AECL EACL

AECL-11453

Hideout of Sea Water Impurities in Steam Generator Tube Deposits: Laboratory and Field Studies

Impuretés d'eau de mer dans les dépôts des tubes de générateur de vapeur : Études en laboratoire et sur le terrain

P.V. Balakrishnan, C.W. Turner, R. Thompson, S. Sawochka

Presented at the Seventh International Symposium on Environmental Degradation of Materials in Nuclear Power Systems -- Water Reactors, Breckenridge, Colorado, USA, 1995 August 6-10.

January 1996 janvier

AECL

HIDEOUT OF SEA WATER IMPURITIES IN STEAM GENERATOR TUBE DEPOSITS: LABORATORY AND FIELD STUDIES

by

P.V. Balakrishnan, C.W. Turner, R. Thompson* and S. Sawochka**

Presented at the Seventh International Symposium on Environmental Degradation of Materials in Nuclear Power Systems--Water Reactors, Breckenridge, Colorado, USA, 1995 August 6-10.

Reactor Chemistry Branch
Chalk River Laboratories
Chalk River, Ontario, CANADA
K0J 1J0

*Florida Power Corporation
Crystal River Energy Complex
15760 W. Power Line St., NR1A
Crystal River, FL 34428-6708
USA

**NWT Corporation
7015 Realm Drive
San Jose, CA 95119
USA

1996 January

AECL-11453

EACL

Impuretés d'eau de mer dans les dépôts des tubes de générateur de vapeur : Études en laboratoire et sur le terrain

P.V. Balakrishnan et C.W. Turner
EACL, Laboratoires de Chalk River
Chalk River (Ontario) Canada K0J 1J0

Rocky Thompson
Florida Power Corporation
Crystal River Energy Complex
15760 W. Power Line St., NR1A
Crystal River, FL 34428-6708

Steve Sawochka
NWT Corporation
7015 Realm Drive
San Jose, CA 95119

Résumé

Des impuretés d'eau de mer se logent dans des couches minces (~ 10 µm) de dépôts sur les tubes des générateurs de vapeur, comme le démontrent les études effectuées en laboratoire sur des tronçons de tubes de générateur de vapeur encrassés prélevés en 1992 à la centrale nucléaire Crystal River-3 et les études de libération des impuretés des dépôts effectuées sur place au cours d'arrêts récents de la centrale.

Les essais en laboratoire effectués à 279 °C (534 °F) et à des flux thermiques allant de 35 à 114 kW/m^2 (11 100 à 36 150 $Btu/h.ft^2$), conditions caractéristiques de la zone entre les plaques tubulaires inférieures et la première plaque support d'un générateur de vapeur à passage direct, ont montré que des impuretés peuvent se loger dans des couches minces de dépôts le long de la portée libre des tubes. La quantité des impuretés augmente avec le flux thermique. Les espèces solubles, comme les ions sodium et chlorure, se délogent rapidement des dépôts pour retourner dans la masse d'eau lorsque le flux thermique cesse, tandis que les espèces moins solubles, comme le sulfate de calcium et l'hydroxyde de magnésium, se libèrent plus lentement.

Les études récentes de la libération des impuretés effectuées à Crystal River-3, où le niveau de l'eau dans les générateurs de vapeur a été maintenu au-dessous de la première plaque support des tubes pendant l'arrêt, ne maintenant ainsi en milieu aqueux que la mince couche de dépôts sur la longueur de portée libre et la petite épaisseur de boue, corroborent les résultats obtenus en laboratoire, montrant que des impuretés se logent effectivement dans ces zones de portée libre des tubes.

Ces résultats impliquent que l'on doit prendre en compte les impuretés dans les dépôts des tubes dans le calcul de la chimie des fissures dérivée des études de libération des impuretés et dans le contrôle chimique global utilisant le critère de rapport molaire.

1996 janvier

AECL-11453

Hideout of Sea Water Impurities in Steam Generator Tube Deposits: Laboratory and Field Studies

P. V. Balakrishnan and C. W. Turner
AECL, Chalk River Laboratories
Chalk River, Ontario, Canada K0J 1J0

Rocky Thompson
Florida Power Corporation
Crystal River Energy Complex
15760 W. Power Line St., NR1A
Crystal River, FL 34428-6708

Steve Sawochka
NWT Corporation
7015 Realm Drive
San Jose, CA 95119

Abstract

Sea water impurities hide out within thin (≈10 µm) deposits on steam generator tubes, as demonstrated by both laboratory studies using segments of fouled steam generator tubes pulled in 1992 from Crystal River-3 nuclear power station and field hideout return studies performed during recent plant shutdowns.

Laboratory tests performed at 279°C (534°F) and heat fluxes ranging from 35 to 114 kW/m^2 (11,100 - 36,150 Btu/h.ft^2), conditions typical of the lower tubesheet to the first support plate region of a once-through steam generator, showed that impurity hideout can occur in thin free-span tube deposits. The extent of hideout increased with increasing heat flux. Soluble species, such as sodium and chloride ions, returned promptly to the bulk water from the deposits when the heat flux was turned off, whereas less soluble species, such as calcium sulfate and magnesium hydroxide, returned more slowly.

Recent field hideout return studies performed at Crystal River-3 where the water level in the steam generators was maintained below the first tube support plate during the shutdown, thus wetting only the thin deposits in the free span and the small sludge pile, corroborate the laboratory findings, showing that hideout does indeed occur in the free-span regions of the tubes.

These findings suggest that hideout within tube deposits has to be accounted for in the calculation of crevice chemistry from hideout return studies and in controlling the bulk chemistry using the molar ratio criterion.

Introduction

Microscopic examinations of secondary-side tube deposits from the Crystal River-3 once-through steam generators (OTSGs) have identified physical evidence that wick boiling had occurred within the deposits[1,2]. Wick boiling is a process whereby liquid water is conveyed from the outer surface of the deposit via a labyrinth of passages (i.e., "capillaries") in the porous deposit structure to pore holes in the walls of "steam chimneys". The water begins to boil as it travels down the capillaries, and evaportates near the tube surface. The steam escapes via the steam chimneys. The outer surfaces of the Crystal River-3 deposits were found to have numerous steam chimneys (see Figure 1) and were very porous, thus indicating that wick boiling is active in the deposits.

Ionic impurities such as sodium, chloride, and sulfate are expected to concentrate within the tube deposit because of the wick boiling. However, numerous laboratory examinations of Crystal River-3 tube deposits found only trace amounts of ionic impurities. Any ionic impurities within the deposits would most likely have been removed by hideout return during shutdown, by leaching during the wet layup periods or by hydraulic cleaning (water-slap), which was applied for the removal of the deposits from the broach holes in the steam generator. Therefore, significant concentrations of ionic impurities in tube deposit samples are not expected.

Crystal River-3 uses salt water from the Gulf of Mexico for condenser cooling. Condenser cooling water inleakage via tube leaks or tube-to-tubesheet joint leakage is the major source of feedwater impurities. Condensate polishing is by full-flow deep-bed demineralizers that are operated in the amine cycle and are not regenerated. Although protection from large tube leaks is afforded by operation of the polishers in this manner, only minimal removal of impurities entering the condensate because of chronic low-level condenser inleakage is achieved during normal operation. Most of these impurities are transported to the steam generators via the feedwater. If these impurities concentrated to corrosive levels within the tube deposits, then corrosion could initiate in the freespan regions of the tubes. With the exception of the first span (between the lower tubesheet and the first tube support plate), which can be influenced by the sludge pile, there has been no freespan corrosion confirmed in OTSGs. However, the possibility of freespan corrosion exists.

The purpose of the laboratory experiments was to determine if, and to what extent, sea water ionic impurities concentrate or hideout in freespan tube deposits. Further, the extent to which the impurities return to the bulk water during reduced heat flux, as during shutdowns, was investigated. For comparison, field hideout return data from the 1994 shutdown at Crystal River-3 (Refuel 9) was evaluated to determine if, and to what extent, sea water impurities were concentrating in the freespan tube deposits of the steam generators.

Laboratory Studies

Experimental

Test Equipment. The tests were carried out in a 1-L stainless steel autoclave. A one-inch-long sample cut from a steam generator tube from Crystal River 3 was mounted on a thermowell on the autoclave head. A cartridge heater placed inside the thermowell, such that the tube sample was centred on the heated length of the heater, boiled the solution in the autoclave on the tube surface, while a water-cooled condenser placed on the autoclave head removed the heat input from the cartridge heater. A conductivity probe monitored the change in ionic solute concentration in the autoclave water during the tests. A desk top computer was used to acquire the on-line conductivity and temperature data.

Test Procedure. Hideout tests were carried out using ASTM sea water diluted 4000 times (i.e., to ≈ 5 mg/kg chloride concentration). The composition of the test solution is given in Table 1.

The conductivity probe was calibrated at room temperature using 0.01 mol/kg KCl. The conductivity of the test solution at room temperature, measured using this probe, was 16 μS/cm, which is close to the calculated value of 18 μS/cm.

The test solution (650 mL) was heated in the autoclave to 279°C using the autoclave heaters. The solution temperature and the conductivity were recorded by the computer data acquisition system at intervals of 0.6 s over the duration of the tests. The power to the cartridge heater was turned on after the autoclave temperature steadied at the set point, and the power was maintained at a value corresponding to the desired heat flux. Water samples for chemical analyses were collected at intervals. The cations were determined in these samples by inductively coupled plasma (ICP) atomic emission spectrometry and the anions by ion exchange chromatography. Unfortunately, the samples for ion exchange chromatography were contaminated so these results are not reliable and will not be used.

To determine the species hiding out in the tube samples, the autoclave was drained (blown down) before turning off the power to the cartridge heater. Thus the sample was dried at the test temperature (279°C), without allowing the water to wash off any solutes deposited in it. The sample was then examined in a scanning electron microscope (SEM). Elemental maps were obtained using the energy dispersive X-ray (EDX) system.

TABLE 1: Composition of the Test Solution

Species	Concentration (mg/kg)
Sodium	2.76
Magnesium	0.16*
Calcium	0.105
Potassium	0.010
Chloride	4.44*
Sulfate	0.69
Bicarbonate	0.037
Fluoride	0.00033
Boric Acid	0.0073

*Slightly different from ASTM sea water composition.

Results

Hideout Under SG Deposit. Figure 2 shows the results of a test to determine hideout under the deposit on a tube sample. A heat flux of 114 kW/m^2 was maintained at the tube sample surface for 24 h, and at the end the autoclave was drained almost completely while the cartridge heater was

was still on. When the autoclave pressure started falling, indicating a superheated condition, the cartridge heater was turned off and the run terminated. The tube sample was removed for microscopic examination. Another run, at a heat flux of 35.4 kW/m^2, was done similarly using another tube sample.

The conductivity fell slowly in both tests over the 24-h period, with indication of steady state being attained after about 15 h. The conductivity dropped by 31% in the first test (heat flux - 114 kW/m^2) and by 10% in the second test (heat flux - 35.4 kW/m^2). A comparable blank test (heat flux - 114 kW/m^2) using a tube sample chemically cleaned of deposit showed about 12% drop in conductivity at steady state, which was reached in about 4 h. Hideout in the blank test presumably took place in the tight crevice between the boiler tube and the thermowell or even in scratches on the bare tube surface. Figure 2 also shows results of a test done using a clean tube, but with a 200-mesh stainless steel wire screen wrapped around it to simulate a porous deposit. Hideout took place under the wire mesh, but because of the more open nature of the mesh the extent of hideout was less than that on a tube covered with deposit. The ICP results for the water samples are shown in Table 2.

The loss of solute concentration during the hideout tests with deposit-covered tubes is higher than that observed during the blank tests, which shows that the solutes did hide out within the deposit. Very little calcium and magnesium returned during the hideout return phase of the tests, which suggests that they precipitated within the deposits as insoluble salts. Previous work by Balakrishnan[3] showed that magnesium and calcium will precipitate as $Mg(OH)_2$ and $CaSO_4$, respectively, from sea water that has concentrated within a deposit or crevice.

SEM/EDX of Deposit After Hideout. Figure 3 shows an SEM micrograph (a) of a polished cross section of the SG tube with deposit that was used in the hideout run at a heat flux of 114 kW/m^2. Also elemental maps (b,c) show the distribution of iron, nickel, chromium, and various sea-water impurities. The polished cross section shows a layer of deposit on the outside of the tube (left-hand side of the micrograph), the SG tube itself (right-hand side of the micrograph), and the corrosion-product layer in between. The micrograph shows that both the outer deposit and the corrosion-product layer are porous.

TABLE 2: ICP Results for Hideout Tests

Species	Start of Test (mg/kg)		End of Test (mg/kg)		Hideout (%)	
	114 kW/m^2	35 kW/m^2	114 kW/m^2	35 kW/m^2	114 kW/m^2	35 kW/m^2
Na	2.90	3.05	2.30	2.90	20.7	4.92
Mg	0.16	0.10	0.10	0.09	37.5	10.0
Ca	0.14		0.06		57.1	

The elemental maps show that the outer deposit is composed primarily of iron oxide, as expected from previous work[1,2]. The sea-water impurities, such as sodium, chloride, and sulfate, that were left within the deposit at the end of the hideout experiment are distributed more or less evenly across the deposit and alloy substrate. That they are not confined to the deposit can be explained by noting that the cross sections had to be polished before examination in the microscope. Although precautions were taken to avoid dissolving solute left within the deposit, by using only an organic solvent for the polishing operation, the solute appears to have been smeared across the entire cross section. Their presence in the cross section does confirm, however, that the sea-water impurities did hide out in the deposit during the experiment.

TABLE 3: Elemental Composition of Corrosion-Product Layer after Hideout

Species	Concentration (atom%)
Magnesium	0
Sulfur	0.94
Chlorine	0.25
Sodium	0
Iron	7.47
Chromium	18.07
Nickel	65.68
Titanium	0.17
Aluminum	4.38
Calcium	3.28

Table 3 shows the results of an EDX spot analysis of the elements in the corrosion-product layer. In addition to Fe, Ni, and Cr, the analysis shows sea-water impurities such as Ca, S, and Cl. Although Mg and Na are also expected to be present (on the basis of the conductivity and analytical data presented in Section 3.3), they did not appear in the spot EDX analysis. This is likely because EDX is not as sensitive to the lighter elements. An order of magnitude increase in sensitivity would be achieved if the deposits were examined by WDX (Wavelength Dispersive X-ray) analysis.

Field Studies

Hideout Return Studies

The most recent hideout return study (1994) at Crystal River-3 corroborated the laboratory findings that hideout occurs in the freespan tube deposits. During the shutdown, the water level was initially maintained at 40 inch (1 m) above the tubesheet, which is about 5 inches (12.5 cm) below the first tube support plate (TSP). It was subsequently increased to 200 inches (5.1 m), that is, just below the fifth TSP. When cooldown was completed, the steam generators were placed in cold wet layup, with the water level initially at about 350 inches (8.9 m) (just below the 9th TSP).

Following the completion of maintenance activities in the main steam lines, the steam generators were filled with water (600 inches (15.2 m)), i.e., full wet layup for the refueling outage. The 1994 hideout return study thus in effect consisted of four phases in which hideout return from four different regions of the steam generators was determined.

TABLE 4. Crystal River 3 1994 "B" Steam Generator Shutdown Hideout Return

	Nominal Steam Generator Water Level											
	40 Inches (1 m)			200 Inches (5.1 m)			350 Inches (8.9 m)			600 Inches (15.2 m)		
Species	ppb	°F	Time	ppb	°F	Time	ppb	°F	Time	ppb	°F	Time
Na	460	533	7:00	5700	531	0:30	1900	127	89:15	400	79	194:20
K	41	531	9:00	300	531	0:30	NA			NA		
Ca	<0.1	531	----	190	443	4:30	NA			NA		
Cl	140	531	9:00	410	531	0:30	300	127	89:15	10	79	194:20
SO_4	94	531	9:00	1,100	531	0:30	900	127	89:15	200	79	194:20
SiO_2	480	531	9:00	12,000	531	0:30	3000	127	89:15	300	79	194:20

NA = Not analyzed.
ppb = Maximum steam generator water concentration at given water level, µg/kg.
°F = Steam generator water temperature at time of maximum concentration.
Time = Hours: minutes from time steam generator water level reached specified level. Note that for 40-inch (1 m) and 350 inch (8.9 m) levels, the sampling was not possible 4 h and 89 h 15 min later, respectively. For the 350-inch level (8.9 m), the first sample taken contained the peak concentrations.

When Crystal River-3 shut down for its ninth refueling outage in April 1994, it had operated continuously for 223 effective full-power days (EFPD) since it tripped at full power in September 1993, and for 336 EFPD since it shut down in March 1993 for a planned mid-cycle outage. The hideout return observed was the result of the accumulation of ionic impurities in the steam generators over this operating time. Table 4 shows the maximum impurity concentration in steam generator water (i.e., hideout return) that was observed at each of the four different steam generator levels.

40-inch level. Significant return was observed from the 1st span of the "B" steam generator (i.e., 40 inch level (1 m)). At this low water level, the hideout return could only be coming from impurities that had concentrated within the thin first-span deposits (<0.5 mil (13 µm)) based on pulled tube measurements and/or from the pile of spalled-off deposits on the lower tubesheet, which is less than 6 inches (15 cm) high, based on measurements performed during visual inspections in 1987 and 1992.

200-inch level. Increased hideout return occurred when the steam generator water level was raised to 200 inch (5.1 m) (just below the 5th TSP). The incremental return observed at this water level would be from both the first four TSPs and the tube deposits. Although it is impossible to distinguish what fraction of the return is from the deposits, and what is from the TSP crevices, it is expected that hideout return from the tube deposits would be greatest at the 3rd - 7th TSP region (123- to 278-inch water level; (3.1 to 7.1 m water level)) where the deposits were observed to be the thickest (2 mils (51 μm) or more) by in situ fiber optic and borescope inspections, and measurement of deposit thickness on pulled tubes. The TSPs in OTSGs have broached flow openings that permit more flow and have less crevice volume than drilled hole designs; therefore less hideout would be expected at OTSG TSPs. Visual inspections in 1992 and 1994 also showed the TSP broaches to be very open, with minimal broach blockage caused by fouling. Small lips of deposit were observed only at the 4th - 6th TSPs. Therefore, most of the return observed at this elevation in the steam generator may in fact be from the tube deposits and not from TSP crevices.

300-inch level. Hideout return continued when the "B" steam generator was placed in wet layup up to just below the 9th TSP (i.e., 350 inches (8.9 m)), although to a lesser extent than that observed at 200 inches (5.1 m) of water. A visual inspection in 1994 using a borescope in the opening left after a tube was pulled, revealed that the TSP broaches were completely open in all nine TSPs inspected, with minimal fouling occurring at the 5th-7th TSPs. Measurement of deposit thicknesses on tubes pulled in 1994 showed the tube deposits to reach a maximum thickness of about 2.25 mils (57 μm) at the 300-inch (7.6 m) elevation in the steam generator (i.e., between the 7th and 8th TSPs), and to rapidly decrease in thickness to less than 0.5 mil (13 μm) at the 350-inch (8.9 m) elevation (or just below the 9th TSP). As at the 200-inch (5.1 m) level, significant return would be expected from this region, since both the tube deposit thickness and TSP blockage, although minimal, are the greatest here. The lower temperature of the wet layup water as well as impurity steam-liquid distribution and mass transfer effects in the OTSGs during normal operation are possible reasons why minimal hideout return is being observed even though fouling is the greatest in this region.

600-inch level. Hideout return continued when the steam generators were filled up to the upper tubesheet (600 inches (15.2 m)), although it was much less than that observed in the mid-section of the steam generator. Above 400 inches (10.2 m) in the steam generator, visual inspections and examination of pulled tubes have shown the tubes to be virtually free of any scale. The TSPs are likewise completely open and free of any fouling. From the 10th TSP (397 inches (10.1 m)) and above, superheated steam is produced in the steam generator, and corrosion product deposition has ceased. The hideout return observed here is most likely from hideout that occurred in the 8th - 10th TSP region, and from entrainment of water droplets in the steam, particularly along the tube-free lane. These entrained water droplets are concentrated in ionic impurities and are transported to the upper elevations (such as the upper tubesheet crevices) where they flash and deposit their impurities.

Discussion

The hideout on tube samples tends towards a steady state, the approach to steady state occurring over a longer period of time on deposit-covered samples than that on clean surfaces (blank tests). Hideout on deposit-covered samples produced lower bulk solute concentrations. This is consistent with a rate of hideout that is determined by a competition between build-up and removal processes. The rate of build-up of solute within the porous deposit should be proportional to the boiling rate which, in turn, is proportional to the heat flux. The rate of return of solute to the bulk is governed by the rate of diffusion of solute from the deposit back to the bulk. Thus the higher solute accumulation and the longer time to reach a steady state with the deposit-covered SG tubes compared with clean tubes are to be expected.

Based on the observations that at a heat flux of 114 kW/m^2 the conductivity of the solution in the autoclave fell by 31% of the value of the original solution and that the corresponding decrease in conductivity during a blank test was 6.5%, 25% of the solutes concentrated under the deposits. A concentration factor of 1.3×10^4 can be calculated for a deposit thickness 10 µm and 50% porosity. This gives a sodium concentration of 3.6×10^4 mg/kg, chloride concentration of 5.8×10^4 mg/kg, a pH of 5.3 (at 279°C) and a superheat of 3°C.

The solute concentration under the deposit will be much higher than that in the autoclave bulk water. Solutes of low solubility (e.g., $Mg(OH)_2$ and $CaSO_4$) will, therefore, precipitate within the deposit. Their release rates to the bulk when the heat flux is turned off will be correspondingly slower than those of solutes, such as NaCl, that do not precipitate. Thus the inventory of magnesium and calcium remaining in the deposit after the return phase will be higher, as observed. The hideout region apparently includes the corrosion film on the SG tube itself, which raises the possibility that some hideout could occur even in the absence of deposits.

The fact that there was significant return at the 40-inch (1 m) water level, which only wetted the thin (<13 µm) deposits below the first TSP and the small sludge pile, is consistent with the laboratory tests that showed hideout return in a tube deposit with a thickness of only 10 µm. The significant hideout return in the 200- to 350-inch level (5.1 to 8.9 m) level is consistent with the thicker deposits in this region. Tube deposits are likely the dominant source of hideout return in the Crystal River steam generators since the TSPs are observed to have only minimal blockage.

Conclusions

The laboratory data shows that a steady state is established with respect to soluble solutes after about 20 h for thin (~10 µm thick) deposits at a heat flux of 114 kW/m^2. Solutes of low solubility precipitate on hiding out. Removal of the heat flux returns the hideout solutes, the soluble ones promptly and the insoluble ones more slowly.

References

1. Rocky H. Thompson and Robert L. Tapping, "Inferring Steam Generator Fouling Mechanisms from Visual Inspections and Deposit Analyses", CORROSION/88, paper no. 255 (Houston, TX: National Association of Corrosion Engineers, 1988).

2. R.L. Tapping, C.W. Turner, R.H. Thompson, Corrosion, 47 6 (1991): p. 489.

3. P.V. Balakrishnan, "Computation of Chemical Equilibria in Steam Generator Water", Proc. 41st Int. Water Conf., Engineers' Society of Western Pennsylavania, Pittsburgh, PA (1980), pp 323-334.

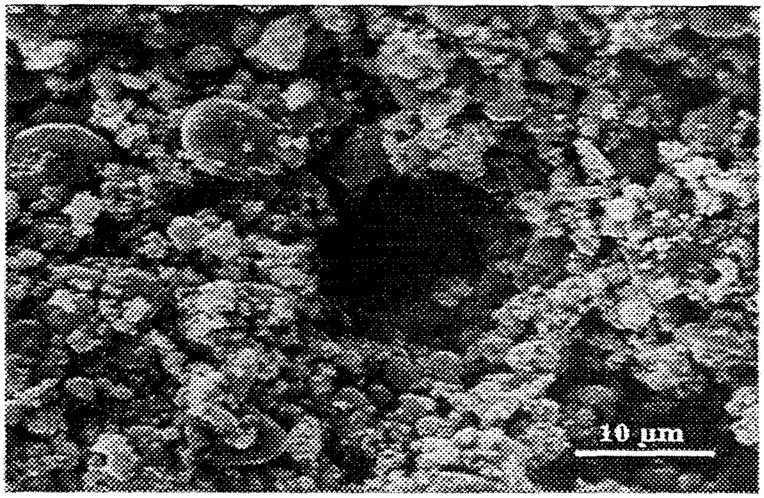


Figure 1: SEM micrograph of the surface of the Crystal River-3 steam generator tube deposit.

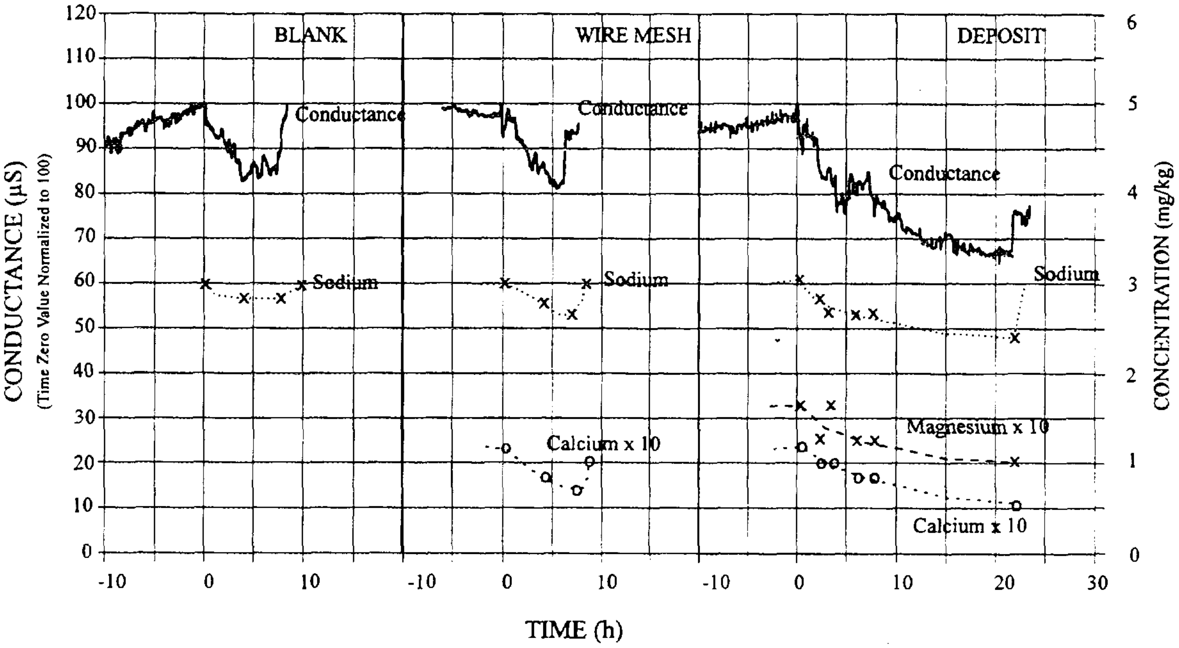
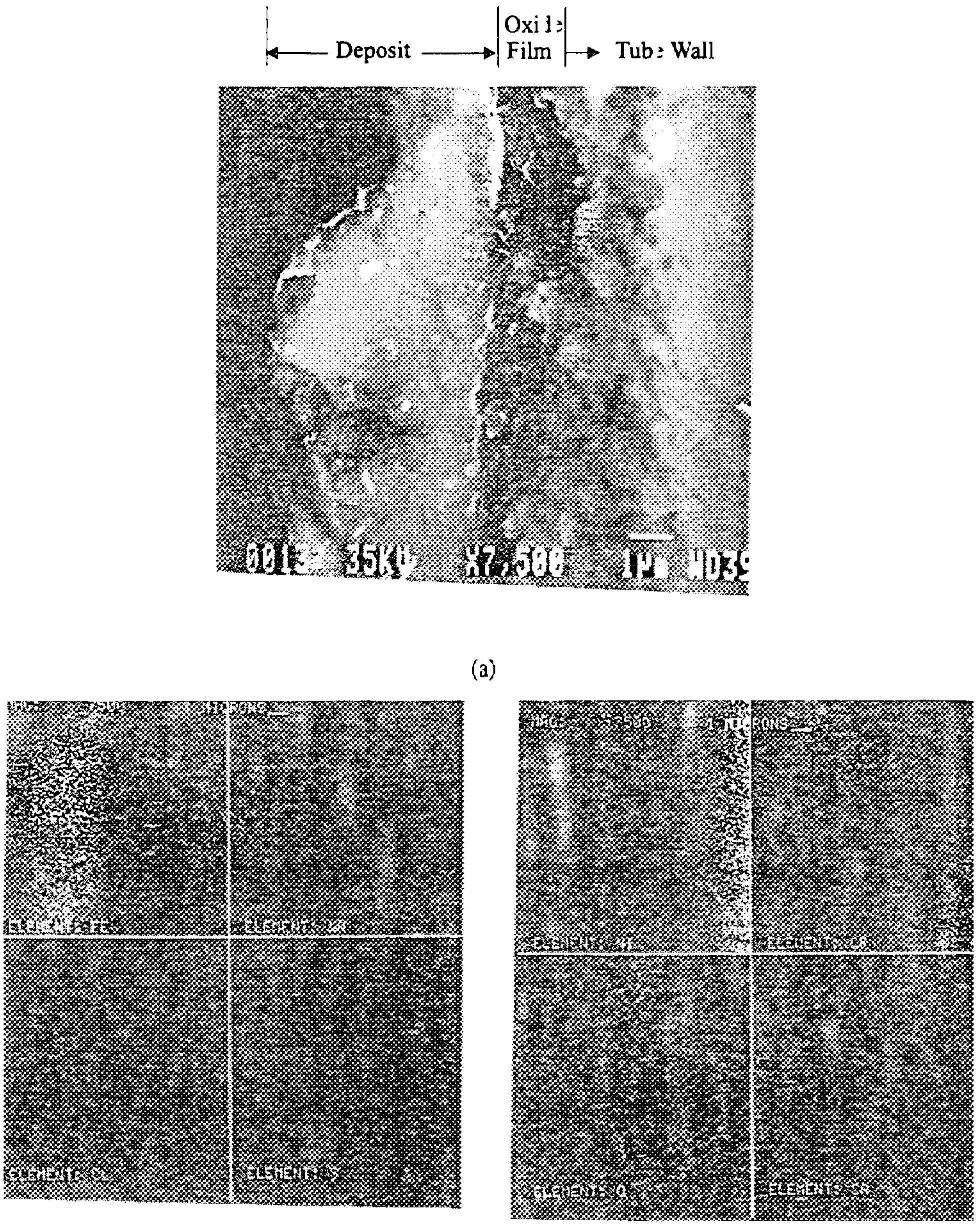


Figure 2: Hideout on tube surface under heat-transfer conditions. (The Time Zero in the plots refers to the time the heat flux - 114 kW/m^2 - was turned on. Values for the ordinate are normalized to give at Time Zero, 100 µS for conductance, 3 mg/kg for sodium, 0.16 mg/kg for magnesium and 0.11 mg/kg for calcium. Temperature = 279°C)



(a)

(b)

(c)

Figure 3: SEM micrograph of a polished cross section of Crystal River-3 steam generator tube with deposit after hideout (a) and elemental maps (b, c) showing distribution of corrosion products and sea-water impurities.

Cat. No. /No de cat.: CC2-11453E
ISBN 0-660-16920-7
ISSN 0067-0367

To identify individual documents in the series, we have assigned an AECL- number to each.

Please refer to the AECL- number when requesting additional copies of this document from:

Scientific Document Distribution Office (SDDO)
AECL
Chalk River, Ontario
Canada K0J 1J0

Fax: (613) 584-1745
Tel.: (613) 584-3311
ext. 4623

Price: A

Pour identifier les rapports individuels faisant partie de cette serie, nous avons affecté un numéro AECL- à chacun d'eux.

Veuillez indiquer le numéro AECL- lorsque vous demandez d'autres exemplaires de ce rapport au:

Service de Distribution des Documents Officiels
EACL
Chalk River (Ontario)
Canada K0J 1J0

Fax: (613) 584-1745
Tél.: (613) 584-3311
poste 4623

Prix: A