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James P. Coughlin and Raymond R. Tsukimura

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James P. Coughlin and Raymond R. Tsukimura

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AFRPL-TR-67-297

Report 1032-81F

LATTICE DEFORMATION FEASIBILITY STUDY

Contract AF 04(611)11548

James P. Coughlin and Raymond R. Tsukimura  
Aerojet-General Corporation  
Sacramento and San Ramon, California

Final Technical Report AFRPL-TR-67-297

December 1967

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Air Force Propulsion Laboratory  
Research and Technology Division  
Air Force Systems Command  
Edwards Air Force Base, California

## FOREWORD

The work reported herein was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, under Contract AF 04(611)-11548, Project No. 3148, Program Element No. 62405184. The program in its initial stages was monitored for the Air Force by Dr. Wm. J. Leahy, RPCS, and is currently monitored by Lt. R. Bargmeyer, RPCS.

This report constitutes both a third quarterly and final report for this program and covers work performed from 1 April 1966 through 30 September 1967. The investigations were performed by Aerojet-General Corporation personnel of the Research and Technology Operations, Sacramento, California, and the Engineering and Development Division, San Ramon, California. The principal investigators are Mr. J. P. Coughlin (Sacramento), who is directly responsible for the Calorimetry and Analysis portions of the program and overall program manager, and Mr. R. R. Tsukimura (San Ramon), who is in charge of the sample irradiation phase of the program. Determination of optical-crystallographic properties were performed by Mr. J. L. McGurk, Sacramento. This report has been given the Aerojet-General report number 1032-81F.

This report contains no classified information.

The distribution list for this report is in accordance with the CPIA Mailing List, May 1967 (CPIA Publication No. 147), Section I (Basic List) and Section II (Categories 1, 2, 3, and 4).

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF  
Chief, Propellant Division

## ABSTRACT

Four samples of reagent grade ammonium perchlorate weighing five grams each were irradiated in the Aerojet-General Nuclear Industrial Reactor (AGNIR) for periods of 37, 78, 187 and 224 hours. Total radiation exposures ranged from  $1.0 \times 10^{17}$  to  $6.1 \times 10^{17}$  neutrons per sq. cm. of neutron exposure, and from  $1.7 \times 10^8$  to  $9.9 \times 10^8$  Rads of gamma exposure.

Sample decompositions were found to be proportional to total radiation exposure. In the experiment of longest duration, 36.5 weight percent of the irradiated sample decomposed into gaseous decomposition products and generated a gas pressure of 19.5 atmospheres in the sealed irradiation pressure vessel. Only 1.5 grams, or 30% of the original sample, was recovered in useable form.

The crystalline samples recovered for analytical and calorimetric measurements all showed excessive radiation damage with extremely porous structures and acidic residues.

The Apparent Lattice Energy Content was determined by measurement of heat of solution before and after the radiation exposure. Measured heats of solution ranged from +68.04 cal/g for the unirradiated sample to a minimum of -34.70 cal/g for the sample of 187 hours exposure. Correspondingly derived values of apparent energy storage ranged from 13.62 cal/g for the 37 hour exposure to a maximum of 102.74 cal/g for the 187 hour exposure sample.

Comparison of measured heats of solution with estimated heats of solution based on chemical analyses of the samples indicated that the derived values of apparent lattice energy could be accounted for on the basis of changes in chemical composition alone, particularly the accumulation of free perchloric acid in the irradiated samples.

It is concluded that under the experimental conditions of this study in which the irradiated sample was continually exposed to water and other products of radiolytic decomposition, no lattice energy was stored.

The mechanism by which the initially induced lattice energy storage was lost is believed to be, not thermal annealing, but rather recrystallization due to contact with water formed by partial sample decomposition.

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## ABBREVIATIONS AND SYMBOLS

AEC	Atomic Energy Commission
AGC	Aerojet-General Corporation
AGN	Aerojet-General Nucleonics, Engineering and Development Division of AGC, San Ramon, California
AGNIR	Aerojet-General Nuclear Industrial Reactor
AP	Ammonium Perchlorate, $NH_4ClO_4$
(sq)	Aqueous solution state
ASME	American Society of Mechanical Engineers
atm	Atmosphere
$^{\circ}C, ^{\circ}F$	Centigrade degrees, fahrenheit degrees
(c)	Crystalline state
cal	Calorie
cm	Centimeter
$\Delta C_p$	Change in heat capacity
d and n	Deviation and number in $\sqrt{\frac{\Sigma d^2}{n(n-1)}}$
DTA	Differential thermal analysis
eq	Equivalentents
ev	Electron volt
"F" and "G" Rings	Positions in the AGNIR reactor pool in close proximity to the active core.
(g)	Gas state
g, Kg	Gram, kilogram
$\Delta H$	Enthalpy change
I.D.	Inside diameter
$I_s$ unit	Specific impulse, the standard measure of propellant performance, pound force-seconds per pound mass
Kcal	Kilocalorie
Kw	Kilowatt
(l)	Liquid state
mg	Milligram
mm	Millimeter

ABBREVIATIONS AND SYMBOLS (cont.)

ml	Milliliter
Meq	Milliequivalents
Mev	Million electron volts
MW = WRT/PV	Molecular weight = $\frac{\text{Weight} \times \text{gas constant} \times \text{temperature}}{\text{Pressure} \times \text{volume}}$
n	Neutrons (or number)
N	Normal, or equivalents per liter
nv	Neutron flux, neutrons per sq. cm. per sec
nvt	Total neutron exposure, neutrons per sq. cm
O.D.	Outside diameter
PBD	Polybutadiene
psi and psis	Pounds per square inch and pcunds per square inch absolute
R	Roentgen units of radiation (or Universal Gas Constant)
RAI	Radiation Applications Incorporated
REON	Rocket Engine Operations - Nuclear; Division of AGC
Type 6061-T6	An aluminum alloy composition particularly well suited for this work, containing minimum amounts of alloying agents or impurities which are capable of forming long life radioactive isotopes in a high neutron source.
Z	Atomic number
low Z	Low atomic number compounds which are relatively unaffected by gamma and neutron radiation; used as container materials for dosimeters.
*	Approximately
uv	Microvolt

## SECTION I

### INTRODUCTION

The practical value of a material as a solid rocket propellant is largely determined by the amount of heat released during combustion to exhaust products. The major emphasis in advanced propellant technology has been directed toward the synthesis of endothermic fuels and oxidizers. Although the phenomena of radiation-induced lattice deformation and bond alteration of crystalline and metallic materials are well known the implications of these effects to rocket propulsion and combustion have not been demonstrated. The practical utility of this concept is limited by two factors: (1) the extent to which extra, available energy can be stored in the material, and (2) the percentage of the material normally used in solid rocket propellant formulations.

The present requirements are the creation of permanent deformations in the lattice of an appropriate model solid material and the subsequent calorimetric demonstration of the extra energy available as heat during combustion.

Much data has been available in recent years regarding disruption of the normal arrangement of crystalline lattices by various forms of radiant energy including that due to accelerated particles as well electromagnetic radiation. Among the various types of radiation for which pertinent data are available are X-ray, gamma rays, beta particles, neutrons, ultraviolet and visible light. However, from an analysis of available data regarding relative effectiveness in disrupting crystalline lattices, it is concluded that pile neutrons offer the best combination of effectiveness, flux and availability.

Previous work on nuclear radiation in materials shows that the amount of stored energy in solids, resulting from prolonged exposure in reactors, varies from a few tenths of a calorie per gram up to five hundred or more calories per gram for graphite. Extensive work on aluminum, beryllium, zirconium, various steels, and tungsten verified that the annealing process in metals is so rapid at room temperature that no more than a few tenths of a calorie per gram of energy is retained. The high value for graphite is also equally well demonstrated, and the rate at which it can be annealed out at various temperatures has been thoroughly investigated, both here and in England.

The energy storage capability of ionic crystalline materials probably lies somewhere between that of graphite and the metals noted above. There is evidence that ionic crystalline materials can and do store measureable amounts of energy due to radiation damage; however, the exact amounts of such storage have not been quantitatively demonstrated to date, particularly for materials of interest as propellant ingredients. The well-known phenomenon of thermoluminescence is now considered as evidence of energy storage due to radiation damage of crystalline lattices. The thermoluminescence pattern of naturally occurring calcite has been duplicated in the laboratory by exposing calcite crystals to gamma or X-rays.

## I, Introduction (cont.)

The propellant ingredients which enter into consideration in this application are the binder, the added metal, the burning rate modifiers, and the oxidizers. Previous irradiation studies on polymers indicate that the binder and its ingredients are most likely to be adversely affected by radiation. In addition the mobility of the polymer structure would not permit retention of any significant amount of stored energy. Metals, such as beryllium and aluminum, are known not to retain more than trivial amounts of stored energy and these two metals are used, as the moderator and structural members, respectively, in high-flux regions of high-power reactors. The moderator and the reflector in the very high power Materials Test Reactor at the Arco, Idaho, test center was made of beryllium blocks. Aluminum cans are used to contain the uranium slugs in the plutonium production reactors. Many metals become converted into radioactive isotopes on exposure to neutrons, and thus would be radioactive for a protracted period after irradiation. Burning rate modifiers such as copper chromite or organometallics are present in propellants in amounts too small to alter propellant energetics, even if they did store large amounts of energy. From these considerations, it is clear that the only ingredient which is a reasonable candidate for irradiation is ammonium perchlorate, an oxidizer most widely used in solid propellants.

This conclusion is also borne out in considerations of propellant performance calculations. For a typical solid propellant containing 12% polybutadiene binder, 15% aluminum and 73% ammonium perchlorate, a stored energy of 200 cal/g in the oxidizer will result in a gain in standard specific impulse of 8.7 units (from 264.4 to 273.1) whereas an equal amount of stored energy in the metal or binder phases would result in corresponding increases of 1.8 or 1.4 units respectively.

Exposure to X-ray and gamma-ray radiation has been shown to significantly alter the thermal stability and decomposition characteristics of ammonium perchlorate in the solid state. Changes in DTA patterns, while not claimed to be quantitative, appear to indicate energy storages of several calories per gram as a result of X-ray radiation. Significant increases in burning-rate activity as a result of gamma radiation of  $\text{NH}_4\text{ClO}_4$  have also been observed.

The major energy storage mechanism with  $\text{NH}_4\text{ClO}_4$  was expected to be displaced atoms which simultaneously produce a lattice vacancy plus an interstitial atom (Frenkel defect). The average neutron flux estimated for the portion of the reactor used in this study was approximately  $2 \times 10^{12}$  neutrons  $\text{cm}^{-2}\text{sec}^{-1}$ , with planned irradiation periods of from 40 to 800 hours. Over the maximum time period planned this would amount to a total dosage of  $5 \times 10^{18}$  incident particles/ $\text{cm}^2$ . Theoretical calculations indicated that the lattice deformation energy storage due to the 800-hour exposure would have an upper limit value of 23.8 cal/g and a probable actual storage in the range from 2.3 to 8 cal/g. This compares with a measured energy storage of 3.6 cal/g from graphite irradiated with the same dosage. Coincidentally, the upper limit value corresponds

I, Introduction (cont.)

closely to the measured value for the heat of transition of  $\text{NH}_4\text{ClO}_4$  from the orthorhombic to cubic phase, 2.3 Kcal/mole or 19.6 cal/g.

Instead of combustion calorimetry as suggested in the proposal request, solution calorimetry was chosen as the best and most accurate means of quantitatively measuring stored energy contents of ammonium perchlorate. This calorimetric technique offers at least a 9:1 advantage in sensitivity compared with the combustion calorimetry technique. With the calorimeter used, energy contents as low as 0.35 cal/g can be detected.

Although the amount of energy storage measured was not sufficient to cause an appreciable increase in solid propellant specific impulse, the calorimetric determination was sufficiently accurate to establish the feasibility of the concept. The real problem encountered, largely unanticipated, was that of distinguishing between genuine lattice deformation energy and apparent lattice deformation energy due to chemical degradation of the sample.

## SECTION II

### SUMMARY AND CONCLUSIONS

#### 1. SUMMARY

Four samples of reagent grade ammonium perchlorate weighing five grams each were irradiated in the Aerojet-General Nuclear Industrial Reactor (AGNIR) for periods 37, 78, 187 and 224 hours.

Total radiation exposures ranged from  $1.0 \times 10^{17}$  to  $6.1 \times 10^{17}$  neutrons per sq cm of neutron exposure, and from  $1.7 \times 10^8$  to  $9.9 \times 10^8$  Rads of gamma exposure.

To prevent annealing of lattice defects formed in the irradiation, the temperature gradient between sample and reactor pool was kept to a minimum. This was accomplished by placing the  $\text{NH}_4\text{ClO}_4$  irradiation samples in direct contact with the aluminum pressure vessels, by filling the pressure vessel with helium before sealing and by maintaining an atmosphere of helium inside the secondary containment capsule. The maximum sample temperature for each of the four samples during irradiation was  $53^\circ\text{C}$ .

In the experiment of longest duration, 36.5 weight percent of the irradiated sample decomposed into gaseous decomposition products and generated a gas pressure of 19.5 atmospheres in the sealed irradiation pressure vessel. Only 1.5 grams, or 30%, of this sample was recovered in useable form; the remainder could not be removed from the capsule without excessive contamination.

The crystalline sample residues recovered for analytical and calorimetric measurements all showed excessive radiation damage with extremely porous structures and acidic residues. The sample of least exposure was recovered as a white porous crystalline product compacted and sintered together, with the individual crystals reduced to about 10% of their original size. This sample contained impurities of approximately 10 mole %  $\text{HClO}_4$  and 7 mole %  $\text{NH}_4\text{Cl}$ , and was somewhat hygroscopic in nature.

The samples of longer radiation exposures showed increasing hygroscopicity and increasing impurity contents, and microscopic examination showed evidence of re-crystallization of portions of the damaged crystals.

Calorimetric measurements indicated heats of solution of  $+68.04 \pm 0.14$  cal/g for the unirradiated sample,  $+55.02 \pm 0.65$  cal/g for the 37 hour irradiated sample and a minimum value of  $-34.70$  cal/g for the 187 hour sample.

Corresponding values of "Apparent Energy Storage," which do not include corrections for the effects of impurities, ranged from  $13.02 \pm 0.67$  cal/g for the 37 hour exposure sample to a maximum of  $102.74$  cal/g for the 187 hour exposure sample.

## II, 1, Summary (cont.)

The chemical analyses were not of sufficient accuracy to permit precise evaluation of meaningful corrections for the effects of impurities on the derived values of Apparent Energy Storage. The general conclusion derived from the analysis results however was that the amounts of free perchloric acid found were sufficient to account for most, if not all, of the Apparent Energy Storage.

### 2. CONCLUSIONS

Under the exact experimental conditions of this study the storage of energy in the form of lattice defects was undetectable and probably negligible because of the overshadowing effect of chemical degradation of the samples.

The apparent storage of lattice energy observed is attributable to the presence of large amounts of decomposition product impurities, particularly free perchloric acid, in the recovered samples.

The disappearance of the lattice defects initially formed by the neutron bombardment is not believed to have been caused by an annealing process, since the sample temperature never exceeded 53°C. Rather the mechanism of loss is believed to have involved recrystallization, since the samples were continually exposed to water and other decomposition products throughout the irradiation.

Microscopic examination showed definite evidence of recrystallization in the samples of 78 hours and greater exposure; the sintering effect observed in the shortest duration experiment is also interpreted as evidence of recrystallization.

In order to prevent this occurrence in future studies, irradiations must be made under anhydrous conditions through the use of either continuous evacuation of sample containers, cold traps or desiccating agents.

### SECTION III

#### THEORETICAL AND EXPERIMENTAL APPROACH

##### 1. SAMPLE IRRADIATION

###### a. Radiation Effects

Prolonged irradiation of crystalline solids by high energy particles produces several changes in the physical properties of the solids. Among these properties are thermal conductivity, electrical resistivity, density, hardness, critical shear stress, tensile strength, and accumulation of stored energy which is of particular interest for propellant materials. The amount of stored energy retained after significant irradiation varies from 0.1 cal per gram for metals(1),(2),(3) to over 500 cal per gram for graphite(4).

All of the effects on physical properties, apart from transient ones associated with electronic transitions, owe their existence to the ability of particle radiation to displace atoms from their equilibrium positions and to destroy local order in the crystalline matrix(5). The amount of stored energy that is accumulated in a solid will therefore depend upon the total flux of particles available and the efficiency with which energy is transferred upon collision.

The phenomenon of thermoluminescence is now believed to be the result of lattice deformations by natural radiation sources. Daniels and co-workers(6)(7) at the University of Wisconsin have shown that the thermoluminescence behavior of naturally activated calcite can be duplicated by means of gamma-ray or X-ray radiation in the laboratory. Heckelsberg and Daniels(8) have shown that 14 alkali halide compounds (fluorides, chlorides, bromides and iodides of Li, Na, K and Rb) also show thermoluminescent response to  $\gamma$ - or X-rays. Artificially induced thermoluminescence has also been observed in the alkaline earth fluorides(9), ZnO(10), CsBr(11), CaSO<sub>4</sub>(12) and many other compounds. Fluorescence and phosphorescence are other examples of stored radiant energy, although the energy levels involved are probably not measurable by calorimetric techniques.

###### b. Comparison of Irradiation Methods

As the following table, based on work on germanium(5) shows, pile neutrons offer the best combination of effectiveness, flux, and availability. Although machine irradiations, especially with the heavier charged particles, can deliver large doses in short times, they are limited to very small samples which can be adequately cooled or else the large energy input will vaporize the sample. In addition, radiation effects are confined to the surface layer because of the low penetration of charged particles.

III, 1, Sample Irradiation (cont.)

TABLE I  
COMPARATIVE RADIATION EFFECTS

<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Radiation	Atoms displaced per incident particle	Useable flux, particles $\text{cm}^{-2}\text{sec}^{-1}$	Practical exposure time, sec	Figure of merit, $2 \times 3 \times 4$
Co-60 photons	$6 \times 10^{-4}$	$1 \times 10^{13}$	$3 \times 10^7$ (1 year)	$1.8 \times 10^{17}$
3 Mev electrons	$11 \times 10^{-2}$	$1 \times 10^{15}$	$10^5$ (1 day)	$1 \times 10^{19}$
1 Mev neutrons	2.5	$2 \times 10^{13}$	$7.5 \times 10^6$ (3 months)	$4 \times 10^{20}$
5.2 Mev alphas	43	$1 \times 10^{13}$	$2 \times 10^5$ (2 days)	$8 \times 10^{19}$

Both neutrons and gamma rays have the advantage of deep penetration into a sample so that radiation effects are produced more or less uniformly throughout. However, the interaction of gamma rays with matter is so much weaker than that of neutrons, that megacurie amounts of Co-60 are required to produce the same results as the neutron flux available from a small nuclear reactor. Such large gamma sources present formidable shielding problems and require considerable mechanical complexity in order to secure uniform irradiation. Nuclear reactors can provide nearly isotropic fluxes of fast neutrons and are much more available for making the long term irradiations of relatively large amounts of material which would be necessary for any practical solid propellant application.

c. Calculation of Stored Energy

When a fast particle traverses the lattice of a crystalline solid the most important means of energy loss is by elastic collision with the atoms of the lattice. If the lattice atom receives an energy  $E_p$  in excess of  $E_d$ , defined as the displacement energy, it is displaced from its normal site. Therefore, the displacement process creates a Frenkel defect (a lattice vacancy plus an interstitial atom), because in most circumstances the recoiling atom comes to rest in a non-equilibrium position. The total amount of useful energy which may be stored in ammonium perchlorate will depend upon the number of Frenkel defects introduced by radiation and the energy released by each defect upon dissolution of the lattice. The latter, which is much less than  $E_d$  because an atom recoil takes place before neighboring atoms can relax, may be taken equal to the energy,  $E_{fd}$ , for thermal generation of a Frenkel defect, between 3 and 6 electron volts(5).

### III, 1, Sample Irradiation (cont.)

Exact theoretical calculation of displacement energy, the number of displacements per primary collision due to secondary collisions of the ejected atoms and the number of collisions per unit flux is complex, and in most cases the density of defects indicated by experiment is smaller than the theoretical value by a factor of 3 to 10. Not all of this discrepancy is due to deficiencies in the theory because in order to make comparisons with experiment it is necessary to reduce the observed physical property changes to concentrations of Frenkel defects. In many instances this reduction requires the use of calculated relationships which cannot be readily verified by experiment. However, even simple theory can be used to predict the order of magnitude of stored energy expected and thus indicate the amount of irradiation required to produce effects that can be measured accurately by calorimetry.

The following treatment is based on the detailed theory developed by Seitz(13) using the formulation given in The Effects of Radiation on Materials(14). The basic equation for the number of displaced atoms,  $N_d$ , is given by,

$$N_d = \phi n' \bar{v} \quad (1)$$

where

$\phi$  is the total number of incident particles

$n'$  is the number of primary collisions per incident particle

$\bar{v}$  is the number of atoms displaced per primary collision.

The stored energy,  $E_s$ , will then be given by,

$$E_s = N_d E_{Fd} \quad (2)$$

where

$E_{Fd}$  is the energy of Frenkel defect.

For irradiations by fast neutrons in the Aerojet-General Nuclear Industrial Reactor (AGNIR), the total number of incident particles,  $\phi$ , may be taken as,

$$\phi = nv t \quad (3)$$

where

$nv$  = the fast neutron flux estimated as  $2 \times 10^{12}$  neutrons  $\text{cm}^{-2}\text{sec}^{-1}$

$t$  = time in seconds.

### III, 1, Sample Irradiation (cont.)

For a nominal 800 hours irradiation near the core,

$$\begin{aligned}\phi &= 2 \times 10^{12} \text{ neutrons cm}^{-2} \text{sec}^{-1} \times 800 \text{ hrs} \times 3600 \frac{\text{sec}}{\text{hr}} \\ &= 5.8 \times 10^{18} \text{ incident particles/cm}^2\end{aligned}$$

For fast neutrons the collisions are of the hard sphere type(15). Only a very small fraction of the struck atoms are not displaced and, therefore, the cross section for producing a primary displacement is the total neutron cross section for scattering, equal to  $3 \times 10^{-24} \text{ cm}^2$  for most atoms. In one gram of ammonium perchlorate, M.W. = 117.5, the number of primary collisions per incident, fast neutron is then,

$$\begin{aligned}n' &= \frac{1 \text{ gm}}{117.5 \text{ gm mol}^{-1}} \times 6 \times 10^{23} \text{ atoms mol}^{-1} \times \frac{3 \times 10^{-24} \text{ cm}^2}{\text{atom}} \\ &= 0.015 \text{ cm}^2/\text{neutron}.\end{aligned}$$

In light elements bombarded by fast neutrons, as in ammonium perchlorate where the average mass number (A) is 11.75, the primary recoil is sufficiently energetic to lose a considerable portion of its energy by ionizing and exciting atoms of the lattice. Any energy lost this way is not available for producing additional displacements and must be taken into account when estimating  $\bar{v}$ , the number of atoms displaced per primary collision. For this situation  $\bar{v}$  is given by,

$$\bar{v} = \frac{E_i}{2 E_d} \left( 1 - \frac{E_i}{2 E_m} \right) \quad (4)$$

where  $E_i$  is a threshold ionization energy above which the particle is assumed to lose energy by electronic events only and below which it is assumed to lose all energy by elastic collisions. A convenient approximation(16) for the threshold ionization energy is,

$$E_i = A \times 10^3 \text{ ev} \quad (5)$$

for ammonium perchlorate for which an average A is 11.75,

$$E_i = 11.75 \times 10^3 \text{ ev}.$$

$E_d$  is the energy required to permanently displace an atom from a stable site in the lattice, which Seitz(13) estimated qualitatively as follows. The energy required to remove a typical atom from an interior site

III, 1, Sample Irradiation (cont.)

in a reversible manner is about twice the energy of sublimation. If, however, the process is carried out dynamically, as in a fast collision, the process is highly irreversible and the energy required is expected to be about four times the sublimation energy. The sublimation energy of  $\text{NH}_4\text{ClO}_4$  into the neutral species  $\text{HClO}_4$  and  $\text{NH}_3$  is only of the order of 2.5 ev(17). However, the energy of sublimation into the ionic species  $\text{ClO}_4^-$  and  $\text{NH}_4^+$  is probably somewhat higher and the further dissociation of  $\text{NH}_4^+$  into  $\text{NH}_3^+$  and  $^1\text{H}$ , as observed by Hyde and Freeman(18) in X-ray irradiation of  $\text{NH}_4\text{ClO}_4$ , could easily lead to a net heat of sublimation of 6 ev or more. Application of the factor of 4, noted above, leads to an estimated value of 25 ev for  $E_d$ .

The remaining term in Equation (4) is  $E_m$ , the maximum energy which may be transferred in an elastic collision. For neutrons which have an energy  $E$  around one Mev, and so lie in the non-relativistic region of velocity, the maximum energy which may be transferred to an atom of mass number  $A$  is given by Seitz and Koehler(19),

$$E_m = \frac{4A}{(1+A)^2} E. \quad (6)$$

For ammonium perchlorate exposed to one Mev neutrons:

$$\begin{aligned} E_m &= \frac{4 \times 11.75}{(1 + 11.75)^2} \times 10^6 \text{ ev} \\ &= 2.9 \times 10^5 \text{ ev.} \end{aligned}$$

Equation (4) may now be evaluated for the number of atoms displaced per primary collision,

$$\begin{aligned} \bar{\nu} &= \frac{11.75 \times 10^3}{2 \times 2.9} \left( 1 - \frac{11.75 \times 10^3}{2 \times 2.9 \times 10^5} \right) \\ &= 230 \text{ atoms/collision.} \end{aligned}$$

The total number of displaced atoms expected for 800 hours irradiation of one gram of ammonium perchlorate in the AGNIR reactor is therefore,

$$\begin{aligned} N_d &= \phi n' \bar{\nu} \\ &= 5.8 \times 10^{18} \frac{\text{neutrons}}{\text{cm}^2} \times 0.015 \frac{\text{cm}^2}{\text{neutrons}} \times 230 \text{ atoms} \\ &= 2.1 \times 10^{19} \text{ displacements/gram.} \end{aligned}$$

### III, 1, Sample Irradiation (cont.)

The major uncertainty in this calculation is in the estimation of  $n' \bar{\nu} = 3.5$ , the number of displaced atoms per incident neutron. This number is not far from the value of 2.5 displaced atoms per incident neutron measured for the neutron irradiation of germanium(20), and suggests that the calculation is reasonably valid.

The stored energy  $E_s$  to be expected from a total nvt of  $5.8 \times 10^{18}$  neutron/cm<sup>2</sup> applied to one gram of ammonium perchlorate is calculated from Equation (2), using 3 ev as the energy of a Frenkel defect, to be,

$$E_s = 2.1 \times 10^{19} \text{ defects/gm} \times 3 \text{ ev/defect} \times \frac{1 \text{ cal}}{2.68 \times 10^{18} \text{ ev}}$$
$$= 23.5 \text{ cal/gm.}$$

Even if this figure is high by an order of magnitude, the stored energy would be of the same order (about 2 cal/gm) as found for potassium chloride irradiated with 350 Mev protons(21). It is of the same order as the stored energy (3.6 cal/gm) found in graphite irradiated to the same nvt(4).

The maximum calculated energy storage is 23.5 cal/g and compares quite closely to the heat of transition (orthorhombic to cubic at 240°C) of 19.6 cal/g as reported by Markowitz and Boryta(22).

Freeman and Anderson(23),(24),(25),(26) in DTA measurements with  $\gamma$ - and X-ray irradiated ammonium perchlorate show one trace with an exotherm indicating a  $\Delta T$  of approximately 25°C. While admittedly the DTA does not give quantitative measures of reaction exotherms, a simple multiplication of  $C_p \times \Delta T$  for this case indicates an exotherm of about 900 calories per mole or over 7.5 cal/g. This exotherm is due primarily to sample decomposition, but may be at least partially due to stored lattice energy.

#### d. Dosimetry

An important factor in all radiation effects experiments is the characterization of the nuclear environment. Such a characterization permits the correlation of the changes observed to the particular radiation field responsible for these changes. In the mixed-radiation field of a reactor, a dose component of interest must be measured independently in the presence of the other. Neutron fluxes are readily measured using the threshold foil system(27 to 32).

Of the many methods available for gamma dosimetry(33), the glass dosimeters(34 to 36) are best suited for determining the gamma contribution to the total dose.

### III, 1, Sample Irradiation (cont.)

Neutron doses are best described by integrated fluxes for specific neutron energy groups. The "sulfur flux", i.e., the neutron flux above the threshold energy (2.9 Mev) for the reaction  $S^{32} + \text{neutron} \longrightarrow P^{32} + \text{proton}$ , is a good index for the fast neutron population. Neutron dose measurements for the AGNIR irradiations were monitored with sulfur neutron detection foils. These foils were placed at appropriate intervals along the entire length of the dummy fuel element irradiation capsule to determine the fast flux gradient for the irradiation position.

Glass dosimeters were used to determine the extent of the gamma contribution to the total dose during the  $NH_4ClO_4$  irradiation. The low-Z silver-metaphosphate glass dosimeters have known thermal and fast neutron responses which were used to determine the gamma dose.

#### e. Reactor Description

The AGNIR is a zirconium-hydride moderated water-cooled pool type reactor licensed for 250 kw(t) maximum operating power. The reactor core is located at the bottom of an aluminum tank 23 ft deep and 10 ft in diameter. In-pool storage is provided for 21 irradiated fuel and/or dummy element irradiation capsules. The entire facility is serviced by a 3 ton bridge crane. A mechanical positioned large component irradiation box can be actuated from the top of the reactor pool.

The performance and design data are:

(1) Power	250 kw, maximum
(2) Critical Mass	2.4 Kg
(3) Cooling	Natural convection
(4) Shielding	17 ft of water over core
(5) Reactor Tank	Aluminum, 10 ft ID by 23 ft deep
(6) Fuel-Moderator Material	Uranium-zirconium hydride
(7) Uranium Enrichment	20% U-235
(8) Active Lattice Dimensions	~17 in. dia. by 14 in. high
(9) Reflector Materials	Aluminum clad graphite & water
(10) Control Rods	3, boron carbide

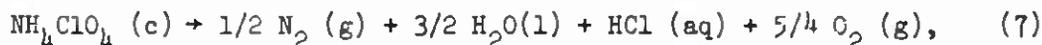
### III, Theoretical and Experimental Approach (cont.)

#### 2. CALORIMETRY

##### a. Choice of Calorimetric Method

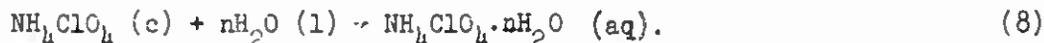
Although a high precision rotating bomb combustion calorimeter (U.S. Bureau of Mines, Bartlesville, Oklahoma, Design<sup>(37)</sup>) and personnel experienced in its use were available for this study, the use of a heat of solution calorimeter offered significant advantages in achieving the highest precision and absolute accuracy.

The maximum anticipated amount of stored energy in the first sample to be studied (1 week exposure) is of the order of 1.25 cal/g. If heat of combustion (or heat of explosion) is used as the basis of comparing the irradiated sample with the untreated sample, the total energy corresponding to the reaction,



will be of the order of -610 calories per gram (exothermic). A stored energy content of 1.25 cal/g therefore represents slightly more than 0.2% of the total measured heat. Furthermore, if the  $\text{NH}_4\text{ClO}_4$  is mixed with a combustible fuel (in order to assure a more reproducible combustion reaction) the total energy release per gram of  $\text{NH}_4\text{ClO}_4$  will be even higher - with a corresponding reduction in the fraction due to  $\text{NH}_4\text{ClO}_4$  energy storage.

Measurement of the heat of solution on the other hand,



involves a heat of reaction of approximately +68 cal/g (endothermic). In this case, an energy storage of 1.25 cal/g represents 1.84% of the total measured heat which is well within the accuracy of the apparatus.

Another advantage of the heat of solution method lies in the fact that the heats of solution of many of the possible impurities present in the irradiated sample (as a result of partial decomposition) have heats of solution nearly equal to that of  $\text{NH}_4\text{ClO}_4$ . Therefore, the analysis for these particular impurities becomes less critical. These heats of solution, derived from data in references (38) and (39) are shown in Table II.

III, 2, Calorimetry (cont.)

TABLE II  
HEATS OF SOLUTION OF POSSIBLE IMPURITIES

<u>Substance</u>	<u>Heat of Solution cal/g</u>	<u>Difference in Heat of Solution</u>	
		<u>cal/g</u>	<u>%</u>
$\text{NH}_4\text{ClO}_4$	+68.09	0	0
$\text{NH}_4\text{Cl}$	+65.99	-2.02	-2.97
$\text{NH}_4\text{ClO}_3$	+94.59	+26.50	+38.92
$\text{NH}_4\text{NO}_3$	+76.71	+8.62	+12.66
$\text{N}_2\text{H}_5\text{Cl}$	+75.91	+6.82	+10.02
$\text{N}_2\text{H}_5\text{ClO}_4$	+71.70	+3.61	+5.30
$\text{NH}_4\text{NO}_2$	+71.825	+3.74	+5.49

Although the rotating bomb combustion calorimeter could be adapted for use as a solution calorimeter, it would necessitate great care to assure that the sample was not prematurely exposed to water vapor. By comparison, the solution calorimeter offers a proven design, ideally suited for this work.

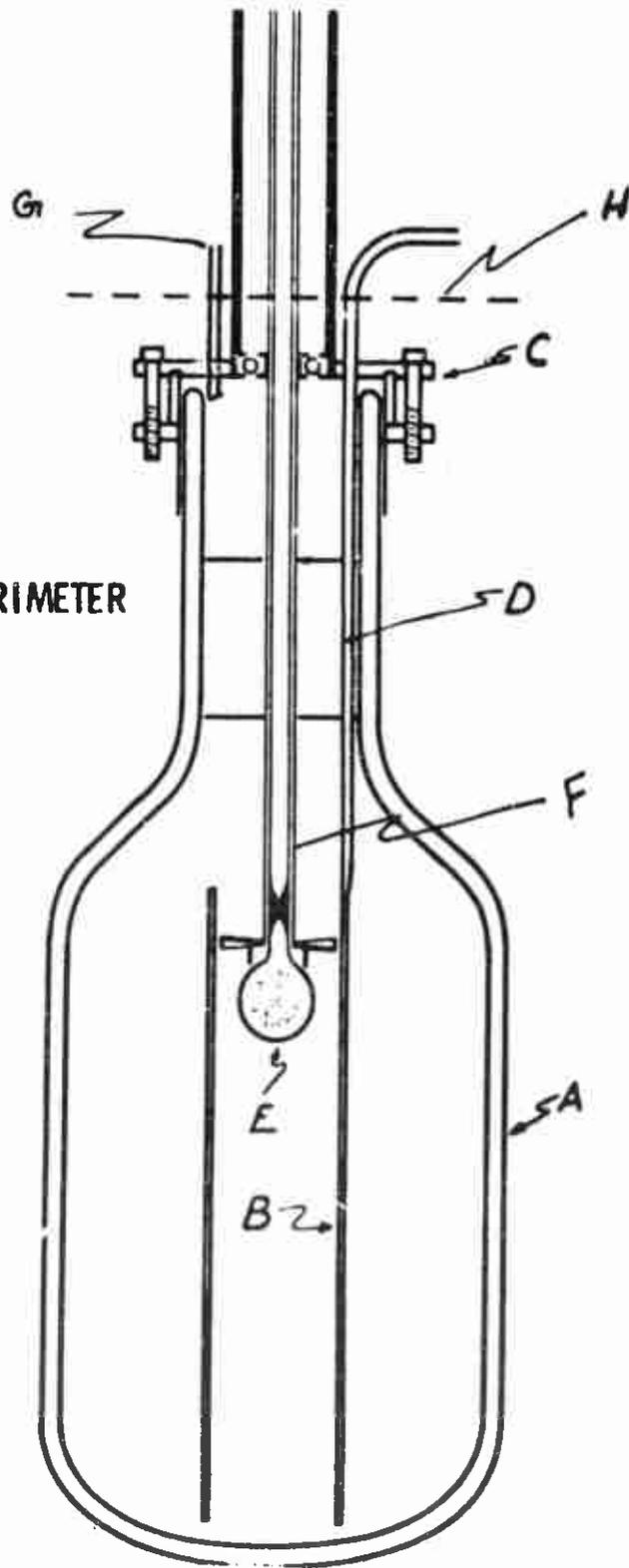
b. Calorimeter Description

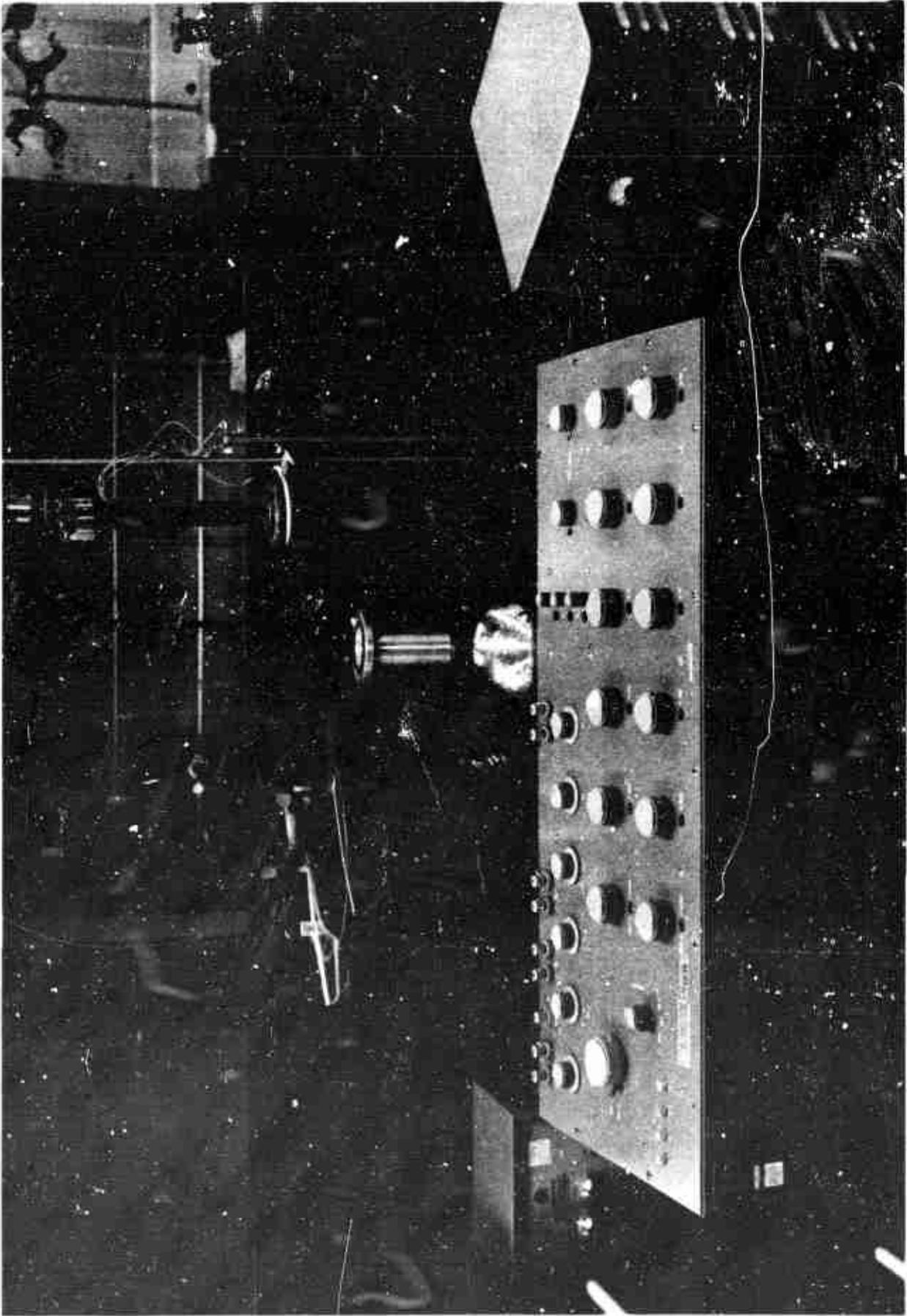
The calorimeter used for this work is identical in all essential details to that originally described by Southard(40) and to an improved version more recently described by Coughlin(41).

The basic design utilizes a 2-quart glass Dewar reaction vessel completely submerged in an isothermal bath (see Figures 1 and 2). Internal metal parts are either made from an inert metal or coated with a layer of "Tygon" paint for protection from corrosion by the acid solutions usually employed for heat of solution work.

Temperature measurements are made with a copper-manganin resistance thermometer of the transposed bridge type originally described by Maier(42) in conjunction with a Rubicon six dial high precision potentiometer,

THE GLASS DEWAR CALORIMETER





HEAT OF SOLUTION CALORIMETER

Figure 2  
Page 16

### III, 2, Calorimetry (cont.)

which is direct reading to 0.01 microvolt ( $\mu\text{v}$ ) when operated at the highest sensitivity range. The sensitivity of the resistance thermometer is approximately  $1500 \mu\text{v}/^\circ\text{C}$  when operated at a constant current of 2000 microamperes. The current is held constant to  $\pm 0.01$  microamp by periodically checking the potential drop across a standard resistor in series with the resistance thermometer and adjusting as required with a pair of resistance boxes in series-parallel arrangement. Since the bridge type thermometer has a null point (a unique temperature at which the potential drop is zero, usually set for about  $2^\circ$  below bath temperature), its principal advantage lies in the combination of high sensitivity and ability to be used with a high-sensitivity, low-range microvolt potentiometer.

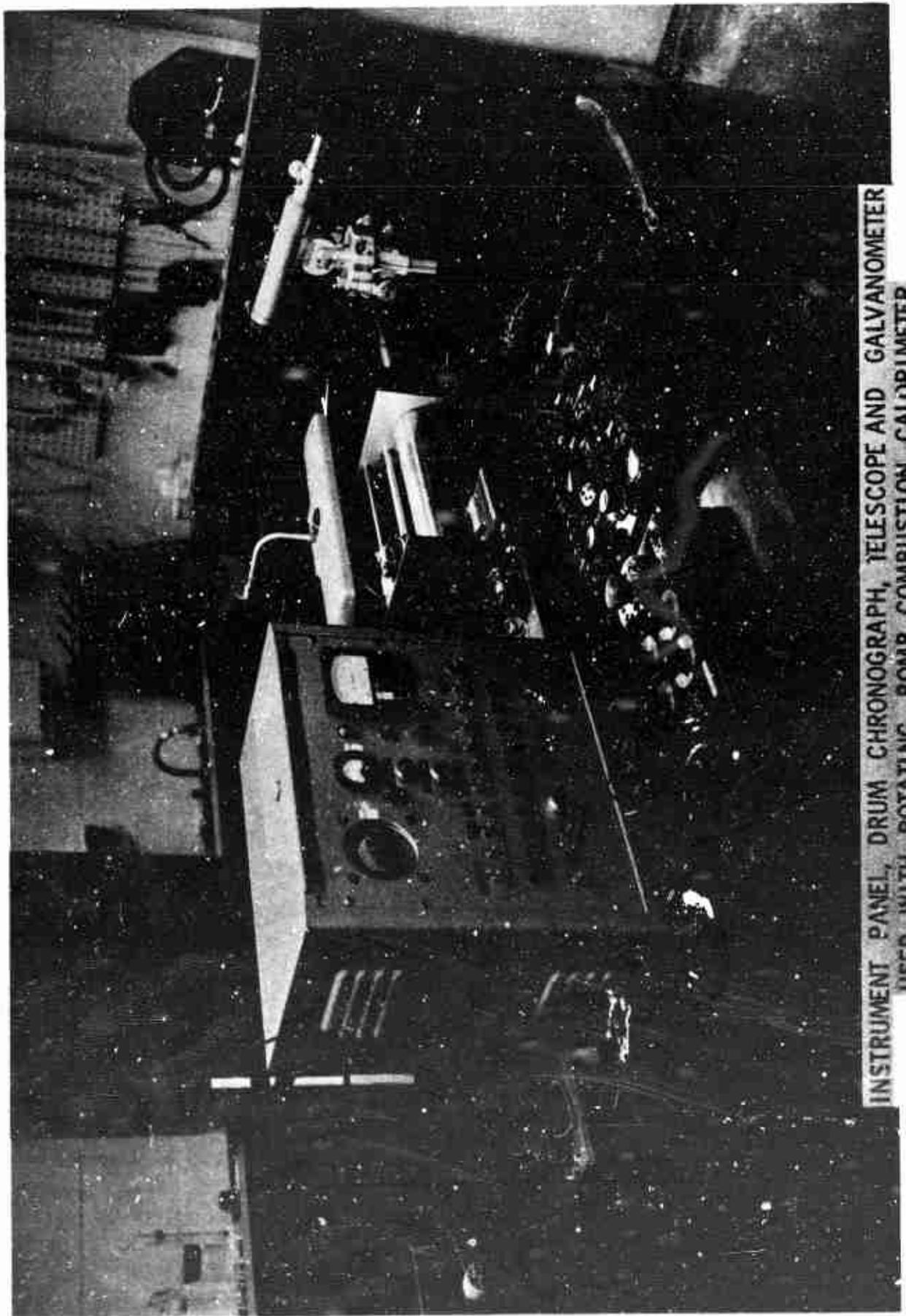
The galvanometer used in the initial measurements with unirradiated AP is a Leeds and Northrup, Type HS, used in conjunction with a telescope and an illuminated scale approximately 8 meters distant from the galvanometer mirror (Figure 3 shows the identical set-up of telescope and instrument panel used with the Rotating Bomb Calorimeter). This arrangement effectively increases the galvanometer sensitivity by a factor of 8 when compared with the normal usage employing a projected light beam and a glass scale at 1 meter distance. In the later measurements with irradiated samples a Keithley Model 147 Nanovolt Null Detector sensitive to 0.001 microvolt was substituted for the galvanometer and telescope in order to gain increased accuracy for the small sample sizes available.

A number of recent improvements not included in the original design(40, 41) are:

- (a) The Keithley Null Detector just described.
- (b) A synchronous motor with nylon gear drive for the calorimeter stirrer.
- (c) The six-dial potentiometer, direct reading to 0.01  $\mu\text{v}$ .

#### c. Precision and Accuracy

An indication of the precision and absolute accuracy attainable with the calorimeter is shown by reference to a typical portion of the work performed in an earlier model of the same design - shown in Table III.



INSTRUMENT PANEL, DRUM CHRONOGRAPH, TELESCOPE AND GALVANOMETER  
USED WITH ROTATING BOMB COMBUSTION CALORIMETER

Figure 3  
Page 18

TABLE III

## PRECISION UNCERTAINTY OF PREVIOUS MEASUREMENTS WITH HEAT OF SOLUTION CALORIMETER

Sample	Molecular Weight	Samp. Wt., grams	Heat of Solution		Precision Uncertainty			Calories (absolute)	Reference
			cal/mole	cal/g	cal/mole	cal/g	%		
Na <sub>2</sub> SO <sub>4</sub> , III	142.05	11.8	-1,363	-9.595	-113	+ 4	+0.028	+0.30	(45)
	14.06	14.06	-1,363	-9.595	-135	+ 4	+0.028	+0.30	(45)
Na <sub>2</sub> SO <sub>4</sub> , V	142.05	13.3	-627	-4.414	-83.4	+ 3	+0.021	+0.48	(45)
	14.9	14.9	-627	-4.414	-93.4	+ 3	+0.021	+0.48	(45)
CaO (c)	56.08	0.48	-47,441	-845.9	-406	+ 29	+0.52	+0.061	(46)
	1.60	1.60	-47,441	-845.9	-1353	+ 29	+0.52	+0.061	(46)
H <sub>2</sub> O (l)	18.016	0.56	-82.6	-4.58	-2.56	+ 2.1	+0.12	+2.54	(46)
	1.05	1.05	-82.6	-4.58	-4.81	+ 2.1	+0.12	+2.54	(46)
$\frac{12}{7}$ CaO·Al <sub>2</sub> O <sub>3</sub> (c)	198.10	1.98	-81,330	-410.5	-813	+ 50	+0.25	+0.06	(46)
3CaO·Al <sub>2</sub> O <sub>3</sub> (c)	270.20	2.70	-199,400	-738.0	-1994	+ 40	+0.15	+0.02	(46)
AlCl <sub>3</sub> (c)	133.35	2.67	-72,510	-543.75	-1450	+ 50	+0.38	+0.07	(47)
AlCl <sub>3</sub> ·6H <sub>2</sub> O (c)	241.45	4.83	-7,610	-31.52	-152	+ 17	+0.07	+0.22	(47)

### III, 2, Calorimetry (cont.)

The uncertainties shown are "Precision Uncertainties," or twice the standard deviation of the mean,

$$2\sqrt{\frac{\sum d^2}{n(n-1)}},$$

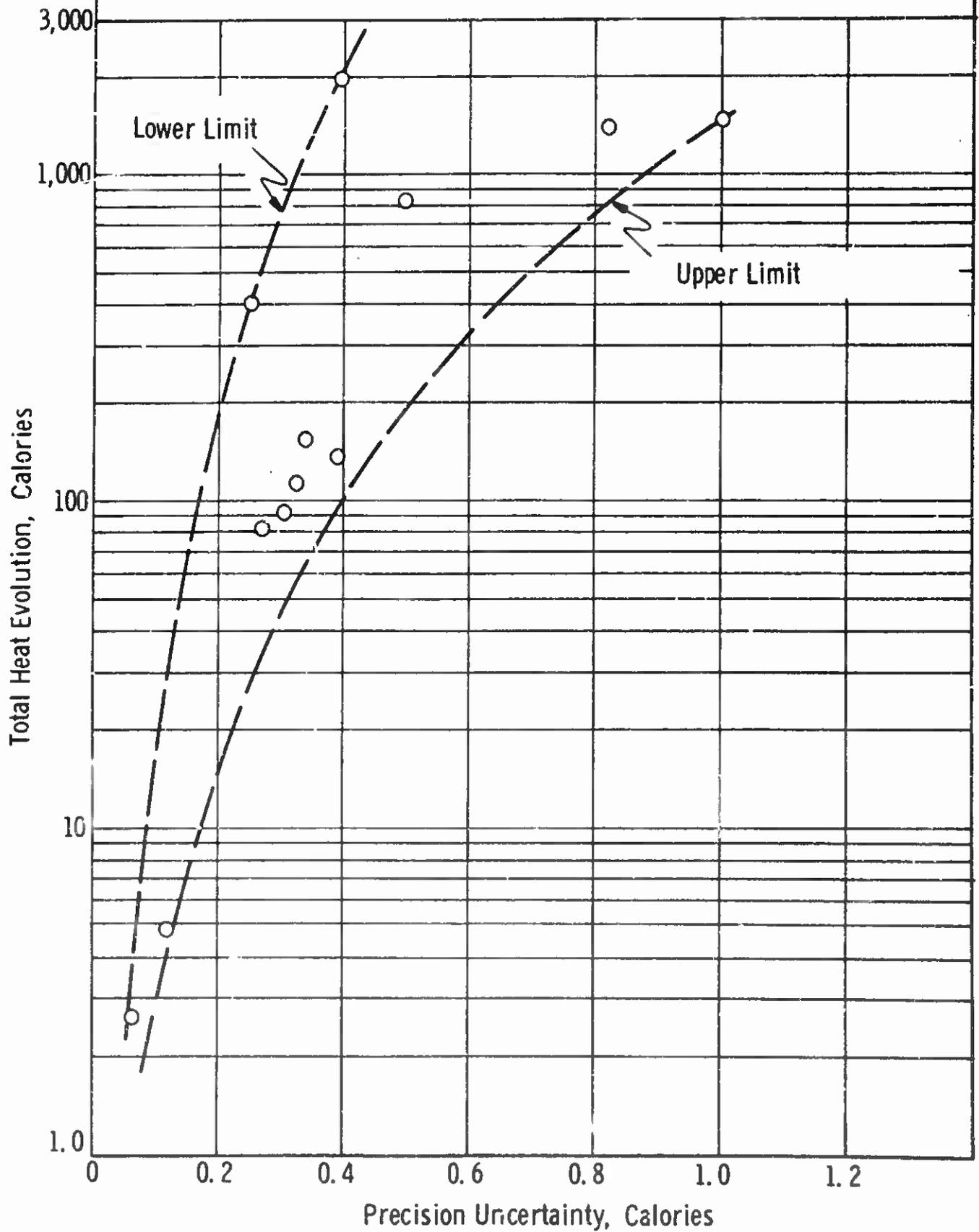
as recommended by Rossini(44) for thermochemical work; in most cases the mean value for the heat of solution represents the average of 5 or more determinations. The data shown (45), (46), (47) cover a wide range of sample sizes, reaction heats and reaction rates. However, aside from experimental difficulties associated with individual samples, the absolute accuracy of a determination is primarily dependent upon the total heat evolution in the measurements. In Figure 4 precision uncertainty is plotted as a function of total heat evolution, with the dotted lines representing the limiting (optimum and worst) cases. Although all of the examples shown apply to exothermic reactions, the method applies equally well to the study of endothermic reactions.

For an  $\text{NH}_4\text{ClO}_4$  sample size corresponding to a heat absorption of 100 to 200 calories the indicated absolute uncertainty from Figure 4 should be less than  $\pm 0.5$  calories. (This estimate of uncertainty is considered conservative since  $\text{NH}_4\text{ClO}_4$ , like  $\text{Na}_2\text{SO}_4$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , is readily soluble with a low heat of solution, and therefore an ideal substance for solution calorimetry.) The original plans based on an assumed sample size of about 10 grams called for a series of five measurements, using about 2 grams per measurement. Under these conditions the total heat evolution (absorption) would be of the order of 140 calories ( $\approx 70$  cal/g) with an anticipated uncertainty of  $\pm 0.50$  cal or  $\pm 0.25$  cal/g. For the smaller sizes actually used ( $\approx 0.3$ g for the irradiated samples) the corresponding anticipated uncertainty is  $\pm 0.3$  cal or  $\pm 1.0$  cal/g.

Since the amount of energy storage is determined from the difference in heats of solution of two samples, the overall uncertainty must include the uncertainties in the measurements with both samples, combined on a root mean square basis according to the recommendations of Rossini(44). Thus, if each series resulted in a precision uncertainty of  $\pm 0.25$  cal/g, the precision uncertainty associated with the difference is  $(0.25^2 + 0.25^2)^{1/2}$  or  $\pm 0.35$  cal/g.

It must be pointed out, however, that this uncertainty summation represents only the precision uncertainty in the measurements and does not reflect possible errors due to decomposition product impurities in the irradiated sample. A proper assessment of the error due to this effect must be made at the time of the measurements, taking into account the amounts of the individual impurities, the heats of solution of the respective impurities and a suitable estimate of the error in analysis for impurities.

PRECISION UNCERTAINTY (ABSOLUTE) vs. TOTAL HEAT EVOLUTION  
(Previous Data from References 45, 46 and 47)



### III, 2, Calorimetry (cont.)

#### d. Auxiliary Thermochemical Data

Since the heat of solution calorimeter is calibrated against an electrical standard as a part of each heat of solution experiment, it is in effect a heat capacity calorimeter. The heat of solution results can then also be used to derive other thermodynamic data for the  $\text{NH}_4\text{ClO}_4 - \text{H}_2\text{O}$  system, such as heat capacity of various concentrations of  $\text{NH}_4\text{ClO}_4$  solution, heat of dilution, apparent molal heat capacity of aqueous  $\text{NH}_4\text{ClO}_4$  solutions, and  $\Delta C_p$  of the solution reaction.

#### 3. ANALYTICAL

The planned analytical approach included not only assessment of the irradiated samples by chemical means but also by X-ray and microscopic techniques. Extensive radiation damage to the single crystal samples to be used for X-ray examination made this technique completely impractical. Valuable qualitative information was obtained from the microscopic examination but the final scope of the program did not permit quantitative examination. In addition problems were encountered in the chemical approach both from equipment failures and from greater than anticipated decomposition of samples under irradiation.

The procedures originally proposed and a discussion of their theoretical aspects are included herein to guide the reader in his evaluation of the ensuing experimental sections. Deviations from the original plan are discussed individually in Section VI.2 which covers the experimental results.

#### a. Chemical Approach

The primary purpose of the analysis is to determine both qualitatively and quantitatively what, if any, chemical impurities are present in the irradiated ammonium perchlorate as a basis for applying accurate corrections to the measured heat of solution. Since a knowledge of the gaseous decomposition products from the AP and of possible container corrosion products was needed to aid in identification of the solid decomposition products remaining in the irradiated AP, sampling and analysis were carried out in three phases as follows:

(1) A gas sample was taken from the irradiation capsule before removal of the sample and subjected to mass spectrometric analysis.

(2) After removal of the sample the capsule was washed and the washings analyzed for metal corrosion products.

### III, 3, Analytical (cont.)

(3) The aqueous liquors remaining after the calorimetric measurements for heat of solution were analyzed for possible decomposition products using standard techniques of quantitative analysis(48), (49). The analysis included the negative ions  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{OH}^-$ , the positive ion  $\text{H}^+$  and the neutral gases  $\text{Cl}_2$  and  $\text{ClO}_2$ , with the  $\text{NH}_4\text{ClO}_4$  purity being computed by difference from 100 percent.

Guidelines for the analyses necessary are embodied in the final report on Contract AF 49(638)-1125, "Radiation Induced Solid Propellant Decomposition"(50), which lists a considerable amount of useful data regarding G values (number of ions or molecules produced per 100 ev) of ammonium perchlorate decomposition products due to Cobalt-60 gamma radiation. This report also lists analytical procedures used in the quantitative analysis for ammonium perchlorate decomposition products.

#### b. Structural Damage Evaluation by X-Ray Techniques

High-energy neutrons may produce disturbances in the arrangement of atoms in a crystal as a result of elastic collisions with atomic nuclei. A struck atom (primary knock-on) will travel through the crystal lattice producing other displaced atoms some of which are capable of further multiplying the process in a paniculate or branching manner. Meanwhile, the initial neutron is capable of producing further knock-ons and permanently displacing atoms until its energy is reduced to about 30 ev. The probability for the initial collision with a  $10^6$  ev neutron is very small but the subsequent chain of reaction may produce appreciable damage of a displacement nature.

It was anticipated that the principal high energy structural defect produced by the aforementioned processes would be the interstitial-vacancy pair (Frenkel defect) and this should amount to a few ev per defect. In addition, there may be a great diversity of minor structural rearrangements of a type producible by thermal energy, i.e.,  $<0.1$  ev/atom.

The planned approach utilized large single crystals which were to be surveyed with X-ray diffraction techniques both before and after sample irradiation.

#### c. Optical Crystallographic Study

In some previous studies at Aerojet-General, it had been shown that deformation of ammonium perchlorate produces multiple twin planes in the initial monocrystalline lattice(51). Thermal deformation produces polysynthetic twins oriented parallel to the (100) and (010) planes while mechanical deformation produces twins parallel to the (110) planes. Analysis

### III, 3, Analytical (cont.)

of the irradiated crystals for possible twinning will give the type of twin from which the type of linear dislocation can be assigned. The concentration of any twinning can also be determined volumetrically with the microscope from which changes in energy can be estimated. These estimates can be recalculated more accurately if the X-ray analysis yields satisfactory results.

Radiation normally produces a series of vacancies in an ionic lattice by the Schottky or Frenkel mechanism. A high concentration of condensed vacancies can be readily recognized under the microscope and their concentration evaluated. These Schottky vacancies have been identified and assigned, on a theoretical basis, to the F, R, M, and Z bands. Frenkel disorder, i.e., vacancies with associated interstitials, have been indicated by three separate observations of either a glassy or liquid ammonium perchlorate phase. If neutron radiation is effective in increasing the enthalpy, as determined by calorimetry, it will be due to a highly concentrated Frenkel disorder. This disorder, recognized as a glassy phase, may be volumetrically determined in single crystals and thus afford a direct correlation with the calorimetric data. Freeman(23) has extensively examined X-irradiated ammonium perchlorate. Correlation can be established between the neutron and X-ray results by use of DTA and the microscope hot stage, or more accurately with TGA if time permits.

#### d. DTA and Drop Test

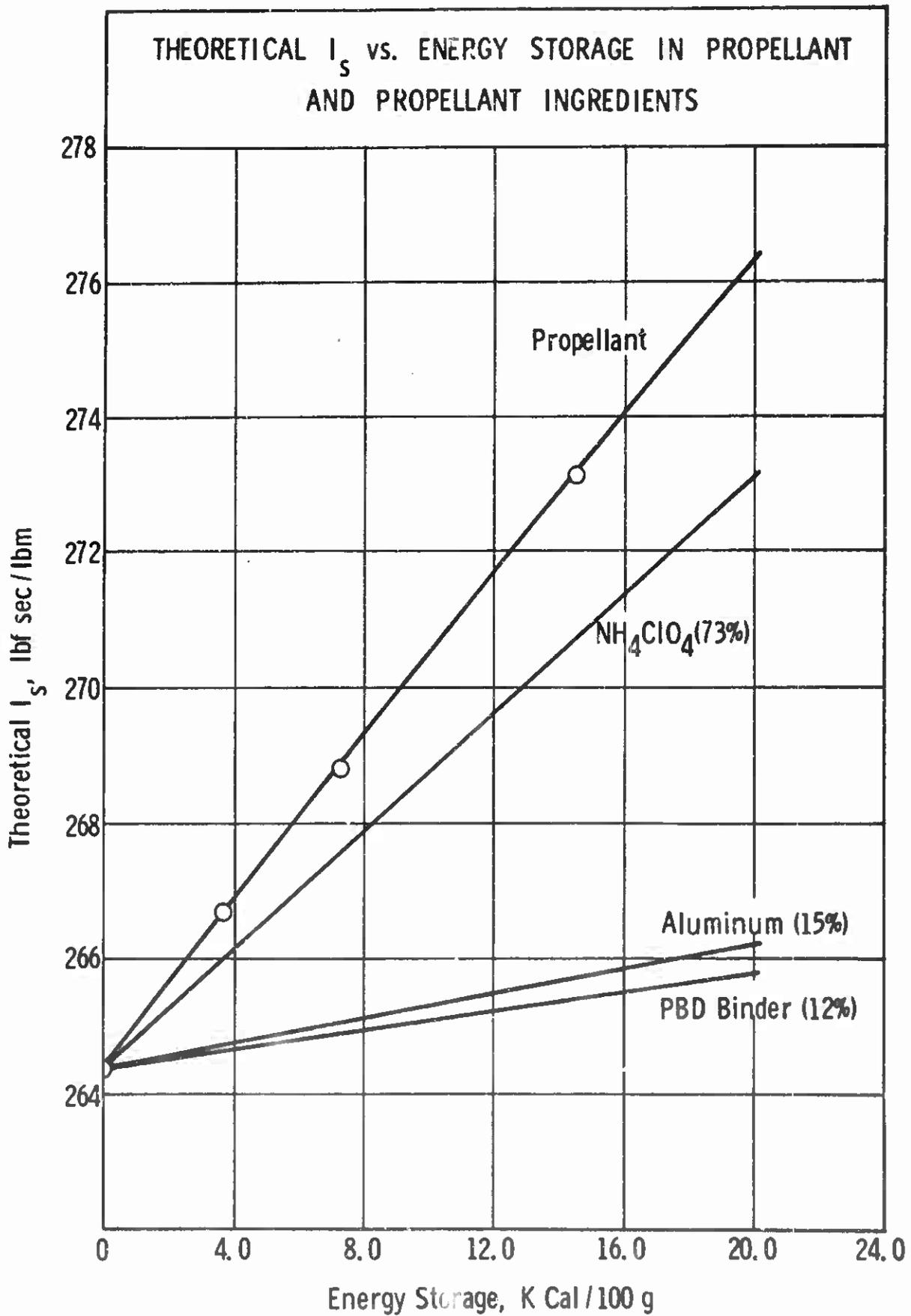
In order to facilitate comparison of data generated on this program with similar data obtained by others with other varieties of activated  $\text{NH}_4\text{ClO}_4$ (23), (52), (53) plans were made to run a standard DTA pattern on each sample of irradiated ammonium perchlorate before the start of calorimetric work. This test was intended to give some preliminary indication of the amount of stored energy to be expected as well as safety information regarding the temperature at which the stored energy is released.

As an added safety precaution, the standard 2Kg weight drop test (Bureau of Mines Apparatus) was planned for each sample before the start of calorimetric work.

### 4. PERFORMANCE POTENTIAL

#### a. Aluminum-Polybutadiene-Ammonium Perchlorate

Theoretical specific impulse calculations were made for a typical modern solid propellant consisting of 12% polybutadiene binder, 15% aluminum fuel and 73% ammonium perchlorate assuming various amounts of stored energy in the propellant or propellant ingredients. The results of these calculations are summarized in Figure 5.



### III, 4, Performance Potential (cont.)

The four lines shown represent the effects of stored energy in (a) the complete propellant, (b) the  $\text{NH}_4\text{ClO}_4$ , (c) the aluminum metal, and (d) the binder, with the 20 Kcal/100g or 200 cal/g the maximum amount considered. Note that a 20 Kcal/100g energy storage, on an overall propellant basis, represents a specific impulse gain of 11.9  $I_s$  units, whereas a 20 Kcal/100g energy storage applied to the aluminum represents a gain of only 1.8  $I_s$  units. A 20 Kcal/100g energy storage applied to the  $\text{NH}_4\text{ClO}_4$ , on the other hand, represents an  $I_s$  gain of 8.7 units. Thus it seems obvious that if the energy storage principle is to be effective it must be applied to the major component of the propellant, namely  $\text{NH}_4\text{ClO}_4$ .

#### b. Graphite-Polybutadiene-Ammonium Perchlorate

It has been previously noted that a considerable amount of lattice defect energy can be stored in graphite. Therefore, a second series of specific impulse calculations were made considering graphite (with various amounts of stored energy up to a maximum of 50 Kcal/100g or 500 cal/g) as a replacement for aluminum. Three graphite concentrations were considered: 8, 12, and 16%, at a constant binder content of 12%. These calculations are summarized in Table IV.

TABLE IV

#### SPECIFIC IMPULSE AS A FUNCTION OF STORED ENERGY IN GRAPHITE

(12% PBD Binder,  $\text{NH}_4\text{ClO}_4$  Oxidizer)

<u>Wt% Graphite</u>	<u>Graphite Stored Energy, Kcal/100g</u>			
	<u>0</u>	<u>+10</u>	<u>+25</u>	<u>+50</u>
16	195.0	196.5	198.5	202.2
12	207.6	208.9	210.8	214.2
8	224.4	225.3	226.6	228.7

These calculations serve to illustrate two distinct points:

(1) Even with a stored energy of 500 cal/g (or 50 Kcal/100g) graphite does not compare with aluminum as a fuel additive.

(2) An energy storage as high as 500 cal/g, when applied to an ingredient which is 16% by weight of the propellant, represents an  $I_s$  gain of only 7.2 units.

### III, 4, Performance Potential (cont.)

This further justifies the choice of an oxidizer as the practical candidate for this study.

#### 5. SAFETY

##### a. Radiation Hazards

Radiation hazards, as well as pressure vessel design and other safety features associated with the use of the reactor were covered in the "Hazards Analysis" which must be submitted to the AGN Safety Committee and the Atomic Energy Commission -- and approved -- before the start of any sample radiation.

After completion of the scheduled nuclear exposure the individual sample pressure vessels were removed from the hot zone and placed in a storage rack in the reactor pool, until such time as appropriate tests indicated negligible radioactivity.

##### b. Explosive Hazards

No explosive hazards were anticipated as a result of the radiation treatment. However, as a precautionary measure, milligram quantities of the irradiated samples were removed (immediately after opening the pressure vessels in the dry box) for standard DTA and Drop Weight tests - before proceeding with the calorimetric and analytical work.

## SECTION IV

### SAFETY ANALYSIS AND TESTING

#### 1. INTRODUCTION

Although in original concept the safety analysis and testing were considered as relatively small portions of the overall program effort, in actual practice this phase of the work proved to be a major effort which was responsible for approximately one half of the total man-hour expenditures. Therefore, this phase of the work is considered separately from the Irradiation and Calorimetry portions of the program.

#### 2. SAFETY ANALYSIS (ORIGINAL)

The original safety analysis was conducted during the initial months of the program and consisted primarily of a literature search for pertinent data and engineering design of the equipment to be used.

Also included were plans for hydrostatically testing of the irradiation capsules at double the anticipated maximum working pressure and a thermal decomposition test of a sealed capsule containing a 10 gram sample of  $\text{NH}_4\text{ClO}_4$ . The temperature planned for this test was  $200^\circ\text{C}$ , or  $95^\circ$  above the maximum anticipated working temperature of  $105^\circ\text{C}$ .

This original safety analysis document, which also contained a heat transfer analysis and an evaluation of all possible nuclear and non-nuclear hazards is included in this report as Appendix A.

This safety analysis had received the tentative approval of the Reactor (San Ramon) Safety Committee, subject to the final approval of the Atomic Energy Commission which controls the use of the reactor.

#### 3. THERMAL DECOMPOSITION TESTS

In the course of preparing for the thermal decomposition test, the procedure to be used was reviewed by an AEC Inspector, who insisted upon carrying this test to the autoignition temperature, rather than the planned prolonged heating at  $200^\circ\text{C}$ .

The revised test procedure called for heating of the sealed pressure vessel containing 10 grams of AP at a rate of  $5^\circ\text{C}/\text{minute}$  until the autoignition temperature was reached. The first three such tests resulted in failure of the irradiation capsules and revocation of the previously granted program approval. (See Figure 6)

IRRADIATION CAPSULE AFTER SECOND IGNITION TEST



#### IV, 3, Thermal Decomposition Tests (cont.)

Appendix B summarizes the results of the autoignition tests to this time, including an analysis of the reasons for failure and a suggested room temperature ignition test designed to more closely simulate the actual reactor conditions.

All other work on the program was suspended during the time period required for carrying out of the room temperature ignition tests, additional elevated temperature testing and rewriting of the Safety Analysis Report for submission to the AEC.

#### 4. ROOM TEMPERATURE IGNITION TESTS

Mixtures of  $\text{NH}_4\text{ClO}_4$  and JPN (Ballistite) were ignited in simulated pressure vessels. The JPN was necessary to initiate the decomposition of  $\text{NH}_4\text{ClO}_4$ ; a fuse wire was used to ignite the JPN. The pressure generated by each mixture was measured by closed-bomb tests in a separate series of measurements conducted at Sacramento and described in detail in Appendix C. Post-ignition examination of the pressure vessel showed that all the  $\text{NH}_4\text{ClO}_4$  was consumed during the test. The test data were normalized to the rating of sample weight-to-free volume projected for the AGNIR experiment. The results are shown in Table V.

The results show that a 10 g sample of ammonium perchlorate will result in a pressure of about 13,700 psi in the pressure vessel; this is significantly less than the demonstrated burst strength of 21,500 psi. Of particular significance is the fact that the  $\text{NH}_4\text{ClO}_4$  did not detonate but completely decomposed at less than sonic velocities.

#### 5. EXPERIMENTS AT ELEVATED TEMPERATURES

Thermal decomposition tests were performed with 2 g and 5 g samples of  $\text{NH}_4\text{ClO}_4$  in the standard pressure vessel without failure. A heating rate of  $\approx 5^\circ\text{C}/\text{minute}$ , supplied by a heating tape, was used to simulate the heating rate of reaction radiation ( $\approx 3 \times 10^7$  Rads/hr) in the reactor. The surface temperature of the pressure vessel was monitored with a chromel-alumel thermocouple and a Leeds & Northrup potentiometer. The experimental data for these tests are shown in Tables VI and VII.

IV, 5, Experiments at Elevated Temperatures (cont.)

TABLE V

NH<sub>4</sub>ClO<sub>4</sub>-JPN ROOM TEMPERATURE IGNITION TEST RESULTS

Experiment	Sample Weights, Grams		Pressure Vessel	Pressure* psia	Remarks
	NH <sub>4</sub> ClO <sub>4</sub>	JPN			
1	-	1.90	No. 1	3,000	No pressure vessel rupture
2	-	3.76	No. 1	7,700	No pressure vessel rupture
3	1.98	2.91	No. 1	10,500	No pressure vessel rupture
4	3.9	2.19	No. 2	12,300	No pressure vessel rupture
5	5.8	1.46	No. 1	12,800	No pressure vessel rupture
6	7.8	0.73	No. 2	13,400	No pressure vessel rupture
7	7.8	0.73	No. 1	13,400	No pressure vessel rupture

\*Values derived from experimental data from AGC-Sacramento tests scaled to AGC-San Ramon test conditions.

A final out-of-pile ignition test was conducted with a 0.73 g JPN-7.8 g NH<sub>4</sub>ClO<sub>4</sub> mixture (13,400 psia) in a simulated pressure vessel whose surface was externally heated to 100°C. The surface temperature was more than twice the temperature (45°C) measured during the thermometry experiments discussed in Section V.2.b. The pressure vessel contained the NH<sub>4</sub>ClO<sub>4</sub> decomposition without any evidence of pressure vessel damage.

6. AEC APPROVAL

After suitable documentation of the safety test experiments described here, the Atomic Energy Commission granted final approval to proceed with the program, using sample sizes equal to 1/2 of the maximum size successfully tested in the "Out of Core" ignition tests.

On this basis since 10 gram samples had been successfully tested, the program was re-activated on the basis of irradiating 5 gram samples instead of the 10 gram size originally planned.

TABLE VI

THERMAL DECOMPOSITION TEST RESULTS - 2 GRAMS OF  $\text{NH}_4\text{ClO}_4$

<u>Elapsed Time, Min.</u>	<u>Temperature, °C</u>		<u>ΔT, °C</u>	<u>Heating Rate, °C/min.</u>
	<u>Inside</u>	<u>Outside</u>		
0	22	27	-	-
5	32	41	9	2
10	63	73	10	6
15	88	100	12	5
20	109	123	14	4
25	124	132	8	3
30	142	153	11	4
35	168	181	13	5
40	193	202	9	5
45	212	222	10	4
50	235	242	7	5
55	259	265	6	5
60	277	284	7	4
65	300*	312	12	5
69	330	340	10	8
70	332	347	15	2
71	337	355	18	50
75	353	380	27	60
78	363	396**	33	3

\*Observed rapid rise of internal temperature.

\*\*Estimated temperature - potentiometer failure.

TABLE VII

THERMAL DECOMPOSITION TEST RESULTS - 5 GRAMS OF  $\text{NH}_4\text{ClO}_4$

<u>Elapsed Time, Min.</u>	<u>Temperature, °C</u>		<u>ΔT, °C</u>	<u>Heating Rate, °C/min.</u>
	<u>Inside</u>	<u>Outside</u>		
0	25	25	..	-
5	39	50	11	3
10	59	72	13	4
15	92	111	19	7
20	122	139	17	6
25	147	161	14	5
30	169	186	17	4
35	198	216	18	6
40	227	243	16	6
45	247	265	18	4
50	275	291	16	6
51	280	296	16	5
52	287	302	15	7
53	292	307	15	5
54	298	312	14	6
55	304	317	13	6
56	312	322	10	8
57	318	327	9	6
58	323	332	9	5
59	330	337	7	7
60	336*	341	5	7
62	358	359	1	6

\*Observed rapid rise of internal temperature.

## SECTION V

### PHASE I - SAMPLE IRRADIATION

#### 1. EXPERIMENTAL TECHNIQUES

The irradiation of four  $\text{NH}_4\text{ClO}_4$  samples was performed in the F-26 position of the Aerojet-General Nuclear Industrial Reactor (AGNIR) located at the San Ramon Plant of AGC. This reactor, described in Section III.1.e was operated at its maximum licensed power of 250 Kw for these irradiations. The primary containment for the  $\text{NH}_4\text{ClO}_4$  was a sealed, aluminum pressure vessel, which, in turn, was contained in a modified aluminum Dummy-Element Irradiation Capsule for secondary containment. A chromel-alumel thermocouple was used to monitor the primary pressure vessel temperature during the irradiation.

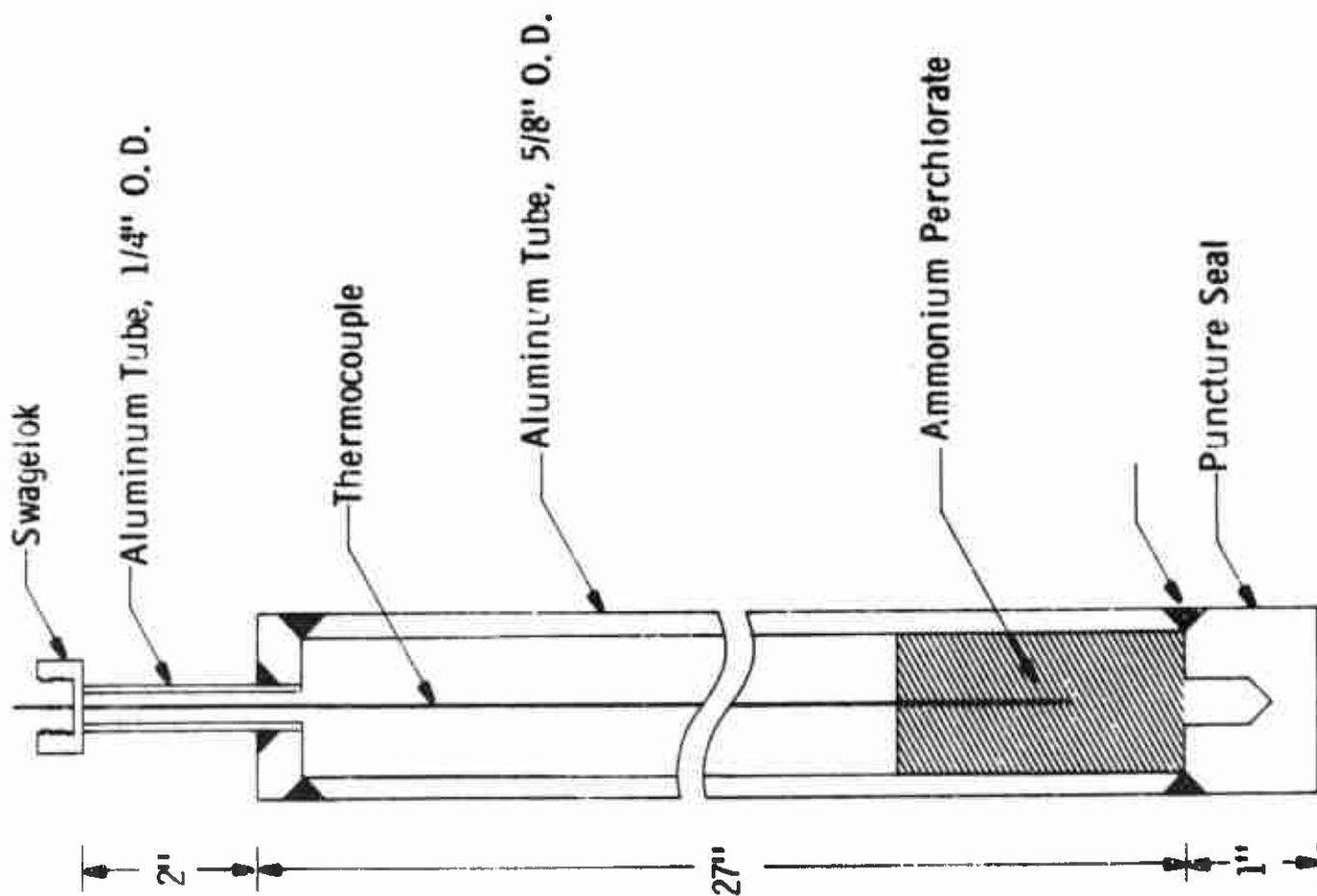
Post-irradiation analyses consisted of sampling the gases from the primary pressure vessel and recovery of the irradiated  $\text{NH}_4\text{ClO}_4$ . The primary pressure vessel was then leached with hot water to insure complete recovery of all undecomposed  $\text{NH}_4\text{ClO}_4$ . The quantity of  $\text{NH}_4\text{ClO}_4$  obtained from the leach solutions was used to facilitate material balance calculations.

##### a. Equipment and Materials

The equipment for this experiment includes aluminum primary pressure vessels, the AGNIR dummy-element irradiation capsule as secondary container, and chromel-alumel thermocouples for temperature monitoring.

##### 1) Pressure Vessel

Type 6061 aluminum tubing and round stock was used to fabricate the pressure vessels used for primary containment of the  $\text{NH}_4\text{ClO}_4$  (Figure 7). These pressure vessels were fabricated in accordance with standards established by the ASME for thin-walled pressure vessels. The design pressure for this pressure vessel was 5375 psia, and the working pressure was 4030 psia. These values were based on an ultimate tensile strength of 64,000 psi calculated from the experimentally determined burst strength (21,500 psi) of fabricated pressure vessels and include an allowance for a tube wall thickness reduction of 0.010 in. to accommodate worst case corrosion conditions. The main body of the pressure vessel was 5/8 in. O.D. tubing with 0.125 in. walls; the assembly was 27 in. long. A 1/4 in. O.D. tube with 0.049 in. walls, 2 in. in length, was welded at one end of the main body for sample loading access. A Swagelok closure was used to seal the pressure vessel. A puncture seal was welded at the opposite end of the pressure vessel to facilitate post-irradiation gas sampling. The overall length of the pressure vessel was 30 in.; the total internal volume was 51  $\text{cm}^3$  (3.1  $\text{in}^3$ ).



PRESSURE VESSEL FOR  
 $\text{NH}_4\text{ClO}_4$  IRRADIATION

## V, 1. Experimental Techniques (cont.)

The complete pressure vessel, before loading of the sample, was tempered to T6 and hydrostatically tested to 8100 psia (twice the working pressure) to verify the mechanical integrity.

The following tests were conducted in support of the development of the design discussed above:

(a) A specimen of 5/8 in. O.D. aluminum tubing was hydrostatically burst test; the burst pressure was 24,000 psi.

(b) A pressure vessel fabricated to the final design was hydrostatically burst test; the burst pressure was 21,500 psi and this value was used to calculate the design and working pressures as indicated earlier.

(c) A series of out-of-pipe ignition tests was performed to verify the pressure vessel integrity (see discussion in Section IV).

### 2) Secondary Container

An AGNIR dummy-element irradiation capsule (Figure 8) was used for the secondary containment for this irradiation. This aluminum capsule is capable of containing two primary pressure vessels (70 in. long, 1.47 in. in O.D., with 0.050 in. walls). The volume is 1690 cm<sup>3</sup> (103 in.<sup>3</sup>). A lead gasket is used to make the seal between the screw cap and the capsule body. The design pressure is 400 psi and the working pressure is 300 psia. This capsule has been hydrostatically tested to 600 psia to verify the mechanical integrity. A stainless steel bulkhead fitting was used as the water-tight connector for passing the thermocouples into the secondary capsule.

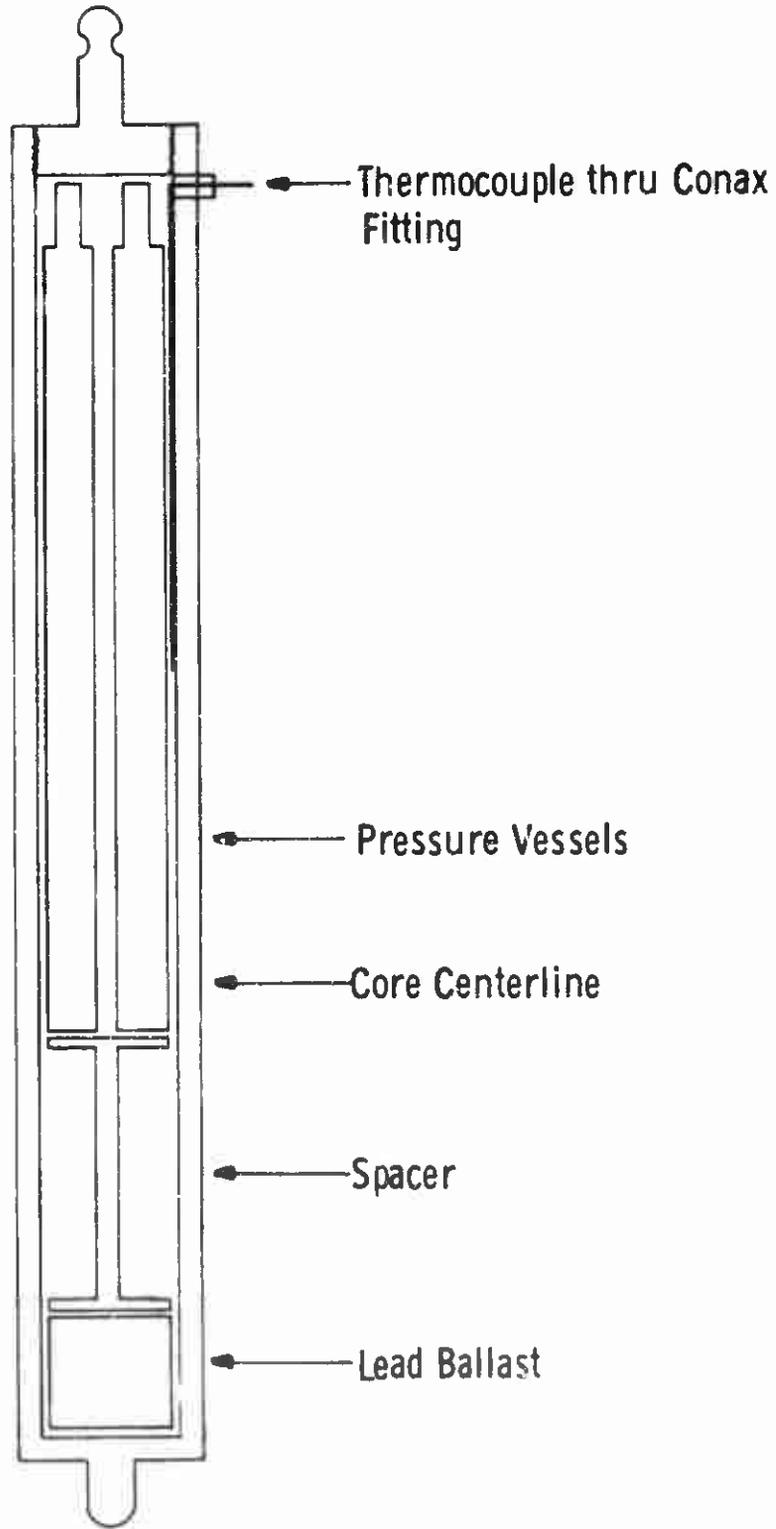
### 3) Instrumentation

The only instrumentation used was a chromel-alumel thermocouple attached to the surface of a primary pressure vessel. The signal from this thermocouple was used to trip (Electronic Trip Control, Rochester Instruments Systems, Model No. 217A) the automatic temperature scram circuit at 80°C. (This scram circuit is separate from that which protects against excessive AGNIR pool temperature.) This temperature was recorded during the entire irradiation period (Recorder, Foxboro Co. Model 64).

### 4) Gas Sampling Valve

A gas sampling valve (Whitey Research Tool Co. Model IVF4-A-316) with a drill-bit stem was used for penetrating the puncture seal

# SECONDARY CONTAINMENT CAPSULE



## V, 1, Experimental Techniques (cont.)

of the primary pressure vessel (see Figure 9). A second valve (Whitey Research Tool Co. Model 4VF4) was used to regulate the gas flow from the primary pressure vessel to the gas-sampling vacuum system.

### 5) Chemicals

Reagent grade  $\text{NH}_4\text{ClO}_4$ , purchased from Matheson, Coleman and Bell, was used for the irradiation samples. Ammonium perchlorate is a colorless crystalline solid and has a density of  $1.95 \text{ g/cm}^3$ . It undergoes a crystalline transition from orthorhombic to cubic at  $240^\circ\text{C}$  ( $\Delta H = 2.3 \text{ kcal/mole}$ ) and its autoignition temperature, as determined by differential thermal analysis, is  $380^\circ\text{C}$  (heating rate =  $5^\circ\text{C/min}$ ). No exotherm is observed below  $240^\circ\text{C}$ .

Both the primary and secondary capsules were pressurized to one atmosphere with helium gas to improve the heat transfer.

## 2. REACTOR IRRADIATIONS

Four samples of  $\text{NH}_4\text{ClO}_4$  were irradiated in AGNIR for periods ranging from 37 to 224 hours. A thermometry experiment, using  $(\text{NH}_4)_2\text{SO}_4$ , was also performed to determine the centerline temperature of the loaded pressure vessel during AGNIR irradiation.

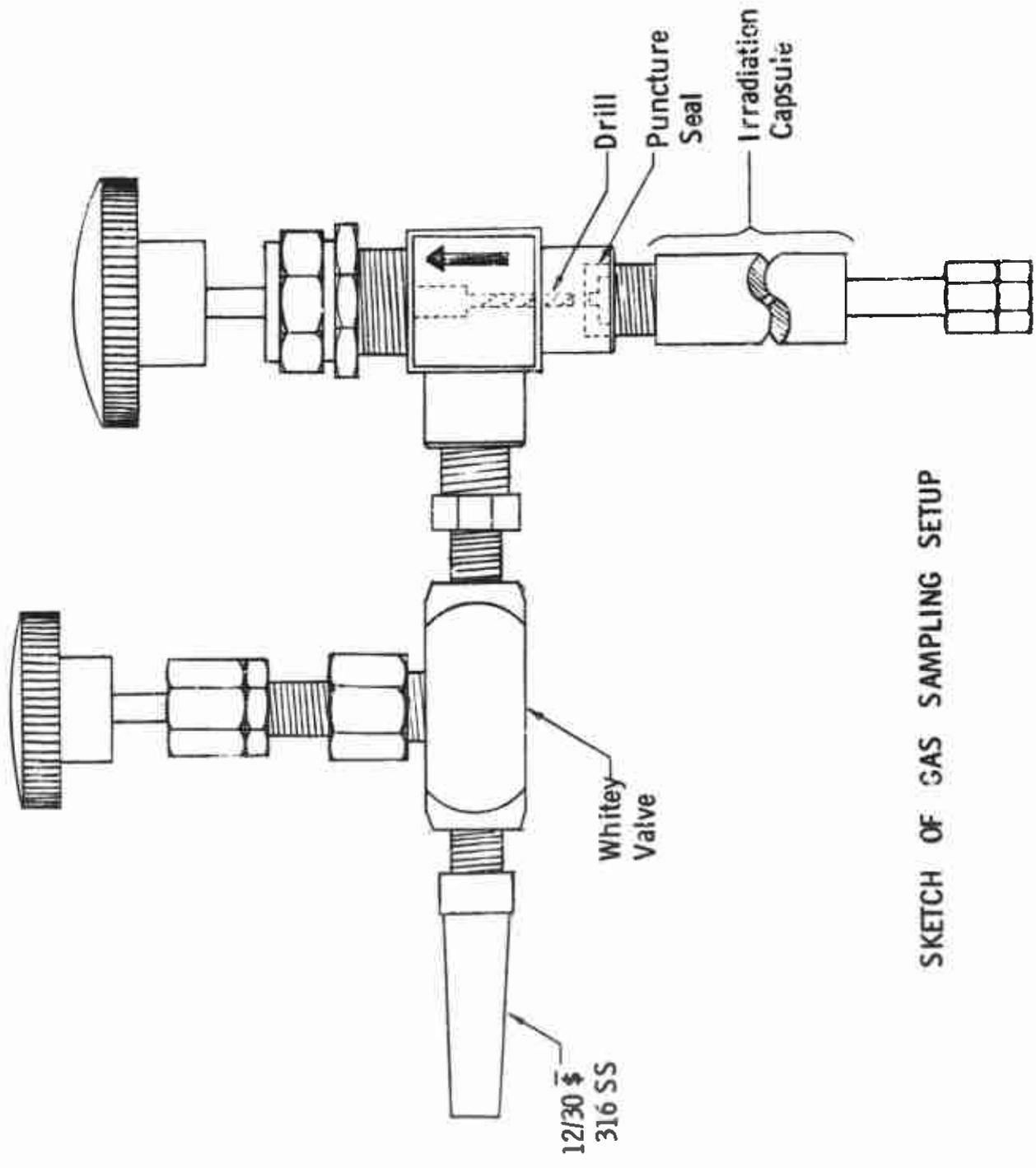
### a. Irradiation Procedure

The samples to be irradiated were loaded into previously cleaned primary pressure vessels in a gloved-bag containing a helium atmosphere. The sample weights were 10 g for the  $(\text{NH}_4)_2\text{SO}_4$  irradiation and 5 g for the  $\text{NH}_4\text{ClO}_4$  irradiations. After the samples were loaded into the pressure vessel, the bag was evacuated, then filled with helium. This purging cycle was repeated three times before the Swagelok end closure was fitted to the tube-end to seal the pressure vessel containing the  $\text{NH}_4\text{ClO}_4$  and 1 atm of He.

Two primary pressure vessels were placed in the secondary capsule and positioned (vertically) to expose the  $\text{NH}_4\text{ClO}_4$  to the highest neutron flux in the F-26 position. Thermocouples were attached to the 224 hr and 78 hr pressure vessels to monitor the temperature during the irradiation.

### b. Temperature Profile Experiment

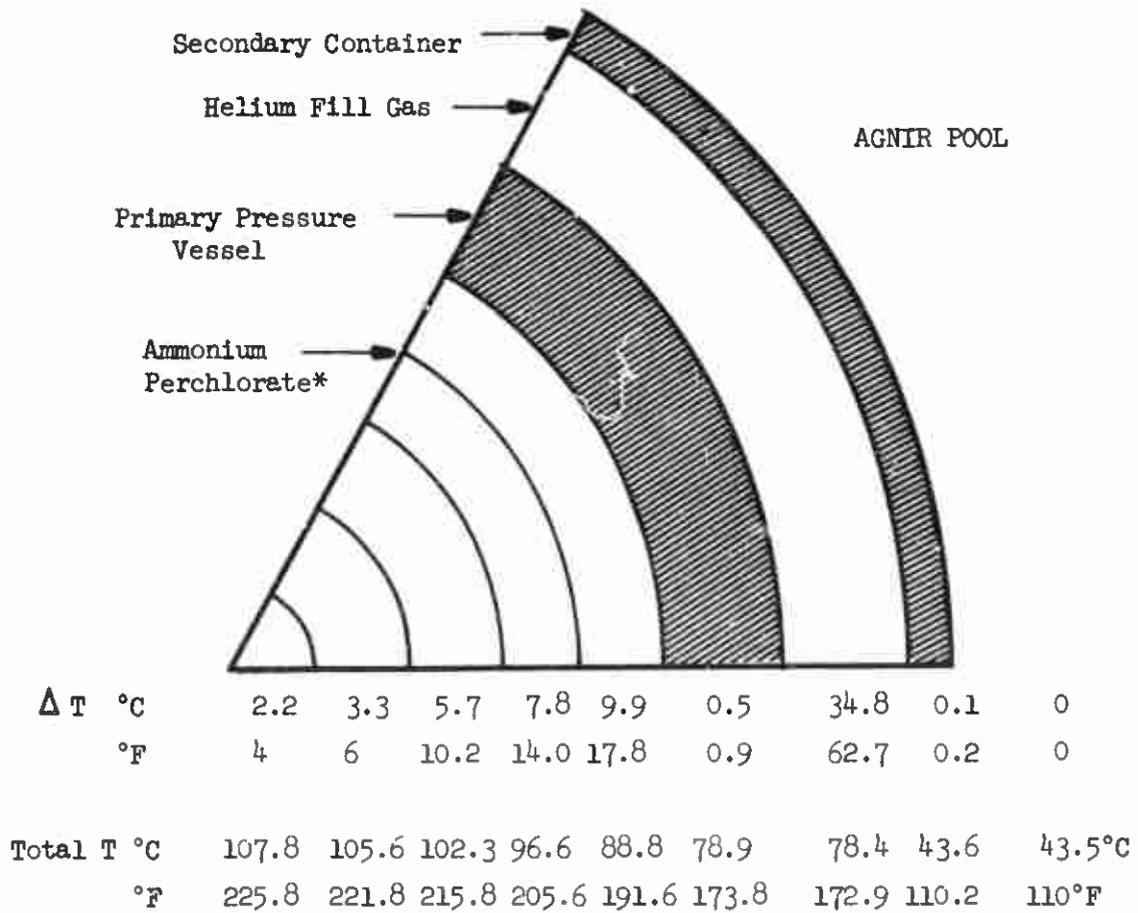
The calculated temperature profile indicated that the centerline temperature of the loaded pressure vessel might be as high as  $108^\circ\text{C}$  (due to gamma heating) during the irradiation (see Figure 10). Such a temperature increases the viability of the pressure vessel due to loss of tensile strength and increased internal pressures. The possibility of annealing of lattice



SKETCH OF GAS SAMPLING SETUP

Figure 9

## TEMPERATURE PROFILE OF IRRADIATION CAPSULE (Estimated)



\*0.01 BTU/ft<sup>2</sup> - sec - °F

was used for the thermal conductivity value (K) for poured ammonium perchlorate

## V, 2, Reactor Irradiations (cont.)

defects also increases with increasing temperature. Therefore, an irradiation of  $(\text{NH}_4)_2\text{SO}_4$  was performed in a pressure vessel containing a centrally located thermocouple and a chromel-alumel thermocouple attached to the outside wall of the pressure vessel. Except for the substitution of  $(\text{NH}_4)_2\text{SO}_4$  for  $\text{NH}_4\text{ClO}_4$  and the internal thermocouple, the experimental conditions were identical to those used for the irradiation of  $\text{NH}_4\text{ClO}_4$ . The irradiation was performed in core position F-26 at a reactor power of 250 Kw for 10 hours.

The results indicate that the centerline temperature of the primary pressure vessel does not differ significantly from that at the outer surface of the pressure vessel. The maximum temperature obtained for this run was 43°C.

### c. Ammonium Perchlorate Irradiation

The irradiation data for the four  $\text{NH}_4\text{ClO}_4$  irradiations are listed in Table VIII.

TABLE VIII  
IRRADIATION DATA

Sample	Length of Irradiation (hours)	Dose		Maximum Temperature During Irradiation
		Neutron E > 1.0 Mev (n/cm <sup>2</sup> )	Gamma (Rads)	
I	37	$1.0 \times 10^{17}$	$1.7 \times 10^8$	53°C (124°F)
II	187	$5.1 \times 10^{17}$	$8.2 \times 10^8$	53°C (124°F)
III	224	$6.1 \times 10^{17}$	$9.9 \times 10^8$	53°C (124°F)
IV	78	$2.1 \times 10^{17}$	$3.4 \times 10^8$	53°C (124°F)

### d. Dosimetry

An important factor in all radiation effects experiments is the characterization of the nuclear environment. Such a characterization permits the correlation of the changes observed to the particular radiation field responsible for these changes. In the mixed-radiation field of a reactor, a dose component of interest must be measured independently in the presence of the other. Neutron fluxes are readily measured using the threshold foil system(27-32).

V, 2, Reactor Irradiations (cont.)

Of the many methods available for gamma dosimetry(33), the glass dosimeters(34-36) are best suited for determining the gamma contribution to the total dose.

Neutron doses are best described by integrated fluxes for specific neutron energy groups. The "sulfur flux", i.e., the neutron flux above the threshold energy (2.9 Mev) for the reaction  $S^{32} + \text{neutron} \rightarrow P^{32} + \text{proton}$ , is a good index for the fast neutron population. Neutron dose measurements for the AGNIR irradiations were performed with sulfur neutron detection foils in the F-26 position. These foils were placed at appropriate intervals along the entire length of the dummy fuel element irradiation capsule to determine the fast flux gradient for the irradiation position. The thermal neutron flux in this position is  $3.3 \times 10^{12}$  n/cm<sup>2</sup>-sec.

Sulfur foils were irradiated in AGNIR at a power level of 2 Kw to determine the fast neutron flux of the selected irradiation position (F-26). The sulfur foils determine the neutron flux above 3 Mev, the threshold energy of the Sulfur-32 (neutron, proton) Phosphorous-32 reaction. The neutron flux for neutrons with energies greater than 1 Mev can be estimated using the Watt(56) or Nereson-Rosen(57) fission spectra. The results from the experiment and the estimated >1 Mev neutron flux for four positions near the centerline of the core are listed in Table IX.

TABLE IX

FAST NEUTRON FLUX OF AGNIR

Position (Inches above or below core centerline)	> 1 Mev		> 3 Mev	
	(Neutron/cm <sup>2</sup> -sec)		(Neutron/cm <sup>2</sup> -sec)	
	<u>2 Kw*</u>	<u>250 Kw*</u>	<u>2 Kw</u>	<u>250 Kw*</u>
-5	$4.7 \times 10^9$	$5.9 \times 10^{11}$	$1.43 \times 10^9$	$1.8 \times 10^{11}$
-1	$6.6 \times 10^9$	$8.2 \times 10^{11}$	$2.00 \times 10^9$	$2.5 \times 10^{11}$
+1	$6.9 \times 10^9$	$8.7 \times 10^{11}$	$2.11 \times 10^9$	$2.6 \times 10^{11}$
+5	$5.1 \times 10^9$	$6.4 \times 10^{11}$	$1.55 \times 10^9$	$1.9 \times 10^{11}$

\*Calculated values

Glass dosimeters were used to determine the extent of the gamma contribution to the total dose during NH<sub>4</sub>ClO<sub>4</sub> irradiation. The low-Z, silver metaphosphate glass dosimeters have known thermal and fast neutron responses which

V, 2, Reactor Irradiations (cont.)

were used to determine the gamma dose. The results from the glass dosimeters, exposed for 15 minutes at 0.1 Kw are listed in Table X.

TABLE X  
GAMMA DOSE DISTRIBUTION (F-26)

<u>Position</u> <u>(in. from top of core)</u>	<u>Dose*</u> <u>(Rads)</u>	<u>Dose Rate</u> <u>(Rads/hr 10<sup>-6</sup>)</u>
4	220	2.2
6	280	2.8
8	330	3.3
10	410	4.1
12	440	4.4
13	430	4.3
14	400	4.0
16	410	4.1
18	360	3.6
20	250	2.5
22	200	2.0

\*Reactor Irradiation - .25 hour at 0.1 Kw.

## SECTION VI

### PHASE II-CALORIMETRY AND ANALYSIS

#### 1. CALORIMETRY

##### a. Introduction

Heat of solution measurements were made with the irradiated samples obtained during this program and with a separate unirradiated portion of the same ammonium perchlorate reagent starting material. In the ideal case, in which the radiation causes no chemical change in the irradiated sample, the amount of lattice deformation energy stored in the sample is obtainable directly from the difference in heats of solution of the irradiated and unirradiated samples. However, in the real case chemical changes do occur and must be taken into account in order to obtain a realistic evaluation of the actual lattice deformation energy storage. Therefore, the measured difference in heats of solution must be referred to as "Apparent Energy Storage" until the effects of the chemical impurities produced in the irradiation can be evaluated.

The apparatus used is described briefly in Section III 2. b. and more completely in the Proposal (55) and in the open literature (40, 41).

##### b. Samples

The starting reagent used in the irradiations and all calorimetric measurements was Matheson, Coleman and Bell, Reagent Crystals, CB 150-AK 1335 with maximum limits of impurities listed as: Ca, 0.01%; Cl<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> (as Cl), 0.01%; Heavy metals (as Pb), 0.001%; Insoluble, 0.01%; Fe, 0.001%; Na, 0.03%; and SO<sub>4</sub><sup>=</sup>, 0.005%. The sample was screened before use and only those portions passing through a 1.0 mm opening screen and retained by a 0.5 mm opening screen were used in subsequent work. Two samples (40 to 45 grams each) after screening were placed in a desiccator over P<sub>2</sub>O<sub>5</sub> for a determination of residual moisture content. Both samples lost about 2.0 to 2.5 mg or 0.005% during the first week, and totals of 0.006% and 0.008% respectively after a period of 53 days. A recrystallized sample, intended for use in the X-ray and microscopic studies was also evaluated in this manner, but this sample was not used because of poor optical crystalline properties. Large single crystals previously grown were used for the X-ray and microscopic work.

##### 1) Irradiated Sample I

The most striking effect of the irradiation was a significant reduction in particle size of the first irradiated sample

VI, 1, Calorimetry (cont.)

(37 hours exposure). Although the  $\text{NH}_4\text{ClO}_4$  was dry, the material was sufficiently compacted so that the powder could not be removed by vigorous tapping of the various sections of the pressure vessel, and, therefore, required the use of a spatula. The  $\text{NH}_4\text{ClO}_4$  crystals did not exhibit the brown color associated with crystals which have been severely damaged by radiation. However, a portion of the  $\text{NH}_4\text{ClO}_4$  had a yellowish tinge similar to that of chlorine and some of its compounds. The amount of sample actually recovered was 3.16 grams of which 2.70 grams was found to be -60 mesh as compared with the starting size of  $>0.5$  mm. The yellow color noted above was probably attributable to a trace of surface moisture or other volatile impurity, as it disappeared after the sample had been exposed to the dry nitrogen atmosphere in the dry box. The coarse fractions from the sample screening appeared to be contaminated with residues from the X-ray sample holder and other unidentified fragments and were, therefore, not used in subsequent measurements. The -60 mesh fraction which was used for the heat of solution measurements was homogeneous in appearance with a uniform white color.

2) Sample II

The irradiated ammonium perchlorate recovered from the second pressure vessel was tinted yellow at removal, but faded to a dirty brownish-green color in a matter of minutes. The powder was not compacted (unlike the first sample which had to be removed with a spatula) and could be p eed into the weighing dish. Only 1.4246 grams were recovered (not including water rinse of pressure vessel) from the original 5 gram sample. During the microscopic examination of the crystals, a great increase in hygroscopicity was noted for the irradiated crystals. Because of high residual radioactivity only a small portion (ca. 0.4 g) could be sent to Sacramento initially. This sample was definitely "wet" in appearance and dried to a crusty material after storage in a desiccator. This crust was easily broken up with a spatula, in the dry box, and the sample was transferred to a single heat of solution bulb. The remainder of this sample, which was shipped later, was similar in appearance and behavior. The hygroscopicity noted in the microscopic studies was definitely confirmed during sample weighings when the samples gained weight at a noticeable rate during exposure to the (25% Relative Humidity Controlled) room air.

3) Sample III

Sample III, which had the greatest radiation exposure, had the same general appearance as Sample II, and showed an even greater hygroscopicity and wet appearance. Unlike Sample II, it had to be removed with a spatula and was contaminated with fragments from the foil wrapping on the X-ray samples. (Capsules I and III, which were loaded and placed in the reactor during the first week of irradiation, contained special foil wrapped samples of single crystals and powdered  $\text{NH}_4\text{ClO}_4$  for the X-ray and microscopic work. When

## VI, 1, Calorimetry (cont.)

Capsule I was removed after the first week of irradiation, it was found that the large single crystals had been completely decrepitated by the neutron bombardment. Therefore, when Capsules II and IV were loaded later, the foil wrapped samples were omitted).

After drying in the desiccator the sample formed a hard crust, which on breaking up with a spatula seemed to separate into large and small sized particles. The sample was screened in the dry box, with the major impurities appearing to remain with the large particles and the small sized fraction used for heat of solution and analysis.

### 4) Sample IV

Sample IV (the second shortest exposure) was similar in appearance to Sample I with somewhat more sintering and also some small grey particles of insoluble matter. The sample was crushed lightly in a small mortar in the dry-box and subdivided directly from the mortar into five heat of solution bulbs. The sample tended to separate into coarse and fine fractions but the entire sample was used and the distribution of coarse and fine particles may not have been uniform throughout the five bulbs.

### c. Equipment Calibration and Auxiliary Data

As noted above in Section III. 2. d, an electrical calibration of the apparatus as a whole is made as an integral part of each heat of solution measurement. As a matter of fact, two such calibrations are made with each run, one before breaking the sample bulb and one after, in order to determine the  $\Delta C_p$  of reaction. During a run the current through the resistance thermometer is periodically checked and maintained at exactly 2.00000 ( $\pm 0.00001$ ) milliamps. Similarly the internal working current of the potentiometer is checked (and re-adjusted if necessary) every few minutes against an external standard cell.

Items of auxiliary equipment requiring calibration are the standard cell, the balance weights used for weighing of samples and the stopwatch used for timing of the electrical energy input. These items are maintained by periodic calibrations according to established procedures.

All weighings included corrections to vacuum, and the results are expressed in terms of the defined calorie, 4.1840 absolute joules.

### d. Results with Unirradiated Sample

Since the calorimeter was used for the first time on this program and several minor changes in design had been made over the previous model (40, 41), the effects of these changes were evaluated before the start of actual measurements.

VI, 1, Calorimetry (cont.)

The only change of significance was that associated with the use of a Dewar vessel of smaller neck diameter than that previously used. While this change produced the desired effect of lowering the heat transfer coefficient (between calorimeter and bath) it also necessitated the use of smaller diameter calorimeter stirrer and resistance thermometer housing and required a series of measurements to determine the optimum combination of propeller blade area, pitch and stirrer speed.

These exploratory tests were made in actual heat of solution measurements with the unirradiated sample, and the results are summarized in Table XI. The first four measurements, which were made with the stirrer as originally fabricated operated at a stirring speed of 672 rpm, indicated that the stirring was inadequate for the coarse sample particles used, as evidenced by the long equilibrium times and poor precision.

The last three measurements shown in Table XI were made after increasing the surface area and pitch of the stirrer blades and showed the desired effect of improved precision and more rapid equilibrium. The average of these three runs, +68.04 cal/g, with a precision uncertainty of  $\pm 0.14$  cal/g, was used as the basis for evaluating the apparent energy storage of the irradiated samples. Likewise, the improved stirrer was used in all subsequent measurements with the irradiated samples and operated at a speed of 845 rpm.

e. Results With Irradiated Samples

Heat of solution measurements were made with four of the six individual sealed glass bulbs containing Sample I. The mean value, as shown in Table XII is +55.02 cal/g with a precision uncertainty of  $\pm 0.65$  cal/g.

Table XI

HEAT OF SOLUTION OF UNIRRADIATED  $\text{NH}_4\text{ClO}_4$   
(Last Three Runs are with Improved Stirrer)

Sample Wt. grams	Temp. $^{\circ}\text{C}$	Heat of Solution cal/g	Equilibrium Time minutes	Stirrer Speed RPM
1.5731	29.70	+67.13	30	672
1.0103	30.17	+67.58	42	672
0.9976	30.17	+69.89	29	672
1.0088	30.16	<u>+68.23</u>	<u>24</u>	672
Average of 1st 4		+68.21	31	
1.5047	30.03	+68.17	24	672
1.5078	29.80	+67.97	14	845
1.5020	29.95	<u>+67.97</u>	<u>12</u>	845
Average of last 3		+68.04	17	

Table XII

HEATS OF SOLUTION OF IRRADIATION SAMPLES I AND IV

<u>Sample I</u>						
<u>Sample No.</u>	<u>Equil. Time minutes</u>	<u>Mass g, in Vac</u>	<u>Calibrations, Cal/μV</u>		<u>ΔT</u>	<u>ΔH</u>
			<u>Initial</u>	<u>Final</u>	<u>μV/g</u>	<u>cal/g</u>
1	4	0.2603	0.94675	0.94492	58.97	55.72
2	2	0.3780	0.94493	0.94355	57.59	54.34
3	2	0.4481	0.94608	0.94608	57.73	54.62
4	2	0.2803	0.94358	0.94278	58.76	55.40
Average		0.3417	0.94533	0.94433	58.26	55.02
Std Dev of Mean*		-	+0.00182	+0.00182	+ 0.35	+0.325
Precision uncertainty*		-	+0.00364	+0.00364	+ 0.70	+ 0.65
Precision uncertainty, %		-	+0.384	+0.384	+ 1.20	+ 1.18

<u>Sample IV</u>						
<u>Sample No.</u>	<u>Equil. Time minutes</u>	<u>Mass g, in Vac</u>	<u>Calibrations, Cal/μV</u>		<u>ΔT</u>	<u>ΔH</u>
			<u>Initial</u>	<u>Final</u>	<u>μV/g</u>	<u>cal/g</u>
1	4	0.3211	0.94502	0.94601	7.26	-6.87
2	2	0.2928	0.94512	0.94796	4.85	-4.60
3	2	0.2605	0.94327	0.94338	6.06	-5.72
4	4	0.2456	0.94391	0.94406	8.92	-8.42
Average		0.2800	0.94432	0.94535	6.77	-6.40
Std Dev of Mean*			+0.00045	+0.00104	+0.87	+0.82
Precision uncertainty*			+0.00090	+0.00208	+1.74	+1.64
Precision uncertainty, %			+0.10	+0.22	+25.7	+25.6

\*The precision uncertainty is defined as twice the standard deviation of the mean, or

$$2 \sqrt{\frac{\sum d^2}{n(n-1)}}$$

## VI, 1, Calorimetry (cont.)

This uncertainty interval, achieved with 4 samples, agrees with the upper limit of uncertainty range predicted in Figure 4 and in the Proposal (55) for replicate measurements with five or more samples. (The heat absorption corresponding to the average sample size of 0.34 g is 19 calories, which from the upper limit curve of Figure 4 corresponds to an uncertainty of  $\pm 0.22$  calories or  $\pm 0.65$  cal/g). Although the uncertainty interval could have been considerably reduced by measurements with the remaining two samples, these samples were reserved for special tests.

The results of the measurements with sample IV are also listed in Table XII. In this case only four of six bulbs filled were actually used for heat of solution measurements with the remaining two being reserved for analysis and a special test. The precision achieved in this case was somewhat poorer than that for sample I, probably because of non-uniform distribution of the coarse and fine particle portions of the sample. The expected uncertainty interval for a sample of this size, based on the previous data in Figure 4 is  $\pm 0.10$  calories or  $\pm 0.35$  cal/g.

Single measurements with samples II and III resulted in values of -34.70 cal/g for sample II and -23.83 cal/g for sample III.

### f. Apparent Energy Storage

Combination of the heat of solution measurements of the irradiated samples with the previously measured heat of solution of the unirradiated sample ( $+68.04 \pm 0.14$  cal/g) leads to the derived values of Apparent Energy Storage shown in Table XIII.

The precision uncertainty shown is the uncertainty in the measurement only, obtained from the root mean square of precision uncertainties of the unirradiated sample and the individual irradiated samples, as for example in the case of sample I,

$$\sqrt{(0.65)^2 + (0.14)^2} = \pm 0.67.$$

## VI, 1, Calorimetry (cont.)

Table XIII

## APPARENT ENERGY STORAGE OF IRRADIATED SAMPLES

Sample Number	I	II	III	IV
Irradiation Exposure hours	36.83	187.17	224	78
$n v t (X10^{17})$	1.0	5.1	6.1	2.1
Apparent Energy Storage, cal/g	13.02	102.74	91.87	77.44
Uncertainty Interval, cal/g	+0.67	-	-	+1.65
Rate of Apparent Energy Storage, Cal/g-hr	0.35	0.55	0.41	0.99

## g. Auxiliary Thermochemical Data

The  $\Delta C_p$  of the solution reaction was measured, as the difference in the average heat capacities of the calorimeter before and after breaking the sample bulb (as shown in Table XII), but the measured difference was not significant since it was less than the combined limits of error in the two sets of measurements. This was because of the extremely small sample sizes used and the correspondingly dilute solutions formed. Even if the apparent molar heat capacity of  $NH_4ClO_4$  were as large as  $-100$  cal/deg-mole, the average amount of sample I dissolved ( $0.34$  grams) would change the heat capacity of the calorimetric system by  $0.34 \times -100/117.5$  or  $-0.29$  cal/deg C, which when compared with the measured heat capacity of approximately  $1760$  cal/ $^{\circ}C$  ( $1865$   $\mu V$ /deg  $\times 0.94533$  cal/ $\mu V$ ) amounts to a change of less than  $0.02\%$ .

## VI, Phase II--Calorimetry and Analysis (cont.)

### 2. ANALYSIS

#### a. Introduction

The sole purpose of the analysis is that of determining the exact chemical composition of the recovered irradiated sample in order to apply appropriate corrections to the measured heat of solution for the effects of decomposition product impurities. It was believed at first that the best analysis of the irradiated sample might be obtained indirectly by separate analysis of the gaseous decomposition products and capsule corrosion products with the recovered sample analysis being computed by difference.

To implement this approach plans were made to make pressure-volume measurements and mass-spectrographic measurements of the collected gaseous decomposition products and standard wet-chemical analyses of the solid corrosion products leached from the irradiation capsule after removal of the sample. This approach was not successful because of failure of the gas-sampling device in two cases and because of the inability of the mass-spectrograph apparatus to produce constant values for the concentrations of gaseous chlorine compounds.

Later in the program an alternate method of gas analysis was developed based on fractionation of the gas sample by liquid nitrogen condensation followed by determination of the average molecular weight and special chemical analysis of the two fractions. Unfortunately this analysis method was applicable to only one of the four irradiated samples.

Because of the difficulties associated with the planned indirect chemical analysis and incomplete data available, the primary emphasis was shifted to that of direct analysis of the irradiated samples.

#### b. Sample Recoveries

The first crude analytical data was in the form of sample recovery data which is summarized in Table XIV. The various handling steps involved (gas sampling, opening capsule with pipe-cutter, scraping sample from container, working in a dry box, screening and separation of sample from aluminum filings and special precautions because of radioactivity) made it extremely difficult to obtain good quantitative data and as a result approximately one gram is unaccounted for in each of the first three samples.

As expected the total solids and total useable solids recovered were inversely proportional to the total radiation exposure (except for a slight reversal in samples II and III). The total extent of decomposition, however, was much worse than originally expected. Although the sample

VI, 2, Analysis (cont.)

of highest radiation exposure (sample III; nvt =  $6.1 \times 10^{17}$  neutrons/cm<sup>2</sup>) received only about 10% of the maximum radiation exposure initially planned, nevertheless only about 30% of the sample was recovered in useable form. On the basis of the data in Table XIV it is estimated that complete sample decomposition would have occurred at a total exposure of much less than  $10^{18}$  nvt (or 367 hours).

TABLE XIV

RECOVERY OF IRRADIATED SAMPLES

<u>Sample No.</u>	I	II	III	IV
Hours irradiated	36.83	187.17	224.0	78.0
Total nvt, neutrons/cm <sup>2</sup> ( $\times 10^{17}$ )	1.0	5.1	6.1	2.1
Original Sample Weight, grams	5.0	5.0	5.0	5.0
Useable sample recovered, grams	3.16	1.42	1.50	2.19
Sample removed by hot water leach, grams	0.6	1.16	0.84	2.35
Total Solids recovered, grams	3.76	2.58	2.34	4.54
Measured weight of gas recovered, grams	-	-	1.825	-
Estimated weight of gas*	0.30	1.52	-	0.64
Total Accounted For	4.06	4.10	4.16	5.18
Unaccounted For	0.94	0.90	0.84	-

\*Linear proportion with hours exposure based on Sample III.

c. Pressure-Volume (PV) Analysis

After the residual radioactivity of the sealed capsule had decayed sufficiently, the capsule was removed from the storage rack in the reactor pool and fitted with the gas sampling device consisting of a standard taper fitting, a threaded seal, a high pressure valve and a hand operated drill shaft sealed with a high pressure packing gland (Figure 9). After drilling through the puncture seal the capsule and gas sampling device were then attached to a vacuum glass manifold system of known volume equipped with a manometer and several calibrated flasks of different volumes. The gases from the capsule were then released through the high pressure valve and standard taper joint into the vacuum manifold system, allowed to reach thermal equilibrium with the room, and final pressure measured.

VI, 2, Analysis (cont.)

From the measured pressure and known volume of the system, the number of moles of gas was computed assuming application of the perfect gas law and also assuming the gases to be at room temperature. Pressure measurements were taken over a period of time to verify the assumption of thermal equilibrium with the room, since the computed adiabatic temperature changes associated with expansion into vacuum amounted to over 100°C in some cases. The results of the final PV measurements are given in Table XV.

Considerable difficulty was encountered in the use of the gas sampling device except for work with Sample III, when it worked perfectly. (1) With Sample I the packing gland on the drill shaft leaked slightly as evidenced by a distinct odor of halogen gases. It was suspected that air leaked into the vacuum system by the same means. (2) With Sample II the drill point broke off and became imbedded in the puncture seal. A slight bubbling was noted around the broken drill immediately after unsuccessfully attempting

TABLE XV

PV ANALYSIS RESULTS

<u>Sample Number</u>	I	II	III
Manometer Pressure, in.*	-	2.88	7.65**
Manometer Pressure, cm.*	44.05	-	-
System Volume, liters*	0.5210	3.068	3.732
PV, liter atm	0.3020	0.2955	0.9549
Millimoles, (PV/RT)x10 <sup>3</sup>	12.34	12.08	39.03
Capsule free volume, liters	0.050	0.050	0.049
Capsule pressure, atmospheres	6.04	6.01	19.48
Sample Decomposition Pressure***	3.26***	5.01	18.48

\*San Ramon measurements were made in inches of mercury; Sacramento measurements were made in centimeters of mercury; system volumes include corrections for movement of the mercury column.

\*\*Previously reported (in error) as 6.65.

\*\*\*Based on Capsule pressure minus one except for Sample I which utilized the Mass Spec Analysis to correct for He and air contamination (.539 x measured P).

VI, 2, Analysis (cont.)

to remove it in the remote handling facility. The capsule and sampling device were immediately attached to the vacuum manifold system and, after determining that the leak rate was quite small, left overnight to reach pressure equilibrium. A small amount of sample was lost, but the exact amount is impossible to estimate; some air contamination probably occurred also because of slight leaks in the glass joints of the manifold during the overnight exposure. (3) With Sample IV the drill point again broke off and the gas sample was lost.

d. Mass Spectrographic Analysis

The mass spectrometric analysis of the gaseous decomposition products of Sample I was inconclusive because of reaction of chlorine containing molecules with metal parts of the inlet system, and unexpectedly large air contamination of the sample. In order to minimize the effect of chlorine compound reactions in the inlet system, the system was passivated by repeated admissions of sample. In repeated scans the mass 36 (HCl) peak increased from zero to a maximum of 7.6 mole%. The results of the scan corresponding to this maximum value are given in Table XVI. The measured argon concentration of 0.4 mole% corresponds to an air contamination of 43%, based on an average air analysis of 0.93 mole% Ar, 78.09 mole% N<sub>2</sub> + 20.95 mole% O<sub>2</sub>. The mass 70 peak (Cl<sub>2</sub>) was not observed, which casts further suspicion on the results, since Cl<sub>2</sub> is believed to be one of the gaseous decomposition products.

TABLE XVI

MASS SPECTROMETRIC ANALYSIS OF IRRADIATION SAMPLE I\*

Molecule	Concentration, Mole %		
	Original	Air Free Basis	Air & He Free Basis
He	3.1	5.4	-
H <sub>2</sub> O	1.6	2.8	3.0
N <sub>2</sub>	42.0	14.7	15.6
O <sub>2</sub>	28.5	34.3	36.2
HCl	7.6	13.3	14.1
Ar	0.4	-	-
N <sub>2</sub> O	16.8	29.5	31.1
Total	100.0	100.0	100.0
Average MW	31.6	33.6	35.3

\*Based on the scan yielding the maximum value for HCl after passivating the gas inlet system by repeated admissions of sample.

## VI, 2, Analysis (cont.)

The mass spectrographic analysis can be reconciled with the gas pressure measurement if it is assumed that a portion of the air contamination occurred during capsule filling and the remainder occurred during the gas sampling operation. This assumption is probably valid since the method used to displace the capsule air with helium before irradiation involved flushing inside of a plastic bag (rather than positive vacuum displacement), and a leak in the drill shaft packing was noted during the gas sampling operation.

### e. Molecular Weight Determination

The average molecular weight of the decomposition product gases from Sample III was determined by accurate weighing (to 0.0001 g) of a 500 ml sample in an especially prepared flask. The flasks used were 500 ml round bottom flasks fitted with vacuum stopcocks and standard taper joints with the total mass kept below 200 grams for weighings on the analytical balance. The difference in weight between the filled and evacuated flask gave the vacuum mass of the gas sample directly since equal volumes of air (presumed to be at equal temperature and pressure) were displaced in both weighings. The average molecular weight was then computed from the perfect gas law relationship,

$$MW = WRT/PV.$$

Since some time had elapsed after taking of the sample, the sample PV measurement was repeated by expansion of the gas sample into the vacuum manifold after weighing of the flask. The molecular weight determination was then repeated by reweighing the flask (at the reduced pressure) followed by evacuation and final weighing. Two additional measurements were made with an enriched portion of Sample III gases obtained by condensing a portion of the higher boiling gases in a liquid nitrogen cold trap. The results are summarized in Table XVII, with the enriched samples designated as III-E. The barometric pressure was checked periodically and found to be in the 753 to 758 mm range.

Portions of the same samples were also quantitatively transferred to other flasks for subsequent chemical analysis.

The disagreement in the duplicate determinations with Sample III is probably due to insufficient care exercised in taking and recording of room temperature and pressure. A 1°C change in room temperature changes the air buoyancy effect on a 500 ml sample flask by 0.33% or 2.0 mg; similarly a 1 mm change in atmospheric pressure changes the buoyancy effect by 0.13% or 0.8 mg. This source of error is particularly critical in the cases of the two smaller sized samples weighing only about 50 mg. Therefore, the 43.1 value (of molecular weight) based on the 0.247 g sample is the preferred value for Sample III.

## VI, 2, Analysis (cont.)

TABLE XVII

## AVERAGE MOLECULAR WEIGHT OF SAMPLE III GASES

Sample No.	III	III	III-E	III-E
Pressure, cm PV, liter atm } San Ramon Meas.	19.44	-	55.35	-
	0.1292	-	0.3645	-
Pressure, cm Flask volume, ml } Sacramento Meas. PV, liter atm }	21.1	4.55	56.80	4.35
	505	502	500	502
	0.1403	0.0300	0.3736	0.0287
Flask + sample, grams	187.0336*	163.3235	188.9804	163.3258
Room Temperature, °C	-	25.7	-	25.0
Flask evacuated, grams	187.7864*	163.2734	188.3013	163.2734
Room Temperature, °C	-	25.0	25.0	25.0
Sample mass, grams	0.247*	0.0501	0.6791	0.0524
Derived sample mass, grams	-	0.0519**	-	-
Molecular Weight***	43.1	42.3**	44.5	44.6
Total mass of gas sample III, grams	1.825	-	-	-

\*Flask too long for analytical balance; weighings made on 10 Kg capacity balance and difference rounded to nearest milligram.

\*\*Based on original mass of 0.247 g and volume ratio used in manifold distribution. 0.0501 g sample weight yielded a molecular weight of 40.8.

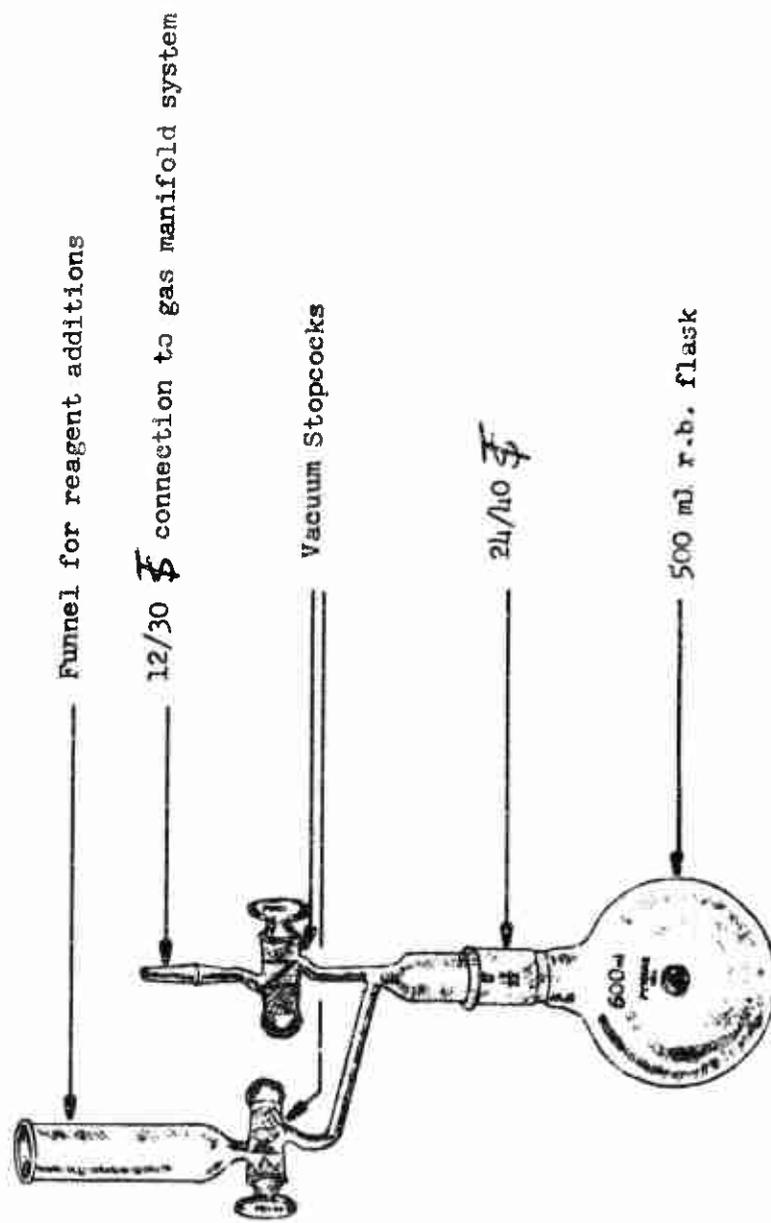
\*\*\*Based on Sacramento Determination of PV which takes into account possible air leak during transportation and storage.

## f. Chemical Analysis of Gases

During the course of the gas molecular weight determinations for Sample III, the gases were also quantitatively sub-divided into several reaction flasks in order to analyze for  $Cl_2$  and  $ClO_2$  and other possible oxidizing gases. The flasks used for this purpose are shown in Figure 11.

After obtaining the gas sample, the flask was removed from the manifold, an excess of a reducing agent solution was pipetted in through the funnel and carefully rinsed in while still retaining a partial vacuum in the flask. After allowing it to stand for some time, the flask was then

# GAS ANALYSIS FLASK



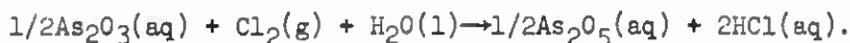
VI, 2, Analysis (cont.)

opened to the air and titrated with either a standard oxidizing or a standard reducing solution. The procedures used were modified versions of those described by RAI (50) and included the following combinations.

- 1) Neutral KI solution added in excess; back titrated with standard 0.1N  $\text{As}_2\text{O}_3$  solution to determine the amount of free iodine produced.
- 2) Acidic KI solution, back titrated with standard 0.1 N thiosulfate solution.
- 3) Standard 0.1 N  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution with unreacted  $\text{Fe}^{++}$  titrated with standard 0.1 N dichromate solution and Barium diphenylamine sulfonate indicator. This was a modification of the RAI method which utilized KCNS as an indicator for  $\text{Fe}^{+++}$  ion and a colorimetric comparison method for determination of concentration. This modification did not yield quantitative results and was dropped. The exact reason for failure is unknown, but the probable cause was oxidation of chloride ion by the dichromate.
- 4) Neutral 0.1 N  $\text{As}_2\text{O}_3$  solution, first re-neutralized with standard 0.1 N NaOH to determine acid content, followed by addition of excess  $\text{NaHCO}_3$  and titration of unoxidized  $\text{As}_2\text{O}_3$  with standard 0.1 N  $\text{I}_3^-$  solution.

The analytical approach was based upon the selectivity of the various reducing agents toward the various Cl and Cl-O compounds as well as other oxidizing species which might be present. According to the RAI report (50):  $\text{Fe}^{++}$  reduces  $\text{Cl}_2$  gas as well as the ions  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ , and  $\text{NO}_2^-$  in acid medium;  $\text{I}^-$  in basic medium reduces  $\text{Cl}_2$  gas and  $\text{ClO}^-$  to  $\text{Cl}^-$  and also partially reduces  $\text{ClO}_2$  gas (to  $\text{ClO}_2^-$ );  $\text{I}^-$  in acid medium reduces  $\text{Cl}_2$  and  $\text{ClO}_2$  gases as well as  $\text{ClO}^-$ ,  $\text{ClO}_2^-$  and  $\text{NO}_2^-$  ions. The use of neutral  $\text{As}_2\text{O}_3$  solution was based on the work of Smith and Hubbard (58) who used this reagent as a selective reducing agent for  $\text{Cl}_2$  gas formed in the oxygen bomb combustion of organic chlorides (this solution does not react appreciably with  $\text{O}_2$  gas even at pressures of over 30 atmospheres). The possible action of  $\text{N}_2\text{O}$  gas on the reagents used is not known but is assumed to be inert in all cases.

Examination of the data in Table XVIII, therefore, appears to indicate that the oxidizing portion of the gas mixtures studied is made up entirely of  $\text{Cl}_2$  gas, since the acid - KI titrations were slightly lower than both the neutral KI and neutral  $\text{As}_2\text{O}_3$  titrations. The HCl content of the gas mixture is obtained from the total acid titration minus the acid resulting from the reduction of  $\text{Cl}_2$  by  $\text{As}_2\text{O}_3$ .



## VI, 2, Analysis (cont.)

TABLE XVIII

## GAS ANALYSIS OF SAMPLE III

Sample	III (Original)		III-E (Enriched)		
	A	B	A	B	C
Flask					
Volume, ml	513	514	513	514	521
Sample mass, g	0.0531	0.0532	0.1450	0.1453	0.1472
Reducing Agent	KI	KI	KI	Fe <sup>++</sup>	As <sub>2</sub> O <sub>3</sub>
Solution Concentration, eq/liter or %	10%	10%	10%	0.1	0.10005
Volume, ml	25	25	50	50.00	50.00
Solution medium	Acid	Neutral	Acid	Acid	Neutral
Titrating Solution	Thio	As <sub>2</sub> O <sub>3</sub>	Thio	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	I <sub>3</sub> <sup>-</sup>
Concentration, eq./liter	0.010046	0.010005	0.10046	0.1	0.096608
Volume, ml	49.9	51.8	18.0	-	32.23
Volume of 0.1008 N NaOH	-	-	-	-	28.34
Meq of H <sup>+</sup> per gram	-	-	-	-	19.408
Meq of Oxidants	0.5013	0.5183	1.808	-	1.911
Meq/g	9.44	9.74	12.47	-	12.98

## g. Chemical Analysis of Recovered Samples

## 1) Introduction

The analyses presented in this section were disappointing and must be viewed with considerable skepticism and considered accurate only insofar as general trends are concerned. Although the analytical schemes worked out are believed to be reliable the results are open to question on a number of points chiefly associated with the limited amounts of sample available, namely: (1) The samples available for analysis were very small,

## VI, 2, Analysis (cont.)

particularly after subdividing into aliquots, and single determinations were made in all cases (2) Sample III is probably not truly representative of the entire irradiated sample since it was of very poor quality and was, therefore, screened through a 0.5 mm screen before use. Less than 1/2 of the sample (the fines) were used for the heat of solution and analytical work. (3) Both samples II and III were noticeably wet when received and were dried in a desiccator before weighing; both were noted to be extremely hygroscopic, absorbing moisture from the air during sample weighings. The degrees of dryness of the samples used for heats of solution and analyses may not have been identical (4) an unused heat of solution sample bulb containing sample IV was saved for the analytical work but it was accidentally broken on the floor of the dry box and swept up with a brush before weighing (5) gases were evolved (and lost) during sample dissolutions (6) the samples used for the  $\text{Cl}^-$  analysis were obtained by boiling down the final solutions from the heat of solution measurements. This process may have resulted in some loss of chloride ion by reaction with  $\text{ClO}^-$  (or other oxidizing anion) to form  $\text{Cl}_2$  gas.

### 2) Procedure

In order to follow the extent of sample contamination as a function of total radiation exposure the following analyses were performed on solutions of irradiation samples II, III, and IV:

- (1) Water insoluble
- (2)  $\text{H}^+$  concentration by titration
- (3)  $\text{Cl}^-$  concentration by  $\text{AgCl}$  gravimetric analysis
- (4) Oxidants reducible by neutral KI
- (5) Oxidants reducible by acidic KI
- (6) Oxidants reducible by acidic  $\text{Fe}^{++}$
- (7) Oxidants (remaining after flash boiling) reducible by acidic KI.

Water insoluble determinations were made with cold water to simulate calorimeter conditions. The chloride determinations were made on samples which had previously been used in heat of solution measurements; these solutions were concentrated by boiling down from the original volumes of 1625 ml to volumes of about 250 to 500 ml before precipitating the silver chloride.

The procedure for titration of oxidants reducible by neutral KI, acidic KI and neutral  $\text{As}_2\text{O}_3$  solutions was essentially the same as that used in the analysis of the gaseous decomposition products (Paragraph VI-2-f.), except that 0.01N reagents were used in all cases.

The procedure with acidic  $\text{Fe}^{++}$  reducing agent was modified to resemble more closely that originally used by RAI (50, 54). To 50 ml

VI, 2, Analysis (cont.)

aliquots of the three solutions were added 50 ml each of 0.1 N KCNS, 1:1 H<sub>2</sub>SO<sub>4</sub> and 0.1N Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solutions in rubber stoppered 250 ml flasks. A blank containing 50 ml of a 0.1% solution of reagent NH<sub>4</sub>ClO<sub>4</sub> was similarly prepared. All four solutions had a distinct pink color (due to Fe<sup>+++</sup> impurity in the Fe<sup>++</sup> reagent in the case of the blank) with sample IV being barely distinguishable from the blank and sample II being the darkest. 0.01 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution was then added dropwise to the blank sample until each of the unknowns were color matched by visual comparison and the corresponding volumes recorded.

One additional analysis was performed, which involved a repetition of the acidic KI analysis, after having first boiled and cooled the unknown solution.

3) Results

The results of these analyses are given in Table XIX.

Interpretation of the analyses is the same as that given in the RAI Report, with one exception, caused by an apparent discrepancy in that interpretation method. The RAI interpretations may be expressed algebraically as follows (with equation numbers corresponding to the data given in Table XIX):

(1) Neutral KI reduces ClO<sup>-</sup> and Cl<sub>2</sub> to Cl<sup>-</sup> and reduces ClO<sub>2</sub> to ClO<sub>2</sub><sup>-</sup>.

$$\text{meq}_1 = \Sigma \text{meq. (ClO}^- + \text{Cl}_2 + 1/5 \text{ClO}_2)$$

(2) Acidic KI (unboiled) reduces ClO<sub>2</sub>, ClO<sup>-</sup>, Cl<sub>2</sub>, and ClO<sub>2</sub><sup>-</sup> to Cl<sup>-</sup>; also reduces NO<sub>2</sub><sup>-</sup>.

$$\text{meq}_2 = \Sigma \text{meq (ClO}_2 + \text{ClO}^- + \text{Cl}_2 + \text{ClO}_2^- + \text{NO}_2^-)$$

(3) Boiling removes the gases Cl<sub>2</sub> and ClO<sub>2</sub> and also ClO<sup>-</sup> (since the samples are acidic); therefore, acidic KI with a boiled solution reduces ClO<sub>2</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>.

$$\text{meq}_3 = \Sigma \text{meq (ClO}_2^- + \text{NO}_2^-)$$

(4) Fe<sup>++</sup> in acid medium reduces Cl<sub>2</sub>, ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup> to Cl<sup>-</sup>; also reduces NO<sub>2</sub><sup>-</sup>.

$$\text{meq}_4 = \Sigma \text{meq (Cl}_2 + \text{ClO}^- + \text{ClO}_2^- + \text{ClO}_3^- + \text{NO}_2^-).$$

VI, 2, Analysis (cont.)

Combining of Equations (1), (2) and (3) leads to a solution for  $\text{ClO}_2$ ,

$$\text{meq}_2 - \text{meq}_1 - \text{meq}_3 = 4/5 \text{ClO}_2 \text{ or } \text{ClO}_2 = 5/4 (\text{meq}_2 - \text{meq}_1 - \text{meq}_3)$$

However, applying this derived value of  $\text{ClO}_2$  to equation (1) leads to an inconsistency since it follows that,

$$\text{meq}_1 > 1/5 \text{ClO}_2,$$

whereas in every case  $\text{meq}_1$  is considerably less than 1/5 of  $\text{ClO}_2$ .

It must be assumed then that neutral KI does not react with  $\text{ClO}_2$ , in which case equation (1) becomes,

$$\text{meq}_1 = \Sigma \text{meq}(\text{ClO}^- + \text{Cl}_2)$$

From this it follows that,

$$\text{ClO}_2 = \text{meq}_2 - \text{meq}_1 - \text{meq}_3,$$

$$\text{ClO}_3^- = \text{meq}_4 - \text{meq}_1 - \text{meq}_3,$$

$$\text{ClO}^- + \text{NO}_2^- = \text{meq}_3,$$

$$\text{and } \text{ClO}^- + \text{Cl}_2 = \text{meq}_1.$$

Finally, since  $\text{meq}_1$  and  $\text{meq}_3$  are relatively small in all cases (compared with  $\text{Cl}^-$  and  $\text{H}^+$ ) it is assumed that

$$\text{ClO}_2^- = \text{NO}_2^- = \text{meq}_3 \div 2$$

$$\text{and } \text{ClO}^- = \text{Cl}_2 = \text{meq}_1 \div 2$$

Table XX shows the corresponding ionic and molecular compositions based on the derivations outlined above. Two further assumptions were involved in the final computed compositions; i.e. that  $\text{ClO}_2$  is present in the crystalline network as an equivalent mixture of  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  ions and that  $\text{Cl}_2$  is similarly present as a mixture of  $\text{ClO}^-$  and  $\text{Cl}^-$  ions.

A complete analysis is not available for sample I but the major impurities of  $\text{H}^+$  and  $\text{Cl}^-$  were analyzed for and based on these analyses the equivalent composition is: 3.57%  $\text{NH}_4\text{Cl}$ ; 9.24%  $\text{HClO}_4$  and 87.19%  $\text{NH}_4\text{ClO}_4$ .

## VI, 2, Analysis (cont.)

TABLE XIX

## ANALYSIS OF IRRADIATED SAMPLES II, III AND IV

Sample	II	III	IV
Weight, grams	0.9593	0.4647	0.3044
Insoluble, grams	0.0116	0.0103	0.0006
Insoluble, %	1.21%	2.22%	0.20%
Sample wt (1/5 aliquot), grams	0.1919	0.0929	0.0609
1. ML of 0.01005 N $\text{As}_2\text{O}_3$ , less blank (Neutral KI)	0.10	0.05	0.05
meq./g sample	0.005	0.005	0.008
2. ML of 0.010046 N Thio, less blank (acid KI- unboiled)	6.05	1.15	0.15
meq/g sample	0.317	0.124	0.025
3. ML of 0.010046 N Thio, less blank (acid KI-boiled)	0.9	0.15	0.10
meq/g	0.047	0.016	0.016
4. ML of 0.01001 N $\text{K}_2\text{Cr}_2\text{O}_7$ ,	4.1	0.25	0.1
meq/g	0.214	0.027	0.016
5. ML of 0.1008 N NaOH, less blank ( $\text{H}^+$ titration)	7.15	0.77	1.28
meq/g	3.94	0.84	2.10
Soluble Aluminum $\text{Al}_2\text{O}_3$ , g	-	-	0
Chloride Sample Weights, g	-	0.1872	0.3098
AgCl precipitate, g	-	0.1554	0.1841
Cl wt, g	-	0.03844	0.04554
Wt% Cl	-	20.54	14.70
meq/g	(6.392)*	5.793	4.146

\*Previous determination

## VI, 2, Analysis (cont.)

TABLE XX

## DERIVED COMPOSITIONS OF SAMPLES II, III AND IV

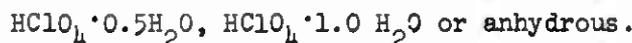
Molecule or Ion	Concentration meq/g			Concentration mmol/g		
	II	III	IV	II	III	IV
$\text{ClO}_2$	.265	.103	.001	.053	.0206	.0002
$\text{ClO}_3^-$	.162	.006	(-.008)	.027	.001	(-.001)
$\text{ClO}_2^-$	.024	.008	.008	.006	.002	.002
$\text{NO}_2^-$	.023	.008	.008	.008	.003	.003
$\text{ClO}^-$	.002	.002	.004	.001	.001	.002
$\text{Cl}_2$	.003	.003	.004	.0015	.0015	.002
$\text{Cl}^-$	6.392	5.793	4.146	6.392	5.793	4.146
$\text{H}^+$	3.94	0.84	2.10	3.94	0.84	2.10

Molecular Composition	Millimoles/g			Weight Percent		
	II	III	IV	II	III	IV
$\text{NH}_4\text{ClO}_3$	.054	.0104	0	0.548	0.106	0
$\text{NH}_4\text{ClO}_2$	.032	.0105	.002	0.274	0.090	0.017
$\text{NH}_4\text{NO}_2$	.008	.003	.003	0.051	0.019	0.019
$\text{NH}_4\text{ClO}$	.002	.002	.003	0.014	0.014	0.028
$\text{NH}_4\text{Cl}$	6.393	5.794	4.146	34.200	30.996	11.179
$\text{HClO}_4$	3.94	0.84	2.10	39.581	8.438	21.096
$\text{NH}_4\text{ClO}_4$	2.156	5.135	4.823	25.332	60.337	56.661

VI, 2, Analysis (cont.)

h. Estimated Heats of Solution

Estimated heats of solution of the four samples based on the derived analysis are listed in Table XXI. Three heats of solution are estimated for each sample based on the assumption that the hydrogen ion found is present as  $\text{HClO}_4$  in one of 3 states of hydration:



Heats of solution of the compounds  $\text{NH}_4\text{ClO}_4$ ,  $\text{NH}_4\text{ClO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_2$ ,  $\text{HClO}_4$ ,  $\text{HClO}_4 \cdot 0.5 \text{H}_2\text{O}$  and  $\text{HClO}_4 \cdot 1.0 \text{H}_2\text{O}$  were obtained from data in References (38) and (39). Heats of solution of  $\text{NH}_4\text{ClO}$  and  $\text{NH}_4\text{ClO}_2$  were estimated as the average of the heats of solution of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{ClO}_3$ . The final estimated heats of solution were based on consideration of the samples as mixtures of the individual components with no consideration of solid solution or other interaction effects.

TABLE XXI

ESTIMATED HEATS OF SOLUTION BASED ON CHEMICAL ANALYSIS  
AND ASSUMED HYDRATION STATE OF  $\text{HClO}_4$  IMPURITY

Sample	Heats of Solution, cal/g			
	I	II	III	IV
Assumed Hydration State of $\text{HClO}_4 \cdot n\text{H}_2\text{O}$				
n = 0	+42.2	-43.0	+44.0	+ 8.7
n = 0.5	+49.0	-13.7	+50.1	+24.3
n = 1.0	+53.4	+ 4.8	+54.1	+34.2

i. DTA and Drop Tests

Differential thermal analysis (DTA) and Bureau of Mines Impact tests (drop test) were run on the unirradiated sample and on Irradiated Sample I only. The results of the DTA tests are shown in Figure 12.

1) Unirradiated Sample

The unirradiated sample showed normal behavior for AP of this purity and particle size in both tests. The DTA (run at a heating rate of  $5^\circ\text{C}/\text{minute}$  with a 20 mg sample) showed the normal endotherm at  $241^\circ\text{C}$ , an exotherm peak at  $378^\circ\text{C}$  and a sharp exotherm (to complete decomposition at  $481^\circ\text{C}$ ).

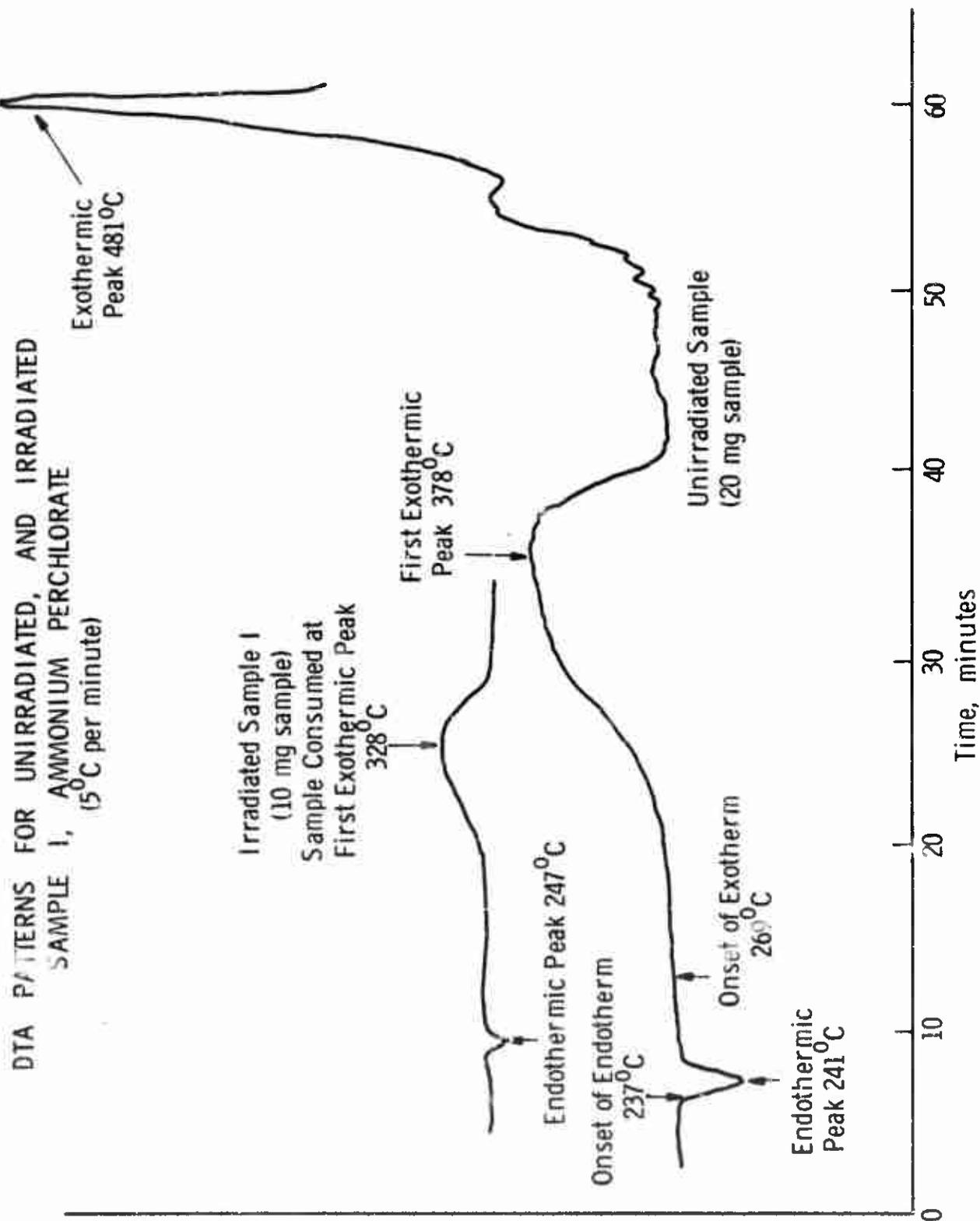


Figure 12

## VI, 2, Analysis (cont.)

The 2 kg drop weight test using the bare anvil was negative at the maximum drop height of 100cm. Addition of #180 grit increased the sensitivity to the measurable range, indicating a 50% point of 72 cm.

### 2) Irradiated Sample I

The DTA for this sample (run at a heating rate of 5°C/minute with an approximately 10 mg sample) showed a small but broad endothermic peak centered at about 143°C (not shown in Figure 12) followed by the normal endothermic peak at 247°C, an exothermic peak at 328°C and no further activity to the maximum temperature of 482°C. The sample was apparently completely consumed at the 328° exotherm. This pattern is similar to that found for porous ammonium perchlorate prepared by thermal decomposition (59).

The 2 kg drop weight test was just in the measurable range for the bare anvil test with a 50% point of 94 cm.

### j. X-ray Tests

Individual large crystals had been selected, mounted and aligned by means of the optical goniometer in preparation for the X-ray studies. Unfortunately the planned studies using these crystals had to be dropped because the crystals were decrepitated during the irradiation.

### k. Microscopic Evaluation of Crystallographic Changes

#### 1) Initial Crystals

Some of the ammonium perchlorate (AP) crystals used were slowly grown from a purified aqueous solution, others were reagent grade. The crystals were either simple aggregates or monocrystalline units 1/2 to 1 mm in size. They were in the orthorhombic system with a rounded to prismatic habit, and contained very few growth pores. No defects were visible and, based on previous experience, the defect concentration was between  $10^8$  and  $10^{12}$  per cc. The refractive indices were within the literature limits and the crystals were perfectly clear and colorless.

#### 2) Radiated Crystals

The crystal structure has been severely damaged by the radiation and individual crystals have crumbled to 20 to 50 micron fragments. The damage is typical of prolonged gamma radiation or heating near the phase transition temperature. As a consequence, anticipated effects such as twinning caused by internal mechanical strains, or the decoration of dislocations by migrating vacancies and other point defects has been obliterated.

## VI, 2, Analysis (cont.)

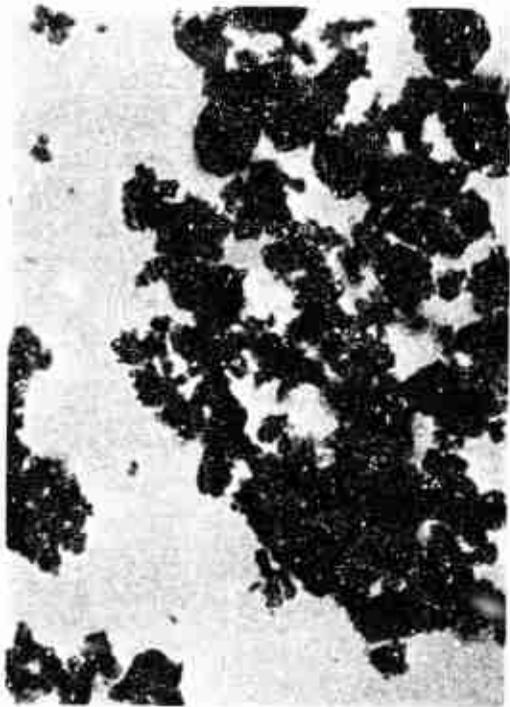
The radiation effect in the sample exposed to the lowest radiation dosage are shown in the photomicrographs, Figure 13 a, b, c, and d. The crumbled fragments of the initial large crystals shown in Figure 13a were mounted in a refractive index media near one of the crystal's principal indices and photographed in plane polarized transmitted light. If any AP particles similar to the initial material had been included in this mounting, they would be invisible, thus the most striking effect of the crystal damage is the opacity induced by the radiation. This opacity is caused by the presence of densely packed pores in the 0.1 to 1.0 micron size range, which act as spherical mirrors blocking transmission of the light. A single rhombohedral fragment a few microns thick is shown in Figure 13b. Several large pores are cleaved open and appear as white circles, the remaining dark part of the crystal contains still smaller sealed pores where some light has been forced through by use of convergent light from the substage-swingout condenser. Some of the crystal fragments have a grid pattern shown by the pores in Figure 13c. This could be the result if some repeated stress-twin structures (thermal twins intersect at  $90^\circ$ ) were selectively eroded by the radiation. The same field of view is again shown in Figure 13d, in doubly polarized light. A dull diffuse gray birefringence is seen at all crystal orientations relative to the planes of polarization. Normal AP crystals of this size would have four orientations of complete extinction and four portions of a clear first order gray-white. Therefore, the remaining percent of the crystal lattice consists of a jumble of randomly oriented mosaic blocks.

### 3) Interpretation

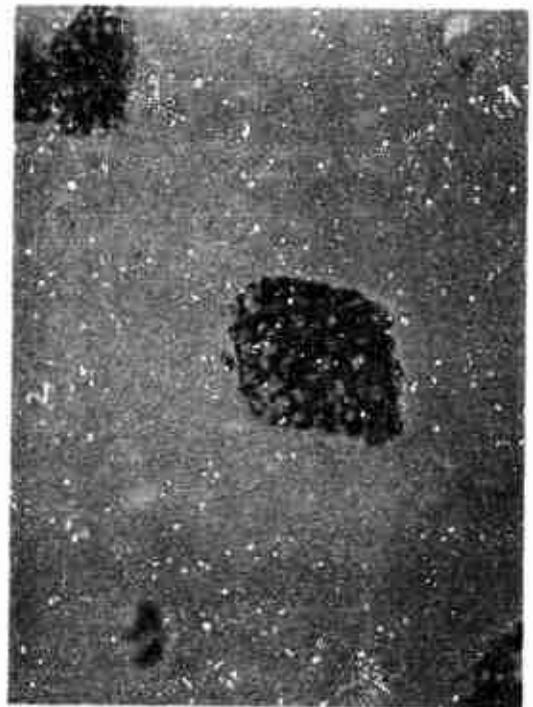
The pores are caused by lattice vacancies, that is missing ions, usually of the same charge. If the vacancy concentration increases, the vacancies migrate to form a spherical aggregate. Further damage causes the unstable matrix of like charged wall ions within the aggregate to collapse leaving a single pore. The concentration of vacancies can increase to a theoretical point of maximum mechanical packing. This disrupts the continuity of the lattice to a condition as it appears in Figure 13d. Any further damage reduces the lattice to a size below the minimum thermodynamically stable mosaic block and the ions recombine into more stable compounds such as chloride or chlorites.

In the crystals exposed to higher radiation (Samples II, III, and IV) some damaged fragments were found with a clear crystalline surface. This observation suggests that the fragments were wet, presumably by some of the decomposition products, and the clear crystalline material is apparently a solution recrystallization product.

CRYSTALLOGRAPHIC CHANGES IN AP CAUSED  
BY NEUTRON RADIATION  
(Sample I; 36.83 hours exposure)



-pol (a) 125X



-pol (b) 500X



-pol (c) 320X



+pol (d) 320X

## VI, Phase II--Calorimetry and Analysis (cont.)

### 3. SPECIAL TESTS

Two special tests were conducted with unused heat of solution sample bulbs of Samples I and IV. Both tests were designed specifically to differentiate between real lattice deformation energy and apparent lattice deformation energy due to chemical impurities.

The first test involved high vacuum de-gassing of Sample I in an attempt to remove the acidic impurity which is the major source of chemical energy contributing to the overall apparent lattice energy. The second test involved recrystallization of a portion of Sample IV in an attempt to completely obliterate all lattice deformation energy (without change in chemical composition) leaving only that portion of the overall apparent lattice energy due to chemical energy alone.

Neither test achieved its desired objective, but both contributed useful data which aided in the understanding of the true nature of the apparent lattice energy.

#### a. Vacuum De-gassing of Sample I

Two unused heat of solution bulbs containing Sample I were re-opened and de-gassed under high vacuum conditions in an attempt to remove the acidic impurity. The sealed bulbs were re-opened and re-weighed with no loss of sample, then de-gassed at room temperature under vacuum conditions which ranged from  $2 \times 10^{-4}$  mm at the beginning to  $8 \times 10^{-6}$  mm at the end of a 3.5 hour period. Condensable gases removed were collected in a liquid nitrogen cold trap and titrated with 0.1008 N NaOH. The data obtained are recorded in Table XXII.

The total acid content of this sample as determined in a previous titration was 0.92 meq/g or 0.708 meq for the combined sample weight of 0.7699 g. The expected weight loss for the sample is 2.58% if the acid is present as HCl or 7.11% if present as  $\text{HClO}_4$ .

Since the actual weight loss was less than 0.8% and only 2% of the total acid was removed, the acid could not have been present as HCl but rather  $\text{HClO}_4$ ,  $\text{Cl}_2\text{O}_7$  or some other nonvolatile form. Since even  $\text{HClO}_4$  or  $\text{Cl}_2\text{O}_7$  might be expected to have distilled over in the vacuum conditions imposed, the acid must have been present as a stable solid solution with AP, or as an acid anhydride impurity substituted in the  $\text{NH}_4\text{ClO}_4$  lattice.

VI, 3, Special Tests (cont.)

TABLE XXII

VACUUM DE-GASSING OF SAMPLE I

Bulb No.	5	6
Sample wt (in vac.)	0.3807	0.3892
Bulb and sample (before)	0.9550	0.9754
Bulb and sample (after)	0.9520	0.9725
Wt loss, g	0.0030	0.0029
Wt loss, %	0.79%	0.74%
Cold trap titration, combined		
mi		0.14
meq		0.014
Combined wt, g		0.0059
Meq/g		2.37
g/eq		421
Total acid content (initial), meq.		0.708
Percent removed in de-gassing		1.98%

b. Re-Crystallization of Sample IV

A portion of Sample IV from one unused heat of solution bulb was transferred to a small beaker, allowed to equilibrate with about 5 ml of distilled water, re-dried over a week-end in a vacuum desiccator, and re-weighed.

The original plan was to re-load the re-crystallized sample in a bulb for a heat of solution measurement. The difference in heat of solution, before and after re-crystallization, would then be a direct measure of the amount of lattice energy stored, provided that the overall chemical composition had not changed. However, a very definite fizzing was noted when water was added to the sample and a distinct odor of halogen gas was observed.

VI, 3, Special Tests (cont.)

Obviously the chemical composition of the re-crystallized sample had changed and the heat of solution of the re-crystallized sample was not measured. The exact weight loss attributable to the gas evolution could not be determined with any certainty because of the extremely hygroscopic nature of the sample, both before and after re-crystallization. The changes in sample weight recorded in this experiment are given in Table XXIII.

TABLE XXIII

RE-CRYSTALLIZATION OF SAMPLE IV

Original Sample Weight, g	0.3532
Weight after 20 days in desiccator (unsealed), g	0.3508
Weight after transfer to beaker, g	0.3523
Weight after re-crystallization and vacuum drying, g	0.3375
Weight after 12.5 minutes exposure to room air, g	0.3407
Weight after 28.5 minutes exposure to room air, g	0.3415

## SECTION VII

### DISCUSSION OF RESULTS

#### 1. ANALYSIS

Although the individual analyses were not of sufficient accuracy to permit the evaluation of precise correction terms for impurities, nevertheless the general trends in the analyses with respect to total irradiation dosage are quite apparent. Table XXIV summarizes the pertinent data with respect to irradiation dosage, analyses and calorimetric results.

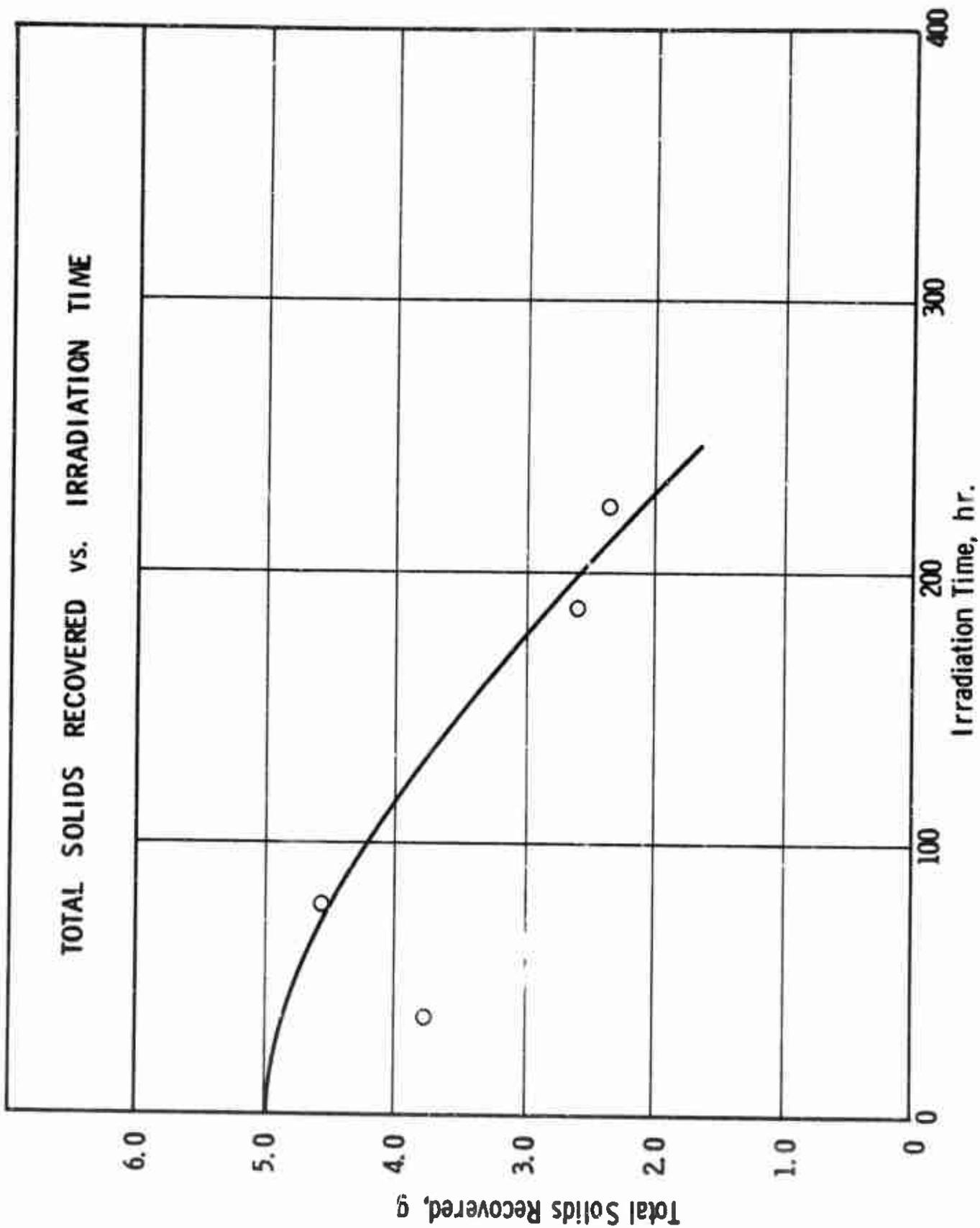
Table XXIV

#### SUMMARY OF DATA FOR IRRADIATED SAMPLES

Sample No.	I	II	III	IV
Hours Irradiated	36.8	187.2	224.0	78.0
Total Solid Sample Recovered, grams	3.76	2.58	2.34	4.54
Heat of Solution, cal/g	+55.02	-34.70	-23.83	-6.40
Apparent Energy Storage, cal/g	+13.02	+102.74	+91.87	+77.44
Analyses: H <sup>+</sup> , Meq/g	0.920	3.94	0.84	2.10
Cl <sup>-</sup> , Meq/g	0.668	6.392	5.793	4.146
Total Oxidants, Meq/g	-	0.317	0.124	0.025

Figure 14 shows the total solid sample (useable solids plus leached solids) as a function of irradiation time and indicates that the entire sample would probably have been decomposed at a total exposure of about 320 hours.

Figure 15 shows the variation of Apparent Energy Storage with irradiation time and indicates a peak value of Apparent Energy Storage at an exposure of approximately 160 hours. Plotting of sample impurity contents as a function of time, as in Figure 16, indicates that the concentrations of the principal impurities also reach peak values at the same point in time.



APPARENT ENERGY STORAGE VS. IRRADIATION TIME

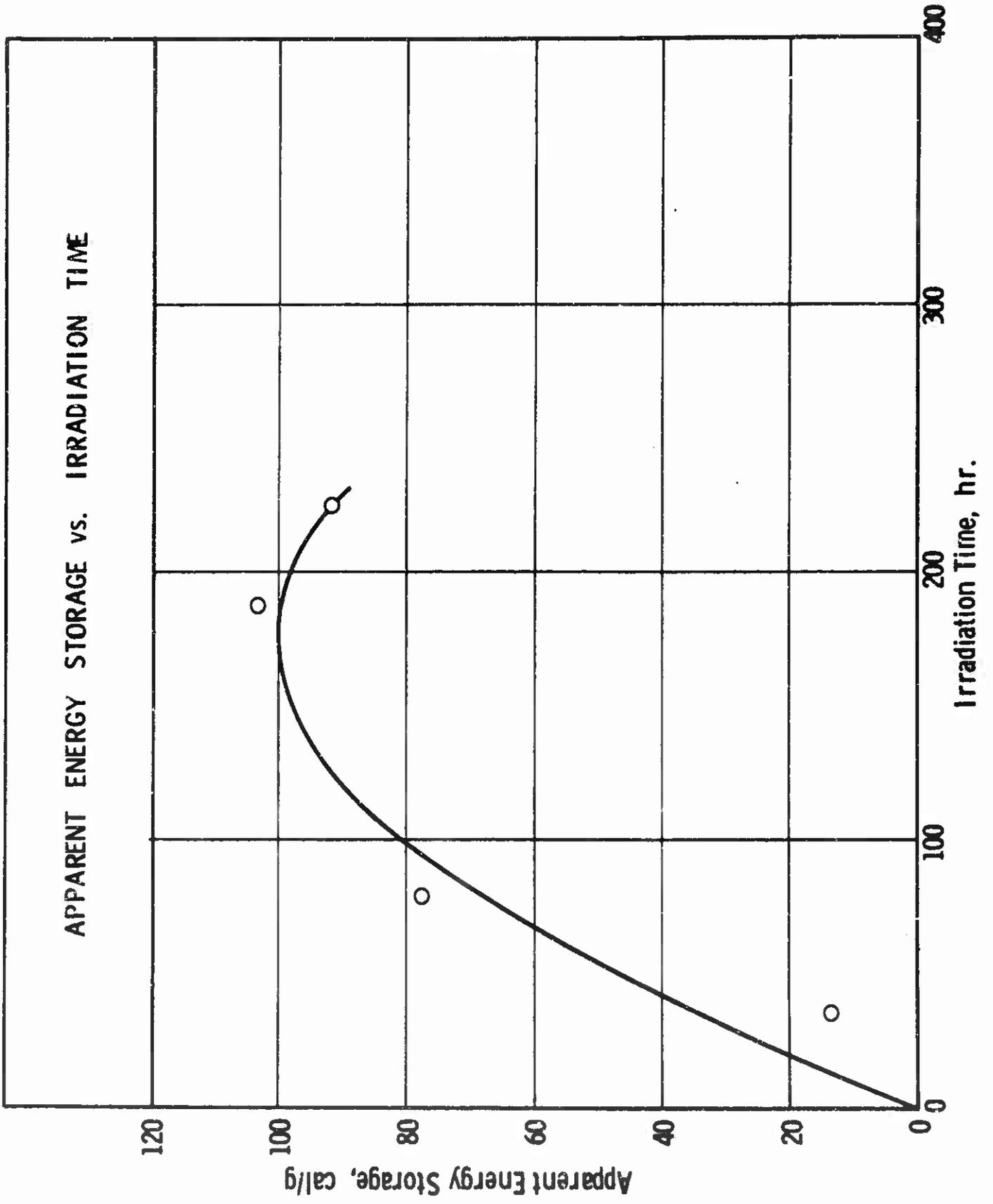


Figure 15

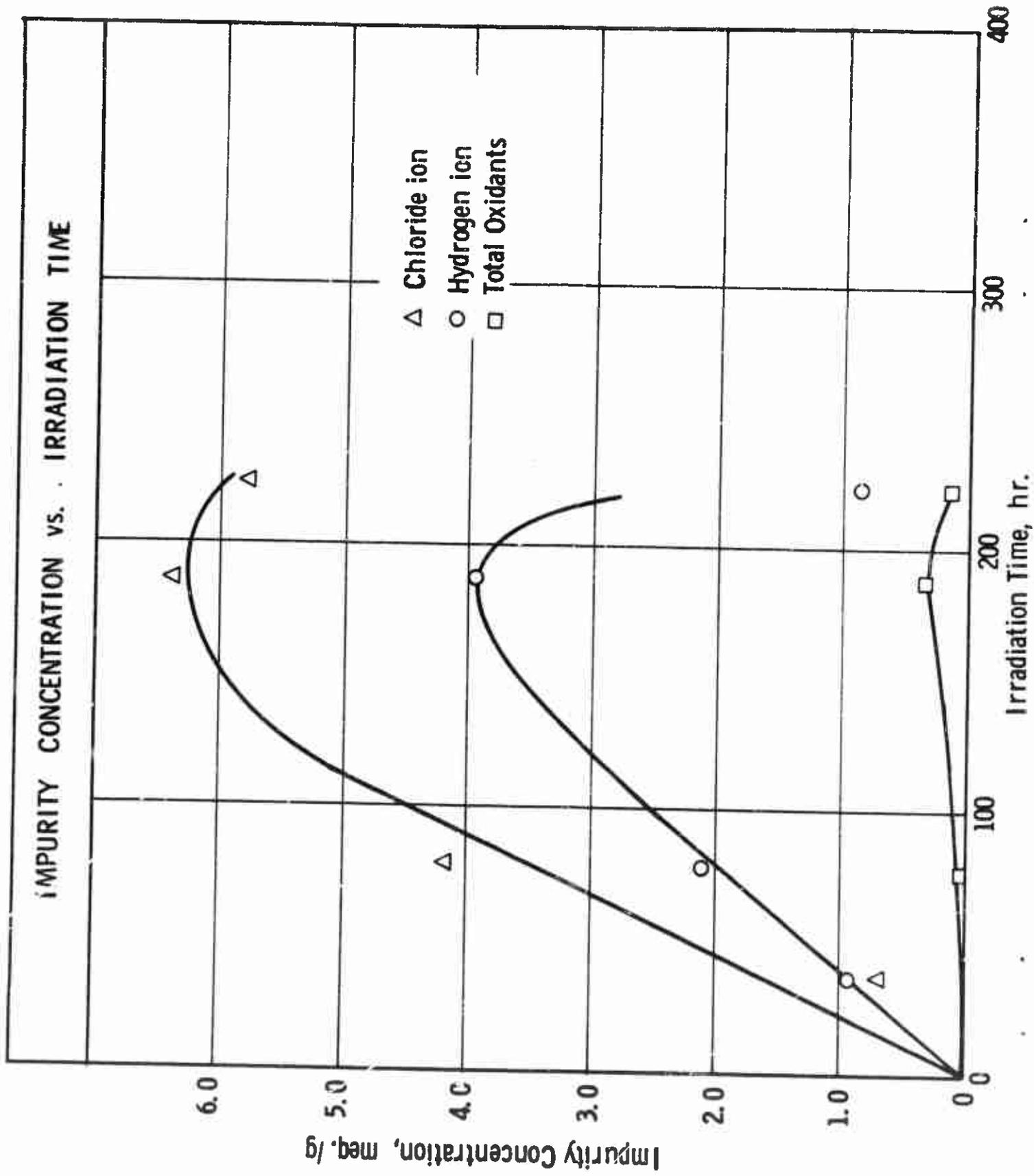


Figure 16

## VII, 1, Analysis (cont.)

### a. Effect of Hydrogen Ion

In Table II of Section III, it was noted that the heats of solution of all possible ammonium and hydrazinium salt impurities were endothermic and fairly close in magnitude to that of  $\text{NH}_4\text{ClO}_4$ . (Initially the formation of acidic residues was not anticipated, and, therefore, data for acidic compounds was not included). Later when the estimations of heats of solution based on sample analyses were made (Table XXI) it was noted that the heat of solution of free perchloric acid, similar to that of other mineral acids, was highly exothermic ( $-209$  cal/g for anhydrous  $\text{HClO}_4$  and  $-66.5$  cal/g for the monohydrate of perchloric acid).

On the basis of these considerations the measured heat of solution was plotted as a function of hydrogen ion analysis in Figure 17. The measured heats of solution are plotted as open circles and the estimated heats of solution from Table XIII (based on  $n = 0$ ) are plotted as triangles. The straight line is drawn as the best fit through the estimated data and is seen to be a reasonably good fit for the measured data as well - except for the anomalous behavior of sample III.

### b. Correlation with Chloride Ion

In Figure 18, the measured heats of solution are plotted as a function of chloride ion concentration. The correlation is remarkably good, but possibly fortuitous, as no theoretical explanation is readily apparent.

## 2. SAMPLE ANNEALING

The theoretical heat transfer analysis which was included as part of the original safety analysis (Appendix A) indicated a probable maximum sample temperature of  $70^\circ\text{C}$  or  $157^\circ\text{F}$  based on a maximum pool temperature of  $110^\circ\text{F}$  and a  $\Delta T$  of  $47^\circ\text{F}$ . A later, more conservative analysis (Figure 10) indicated a possible maximum sample temperature of  $108^\circ\text{C}$  or  $226^\circ\text{F}$  based on an assumed  $\Delta T$  of  $126^\circ\text{F}$ .

All reasonable precautions had already been taken to keep the sample temperature as close to pool temperature as possible, including placing the AP sample in direct contact with the pressure vessel and filling both the pressure vessel and the secondary container with helium gas. Because of the uncertainty of the heat transfer calculations and the importance of keeping the sample cool during irradiation, a separate experiment (with ammonium sulfate in place of AP) was run to determine the actual sample temperature and more particularly the temperature difference between the sample center and pressure vessel.

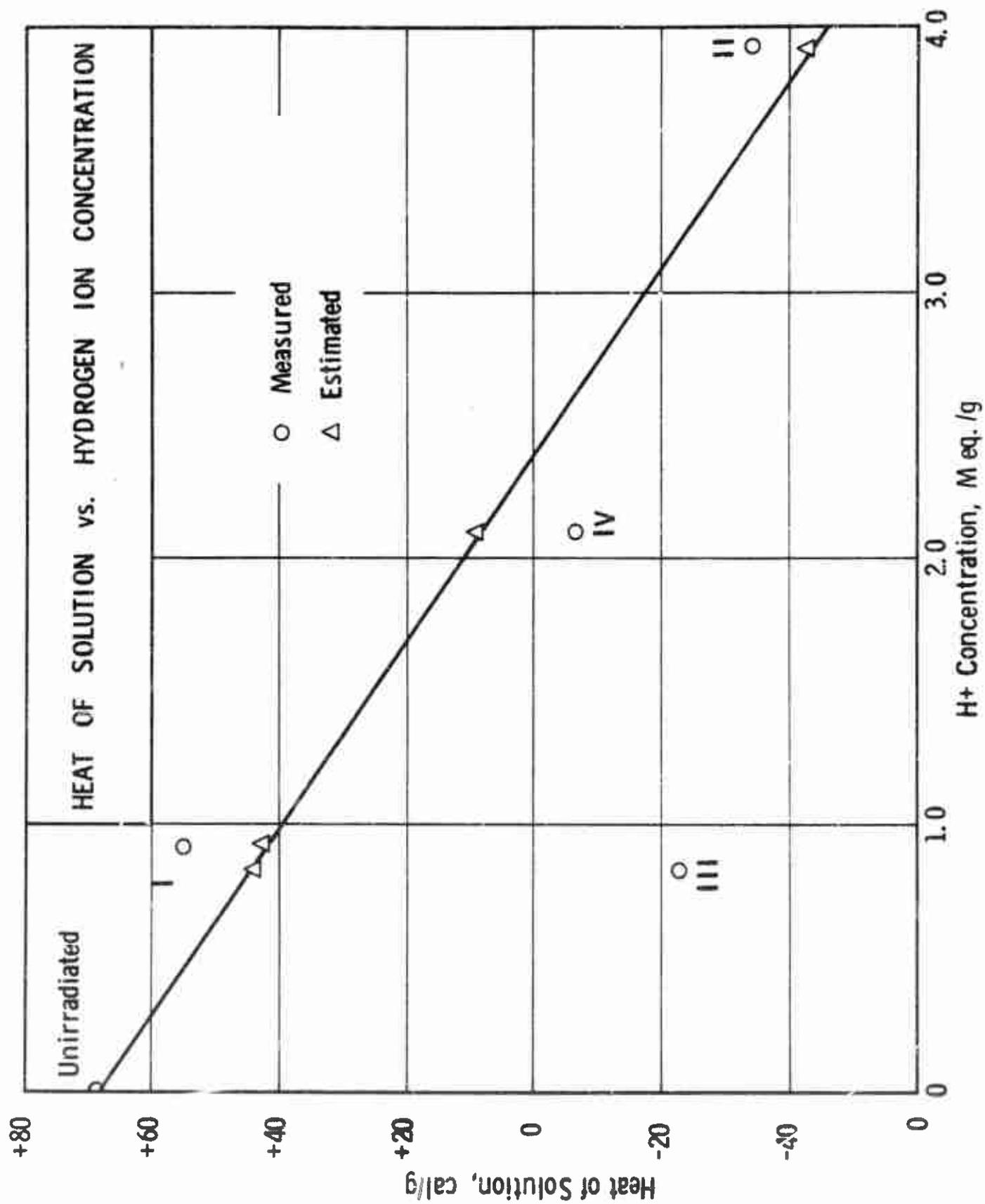


Figure 17

HEAT OF SOLUTION VS. CHLORIDE ION CONCENTRATION

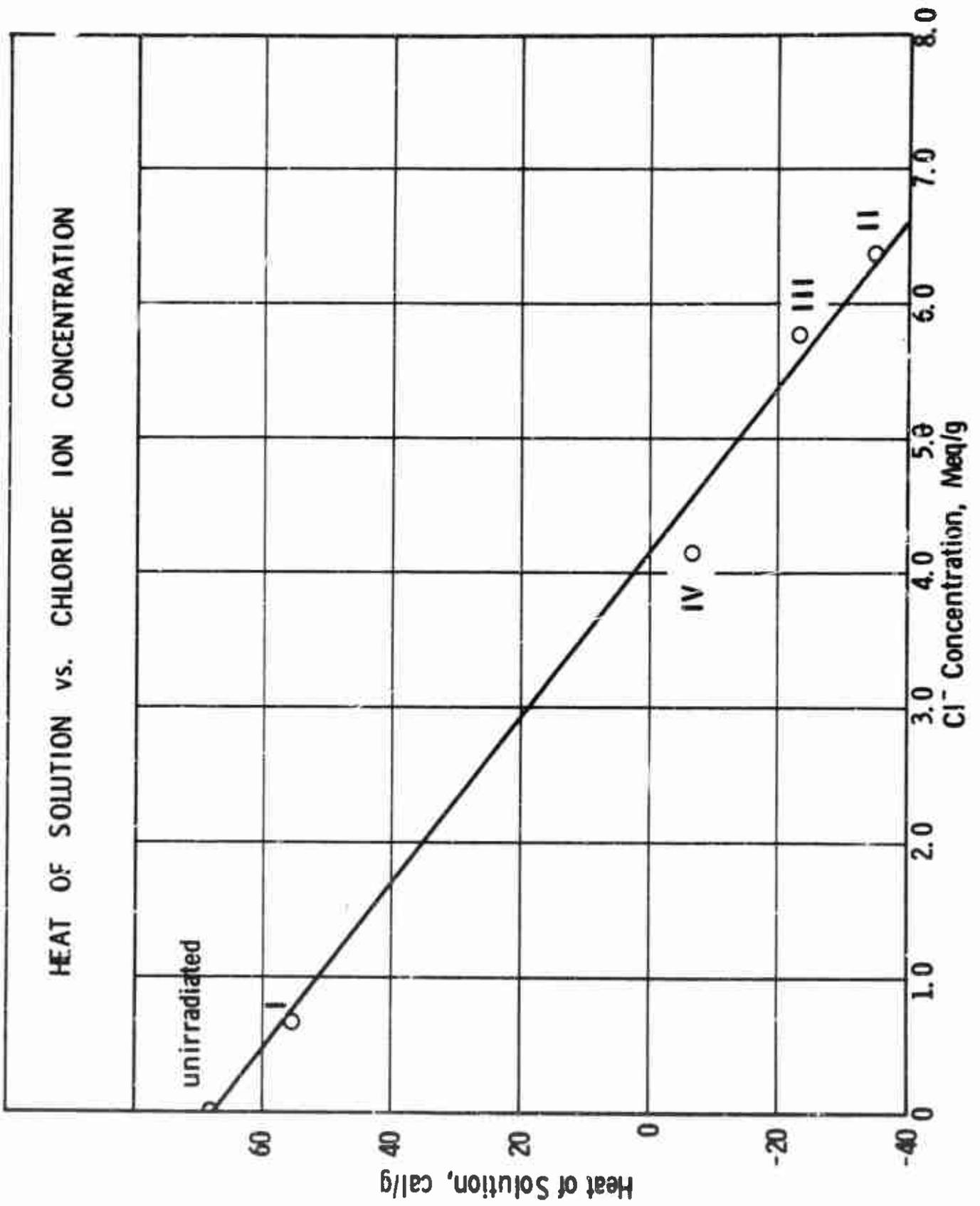


Figure 18

## VII, 2, Sample Annealing (cont.)

On the basis of these preliminary calibration experiments and thermocouple measurements made during AP irradiation, it was found that the maximum sample temperature never exceeded 53°C thus indicating that the theoretical heat transfer calculations were extremely conservative.

### 3. MICROSCOPY

Evidence available from microscopic examination of the irradiated samples tends to substantiate the conclusions drawn from the calorimetric and analytical data, i.e., that the Apparent Energy Storage is due primarily to chemical changes taking place in the sample rather than to lattice deformation.

Moreover, the microscopic evidence suggests a mechanism by which the lattice defect energy initially present was dissipated, namely by re-crystallization due to the exposure of the samples to water produced by the partial radiolytic decomposition of the sample.

## SECTION VII

### RECOMMENDATIONS FOR FOLLOW ON WORK

A follow on program involving a series of short duration irradiations under a wide variety of environmental conditions, together with appropriate calorimetric and analytical work is recommended.

The feasibility of storing lattice energy by neutron irradiation of  $\text{NH}_4\text{ClO}_4$  has still not been completely resolved. Any follow-on effort should, therefore, be primarily directed toward irradiation under anhydrous conditions in order to prevent loss of lattice defect energy through re-crystallization.

Several means of achieving anhydrous conditions should be used. Among those most apparent are: (a) Continuous evacuation of the sample container during irradiation, with a cold trap for collection of evolved gases and prevention of radioactive contamination (b) A sample container vented to an external cold trap and manometer for measurements of pressure increase due to generation of noncondensable gases (c) Use of a desiccant (in place of cold trap) with a manometer to register decomposition pressure of nonaqueous gases.

The follow on effort should also include a repetition of the work with Sample I of this program (with greater emphasis on the analytical work) in order to better correlate with the results of the two programs.

A small side effort should also be expended to investigate the use of neutron irradiated ammonium perchlorate as a burning rate catalyst in propellants. The sample irradiated for one week (Sample I) was very similar in appearance under the microscope and in DTA behavior to porous ammonium perchlorate (PAP) prepared by thermal decomposition in an Aerojet IR&D program (59).

Safety analysis and testing should present no further problems to any future program because of the extensive amount of such work documented in connection with this program. The follow-on program would involve only short duration irradiations for which an adequate margin of safety has already been demonstrated.

The irradiation costs should, therefore, be considerably reduced, thereby permitting use of a greater percentage of available funding for calorimetry and analysis.

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## APPENDIX A

### SAFETY ANALYSIS OF $\text{NH}_4\text{ClO}_4$ IRRADIATION IN AGNIR

#### 1. INTRODUCTION

The effect of fast neutrons on ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) will be evaluated by irradiating four samples of  $\text{NH}_4\text{ClO}_4$  in AGNIR. These fast-neutron interactions will create vacancy - interstitial pairs which are expected to increase the energy content of  $\text{NH}_4\text{ClO}_4$  above that of unirradiated  $\text{NH}_4\text{ClO}_4$ .

The irradiations will be performed in either the "F" or "G" rings of the AGNIR. The nominal fluxes for both fast and thermal neutrons is  $\approx 10^{12}$  neutrons/cm<sup>2</sup>-sec.

During irradiation the  $\text{NH}_4\text{ClO}_4$  will be contained in aluminum pressure vessels which will be contained in a modified dummy-element irradiation capsule (secondary containment). Two capsules, each containing approximately 10 grams of  $\text{NH}_4\text{ClO}_4$ , will be irradiated, simultaneously. The longest irradiation is scheduled for 600 hours, with other capsules scheduled for 40, 200 and 360 hour irradiations.

This appendix contains the results of the safety evaluation of various hazards, both nuclear and non-nuclear, associated with the irradiation of  $\text{NH}_4\text{ClO}_4$ .

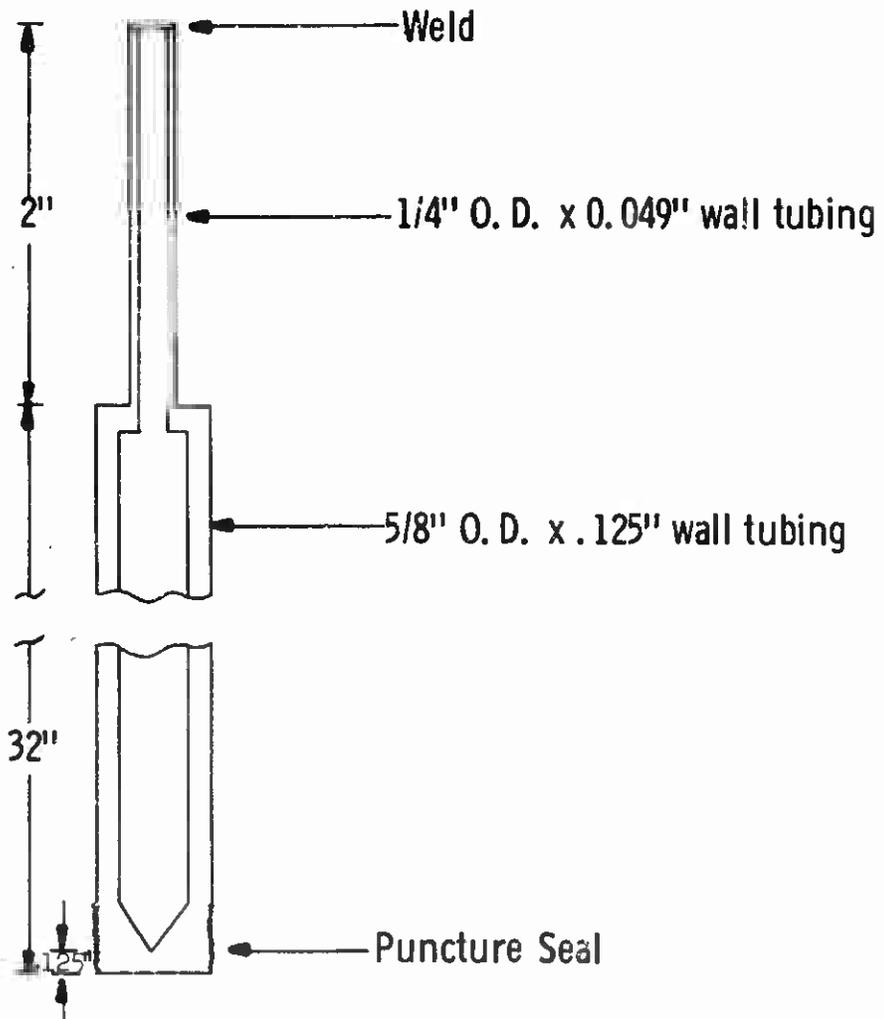
#### 2. EQUIPMENT AND MATERIALS

The pressure vessels will be fabricated from aluminum to keep the radiation dose rate from induced activities at a minimum. An iron-constantan thermocouple will be used to monitor the pressure vessel temperature during the irradiation.

##### a. Pressure Vessel

Type 6061 aluminum tubing and round stock will be used to fabricate the pressure vessels used for primary containment of the  $\text{NH}_4\text{ClO}_4$ . These pressure vessels will be fabricated in accordance with standards established by ASME for thin-walled pressure vessels. The design pressure for this pressure vessel is 4038 psia and the working pressure is 3029 psia. The main body of the pressure vessel will be 5/8 in. O.D. tubing with 0.125 in. walls by  $\approx 32$  in. long (see Figure 1). A 1/4 in. O.D. with .049 in. wall tube,  $\approx 2$  in. in length, will be welded at one end of the main body for sample loading access. This tubing will be welded shut after the loading operation. A puncture seal will be placed at the opposite end of the pressure vessel for post-irradiation gas sampling.

PRESSURE VESSEL FOR  $\text{NH}_4\text{ClO}_4$  IRRADIATION



APPENDIX A - FIGURE 1

The complete pressure vessel, before loading of the sample, will be tempered to T6 and then hydrostatically tested to 6058 psia (2 times the working pressure) to ensure the integrity of the pressure vessel. Auxiliary tests include the hydrostatic testing of the 5/8 in. O.D. tubing to the burst pressure (expected to be >6060 psia) and the thermal decomposition of  $\text{NH}_4\text{ClO}_4$  in a fabricated and hydrostatically-tested pressure vessel.

The only instrumentation used will be an iron-constantan thermocouple attached to the pressure vessel used for the 600 hour irradiation. The signal from the thermocouple will be used to actuate an annunciator on the AGNIR control console when the capsule temperature is  $150^\circ\text{C}$ .

#### b. Secondary Container

The dummy-element irradiation capsule will be used for the secondary container for these  $\text{NH}_4\text{ClO}_4$  irradiations. The capsule is capable of containing 2 primary pressure vessels at any single moment (see Figure 2). A stainless steel bulkhead fitting will be used as the water-tight connector for passing the thermocouple into the secondary container.

#### c. Chemicals

Reagent grade  $\text{NH}_4\text{ClO}_4$ , purchased from Matheson, Coleman and Bell, will be used for the irradiation samples. The particle size of the  $\text{NH}_4\text{ClO}_4$  will be  $>500\mu$ , with additional larger particles, recrystallized from  $\text{H}_2\text{O}$ , added for X-ray analysis.

Approximately 10 grams of  $\text{NH}_4\text{ClO}_4$  will be irradiated in each pressure vessel for a total  $\text{NH}_4\text{ClO}_4$  loading of  $\approx 20$  grams during a single irradiation experiment.

Helium gas at 1 atm will be added over the  $\text{NH}_4\text{ClO}_4$  and in the secondary container to enhance the heat transfer within these containers.

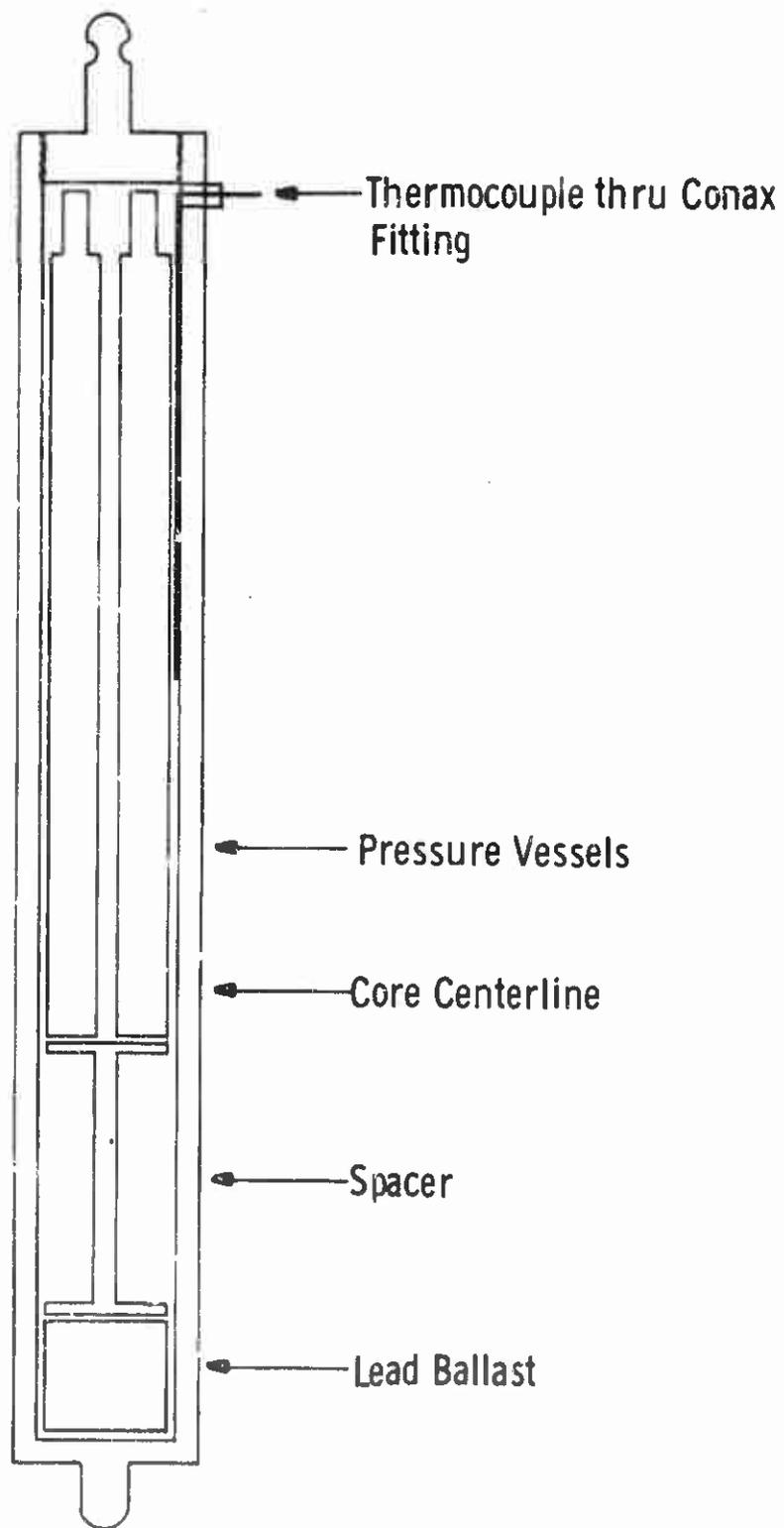
### 3. HEAT TRANSFER

Gamma heating will be the major source of heat generation in the pressure vessels. Based on the gamma heating rates calculated for the "F" ring, (4) the heat generation rate for a single pressure vessel will only be 2.36 Stu/hr-in. This heat, generated mainly in the walls of the pressure vessel will result in centerline temperatures of  $70^\circ\text{C}$  ( $157^\circ\text{F}$ ). This quantity of heat will not result in any excessive heating (within the pressure vessel) which might result in an exotherm or excessive pressure. Details of the heat transfer calculations are included in Paragraph 7.

### 4. SAFETY ANALYSIS

The major areas of concern when irradiating  $\text{NH}_4\text{ClO}_4$  are the pressure buildup caused by radiolysis of the compound and the possibility of detonation

DUMMY-ELEMENT IRRADIATION CAPSULE CONTAINING  
2 PRESSURE VESSELS AND A THERMOCOUPLE



APPENDIX A - FIGURE 2

during irradiation. Both of these problems can be solved by appropriate engineering design. The reactivity effect caused by the irradiation capsule and the  $\text{NH}_4\text{ClO}_4$  is negative and negligible for this experiment.

a. Nuclear Hazards

The dose rates from neutron activation of two pressure vessels after irradiations of 1, 10 and 600 hours are shown in Figure 3. Although the dose rates at 1 foot are initially high, decay periods of one week or less will be sufficient to reduce the radiation field to a convenient, working level. The activation of the chlorine in  $\text{NH}_4\text{ClO}_4$  produces a radiation field of  $\approx 5$  R/hr at 1 foot at the end of the experiment. This dose rate is small compared to the dose rate from the irradiated pressure vessel and will diminish with a 37 minute half-life.

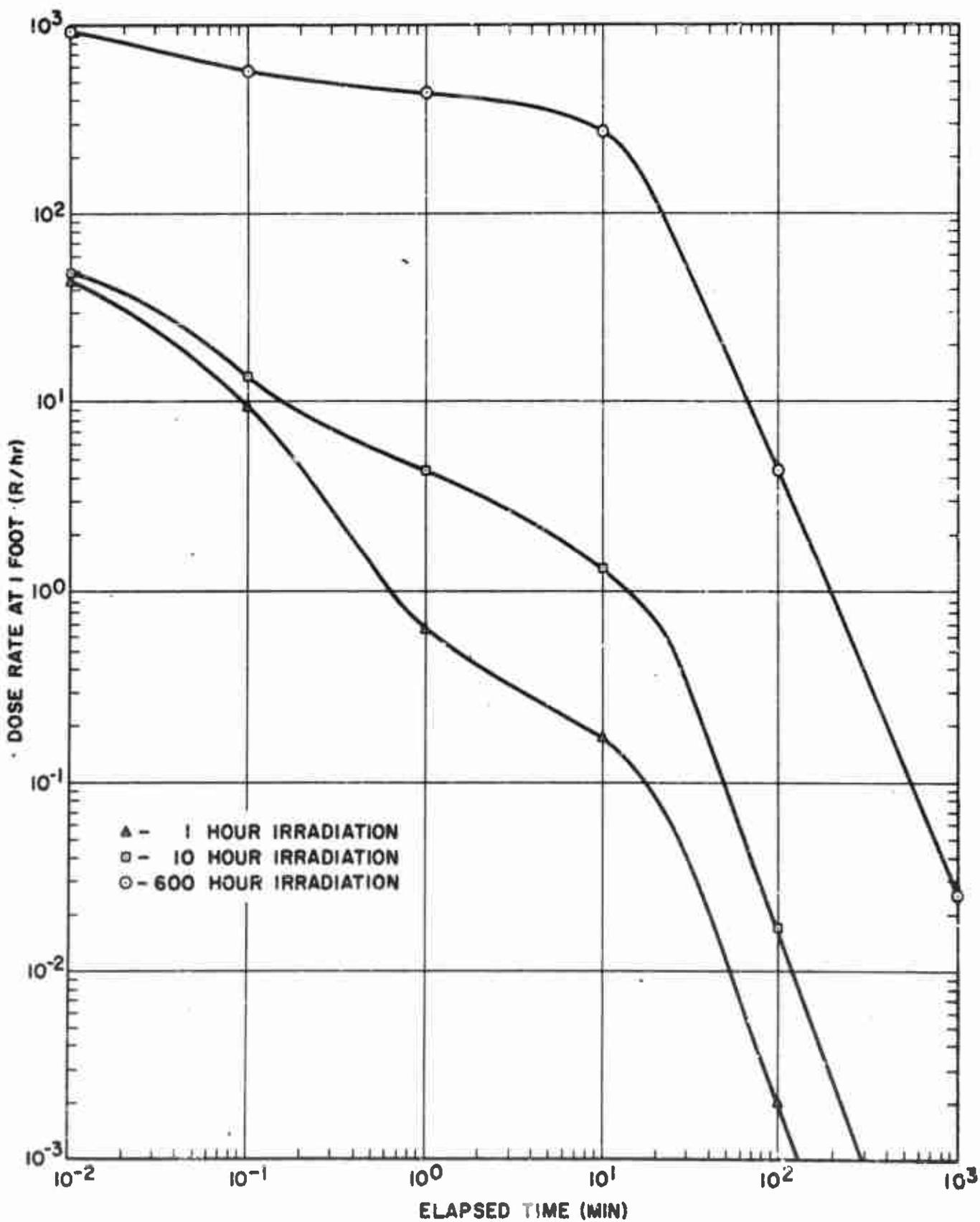
b. Non-Nuclear Hazards

The explosive properties of  $\text{NH}_4\text{ClO}_4$  are well known because of the extensive use of the compound in the formulation of solid propellants. Ammonium perchlorate is a low-grade explosive, listed as a Class 1.2 explosive according to Ordnance Standard 1724-C of the Ordnance Safety Manual (AMCR-385-225). The auto-ignition temperature for reagent grade  $\text{NH}_4\text{ClO}_4$  is  $380^\circ\text{C}$  ( $310^\circ\text{C}$  for practical grade) with no exotherm occurring below  $240^\circ\text{C}$ . Of particular significance is the work performed by Andersen and Pesante on critical diameter as a function of particle size and tamped-density. (1) Their results showed that for  $12\mu$  particle size and 0.6 g/cc density,  $\text{NH}_4\text{ClO}_4$  would not detonate (after use of No. 8 blasting caps to initiate the detonation) if the charge diameter were below 0.6 in. For an  $\text{NH}_4\text{ClO}_4$  density of 1.75 g/cc, no detonation occurred below 2.5 in. Since the pressure vessel internal diameter is  $3/8$ " and the particle size is  $>500\mu$ , no detonation will occur during the proposed irradiation.

The radiolysis experiments of Freeman, et al, (5,8) and Odian, et al. (9,10) show that no detonation occurred during their experiments. Although the dose rates used by these experimenters are a factor of  $10^2$  lower than those calculated for this experiment, the effect of decomposition rate on pressure vessel integrity can be qualitatively evaluated by a thermal decomposition test. The heating rate will be selected to simulate the radiolytic decomposition rate at  $3 \times 10^7$  Rade/hr. This thermal decomposition test plus the examination of the pressure vessels after each irradiation should provide meaningful data about the pressure vessel used for the 600 hour irradiation. The fact that the total exposure dose for these experiments is also a factor of  $10^{-2}$  higher than those of the other experimenters should not be significant since complete decomposition of  $\text{NH}_4\text{ClO}_4$  to the elements has been assumed for the purposes of this safety analysis.

The possibility of pressure vessel rupture caused by excessive pressure buildup by the non-condensable gases formed during the radiolysis of  $\text{NH}_4\text{ClO}_4$  is miniscule. The pressure vessels have been designed to

DOSE RATES FROM IRRADIATION OF ONE POUND OF ALUMINUM (TYPE 6061)



APPENDIX A - FIGURE 3

accommodate the pressure at 70°C (157°F) caused by products formed by radiolytic decomposition of  $\text{NH}_4\text{ClO}_4$  to the elements. Although thermal decomposition of  $\text{NH}_4\text{ClO}_4$  results in 4.75 moles of product (including 1.5 moles of  $\text{H}_2\text{O}$ , the pressure vessels have been designed to contain 5 moles of product, the theoretical limit, for every mole of  $\text{NH}_4\text{ClO}_4$  irradiated. The effects of pressure vessel corrosion caused by the radiolysis products will also be evaluated by thermally decomposing  $\text{NH}_4\text{ClO}_4$  in a replica of the pressure vessel. Post-irradiation examination of the pressure vessel will be performed after 40, 200 and 400 hours of irradiation to determine the integrity of the pressure vessels against any corrosion.

#### 5. LIMITING CONDITIONS

The irradiations will be performed on an 8-hr/day basis in either the "F" or "G" rings of AGNIR. The temperature of one of the pressure vessels will be monitored at  $\approx 1$  hr. intervals during the length of the irradiation. The limiting pressure vessel temperature will be 200°C, which is below the 240°C transition temperature. The experiment will be discontinued if post-irradiation examination indicates excessive corrosion of the pressure vessels.

#### 6. DISCUSSION

Since  $\text{NH}_4\text{ClO}_4$  is widely used as the oxidizer in solid-propellant formulations, its explosive properties as a compound are readily overrated by the casual observer. The experimental results compiled by Anderson and Pesante on particle size-critical diameters and the extensive irradiation experiments performed by Freeman and Odian and their co-workers attest to the inherent safety of the irradiations discussed here. The pressure vessel diameter is less than the critical diameter of 1.52 cm (0.6 in.) required to sustain a detonation for even low-density  $\text{NH}_4\text{ClO}_4$ . The  $\text{NH}_4\text{ClO}_4$  particle size is an order of magnitude greater than the particle size (12 $\mu$ ) associated with the 1.52 cm critical diameter.

The temperature inside the pressure vessel (70°C) is well below the 240°C temperature below which no exotherms have ever been observed. By assuming complete radiolysis of  $\text{NH}_4\text{ClO}_4$  to the elements, the highest possible pressure is calculated. This pressure of 206 atm (3100 psia) at 70°C (157°F) is readily contained by both the primary and secondary containers. The minor problem of dose rates from induced activities is easily solved by allowing the appropriate time interval to elapse before handling.

The results of this safety analysis show that irradiation of  $\text{NH}_4\text{ClO}_4$  can be performed in AGNIR without any danger to the reactor itself, or the personnel associated with the experiment.

## 7. HEAT TRANSFER CALCULATIONS

The major source of heating during the AGNIR irradiation of  $\text{NH}_4\text{ClO}_4$  is from gamma radiation. The heating caused by the disintegration of the  $\text{NH}_4\text{ClO}_4$  ( $\Delta H = 665 \text{ cal/g}$ ) is only 0.7 Btu/hr (over a 40 hr irradiation) or  $\approx 1\%$  of the total heat generation rate.

For an aluminum tube, .625 in. O.D. x .125 in. walls, the heating rate per unit length is

$$\begin{aligned}\text{wt Al} &= 16.387 \pi D \rho \\ &= 8.7 \text{ g/in.}\end{aligned}$$

where  $\rho = 2.7 \text{ g/cc}$

$$t = .125 \text{ in.}$$

$$D = .50 \text{ in.}$$

Since the  $\gamma$ -heating rate for the "F" ring is .079 watts/g (see EAD-268, J. K. Witthaus), the heating rate is

$$Q = (.079)(8.7)(3.41) = 2.4 \text{ Btu/hr-in.}$$

Assuming that the average distance between the pressure vessel and secondary capsule walls is .5r ( $L = .027 \text{ ft}$ ), the  $\Delta T$  is readily calculated as

$$\Delta T = \frac{QL}{kA} = \frac{(2.4)(.027)}{(.014)(.1)} = 47^\circ\text{F}$$

where  $k = .1 \text{ Btu/hr-ft-}^\circ\text{F}$  (for helium)

$$A = .014 \text{ ft}^2.$$

Therefore, the pressure vessel temperature is  $70^\circ\text{C}$  ( $157^\circ\text{F}$ ), well below the lowest exotherm temperature ( $240^\circ\text{C}$ ) for  $\text{NH}_4\text{ClO}_4$ . The gamma-heating in 10 grams of  $\text{NH}_4\text{ClO}_4$  is 3 Btu/hr,  $< 1\%$  of that for the pressure vessel.

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## APPENDIX B

### CURRENT STATUS OF "LATTICE DEFORMATION FEASIBILITY STUDY" PROGRAM

AF 04(611)-11548

Sept. 30, 1966

#### 1. INTRODUCTION AND SUMMARY

On September 21, 1966, as a result of radiation capsule failure in a modified thermal decomposition test, the AGN Reactor Safeguards Committee revoked its previously granted approval for radiation experiments in this program - which had been contingent upon successful completion of the thermal decomposition test.

In reviewing the safety testing plans for the aluminum pressure vessel to be used in this work, it was the judgment of the AEC Inspector and the Reactor Supervisor that the planned thermal decomposition test at 200°C would not give adequate assurance that "no damage to reactor components could occur". In their judgment an actual ignition of the  $\text{NH}_4\text{ClO}_4$  in a sealed irradiation capsule was needed to satisfy this requirement. The key sentence of the Technical Specification Section of the AEC License Agreement (Revision 1, March 17, 1966) reads as follows: "Reactive materials shall not be irradiated without out-of-core ignition tests which shall verify that the encapsulation will insure that no damage to reactor components could occur". Therefore the planned test was modified to continue heating the sealed sample container (beyond 200°C) until the autoignition temperature of  $\text{NH}_4\text{ClO}_4$  was reached.

The first three tests with actual or simulated pressure vessels resulted in explosive decomposition of the ammonium perchlorate and resultant capsule failure (see Figure 3 of text). In the first two tests, actual pressure vessels were used and the sample was heated internally with a temperature monitor mounted on the outer surface of the vessel (no internal temperature measurement). Based on a previous thermocouple calibration with an inert filler in place of the  $\text{NH}_4\text{ClO}_4$  sample it appeared that the capsules had failed at an internal temperature of less than 200°C. The third test was performed more carefully with a simulated capsule made from the same aluminum tubing used in capsule fabrication, closed with steel Swagelok end caps and heated externally. In this test in which both the internal and external temperatures were monitored, the container failed, with an audible ignition, at an internal temperature of 311°C (external temperature = 317°C).

Failure of the capsules under the conditions of these tests was not surprising since the capsules were designed to withstand an internal pressure (due to slow radiolytic or thermal decomposition at 200°C) of about 4000 psia and hydrostatically tested to 8100 psia. The estimated pressure due to rapid ignition of a sample pre-heated to 311°C on the other hand

is over 13,000 psia. In addition the tensile strength of the alloy used in fabrication is considerably reduced at a wall temperature of 300°C, compared with corresponding values at 100° or 200°C.

When the results of the first three experiments were made known to the Reactor Safeguards Committee, they revoked their previously granted provisional approval.

Before suspending work on the program two additional tests were performed in a simulated pressure vessel with ammonium perchlorate sample weights of two and five grams respectively. Both of these tests were successful.

Five alternative courses for completion of the program are discussed - all of which involve program delays and increased cost, and in some cases, decreased sample size. However, a decrease in sample size does not appear to be objectionable since the calorimetric work to date has shown better precision than expected and it now appears that the program objectives can be achieved with a smaller sample than originally planned.

## 2. PROGRAM ALTERNATIVES

The program cannot be continued in its present form without a considerable amount of additional testing designed to satisfy the committee that no real hazard exists. Even if such additional tests were performed successfully, the committee would now be reluctant to grant approval at the local level, and would probably insist upon obtaining specific AEC approval in the form of an Amended License Agreement.

Several alternatives are possible, all of which involve some program delay as well as probable increases in cost and possible reduction in the size of sample to be irradiated. Results of calorimetric measurements to date indicate that some reduction in sample size could be tolerated - while retaining all of the original program objectives.

Five possible program modifications are outlined below. The first three involve modified program with the irradiation to be carried out at AGN while the last two approaches involve subcontracting of the irradiation phase of the work to the General Electric - Vallecitos Facility.

- a. Irradiation of Reduced Size AP Sample in the Same Portion of the AGN Reactor with Original Capsule Design

Additional effort involved in this approach will involve  
(1) fabrication and testing of additional capsules with reduced loads -

in both room temperature and elevated temperature ignition tests, (2) writing and submission of an application for amendment of the AEC License Agreement, and (3) possibly some additional calorimetry work to establish new limits of precision with unirradiated AP in smaller sample sizes.

If a suitable ambient temperature ignition test can be devised (involving either pure AP or an equivalent mixture of AP and an ignition aid such as JPN) it may be possible to qualify the present capsule design for the full 10-gram loading. However, at the present time it appears that the permissible sample loading will be in the range of 4 to 8 grams.

- b. Irradiation of 10-Gram AP Samples with a Heavier Wall Capsule in the Same Portion of the AGN Reactor

Additional effort involved in this approach will involve (1) design, fabrication and testing of heavier-wall capsules (2) amending the AEC License Agreement and (3) irradiation and Calorimetry as originally planned.

- c. Irradiation of 10-Gram AP Samples with Capsules of Larger Outside Diameter and Heavier Wall in an Increased Flux Region of the AGN Reactor

This approach involves (1) design, fabrication and testing of special capsules of larger outside diameter and heavy wall, (2) amendment of the AEC License Agreement, (3) irradiation at a flux rate of approximately three times the originally planned rate for 1/3 the total time, (4) calorimetry as originally planned.

- d. Irradiation of 4- to 5-Gram Samples of  $\text{NH}_4\text{ClO}_4$  in the GE Reactor with REON Designed and Qualified Capsules; Two Capsules Per Exposure

This approach involves irradiation in the Z-Trail Cable area of the GE reactor at flux levels 10 times higher than originally planned. The REON designed capsules have been fully qualified for use with 1.8 grams of high explosive in detonation tests with 3.6-gram (and larger) quantities of high explosive. The official price quotation from GE will specify the sample size limit for irradiation of AP - as determined by the GE Reactor Safety Committee. This judgment is within their area of jurisdiction since GE is already licensed to irradiate high explosives. The ROM cost estimate is based on irradiation of two capsules at each planned exposure level, thus making available from 8 to 10 grams of irradiated sample.

- e. Irradiation of 4- to 5-Gram Samples in the GE Reactor with REON Designed and Qualified Capsules; One Capsule Per Exposure

In order to remain as close as possible to the original program budget, it may be possible to perform the analytical and calorimetric measurements within the desired limits of accuracy - with 4 to 5 grams of sample from each exposure level. This would then permit the use of one capsule for each exposure level and reduce the cost of irradiation by about 40%.

### 3. EXPERIMENTAL DETAILS

#### a. Summary

The Technical Specifications (Revision 1, 17 March 1966) for AGNIR require that out-of-core ignition tests must be performed before reactive materials can be irradiated in AGNIR. This test is performed to "verify that the encapsulation will ensure that no damage to reactor components could occur". To comply with this stipulation, a total of five ignition tests have been performed with ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ). In the first two tests, hot filament heaters were sealed into the pressure vessel. A tape-type heater was used to heat the pressure vessel from the outer surface in the last three tests. These tests verify the fact that  $\text{NH}_4\text{ClO}_4$  can indeed be ignited if the temperature is sufficiently high. They also verify that the encapsulation for the  $\text{NH}_4\text{ClO}_4$  irradiation experiments discussed in the hazards analysis does ensure, within the anticipated experimental limits, that no damage will occur to reactor components.

#### b. Experimental Methods

Two experimental approaches were used for the ignition tests - internal heating and external heating. The heating rates, in all cases, were calculated to represent the heating rate caused by reactor radiation ( $\sim 3 \times 10^7$  Rads/hr) in the irradiation position (F ring). This rate is  $\sim 5^\circ\text{C}/\text{min}$ .

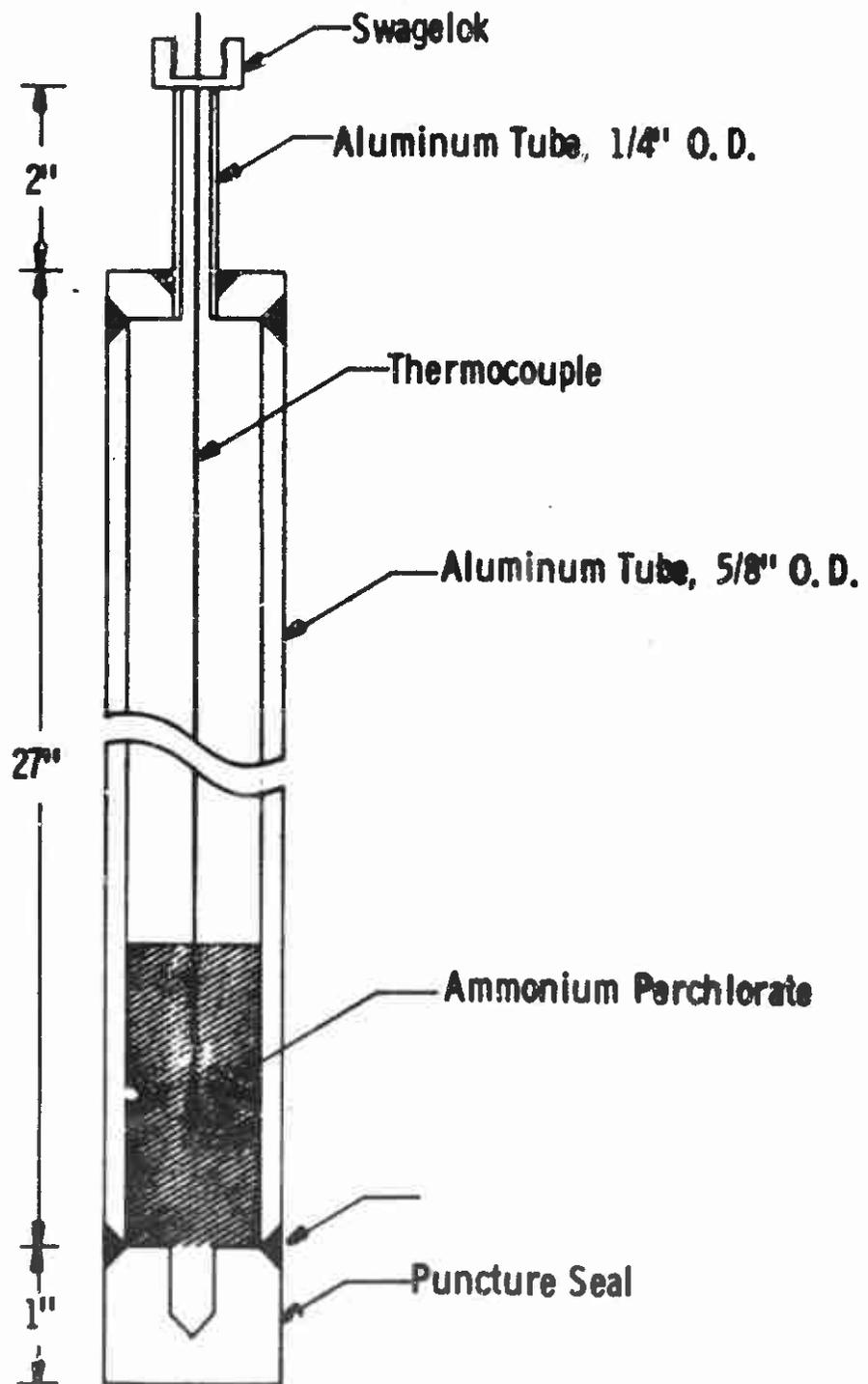
##### (1) Pressure Vessel

The aluminum pressure vessels designed for this program were used for the internally-heated experiment (see Figure 1). They were hydrostatically tested to 8100 psig. A simulated vessel consisting of a 30 in. section of the same 5/8" O.D. Type 6061-T6 aluminum tube, used for the pressure vessels with stainless steel Swagelok caps was used as the container for the externally-heated tests (since no more spare pressure vessels were available at this time). This type of container had been previously tested to 24,000 psig before tube rupture occurred. A Heise gauge capable of measuring pressure to 4000 psig was used for pressure measurements. An atmosphere of helium was added to each vessel to simulate the proposed experimental conditions.

##### (2) Heaters

Three types of heaters were used for the experiments. A heater which was fabricated from nichrome wire (0.10 in. dia) and copper leads (0.013 in. dia) and encased in ceramic insulation was used for the first of the internally-heated experiments. A chromel-alumel thermocouple, sheathed in stainless steel, was used for the second internally-heated experiment. These heaters were calibrated for heating rate by heating a 5/8" O.D. aluminum tube containing sodium chloride and measuring the centerline and external temperatures. During the ignition test, only the external temperature was recorded, the

# PRESSURE VESSEL FOR $\text{NH}_4\text{ClO}_4$ IRRADIATION



APPENDIX B- Figure 1

centerline temperature being estimated from the calibration data. The power supply used was an AB Electro Polisher Power Source, Cat. No. 1715-1, made by Buehler, Ltd., Chromel-Alumel thermocouples and Millivolt Potentiometers, Cat. No. 8686 made by Leeds and Northrup, were used for temperature measurements.

For the externally-heated experiments, a heating tape with variac power supply was used. The internal temperature was monitored with a copper constantan thermocouple; the external temperature with an iron-constantan thermocouple. The Leeds and Northrup potentiometers were used for thermocouple readout.

### c. Results

The first three ignition tests, each conducted with 10-gram samples of AP, resulted in pressure vessel failure of one form or another. In two additional tests, using reduced AP sample sizes (2 and 5 grams, respectively) the pressure vessel remained intact at maximum temperatures of 396°C and 359°C respectively.

The first internally-heated test, using the nichrome heater, was terminated at 96° external temperature (apparent internal temperature of 180°C) when the 1/4" O.D. tube separated from the main body of the pressure vessel, at the weld, with a loud report. The tube was also severed at the Swagelok connector and was not found after the experiment. The measured pressure was 4 psig just before the failure of the container.

The second internally-heated experiment (using a sheathed heater) was abruptly terminated when the puncture seal left the main body of the pressure vessel. Further pressure vessel damage occurred in the form of 1.5 in. axial split with subsequent opening of the tube in the radial direction. This rupture occurred at 124°C external temperature corresponding to an apparent internal temperature of ~ 170°C. A noticeable pressure reading was obtained at ~ 76°C and increased to 76 psig just before the pressure vessel rupture.

The first externally heated experiment also ended in an audible fashion when a brass reducing-coupling gave way. This failure occurred at a measured internal temperature of 311°C and an external temperature of 317°C (see Table I). The pressure reading was 40 psig just before the failure and rose to > 4,000 psig.

The results from the ignition tests verify the fact that when any reactive compound is heated high enough, the compound will decompose rapidly or deflagrate.

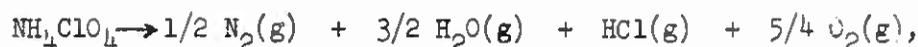
The apparent temperatures at which failure occurred in the internally heated experiments are disturbingly low. This phenomena may be attributed to hot spots such as the nichrome-copper junction and the fact that the thermocouple heater was glowing red when the measured temperature in NaCl was only 300°C. Under these conditions exothermic decomposition of the

$\text{NH}_4\text{ClO}_4$  undoubtedly occurred and the externally measured temperature could be of no value in determining the actual AP sample temperature. For this reason the third test was run using an external heater with thermocouples mounted both inside and outside.

The fact that pressure vessel failures were not detonations (no shrapnel) but deflagrations is rather encouraging. The results from the externally heated capsule show that at  $150^\circ\text{C}$ , the experiment scram temperature, there is no pressure rise. Significant decomposition (or pressure rise) did not occur until  $295^\circ\text{C}$ . Therefore, the ignition test has shown that the capsule can contain the reactive material at both the operating temperature ( $105^\circ\text{C}$ ) and the automatic scram temperature ( $150^\circ\text{C}$ ).

#### 4. DISCUSSION OF TESTS

The pressure generated within the irradiation capsule by the decomposition of  $\text{NH}_4\text{ClO}_4$  can be estimated from the decomposition reaction,



which evolves a heat of 38.07 Kcal, and generates 4.25 moles of gas, per mole of  $\text{NH}_4\text{ClO}_4$ . Assuming the perfect gas law, the corresponding equilibrium pressure in atmospheres is,

$$P = \frac{W}{117.497} \times 4.25 \times \frac{22,412}{V} \times \frac{T}{273} = 2.969 T \times \frac{W}{V}$$

where T is the temperature in degrees Kelvin, W is the sample weight in grams and V is the capsule volume in cubic centimeters.

In a slow decomposition reaction (thermal or radiolytic) the process may be considered as isothermal with the effective temperature being that of the pressure vessel. Under these conditions the pressure corresponding to complete decomposition of 10 grams of  $\text{NH}_4\text{ClO}_4$  in a container of 54.3 cc internal volume at a capsule temperature of  $105^\circ\text{C}$  (the assumed operating conditions) is 206.7 atmospheres or 3038 psia. At the reactor scram temperature of  $150^\circ\text{C}$ , the corresponding pressure is 3400 psia, while at the originally planned thermal decomposition test temperature of  $200^\circ\text{C}$ , the corresponding pressure is 3802 psia.

Since the pressure vessels had been hydrostatically tested to 8100 psia and there is no literature evidence of  $\text{NH}_4\text{ClO}_4$  auto-ignition below the orthorhombic to cubic phase transition temperature of  $242^\circ\text{C}$  - the capsules were expected to pass the  $200^\circ\text{C}$  thermal decomposition test.

However, when ammonium perchlorate is heated to the auto-ignition temperature, the situation is entirely different. In this situation adiabatic

Table IRESULTS OF EXTERNALLY-HEATED EXPERIMENT  
(Test No. 3)

<u>Temperature Inside (°C)</u>	<u>Outside (°C)</u>	<u><math>\Delta T</math> (°C)</u>	<u>Heating Rate °C/min</u>	<u>Pressure (psig)</u>
21	24	3	-	0
23	28	5	2	0
38	47	9	4	0
61	72	11	5	0
88	99	11	5	0
113	124	11	5	0
132	143	11	4	0
150	162	12	4	0
178	192	14	6	2
208	217	9	5	2
218	228	10	4	2
225	237	12	5	2
233	243	10	8	2
236	249	13	6	2
238	252	14	3	2
241	257	16	5	2
246	261	15	4	2
252	266	14	5	2
259	271	12	5	2
264	275	11	4	2
276	286	10	5	2
280	295	15	5	6
289	299	10	4	12
297	304	7	5	17
301	309	8	5	25
306	313	7	4	32
311	317	6	4	40

conditions may be assumed and the heat of reaction of 38.07 Kcal/mole corresponds to a temperature rise of 1066°C. If 10 grams of  $\text{NH}_4\text{ClO}_4$  were ignited at an initial temperature of 298°K in the capsule of 54.3 cc volume, the corresponding adiabatic flame temperature and pressure would be 1364°K and 10,962 psia respectively. Under conditions corresponding to Test #3, with the sample and container preheated to 311°C at the time of ignition, the corresponding temperature and pressure are 1650°K and 13,261 psia, respectively.

In addition to the pressure generated in the ignition, the tensile strength of the aluminum alloy is considerably reduced at the temperature corresponding to auto-ignition. Table II lists literature values of tensile strength as a function of temperature for the alloy used and shows that at 315°C the tensile strength is only 10% of that at 24°C.

The loss in tensile strength with temperature was the chief reason for conducting the first two pages with an internal heater - to keep the capsule temperature below that of the AP and thus retain as much capsule strength as possible. However, direct contact of the heater wire with the AP led directly to auto-ignition and capsule failure.

In view of the data discussed above, it is not surprising that the capsules failed in the auto-ignition test.

It should be possible, however, to devise a less severe test - more closely resembling actual conditions in the reactor - as a qualification for the capsules. Room temperature ignition of  $\text{NH}_4\text{ClO}_4$  should be an acceptable test; however, it may not be possible to ignite pure AP without an ignition aid of some sort. Ignition of an energetically equivalent mixture of AP and an ignition aid such as JPN double base propellant should provide a suitable test.

TABLE II

TENSILE STRENGTH OF TYPE 6061-T6 ALUMINUM  
ALLOY AT VARIOUS TEMPERATURES

<u>Temperature,</u> <u>°C</u>	<u>Tensile Strength,</u> <u>lb/sq. in.</u>
24	45,000
100	42,000
149	34,000
205	19,000
260	7,500
315	4,500
370	3,000

5. STATUS OF CALORIMETRY

Since the last monthly report, the calorimeter stirrer has been improved by increasing the surface area of the blades - resulting in more rapid attainment of equilibrium and greatly improved precision. Table III (of the text) shows the results of the four measurements made before and three measurements made after the stirrer modification. Several more sample bulbs had been prepared for additional measurements this month; however, all work on the program was suspended following the September 21 meeting of the Safety Committee.

On the basis of the first three measurements with the improved calorimeter stirrer it now appears that the desired precision uncertainty of  $\pm 0.25$  cal/g could be achieved with a sample size as low as 0.5 gram - if it becomes necessary to reduce the sample size for irradiation.

## APPENDIX C

### CLOSED BOMB PRESSURE TESTS

#### INTRODUCTION AND SUMMARY

As an aid in developing a suitable ambient temperature ignition test for the ammonium perchlorate irradiation capsules, a series of closed bomb ignition tests were run in which the peak pressure corresponding to various compositions and specific volume conditions were determined. Since pure ammonium perchlorate, particularly in large particle size, is difficult to ignite it was necessary to mix the  $\text{NH}_4\text{ClO}_4$  sample with an ignition aid to ensure complete combustion. The well characterized double base propellant JPN (Ballistite) was used for this purpose.

A series of JPN-AP mixtures and corresponding sample loading densities were chosen to approximate the peak pressure of 11,000 psia which was estimated for the combustion of 10 grams of pure ammonium perchlorate in an enclosed volume of 54 cc (the approximate free volume of the irradiation capsule). Within the range of compositions tested, from 100% to 8.57% JPN or 0 to 91.43% AP, the actual measured pressures ranged from a maximum of 13,400 for 91.43% AP to a minimum 7,740 for 100% JPN.

The deviations between the measured and originally estimated pressures were due to two major effects: (a) the originally estimated theoretical value for  $\text{NH}_4\text{ClO}_4$  was in error - exact theoretical calculations made later indicated a pressure of 14,000 rather than 11,000 psia, and (b) the pressure efficiency (ratio of measured to theoretical) decreased with increasing concentrations of JPN in the sample mixture - probably because of increasing heat loss associated with higher flame temperatures and smaller sample masses.

The extrapolated pressure corresponding to combustion of 100%  $\text{NH}_4\text{ClO}_4$  in a free volume of 5.4 cc per gram of sample is 13,700 psia.

## EQUIPMENT

The measurements were made in a closed cylindrical steel bomb of 2-3/8" inside diameter and inside length variable from 1" to 25" by means of removable aluminum spacer rods. For these tests 7" of free space was used which corresponded to an internal volume of 31.6 cubic inches or 508.2 cubic centimeters.

Pressures were recorded by means of a rapid response pressure transducer at a chart speed of 80 in. per second, or .08 in. = 1 millisecond. Figure 1 shows a typical trace of pressure vs time for one of the mixtures studied.

## MATERIALS

The ammonium perchlorate sample used in these tests was an unscreened portion of the same reagent grade material to be used in the irradiation studies. A sieve analysis conducted earlier indicated that only 49% of the original reagent was in the particle size range of 0.5 to 1.0 mm which is being used for the irradiation and calorimetric work. Therefore, the unscreened material might reasonably be expected to burn faster, resulting in a higher peak pressure than that of the relatively coarse particles to be used in actual irradiation studies.

The ignition material used in these studies is the well-known double base gun propellant JPN (or Ballistite)<sup>1,2</sup> which consists of 51.5% nitrocellulose, 43% nitroglycerin and other additives. The actual sample used was from a large roll of 1/16 in. sheet material of about the consistency of tough shoe leather. It is quite stable in storage and handling, can be readily ignited with a hot wire, and can be cut to any desired shape with a sharp knife or cork borer. The sample used in these tests consisted of circular discs weighing approximately 0.1 gram each.

In order to simplify the tests and assure rapid ignition with minimum heat loss, a standard ignition system consisting of a 0.1 gram electrically ignited Mark II squib and 2 grams of red dot powder was used in each of the tests. Theoretical calculations indicate that the squib contributes 7 psia and the red dot powder contributes 613 psia to the overall measured pressure

1. Wimpres, R., Internal Ballistics, McGraw Hill, New York, 1950.

2. Sarner, S. F. Propellant Chemistry, Reinhold, New York, 1966.

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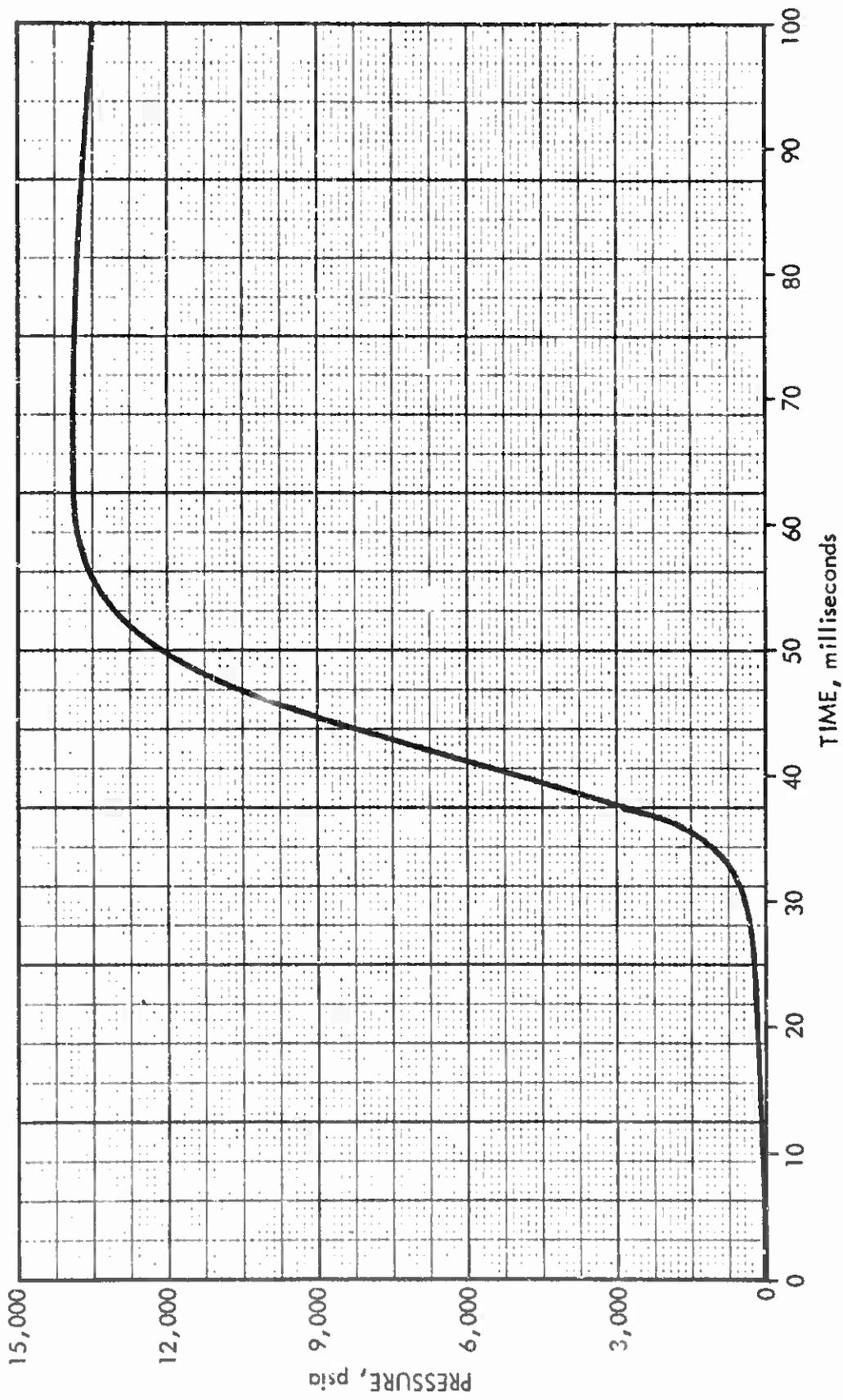


FIGURE C-1. PRESSURE VERSUS TIME TRACE FOR SAMPLE NO. 7, 91.43% NH<sub>4</sub>ClO<sub>4</sub>

peak. A nominal correction of 500 psia (which assumes about 20% heat loss) was applied to the measured peak pressures to account for the effect of the squib and red dot.

## RESULTS

The results of the closed bomb pressure tests, including the extrapolation to 100%  $\text{NH}_4\text{ClO}_4$  are shown in Table 1, while Table 2 shows the equivalent sample weights for tests in the irradiation capsule of 54 cc free volume.

Figure 1 shows the pressure vs time trace for Run #7 indicating a peak pressure of 13,900 (uncorrected for the squib and red dot) and an elapsed time of about 50 milliseconds from initiation to peak pressure.

Figure 2 (peak pressure vs weight percent  $\text{NH}_4\text{ClO}_4$ ) summarizes the results for Runs 2, 4, 5, 6 and 7 and indicates that the extrapolated value for 100%  $\text{NH}_4\text{ClO}_4$  is probably accurate to within  $\pm 500$  psia. Theoretical peak pressures corresponding to adiabatic conditions are also shown for comparison.

## THEORETICAL CALCULATIONS

The original theoretical pressure calculations were based on an accurate equation of state of JPN, combined with a rough estimate for AP and assumed no interaction of the combustion products. On this basis, a series of compositions were chosen for tests designed to yield identical peak pressures of 11,000 psia.

Later calculations of actual mixtures were made utilizing the IBM computer program for propellant thermodynamic calculations which incorporates the latest data for thermodynamic properties of the combustion products and includes the effects of interactions. Exact calculations were made for the constant volume adiabatic conditions covering the entire range of compositions and specific volumes of interest.

The calculations were made assuming applicability of the perfect gas law which appeared to be reasonable for the pressures of interest. The results of these calculations are shown in Figure 3.

Comparison of the perfect gas calculation for pure JPN with calculations based on the equation of state,  $P = wRT/(V-bw)$ , indicated exact agreement at pressures up to 15,000 psia.

TABLE 1 - RESULTS OF CLOSED BOMB PRESSURE TESTS  
(508.2 cc Free Volume)

Run No.	Sample Weight, grams		Weight Percents		Specific Volume	Measured Peak Pressure
	JPN	$\text{NH}_4\text{ClO}_4$	JPN	$\text{NH}_4\text{ClO}_4$	cc/g	psia*
1	18	-	100	-	28.7	3,000
2	36	-	100	-	14.4	7,740
3	54	-	100	-	9.6	14,200
4	28	19	60	40	10.8	10,500
5	21	37.5	36	64	8.65	12,300
6	14	56	20	80	7.2	12,800
7	7	75.5	8.57	91.43	6.2	13,400
	-	-	0	(100)**	5.4	(13,700)**

\* Includes correction of 500 psia for squib and red dot.

\*\* Extrapolated from Runs 2, 4, 5, 6, and 7.

TABLE 2 - EQUIVALENT SAMPLE WEIGHTS FOR 54 cc IRRADIATION CAPSULE

Run No.	Sample Weight, grams		Specific Volume, cc/g
	JPN	$\text{NH}_4\text{ClO}_4$	
1	1.875	0	28.6
2*	3.75	0	14.4
3	5.625	0	9.6
4*	3.00	2	10.8
5*	2.25	4	8.65
6*	1.50	6	7.2
7*	0.75	8	6.2
	(0)	(10)	(5.4)

\* Based on originally estimated peak pressures, the series of Runs 2, 4, 5, 6 and 7 were designed to yield identical peak pressures of 11,000 psia with  $\text{NH}_4\text{ClO}_4$  added in successive 2 gram steps.

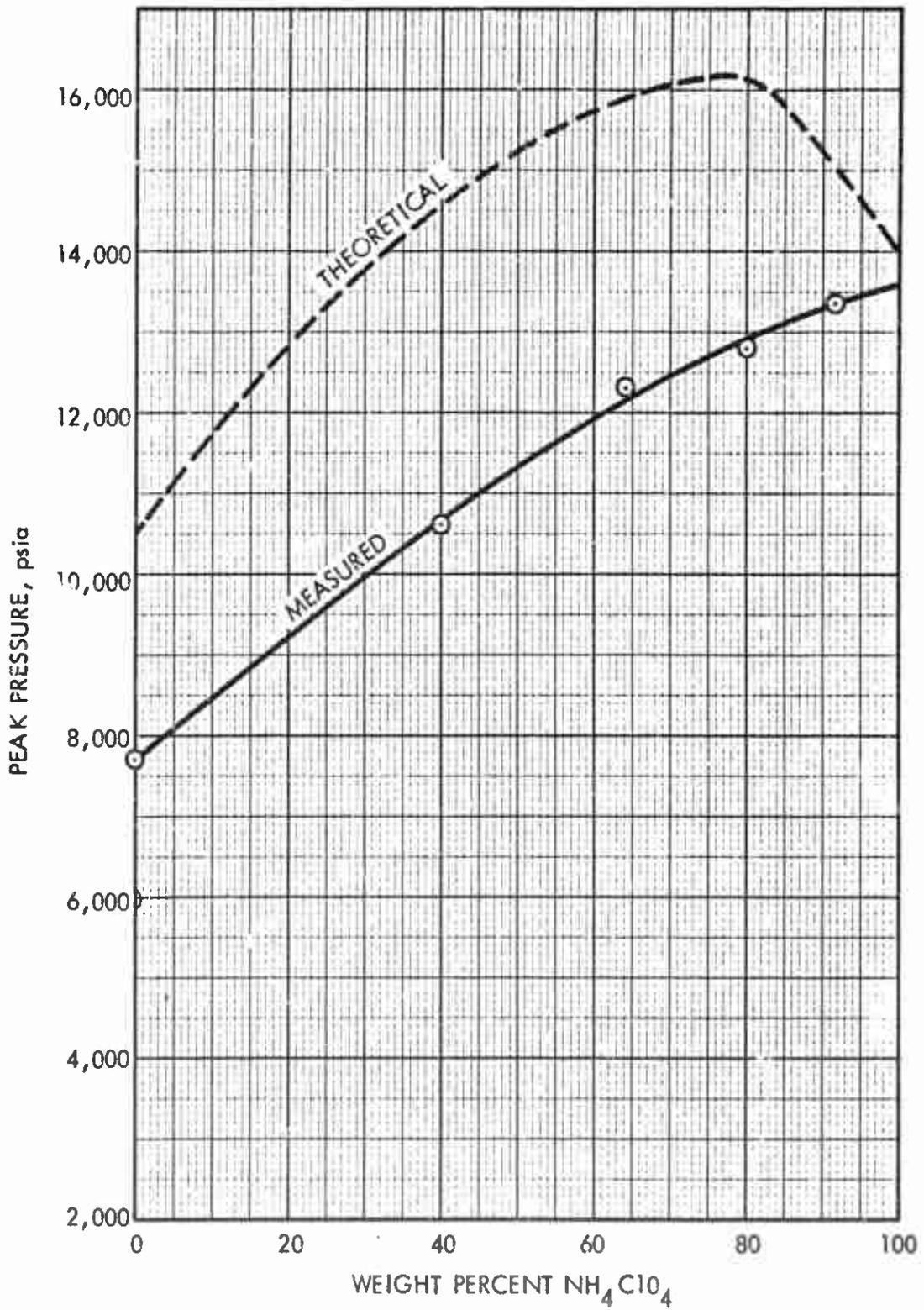


FIGURE C-2. THEORETICAL AND MEASURED PEAK PRESSURES VERSUS WEIGHT PERCENT  $\text{NH}_4\text{ClO}_4$

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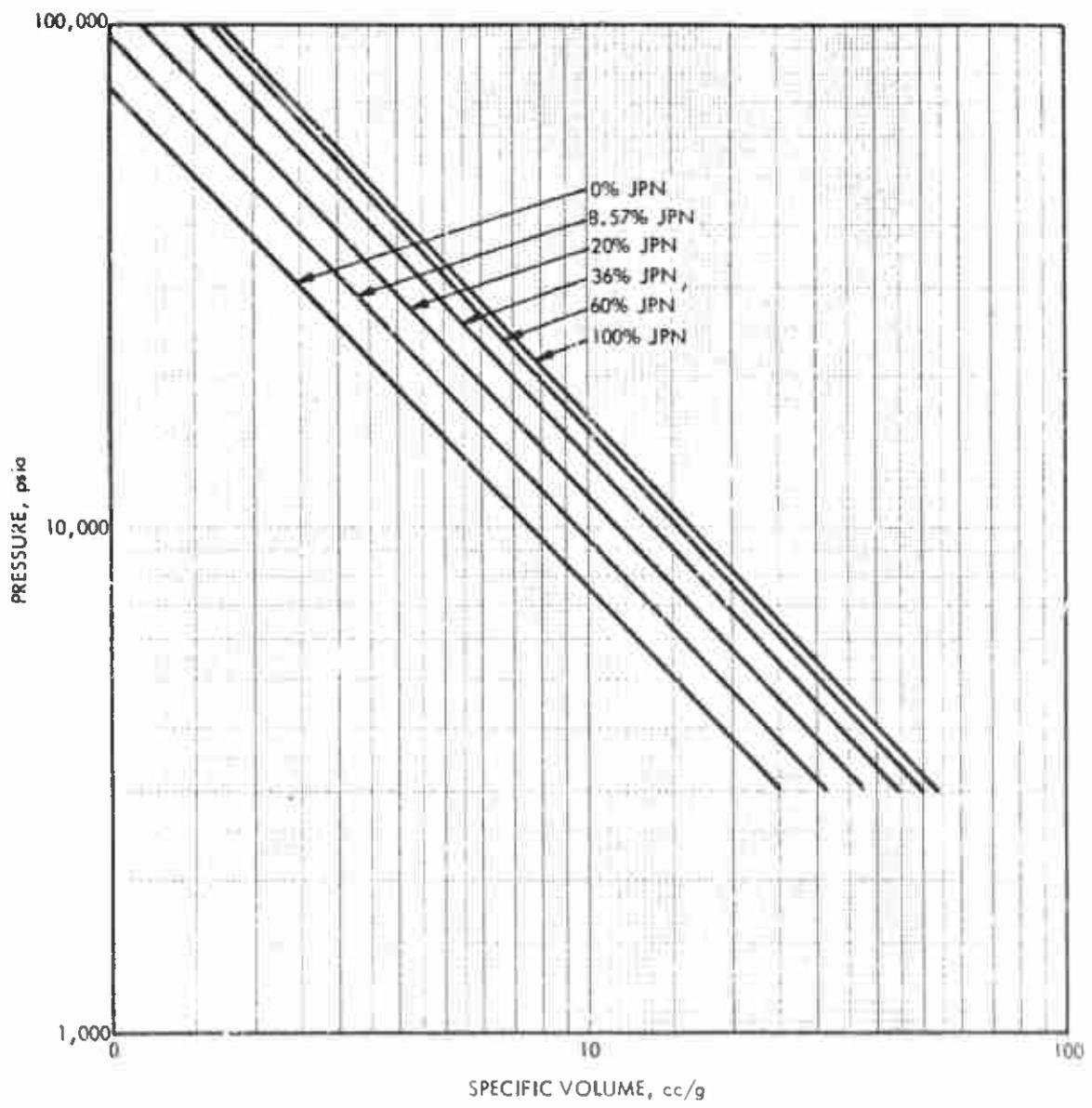


FIGURE C-3. THEORETICAL PRESSURE VERSUS SPECIFIC VOLUME FOR ADIABATIC COMBUSTION OF JPN-AP MIXTURES

3 DI-67-060

## DISCUSSION

The peak pressures recorded under the conditions of these tests are probably higher than those which might be expected under conditions existing in the sealed irradiation capsule (0.5 to 1.0 mm crystals and no ignition aid). The combination of ignition aids (JPN and red dot powder) and the average particle size of the AP sample contributed to higher peak pressure through rapid combustion and resultant minimum heat loss.

In addition, interaction of the combustion products of  $\text{NH}_4\text{ClO}_4$  (containing excess  $\text{O}_2$ ) with those of the red dot powder (containing unburned  $\text{H}_2$  and  $\text{CO}$ ) results in a higher temperature and pressure than would be predicted on the basis of no interaction. Although this effect has not been theoretically evaluated for mixtures of AP and red dot, it has been evaluated for corresponding mixtures of AP and JPN which are nearly identical chemically.

Figure 4 shows the variation in adiabatic flame temperature with composition for constant pressure combustion of AP-JPN mixtures at 1500 psia. The curve shows the results of actual theoretical equilibrium calculations with a peak temperature corresponding to about 30% AP, whereas, the dotted straight line shows the temperatures which would be predicted on the basis of no interaction. From the shape of the curve it appears that the effect of interaction is not pronounced at compositions near 100% AP. Comparison of the two lines at a composition of 98% AP which corresponds roughly to the effect of 2 grams of red dot indicates an additional temperature increase (due to interaction) of  $60^\circ\text{K}$  or 4.3%. The applied (pressure) correction for the effect of red dot therefore is probably low by about the same percentage. Thus, the extrapolated measured value of 13,700 psia for pure AP may be slightly high because of neglecting to correct for interaction of the red dot and AP combustion products.

The results of the closed bomb tests indicate that combustion of mixtures of JPN and  $\text{NH}_4\text{ClO}_4$  in the irradiation capsule should provide an accurate simulation spontaneous ignition of 10 grams of  $\text{NH}_4\text{ClO}_4$  in the same capsule. Survival of the capsule under these conditions should provide an adequate margin of safety for all irradiation work planned.

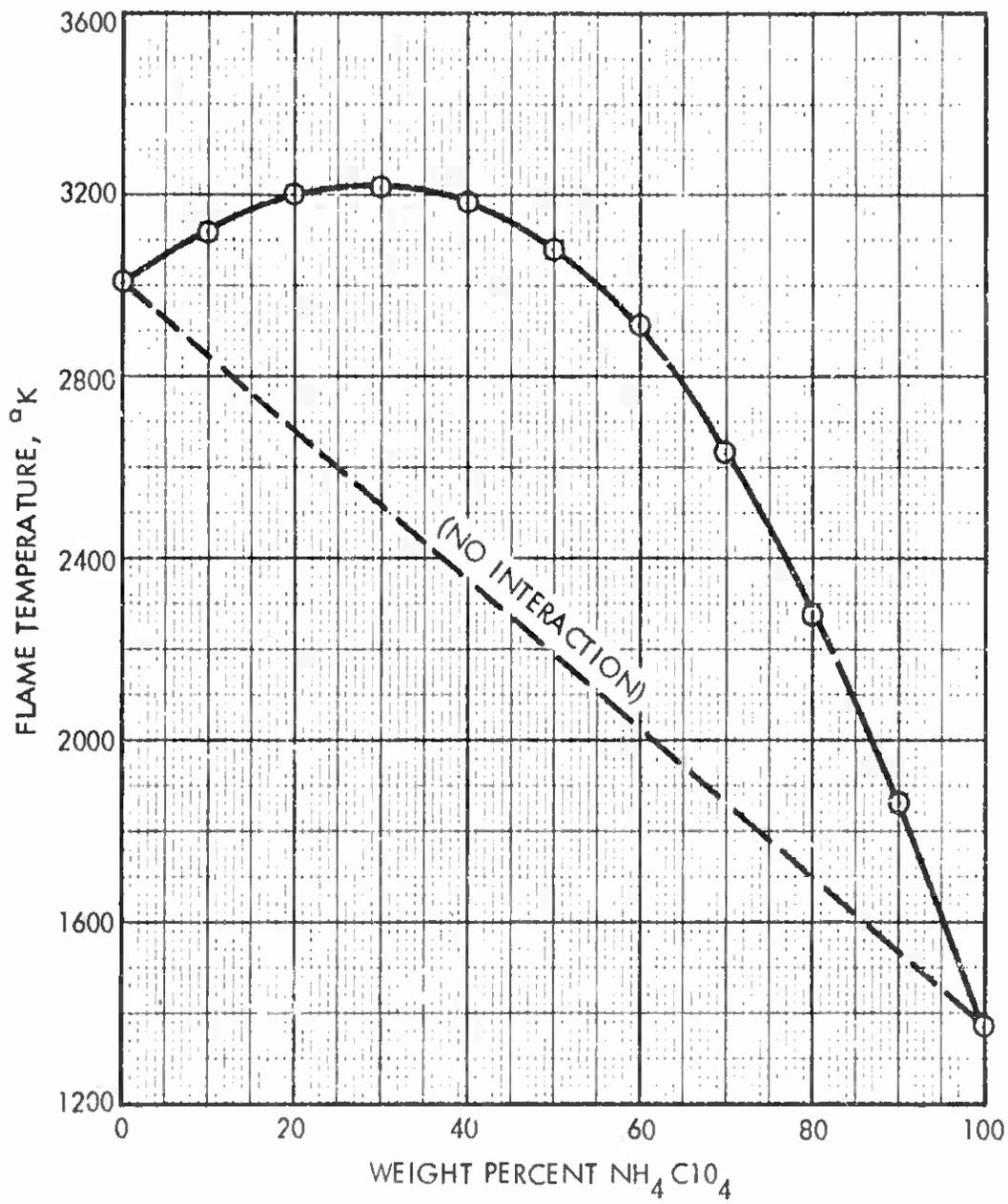


FIGURE C-4. THEORETICAL FLAME TEMPERATURE AT 1500 psia FOR CONSTANT PRESSURE COMBUSTION OF JPN-AP MIXTURES

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13. ABSTRACT Four samples of reagent grade ammonium perchlorate weighing five grams each were irradiated in the Aerojet-General Nuclear Industrial Reactor (AGNIR) for periods of 37, 78, 187 and 224 hours. Total radiation exposures ranged from $1.0 \times 10^{17}$ to $6.1 \times 10^{17}$ neutrons per sq cm of neutron exposure, and from $1.7 \times 10^8$ to $9.9 \times 10^8$ Rads of gamma exposure.		
<p>Sample decompositions were found to be proportional to total radiation exposure. In the experiment of longest duration, 36.5 weight percent of the irradiated sample decomposed into gaseous decomposition products and generated a gas pressure of 19.5 atmospheres in the sealed irradiation pressure vessel. Only 1.5 grams, or 30% of the original sample, was recovered in useable form.</p> <p>The crystalline samples recovered for analytical and calorimetric measurements all showed excessive radiation damage with extremely porous structures and acidic residues.</p> <p>The Apparent Lattice Energy Content was determined by measurement of heat of solution before and after the radiation exposure. Measured heats ranged from +68.04 cal/g for the unirradiated sample to a minimum of -34.70 cal/g for the sample of 187 hours exposure. Correspondingly derived values of apparent energy storage ranged from 13.02 cal/g for the 37 hour exposure to a maximum of 102.74 cal/g for the 187 hour exposure sample.</p>		
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<p>Comparison of measured heats of solution with estimated heats of solution based on chemical analyses of the samples indicated that the derived values of apparent lattice energy could be accounted for on the basis of changes in chemical composition alone, particularly the accumulation of free perchloric acid in the irradiated samples.</p> <p>It is concluded that under the experimental conditions of this study in which the irradiated sample was continually exposed to water and other products of radiolytic decomposition, no lattice energy was stored.</p> <p>The mechanism by which the initially induced lattice energy storage was lost is believed to be, not thermal annealing, but rather recrystallization due to contact with water formed by partial sample decomposition.</p>		

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