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SUBJECT: HRT Mockup Iodine Removal and Recombiner Tests

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FROM: P. H. Harley

ABSTRACT

Tests have been run in the HRT core system mockup which demonstrate that iodine can be successfully removed from dry steam by a silver bed. Such a bed is recommended to prevent iodine poisoning of the HRT recombiner catalyst. An added advantage will be removal of I-135 from circulation, whereby reducing neutron losses to Xe-135, a daughter.

Four experiments were made with the silvered Alundum pellets during which experimental mass transfer coefficients were determined. At 110°C the experimental k_g was 25% of the theoretical value, and at 150°C the k_g was 52% of the theoretical. The experimental efficiencies were 68% and 97.8% of the theoretical efficiencies at the above temperatures. Increasing the gas temperature greatly improved the correlation of the theoretical and experimental data.

Two iodine removal tests were made using silver-plated stainless steel wire mesh. These two tests gave higher removal efficiencies than the corresponding tests with the silvered Alundum rings (see Table II). The metal support is preferred also because of its greater mechanical and chemical stability. In particular, leaching of Na_2O from Alundum rings was noted in the HRT.

In a test of the stability of the silver-plated wire mesh, only 0.0025% of the silver was lost in a 650 hour run. During mockup tests without a silver bed, iodine poisoning lowered the recombiner efficiency from 99.97% to 98% at the HRT design conditions. Increasing the recombiner temperature to 650°C was found to be effective in removing iodine poison from the platinum catalyst.

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Introduction

In an aqueous homogeneous reactor designed for breeding, the breeding ratio would be lowered excessively if the xenon poison was allowed to build up to the normal equilibrium level. Since xenon is a daughter of fission-product iodine, an effective method of lowering the xenon level would be to remove iodine from the circulating system.

Another inducement for the removal of iodine is the need to prevent poisoning of the platinum catalyst used in the recombination of radiolytic gas. Unrecombined deuterium would create an explosion hazard in the off-gas system, and of course it would represent an economic loss.

Experience in the Chemical Technology Division[1] and subcontract work by the Vitro Corporation[2] have shown that silver supported on Alundum pellets would remove iodine from a vapor stream.

This report describes theoretical and experimental determinations of the mass transfer coefficients and efficiencies of two types of silver beds used to remove iodine in the HRT mockup. The type of removal system tested could be used to remove iodine in the HRT.

Theory

For a reaction between a gas (iodine) and a solid (silver) in which the gas is carried by an inert vapor (steam), the reacting gas must diffuse through the vapor to the solid in order for an appreciable reaction to take place. If the rate of diffusion were slower than the chemical reaction, then the diffusion rate would control the overall reaction rate. This was assumed to be true in analyzing these tests.

Chilton and Colburn[3] developed a relationship for the mass transfer coefficient, k_g, in terms of a "j_D" factor. Gamson, Thodos and Hougan[4] presented the "j_D" factor for the diffusion of a gas through vapor to the solid surface in a packed bed, based on a Reynolds number dependent upon the size and shape of the packed material. These two "j_D" expressions for turbulent flow were equated to give Equation 1.

$$\frac{k_g M_m P_f}{G} \left(\frac{\mu}{\rho D_{am}}\right)^{2/3} = 0.99 \left(\frac{D_p G}{\mu}\right)^{-0.41} \qquad 1$$

k_g = mass transfer coefficient, moles/hr, ft^2 (mole fraction)

M_m = mean molecular weight, pounds/mole

P_f = film pressure factor = 1 for very dilute diffusants

G = mass flow rate, pounds/hr, ft^2 (based on open area)

μ = viscosity, pounds/hr, ft

ρ = density, pounds/ft^3

D_{am} = diffusivity, ft^2/hr

D_p = equivalent spherical diameter of one ring, ft.

This equation was used to determine the theoretical value of k_g. The mass transfer coefficient can also be expressed by the following relation:

$$k_g = \frac{\ln(P_{ao}/P_a)\ G}{M_m A_v L} \qquad 2$$

P_{ao} = partial pressure of reacting gas entering the bed, atm.

P_a = partial pressure of reacting gas leaving the bed, atm.

A_v = surface to volume ratio of the bed, ft^2/ft^3

L = length of bed, ft

Equation 2 was used to calculate the theoretical percentage of iodine removed, and the values for k_g based on experimental data.

Silver Alundum Bed

In the theoretical calculations it was assumed that the surface of the rings was completely coated with silver. The porosity of the pellets was neglected which, it was assumed, would off-set any incompletely silvered surfaces.

Based on these assumptions, the mass transfer coefficient for the 1/8 in. x 1/4 in. x 1/4 in. rings was calculated by Equation 1 as 2.96 and 2.90 moles/hr, ft^2 (mole fraction) at 150°C and 110°C. Equation 2 was used to relate the mass transfer coefficient of the bed to an expected efficiency of iodine removal.

Wire Mesh Bed

There was no theoretical mass transfer information available for beds packed with wire mesh so no theoretical calculations were made for the silver plated wire-mesh beds. The surface to volume ratio of the two wire-mesh beds were estimated to be 158 and 209 ft^2/ft^3, with corresponding densities of 22 pounds and 29 pounds/ft^3, respectively. Equation 2 was used to calculate experimental values of k_g from the test data.

Silvered-Alundum Preparation

The silvered-alundum pellets were prepared by soaking the alundum rings in 1 m silver nitrate solution under 25 in. of Hg vacuum for 3 hr and air drying overnight. The pellets were then heated slowly to 550°C in a furnace and held at this temperature for 3 hr. Finally, the pellets were cooled under a nitrogen atmosphere to prevent oxidation.

Silver-Plated-Mesh Preparation

Wire mesh knitted from 0.011 in. diameter 304 stainless steel wire and designed for use in entrainment separation was plated with a 2-mil coating of porous silver. To obtain a uniform plating, a copper wire electrode was laced around each portion of wire mesh. A thin nickel plate was used to obtain a surface to which the silver would adhere.

The plated mesh was rolled by hand. The tightness of the roll determined the final density of the bed obtained. However, the two beds of different density used in the mockup runs were obtained by using a crimped and an uncrimped wire mesh.

General Loop Operation

Uranyl sulfate solution was circulated in the high-pressure system of the HRT mockup at 280°C and 1700 psi, with a side stream of 1 gpm letdown to a low-pressure storage tank. The solution in the storage tank was boiled at atmospheric pressure, giving 3.34 pounds of steam per minute which in these experiments passed through the silver bed, through a recombiner containing platinized alundum catalyst and to the condenser and condensate tank. Condensate was fed at a rate of 0.25 gpm to the circulating pump and pressurizer of the high pressure system; the excess was returned to the storage tank. To compensate for the letdown stream, 0.75 gpm of solution from the storage tank was continuously pumped into the high-pressure loop.

Procedure for Iodine Addition

Two different methods were used for the addition of iodine to the mockup. The first method was to add potassium iodide solution from a bomb directly into the high-pressure system. The bomb was flushed for 30 minutes. The second method was to add the potassium iodide solution continuously to the feed-pump suction over a 4- to 5-hr period. The amount of iodine added in the test varied from 0.8 to 1.4 g. A 1.4 g addition was equivalent to the 100-day concentration calculated for the HRT assuming no removal.

In all the tests the iodine distribution was followed by taking samples from various parts of the system at frequent intervals.

Recombiner Tests

Operation

In preparation for the tests of the iodine removal beds, the recombiner efficiency was first measured with no iodine present. Hydrogen (0.4 scfm) and oxygen (0.28 to 0.4 scfm) were injected into the low pressure letdown line and passed through the recombiner, Fig. 1, with steam evaporated from the storage tank. The vapors entered the bed at 110°C and left at 450°C. The efficiency, as measured by a Davis explosion meter in the off-gas line, was 99.97%.

Recombiner Poisoning

The recombiner was poisoned by adding 1.4 g of iodine from a bomb to the high-pressure system. The iodine was traced by the addition of 25 millicuries of I^{131}. With the recombiner operating, the iodine was absorbed on the catalyst and lowered the efficiency to 98%. There was no silver alundum bed in the system during this test.

After the test, eight samples of approximately 100 catalyst pellets each, which represented the top and bottom of each quadrant of the bed, were analyzed for iodine. The results showed no correlation based on the location of the samples in the recombiner. However, from the average of all eight samples, 87% of the iodine charged was accounted for in the bed. No iodine was detected in the system off-gas samples.

Silvered Alundum Bed Tests

Preliminary Iodine Removal and Recombiner Regeneration Tests

A preliminary iodine removal test was made by installing a 2-in. depth of silvered alundum ahead of the recombiner. New platinized-alumina pellets were used in the recombiner.

In this test 1.4 g of traced iodine were added to the high pressure system as before. Within 2 hours the iodine concentration in the circulating solution had dropped by a factor of 10 and after 5 hours by a factor of 100. However, enough iodine had passed through the silvered alundum to partially poison the recombiner, which was operating at 450°C.

The recombiner was regenerated by lowering the steam diluent flow slowly until the vapors leaving the recombiner reached 650°C. Iodine was released from the recombiner bed at the high temperature. The iodine was recirculated through the Mockup until it was removed by reaction in the silver bed. After 1 hour of operation at 650°C the Davis meter showed no hydrogen in the off-gas; when the steam flow was subsequently increased to its normal rate, the recombiner operated at its normally high efficiency.

Samples removed from the two beds after the recombiner was poisoned indicated that 17% of the iodine was in the silver bed and 21% was in the platinized alumina. However, after regenerating the recombiner, samples of the two beds showed that 32% of the iodine was in the silver and 2% was in the recombiner. The reason for the low accountability of the iodine in this test was not determined. Only trace amounts were found in the off-gas samples.

Silvered Alundum Bed Efficiency Tests

The next three tests, runs 1, 2, and 3 had two purposes:

1. To verify the theoretical mass transfer coefficient and the relation between bed depth and degree of iodine removal.

2. To check the effect of temperature in the bed on the efficiency of iodine removal.

In these tests no recombiner was used, so that the amount of iodine removed per pass could be determined by a material balance based on the flow rates and solution analyses of the system.

Runs were made with 5- and 8-in. bed depths and at 110, 120 and 150°C. The traced iodine was added continuously to the feed-pump suction at 50 cc/min (~0.25 g of iodine per hour) for 4 to 5 hours. The iodine behavior was followed by sampling various parts of the system periodically and analyzing for I^{131} tracer.

Figure 2 shows the iodine distribution in the system for a typical run. In the high pressure system and the letdown stream, the iodine concentration increased until the concentration was equal to the iodine feed concentration. The letdown stream showed a lower concentration than the high-pressure system because some of the iodine was flashing to the vapor phase at the letdown valve. The condensate tank and pressurizer samples indicated the iodine concentration which passed through the silver bed. The iodine in the storage tank, not shown in the graph, remained at about 0.15 of the high-pressure sample. The sharp break at 4.25 hours came when the I_2 feed was stopped.

At the end of each run, samples from different depths of the bed were counted for I^{131} tracer. The results are shown in Fig. 3.

The bed efficiency (iodine removed per pass) was calculated for each run from the iodine analysis of samples from the silver bed. The efficiency is defined as 100 $\left(1 - \frac{I_2 \text{ conc. at outlet}}{I_2 \text{ conc. at entrance}}\right)$. As a check, the bed efficiency was also obtained from an iodine material balance of the whole system based on the solution analyses and system flow rates. The results of both methods are shown in Tables I and II.

The bed efficiency increased as expected both with increase in bed depth and bed temperature. With increase in temperature the results gradually approached the theoretical efficiency, as developed above.

Wire Mesh Bed Efficiency Tests

These two runs were made at 120°C with two different bed densities and two different bed volumes. In the first test a 6-in.-diameter by 10-in.-deep bed was packed with plated wire mesh having a density of 22 lb/ft^3. The second test was made with a bed 6 in. in diameter by 6 in. deep packed with plated mesh having a density of 29 lb/ft^3.

The first run gave bed efficiencies of 97.0% and 98.2%, respectively, based on the bed analysis and material balance. In the second run, efficiencies were 99.6% and 99.8% by the bed analysis and material balance, respectively.

Wire Mesh Bed Stability

As a final test a 6-in.-deep bed was packed with the 29-lb/ft^3 mesh, loaded with 20 g of iodine, and left in the mockup during a 620-hr run. During this run no iodine was detected in the loop samples. Analysis of solution samples at the end of the run indicated only 1 ppm of silver. Based on the volume of the mockup and the weight of silver in the bed, the loss of silver was only 136 mg, or 0.0025% of the amount in the bed.

Discussion of Results

The recombiner tests have shown that the degree of iodine poisoning was inversely related to the bed temperature. If a high bed temperature were maintained (650°C) there would be little danger of poisoning. In the HRT the present trend has been the reverse. That is, less radiolytic gas than originally designed would be recombined externally and as a result a lower recombiner temperature and a higher probability of iodine poisoning would be encountered.

During these tests only minor amounts of iodine were found in the off gas which indicates that all the iodine would stay in the system until it had decayed. So, in a breeder type reactor without an iodine removal system, the xenon poison level would be high and the breeding ratio would be lowered as a result. However, an iodine removal bed would hold the iodine until it decayed to Xe, which could leave through the offgas system.

Although the experimental results with silvered alundum pellets, Table I, showed lower mass transfer than the theoretical calculations, the theoretical method can be used satisfactorily to design a silver bed; a suitable safety factor is recommended.

The test results indicate that the iodine removal bed efficiency increases with temperature and at higher temperatures would probably approach the theoretical value. This may mean that at the lower temperatures the diffusion rate was not the only important mechanism.

The tests indicate that the silver-plated wire mesh is superior to the silvered alundum pellets for a given volume of bed, considering the surface to volume ratio of the packing, Table II.

This report is based on a minimum number of experiments, and suggestions for further studies have been made under the Conclusions and Recommendations.

Conclusions and Recommendations

The following conclusions have been made:

1. Silver beds will efficiently remove iodine from a dry vapor stream.

2. Of the two materials tested, the silver-plated wire mesh was superior to the silvered Alundum rings.

3. With no silver bed the iodine will remain in the system until it decays.

4. Iodine will lower the recombiner efficiency slightly at 450°C.

5. The iodine poison can be removed from the recombiner bed by increasing the vapor temperature in the bed to 650°C.

The following recommendations are made based on the above work:

1. The HRT should use a silver-plated wire mesh bed with a bed density of about 29 pounds per cubic foot. The bed should be sized to hold the stable iodine produced in a reasonable time (1 to 2 years).

2. With wire mesh for a silver support, a theoretical mass transfer correlation should be developed.

3. The effect of iodine removal bed temperature should be extended to the higher temperatures expected in a reactor.

4. The effect of mass flow rate on the reaction should be determined. (Only one mass flow rate was used in these tests.)

5. The accurate determination of the reaction controlling mechanism should be made over the temperature range expected in a reactor.

Acknowledgment

The assistance and cooperation received from the Chemical Technology Division in sampling and analyzing the data during these tests were greatly appreciated.

Table I

Comparison of Theoretical and Experimental Results

for 6 in. Diameter Silver Alundum Beds

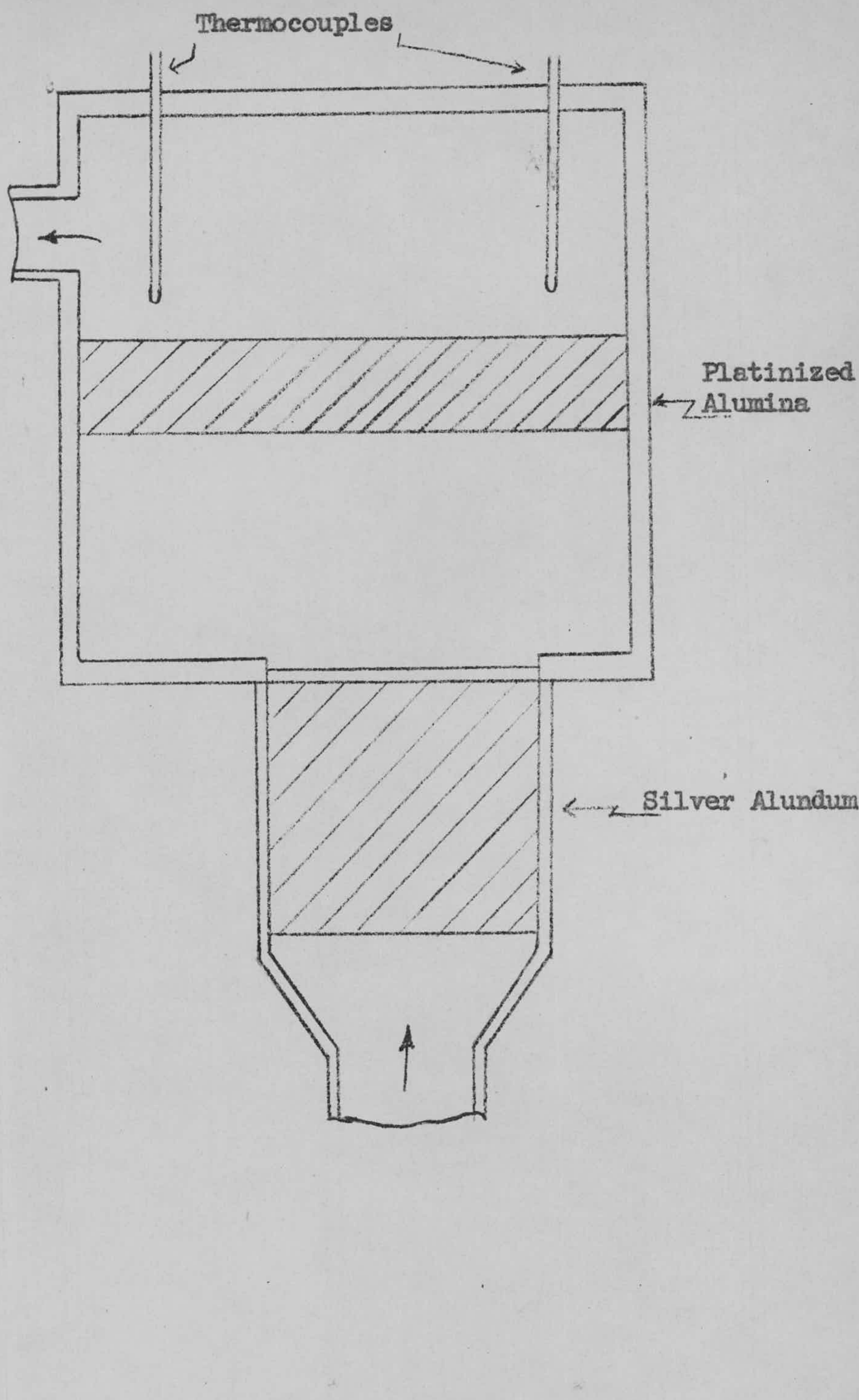
Run	Temp.	Bed Depth	kg Calc.	kg Exptl.	Efficiency - % Calc.	Efficiency - % Exptl. Bed I Analysis	Efficiency - % Exptl. Material Balance
1	110	5	2.90	0.72	98.65	67.0	35-74
2	150	8	2.96	1.54	99.91	97.7	86
3	120	8	2.89	0.68	99.86	81.0	80

Table II

Comparison of Experimental Efficiency of Silvered Alundum

and Silver Plated Wire Mesh Beds at 120°C

Run	Support Material	Surface/Volume ft^2/ft^3	Bed Depth ft	Efficiency Iodine Analysis in Bed	Efficiency Material Balance
3	Alundum	208	0.67	81%	80%
4	Stainless	159	0.83	97%	98.2%
5	Stainless	209	0.5	99.6%	99.8%



RECOMBER AND IODINE SCRUBBER

Fig. 1

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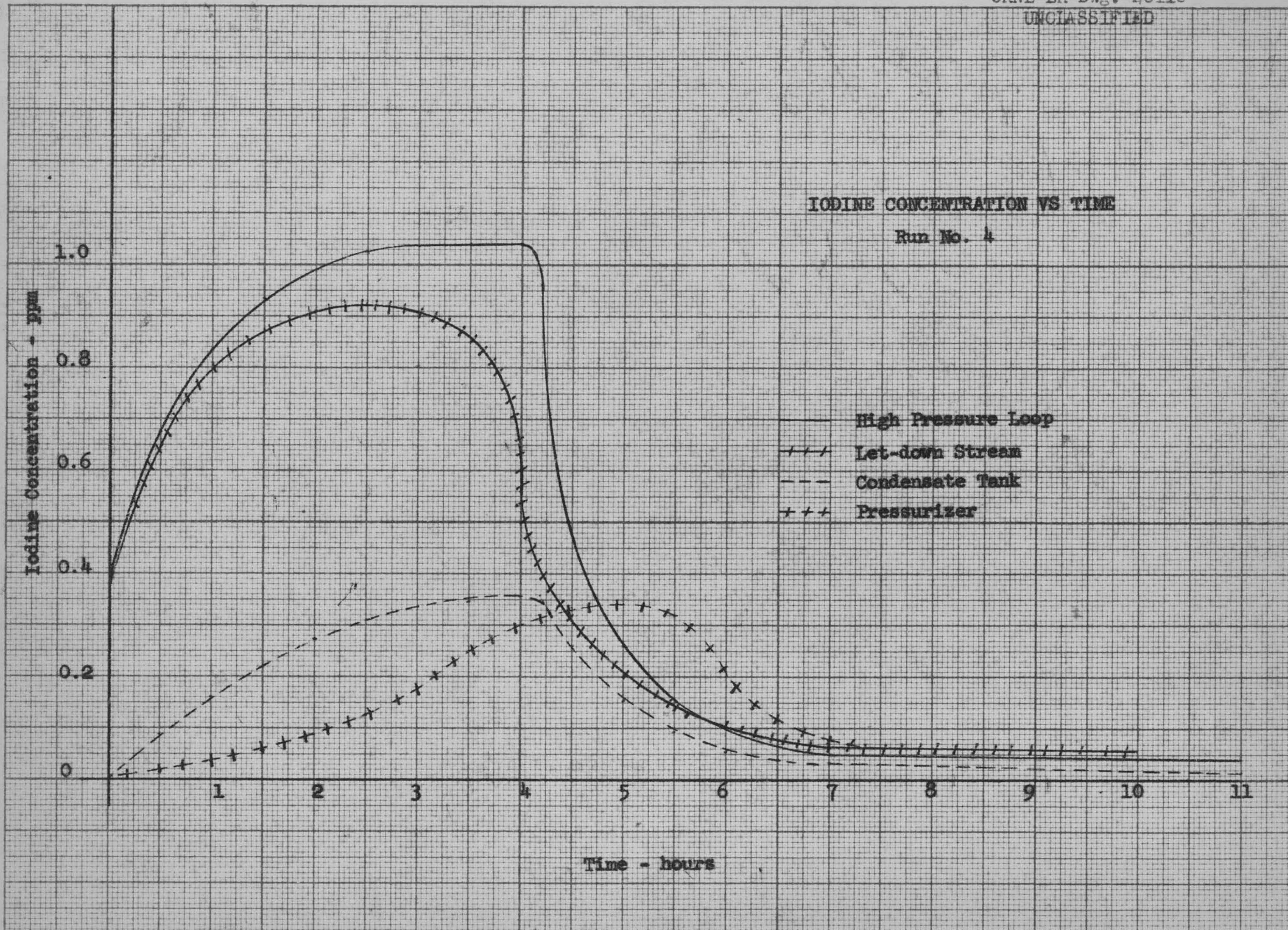

Fig. 2

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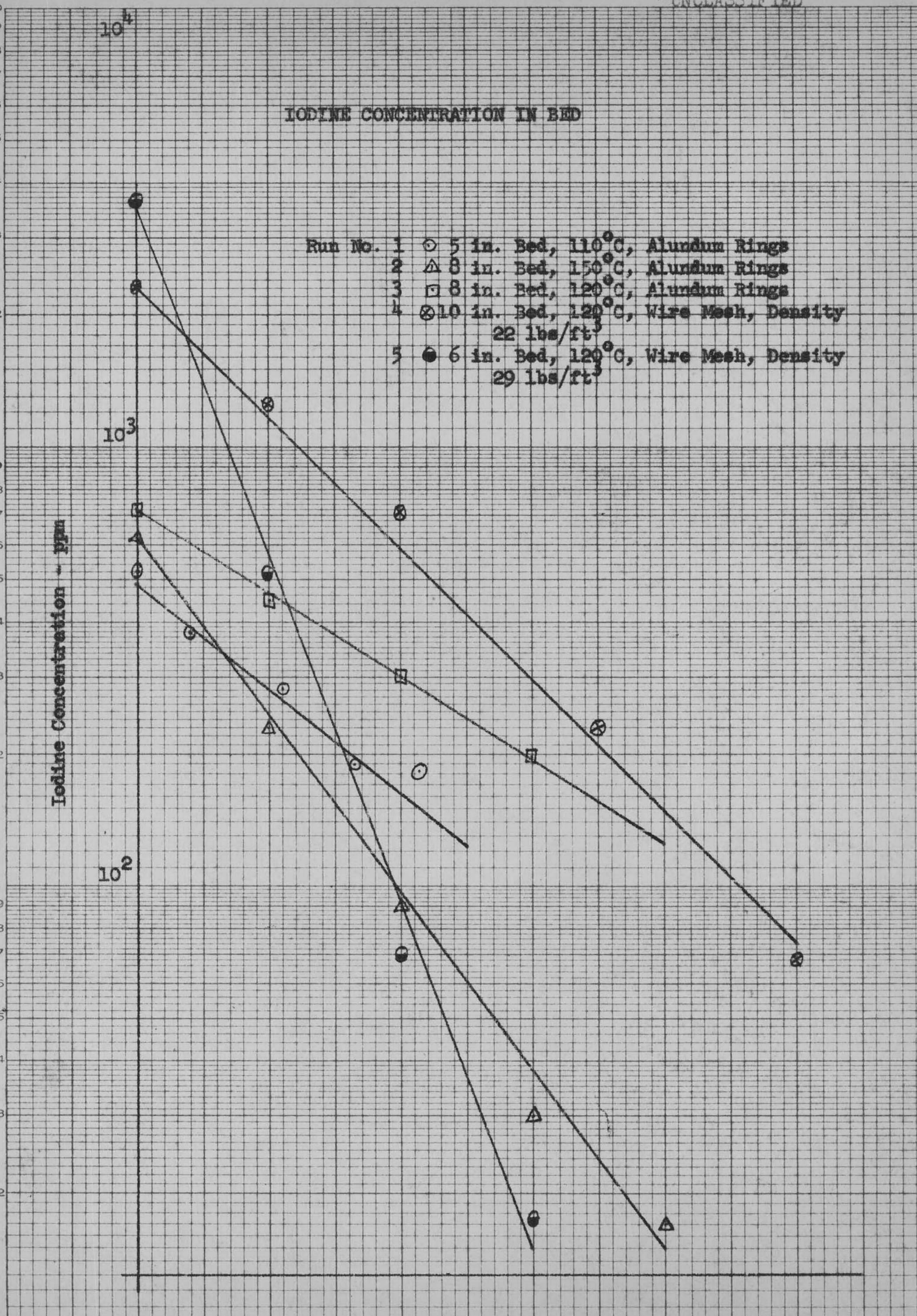

Fig. 3

REFERENCES

1. Vitro Laboratory, HRP Quarterly Report July to September, 1956, KLX-10045.

2. D. E. Ferguson et al., HRP Quarterly Progress Report October 31, 1956, ORNL-2222, p 137-138.

3. Hougen and Watson, Chemical Process Principals, Part III, John Wiley and Sons, London, September, 1955, p 975-995.

4. B. W. Gamson, G. Thodas, O. H. Hougen, Trans. Am. Inst. Chem. Engrs., 39, 1 (1943).

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