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MERCURY RANKINE POWER CONVERSION PROGRAM (SNAP 2)

TOPICAL REPORT No. 35

MASTER

CORROSION PRODUCTS IN THE

SNAP 2/MRPCP

CRU V TEST SYSTEM

AEC RESEARCH AND DEVELOPMENT REPORT

Prepared under Subcontract AT(04-3)-690

for

Atomic Energy Commission

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By

R. C. SCHULZE
E. J. VARGO

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ABSTRACT

The results of a study of the mercury corrosion product problem in the MRP/SNAP 2 system are presented and discussed in this report. It was established in this study that the primary source of corrosion products in the system mercury was the boiler. High quality mercury vapor must be maintained in order to prevent the introduction of an inordinate amount of corrosion products into the turboalternator (CRU V) by liquid carryover.

Spectrographic analysis of hot mercury samples taken during operation was used to monitor the corrosion product level. Upon startup of a test the corrosion product level in the system mercury is relatively high. However, steady state operation soon produces a very low level of corrosion products in the liquid mercury. Careful control of system materials, vacuum integrity and cleanliness significantly reduce the corrosion product burden.

The characteristics of the corrosion product deposition in the vapor regions of the system vary from those found in the liquid region. The deposits in the former were metallic (Cr, Ni, Fe, and Co) and those which deposited in the liquid section were present as spinels (Fe_2O_3 and Me_3O_4). Electron microscopy, electron diffraction and electron beam microprobe techniques were used to evaluate the corrosion and corrosion products.

I INTRODUCTION

Corrosion product deposition in the CRU V has presented itself as a major system design problem. During the initial stages of CRU V development, the problem was not critical. However, as the test systems became more compact, problems associated with corrosion product deposition became more evident.

Table I presents a summary of CRU V operation and the effects of corrosion product deposition on operation. Of the twenty-six CRU V units operated, corrosion product deposition caused interruption during nine tests, and termination in two tests. Figure 1 shows a schematic of the CRU V detailing the areas of interest.

As shown in Table I, the majority of the test interruptions resulted in the reduction or loss of lubricant flow to the three CRU V bearings (turbine and alternator journal bearings, and the thrust bearing). This reduction in flow usually occurred through corrosion product deposition on:

- 1) The journal bearing bushing and sleeve surfaces causing a reduction in bearing clearance.
- 2) The bearing orifices causing a reduction in orifice cross sectional area.
- 3) The lubricant line filters (2 micron nominal - 18 micron absolute 1.5 inch² filtering surface).

In all three cases, the reduction of lubricant flow, through increased resistance, decreased the load carrying capacity of the bearings; and indicated a potential for failure through bearing seizure. During the CRU V test program, corrosion product deposition in the bearings and associated hardware has caused temporary shutdowns during testing. However, no CRU V failures have occurred as a result of corrosion product deposition in the bearings.

Another region associated with the loss of flow resulting from corrosion product deposition was the CRU V pump. In almost every CRU V pump operated traces of corrosion product deposition have been found. The effect of the deposition in general has been a minor loss in pumping capacity. The loss, however, has never been great enough to warrant corrective measures.

The other major CRU V region where corrosion product deposition effects have been felt is the vapor turbine region. The effects in this region have been twofold. As shown in Table I, the major effect has been the loss (temporary and permanent)

TABLE I CHRONOLOGICAL SUMMARY OF CORROSION PRODUCT EFFECTS IN CRU V MODULES

CRU V No.	Test System No.	Total CRU V Oper. Time (Hrs.)	No Of Corrosion Product Induced Shut-Downs	CRU V Performance Effects Resulting From Corrosion Product Deposition	Corrosion Product Deposition Observed At Disassembly
-1	4	27.6	0	None Noted	Slight amount of black powdery deposit on bearings, turbine nozzles and pump impeller.
-3	4	208.4	0	Decay in CRU efficiency. Increase in turbine and alternator bearing impedance.	None Reported
-2A	5	0	0	- - -	- -
-3A	5	0	0	- - -	- -
-4	5	2.6	0	None Noted	None Noted
-2B	5	438.7	1	Turbine bearing flow regulator plugged by deposits.	Heavy black powdery deposit on alternator bearing. Slight deposit on pump impeller.
-1A	4	2557.5	0	Decay in CRU efficiency. Increase in turbine bearing impedance.	Hard adherent metallic deposit on turbine nozzle. Light black powdery deposit on alternator bearing. Heavy black deposit on pump diffuser.
-5	3	860.7	2	Plugging of the turbine bearing flow regulator, jet pump and turbine bearing filter. Increase in alternator and turbine bearing impedance. Plugging of jet pump filter.	Black powdery deposit on the turbine and alternator bearings.
-3B	5	2049	2	Increase in the turbine and alternator bearing impedance. Plugging of bearing lube line filters.	Light black powdery deposit on the alternator and turbine bearings.

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(CONT'D) TABLE I CHRONOLOGICAL SUMMARY OF CORROSION PRODUCT EFFECTS IN CRU V MODULES

CRU V No.	Test System No.	Total CRU V Oper. Time (Hrs)	No of Corrosion Product Induced Shut-Downs	CRU V Performance Effects Resulting From Corrosion Product Deposition	Corrosion Product Deposition Observed At Disassembly
-4A	4	176.8	0	None Noted	None Noted
-2C	3	111.8	0	Increase in turbine and alternator bearing impedance.	Light black powdery deposit on turbine and alternator bearings.
-5A	3	135.5	0	None Noted	Light black powdery deposit on the alternator bearing and the pump impeller.
-4B	4	209.6	0	Decay in CRU efficiency.	Light black powdery deposit on the turbine nozzle vanes and the turbine bearing.
-2D	4 & 3	202.2		Decay in CRU efficiency after 101 hours operation in test system 4.	Slight black powdery deposit on the turbine nozzle, turbine and alternator bearings.
-3C	3	.5	0	None Noted	None Noted
-1B	5	3153.4	0	Decay in CRU efficiency	Hard adherent metallic deposit on turbine nozzles and light black powdery deposit on the alternator bearing.
-5B	4	1277.4	0	Decay in CRU efficiency	Light black powdery deposit on both alternator and turbine bearings.
-4C	3	55.9	0	- - -	- -
-3D	3 4	87.3 2412.7	2 2	No permanent effects. Plugging of thrust bearing filter. Increase in turbine bearing impedance.	Light black powdery deposit on the turbine and alternator bearings.
-1C	5	759.5	3	Increase in turbine and alternator bearing impedance.	Black powdery deposit on the alternator and turbine bearings.

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(CONT'D) TABLE I CHRONOLOGICAL SUMMARY OF CORROSION PRODUCT EFFECTS IN CRU V MODULES

CRU V No.	Test System No.	Total CRU V Oper. Time (Hrs)	No of Corrosion Product Induced Shut-Downs	CRU V Performance Effects Resulting From Corrosion Product Deposition	Corrosion Product Deposition Observed At Disassembly
-4D	4	408.6	0	None Noted	None Noted
	3	589.6	5	Increase in alternator and turbine bearing impedance.	Black powdery deposit on the alternator and turbine bearings. Heavy black deposits in the CRU pump.
-2E	3	20.5	2	Increase in turbine and alternator bearing impedance.	Heavy black powdery deposit in alternator and turbine bearings and CRU pump.
-1D	4	683.0	0	None Noted	Black powdery deposit on alternator and turbine bearings.
-5C	5	4767.2	1	Increase in turbine and alternator bear- ing impedance.	Black powdery deposit in alternator and turbine bearings.
-3E	3	3500	1	Turbine efficiency decreased because of corrosion product deposits.	Metallic spheres in turbine housing. Black powdery deposit in alternator and turbine bearings.
-4E	5	1100	0	Turbine efficiency decreased because of corrosion product deposits.	Metallic spheres in turbine housing. Black powdery deposit in alternator and turbine bearings.

CRU V

FIGURE 1 SCHEMATIC OF THE CRU V

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in turbine output power. This loss has resulted from corrosion product deposition on the turbine nozzles and vanes causing an increased resistance to vapor flow through the turbine. In the last two tests (CRU V-3E and CRU V-4E) deposition of corrosion products in the turbine caused power losses and was partly responsible for the termination of both tests.

During the early stages of the mercury power system development there was little indication of the problem of corrosion product deposition in CRU V operation. This was probably attributable to the breadboard type design of the test systems. These systems had a very large mercury inventory and also had several large sumps and reservoirs to contain the mercury. Because of this, the rate of mercury turnover was small and there were innumerable quiescent areas for the corrosion products to settle out and thus separate.

More recent test systems, by comparison, were quite compact, and were equipped with flight-type mercury boilers. In these test systems there was very little excess inventory of mercury. This resulted from shorter lines and the removal of sumps and reservoirs. Thus, since the turnover rate of mercury in such test systems was quite high, the corrosion products tended to be retained in circulation within the flowing mercury.

From the total test experience accumulated, the effects of corrosion product deposition have been varied. However, there appeared to be a general relation between corrosion product deposition and combined test system and CRU V sophistication. Undoubtedly, a significant part of this deposition was the result of test system induced problems (includes everything other than the CRU V module). The remainder is associated with the CRU V.

However, for a CRU V to operate in an integrated power system, the problem of corrosion product formation and deposition needed to be solved. The solution of the total problem depended upon answering several basic questions.

- 1) What is the tolerance limit of the various regions of the CRU V to corrosion product deposition?
- 2) How does the corrosion product level vary in the various parts of the total test system?
- 3) What are the characteristics of the corrosion products and how can they be controlled?
- 4) What is the tolerance limit of the various regions of the CRU V to corrosion product deposition?

A. TECHNICAL APPROACH

As a result of the above questions, a multi-faceted program was conducted to obtain the answers and eliminate corrosion product deposition as a potential failure mode. The areas of investigation included:

- 1) A study of the fundamental characteristics of corrosion products.

- 2) Monitoring of the CRU V test systems for the purpose of studying the composition, characteristics, concentration level and variation in concentration level as of function of time. Also, included in this phase was the metallurgical evaluation of the test system hardware for mercury corrosion and/or corrosion product deposition.

- 3) Examination of CRU V's after test to determine the location of corrosion product deposits, composition of the deposits and the type of deposit.

- 4) Post test examination of the Test Systems 3 and 5 flight type boilers for mercury corrosion and/or corrosion product deposition effects.

- 5) Monitoring of the test system and CRU V module filters during operation and post test evaluation of the filters to determine the effects of corrosion products on the filters.

- 6) A study of corrosion product separation and the development of potentially useful corrosion product separators.

These various phases were investigated concurrently; however, the approach and the results of each phase will be discussed separately.

II CORROSION PRODUCT PROPERTIES AND CHARACTERISTICS

The expression "corrosion product" as used in this report is the term applied to the contaminants found in a mercury Rankine system. These contaminants have been found in the mercury as solutes or suspensoids; or as deposits on the container walls of system components. The principal source of corrosion products in a mercury system is the leaching of susceptible elements from container materials by the mercury. The leaching is a result of the solubility which most elements have in liquid mercury to varying degrees. This solubility is temperature dependent as is, consequently, the corrosion rate. The corrosion rate for various materials of construction is given in Figure 2 in terms of weight loss per unit area per unit time as determined by laboratory tests. From these curves the corrosion product quantity may be estimated as a function of temperature for a time of one year.

The presence of corrosion products as dissolved in mercury does not necessarily constitute a problem in the performance of a Rankine system such as the MRPC. If the corrosion products present in the mercury remained in solution, they would be harmless. However, the solute contaminants can and do precipitate out resulting in heterogeneous particles of varying size and shape. It is the deposition of these particles that causes trouble in critical areas of rotating systems.

In the interest of clarity the definition of the terms which will be used in this report to describe the corrosion product particles found in mercury systems are presented below.

A. PARTICULATE MATTER PRESENT IN MERCURY

a) Ultimate Particle

The ultimate particle of a substance is the smallest state of subdivision which retains all the physical and chemical properties of the substance. For a crystalline substance the ultimate particle is normally an assembly of unit cells and approaches molecular dimensions.

b) Aggregate

An aggregate is a particle or an assembly of particles held together by strong inter- or intramolecular forces or atomic cohesive forces. The particles may be joined by metallic bonds, covalent bonds, ionic bonds or by much weaker van-der-Waals' forces or by mixtures of the various bond types. An aggregate is stable to normal handling.

FIGURE 2 CORROSION RATE OF SEVERAL ALLOYS IN MERCURY AS A FUNCTION OF TEMPERATURE

c) Agglomerate (Floc)

An agglomerate (or floc) is composed of two or more particles and/or aggregates held together by relatively weak cohesive forces. These cohesive forces may be coulombic (i.e., electrostatic, magnetic, or vand-der-Waals' forces). Agglomerates can be easily broken up by dispersion methods.

Dispersions of particles in a liquid are generally classified arbitrarily(1) into three states of subdivision as follows:

- True solutions - Particle diameter less than 10^{-3} microns (10^{-7} cm)
- Colloids - 10^{-3} micron to 2×10^{-1} micron diameter (10^{-7} to 2×10^{-5} cm)
- Suspensions - 2×10^{-1} micron diameter and over

Unlike true solutions, which are homogeneous, colloidal systems and suspensions are considered to be heterogeneous.

B. SOLUBILITY

The solubility of a metal in mercury (atomic dispersion or true solution) depends upon the electron configuration of the metal. The solubility of metals in mercury shows periodic variation with increase in atomic number.(2) The best solubility is shown by those metals which are nearest to mercury in the periodic system. One must, however, distinguish between real solubility and the apparent solubility of colloids. Furthermore, the formation and dissociation of mercury compounds also have an effect on real solubility.(3)

The solubility of several of the common alloying elements of constructional materials as determined by various investigators (3, 4, 5, 6, and 7) shows poor agreement. Nevertheless, it is indicated that element solubility is affected by the materials in contact with the mercury (Figure 3). For example, the solubility of chromium varies according to its presence as an element alone or as an alloying agent in L-605, L-605 plus Type 316 SS, and Type 316 SS. The same effect is found to be true for cobalt and for nickel solubility. Also, it appears that element solubility is affected by the presence of other metals.

C. COLLOIDAL DISPERSIONS

Colloidal dispersions may be stable over long periods of time. The stability of colloidal dispersion is due to extensive solvation. As a result of chemical and physical reaction the colloidal particle becomes encased in a sheath of solvent which acts as a barrier to contact with aggregates of the dispersed phase. By solvation the interfacial energy (surface energy) of the solid is reduced to that of the liquid. This removes the

FIGURE 3 SOLUBILITY OF CHROMIUM IN MERCURY AS A FUNCTION OF ALLOY AND INVESTIGATOR

1. Elemental Chromium (Ref. 3)
2. Elemental Chromium (Ref. 5)
3. Chromium in Type 316 Stainless Steel (Ref. 4)
4. Chromium in Bi-Metallic Type 316 Stainless Steel - L 605 System (Ref. 4)
5. Chromium in L-605 (Ref. 4)

incentive for flocculation and thus creates the stability of colloidal dispersions. The solubility of small particles of colloid sizes is greater than that of particles of larger dimensions, owing to the greater surface energy of the former.(8) As compared to the solubility of the colloid, the solubility of particles of atomic or molecular size (true solutions) is less. As a result, when corrosion products first enter the mercury, they are of atomic size and wetted by the mercury. However, because of the low solubility and corrosion kinetics, these particles grow by diffusion, aggregation and agglomeration into colloidal sized dispersions.

D. SEDIMENTATION

In a gravitational field or centrifugal force field, suspensions will separate until a state of equilibrium is reached whereby sedimentation and diffusion balance each other. The particles lighter than mercury will tend to concentrate near the top because of buoyancy. When a suspension is sufficiently dilute to prevent significant physical interaction between particles, the process of sedimentation conforms to Stokes' law. The complexities of shape are avoided by assigning to the particles the spherical shape. Accordingly, the radius of the particles is given by(1):

$$r = \left(\frac{9NU}{2(P-P')g} \right)^{1/2}$$

where r is the radius of the idealized spherical particle, N is the coefficient of viscosity of the fluid, U is the settling rate, P-P' is the difference in density between the particle and the fluid, and g is the acceleration of gravity.

E. GROWTH

Growth in particulate systems occurs by diffusion of atoms from surfaces of high energy (corresponding to a small radius of curvature) to surfaces of low energy (large radius of curvature). Small particles tend to dissolve and large particles tend to grow, thus increasing the average diameter of the particles. The growth kinetics of iron and cobalt particles in mercury has been studied by Luborsky(9, 10). He postulates that the growth may take place by accretion through the following sequence of steps: (1) atoms dissolve from the surface of the particles, (2) these atoms diffuse through the mercury; and finally, (3) these atoms deposit on another particle. The diffusion of the atoms through the mercury is assumed to be the rate-controlling step. He further concluded as a result of this work that the coagulation mechanism is not a major factor in the growth of these particles.

F. EFFECT OF OTHER METALS

A factor which strongly affects the problem of corrosion product separation is the extremely small size of the particle in mercury. These particles have been determined to be as small as 0.001 micron in size. Falk and Luborsky(11) have reported results of their work whereby the effect of a third metal on inhibiting the growth of small iron particles in mercury was revealed. These additives were classified according to whether they produced (1) negligible inhibition, (2) some inhibition, or (3) marked inhibition of the growth rate. Metal additives which resulted in a marked inhibition of iron particle growth are found to form a stable monolayer on the particles. Only those metals which may form intermetallic compounds were effective inhibitors. These included Sn, Mn, Zn, Al, Ti and Sb. Metal additives which resulted in no inhibitions of growth showed no evidence for adsorption, and could not form compounds with iron. These included Ag, Pb, Cr, Cd and Ba. The elements which had a small effect on iron-particle growth included In, Cu, Bi, Mo, As and Ni.

However, those elements such as Zn and Sn which inhibit particle growth may increase the tendency of the particles for agglomeration. For example, Rabinowitsch and Zywotinski(12) found that iron particles with Zn and Sn additives showed greater sedimentation rates. The true solution as such is only a temporary condition since the atoms will tend to deposit on larger particles and form colloids. The colloid solubility is much greater than that of the atom (true solution) as shown in Figure 3. Thus, the elements dissolved in mercury must be considered predominantly colloidal systems or suspensions(12, 13) since the true solubility is usually low for most alloying elements of constructional materials.

G. ARTIFICIAL CORROSION PRODUCTS

The study of the characteristics of the corrosion products found in the CRU V or test system is a complicated subject. Previous studies(13) have shown the presence of particles of varied physical appearance and size. As has been discussed, many factors affect the physical characteristics.

Because of these factors, a series of mercury solutions containing artificial corrosion products were prepared and studied under the electron microscope. These artificial corrosion products were prepared under controlled conditions by the electrodeposition of the metals chromium, cobalt, iron and nickel in mercury. Care was used to maintain a high level of purity. This care in purity was exercised because the presence of several metal elements as well as their compounds associated with mercury can affect the physical characteristics of the particles present.

Spectrographic analyses revealed only trace quantities of extraneous elements as listed in the table below:

<u>Major Corrosion Product Element</u>	<u>Impurities - PPM</u>
Co	Ni - 0.2
Cr	Fe - 0.02, Ni - 0.35
Fe	Ni - 0.02
Ni	Fe - 0.01, Co - 0.02

The mercury specimens containing the electrodeposited elements were exposed to ambient atmosphere in order to dewet the suspended particles by controlled oxidation and thus permit them to separate. These particles were separated from the mercury on a glass slide and coated with carbon for electron microscope replica examination. Representative electron photomicrographs of the corrosion product obtained by this means are presented in Figures 4, 5 and 6. These photomicrographs include one which represents the particles separated from as-received mercury which was reported to contain only iron as an impurity at a level of 0.02 ppm.

Evaluation of each of the samples was made on the basis of:

- 1) Size of individual particle
- 2) Shape of individual particle
- 3) Presence of agglomerations
- 4) Size of agglomerations

The results are tabulated and listed in Table II.

It was noted that both iron and nickel were found to be present only as spherical particles, whereas the cobalt and chromium contaminants in mercury were present in two particle configurations, spherical and platelet. The sub-micron size of the spherically shaped particles contrasts very significantly with the size of the platelet (essentially two dimensional). These data and observations were used as tools to aid in the identification and study of the typical corrosion product found in the mercury sampled from test systems.

A. IRON-MERCURY SYSTEM

6000 X

B. NICKEL-MERCURY SYSTEM

6000 X

FIGURE 4 ELECTRON PHOTOMICROGRAPHS SHOWING TYPICAL PARTICLES FOUND IN THE IRON-MERCURY (A), AND NICKEL MERCURY (B) SYSTEMS

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A. COBALT-MERCURY SYSTEM

6000 X

B. CHROMIUM-MERCURY SYSTEM

6000 X

FIGURE 5 ELECTRON PHOTOMICROGRAPH SHOWING TYPICAL PARTICLES FOUND IN THE COBALT-MERCURY AND CHROMIUM MERCURY SYSTEMS

6000 X
03336

FIGURE 6 ELECTRON MICROGRAPH SHOWING THE PARTICLES FOUND IN THE AS-RECEIVED MERCURY

TABLE II CHARACTERISTICS OF CORROSION PRODUCT TYPE
CONTAMINANTS PREPARED BY ELECTRODEPOSITION

Type	Particle Configuration	Individual Particle Size <u>-u-</u>	Size Distribution <u>-u-</u>	Agglomeration	Size of Agglomeration <u>-u-</u>	Impurities ppm
1. As received Hg	spherical	0.5 dia.	uniform	none	--	Fe-0.02
2. Fe-Hg	roughly spherical	0.05 to 2.0	majority < 0.25	yes	4	Ni-0.02
3. Ni-Hg	spherical	0.05 to 1.0	majority < 1.0	yes	1 to 4	Fe-0.01 Co-0.02
4. Co-Hg	spherical platelets	0.05 to 0.5 3.0 to > 5.0 by < 1.0 thickness	majority < 0.1	yes	3.5 to < 5.0	Ni-0.02
5. Cr-Hg	spherical platelet	0.05 to 1.0 6.0 to 13 by < 1.0 thickness	majority < 0.25	yes	very massive	Fe-0.02 Ni-0.35

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III RESULTS

The need for hot mercury sampling was recognized during the earlier phases of test system operation. After exploring the feasibility, it was determined that hot mercury sampling could be employed in the liquid mercury portion of the test system during CRU V operation. The development of the sampling and the analytical techniques have been reported previously.(8)

In addition to hot sampling of the liquid mercury, provisions were included in several boiler tests to obtain samples of the mercury vapor exiting the boiler. However, sampling of the hot mercury vapor was not extended to CRU V testing, because it was feared that the sampling ports could cause unnecessary perturbations in the CRU V turbine.

The other segment of test system monitoring was the examination of test system components when made available. This examination included visual and metallographic examinations for the presence of mercury corrosion effects or corrosion product deposits.

A. TEST SYSTEM MONITORING

The problem of corrosion products affecting the operation of CRU V in the test systems prompted the need for acquiring more knowledge of mercury corrosion occurring in the test systems and the distribution of corrosion products during and after test. In order to satisfy this need, provisions were incorporated in the test system plumbing to obtain mercury samples during system operation. The specific purpose of hot sampling the system mercury during operation was to determine the following:

- a) The corrosion product burden as a function of time.
- b) The chemical composition of the corrosion product present in the mercury.
- c) The effectiveness of the various corrosion product control devices.

In addition, various plumbing components of the modified Test Systems 3 and 5 (L-605 material) were examined for mercury corrosion and corrosion product deposition after the CRU V-3E and -4E test operations.

B. TEST SYSTEM CHEMISTRY

Sampling ports were established in the modified test systems at the condenser outlet, after the corrosion product separator,

and at the intermediate filter outlet. (See Figures 10 and 21) The sample obtained from the latter port was considered to be closely representative of the mercury entering the lubrication system of the CRU V.

Samples were taken at frequent intervals at the beginning of each run. These were at the 1, 24, 48, 100 and 200 hour mark. Thereafter, samples were taken at intervals of about 250 hours for the balance of the test.

Sample size varied between 0.5 to 2.0 pounds. The temperature of the mercury was at least 350°F at the sampling ports. An argon cover was used to protect the hot mercury from oxidation during and after the sampling operation.

Analysis of the samples was made by spectrographic techniques. The corrosion product present in the mercury sample was carefully separated by oxidation, dewetting and filtration. The filtrate was sparked on the spectrograph. All results were based on the total weight of the sample.

The spectrographic analysis of the mercury samples revealed contaminant contents which were usually at the level of less than one ppm regardless of the sampling location. However, of the three locations the condenser discharge revealed less contaminant content than the intermediate filter outlet and the gravity-magnetic separator discharge in that order. Obviously, the cleanliness of the mercury discharging from the intermediate filter is most important to the CRU V operation. Also, since the chemistry of these post-intermediate filter samples are the most representative of the mercury contamination only these results are presented in tabular form (Tables III and IV) and plotted in Figures 7 and 8.

As indicated, the contaminant level of a system fabricated principally of Type 316 SS is slightly greater than the one built of L-605 material. Of equal significance is the dominating presence of iron as a contaminant regardless of the test system container metal, Type 316 SS an iron base alloy or L-605 a cobalt base alloy. This persistent presence of iron as a principle contaminant was true also for the samples taken elsewhere from the system during CRU V operation.

The other elements present in the mercury samples were nickel and chromium in both the Type 316 SS and L-605 test systems. The infrequent presence of cobalt, silicon, manganese and molybdenum was noted.

The plots of the total corrosion product present in the samples collected at the outlet side of the intermediate filter illustrates the initial surge of the corrosion product level upon startup of a CRU V, particularly when the mercury has been replaced in the system. This surge is shortly followed by a

TABLE III SPECTROGRAPHIC ANALYSES OF TEST CELL 3 MERCURY SAMPLES
REMOVED DURING CRU V-3E TESTING AT INTERMEDIATE FILTER OUTLET

Run No.	Oper. Time (hr)	Acc. Oper. Time (hr)	Total Metallic Impurity	Spectrographic Analysis (ppm)								
				Fe	Ni	Cr	Co	Ti	V	Mn	Mo	Si
5	0(1)	0	0.118	0.068	0.015	-	-	0.025	0.010	-	-	-
5	1	1	0.195	0.125	0.070	-	-	-	-	-	-	-
5	50	50	0.210	0.150	0.050	0.010	-	-	-	-	-	-
7	0(2)	99	0.161	0.080	0.080	0.001	-	-	-	-	-	-
9	0(3)	120	0.186	0.080	0.080	0.010	-	-	-	-	0.008	0.008
9	1	121	0.035	0.035	-	-	-	-	-	-	-	-
9	50	171	0.030	0.030	-	-	-	-	-	-	-	-
9	100	221	0.232	0.125	0.062	0.031	-	-	-	0.001	0.001	0.012
9	275	395	0.020	0.020	-	-	-	-	-	-	-	-
9	790	910	0.050	0.040	-	-	-	-	-	-	-	0.010
9	880	1000	0.035	0.030	0.005	-	-	-	-	-	-	-
9	1460	1580	0.020	0.015	0.005	-	-	-	-	-	-	-
9	1954	2074	0.039	0.037	0.002	-	-	-	-	-	-	-
9	2033	2153	0.037	0.025	0.010	.002	-	-	-	-	-	-
9	2290	2420	0.010	0.010	-	-	-	-	-	-	-	-
11	1	2591	0.005	0.003	0.002	-	-	-	-	-	-	-

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(Cont'd) TABLE III SPECTROGRAPHIC ANALYSES OF TEST CELL 3 MERCURY SAMPLES
REMOVED DURING CRU V-3E TESTING AT INTERMEDIATE FILTER OUTLET

Run No.	Oper. Time (hr)	Acc. Oper Time (hr)	Total Metallic Impurity	Spectrographic Analysis (ppm)								
				Fe	Ni	Cr	Co	Ti	V	Mn	Mo	Si
11	96.5	2686	0.015	.010	.005	-	-	-	-	-	-	-
11	412	3002	0.150	.015	.135	T	-	-	-	-	-	-
11	619	3209	0.025	.025	T	-	-	-	-	-	-	-
11	508	3098	0.032	.012	.020	-	-	-	-	-	-	-
11	675	3265	0.001	T	.001	-	-	-	-	-	-	-
13	2	3268	0.035	.035	T	-	-	-	-	-	-	-
13	22	3288	0.030	.030	-	-	-	-	-	-	-	-
13	140	3406	0.113	.075	.025	.010	.003	-	-	-	-	-
13	233	3499	0.010	.010	-	-	-	-	-	-	-	-

- (1) Sample taken just prior to startup of run No. 5.
(2) Sample taken just prior to run No. 7.
(3) Sample taken just prior to run No. 9.

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TABLE IV SPECTROGRAPHIC ANALYSES OF TEST SYSTEM 5 MERCURY SAMPLES
REMOVED DURING CRU V-4E TESTING AT INTERMEDIATE FILTER OUTLET

Run No.	Oper Time (Hrs)	Acc Oper Time (Hrs)	Total Metallic Impurity	<u>Spectrographic Analysis (ppm)</u>			
				<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Co</u>
4	15	15	.016	.010	.006	T	-
6	0.5	58	.010	.010	-	-	-
6	6.0	64	.010	.010	-	-	-
6	97.0	155	.010	.010	-	-	-
10	1	172	.006	.006	-	-	-
10	12	183	.005	.005	-	-	-
10	50	221	.040	.025	.015	-	-
10	121	292	.012	.012	-	-	-
10	368	539	.005	.005	-	-	-
10	543	724	.020	.020	-	-	-
14	5.5	894.5	.024	.022	.002	-	-
14	28.5	917.5	.034	.033	-	.001	-
14	101.8	990.8	.024	.024	-	-	-
14	211	1100	.013	.011	.002	-	-

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FIGURE 7 TOTAL CORROSION PRODUCT CONTENT PRESENT IN THE MERCURY
(INTERMEDIATE FILTER OUTLET) DURING CRU V-3E AND
CRU V-5C TESTS

FIGURE 8 TOTAL CORROSION PRODUCT CONTENT PRESENT IN THE MERCURY (INTERMEDIATE FILTER OUTLET) DURING CRU V-4E TEST

decline to a relatively low plateau. The plots of the CRU V-4E illustrate this tendency. Each of the startups after a hot flush and drain resulted in this spike. A similar surge occurred with the CRU V-3E-13 test. Prior to this latter test the entire system mercury had been replaced.

The absolute acme of the corrosion produce concentration or "time-after-start" of same cannot be determined with the batch type sampling techniques used. The data obtained merely indicate the existence of the initial spike as illustrated.

After several hundred hours of operation the corrosion product content in the liquid mercury leveled out to about 0.06, 0.02, and 0.01 ppm for the CRU V-5C, CRU V-3E and CRU V-4E tests respectively. Apparently, a condition of equilibration of corrosion product in the mercury is attained since these values are approaching the limits of solubility of iron, nickel, chromium, etc., in mercury at 400°F. (3, 4, 5)

The differences in the equilibration levels of the mercury as indicated in the plots of the CRU V-5C, 3E, and 4E corrosion product data may be the result of the effect caused by the system construction materials, the system mercury inventory, the vacuum integrity of the system, the system configuration and the operating temperatures.

C. TEST SYSTEM METALLURGICAL EXAMINATION

1. Type 316 Stainless Steel Test Systems

Following the 5C-8A boiler test in Test Cell 3 and CRU V-5C operation in Test Cell 5, both test systems were completely dismantled for modification and improvement. The purpose of this activity was to replace the Type 316 stainless steel with L-605 material and to improve the test system integrity and reliability. During the dismantling of both test systems, segments of the plumbing were retained for metallurgical analysis. This analysis was conducted to determine the presence of corrosive attack and/or deposition of corrosion products in the test system hardware.

The plumbing segments that were examined from test systems were as follows:

<u>Test System 3</u>	<u>Test System 5</u>
1) Boiler Inlet Line	1) Boiler Inlet
2) Boiler Discharge Line	2) Boiler Discharge
3) Condenser Sump	3) CRU Discharge Line
4) Condenser Discharge Filter	4) Condenser Inlet Line

5) Condenser Discharge Filter Line	5) Condenser Sump Discharge
6) Simulated Bearing Lube Line (used during 5C-8A boiler tests, runs 12 through 17)	6) CRU Can Drain Lines
	7) Bearing Drain Lines
	8) Regulator Tank Drain Line

The specific regions examined are listed in Tables V and VI along with the results obtained from the metallographic examination of the various Type 316 stainless steel tube sections. These regions are indicated in Figure 9. In general, all the tube sections examined suffered corrosive attack. No deposition was noted.

For most of the tube sections, corrosion penetration was generally much lower than anticipated from laboratory tests.

The presence of corrosive attack in the boiler discharge line indicates that there was some liquid mercury present with the vapor in this region. Results of laboratory tests have shown that dry mercury vapor alone is noncorrosive.(14)

2. L-605 System

Following the operation of the CRU V-3E in Test System 3 and CRU V-4E in Test System 5, both test systems were completely dismantled. During the dismantling of both systems, the various plumbing segments were visually and microscopically examined. This examination was conducted to determine the presence of corrosive attack and/or deposition of corrosion products in the test system hardware.

a. Test System 3

The test system plumbing segments from Test System 3 which were examined included:

- 1) Turbine Inlet Line
- 2) Turbine Discharge Line
- 3) Condenser
- 4) Condenser Sump
- 5) Heat Exchanger
- 6) Accumulator Tank

TABLE V RESULTS OBTAINED FROM METALLOGRAPHIC EXAMINATION OF SPECIMENS
REMOVED FROM VARIOUS REGIONS OF TEST SYSTEM 3 PLUMBING
(MATERIAL - TYPE 316 STAINLESS STEEL)

Section	Specimen	Location	Approx. Oper. Temp. (°F)	Exposure Time (Hr)	Approx. Hg Flow Rate (lb/min)	Hg * Phase	Max. Corrosion Penetration (in.)	Attack Mode
a	1	Boiler Inlet	500	1039	20	L	.0011	Layer and crevice
b	2	Boiler Discharge	1100	1039	20	V	.001	Layer and crevice
c	3	Condenser Sump	600	1039	20	V	.0005	Crevice and wedge
	4	Condenser Sump	600	1039	20	L	.0003	Crevice and wedge
d	5	Condenser Discharge Filter Inlet Tube	400	1127	20	L	.0003	Crevice and wedge
e	6	Condenser Discharge Filter Outlet Tube	400	1127	20	L	.001	Crevice and wedge
f	7	Simulated Bearing** Lube Line	400	106	20-25	L	.0006	Crevice and wedge

* Hg Phase; V-Vapor, L-Liquid

** During the 5C-8A Boiler Test (Runs 12 Thru 17) this line was installed to mock-up the plumbing required for the CRU. Figure 2 shows the placement of this tubing.

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TABLE VI RESULTS OBTAINED FROM METALLOGRAPHIC EXAMINATION
OF SPECIMENS REMOVED FROM TEST SYSTEM 5 PLUMBING (TYPE 316 STAINLESS STEEL)

Region	Specimen	Location	Material	Approx. Oper. Temp. (°F)	Exposure Time (Hr)	Approx. Hg Flow Rate (lb/min)	Hg* State	Max. Corrosive Penetration (in.)	Attack Mode	Comments
a	1	Boiler Inlet	316 SS	440	4770	20	L	0.0001	Crevice	Very scattered attack
	2	Boiler Discharge	316 SS	1170	4770	20	V	0.0002	Crevice	Scattered attack
b	3	Turbine Inlet	316 SS	1150	4770	20	V	0.0002	Crevice	Uniform attack
	4	Turbine Exhaust	316 SS	640	5530	20	V	0.0002	Pitting & Crevice	Uniform attack
c	5	Exhaust Nozzle Discharge	17-4 PH	630	5530	20	V	0.0002	Pitting	Scattered attack
	6	Condenser Inlet	316 SS	630	5530	20	V	0.0005	Crevice	Heavy uniform attack
d	7	Cond. No. 1 Tube	L-605	600+	5530	20	V+L	0.0005	Crevice	Scattered attack
	8	Cond. No. 2 Tube	L-605	600+	5530	20	V+L	0.0005	Crevice	Scattered attack
	9	Cond. Lower Man	316 SS	600+	5530	20	V+L	0.0003	Crevice	Scattered attack
e	10	Top Condenser Sump	316 SS	600	5530	20	V+L	0.0011	Crevice	Uniform and heavy
	11	Bottom Cond. Sump	316 SS	600	5530	20	L	0.0001	Crevice	Uniform attack
	12	Cond. Sump Discharge	316 SS	535	5530	20	L	0.0003	Crevice	Scattered attack
f	13	Can Drain - Pump End	316 SS	625	5530	-	L	0.0002	Crevice	Scattered attack
	14	Can Drain - Turbine End	316 SS	630	5530	-	L	0.0004	Crevice	Scattered attack

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(CONT'D) TABLE VI RESULTS OBTAINED FROM METALLOGRAPHIC EXAMINATION
OF SPECIMENS REMOVED FROM TEST SYSTEM 5 PLUMBING (TYPE 316 STAINLESS STEEL)

Region	Specimen	Location	Material	Approx. Oper Temp. (°F)	Exposure Time (Hr)	Approx. Hg Flow Rate (lb/min)	Hg* State	Max. Corrosive Penetration (in.)	Attack Mode	Comments
f	15	Combined Can Drain	316 SS	625	5530	.8	L	0.0003	Crevice	Very scattered attack
	16	Alt. & Thrust Brg. Drain	316 SS	470	5530	17	L	0.0002	Crevice	Uniform attack
g	17	Turbine Brg. Drain	316 SS	585	5530	7.5	L	0.0002	Crevice	More intense than (16)
	18	Combined Brg. Drain	316 SS	400	5530	24.5	L	0.0005	Crevice	Uniform attack
h	19	Reg. Tank Discharge	316 SS	310	5530	25.3	L	0.0002	Crevice	Uniform attack

* V - Vapor
L - Liquid

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TABLE VII RESULTS OBTAINED FROM METALLUGRAPHIC EXAMINATION OF
SPECIMENS REMOVED FROM TEST SYSTEM 3 PLUMBING (MATERIAL L-605)
AFTER CRU V-3E OPERATION

Component	Location	Approx. Oper. Temp. (°F)	Mercury State	Corrosive Attack		Deposition (In)	Remarks
				Max. Penetration (In)	Attack Mode		
Turbine Inlet	2 ft. down stream	1150	V	.0006	Inter.	None	-
Turbine Inlet	"J" Tube	1150	V	None .001	- Erosion	Deposit	Corrosion & Deposition (See Figure 12)
Turbine Exhaust	Upper Leg	630	V	None	-	Deposit	Black powdery deposit, unable to obtain a thickness
Condenser	Upper Header Tube	626	V	.0006	Layer	-	Non-wetted surface
		626	V & L	<.0001	Pitting	-	Wetted surface
		626	V & L	<.0001	Pitting	-	Wetted surface
	Lower Header Sump	626	L	.0004	Layer	-	Wetted surface
		600	L	<.0002	Pitting & Crevice	Deposit	Loosly adherent powdery deposit at the liquid- vapor interface
Heat Exchanger	Inner Tube (Bearing Flow Return Line)	450	L	<.0001	Pitting	-	-
Accumulator Tank		375	L	.001	Inter.	-	-
Regulator Tank		143	L	<.0001	Pitting	-	-
Magnetic-Gravity Separator		360	L	.003	Layer	-	Corrosion found on ALNICO V magnet, magnet was wetted.
Bearing Lube Inlet Manifold		350	L	None	-	-	Specimen examined was up stream of the turbine bearing line

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FIGURE 9 TEST SYSTEM 3 AND 5 (TYPE 316 SS) SCHEMATIC SHOWING THE LOCATIONS WHERE SAMPLES WERE REMOVED FOR METALLOGRAPHIC EXAMINATION

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- 7) Regulator Tank
- 8) Gravity-Magnetic Separator
- 9) Bearing Lube Manifold
- 10) Various Test System Filters

The specific regions examined are listed in Table VII along with the results of visual and microscopic examinations. These regions are indicated in Figure 10. The results obtained from the examinations of the above plumbing segments are as follows:

(1) Turbine Inlet Line

The entire length (7 feet) of the turbine inlet line was cut into 14 sections of from 4 to 8 inches in length. After metallographic samples were taken from each, the tube sections were cut longitudinally and the exposed inside diameter surfaces were examined visually. No wetting was observed (Figure 11). However, in one section immediately before entering the turbine housing a deposit was observed at a 90 degree bend (Figure 12). Although some erosion also may be present the dominant characteristic of this surface at the bend was the deposit illustrated in Figure 13. This deposit had a maximum thickness of 5.0 mils. Mercury corrosion to a depth of 0.6 mil was noted only in an area 2 feet from the boiler exit.

(2) Turbine Exhaust Line

The examination of this component did not reveal any deleterious effect of mercury. However, a slight amount of black corrosion product deposit was noted as illustrated in Figure 14.

(3) Test System Condenser

The condenser, which was fabricated of L-605 sheet, was dissected and examined visually before samples were cut for metallographic examination. Wetting was noted in both the top and bottom headers (See Figure 15) as well as the condenser tubes and sump (Figures 16 and 17 respectively). In addition a loosely adherent black corrosion product deposit was noted along the wall at the liquid/vapor interface of the sump.

Metallographic examination of samples cut from the wetted portions of the condenser revealed corrosive penetration of from less than 0.1 to a maximum of 0.6 mil. The maximum corrosion was noted in the upper header and revealed itself as a layer type, Figure 18. The results of the metallographic examination are listed in detail in Table VII.

(4) Accumulator Tank and Regulator Tank

The accumulator tank exhibited intergranular mercury corrosion damage to a depth of 1.0 mil although the inlet and outlet tube only had 0.2 mil penetration. The regulator tank and its outlet line revealed very little corrosion effect. The penetration was less than 0.1 mil.

(5) Mercury Lubrication System

Metallographic examination of several portions of the CRU V mercury lubrication system was made. A sample of the lube manifold just upstream of the turbine bearing line revealed no detectable corrosion. The heat exchanger (inner tube) indicated a slight amount of pitting with penetration of less than 0.1 mil. However, examination of the Modified Gravity-Magnetic separator magnet revealed corrosion attack of the layer type (Figure 19) to a depth of 3.0 mils. The permanent magnet is cast Alnico V which has a nominal composition of 8Al, 14 Ni, 24 Co, 3 Cu, balance Fe.

Based on 3850 hours of operation of Test System 3, which includes both the CRU V-3E and the 5C-8B boiler tests, the parabolic penetration rate constant for this corrosive attack of the Alnico V magnet at 500°F is 0.002 mils²/hr. This would indicate a lower resistance to mercury corrosion than that indicated for the similar alloy Alnico VI.(15). Apparently, variations in composition due to segregation in the cast material may cause such an anomaly or else the original laboratory data obtained from short time bent reflux tube capsule tests were inadequate.

(6) Auxiliary Pump

The auxiliary pump used in Test System 3 for the period November 5, 1966 to July 18, 1967, was dismantled. The mercury wetted surfaces of this component's interior were the rotor, end plate, and both front and rear bearing housings. A light black surface deposit was present on the impeller. Analysis of this black powder revealed that the metallic elements iron, chromium, cobalt and nickel were present in near equal quantities. Only traces of other metallic elements were noted.

Transmission electron photomicrographs, Figure 20, reveal that the corrosion product deposit consisted of agglomerations of round particles less than 0.1 micron in diameter.

b. Test System 5

The Test System No. 5 plumbing segments which were examined included:

- 1) Turbine Inlet Line
- 2) Turbine Discharge Line

P - PHOTOGRAPHY
C - CHEMISTRY
M - METALOG.
V - VISUAL
M.E. - METALLURGICAL EVAL.

TEST CELL #3 , SYSTEM SCHEMATIC

FIGURE 10. TEST SYSTEM 3 (L 605) SCHEMATIC SHOWING THE LOCATIONS WHERE SAMPLES WERE REMOVED FOR EXAMINATION.

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FIGURE 11 PHOTOGRAPH SHOWING THE CONDITION OF THE ID SURFACE OF THE TURBINE INLET LINE (CRU V-3E)

07-270

MERCURY FLOW →

FIGURE 12 MACROGRAPH SHOWING THE PRESENCE OF THE DEPOSIT AND EROSION
FOUND IN THE 'J' TUBE FROM TEST SYSTEM 3

MAGNIFICATION: 2X

B-4781

FIGURE 13 DEPOSIT FOUND IN THE 'J' TUBE FROM TEST SYSTEM 3

MAGNIFICATION: 250X ETCHANT: NONE

FIGURE 14 PHOTOGRAPH SHOWING THE APPEARANCE OF THE ID SURFACE OF THE TEST SYSTEM 3 CRU V-3E
TURBINE EXHAUST LINE

FIGURE 15 PHOTOGRAPH SHOWING THE MERCURY WETTED REGION FOUND ON THE INSIDE OF THE LOWER CONDENSER HEADER FROM TEST SYSTEM 3 AFTER CRU V-3E OPERATION

FIGURE 16 PHOTOGRAPH SHOWING THE MERCURY WETTED REGION FOUND ON THE ID SURFACE OF ONE OF THE TWO TEST SYSTEM 3 CONDENSER TUBES (CRU V 3E TEST)

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FIGURE 17 PHOTOGRAPH SHOWING THE MERCURY WETTED REGION FOUND ALONG THE ID SURFACES OF THE CONDENSER SUMP OF TEST SYSTEM 3 AFTER CRU V-3E OPERATION

B-4878

FIGURE 18 LAYER CORROSION FOUND IN THE UPPER HEADER OF THE
CONDENSER OF TEST SYSTEM 3 AFTER CRU V-3E OPERATION

MAGNIFICATION: 250X

ETCHANT: NONE

3.0 MILS

B-4777

FIGURE 19 LAYER CORROSION FOUND ON THE ALNICO V MAGNET FROM THE GRAVITY-MAGNETIC SEPARATOR USED IN TEST SYSTEM 3 DURING CRU V-3E TESTING

MAGNIFICATION: 100X

ETCHANT: NONE

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04883

04884

FIGURE 20 ELECTRON TRANSMISSION PHOTOMICROGRAPH SHOWING TYPICAL CORROSION PRODUCT PARTICLES
FOUND IN THE MERCURY FROM TEST SYSTEM 3 AUXILIARY PUMP AFTER CRU V-3E OPERATION

MAGNIFICATION: 10,000X

- 3) Condenser
- 4) Condenser Sump
- 5) Heat Exchanger
- 6) Regulator Tank
- 7) Gravity-Magnetic Separator
- 8) Bearing Lube Manifold
- 9) Various Test System Filters

The specific regions examined are listed in Table VIII along with the results of visual and microscopic examinations. These regions are indicated in Figure 21. The results obtained from the examinations are as follows:

(1) Turbine Inlet Line

In a manner similar to Test System 3, the entire length (7 feet) of the turbine inlet line was cut into 14 sections of from 4 to 8 inches in length. After metallographic specimens were removed from each tube, the tube sections were cut longitudinally and the exposed inside diameter surfaces were examined visually.

There was no evidence of mercury wetting or deposition along the I.D. surface, as illustrated in Figure 22. Metallographic examination revealed the presence of a light corrosive attack to the surface. The corrosion in the form of crevice, pitting and intergranular attack varied in depth from 0.1 mil up to a maximum of 0.8 mil. The greatest depth occurred in a region approximately 3 to 4 feet away from the boiler exit.

(2) Turbine Exhaust Line

The examination of this component did not reveal any gross mercury effects. Examination of the lower leg, however, did reveal the presence of a light black powdery corrosion product deposit as shown in Figure 23. Metallographic examination of specimens removed from the turbine exhaust line revealed a crevice type of corrosion attack of 0.2 mil.

(3) Condenser

The condenser, fabricated of L-605 sheet, was sectioned and visually examined before samples were removed for metallurgical examination. Mercury wetting was noted only in the lower halves of the condenser tubes and the bottom plate of the lower condenser header. A light black powdery corrosion product deposit was found along the I.D. surfaces in the upper half of both condenser tubes. Figure 24 illustrates the condition of the

TEST CELL #5 - SYSTEM SCHEMATIC

C - CHEMISTRY
V - VISUAL
M - METALOG.
P - PHOTOGRAPHY
M.E. - METALLURGICAL EVAL.

NOTE: ALL TUBING LINES L 605

FIGURE 21. TEST SYSTEM 5 SCHEMATIC SHOWING THE LOCATIONS WHERE SAMPLES WERE REMOVED FOR EXAMINATION.

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TABLE VIII RESULTS OBTAINED FROM METALLOGRAPHIC EXAMINATION OF
SPECIMENS REMOVED FROM TEST SYSTEM 5 PLUMBING (L - 605) AFTER
CRU V-4E OPERATION

Component	Location	Approx. Oper. Temp. (°F)	Mercury State	Corrosive Attack			Remarks
				Max. Penetration (In.)	Attack Mode	Deposition (In.)	
Turbine Inlet	2 ft. from boiler	1150	V	.0008	Inter.	None	-
	"J" Tube	1150	V	.0001	Pitting	None	-
Turbine Exhaust	-	640	V	.0002	Crevice	Deposit	Black powdery deposit, too thin & scattered to measure.
Condenser	Upper Header	625	V	None	-	None	-
	Tube	625	V&L	.0002	Crevice	None	Non wetted surface
			V&L	.0005	Crevice	Deposit	Wetted surface - Black powdery deposit present
	Lower Header	625	L	.0008	Crevice	-	-
	Sump	600	L	.0012	Layer	-	Wetted surface
			L	.0005	-	Deposit	Non wetted surface - Loose black powdery deposit present.
Heat Exchanger	-	450	L	.0006	Crevice	-	-
Regulator Tank	-	150	L	None	-	-	-
Magnetic-Gravity Separator	-	350	L	None	-	-	-
Bearing Lube Inlet Manifold	-	350	L	None	-	-	-

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FIGURE 22 PHOTOGRAPH SHOWING THE CONDITION OF THE ID SURFACES OF TEST
SYSTEM 5 TURBINE INLET LINE AFTER CRU V-4E OPERATION

FIGURE 23 PHOTOGRAPH SHOWING THE CONDITION OF THE ID SURFACES OF THE TEST
SYSTEM 5 TURBINE EXHAUST LINE AFTER CRU V-4E OPERATION

FIGURE 24 PHOTOGRAPH SHOWING THE CONDITION OF THE ID SURFACES OF ONE OF THE TEST SYSTEM 5 CONDENSER TUBES AFTER CRU V-4E OPERATION

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condenser tube surface.

Metallographic examination of samples cut from the wetted portions of the condenser tubes revealed a maximum corrosive penetration of 0.5 mil. The greatest depth of attack was found in the wetted region along the bottom surface of the lower condenser header. The penetration in the form of crevice attack occurred to a depth of 0.8 mil.

(5) Condenser Sump

Visual examination of the condenser sump revealed the presence of considerable mercury wetting of the top I.D. surface. A very light, black powdery corrosion product deposit was found on the unwetted surfaces of the condenser sump. Figure 25 illustrates the condition of the I.D. surfaces. Metallographic examination of specimens removed from the condenser sump revealed varied amount of corrosive attack. At the top of the sump, in the wetted region, a corrosive penetration in the form of layer attack was found to a maximum depth of 1.2 mil. At the bottom of the sump in the unwetted regions, layer and intergranular attack was found to a maximum depth of 0.5 mil.

(5) Regulator Tank

Visual examination revealed the inside surfaces to be clean. No metallographic samples were removed from this component.

(6) Mercury Lubrication System

Metallographic examinations were made of several of the CRU mercury lubrication system components. A sample from the mercury lubricant manifold revealed no detectable corrosion. The heat exchanger (inner tube) suffered mercury attack to a maximum depth of 0.6 mil. The corrosion found was in the form of crevice attack. No significant evidence of corrosion product deposits or evidence of mercury attack were found in the Gravity-Magnetic Separator.

D. CRU V EVALUATION

Throughout the CRU V program, post test analysis of the CRU V's have shown the presence of mercury corrosion product deposits in both the liquid and vapor regions. The location of the deposits has usually been uniform, but the amount, composition and physical characteristics of the deposits varied.

The CRU V regions most affected by corrosion products have been:

- 1) The turbine, nozzles and vanes

FIGURE 25 PHOTOGRAPH SHOWING THE CONDITION OF THE ID SURFACES OF THE CONDENSER
SUMP OF TEST SYSTEM 5 AFTER CRU V-4E OPERATION

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- 2) The CRU V pump
- 3) Flow regulators and restrictors
- 4) Bearings

In general, the type of corrosion product deposit found depended upon the CRU V region. In the liquid regions of the CRU V such as the pump, the bearings and the flow regulators and restrictors, the deposits were loosely adherent and partially wetted with mercury. The deposits in the pump and flow regulators and restrictors tended to be more powdery than the deposits found on the bearings. The deposits on the bearing journal and bushing surfaces were usually more dense and tightly adherent, which probably resulted from the mercury flow conditions present in the bearings.

Because of these generalizations on CRU V operation, the CRU V hardware was routinely examined after each test. In earlier tests the examination included visual examination, notation of the location and measurement of corrosion product deposition thickness. And, if possible, semi-quantitative spectrographic analyses were made on specimens of the deposit. However, starting with the units CRU V-4D and continuing through with the CRU V-5C, -2E, -1D, -3E, and -4E, the corrosion product deposits were studied more thoroughly through the use of:

- 1) Electron microscopy for,
 - a) Particle configuration, and
 - b) Particle size
- 2) Electron beam microprobe analysis for,
 - a) Composition
- 3) Selected area electron diffraction for,
 - a) Compound identification

The various deposits were prepared for analysis by: 1) stripping the particles from the bearing with thick films of nitrocellulose, 2) vapor depositing a thin film of carbon normal to the surface, and 3) dissolving the plastic to leave the particles on a thin carbon supporting film.

1. CRU V Visual Examination

The depth of deposits found in the various regions of the CRU V varied. In the CRU V pump the deposits varied from 0.1 mil to 0.4 mil. This included the impeller, the impeller housing and the pump diffuser and collector. In the bearings, the deposits

varied from 0.1 mil up to 0.6 mil on both the journal and bushing surfaces. A characteristic of these corrosion product deposits on the bearing surfaces is their moderate adhesion to the base metal surface. A typical bearing surface is illustrated in Figure 26 (Turbine sleeve bearing CRU V-4E). No definite correlations could be established between the depth of deposition in a given area of the liquid portion of the CRU V as a function of time.

Of the CRU V's examined, the CRU V-2E, which operated for 22.5 hours, and the heaviest layer of corrosion product deposit (0.2 to 0.4 mil in depth).

In contrast to the liquid regions of the CRU V, the deposits found in the vapor regions, i.e., the turbine nozzles and vanes, tended to be more metallic in nature. The metallic deposits when found were usually tightly adherent. In general, deposits in the vapor regions were not as prevalent as those found in the liquid regions.

The results obtained from examining the CRU V-3E and 4E are reported in the following sections.

2. CRU V-3E

After removal from Test System 3, the CRU V-3E was opened for post-test inspection. A visual inspection of the alternator and turbine bearing surfaces revealed the presence of a light to moderate layer of corrosion products. The thicknesses of the corrosion product deposits on the bearing surfaces could not be measured.

Similar corrosion product deposits were also found on the CRU V pump diffuser-collector and impeller housing.

Examination of the turbine region of the CRU V revealed the presence of metallic deposits in the turbine inlet "J" tube, on both the first and second stage nozzles, the turbine housing and the first and second stage turbine wheels. Most significant, was the presence of 9 relatively large metallic spheres in the first stage nozzle. Six of the spheres were wedged between the vanes in 6 of the 8 nozzle passages. Another sphere was found inside the nozzle. Two more relatively large spheres were found in the turbine inlet scroll at disassembly. Specimens of both the metallic deposit and spheres were submitted for analysis.

3. CRU V-4E

The general condition of the CRU V-4E was similar to that found in the CRU V-3E. Corrosion product deposits were found in the journal bearings, the CRU V pump, diffuser-collector and impeller housing. The thicknesses of the corrosion product deposits on the bearing surfaces could not be measured.

FIGURE 26 CRU V TURBINE SLEEVE BEARING SHOWING A TYPICAL CORROSION PRODUCT DEPOSIT

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Again, as reported with the CRU V-3E, examination of the CRU V-4E turbine region revealed the presence of adherent metallic deposits on both nozzle stages and turbine wheels and the turbine housing. Also, spheres similar to those found in the CRU V-3E were found to be present in the first-stage nozzle of the CRU V-4E. Of the eight nozzle passages present, six were partially blocked by spheres. Two spheres were found along the inside wall of the nozzle and two spheres were found in the inlet scroll.

E. CRU V DEPOSIT ANALYSIS

1. Mercury Vapor Regions

Because of the distinctive nature of the metallic deposits found in the turbine housings of the CRU V-3E and CRU V-4E, the results of the analyses of the deposits are reported separately.

a. Hollow Spheres

A total of 9 and 10 spheres were recovered from the CRU V-3E and -4E respectively. The photograph in Figure 27 illustrates the typical appearance of these spheres which varied between 0.060 and 0.120 inch in diameter. Metallographic examination of several of these spheres confirmed the initial radiographic results which indicated that they were hollow. The wall thicknesses varied between 6 and 10 mils as illustrated in Figure 28. Micro-examination revealed that the walls of the spheres consisted of a heterogeneous mixture of two phases. One phase appeared white in nature; whereas the second phase had a gray mottled appearance. This appearance is illustrated in Figures 29 and 30 which are photomicrographs of two of the spheres.

The electron microprobe analyses of these are listed in Table IX. These analyses represent the composition of the spheres in the white and the gray mottled areas as illustrated in the photomicrographs shown in Figures 29 and 30. The significant difference in composition of the marbling microstructure is evident; higher percentage of chromium and nickel but lower content of cobalt in the white areas as compared to the gray mottled areas.

TABLE IX
ELECTRON MICROPROBE ANALYSES CONDUCTED ON THE
SPHERES FOUND IN THE CRU V-3E AND CRU V-4E

	<u>Composition (Weight Per Cent)</u>				
	<u>Co</u>	<u>Ni</u>	<u>Cr</u>	<u>Fe</u>	<u>Mn</u>
CRU V-3E (1 sphere					
White phase	57.8	11.6	26.0	2.6	2.0
Mottled phase	86.4	0.5	2.4	10.4	0.2
CRU V-4E (2 spheres)*					
White phase	21.3/61.4	17.0/36.9	16.2/21.4	2.5/4.4	0.9/16.6
Mottled phase	89.9/92.0	0.9/1.1	1.6/1.2	5.4/9.6	0.2

W - Segregated regions of tungsten in all three spheres.

*Analyses show the range of composition in the two spheres analyzed.

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FIGURE 27 PHOTOGRAPH SHOWING THE APPEARANCE OF THE SPHERE FOUND IN THE
FIRST STAGE NOZZLE OF THE CRU V-3E

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FIGURE 28 PHOTOMACROGRAPH OF HOLLOW SPHERES FOUND IN THE CRU V-3E
AND CRU V-4E TURBINE NOZZLES

MAGNIFICATION: 10X

B-4198

MAGNIFICATION: 100X

B-4199

MAGNIFICATION: 500X

FIGURE 29 STRUCTURE FOUND IN ONE OF THE SPHERES REMOVED FROM THE FIRST STAGE TURBINE NOZZLE OF THE CRU V-3E

B-4200

MAGNIFICATION: 100X

B-4201

MAGNIFICATION: 500X

FIGURE 30 STRUCTURE FOUND IN ONE OF THE SPHERES REMOVED FROM THE
FIRST STAGE NOZZLE OF THE CRU V-4E

b. Turbine Inlet Nozzle Housing Deposit

The deposit of corrosion products present in both the CRU V-3E and 4E turbine inlet nozzle housings is illustrated in Figure 31. It is obvious from this photograph that centrifugal force generated by the turbine separated the liquid mercury from the vapor and caused it to impact on the periphery of the housing. The corrosion product deposit thus was initiated and increased in size by subsequent nucleation and growth. The electron microprobe analyses of samples from the deposit in both the CRU V-3E and 4E turbine housings are presented in Table X. The results of the microprobe analyses are given as ratios (in percent) of the observed intensity over the intensity from a pure element (standard). Because of the complexity of the system corrections of the intensity values were not attempted.

TABLE X
Composition (Weight Per Cent)

	<u>Co</u>	<u>Cr</u>	<u>Fe</u>	<u>Ni</u>
<u>CRU V-3E</u>				
a	12	3	7	0.2
b	26	5	3	0.4
c	81	2	6	0.5
d	25	31	4	7.0
<u>CRU V-4E</u>				
a	92	3	5	4.0
b	2	67	0.1	31.0

It can be seen that the particles varied widely in composition. Some of this variation may have been caused by the topographical features of the pieces and by possible surface films, i.e., oxide films. However, because of the large variations, it is believed the pieces must also have had variations in basic composition.

The particles were also identified by electron diffraction analysis. The particles from both of the CRU V's indicated multiphase material, a face centered cubic and a body centered cubic structure. The FCC material was probably the cobalt or cobalt rich phase and the BCC material was the chromium or chromium rich alloy.

FIGURE 31 PHOTOGRAPH SHOWING THE ADHERENT METALLIC DEPOSIT FOUND ON THE INSIDE DIAMETER OF THE CRU V-3E TURBINE INLET NOZZLE HOUSING

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c. Turbine Inlet Line

The corrosion product deposit present in the turbine inlet line was restricted to that section of the tubing where a 90 degree bend exists prior to entrance into the turbine inlet-nozzle housing. The photomicrograph in Figure 13 illustrates the pattern and quantity of deposit.

The electron microprobe analysis of the deposit revealed a weight per cent composition consisting principally of chromium (31.1) and nickel (37.9) with a surprising amount of tungsten (18.3). Cobalt (10.6) was present but not in a quantity which reflects the basic composition of L-605. Smaller amounts of iron (5.1) and manganese (2.7) were also found. Although, the presence of high nickel and chromium may indicate the preferential leaching of these elements from the upstream portion of the system by mercury, it also indicates that deposition in this section may have occurred only during those periods when these elements were present as corrosion product in the vapor.

2. Liquid Mercury Region

The deposits of corrosion product found in the liquid mercury regions of the CRU V's have been examined by means of electron microscopy, electron beam microprobe and by electron diffraction analysis. The purpose of these analyses was to determine the size, configuration and composition of the corrosion products deposited in such areas as the pump and the bearings.

In general, these analyses have shown the deposits to be similar. For example, the deposits present in the pump region are similar to those found on the bearing surfaces. The improvement incorporated in the test systems prior to CRU V-3E and -4E tests resulted in some change of composition. These improvements were 1) greater vacuum integrity, and 2) more corrosion resistant plumbing material. However, because of the similar nature of the corrosion products the detailed results and discussion will be presented according to the method of analysis.

Electron Microscopy

Electron photomicrographs of the typical deposits found on the bearing surfaces of various CRU V's are illustrated in Figures 32 and 33. The particles removed from all the various surfaces (including the CRU V bearing sleeves and bushings, and the CRU V pump components) were similar in appearance and distribution. Examination at very high magnifications showed the ultimate particle size to be usually in two size ranges; those of 0.01 microns or less and those ranging in size from 0.1 to 1.0 microns. Almost all of the particles appeared as flocculates which are composed of a mass of fine particles surrounding larger particles. In general the particles of both size ranges were rounded although thin platelets with a thickness of less than

FIGURE 32 ELECTRON MICROGRAPH OF PARTICLES REMOVED FROM THE CRU V-4D TURBINE BEARING SLEEVE O.D. SURFACE. THE DEPTH OF THE DEPOSIT WAS APPROXIMATELY 0.0001 INCH THICK

10,000X

FIGURE 33 PARTICLES REMOVED FROM CRU V-5C ALTERNATOR BEARING SLEEVE AS DISPERSED

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0.01 microns have been observed.

The detailed data for each of the CRU V's examined are listed in Table XI.

Electron Microprobe

Electron microprobe analyses were performed on the same specimens examined by electron microscopic analyses. Within any given sample, variations of elemental distributions were found. These data are summarized in Table XI and reveal that, though the same elements were found in the corrosion product deposits analyzed, a significant difference exists between those CRU V's operated in test systems constructed of Type 316 SS and those operated in systems fabricated of L-605. The predominate metallic element present in the bearing surface deposits of the CRU V's tested in Type 316 SS systems was iron as compared to chromium for the CRU V's operated in the L-605 test systems.

Electron Diffraction Analyses

The particles from the various surfaces (including the CRU V bearing bushing and sleeve, and the CRU V pump components) were identified by electron diffraction analyses. Areas for analyses were similar to those used for the electron microscopy and microprobe studies. Select areas containing large particles, small particles as well as combinations were analyzed. The data are summarized in Table XI.

The results of the electron diffraction analyses of the deposits on the CRU V component surfaces indicate that the mercury corrosion products deposit as ferrites possessing the crystallographic structure of the spinels. A brief discussion of these ceramic ferrimagnetic materials of the spinel structure is presented below in order to clearly establish the subtle differences of the spinel compounds identified in the CRU V's examined.

The composition of the ferrites possessing the spinel structure can be presented by the general chemical formula MeFe_2O_4 where Me is a divalent metal ions such as Fe, Mn, Mg, Ni, Zn, Cd, Co, Cu, or a mixture of these. The formula also can be expressed as $\text{MeO} \cdot \text{Fe}_2\text{O}_3$. Typical examples of such ferrites are the spinels:

TABLE XI CORROSION PRODUCT DEPOSITS IN THE CRU-V MODULE

CRUV	Component	Test System Material	Ultimate Particle Size -Microns-	Particle Configuration	Electron Microprobe Analyses	Crystal Structure
-4D	Alternator Bearing	Type	0.005	Round	Major - Fe	Spinel,
	Turbine Bearing	316 SS	to 0.01		Minor - Cr, Co, Ni, Si	Me Fe ₂ O ₄ and γ Fe ₂ O ₃
-1D	Alternator Bearing Sleeve	Type 316 SS	(a)0.05 to (b)0.5	(a)Round (b)Platelet	Fe,Ni,Co, Cr,andMn	Spinel, γ Fe ₂ O ₃
-5C	Alternator Bearing Sleeve	Type 316 SS	(a)0.01 (b)1.0	(a)Round (b)Platelet	Major - Fe Minor - Ni, Cr, Co, Mn	Spinel, γ Fe ₂ O ₃
-2E	(1)Turbine Bearing (Sleeve)	Type 316 SS	0.01	Round	Fe,Cr,Co, NiandSi	Spinel
	(2)Alternator Bearing (Sleeve)	Type 316 SS	-	-	-	γ Fe ₂ O ₃
	(3)Pump Housing	Type 316 SS	-	-	-	
	(4)Alternator Bearing (Bushing)	Type 316 SS	-	-	-	
-3E	(1)Impeller Housing	L 605	(a)<0.01	Round	Major - Cr	Spinel Me, Me ₂ O ₄
	(2)Alternator Bearing (Bushing)	L 605	(b)0.1 -	-	Minor - Mn, Fe, - Co, Ni	
	(3)Turbine Bearing (Bushing)	L 605	-	-	-	
	(4)Exhaust Core	L 605	-	-	-	

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(CONT'D) TABLE XI CORROSION PRODUCT DEPOSITS IN THE CRU-V MODULE

CRUV	Component	Test System Material	Ultimate Particle Size -Microns-	Particle Configuration	Electron Microprobe Analyses	Crystal Structure
-4E	(1)Impeller Housing	L 605	(a)<0.01 (b) 0.1	Round	Major - Cr Minor - Mn, Fe Co, and Ni	Spinel, Me Me ₂ 'O ₄
	(2)Alternator Bearing (Bushing)	L 605	-	-	-	-
	(3)Turbine Bearing (Bushing)	L 605	-	-	-	-

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CoFe_2O_4 or $\text{CoO} \cdot \text{Fe}_2\text{O}_3$

MnFe_2O_4 or $\text{MnO} \cdot \text{Fe}_2\text{O}_3$

$\text{Co Ni Fe}_2 \text{O}_4$ or $(\text{CoNi})\text{O} \cdot \text{Fe}_2 \text{O}_3$

The symbol Me also can represent a combination of ions which have an average valency of two. A particular case is the ferrimagnetic $\gamma \text{Fe}_2\text{O}_3$ which has the spinel structure and whose chemical formula can be written as $\square \frac{1}{3} \text{Fe}_{8/3} \text{O}_4$, the symbol $\square$ representing a vacant lattice site. The trivalent iron ions (ferric) in $\text{Me Fe}_2 \text{O}_4$ can be replaced by another trivalent ion such as Cr. A typical example would be $\text{Me} (\text{Cr Fe}) \text{O}_4$. These compounds are also ferrimagnetic if the nonmagnetic ions are present in not too large concentration. (16) The general formula $\text{Me Me}'_2 \text{O}_4$ is used in this report to designate this form of spinel where Me represents a divalent metal ion or mixtures of same and Me' represents the trivalent metal ions.

The results of the electron diffraction study made of the corrosion product deposits in the CRU V module reveal a difference in the ferrites present as spinels. Those units which were operated in the test systems principally fabricated of Type 316 SS had deposits which were composed of the $\gamma \text{Fe}_2\text{O}_3$ type spinel. Both of the CRU V's which were operated in the L-605 test systems had deposits composed of the $\text{Me Me}'_2 \text{O}_4$ type spinel. The reason for this difference is not clear. However, it could be associated with the dominating concentration of iron in the corrosion product of the Type 316 SS as compared to chromium in the corrosion product found in the L-605 test system; or, a result of increased vacuum integrity of Test Systems 3 and 5 after rebuilding with L-605 plumbing hardware.

The expansion of the crystal lattice noted in the diffraction study indicated substitution of the iron ion of the $\gamma \text{Fe}_2\text{O}_3$ spinel by the other metals present. Similarly, Mn, Fe, Co and Ni are present in the $\text{MeMe}'_2\text{O}_4$ type spinel.

F. BOILER CORROSION

The Model 5C boiler consisted of four concentric helical coils of L-605 tubing in which the mercury boiled. Each tube had a total developed length of 29 feet. The tubes were contained in an annular space between an outer shell and an evacuated cylindrical inner can. NaK flowed through the annular space counter current to the mercury flow. Typical values for the operating parameters of this model boiler are listed in Table XII below:

TABLE XII
MODEL 5C BOILER OPERATING PARAMETERS

Hg Inlet Flow	18-22 ppm
Hg Inlet Pressure	180-240 psia
Hg Inlet Line Temperature	750°F
Hg Discharge Line Temperature	1180-1200°F
NaK Inlet Flow	74 - 78 ppm
NaK Inlet Line Temperature	1220 - 1260°F
NaK Discharge Line Temperature	1020 - 1080°F

A total of 7 Model 5C boilers have been metallurgically evaluated for mercury corrosion, mass transfer and deposition of corrosion products. These boilers have been exposed to boiling and superheated mercury for accumulative times extending to 6600 hours. Operating parameters such as mercury pressure and temperature were varied. An operating characteristic, the ability to perform in a "conditioned" manner, was continuously monitored during boiler operation. A "conditioned" boiler has been defined as one which operates in accordance with performance that is predicted from the nonwetting design correlations.(17) In practice the performance of a boiler could be monitored by the characteristics of the plot of the NaK temperature as determined by the data acquired from thermocouples mounted on the boiler shell. An ideal temperature profile for the Model 5C boiler operating in a conditioned manner is illustrated in Figure 34.

1. Metallurgical Examination

Metallurgical evaluation of the boilers was made by extensive metallographic examination and careful electron microprobe analysis. After dismantling the boiler, metallographic samples were taken of the tubes at intervals of two feet throughout the entire length. Thus, the cross sections of the tubes were examined and the degradation, if any, of the L-605 material was observed and measured. Selected specimens subsequently were subjected to electron microprobe analysis.

The data obtained from these evaluations of 7 Model 5C boilers revealed a repetitive pattern of corrosion and deposition which was closely related to the location of exposure to two phase mercury in the boiling zone. Significant corrosion always occurred in that portion of the tube where the mercury was at or slightly above the saturation temperature and the vapor quality was estimated to be from 0 to 30 per cent. The deposition of the

FIGURE 34 IDEAL NaK TEMPERATURE PROFILE FOR THE MODEL 5C BOILER

corrosion products always occurred within 3 feet downstream of the corroded area and was associated with the mercury in the vapor state at a quality in the range of 30-80 per cent. The relationship between the location of corrosion and deposition in the boiler tube and the physical state of the boiling mercury is graphically illustrated in Figure 35. Here, the plot of the depth of corrosion and the thickness of deposition of a 5C-9 boiler tube has been superimposed on the NaK shell temperature profile. Intermittent use of a boiler may result in a variable NaK temperature profile. For example, such a boiler may have an excess superheat length of 18 to 21 feet during one period of operation whereas after a shutdown and subsequent startup may only have 6 feet. The operational history of the 5C-7 boiler illustrated this characteristic behavior (see Table XIII). During the 1260 hour test of the CRU V-3B-10 this system boiler had an excess superheat length of 18 to 21 feet, but during the subsequent 3153 hour test of the CRU V-1B-2 the excess superheat length had a maximum value of only 6 feet. The vapor quality of the mercury was 94.5 and 87 per cent respectively for these two tests. The effect on the location of the corrosion and deposition is illustrated in the superimposed plots in Figure 36.

The corrosion of the L-605 boiler tubes is of the characteristic layer type as illustrated in Figure 37. Selective leaching of alloying elements by the mercury during the boiler operation resulted in a significant depletion of chromium and nickel, a moderate depletion of cobalt and an indicated increase in tungsten content. The electron beam microprobe analysis of a characteristic mercury boiler tube corrosion layer is presented graphically in Figure 38. The indicated increase in the tungsten content in the corrosion layer is probably grossly exaggerated because of the elimination of the effect of the nickel K absorption edge on the L radiation of tungsten. Nevertheless, the electron beam microprobe analyses do reveal that the corrosion layer consists essentially of tungsten and cobalt. X-ray diffraction studies indicate that these elements are present as a carbide of the form $(Co, W)_6 C$.

The typical appearance of the deposit found in the boiler tubes immediately downstream of the corroded section is illustrated in Figure 39. The deposits are obviously porous. The thickness of the deposits observed in the various boilers evaluated appear to be directly related to the time of boiler operation provided other conditions such as boiler stability remain constant.

The composition of the deposits may be quite complex as revealed by electron beam analyses. The electron microprobe traces taken at the 31 mils thick deposit of a boiler tube illustrate this complexity (Figure 40). These traces reveal a banded structure which on the basis of the indicated chromium, nickel and cobalt content can be divided into 6 zones. The elements chromium and nickel are dominant in the first 5 zones. The final layer or zone has a high concentration of cobalt. This banded

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FIGURE 35 PENETRATION AND DEPOSITION AND NAK SHELL TEMPERATURE
PROFILE VERSUS DEVELOPED LENGTH FOR THE MODEL 5C-9 BOILER

FIGURE 36 PENETRATION AND DEPOSITION AND NaK SHELL TEMPERATURE PROFILE
VS. DEVELOPED LENGTH FOR THE MODEL 5C-7 BOILER

FIGURE 37 TYPICAL CORROSION LAYER FROM THE MODEL 5C
TYPE BOILER

MAGNIFICATION: 100X ETCHANT: NONE

FIGURE 38 ELECTRON BEAM MICROPROBE ANALYSIS OF A TYPICAL CORROSION LAYER OF THE MOD 5C TYPE BOILER

FIGURE 39 TYPICAL CORROSION PRODUCT DEPOSIT FOUND IN A BOILER TUBE
FROM THE MODEL 5C TYPE BOILER

MAGNIFICATION: 100X

ETCHANT: NONE

FIGURE 40 ELECTRON BEAM MICROPROBE ANALYSIS OF A TYPICAL CORROSION DEPOSIT
FOUND IN A BOILER TUBE FROM THE MOD 5C TYPE BOILER

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FIGURE 40 (Cont.) ELECTRON BEAM MICROPROBE ANALYSIS OF A TYPICAL CORROSION DEPOSIT FOUND IN A BOILER TUBE FROM THE MOD 5C TYPE BOILER

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structure is indicative of the selective leaching process of mercury corrosion of the L-605. The tungsten electron microprobe trace only indicates occasional spikes of high radiation intensity.

The mercury corrosion of L-605 follows the parabolic rate law:

$$p = kt$$

where

$$p = \text{depth of penetration}$$

$$t = \text{time exposed to liquid mercury at constant temperature, and}$$

$$k = \text{rate constant(18, 19)}$$

The decelerating effect on the corrosion rate is attributed to the adherent corrosion layer since contact between the liquid mercury and the alloy is maintained solely by diffusion of the alloying elements across this barrier.

The values of k for the boilers evaluated have been determined and are listed in Table XIII. These values are plotted and compared with the laboratory data (18) in Figure 41. Except for two exceptions, the 5C-7 and 5C-10 boilers, the data compare favorably with the laboratory results obtained from L-605 convection loop and metal capsule tests. In general, the boiler corrosion data agree more favorably with the metal capsule and convection loop than with the glass capsule results.(20)

The data obtained from the 5C-8 boiler evaluation reveal a significantly low level in corrosion rate after a hydrogen anneal of the boiler. This boiler was hydrogen annealed after 2617 hours of previous operation during which time it had behaved erratically with excess superheat lengths of 0 to 21 feet. After the hydrogen anneal the boiler (now designated as 5C-8B) was operated for an additional 3805 hours during which time the boiler was stable with an excess superheat length of 13 to 18 feet. Thus, the exact position of the corrosion which took place during these 3805 hours was identifiable. Metallurgical examination revealed only a 3 mil penetration. The plot of this data point in Figure 43 shows that the rate of corrosion for the 5C-8B boiler operation was lower than the other boilers except the 5C-10. Thus, it is strongly indicated that not only does a hydrogen anneal of a boiler create a surface favorable for "conditioned" operation but the intermetallic compounds formed on the surface as a result of the anneal also inhibits mercury corrosion upon subsequent operation.

No clear explanation can be given for the excellent and poor corrosion rates of the 5C-10 and 5C-7 boilers respectively.

TABLE XIII MODEL 5C TYPE BOILER CORROSION DATA

Boiler	Saturation Hg Temp. -°F-	Time Of Operation -Hrs-	Calculated Vapor Quality	Excess Super Heat Length -ft-	Location Of Corrosion From Inlet -ft-	Corrosion Penetration -mils-	Parabolic Rate Constant mils ² /hr	Remarks
5C 2	1035	1000	-	20	1 to 5	2.5	6.25×10^{-3}	Boiler Endurance Test
5C 4	1010	740	-	20(a)	1 to 5	2.2	6.55×10^{-3}	PSM-1 System At A.I.
5C 7 (a)	970	770	94	6 to 18	-(b)	-(b)	-(b)	CRUV-3B-7
(b)	1015	1260	94.5	18 to 21	7	4.0	1.27×10^{-2}	CRUV-3B-10
(c)	990	3153	87	0 to 6	22	7.5	1.78×10^{-2}	CRUV-1B-2
(d)	980	742	93.5	1 to 20	-(b)	-(b)	-(b)	CRUV-1C-33
5C 8	1005	1300	84.5	0 to 21	-(b)	-(b)	-(b)	CRUV-5-11
5C 8A	1010	1317	89	0 to 21	-(b)	-(b)	-(b)	CRUV-4D-23
5C 8B	1025	3805	86.5	13 to 18	10-12	3.0	2.4×10^{-3}	CRUV-3E-9 (H ₂ - Annealed)
5C 9	1010	2200	-	17	8	3.2	4.65×10^{-3}	Boiler Endurance Test
5C 10	1020	5038	90	18-21	10	2.1	8×10^{-4}	CRUV-5C
5C 13	1020	1365	81	20-21	6-8	3.2	7.5×10^{-3}	CRUV-4E

(a) During acceptance test only. Subsequent operation in the PSIG-1 test system necessitated the use of Mg in order to achieve and maintain conditioned operation.

(b) Cannot be determined

FIGURE 41 COMPARISON OF CORROSION RATE CONSTANT AT MAXIMUM PENETRATION WITH LABORATORY DATA ON L605 (HAYNES ALLOY 25) CORROSION

FIGURE 42 CORROSION PRODUCT CONCENTRATION IN CIRCULATING MERCURY DURING 5C-8B BOILER TEST IN TEST SYSTEM 3

FIGURE 43 SCHEMATIC SHOWING THE CRU V BEARING LUBRICANT LINE
FILTERS IN THE SERIES - PARALLEL ARRANGEMENT

The presence of corrosion products in the mercury vapor exiting from the boiler has been demonstrated by analyses made of mercury vapor samples taken during boiler test operations.(21) The data obtained from the analyses of samples taken during a typical boiler test prior to operation with a CRU V unit included in the system are listed in Table XIV and graphically illustrated in Figure 42. All sample locations showed a peak in corrosion product concentration early in the test which rapidly diminished after 100 hours of operation. The corrosion product concentration in the mercury samples taken from the liquid mercury phase portion of the system (condenser discharge, etc.) attained an indicated level of contamination which was less than 0.02 ppm. However, the boiler outlet sample (vapor) diminished to a level of 0.20 ppm only after 300 hours of operation. The ultimate effect of this corrosion product carried over in the vapor exiting from the boiler will be discussed in a later section. Obviously, the boiler is a major source of corrosion products in the system.

G. TEST SYSTEM FILTRATION

As discussed earlier, filters have been utilized throughout the CRU V test program to protect sensitive regions of the CRU V from occasional loose chips, weld spatter, wear debris or other such particulate matter. In general, the regions to be protected by this method included:

1. CRU V Bearings
 - Thrust
 - Turbine
 - Alternator
2. The CRU V Jet Pump
3. The Inlet to the CRU V pump
4. The Combined Bearing and Boiler Flow Line

During the course of the CRU V test program, the types of filters utilized and their locations changed. The reasons were several. The major problem encountered was that at times the filters inadvertently became corrosion product separators. The other major reason was that a specific region was not sufficiently protected.

The major changes evolved were:

1. The elimination of the CRU V jet pump filter.

Starting with the CRU V - build this filter eliminated because it consistently became plugged with corrosion products.

TABLE XIV SPECTROGRAPHIC ANALYSES OF TEST SYSTEM 3 MERCURY SAMPLES
REMOVED DURING 5C-8B BOILER TESTING

Location of Sample	Operating Time (hr.)	Sample Weight (lb)	Total Metallic Content	Spectrographic Analyses (ppm)							
				Fe	Ni	Cr	Co	Mo	W	Mn	Other
Boiler Discharge	1	2.0	5.405	0.35	0.15	2.75	1.65	0.10	0.35	0.35	0.02(V)
	21	1.5	5.430	0.25	0.75	3.00	1.25	0.02	0.01	0.15	--
	46	1.5	39.10	1.25	3.75	30.0	3.75	--	--	0.35	--
	96	2.0	0.474	0.002	0.050	0.110	0.275	0.011	--	--	--
	203	1.75	0.486	0.015	0.075	0.125	0.250	--	0.001	--	0.01(A1)
	306	1.5	0.18	0.010	0.025	0.100	0.025	0.010	--	--	--
Condenser Discharge	1	1.25	0.085	0.025	0.010	0.040	0.010	--	--	--	--
	21	3.0	0.056	0.040	0.005	0.010	--	0.001	--	--	--
	46	2.25	0.10	0.075	0.010	0.050	0.010	--	--	--	--
	96	1.75	0.075	0.025	0.050	--	--	--	--	--	--
	203	1.25	0.010	0.010	--	--	--	--	--	--	--
	306	1.25	0.005	0.005	--	--	--	--	--	--	--
Inlet to Franz Separator	1	2.75	0.037	0.025	0.010	0.002	--	--	--	--	--
	21	8.25	0.037	0.027	0.010	--	--	--	--	--	--
	46	3.25	0.130	0.070	0.050	0.010	--	--	--	--	--
	96	3.0	0.070	0.060	0.005	0.005	--	--	--	--	--
	203	3.0	0.015	0.015	--	--	--	--	--	--	--
	306	2.5	0.011	0.010	0.001	--	--	--	--	--	--
Between Franz Separator and Intermediate Filter	1	4.25	0.230	0.050	0.050	0.100	0.005	--	--	0.025	--
	21	7.0	0.842	0.320	0.250	0.250	0.002	--	--	0.020	--
	46	5.5	0.070	0.040	0.010	0.020	--	--	--	--	--
	96	3.75	0.062	0.040	0.020	0.002	--	--	--	--	--
	203	4.5	0.008	0.005	0.002	0.001	--	--	--	--	--
	306	1.5	0.008	0.005	0.002	0.001	--	--	--	--	--

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(CONT'D) TABLE XIV SPECTROGRAPHIC ANALYSES OF TEST SYSTEM 3 MERCURY SAMPLES
REMOVED DURING 5C-8B BOILER TESTING

Location of Sample	Operating Time (hr.)	Sample Weight (lb)	Total Metallic Content	Spectrographic Analysis (ppm)							
				Fe	Ni	Cr	Co	Mo	W	Mn	Other
Intermediate Filter Outlet	1	4.5	0.630	0.500	0.100	0.025	0.005	--	--	--	--
	21	3.25	0.580	0.500	0.070	0.010	--	--	--	--	--
	46	5.5	0.510	0.300	0.200	0.010	--	--	--	--	--
	96	4.5	0.008	0.005	0.002	0.001	--	--	--	--	--
	203	3.5	0.008	0.006	0.002	--	--	--	--	--	--
	306	2.0	0.016	0.011	0.005	--	--	--	--	--	--

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The results of analyses conducted on this filter have been discussed previously.

2. The addition of the CRU V pump inlet filter.

This filter was added to protect the pump impeller from particles large enough to jam up the pump.

3. The auxiliary lubricant pump filter was originally fabricated of sintered metal powder. However, during the CRU V-5C test this filter ruptured because of excessive overloading. Because of this incident this filter was changed to a pleated metallic screen type.

4. During the operation of the CRU V-5C, an intermediate filter was installed in the plumbing line between the CRU V pump and the combined boiler bearing flow manifold. This filter was installed to prevent the CRU V lubricant line filters from becoming plugged as the result of an inadvertent introduction of a large quantity of debris upon startup. This filter was utilized also as a backup device for the corrosion product separators utilized in the 5C-8A, CRU V-3E and CRU V-4E tests.

5. Originally each lubricant line (turbine bearing, alternator bearing, thrust bearing) had one filter for protection. However, because of problems associated with the buildup of excessive amounts of corrosion products on the CRU V lubricant line filters during the CRU V-5C test the arrangement of the filters was changed.

The new arrangement, shown in Figure 43, was utilized during the operation of the CRU V-5C, the CRU V-3E and CRU V-4E tests. This arrangement allows for the replacement of one of the lubricant line filters in the event that severe plugging of an element occurs. As illustrated in Figure 43, three filters were installed in each lubricant line in a series-parallel combination. Thus, filters 1 and 2 would be the primary collectors of debris. In the event of plugging, filter 2 would be replaced with a new filter. Filter 3 should remain relatively clean. Filter 3 was installed to protect the bearings in the event filter 2 had to be replaced.

The basic designs of the various filters utilized (except for the jet pump filter which was deleted) during the final CRU V tests are illustrated in Figure 44 and Figure 45. Table XV lists the design data for the filters. All the filter elements were of a Dutch twill weave fabricated of a Type 300 series stainless steel wire.

1. Filter Evaluation

a. Test System 3-CRU V-3E

FIGURE 44 PHOTOGRAPH SHOWING THE INTERMEDIATE, CRU V PUMP INLET AND AUXILIARY PUMP DISCHARGE FILTERS

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FIGURE 45 - PHOTOGRAPH SHOWING THE POST TEST CONDITION OF THE CRU V-3E THRUST BEARING LUBRICANT LINE FILTER

TABLE XV TYPES OF TEST SYSTEM FILTERS

Filter	Type	Filter Screen Material	Filter Rating		Filter Surface Area (in ²)
			Nominal*	Absolute**	
CRU V Jet Pump	Woven Wire Cylinder	Type 316 Stainless Steel	5 μ	18 μ	6
CRU Pump Inlet	Woven Wire Pleated Screen	Type 316 Stainless Steel	40 μ	75 μ	100
Auxiliary Pump	Sintered Metal Powder Cylinder	Type 316 Stainless Steel	10 μ	-	36
Auxiliary Pump	Woven Wire Pleated Screen	Type 316 Stainless Steel	5 μ	18 μ	148
Intermediate	Woven Wire Pleated Screen	Type 316 Stainless Steel	5 μ	18 μ	330
Lubricant Line	Woven Wire Pleated Screen	Type 316 Stainless Steel	2 μ	10 μ	6

Of the four test system filters from Test System 3, only two, the pump inlet and the intermediate, exhibited evidence of corrosion product entrapment as illustrated in Figure 46 (pump inlet filter) which shows a typical post test surface. The boiler inlet and the auxiliary pump discharge filter were both clean. This freedom from corrosion product entrapment may be partly due to the relatively short period of activity for both filters. The boiler inlet filter and the auxiliary pump discharge filter operated for approximately 500 hours. In contrast, the CRU V inlet filter and the intermediate filter operated for 4000 plus hours.

The CRU V pump inlet filter trapped out a significantly larger quantity of corrosion product as compared to the intermediate filter. This difference in quantity of corrosion product present on the screens indicated either a higher burden of corrosion products in the mercury entering the CRU V pump inlet filter or that the corrosion products were physically in a form more amenable to filtration at the CRU V pump inlet filter.

Chemical analyses conducted on the periodic mercury samples removed upstream of both filters indicated a relatively low burden of corrosion products entering each filter. However, electron microscopy conducted on specimens of corrosion product removed from the CRU V pump inlet filter revealed that the corrosion product consisted of large agglomerates composed of a mixture of small spherical particles and thin platelets. Thus, it would appear that the corrosion products entering the CRU pump inlet filter were in a physical state more amenable to filtration.

Examination of the CRU V-3E bearing lubricant line filters (9 total) revealed all to be relatively clean. Figure 45 is typical of the post test condition of the CRU V-3E filter screens. This lack of corrosion product buildup tends to confirm the low level of corrosion product detected in the periodic mercury samples removed from the inlet to the bearing lubricant lines during test operation.

b. Test System 5 - CRU V-4E

Of the three test system filters, only one, the CRU V pump inlet filter exhibited evidence of corrosion product entrapment. The boiler inlet and intermediate filter were clean. This experience is similar to that found in the filters removed from Test System 3. Metallographic specimens removed from all three filter elements revealed no corrosion attack.

Examination of the CRU V-4E bearing lubricant line filters (9 total) revealed all to be relatively clean. The post test condition of the CRU V-4E filter screens was similar to that shown in Figure 45 (CRU V-3E thrust bearing filter).

FIGURE 46 PHOTOGRAPH SHOWING THE POST TEST CONDITION OF THE TEST SYSTEM 3
CRU PUMP INLET FILTER

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H. CORROSION PRODUCT SEPARATOR DEVELOPMENT

1. Preliminary Corrosion Product Separation

Various separation techniques for mercury corrosion product removal were first investigated at TRW (15,20) as a part of the materials corrosion studies on the MRPC Program. The separation techniques studied were:

1. Magnetic action
2. Chemical gettering and filtering
3. Centrifugal forces
4. Settling chamber
5. Change in direction or impingement, and
6. Thermal diffusion (Soret effect)

Experimental corrosion product separator units utilizing these techniques were tested in several natural circulation and forced circulation loops. The results of these series of loop tests established the most favorable principles of corrosion product separation to follow in system testing.

2. System Corrosion Product Separator Development

The first experiences with mercury Rankine power CRU V and component operation in test systems were not hampered by the harmful deposition of corrosion products. The use of large inventories of mercury in the systems and the presence of stagnant regions allowed the corrosion products to separate by gravity harmlessly in out-of-the-way regions. However, the need for corrosion product separation devices became obvious as the test systems became more flight oriented (compact) and the tests became longer in duration.

a. Wire Cloth Barriers

The first technique of corrosion product separation utilized in a test system was that of wire cloth filters. Primarily, the usage of these devices was to protect sensitive regions of the CRU V from ingestion of particles 10 microns and larger. In several instances, however, these filters unintentionally became corrosion product separators.

The intermediate filter was the exception. This filter, utilized during the latter stages of CRU V-5C and CRU V-4D testing, was installed primarily to protect the bearing lubricant line filters from corrosion product deposition. Figure 47 shows the placement of this filter in the test system plumbing. Later, the intermediate filter was utilized as an integral part of the

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FIGURE 47 SCHEMATIC SHOWING THE INTERMEDIATE FILTER CONFIGURATION

modified magnetic-gravity separator.

b. Gravity Plus Magnetism

The second method of separation utilized in test systems was gravity plus magnetism. This method made use of a commercial filter consisting of permanent magnets and a large reservoir which was modified for mercury usage. Actually, three different modifications were investigated.

1) The first modification consisted of reversing the flow through the separator. Figure 48 illustrates the construction of the separator. This device was used with the following CRU V Tests.

- a. Test System 3 - CRU V-2 and CRU V-2D
- CRU V-3C
- CRU V-5 and CRU V-5A
- b. Test System 4 - CRU V-2D and CRU V-4A
- c. Test System 5 - CRU V-3E

In Test Systems 3 and 5 the separators were located in the CRU V pump discharge line. In Test System 4, the separator was installed at the inlet to the CRU V bearing manifold. (In Test System 4, the CRU V pump operated independently of the remainder of the test system. The operating mercury was supplied by an auxiliary pump.)

2) The second modification consisted of removing the top magnet, and packing tantalum wool into the open spaces. Figure 49 illustrates the configuration of the second modification. The purpose of the tantalum wool was to retain the separated corrosion products through either mechanical trapping and/or gettering. A woven metal screen was placed over the top of the stack of grids to prevent the possible migration of tantalum particles into the rest of the system. This separator was utilized during CRU V-1B testing in Test System 5.

3) The third modification investigated was similar to the second, except that the inside grid network was shortened and the top magnet was used. Figure 50 shows the configuration of the third modification. The intermediate filter was installed downstream of the separator as illustrated in Figure 51 to prevent possible migration of tantalum particles into the remainder of the test system. This separator was utilized during the following tests:

- a. 5C8A boiler test and CRU V-3E operation in Test System 3 (upgraded).

FIGURE 48 SKETCH OF THE FIRST MODIFICATION OF THE GRAVITY-MAGNETIC SEPARATOR

FIGURE 49 SKETCH OF MODIFICATION II OF THE GRAVITY-MAGNETIC SEPARATOR

FIGURE 50 SKETCH OF MODIFICATION III OF THE GRAVITY MAGNETIC SEPARATOR

FIGURE 51 SCHEMATIC SHOWING THE MANNER IN WHICH THE GRAVITY-MAGNETIC SEPARATOR AND THE INTERMEDIATE FILTER WERE UTILIZED

b. CRU V-4E operation in Test System 5 (upgraded).

c. Depth Filters

The concept of filters serving as a corrosion product separating device led to the initial development of compact depth filters. These filters contained stainless steel felt-metal elements ranging in pore size from 285 microns down to a minimum of 15 microns. The filter was developed on a graded structure concept combining the trapping aspects of a depth filter at the inlet end and the barrier aspects of a screen on the outlet end. To prevent the migration of any metal fibers, a 10 micron screen element was placed after the last filter element in the assembly. Figure 52 shows the general arrangement of this design.

A modification of the above depth filter was to incorporate a magnetic field in order to increase the efficiency of the device. This later design is illustrated in Figure 53. Basically, the filter consists of a 3" long permanent magnet sleeve (axially magnetized) with magnetic filter elements inside the sleeve. The magnetic filter element is the return path for the lines of flux created by the permanent magnet. There are pole pieces on each end to prevent the loss of magnetization. Magnetism was added to aid in the filtering of particles.

Depth filters were used in the following tests.

- 1) CRU V-4B and CRU V-5B operation in Test System 4
- 2) CRU V-3D operation in Test System 3

The magnetic depth filter was used during 5C-10 boiler testing in Test System 3.

d. Cyclone Separator

This concept was developed through the observation and examination of corrosion product deposition in the test systems and CRU V hardware. In the course of examination of system hardware it was observed that corrosion product deposits tended to occur where:

- 1) Centrifugal forces were created by flow through components such as the Model 5C boiler.
- 2) The centrifugal force was imparted from a rotating body such as the mercury pump and the journal bearings.
- 3) Where there is eddying turbulence from the rapid deceleration of mercury flow. This eddying turbulence forms vortices which create centrifugal forces.

In all three cases, separation of corrosion products has occurred as the result of centrifugal forces acting upon and

FIGURE 52 SKETCH SHOWING THE ASSEMBLY OF THE COMPACT DEPTH FILTER

FIGURE 53 SKETCH SHOWING THE ASSEMBLY OF THE MAGNETIC DEPTH FILTER ASSEMBLY

multiplying the differences in density between corrosion products and mercury.

These observations led to the conception of the cyclone separator. The cyclone was selected as the separator because it has the capability of producing high centrifugal forces without the need for moving parts. The mercury is introduced tangentially into the cyclone at a velocity sufficient to create a vortex effect. (See Figure 54) Presumably clean mercury would be forced to the walls of the cyclone and pass down and out of the conical body. The less dense corrosion products, with the remaining mercury would move into the vortex and be discharged upward toward a second outlet. Both the nonmagnetic and magnetic depth filters previously discussed were used with the cyclone to store the corrosion products that the cyclone separated. The various combinations of cyclone and depth filters tested are listed in Table XVI. Figure 55 illustrates the manner in which the cyclones were mounted in the test system.

As shown in Table XVI, one cyclone (S/N 3) was tested initially with the CRU V-4C (55.9 hours) in Test System 3. This cyclone was then tested for 87 hours with the CRU V-3D in Test System 3. Following this test the cyclone was moved to Test System 5 and tested with the CRU V-1C for 759.6 hours. In all, the cyclone operated for 902 hours.

The second cyclone (S/N 1) was operated for 240 hours with the 5C-8 boiler test in Test System 3.

3. Results

Table XVII summarizes the operation of the various separators and the results obtained from the testing. In general, the results obtained from system testing of the various corrosion product separators was not encouraging.

a. Gravity Plus Magnetism

Modification I

The first modification of the gravity-magnetic separator was examined after 500 hours of operation in Test System 3 with the CRU V-5. Examination of the inside surfaces of the separator showed no evidence of trapped corrosion products. However, examination of the gravity-magnetic separator that was used with the CRU V-3B for 2049 hours in Test System 5 revealed the presence of a uniform coating of corrosion products throughout the separator 0.001 to 0.002 inch thick. The corrosion products found in the bottom magnet were wetted; whereas, the corrosion products deposited on the top magnet were a black powder. The presence of corrosion product on all of the surfaces indicated that before the separator was drained corrosion products were concentrated in this region probably by gravity separation.

FIGURE 54 CROSS-SECTIONAL VIEW OF THE CYCLONE CORROSION PRODUCT SEPARATOR
TESTED IN TEST SYSTEMS 3 AND 5

TABLE XVI RESULTS OF THE VISUAL EXAMINATION OF THE
CYCLONE CORROSION PRODUCT SEPARATORS

<u>Cyclone</u>	<u>Time Operated (hr)</u>	<u>Unit Tested With</u>	<u>Test System</u>	<u>Associated Depth Filters</u>	<u>Results of Visual Examination</u>
S/N 1	250	5C-8 Boiler Test	3	814355*	Pitting of the ID wall. Also, the ID wall was covered with a very light layer of corro- sion products.
S/N 3	55.9	CRU V-4C	3	814355*	The inside wall was covered with a coating of corrosion products as illustrated in Figure 34.
	87.3	CRU V-3D	3	814555 (magnetic)**	
	<u>759.6</u> 902.8	CRU V-1C	5	814555 (magnetic)**	

*These filters were initially operated in conjunction with the S/N 1 cyclone in Test System 3 during the CRU V-4C test which operated for 55.9 hours. These filters were then operated in conjunction with the S/N 2 cyclone in Test System 3 during the 5C-8 Boiler Test.

**This cyclone-magnetic depth filter assembly was originally tested with the CRU V-3D in Test System 3. After the CRU V-3D was moved to Test System 4, the filter assembly was installed with the CRU V-1C in Test Cell 5.

CRU V-4C - 55.9 HR (TEST SYSTEM 3)
FILTERS - 8I4355

CRU V-3D - 87.3 HR (TEST SYSTEM 3)
FILTERS - MAGNETIC

5C-8 BOILER - 240 HR (TEST SYSTEM 3)
FILTERS - 8I4355

CRU V-IC - 600 + (TEST SYSTEM 5)
SAME ASSEMBLY AS TESTED IN CRU V-3D

FIGURE 55 CYCLONE CORROSION PRODUCT SEPARATOR FLOW DIAGRAM

Modification II

The one separator of this modification was examined after 3130 hours of operation. Amalgamated particles were present in the wool, black powder deposits were present on the woven metal screen and an amalgam deposit was present on the magnet.

The analytical results showed that cobalt, chromium, iron, nickel and tungsten were the elements removed in quantity. Of these elements, cobalt was the most predominant, with iron second. The tantalum wool appeared to be the most effective separator element in this device since it contained 50 per cent of the corrosion products found in the separator. The worth of this separation device is indicated by the amount of leached metal present in the separator, 2.6 grams. The CRU V-1B test operation was terminated at the end of 3130 hours because of turbine inlet tube failure. It should be noted that the test data indicated that the bearing flow was decreasing at the end of the test probably because of corrosion product deposition.

Modification III

Two separators of modification III were evaluated during the following tests:

S/N 1 - Test System 3; 5C-8A and CRU V-3E testing
(total of 5000 hours operation)

S/N 2 - Test System 5; 5C-13 and CRU V-4E testing (1500
hours operation)

Results obtained from mercury samples removed from the inlet and exit of both separators during the various tests were mixed. In general, the results indicated either only a slight reduction of corrosion product level or no reduction. Also, under startup transient conditions, the mercury leaving the separator at times showed a higher corrosion product concentration than the mercury entering the separator. During steady state operation the corrosion product level entering and leaving separators was in the range of 0.01 to 0.02 ppm total metallic impurity.

Depth Filters

As discussed and shown in Table XVII, various depth filters and depth filter combinations were tested. In general, the results obtained were inconclusive. Visual examination of the various depth filters revealed the presence of some entrapped corrosion products. In order to more accurately assess the effectiveness of the magnetic depth filters, two of the magnetic type depth filters were fabricated and installed in parallel in Test System 3. These filters were tested in conjunction with the 5C-10 boiler and nozzle test for a period of 261 hours. During this test, provisions were included such that mercury samples could be extracted before and after the depth filters. Figure 56

TABLE XVII CORROSION PRODUCT SEPARATION SUMMARY

<u>Device</u>	<u>Time (hours)</u>	<u>Test System</u>	<u>CRU V Unit</u>
1. Gravity Magnetic Mod. I	500	3	5
2. Gravity Magnetic Mod. I	350	3	2C, 5A, 2D
3. Gravity Magnetic Mod. I	280	4	4A, 2D
4. Gravity Magnetic Mod. I	2049	5	3B
5. Gravity Magnetic Mod. II	3153	5	1B
6. Depth Filters	210	4	4B
7. Depth Filters	0.5 3690	3 4	3C 5B, 3D
8. Cyclone - Depth Filters	55.9	3	4C
9. Cyclone - Depth Filters	240	3	5C-8 Boiler
10. Cyclone - Magnetic Filters	87.3	3	3D
11. Cyclone - Magnetic Filters	759	5	1C
12. Gravity - Magnetic Mod. III	3810	3	5C - 8A Boiler Test and 3E
13. Gravity - Magnetic Mod. III	1110	5	4E

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FIGURE 56 SAMPLING SYSTEM SCHEMATIC USED DURING THE 5C-10 BOILER TEST

shows the manner in which the depth filters were mounted and also shows the mercury sampling points.

The results of the mercury sampling indicated that the concentration of corrosion products in the mercury exiting the separators was higher than the concentration of the corrosion products in the mercury entering the separators. The cause for this behavior was not established. However, the results obtained indicated a doubtful ability of either magnetic or non-magnetic depth filters to effectively remove corrosion products from flowing mercury.

Cyclone Separator

Efforts to evaluate the effectiveness of the cyclone were inconclusive. During the period when the cyclones were in use, there were no provisions for obtaining mercury samples to evaluate the separating efficiency of the cyclone. Also, the cyclone did not appear to have any positive or negative effects on CRU V corrosion product deposition. Post test evaluation of the two separators (listed in Table XVII) revealed evidence of either 1) a light layer of corrosion product deposition on the cyclone I.D. surface, or 2) light corrosion pitting of the cyclone I.D. surface. Because of these results and the fact that the cyclone design was still experimental, it was decided not to continue testing the cyclones in the CRU V test systems.

IV TECHNICAL DISCUSSION

A. MECHANISM OF METALLIC SPHERE FORMATION

The presence of spheres had been observed previously in the CRU IVM-1A. This test was operated with a cyclone separator in the vapor portion of the test system. Investigation of the problem disclosed that the formation of the hollow metal spheres was the result of; 1) erosion of the sidewall of the separator; 2) agglomeration of the resultant debris upon nuclei of droplets of liquid mercury in the vapor; and 3) adhesion and welding of these particles by the collisions of these agglomerates with the container walls and themselves, and subsequent evaporation of the liquid mercury(22) because of elevated temperature exposure.

Thus the following requirements must be fulfilled for hollow metal sphere formation in mercury vapor: 1) a source of material, 2) the presence of nuclei, and 3) adequate residence time in an environment of turbulence and elevated temperature.

These criteria apparently were met in the operation of the test systems during the CRU V-3E and -4E tests. Reference is made to Figure 57 which is a sketch of the boiler and turbine inlet line portion of the test systems. The fact that the boilers, 5C-8B and the 5C-13, operated at a relatively inferior quality even though the thermal profile indicated excess superheat lengths of 15 to 20 feet has been reported earlier in this report.

As a result, liquid mercury in the form of fine droplets (fog flow) was present in the upper regions of the vertical boilers.

These fine droplets contained small amounts of corrosion product; the result of mercury corrosion of the boiler tubes, which escaped deposition in the boiling section of the boiler tubes. Thus, two of three criteria necessary, source of material and the presence of nuclei, were present because of subdesign boiler performance.

As reported by Ziobro and Oberacker,(23) the boiler section under discussion is an area of extreme turbulence. Also, the temperature is high in that NaK at 1250°F enters the boiler from this end. Therefore, the third criteria is met whereby residence time in an environment of turbulence and elevated temperature is attained.

It is hypothesized that the droplets of mercury are levitated in this turbulent section of the boiler. During the period of residence a few of these mercury droplets become nuclei for the agglomeration of corrosion products. If ideal conditions persist for an adequate length of time the droplet

FIGURE 57 BOILER AND TURBINE INLET LINE OF TEST SYSTEMS 3 AND 5

will become coated with corrosion products or form a significant mass of mercury amalgamated with the metallic corrosion products. Impact with each other or the container wall will result in the welding of the corrosion particles. Further exposure to the elevated temperature environment will result in the eventual expulsion of mercury from the agglomerate as a vapor. Thus, the hollow "sphere" is formed. Because of its density change the sphere is now easily removed from the vapor portion of the boiler by entrainment in the high velocity mercury vapor. There are carried through the turbine inlet line, enter the turbine nozzle inlet housing and become lodged in the nozzle openings which act as a physical barrier. The ultimate result is a reduction in power output.

B. MECHANISM OF CORROSION PRODUCT FORMATION AND DISTRIBUTION

The results obtained in the corrosion product study of the test systems and the CRU V's present a consistent story about the formation, distribution and deposition of corrosion products, which is:

- 1) The major source of corrosion products is the boiler.

The data obtained from mercury sampling during boiler testing indicate that during operation, significant quantities of corrosion product are carried over into the condenser from the boiler. (21) Although the data are too insufficient to predict, the absolute amount carried over at any given moment is probably directly dependent upon the quality of the vapor exiting the boiler. Also, examination of the liquid regions of the CRU V test system, as discussed in Section III-B, have revealed a minimal amount of mercury corrosion.

- 2) During steady-state operation, the major portion of the corrosion product is trapped in the condenser sump. Analyses conducted during various test system operations revealed the concentration of corrosion products within the mercury exiting the condenser sump was significantly less than that present in the mercury coming out of the boiler.

- 3) In the region of the CRU V module and condenser, the corrosion products carried over from the boiler are converted to oxides. Prior to the rebuilding of Test Systems 3 and 5, the primary oxide species found was γ - Fe_2O_3 with iron being the major constituent. After the rebuild with L-605 hardware and increased vacuum integrity the primary species found was Me_3O_4 with chromium being the predominant element. In the past there have been air leaks of various magnitude in the low pressure mercury vapor regions of the CRU V modules and the test systems during past operations (leak rates varied from 12 to 200 microns/hr). As a result of these air leaks, there was a

significant partial pressure of oxygen present in the vapor regions of the CRU V and test system. This readily available oxygen reacted with the corrosion products which were carried over into the vapor region from the boiler. These products, consisting of very fine solid particles suspended in the vapor and small mercury droplets saturated with corrosion products, acted as a gettering agent toward the oxygen. In doing so, the corrosion products were converted to finely dispersed oxide particles which then tend to become trapped in the condenser sump. As a part of the rebuilding of Test Systems 3 and 5, the vacuum integrity was improved. Thus, the ultimate vacuum attainable was increased, and the system leak rates were lowered. The effect of the harder vacuum and lower leak rate (i.e., less oxygen) appeared to change the order of oxide found.

As discussed, the oxide found during the CRU V-3E and CRU V-4E tests was the Me_3O_4 variety. This oxide has 1.3 atoms of oxygen combined with one atom of metal. In comparison, the Me_2O_3 variety found previously has 1.5 atoms of oxygen combined with 1 atom of metal.

4) At system shutdown, the corrosion products which have been trapped in the condenser are redistributed in the plumbing lines as the mercury is drained. Thus, some of the corrosion product is transferred to the system reservoirs.

5) At the time of a test system restart, this deposited corrosion product is stirred up and carried into the other regions of the test system. Part of this is picked up and added to the circulating mercury. This occurrence has been indicated by the peaks in corrosion product content found in the circulating mercury during testing (Section III-A). As discussed, the corrosion product concentration at the start of a test (less than 0.1 ppm typical for both boiler and CRU V testing) increased rapidly, reached a peak (0.2 ppm typical) and then started dropping off to a steady state concentration (0.01 to 0.06 ppm), significantly lower than that at initial startup.

6) There appears to be a limiting thickness of corrosion product deposit on the various rotating elements in the liquid mercury regions. After 5000 hours of operation, the thickness of corrosion product deposit present in the CRU V-5C bearings (0.0001 to 0.00025 inch) was approximately the same as that found on the CRU V-1D bearing surfaces (683 hours, 0.0001 to 0.00020 inch). In fact, the thickest deposit was found on the CRU V-2E bearings (0.00015 to 0.0004 inch) which operated for 21 hours. In the same manner, all the deposits found in the CRU V pump region have been similar in thickness. However, in no case has the deposit in the pump region become thick enough to cause a serious drop in pump output.

C. CORROSION PRODUCT DEPOSITION MECHANISM

Corrosion products present in the liquid mercury (solution or suspension) have been studied by electron microscopy in the same manner as those corrosion products found as deposits. Mercury samples obtained from the test system after 1580 continuous hours of the CRU V-5C-25 test revealed the presence of corrosion products. These were found to be in the form of agglomerates up to 2.5 microns in diameter or as particles, presumably ultimate particles, of 0.004 to 0.01 microns in diameter, as illustrated in Figure 58. The particle size indicates that the contaminant in the mercury was probably present as a colloidal dispersion. The presence of the corrosion products in the form of these small particles is in agreement with the low level of contamination revealed by spectrographic analysis. The results are presented in Figure 7 as a plot of total contamination in ppm versus time of test operation.

A mathematical analysis of the lubrication system has revealed several interesting aspects of corrosion product deposition on the bearing surfaces.

As discussed previously, examination of the various CRU V journal bearings has revealed the corrosion product deposit to vary in thickness from 0.0001 to 0.0004 inch in depth. Using the deposits found on the CRU V-5C bearings (this CRU V test had the largest accumulated operating time) an analysis was conducted to determine the approximate weight of corrosion product deposited. The corrosion product deposit thicknesses found were as follows:

Alternator Bearing - Bushing	0.0001 - 0.00012 inch
Sleeve	0.0001 - 0.00025 inch
Turbine Bearing - Bushing	0.0001 - 0.00013 inch
Sleeve	0.00015 - 0.0002 inch

Before the analysis could be conducted, several assumptions were required:

- 1) That the corrosion product thickness was uniform on both the bushing and the sleeve, (to do this an average thickness was used); and
- 2) That the corrosion product deposit was uniform and had a theoretical density of Fe_2C_3 (this was the principal component found on the bearing surfaces).

The surface areas for the bearing bushing and sleeve surfaces were calculated to be:

- 1) Bushing - 0.704 inch²

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FIGURE 58 TYPICAL CORROSION PRODUCT PARTICLES AFTER SEPARATION
FROM THE SYSTEM MERCURY SAMPLE (CRU V-5C-25 TEST)

MAGNIFICATION: 20,000

2) Sleeve - 0.735 inch²

Using the average thickness of the deposit and a uniform composition of Fe₂O₃ the deposit weights were found to be:

Surface area (inch²) X average height (inch) X Fe₂O₃ density (lb/inch³) = weight of deposit (lb). The weights were then converted to milligrams.

The amount of deposit calculated for each surface is as follows:

Alternator Bearing - Bushing	3.5 mg
Sleeve	6.15 mg
Turbine Bearing - Bushing	3.85 mg
Sleeve	<u>6.15 mg</u>
Total Weight of corrosion product deposited	19.30 mg

It is apparent from this mathematical analysis that the weight of the corrosion product deposits on the bearing surfaces is extremely small, 20 mg, as compared to the corrosion contamination normally present in the mercury lubricant and presumably available for deposition. For example, the weight of corrosion products in the lubricant mercury which flowed through the bearings during the CRU V-5C-25 test operation would be 29.3 mg in just one hour. In ten hours there would be 293 mg of corrosion product theoretically available for deposition. With more time the corrosion product available for deposition increases linearly as shown below:

<u>Time in Hour</u>	<u>Wt. of Corrosion Products in gms</u>
1 (sec)	0.00044
1	0.0293
10	0.293
100	2.93
5000	146.5

Obviously, if it assumed that deposition takes place continuously, the rate of deposition would be extremely slow. However, this is not true since the test data usually indicate a sharp decline in the mercury bearing flow in the first few hours of a test operation as indicated in Table III. Thus, we must assume that the most significant deposition takes place in the early part of a test because the corrosion products are present

in a form other than colloidal dispersion. Based on the results of the electron microscopic studies it is indicated that the corrosion products which do deposit on the bearing surfaces are present as agglomerates of a size approaching one micron. Furthermore, these studies also show that the flocs consist of small particles (0.01 microns or less) attached to a larger particle (0.1 micron or larger).

The growth of the floc in mercury is not entirely understood. However, Luborsky(9, 10) has postulated that the growth of iron and cobalt particles in mercury takes place by accretion through the following series of steps:

- 1) atoms dissolve from the surface of the particles,
- 2) these atoms diffuse through the mercury; and finally
- 3) these atoms deposit on another particle.

The diffusion of the atoms through the mercury is assumed to be the rate-controlling step. Regardless of the growth mechanism, the particles of corrosion product now are present in a form more susceptible to separation and subsequent deposition on a component. Thus, a high rate of deposition can occur in the initial stage of a CRU V test.

Once these deposition-prone corrosion products in the system mercury have been eliminated or reduced by deposition or separation (filters, etc.) the system achieves a steady-state condition. It is during this stage that the system mercury contamination level is at the minimum plateaus illustrated in Figures 7 and 8. It is very likely that the mere existence of corrosion products as colloidal dispersions in the liquid mercury at these low concentration levels preclude any deposition during system operation.

The level of contamination at which the CRU V can operate without problems associated with corrosion product deposition on critical component surfaces appears to be between 0.02 to 0.06 ppm. Numerous analyses of mercury samples taken during the CRU V-5C-25 test resulted in data which indicate an equilibrium condition of 0.06 ppm (Figure 7). Since a slow increase in the pressure drop across the lubricant line filter complex took place during the test operation (Figure 59) we must conclude that the safe contamination level of the liquid system mercury must be below 0.06 ppm. The data from the CRU V-3E test, which had a steady state contamination level of 0.02 ppm, did not disclose any potential operating problems.

The plateau of corrosion product content to which the systems equilibrated after each startup is listed below:

FIGURE 59 PRESSURE DROP ACROSS CRU V-5C TURBINE BEARING LUBRICANT LINE FILTER COMPLEX
VERSUS TIME DURING RUN NO. 25

TS/5 (CRU V-5C-25)	-	0.06 ppm
TS/3 (CRU V-3E)	-	0.02 ppm
TS/5 (CRU V-4E)	-	0.01 ppm

The cause of the variation in corrosion product levels is not entirely clear. However, the basic material of construction of the system and the test system configuration are undoubtedly major contributing factors.

Test System 5 at the time of the CRU V-5C-25 test operation was constructed principally of Type 316 SS. Test System 3 was built of L-605 material except for a few isolated components, such as the regulator tank, which were fabricated from Type 316 SS material. Test System 5, rebuilt for the CRU V-4E test, was entirely of L-605 material and also was of much more improved design than any of the previous test systems.

V CONCLUSIONS

The study of the mercury corrosion product problem in the MRP/SNAP 2 system has answered several questions; such as what component(s) is the principle source of corrosion product in the system and what effect does the contaminant have on the CRU V unit? Furthermore, the study has enabled the achievement of a practical application of the laboratory corrosion study results to the engineering system. Specific conclusions which have been drawn from this study are:

1) At operating temperatures up to 600°F, mercury corrosion experienced in the liquid regions of the CRU V test system was minimal, and usually the depth of attack found was less than that predicted by laboratory tests. In those regions where the liquid mercury temperature was over 600°F, i.e., boiler and condenser inlet, the depths of penetration from mercury corrosion were in agreement with the depths predicted by laboratory tests.

2) The maximum level of corrosion products present in the circulating mercury occurs around 100 to 200 hours after initiation of test system operation. Once this maximum level has been reached, the concentration of corrosion products present in the liquid region of the test system drops to a steady state level between 0.01 and 0.06 ppm.

3) Increasing the vacuum integrity of the CRU V test system and utilizing L-605 as plumbing material resulted in a definite decrease in the steady state corrosion product level present in the liquid region of the test systems from 0.06 to 0.010 ppm.

4) Deposition in the liquid mercury portion of the system probably occurs in the initial portion of a test run. The rate of deposition is not linear; both because of the presence of an excessive amount of residual corrosion products present in the system at the start and also because the rate of corrosion thereafter is nonlinear (parabolic).

5) In order to minimize corrosion product buildup, the test systems should first be operated for no less than 200 hours without a CRU V installed. This operation allows for breaking in of the test system. After this operation and prior to any subsequent CRU V testing the test system should be flushed with liquid mercury. To gain the greatest benefit from the flushing, the test system should be constructed so that during flushing the mercury could enter at the lowest point and exit at the highest point.

6) As the cleanliness of the liquid regions of the test system increases, the usefulness of liquid corrosion

product separators appears to decrease.

7) The major source of corrosion products in the MRP/ SNAP 2 test system is the boiler. Some of the corrosion products generated by corrosion of the boiler tubes are carried from the boiler into the remainder of the test system with the mercury vapor.

8) In order to achieve 10,000 hour life in a mercury test system, the mercury boiler and superheater should be capable of producing vapor quality in excess of 95 per cent. This quality is necessary to insure minimal carryover of corrosion products from the boiler.

9) Corrosion product separators should be designed for operation in the vapor portion of the system (boiler discharge) in order to prevent corrosion product deposition in the turbine housing.

10) The corrosion product deposits found on the CRU V liquid component surfaces have been determined to be ferrites possessing the crystallographic structure of the spinels. These spinels are of either the γ Me_2C_3 or the Me_3C_4 types.

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