o C in the absence of any catalysts, is shown in Fig. 2. As the solutions were kept in amber colored bottles and inside an incubator possibility of degradation due to ultraviolet radiation was excluded. While about 3% degradation was observed after 24 hrs, 25 and 40% of the original hydrazine was found to have decomposed after 30 and 60 days, respectively. Hydrazine could decompose through reactions l-3, to give nitrogen and ammonia. But these reactions in the absence of O_2, catalysts etc. appear to be slow as found in Fig. 2. Monitoring of ammonia does not appear to provide quantitative data of the decomposition reactions. Though traces of NH_3 was detected in the test solutions concentrations were less than those expected by equations 2 and 3. This may also be due to the escape of some NH_3 during handling etc. and pH changes were too low to be of any significance.

Decomposition of hydrazine in the presence of ferric ions (Fe+= 100 ppb) is shown in Fig. 3.

The results show that decomposition of hydrazine is not catalyzed by the presence of Fe^{+++} ions, with losses of 3, 22 and 22%, after 1, 30 and 60 days contact times, respectively. The magnitude of decomposition is similar to that found in the blank experiments (Fig. 2). But in the presence of Cu^{++} ions (Fig.4) decomposition was found to be quite rapid and quantitative within 60 days. Here again the ammonia content did not indicate proportionate increase. But the presence of substantial amount of ammonia (21.7 ppm) after 60 days contact time indicates that the decomposition in the presence of cupric ions proceeds through a catalytic reaction.

Experiments with precorroded iron and Cu/Ni turnings are shown in Figure 5 and Figure 6 respectively. The decomposition in the presence of Cu/Ni turnings was much more rapid and quantitative than found in the presence of iron turnings, Both iron and Cu/Ni turnings exhibited better catalytic property than their respective ions in solution. It appears that the thin oxide films on the surface of the corroded alloy turnings provide a more favourable catalytic environment than the dissolved ions, though copper even in the ionic form exhibited strong catalytic property.

To study the effect of temperature on the decomposition reactions, $N_2 H_4$ solutions were kept in contact with rusted iron and Cu/Ni turnings for 14 days at 20, 30 and 45oC. The results (Fig. 7 and Fig. 8) show that the decomposition of N_2H_4 depends significantly on the temperature and increases proportionately as the temperature increases. The effect was quite dramatic in the presence of Cu/Ni turnings while in the case of iron turnings the increase was marginal.

Due to the instability of hydrazine used for preservation of the Al Jubail boilers, a new product, Betz Layup-1, was used for a period of time. After draining out this chemical, the boiler drum was inspected and was found to have a uniform black coating of magnetite. The boiler was then filled with hydrazine and subsequent analysis indicated that hydrazine degradation had significantly reduced. To check this, small test specimens of iron and Cu/Ni alloy, previously corroded by exposing to the atmosphere for a few days, were first immersed in Betz Layup-l solution (1000 ppm) for a week, removed and rinsed in DM water, and then immersed in 300 ppm $N_2 H_4$ for a week at 45^0C. The results Table-l indicate that Betz Layup-l treatment did not have noticeable effect on N_2H_4 degradation. While approximately 87% of N_2H_4 was found to be decomposed in the presence of Cu/Ni, only 20% degradation occurred in the presence of Fe. These results are similar to those obtained in previous tests conducted without Betz Layup-l treatment. The results also indicate that Betz Layup-l is slightly aggressive to the alloys, dissolving Cu, Ni and Fe from the specimens. In comparison, attack by hydrazine was milder, as indicated by much lower concentrations of the metal ions in the solution.

CONCLUSIONS

The studies indicate that both cupric ions in solution and CuO film on rusted Cu/Ni turnings significantly enhance the decomposition of hydrazine. Decomposition is much faster at 45° C than at lower temperatures. Though Fe does not influence the degradation of N_2H_4, its oxides formed on the rusted carbon steel surface appear to have significant effects on the kinetics of decomposition. Wide variations in the ammonia concentrations did not help to suggest which of the several reactions proposed above play a prominent part in the decomposition. But the presence of high concentration of ammonia in N_2H_4 solution degraded in the presence of Cu^{++} ions and the oxides on the alloy turnings indicate that these species might be acting as catalysts rather than taking part in chemical reactions resulting into stable compounds such as Fe_3O_4 or Cu_2O as indicated by reactions 4 and 5.

A treatment with Betz Layup-l did not improve the stability of hydrazine as indicated by our studies. In addition, this chemical appears to be aggressive to the alloys and should be used with caution. The improvement in the stability of hydrazine found in boiler #66 after Betz Laynp-l treatment may possibly be explained as follows:

Traces of Cu^{++} ions present in boiler water originating from the Cu/Ni tubes in the desal brine heaters or boiler H.P. heaters could deposit on the carbon steel internals of the boiler as copper is a nobler metal than carbon steel. As the boilers have been in service for a long period of time, thin layers of Cu or CuO might have been formed on the surface of the boiler parts that had acted as catalysts enhancing N_2H_4 decomposition. When the boiler was treated with Betz Laynp-l it acted in two possible ways : (a) removed all copper deposits from the boiler surface by dissolution or dispersion as indicated by high increase of copper content in the solution phase, thereby diminishing the catalytic activity; (b) Betz Laynp-l helped to form a passive magnetite layer on the metal surface, as indicated by the presence of a black film on the surface of the steam drum. Both of these will virtually stop decomposition of the N_2H_4 if proper nitrogen blanketing is maintained.

RECOMMENDATIONS

(1) Regular monitoring of N_2H_4 copper and iron contents in the preserved boilers needs to be continued.

(2) If decomposition of N_2H_4 is unusually high cleaning of the boiler internals should be considered to remove the corrosion deposits. A short period of Betz Layup-l treatment appears to be useful in removing any possible Cu deposits

from the boiler internals as well as to provide passivation. Further work in these lines should be done with caution and the R & D Center Should be involved to carry out detailed studies.

(3) If the boiler has been under long time preservation using N_2H_4 care Should be taken to drain the boiler before returning to load, to prevent ammonia getting into brine heaters causing corrosion of Cu/Ni tubes.

REFERENCES

1. Encyclopedia of Chemical Technology, Vol. 12, III Edit. p.53.

2. ASTM Power Plant Water Analysis Manual sponsored by ASTM Committee D-19 on water; I Edit (1984) p.27.

Table 1:N2H4 decomposition after Betz Layup treatment

Initial Concentrations: N2H4 = 245 ppm

NH3 = 0.95 ppm

pH = 9.6

Specimens	Betz Lay up Filtrate	Analysis in Hydrazine solution			
		N2H4	NH3	pH	Metals
Cu/Ni	Cu =1.95 ppm Ni =0.08 ppm	30 ppm 30 ppm	105.8 ppm 106.1 ppm	10.2	Cu=0.04ppm Ni =0 ppm
Carbon Steel	Fe =1.15 ppm	196 ppm 196 ppm	40.9 ppm 41.3 ppm	10.0 ppm	Fe=0.28 ppm

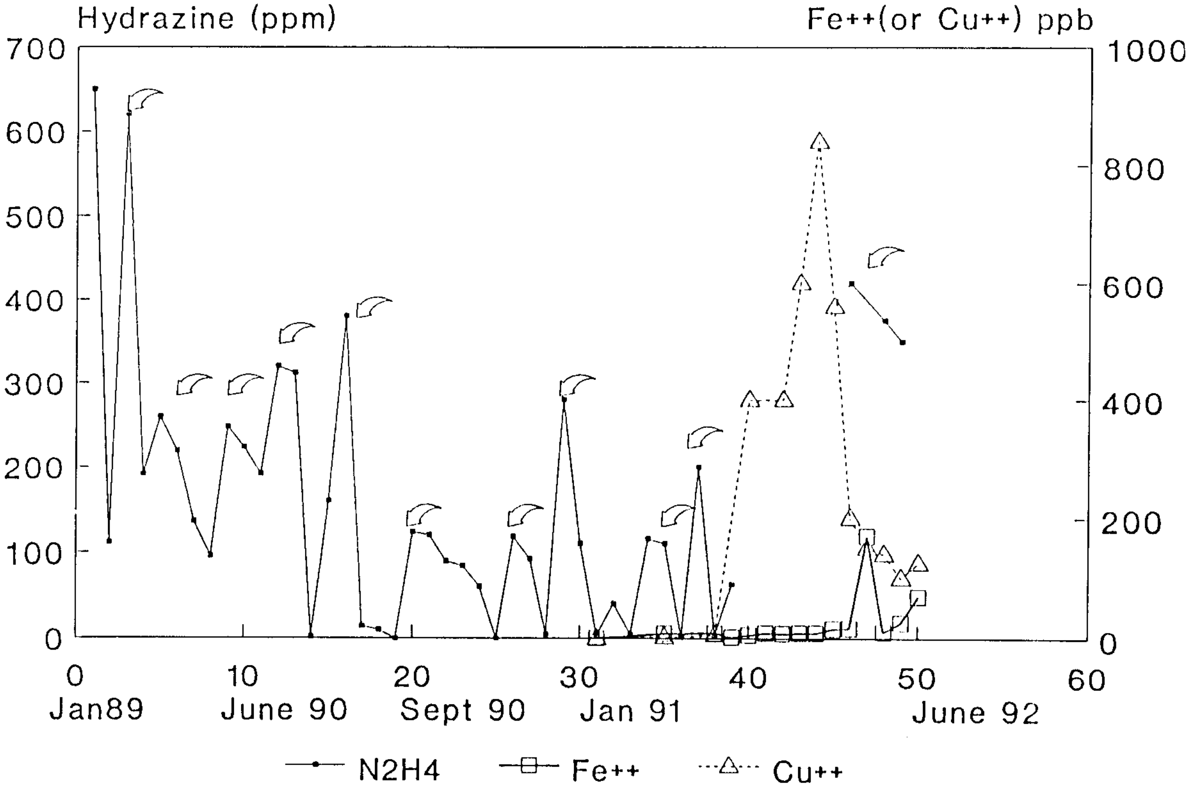


Fig.1 Analysis of N2H4 in Boiler #66, Al Jubail

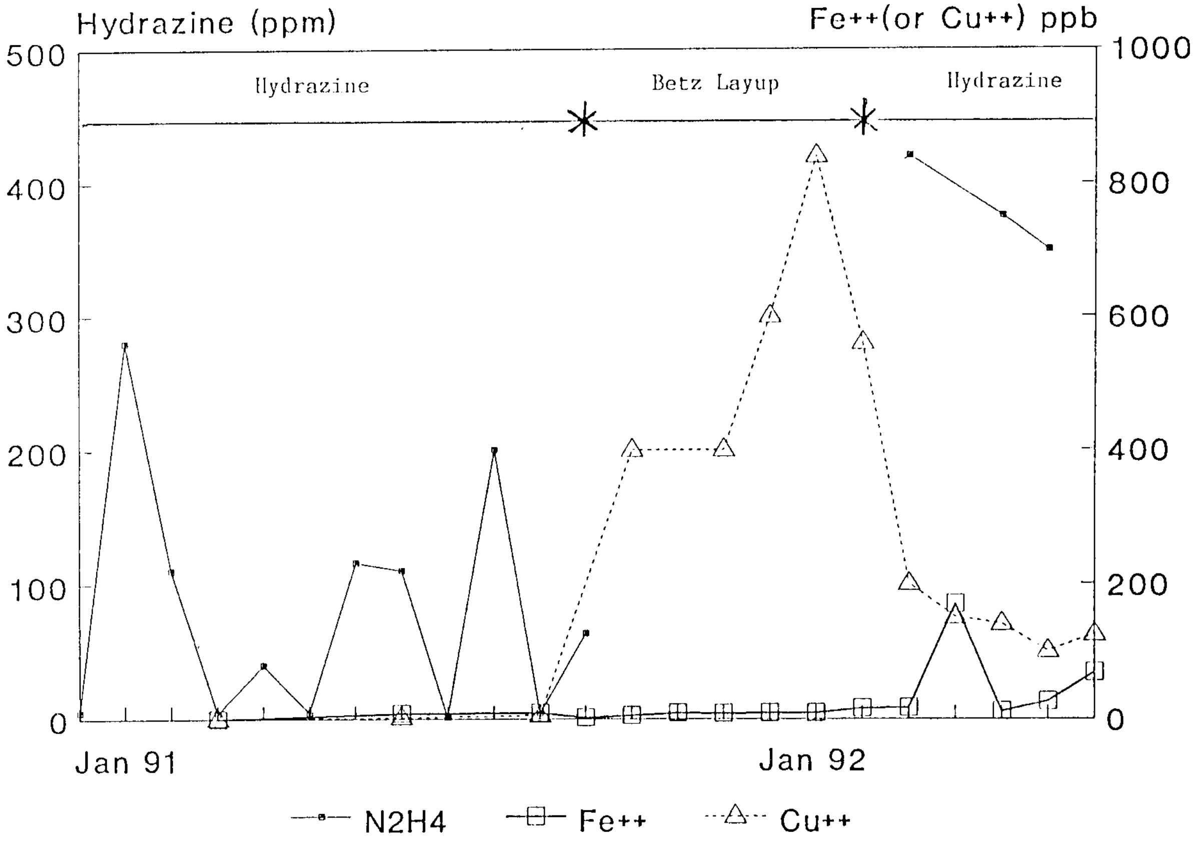
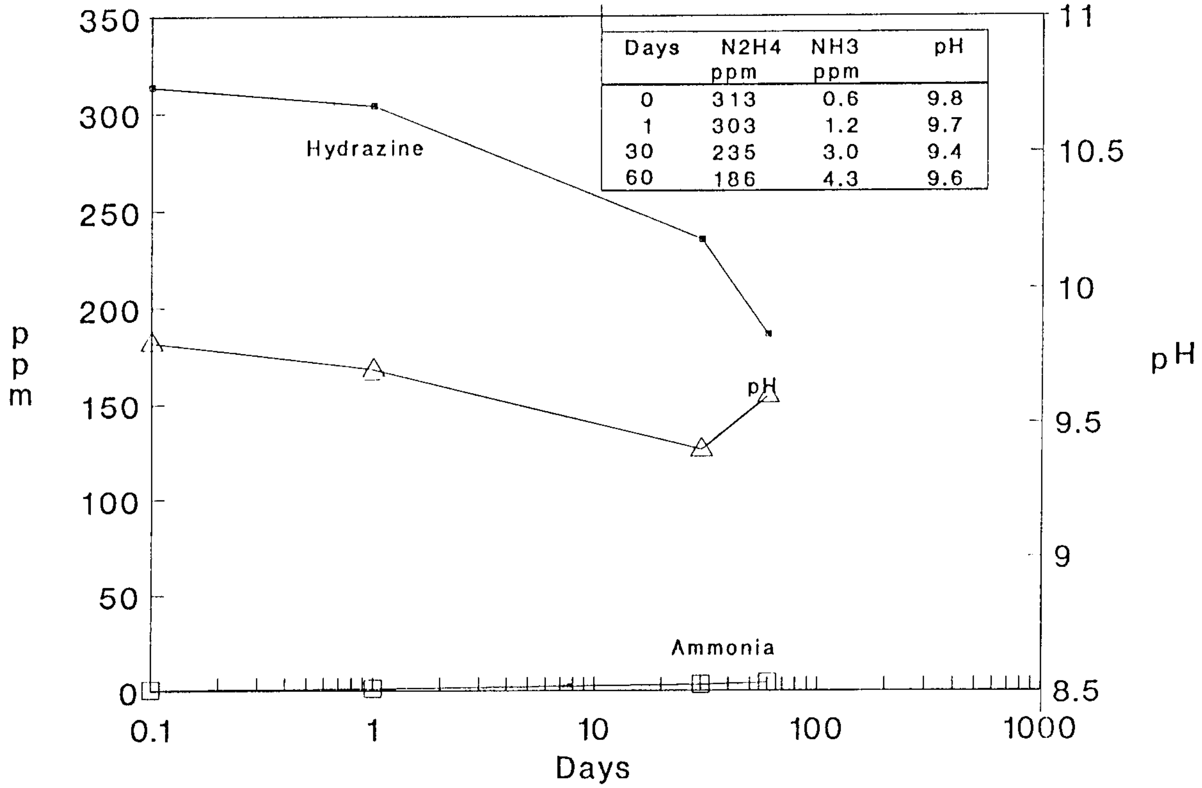
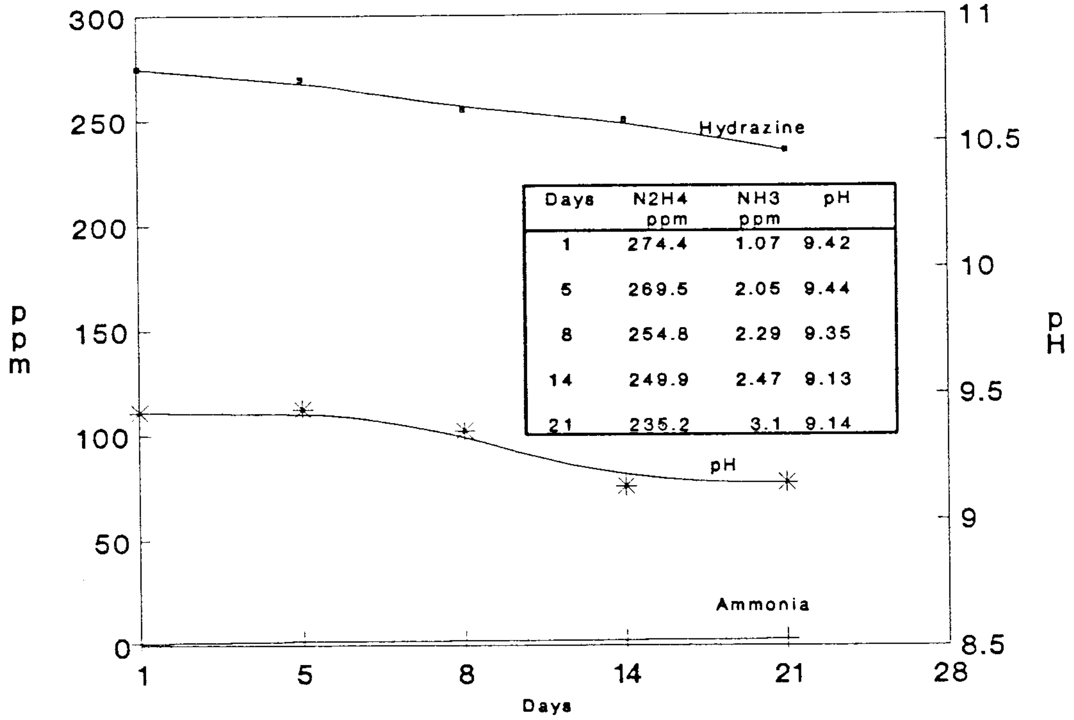


Fig.1 (Contd.) Deatails for period after Jan 91



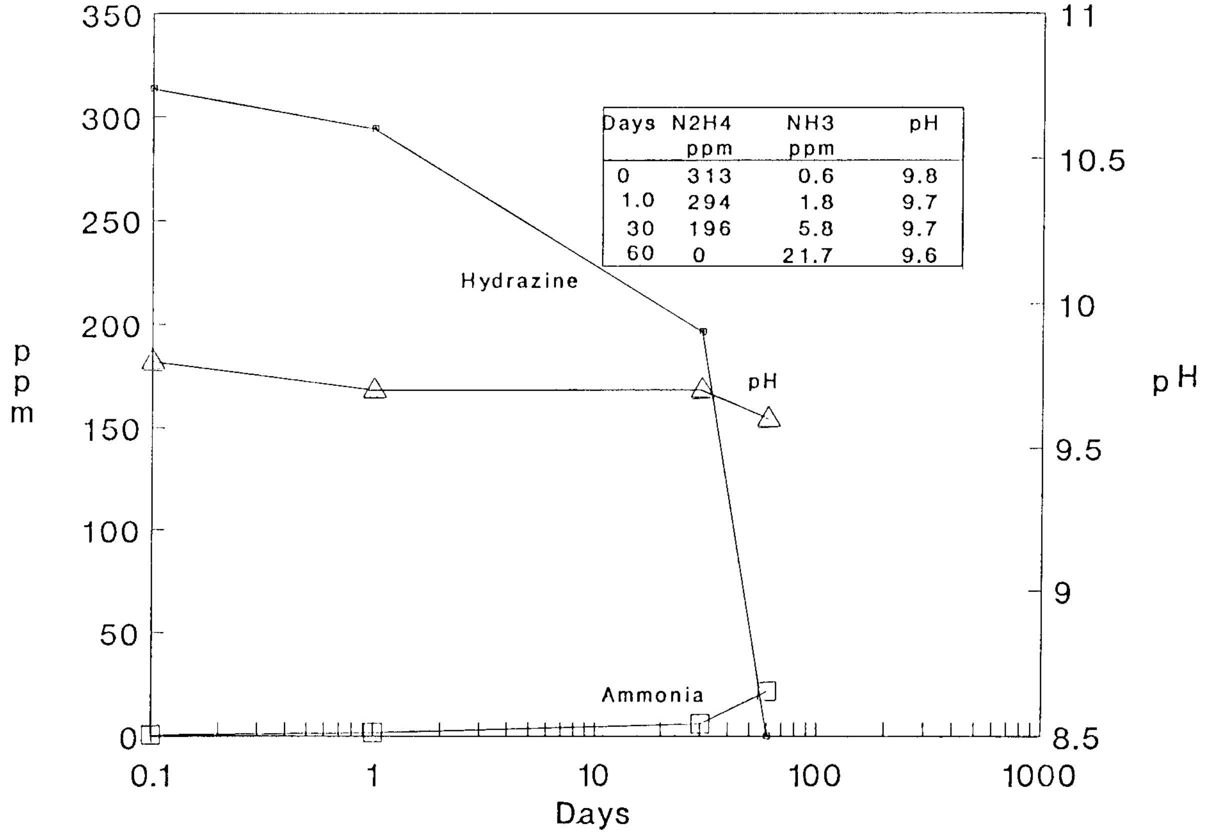
Days	N2H4 ppm	NH3 ppm	pH
0	313	0.6	9.8
1	303	1.2	9.7
30	235	3.0	9.4
60	186	4.3	9.6

Fig.2 Hydrazine degradation vs contact time-Blank(45oC)



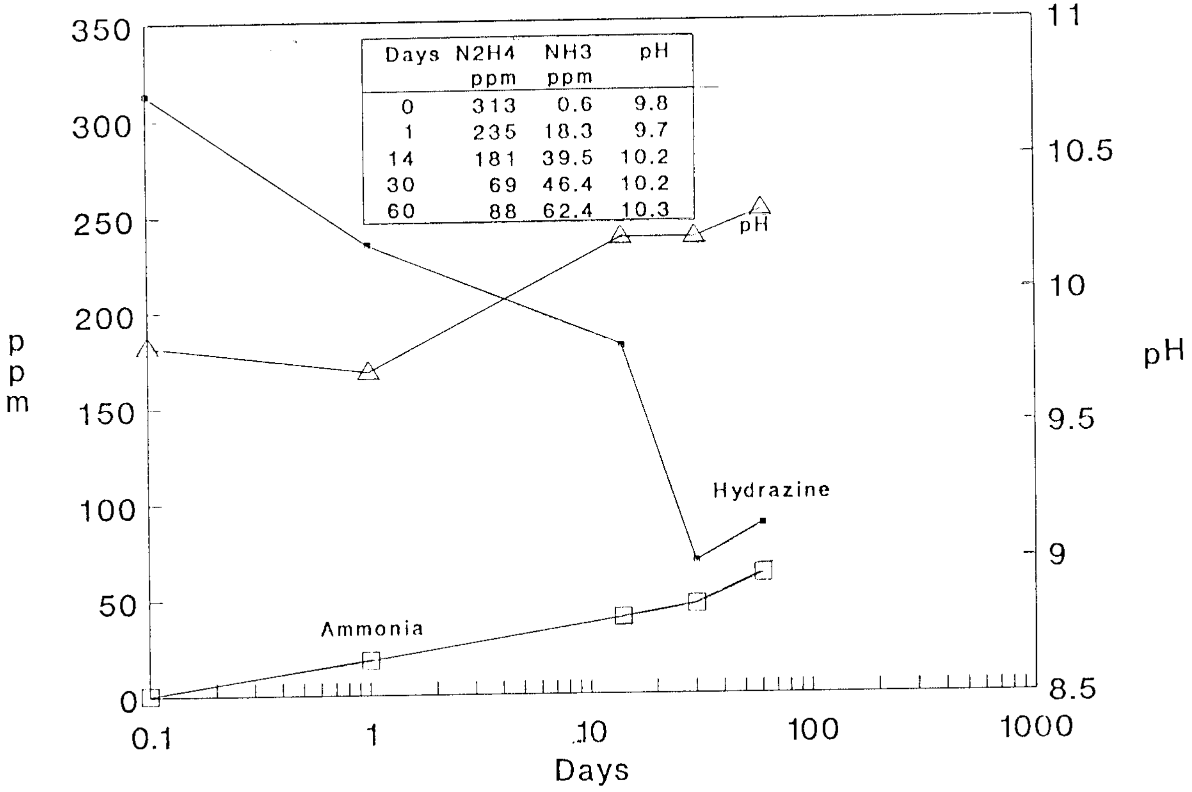
Days	N2H4 ppm	NH3 ppm	pH
1	274.4	1.07	9.42
5	269.5	2.05	9.44
8	254.8	2.29	9.35
14	249.9	2.47	9.13
21	235.2	3.1	9.14

Fig.3 Hydrazine degradation vs contact time(Fe+++) 45 oC



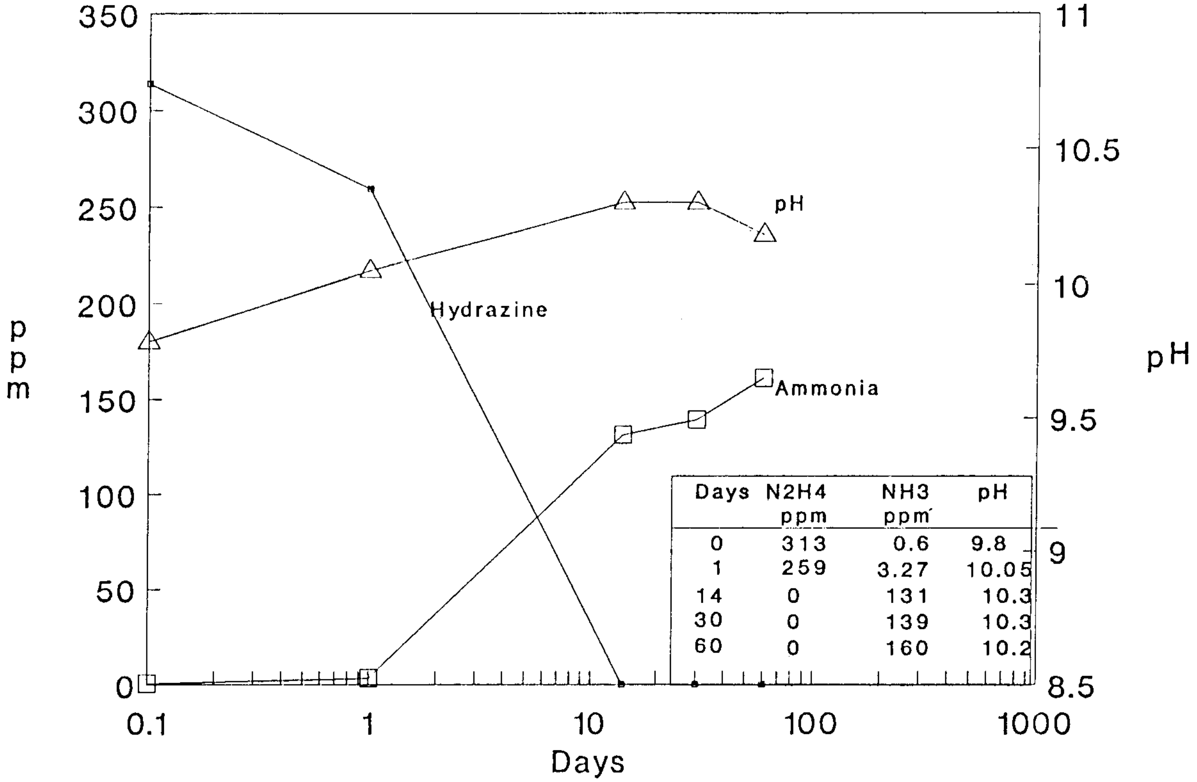
Days	N2H4 ppm	NH3 ppm	pH
0	313	0.6	9.8
1.0	294	1.8	9.7
30	196	5.8	9.7
60	0	21.7	9.6

Fig.4 Hydrazine degradation vs contact time (Cu++) 45o C



Days	N2H4 ppm	NH3 ppm	pH
0	313	0.6	9.8
1	235	18.3	9.7
14	181	39.5	10.2
30	69	46.4	10.2
60	88	62.4	10.3

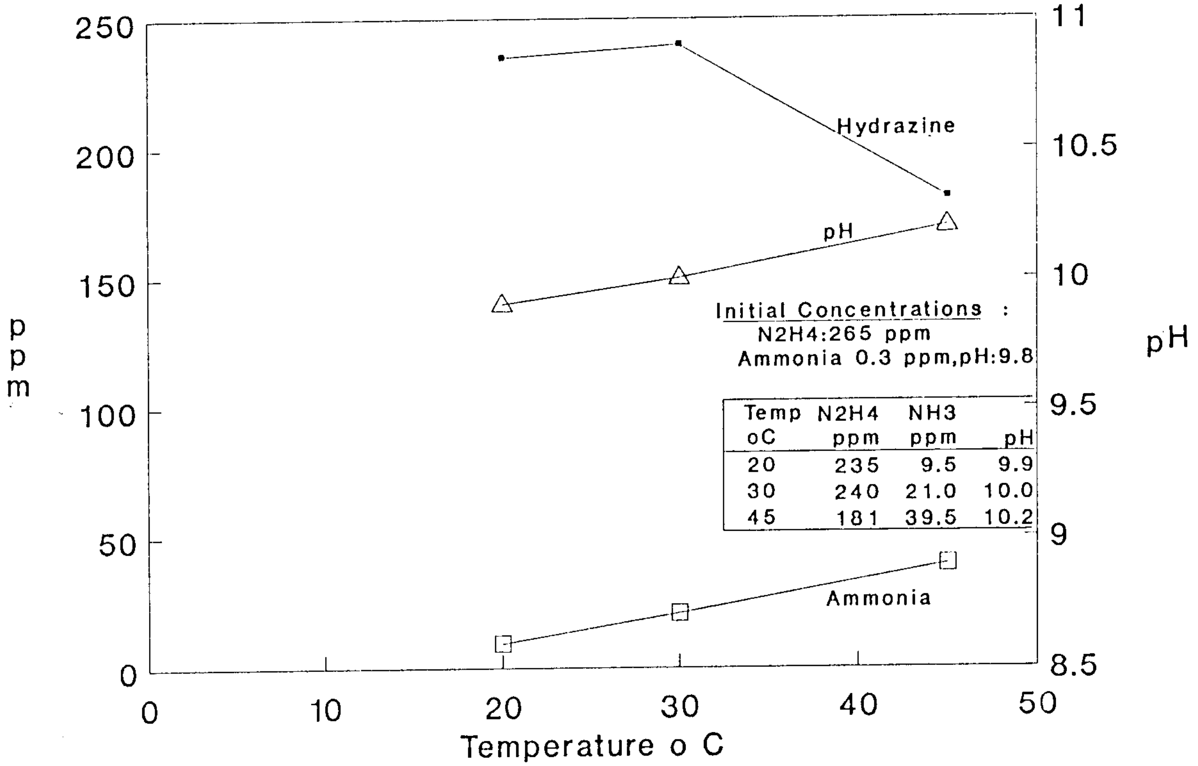
Fig.5.Hydrazine degradation vs contact time Fe (45oC)



Days	N2H4 ppm	NH3 ppm	pH
0	313	0.6	9.8
1	259	3.27	10.05
14	0	131	10.3
30	0	139	10.3
60	0	160	10.2

Fig.6 Hydrazine degradation vs contact time -Cu/Ni (45oC)

Fe

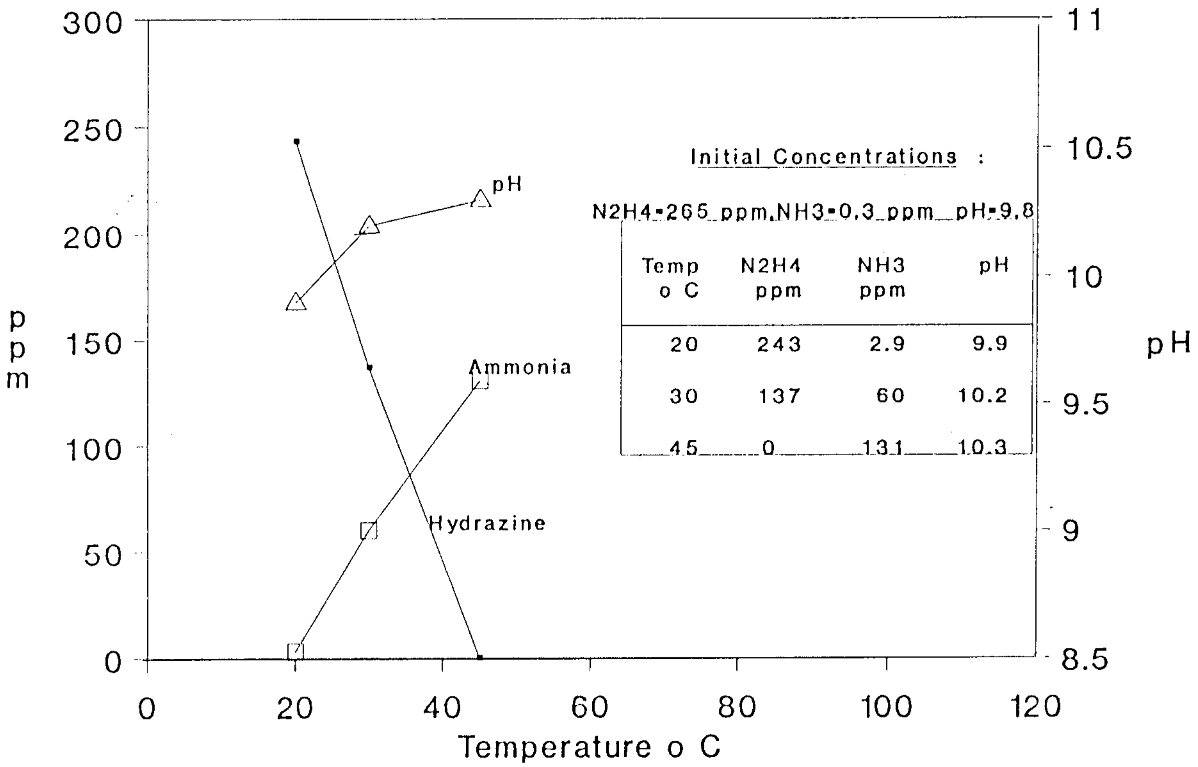


Initial Concentrations :
N2H4:265 ppm
Ammonia 0.3 ppm,pH:9.8

Temp oC	N2H4 ppm	NH3 ppm	pH
20	235	9.5	9.9
30	240	21.0	10.0
45	181	39.5	10.2

Fig.7 Hydrazine degradation vs Temperature

Cu/Ni



Initial Concentrations :

N2H4=265 ppm,NH3=0.3 ppm pH=9.8

Temp o C	N2H4 ppm	NH3 ppm	pH
20	243	2.9	9.9
30	137	60	10.2
45	0	131	10.3

Fig 8. Hydrazine degradation vs Temperature