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AUGUST 2, 1945

MEMORANDUM REPORT - SE-PC-#74

THE EVOLUTION OF IODINE DURING METAL DISSOLUTION

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I Introduction

During the dissolution in nitric acid of uranium metal which has been irradiated in a pile, radio-iodine (8.0 day) and radio-xenon (5.3 day) are liberated along with the oxides of nitrogen. Since in the plant these gases are discharged into the atmosphere, the presence of the activities (particularly radio-iodine because of its greater chemical reactivity) presents a physiological hazard. As a consequence, the cooling period (that is, the time between the discharge of the metal from the pile and the dissolution of the metal in nitric acid for the extraction of the product) should be sufficiently long so that the activities will have decreased through decay to the point where their concentrations in the atmosphere will not exceed 2.5×10^{-13} curies/cc* and 5×10^{-11} curies/cc* for radio-iodine and radio-xenon, respectively. Before the start of operations at H.E.W. a study was made of the existing information (largely from Site X) concerning the liberation of iodine and xenon during the dissolution of the metal and the information was summarized in a memorandum.(1) At that time it was apparent that radio-iodine would present the greater hazard, and that very little was known about the factors governing the liberation of iodine during the metal dissolution. For this reason, an investigation of the factors involved in the liberation of iodine during metal dissolution was undertaken in the laboratory.

At the start of the investigation it appeared that the problem could be divided in two parts: (1) evolution of iodine from the uranyl nitrate solution, and (2) escape of the iodine past the reflux in the dissolver column and through the off-gas line. It was considered that the following factors might possibly influence the evolution of iodine from the uranyl nitrate solution: (1) concentration of iodine, (2) concentration of nitric acid, (3) concentration of uranyl nitrate, (4) the ratio of the surface of the metal to the volume of the solution, and (5) the temperature. Since the temperature is fairly definitely established in the plant at 105°C-110°C, and since the rate of evolution is probably dependent on the surface to volume ratio to no more than first power, the investigation was focused on the first three variables. Of the many factors that might possibly influence the escape of the iodine, only the absorption of iodine in the reflux was investigated, since data obtained by the Health Instrument Section suggested that the reflux in the dissolver column greatly retarded the rate of discharge of the iodine.

II Summary and Conclusions

From the data presented in this report and discussed more fully under the heading "Discussion", the following conclusions may be drawn with respect to the discharge of iodine during the dissolution of irradiated uranium metal in nitric acid:

(1) The evolution of iodine from the uranyl nitrate solution is principally influenced by the concentration of iodine and is substantially independent of the concentration of nitric acid or uranyl nitrate. The reaction involved in the evolution of iodine appears to be approximately a second order reaction with respect to the concentration of iodine and to have a reaction rate constant of 0.05 l./mg. of iodine/min.

(2) The above conclusion is qualitatively substantiated by plant data.

* Tolerance concentration for an eight hour day (cf. CE-690 and CH-504).

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(3) The addition of iodine (inactive) either as iodide or as iodate only slightly increases the rate of evolution of the active iodine from the uranyl nitrate solution. By visual observation, the added iodine, however, is evolved quickly from the solution. This suggests that the active iodine in the uranyl nitrate solution does not exist as either iodide or iodate. Although the state in which iodine exists in the uranyl nitrate solution is not known, very likely the iodine exists in a complex ion, and in an oxidation state higher than I_2 (since concentrated HNO_3 oxidizes iodine to iodate).

(4) Under simulated dissolver conditions in the laboratory the reflux removed a large fraction (70% to 90%) of the iodine from the off-gases.

(5) Analyses of the plant solutions (Run T-5-03-B-1) through the extraction step indicates (a) that about 48%* (on the basis of a fission yield of 2.8% for 8.0 day iodine) of the iodine remains in the metal solution after the metal dissolution step, (b) that about 25% of the iodine remaining is evolved from the uranyl nitrate solution before the extraction step, and (c) that a decontamination factor, with respect to iodine, of about 60 is obtained in the extraction step.

III Discussion

A Order of the Reaction and the Reaction Rate Constant

On the assumption that the evolution of iodine would involve only the concentration of iodine and nitric acid, the appropriate data obtained in the experiments were substituted in the equation $-dI/dt = K \times I^a \times HNO_3{}^b$. If values for "a" and "b" which resulted in a constant value for K could be determined, the dependency of the reaction involving the evolution of iodine from uranyl nitrate solutions during the dissolution of metal would be established. For this purpose the concentration of iodine and nitric acid during the course of the runs (at various concentrations of iodine, nitric acid, and uranyl nitrate) were plotted in Figures 1, 2, 3, and 4. At a given time, t, the concentration of iodine (I), the concentration of HNO_3, and dI/dt (the slope of the curve representing the concentration of iodine) were substituted in the above equation. The results of this substitution, using values of "a" from 1 to 3 and values of "b" from 0 to 1, are shown in Tables 1a, 1b, 1c, and 1d. An inspection of the values of K given in the tables show that under all the varied conditions the most constant value is obtained when "a" equals 2, and "b" equals 0, that is, the reaction is approximately second order with respect to the concentration of iodine and independent of the concentration of nitric acid.

The values of K calculated from the equation $-dI/dt = KI^2$ lack accuracy because of the freedom permitted by the data in the drawing of the curve representing the concentration of iodine. For this reason, after establishing that the reaction was most likely a second order reaction, the reaction rate constant was determined by plotting the reciprocal of the concentration of iodine with respect to the reaction time.** The straight lines obtained as a result of this plot are also shown in Figures 1, 2, 3, and 4. The average reaction rate constant determined from the slopes of the straight lines is 0.05 l/mg/min.

* At higher concentrations of product in the metal, and hence at higher concentrations of iodine, the percentage remaining in solution should be less.

** If $-dI/dt = KI^2$, then $\int -dI/I^2 = K\int dt$. Since the $\int -dI/I^2 = 1/I - 1/I_0$ and the $\int dt = t$, $1/I = Kt + 1/I_0$. Hence, the plot 1/I vs. t would be a straight line, and the slope of the line representing K.

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The ratio of the surface of the metal to the volume of the nitric acid solution was approximately 0.1cm^2 per ml, in the experiments from which the above reaction constant was obtained. Approximately the same surface to volume ratio exists in the plant when 480 gal. of nitric acid (usual charge) is added to three tons of metal, without any remaining metal heel. Although time did not permit the study of the effect of the surface to volume ratio on the reaction rate constant, it appears quite probable that reaction rate constant may vary in direct proportion to the ratio.

B Correlation with Plant Data

Direct correlation between the laboratory data and plant data is difficult because the concentration of iodine in the dissolver solution during the course of dissolution of the metal is not known. Thus, in the plant, during the course of dissolution of the metal, iodine is liberated from the metal and, in part, is evolved from the uranyl nitrate solution. In addition, the reflux in the packed column on the dissolver apparently returns a considerable fraction of the evolved iodine to the solution. However, if the dissolution time is reduced by estimation to an "effective reaction time"*, some correlation between laboratory data and plant data is obtained.

Thus, in T-5-03-B-1 the metal had been irradiated for a total of 64.4 megawatt days per ton[2], which would result in an iodine content of 0.2g to 0.6g per ton**. The corresponding concentrations of iodine in the dissolver solution would be 0.1mg/l and 0.3mg/l, if none of the iodine had evolved during the dissolution of the metal. Analysis of the metal solution (4-7-M) in T-5-03-B-1 showed that 48% (on the basis of 2.8% fission yield for 8 day iodine***) of the iodine remained in the uranyl nitrate solution following dissolution. The curves shown in Figure 5 indicate that 48% would have remained in the solution after about 4 hours if the initial iodine concentration had been 0.1mg/l, and after about 1 hour if the initial concentration had been 0.3mg/l. It appears quite probable that with a dissolution time of 6-9 hours, the "effective reaction time" would be in the order of 1-4 hours. On the other hand, data from the plant operation at Site X[3] indicate that only 5%-10% of the iodine was evolved during the dissolution of the metal. The average exposure of the metal was about 3.2 megawatt days per ton which would result in an iodine content of 0.01 g/ton to 0.03 g/ton, depending upon the fission yield used. In turn, on the basis of no iodine evolution, the concentration of iodine in the dissolver solution would be 0.006 mg/l and 0.017 mg/l. The curves in Figure 5 indicate that, at these concentrations of iodine, 10% of the iodine would have evolved (90% remaining in solution) in 2 hours to 8 hours, which appears to be a reasonable "effective reaction time" under the conditions the dissolver operated. As a result of this correlation, it can be predicted that at full power level (250 megawatt days per ton, which corresponds to a concentration of iodine of 0.4 to 1.2mg/liter of solution) about 80% of the iodine will be evolved during metal dissolution.

* During the dissolution of the metal a given amount of iodine is evolved. The "effective reaction time" is defined as the time required for the evolution of that same amount of iodine, if all of the iodine in the metal had been initially present in the solution.

** According to the project handbook (CL-697, Chap.III, Part D,1) the combined fission yield of I^{127}(stable) and I^{129}(long lived) is 0.69%; however, this value is probably low and according to smoothed fission yield curves the yield should be about 1.6%. [Although 8.0day iodine has a greater fission yield(ca. 2.8%), under normal process conditions, because of decay, the 8.0 day iodine represents only a small fraction of the total iodine.] The iodine content is calculated from the total megawatt days of irradiation as follows:

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$$64.4 \times \frac{0.91}{0.88} \times \frac{128}{239} \times 0.0059 = 0.2g \text{ of I per ton, where}$$

64.4 = megawatt days of irradiation per ton of metal,
0.91 = grams of product per megawatt day,
0.88 = capture to fission ratio
128 = average molecular weight of iodine,
239 = molecular weight of product, and
0.0059 = combined fission yields of the long lived and stable iodine.

*** It is generally recognized that the fission yield of 8.0 day iodine is not definitely known. The latest yield based on experimental evidence is 2.3%, however, that value was determined without the benefit of improved methods of iodine analysis. From smoothed fission yield curves the yield for I^{131} (8.0 day) has been estimated to be from 2.7% to 3.0%.

C Addition of Iodine (either as Iodide or Iodate) During Dissolution

In one experiment, after about 50% of the iodine which had been added to the laboratory dissolver had evolved, sufficient inactive iodine as potassium iodide was added to give a concentration of about 100mg/l in the solution. If the evolution of iodine depended upon a second order reaction with respect to the concentration of iodine (with a reaction rate constant of 0.05 l/mg/min) and if the added iodine quickly equilibrated with the iodine in the solution, the addition of the iodine should have resulted in the evolution of over 98% of the iodine in the solution within 10 minutes. However, only about 20% of the iodine in the solution was evolved within 10 minutes. In a similar experiment, when an equal amount of iodine as potassium iodate was added, only about 15% of the iodine in the solution was evolved within 10 minutes. In both experiments, however, visual evidence indicated that the added iodine was quickly evolved. Since it has been fairly definitely shown the evolution of iodine from the solution is dependent upon the concentration of iodine to approximately the second power, it follows that interchange between the added iodine and the iodine in the solution was not quickly attained and therefore that the iodine in the solution was not present either as iodide or as iodate. In addition, since laboratory experiments have shown that concentrated nitric acid oxidizes iodine to iodate, it appears that the iodine in the uranyl nitrate solution existed in an oxidation state higher than I_2, and probably was complexed in some manner.

D Removal of Iodine from the Off-Gases by the Reflux

Typical data obtained by the Health Instruments Section in the monitoring of the dissolver off-gases are shown in Figure 6. The dip in the rate of discharge of iodine has been attributed to the removal of iodine from the off-gases by the reflux in the packed column on the dissolver. That the iodine is removed by the reflux has been shown by a laboratory experiment in which, during the first part of dissolution (the concentration of HNO_3 in the dissolver solution decreased from 11.3N to 6.2N during the experiment), 70% to 90% of the iodine was removed from the off-gases. The same fraction may not be removed in the plant since the extent of the removal is dependent upon the relative amounts of the reflux and the relative efficiency of the columns. However, in the plant a large fraction of the iodine is no doubt absorbed by the reflux during the stage of dissolution where vigorous boiling occurs.

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E Analysis of Plant Solutions for 8.0 Day Iodine

The following solutions from the plant run T-5-03-B-1 were analyzed for 8.0 day iodine: 40% UNH solution without H_2SO_4(4-7M), 40% UNH solution with H_2SO_4(8-1M), 20% UNH solution after pre-reduction with $NaNO_2$(8-1MR), extraction waste solution (8-3WS), and the extraction cake solution (8-4P). The analytical method, which was shown to give greater than 90% interchange between the active iodine and the carrier iodine added, is described in the "Experimental Details" section of this report. The results, corrected for decay to 3/5/45, indicate that the solutions contained the following amounts of 8.0 day iodine:

Solution	Activity (curies)
4-7M	260*
8-1M	220
8-1MR	219
8-3WS	192
8-4P	3.1

The value for 8-1M is not based on direct measurement but on an extrapolation of the data obtained. Thus, analysis of the 8-1M solution on 3/15, 3/19, 3/21, and 3/27 gave values (corrected to 3/5/45) of 176 and 177, 161, 142, and 126 and 124 curies, respectively. These results indicate that the sample was losing iodine (perhaps by evolution), hence the data were extrapolated to 3/5 and the value of 220 curies was obtained.

It was estimated by I.Perlman that the metal (discharged after pile shutdown on 1/18/45) dissolved for the runs T-5-03-B-1, 2, and 3 had been irradiated at a rate of 1250 KW/ton/day for a sufficient length of time prior to shutdown of the pile to approach near equilibrium concentrations of 8.0 day iodine. The activity of 8.0 day iodine in three tons of metal at time of dissolution (3/5/45 taken as the average date) would therefore be

$$\frac{1250 \times 3 \times 3.1 \times 10^{13} \times 0.028}{3.7 \times 10^{10} \times 2^{46/8}} = 1640 \text{ curies, where}$$

1250 = KW/ton/day; 3 = number of tons; 3.1×10^{13} = fissions/sec./KW; 0.028 = branching ratio of 8.0 day iodine; 3.7×10^{10} = disintegrations/sec./curie; 46 = days of decay; 8 = half life of iodine in days.

Since analytical data showed that the one ton processed in T-5-03-B-1 contained 260 curies on 3/5/45, the percentage of iodine remaining after the dissolution of three tons was 3 x 260 x 100/1640 = 48%.

The data also indicate that about 25% of the remaining iodine is evolved in Cell 8** and that a decontamination factor with respect to iodine of 60-70 is obtained in the extraction step.

* Activity in that fraction (1/3) of 4-7M solution which was processed in T-5-03-B-1.

** Data reported in SE-PC-78 (File No. 3-1943) indicate that the walls of Cell 8 were contaminated by spray from the metal solution, however, the iodine activity present with the other fission product elements represented an enrichment.

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IV Experimental Details

A Apparatus and Procedure for the Determination of the Order of the Reaction

A schematic drawing of the apparatus used in these experiments is shown in Figure 7. A normal experiment was conducted as follows. Two pieces of uranium metal* were placed in the flask. The transfer line and the scrubbers (containing sufficient NaOH solution so that the NaOH would not be depleted within a reasonable length of time) were attached to the flask. The nitric acid or a nitric acid-uranyl nitrate solution (300 ml) was added to the flask through the inlet tube. By means of a water aspirator, air was swept through the system at a rate of 100-270ml/min. (In order to duplicate the reduced pressure in the plant dissolver, the air was drawn through 15-18 inches of water as shown in the figure). Heat was applied to the flask to raise the temperature to 105°C, and when the reaction had subsided sufficiently so that the temperature could be maintained at 105°C, a given amount of iodine with radio-iodine** was added. Before the NaOH was depleted in one scrubber, the off-gas flow was diverted to the alternate scrubber. During the course of a run, water was added to the flask at a rate estimated to compensate for the evaporation. For analysis, two sets of samples of the uranyl nitrate solution were taken. One set, withdrawn about one-half minute before the other, was used for the determination of the concentration of HNO_3 and UNH; the other set was withdrawn into 25-30 ml. of a NaOH solution for the determination of the iodine concentration. From the concentration of UNH in the solution (obtained by the analysis of the first set of samples) and the UNH content of the samples in the second set, the volume of the samples withdrawn into NaOH was calculated. At the completion of a run the remaining solution in the flask was withdrawn for the measurement of the volume. This volume was always in good agreement with the initial volume minus the volume of the samples taken.

The iodine content of the second set of samples was determined by measuring the entire activity (due to radio-iodine and UNH) of the sample in the high pressure, liquid, gamma chamber(*) and by correcting for the activity due to UNH. The concentration of UNH in both sets of samples and the concentration of HNO_3 in the first set were determined by the Analytical Group. Because the accuracy of the iodine determination was largely dependent upon the accuracy of the UNH determination, the UNH was analyzed by a gravimetric method, at least in duplicate.

With the use of the High pressure, liquid, gamma chamber, except in Run 126(data shown in Figure 1), satisfactory material balances with respect to iodine were obtained. In Run 126, the material balances, calculated at several points during the run, decreased as the run progressed. This decrease was attributed to the lack of complete absorption of the iodine in the scrubber, because of the high rate of evolution of the off-gases; however, the concentration of iodine in the uranyl nitrate solution was considered to be of sufficient accuracy nevertheless for reaction rate determinations.

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The results of the runs made under various concentrations of nitric acid, uranyl nitrate, and iodine are shown in Figures 1, 2, 3, and 4.

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* The pieces together weighed about 50 grams, and had a total surface of about 27 cm^2 so that the addition of 250-300ml of solution resulted in a surface to volume ratio of 0.1cm^2/ml.

** Interchange between the active and inactive iodine was achieved by oxidation with H_2O_2 in an alkaline medium. After the H_2O_2 had been completely decomposed by heating, the solution was acidified and added to the flask. The solutions of radio-iodine was supplied by Site X. One solution was concentrated HNO_3, the other was slightly acid in HCl. In order to avoid the possibility of the formation of a complex ion between iodine and chlorine, the radio-iodine on the latter case was purified by CCl_4 extraction.

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B Absorption of Iodine by the Reflux

In the investigation of the effect of the reflux, the apparatus was modified to include the reflux attachments shown in Figure 7. Samples of uranium metal were placed in the flask and the apparatus was assembled. Air was swept through the system by means of a water aspirator, however, the system was not placed under a reduced pressure as in the reaction rate experiments. Concentrated nitric acid (300 ml) was added to the flask and, after reflux had commenced, the equilibrated radio-iodine and carrier iodine (0.28mg./l. of HNO_3 solution) were added. Periodically the condensate was drained from the well beneath the reflux condenser, and simultaneously the scrubber solutions were changed. Also, occasionally, samples of the uranyl nitrate solutions were withdrawn from the flask for the determination of the nitric acid concentration. The results of the experiment are shown in the table below:

Time* (min.)	2	7	12	17	22	27	32	37
Conc. of HNO_3 in solution (N)	11.3	10.3	9.8	8.9	8.1	7.4	6.7	6.2
Volume of reflux (ml.)	7.0	14.4	11.6	8.7	7.2	7.2	6.2	6.4
Activity in reflux (mv/sec)	1.37	3.20	2.06	1.32	1.01	0.90	0.58	0.58
Activity in scrubbers (mv/sec)	0.69	1.40	0.49	0.24	0.21	0.11	0.16	0.18
Percent of activity in reflux**	67	70	81	85	83	89	78	78

* After the addition of the iodine.
** Percent of the sum of the activities in the reflux and the scrubber.

These results show that the reflux removes a large fraction of the iodine from the off-gases. It is quite likely that the reflux would contain a high concentration of HNO_3, not only because of the boiling nitric acid solution but also because of the passage of NO_2, NO and air. It would be supposed, therefore, that the absorption is due to the conversion of the evolved I_2 to iodate*. Although time did not permit a thorough investigation of the factors involved, the data suggest that in the plant the reflux, during vigorous dissolution, removes a large fraction of the iodine from the off-gases.

C Analytical Procedures

1. Analytical Procedure for the Determination of Iodine

Preliminary experiments showed that the concentrations of iodine (generally less than one milligram per liter) involved in this investigation would be too low for accurate analysis by conventional methods. Because of this fact radio-iodine was employed as a tracer. A known amount of iodine plus sufficient radio-iodine (in the same state as the inactive iodine) to permit radiation measurements were added in an experiment. The concentration of iodine in an aliquot was then determined from the fraction of the total activity in the aliquot.

The amount of activity in the scrubber solutions (usually NaOH solutions) were determined by two methods: (a) acidification of an aliquot with HNO_3, addition of carrier iodine, reduction by bisulfite, precipitation of AgI**, transference of AgI through dissolution in KCN to a watch glass, evaporation, and measurement of the activity with a Geiger-Muller counter, (b) direct measurement of an aliquot (up to 70 ml) by the high pressure, liquid, gamma chamber. Since the two methods gave comparable results, complete interchange between the active iodine and the carrier iodine must have been obtained in the precipitation method (a). Generally, the

* Experiments in the laboratory showed that boiling 13N HNO_3 (60%) solution converted iodine (added as KI) quantitatively to iodate. Boiling 5N HNO_3, on the other hand, converted only 2% of the iodine (added as KI) to iodate within one hour, with 98% being converted to I_2.
** Precipitate was washed with 10N HNO_3 to remove any silver sulfite.

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latter method was employed.

When the above precipitation procedure was used for the analysis of solutions of uranyl nitrate for iodine, erratic and low results were obtained. Work at Sites C and X show that the erratic and low results were due to lack of interchange between the normal and radio-iodine atoms. A procedure for equilibration of the carrier iodine and the radio-iodine has been developed by Glendenin[5]. The procedure consists of the oxidation of the carrier and active iodine with NaOCl in an alkaline medium (Na_2CO_3), acidification, reduction with bisulfite, oxidation with $NaNO_2$ to I_2, and extraction with CCl_4. When solutions of uranyl nitrate contains other activities in addition to iodine, the above method is necessary in order to obtain quantitative analysis for the radio-iodine. However, when the only activity in the solution is radio-iodine, the solution can also be analyzed by means of the high pressure, liquid, gamma chamber. In that case a correction has to be made for the radiation to the UNH. Because of the simplicity of the latter method, it was used in all experiments involving activities due only to iodine and UNH.

2. Analysis of Plant Solutions for 8.0 Day Iodine

In order to separate the iodine from the other fission product elements and in order to obtain a quantitative yield, the procedure developed by Glendenin (briefly described above) for equilibration of active and carrier iodine was used. After extraction into CCl_4 and re-extraction into bisulfite water, the iodine was further purified by at least two similar extraction cycles. Despite this treatment the final aqueous solution sometimes contained other activity (as shown by decay measurements with the high pressure, liquid, gamma chamber) than 8.0 day iodine. When other activity was evident, the amount of 8.0 day iodine present was calculated from the rate of decay, on the assumption that the other activity was representative of all the other fission product elements. According to Figure 16, Cl-697 (Chap. III, Part D,6) the overall rate of decay of fission product elements produced in metal which has been irradiated for 50-60 days and which has been cooled 50-60 days is about 1.7% per day. On that basis, the activity due to 8.0 day iodine in a solution was calculated by the equation:

$$2^{d/8}X + \frac{A'-X}{(1.0-0.017)^d} = A$$

where d = period in days during which the decay of the activity was followed, X = amount of activity due to 8.0 day iodine after d days, A = total activity at the start of the period, and A' = the total activity at the end of the period. That this method of correction was valid within the accuracy of the experiments is shown by the table below:

Analysis No.	1	2	3
Volume of aliquot (ml)	0.01	0.01	0.025
Total activity at 10 AM, 3/15 (mv/sec)	5.84	4.42	--
Total activity at 2 PM, 3/21 (mv/sec)	3.02	2.54	6.20
Calculated iodine activity per 0.01 ml at 2 PM, 3/21 (mv/sec)	2.48	2.66	2.58

A factor (1.35×10^6 d/m/mv/sec.) for the conversion of mv/sec to d/m (and hence curies) was determined by the measurement of the activity in a number of AgI precipitates containing 8.0 day iodine both with the high pressure, liquid, gamma chamber and with a Geiger-Muller chamber. In the measurement with the Geiger-Muller chamber, a correction for the absorption of the beta particles was made, using a half-thickness of 20mg./cm^2.

The detailed experimental data upon which this report is based is contained in notebooks HEW-130-T, HEW-86-T and HEW-402-T. The experimental work was performed by H.J.Kamack and J.L.Dreher.

V References

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3) Beall and Adams: "205 Stack Gas Monitoring", (CE-2205).

4) LaViolette: "Liquid Sample Pressure Chamber", Feb. 6, 1945 (File No. 3-1602).

5) Glendenin: "The Interchange of Radioactive Iodine with Carrier; a Procedure for the Quantitative Separation of Radioactive Iodine from Fission Material", (CC-2218).

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Table 1a

Calculation of Order of Reaction

(Data from Run 126 shown in Figure 1)

Reaction Time (Min.)	10	20	30	40
Conc. of Iodine (mg./l.)	0.248	0.224	0.207	0.194
Conc. of HNO_3 (N)	9.1	7.6	6.6	5.7
dI/dt (mg./l./Min.)	0.00290	0.00194	0.00149	0.00120
dI/dt / I (1/Min.)	0.0117	0.0087	0.0072	0.0062
dI/dt / I^2 (l./mg./Min.)	0.047	0.039	0.035	0.032
dI/dt / I^3 (l^2/mg^2/Min.)	0.19	0.17	0.17	0.16
dI/dt / I x HNO_3 (1/Min.xN)	0.0013	0.0011	0.0011	0.0011
dI/dt / I^2x HNO_3 (l./mg./Min.x N)	0.0052	0.0051	0.0053	0.0056
dI/dt / I^3x HNO^3 (l^2/mg^2/Min.xN)	0.021	0.022	0.026	0.028

Table 1b

Calculation of Order of Reaction

(Data from Run 129 shown in Figure 2)

Reaction Time (Min.)	10	20	30	40	50
Conc. of Iodine (mg./l.)	0.260	0.232	0.208	0.190	0.176
Conc. of HNO_3 (N)	2.52	2.25	2.03	1.83	1.63
dI/dt (mg./l./Min.)	0.00309	0.00257	0.00212	0.00160	0.00127
dI/dt/I (1/Min.)	0.0119	0.0111	0.0102	0.0084	0.0072
dI/dt / I^2 (l./mg./Min.)	0.046	0.048	0.049	0.044	0.041
dI/dt / I^3 (l^2/mg^2/Min.)	0.18	0.21	0.24	0.23	0.23
dI/dt / I x HNO_3 (1/Min.xN)	0.0047	0.0049	0.0049	0.0044	0.0041
dI/dt / I^2x HNO_3 (l./mg./Min.xN)	0.018	0.021	0.024	0.023	0.023
dI/dt / I^3x HNO_3 (l^2/mg^2/Min.xN)	0.072	0.093	[redacted] 0.13	0.12	0.13

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Table 1c

Calculation of Order of Reaction

(Data from Run 24 shown in Figure 3)

Reaction Time (Min.)	10	20	30	40
Conc. of Iodine (mg./l.)	0.687	0.555	0.496	0.385
Conc. of HNO_3 (N)	8.30	6.85	5.50	4.85
dI/dt $(\frac{mg./l.}{Min.})$	0.0149	0.0102	0.0084	0.0065
$\frac{dI/dt}{I}$ $(\frac{1}{Min.})$	0.022	0.018	0.018	0.017
$\frac{dI/dt}{I^2}$ $(\frac{l./mg.}{Min.})$	0.032	0.033	0.040	0.044
$\frac{dI/dt}{I^3}$ $(\frac{l^2/mg^2}{Min.})$	0.046	0.060	0.087	0.114
$\frac{dI/dt}{I \times HNO_3}$ $(\frac{1}{min. \times N})$	0.0026	0.0026	0.0032	0.0037
$\frac{dI/dt}{I^2 \times HNO_3}$ $(\frac{l./mg.}{Min. \times N})$	0.0039	0.0048	0.0071	0.0097
$\frac{dI/dt}{I^3 \times HNO_3}$ $(\frac{l^2/mg^2}{Min. \times N})$	0.0065	0.0088	0.0156	0.025

Table 1d

Calculation of Order of Reaction

(Data from Run 28 shown in Figure 4)

Reaction Time (Min.)	10	20	30	40	50	60
Conc. of Iodine (mg./l.)	0.49	0.39	0.325	0.27	0.22	0.19
Conc. of HNO_3 (N)	4.39	4.19	4.00	3.85	3.68	3.44
dI/dt $(\frac{mg./l.}{Min.})$	0.0168	0.0068	0.0062	0.0053	0.0040	0.0030
$\frac{dI/dt}{I}$ $(\frac{1}{Min.})$	0.034	0.018	0.019	0.020	0.018	0.016
$\frac{dI/dt}{I^2}$ $(\frac{l./mg.}{Min.})$	0.070	0.045	0.059	0.073	0.082	0.083
$\frac{dI/dt}{I^3}$ $(\frac{l^2/mg^2}{Min.})$	0.143	0.116	0.18	0.27	0.37	0.44
$\frac{dI/dt}{I \times HNO_3}$ $(\frac{1}{Min. \times N})$	0.0078	0.0043	0.048	0.052	0.049	0.047
$\frac{dI/dt}{I^2 \times HNO_3}$ $(\frac{l./mg.}{Min. \times N})$	0.016	0.011	0.015	0.019	0.022	0.024
$\frac{dI/dt}{I^3 \times HNO_3}$ $(\frac{l^2/mg^2}{Min. \times N})$	0.033	0.028	0.045	0.070	0.10	0.13

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FIGURE 1

Evolution of Iodine from a Uranyl Nitrate Solution During the Dissolution of Uranium Metal in Nitric Acid

(Temperature=105°C; Initial concentration: I=0.304 mg./l.; HNO_3=11.0N; UNH=156g./l.)

(Run 128)

Time (min.)	I Conc. (mg/l)	HNO_3 Conc. (N)	di/dt (mg/l/min.)
10	0.248	9.1	0.00290
20	0.224	7.6	0.00194
30	0.207	6.8	0.00148
40	0.194	6.7	0.00120

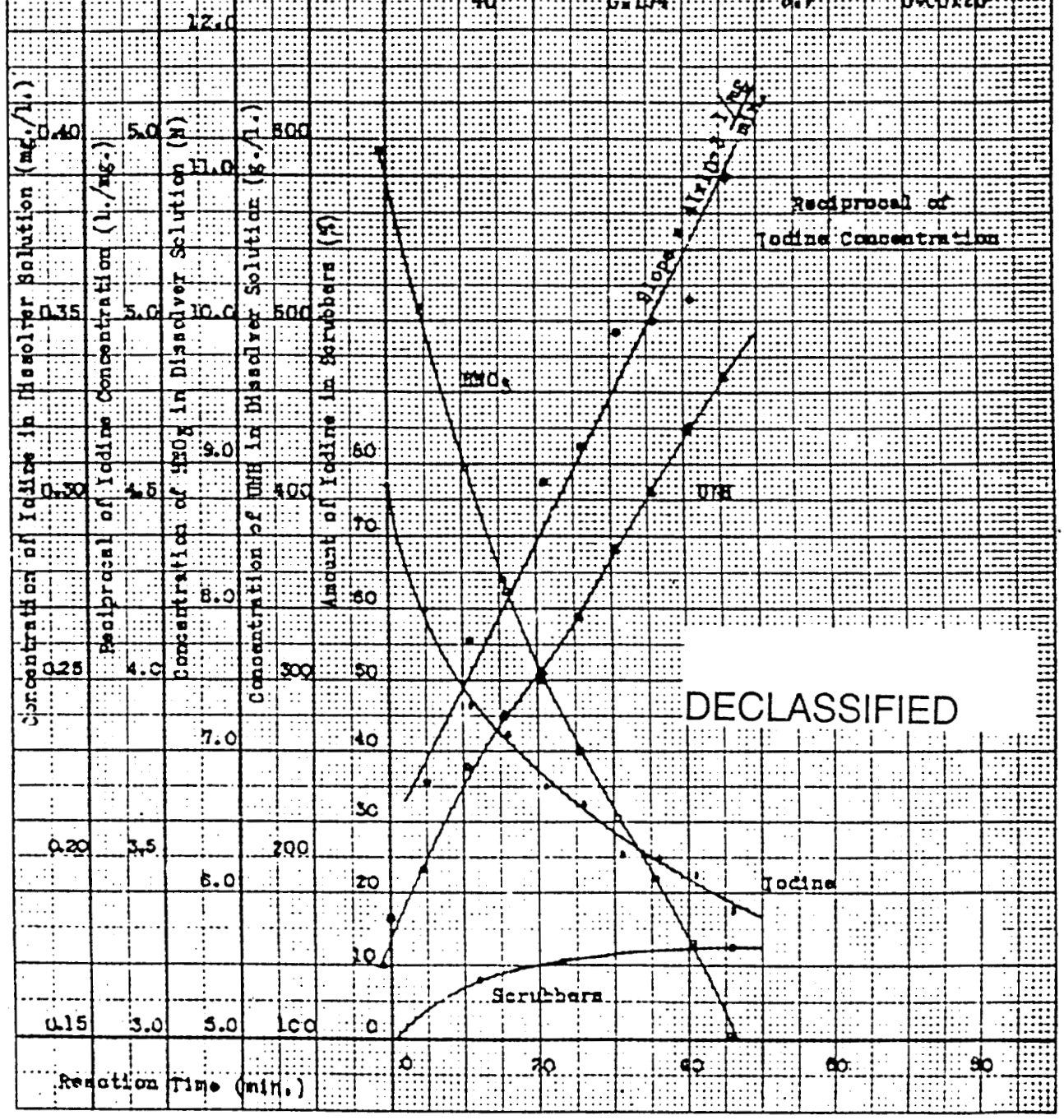

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FIGURE 2

Evolution of Iodine from a Uranyl Nitrate Solution During the Dissolution of Uranium Metal in Nitric Acid

(Temperature =105°C; Initial concentrations: I=.304 mg/l; HNO_3=2.8M; UNH=200g/l)

(Run 129)

Time (min.)	I Conc. (mg/l)	HNO_3 Conc. (M)	dI/dt ($\frac{mg/l}{min}$)
10	0.280	2.52	0.00303
20	0.232	2.38	0.00257
30	0.206	2.03	0.00212
40	0.190	1.33	0.00160
50	0.176	1.03	0.00127

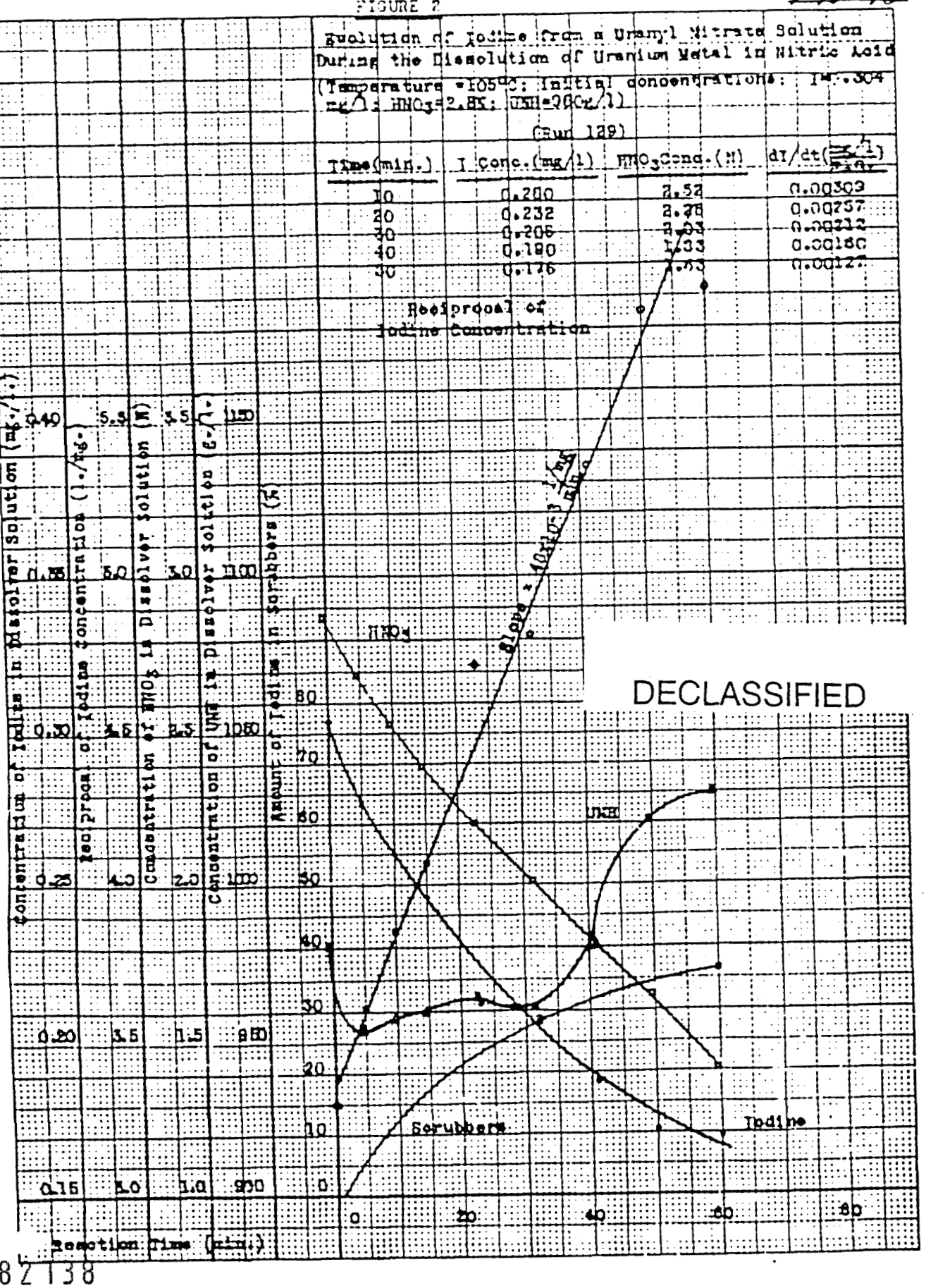

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FIGURE 3

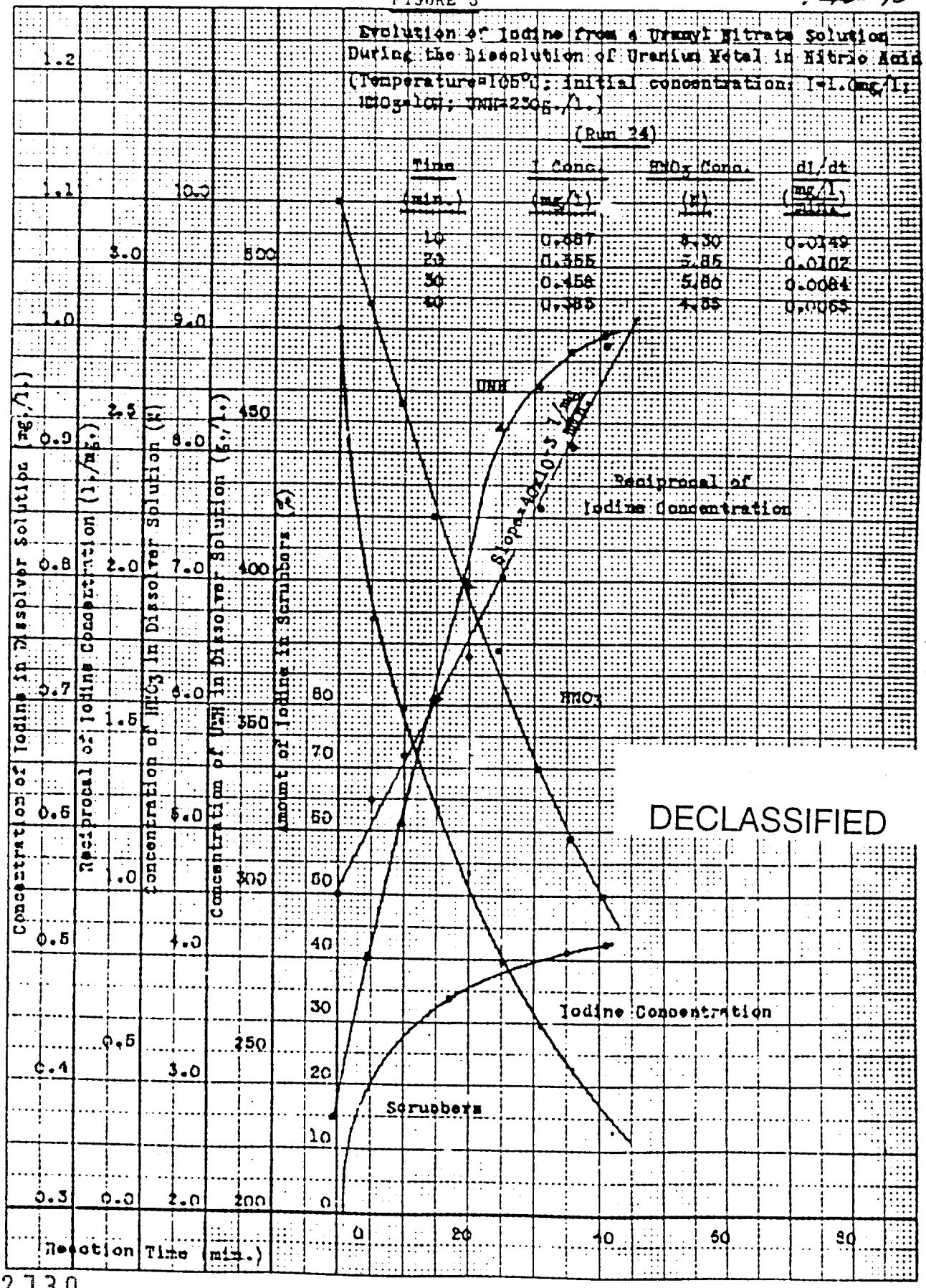
Evolution of Iodine from a Uranyl Nitrate Solution During the Dissolution of Uranium Metal in Nitric Acid
(Temperature=105°C; initial concentration: I=1.0mg/l; HIO3=10g; UNH=250g./l.)
(Run 24)
Time (min.) | I Conc. (mg/l) | HNO3 Conc. (M) | dI/dt (mg/l / min.)
10 | 0.687 | 6.30 | 0.0149
20 | 0.355 | 5.85 | 0.0102
30 | 0.158 | 5.80 | 0.0064
40 | 0.085 | 4.85 | 0.0063
UNH
Slope=4.0x10-3 l/mg.
Reciprocal of Iodine Concentration
HNO3
Iodine Concentration
Scrubbers
Concentration of Iodine in Dissolver Solution (mg./l.)
Reciprocal of Iodine Concentration (l./mg.)
Concentration of HNO3 in Dissolver Solution (M)
Concentration of UNH in Dissolver Solution (g./l.)
Amount of Iodine in Scrubbers (%)
Reaction Time (min.)
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FIGURE 4

Evolution of Iodine from a Uranyl Nitrate Solution During the Dissolution of Uranium Metal in Nitric Acid

(Temperature=105°C; initial concentration: I=1.24 mg./l.; HNO_3=5.6N; UNH=330g./l.)

(Run 28)

Time (min.)	I Conc. (mg/l)	HNO_3 Conc. (N)	dI/dt (mg/l/min.)
10	0.49	4.39	0.0168
20	0.39	4.19	0.0088
30	0.325	4.00	0.0082
40	0.27	3.83	0.0055
50	0.22	3.65	0.0080
60	0.19	3.44	0.0150

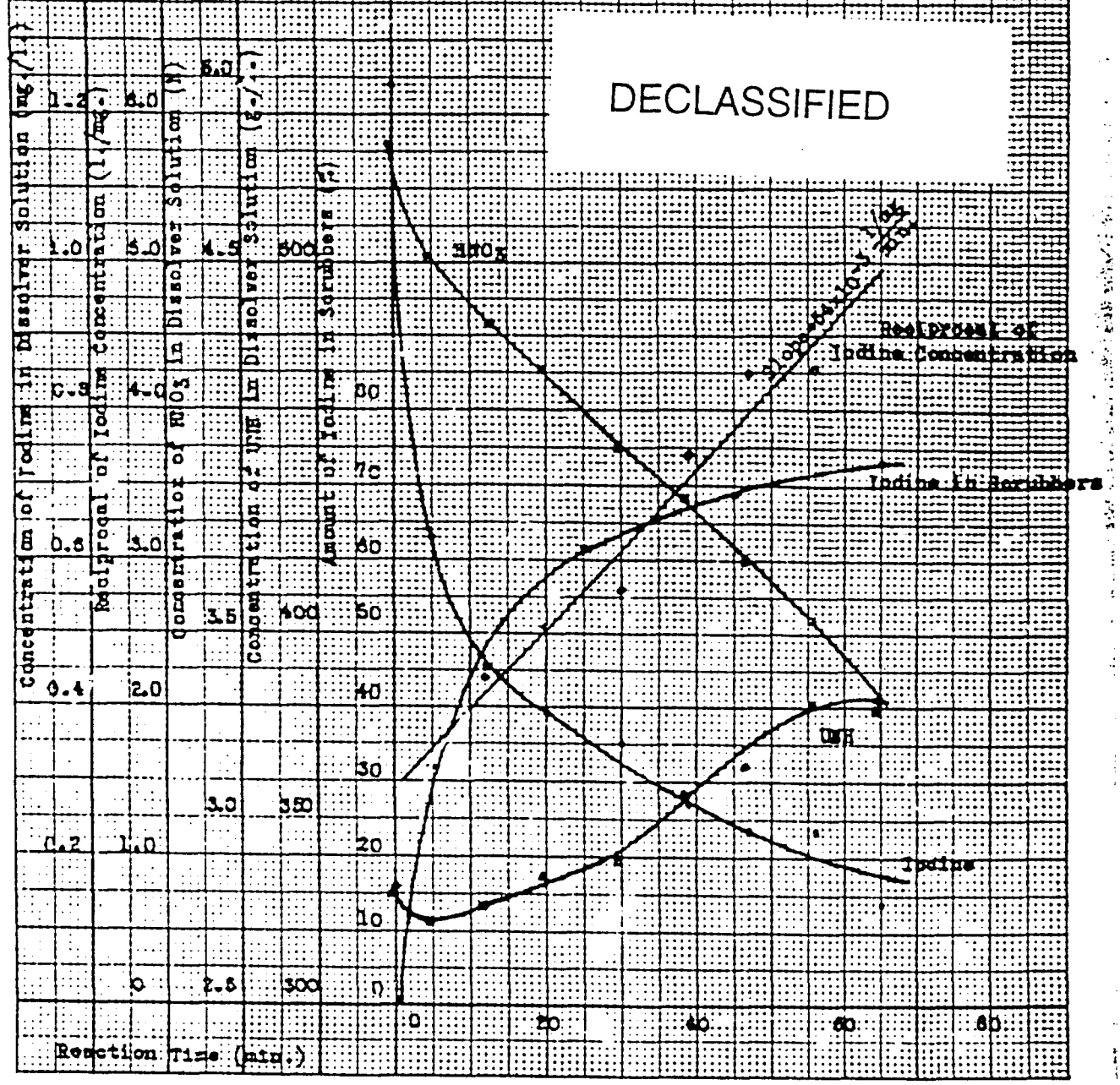

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FIGURE 5

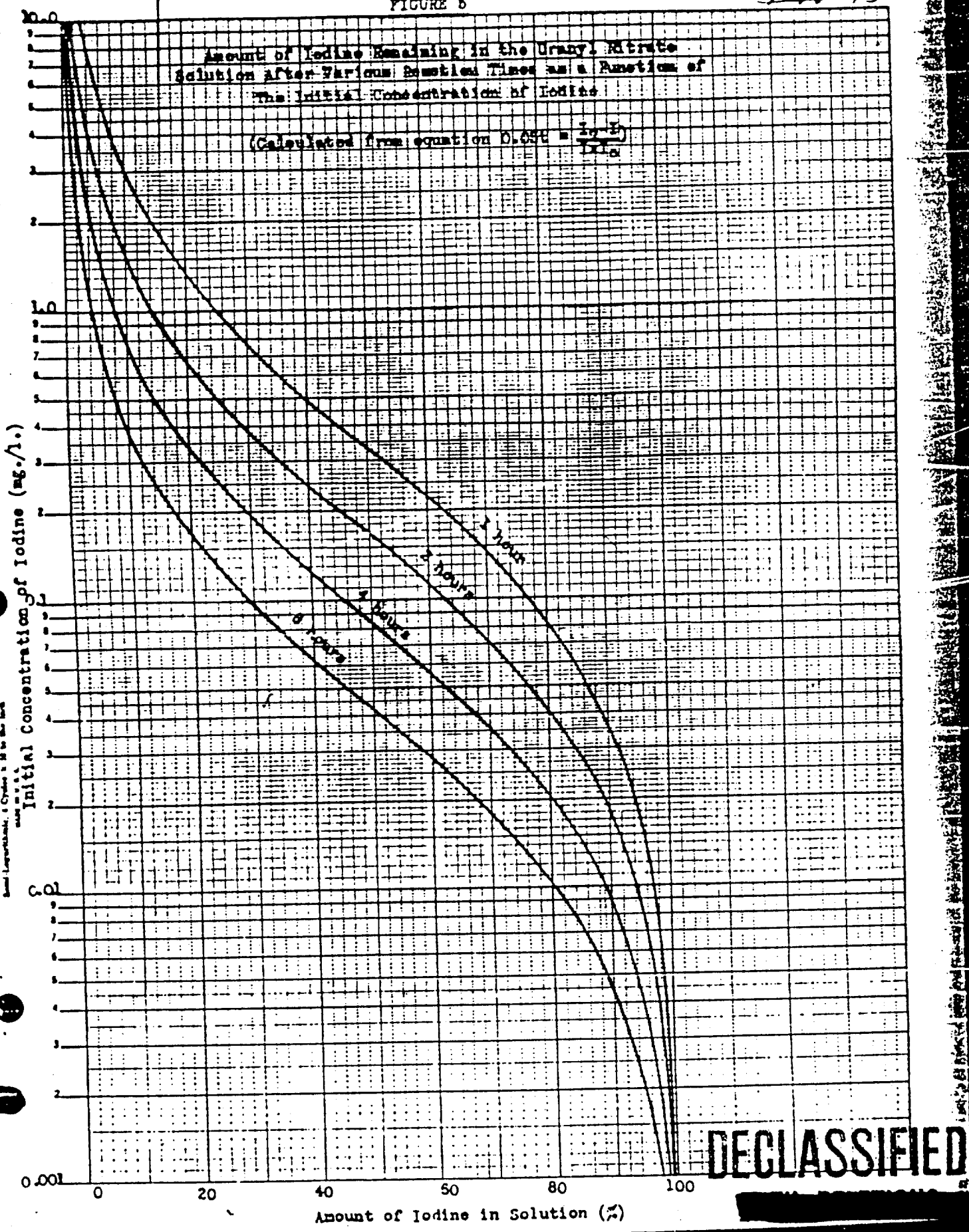

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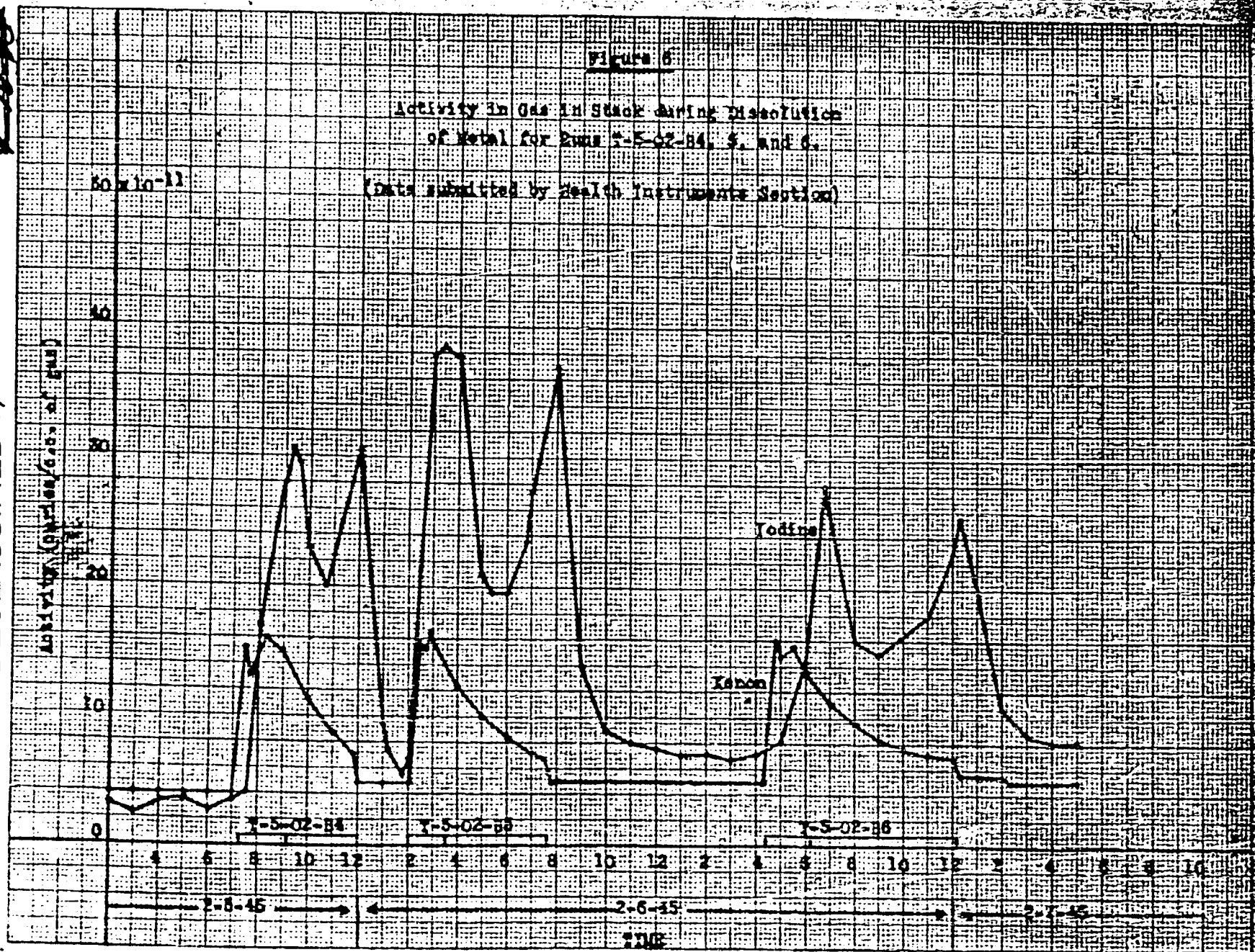
Figure 6

Activity in Gas in Stack during Dissolution of Metal for Runs Y-5-02-84, 5, and 6.

(Data submitted by Health Instruments Section)



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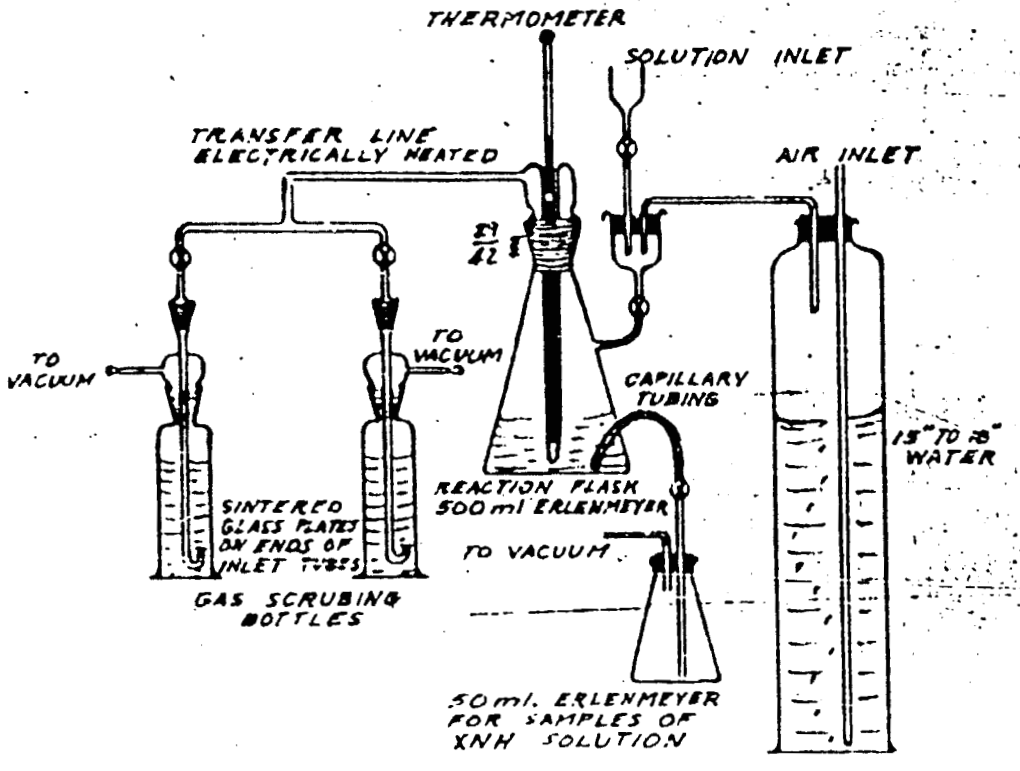
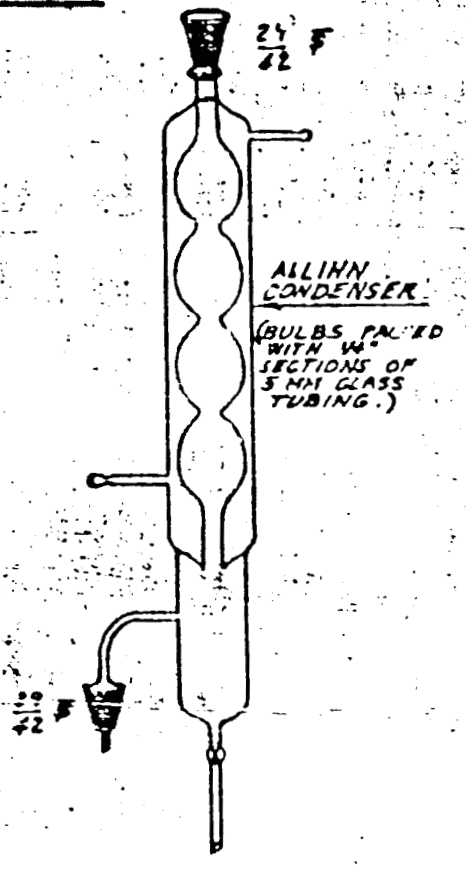
SCHEMATIC DRAWING OF APPARATUS





APPARATUS FOR REACTION RATE STUDIES

REFLUX ATTACHMENT

FIGURE 7

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