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A CRITICAL REVIEW
OF STRESS-CORROSION CRACKING
AS ASSOCIATED WITH THE FFTF
DRIVER FUEL CLADDING

October 1969

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AS ASSOCIATED WITH THE FFTF DRIVER FUEL CLADDING

by

R. V. Bowersock

Corrosion Research Section
Chemistry Research Department

October 1969

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A CRITICAL REVIEW OF STRESS-CORROSION CRACKING
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ABSTRACT

A review of the literature pertaining to stress corrosion of austenitic stainless steel was made. This review failed to reveal either a threshold concentration level required to induce stress corrosion or specific information on how halides are attached to the metal surface. Applicable process specifications and analytical procedures for the determination of residual halide were reviewed and found to be responsive to the needs of the Fast Flux Test Facility.

A CRITICAL REVIEW OF STRESS-CORROSION CRACKING
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INTRODUCTION

The selection of austenitic stainless steels for some of the critical components of the Fast Flux Test Facility (FFTF) presents a potential problem of component failure from stress-corrosion cracking. During the pre-operational period of fabrication, delivery, storage, construction, and testing, the potential for stress corrosion is as great if not greater than during actual plant operation. Problem areas, possible solutions, and recommendations concerning stress corrosion of the Type 304 stainless steel FTR vessel have been discussed by O'Keefe.⁽¹⁾ Another area of concern is the ~200 miles of Type 316 stainless tubing being procured for the driver fuel cladding. Tentatively, this tubing will be 0.230 inch OD $\times$ 0.200 inch ID $\times$ 10 feet long and will be furnished in the 20 percent cold worked condition.

The most effective way to prevent stress corrosion is to exclude the presence of halides from the metal surface. A critical review of applicable specifications and of various analytical procedures for the determination of residual halide was deemed necessary. Analytical procedures sensitive enough to detect concentrations equivalent to 0.5 μg halides/in.² of tube surface are primarily emphasized in this review.

OBJECTIVES

The objectives of this study were:

- To review the literature pertaining to stress corrosion of austenitic stainless steel in search of a threshold limit for halides.

- To review FFTF specifications pertaining to surface cleanliness and determine their adequacy.
- To review the various analytical techniques presently available to determine their sensitivity and adaptability for measuring residual halides on the inner surface of small diameter stainless steel tubing.
- To recommend acceptable procedures, and
- To define areas where future development is required.

SUMMARY AND CONCLUSIONS

By far the largest number of halide-induced, stress-corrosion failures has been traced to chlorides, either known or suspected to be present. A few failures have been attributed to fluoride contamination, but none were found reported as caused by either iodides or bromides. A threshold concentration level required to induce stress-corrosion has not been established. If conditions are such that concentration of chlorides can occur, then conceivably, any chloride concentration could promote stress-corrosion cracking. However, no stress-corrosion failures of austenitic stainless steel cladding of pellet-type fuels have been reported in which the failure originated on an interior surface of the fuel cladding; nor could any incidence of stress-corrosion cracking be found that was attributable to reaction with liquid metal environments, even though appreciable quantities of chlorides are available in both of these environments.

Present FFTF specifications limit surface contamination by halides to $0.5 \mu\text{g halides/in.}^2$ of surface. This permissible concentration level is based upon minimum detection limits and is consistent with similar limits used by others within the industry. Practical techniques for the administration of this limit by direct analysis of the surface have not been developed. However, several analytical techniques have been established that permit detection of halide indirectly by analysis of rinse

solutions. The procedure recommended to determine halides on the FFTF driver fuel cladding tubes is to carefully wash a full length tube (preferably by using pyrohydrolysis* techniques) in high quality deionized water, and to analyze this wash solution for fluorides by use of the specific ion electrode technique. The combined chloride, iodide, and bromide content can be determined collectively by either turbidity analysis of their insoluble silver salts or by any of three available colorimetric techniques.

Further development work is recommended to provide better understanding of halides and their relationship to austenitic stainless steels. Of particular interest would be additional information concerning the nature of how the halides are attached to the metal surface and the effectiveness of their removal by various cleaning procedures.

DISCUSSION

STRESS-CORROSION CRACKING

When static stresses combine with corrosion to produce cracking, the resulting phenomenon is termed stress-corrosion cracking. It is the susceptibility of the austenitic stainless steels to this mode of failure that concerns us here. Stress corrosion is a complex phenomenon involving numerous interrelated factors. Although there is a wealth of information published on this subject, the only affirmative statement that one can make without fear of contradiction is that complete understanding of the subject has not yet been achieved. A brief review of the major contributing factors is presented in hopes of providing the proper orientation and understanding necessary

* *Pyrohydrolysis is a technique for converting metal halides to metal oxides plus volatile hydrogen halides by passing water vapor over the heated specimen. The volatile hydrogen halides are collected in the condensed water vapor for subsequent analysis.*

to better appreciate how rather subtle combinations of stress and environment can result in a brittle fracture of a normally ductile material.

As the name implies, a basic requirement for stress corrosion is the presence of tensile stress. Although any reduction of stress levels is an important step in reducing the potential for stress-corrosion behavior, this technique alone is not considered to be a practical approach to the problem. Threshold levels as low as 1000 psi have resulted in failures, as have residual stresses resulting from the straightening of annealed tubing.⁽²⁾

The other basic requirement for stress corrosion is the presence of a corrosive medium. Industrial failures of stainless steel equipment have been attributed to a number of corrosive media, but by far the largest number of failures have been traced to chlorides which were known or suspected to be present. It is generally accepted that stress corrosion initiates from points of localized attack such as deep pits. Pitting attack is more prevalent in solutions containing chlorides than in solutions of the other halides. Pitting is also more pronounced in oxidizing solutions. Most organic halides when dry have no effect on stainless steels. When they are wet, however, pitting and stress-corrosion cracking can occur from the hydrolysis of the halides to their respective acids.⁽³⁾ No threshold limit for chloride ion concentration has been established. If conditions are such that concentration of chlorides can occur, i.e. localized boiling, alternate wetting and drying, crevice corrosion, etc., it is conceivable that any medium having chlorides present could promote stress-corrosion cracking.

As stated above, there is a definite relationship between chloride and oxygen contents. Williams⁽⁴⁾ in comparing autoclave test data by ignoring all variables except oxygen and

chloride contents concluded:

- Both oxygen and chloride must be present for stress corrosion to occur,
- High oxygen. can be tolerated if the chloride is very low, and
- High chloride can be tolerated if the oxygen is very low.

These results are shown graphically in Figure 1. This work has resulted in the widespread acceptance of the need for maintaining strict control of oxygen and chloride in both nuclear and non-nuclear steam generator operations.

Other factors contributing to stress-corrosion cracking include metal composition, surface condition, and temperature. Austenitic stainless steels that contain approximately 8 percent Ni show the highest susceptibility to this type of attack. As the nickel content is either increased or decreased from the 8 percent value, the susceptibility to cracking decreases.⁽⁵⁾ Very little improvement is obtained by changing from Type 304 to Types 309, 310, or 316. Surface conditioning as affected by rolling practice, heat treatment, and surface finish all have some influence on behavior. Extension of the incubation period for initial attack in dilute chloride solutions from a few minutes for dry-ground surfaces to that of several hundred hours for polished-and-etched surfaces has been reported by Louthan.⁽⁶⁾ Although time to failure is lessened by increased temperature, tests at the DuPont Engineering Materials Laboratory using the wick-test method have resulted in cracking at metal temperatures as low as 40 °C.⁽⁷⁾

EXAMPLES OF FAILURE

Examples of actual stress-corrosion cracking failures are presented to illustrate the importance of minor details that might otherwise be considered innocuous. The first two examples

FIGURE 1. Relationship Between Chloride and Oxygen Content of Alkaline Phosphate-Treated Boiler Water and Susceptibility to Stress-Corrosion of Austenitic Stainless Steel Exposed to the Steam Phase with Intermittent Wetting at 500 °F.⁽⁴⁾ (This figure taken from an article by W. Lee Williams, *Corrosion*, vol. 13, p. 70.)

cite cases where stress corrosion was attributed to improper cleaning. The first failure resulted from incomplete removal of a chlorinated hydrocarbon prior to an anneal; the second failure resulted from acid pickling of sensitized material. The third example, taken from the operating experience of the Agesta Nuclear Power Station, relates where stress corrosion was attributed to fluoride contamination. The fourth example illustrates the importance of environmental control during storage of cleaned components, particularly if the material has been sensitized during fabrication. The last two examples illustrate how use of halogenated materials other than cleaning agents resulted in stress-corrosion failure; i.e., the last case simply involves the use of normal process water for hydrostatic pressure testing. Other such examples may be found in References 8 and 9.

Homogeneous Reactor

Transgranular stress-corrosion cracks were detected in Type 304 and Type 347 stainless steel components of the Homogeneous Reactor prior to actual startup of the reactor. Apparently, a chlorinated hydrocarbon lubricating compound was not removed during fabrication and was baked in during subsequent annealing. The stress-corrosion cracking was attributed to these chlorides. (10)

Savannah River Reactor Plant

Intergranular stress-corrosion cracking was detected in two Type 304 stainless steel outlet nozzles in high-purity heavy-water moderator service at the Savannah River Reactor plant. The cracks propagated from general intergranular attack that apparently occurred at sensitized grain boundaries as the result of acid pickling during initial fabrication of the nozzles. Cracking was attributed to chlorides, although the bulk heavy water contained only about 6 ppb chloride. The

chloride ions were believed to have concentrated in the intergranular pickling cracks. Laboratory tests conducted with sensitized U-bend specimens pickled to produce intergranular attack, showed intergranular cracking within 450 hours in water containing only 2 ppm chloride at 90 °C.(8)

Agesta Nuclear Power Station

Stress-corrosion cracking was found in crevices and on fully exposed surfaces of highly stressed Inconel 600 tubes. Cracks originated on the outside surface in contact with light water at pH 10 and 217 °C for about 150 days. Surface contamination at the crack was limited to 1 $\mu\text{g}/\text{cm}^2$ of fluorine.(11)

Sodium Component Test Facility

At the Atomics International Sodium Component Test Facility, three Type 304 stainless steel bellows failed after relatively short service. Investigation disclosed the bellows to have been sensitized during fabrication when a 700 °C baking operation was employed to volatilize and remove materials between the two plies of the bellows. Subsequent intergranular attack was judged to have occurred from atmospheric moisture in contact with the sensitized steel during the 30-month storage period between fabrication and installation. The exposure to sodium was apparently in no way responsible for the failures.(12)

Plutonium Recycle Test Reactor

Plastic sheeting was used as a shroud to collect heavy water leaking from fittings until permanent repairs could be made. This condition prevailed for approximately 6 months. During repairs of the leaky fittings, a pressure test revealed a leak had developed in the wall of a tube exterior to the heat exchanger on the cooled side. Investigation revealed an apparent stress-corrosion cracking failure. The most likely cause of failure was traced to the use of a green,

clothbacked tape which on chemical analysis was found to be high in chlorides. The tape had been used to secure the plastic sheeting. (13)

Atomic Energy Research Establishment--United Kingdom

An experimental sodium-steam heat exchanger being tested for the AERE-Harwell developed a leak after 348 hours of operation. The heat exchanger was operated as a sodium heater to raise the temperature of the sodium from 680 to 896 °F by using 1000 psi steam. The tube plate that failed was of niobium-stabilized 18/10 chromium-nickel steel. Similar plates of 18/8 chromium-nickel titanium stabilized steel also used in the heat exchanger were found sound. The general conclusion was that the failure arose from stress corrosion which originated from the steam side, and, in particular, from crevices between the tubes and the tube plate. Although not definitely confirmed, the failure was believed to have been caused by chlorides introduced during hydraulic pressure testing that was retained within the crevices and became concentrated when the heat exchanger was placed in operation. (9)

APPROACH TO THE PROBLEM

From the above discussion, one can conclude that the presence of any halides on the surface of austenitic stainless steel is undesirable. One approach to achieve this utopian state would be to exclude all contact with halogenated materials from the winning of the raw materials through final use of the fabricated assembly. Carried to extremes, this approach is probably neither feasible nor practical. The other extreme is to rely solely on cleaning procedures for complete removal of any halide that may be present. Again the feasibility of such an approach is highly questionable, particularly when one considers assemblies having complex geometries containing crevices

and other inaccessible areas. Therefore, one is forced to compromise and adopt procedures that incorporate some of the aspects of both extremes.

Although one can find general agreement that needless exposure of austenitic stainless steel to halides is not a good practice, such needless exposures occur routinely. For example, use of chlorinated hydrocarbons for degreasing may be the most convenient choice of cleaner but may not be the only choice available; or the use of an agent when one is ignorant of its halide content may subject the Steel to an environment that could have been avoided or appreciably lessened had proper attention been made in the selection of that or a substitute agent. Indiscriminate use of tapes, lubricants, marking inks, dye penetrants, etc., fall into this latter category. However, standards and specifications are provided to help identify the many pitfalls associated with fabrication.

A review of the specifications associated with the procurement and processing of FFTF Driver Fuel Cladding⁽¹⁴⁻¹⁶⁾ revealed their authors to be both knowledgeable and concerned about the potential problems associated with halide contamination. The limits and restrictions so specified were found to be consistent with other standards⁽¹⁷⁾ and specifications⁽¹⁸⁾ used within the industry. The exact origin of the 0.0005 mg/in.² for total residual halide surface **contamination** is somewhat in doubt; however, it has been stated to be based upon the minimum detectable concentration.⁽¹⁹⁾ Since any halide contamination is undesirable, minimum detection limits are valid bases for the establishment of limits. Also the use of a similar limit by another site⁽¹⁸⁾ was probably taken into consideration when specifications for the FFTF were established. The maximum permissible halide content of cleaners and other agents used in contact with the metal surface is not specified. Current practices followed by other sites restrict actual cleaners to

less than 30 ppm which represents an upper limit that is acceptable under conditions favorable to removal of the cleaner by standard rinsing techniques. Agents other than cleaners, such as marking ink and dye penetrants, are restricted to halide levels of less than 50 ppm.

REVIEW OF ANALYTICAL PROCEDURES FOR HALIDE DETERMINATION

Specifications that limit the residual halide contamination present on a metal surface are only meaningful if techniques are available for detection of halide at or below the level specified. A review of various analytical procedures was made by A. S. Wilson of the Inorganic Analytical Chemistry Section (see Appendix). A summary of that review is presented in Table I.

Of the two procedures that allow direct measurement of the halides in place, only the induced electron emission spectroscopy method has the required sensitivity. This is a relatively new analytical technique still more or less in the developmental stage. The surface to be analyzed is placed within a chamber, evacuated, and X-rays of precisely known energy are impinged on the surface. By analyzing the energy range of the electrons emitted from the surface, one can determine the element from which the electrons were bound. Although this technique has exciting possibilities in support of basic research, it is not considered practical for routine quality analysis of the inner tubular surface. The X-ray fluorescence technique is about a factor of 60, too insensitive to be used in direct surface analysis. Also this technique is limited to exposed surfaces and would require destruction of the tube to permit analysis of the inner surface.

TABLE I. *Sensitivity of Analytical Procedures*

<u>Analytical Procedure</u>	<u>Lower Detectable Limit</u>
Direct Surface Analysis	
X-Ray Fluorescence	32 μg $\text{Cl}^-/\text{in.}^2$
Electron Emission Spectroscopy	0.32 μg $\text{I}^-/\text{in.}^2$
Analysis of Surface Rinse Solutions	
Potentiometric:	
Specific ion electrode, Cl^-	10^{-5}M or 35 μg in 100 ml
Specific ion electrode, F^-	10^{-6}M or 0.2 μg in 100 ml
X-Ray Fluorescence	3 μg
Turbidimetric	0.6 μg
Colorimetric:	
Method 1	0.7 μg
Method 2	0.5 μg
Method 3	0.5 μg

An indirect approach to measuring of surface contamination is to leach the contaminants into a suitable solvent and analyze the solvent for the presence of halides. This, of course, has the obvious drawback of "averaging" the contaminant over the entire surface tested and is not sensitive to contaminants that are insoluble in the rinse solution. However, such techniques are all that are available at the present time. The sensitivity requirement for this approach is a function of total surface area tested. For the case of a 10-foot length of 0.230-inch OD $\times$ 0.200-inch ID tubing, the inner surface is 75.4 in.^2 . Should this surface be contaminated to the maximum permissible limit (0.5 $\mu\text{g}/\text{in.}^2$) the total quantity of halide present would be only 38 μg . All of the analytical procedures listed in the lower portion of Table I have a detection limit below 38 μg . However, the detection limit of chloride by the potentiometric method would be borderline and therefore is not recommended. The

potentiometric method for detection of fluoride is adequate and is recommended for use because of its simplicity.

MISCELLANEOUS OBSERVATIONS

Restricting surface contamination to $0.5 \mu\text{g halides/in.}^2$ is reasonable from the viewpoint that the ultimate goal is to achieve a true halide free state. For components having simple geometries, this level of cleanliness should be attainable with reasonable care and proper selection of cleaning agents. However, as geometries become more complex, and subsequent **post-cleaning** handling requirements increase, both in number of processing steps and in duration of storage time between final clean and ultimate use, the effort required to maintain this level of cleanliness increases exponentially. Although one should apply reasonable care to limit surface contamination to a minimum, the question arises: what is reasonable care? Perhaps this question can be better answered after a review of the environments that the cleaned, driver-fuel, cladding tube will encounter. Assuming the metal surfaces only meet the bare cleanliness requirements ($0.5 \mu\text{g halide/in.}^2$), the combined surfaces of the fuel cladding inner surface (approximately 69 inches long), both outer and inner surface of the plenum tube, the outside of the reflector rod, and the surface of the spring would together represent a total contamination potential of about $40 \mu\text{g}$ of halides. Into this assembly will be loaded 190.6 g of mixed oxide fuel. The halide specification limit on the fuel material is 22 ppm Cl and 22 ppm F, which represents a total of $8,400 \mu\text{g}$ halides or a factor of 200 more than allowed on the metal parts. The outer surface of the fuel cladding could be contaminated with about $27 \mu\text{g}$ of halides and still be within specifications. This surface will be exposed to reactor grade sodium having a chloride content of 25-30 ppm. Although the above halide level from sources other than surface contamination seem at first to be overwhelming, it is of interest to note that

the author could find no incidence of fuel element failure due to stress-corrosion cracking originated from either the sodium coolant side or from the inside surface of pellet-type fuels. Intergranular cracking of Type 304 stainless steel clad, pellet-type fuels has occurred at both the Vallecitos Boiling Water Reactor and the Dresden Reactor. However, it was concluded from detailed metallurgical examination of the failures that the cracks originated at the fuel rod outer surface and progressed inwardly through the cladding wall. (20)

FUTURE WORK

A review of the literature failed to reveal a threshold concentration level of halides required to induce stress-corrosion cracking of the austenitic stainless steels. Very limited data was available concerning the nature of the attached halide or effectiveness of various cleaning procedures in removal of other than readily water-soluble halides. In addition, techniques for the direct detection of trace quantities of halides on metal surfaces are not readily available. All of these shortcomings have direct bearing not only upon the FFTF project and other LMFBR programs, but also to other nuclear and non-nuclear applications where austenitic stainless steels are being used. In this regard the following recommendations for future work are submitted.

- Joint informational exchange meetings should be held between LMEC, ORNL and BNW personnel concerning all of the above items.
- Additional development work should be conducted to provide the necessary data required to answer all of the above questions. Procurement of an induced electron emission spectrometer (approximate cost \$80,000) would be a very valuable addition to the Laboratory for support of this endeavor.

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APPENDIXA LITERATURE SURVEY OF THE ANALYTICAL PROCEDURES FOR HALIDE DETERMINATION ON STAINLESS STEEL SURFACES- A. S. Wilson

The expeditious, rational development of an analytical procedure for halide determinations on stainless steel surfaces requires that the nature of the halide attachment to the surface be known. No references were found in which the nature of the halide attachment was experimentally examined. One study* showed that chloride ion which originated from the residue of a halogenated hydrocarbon cleaning agent could be removed by soaking in water. Hypothetically, halogens could be present as absorbed salts such as sodium chloride or as halide salts of one of the steel constituents; for example, FeCl_3 , FeCl_2 , FeOCl , etc. In any case, the salt would be expected to be soluble in water made slightly acid to maintain hydrous oxides and halides in solution. Conceivably, the halide might be present as a difficulty soluble salt. In this case, pyrohydrolysis might be used. In this technique water vapor is passed over the sample which is maintained at a high temperature, 300-500 °C. Under these conditions metal halides are converted to oxides and the volatile hydrogen halide collected in the condensed water vapor. The details of the best technique are still to be verified experimentally.

The question of "included halides within the metal matrix" was not considered in this report except to note that currently available analytical schemes require that the metal piece be destroyed in order to analyze it.

Existing analytical procedures can be placed in these two main classifications; the one which examines the surface as it exists; and the second which analyzes the wash solution from the surface.

*KAPL-M-ELS-9 (1958).

Two methods are known for surface examination. The one which is currently available will detect 5 to 6 $\mu\text{g Cl}^-/\text{cm}^2$ (32 to 39 $\mu\text{g}/\text{in.}^2$) of surface via X-ray fluorescence of the chlorine X-ray? The other method which sorts according to energy the electrons ejected from the valence shells of atoms by soft X-rays is called electron spectroscopy. Commercial instruments for this technique are not now currently available, but may be in a year or so. This technique is reported to measure halides, at least iodide, at a concentration of less than 0.32 $\mu\text{g}/\text{in.}^2$.⁽²¹⁾ The maximum permissible concentration of halide ion is 0.5 $\mu\text{g}/\text{in.}^2$ of surface.** At present neither of the methods just mentioned is practical.

Several methods are available for measuring halides at low concentrations in water. A successful method must be sensitive enough to detect at least the maximum amount of halide to be found in the wash solution. Moreover, the adopted method would be expected to determine an amount of halide ion which brackets the value of the maximum permissible amount. In the case of the fuel pin cladding, the maximum permitted value of halogen on the inner surface is 38 μg .[†] Those analytical procedures which would measure an amount of halide ion which would bracket 38 μg are listed here. In this comparison halide is taken to be chloride except where noted.

[†]Private communication, D. S. Skeie, Battelle-Northwest, June 1969.

**BNW Specification A-0086, Rev. 1.

[†]Maximum permissible amount calculated as follows:

cladding length	120 in.
cladding OD	0.230 in.
cladding ID	0.200 in.
outer surface area	(120) (0.230) (3.1416) = 87 in. ²
inner surface area	(120) (0.200) (3.1416) = 75 in. ²
Specification	<u>0.5 $\mu\text{g}/\text{in.}^2$</u>
μg on outer surface	(0.5) (87) = 44 μg
μg on inner surface	(0.5) (75) = 38 μg
Total	<u>82 μg</u>

- Colorimetric; lower detection limit: 0.7 μg ; uses the bleaching of the mercury (II) diphenylcarbazone complex by Cl^- . Other halides interfere.(22)
- Colorimetric; lower detection limit: 0.5 μg ; uses the formation of the blue violet mercury II diphenylcarbazone as an endpoint in the titration of chloride solutions with a mercury II solution. Br^- and I^- interfere. (Referee Method A: ASTM method for Chloride Ion in Industrial Water)
- Colorimetric; lower detection limit: 0.5 μg ; uses the formation of the red ferric thiocyanate complex when chloride ion releases thiocyanate ion from mercury thiocyanate. Br^- and I^- interfere. (Referee Method C: ASTM method for Chloride Ion in Industrial Water)
- Turbidimetric; lower detection limit; 0.6 μg ; uses the turbidity of a solution in which silver chloride is precipitated. Br^- and I^- interfere.(23)
- X-Ray fluorescence; lower detection limit: 3 μg ; uses the characteristic chlorine fluorescent X-ray from silver chloride collected on a filter.(24)
- Potentiometric; lower detection limit: 10^{-5}M equivalent to 35 μg in 100 ml solution; uses a specific ion electrode whose potential versus a calomel electrode is sensitive to chloride ion concentration."
- Potentiometric; lower detection limit for fluoride ion; 10^{-6}M equivalent to 2 μg in 100 ml solution; uses a specific ion electrode whose potential versus a calomel electrode is sensitive to fluoride ion concentration.*

Recommendations

Currently it would appear that the best process for the analysis of surface halides would be their removal through a

*"ORION Specific Ion Electrode, Chloride Ion Activity Electrode.
11 Blackstone St., Cambridge, Mass., 02139.*

combination of washing and steaming and the resulting collection of the wash water. This liquid could be concentrated to at least 100 ml and the solution analyzed for chloride and fluoride ion. The analysis for fluoride uses the specific ion electrode. The analysis for chloride ion uses analytical colorimetric methods listed above.

Long range development efforts should be applied to:

- The detailed investigation of the halide removal technique.
- The further refinement of the X-Ray Fluorescence technique as a means of measuring the sum of $\text{Cl}^- + \text{Br}^- + \text{I}^-$ via AgX precipitation with a measure of the Ag fluorescence.
- The use of the electron spectrometer for elucidating the nature of halides attached to surfaces.

The method of analysis proposed here would examine the entire 10-foot length of tube by washing it and analyzing the wash water. This would also clean the tube. Thus, after this process the tube must not contact any source of chloride ion. For example, 10 to 60 μ liters of human sweat contains about 38 μg of chloride ion which is the maximum permissible amount. It would seem more reasonable to relax the specification of halide contamination on tubes coming from vendors and to carry out the final cleaning and testing of the tubes on-site under vigorously controlled conditions of halide-free rooms.

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