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TRITIUM PERMEATION THROUGH CHARACTERIZED FILMS ON TYPE 304L STAINLESS STEEL

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SUBJECT DESCRIPTORS

Acid Etch Cleaning
Nitradd®
Nitric Acid
Passivation
304L Stainless Steel
Tritium

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TRITIUM PERMEATION THROUGH CHARACTERIZED FILMS ON TYPE 304L STAINLESS STEEL

A. J. Kallas, T. L. Rising, and E. L. Childs

ABSTRACT

Rocky Flats is looking for an optimum method for surface treating 304L stainless steel to increase its resistance to tritium permeation. Tritium exposure and analysis is very expensive and time consuming. Therefore, alternate surface characterization methods were sought that would correlate to tritium permeation. These alternate characterization methods will be employed initially to characterize treated surfaces prior to tritium analysis. In the future, these characterization methods will be used to screen candidate passivation processes. The best candidates will then be evaluated by exposing them to tritium and measuring permeation.

Selected surface treatments were applied to 304L samples at the Rocky Flats Plant. One set of samples was shipped to the Rockwell Corporate Science Center for alternate characterization analysis. Another set of samples was sent to Los Alamos National Laboratory for tritium exposure and ion beam spectrographic analysis. The Science Center performed the following analyses: ellipsometry, contact potential, photoelectron emission, surface energy, surface activation, cathodic polarization, electrochemical impedance, and open-circuit potential. Excellent correlation was found between type of treatment and surface activation and electrochemical impedance. As shown below, results of the Science Center tests correlate well with actual tritium permeation measurements made at Los Alamos. The treatments are listed in order of decreasing permeation resistance.

MOST STABLE - LEAST PERMEABLE

Science Center Tests	Los Alamos Tritium Measurements
Electropolish and Nitric Acid	Electropolish and Nitric Acid
Electropolish	Electropolish
Electropolish and Nitric/Nitradd	Electropolish and Steam
Electropolish and Steam	Electropolish and Nitric/Nitradd

LEAST STABLE - MOST PERMEABLE

Future work will involve screening new treatments, testing different stainless steel alloy substrates, and investigating the effects of aging and environment on as-deposited passive oxide films. Results from future work will dictate which cleaning or passivation treatments 304L stainless steel parts will receive during final cleaning processes.

INTRODUCTION

The Rocky Flats Plant uses different techniques to passivate the surfaces of 304L stainless steel (304L SS) parts. Passivation, the formation of protective surface oxides, is generally accomplished by exposing the steel to an acid mixture, followed by deionized water rinsing and air drying. Los Alamos National Laboratory and Sandia National Laboratory, Livermore, require passivation of some of their containers during final cleaning operations at Rocky Flats. Although Rocky Flats has used some of the passivation procedures for years, the Laboratories question whether optimum passivation techniques are used.

A development effort is under way at Rocky Flats to determine one optimum method of passivating 304L SS that will be acceptable to both Los Alamos and Sandia. The determination of an optimum method will enable Rocky Flats to clean and passivate most stainless steel parts in one acid passivation line. This will reduce the number of procedure documents required in the stainless steel cleaning area, while increasing operator efficiency. Determining an optimum passivation technique will also prolong the service life of parts. Passive surfaces will effectively reduce tritium permeation into the stainless steel wall, thereby reducing hydrogen and helium embrittlement. In addition, passive surfaces enhance corrosion resistance, although corrosion resistance is not the main thrust of this study.

Chemically processing or heat treating stainless steel causes the formation of a passive, chromium-oxide-enriched outer surface. To characterize the tritium permeation resistance of this passive oxide layer, it is essential that all oxide surfaces studied are of the same quality and consistency. Treated samples eventually will be exposed to tritium or analyzed via electron optics. Uniform oxide surfaces will enable direct correlation between tritium exposure and electron optical measurements.

A rapid, inexpensive method for surface characteriztion was sought to verify consistent oxide surfaces (depending upon surface treatment). Early in this program, experimentation at Rocky Flats with electropotential measurement across the passive oxide layer of a group of similarly treated samples demonstrated that there are measurable, reproducible potential differences characteristic to each passivation treatment.

During the past year, the Rockwell International Science Center, Thousand Oaks, Calif., extended this work. Based on electrochemical measurements, inferences now can be made between surface treatment and oxide layer thickness, integrity, and chemical stability.[1] The Science Center characterization methods were used in this project to characterize samples used for tritium exposure. In the future, some of these studies will be used to evaluate the changes that oxide surfaces undergo when exposed to air and hydrogen environments over an extended period. The Science Center's methods will also be used to verify that given passivation treatments consistently yield the same type of oxide layer.

When reliable correlations between electrochemical characterization and tritium permeation are established, these inexpensive methods will be used for screening large numbers of passivation treatments and subsequent exposure conditions. Potentially, they can act as quality assurance tools in applications where passivated materials are used for their resistance to hydrogen isotope permeation.

The usefulness of these characterization tools is also evident when one realizes that for most passivated stainless steel systems, hydrogen permeation through the oxide layer is the rate controlling step. Researchers[2, 3] found that stainless steel without a passive layer has two to three orders of magnitude greater permeability to hydrogen isotopes than steels with passive layers. In each case, the investigators removed the oxide layer by vacuum sputtering and then plated the samples with palladium.

Undoubtedly, a major portion of the permeability increase was due to the catalytic nature of palladium. Swansiger and Bastasz[2] found that a palladium layer over the oxide surface still increased the permeability of the material, although not as much as the oxide-free, palladium-coated samples. This current work confirms these findings with regard to increased permeability of palladium-oxide-coated samples. Their work reinforces the observation that surface reactions are rate controlling for hydrogen permeation.

Thin, cohesive, and stable oxides appear to have greater resistance to permeation than thicker and more defective coatings.[1, 2] Apparently, the differences in tritium permeability among different coherent oxide coatings is less than the observed difference between palladium-coated and oxide-coated samples.[4] Since thickness and stability are the attributes that the Science Center measured, one would expect a good correlation between their results and tritium permeability.

This hypothesis was tested by studying the effect of surface treatment versus tritium permeation into the surface. Sets of chemically and thermally treated samples were exposed for a specified period to tritium at Los Alamos. The method chosen to measure tritium diffusion was ideal for this study. Unlike the permeation method for measuring tritium flux through stainless steel foils,[2, 4] ion beam analysis avoids complications associated with material transport through two surfaces; namely, the upstream and downstream surfaces. The ion beam analysis has the further advantage that it is less destructive than the thermal release[5] and acid etching[6] methods for measuring tritium permeation.

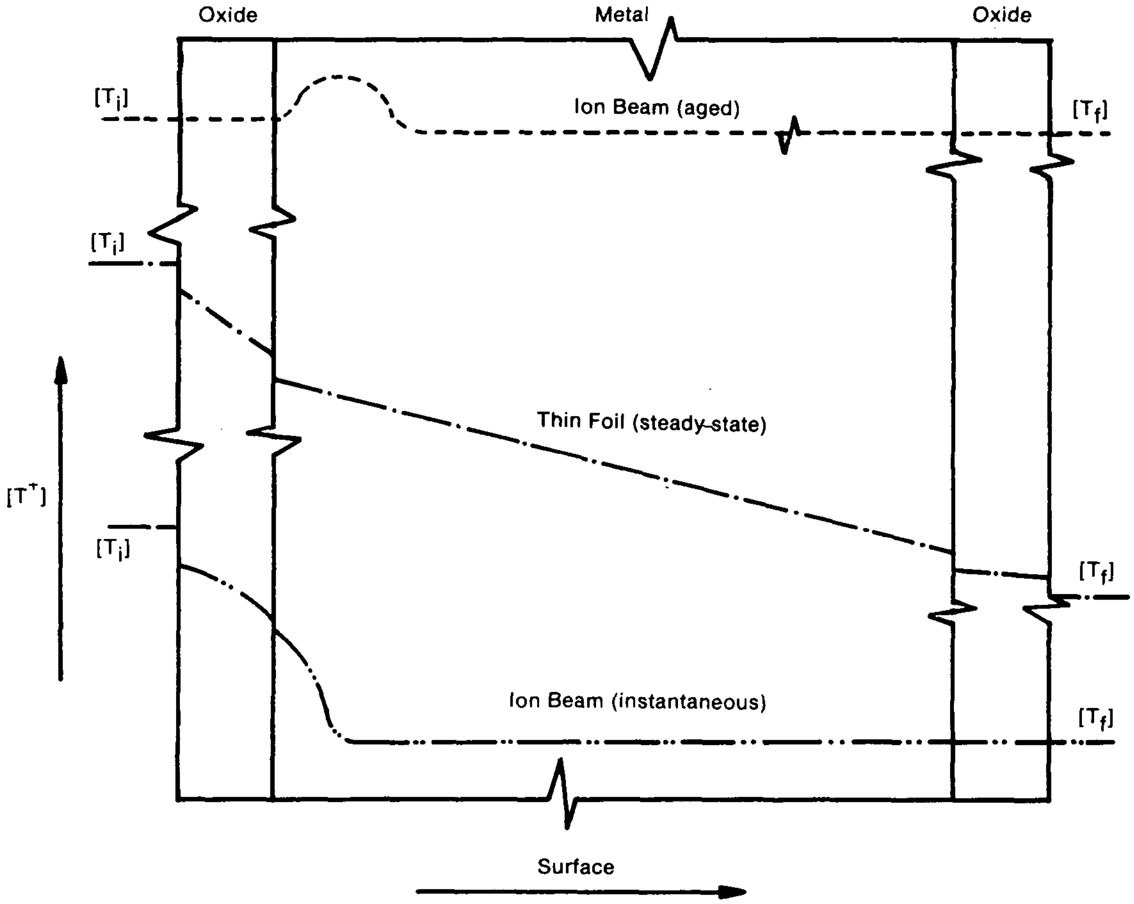

FIGURE 1. Thin Foil Versus Ion Beam Analysis for Tritium Permeation Evaluation

Figure 1 is a schematic illustrating the difference between the ion beam and the thin foil techniques. The thin foil is shown at steady state; the initial $[T_i]$ and final $[T_f]$ tritium concentrations are known, and the overall flux is measured. However, it is very difficult to measure tritium concentration at the oxide/tritium and oxide/metal interfaces and within the oxide and metal. Without concentration measurements, inferences about the mechanisms that control permeation throughout the system are difficult to make.

On the other hand, ion beam analysis measures the tritium profile as a function of depth under both steady-state and nonsteady-state conditions. Thus, the ion beam method is ideally suited to studying the influence of passive oxide film structure on tritium permeation.

The initial correlation between the Science Center results and tritium permeation results from Los Alamos is excellent. The thick, porous oxide films produced by heat treating are much more permeable than the thin, stable oxide films produced by nitric acid. It appears that the inexpensive characterization methods do provide a correlation with measured tritium permeation.

In the future, this correlation will be exploited to reveal more information about passive films. Electrochemical characterization methods will be used to screen potential passivation agents, evaluate environmental effects on films, and perhaps even be used as quality assurance for production passivation processes. Results from this study will enable Rocky Flats to implement one optimum passivation procedure for cleaning stainless steel parts. Ion beam analysis will continue to be used to ensure that correlations are valid.

PROJECT HISTORY

Previous work on this effort focused on determining a correlation between the chemical or thermal processing of a 304L stainless steel surface and its electrochemical potential qualities. This work was performed rather inexpensively by use of an EG&G Model 350A potentiostat. The work proved to be a sensitive and rapid method of evaluating hydrogen isotope barrier qualities on pretreated 304L SS surfaces. The ability to distinguish between different surface treatments by use of electrochemical potential was established at Rocky Flats in 1984.

The results of the above study showed that relating tritium permeation to surface treatment by use of potentiometric techniques was possible. More advanced and accurate electrochemical techniques are required, however, to enable a practical correlation of tritium permeation versus surface treatment. This report outlines how these correlations were obtained and what they signify. Future work will focus on the most promising surface treatments and electrochemical tests to determine an optimum passivation technique for production purposes.

Chemical Process Systems Development at Rocky Flats is coordinating all of the efforts involved with this study. Surface characterization studies were performed by the Science Center and by Rocky Mountain Analytical Research Laboratories, Inc. Tritium permeation studies were performed by Los Alamos. Rocky Flats prepared the 304L SS samples used by all three laboratories. All samples were electropolished using the same procedure prior to subsequent treatment. Electropolishing was intended to eliminate the surface variability inherent in the as-received specimens.

EXPERIMENTAL

Rockwell Science Center

Sample coupons for the Science Center, 1/2 X 1/8 X 7 inches, were electropolished for 10 minutes in a 90 vol% phosphoric acid mixture at 60 °C, rinsed in a 10% mixture of boric/sulfamic acid for 10 minutes, cascade rinsed in two deionized (DI) water baths at 60 °C for 10 minutes, then air dried. The coupons (in sets of 15) were then treated in the following manner:

1. Electropolished (EP)
2. Electropolished, then vacuum plated with approximately 250 Å of palladium (EP + Pd)
3. Electropolished, heated to 200 °C for 1 hour, then allowed to cool to room temperature (EP + 200 °C)
4. Electropolished, then exposed to 50 vol% concentrated nitric acid (HNO_3) at room temperature for 5 minutes, followed by a 5-minute exposure to a 30 °C solution composed of: 20 vol% of 6.0*M* Nitradd®, 30 vol% HNO_3, and 50 vol% DI water. The samples were then rinsed with DI water at room temperature and air dried. (EP + nitric-Nitradd)
5. Same as Step 4, except reverse acid treatments (EP + Nitradd-nitric)
6. Electropolished, then exposed to 50 vol% HNO_3 at room temperature for 1 hour, followed by a DI water rinse and air drying (EP + nitric)
7. Electropolished, then placed in a DI steam environment in a reflux chamber for 1 hour, followed by air drying (EP + Steam)

All coupons were wrapped in separate plastic bags and sent to the Science Center. The following analyses were performed on the coupons, as described in Reference 1, which details each analysis:

1. Ellipsometry – evaluates film thickness and optical properties
2. Contact Potential Difference (CPD) – relates to the work function/outer dipole structure

3. Photoelectron Emission (PEE) - relates to film thickness and chemistry
4. Surface Energy Analysis - evaluates the relative hydrophilic/hydrophobic nature of the surface
5. Surface Activation - evaluates the stability of the film to acid attack
6. Cathodic Polarization Curve - evaluates the kinetics of film reduction/hydrogen evolution
7. Electrochemical Impedance Spectroscopy (EIS) - determines the capacitance of the film in an electrolyte
8. Open-Circuit Potential - relates to electrochemical and corrosion reactions

The objectives of the analyses performed by the Science Center were twofold: first, to determine which method(s) best characterize the passivated surface of 304L SS; second, to determine the chemical and electrochemical kinetic properties of the treated surfaces. The first objective's results are summarized in Table 1, an application matrix that shows how well the different analysis techniques meet the following test criteria:

1. Sensitivity of test equipment
2. Nondestructivity to sample or specimen
3. Ease and speed of measurement
4. Ease of data interpretation

The second objective, determining chemical and electrochemical properties of the treated surfaces, can best be summarized by examining each individual treatment. The EP sample had the most hydrophilic surface that was readily depassivated, as observed by the activation test. It also had the highest capacitance and the lowest open-circuit potential, both indicative of a thin oxide film, but had an anomalously low PEE for a presumably thin oxide film.

In contrast with the EP sample, the EP + 200 °C specimen appeared to be the most hydrophobic. This specimen had the lowest capacitance indicative of a thick oxide film and the highest open-circuit potential in deaerated potassium nitrate. Despite these indications of a thick oxide film, the EP + 200 °C specimen showed only moderate resistance

TABLE 1. Application Matrix
(Table supplied by Rockwell Science Center)

	Sensitivity	Nondestructive	Rapid	Easily Interpreted	Sum*
Ellipsometry	0	2	1	0	3
Contact Potential	1	2	2	0	5
Photoelectron Emission	0	2	2	0	4
Surface Energy	1	2	0	2	5
Surface Activation	2	0	2	2	6
Cathodic Polarization	2	0	1	0	3
Electrochemical Impedance	2	1	1	2	6
Open-Circuit Potential	2	1	2	0	5

KEY: 0 Method fails
1 Partial success
2 Meets objective

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*Since the selection factors have unequal weight, the sum is only a rough guide to the suitability of a given procedure.

to activation. EIS showed a substantial loss of capacitance at low frequencies indicating that, even though the film on the sample may be thick and hydrophobic, it is probably highly defective.

The EP + nitric sample appears to have one of the least reactive and therefore most stable surfaces, as evidenced by the low value for the anodic activation current observed by the polarization experiment and long average time for surface activation. EIS showed minimal loss of capacitance at low frequencies.

The EP + Nitradd-nitric specimen also showed a relatively long time on the average for surface activation in 70 °C 25 vol% sulfuric acid and a relatively low loss for the capacitance of its interface. This indicates a good oxide film that is relatively stable to corrosion. However, this specimen was somewhat hydrophilic.

The EP + nitric-Nitradd samples differed considerably from the Nitradd-nitric in that they were the most readily depassivated specimens and showed the greatest tendency for reactivation, in addition to being somewhat hydrophilic. Nitradd-treated specimens showed low CPDs, but the EP + nitric-Nitradd specimens had the lowest average CPD. Other evidence for high reactivity appears in the high value for apparent corrosion rate in dilute sulfuric acid.

The EP + steam-treated specimen was also readily depassivated. This treatment showed the highest average CPD close to that for the EP + 200 °C and relatively low-phase angle behavior at low frequencies both indicative of a defective film.

Rocky Mountain Analytical Research Laboratories

Two 304L SS samples were submitted to this laboratory for compositional analysis of the treated surface and to determine oxide layer thickness. Both stainless steel samples were the same dimensions as those submitted to the Science Center and electropolished according to the same procedure. Sample 240 was heated to 200 °C for one hour, then allowed to cool (EP + 200 °C). Sample 239 was submitted to the laboratory in the electropolished (EP) condition. X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) surface analysis techniques were used on these samples. The AES depth profile of these samples resulted in approximate (assuming a sputter rate of 60 angstroms per minute) thicknesses of 18 and 37 angstroms for EP and EP + 200 °C, respectively.

AES showed a substantial difference in the surface composition of the two samples. EP had a higher nickel content in the oxide layer, which extended further from the surface than did the nickel in the EP + 200 °C sample. In addition to exhibiting a lesser and deeper nickel content in its oxide layer, EP + 200 °C also showed a considerably higher iron content in the oxide layer, especially at near-surface depths. AES showed that the EP sample had greater phosphorus and chromium concentrations and lower iron concentration, which was in good agreement with the XPS data.

The XPS surface analysis showed that the EP sample had higher chromium, phosphorus, carbon, and nitrogen concentrations than the EP + 200 °C. The analysis also showed 0.3 at.% sulfur on EP, which was not found at all on EP + 200 °C. EP + 200 °C showed markedly higher iron and oxygen conentrations on the surface. The presence of oxygen after the oxide/metal interface was most likely caused by *in-situ* adsorption of molecular oxygen present in the residual gases within the analysis chamber and not from any oxygen being present in the base metal. The XPS profile of EP + 200 °C also showed that the outermost portion of the oxide layer was primarily composed of chromium and iron oxides with nickel not substantially present until near the oxide/metal interface. A small amount of phosphorus was found just slightly into the oxide layer, and nitrogen was found near the oxide/metal interface as a metal nitride.

Los Alamos National Laboratory

Eight 1.0 cm^2 by 0.3 cm 304L SS samples were submitted to Los Alamos for exposure to tritium (T_2) gas for an eight-month period. All the samples were electropolished according to the procedure used for the Science Center samples. The following treatments were performed on the samples (each treatment is also described in more detail earlier in the report):

1. Electropolished (EP)
2. 200 °C treatment (EP + 200 °C)
3. Palladium coated, approximately 250-Å thickness (EP + Pd)
4. Nitric acid treatment (EP + nitric)
5. Nitric-Nitradd treatment (EP + nitric-Nitradd)
6. Steam treated (EP + steam)
7. A sample with a full penetration electron beam weld across the center and treated with nitric-Nitradd (EP + nitric-Nitradd, weld)
8. Sample coupon also welded as described in Step 7, with 200 °C treatment (EP + 200 °C, weld)

The fill gas was 97.15 mol% T_2, 1.98 mol% deuterium (D_2) at 46.11 psia. The volume of the gas was 290 cm^3 at 19.9 °C. The samples were placed in the exposure chamber on April 15, 1985 and taken out on December 12, 1985. The temperature of the gas during the eight-month exposure period was maintained at 22 °C. After removal, the samples were allowed an offgas period until January 21, 1986 (1.2 months).

The extent of T_2 permeation into the surface of the samples was then determined by ion beam analysis. The samples were irradiated with deuterons, producing alpha particles according to the reaction $^3H(^2H,n)^4He$. Figure 2 shows the experimental setup used for this analysis. The alpha particles were collected and processed to yield a tritium depth profile for each sample. The results are shown in Figures 3 through 7. The two weld samples and EP + 200 °C were not analyzed for technical reasons.

Results from Los Alamos indicate that the EP + Pd sample absorbed far more tritium than any of the other four samples. Integration of the curve in Figure 3 shows a total of 910 counts detected in the test area of the sample. One theory that may explain this phenomenon is that palladium acts as a catalyst, dissociating T_2 into mobile atomic and ionic species. The presence of these relatively large quantities of mobile species increases tritium permeation. Integration of the curves in Figures 4 through 7 shows that EP + nitric-Nitradd had the second highest tritium concentration, followed by the EP + steam, EP, and EP + nitric. Table 2 shows the number of counts detected from each sample and peak tritium concentration in atom parts per million (peak concentration measured at a uniform 0.75 micrometer from the surface).

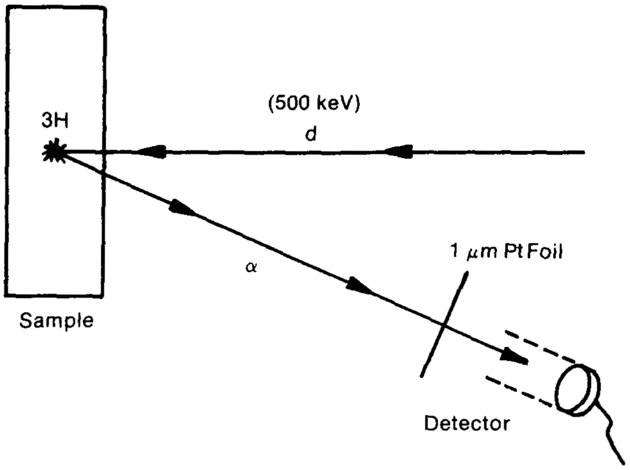


FIGURE 2. Experimental Setup Used for Ion Beam Analysis (Diagram provided by Los Alamos)

Figure 8 is an Auger oxygen depth profile of four of the five samples Los Alamos exposed to tritium. The profile confirms the existence of an oxygen film on these treated samples. The presence of oxygen beneath the palladium on the palladium-coated sample is evident. The 200 °C sample had an oxygen layer approximately twice as thick as the others. This finding is consistent with the results from both the Science Center and Rocky Mountain Analytical Laboratories.

RESULTS

Numerous interesting correlations were observed when the results from Los Alamos and the Science Center were compared. The Science Center completed its studies first. Based upon its surface characterization results, the treatments were placed in series. The series places each treatment in order from the least reactive, most stable surface (relatively low tritium permeation) to the most

FIGURE 3. Counts Detected From the EP + Pd Sample
(Figure supplied by Los Alamos)

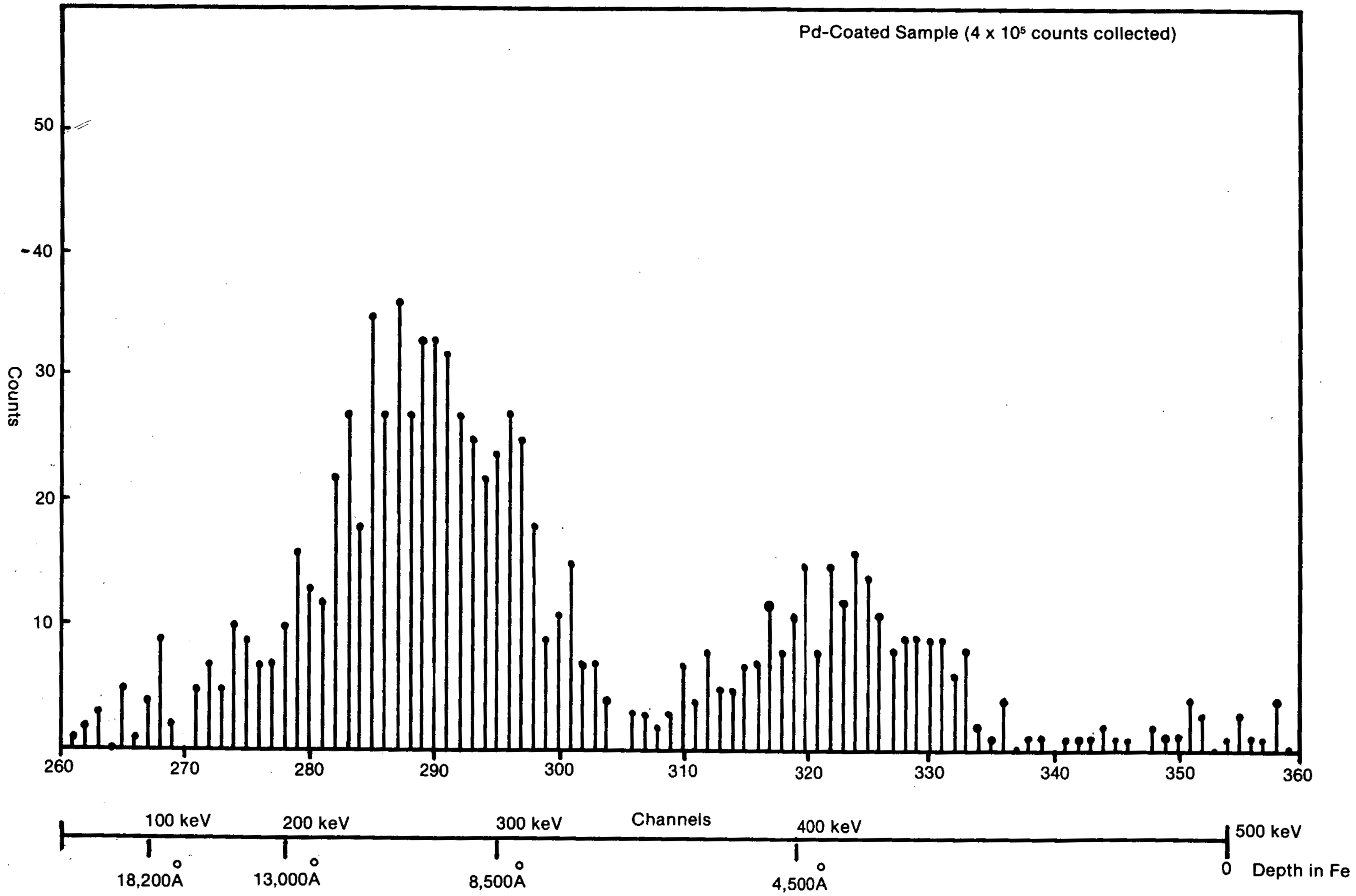


FIGURE 4. Counts Detected From the EP + Nitric-Nitradd
(Figure supplied by Los Alamos)

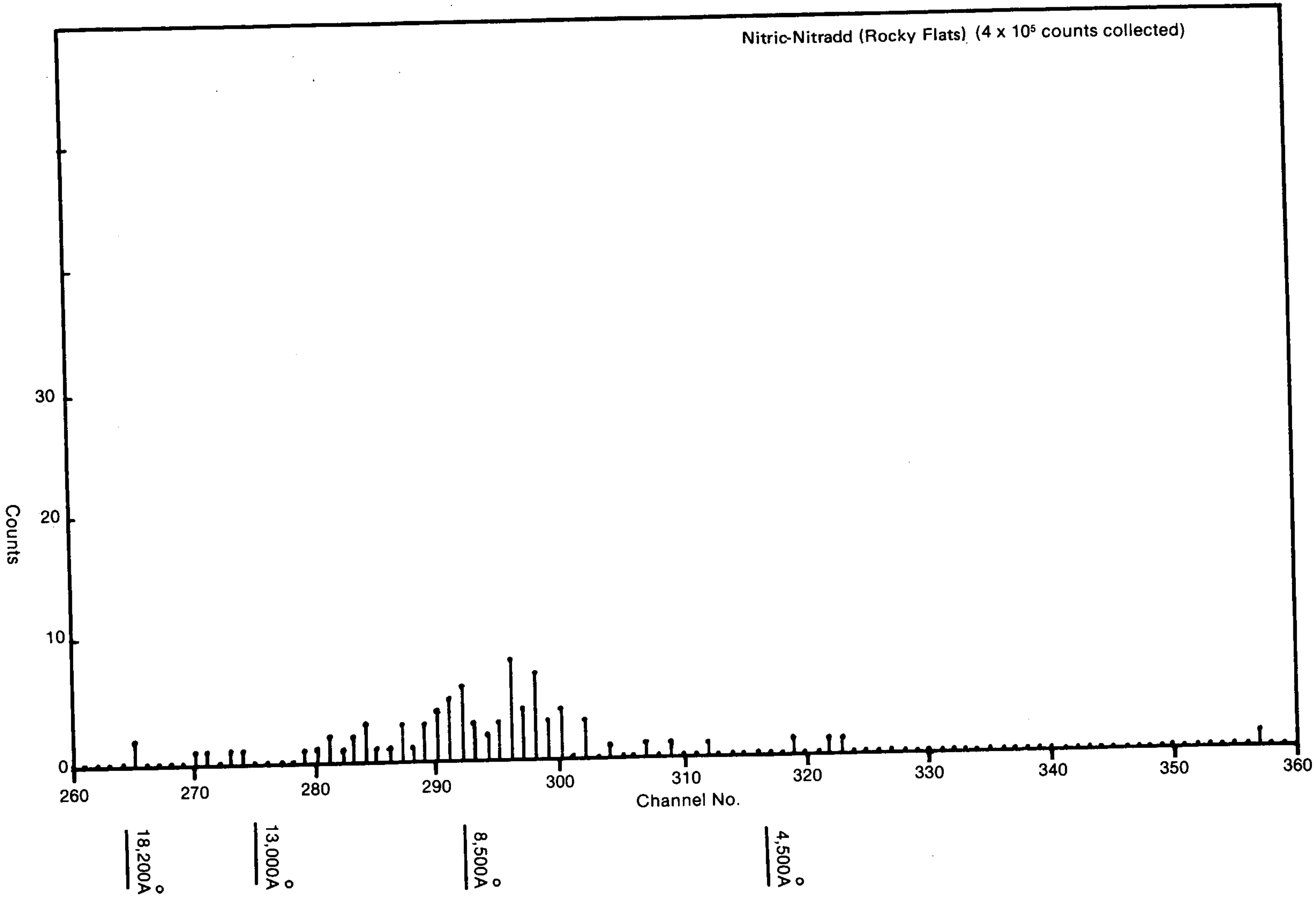


FIGURE 5. Counts Detected From the EP + Steam Sample
(Figure supplied by Los Alamos)

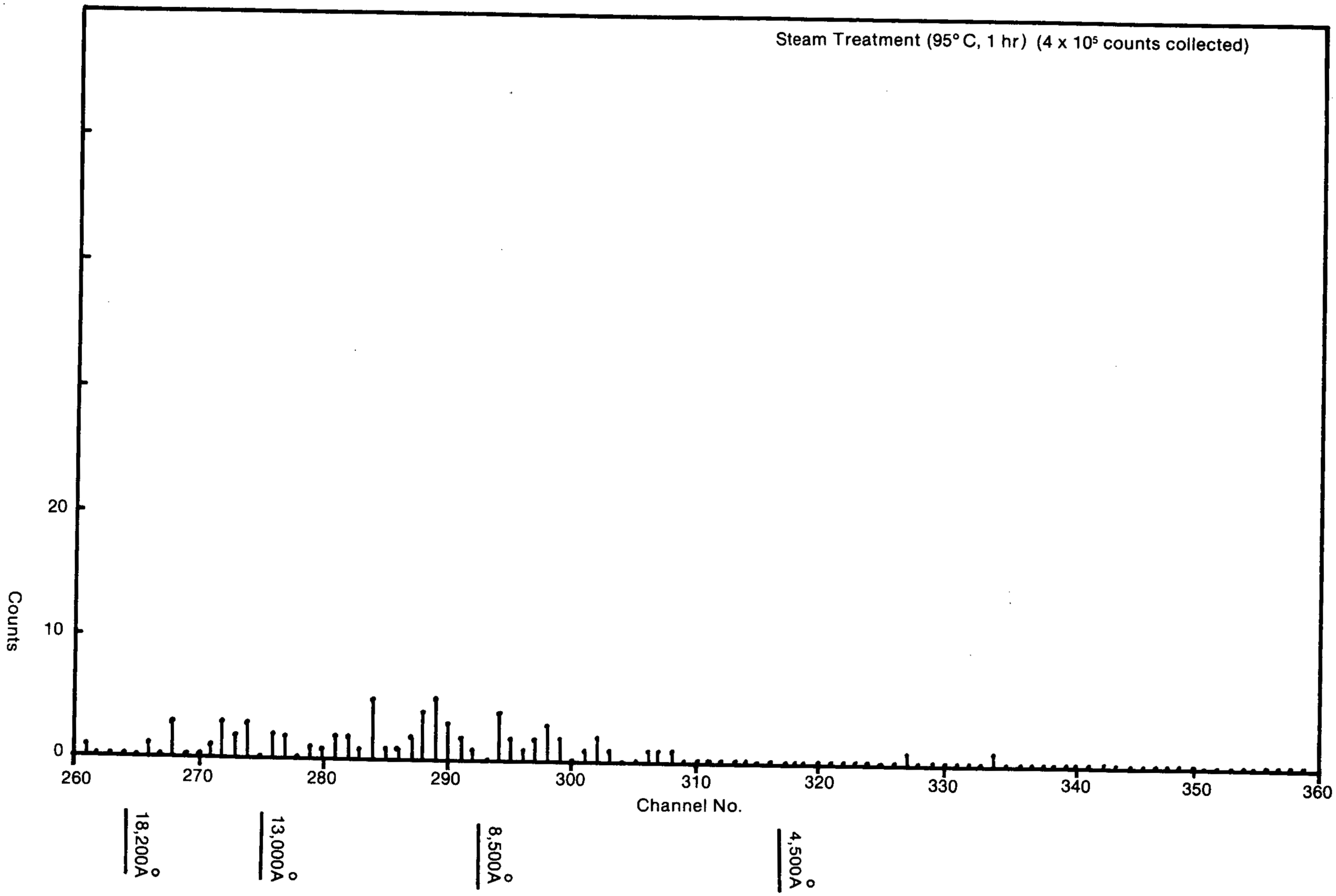


FIGURE 6. Counts Detected From the EP Sample
(Figure supplied by Los Alamos)

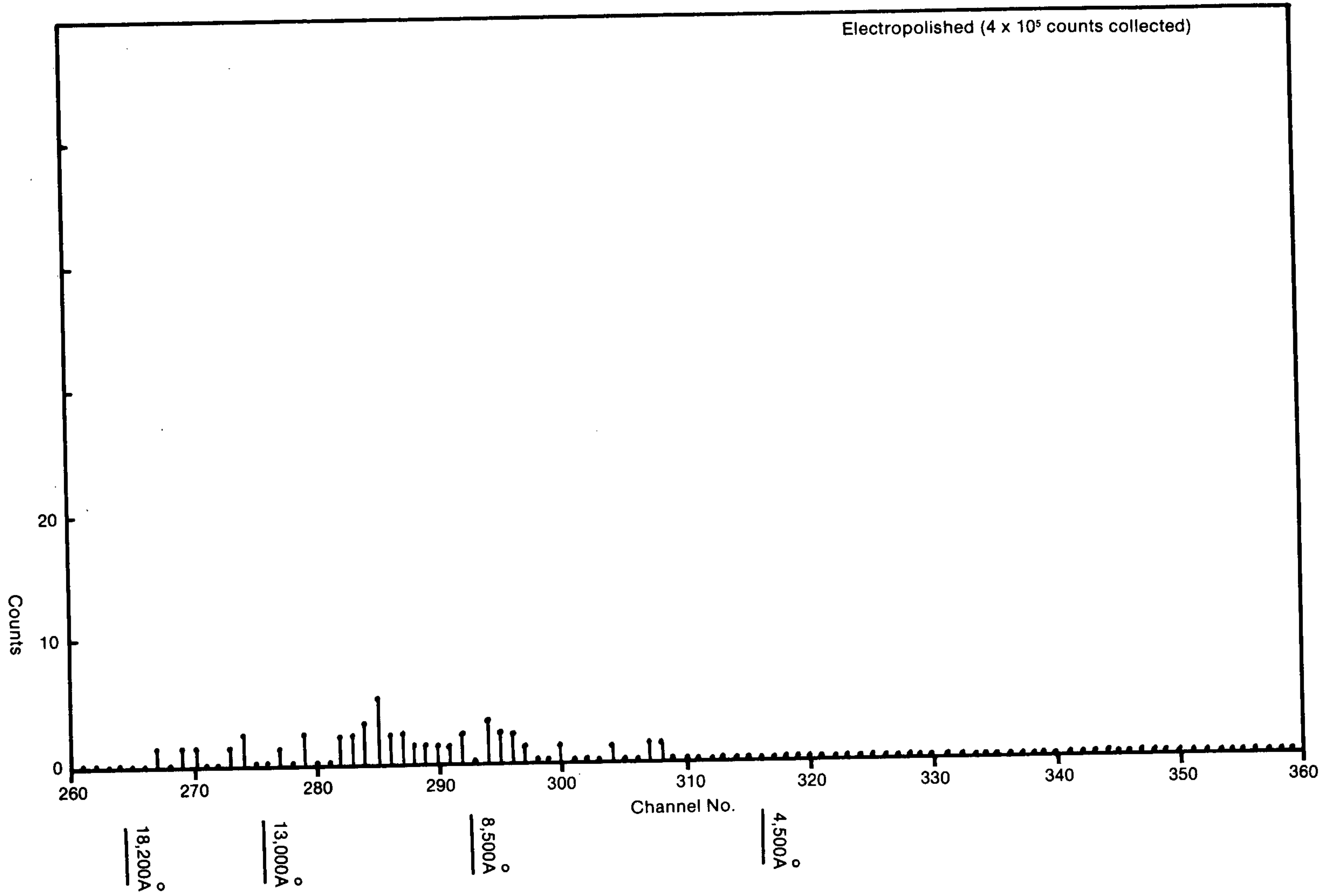


FIGURE 7. Counts Detected From the EP + Nitric Sample
(Figure supplied by Los Alamos)

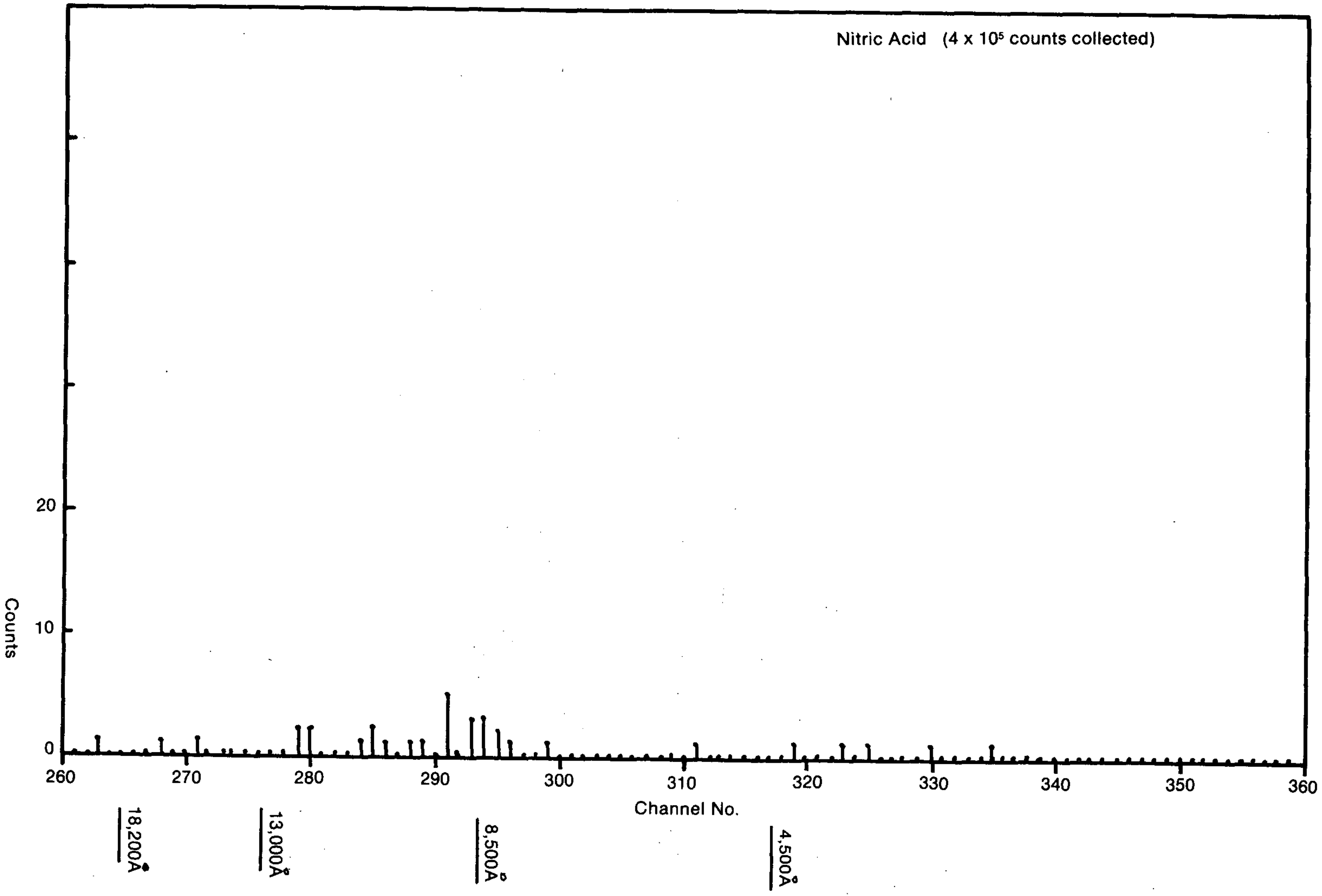
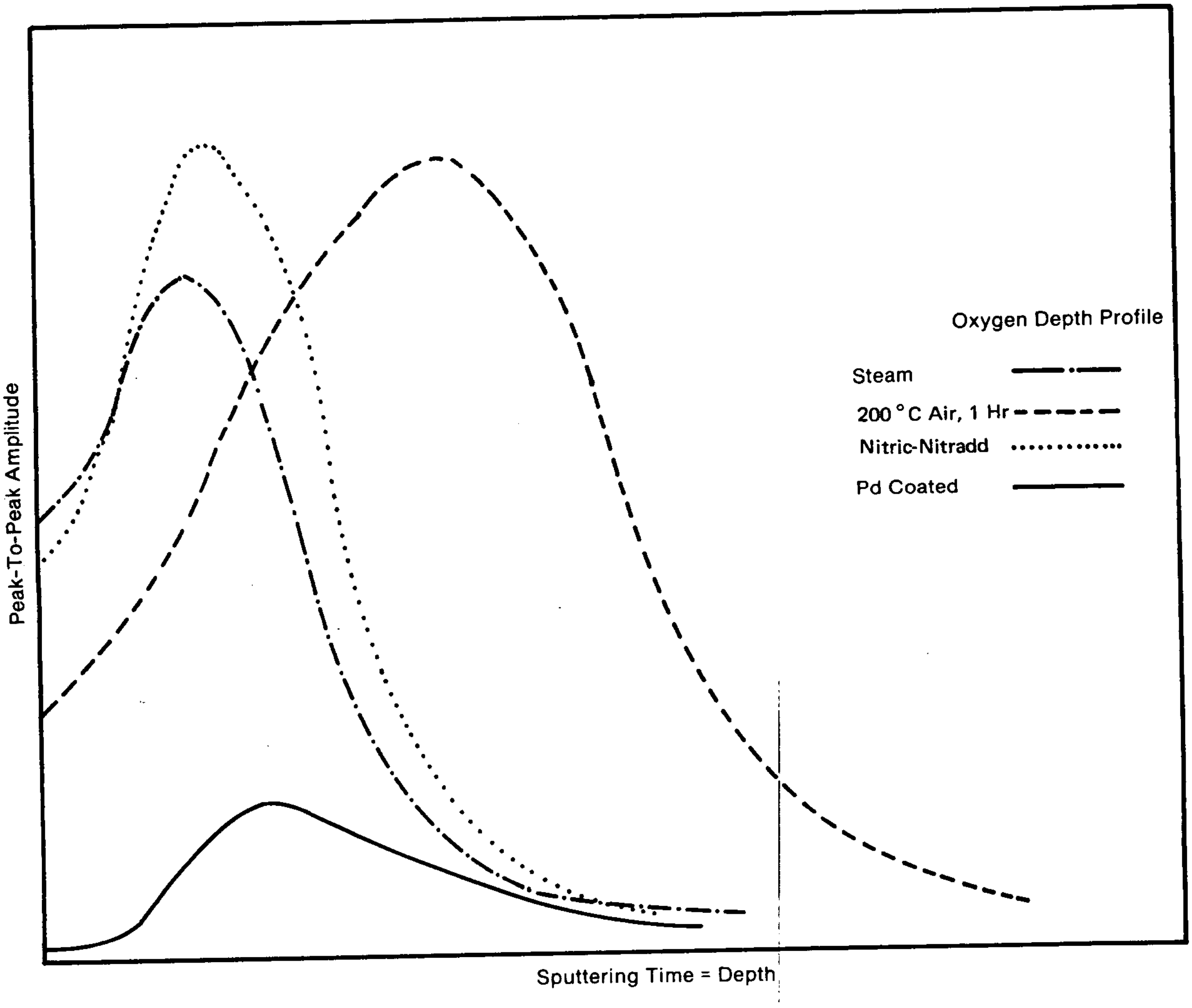


TABLE 2. Tritium Concentration on Treated 304L SS Samples

Treatment	Peak Concentration (ppm)	Counts
EP + Pd	30	910
EP + Nitric-Nitradd	4.2	84
EP + Steam	2.0	70
EP	1.3	43
EP + Nitric	1.3	34

FIGURE 8. Auger Oxygen Depth Profile for Four Treatments (Diagram provided by Los Alamos. Units normalized)



reactive, least stable surface (relatively high tritium permeation), as shown below. The EP + 200 °C and EP + Pd samples were not included because of their highly defective nature. (This is discussed in more detail later in the report.)

LEAST REACTIVE, MOST STABLE SURFACE

EP + Nitric
EP + Nitradd-Nitric
EP
EP + Nitric-Nitradd
EP + Steam

MOST REACTIVE, LEAST STABLE SURFACE

The tritium permeation studies were completed by Los Alamos after the work at the Science Center was completed. Based upon the results from the Science Center and referencing the above listing, the expectation was that the nitric sample would absorb the least amount of tritium, followed by the EP sample and so on. Actual results (from Table 2) shown in the following listing correspond very well with the results from the Science Center:

LEAST REACTIVE, MOST STABLE SURFACE
(relatively low tritium permeation)

EP + Nitric
EP
EP + Steam
EP + Nitric-Nitradd

MOST REACTIVE, LEAST STABLE SURFACE
(relatively high tritium permeation)

The results from the Rocky Mountain Laboratory and the Science Center show that heat treatment (EP + 200 °C) forms a poor barrier on the 304L SS surface. Science Center results also show that steam treatment forms a defective film. Los Alamos results indicate that palladium behaves like a catalyst, entrapping an appreciable amount of tritium. Although palladium plating would not be considered for production purposes, more samples will be prepared for further development work at Los Alamos. Los Alamos will sputter-clean stainless steel samples to remove any oxide film, then vacuum plate palladium onto the surfaces. These samples will be used as controls in their development work.

The remaining four treatments are the most interesting since they more closely duplicate existing production procedures. The EP sample can best be used as a reference in comparing the last three treatments: nitric, nitric-Nitradd and Nitradd-nitric. Both Science Center and Los Alamos results indicate that of the treatments studied, a final treatment of nitric acid forms the most stable, passive layer that allows permeation of the least amount of tritium. A final treatment of Nitradd, on the other hand, forms a surface that is relatively more reactive than the nitric-acid-treated surface. Los Alamos detected nearly a three-fold greater increase in the amount of tritium in the Nitradd-treated surface than the nitric-treated surface. The EP-treated sample exhibited nearly the same characteristics as the Nitradd-nitric and the nitric. Combining the results from the Science Center and Los Alamos leads to the following listing:

LEAST REACTIVE, MOST STABLE SURFACE

EP + Nitric
EP + Nitradd-Nitric
EP
EP + Nitric-Nitradd

MOST REACTIVE, LEAST STABLE SURFACE

DISCUSSION

Passivation of stainless steel components at Rocky Flats has included the Nitradd exposure procedure for a number of years. Nitradd is an aqueous solution composed of ammonium bifluoride, ammonium fluoride, ammonium acetate, acetic acid, and hydrofluoric acid (HF). The HF concentration alone is approximately 6*M*. The HF present in Nitradd attacks a passive stainless steel surface, breaking the protective chromium-rich oxide bond structure. Trace fluorine has been detected on experimental samples exposed to HNO_3/HF, then rinsed with high purity water.[7] Any fluorine ions present in the oxide surface contaminate the customer's fill product and enhance corrosion rates. Previous tests performed at Rocky Flats show that

Nitradd etches the surface of 304L SS, resulting in measurable weight loss. The term *passivation* is an obvious misnomer when used to describe Nitradd acid cleaning processes in use at the Rocky Flats Plant.

Theoretically, the most desirable finish on the surface of 304L SS components is a thin, coherent chromium-rich oxide layer. The enrichment or depletion of chromium on the stainless steel surface will dictate the surface's relative corrosion resistance and service life. Other treatments that form chromium-rich oxide surfaces include nitric acid mixed with sodium or potassium dichromate.[8]

Formation of a new oxide layer is not particularly required for the purposes of the customer. Components may be alkaline detergent cleaned, then rinsed, omitting the passivation procedure. The use of ultrasonic agitation during the cleaning operation enhances particulate removal. Detergent cleaning, like Nitradd, also effectively reduces the contaminant level present on these parts after welding operations.

CONCLUSION

The thrust of this project focused on developing a correlation between surface characterization work performed at the Science Center and tritium permeation studies performed at Los Alamos. This was accomplished with great success. Thick, porous oxide films (Science Center characterization work) are more permeable to tritium (Los Alamos work) than thin, stable oxide films. This correlation will assist in determining an optimum passivation procedure for cleaning or passivating stainless steel parts at Rocky Flats.

Results from this study verify that Nitradd should not be considered for use in passivating 304L SS. Nitradd is an effective acid-etching solution. Nitric acid effectively passivates a stainless steel surface. Other solutions that form highly protective oxide surfaces, such as the nitric acid mixed with potassium dichromate, should be considered. Treatments that formed defective oxide films (200 °C and steam) will not be considered for production implementation. Palladium plating, however, should be considered for use as a control in observing what happens when there is no effective oxide barrier to reduce tritium permeation.

FUTURE WORK

Meetings to plan future work have been held with personnel from the Science Center, Los Alamos, and Rocky Flats. Members concluded that future work should involve more tritium permeation and surface characterization studies on both welded and unwelded samples. Other stainless steels that will be tested include 21-6-9, 316L and JBK-75. Those treatments damaging (or not forming) a protective oxide layer (steam and 200 °C) will not be electroplished; as-machined samples will be used to more closely simulate actual production parts.

The three treatments that may potentially be used by production are the nitric, nitric-Nitradd (current method), and Nitradd-nitric. Other treatments that will be examined in future studies include alkaline solution exposure (detergent cleaning), machined stainless steel samples that have not been cleaned (control sample), and dichromate treatments. Palladium coating of future samples will be tested by Los Alamos, however, to elucidate catalytic, adsorption, and permeation phenomena associated with tritium/stainless steel exposure.

Surface characterization work will be limited to the techniques that provide the most consistent and easily attainable information. XPS, SEM, surface energy, surface activation, and electrochemical impedance are the methods that may be used on future characterization studies. Some or all of the methods will be used, depending upon equipment availability and/or information required.

Listed below are the proposed treatments to which the next set of samples will be exposed:

1. As machined (All samples will be machined prior to treatments. These first two samples will be wipe-cleaned with alcohol.)
2. A tungsten inert gas (TIG) weld across half the sample will simulate production conditions. This will be designated by TIG.

3. Nitric acid
4. Nitric (TIG)
5. Nitric-Nitradd
6. Nitric-Nitradd (TIG)
7. Nitradd-nitric
8. Nitradd-nitric (TIG)
9. Nitric acid mixed with potassium dichromate
10. Nitric acid mixed with potassium dichromate (TIG)
11. Aqueous detergent ultrasonically cleaned
12. Aqueous detergent ultrasonically cleaned (TIG)
13. Aqueous detergent ultrasonically cleaned, nitric acid
14. Aqueous detergent ultrasonically cleaned, nitric acid (TIG)

The treatment parameters will be derived from literature and American Society for Testing and Materials standards for passivating stainless steel surfaces. This set of samples will be sent to Los Alamos for tritium studies. Three samples will be exposed to each treatment. Some samples will be treated but not exposed to tritium for 6 to 12 months. This will provide information on what effect aging has on treated stainless steel surfaces that do not come into contact with tritium over this time frame. The tritium exposure pressure will be increased to accelerate tritium permeation. All other parameters generally will remain the same as those used in this study.

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