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GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

DESTRUCTION OF NITRIC ACID IN PUREX PROCESS STREAMS BY
FORMALDEHYDE TREATMENT

by

S. V. Kumar, M. N. Nadkarni, P. C. Mayankutty,
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ABSTRACT

Efficiency of destruction of nitric acid in Purex Process streams with formaldehyde has been studied as a function of initial acidity, urexium concentration, rate of addition of formaldehyde and temperature in the range 6 - 0.5M acid. Guidelines are suggested for the accurate calculations of the volume of formaldehyde needed to effect the required change of acidity at 100°C. Sodium nitrite has been established as a "key" to initiate the reaction and water as an effective scrubber for collecting the acid fumes emanating from the reaction vessel.

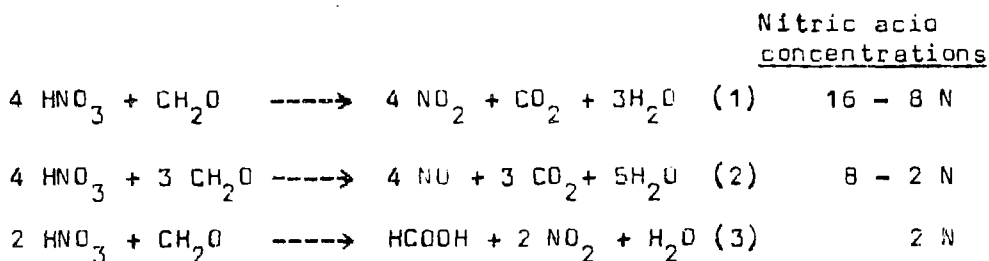
DESTRUCTION OF NITRIC ACID IN PUREX PROCESS STREAMS BY FORMALDEHYDE TREATMENT

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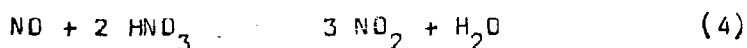
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1. INTRODUCTION

Destruction of nitric acid with formaldehyde had been known since long as an effective means of destroying nitric acid in Purex process solutions. T.V. Healy⁽¹⁻³⁾ from Harwell and later Evans⁽⁴⁾ and Forsman and Oberg⁽⁵⁾ from Hanford had extensively studied the mechanism and kinetics of the reactions between nitric acid and formaldehyde and the extension of the results to pilot plant scales for the denitration of Purex radioactive wastes. The reaction was reported by Healy as different equations depending upon the concentration of nitric acid reacting. The equations are:

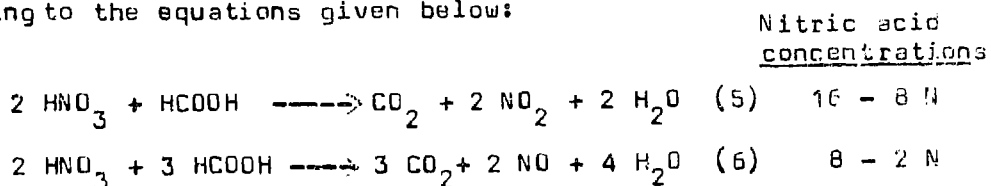


the equations (1) and (2) are linked by the equilibrium,



Below 2N nitric acid the formation of formic acid becomes significant particularly when the nitric acid concentration falls below 0.5 N.

Formic acid also was reported to be reacting with nitric acid according to the equations given below:



Efficiency and rates of these reactions are much low comparing to those of formaldehyde with nitric acid and hence formaldehyde is always preferred for the purpose of acid destruction.

Presence of ferric or uranyl nitrate catalyses the speed of the reactions of the concentrated or dilute nitric acid with both formaldehyde and formic acid. At low acidities these salts also catalyse the oxidation of formaldehyde and formic acid so that the amount of formic acid present in solution after reaction is negligible⁽²⁾.

The range of nitric acid concentrations that is of interest in the Purex Process Solutions is 1-6 M. According to equation (2) the destruction of nitric acid takes place at the ratio of 1.33 mole of nitric acid per mole of formaldehyde added. But this is a gross approximation and the ratios may vary widely depending upon the initial acid concentration and the temperature at which the reaction was allowed to take place. Therefore, addition of formaldehyde on the basis of equation (2) will yield product solutions with acidities far off from the set target in this range. This will cause unnecessary waste of time, chemicals and set in other complications.

The reaction between formaldehyde and nitric acid is exothermic and under certain conditions could be quite violent. Therefore maximum care must be taken to conduct the operation with strict control over the reaction especially while treating solutions from fuel reprocessing plants containing radioactive materials. Detailed informations regarding the efficiency of the reaction at the operating temperature and the initial nitric acid concentrations, rate of addition of formaldehyde to the reacting vessel and the magnitude of induction periods at the given conditions should be provided to the operator for the most effective and trouble-free utilisation of the process.

The present studies were undertaken to collect further data with the above points in mind. Studies were carried out in the nitric acid molarity ranging from 0.5 to 6 and temperatures 90 and 100°C. At 80°C and below the induction period is quite significant and hence considered unsafe for operation. Ratios of the mole of nitric acid destroyed per mole of formaldehyde added were determined in this range and the effects of temperature and the rates of formaldehyde addition on this ratios were studied. Destruction of nitric acid in $\text{UO}_2(\text{NO}_3)_2$ solutions in the range of 50 - 300 mg. U/ml was also studied in a similar manner. Induction period was noted in each case and the effect of the presence of sodium nitrite in the reaction mixture on the induction period was also investigated. An empirical formula to calculate the volume of formaldehyde required to change the concentration of the acid from an initial to a final value was suggested and the accuracy of the formula was tested experimentally.

2. EXPERIMENTAL

All chemicals used were AR grade, the aqueous formaldehyde used was 37 - 40% having a methanol content of 11 - 14% w/w. Nitric acid was used as such without any effort to remove the dissolved nitrous fumes that may be present. 100 ml of pure nitric acid or uranyl nitrate in nitric acid was placed in a 500 ml, three necked round bottom flask and heated on an isomantle to the required temperature; known amounts of formaldehyde were added from a burette at a definite flow-rate while maintaining the temperature steady. Normally a simmering period of 60 minutes was given after the addition of formaldehyde was completed. The reaction mixture was agitated with a jet of air and the evolved gases were passed through a Leibig's condenser and bubbled through a series of alkali or water traps (fig.1). Nitric acid was estimated titrimetrically and the free acidity in uranyl nitrate solution was determined by potentiometric titration in

neutral oxalate medium using a Beckman pH metre. Formaldehyde was analysed by oxidising with H_2O_2 in excess of standard sodium-hydroxide and back titration of the alkali with standard sulphuric acid⁽⁶⁾.

3. RESULTS AND DISCUSSIONS

3.1 Pure Nitric Acid Solutions

Destruction of nitric acid in the range of 6 - 0.5 M in steps of 1M was studied at 90°C, 100°C and the boiling point and the results are presented in table 1. It can be observed that the rates of addition of formaldehyde and the temperatures above 90°C do not have significant influence on the efficiency of destruction. However as the temperature goes down the efficiency tends to decrease and at temperatures lower than 90°C, the efficiency could be too low which is not favourable. The extent of destruction considerably varies at each step of the range studied as is evident from columns 7 and 8 of table 1.

On the basis of the data in table 1, the following formula can be employed to calculate the amount of formaldehyde needed to bring about a change of acidity from a known initial to a required final concentration at 100°C and in the absence of any loss of acid by evaporation.

$$\text{Formaldehyde required in ml} = \frac{\frac{X(6-5)}{1.65} + \frac{X(5-4)}{1.43} + \frac{X(4-3)}{1.36} + \frac{X(3-2)}{1.32} + \frac{X(2-1)}{1.07}}{M_{HCHO}}$$

where X = total acid in m Moles to be destroyed at the individual steps of 6-5 M, 5-4 M, etc.

M_{HCHO} = Concentration of formaldehyde in M.

Exemple:-

Calculate the amounts of formaldehyde required to bring down the acidity of (a) 100 ml 5.94 M HNO_3 to 1.09 M and (b) 100 ml of 4.18 M HNO_3 to 1.17 M without any reduction in volume.

a) Volume of formaldehyde required:

$$= \frac{94}{1.65} + \frac{100}{1.43} + \frac{100}{1.36} + \frac{100}{1.32} + \frac{11}{1.07} \text{ mls.}$$
$$= \frac{12.54}{12.54} \text{ mls.}$$
$$= \underline{\underline{22.85 \text{ mls}}}$$

b) Volume of formaldehyde required:

$$= \frac{18}{1.43} + \frac{100}{1.36} + \frac{100}{1.32} + \frac{83}{1.07} \text{ mls.} = \underline{\underline{19.1 \text{ mls.}}}$$

In the actual experiments volumes of formaldehyde required were 21.9 and 18.6 mls for (a) and (b) respectively. The errors are within acceptable limits.

As can be seen from table 1 induction periods at 90°C and above are sufficiently low. However, at lower temperatures the induction periods are quite considerable (fig.2) and it is this time delay which may be responsible for the reaction getting out of control. But if care is taken to bring up the temperature above 90°C before the commencement of formaldehyde addition, the reaction will become quite safe and smooth provided it is not added in bulk quantities. Though the rate of addition of formaldehyde does not influence the efficiency of destruction, it is quite necessary to maintain a steady flow-rate, possibly by way of a metering device, in order to avoid unnecessary accumulation of formaldehyde in the acid solution thereby causing explosive reactions.

It has been reported⁽³⁾ that passing NO₂ gas through the reaction mixture helps reduce the induction period. Present studies indicate that addition of sodium nitrite also has the same effect. It can be seen from fig.2 that the reaction can be 'forced' to start almost instantaneously by the addition of 0.015 M NaNO₂ solution even at 60°C.

As mentioned above the reaction is much slow at 1M and below due to the build up of formic acid (equation 3). In a separate study 25 ml of 1M HNO_3 was mixed with 2 ml formaldehyde at the boiling temperature and refluxed for different durations. The results were calculated as m Mole of nitric acid destroyed per ml of formaldehyde added (fig. 3). It can be seen that prolonged simmering period is required for the reduction of acidities to much lower values. Addition of NaNO_2 does not have much influence on the over all efficiency of destruction in this region but the simmering period can be reduced to a certain extent by its presence.

3.2 Uranyl Nitrate Solutions

Efficiency of acid destruction and induction period were determined with uranyl nitrate solutions as a function of Uranium concentration in the free acid range 5 - 0.5 M in steps of 1M. The results are given in table 2 and fig.4. It can be seen that the reaction starts almost instantaneously in uranyl nitrate solutions thereby demonstrating that uranium nitrate must be acting as a catalyst. At 1M acid the induction period was quite considerable, but the overall efficiency of destruction showed significant improvement in the presence of uranyl nitrate over pure 1M HNO_3 (fig.4). In the case of higher acidities also presence of uranyl nitrate enhances the ratios of acid destruction per formaldehyde added and these ratios increase as the uranium concentrations increase.

The amount of formaldehyde required to effect a change between two given acidities can be calculated, as in the case of pure nitric acid, by using the figures in column 4 of table 2.

The above experiments were conducted avoiding evaporation during the treatment. But during plant operations it is quite often necessary to adjust the acidity simultaneously increasing the uranium concentration to a certain level which necessitates a reduction in

volume of the product solution. Two relevant examples are (1) in Inter cycle evaporators where solutions containing 50 mg/ml U in 1 M HNO_3 have to be concentrated to 300 mg/ml U in 2 M HNO_3 and (2) Final uranium cycle where solutions containing 50 mg/ml U in 1M HNO_3 have to be converted to 300 mg/ml U in 0.6 M HNO_3 with a view to favouring the recovery of neptunium.

Experiments were conducted to determine the mole/mole ratios in such cases and compared the data with those of table 2. The results are given in table 3. Here, 100 ml each of uranium solution of known acidity was treated with formaldehyde in a three necked round-bottomed flask with one of the necks kept opened and heating continued until the required concentration of the product solution with respect to U was attained. No attempt was made to account for the reduction of acidity due to the loss of HNO_3 by way of direct evaporation as it is negligible. In the actual plant conditions where the treatment is a continuous process, it will be difficult to know the actual acidity and U concentration of the solutions as they come in contact with formaldehyde. To test the extent of influence of these differences in concentrations on the destruction ratios, four experiments were conducted in each case (column 5, a to d, table 3) by keeping the test solution at 100°C for different durations before the addition of formaldehyde was commenced. In each of these cases, though the initial conditions of the test solutions are the same, they are actually different at the time of formaldehyde addition. It can be seen from the results that whatever be the concentration of U and HNO_3 in the solutions when formaldehyde comes in contact with them, mole/mole ratios do not vary much. Hence it can be assumed with a reasonable accuracy that the ratios depend mainly on the final state of the product solutions rather than the initial state. In the first example where the aim is 300 mg/ml U in 2M HNO_3 , a ratio of 1.59 (table 2) can be accepted for the purpose of calculations. The same principle can be applied for the entire range of 5 - 1 M HNO_3 .

In the second example though the overall ratio is around 1.1 in all the four cases, the observed results may be rather misleading. For cases where the final acidity is aimed between 1 - 0.5 M it is advisable to split the calculations into two parts: (1) Calculate the amount of formaldehyde required to bring down to 1M. In the present case the ratio 1.40 can be accepted since U concentration is aimed at 300 mg/ml, (2) Calculate the formaldehyde required to bring down the acidity below 1 M. using the ratios in the range 1 - 0.5 M. In the present case 0.83 can be used. In this manner data in table 2 can be made use of in general for any calculations involving uranyl nitrate solutions.

3.3 Acid Recovery

It was considered worthwhile to collect the large amount of acid fumes let off from an acid destruction system in proper absorbers and reuse them elsewhere in the plant. During the course of the present studies the acid fumes were passed by way of a Leibig's Condensor and allowed to bubble through water or alkali. The collected acid was analysed by volumetric titrations in each case and the recovery was calculated as percentage of the total destroyed. The recovery varied from 50 - 70% depending upon the length of the liquid column used for collecting and the rate of bubbling. The results indicated that water was as efficient as alkali for the purpose of collecting acid fumes. In the case of alkali large amount was used up for the absorption of CO_2 thus causing considerable wastage. Water has another advantage in that it can be used directly as pure nitric acid elsewhere in the plant whereas alkali has to be discarded as waste thereby causing less economy. Efficiency of recovery can be increased in plant scale operations by scrubbing down the acid fumes from the top of a column and recirculating the same acid solution repeatedly.

4. CONCLUSIONS

The following conclusions can be drawn from the present studies:

1. The efficiency of acid destruction by formaldehyde is a function of initial and final acidities of the solution treated.

2. Rate of addition of formaldehyde does not affect the efficiency of destruction. However, care must be taken to maintain a steady flow rate and strictly avoid the addition in bulk quantities as it may cause violent reactions due to local concentration of formaldehyde.
3. Care must be taken to maintain the temperature above 90°C before the commencement of formaldehyde addition. At higher temperatures the reaction proceeds quite smoothly without any danger of the reaction getting out of control.
4. Addition of 0.015M NaNO_2 induces the reaction at an early stage even at low temperatures. This can be used as a 'Key' to start the reaction at any stage if the commencement of the reaction is delayed due to any reason.
5. Presence of $\text{UO}_2(\text{NO}_3)_2$ not only induces the reaction but also increases the efficiency of destruction. Water was found to be as efficient as alkali and more advantageous for the purpose of collecting acid fumes let off from the reaction vessel.

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Table 1

DESTRUCTION OF NITRIC ACID IN PURE SOLUTION WITH FORMALDEHYDE

100 ml HNO₃ + 8.0 ml HCHO

| Initial concentration (M) | Temperature °C | Flow rate ml/hr | Induction period (mt) | Final concentration (M) | Acid destroyed Mole/mole CH ₂ O | Range | Average destruction mole/mole CH ₂ O |
|---------------------------|----------------|-----------------|-----------------------|-------------------------|--|--------|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 6.04 | 90 | 5 | 11 | 4.39 | 1.65 | 6 - 5M | 1.62 |
| 5.94 | 90 | 10 | 7 | 4.31 | 1.62 | | |
| 6.04 | 90 | 20 | 7 | 4.44 | 1.59 | | |
| 6.04 | 100 | 5 | 5 | 4.41 | 1.61 | 6 - 5M | 1.65 |
| 6.04 | 100 | 10 | 2 | 4.36 | 1.65 | | |
| 6.04 | 100 | 20 | 3 | 4.34 | 1.70 | | |
| 6.04 | BP(111°C) | 10 | 1 | 4.26 | 1.78 | 6 - 5M | 1.78 |
| 4.99 | 90 " | 10 | 10 | 3.63 | 1.36 | 5 - 4M | 1.36 |
| 4.99 | 100 | 10 | 4 | 3.56 | 1.43 | 5 - 4M | 1.43 |
| 4.09 | 90 | 5 | 9 | 2.90 | 1.19 | 4 - 3M | 1.27 |
| 4.18 | 90 | 10 | 7 | 2.84 | 1.29 | | |
| 4.12 | 90 | 20 | 10 | 2.70 | 1.33 | | |
| 4.12 | 100 | 5 | 5 | 2.82 | 1.30 | 4 - 3M | 1.36 |
| 4.12 | 100 | 10 | 4 | 2.73 | 1.38 | | |
| 4.18 | 100 | 20 | 2 | 2.66 | 1.42 | | |
| 4.09 | BP(107°C) | 10 | 4 | 2.62 | 1.47 | 4 - 3M | 1.47 |
| 3.15 | 90 | 5 | 12 | 1.95 | 1.20 | 3 - 2M | 1.19 |
| 3.16 | 90 | 10 | 13 | 1.98 | 1.18 | | |
| 3.04 | 90 | 20 | 13 | 1.85 | 1.18 | | |
| 3.16 | 100 | 5 | 6 | 1.85 | 1.30 | 3 - 2M | 1.32 |
| 3.16 | 100 | 10 | 5 | 1.84 | 1.31 | | |
| 3.16 | 100 | 20 | 4 | 1.70 | 1.35 | | |
| 2.09 | 90 | 5 | 10 | 1.29 | 0.80 | 2 - 1M | 0.78 |
| 2.09 | 90 | 10 | 11 | 1.30 | 0.79 | | |
| 2.09 | 90 | 20 | 13 | 1.34 | 0.75 | | |
| 2.09 | 100 | 5 | 11 | 1.04 | 1.05 | 2 - 1M | 1.07 |
| 2.09 | 100 | 10 | 7 | 1.07 | 1.07 | | |
| 2.09 | 100 | 20 | 5 | 0.99 | 1.09 | | |

B.P. = Boiling point

Table 2

DESTRUCTION OF FREE NITRIC ACID IN $UO_2(NO_3)_2$
SOLUTIONS

Temperature = 100°C
 HCHO addition rate = 6 drops/mt(10 ml/hr)
 100 ml solution + 4 - 6 ml HCHO

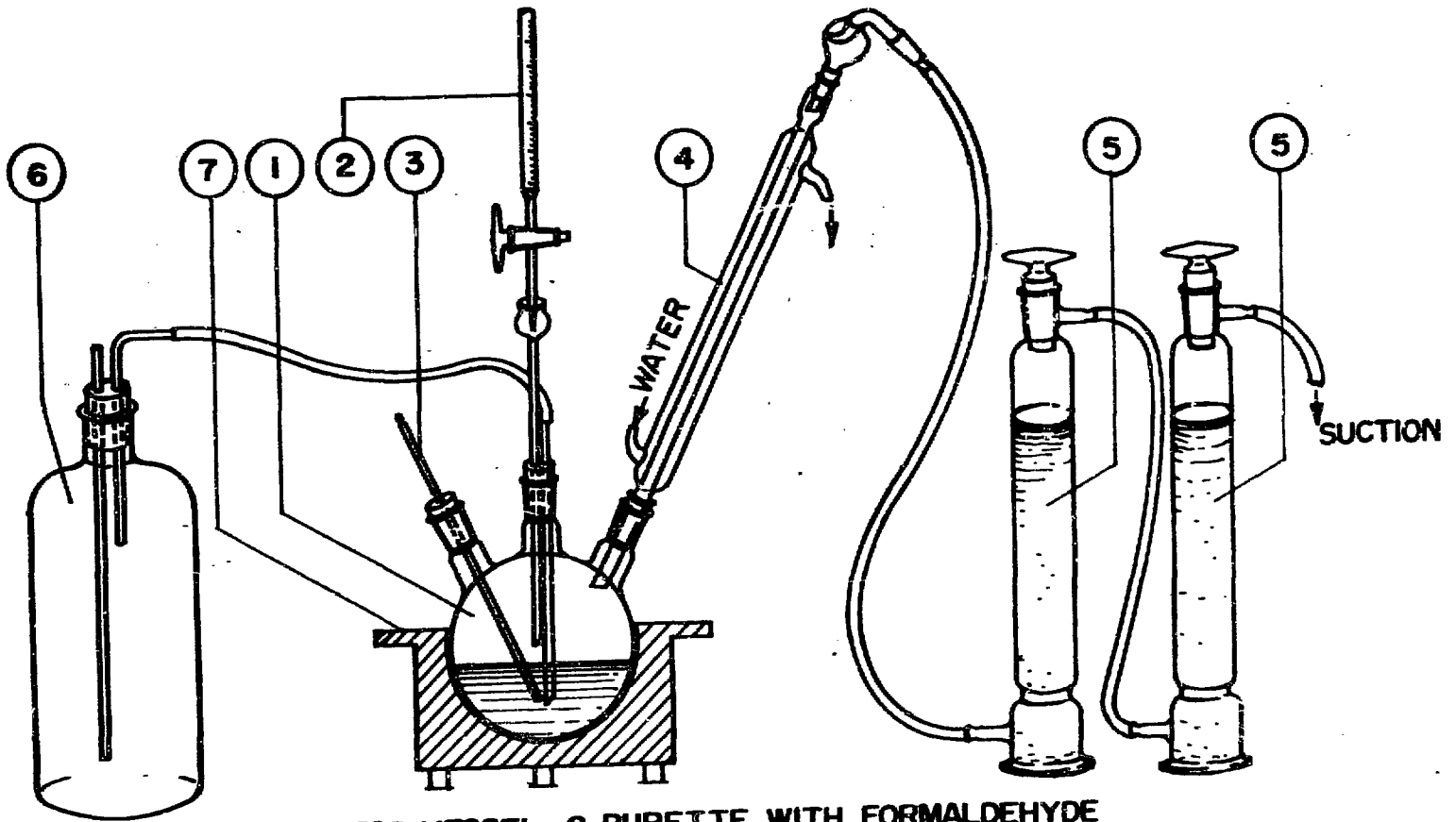
| Acid Range | U concentration (mg/ml) | Induction period (mt) | Acid destroyed Mole/Mole HCHO |
|------------|----------------------------|--------------------------|----------------------------------|
| 1 | 2 | 3 | 4 |
| 5 - 4 M | 0 | 4 | 1.43 |
| " | 50 | 3 | 1.72 |
| " | 100 | 3 | 1.74 |
| " | 200 | 2 | 1.85 |
| " | 300 | 1 | 1.88 |
| 4 - 3 M | 0 | 4 | 1.38 |
| " | 50 | 4 | 1.52 |
| " | 100 | 3 | 1.58 |
| " | 200 | 3 | 1.68 |
| " | 300 | 3 | 1.66 |
| 3 - 2 M | 0 | 5 | 1.35 |
| " | 50 | 5 | 1.38 |
| " | 100 | 5 | 1.44 |
| " | 200 | 3 | 1.55 |
| " | 300 | 3 | 1.59 |
| 2 - 1 M | 0 | 7 | 1.07 |
| " | 50 | 6 | 1.25 |
| " | 100 | 5 | 1.29 |
| " | 200 | 5 | 1.37 |
| " | 300 | 3 | 1.40 |
| 1 - 0.5M | 0 | 15 | 0.10 |
| " | 50 | 12 | 0.34 |
| " | 100 | 10 | 0.55 |
| " | 200 | 7 | 0.71 |
| " | 300 | 6 | 0.83 |

Table 3

SIMULTANEOUS DESTRUCTION OF FREE HNO_3 AND CONCENTRATION OF $\text{NO}_2(\text{NO}_3)_2$ SOLUTIONS
IN THE PRESENCE OF HCHO

Temperature = 100°C
Rate of HCHO addition = 6 drops/mt (10 ml/hr)

| Exam- ple | Initial | | | Addition of HCHO after | Volume HCHO added (ml) | Final | | | Acid destroyed (mole/mole HCHO) |
|--------------|----------------|----------------|--------------------|--|--|----------------|----------------|-------------------|--|
| | Volume (ml) | Acidity (M) | U Conc. (mg/ml) | | | Volume (ml) | Acidity (M) | U Con. (mg/ml) | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | 100 | 1.10 | 50 | a) 0 Min. | 4.1 | 18.56 | 2.18 | 269.6 | 1.47 |
| | 100 | 1.10 | 50 | b) 30 " | 4.1 | 18.56 | 2.01 | 269.6 | 1.54 |
| | 100 | 1.10 | 50 | c) 60 " | 3.6 | 18.62 | 2.41 | 268.8 | 1.57 |
| | 100 | 1.10 | 50 | d) 90 " | 4.1 | 19.53 | 1.57 | 256.0 | 1.65 |
| 2 | 100 | 1.00 | 50 | a) 0 " | 7.1 | 15.85 | 0.69 | 315.2 | 1.09 |
| | 100 | 1.00 | 50 | b) 30 " | 7.1 | 20.84 | 0.56 | 240.0 | 1.08 |
| | 100 | 1.00 | 50 | c) 60 " | 7.1 | 14.15 | 0.54 | 353.6 | 1.15 |
| | 100 | 1.02 | 50 | d) 90 " | 7.1 | 19.17 | 0.51 | 260.8 | 1.11 |



1. REACTOR VESSEL 2. BURETTE WITH FORMALDEHYDE
 3. THERMOMETER 4. LIEBIGS CONDENSER 5. ACID FUMES TRAPS
 6. SAFETY VENT 7. HEATING MANTLE

FIG.1 EXPERIMENTAL SET-UP

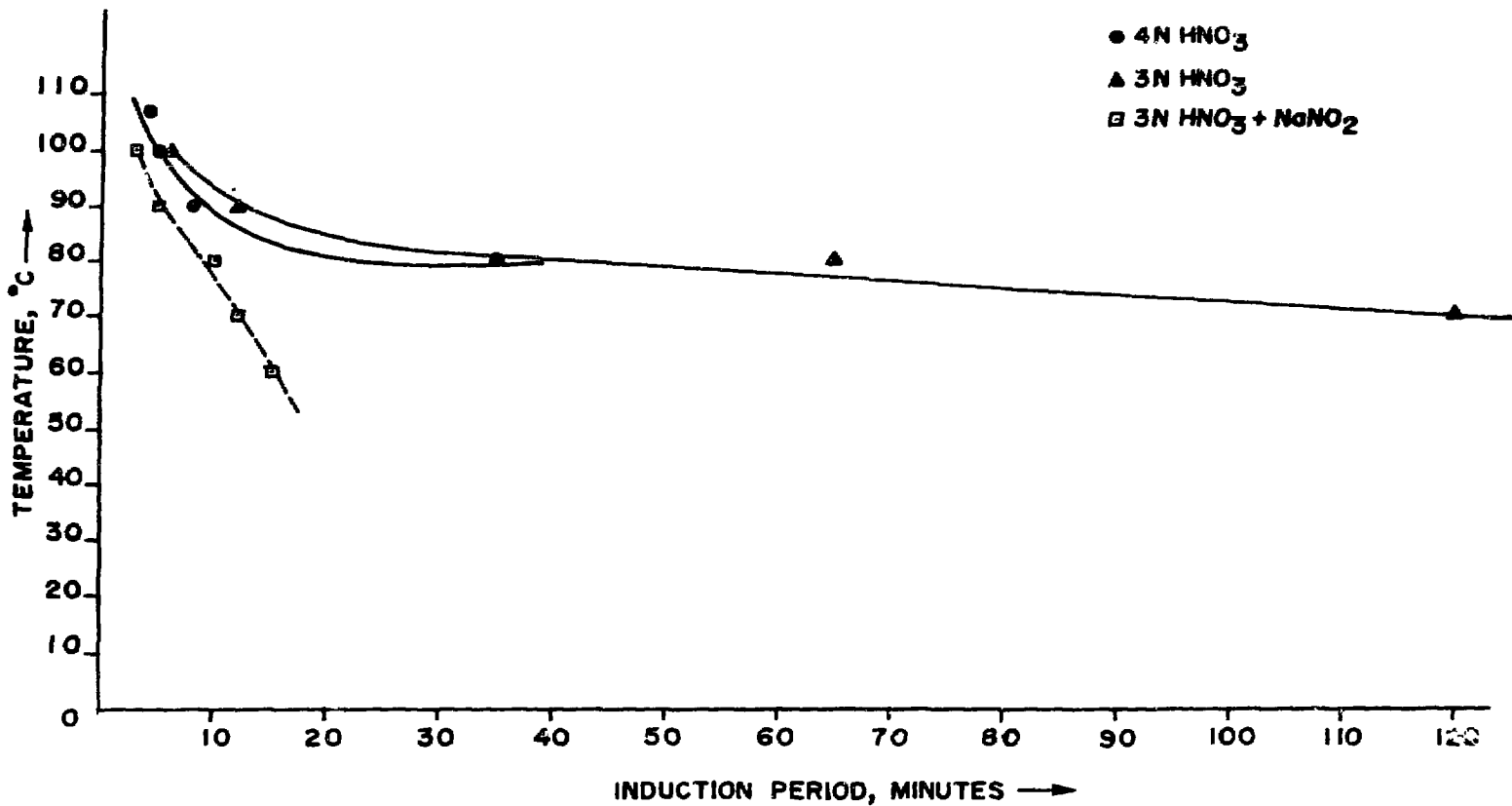


FIG. 2 DESTRUCTION OF HNO₃ WITH FORMALDEHYDE -
EFFECT OF NaNO₂ ON INDUCTION PERIOD

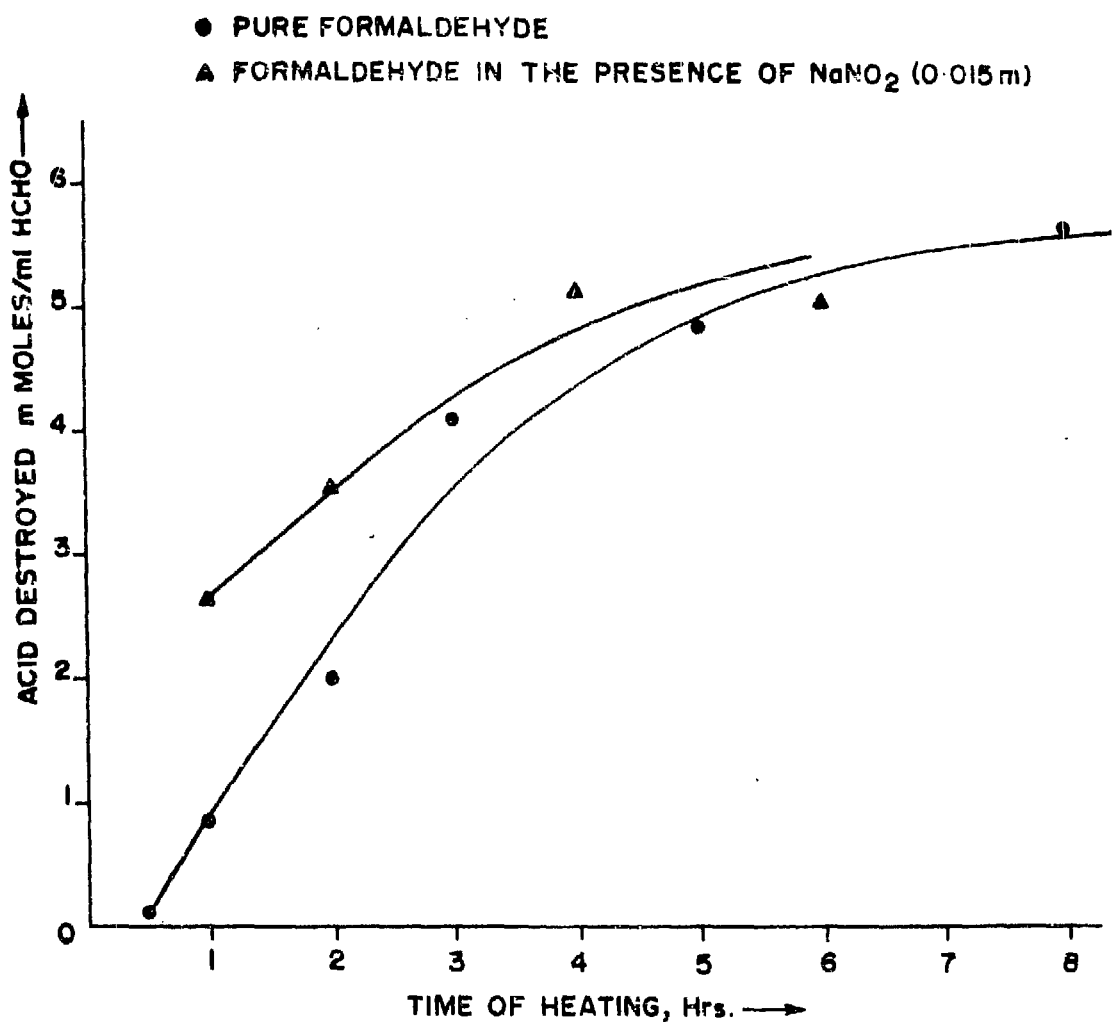


FIG.3 DESTRUCTION OF HNO_3 WITH HCHO -
 EFFECT OF SIMMERING TIME AND NaNO_2
 ON THE EFFICIENCY OF DESTRUCTION

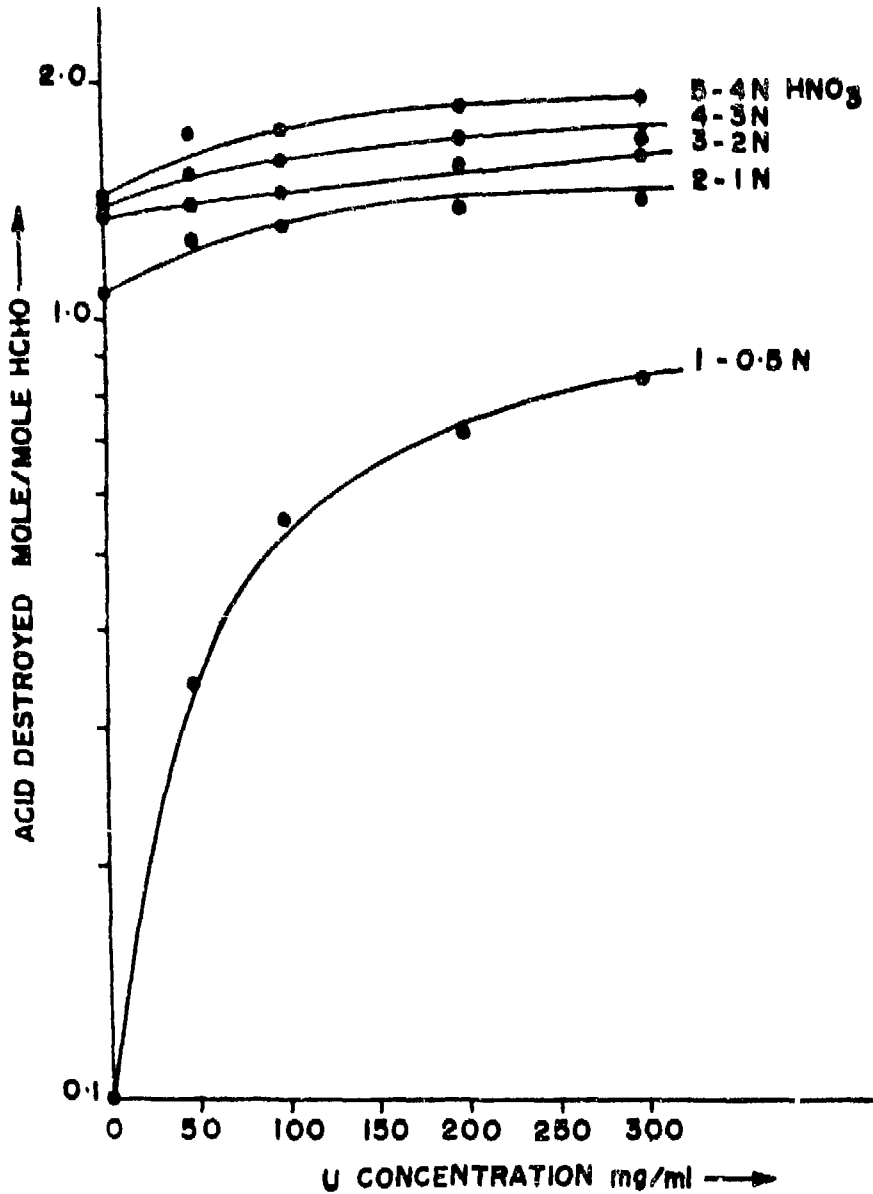


FIG. 4 DESTRUCTION OF HNO_3 WITH FORMALDEHYDE - EFFECT OF $UO_2(NO_3)_2$ CONCENTRATION

