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I   THE EFFECT OF METAL SURFACE CONDITION ON THE APPEARANCE OF NITRIC ACID-
    TREATED SPECIMENS

OBJECT   To determine the cause for variations in the physical appearance
              of nitric acid-pretreated 347 stainless steel specimens

METHOD   It was observed that the physical appearance of Type 347
              stainless steel specimens, pretreated for 24 hours in 1% by
              weight of 70% nitric acid at 250°C, varied occasionally from
              the normal condition. Generally, the specimens exhibited highly
              lustrous interference tints with extremely adherent films. More
              frequently, however, the stainless steel specimens were removed
              from the nitric acid pretreatment solutions with uniform, dull
              black films which sometimes were coated with a loose brown smut.
              The films were thicker than those observed on the lustrous
              specimens, but showed the same excellent degree of passivity in
              subsequent exposure to uranyl sulfate at 250°C as was character-
              istic of the lustrous samples.

              The variations were suspected to be a function of the surface
              condition of the stainless steel bombs used for pretreating.
              These bombs were used almost continually for a period of 9 to
              12 months in the uranyl sulfate corrosion testing program, and
              had been subjected to numerous nitric and chromic acid pre-
              treatments, routine uranyl sulfate corrosion tests, and chemical
              cleaning operations. As a result of these exposures, great vari-
              ations in surface condition could be expected.

              In order to determine definitely if surface condition in the
              test bombs was a contributing factor to the difference in pre-
              treatment appearance on test specimens, four old bombs were
              remachined internally to remove all previously-exposed surfaces.
              Four other old bombs were first cleaned for 15 minutes in a
              mixture of 15% HNO_3 and 15% H_2O_2 (by volume) to remove adherent
              uranium oxides and then washed and scrubbed thoroughly in
              distilled water.

              Type 347 stainless steel specimens were prepared in identical
              manner for all tests. Specimens were 3.2 cm in diameter by
              0.5 cm thick. They were abraded on No. 80 and 120 grit papers,
              degreased in acetone, rinsed in alcohol, dried and weighed.

The test plan was to expose four test samples in four of the newly machined bombs for periods of 1, 4, 8, and 24 hours at 250°C. A similar procedure was used with the new bombs. Each bomb contained 150 ml of 1% by weight of 70% nitric acid. The average specimen area was 20 cm^2. The total (bomb plus sample) exposed surface area ratio to solution volume was 2.0 cm^2 to 1.2 ml.

DATA   At the end of the respective runs, the solutions were analyzed for total dissolved iron, nickel, and chromium. The results of the analyses are included in Table 1. Test data for the 347 stainless steel specimens appear in Table 2.

TABLE 1

CHEMICAL ANALYSES OF NITRIC ACID TEST
SOLUTIONS AFTER EXPOSURE AT 250°C
(Initial solution pH 1.1)

Bomb Type	Exposure hr	Final pH	Dissolved Ions, ppm			Solution Appearance
			Fe	Ni	Cr	
New	1	1.1	5	59	4	Water-white; slight brown residue
New	4	0.8	1	65	1	Water-white; slight brown residue
New	8	1.2	1	60	89	Water-white; fine black residue
New	24	0.5	1	97	9	Water-white; slight brown residue
Old	1	1.1	4	32	7	Water-white; brown residue
Old	4	0.7	1	11	20	Pale yellow; slight brown residue
Old	8	1.2	1	19	6	Pale yellow; brown residue
Old	24	0.5	1	8	33	Strongly yellow; brown residue

TABLE 2

THE CORROSION OF 347 STAINLESS STEEL
IN 1% NITRIC ACID AT 250°C

Bomb Type	Exposure hr	Wt. Change, mg/cm^2	Thickness Change, mils	Sample Condition
New	1	-0.015	-0.0007	Lustrous golden-pink tint
New	4	+0.086	+0.022	Lustrous pink tint
New	8	+0.015	+0.004	Lustrous green-pink tint
New	24	-0.056	-0.003	Lustrous metallic black color
Old	1	-0.127	-0.007	Shiny brown-black streaks
Old	4	-0.030	-0.002	Dull gray-black color
Old	8	-0.015	-0.0007	Dull gray-black color
Old	24	-0.066	-0.003	Shiny brown-black color

The mean film thickness is calculated on the basis that the film is essentially Fe_2O_3 with a density of 5.24. Pretreatment films using nitric acid have been found to contain $> 90\%$ $\alpha.Fe_2O_3$ by X-ray diffraction examination. On this basis, the approximate mean film thickness can be determined by using the expression:

$$T = \frac{400\ W\ M}{(M - m)\rho}$$

where T = film thickness, mils
        W = weight increase, gm/cm^2
        M = molecular weight of the film, gm
        m = molecular weight of metal in film molecule, gm
        ρ = density of film, gm/cm^2

This relationship does not give an absolute value for oxide film thickness since an oxide film was present initially on the stainless steel when it was weighed prior to pretreating.

DISCUSSION   An examination of the exposed test specimens showed that the lustrous films formed in the newly machined stainless steel bombs appeared thinner than the dull gray-black films produced by exposure in the old bombs. Another observed difference was that on the lustrous samples there were no loosely adherent oxides present while on the dull-appearing specimens, a smut of iron oxides was removed during the scrubbing in water operation. This smut was brown-black in color.

Weight changes on the lustrous specimens were erratic; no definite pattern of increased corrosion losses with exposure time was observed. A loss in weight occurred during one hour of exposure; weight gains were observed on the 4 and 8-hour exposure specimens, while the sample exposed 24 hours exhibited a weight loss three times greater than the weight loss incurred during the first hour. In the case of specimens exposed in old bombs, weight losses were observed with the greatest attack occurring during the first exposure period of 1 hour. A decrease in attack was evident on the 4 and 8-hour specimens while the magnitude of attack on the 24-hour sample was comparable to that exhibited by the specimen exposed 24 hours in a newly machined bomb.

The effect of surface condition in test bombs on the exposed specimens is more fully marked in consideration of the facts that all test specimens were prepared in the same manner before testing and that the specimens were electrically insulated from the bomb mass by means of quartz holders.

Several conclusions may be drawn from the results of the tests and chemical analyses of the test solutions.

1) Corrosion iron was found as a precipitate of $\alpha.Fe_2O_3$ (possibly a hydrated form) after one hour's exposure at $250^{\circ}C$. Thus the total time required for the transition of metallic iron to the ferric state was two hours from the start of the test, allowing one hour for the test bomb and solution to come to operating temperature. It was during this period that the dissolved iron concentration was highest in both old and new bombs. During subsequent exposure times, the dissolved iron contents were > 1 ppm although precipitated iron oxides were found in all solutions.

One mechanism for the formation of ferric oxide in the solutions may be the initial oxidation of iron in the stainless steel by the dilute nitric acid at moderate temperature to form soluble ferrous state products. Metallic iron can be oxidized by hydrogen ions to the ferrous state but not appreciably to the ferric state from the ferrous state. As the temperature is increased, thermal decomposition of the nitric acid occurs, resulting in the formation of gaseous products, including oxygen. If polarization of the stainless steel was part of the initial corrosion process, the protective blanket of hydrogen is removed by the presence of oxygen, and corrosion attack on the stainless steel continues. Any existing soluble state ferrous compounds are oxidized to the ferric state and precipitate from solution as insoluble oxides. The metal surface also undergoes oxidation of metallic iron to ferrous and finally ferric oxides. The oxidation process on the surface forms a protective oxide film which remains as an extremely adherent layer.

In view of the results obtained from numerous pretreatment tests, it would seem that the presence of insoluble iron oxides in the solution may be at least partially attributed to the formation of soluble ferrous compounds during the initial phase of the exposure. Many pretreatment tests have been run in bombs which were used only for pretreating in which the final solutions have been water-white in color and free of insoluble residues. Some precipitate, very slight in quantity, may be present from exposure of the freshly abraded test specimen. These results indicate that the bomb surface still had retained a protective layer which was very resistant to attack by new solutions. As a bomb is subjected to repeated exposures in uranyl sulfate,

with infrequent solution reductions, this phenomenon no longer exists and pretreatments conducted on such surfaces invariably produce more insoluble oxides of iron than are normally encountered.

In cases where weight gains rather than losses were observed in the new bombs, the oxidation rate on the samples may exceed the dissolution rate of the base metal. The dissolution rate, in turn, is affected by variations in chemical composition of the stainless steel, non-homogeneities of the surface, and other factors.

2) The high concentrations of nickel encountered in the solutions taken from the new bombs indicate selective corrosion attack in preference to chromium. This would be expected since chromium is more passive to the action of nitric acid than nickel. This same effect was less noticeable in the solutions taken from old bombs. The dissolved chromium analyses are not truly representative of the actual amount of chromium removed from the stainless steel since it is suspected to precipitate from solution as an oxide. The nickel analysis is a better criterion for evaluation of corrosion attack because it does not remain as an inherent component of the protective film and is soluble in nitric acid as are its oxides, if formed.

If one takes a nickel content of 9.5 percent (determined by analysis) in the 347 stainless steel bomb and sample, a nickel balance can be calculated between the weight loss of metal during the exposure and the amount of nickel determined analytically in the test solutions. The total exposed area of the test bomb and sample was 335 cm^2. Corrosion attack on the test coupons is considered to be representative of the type and magnitude of corrosion attack occurring on the walls of the bombs. The weight losses included in Table 3 represent an estimated total weight loss for the bomb and sample. Data were not calculated for specimens showing weight gains. The reported nickel analyses are based on a test volume of 150 ml.

TABLE 3

A COMPARISON BETWEEN ESTIMATED NICKEL LOSSES AND REPORTED NICKEL ANALYSES IN NITRIC ACID SOLUTION AT 250°C

Bomb Type	Exposure, hr	Wt. Loss, mg/cm^2	Total Wt. Loss, mg	Estimated Nickel Loss, mg	Reported Nickel, mg	Discrepancy Factor
New	1	0.015	5.03	0.48	8.85	18.4
New	24	0.056	18.76	1.78	14.55	8.2
Old	1	0.127	42.55	4.04	4.80	1.1
Old	4	0.030	10.05	0.96	1.65	1.7
Old	8	0.015	5.03	0.48	2.85	6.0
Old	24	0.066	22.11	2.10	1.20	0.6

The discrepancy factor is the ratio of estimated nickel loss to the reported nickel analysis.

A greater discrepancy in nickel balance occurred in the new bombs than in the old test bombs. It must be realized that a true balance on nickel is not possible unless the pretreatment films were stripped from the metal surfaces to more closely approximate actual weight losses. A very good balance was obtained on the 1 hour test conducted in an old bomb; estimated loss and reported value compared closely. Results on 4 and 24-hour tests were not in quite as good agreement, while the greatest difference was found in the 8-hour test.

Using the values obtained from nickel analyses of the test solutions, the thickness losses on the test samples can be calculated. These losses are compared with actual thickness losses in Table 4. Corrosion attack is assumed to be uniform.

5 5 4 - 7

TABLE 4

A COMPARISON OF ACTUAL AND CALCULATED
METAL THICKNESS LOSSES

Bomb Type	Exposure hr	Actual Thickness Loss, mil	Calculated Thickness Loss, mil
New	1	0.0007	0.013
New	24	0.0030	0.025
Old	1	0.0070	0.008
Old	4	0.0020	0.003
Old	8	0.0007	0.004
Old	24	0.0030	0.002

These results again indicate that selective corrosion attack of nickel occurs in new bombs to a greater degree than it does in old bombs. Greater metal thickness losses are indicated than actually obtained in the new bombs. Good agreement between actual and calculated thickness losses was obtained in the old bombs.

These data, accumulated on a total of 8 tests, will be supplemented by the results of analyses of numerous pre-treatments being conducted in new and old bombs. It will be determined if the same type of behavior as exhibited by the tests herein described is characteristic of nitric acid pretreatment operations in the two types of bombs.

CONCLUSION   The conclusions derived from this series of tests were:

1- The physical appearance of nitric acid pretreatment films formed at 250°C is influenced by the surface condition of the test bombs in which the pretreatment is conducted. Newly machined stainless steel bombs produce highly lustrous surfaces with brilliant interference tints; old and often-exposed surfaces invariably result in dull gray-black surfaces which show equally good passivity in uranyl sulfate solutions at 250°C.

2- The magnitude of corrosion attack by nitric acid on test specimens exposed in old bombs is generally greater than observed on specimens exposed in newly machined bombs.

3- The amount of dissolved nickel found in solutions used in new test bombs was greater than that found in old bomb test solutions. Test data indicate selective attack of nickel in new bombs; the magnitude of this attack was less pronounced in old bombs.

554-8

4- The metal thickness losses in new bombs, calculated on the basis of dissolved nickel concentrations in the test solutions, were greater than losses determined by specimen weight losses, assuming corrosion attack to be uniform. Agreement was good between actual and calculated metal thickness losses on specimens exposed in old bombs as determined by nickel analyses.

Note The 347 test coupons used in this study have been submitted for optical and X-ray examination to determine:

1- Basic constituents in films and approximate concentrations of each.

2- Film thicknesses as a function of exposure time.

3- General metallographic examination of film and metal structures.

II THE CORROSION OF 347 STAINLESS STEEL IN HIGH CONCENTRATIONS OF URANYL SULFATE AT 250°C

OBJECT   To determine the corrosion behavior of HNO_3-treated Type 347 stainless steel at 250°C in uranyl sulfate containing 100 and 200 g uranium/liter

METHOD   Concentrated solutions of uranyl sulfate were prepared by dissolving calculated quantities of salt in distilled water. These solutions were made approximately 0.44M and 0.86M in uranyl sulfate and contained 103.8 gm and 203.8 gm of uranium/ liter, respectively.

Test specimens of Type 347 stainless steel were prepared by abrading on No. 80 and 120 grit papers, degreased, rinsed in alcohol, dried, and weighed. Quartz hooks were used to suspend the specimens in the test solutions.

A solution volume of 150 ml was used for each test and the same solution was used throughout the test runs of 11 weeks. The solutions were analyzed at the end of the tests.

Stainless steel test bombs were used to contain the samples and solutions. After chemical cleaning, the bombs were pretreated for 24 hours at 250°C in 1% by weight of 70% concentrated nitric acid. This single initial pretreatment proved satisfactory for the entire test period.

The test bombs were heated to 250°C and run at this temperature for weekly periods. The solutions were examined at the end of each week for signs of reduction; specimens were inspected and weighed at this time.

DATA

The final solution analyses are included in Table 1.

TABLE 1

CHEMICAL ANALYSES OF URANYL SULFATE SOLUTIONS AFTER 11 WEEKS AT 250°C

	Solution 1	Solution 2
Initial U, gm/l	103.8	203.8
Final U, gm/l	103.0	200.0*
Initial pH	1.95	1.55
Final pH	1.90	1.52
Final Fe, mg/l	15.0	9.0
Final Cr, mg/l	1.0	1.0
Final Ni, mg/l	5.0	18.0
Final U(IV), mg/l	236.0	346.0

*This result was beyond the accuracy of the analytical method for high uranium concentrations.

Corrosion data on the test specimens are shown in Table 2. The average exposed specimen area was 19.7 cm^2.

554-10

TABLE 2

THE CORROSION OF NITRIC ACID-PRETREATED 347 STAINLESS STEEL IN CONCENTRATED URANYL SULFATE SOLUTIONS AT 250°C

Exposure, wk	0.44M UO_2SO_4		0.86M UO_2SO_4	
	mdd	mpy	mdd	mpy
1	-1.40	0.25	-1.96	0.35
2	-0.29	0.05	-0.73	0.13
3	-0.14	0.03	-0.56	0.10
4	-0.13	0.02	-0.47	0.08
5	-0.32	0.06	-0.56	0.10
6	-0.25	0.05	-0.43	0.08
7	-0.42	0.08	-0.38	0.07
8	-0.22	0.04	-0.35	0.06
9	-0.19	0.03	-0.31	0.06
10	-0.18	0.03	-0.29	0.05
11	-0.20	0.03	-0.31	0.06

The test solutions did not exhibit any of the usual signs of reduction during the run and remained clear and yellow in color. The test specimen removed from the 0.44M solution was dull black in color; the sample removed from the 0.86M solution was a lustrous, metallic gray-purple color. Neither of the samples had visible signs of corrosion attack. The difference in appearances may have resulted from the initial nitric acid pretreatment since it has been determined that metal surface condition influence on the physical appearance of the test specimens.

DISCUSSION   Results of chemical analyses show no reduction in total uranium content during the 11 weeks. The analysis on the 0.86M solution could not be obtained any closer than 200 gm/liter due to limitations of the analytical method. New methods are now being prepared for analyses of highly concentrated uranyl sulfate solutions that will have greater accuracies. The dissolved ions such as iron, nickel, and chromium, were low in concentration indicating negligible corrosion attack on the stainless steel. The nickel analysis is most important since it remains in solution and does not precipitate as do iron and chromium. The solution pH showed negligible change between initial values and values obtained at the end of 11 weeks.

Weight losses, mg/cm^2, are plotted in Fig. 1 as a function
of exposure time. Corrosion attack was slightly more
pronounced in the 0.86M uranyl sulfate solution. Samples
in the two solutions showed similar behavior. After the
initial exposure of one week, the weight losses decreased
during the ensuing 1 to 3 weeks. This period was then
followed by a gradual increase in corrosion attack for the
remainder of the tests. Little difference in corrosion
rates for the two specimens was apparent at the end of
11 weeks. The rate in the 0.44M solution was 0.03 mil/year
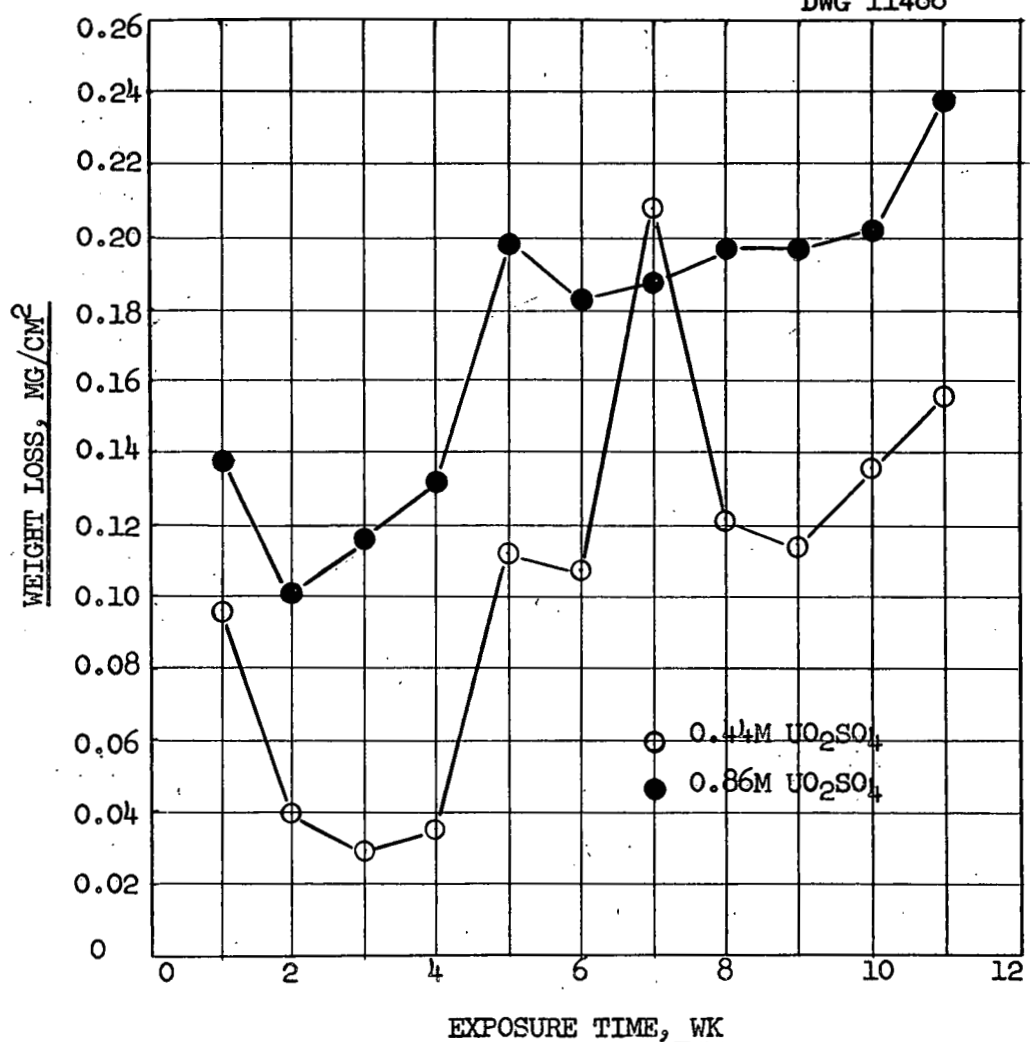as compared to the 0.06 mil/year obtained in the 0.86M uranyl
sulfate.

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FIG. 1 Weight Losses on Nitric Acid-Pretreated 347
         Stainless steel Exposed to Concentrated
         Uranyl Sulfate Solutions at 250°C

554-12

A straight-line relationship was obtained by plotting uranium concentrations of 40, 103.8 and 203.8 gm/l against corrosion rates on 347 stainless steel pretreated in 1% nitric acid. Data are for an exposure period of 11 weeks, and are shown in Fig. 2. Increasing the uranium concentration resulted in a slight intensification of corrosion attack; at 203.8 gm/l the rate was six times greater than the rate for 40 gm/U solution. However, the magnitude of this attack was extremely low, 0.06 mil/year, and cannot be considered as a serious increase.
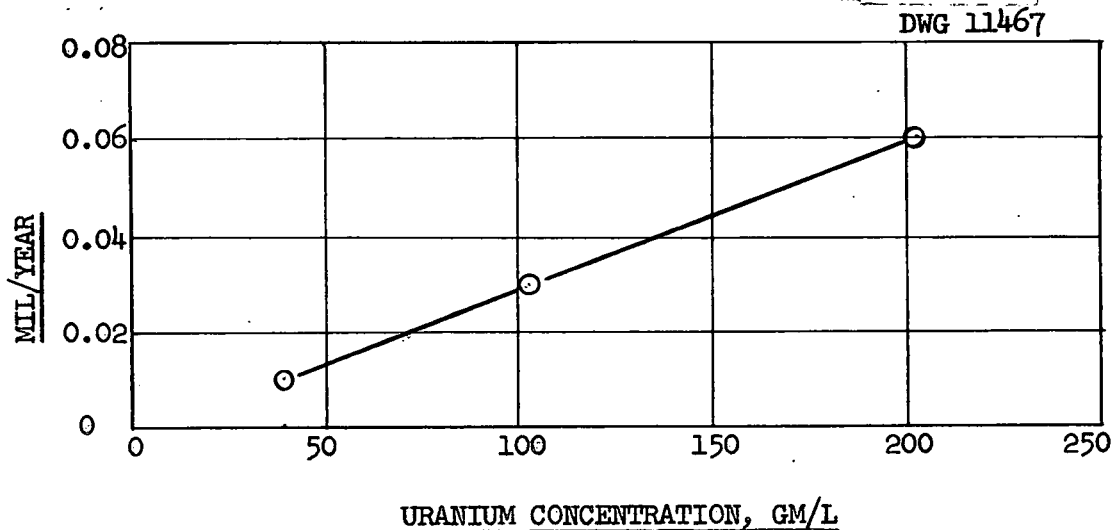

FIG. 2 The Corrosion of Nitric Acid-Pretreated 347
Stainless Steel as Determined by Total
Uranium Content in Uranyl Sulfate Solution
at 250°C
(Exposure Time, 11 Weeks)

Additional studies with uranyl sulfate solutions containing 100 to 400 gm of uranium/liter will include:

1) The effect of solution stability in untreated stainless steel surfaces at 250°C.

2) The use of chromic and nitric acid pretreatments as affecting solution stability at 250°C.

3) The presence of oxygen as a solution stabilizer.

CONCLUSIONS The results of this investigation are summarized as follows:

1- Nitric acid-pretreated surfaces will satisfactorily contain 103.8 to 203.8 gm of uranium/liter uranyl sulfate solutions at 250°C.

2- Corrosion attack on pretreated 347 stainless steel is very slightly accelerated as the uranium concentration is increased from 103.8 to 203.8 gm/liter. The corrosion rate in 0.44M uranyl sulfate was 0.03 mil/year as compared to 0.06 mil/year obtained in 0.86M uranyl sulfate at 250°C for 11 weeks.

3- Corrosion rates on pretreated 347 stainless steel were a straight-line function of uranium concentration, gm/liter. Rates of 0.01, 0.03, and 0.06 mil/year were obtained in 40, 103.8, and 203.8 gm of uranium/liter solutions, respectively, for 11 weeks at 250°C.

III EXAMINATION OF INSOLUBLE RESIDUES REMOVED FROM URANYL SULFATE-STAINLESS STEEL SYSTEMS OPERATED AT 250°C

OBJECT   To determine the identity of insoluble residues removed from the liquid-vapor interface region of stainless steel systems operating with uranyl sulfate at 250°C

DESCRIPTION   Insoluble yellow-colored precipitates have been observed recently in two stagnant corrosion tests operating with uranyl sulfate at 250°C. These residues were found at the liquid-vapor interface after the tests were cooled and dismantled. The quantity of residues found in each case was small, 50 to 60 mg. The precipitates were collected carefully and submitted to H. Dunn for X-ray diffraction studies. A resumé of the test history leading to the finding of the residues follows.

Test 970 A stainless steel bomb with a solution capacity
of 150 ml, was pretreated for 24 hours at 250°C in 0.1M Na NO3.
Uranyl sulfate containing 40 gm of uranium/liter was placed
in the bomb and heated to 250°C. The test was run suc-
cessfully for eight weeks with weekly replacement of the
sulfate solution. Solution reduction was not detected and
corrosion attack on the 347 stainless steel specimen was
negligible. At the end of the final week, a slight ring of
yellow, insoluble crystals was observed at the solution-vapor
interface. Approximately 60 mg were removed and sent for
X-ray diffraction inspection. The results of the diffraction
study showed that the crystals were predominantly a mono-
hydrated form of UO_3. A trace quantity of UO_4 . x H_2O was
found also.

Test S203 A stainless steel bomb, solution capacity 750 ml,
was pretreated for 24 hours in 1% HNO_3 at 250°C. Uranyl
sulfate containing 38 gm of uranium/liter was introduced
and heated to 250°C. Samples were taken at temperature. –
After 18 hours of operation, the total uranium content de-
creased to 25 gm/liter and solution pH decreased from 2.4
to 1.9. The test was cooled to room temperature, and without
opening the bomb, 50 psi of oxygen pressure was added. After
heating back to 250°C, an operation requiring 1.5 hours, the
total uranium content returned to a value of 38.8 gm/liter and
remained approximately at this concentration for an additional
42 hours at which time the test was stopped. After cooling,
the solution pH was 2.4. An insoluble precipitate of iron
oxide was noted in the solution as a result of corrosion attack
on the stainless steel during the initial phase of the run when
the uranium concentration decreased.

A small deposit of yellow crystals was observed on the walls
of the bomb at the solution-vapor level. An X-ray diffraction
study disclosed them to be UO_3 . H_2O.

CONCLUSIONS An infrequent appearance of yellow-colored, insoluble crystals
was observed at solution-vapor levels in several stagnant
corrosion test runs. These crystals were found to be
predominantly UO_3. H_2O with traces of UO_4 . x H_2O. No definite
correlation between the specific history of a corrosion test
with the formation of the UO_3 . H_2O has yet been observed.
Since this compound is easily dissolved in acid solutions, its
presence may be due to a cooling phenomenom which leaves it
suspended out of the test medium as the solution cools and
returns to its original volume.

James L. English

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