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PROGRAM FOR INVESTIGATION OF ZIRCALLOY-2 HYDRIDING

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PROGRAM FOR INVESTIGATION OF ZIRCALOY-2 HYDRIDING

Classification Cancelled and Changed To

S. M. Graves

W. K. Alexander

Research and Engineering Section
Irradiation Processing Department

May 5, 1965

**HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON**

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PROGRAM FOR INVESTIGATION OF ZIRCALOY-2 HYDRIDING

I. INTRODUCTION

During the week of March 1, 1965, KW Reactor shut down with indications of a tube leak. Leak testing during the shutdown indicated a front Van Stone flange leak on tube 3065 and a suspect internal leak on tube 3075. During the tube removal process, there was indication of Zircaloy embrittlement on both tubes. Subsequent metallographic examination of samples taken from these tubes indicated the presence of case hydriding on the internal tube surface extending from approximately the end of the active fuel column to the rear Van Stone flange. Vacuum analysis of selected samples revealed the total hydrogen concentration, including the hydrogen present in the hydrided layer, ranged from approximately 50 ppm at the end of the active charge location to approximately 1300 ppm at the rear Van Stone flange. Since examination of these first two Zircaloy tubes removed from KW Reactor, two additional tubes have been removed from KW Reactor, two tubes have been removed from KE Reactor, and one C-size Zircaloy tube has been removed from C Reactor. The presence of hydriding has been observed on the seven Zircaloy-2 tubes removed to date.

It is the purpose of this document to review in some detail the data obtained from laboratory examination of these tubes and to review the scope of the program that has been initiated to determine the mechanism causing hydriding in the Hanford reactors. The program which has been initiated to evaluate the effect of hydriding on the mechanical properties and service life of the Zircaloy tubes, together with investigations of possible remedial action, is also discussed. It should be recognized that the program presented herein is of tentative nature and subject to reorientation as additional data become available.

Conclusions regarding the implications of hydriding on the service life of the Zircaloy tubes may be inferred from the data available to date and the general knowledge available regarding the hydriding process. These conclusions must be considered of tentative nature and are subject to change as more data become available and a better understanding of the hydriding mechanism affecting the Hanford Zircaloy tubing is achieved. The hydriding observed to date not only raises questions regarding the service life of the K Reactor Zircaloy tubing but can markedly influence the direction of future reactor programs, such as overboring, which have been based on the use of Zircaloy tubes. As discussed in this document, preliminary investigation has been initiated to evaluate the hydriding resistance of alternate processes and materials such as autoclaving, Zircaloy-4, and zirconium-niobium alloys.

II. SUMMARY

The following tentative conclusions may be inferred from examination of K and C Reactor Zircaloy tubing and from the general knowledge available of the

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hydriding process. As mentioned previously, these conclusions must be considered tentative and subject to change as additional data and understanding of the hydriding mechanism in the Hanford reactors become available.

1. It appears that hydriding is present to some degree in all Zircaloy tubing in the K and C Reactors. There is no evidence of hydriding in the front end of the process tubes or in that portion of the tubes containing the active fuel charge. Hydriding appears to be maximum at the rear end of the process tube and decreases within approximate linear gradient to the end of the active fuel section.
2. There is an apparent large variation in the amount of hydriding present in the Zircaloy tubes and with no obvious exposure dependency. It appears unlikely that all Zircaloy tubes will reach a limiting hydrided condition or failure within a narrow time period. It can be conjectured that should tube failures result from hydriding, there will be sufficient early indication of a failure problem to permit procurement of replacement tubes before large-scale failure rates become prevalent.
3. Preliminary mechanical properties tests of reactor hydrided Zircaloy tubing indicate, for our service conditions, acceptable ductility remains on tubes having the maximum degree of hydriding observed to date. Hydriding of the reactor tubing appears largely a surface phenomenon with the base metal containing a relatively small amount of the total hydrogen. Provided the hydrogen absorption in the base metal remains low, and the stresses imposed by the hydride layer are not limiting, substantial service life of the Zircaloy tubes may remain despite a fairly thick internal case hydride layer. If hydriding can be arrested or the rate of hydriding markedly reduced within the next few months, substantial service life of the Zircaloy tubes will probably remain.
4. Techniques are being evaluated for reconditioning the K Reactor Zircaloy tubes, including removal of the hydride layer and application of a protective film. Although these techniques appear technically feasible, it appears doubtful that their application on a large-scale program will be economically competitive with tube replacement.

III. DISCUSSION

The data, plans, and proposals discussed in this section represent the status of the hydriding investigation as of May 5, 1965.

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A. Background and Data Review

1. Historical Background

Development of Zircaloy process tubes for Hanford production reactors has been carried on since about 1950. The bulk of the work was aimed at producing ribbed tubes. The switch to ribless tubes eliminated most of the fabrication problems which had been plaguing the development of ribbed tubes. The history of the procurement and installation of the K ribless tubes has been documented¹.

Prior to the full-scale installation recorded in the above reference document, two prototype tubes were installed in KW in mid-1961. Sixty-nine ribless "C-size" Zircaloy tubes were installed in the C Reactor in 1960. Earlier work concerning development and installation of ribbed tubes and KER loop tubes can be found in the records^{2,3,4}.

The K Zircaloy process tubes were made by the Wolverine Tube Company. A brief stepwise listing of the fabrication process is given below:

1. The machined Zircaloy billets were canned in copper, evacuated, heated, and extruded to "blooms." Each billet contained sufficient material for four finished tubes. Some of the earlier billets were double canned with steel between the copper and Zircaloy to prevent alloying of the copper and Zircaloy.
2. The blooms were declad by pickling in HNO_3 and were mechanically conditioned if required.
3. The blooms were annealed in vacuum at 750 C for one hour.
4. The blooms were given one pass through the tube reducing machine, cut into four pieces, and again annealed and pickled in $\text{HNO}_3\text{-HF}$.

1. R. S. Bell. K Reactor Zirconium Tube Program Summary Report, HW-82333. June 9, 1964. (Confidential)
2. D. H. Curtiss and J. W. Riches. Ribbed Zircaloy-2 Process Tubes for Production Reactors, HW-57708. October 10, 1958. (Unclassified)
3. D. H. Curtiss. Summary Report on BDF Zircaloy Process Tube Procurement, HW-61186. July 21, 1959. (Unclassified)
4. D. H. Curtiss and J. W. Riches. Highlights of Zircaloy Tubing Procurement and Utilization at Hanford, HW-67780 RD. December 14, 1960. (Unclassified)

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5. The tube sections were given the second pass through the tube reducer, and again annealed and pickled.
6. The third and last reducing operation left the tube with at least 35 per cent cold work. They were neither annealed nor etched after this final reducing operation.
7. During inspection it was found advisable to sand the surfaces to get uniform appearance. Originally the outer surface was belt sanded, but this practice was discontinued largely after the program was underway. However, the inner surfaces were 100 per cent polished with an emery cloth covered plug.
8. Hydrogen, nitrogen, and corrosion tests were run on samples cut from finished tubes.

After receipt at Hanford the tubes were vidigaged for wall thickness, borescoped to detect internal flaws, and thoroughly inspected for conformance to specifications⁵. Before shipment to the reactors the tube ends were dry honed and annealed. A Van Stone flange was turned on the upstream end of each tube. Both flanges were inspected with fluorescent penetrant test to detect flaws before putting on the nozzles.

The neutron flux, gamma radiation, and temperature to which the K process tubes are exposed is shown in Figure 1. There is very little difference in the conditions the Zircaloy tubes see since aluminum tubes were left in the fringes. The values shown are maximum conditions.

There have been a number of changes made in process water treatment or additions during the life of the C and K Reactor Zircaloy tubes. These are summarized in Table I. The possible implications of some of these changes will be discussed in more detail later in this report.

2. Data Collected to Date

The initial discovery of the presence of hydride was made during the inspection of tubes 3065 and 3075 KW which were removed due to leaks. The front Van Stone flange of 3065 was found to be cracked and could not be repaired. Tube 3075 was found to leak somewhere between the Van Stones; however, the exact location or nature of the leak was

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5. A. W. Fraser. The Nondestructive Testing of the Zircaloy-2 Tubes for K Reactors, HW-82774. April, 1964. (Unclassified)

FIGURE 1

RELATIVE FLUX AND TEMPERATURE LEVELS
SEEN BY THE COOLANT

TABLE I
WATER PLANT OPERATING CONDITIONS

Alum Feed Rate Changes, ppm

Initially all reactors variable from 3 to 14.

7-1-61	C to 18	4-12-62	KE to 13
7-6-61	KE and KW to 18	4-30-62	KW to 18
7-15-61	D to 18	5-21-62	KW to 20, KE to 18
9-6-61	KW to 8	9-1-62	KW to 18
10-6-61	KW to 12	2-15-63	KE, KW Variable 6 to 18
12-6-61	KW to 18	4-1-63	KE, KW to 12
3-9-62	KE and KW to 10	5-1-63	KE, KW Variable 12 to 18

pH Changes

Initially all reactors 7.0.

6-23-61	KW to 6.6	6-24-64	1/2 D to 6.6
9-26-61	KE to 6.6	9-25-64	KE, KW to 7.0
3-1-63	C to 6.6	12-5-64	KW to 6.6
10-18-63	1/2 D to 6.6	12-6-64	KE to 6.6
12-20-63	1/2 D to 6.2		

Dichromate Changes, ppm

Initially all reactors 1.8.

9-20-60	1/2 C to 1.0	3-19-63	D to 1.8
7-1-61	KE to 1.0, KW to 1.8	9-5-63	D, KE, KW to 1.4
9-26-61	KE to 1.8	4-14-64	1/2 C, D, KE, KW to 1.0
12-61	D to 1.0		

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never determined. Two additional tubes were removed from KW plus two from KE. Tube 3074 KW was selected for removal because it was one of the first Wolverine tubes installed and also because it was in row 30 where the first two tubes had been located. It was felt that abnormal conditions might have occurred on row 30 at some time in the past. Tube 0868 KW was selected as one of the youngest tubes in KW. Tubes 2169 KE and 4372 KE were selected as the oldest and youngest, respectively, from KE.

All of the hydride data collected to date have been obtained by removing samples from these tubes and destructively analyzing for the presence of hydrogen. Both metallurgical inspection and vacuum extraction analyses have been used for hydrogen determinations. The metallurgical inspection gives a qualitative indication of the amount and distribution of hydrides in the tube wall. Figure 2 shows typical photomicrographs taken at indicated locations. These inspections have revealed the following pertinent facts:

1. A layer, or case, of massive hydrides is generally found on the inner surface in the downstream end of the tubes.
2. This hydride layer varies in thickness from negligible to about 5 mils maximum. It has been found that near the rear Van Stone flange of the more heavily hydrided tubes this layer is continuous over the entire surface. Further upstream, and in the more lightly hydrided tubes, the layer becomes discontinuous and uneven.
3. The hydride distribution in the base metal is quite uniform and is relatively low when compared to the total hydride values determined by chemical analysis. It is estimated that approximately 90 per cent of the hydride is contained in the surface layer.

The results of the vacuum extraction analyses are shown in Figure 3. The location of the sample and the analytical results are shown for the downstream 12 feet of the 7 tubes studied to date. Inspection of the data displayed in this chart indicates the following:

1. Hydriding in that portion of the tube containing fuel elements is negligible. The chart does not show values upstream of the 12-foot mark but these have all been below specifications for new tubes. There is some evidence of slight hydrogen pickup in the downstream half of the metal charge, but as stated above, it is below the amount allowed by tube specifications.
2. The extent of hydriding increases in a linear manner from the end of the active metal to the Van Stone flange. The maximum reading in all cases has been found within a few inches of the flange.

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Typical section near downstream end

Typical section near 8 foot point

Typical section from upstream area (beyond 8 feet)

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FIGURE 2

DISTRIBUTION OF HYDRIDES IN "K" TUBE

HYDRIDE ANALYSES

FIGURE 3

(ppm Hydrogen)

Tube No. and
Installation
Date

3065 KW
8-61

3075 KW
8-63

3074 KW
2-63

0868 KW
2-64

2169 KW
5-63

4372 KW
1-64

3679 C
1-60

Distance from Rear Van Stone - Feet

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3. There does not appear to be any correlation between amount of hydrogen found and length of exposure, e.g., tube 2169 C had a rate of 4 ppm/mo. compared to a rate of 50 ppm/mo. for tube 3075 KW. This assumes that the uptake rate is uniform for any particular tube. This assumption may be invalid. Figure 4 is a plot of maximum hydride versus length of time in reactor.

The data to date indicate a general hydriding problem throughout the K Reactors. The maximum amount has been found to vary widely between tubes, and there is no good reason to believe that the worst tube has been found. Although the highest concentration measured was in 3075 KW, the tube which developed a leak, there is no positive proof that the leak resulted from hydride formation.

Observations by maintenance personnel during removal of tubes 3075 and 3065 KW were that these tubes were "like glass." The literature certainly does not indicate that the amount of hydrogen found in the base metal should change the ductility drastically. The presence of the case layer, which apparently stresses the base metal, may decrease the flexural strength of the metal. Physical tests on specimens taken from hydrided tubes indicate some reduction in ductility but no drastic changes. These results will be discussed in more detail later.

3. Future Data Acquisition

As mentioned above, it has been quite conclusively established that a general hydride problem exists in the K Reactors. It may be necessary to remove additional tubes for further data acquisition but this will only be done to evaluate the effects of certain parameters thought to bear on the problem. For example, if differences in tube fabrication can be found, then tubes representing such differences would be examined to evaluate the effects of these differences. At the present time it has not been possible to identify any variables which could conceivably account for the apparent differences in susceptibility of various tubes.

A study is now in progress to determine if the perforated Zircaloy inserts (carrot scrapers) in the rear nozzle pick up hydrogen at the same rate as the tubes they are associated with. Twenty-four of these inserts have been removed from KE and are being analyzed for hydrogen content. If the hydrogen levels found approximate those found in the tubes already removed, then it may be advisable to remove tubes from the same channels as the inserts to see how exact the relationship is. If a good correlation can be found between the hydrogen content of the tubes and their nozzle inserts, then a relatively simple and inexpensive method for determining the total picture may be available.

A metallurgical examination of the Van Stone flange from 3065 KE indicated that the hydrides were continuous over the curve of the flange

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FIGURE 4
HYDROGEN CONTENT VS. LENGTH OF SERVICE

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until the point of contact with the gasket was reached. This observation suggests the possibility that removal of the flange may provide sufficient material for determining the extent of hydride formation in the tube. This would be a much less expensive way to detect hydride than removal of the entire tube; this approach has not been tried yet.

The first Zircaloy tube ever installed in a Hanford reactor, 3586 D, is still in operation. This tube probably represents the longest irradiation of Zircaloy in the free world. There is considerable interest in leaving this tube in service as long as possible. On the otherhand, it would be extremely interesting to find out if it has also been hydrided. In an attempt to "have our cake and eat it too," plans are being made to remove four inches from the downstream end without molesting the remainder of the tube.

All of the above mentioned means of securing additional data could be dispensed with if an instrument were available for nondestructively detecting and measuring hydride in the tubes. Several simple approaches to this problem have been tried and found unsatisfactory. A rather complex, high frequency eddy current device is being assembled by Battelle personnel. It is hoped that by using 5 megacycle equipment that the eddy currents will be generated on the inner surface of the tube only. The usual interference of the gunbarrel on the outside of the tube will be eliminated.

Another instrument being developed by IPD personnel is based on the usual difference in thermoelectric potential between dissimilar metallic materials.

It should be emphasized again that reliable, nondestructive instrumentation is desperately needed to determine the location and degree of hydriding now present and more importantly to determine at what rate the uptake is proceeding.

B. Hydriding Mechanism Investigation

The first requirement to successful solution of the K Reactor problem is to gain an accurate understanding of the mechanism by which hydrogen is being absorbed by the Zircaloy. This phase of the over-all program is being carried on by Battelle-Northwest Laboratories.

There are practically no data in the literature bearing on this particular problem. The vast bulk of the work on Zircaloy hydriding has been done at higher temperatures. One piece of information⁶ was found which may be helpful. It is shown in Figure 5. This curve establishes an upper limit

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6. A. Sawatzky. Rate of Growth of a Hydride Layer by Electrolysis at 100°C.
CRMET-924.

FIGURE 5

RATE OF GROWTH OF A HYDRIDE LAYER
BY ELECTROLYSIS AT 100 C

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to the rate at which a hydride layer can be built up by any process at 100 C. The limit is determined by the rate at which hydrogen will diffuse through the layer as it builds up. The parabolic form of this curve indicates that the rate of uptake will diminish with time.

The Chemical Metallurgy Unit of BNW is working in the following areas in an attempt to understand the mechanisms of hydriding better:

1. Determination of Oxide Thickness

Anodizing techniques have been developed which have been demonstrated on both out-of-reactor and in-core samples. An oxide thickness profile over the length for one or more tubes will be determined. This study will determine by mid-May if the hydriding profile will satisfactorily correlate with oxide thickness.

2. Deposited Crud Film

A deposited crud film has been observed on both irradiated and downstream out-of-reactor portions of the discharged K process tubes. This film consists of a loose outer film and a hard inner varnish. While the outer film is readily removed by a plastic fiber brush, the inner film is difficult to remove, even by decontaminating chemicals. A systematic evaluation of crud film thickness along the length of the tube will be undertaken during the determination of oxide thickness, by mid-May.

3. Hydrogen Pickup from Low Temperature H_2 - H_2O Mixtures

The previous studies of hydrogen pickup from a low temperature moist hydrogen atmosphere will be repeated with a liquid phase environment; reactor process water plus H_2 . A variety of surface conditions will be included ranging from vapor blasted to various thicknesses of anodized or autoclaved films and aluminum-zirconium couples. These studies are in progress and significant results will be reported periodically. Estimated time for completion of the test - one year.

4. Electrically Coupled Zircaloy-2 Samples

Electrically coupled Zircaloy-2 samples with sensitized (vapor blasted, punched) surfaces will be exposed to refreshed process water at about 100 C. The experiment is being prepared and will start up about May 1. The test will be periodically sampled. The experiment will be continued until positive results are obtained or one year has elapsed.

5. Gamma Irradiations

Zircaloy samples with a variety of surface treatments have been suspended in a process water filled can at 60 C, in the 3730

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gamma facility. The γ flux is estimated at 10^7 R/hr at the sample surfaces. If γ radiation is necessary to the hydriding mechanism, or an important accelerating factor, this test should produce positive results. This experiment has been sampled twice without positive results. It will be continued for six months.

6. In-Reactor Coupons

Insertion of aluminum spacers supporting zirconium alloy coupons of varying composition and surface treatment is in progress. The purpose of this program is several-fold. It will provide information on: (1) the current progress of the hydriding attack, (2) the effect of both sensitizing and (hopefully) inhibiting surface treatments on initiation of attack, (3) the susceptibility of various alloys, (4) the rate of attack by programmed sample withdrawal information, and finally (5) the distribution of conditions conducive to hydriding within a reactor. This feature duplicates to some degree the carrot scraper evaluation, but offers some advantages in choice of sample surface preparation and in knowledge of the current situation.

The in-reactor coupon program will be supplemented with charges of coupons mounted in specimen holders cathodic to zirconium rather than anodic as are the aluminum spacers in which coupons are currently supported. Secondly, coupons of hydrided tubing will be re-exposed to accelerate our knowledge of how fast hydriding attack, once initiated, proceeds.

In addition to the above outlined work by CMU, the following somewhat similar investigations are being made by Battelle's Coolant Systems Development Unit.

1. Coupon Exposure

Coupons have been pretreated to sensitize the surface and induce hydriding during in and out-of-reactor exposure. The pretreatment techniques are listed below:

1. Etching
2. Polishing
3. Etching plus scratching and smearing with aluminum
4. Treatment 3 plus contact with a paste of decontaminant mixture containing fluoride at 100 C for several minutes
5. Etching plus the fluoride paste treatment

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2. Out-of-Reactor Tests

Sensitized specimens are being exposed in the TF-20 facility at reactor effluent conditions. The first specimens were discharged on April 16 after 360 hours exposure. The samples are being analyzed for hydriding; however, no data are available at present. The test will continue for another six weeks and the final data will be available in seven to eight weeks. Interim data will be available during the course of the test.

Sensitized specimens will be exposed to solutions of Turco 4306-C. The test will start about May 1 and continue for six to eight weeks. Interim data will be available during the course of the test.

3. In-Reactor Tests

Zr-2 coupons have been exposed in-reactor from 3 to 14 months as part of CSDU coolant quality and corrosion programs. These coupons will be analyzed for hydriding, the first information will be available by the end of May.

Specimens were charged in the 1706-KE single-pass tubes, including tube 3050 KE. The corrosion will be monitored by periodic discharge and examination. The discharge and examination schedule for tube 3050 KE will be co-ordinated with the water-quality test program.

4. Zr-2 Fretting

Analyses indicate that the hydriding starts where the fuel charge stops. Factors associated with this demarcation are reactor radiations, geometry, velocity, mass, and materials. The factors of geometry, mass, velocity, and materials can be linked to fretting corrosion or combination fretting-electro-chemical corrosion if it is assumed that the demarcation results in intimate contact between the Al spacers and the Zr tubes. Relative movement between two surfaces in intimate contact could accelerate the attack in two ways: (1) by continuous abrasion and even continuous removal of the already extremely thin zirconium oxide film, by aluminum oxide particles trapped between the surfaces, and (2) by impregnation of the Zr with Al by metal transfer, perhaps by cold welds which are subsequently destroyed by shear associated with the relative movement.

An experimental facility has been set up to determine if relative movement between pieces of Zr-2 process tube and aluminum spacers can result in hydriding. Relative movement will be achieved by externally applied vibration. The hydride concentration of sections of the Zr-2 tubes will be determined after each two-week operating period.

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The test will continue for 18 weeks or 9 operating periods. Interim data will be available while the test is in progress; final data will be available in 20-22 weeks.

5. Corrosion Probes

Coolant Systems Development Unit is developing a corrosion probe to detect Zr-2 hydriding. The development will probably not be completed in time to assist significantly in the present problem; however, it should be a valuable tool during future reactor operation.

C. Water Chemistry Program

1. Dichromate Addition and Coolant pH

As mentioned earlier, the sodium dichromate feed rate and the coolant pH at the K Reactors have been changed since the installation of some or all of the Zircaloy tubes. The sodium dichromate feed rate was decreased from 1.8 to 1.4 ppm in September, 1963 and from 1.4 to 1.0 ppm in April, 1964. The pH of the coolant was at 6.6 since mid-1961 except for the months of October and November, 1964. In order to determine the effect of varying dichromate feed rate and coolant pH on the hydrogen peroxide and hydrogen contents of the effluent, single-pass tube tests have been initiated. A one-week operating period using 1.0 ppm sodium dichromate and pH 6.6 has been completed. It appears that a week is adequate to establish equilibrium. Conditions have been shifted to 1.0 ppm dichromate and a pH of 7.0. About six sets of conditions are planned, and they should be completed in from five to six weeks.

2. Chemical Additions

A program of in-reactor single-tube tests is planned to investigate the effectiveness of various chemical additions to the coolant in suppressing hydrogen formation. The use of hydrogen peroxide, hydrazine, metallic ions, carbon dioxide, and oxygen are tentatively planned. A production test authorizing the additions has been prepared. It is estimated that the tests will get underway in about two weeks. The duration of the program is indefinite and will be dictated by the results obtained. It is worth noting that results will have to be obtained by the use of small quantities of additive even if they are moderately priced or prohibitive costs will result.

3. Sampler

A sampler has been designed and is being fabricated to sample coolant at the end of the fuel charge, half-way between the end of the fuel charge and the rear Van Stone flange, and at the rear Van Stone flange. Completion is anticipated in about a month. The sampler will be used to investigate whether changes in coolant composition occur between the end of the fuel charge and the rear nozzle.

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D. Mechanical Properties Evaluation

A program has been started for testing the mechanical properties of the hydrided tubing from the reactor. Specimens of the entire tube section have been tested to failure in axial tension and ductility. Ring specimens have been pulled in tension to determine transverse properties and ring crush tests will be performed to determine susceptibility to cracking under that mode of deformation. Measurements will also be made to determine the magnitude of residual stresses in the tube wall caused by expansion of the hydride case. All these tests will be repeated on material from which the hydride case has been removed to test the properties of the underlying metal. This same case-free material will then be subjected to a thermal or anodizing treatment to produce a protective film, a treatment such as might be proposed for application to the reactor tubes in-situ, and again tested.

The program of tests for characterizing the tubes as removed from reactor can be completed by the first of May on those tubes presently discharged. Removal of the hydride layer and tests to provide a protective film will follow through May and June. As the surveillance testing of carrot scrapers proceeds, additional tubes will be sampled as indicated. Special tests such as fatigue flexure tests on tube sections can be implemented as the need arises.

The data collected to date indicate that tensile properties have not been changed significantly. The most drastic change has been in the decrease in Reduction in Area value for the tensile specimens. Figure 6 is a plot of the values obtained to date. It can be seen that where unirradiated tube samples give RA values of 45-47 per cent, samples from tube 3075 with 1380 ppm hydrogen give only 15 per cent RA values.

E. Factors Affecting Tube Life

When data are available on the mechanical properties of hydrided tubes, an attempt will be made to assess the over-all effect of the hydriding problem on tube serviceability and life. To facilitate this study, it is planned to take the most accurate readings possible of tube distortion. It will be quite straightforward to plug any given set of mechanical properties into the appropriate flexure formulas to get a calculated limit on distortion. Whether the calculated allowable loads are reliable for predicting tube life will remain to be seen.

There are several factors affecting in-reactor tube life which cannot be factored into calculations; these are:

1. Exact Amount and Distribution of Hydride

Unless nondestructive instrumentation can be developed which gives us this information in all tubes, we can only estimate, from the limited number of tubes removed, what the situation really is.

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FIGURE 6
THE EFFECT OF HYDRIDE ON REDUCTION IN AREA

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2. Creep

If stresses become high enough in the base metal of the tube wall to cause failure, some creep should occur tending to relieve these stresses. If the highest stresses are near the end of the gunbarrels, then the effects of the neutron field may be important.

3. Stress Risers

It is conceivable that during installation the tubes could have received some mechanical damage in the form of nicks, scratches, or gouges which may act as stress risers. It may be that the differential thermal expansion between the gunbarrel and the tube is causing galling at the inner end of the gunbarrel.

4. Stuck Gunbarrels

At the time the Zircaloy tubes were installed, a small per cent of the rear gunbarrels were found to be stuck. It is to be expected that this condition will become worse (e.g., F Area where nearly 100 per cent are stuck). The stress patterns with stuck gunbarrels will be different than with free ones. If both the front and rear gunbarrels stick then the stresses will be very much different. Unless a program of "gunbarrel exercising" is initiated, there will be no way of knowing how many, or which ones are stuck.

5. Graphite Damage

When the Zircaloy tubes were installed, the channels were reconditioned and all tubes were installed with forces below the 1500 pound limit. Out of the six tubes removed from the K Reactors, one was found to be stuck in the graphite. This was believed to be due to wedging action of a broken trunion block. Such binding in the graphite can also introduce abnormal stresses in the tubes. We don't know if the one in six means that 16-2/3 per cent of the tubes are stuck in the graphite or if it was just a happenstance that this tube was picked for removal.

It would appear that the most likely places for tube failure would be at the rear Van Stone flange, or in the immediate vicinity of the inner end of the gunbarrel. If the tube is subjected to high tensile loads, the rear Van Stone will be vulnerable since it is normally weaker than the tube, due to annealing, and also, the highest hydride concentrations have been found at the rear Van Stone. The maximum bending of the hydrided portion of the tube is at the inner end of the gunbarrel. Fortunately, the hydride levels are lower at this point than further downstream.

The foregoing discussion leads one to believe that it will be very difficult to predict accurately at what hydride levels, or at what date, we can expect tube failures.

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F. Tube Reconditioning

The data on hand at the present time indicate that the amount of hydrogen in the base metal is not sufficient to affect the serviceability of the tubes to any great extent. The hydride layer seems to be the biggest offender and the tentative conclusion that its removal, and subsequent passivation of the inner surface, would result in an acceptable condition for indefinite future life seems well founded. A number of means of achieving this goal have been suggested and are discussed briefly below:

1. Passivation Without Hydride Layer Removal

It is possible that we could live with the present amount of hydride if it could be guaranteed that no further hydriding would occur. Two possible methods for doing this would be oxidation and anodic protection. Neither of these possibilities have been demonstrated as possible, even on a laboratory scale. These two methods will be investigated as means of preventing further hydrogen uptake but the chances of their being satisfactory appear quite remote.

2. Hydride Removal and Surface Treatment

Since it appears possible that it will be necessary to remove the hydride layer before a passive surface can be obtained, much thought is being given to means for its removal. Three suggested mechanical removal techniques in descending order of promise are grit blasting, grinding, and broaching or scraping. All of these methods can be used to remove metal but none of them will remove hydride selectively in preference to base metal. This means control of material removed would depend solely on operation of the equipment. Grit blasting seems to be the preferred one of the three mentioned since it would be relatively insensitive to variations in tube ID or roundness. Development of these techniques is being carried out by IPD's Equipment Development Subsection.

Chemical removal of the hydride layer is also being considered. No selective reagent for removal of hydride in the presence of bare metal is now available. Hydride etching rates in the standard HNO_3 - HF - H_2O solution, which now appears to be the most likely candidate etchant, are similar to those of the base metal. Thorough removal of the crud film is necessary prior to etching. There are serious problems associated with chemical removal of hydrided areas, principally in protecting the non-Zircaloy materials from the etchant, in preventing nonetched areas at the top of the tube due to gas collection during etching, and in proper control of the etching rate. These problems appear to be solvable but are comparable to those associated with mechanical removal of the layer. Consideration is also being given to use of some of the proprietary chemicals which are suitable for etching Zircaloy. This work is also being done by Equipment Development Subsection.

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Subsequent to removal of the hydride layer, either mechanically or chemically, it will be necessary to passivate the surface to prevent further hydride formation. It is quite well established that a substantial oxide layer, such as that obtained by autoclaving in steam at 400 C for 72 hours, will act as an effective barrier to hydrogen. It has not yet been shown that such an oxide layer will remain effective at our relatively low temperature for long periods of time. Also, the charge-discharge operations with SSF elements may damage the oxide film extensively. This latter point is being evaluated by charging tests in an autoclaved tube in the 189-D Laboratory.

To form such an oxide coating by autoclaving "in situ" would require holding the tubes at approximately 400 C for three days. This would be a task of considerable magnitude in just supplying the steam. The problem of overheating the rear biological shield may rule out this method. A more practical method of oxidizing the tubes may be to use local heating to give temperatures sufficient to form the oxide layer in a matter of minutes. This would prevent overheating of the shields. A temperature in the 600-700 C range with a pure oxygen atmosphere gives the required oxide layer almost instantly. Such temperatures may be attainable with internal induction coils.

The deposition of an oxide film by electrical means (anodizing) at room temperatures is being investigated. It does not appear practical to get as heavy a film in this way but the attainable film may still be effective. Battelle's Chemical Metallurgy Unit is investigating this possibility.

Other possible means of extending tube life includes re-Van Stone flanging on the rear if the Van Stone flanges prove to be the most vulnerable part of the tube. In addition to simply forming a new Van Stone, it may be practical to recondition the downstream few inches of the tube by any one of the methods described earlier.

The possibility of welding a new section of tube to the rear is also being considered. It is proposed that the tube be pushed to the rear, the hydrided portion removed, and a new section attached. As mentioned previously, it is most likely that the tubes will fail either at the Van Stone flange or near the end of the gunbarrel. It would therefore be necessary to remove approximately 10 to 12 feet of tube to eliminate the tendency for failure at the inner end of the gunbarrel. The induced radioactivity of the tube at this point would require remote cutting and welding.

G. Tube Replacement Possibilities

If it should become necessary to replace large numbers or possibly all of the present Zircaloy tubes, the door would be opened to consideration of

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further reactor modifications. The present tubes were installed for the "life" of the K Reactors. The current interest in channel enlargement would certainly have a bearing on the possible tube replacement problem, or vice versa. In any case, a decision on replacement tube materials would be required. The alternates are discussed below in the light of present knowledge.

1. Zircaloy-2

If large numbers of the present tubes fail with less than five years' use, it would appear pointless to replace them with similar tubes. However, there are data which indicate that autoclaved tubes are much more resistant to hydriding than unautoclaved ones. The unknown associated with this approach is "will an autoclave film remain effective at these low temperatures?" Our charge-discharge operation with self-support fuel may seriously damage any preinstallation oxide film. Only in-reactor tests will determine this, and two autoclaved tubes are already in KE. It does appear to be within the realm of possibility that such tubes would have a satisfactory service life.

2. Zircaloy-4

Zircaloy-4 has been developed to minimize the tendency of Zircaloy to hydride. The nickel content of Zircaloy-2 has been found to have a "sensitizing" action toward hydrogen pickup. It is possible that this modification, particularly when coupled with autoclaving, would result in tubes sufficiently resistant to hydride formation to last the life of our reactors. In-reactor tests will be required.

3. Other Zirconium Alloys

Various other alloys of zirconium have been developed as possible cladding or pressure tube candidate materials. The Zr-2% Nb alloy is receiving considerable attention. These possibilities should be carefully screened. Pure zirconium may also fall in this class.

4. Aluminum Alloys

If no satisfactory zirconium alloy can be found which is impervious to hydrogen, we can always fall back on aluminum. Two questions would need to be answered before resorting to aluminum tubes. First would be the question of geometry. Would we use a smooth-bore tube or go back to ribs? We don't have a proven technology for smooth-bore aluminum tubes. The overbore ribless tubes gave considerable charge-discharge trouble. In addition, it was indicated that tube life was greatly reduced by the combined wear and corrosion. The use of ribbed tubes would mean elimination of the self-support element.

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Secondly, the alloy and/or surface treatment would need to be specified. This would be a problem if an attempt were made to use smooth-bore aluminum tubes, since it would be necessary to have the best possible wear and corrosion properties. Anodizing has been suggested as a means of improving the performance of aluminum tubes.

In any case, the use of aluminum tubes would require the use of smaller diameter fuel elements with attendant production losses.

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