UNCLASSIFIED

~~CONFIDENTIAL~~

HW-52796

CARRYOVER

CHEMISTRY-SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM

This document classified by
A. Brunstad

AEC RESEARCH AND DEVELOPMENT REPORT

REDUCTION AND STABILIZATION OF PLUTONIUM NITRATE IN CATION EXCHANGE FEED AND PRODUCT SOLUTIONS

~~C. 1 thru 3 Extra~~

Photostat Charge $ ~~5.98~~
Microcard Charge $ ~~______~~
for Access Permittees

Available from
Technical Information Service Extension
P. O. Box 1001, Oak Ridge, Tennessee

~~This document consists of 18 pages, No. 1 of 3 copies, Series B~~

By

A. Brunstad
and
R. C. Smith

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.~~

~~This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.~~

234-5 Development Operation
Research and Engineering Operation

September 24, 1957

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the General Electric Company under Contract #W-31-109-Eng-52

Classification cancelled (or changed to UNCLASSIFIED)
by authority of Std. In. Decl. Bd. dtd 11-10-58
by J. C. Ridderson, TIE, date 11-17-58

534 001

UNCLASSIFIED

DISCLAIMER

REDUCTION AND STABILIZATION OF PLUTONIUM NITRATE IN CATION EXCHANGE FEED AND PRODUCT SOLUTIONS

I. INTRODUCTION

In the concentration and purification of plutonium by cation exchange, the plutonium ions are adsorbed on the resin from a dilute nitric acid solution (about 0.3 M) and eluted by more concentrated nitric acid (about 5.8 M). Plutonium for the feed solution must be in the plus three valence state, but the nitrate solution from a solvent extraction process contains a high percentage of plutonium(IV) and a small amount of plutonium(VI). An effective reductant is sought to reduce these higher valence states.

The higher nitric acid concentration used to elute the plutonium is a source of oxidant tending to reoxidize the plutonium(III) to plutonium(IV). If oxidation is allowed to occur in the stripping column, waste losses will be increased and the gaseous by-products of the oxidation will hinder column operation. A holding reductant must, therefore, be provided to remove oxidants from the nitric acid. This paper described experimental work with a number of reductants thought useful in meeting these requirements.

II. OBJECTIVE

It was desired to find a reducing agent satisfactory for the reduction of plutonium in Purex product streams and to make these streams suitable as cation exchange feeds. A suitable holding reductant for use in the high acid elutant stream of the ion exchange cycle and a stabilizer for the product was also sought.

The desired reductant should:

1. Reduce plutonium rapidly and completely to the plus three state.
2. Not add metal ions to the system.
3. Have a low exchange potential with the resin.
4. Product no gaseous oxidation products or form precipitates in any part of the ion exchange cycle, feed, or product.
5. Allow plutonium eluates to be reoxidized safely and concentrated without formation of tars or precipitates.
6. Cause no serious corrosion difficulties.
7. Be inexpensive, safe to handle, and readily available.

III. SUMMARY AND CONCLUSIONS

The bisulfites met the requirements for speed and completeness of reduction of plutonium in the feed material. They are cheap and readily available. Ammonium bisulfite adds no metallic ions and is considered most suitable. The sulfites are a source of sulfate ions, however, which may result in precipitation of plutonium sulfate if the product is concentrated.

Qualitative tests with sulfurous acid indicated rapid and complete reduction of low concentration plutonium solutions but this reagent adds undesirable sulfate ions.

Hydrozylamine sulfate reduced plutonium(IV) to plutonium(III) at a rate too slow to be practical and the reduction was not complete at any concentration of reductant. This reductant is also a source of sulfate ion which is undesirable in the final product.

Hydroxylamine hydrochloride is only slightly better than the sulfate with respect to speed and completeness of reduction and the chloride ion is highly undesirable in stainless steel equipment.

Ascorbic acid affected rapid and complete reduction of plutonium(IV) to plutonium(III). Precipitates were formed, however, which plugged the filters, accumulated in the resin column, or passed into the waste stream with consequent plutonium losses.

Semicarbazide reduced plutonium(IV) to plutonium(III) rapidly and completely. A 2BP solution was completely reduced in one-half minute with 0.10 $\underline{M}$ semicarbazide. Ion exchange feeds reduced with semicarbazide at times formed an unidentified precipitate. Semicarbazide is expensive and requires special handling procedures.

Qualitative tests with amino-guanidine indicated slow reduction of plutonium(IV) to plutonium(III).

Amino-guanidine and sulfamic acid were used as holding reductants. The stabilizing effect of these agents was found to be proportional to their own concentration and inversely proportional to the nitric acid concentration. Gas liberation was evidenced with product solutions stabilized with amino-guanidine and with sulfamic acid. Gas evolution was linear with time. Gassing is explained by the reaction of the reductant with nitrous acid to form nitrogen gas and the gassing is, therefore, an inherent part of the stabilizing behavior. Oxidation of plutonium(III) to plutonium(IV) enters into the gassing phenomena through an increase in nitrous acid, due to the autocatalytic mechanism of plutonium oxidation.

IV. DISCUSSION

A preliminary survey was made with five reducing agents: hydroxylamine sulfate, ascorbic acid, sulfurous acid, semicarbazide, and amino-guanidine. The effectiveness of these agents was measured by visual observation of color change, formation of precipitate, and gas evolution. A subsequent study was made using a recording spectrophotometer to obtain more specific information on rates of reduction and reoxidation. Hydroxylamine sulfate, hydroxylamine hydrochloride, sodium bisulfite, sodium metabisulfite, ammonium sulfite, ammonium bisulfite, and semicarbazide were studied.

Observance of the performance of these agents when employed in the operation of the laboratory continuous ion exchange columns comprised the third phase of the study.

A. Preliminary Survey

Ascorbic acid was tested at several reducing concentrations and at various acidities from 0.3 M to 6.0 M. It reduces plutonium rapidly and completely. For ion exchange feeds containing up to 10 g/l Pu, a concentration of 0.05 M ascorbic acid appeared satisfactory. Reduction of 5 g/l Pu in 0.3 M HNO_3 was obtained with 0.01 M ascorbic in most cases, but completeness of reduction was not assured and reoxidation sometimes occurred within two hours. Solutions reduced with 0.05 M ascorbic acid required from 15 to 20 days to become completely reoxidized. Unattractive features of ascorbic acid included the occasional formation of a precipitate ranging in color from orange to grey-white as the plutonium solution reoxidized. The precipitates were not identified but appeared to be formed by plutonium and one of the oxidation products of ascorbic acid. At 6 M HNO_3, 0.10 M ascorbic acid would not reduce the plutonium without the addition of sulfamic acid to destroy the nitrite ion.

Sulfurous acid made by bubbling sulfur dioxide through water was tested and found to reduce lower concentrations of plutonium rapidly and completely at low nitric acidities. It was not found as effective as either hydroxylamine or ascorbic acid, however, and was not tested in the continuous ion exchange system.

Semicarbazide was found to reduce plutonium(IV) rapidly without appreciable gas formation at plutonium concentrations up to 10 g/l. Reduction with semicarbazide at 0.05 M was found to keep the plutonium solution blue for up to 19 days. It also reduced plutonium in 6 M nitric solutions, but at slower reduction rates. Semicarbazide is a somewhat unstable compound and should be kept under refrigeration. The manufacturer's recommended shelf life is three months. The normal use for this reagent is for drugs and probably not greater than one per cent decomposition occurs in a 90-day period if the semicarbazide is kept under refrigeration.

Amino-guanidine (obtained as the bicarbonate) in all preliminary tests proved to have a much slower reducing rate than any of the other agents tested. It did not reduce plutonium in 6 M HNO_3. Time for reduction of 15 g/l Pu in 0.3 M HNO_3 ranged from one hour to several days. It was, therefore, not tested as a reducing agent in column operation but retained as a possible holding agent for use in elutriant solutions.

Addition of 0.3 M sulfamic acid to the reducing agent solutions tested did not increase the rate of reduction of the plutonium by the individual reductants tested. Addition of sulfamic acid did approximately double the length of time the plutonium remained in the three valence state.

B. Reduction During Simulated Purex 2B Column Strips

Reduction of the Purex product during the stripping step in the 2B column would simplify feed preparation for ion exchange. Sulfurous acid, hydroxylamine, and ascorbic acid were tested on simulated 2AP streams. The sulfurous acid did not reduce the plutonium under these conditions. Both hydroxylamine hydrochloride and ascorbic acid at a concentration of 0.05 M and a 2AP to strip ratio of 2 to 1 appeared to reduce the plutonium rapidly and completely. There was no visible gas formation and the solutions were still reduced after an interval of one week.

C. Spectrophotometric Studies

1. Hydroxylamine Sulfate

Information obtained from Savannah River* indicated hydroxylamine sulfate to be a promising reductant. However, spectrophotometric determinations on feed prepared for ion exchange showed incomplete reduction. Reduction with hydroxylamine sulfate was actually retarded by increasing the reductant concentration (Figure 1). This is explained by the formation of a plutonium(IV) sulfate complex which is difficult to reduce. If the sulfate complex is formed more rapidly than the plutonium(IV) is reduced, the complexing effect might be expected to adversely influence the reduction rate according to sulfate concentration, during an initial period of complex formation. If reduction is through the uncomplexed plutonium(IV) ion, the reaction should be fast at first and decrease sharply when the complexing equilibrium is established. Reduction thereafter should not be affected by reductant concentration because of its great excess over uncomplexed plutonium. The different concentrations of hydroxylamine sulfate (H.A.S.) yielded curves of similar slope after the initial rapid reduction. The retarding effect is proportional to the initial sulfate concentration.

The semilog plot, Figure 1, was used for convenience only. The break in the curves after the short initial period would indicate that no simple rate law could be devised from reactant concentrations. Some values of k, the reaction velocity constant, based on the rate expression:

$$-\frac{dPu(IV)}{dt} = k\left[Pu(IV)\right]\left[H.A.S.\right]$$

were calculated to show the discontinuity in the reduction rate and an approach to equilibrium.

(*) Private communication

TABLE I

REDUCTION WITH H.A.S. - SECOND ORDER RATE CONSTANT

Time - Minutes	1/(g mole)(min)
0	-
1	12.74
5	1.04
30	0.32
180	0.04
0	-
1	4.09
5	0.58
30	0.15
180	0.03
0	-
1	1.39
5	0.25
30	0.06
180	0.01

There was no significant difference in valence state at three hours and at three days. It is postulated that sulfate complexing caused a sufficient shift of potential to prevent reduction of plutonium(IV) to plutonium(III). The introduction of sulfate ion is objectionable both from the standpoint of reaction kinetics and also because of the possible precipitation of plutonium sulfate.

Sulfamic acid did not adversely affect the rate of reduction with hydroxylamine sulfate as it did with the bisulfites. This might be expected, as the H.A.S. will more quickly furnish sulfate ions to complex the plutonium(IV) and further addition of sulfate ions by hydrolysis or oxidation of sulfamic acid will have no effect.

Hydroxylamine hydrochloride was tried at one concentration only--0.05 $\underline{M}$. The reaction mechanism must be similar to that found for the sulfate, as evidenced by the similarity of the respective curves (Figures 1 and 3).

2. Sulfite Reductions

Reduction with sodium bisulfite and ammonium bisulfite was studied by spectrophotometer when it became apparent that reduction by H.A.S. was unsatisfactory.

A reddish-brown color develops when sulfite solution is added to plutonium(IV) nitrate solution. The blue color of plutonium(III) becomes predominant within one-half minute, however. In spite of this apparent delay in the reduction, the reaction rate is greatest during the first minute. Reduction during this period was not significantly affected by reductant concentration (0.026 M - 0.081 M $NaHSO_3$), Figure 2. The reaction rates thereafter are proportional to reductant concentration. The behavior is somewhat different at 0.107 M sulfite. The initial rapid period is less pronounced, but the rate thereafter follows the concentration rule.

Calculations of the second order velocity rate constant was done as with H.A.S.

Values of the rate constant corresponding to data for two curves shown in Figure 2 are given in Table II.

TABLE II

REDUCTION WITH SODIUM BISULFITE - SECOND ORDER RATE CONSTANT

Time - Minutes	k 1/(g mole)(sec.)
0	-
1	21.1
2	5.6
3	4.4
4	2.5
5	2.9
6	2.0
7	2.7
0	-
1	12.50
2	5.51
3	4.04
4	3.45
5	3.03
6	3.05
7	3.16

The higher value of k at one minute for the lower concentration of reductant indicates a complexing effect similar to that observed with different concentrations of H.A.S. The values of k level out with the sodium bisulfite reductant, however, and are constant after about three minutes, indicating a true second order reaction and complete reduction.

A 5 g/1 Pu(IV), 0.28 M HNO_3 solution was reduced with 0.05 M sodium bisulfite with and without sulfamic acid. The sulfamic acid

(SA) delayed the reduction. The remaining plutonium(IV) concentration was similar at 30 minutes (no SA) and at 16 hours (0.05 M SA). The adverse effect is attributed to sulfate ion formed by hydrolysis and oxidation of the sulfamate.

D. Reduction Performance With Continuous Ion Exchange Equipment

The ion exchange prototype was a Higgins(1)-type continuous unit wherein the feed is added continuously to one column and the loaded resin pushed to a second column where it is eluted. When the resin has been eluted, it is fed back to the first column for reloading, making a complete loop of resin and allowing continuous operation of the columns.

The ion exchange feed was made up and reduced in a critically safe 6" I.D. glass pipe. Each batch of feed contained approximately 28 liters of feed and ranged from 2.5 - 8.0 g/l in Pu and 0.2 - 0.4 M HNO_3. The feeds were agitated by air or nitrogen sparging during the 20 - 60 minute period allowed for reduction.

The first batch of feed was reduced with 0.05 M hydroxylamine hydrochloride. The reduction appeared to be rapid and satisfactory. Due to improper feed make-up technique, a considerable amount of plutonium polymer formed and the feed was set aside for later use. In subsequent runs, the reducing agent was added in solution with 0.1 M HNO_3 to reduce polymer formation.

Five batches of feed were reduced with hydroxylamine sulfate at hydroxylamine concentrations ranging from 0.03 - 0.05 M. In all cases it was necessary to add a small amount of ascorbic acid to produce greater than 70 percent reduction within two hours. When used with hydroxylamine sulfate, 0.005 to 0.01 M ascorbic acid was found adequate to complete the reduction. A milky precipitate believed to be plutonium(IV) polymer formed in three of the five solutions.

Five feeds were reduced with ascorbic acid alone. Rapid reduction, complete within 20 - 60 minutes was accomplished with concentrations from 0.05 M down to 0.033 M. In three of these feeds, plutonium polymer was formed and in at least one, an unidentified grey precipitate plugged filters and caused considerable operational difficulty. The polymer, when formed, causes slight filter plugging, but goes through both filters and the resin into the waste streams, increasing waste losses.

Two feeds were reduced with semicarbazide 0.07 M and 0.09 M respectively. The reduction was rapid and complete within one-half hour, but a milky precipitate was formed in both feeds.

Four batches of feed were reduced by making them 0.058 M in sulfur dioxide with sodium meta bisulfite. The reductions were rapid and com-

---

(1) Higgins, I. R. Mechanical Features of the Higgins Continuous Ion Exchange Column. ORNL-1907 (Unclassified)

plete within one-half hour and the feeds remained clear. This was considered a very satisfactory reductant.

One batch of feed was reduced with 0.10 M ammonium sulfite. The reduction was rapid--but again a milky precipitate was formed. Further study would be necessary to determine how much of the milky cloudiness obtained in such feeds is plutonium polymer. It was noted in the preliminary work with ascorbic acid that precipitates were formed on several occasions from reactions with the plutonium and oxidation products of the reductant. Precipitates were also obtained on a few experiments made with semicarbazide, especially in high plutonium concentrations.

The problem of polymer formation possibly can be overcome with proper reductant solution addition technique or by adding the reductant as a solid.

E. Product Stability

Oxidation to the plutonium(IV) state has been associated with gassing. A study was made of the rate of oxidation as affected by acidity, and the relation of gassing to valence change. The liberation of gas and valence change of plutonium were noted for two ion exchange product solutions. Results are shown in Table III and Figure 4.

TABLE III

PLUTONIUM OXIDATION AND GASSING

	Holding Reductant	
	Amino-guanidine	Sulfamic Acid
HNO_3 concentration	2.80 M	4.84 M
Percent plutonium(IV) at 10 days	2 %	50 %
ml of gas/g Pu oxidized	1530	67

The liberation of gas appears to be linear with time and not directly related to the plutonium oxidation. The presence of stainless steel did not affect the rate of gassing.

Samples were taken for valence state determination from six bottles representing consecutive product solutions from one ion exchange run using 0.33 M SA and 5.0 M HNO_3 as elutant. Results are shown in Table IV.

TABLE IV

STABILITY OF ION EXCHANGE PRODUCT

Bottle Number	Pu/l Grams	HNO_3 M	% Pu(IV) 0 days	% Pu(IV) 1 day	% Pu(IV) 6 days
1	17	2.60	5	6	10
2	35	3.80	6	9	33
3*	37	3.80	39	41	51
4	35	4.00	7	10	33
5	44	4.50	5	10	44
6	40	4.30	4	9	30

(*) The high oxidation of samples from this bottle was due to overheating of the resin column during the ion exchange run.

Samples from bottle No. 2 were acidified to 7 M and 8 M HNO_3 and the rates of oxidation were compared with the original 3.8 M acid solution. Results are shown in Figure 5. Figure 6 shows the effect of nitric acid concentration on the oxidation of plutonium solution eluted with 0.30 M amino-guanidine.

Plutonium(III) solutions reduced with ammonium sulfite were noted to remain reduced longer than similar solutions reduced with sodium bisulfite. It appears that in this case the ammonium ion acts as a holding agent by decreasing the nitrite ion concentration. Three test tubes were made up to test for gaseous by-products of a possible reaction between the ammonium ion and an oxidant of the nitric acid system. Results are given below:

TABLE V

NITRATE-AMMONIUM ION REACTION

HNO_3	$(NH_4)_2SO_4$	$NaNO_2$	VISIBLE REACTION
1.0 M	0.5 M	0.5 M	Gassing
1.0 M	---	0.5 M	None
---	0.5 M	0.5 M	None

A simple explanation of the above observation is as follows:

$$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2H_2O$$

The rate of liberation of N_2 gas in a nitric acid solution has been represented by the following expression(2):

$$\frac{d(N_2)}{dt} = k(NH_4^+)(NO_2^-)(HNO_2)$$

---

(2) Yost, D. M. and H. J. Russel, Systematic Inorganic Chemistry. New York: Prentice-Hall, Inc., 1946, pp. 67-68.

The ammonium ion is, therefore, a means of eliminating the nitrite ion and nitrous acid.

The effectiveness of a holding reductant has been assumed to be due to its rate of reaction with the oxidants in the nitric acid system. Thus, sulfamic acid is similarly effective because of the following very rapid reaction:

$$HNO_2 + NH_2SO_3^- \rightarrow N_2\uparrow + HSO_4^- + H_2O$$

Gassing is, therefore, an integral part of the stabilization of plutonium(III) in a nitric acid system. The effectiveness of the holding reductant is related to its rate of oxidation compared with that for plutonium.

It is evident that plutonium solutions containing the holding reductants used in these experiments cannot be safely sealed for storage or shipment. A satisfactory method of concentrating solutions for storage and shipment is given below.

F. Continuous Concentration of Product Solutions

Product solutions containing sulfamic and nitric acids were continuously concentrated in the following manner by R. E. Latta(3):

> A feed containing plutonium nitrate, nitric acid, and sulfamic acid was added dropwise to a boiling solution. The composition of the feed is given in Table VI. As the feed was added, distillate and heel were removed. The rate of volume removed equaled the rate of feed addition. The final concentrations of the heels removed are given in Table VII. Although the concentrated product was stable at boiling temperatures, plutonium sulfate precipitation occurred upon cooling. A study of the precipitation of plutonium sulfate from these solutions has been reported(3).

TABLE VI

COMPOSITION OF FEED IN CONTINUOUS CONCENTRATIONS

Run No.	Plutonium Grams/liter	HNO_3 M	Sulfamic Acid M
1	24.4	2.20	0.20
2	18.0	1.80	0.16
3	11.8	1.90	0.15
4	3.0	0.40	0.015
5	63.2	3.45	0.30

(3) Latta, R. E. and H. H. Hopkins, Jr., Continuous Concentration of Cation Exchange Product." HW-50280 (Secret), May 20, 1957.

TABLE VII

COMPOSITION OF HEEL AT END OF CONTINUOUS CONCENTRATION

Run No.	Plutonium Grams/liter	HNO_3 M	Sulfamic Acid (Sulfate) M
1	85	5.6	0.51
2	106	6.5	0.69
3	82	7.3	0.85
4	120	7.6	0.55
5	165	8.6	0.79

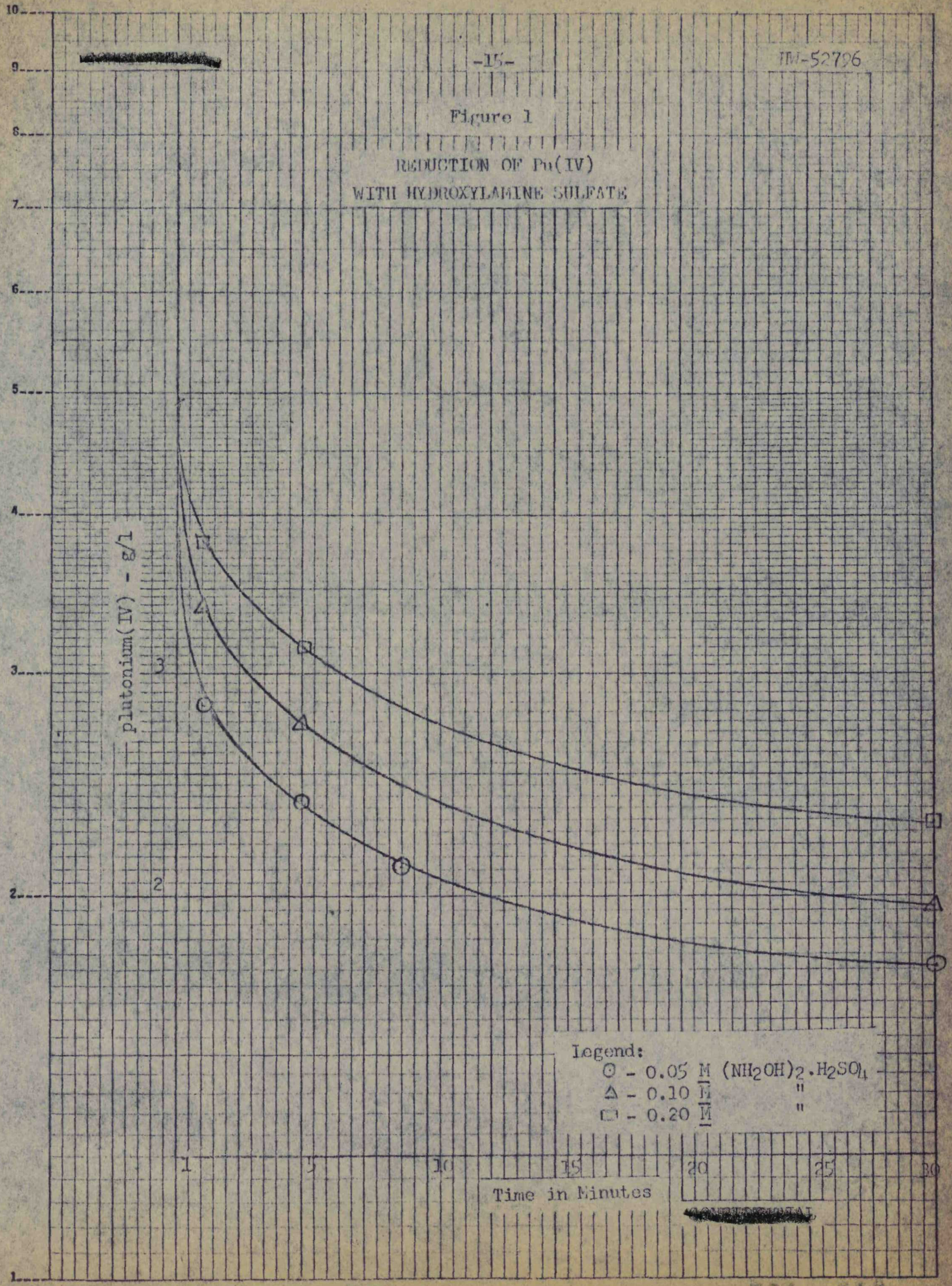


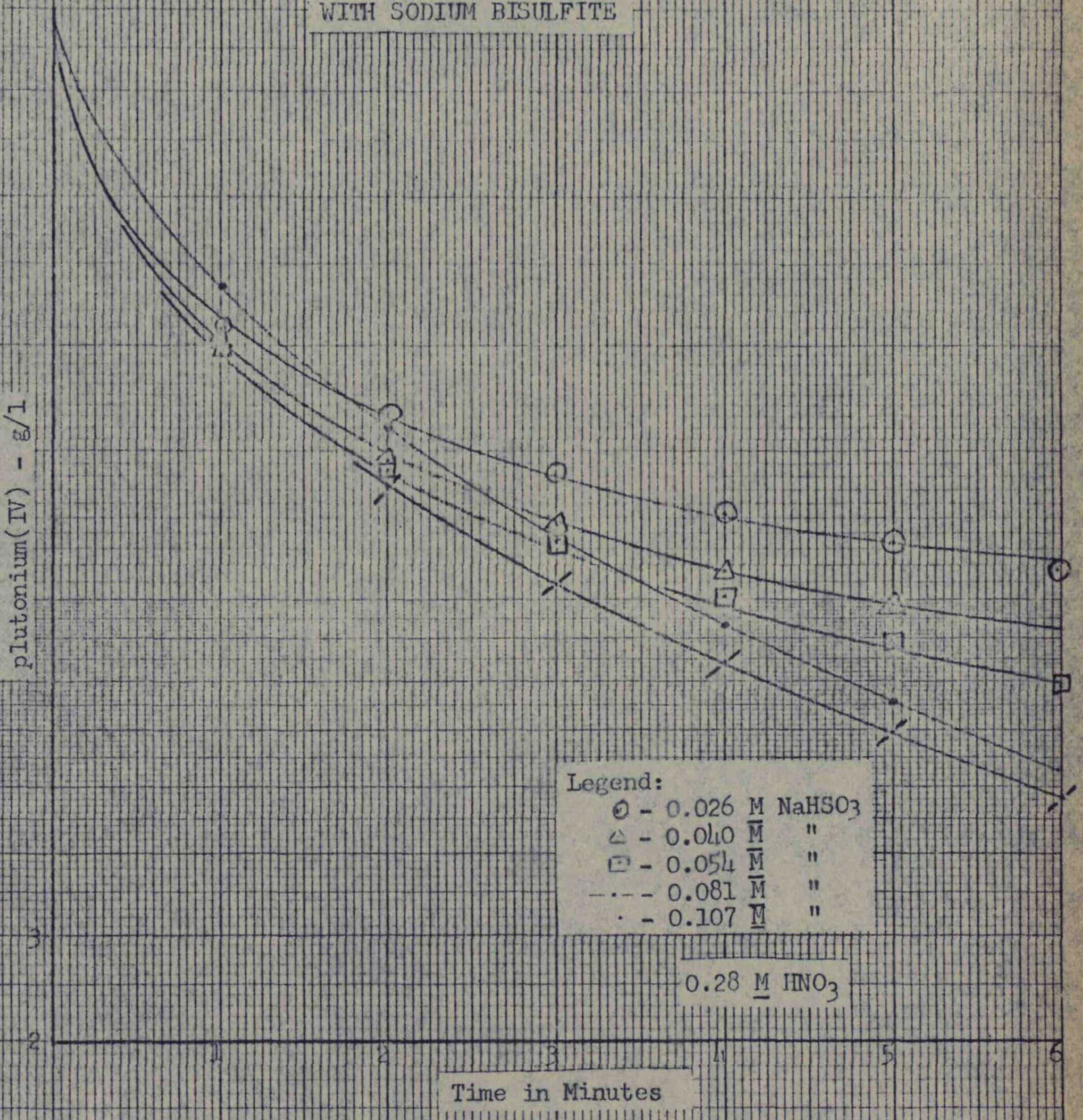
Figure 1

REDUCTION OF Pu(IV)
WITH HYDROXYLAMINE SULFATE

[redacted]

Figure 2

REDUCTION OF Pu(IV)
WITH SODIUM BISULFITE

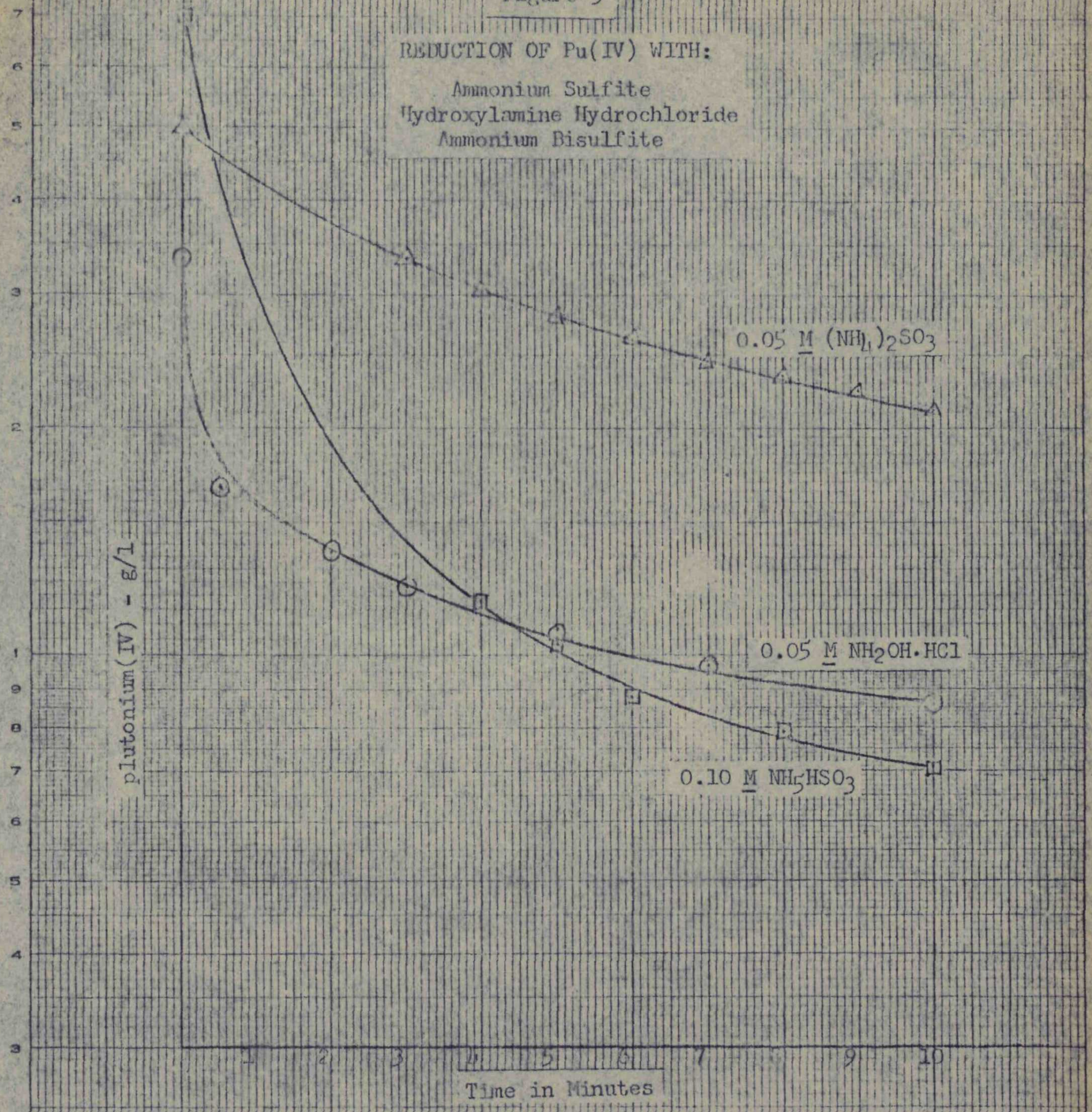


~~CONFIDENTIAL~~

Figure 3

REDUCTION OF Pu(IV) WITH:

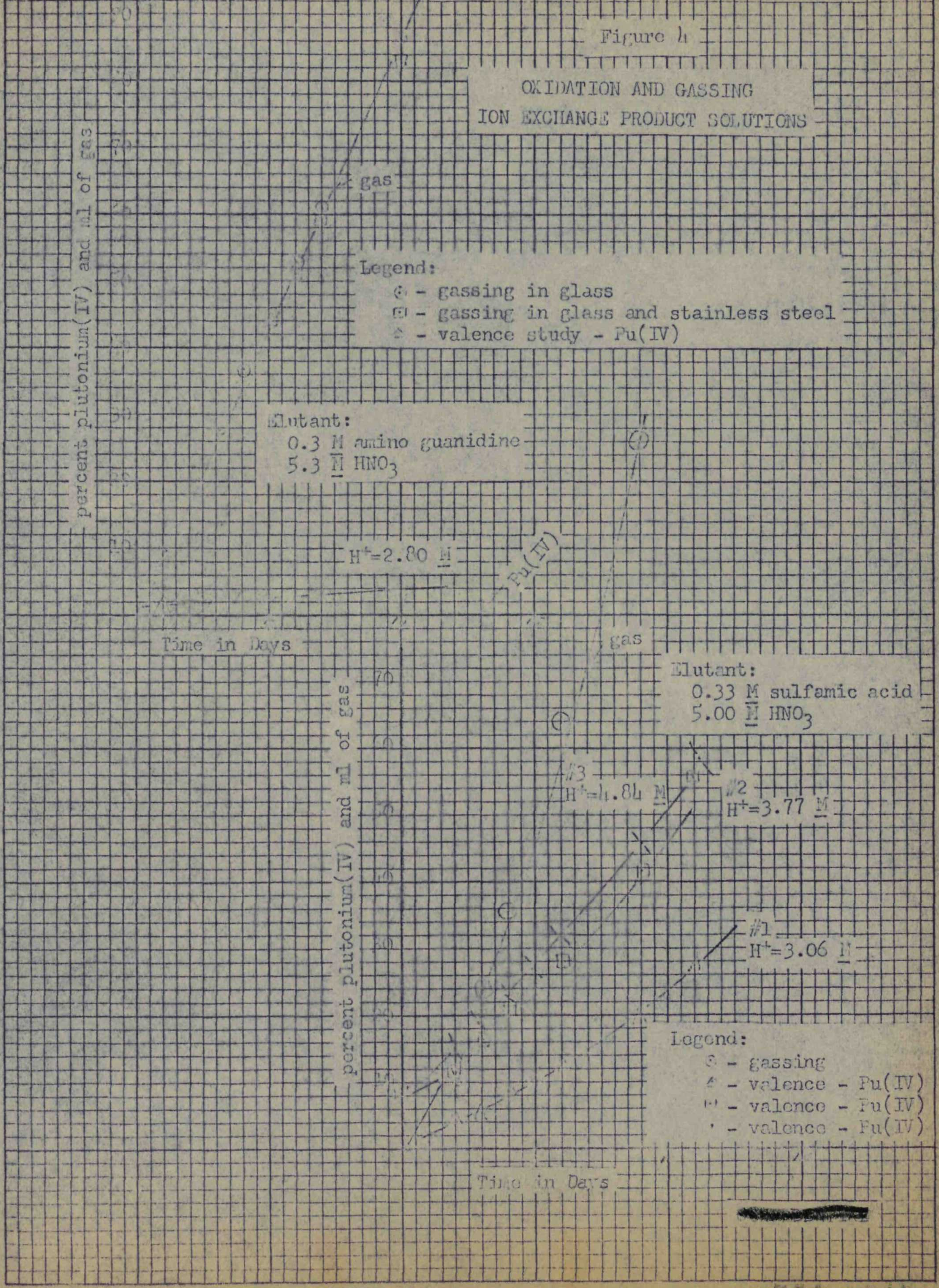
Ammonium Sulfite
Hydroxylamine Hydrochloride
Ammonium Bisulfite



[redacted]

Figure 4

OXIDATION AND GASSING
ION EXCHANGE PRODUCT SOLUTIONS



[redacted]

Figure 5

OXIDATION RATES
ION EXCHANGE PRODUCT

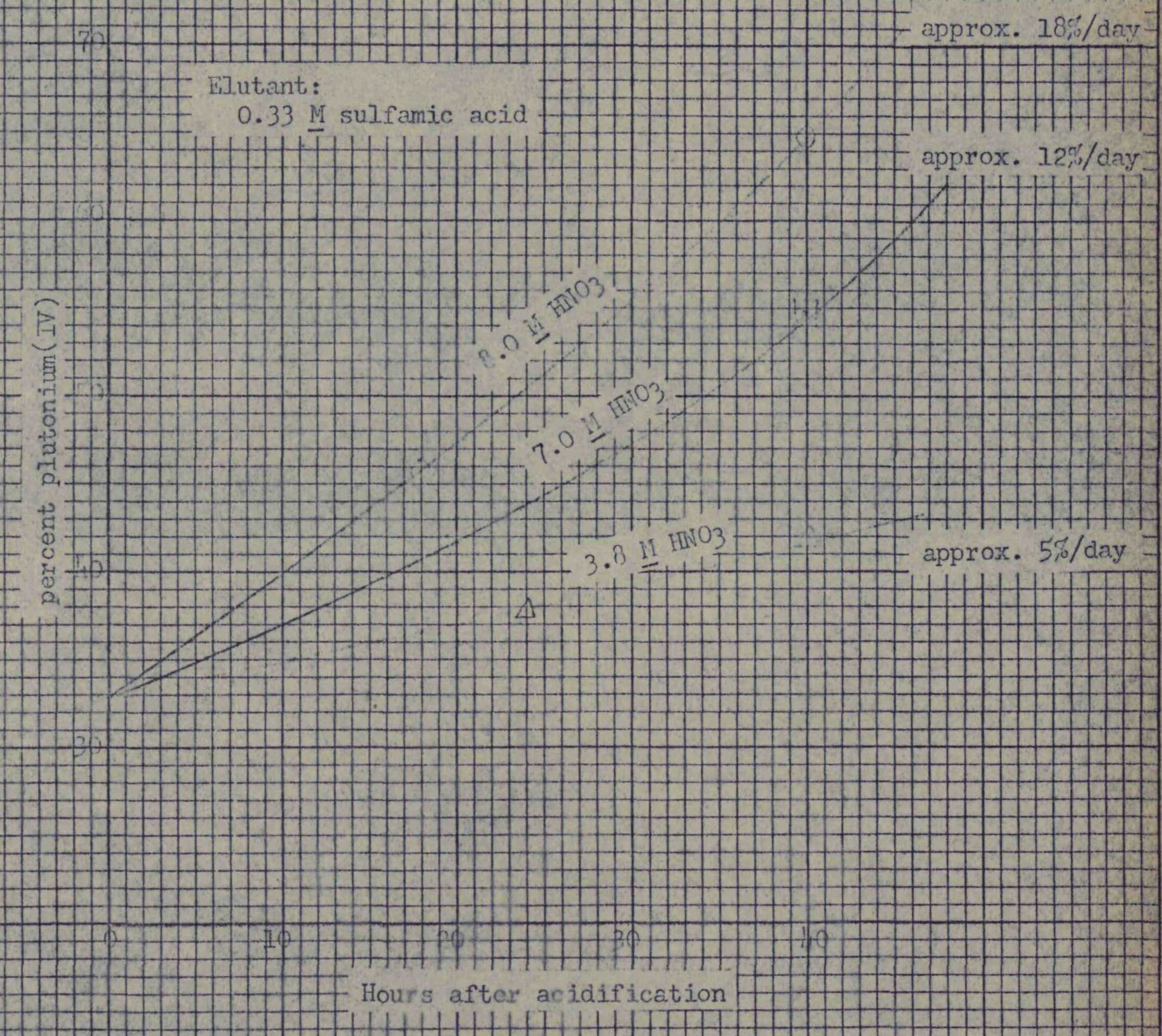


Figure 6

OXIDATION RATES ION EXCHANGE PRODUCT