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Corrosion analysis and diagnosis – useful tools for plant life management and long term operation programmes in nuclear power plant

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Abstract Steam Generator degradation has caused substantial losses of power generation, resulted in large repair and maintenance costs. Institute for Nuclear Research has carried out an extensive R&D program focused on the understanding of the degradation processes especially for the tubing material and on developing remedial actions in the purpose to prevent and diminish the ageing process of which evolution supposes some considerable economic costs. Because of the huge impact of corrosion, it is imperative to have a systematic approach to recognizing and diminish corrosion problems as soon as possible after they become apparent. A proper failure analysis includes collection of pertinent background data and service history, followed by visual inspection, photographic documentation, material evaluation, data review and conclusion procurement. In analyzing corrosion failures, one must recognize the wide range of common corrosion mechanisms. The features of any corrosion failure give strong clues as to the most likely cause of the corrosion. The principal steps of analysis and diagnosis of the steam generator tubes degradations consist in: visual inspection, chemical analysis, cross section examination by optical and scanning electron microscopy (SEM) and X-ray diffraction (XRD), data review, conclusions and recommendations. The paper details a proven approach to properly determining the root cause of a failure, and includes metallographic illustrations of the most common corrosion mechanisms, including general corrosion, pitting, crevice corrosion, corrosion fatigue and intergranular corrosion.

Keywords: corrosion degradations, corrosion analysis and diagnosis, structural materials failures, steam generator tubing

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Introduction

Plant Life Management (PLIM) has like principal objective the assurance of Long Term Operation (LTO) for a Nuclear Power Plant (NPP). The diagnosis and analysis of corrosion degradations methodology is an important step for PLIM Programme.
A logical and systematic approach is extremely important in determining the root cause of any failure, whether it is due to corrosion, fracture, wear, or any other mechanism. The use of such an approach will minimize the likelihood that important details and features will be overlooked during the course of the failure investigation; as such details may not be recoverable once the failed component has been dissected. In the purpose of maximizing the chance of an accurate prognosis in a failure investigation is absolutely necessary to respect an investigation methodology. Diagnosis of corrosive phenomena in Nuclear Power Plants (NPPs) implies: a) structural materials corrosion processes investigation, in different conditions of materials, water chemistry, pressure and temperature; b) understanding of the corrosion degradation phenomena which conduct to failure of some structural components; c) corrosion analyses on corroded structural materials and components from NPPs. The paper presents the principal steps of the methodology concerning the analysis and diagnosis of the CANDU steam generator tubing material and some examples of the most common corrosion mechanisms [1] ÷ [7], Fig. 1.

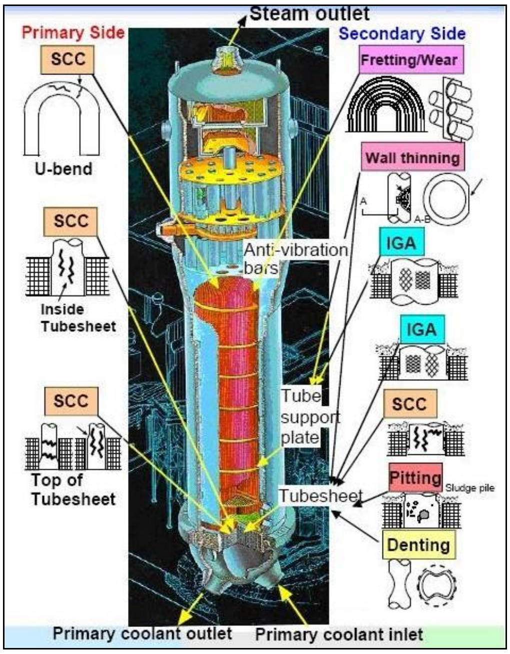


Fig. 1. Degradations of CANDU steam generator tubing [1]

1. The failure analysis process

The experience accumulated during the operation of some NPPs showed that even, in normal operation conditions could appear no-desired effects especially due to corrosion, erosion, hydriding and deposition of corrosion products on heat transfer surfaces. During the investigation of the structural materials corrosion processess, in different conditions of water chemistry, pressure and temperature, it is necessary to understand the corrosion degradation phenomena that conduct to failure of some components from primary and secondary circuits of CANDU (**CAN**adian **D**euterium **U**ranium) reactor. The principal objectives of structural materials corrosion testing programme are: elaboration of the evaluation methodology of structural materials corrosion behaviour, development of a database concerning the structural materials corrosion behaviour and mathematical modelling of the corrosion processes, and assessment of the causes that conduct to failure of some components and possible remedies. In this aim, in Nuclear Materials and Corrosion Department from Institute for Nuclear Research, corrosion experiments in different conditions of water chemistry and temperature and corrosion analyses on some corroded components were performed, [8] ÷ [12].

1.1. Background Data Collection

The first logical step to any failure analysis is to gather as much background information as possible, as it relates to the failed component. A simple way reduce the occurrence of this is to go into a case well informed on how similar systems have failed. An excellent source of for this type of information is the specialty literature consisting in articles, standards, procedures etc.

Details such as part information and identification, including pertinent drawings and specifications, should be collected and kept on-hand for future reference. The known service history of the component is also important, and should include details about how the part was manufactured, as well as what stresses and service conditions the component experienced during its lifetime. In cases involving machines and equipment, details about the maintenance schedule and repair history should be recorded, along with any anomalous service events. Information about the frequency of the observed failure is also important, as it can provide clues as to whether the failure is due to production lot or unusual service conditions.

1.2. Initial Inspection and Scope Definition

With a good handle on the background information and component history, the initial inspection may be performed. The initial inspection involves review of the failed component and adjacent components, including documentation of wear patterns, unusual surface damage, corrosion features, etc. Photographic documentation should also be conducted to clearly illustrate the nature of the problem and provide visual aides for the analyst to review and discuss. It is during this stage that the scope of the investigation is determined. The scope will be based upon parameters such as the available amount of time to complete the analysis, the number and condition of representative failed and nonfailed components, and the available funds to complete the material evaluation.

1.3. Material Sampling and Shipment

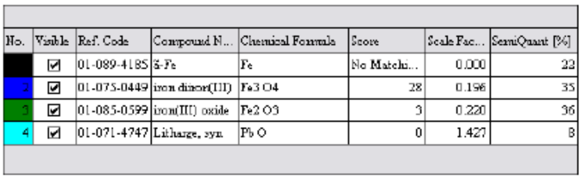
The most majority of failed components including sample tube can easily be shipped to a laboratory for in-depth analysis. It is of great importance that the evidence not be damaged during the sectioning process, and that the failed areas be preserved in their original form as much as possible. In cases involving fractured components, careful sectioning practices should be employed to avoid damaging the fracture surface. It should be noted that some fractures could potentially be corrosion related; because of this, the use of cutting fluids and coolants should be minimized, as they will contaminate the corrosion deposits. If cooling is necessary to avoid altering the part microstructure, clean water should be used instead of cutting fluids. The size of the sample should also be considered, and adequate material should be removed as to allow for mechanical testing, as it may be appropriate. It is also prudent at this stage to photograph the failed component prior to and after the sectioning process, in order to clearly illustrate where the failed component was situated while it was in service. Once the samples have been extracted, they should be identified and placed into protective packaging materials prior to being sent to the laboratory.

1.4. Visual Inspection

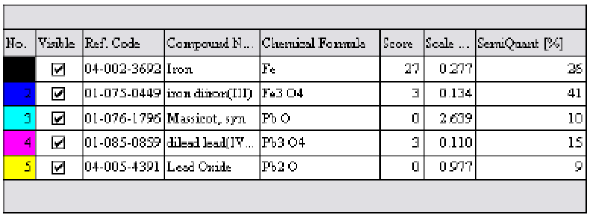
Once the failed component has reached the laboratory, the analyst can proceed with the detailed visual inspection process. During this stage, careful observations are made as to the condition of the component and the appearance of the damage which apparently led to or contributed to the failure. Low and high magnification photographic documentation should also be conducted at this stage to illustrate the morphology and color details. In cases where laboratory cleaning is necessary, the failed areas should be documented before and after cleaning, as the cleaning process can obscure the original color of any corrosion deposits. The component should also be photographed prior to and following any sectioning. In cases involving corrosion where adequate amounts of corrosion products are present, such products should be physically sampled. Care should be taken to preserve the original form of the corrosion deposits as much as possible, as they sometimes exhibit microscopic features that can give clues as to how they were formed. Whatever sampling method is used, it is imperative that the corrosion products not be contaminated.

1.5. Chemical Analysis

In most investigations, it is prudent to analyze the base material of the failed component for elemental makeup. Several different techniques are available for this process. When completely nondestructive analysis is desired, approximate chemical compositions can be obtained using scanning electron microscopy (SEM) or energy dispersive X-ray spectroscopy (EDS).



No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale Fac...	SemiQuant [%]
■	☑	01-089-4185	δ-Fe	Fe	No Matchi...	0.000	22
2	☑	01-075-0449	iron diiron(III)	Fe3 O4	28	0.196	35
3	☑	01-085-0599	iron(III) oxide	Fe2 O3	3	0.220	36
4	☑	01-071-4747	Litharge, syn	Pb O	0	1.427	8



No.	Visible	Ref. Code	Compound N...	Chemical Formula	Score	Scale ...	SemiQuant [%]
■	☑	04-002-3692	Iron	Fe	27	0.277	26
2	☑	01-075-0449	iron diiron(III)	Fe3 O4	3	0.134	41
3	☑	01-076-1796	Massicot, syn	Pb O	0	2.639	10
4	☑	01-085-0859	dilead lead(IV...	Pb3 O4	3	0.110	15
5	☑	04-005-4391	Lead Oxide	Pb2 O	0	0.977	9

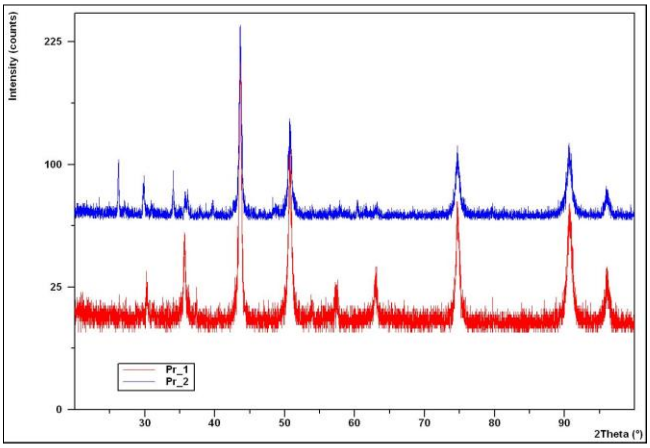


Fig. 2. X-Ray Diffraction analysis for Iy-800 sample tested in the presence of impurities

X-ray diffraction (XRD) can be used to identify compounds in corrosion deposits by analyzing crystal plane spacing, Fig. 2.

1.6. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

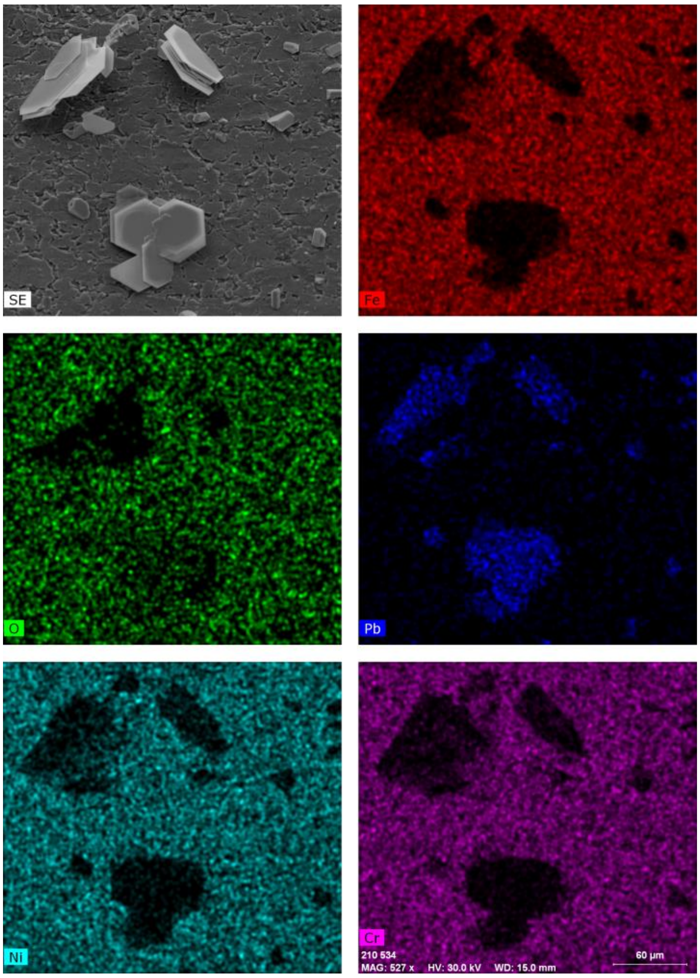
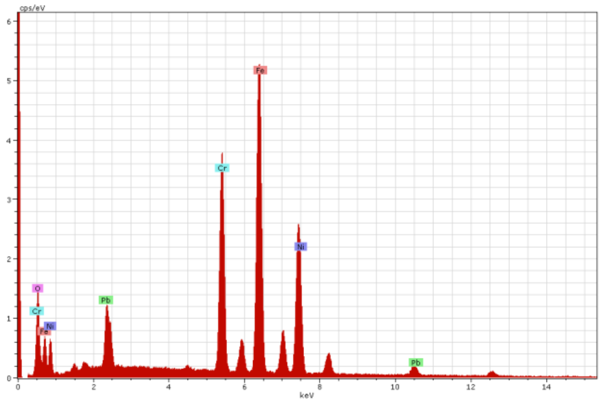


Fig. 3. Elemental distribution on Iy-800 tested in the presence of impurities

High magnification characterization of the component surface is conducted using a scanning electron microscope. This instrument allows for positive determination of the fracture mode in cases involving fractures, and also facilitates detailed characterization of corrosion features that cannot be discerned under light microscopy. This microscope enables the analyst to view the sample at magnifications of up to 5,000X in most circumstances. Under good instrumental conditions and in the absence of residual vibration, magnifications of 20,000X can reasonably be reached while maintaining high quality imaging; however, these magnifications are seldom needed for adequate characterization of the fracture or corrosion features. Some SEM’s are equipped with an EDS (Energy-Dispersive X-Ray Spectroscopy) or WDS (Wavelength Dispersive Spectroscopy) feature, which enables elemental characterization of inclusions and corrosion deposits. This is useful for determining possible causes of the corrosion, as well as identifying the most likely corrosion mechanisms, Fig. 3 and Fig. 4.



Elements	Masic percents
Fe	38
Ni	18
Cr	18
Pb	10
O	8

Fig. 4. EDS spectre and and chemical compozition of the layer formed on the Iy-800 tested in the presence of impurities

1.7. Metallographic Examination

A wide range of information can be obtained from evaluating a failed component in cross section. In cases involving fractures, cross section examination is commonly conducted at the fracture origin, in order to identify any material anomalies that may have served as crack initiation sites. In corrosion failures, examination of the surface profile at the corroded areas can give helpful clues as to what caused the corrosion, and can also reveal any localized features in the microstructure that may have contributed to the problem. Features such as pits, cracks, inclusions and inter-metallic precipitates are identified and characterized using metallographic techniques, and etching is often needed in order to reveal the heat treat condition, as well as potentially deleterious metallic phases. Lower magnifications of up to 100X can be used to characterize overall microstructure uniformity, while higher magnifications of 1,000X to 2,000X can be used to characterize carbide dispersion and appearance.

1.8. Mechanical Testing

It is often dificil to measure the mechanical properties of a failed component, particularly in instances where fracture or wear are involved. Relatively common test methods are used to determine the durability of a material under a variety of stress and temperature conditions. Hardness can be used to provide an estimate of the ambient temperature ultimate tensile strength in most instances, although tensile testing can be performed in order to directly measure the tensile strength, yield strength and ductility under a low strain rate. If the part is too small to allow for tensile or standard hardness testing, it can be prepared in a metallographic mount and subjected to microhardness testing, which can also be used to approximate the ultimate tensile strength.

1.9. Data Review, Conclusions and Recommendations

Once all of the data has been collected, and reviewed, logical conclusions need to be drawn by the analyst. The conclusions must be based on solid engineering principles, and should take into account all of the reported background information, service history and evaluation data. It is imperative that all of the test data be considered during formation of the conclusions, in order to avoid misinterpretation of the results. After the proper conclusions have been reached, the analyst can recommend corrective measures which, if properly followed, should greatly reduce or eliminate the likelihood of future failures. This step involves common sense and sufficient experience on the part of the analyst, in order to avoid unnecessary expenses and, more importantly, the development of other problems. In general, the simplest solution is often the best solution.

2. Some exemples of steam generator tubing analysis

The purpose of this paper is to demonstrate by examples the principal types of tubing degradations and in the same time to show the techniques that where used when obtaining.

The features of any corrosion failure give strong clues as to the most likely cause of the corrosion. An understanding of the common corrosion mechanisms will greatly aid in interpreting the features and observations that are revealed in any corrosion investigation. Common corrosion mechanisms include general corrosion, pitting, crevice corrosion, corrosion fatigue, stress corrosion cracking (SCC), intergranular corrosion (IGC), fretting and flow assisted corrosion (FAC) or erosion corrosion, [13] ÷ [35].

3.1 General Corrosion

This type of corrosion is easily predicted via laboratory testing, and corrosion rates can be directly calculated by weight loss measurements, due to the uniformity of the attack.

3.2 Pitting Corrosion

Many metals and alloys have a tendency to form a tenacious passive film on their surfaces, which protects them from general corrosion in certain environments. Pitting occurs when anodic sites develop on the surfaces of such metals, and remain anodic due to the robustness of the protective film in the surrounding areas, Fig. 5 and Fig. 6. Firstly, pitting is difficult to predict via laboratory testing. Although some electrochemical test methods have been developed to determine whether various metals are prone to pitting in certain environments, these methods often do not produce results that correlate well to actual components under true service conditions. Secondly, the corrosion rates within the pits tend to be rather high due to localized galvanic effects and acidic conditions; therefore, pits can quickly penetrate through vessel walls and cause leaks without warning. Thirdly, even if pits are detected well before they cause leaks, they can lead to expensive and labor-intensive repairs.

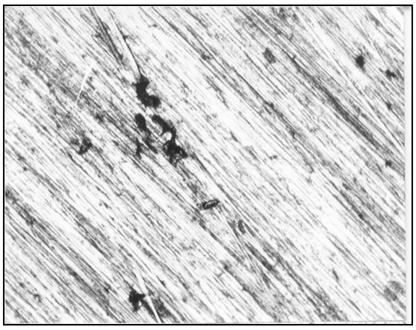


Fig. 5. Pitting on the surface of Iy-800 (x 100)

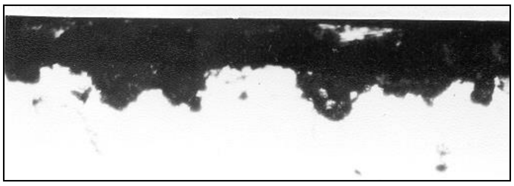


Fig. 6. Microscopic aspect of the oxide layer formed on Iy-800 sample tested 1200 hours in 10g/l NaCl solution, pH=10.5 (x100)

3.3 Crevice Corrosion

When crevices are present between a metal surface and another component, the environment within the crevice can differ significantly from the environment in the boldly exposed areas. The environmental variations effectively alter the localized electrochemical potential, causing the material within the crevice to have a more anodic potential than the material that is exposed to the general environment. Furthermore, the absence of oxygen impairs development of a protective oxide film within the crevice. As a result of these factors, localized corrosive attack occurs to the metal surface within the crevice. A optical micrograph illustrating the effects of crevice corrosion is shown in Fig. 7.

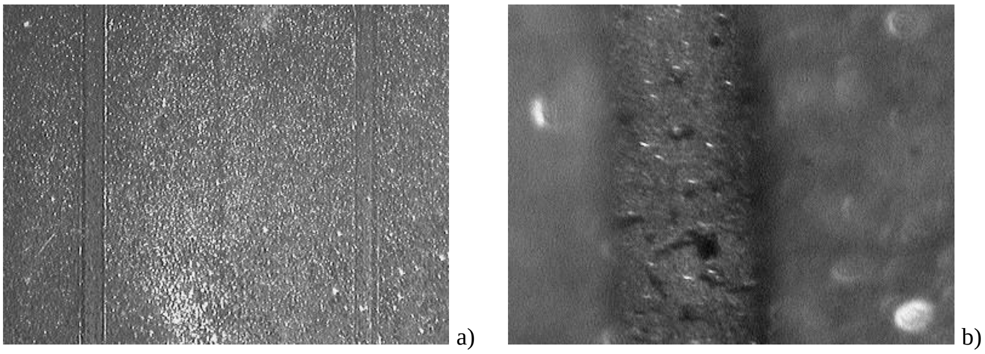

a) b)

Fig. 7. Examples of crevices corrosion (a and b)

3.4 Stress Corrosion Cracking

Passive film-forming metals that are subjected to sustained tensile stress may undergo rapid catastrophic stress corrosion cracking (SCC) while they are exposed to certain mildly corrosive environments. This cracking mechanism is rather rapid, and can thus lead to rapid failures without warning. A variety of materials are susceptible to SCC, including stainless steels, carbon steels, copper alloys, aluminum alloys and titanium alloys. Transgranular SCC commonly occurs in austenitic stainless steels that are subjected to sustained tensile stress and exposed to aqueous chloride-containing substances, particularly steam. SCC is characterized by numerous branched cracks that penetrate deep into the cross section of the material. A metallographic cross section showing such cracks is presented in Fig. 8.

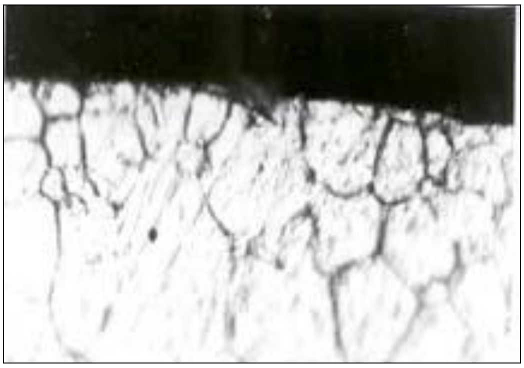


Fig. 8. Microcracks on a sample stressed at 490 MPa tested 48 hours at 850C at (-100) mV (x800) [35]

3.5 Corrosion Fatigue

Like SCC, corrosion fatigue requires stress and a corrosive environment to occur. However, corrosion fatigue occurs under conditions of cyclic stresses, rather than sustained stress. Corrosion fatigue cracks usually initiate at corrosion pits in the surface, and corrosion occurs to the fractures as often show features that are similar to fatigue fractures, along with severe corrosion of the fracture surface. The crack propagation rate varies with a number of factors, including stress intensity, load frequency, environmental conditions and metallurgy.

3.6 Fretting

When two metal surfaces are subjected to vibration and slip while exposed to oxidizing environments, surface damage may occur in the form of fretting. This process involves shearing of the microscopic surface asperities of the mating surfaces, followed by oxidation of the resulting particles. Once oxidized, these particles become abrasive, and cause wear of one or both of the mating surfaces. Fretting can be particularly problematic on sensitive surfaces such as electrical contacts, where sufficient damage can cause intermittent poor contact.

4. Conclusion

Components can fail by a large number of corrosion mechanisms. In any corrosion failure, proper analytical practices and techniques will provide valuable information which, if properly understood, will lead to identification of the failure mode. Once the failure mode has been established, a review of the background history and service conditions will aid in the procurement of sensible corrective measures. Obtaining proper background information and performing the appropriate analyses, combined with an understanding of the material behavior as well as pertinent experience, will produce the best chance of obtaining the accurate conclusions in any failure investigation. All these information are usefull for the PLIM Programme and LTO of a NPP. Applying the methodology described in this paper, one can evaluate the intensity of a component's degradation and estimate the residual time for its safe operation.

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