出國報告（出國類別：開會）

赴福島國際會議出國報告

服務機關： 核能研究所
姓名職稱： 黃俊源　研究員
派赴國家/地區：日本/福島縣
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報告日期： 109年2月7日

摘 要

本次赴日本福島縣富岡鎮(Tomioka Town)參加 2019 Fukushima Research Conference on “Corrosion Prediction and Mitigation for Key Components of Fukushima Daiichi NPS”—Key Corrosion Issues to Maintain Structural Integrity for the Next Three Decades?—國際會議，12 月 9 日～11 日，為期 3 天會議。第三日參觀福島 Daiichi 核電廠。Fukushima Research Conference 每年約主辦 5-6 次，主題涵蓋 ①核種分析(Analysis of nuclear species), ②嚴重事故分析(Severe accident analysis), ③輻射暴露及除汙保護(Protection of radiation exposure and decontamination), ④遠端遙控技術(Remote control technology), ⑤ 計劃管理(Project management), ⑥混泥土結構材料保存(Conservation of concrete structural materials), ⑦ 腐蝕及腐蝕防護預測(Prediction of corrosion and corrosion protection), ⑧ 檢測技術(Inspection technology), ⑨修補技術(Repairing technology), ⑩ 核燃料爐屑及處置(Property of fuel debris and its disposal), ⑪ 放射性廢料處置(Disposal of radioactive waste), ⑫ Management of critical condition，由於福島放射性廢料處理是棘手問題，因此需各國先進、學者、專家共聚一堂，貢獻心力。此次會議由 JAEA (JAPAN ATOMIC ENERGY AGENCY)與 TOHOKU UNIVERSITY 主辦，會議主席是 CEA, France 的 Dr. Damien Feron，材料腐蝕議題是第二屆舉辦，上次會議是 2017 年。此次會議由受邀演講者(Invited Speaker)，東京電力的 T. Arai，主講 “Daiichi 福島電廠去污、除役現況”，揭開專業論文發表序幕。第一天會議分為三個階段，第一階段為 PCV(Primary Containment Vessel)的均勻腐蝕(General Corrosion) 有兩篇論文發表。第二階段主題是微生物誘發腐蝕，計有兩篇論文發表。下午的場次是第三階段，主題是水解(Radiolysis)效應對腐蝕的影響，也有兩篇論文發表。第二天早上繼續前一天水解(Radiolysis)效應對腐蝕的影響，有四篇論文，中午休息時間 11:40~13:20 為海報發表，計有 17 篇論文，本所發表的論文亦在此列。各學者至海報區與作者互動，討論海報論文內容，極為熱絡。最後一個階段為 RC 結構的腐蝕，有兩篇論文發表。

主辦單位安排住宿旅館位於 Iwaki Town (磐城市)，距離開會的富崗鎮會議中心(Tomioka Town Art and Media Center))約有 50 分鐘車程。每天早晨 7:30 就需至指定地點搭遊覽車至 Tomioka 鎮，沿途接送住宿於 Tomioka 鎮的 Hotel Hojinkan 的學者至富崗鎮會議中心，中午休息時間，則以遊覽車載與會學者至富崗購物中心用餐，為此次國際會議特殊之處。由於開會的富崗鎮會議中心距離福島第一核電廠僅約 10 公里，表示福島核災發生至今，去污恢復已有相當成果。

透過此國際會議，關注福島第一核能電廠腐蝕劣化及防治研究現況，並發表發表本所論文：「Corrosion Behavior of Carbon Steel A106B in Still Water Environment after Decommissioning of Nuclear Power Plant」，與國際核能材料、腐蝕、土木、水化學等專家學者交換研發心得，參訪福島電廠，更親身經歷核災現場的恢復狀況，成果頗為豐碩。

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一、 目的

本所長期從事於核能材料環境效應促進材料劣化研發工作，致力於運轉中及除役過渡期核材料老劣化機制與防治之研究。電廠運轉或進行功率提升均需清楚材料老劣化機制，方能有效進行老化管理及組件壽命評估。國內核一廠兩個機組均已達使用年限，處於停機、除役過渡階段，用過核子燃料仍處於爐心位置，相關之安全維護仍不可忽視，是核管單位安全管制重點。福島電廠由於核燃料裸露，造成爐心熔毀，熔融的核燃料熔穿反應爐壓力槽，掉落至主圍阻體(PCV，Primary Containment Vessel)底部，其中的海水及熔融的核燃料對主圍阻體鋼板的腐蝕議題，不容忽視。藉參加此會議可獲取福島電廠、研發機構、學者專家、管制單位等對福島電廠腐蝕議題之研發現況及關注方向，提供國內電廠管制參考及學習日本針對核災事故後群策群力，將災害降至最低，並盡力降低受汙染地區之危害。此行主要目的如下：

(一) 參加 2019 Fukushima Research Conference on “Corrosion Prediction and Mitigation for Key Components of Fukushima Daiichi NPS”—Key Corrosion Issues to Maintain Structural Integrity for the Next Three Decades?--會議，發表本所論文：「Corrosion Behavior of Carbon Steel A106B in Still Water Environment after Decommissioning of Nuclear Power Plant」；

(二) 了解碳鋼於空氣-水之介面腐蝕、微生物腐蝕、輻射水解誘發腐蝕之關鍵議題；

(三) 與會議專業人員交換電廠組件材料老劣化、乾貯筒、最終處置銅腐蝕之研發經驗與技術細節探討；

(四) 會議安排參訪福島第一核電廠(1F, Fukushima Daiichi Nuclear Power Station)，了解福島電廠復原進度。

二、過程

(一) 行程

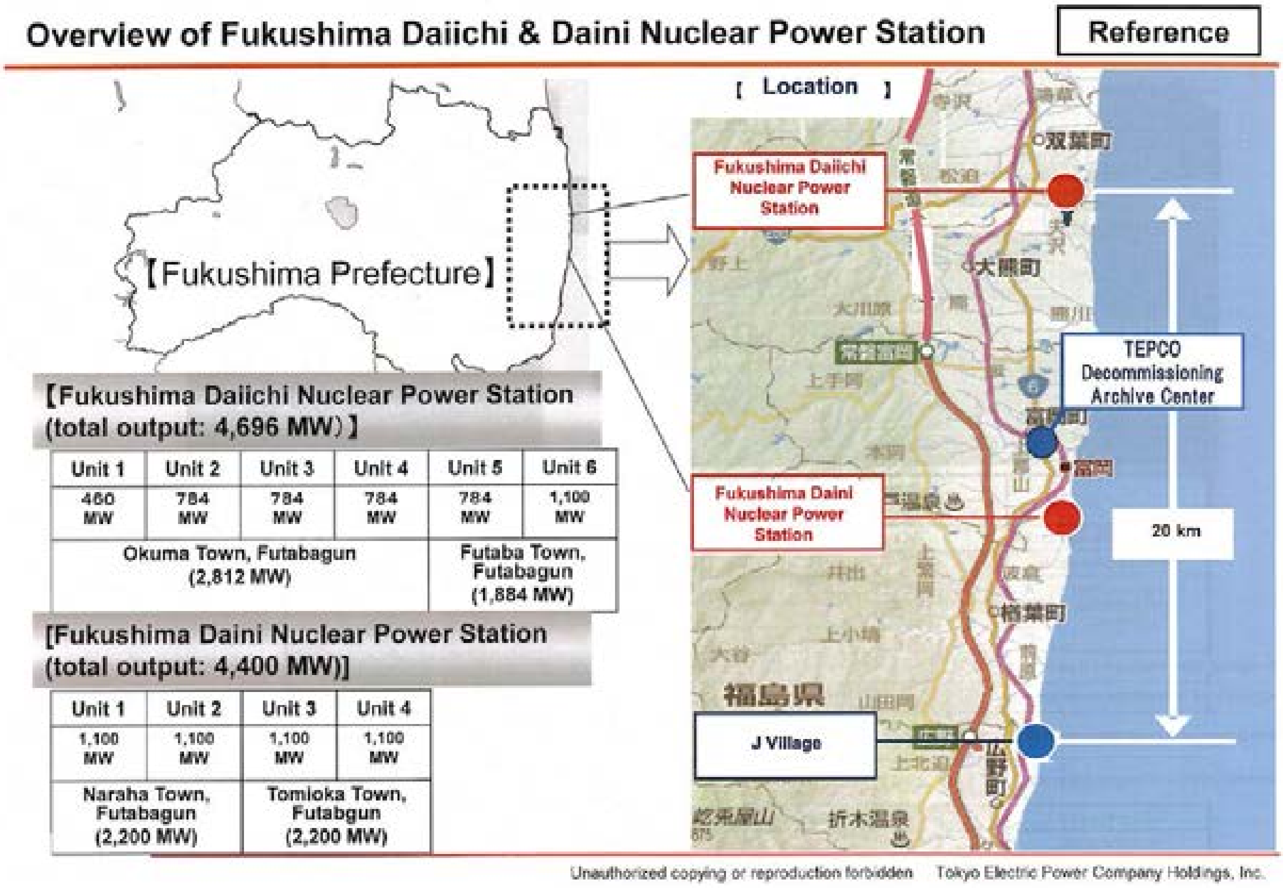
日　期	地　點	內　容
12 月 8 日	桃園→福島機場→磐城市(Iwaki city)	去程
12 月 9-10 日	磐城市→富崗鎮(Tomioka)	FRC-Corrosion 2019 “Corrosion Prediction and Mitigation for Key Components of Fukushima Daiichi NPS” 會議
12 月 11 日	磐城市→福島第一核電廠	東京電力廢爐資料館聽取簡報及巴士遊覽福島第一核電廠廠區(1F)
12 月 12 日	磐城市→福島機場→桃園	回程

108年12月8日週日下午14：00由桃園國際機場搭遠東航空班機赴日本福島縣，另外，國立清華大學核子工程與科學研究所葉宗洸教授則由日本成田機場入境至東京搭新幹線至福島磐城市，台灣參加者總計二人。飛機行程去程約3小時，抵達日本福島機場後，原先約定的機場接送司機爽約未出現，所幸在台灣桃園機場認識的日本Owada先生熱心陪伴本人在機場等候約一個小時，確定司機沒出現後，開車送本人至磐城市(Iwaki city)，耗時約1 小時。

12月9日上午10：30會議由CEA, France 的 Damien Feron 擔任此次大會主席，宣布會議開始並致歡迎詞。主辦國的日本東北大學 Yutaka Watanabe教授介紹此會議目的有四個:1. 提升1F除役相關的學術研究，2. 鼓勵學生及年輕學者投入，3. 對福島靠海區之恢復作出貢獻，4. 協助東電1F除役。接著由受邀演講者(Invited Speaker)--東京電力的T. Arai，主講 “Daiichi福島電廠去污、除役現況”，揭開專業論文發表序幕。第一天會議分為三個階段，第一階段為PCV(Primary Containment Vessel)的均勻腐蝕(General Corrosion)有兩篇論文發表。第二階段主題是生物誘發腐蝕，計有兩篇論文發表。下午的場次是第三階段，主題是水解(Radiolysis)效應對腐蝕的影響，也有兩篇論文發表。第二天早上繼續前一天水解(Radiolysis)效應對腐蝕的影響，有四篇論文，中午休息時間11:40~13:20為海報發表，計有17篇論文，筆者發表的論文亦在此列，各學者至海報區與作者們互動討論海報論文內容，極為熱絡。本所的海報發表約有5-6位學者蒞臨討論，來自Savannah River

National Laboratory 的Dr. Robert Sindelar詢問不同A106鋼材氧化層對腐蝕速率的影響。另外，JAEA的Mr. Shoya Suda對本所提出氧化層於1000小時後，有一段重量損失保持固定的論述，持肯定的看法。最後一個階段為RC結構的腐蝕，探討PCV內的溶融核燃料對鋼筋混泥土的腐蝕，有兩篇論文發表。會議每天從AM 9：30至12：00，下午從1：10至PM 16：10，於10日下午結束，內容相當精彩豐富。

11日上午7：30由磐城市出發至福島第一核電廠參觀，相關位置圖如圖一。巴士先抵達位於富崗鎮的東電除役檔案中心(TEPCO Decommissioning Archive Center)，聽取福島核災及善後處理簡報，影片一開始就放出Quote of the Day:「Arrogance and overconfidence are the real cause of the Fukushima nuclear accident! 」（自大與過度自信才是福島核子事故的真正肇因！）。日本一直對他們核電廠安全設計非常有信心。但人類在大自然面前，不得不謙卑。隨後至福島第一核電廠(簡稱1F)行政大樓辦理入場參觀手續及必要的防護設施與領取劑量佩璋。參訪人員在遊覽車內，由TEPCO人員負責解說。車子在廠區內緩慢進行，目前1F電廠及重度汙染區域周邊的通行管制已由事發的10公里，進一步縮小為3公里，3公里邊界的環境輻射劑量率為每小時1.775微西弗 (µSv/h)，車內量測值為每小時0.72微西弗；持續往電廠方向移動，會經過特定熱區（Hot Spot, 主因為周邊受汙染樹木未除污），車內劑量率為每小時達6微西弗。(註：台灣地區平均背景值為每小時0.05微西弗，因地理位置差異，日本地區平均背景值為每小時0.10微西弗。一般人可接受的有效劑量不超過1000微西弗/年)。汙染地區的表層土刨除工作仍在進行，目前每天仍有約3000車次卡車運送廢土，廢土被集中於露天暫存場。參訪途中，不時看到卡車頻繁進出。參觀完回到磐城市約下午5:00，隔日12日約六點由Owada友人載至福島機場搭乘10:00遠東航空班機返台，沒想到一抵達中正機場，就接到遠東航空因為財務危機停止飛行的消息，真是萬幸!



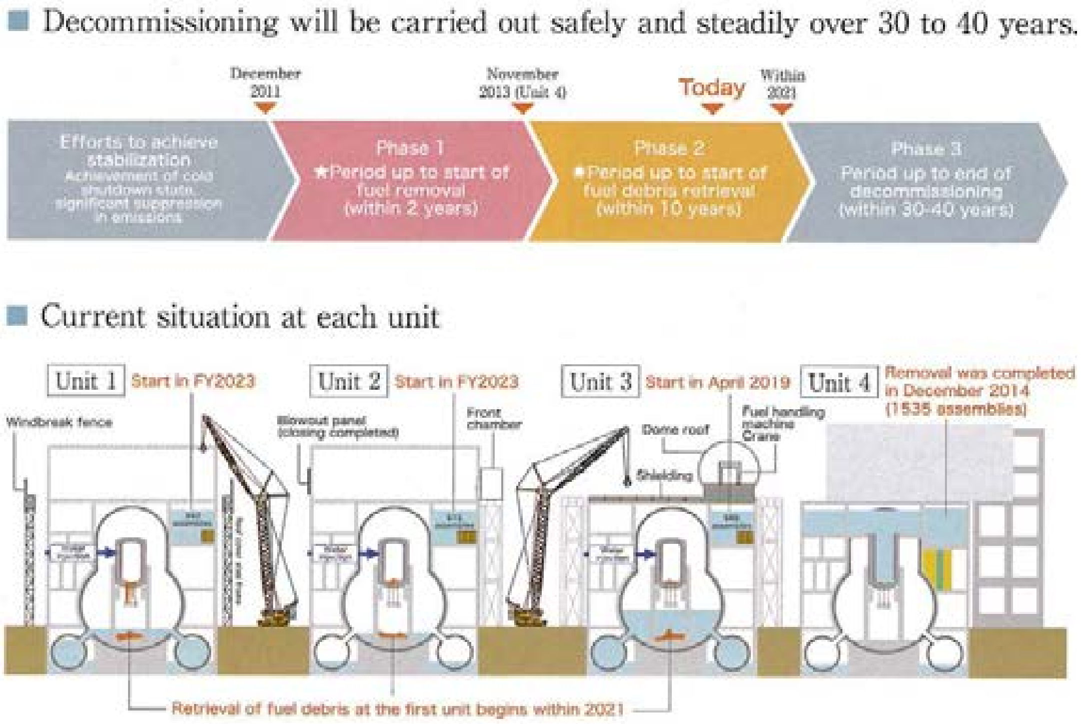
【Fukushima Daiichi Nuclear Power Station (total output: 4,696 MW)】

Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6
460 MW	784 MW	784 MW	784 MW	784 MW	1,100 MW
Okuma Town, Futabagun (2,812 MW)				Futaba Town, Futabagun (1,884 MW)	

[Fukushima Daini Nuclear Power Station (total output: 4,400 MW)]

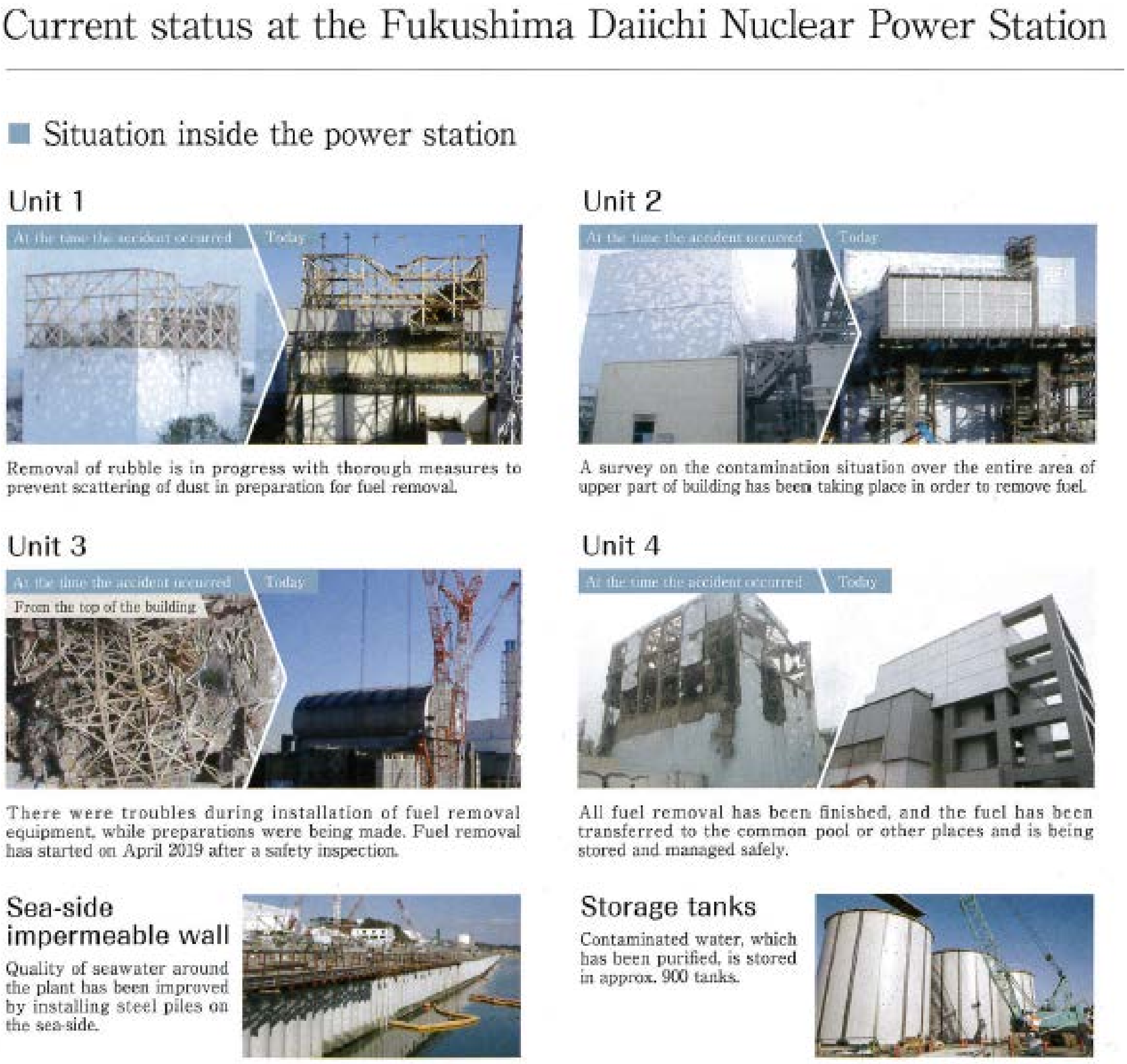
Unit 1	Unit 2	Unit 3	Unit 4
1,100 MW	1,100 MW	1,100 MW	1,100 MW
Naraha Town, Futabagun (2,200 MW)		Tomioka Town, Futabgun (2,200 MW)	

圖1：Iwaki、Tomioka與福島第一、二核電廠相關位置圖



圖二 1F電廠目前燃料移出進度

圖二顯示1F電廠目前燃料移出進度:4號機已完全移除，3號機2019年4月開始進行，1、2號機預定至2023年開始清除。圖三則為1F4個反應爐機組外觀及預防地下水滲透之圍堵設施，藉由地下冷凍管路形成一個低溫凍土牆，避免放射性物質透過地下水外洩。經過反應爐冷卻污染的水藉由過濾純化，收集已有近900個大桶子。



Current status at the Fukushima Daiichi Nuclear Power Station

■ Situation inside the power station

Unit 1

Removal of rubble is in progress with thorough measures to prevent scattering of dust in preparation for fuel removal.

Unit 2

A survey on the contamination situation over the entire area of upper part of building has been taking place in order to remove fuel.

Unit 3

There were troubles during installation of fuel removal equipment, while preparations were being made. Fuel removal has started on April 2019 after a safety inspection.

Unit 4

All fuel removal has been finished, and the fuel has been transferred to the common pool or other places and is being stored and managed safely.

Sea-side impermeable wall

Quality of seawater around the plant has been improved by installing steel piles on the sea-side.

Storage tanks

Contaminated water, which has been purified, is stored in approx. 900 tanks.

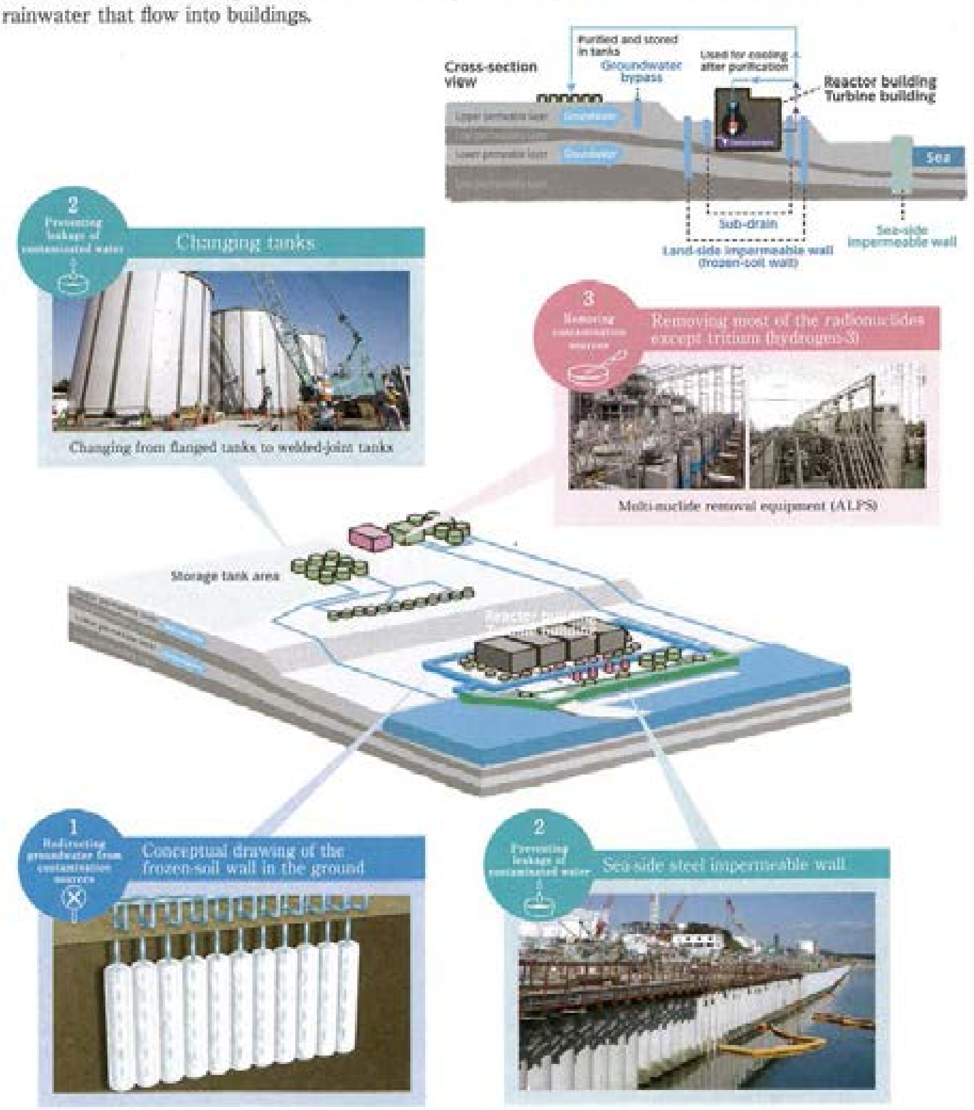
圖三　1F4個反應爐機組外觀及預防地下水滲透之圍堵設施

冷凍土技術及示意圖如圖四，除了冷凍土管路，在靠近反應器廠房的廠區表土，鋪設低滲透的柏油，防止雨水滲透至地底下成為污染的地下水。

Management of contaminated water

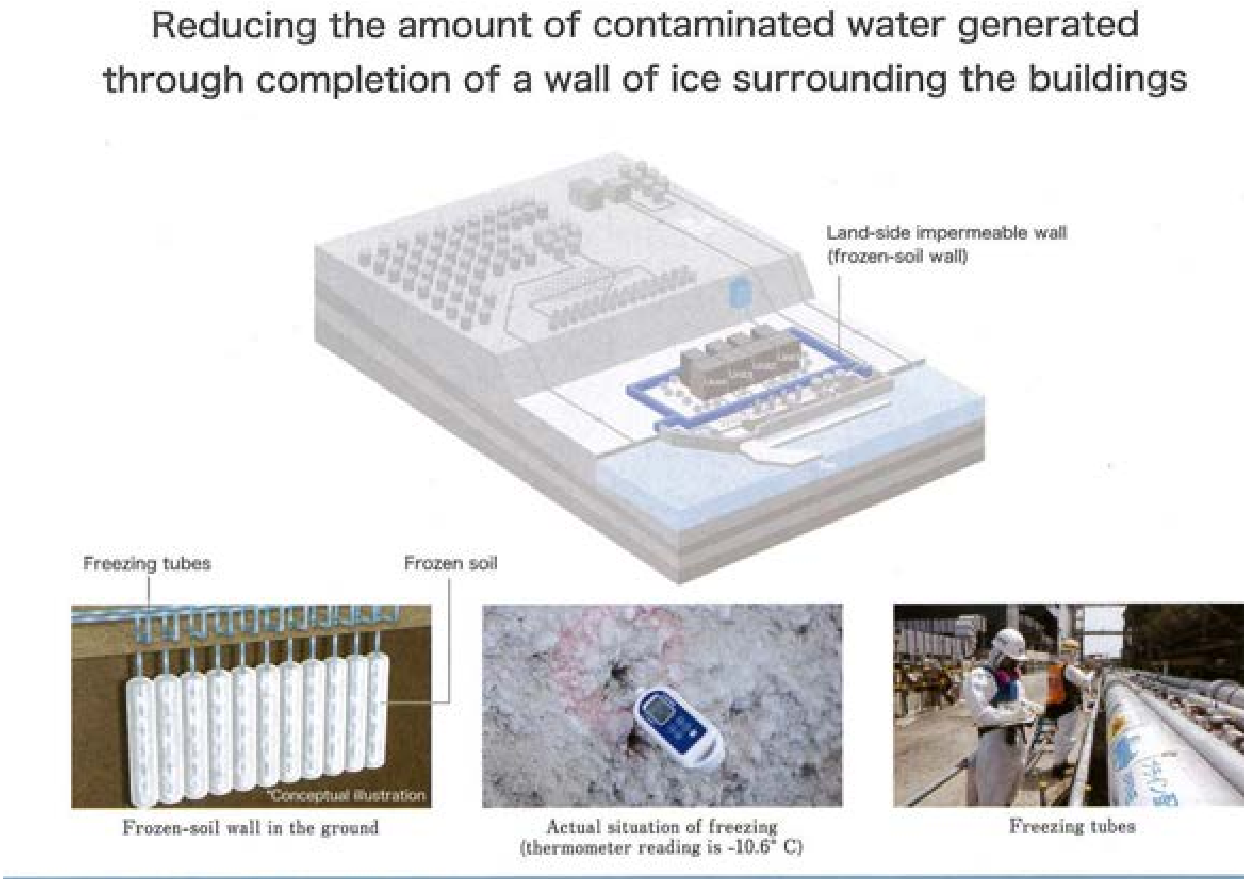
Mechanism of generation of contaminated water

Water for cooling fuel debris touches that debris, and thereby becomes highly contaminated water containing highly concentrated radioactive materials.
New contaminated water is generated due to mixing of this highly contaminated water with groundwater and rainwater that flow into buildings.



圖四　1F汙染水處置凍土牆及海邊不滲水牆示意圖及照片

圖五為1F汙染水處置凍土牆溫度量測約為-10.6 ºC，及冷凍管路現場照片圖



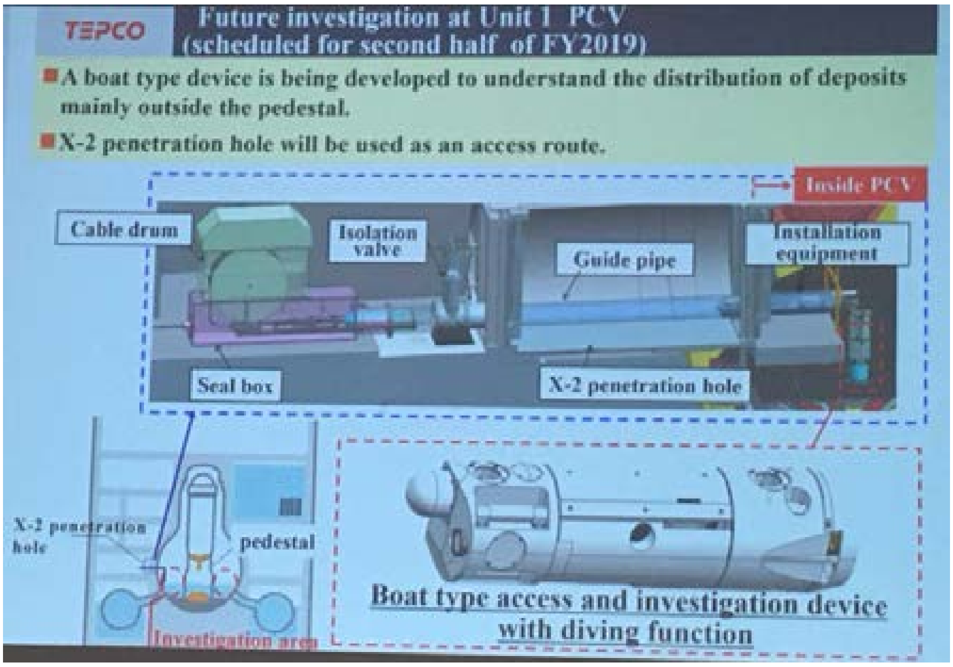
圖五　1F汙染水處置凍土牆溫度量測及冷凍管路

三、心得

此次FRC-Corrosion 2019會議論文，有四大方向: 1. PCV(Primary Containment Vessel)的均勻腐蝕(General Corrosion)，2. 生物誘發腐蝕，3. 水解(Radiolysis)效應對腐蝕的影響，4. RC結構的腐蝕。本次出席該會議心得就會議內容摘錄如下:

會議由邀請演講者(Invited Speaker)--東京電力的T. Arai，主講 “Daiichi福島電廠去污、除役現況與挑戰”，揭開專業論文發表序幕。1F汙染水質處理是第一要務，分為三大部分，1. 移除汙染物質，2. 隔絕地下水接觸汙染物質，3. 防止汙染水質外洩。藉由凍土牆及防水層柏油及海邊不滲水牆多重障蔽，已成功將汙染水從2014年470噸/年降低至2018年170噸/年。

4號機用過核燃料已由燃料池完全移除，3號機2019年4月開始進行，1、2號機預定至2023年開始清除。熔融的核燃料因已由反應爐掉至主圍阻體 (PCV, Primary Containment Vessel)，如何取出，是前所未見的工作。2019年1月，2號機探索設備(Investigation Device)於X-2穿越管(Penetration)藉由導管(Guide Tube)傳輸，使觀測設備進入PCV底部進行觀察及取樣，如圖六。檢測結果確定是核燃料與RPV的成分。


TEPCO

Future investigation at Unit 1 PCV
(scheduled for second half of FY2019)

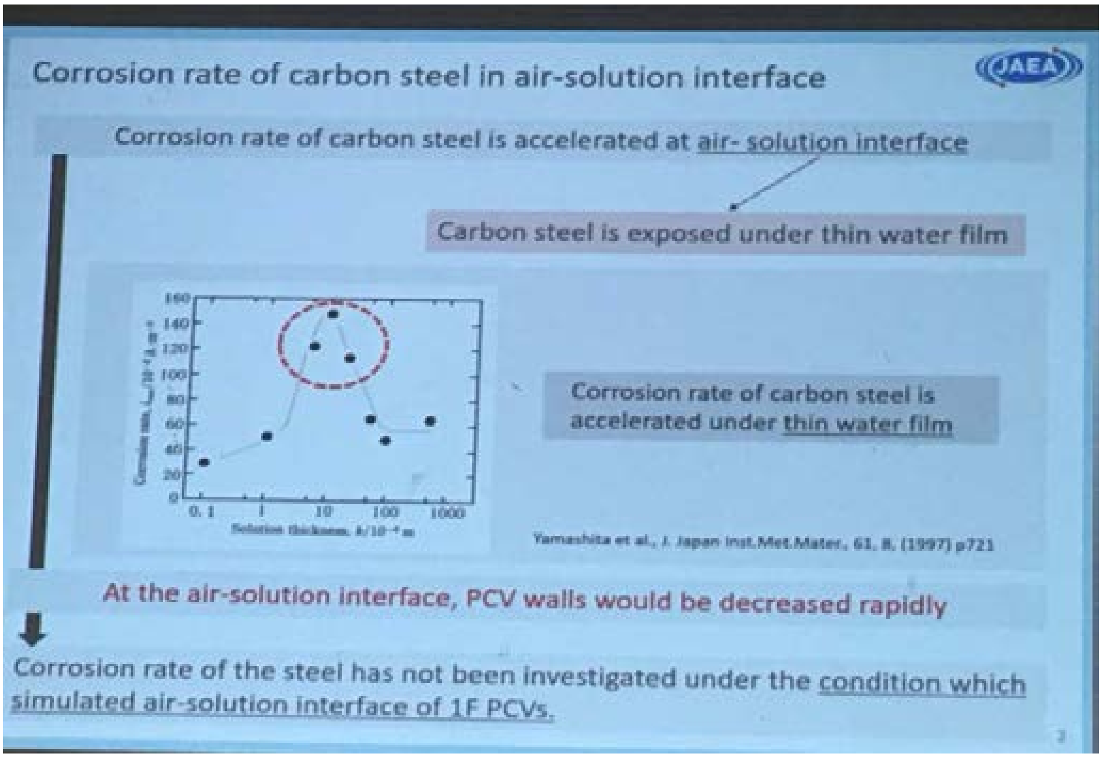
- A boat type device is being developed to understand the distribution of deposits mainly outside the pedestal.
- X-2 penetration hole will be used as an access route.

圖六　進入2號機取樣、觀測之探索設備示意圖

加拿大Integrity Corrosion Consulting Ltd., 的Fraser King與核研所有許多合作計畫，亦受邀報告 “Prediction of Joint Mechanical-Corrosion Failures of Carbon Steel Components and Structures” ，他提出碳鋼的腐蝕可能導致結構無法支撐，是機械與腐蝕結合的重點，另外要考慮的是氫脆議題，由於鐵基材料特別是碳鋼腐蝕時會產生氫氣，可能進入材料內部，使材質變脆，也可能發生機械與腐蝕結合的劣化，是需考慮的重點。會後筆者也與Fraser King博士交換意見，因他是加拿大NWMO (Nuclear Waste Management Organization)的顧問，也長期與本所有合作計畫，曾參訪本組實驗室兩次。筆者問及加拿大採用碳鋼

以5mm 電鍍層或冷噴塗層是否足夠形成保護，尤其電鍍層的鍵結力是否可阻擋摩擦或外力刮傷的衝擊? 他也同意筆者的顧慮，但因加拿大的燃料較短，處置方式與台灣不同，所以考慮的點不太一樣。另外，問及銅罐是否發生氫脆的議題，他個人表示機率應是非常小，因為反應速率太慢，但因他是作Model 的人，對實驗數據仍採保守態度，仍需有更多實驗數據佐證，目前僅有少數實驗數據持此論點。

JAEA的 Kyohei Otani 發表 “A mechanism of the accelerated corrosion of carbon steel in the simulated condition of air-solution interface”，1F核電廠發生核災後，以遙控機器人深入PCV觀測，發現PCV碳鋼處於汙染水與空氣(Air-Solution)交界的環境，之前的研究顯示，當碳鋼表面有水膜時，其腐蝕速率會加速，如圖七，


Corrosion rate of carbon steel in air-solution interface

Corrosion rate of carbon steel is accelerated at air- solution interface

Carbon steel is exposed under thin water film

Corrosion rate of carbon steel is accelerated under thin water film

Yamashita et al., J. Japan Inst.Met.Mater., 61, 8, (1997) p721

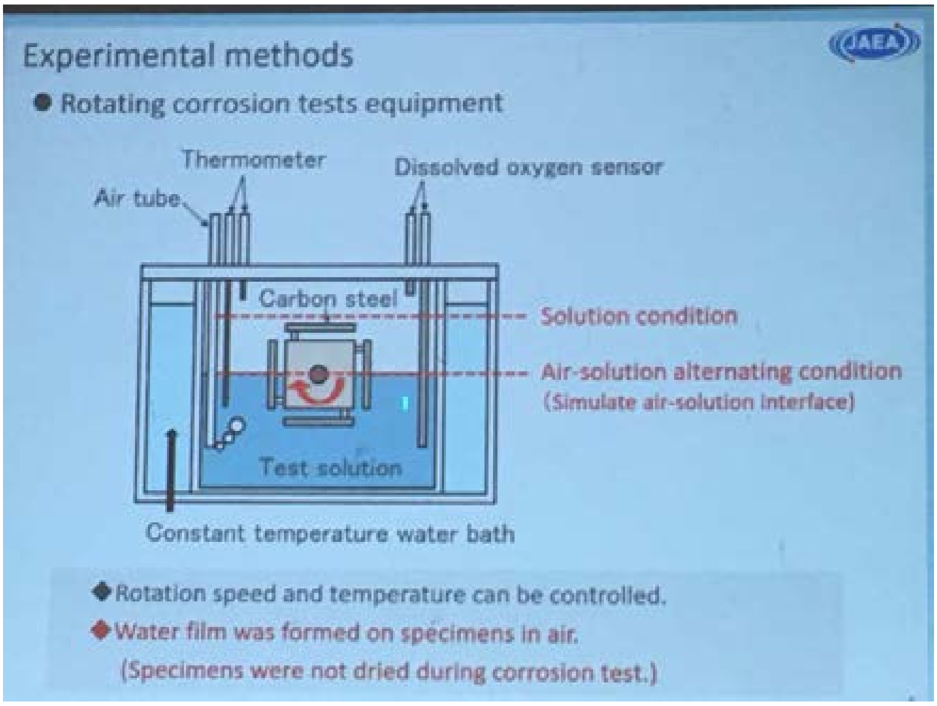
At the air-solution interface, PCV walls would be decreased rapidly

Corrosion rate of the steel has not been investigated under the condition which simulated air-solution interface of 1F PCVs.

圖七　碳鋼表面水膜會促使腐蝕速率加速

實驗裝置示意圖如圖八，實驗結果顯示，碳鋼在液-氣交替環境的腐蝕速率，約為溶液中的3倍。有報告指出碳鋼上薄薄的水膜可加速水中溶氧的傳輸，使氧的還原反應加速，根據混和電位理論(Mix-potential Theory)，會使腐蝕速率變快。圖九為經500

小時液-氣介面測試後試片表面，可發現氧化層內有奈米顆粒。經由成分分析如圖十，外層以Fe_2O_3為主，內層則為Fe_3O_4。



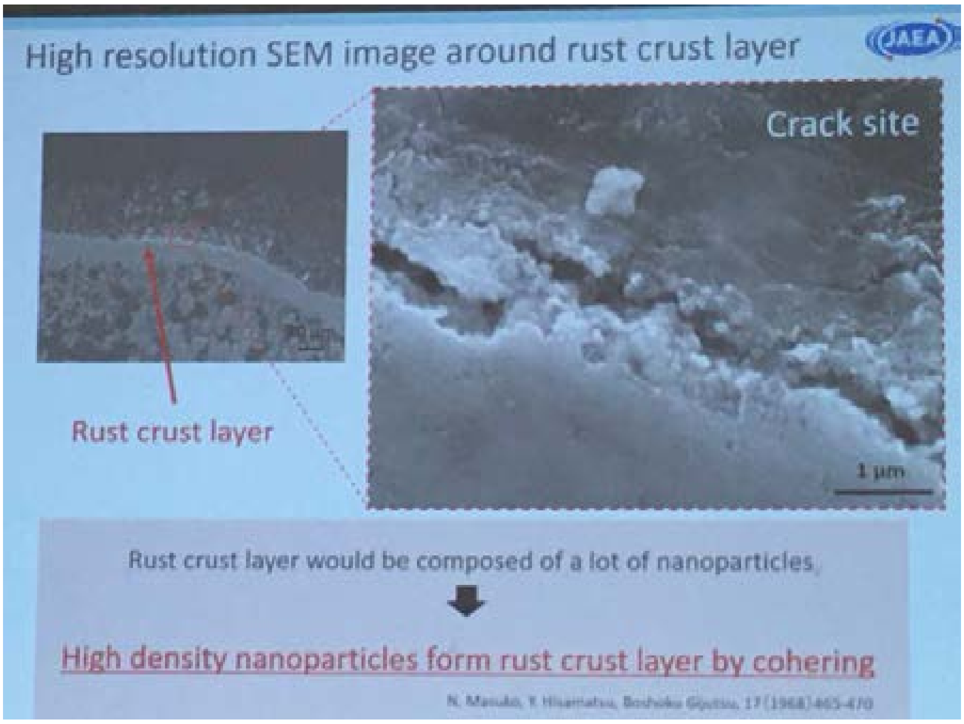
Experimental methods

- Rotating corrosion tests equipment

◆Rotation speed and temperature can be controlled.

◆Water film was formed on specimens in air.
(Specimens were not dried during corrosion test.)

圖八　碳鋼試片於液-氣介面旋轉腐蝕示意圖



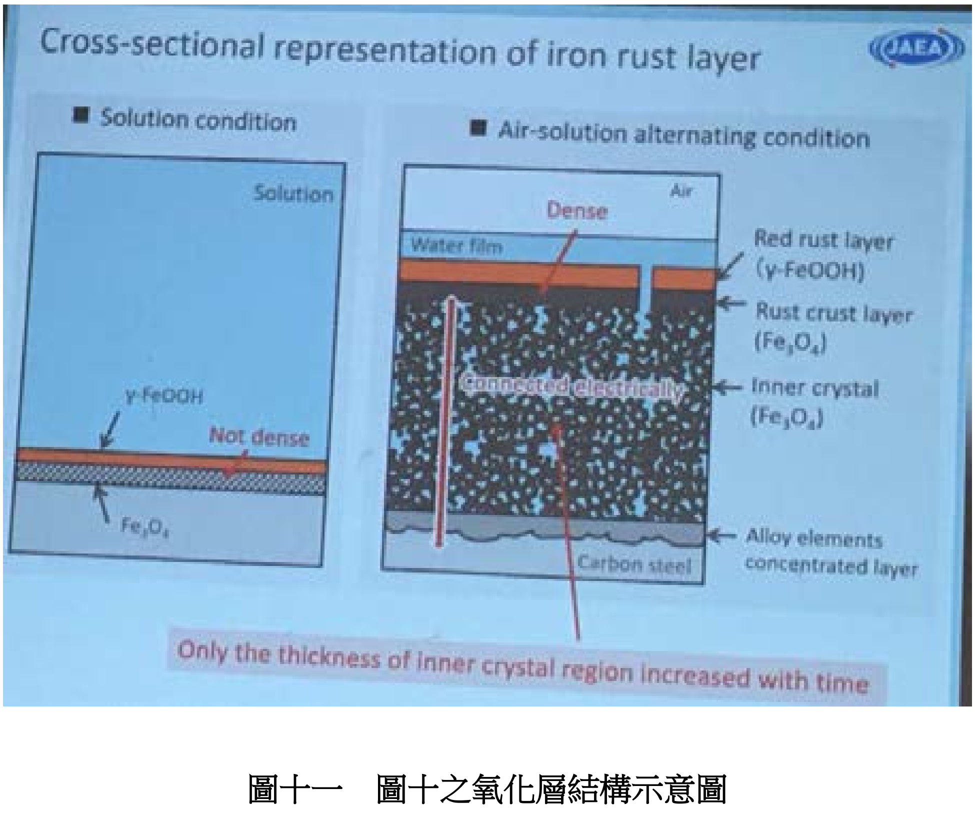
High resolution SEM image around rust crust layer

Rust crust layer would be composed of a lot of nanoparticles

High density nanoparticles form rust crust layer by cohering

圖九　經500小時液-氣介面測試後試片表面

圖十 外層以Fe_2O_3為主，內層則為Fe_3O_4



Cross-sectional representation of iron rust layer

■ Solution condition

■ Air-solution alternating condition

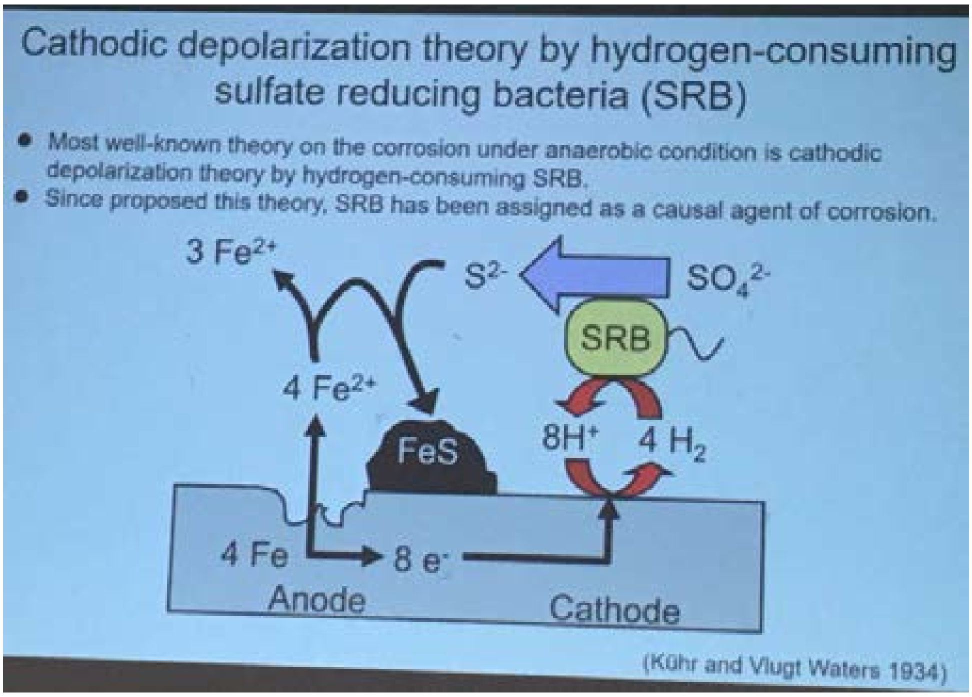
Only the thickness of inner crystal region increased with time

圖十一　圖十之氧化層結構示意圖

氧化層結構如圖十一之示意圖，紅色鬆散的氧化層內部有一連續的Fe_3O_4。

來自澳洲The university of Newcastle，Robert E. Melchers，原為土木結構工程師，後來轉而研究鋼材的微生物腐蝕，發表的題目為 “Microbiologically Influenced Corrosion (MIC) of Steels and Alloys in Seawaters”， 傳統的微生物腐蝕理論之一是硫酸鹽還原菌(Sulfate Reducing Bacteria, SRB)，其厭氧性的細菌與金屬鐵的反應式如下，如圖十二:

$4Fe \rightarrow 4Fe^{2+}+8e^{-1}$（陽極過程）
$8H_2O \rightarrow 8H^{+1}+8OH^{-}$（水電離）
$8H^{+}+8e^{-1} \rightarrow 4H_2$（陰極過程）
$SO_4^{-2}+4H_2 \rightarrow S^{2-}+4H_2O$（細菌的陰極去極化）
$Fe^{2+}+S^{2-} \rightarrow FeS$（腐蝕產物）
$3Fe^{2+}+6OH^{-} \rightarrow 3Fe(OH)_2$（腐蝕產物）



Cathodic depolarization theory by hydrogen-consuming sulfate reducing bacteria (SRB)

- Most well-known theory on the corrosion under anaerobic condition is cathodic depolarization theory by hydrogen-consuming SRB.
- Since proposed this theory, SRB has been assigned as a causal agent of corrosion.

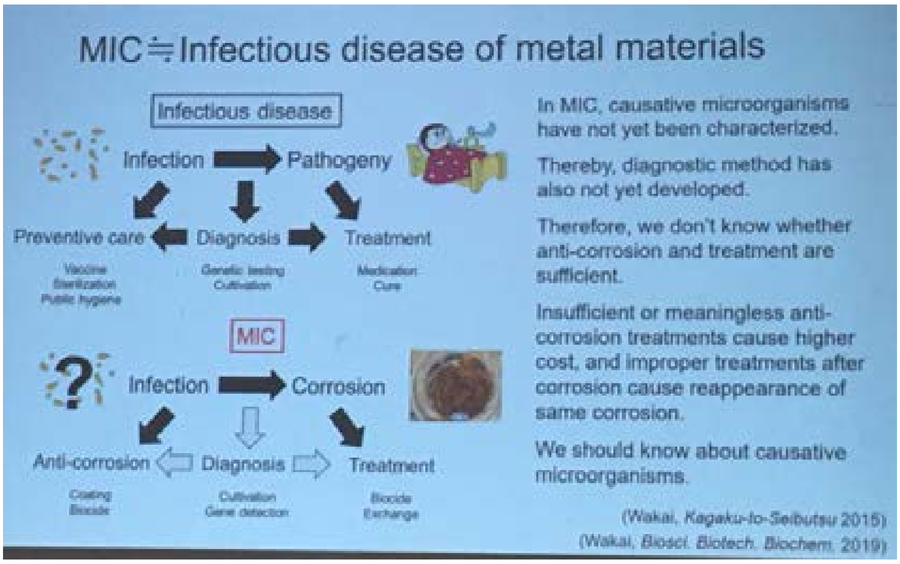
(Kühr and Vlugt Waters 1934)

圖十二 SRB與鐵反應的陰、陽極反應示意圖

作者提出微生物腐蝕牽涉化學反應稱之為 cMIC，而涉及電子轉移者稱之為 eMIC。海洋的微生物腐蝕，涉及海水溫度及營養物的補充(通常為鐵)及溶解無機氮(DIN, Dissolved Inorganic Nitrogen)。作者也提出CuNi合金因內部含鐵，會有微生物腐蝕，鋁合金一般不含鐵，所以耐微生物腐蝕。會後休息時筆者向作者詢問，他如何由結構工程師轉向微生物腐蝕，他表示初入門的確困難，但他推薦參考資料: T. Liengen, D. Feron,

R. Basseguy and I. B. Beech, (Eds.) (2014) Understanding Biocorrosion European Federation of Corrosion Publications, Number 66, Cambridge, Woodhead Publishing in Materials, 213-242. 縮短他摸索的距離。

來自 Japan Agency for Marine-Earth Science and Technology, Dr. Satashi Wakai發表 “MIC is infectious disease of metal Materials” ，提出: 目前對微生物腐蝕的機制仍有許多不清楚處，如同人體受病菌感染，經過正確診斷，採取正當的治療，即可得醫治。但微生物腐蝕機制不清楚，耗費財力處理，但可能腐蝕再度出現，如圖十三。近期，腐蝕鐵的微生物與硫酸鹽還原菌SRB被提出，另外，iron-corrosive methanogen(產甲烷菌), iron-corrosive nitrate-reducing bacteria(硝酸鹽還原菌), iron corrosive acetogen(產乙酸菌), iron-corrosive neutrophilic(嗜中性白血球) iron-oxidizing bacteria, iodide-oxidizing bacteria等等也被報導，日後結合大數據的技術是未來發展的策略。



MIC≒Infectious disease of metal materials

In MIC, causative microorganisms have not yet been characterized.

Thereby, diagnostic method has also not yet developed.

Therefore, we don't know whether anti-corrosion and treatment are sufficient.

Insufficient or meaningless anti-corrosion treatments cause higher cost, and improper treatments after corrosion cause reappearance of same corrosion.

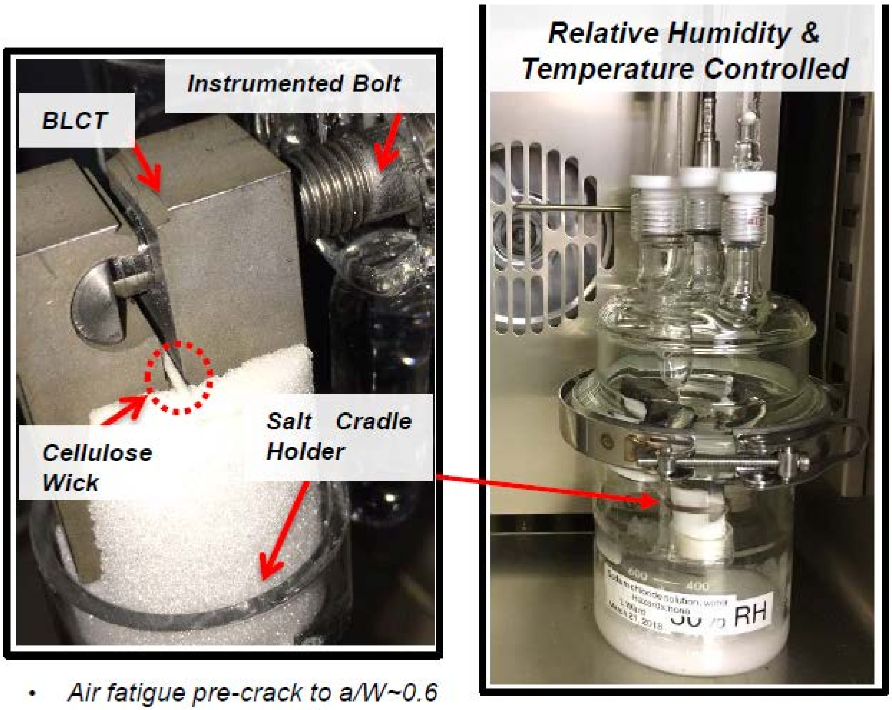
We should know about causative microorganisms.

(Wakai, *Kagaku-to-Seibutsu* 2015)
(Wakai, *Biosci. Biotech. Biochem.* 2019)

圖十三 金屬微生物腐蝕與人類傳染疾病示意圖

來自Savannah River National Laboratory 的Robert Sindelar以海報形式發表 “Chloride-induced Stress Corrosion Cracking-Growth rates for application to Canister Flaw Disposition” ，由於作者的文章曾在ESCP (Extended Storage Cooperation Program)會議發表過類似文章，當初讀的時候就發現許多疑問，所以筆者向作者提了許多問題，互

相交換意見。作者的試片設計是以WOL(Wedge Open Loading)試片，或稱之為BLCT(Bolt Load Compact Tension)，以螺絲施加應力，如圖十四。而環境以纖維素(Cellulose)含鹽沾濕後置於自製的實驗玻璃槽控制溫、濕度，由於含鹽量不易控制，且作者也同意此實驗不易做，一般的數據大都是水溶液環境中，測試而得的數據，但潮解的海鹽，與水溶液環境不同，是否滲透至裂縫尖端，不易得知。仍有待更多數據佐證。

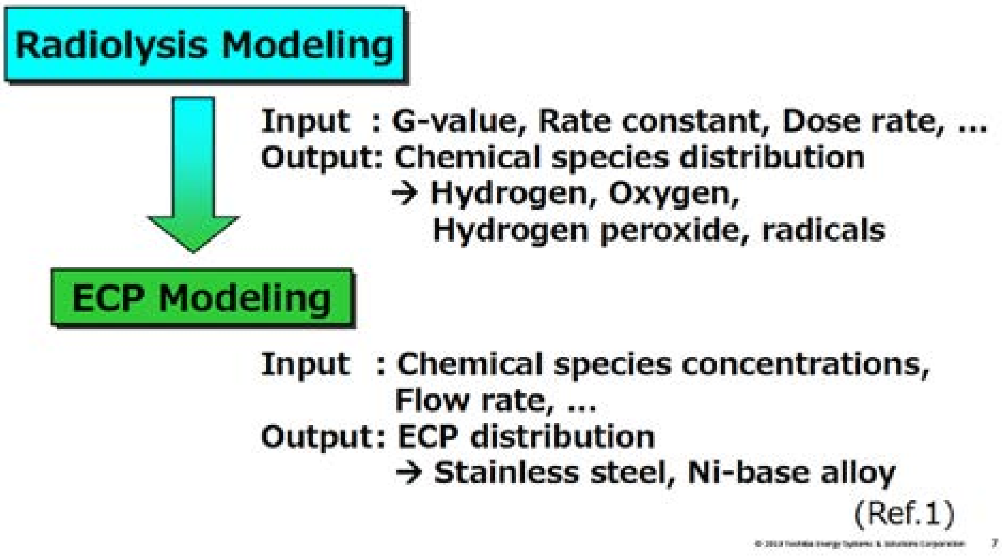


- Air fatigue pre-crack to a/W~0.6
- Loaded to ~33 MPa $\sqrt{m}$
- Test initiated March 2018

Each condition has companion teardrop specimen

圖十四 WOL試片加鹽及負載方式

來自Toshiba Energy Systems and Solution Corporation的Dr. Junichi Takagi 發表 “Water Radiolysis and Its Effect on BWR Plant Materials and Radioactive Wastes” ，有兩種model輸入模式:水解(Radiolysis) 及ECP(電化學電位)，而單位能量的水解產物定義為G值，是輸入model 的重要參數。由於輻射水解會產生不同的H^+、H_2O_2、HO_2、H_2、e_{aq}^{-1}、H、OH產物，所以藉由Modeling可得出水解產物。再輸入ECP modeling可算出裂縫的生長速率，流程如圖十五。G值定義如圖十六。



Radiolysis Modeling

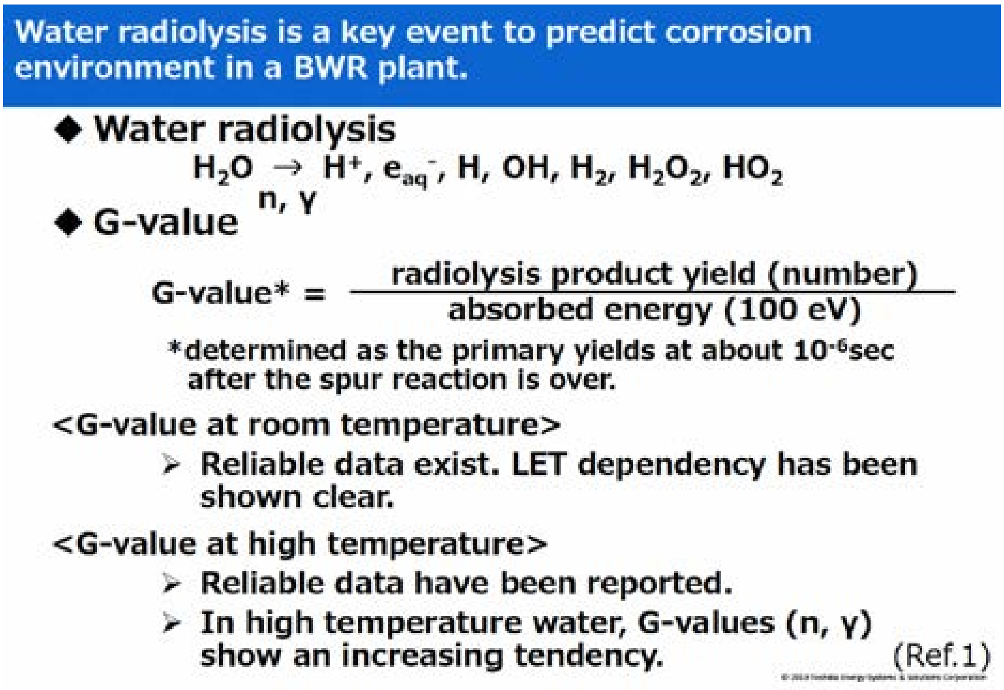
Input : G-value, Rate constant, Dose rate, ...
Output: Chemical species distribution
→ Hydrogen, Oxygen,
Hydrogen peroxide, radicals

ECP Modeling

Input : Chemical species concentrations,
Flow rate, ...
Output: ECP distribution
→ Stainless steel, Ni-base alloy

(Ref.1)

圖十五　Modeling輸入參數



Water radiolysis is a key event to predict corrosion environment in a BWR plant.

◆ Water radiolysis

$$H_2O \xrightarrow[n,\ \gamma]{} H^+,\ e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2,\ HO_2$$

◆ G-value

$$\text{G-value}^* = \frac{\text{radiolysis product yield (number)}}{\text{absorbed energy (100 eV)}}$$

*determined as the primary yields at about 10^{-6}sec after the spur reaction is over.

<G-value at room temperature>

- Reliable data exist. LET dependency has been shown clear.

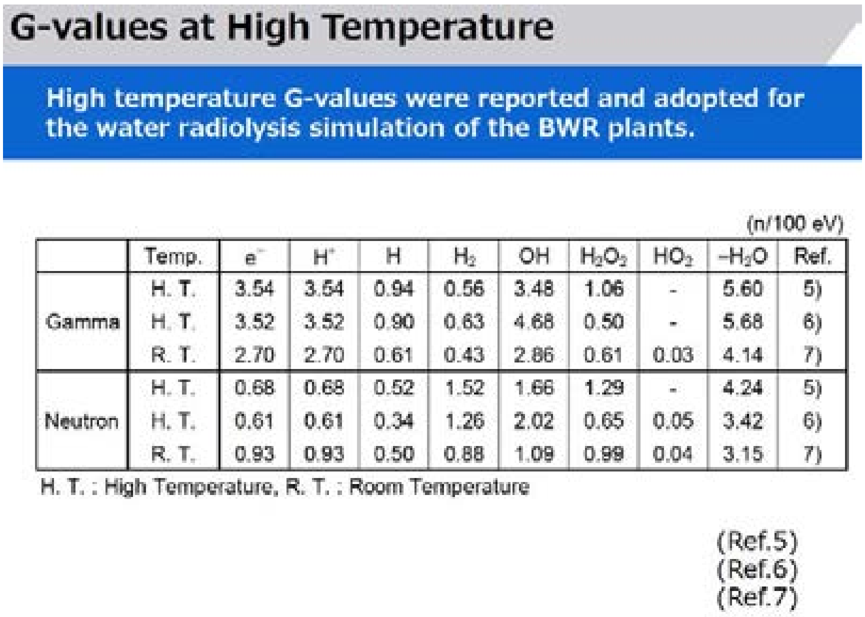
<G-value at high temperature>

- Reliable data have been reported.
- In high temperature water, G-values (n, γ) show an increasing tendency.

(Ref.1)

圖十六 G值定義

由於G值會隨生成物、環境溫度與中子(n)或加馬(γ)射線而不同，如下表



G-values at High Temperature

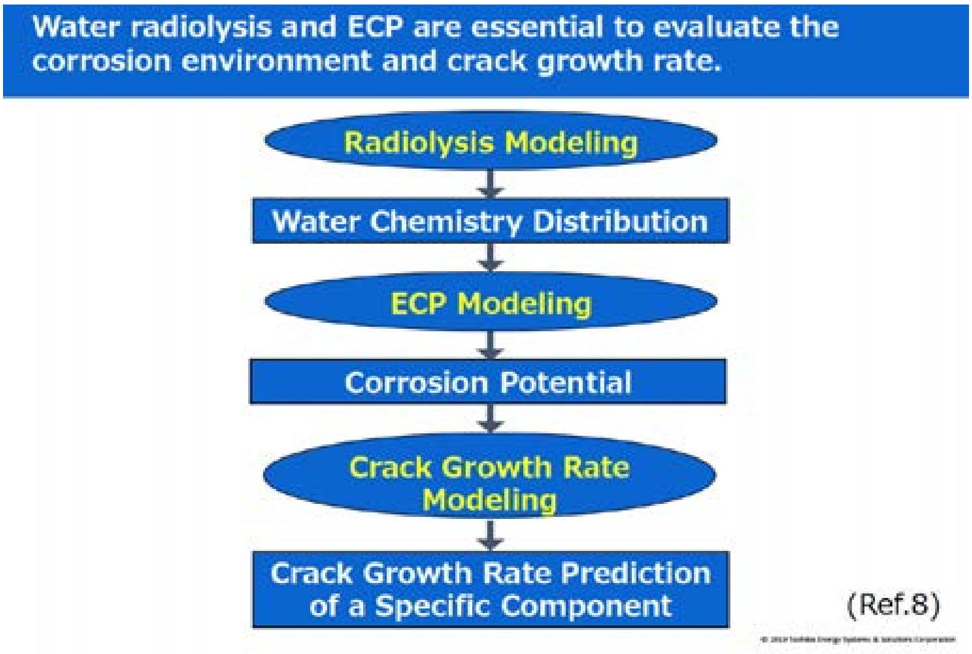
High temperature G-values were reported and adopted for the water radiolysis simulation of the BWR plants.

(n/100 eV)

	Temp.	e^-	H^+	H	H_2	OH	H_2O_2	HO_2	$-H_2O$	Ref.
Gamma	H. T.	3.54	3.54	0.94	0.56	3.48	1.06	-	5.60	5)
	H. T.	3.52	3.52	0.90	0.63	4.68	0.50	-	5.68	6)
	R. T.	2.70	2.70	0.61	0.43	2.86	0.61	0.03	4.14	7)
Neutron	H. T.	0.68	0.68	0.52	1.52	1.66	1.29	-	4.24	5)
	H. T.	0.61	0.61	0.34	1.26	2.02	0.65	0.05	3.42	6)
	R. T.	0.93	0.93	0.50	0.88	1.09	0.99	0.04	3.15	7)

H. T. : High Temperature, R. T. : Room Temperature

(Ref.5)
(Ref.6)
(Ref.7)

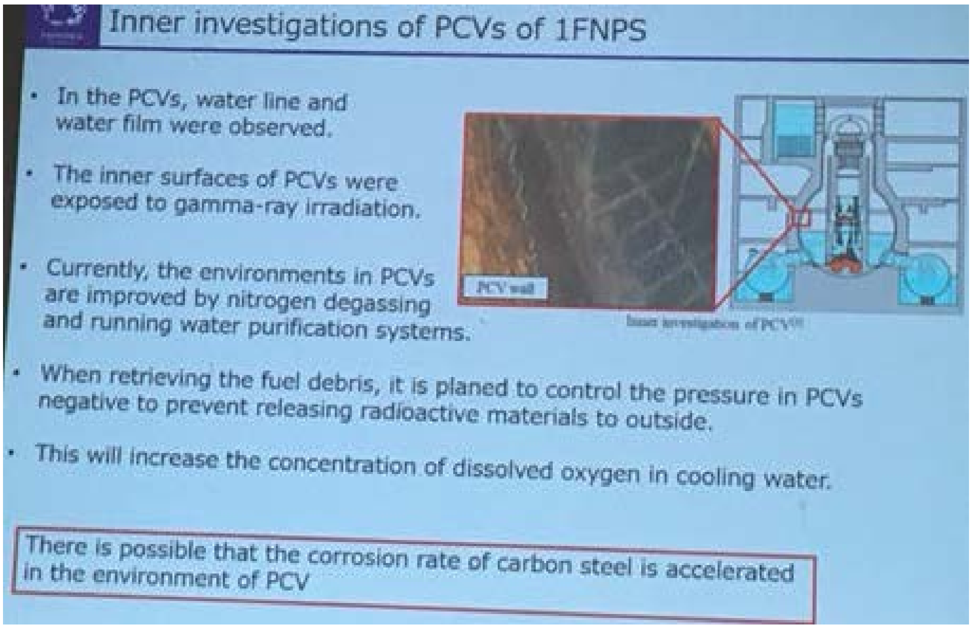


Water radiolysis and ECP are essential to evaluate the corrosion environment and crack growth rate.

Radiolysis Modeling
Water Chemistry Distribution
ECP Modeling
Corrosion Potential
Crack Growth Rate Modeling
Crack Growth Rate Prediction of a Specific Component

(Ref.8)

東北大學的Hiroshi Abe發表 “Effect of gamma-ray irradiation on corrosion rate of carbon steels at water line”，由於1F電廠爐心冷卻水失效，故緊急注入海水，而爐心PCV處有溶融的核燃料，會放射gamma-ray，1F屬MarkII主圍阻體，PCV是由碳鋼材SA7388鋼板製之，PCV內通氮氣除氧，但取出爐屑(Debris)時會使PCV內部保持負壓，防止輻射物質外洩，但此舉會造成PCV溶氧增加，本研究探討於海水(半浸泡)環境及gamma-ray照射，對鋼材的腐蝕速率之影響，如圖十七。



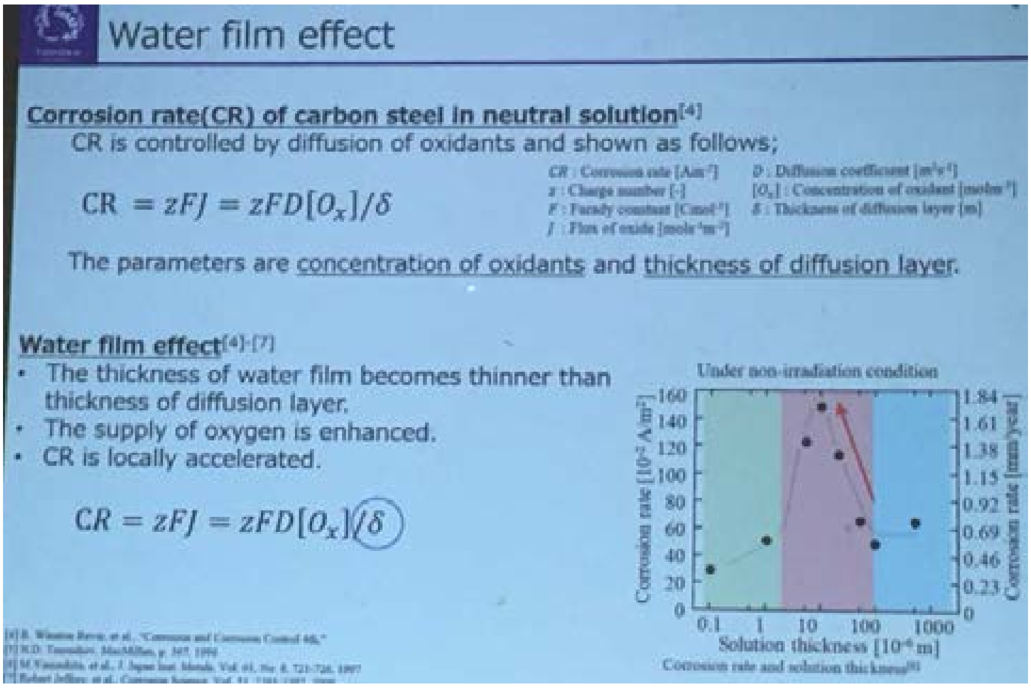
Inner investigations of PCVs of 1FNPS

- In the PCVs, water line and water film were observed.
- The inner surfaces of PCVs were exposed to gamma-ray irradiation.
- Currently, the environments in PCVs are improved by nitrogen degassing and running water purification systems.
- When retrieving the fuel debris, it is planed to control the pressure in PCVs negative to prevent releasing radioactive materials to outside.
- This will increase the concentration of dissolved oxygen in cooling water.

There is possible that the corrosion rate of carbon steel is accelerated in the environment of PCV

圖十七　PCV鋼板內部示意圖

碳鋼與水膜(Water Film)的厚度在某一厚度時，由於氧的擴散加速，導致腐蝕速率加速，另外，輻射水解發生時，會生成H_2O_2及O_2氧化劑，也會使腐蝕速率加速，如圖十八、十九。



Water film effect

Corrosion rate(CR) of carbon steel in neutral solution[4]

CR is controlled by diffusion of oxidants and shown as follows;

$$CR = zFJ = zFD[O_x]/\delta$$

CR : Corrosion rate [Am^{-2}]
z : Charge number [-]
F : Farady constant [$Cmol^{-1}$]
J : Flux of oxide [$mol\,s^{-1}m^{-2}$]
D : Diffusion coefficient [m^2s^{-1}]
[O_x] : Concentration of oxidant [$mol\,m^{-3}$]
δ : Thickness of diffusion layer [m]

The parameters are concentration of oxidants and thickness of diffusion layer.

Water film effect[4]-[7]

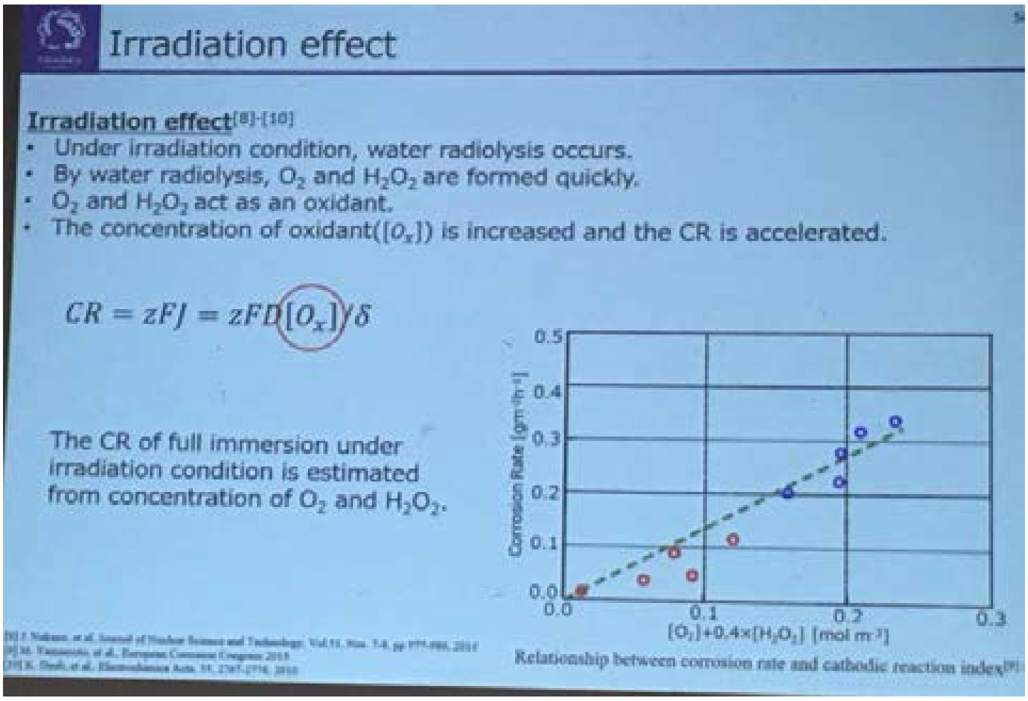
- The thickness of water film becomes thinner than thickness of diffusion layer.
- The supply of oxygen is enhanced.
- CR is locally accelerated.

$$CR = zFJ = zFD[O_x]/\boxed{\delta}$$

[4] R. Winston Revie, et al., "Corrosion and Corrosion Control 4th"
[5] N.D. Tomashov, MacMillan, p. 397, 1966
[6] M.Yamashita, et al., J. Japan Inst. Metals, Vol. 61, No. 8, 721-726, 1997
[7] Robert Jeffrey, et al., Corrosion Science, Vol. 51, 1361-1367, 2009

Corrosion rate and solution thickness[6]

圖十八 碳鋼腐蝕速率受水膜厚度影響示意圖



Irradiation effect

Irradiation effect[8]-[10]

- Under irradiation condition, water radiolysis occurs.
- By water radiolysis, O_2 and H_2O_2 are formed quickly.
- O_2 and H_2O_2 act as an oxidant.
- The concentration of oxidant($[O_x]$) is increased and the CR is accelerated.

$$CR = zFJ = zFD[O_x]/\delta$$

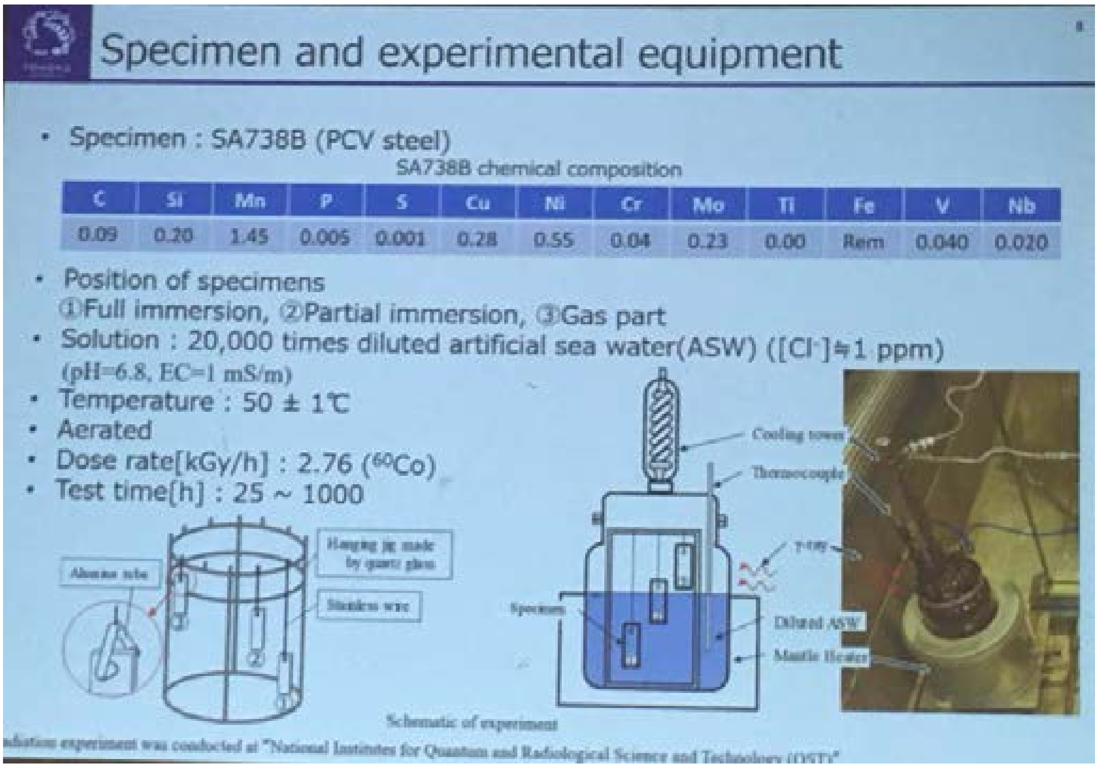
The CR of full immersion under irradiation condition is estimated from concentration of O_2 and H_2O_2.

Relationship between corrosion rate and cathodic reaction index[9]

圖十九 碳鋼腐蝕速率受輻射效應水解影響關係式

作者將碳鋼試片分別置於水槽中，位置如圖二十，探討完全浸泡、半浸泡及空氣中之腐蝕速率差異。以^{60}Co照射γ ray(劑量率為2.76kGy/h)，測試溫度50^{o}C，時間為25-1000小時。測試結果如圖二十一 :浸泡與半浸泡之腐蝕外觀無明顯差異，外層為γ-FeOOH，內層為Fe_3O_4，但由3D Shape Measurement影像分析技術及重量損失可分辨出半浸泡及γ射線照射之腐蝕情況較嚴重，如圖二十二。3D Shape Measurement影像分析技術經詢問作者係由Keyence的產品Wide-Area 3D Measurement System VR-5000，量測而得，先將表面的氧化物清洗乾淨，利用深度的量測得知腐蝕速率。

圖二十三與二十四為筆者海報現場照片及全體合照。



Specimen and experimental equipment

- Specimen : SA738B (PCV steel)

SA738B chemical composition

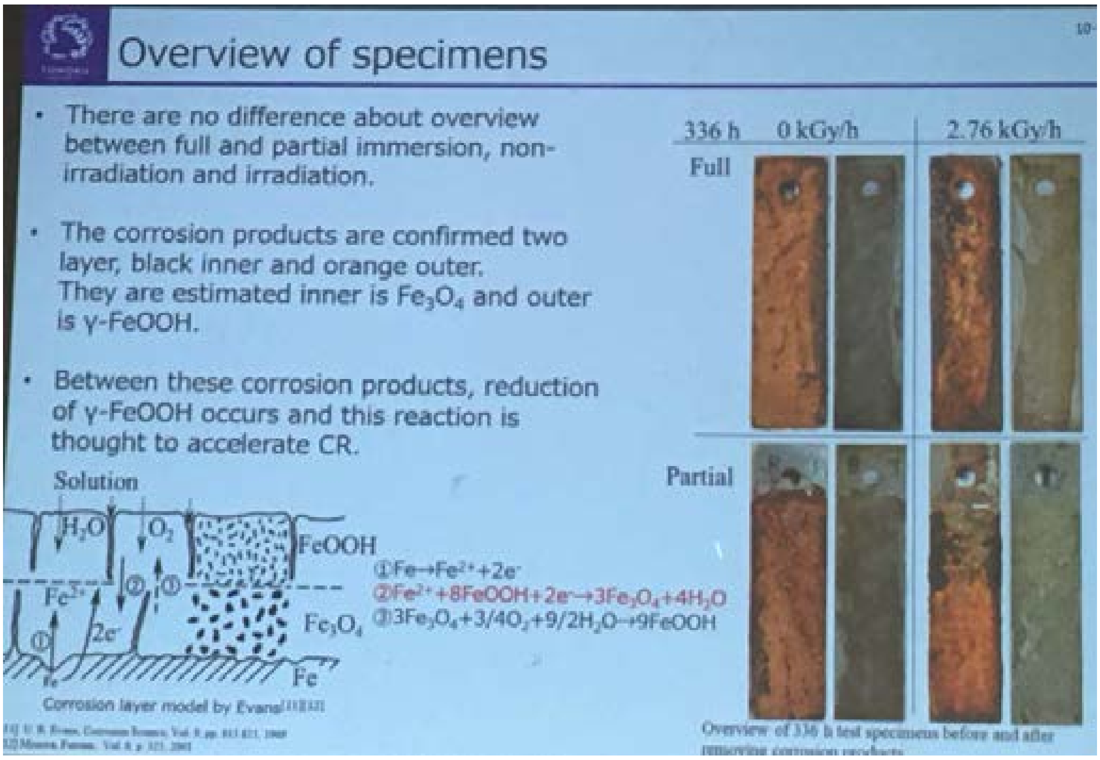
C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Ti	Fe	V	Nb
0.09	0.20	1.45	0.005	0.001	0.28	0.55	0.04	0.23	0.00	Rem	0.040	0.020

- Position of specimens
  ①Full immersion, ②Partial immersion, ③Gas part
- Solution : 20,000 times diluted artificial sea water(ASW) ([Cl^-]≒1 ppm)
  (pH=6.8, EC=1 mS/m)
- Temperature : 50 ± 1℃
- Aerated
- Dose rate[kGy/h] : 2.76 (^{60}Co)
- Test time[h] : 25 ~ 1000

Schematic of experiment

adiation experiment was conducted at "National Institutes for Quantum and Radiological Science and Technology (QST)"

圖二十 **PCV**鋼材測試條件及試片放置示意圖



Overview of specimens

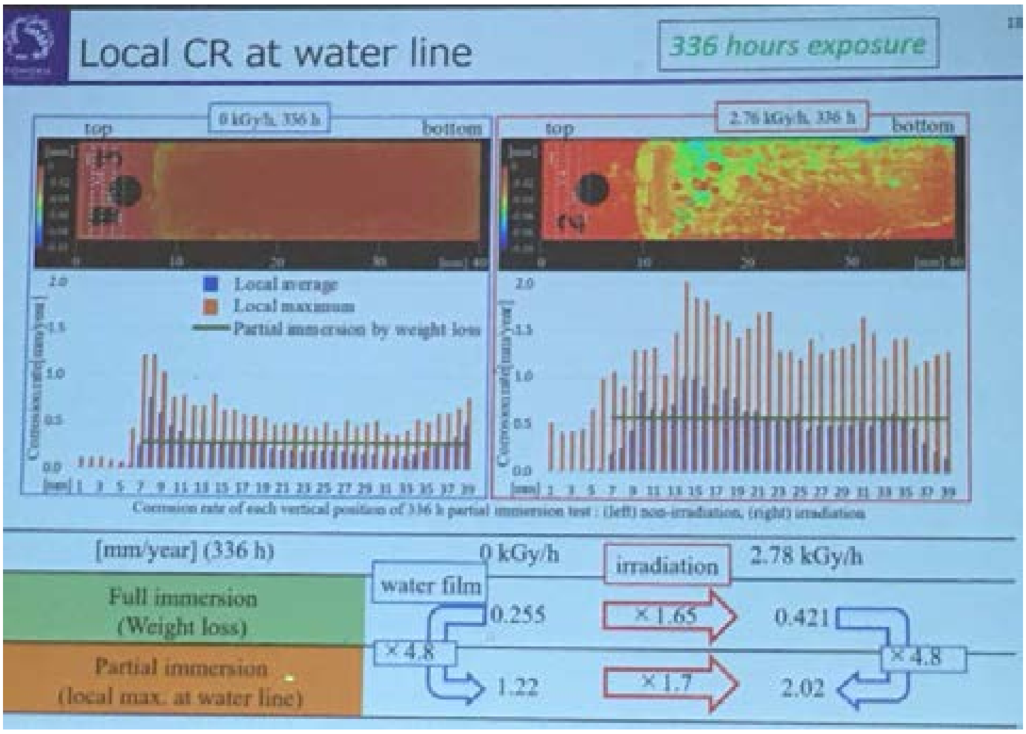
- There are no difference about overview between full and partial immersion, non-irradiation and irradiation.
- The corrosion products are confirmed two layer, black inner and orange outer.
  They are estimated inner is Fe_3O_4 and outer is γ-FeOOH.
- Between these corrosion products, reduction of γ-FeOOH occurs and this reaction is thought to accelerate CR.

①$Fe \rightarrow Fe^{2+} + 2e^-$
②$Fe^{2+} + 8FeOOH + 2e^- \rightarrow 3Fe_3O_4 + 4H_2O$
③$3Fe_3O_4 + 3/4O_2 + 9/2H_2O \rightarrow 9FeOOH$

Corrosion layer model by Evans[1][2]

Overview of 336 h test specimens before and after removing corrosion products

圖二十一 浸泡與半浸泡之腐蝕外觀無明顯差異，外層為γ-FeOOH，內層為Fe_3O_4



Local CR at water line

336 hours exposure

Corrosion rate of each vertical position of 336 h partial immersion test : (left) non-irradiation, (right) irradiation

[mm/year] (336 h)　0 kGy/h　irradiation　2.78 kGy/h

water film

Full immersion (Weight loss)　0.255　×1.65　0.421

×4.8　×4.8

Partial immersion (local max. at water line)　1.22　×1.7　2.02

圖二十二 半浸泡及γ射線照射之腐蝕情況較嚴重

圖二十三 筆者於海報現場照片

圖二十四 FRC-Corrosion 2019全體合照照片

四、建議事項

(一) FRC-Corrosion 會議邀請核管單位、電廠、廠商、研究機構、學術團體之專家學者齊聚一堂，對福島特殊事故之腐蝕議題進行研發成果心得分享。集結日本及國際力量共同解決福島核子事故問題，日本政府針對特殊環境之腐蝕仍願意花費人力、物力進行研究，可看出對學術之尊重及嚴謹，對核能材料劣化機制與防治，能夠更進一步了解，值得我方定期派員學習效法。

(二) 因應日本福島核子事故事件，核能機組運轉安全為各界關注之議題，福島後續善後亦為世界各國觀摩學習之機會。材料老劣化機制之研究與防治技術開發，實刻不容緩，但國內從事此一領域的研究人員逐漸凋零，值得加以重視，另外，藉由參加會議熟悉相關專業知識與最新技術，可提升核能管制及研發能力。

附件

附件一：FRC-Corrosion 2019 年國際會議議程及摘要

FRC-Corrosion 2019

Cherry Tunnel in Tomioka (提供 富岡町役場、provided by Tomioka Town Hall)

Fukushima Research Conference
on
“Corrosion Prediction and Mitigation for Key Components of Fukushima Daiichi NPS”

- Key Corrosion Issues to Maintain Structural Integrity for the Next Three Decades? -

December 9-11, 2019
Tomioka Town, Fukushima Prefecture, Japan

JAPAN ATOMIC ENERGY AGENCY
TOHOKU UNIVERSITY

Scope

Eight years have passed since Fukushima Daiichi NPS (Nuclear Power Station) accident. Decommissioning is progressing step by step and safety. Also, the procedures to retrieve nuclear fuel debris from the reactor are almost prepared. It is, however, considered to take more than thirty years to complete the decommissioning. There are number of important components which bear the safety functions, such as primary containment vessel, piping system etc. One of the potential concern about ageing degradation of the important components of is “corrosion” of metals and alloys. The conference focuses on potential corrosion phenomena to predict and mitigate those to maintain the key components for the next three decades.

The key topics

- ✧ Long-term prediction of uniform corrosion of carbon steels
- ✧ Passivation and localized corrosion of carbon steels in borate-containing solution
- ✧ Critical condition for re-passivation of crevice corrosion of stainless steels and other corrosion resistant alloys
- ✧ Radiolysis effect on corrosion
- ✧ Microbially induced corrosion
- ➢ Corrosion management of piping systems
- ➢ Corrosion management of primary containment vessels
- ➢ Corrosion deterioration of reinforcing steel bars in damaged RC structures

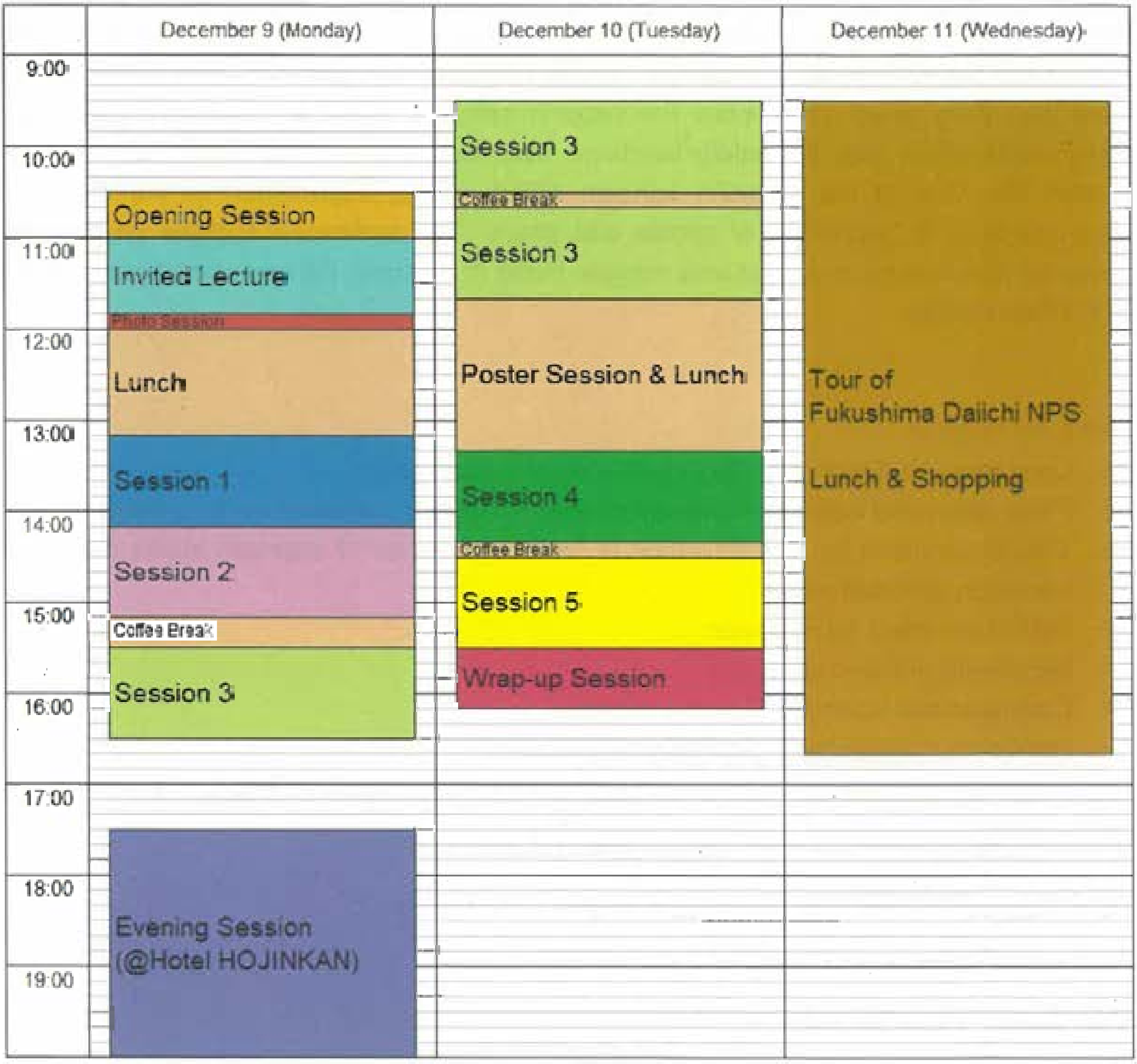
and others

(✧ : Topics more general and fundamental
➢ : Topics more specific to the particular components)

Sessions

Opening Session
Session 1 : General Corrosion of PCV materials (Carbon steel)
Session 2 : Microbially Induced Corrosion
Session 3 : Radiolysis Effect on Corrosion
Session 4 : Passivation and Localized Corrosion
Session 5 : Corrosion of RC Structure in Radiation Condition.
Poster Session
Wrap-up Session

Schedule



	December 9 (Monday)	December 10 (Tuesday)	December 11 (Wednesday)
9:00		Session 3	Tour of Fukushima Daiichi NPS Lunch & Shopping
10:00	Opening Session	Coffee Break Session 3	
11:00	Invited Lecture Photo Session	Poster Session & Lunch	
12:00	Lunch		
13:00	Session 1	Session 4	
14:00	Session 2	Coffee Break Session 5	
15:00	Coffee Break Session 3	Wrap-up Session	
16:00			
17:00	Evening Session (@Hotel HOJINKAN)		
18:00			
19:00			

Venue

Main Conference Room : Tomioka Town Art & Media Center "MANABI-NO-MORI",
Tomioka Town, Fukushima Prefecture.

Evening Session : Hotel HOJINKAN, Tomioka Town, Fukushima Prefecture

Chairperson

Prof. Damien FÉRON, Commissariat à l'énergie atomique et aux énergies alternatives (CEA)
Director of Research, INSTN Professor,
President of World Corrosion Organization, France

Vice-chairs

Prof. Yutaka WATANABE, Tohoku University, Japan
Prof. Masahiro YAMAMOTO, JAEA & Tohoku University, Japan

Keynote and invited lecturers

From abroad

- Prof. Damien FÉRON, CEA, France
- Dr. Frazer KING, Integrity Corrosion Consulting Ltd., Canada
- Dr. Young-Jin KIM, FNC Technology Co., Ltd., Korea
- Dr. Yan LE PAPE, Oak Ridge National Laboratory (ORNL), USA
- Prof. Robert MELCHERS, University of Newcastle, Australia
- Prof. Bernard NORMAND, Institut National Des Science Appliquées (INSA) Lyon, France
- Prof. Tsung-Kuang YEH, National Tsing Hua University, Taiwan

From Japan

- Senior Assist. Prof. Hitoshi ABE, Tohoku University
- Mr. Tomoyuki ARAI, Tokyo Electric Power Company Holdings (TEPCO)
- Dr. Kuniki HATA, JAEA
- Assoc. Prof. Tomoya NISHIWAKI, Tohoku University
- Dr. Kyohei OTANI, JAEA
- Assoc. Prof. Eiji TADA, Tokyo Institute of Technology (TITECH)
- Dr. Junichi TAKAGI, Toshiba Energy Systems & Solutions Corporation
- Dr. Satoshi WAKAI, Japan Agency for Marine-Earth Science and Technology (JAMSTEC)
- Prof. Yutaka WATANABE, Tohoku University

Organizer

Collaborative Laboratories for Advanced Decommissioning Science (CLADS),
JAPAN ATOMIC ENERGY AGENCY (JAEA)

Center for Fundamental Research on Nuclear Decommissioning (CFReND),
TOHOKU UNIVERSITY

Contact

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Conference Program Dec. 9-11th

Fukushima Research Conference on Corrosion of Key Components of Fukushima Daiichi NPS

― Key Corrosion Issues to Maintain Structural Integrity for the Next Three Decades? ―

1st Day : December 9th, Mon.

10:30-11:00

✧ **Opening Session**

Chair : Masahiro YAMAMOTO (JAEA, Japan)

- Opening Remarks

Damien FÉRON (Conference Chair, CEA, France)

- Main Discussion Targets of FRC-Corrosion 2019

Yutaka WATANABE(Tohoku Univ, Japan)

11:00-11:50

Invited Lecture : Status of Fukushima Daiichi NPS

Chair : Shunichi SUZUKI (Univ. Tokyo, Japan)

- "Fukushima Daiichi Decontamination and Decommissioning Current Status and Challenges"

Tomoyuki ARAI (TEPCO)

11:50-12:00

✧ **Photo Session**

12:00-13:10

✧ **Lunch**

13:10-14:10

✧ **Session 1 : General Corrosion of PCV materials (Carbon steel)**

Chair : Takayuki AOKI (Tohoku Univ., Japan)

- "Prediction of Joint Mechanical-Corrosion Failures of Carbon Steel Components and Structures"

Frazer KING (Integrity Corrosion Consulting Ltd., Canada)

- "A mechanism of the Accelerated Corrosion of Carbon Steel in the Simulated Condition of Air-Solution Interface"

Kyohei OTANI (JAEA, Japan)

14:10-15:10

✧ **Session 2 : Microbially Induced Corrosion**

Chair : Hideki KATAYAMA (NIMS, Japan)

- "Microbiologically Influenced Corrosion (MIC) of Steels and Alloys in Seawaters"

Robert MELCHERS (Univ. of Newcastle, Australia)

- "MIC Is Infectious Disease of Metal Materials"

Satoshi WAKAI (JAMSTEC, Japan)

15:10-15:30

✧ **Coffee Break**

15:30-16:30

✧ **Session 3 : Radiolysis Effect on Corrosion**

Chair : Shinichi YAMASHITA (Univ. Tokyo, Japan)

- "Radiolysis & Irradiation Influences on Water-saturated Corrosion of Carbon Steels at 80°C "
  Damien FÉRON (Conference Chair, CEA, France)

- "Water Radiolysis and Its Effect on BWR Plant Materials and Radioactive Wastes "
  Junichi TAKAGI (Toshiba ESS, Japan)

17:30-20:00

✧ **Evening Session**

- Working Dinner at Hotel HOJINKAN

※Participants of the Evening Session are required to move the venue. Bus ride for a several minutes. Participation fee is required.

2nd Da : December 10th Tue.

9:30-10:30

✧ **Session 3 : Radiolysis Effect on Corrosion** (Continued)
Chair : Yoshiyuki KAJI (JAEA, Japan)

- "Water Chemistry in the Core of a Boiling Water Reactor Experiencing a Long-Term Shutdown"
Tsung-Kuang YEH (National Tsing Hua University, Taiwan)

- "Estimation of the Production of Oxidants from Radiolysis of Solutions Containing Ferrous Compounds" Kuniki HATA（JAEA, Japan)

10:30-10:40

✧ **Coffee Break**

10:40-11:40

✧ **Session 3 : Radiolysis Effect on Corrosion** (Continued)
Chair : Satoshi HANAWA (JAEA, Japan)

"Gamma Radiation Induced Corrosion of Candidate Alloys for Nuclear Waste Packages"
Young-Jin KIM (FNC Technology Co., Ltd., Korea)

"Effects of Gamma-Ray Irradiation on Corrosion Rate of Carbon Steels at Water Line"
Hiroshi ABE (Tohoku Univ., Japan)

11:40-13:20

✧ **Poster Session and Lunch**

13:20-14:20

✧ **Session 4 : Passivation & localized corrosion**
Chair : Masatoshi SAKAIRI (Hokkaido Univ. Japan)

- TBD
Bernard NORMAND (INSA-Lyon, France)

- "Corrosion Behavior of Carbon Steel in Sodium Borate Solutions Containing NaCl under Gamma-ray Irradiation" Eiji TADA (TITECH, Japan)

14:20-14:30

✧ **Coffee Break**

14:30-15:30

✧ **Session 5 : Corrosion of RC Structure in Radiation condition**
Chair : Chiaki KATO (JAEA, Japan)

- "Possible Synergies between the Effects of Irradiation and Corrosion on Reinforced Concrete"
Yann Le Pape (ORNL, USA)

- "Chloride Ion Penetration via Concrete Cracks and a Countermeasure"
Tomoya NISHIWAKI (Tohoku Univ., Japan)

15:30-16:10

✧ **Wrap-up Session**

Chair : Yutaka WATANABE (Tohoku Univ., Japan)

- General Discussion (Towards evaluation and measures for degradation in structural reliability)

- Concluding Remarks

Damien FÉRON (Conference Chair, CEA, France)

3rd Day : December 11th, Wed.

✧ **Tour of Fukushima Daiichi Nuclear Power Station**

9:30-13:20
Tour of Fukushima Daiichi Nuclear Power Station

13:40-16:00
Lunch at the cape "TENJIN-MISAKI"
and Shopping at the roadside rest area "MICHINOEKI-YOTSUKURA PORT"

16:40
Arrival at IWAKI Station.

Invited Lecture : Status of Fukushima Daiichi NPS

Fukushima Daiichi Decontamination and Decommissioning Current Status and Challenges

Tomoyuki Arai [1]
[1] *Tokyo Electric Power Company Holdings, Inc.;* ARAI.TOMOYUKI@tepco.co.jp

In the Fukushima Daiichi Nuclear Power Station, more than eight years have passed since the accident on March 11, 2011. The reactors have been maintained in a stable cooling state, and the work environment have been greatly improved, being able to work with regular work clothes instead of protective clothes in the most area of Power Station.

Countermeasure for Contaminated Water

In Fukushima Daiichi, responding to contaminated water has become a major issue, since the ground water flows into the reactor building and touches with contamination sources and then becomes new contaminated water, etc. Therefore, Multi-layered countermeasures have been implemented to reduce the risk with the three basic policies (1) "Removing the contamination source", (2) "Isolating groundwater from the contamination source" and (3)"Preventing leakage of contaminated water".
As an example of (2)"Keep water away from the pollution source", there are countermeasures such as paving the ground so that the rain does not penetrate in to the ground and become groundwater, Land- side impermeable wall (ice wall) surrounding with the frozen soil with a depth of about 30m so that groundwater does not approach the building, and sub-drains that pump up and purify the groundwater around the building.
As a result of the combined effects of these countermeasures, the amount of contaminated water has been reduced by over 60% from FY2014 (470 tons / year) to FY2018 (170 tons / year).

Fuel Removal

The focus of decommissioning has shifted to preparation for fuel removal from the spent fuel pool and fuel debris retrieval. The removal of fuel (1,535) from the spent fuel pool of Unit 4 was completed in December 2014, and the removal of the Unit 3 pool fuel started in April 2019. We will continue to work for removal in Unit 1 and Unit 2.
On the other hand, the retrieval of the molten fuel is an unprecedented work in the world. So far, the position of fuel debris has been analyzed, and various types of robots have been used for investigation. In January 2019, a survey was carried out at Unit 2 by hanging a survey device attached to the tip of a guide pipe with a telescopic pipe at the bottom of the containment vessel. From the obtained image, it was confirmed that a part of the fuel assembly, which is a structure in the reactor, was dropped, and there are deposits that looked like pebbles or clay on the entire bottom
The structure is thought to be an offshoot of that molten fuel damaged the pressure vessel. In addition, the deposit seems to contain fuel debris from the situation. On the other hand, since no major damage was observed in the CRD housing on the under part of the reactor pressure vessel, it was estimated that most of the fuel debris remained in the pressure vessel as well as the analysis results. In the future, we are proceeding with a plan to start the retrieval of fuel debris according to the medium- to long-term roadmap.

Prediction of Joint Mechanical-Corrosion Failures of Carbon Steel Components and Structures

Fraser King

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Abstract

Failure of metallic components and structures can result from either corrosion or mechanical degradation modes. Perhaps more commonly, however, failure is the result of mechanical overload following a period of degradation of the material due to corrosion. For some materials, corrosion may simply result in the reduction in thickness of the load-bearing membrane. In other cases, exposure to the corrosive environment (or other environmental condition) may also result in the degradation of the material properties, such as the fracture toughness or ductility. Carbon and low alloy steels may exhibit this type of interaction between corrosion and mechanical failures modes, typically as a result of the effects of absorbed hydrogen on the material properties. An example will be given of how this type of interaction has been accounted for in the lifetime prediction of nuclear waste containers. Possible implications for the degradation of steel structures and components over the next 30 years at Fukushima Daiichi NPS will also be discussed.

Carbon steel nuclear waste containers will be subject to both corrosion and mechanical loads during their long service life extending for periods of thousands of year [1]. Environmental conditions within the deep geological repository are expected to lead to a combination of general and localized corrosion, accompanied by the absorption of hydrogen. In addition to residual stress from the final closure weld, the containers will be subject to external loads from the swelling of the bentonite clay and the hydrostatic (and, for some rock types, lithostatic) loads at the typical repository depth of 500-900 m. The time-dependent structural integrity of the canister has been assessed using the Failure Assessment Diagram (FAD) approach for components with defects (e.g., [2]).

The application of this methodology to the long-term structural integrity of steel structures at Fukushima Daiichi NPS will be discussed. Among the factors that need to be considered are:

- The current size, shape and location of defects in the PCV, piping, and other steel components (based on construction records or recent inspection).
- Mechanical and fracture properties of the PCV and other components exposed to neutron irradiation during service.
- The effect of 30 years of general corrosion in (i) reducing the load-bearing capacity, (ii) generating absorbable hydrogen, and (iii) either removing surface defects or exposing sub-surface defects.
- Absorption of hydrogen due to atmospheric corrosion and/or localised corrosion.
- External loads and the levels of residual stress.
- Magnitude of handling stresses during decommissioning or possible dynamic loads due to future seismic activity.
- Definition of failure and of a suitable safety factor.

References

[1] King, F. et al., Corros. Eng. Sci. Technol. 49, 2014, 442-449.

[2] British Standards Institute, BS 7910:2005, Guide to methods for assessing the acceptability of flaws in metallic structures (2005).

Session 1-2

A mechanism of the accelerated corrosion of carbon steel in the simulated condition of air-solution interface

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Introduction

In Fukushima Daiichi nuclear power station, cooling water is constantly injected into the reactor pressure vessels (RPVs) for cooling the fuel debris after the severe accidents in March 2011. Inner components of the primary containment vessels (PCVs) was observed by remote-controlled robots and the observation showed that carbon steels of the PCVs wall above the contaminated water level was exposed to an air-solution alternating condition. Previous studies [1] have reported that the corrosion rate of carbon steel is accelerated in case of the steel with thin water film exposed in air under the an air-solution alternating condition. This suggests that the corrosion rate of carbon steel will be accelerated in the air-solution alternating condition. However, the corrosion rate of the steel on the corrosion tests which simulated the air-solution alternating condition has not been clarified. In the present study, an alternating corrosion test of carbon steel which simulated the air-solution alternating condition was carried out.

Experimental methods

The carbon steel was alternately exposed to air and solution for 144 h by rotating in a water tank which was not completely filled with solution. The surface morphology of the specimen after the tests were observed by digital camera and optical microscope, and the corrosion rate of the steel in the alternating condition was obtained from mass loss measurement. The cross-sectional observation and analysis for the iron rust layer formed on the specimen were carried out by a scanning electron microscopy (SEM) and an Auger electron spectroscopy (AES).

Results and discussions

The cross-sectional SEM images show that the rust layer formed on the steel after the tests in the alternating condition was thicker than 400 μm. (Fig. 1) The corrosion rate of carbon steel in the alternating condition was more than three times larger than that of the steel rotated always in solution. A thin water film was confirmed on the steel when the specimen exposed to the air during the tests. It has been reported that the mass transfer of dissolved oxygen to the carbon steel surface is accelerated in case of the carbon steel covered by a thin water film and corrosion of carbon steel is accelerated by the acceleration of oxygen reduction reaction (cathodic reaction) [2]. This suggests that the accelerated corrosion of the steel in the alternating condition would be caused by the thin water film on the steel during the tests.

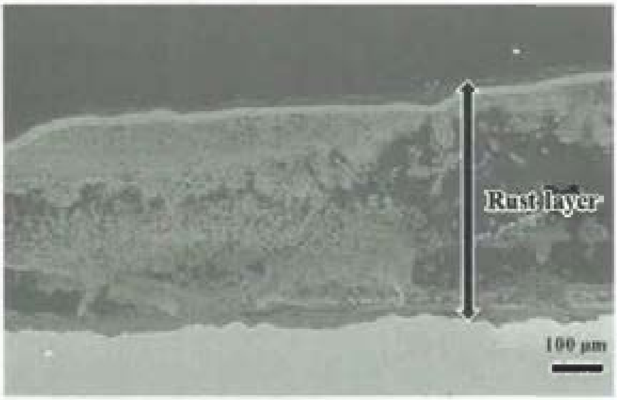

Fig. 1 Cross-sectional SEM images of the rust layer formed [illegible]

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2. A. Nishikata *et al.*, J. Electrochem. Soc., 144 (1997) 1244-1252.

Session 2-1

Microbiologically Influenced Corrosion (MIC) of Steels and Alloys in Seawaters

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Some History

This section provides a very brief overview of the development of understanding of the concept of microbiologically influenced corrosion (MIC). The emphasis is on the main critical aspects in the development of the MIC concept and its practical occurrence. The present paper does not consider detailed microbiological aspects but focuses on the effect of microbiological activity as expressed in terms of general and pitting corrosion.

Background to MIC studies

The traditional or classical understanding of MIC for ferrous metals follows from sulphate reducing bacteria since these are easy to detect in practice and leave sulphur deposits, usually taken as singles of their presence. This grouping of bacteria is by phenomenon and may include a very wide range of species. In the 1930s the so-called cathodic depolarization theory was proposed to explain the corrosion mechanisms involved. This led to furious scientific disputes for many decades until in the 1980s when after much observation and inconsistencies a much simpler explanation was proposed. This has the metabolites (waste products) of bacteria lowering the pH at the metal surface and causing the observed corrosion damage [1,2]. It is an essentially chemical process and has been termed cMIC. It is still considered the most important from practical MIC cases. Some laboratory work has shown the existence also of microorganisms that directly consume electrons and this has been termed eMIC. Because of the on-going difficulty of correlating microbiological species with their effect on corrosion, detailed microbiological aspects are not considered herein. Emphasis is on the effect of microbiological activity in terms of its result as general and pitting corrosion.

Marine corrosion

This section reviews the bi-modal model for the longer term corrosion of steels (and various other alloys) in seawater exposure conditions. It shows the effect of MIC. The model has been calibrated to a wide variety of (mainly field) data, and is influence primarily by water temperature and seawater nutrient exposure [1,2].

Nutrients

The essential requirements for all living things include shelter, energy supply and appropriate nutrients. In most seawaters the critical nutrients are Fe ions and dissolved inorganic nitrogen (DIN). For steels the corrosion process supplies the Fe irons. A high degree of correlation has been found between DIN and corrosion loss, including over extended exposure periods [2,3]. This has been shown in long-term laboratory tests [4] and in various practical applications.

Accelerated Low Water Corrosion (ALWC)

This section gives a summary of the early effort to determine the origin of severe loss of steel for driven sheet piling in UK and later other harbours. Despite early identification that MIC was likely involved, procedures to predict the occurrence of ALWC did not come about until relatively recently [3,4] with demonstration of correlations with DIN concentrations in the local seawaters.

Offshore Mooring Chains

There is increasing use of Floating Production Storage and Offloading (FPSO) vessels for offshore oil and gas production. These are moored, often in deep waters, using mooring lines composed of wire rope and of large sized chains. The corrosion of the chains in the surface water region has been observed sometimes to be very high. This can be shown to be related to local water quality, in particular the concentration of DIN [5,6].

Water Injection Pipelines

Water injection pipelines are widely used in the oil and gas industry to help extract remaining oil and gas in wells by pumping in seawater, fresh water or aquifer waters under high pressures, and very low oxygen conditions, the latter in an attempt to reduce internal corrosion. However, in some cases severe channeling corrosion is observed. For many years this has been attributed to MIC but clear proof was difficult to find. Data from actual operational pipelines and from special experiments shows that MIC can be involved but only if DIN is present. Most of the corrosion appears to be due to settlement within the pipes during periods of shut down [7,8]. In practice the use of biocides has declined owing to environmental impacts and some operators have switched back to greater use of pigging to clean the pipes and reduce both bacterial content and hence proneness to MIC as well as the sediments that can cause serious under-deposit corrosion.

Corrosion in Soils

The external corrosion of cast iron water pipes is a problem with a very long history (>>100years) yet understanding of its influencing factors has, until recently, remained unclear. It has now been shown that the inter-contact region between the soil and the ferrous metal (cast iron and steels) plays a crucial early role and has long-term implications. The rate of supply of surface water to the corrosion interface is critical for the (almost constant) rate of long-term corrosion. The rate of supply of oxygen is seldom critical owing to longer-term corrosion being largely in the anaerobic domain [9,10]. Although MIC was considered in the early 1900s to be critical for in-ground corrosion, evidence from a large number of actual field sites shows that MIC often is not involved - it depends on the availability, at pipe depth, of critical nutrients.

Other Alloys

Alloys such a CuNi are prone to MIC in seawater owing to a small content of Fe, while Al alloys cannot contain any Fe are not prone to MIC in seawater. However, they may be subject to macro-fouling, irrespective of Cu or Al content.

References

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[2] R.E. Melchers, Long-term immersion corrosion of steels in seawaters with elevated nutrient concentration, Corrosion Science, 81 (2014) 110-116.

[3] R.E. Melchers, R.J. Jeffrey, Corrosion of steel piling in seawater harbours, Proc. Instn. of Civil Engineers, Maritime Engineering, 167 (2014) MA4, 159-172.

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Session 2-1

Session 2-2

MIC is infectious disease of metal materials

Satoshi Wakai [1]

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Microbiologically influenced corrosion (MIC) refers to the corrosion of metal materials caused by microorganisms. We have empirically known MIC, but little is known about MIC. Almost all of case that are considered to be caused by microorganisms are based on elimination methods. When we cannot explain the corrosion by physicochemical factor, the corrosion is considered as MIC. Namely, systematic methods for diagnosis of MIC have not yet been established.

I have proposed that MIC is infectious disease of metal materials by microorganisms [1]. In the case of human infectious disease, pathogenic microorganism infects to human body and takes place pathogeny. In many infectious diseases, preventive care, diagnosis, and treatment are established because causative microbes are well characterized. Accurate diagnosis would give proper treatment and lead to proper preventive care. By contrast, in MIC, causative microorganisms have not yet been characterized, and then diagnostic method have also not yet developed. Therefore, we cannot evaluate whether anti-corrosion and treatment are sufficient. Insufficient or meaningless anti-corrosion treatments cause higher cost, and improper treatments after corrosion would cause reappearance of same corrosion. Therefore, we must know about causative microorganisms and develop proper diagnosis and meaningful treatment techniques.

Unfortunately, we don't know about whole view of iron-corrosive microorganisms, but recently various types of iron-corrosive microorganisms in addition to sulfate-reducing bacteria (SRB) have been reported. For examples, there are iron-corrosive methanogen [2-4], iron-corrosive nitrate-reducing bacteria [5], iron corrosive acetogen [6], iron-corrosive neutrophilic iron-oxidizing bacteria [7], iodide-oxidizing bacteria [8], and so on. These reports allow to change the mind about overview of iron corrosive microorganisms. Namely we should not focus only SRB, we have to pay the attention of the corrosion by other microorganisms, because we have to protect metal materials from various types of corrosive microorganisms.

In addition to isolate and characterize novel iron-corrosive microorganisms, author has studied on microbial community of various corrosion environments [9,10]. In this lecture, I will introduce about latest knowledge of corrosive microorganisms and gene analysis for microbial communities in corrosive environments.

References

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[10] S. Wakai, et al., *EUROCORR proceedings*, paper No. 105117, 1-13 (2018)

Session 3-1

Radiolysis & irradiation influences on water-saturated corrosion of carbon steels at 80°C

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The degradation of iron-based materials by atmospheric corrosion is a well-known issue that has to be taken into account, including for the disposal of high-level radioactive nuclear waste. In specific conditions (deep geological disposal for instance), the environment will be saturated with water either in an atmosphere with 100% humidity or with liquid water. During these periods, it is important to determine the corrosion damages and evaluate whether irradiation may influence these damages. In particular, the radiolysis of the water film in contact with air can lead to the formation of oxidizing species and to an increase in corrosion rates.

Experimental conditions are close to those expected in the French concept of nuclear waste disposal (temperature and alloy) and are chosen to study the impact of some parameters, but these conditions may be find also in other environments like in the Fukushima cooling systems :

- Two carbon steels (API 5LX65 for the micro-tunnel casing and P285H for the overpack);
- Temperature 80°C;
- Two irradiation dose rates (10 and 20 Gy/h) and of course one set of experiments without irradiation for comparison;
- The experiments were performed with coupons exposed in autoclaves with two initial gas compositions ($O2/N2$ = 20/80 and 40/60) and two pressures (2.2 and 4.4 bar) in order to look at the influence of oxygen initial partial pressure (which is directly related to the quantity of oxygen available for corrosion);
- In some experiments, coupons were exposed in 100% humid atmosphere (CASIMIR 2 experiments), but other coupons were half or totally immersed in a liquid solution (CASIMIR 3 experiments).

The coupons have been exposed between 3 months and 18 months. At the end of the experiments, gas and aqueous solutions were analyzed. After exposure, weight gain and weight loss after desquamation were performed on some coupons as well as visual examinations including binoculars. On other coupons, X-ray corrosion analysis were performed and observations by Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectroscopy were also performed.

The paper will include details of various results that can be summarized as follows:

- No major differences are found between irradiated and non-irradiated coupons; corrosion rates obtained without irradiation are nearly highest than those obtained under 10 or 20 Gy/h, the lowest ones being under 10 Gy/h;
- No significant differences between the two steels, neither between the two gas pressures, nor between the two oxygen concentrations (20% and 40%);
- The oxygen concentration decreases and the hydrogen concentration in the gas phase increases when the corrosion damages increased, as expected, but oxygen and hydrogen are found together in the atmosphere of several autoclaves, showing that the cathodic reaction with water occurs before the end of the cathodic reaction with oxygen.

- The corrosion products are mainly based on hematite at the beginning of exposure and on magnetite after longer periods of exposure, in accordance with the evolution of redox conditions;
- Large scattering is found regarding the damages of the coupons under the same conditions exposed to O2/N2 gas with 100% humidity: it is linked to the heterogeneity of atmospheric initiation on these non-previously corroded coupons;
- For the immersed or semi-immersed coupons, the metal below the waterline exhibits wide strongly corroded areas neighboring no corroded areas.

In summary, no detrimental effect of radiolysis was found on water-saturated corrosion of carbon steel at 80°C between 0 to 20 Gy/h, while the evolution of oxygen and hydrogen in the gaseous atmospheres is as expected as well as the evolution of corrosion products.

Acknowledgments: the authors thank very much DM2S/LPEC team for dose rate calculations and DPC/LABRA team for the irradiation experiments made in Poseidon facility. They would like also to thank very much EDF, French waste producer, and Andra, French radioactive waste management organization, for co-defining and co-funding this work.

Session 3-2

Water Radiolysis and Its Effect on BWR Plant Materials and Radioactive Wastes

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Introduction

Comprehension of the radiation chemistry of water is essential to understand the corrosion environment of BWR plant materials and radioactive wastes. In this paper, basics of radiation chemistry of water is briefly reviewed. Both radiolysis and ECP models are strong tools to evaluate the corrosion environment of BWR plant materials and radioactive wastes. Finally, recent activities for Fukushima recovery are reviewed.

Basics of radiation chemistry and water radiolysis [1]

Two types of modeling have been developed and utilized to estimate the BWR corrosion environment. Water radiolysis is a key event to predict corrosion environment in a BWR plant. G-values are essentially necessary for the water radiolysis simulation of the BWR plants. Then, the generated chemical species react with each other subject to the reaction rate constants.

Final molecular products are generated as a result of various secondary reactions.

Radiolysis and ECP modeling [2]

Radiolysis Model and ECP Model have been developed to predict plant water chemistry response. For Radiolysis Model G-values at high temperature and key reaction rate constants are important parameters. ECP Model has been developed based on the mixed potential theory. Flow rate and hydrogen peroxide are contributing factors. Mitigations by cathodic current control and anodic current control are both well described by the model.

Radiolysis behavior regarding radioactive waste and fuel debris [2, 3]

In the case of pure water γ-radiolysis, the hydrogen concentration reaches the equilibrium concentration with time. Under only α-radiolysis condition, the hydrogen yield is largely enhanced due to the high G-value for hydrogen. Under 100% sea water condition, the hydrogen generation is accelerated significantly by the effect of halogenated ions. However, the effect of the sea water becomes negligible when it is diluted to 0.1% of the original concentration.

From the material corrosion viewpoint, oxygen and hydrogen peroxide behaviors are more critical. It seems that hydrogen peroxide concentration also becomes higher when hydrogen concentration becomes high. Therefore, i) hydrogen is important from the viewpoint of safety evaluation, while ii) hydrogen peroxide is important from the material corrosion viewpoint. **Conclusions**

Basics of radiation chemistry and water radiolysis were briefly reviewed. Radiolysis modeling is a useful tool to predict the corrosion environment of the BWR primary system. Together with ECP modeling in series, ECP distribution has been obtained. After the Fukushima accident, radiolysis modeling has been applied to show the hydrogen accumulation risk. Seawater effect and alpha radiolysis effect have been evaluated. Furthermore, hydrogen peroxide behavior should be investigated from the material corrosion viewpoint.

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Session 3-3

Water Chemistry in the Core of a Boiling Water Reactor Experiencing a long-Term Shutdown

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Introduction

The operation licenses of the two reactor units at Chinshan Nuclear Power Plant (NPP) have expired one after another in the past one year. Although Taiwan Power Company has obtained the decommissioning permit from the regulatory body, Atomic Energy Council, this year, the fact is that no parts pertinent to the pressure boundary components has been dismantled so far since the fuel assemblies are still in the boiling water reactor (BWR) cores of both units. This awkward situation happens because the New Taipei City government has not issued the operation permit of the dry storage facility at this NPP. Under the current circumstances of decommissioning transition, the core components of the reactor is inevitably exposed to a highly oxidizing coolant for a very long time, though at a temperature much lower than the operating temperature and at much lower radiation fields. In order to explore the long-term water chemistry in the primary coolant circuit of a shutdown BWR, we conducted necessary thermal hydraulic, radiation field, and water chemistry analyses. The outcome would assist in evaluating the long-term integrity and safety of core fuels and comportments during the decommissioning transition phase. The results of thermal-hydraulic and radiation field analyses (e.g., temperature, flow velocity, and dose rates of neutron and gamma) were adopted in the subsequent water chemistry analysis to calculate the concentrations of the two major oxidants (namely oxygen and hydrogen peroxide). The preliminary prediction results show that the integrity of reactor core components will not be affected by corrosion at various coolant conditions during the decommissioning transition phase.

Theoretical Analysis on Thermal Hydraulics

The conceptual schematic of the modeled regions in the selected BWR is shown in Figure 1, and the temperature variations in each region is shown in Figure 2.

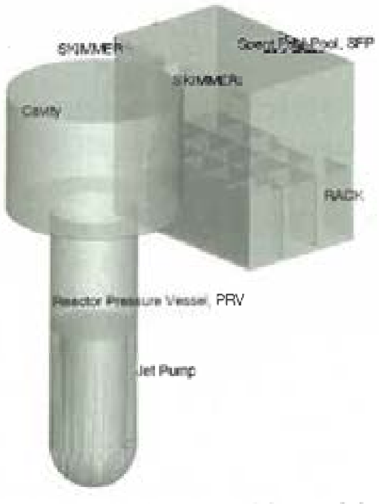

Figure 1. Conceptual schematic of the modeled regions in the selected BWR.

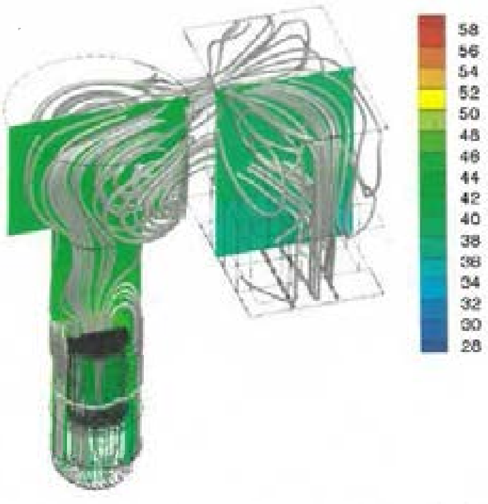

Figure 2. Temperature variations in the modeled regions of the selected BWR.

Theoretical Analysis on Water Chemistry

The structure of the theoretical model (DEMACE_BWR) is shown in Figure 3, and the coolant flow path in the selected BWR is shown in Figure 4.

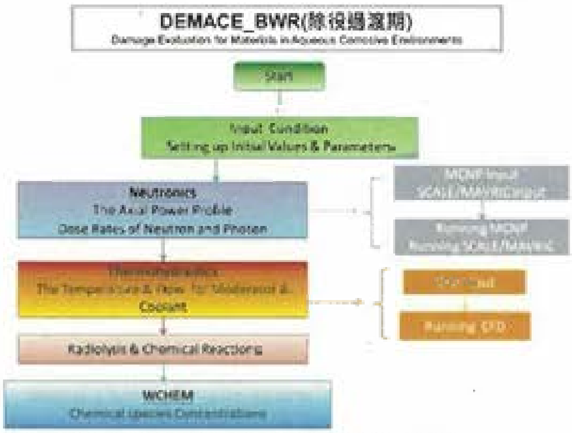

Figure 3. Structure of the DEMACE_BWR model.

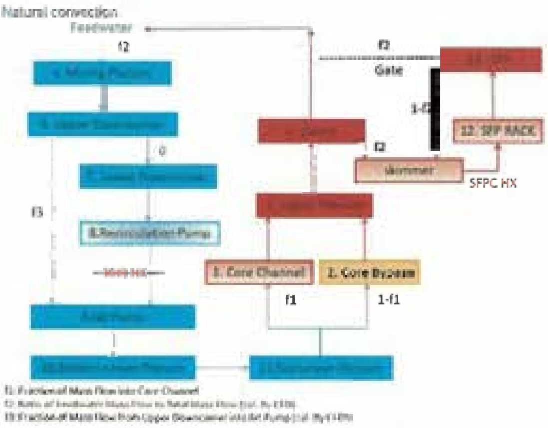

Figure 4. Coolant flow path in the selected BWR.

Results

The preliminary prediction results show that the integrity of reactor core components will not be affected by corrosion at various coolant conditions during the decommissioning transition phase. The concentration variations of oxygen and hydrogen peroxide in the primary coolant circuit of the selected BWR are shown in Figures 5 and 6, respectively. The concentrations of these two major oxidants are predicted to be much less than those under operating conditions. Accordingly, no serious degradation in terms of corrosion is expected during the decommissioning transition stage.

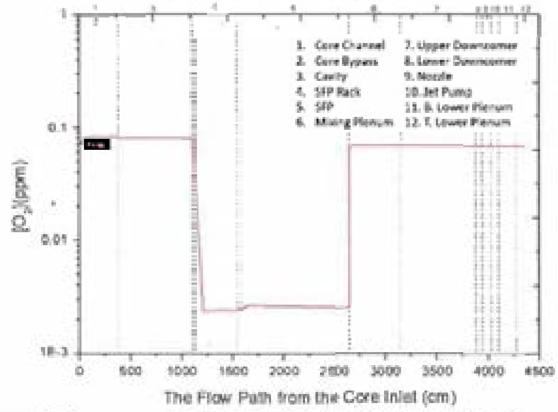

Figure 5. O_2 concentration variations along the circuit.

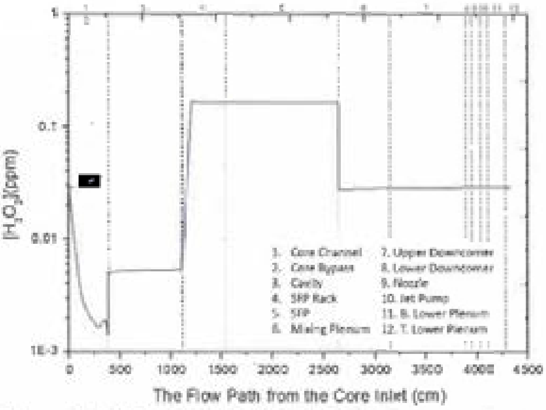

Figure 6. H_2O_2 concentration variations along the circuit.

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Session 3-4

Estimation of the Production of Oxidants from Radiolysis of Solutions Containing Ferrous Compounds

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Introduction

It will take several decades to accomplish the decommissioning of Fukushima Daiichi Nuclear Power Station (NPS). Through this log-time project, the prevention of the leakage of radioactivity is one big issue. To keep the radioactivity in the reactors, corrosion of primary containment vessels (PCVs) and piping should be estimated and inhibited in a proper way. In the PCVs, it is considered that materials are subjected to a corrosive environment due to stagnant water. Moreover, hydrogen peroxide (H_2O_2) and oxygen (O_2) produced from radiolysis of the stagnant water can enhance the oxidation of steels. Radiolysis effect of pure water has been well identified to estimate corrosion potentials in reactors in operation. On the other hand, the stagnant water contains some impurities, which would affect the radiolytic process and the production of H_2O_2 and O_2. The objective of this study is to understand radiolysis of the stagnant water for the estimation of radiolysis effects on corrosion of steels in PCVs at Fukushima Daiichi NPS. In this report, we show our recent work on radiolysis of solutions containing ferrous compounds, which we assumed as one candidate for chemical species affecting the radiolytic process of the stagnant water.

Methods

Radiolysis simulations were carried out using COMSOL multiphysics® Chemical Reaction Engineering Module. Chemical reactions and their rate constants prepared by Elliot[1] and Lundström[2] were employed. In this simulation, a 20 ml solution in a 30 ml glass vial was assumed. To estimate the volatilization of O_2 and H_2, interfacial mass transfer model developed by Yakabuskie was implemented[3].

Results and Discussion

A radiolysis simulation of a deaerated 5.0×10^{-4} mol/l ferrous sulfate ($FeSO_4$) solution irradiated with gamma ray (1.2 kGy/h) was carried out. Fig. 1 shows concentrations of O_2 and H_2 in the gas phase and a concentration of H_2O_2 in the liquid phase during irradiation. The result showed that H_2 was rapidly produced by radiolysis of the $FeSO_4$ solution. In contrast with H_2, the concentrations of H_2O_2 and O_2 were very low. It is known that the following chain reaction controls the production of H_2 and H_2O_2 in water radiolysis.

$$H_2 + {}^{\bullet}OH \rightarrow H^{\bullet} + H_2O$$

$$H_2O_2 + H^{\bullet} \rightarrow {}^{\bullet}OH + H_2O$$

Because of high reactivity of Fe^{2+} with ${}^{\bullet}OH$, this chain reaction is inhibited in the $FeSO_4$ solution; H_2 can easily escape to the gas phase. On the other hand, the reaction of Fe^{2+} with H_2O_2 also controls the amounts of H_2O_2. It is inferred that the consumption of H_2O_2 by this reaction resulted in the suppression of the total amount of these radiolytic oxidants (H_2O_2 and O_2).

Conclusion

In this study, we carried out radiolysis simulations of $FeSO_4$ solutions and found that the production of H_2O_2 and O_2 was suppressed by addition of Fe^{2+}. We also have been investigating effects of other impurities, such as seawater constituents and nitrogen. Taking into account effects of these impurities, we will discuss the corrosive environment in the stagnant water.

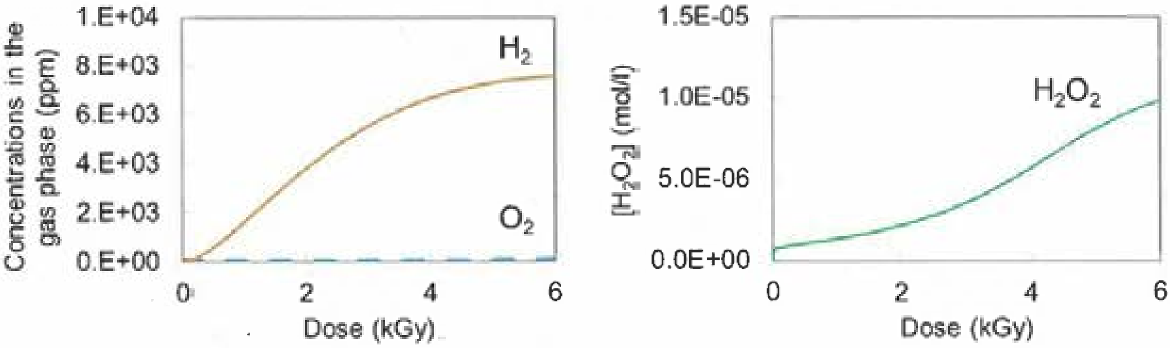

Fig.1 The production of radiolytic products from a deaerated 5.0×10^{-4} mol/l $FeSO_4$ solution irradiated with gamma ray (1.2 kGy/h)

Acknowledgment

This work was partially supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan, "Construction of corrosion database under radiation environment" for Nuclear S&T and Human Resource Development.

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Session 3-5

Gamma Radiation Induced Corrosion of Candidate Alloys for Nuclear Waste Packages

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Commercial nuclear power uses an uranium oxide clad into Zr-based alloy tubes. This fuel bundles used for approximately 5 years at plants, removed/stored first in the water pools and later transferred to dry cask storage. Spent fuel generates heat during storage and this creates elevated temperatures in ranges of 50-150°C, and eventually, the storage container cools down to the ambient geolcgical storage temperature (assumed to be ~30°C). The gamma field is produced by the radioactive decay of radionuclides within the nuclear waste form in the container, and its magnitude depends on the nature and age of the waste form and the waste package.

The corrosion performance of nuclear waste package is determined by the exposure environment established within the geological environmental conditions. When water contacts the surface of the waste package, its gamma radiolysis could produce an additional supply of corrosive agents. Gamma irradiation of the package surface and the surrounding environment is known to affect the corrosion behavior of the package: radiolysis of the vapor and aqueous phases to produce oxidizing and reducing radicals and molecular products, interaction with passive oxide films, and reduction in the number of viable microbes at/near the waste package surface [1].

The nature of the radiolytic products and their concentrations depend on the environment undergoing radiolysis. For relatively dilute groundwater, the predominant oxidants would be OH^*, O_2^-, H_2O_2, and O_2, while the predominant reductants would be H^*, e_{aq}^-, and H_2. Figure 1 shows the effect of gamma radiation on
the corrosion potential (e.g., open circuit potential: OCP) of Ti-Grade 12 in brine solution, shifting the OCP in the positive direction under the gamma irradiation; conversely, being active when the radiation was removed [2]. This phenomenon indicates that the radiolysis products may increase either the cathodic reactions or the rate hydrogen reduction reaction, so that the mixed potential (e.g., OCP) moves in the anodic direction. This hypothesis can be explained by the presence of H_2O_2 produced by the gamma irradiation and clearly shown in Figure 2; the small amount addition of H_2O_2 produces the positive OCP shift and eventually a maximum effect is attained in an intermediate time; confirming the important role of radiolytic products, such as H_2O_2, for altering the OCP of Ti Grade 12. This behavior is very similar to one under gamma radiation (see Figure 1)

This paper will review more details on the radiolysis of water and its effect on the corrosion behaviors of various candidate alloys for nuclear waste packages.

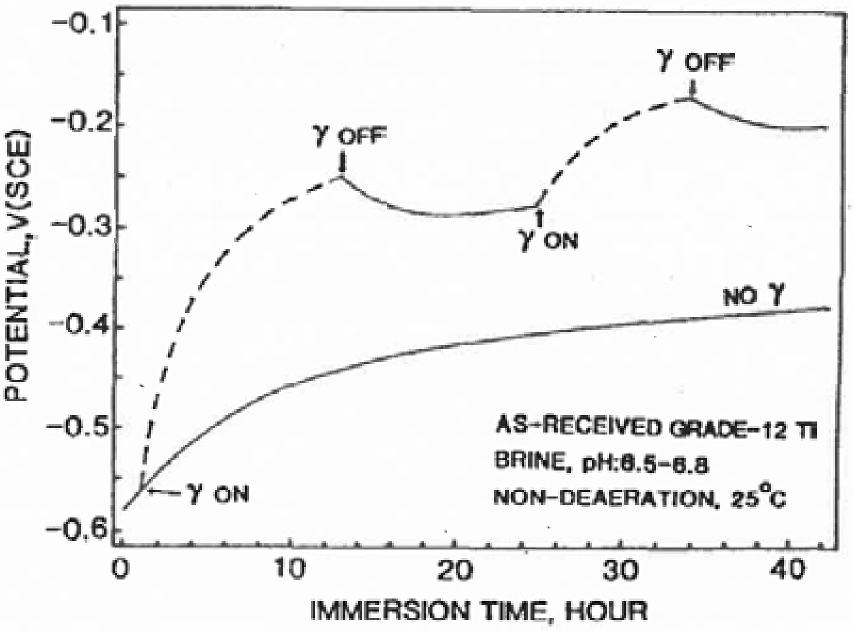

Figure 1: Effect of gamma radiation on the OCP of Ti Grade 12 in brine at 25°C [2]

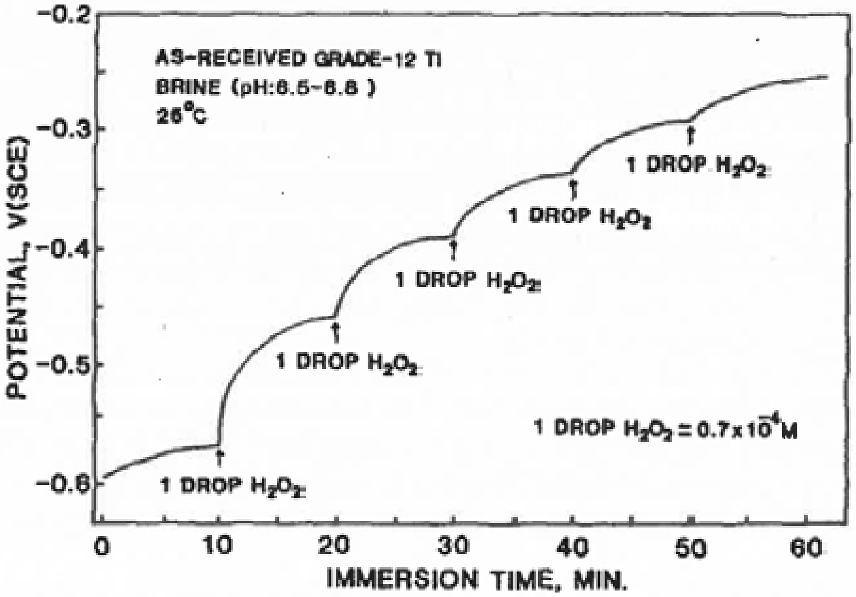

Figure 2: Effect of H_2O_2 addition on the OCP of Ti Grade 12 in brine at 25°C [2]

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Session 3-6

Effects of gamma-ray irradiation on corrosion rate of carbon steels at water line

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Introduction

After the accident at the Fukushima Daiichi Nuclear Power Station, seawater was injected into the reactor vessels and the spent fuel pools as an emergency cooling measure. Environmental conditions at the site have been improved by reducing the concentration of dissolved oxygen and removing the chloride ions. The inner walls of the primary containment vessels (PCVs) made of carbon steel were either immersed in water or covered with a water film. Moreover, the inner surfaces of the PCVs were exposed to gamma-ray irradiation. In this study, corrosion rate at water line under a gamma-ray irradiation has been investigated.

Experimental details

SA738B steel plate was used for the PCV of type Mark II primary containment. The fully and partially immersed specimens were fixed in the cell. The corrosion experiments were conducted in a diluted artificial seawater with 1 ppm chloride ion at 50 °C under aerated condition. The dose rate in the experiments under gamma-ray irradiation was up to 2.76 kGy/h. The average and local corrosion rates were evaluated by weight loss and 3D shape measurement, respectively. Other detailed information for the experiment is described in another paper [1].

Results and discussion

The partially immersed specimen showed higher corrosion rate compared with the fully immersed specimen in both non-irradiation and irradiation conditions, because the highest corrosion rate was observed at water line (Fig.1). In addition, the corrosion rate was accelerated by gamma-ray irradiation regardless the position of the specimen. The both water film effect (acceleration of oxidant diffusion through a boundary layer) and irradiation effect (hydrogen peroxide formation by water radiolysis) were clearly observed in the water line corrosion.

References

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Acknowledgement

This study was partly supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan, "Construction of corrosion database under radiation environment" for Nuclear S&T and Human Resource Development.

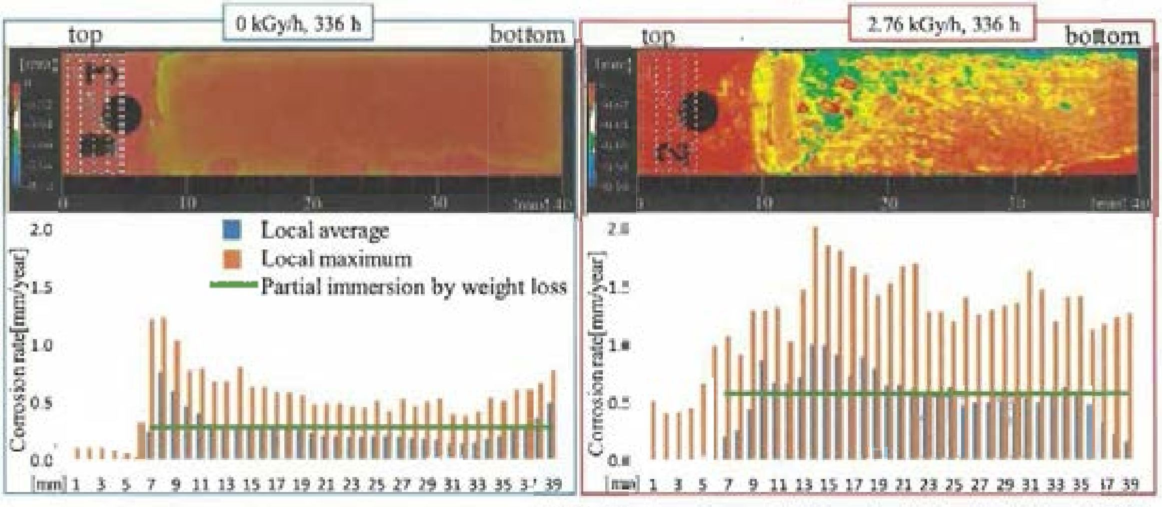

Fig. 1 Corrosion rate of each vertical position of the partially immersed specimens: (left) non-irradiation, (right) irradiation

Session 4-2

Corrosion Behavior of Carbon Steel in Sodium Borate Solutions Containing NaCl under Gamma-ray Irradiation

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Decommissioning work at the Fukushima Daiichi Nuclear Power Station will continue very long of several decades. In the decommissioning process, stable and continuous cooling of fuel and fuel debris in the vessels and the radioactive waste storage facility is one of the critical issues. Therefore, corrosion deterioration of cooling system can be a problem to promote the decommissioning process steadily and it is important to evaluate corrosion degradation of carbon steel, which is main material of the reactor pressure vessel (RPV), primary containment vessel (PCV), pipes, and tubes in the cooling system.

From the view point of the criticality management of fuel debris in the decommissioning process, the use of boron compounds like borate, boron is a neutron absorber, can be injected to the cooling system. In this case, carbon steel gets passivated, however, in the presence of chloride ions, passivation may be broken down, resulting in localized corrosion like pitting corrosion and crevice corrosion. In addition, it is assumed that in the radiation environments, corrosion potential of carbon steel can shift to higher values due to the generation of hydrogen peroxide by radiolysis of water. This might enhance the initiation of localized corrosion even when the chloride ion concentration is in a low level.

In this study, the corrosion behavior of carbon steel in the irradiation environment was investigated by immersion test and electrochemical measurements in sodium borate ($Na_2B_4O_7$) containing sodium chloride (NaCl).

It was found from the results of the immersion test conducted in the mixtures of $Na_2B_4O_7$ and NaCl under gamma-ray irradiation that corrosion behavior of carbon steel depended on the concentration ratios of $Na_2B_4O_7$ and NaCl. Carbon steel was basically in a passive state in ($Na_2B_4O_7$) without NaCl, however uniform corrosion was observed when the concentration of ($Na_2B_4O_7$) is low less than 0.5 mM. In the presence of NaCl in the solution, pitting corrosion was initiated depending on the concentration ratio of $Na_2B_4O_7$ and NaCl. The corrosion behavior of carbon steel observed under gamma-ray irradiation was in good agreement with electrochemical behavior investigated by electrochemical polarization and open circuit potential measuremnt.

This project is conducted as a part of "Analysis of Corrosion Mechanism in Specific Environment" supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

Session 5-1

Possible Synergies between the Effects of Irradiation and Corrosion on Reinforced Concrete

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Light Water Reactors (LWRs) concrete biological shields (CBSs) are exposed to high neutrons and gamma irradiations potentially reaching levels for which degradation has been reported in the literature, i.e., > 5 x 10^{18} n.cm^{-2} at E > 0.1 MeV. At 80 years of operation, it is estimated that the bounding fluence approaches 6 x 10^{19} n.cm^{-2} (E > 0.1 MeV) [1], i.e., about 12 times, the potentially critical dose for irradiation-induce damage onset (As countries other than the U.S. may consider different operation extension periods, the bounding fluence can be estimated proportionally). The tolerance of concrete against neutron irradiation greatly varies as a function of its constituents, i.e., coarse aggregates, sand, and hardened cement paste (hcp). The first-order degradation factor was found to be aggregates radiation-induced volumetric expansion (RIVE) [2], i.e., the propensity of swelling under neutron exposure as a function of their minerals contents, structures and textures. Irradiation-induced *amorphization*, also referred to as metamictization is the mechanism of gradual disordering of the minerals' crystalline structures accompanied by significant expansion, especially in silicates. For example, the maximum volumetric expansion of quartz and feldspars – a group of rock-forming tectosilicate minerals that make up as much as 60% of the Earth's crust – has been shown to be as large as ~18% and ~8%, respectively, while the change of density in calcite remains rather low (~0.3-0.5%). The main reason for higher swelling is the number of covalent bond (Si-O) and the degree of polymerization of [SiO_4] tetrahedrons [3]. Depending on the mineralogical content, considerable variations in aggregate RIVE have been observed. Because rock-forming aggregates are a complex assemblage of minerals varying in nature and dimension, local RIVE rates may significantly differ leading to internal mismatched strains causing internal cracking. Moreover, some observed post-irradiation expansions exceed what is considered as detrimental by alkali-silica reaction (ASR) researchers. Because structural concrete is made of ~70% of aggregates by volume, RIVE can impose severe stresses on the surrounding hcp leading to micro-cracking. A number of time-dependent factors can affect the irradiation-induced damage formation in concrete constituents. Despite the lack of data and observation, it is currently hypothesized that the thermal annealing of relatively low neutron flux can significantly heal the irradiation damage [4] and that the hcp creep rate is accelerated by the neutron bombardment leading to the relaxation of the RIVE-induced stress in the paste. At the structural level, the radiation field's strong attenuation produces a high RIVE gradient causing high biaxial compressive elastic stresses near the reactor cavity. Simultaneously, the prolonged moderate temperature exposure (< 65°C by design) and strong internal moisture content gradient affect the degree of hydration of concrete, and thus, its mechanical properties. In particular, it leads to the development of lower strengths toward the reactor cavity. Although, the extent of radiation-induced concrete damage appears to be limited to a depth of about < 20 cm of the CBS, the consequences of this damage to the structural performance under seismic conditions (e.g., impact on the reactor pressure vessel (RPV) supports, or accident conditions; e.g., sudden increase of temperature in the cavity, or seismic events) still remain to be investigated. It must be noted that the estimated damage area extends beyond the inner layer of reinforcement and appears strongly oriented along 'parallel' planes to that layer, questioning its ability to transfer effectively stresses due to possible degradation of the steel-concrete bond. In the context of exposure to aggressive corrosive agents such as chlorides, the irradiation-induced cracking may increase the diffusivity of those agents and increase the risk of corrosion of the embedded reinforcement. It must also be noted the irradiation-induced amorphization greatly increase the solubility of silicates at all pH [5].

At gamma doses under 100 MGy, no literature data indicates significant loss of mechanical properties. Radiolysis [6] can affect the free and absorbed capillary water and also may affect the hydrates' chemically bonded water, causing the formation of gas, primarily H_2 in alkaline medium. In Portland cement, the oxygen is consumed by a redox sequence forming peroxide [7]. The latter is captured by the calcium found in the interstitial solution and hydrates to form peroxide octahydrate $CaO_2.8H_2O$, which is very slightly soluble, but is capable of easily losing its water during crystallization in air and then decomposing with simultaneous carbonation. The presence of residual oxygen can potentially increase the risk of corrosion of the embedded reinforcement although no observation of such phenomenon has been observed yet.

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Session 5-2

Chloride ion penetration via concrete cracks and a countermeasure

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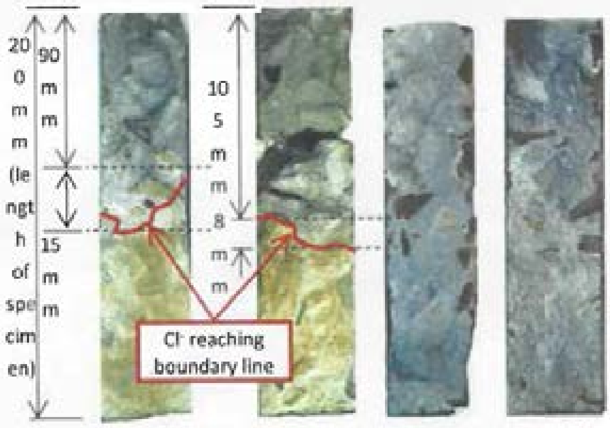
Introduction

Reinforced concrete (RC) structures are widely used not only in nuclear power plants but also in buildings and infrastructures. RC structures consist of reinforcing bars and concrete. Here, reinforcing rebar provides tensile strength and ductility, while concrete offers compressive strength and protective layers of rebars. Therefore, corrosion of the reinforcing bar directly affects the degradation of the performance of RC structures. In general, cover concrete provides a strong alkaline environment and serves as a protective layer against corrosion of reinforcing bar. On the other hand, when cracks occur in concrete due to some external force, e.g., chloride ions reach reinforcing bars, or the alkaline environment is lost due to neutralization of concrete, concrete cannot give enough performance as a protective layer. In this case, the risk of reinforcing bar corrosion may drastically increase.

Here, some experimental results of chloride ion penetration into concrete are presented, which is exposed to elevated temperature simulated the situation of the Fukushima Daiichi Nuclear Power Plant (1F) accident in March 2011. In addition, a concept of self-healing concrete to prevent the ingress of aggressive substances via cracks is introduced.

Penetration of chloride ion into concrete exposed to elevated temperature

The 1F was severely damaged by the earthquake and tsunami due to the Great East Japan Earthquake in 2011. It has been pointed out that some concrete members of the power plant were exposed to elevated temperatures, and water with chloride ions were penetrated concrete supplied by tsunami and cooling seawater. Generally, when concrete is exposed to elevated temperature, cracks occur, and mechanical properties decrease. In addition, these generated cracks allow rapid penetration of chloride ions into concrete. Here, concrete specimens were prepared with the mix proportion which is assumed to be employed in the 1F concrete. These concrete specimens were subjected to elevated temperature, 150, 300, 450, and 600 °C. And then, these specimens were immersed in 3 % sodium chloride solution. Penetration behavior of chloride ion was evaluated by $AgNO_3$ solution spray method and the EPMA and SEM measurement. As the results, in case of the specimen exposed to elevated temperature of 600 °C, chloride ions penetrated to the whole specimen (200 mm from the penetration surface) as shown in Fig. 1. Moreover, measured chloride ions exceeded 1.2 kg/m³, which is a general corrosion limit as shown in Fig. 2. These results were drawn due to fine cracks generated around the aggregate, which is observed as Fig. 3.



a) 150 °C, 1 and 4 weeks b) 600 °C, 1 and 4 weeks

Fig. 1 Penetration of chloride ion

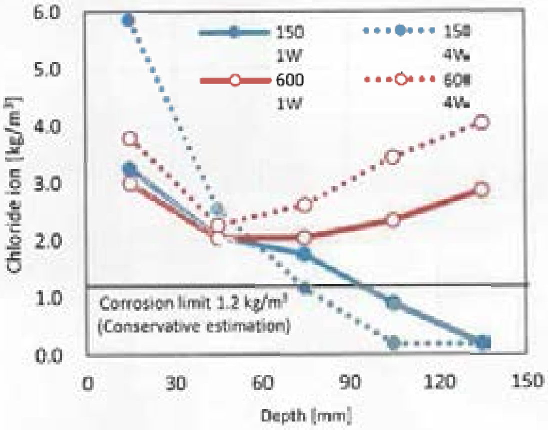
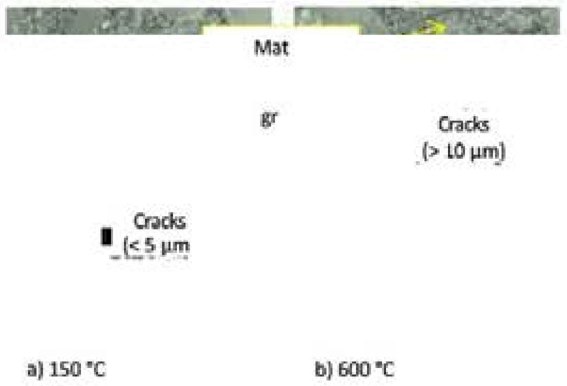


Fig. 2 Distribution of chloride ion



a) 150 °C b) 600 °C

Fig. 3 Microcracks observed by SEM

Fig. 4 Self-healing of crack on FRCC

Self-healing concrete to prevent penetration of chloride ion

Generally speaking, cracks in concrete can occur in any stage of the service life of concrete structures due to various factors such as the above-mentioned elevated temperature, external load, drying shrinkage and so on. Once cracking occurs in reinforced concrete members, not only the mechanical performances reduce but corrosion of reinforcing rebars also occur due to the permeation of water, oxygen, and aggressive substances like chloride ions. On the other hand, concrete inherently has a "self-healing" capability to close cracks by itself[1]. This phenomenon has been known for a long time and can be found even in some old literature[2]. In recent years, many studies have been conducted to evaluate this function from an engineering point of view. The concept of self-healing concrete can be roughly divided into two directions. One is to strengthen the phenomenon observed in conventional concrete such as rehydration of cement and precipitation of calcium carbonate, and the other is to provide means for automatic repair and reinforcement by adding some functional materials and devices to concrete. For the former concept, fiber-reinforced cementitious composites (FRCC), which can sufficiently reduce and keep crack width narrow enough, is one of promising approaches[3]. For the latter one, methods using bacteria as admixture is widely studied[4]. And a lot of different concepts are proposed all over the world[5]. Considering the characteristics of nuclear power plants, the technology of self-healing concrete that enables unmanned crack repairing and closure treatment can be one of the promising countermeasures against harmful cracks on concrete members. Figure 4 shows an example of self-healing on cracked FRCC, which is provided by precipitation of calcium carbonate and rehydration of unhydrated cement[6]. Even though the mechanical properties are not regained by this self-healing phenomenon, closure of crack can recover its tightness against penetration of aggressive substances.

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Poster Program

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P-01

Corrosion behavior of Carbon Steel A106B in Still Water Environment after Decommissioning of Nuclear Power Plant

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Abstract

Carbon steels have been extensively used in nuclear power plants as auxiliary coolant system, reactor coolant pressure boundary piping and control rod drive system, etc. However, corrosion has been reported to be an important degradation mechanism for the carbon steels in nuclear power plants due to their low Cr content. This study focused on corrosion behavior of carbon steel in still water environment after decommissioning of nuclear power plant using cold-drawn and hot-rolled A106 B tubing. The experimental results show that the corrosion rates of A106 B in 45 °C still water environment are divided into three stages. The corrosion rates of cold-drawn and hot-rolled A106 B in Stage 1 are $8.69 * 10^{-3}$ μm hr^{-1} and $9.75 * 10^{-3}$ μm hr^{-1}, and in stage 3: $2.47 * 10^{-3}$ μm hr^{-1} and $2.91 * 10^{-3}$ μm hr^{-1}, respectively. The corrosion rates in Stage 1 are higher than those in Stage 3 because the dissolved oxygen level was higher in Stage 1 and the Fe_3O_4 oxide layer had gradually formed in stage 3 during corrosion. In addition, no pitting corrosion was observed and general corrosion was the prevalent feature.

原子力発電プラント廃炉後の A106B 鋼の静止水環境の腐食挙動

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要　旨

炭素鋼は、原子力発電所では、補助冷却系、原子炉冷却材圧力バウンダリ配管、制御棒駆動系などに広く使用されている。しかし、炭素鋼は、低Cr含有量であるために、その腐食は原子力発電所の重要な劣化メカニズムであると報告されている。本研究では、冷間引抜き及び熱間圧延されたA106B鋼配管における静止水環境中の腐食挙動に着目した。試験の結果、45℃静止水環境中のA106B鋼の腐食速度は、3段階に分けられることを示した。冷間引抜き及び熱間圧延したA106B鋼の腐食速度は、ステージ1ではそれぞれ8.69×10^{-3} μm hr^{-1} 及び 9.75×10^{-3} μm hr^{-1}, ステージ3ではそれぞれ 2.47×10^{-3} μm hr^{-1} 及び 2.91×10^{-3} μm hr^{-1} であった。ステージ1の腐食速度がステージ3よりも大きい理由は溶存酸素濃度がステージ1の方が高いこととステージ3の腐食進行中にFe_3O_4 酸化物層が徐々に形成されるためである。さらに、孔食は観察されず、全面腐食が一般的な特徴であった。

P-02

Stress corrosion cracking susceptibility of carbon steel in sodium pentaborate environment

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Abstract

Carbon steel is used as a primary containment vessel (PCV). In the Fukushima Daiichi Nuclear Power Station, addition of sodium pentaborate having neutron absorption function to cooling water is being considered to prevent recriticality of fuel debris during fuel debris removing process. Sodium pentaborate is known to passivate carbon steel, so stress corrosion cracking (SCC) may potentially occur and progress depending on environmental conditions. Knowledge about SCC susceptibility of carbon steel in sodium pentaborate environment is necessary to maintain the soundness of PCV. In this study, SCC susceptibility was investigated under different sodium pentaborate concentration. First, the potentiodynamic anodic polarization measurement at sweep rates 20mV/min and 1000mV/min was conducted to estimate potential regionwhere SCC susceptibility may appear, because the previous study reported that carbon steel shows SCC susceptibility in the transition potential region from uniform corrosion to passive state. Next, the SSRT was conducted at the several potentials in the estimated potential range at 80℃. At the sodium pentaborate concentration 30000ppm as B, SCC was developed in the transition potential range (-0.425$V_{Ag/AgCl}$, -0.375$V_{Ag/AgCl}$, -0.325$V_{Ag/AgCl}$). At the sodium pentaborate concentration 12000ppm as B which is considered the maximum concentration when the sodium pentaborate is added to the actual plant, no SCC was found in transition potential at -0.45$V_{Ag/AgCl}$.

五ホウ酸ナトリウム環境中における炭素鋼の応力腐食割れ感受性の評価

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要　旨

炭素鋼が原子炉格納容器（PCV）等に使用されている．福島第一原子力発電所では燃料デブリ取り出しの際，燃料デブリの再臨界を防止するために中性子吸収作用を有する五ホウ酸ナトリウムを冷却水に添加することが検討されている．五ホウ酸ナトリウムは炭素鋼に対して不働態化作用を有することが報告されており，環境条件によって応力腐食割れ（SCC）感受性が現出する可能性があるか否かを検討しておくことは有益である．そこで本研究では，異なる五ホウ酸ナトリウム濃度条件で炭素鋼のSCC感受性評価を実施した．動電位アノード分極曲線において，全面腐食ー不働態遷移電位領域でSCC感受性を示すという既往知見に基づき，掃引速度20mV/minと1000mV/minでアノード分極測定を行い，SCC感受性が現れる可能性のある電位領域を推定した．そして推定された電位領域において80℃でSSRT試験を実施した．五ホウ酸ナトリウム濃度30000ppm as Bでは遷移電位領域内の-0.425$V_{Ag/AgCl}$, -0.375$V_{Ag/AgCl}$, -0.325$V_{Ag/AgCl}$でSCC感受性を示した．一方，実機に添加する際の最大濃度とされる12000ppm as Bでは遷移電位領域内の-0.45$V_{Ag/AgCl}$ではSCC感受性を示さなかった．

P-03

Corrosion Investigations for Aging Management of Fuel and Structures in Nuclear Service

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Abstract

Researchers at the Savannah River National Laboratory have conducted investigations over the years to characterize corrosion of materials with objectives to maintain the integrity of materials in nuclear service. The materials and applications include carbon steel for waste storage tanks; aluminum cladding of spent fuel in basin storage; and stainless steel for spent fuel dry storage canisters. Characterization of the thermal, chemical, and radiation conditions of exposure is the first step in evaluation of the materials' behavior; the characterization of the various types of corrosion attack under these conditions that can cause thinning, pitting, cracking, and/or embrittlement of the material is the next step to manage the corrosion in service. Corrosion control, and inservice inspection are methods to mitigate and monitor the corrosion, respectively.

This poster presents the following 4 case studies of recent work in characterization of corrosion phenomena and management thereof for fuel and structures in nuclear service:

- Waste chemistry control for mitigation of carbon steel corrosion of liquid radioactive waste storage tanks
- Corrosion surveillance and monitoring for extended storage of fuel in a water basin
- Radiolysis of free and chemically-bound water in dry canister storage of spent fuel
- Chloride-induced stress corrosion cracking growth rates in austenitic stainless steel for application to aging management of dry storage canisters

核施設における燃料及び構造物の経年劣化管理のための腐食調査

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要旨

サバンナリバー国立研究所では、核施設における材料の健全性維持を目的に長年にわたって材料腐食の調査を行ってきた。材料及び用途には、廃棄物貯蔵タンク用の炭素鋼、使用済み燃料のアルミ製被覆管の流水中貯蔵、ステンレス鋼製の使用済み燃料乾式貯蔵キャニスターが含まれる。熱的、化学的及び照射環境の分析は材料の挙動調査の第一歩である。減肉、孔食及び割れ、あるいは材料の脆化を引き起こすこれらの条件下における様々なタイプの腐食の分析は、施設における腐食を管理するための次のステップである。腐食制御や供用中検査は、それぞれ腐食の緩和や監視する方法である。

このポスターでは、各施設における燃料と構造物の腐食現象の分析と管理に関する最近の4つのケースを示す。

・炭素鋼製放射性液体廃棄物貯蔵タンクの腐食を軽減するための廃棄物化学管理
・流水中の燃料の長期保管のための腐食監視とモニタリング
・使用済み燃料乾式貯蔵キャニスター中の化学結合水と遊離水の放射線分解
・乾式貯蔵キャニスターの経年劣化管理に適用するためのオーステナイト系ステンレス鋼の塩化物誘起応力腐食割れ進展速度

P-04

The development of the remote measuring device and the heat resistance of continuous measurable ultrasound probe for pipe wall thickness

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Abstract

The online monitoring for the thickness of pipe wall is effective for achieving the more safety operation of power plant under running. The objective of this research is to confirm the risk of thinning phenomenon by monitoring the thinning area in the pipe under high temperature environment. The monitoring device and the new ultrasound sensor have been developed to obtain the heat resistance, flexibility and continuous measuring function. These characteristics also have been evaluated not only by conducting tests by simulating the pipe thinning in laboratory but also by applying to the power plant to verify performance. As these test results, the vital performance for the monitoring is confirmed.

連続配管肉厚測定可能な超音波探触子の耐熱性機能および遠隔測定装置の開発

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要　旨

発電所の安全な稼働に寄与するためには，運転中の連続配管肉厚測定（オンライモニタリング）が有効である。本研究では，高温環境下における配管減肉部監視による減肉リスクの把握を目的とし，耐熱性と柔軟性を有する超音波探触子および連続肉厚測定装置を開発し，性能試験，減肉試験，発電所における実証試験を行い，連続配管肉厚測定に必要な性能を確認した。

P-05

Microbial Influences on Corrosion in Radioactive Environments

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Abstract

Microbial influences on corrosion of materials is an important consideration in maintaining the safe operation of aging nuclear facilities. At the U.S. DOE Savannah River Site, microbial contributions to corrosion are carefully monitored and controlled. Examples of issues identified with microbial contributions to corrosion, filter fouling, etc. and solutions developed in response to these issues will be described. Novel methods for in-situ characterization and monitoring of biofilms will be presented.

放射線環境中の腐食に及ぼす微生物の影響

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要　旨

材料の腐食に対する微生物の影響は、老朽化した原子力施設の安全な運用を維持する上で重要な課題である。 米国DOEサバンナリバーサイトでは、腐食に対する微生物の寄与を注意深く監視および制御している。微生物の寄与が特定された問題の例として腐食、フィルター汚損などのほか、これらの問題に対応するために開発した解決策について説明する。 バイオフィルムのその場特性評価とモニタリングのための新しい方法を紹介する。

P-06

Corrosion behavior evaluation for an isolated corrosive bacterium in a bio corrosion inducing environment

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Abstract

Austenitic stainless steels are high corrosion resistant materials used in the power and chemical plants. Even so, stainless steel does not necessarily have corrosion resistance in the natural environment. Especially bio corrosion susceptibility of stainless steel welds is not necessarily clarified. From this point of view, it is very important to clarify the initiation and propagation behavior of corrosion of stainless steel in bio corrosion inducing environments. The effect of solute content, corrosive bacteria (FT01) and microstructure on the pitting potential in artificial seawater solution was studied. In-situ dynamical observation of corrosion behavior of austenitic stainless steel welds / HAZ (Heat Affected Zone) was carried out. From the results of electrochemical analysis, the significant reduction of the pitting potential was confirmed in the biotic condition compared to the abiotic conditions. From the results of dynamic observation, the high correlation between the bacterial attachment region and corrosion generate area was confirmed. Then the difference of height of corrosion area was investigated by a CSLM equipped with a high-resolution three-dimensional height analysis function. Moreover microstructural analysis by FE-SEM/EBSD was performed on the corrosion damaged area, then the traces of corrosion distributed corresponding to the grain boundaries was confirmed.

微生物腐食誘導条件における腐食性単離細菌の腐食挙動評価

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要　旨

オーステナイト系ステンレス鋼は、エネルギープラントおよび化学プラントで使用される代表的な高耐食性材料である。しかしながら、微生物腐食に代表されるように、ステンレス鋼の自然環境での耐食性が必ずしも十分とはならない場合がある。特に、ステンレス鋼溶接部の微生物腐食感受性は明確ではない。この観点から、微生物腐食誘導条件におけるステンレス鋼の腐食発現と進展挙動を明らかにすることを目的とした。本研究では、腐食性単離細菌を含む海水組成培地条件での孔食電位測定を実施し、材料の微生物腐食感受性を評価した。また、生物環境条件におけるオーステナイト系ステンレス鋼浴接部/ HAZ（熱影響部）の腐食挙動をその場観察で調査した。電気化学的調査の結果から、非生物環境条件と比較して生物環境条件では孔食電位の有意な減少が確認された。その場観察の結果からは、微生物付着領域と腐食発生領域との高い相関が確認された。腐食領域を超深度測定装置で解析し、腐食損傷を調査した。同腐食領域に対しFE-SEM/EBSDによる組織解析を行い、粒界に対応した腐食形態を形成していることを確認した。

P-07

Electrochemical analysis of novel sulfate reducing bacteria with novel corrosion activity

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Abstract

We have enriched a sulfate-reducing consortium with corrosion activity from marine sediment even in the absence of hydrocarbons as a carbon source. We explored sulfate reducing bacteria with corrosion activity included in the consortium. *Desulfovibrio* sp. and *Desulforhabdus* sp. were isolated from the consortium with using elemental iron as an electron donor and bicarbonate as a carbon source. The corrosion of carbon steel by both isolates were electrochemically characterized. Relative to the abiotic control, polarization resistance decreased in both isolates and a 4 and 50.5 fold increase in the corrosion current was noted with the *Desulfovibrio* and the *Desulforhabdus*, respectively. The corrosion potential of the *Desulfovibrio* decreased from -650 mV to -900 mV over 2 months incubation, while that of the *Desulforhabdus* decreased from -650 mV to -850 mV in a week, after which it increased to -750 mV. Cyclic voltammetry measurements confirmed that electrons could be transferred between the isolates and carbon steel. These findings are consistent with the view that the *Desulforhabdus* isolate exhibited a higher corrosion activity than the *Desulfovibrio* isolate and suggests that both bacteria promote corrosion by forming conductive biofilms that extract electrons directly from corroding metal surfaces.

新規腐食性硫酸還元菌の単離とその電子獲得型腐食プロセスの電気化学的解析

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要　旨

我々は炭素源として有機炭素(炭化水素)が存在しない場合においても硫酸還元活性および腐食活性を有する微生物群集を海底堆積物から集積することに成功している。本研究ではこの微生物群集に含まれている硫酸還元菌の特性解析を行った。まず、この微生物群集より鉄を単一電子供与体として増殖可能な2株の硫酸還元菌を単離し、それぞれ*Desulfovibrio*および*Desulforhabdus*と同定した。両単離株による炭素鋼の腐食過程を電気化学的に解析した。その結果、滅菌区と比較して、*Desulfovibrio*と*Desulforhabdus*培養区では分極抵抗が減少し、それぞれ腐食電流の4倍と50倍の増加が検出された。*Desulfovibrio*培養区の腐食電位は2か月間の培養試験において-650 mVから-900 mVに減少したのに対して、*Desulforhabdus*培養区の腐食電位は1週間で-650 mVから-850 mVに減少した後、増加に転じ-750 mVに達した。サイクリックボルタンメトリー測定により、炭素鋼と炭素鋼表面に形成されたバイオフィルム間での電子移動が確認された。これら電気化学的な知見は、*Desulforhabdus*が*Desulfovibrio*よりも高い腐食を示すことと一致し、本研究で得られた単離株が炭素鋼表面に導電性バイオフィルムを形成しながら炭素鋼から直接電子を抽出することで腐食を促進するメカニズムを示唆する。

P-08

Corrosion of carbon steel in compacted bentonite buffer materials using anaerobic corrosive microbial consortium.

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Abstract

Microbially influenced corrosion of metallic container is one of concerns for nuclear waste disposal. Corrosion of carbon steel buried in compacted bentonite buffer materials was investigated using anaerobic corrosive microbial consortium. The buffer material was composed of 70% bentonite (Kunigel V1) and 30% silicate sand with different dry densities in test cells. Compacted buffer materials were incubated in nutrient medium with or without inoculation for one year at 30°C and 50°C. Corrosion rates were suppressed (9.4 – 12.9 $mg/cm^2/year$) with compacted densities of 1.3 and 1.6 Mg/m^3 at 50°C. In contrast, a high corrosion rate (52.0 $mg/cm^2/year$) was observed in the inoculated 1.0 Mg/m^3 compacted buffer materials at 30°C, and microbial analysis showed the highest microbial abundance and the high relative ratio of sulfate-reducing bacteria, such as *Desulfovibrio* sp.. These results are demonstrated that a sufficiently high dry density is one of the important key factors to suppress microbial activity in buffer material surrounding metallic containers, because of the physical characteristics such as small pores, low water activity, less nutrient supply caused by low hydraulic conductivity.

This study was funded in the "Project on Research and Development of Spent Fuel Direct Disposal as an Alternative Disposal Option" by Ministry of Economy, Trade and Industry of Japan in FY 2015-2017.

圧縮ベントナイト中における鉄腐食性菌叢による炭素鋼の腐食挙動

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要　旨

地層処分における金属製処分容器の腐食挙動への微生物の影響が懸念されている。湖沼底泥試料から金属鉄により集積培養した微生物群集を用いて圧縮ベントナイト中における炭素鋼片の腐食試験に実施した。腐食試験では、異なる乾燥密度に圧縮成型した緩衝材(クニゲルV1:5号珪砂=7:3)中に炭素鋼試験片を包埋した試験セルを、無菌の培養液に浸漬して飽和させた後、培養液に上述の集積培養した微生物群集を植菌し、嫌気性雰囲気下、30℃あるいは50℃恒温下で静置して、最長1年間、炭素鋼試験片の重量減損量を測定するとともに、緩衝材中の菌叢解析を行った。その結果、乾燥密度1.0Mg/m^3、試験温度30℃、試験期間1年の場合において顕著な重量減損 (52.0 $mg/cm^2/year$)が認められた。また菌叢解析の結果、微生物群集の構成比は試験前後で大きく変化するとともに、硫酸還元菌の存在割合が経時的に増大することが明らかとなった。一方、その他の乾燥密度条件(1.3, 1.6 Mg/m^3)の場合には顕著な変化は認められなかった。以上より、乾燥密度が高くなるに伴い、緩衝材内の膨潤圧が増大することで、空隙サイズ、栄養塩供給速度、水分活性等が低下し、微生物活性が抑制されることで腐食速度が低下した可能性が示唆された。

本成果は、経済産業省資源エネルギー庁の委託事業である「使用済燃料直接処分技術開発（平成26年度）」および「直接処分等代替処分技術開発（平成27～29年度）」の一部である。

P-09

Effects of Gamma-Ray Irradiation on Spontaneous Potential of Stainless Steel in Zeolite-Containing Diluted Artificial Seawater

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Abstract

With respect to the long-term storage of the zeolite-containing spent Cs adsorption vessels used at the Fukushima Daiichi nuclear power station, the corrosion of the vessel material is one of the most important issues. This is because the chloride ions (Cl^-) present in the contaminated water, which is mixed with seawater and is exposed to radiation from the adsorbed radioactive Cs, can accelerate the corrosion of the stainless steel in the vessels. In this study, we performed electrochemical tests on stainless steel (type 316L) specimens in zeolite-containing artificial seawater under gamma-ray irradiation. The spontaneous potential (E_{SP}) and critical pitting potential (V_C) of the type 316L steel in systems in contact with various zeolites were measured in order to evaluate the corrosion resistance of the steel. The E_{SP} value under irradiation, which can also be defined as the steady-state rest potential, increased with an increase in the dose rate; however, the increase was suppressed in contact with the zeolites. The concentration of H_2O_2 in the bulk water under irradiation also increased with the increase in the dose rate. This increase was suppressed in the systems in contact with the zeolites, owing to the decomposition of the H_2O_2 by the zeolites. A clear relationship was observed between E_{SP} and the H_2O_2 concentration. As contact with the zeolites caused the increase in ESP under irradiation to be suppressed, it can be concluded that the presence of zeolites in the spent Cs adsorption vessels can reduce the probability of the localized corrosion of the stainless steel in the vessels.

希釈人工海水中のゼオライト接触ステンレス鋼の自然電位に対するガンマ線照射の影響

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要　旨

福島第一原子力発電所の事故対応で発生する使用済みセシウム吸着容器の長期保管に関して、容器材料の腐食は最も重要な問題の1つです。これは、吸着された放射性セシウムからの放射線と汚染水に存在する塩化物イオン（Cl^-）が、容器内のステンレス鋼の腐食を促進する可能性があるためです。本研究では、ガンマ線照射下のゼオライト含有人工海水中のステンレス鋼（SUS316L）の電気化学試験を実施しました。ステンレス鋼の耐食性を評価するために、ゼオライトと接触する条件で定常自然浸漬電位（E_{SP}）および孔食発生電位（V_C）を測定しました。照射下のE_{SP}は、線量率の増加とともに貴化しました。しかし、ゼオライトとの接触ではその貴化が抑制されました。照射下のバルク水中のH_2O_2の濃度も線量率の増加とともに増加するが、ゼオライトによるH_2O_2の分解により、ゼオライト接触条件では抑制された。E_{SP}とH_2O_2濃度の間には明確な関係が観察されました。ゼオライトとの接触により、照射下でのE_{SP}の増加が抑制されるため、使用済みCs吸着容器に存在するゼオライトにより、容器内のステンレス鋼の局所腐食の確率を低減できる可能性があることが示された。

P-10

Corrosion Monitoring in Ozone-Containing Humid Environment Simulating Gamma Ray Irradiation

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Abstract

To evaluate the effect of oxidants, which are formed by radiolysis of water under gamma ray irradiation, on the corrosion of a carbon steel in humid environment, ozone was introduced as a model oxidant in to humidity-controlled air at 50 °C in a thermo-hygrostat chamber. Corrosion monitoring was performed by using an Atmospheric Corrosion Monitor-type (ACM) sensor consisting of a carbon steel anode and an Ag cathode. The output current of the ACM sensor was increased with the increase in relative humidity and it was obviously increased with the increase in the introduced ozone concentration at each relative humidity. The results indicate that ozone accelerates the corrosion of the carbon steel. The effect of ozone on the corrosion acceleration is attributed to the fast reduction reaction and fast dissolution reaction in to water compared to that of oxygen.

ガンマ線照射を模擬したオゾンを導入した湿潤環境での腐食モニタリング

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要　旨

ガンマ線照射下での水のラジオリシス によって生成する酸化剤が湿潤環境での炭素鋼の腐食に及ぼす影響を評価するために，温度を50℃とした恒温恒湿槽中にオゾンを模擬的な酸化剤として導入した．腐食モニタリングにはアノードが炭素鋼でカソードがAgであるAtmospheric Corrosion Monitor型 (ACM)センサを利用した．ACM電流は相対湿度とともに上昇するが，それぞれの相対湿度でのACM電流はオゾンの導入によって明らかに高くなった．この結果は炭素鋼の腐食をオゾンが促進することを示す．オゾンによる腐食促進の効果は，オゾンの還元反応の速度もしくはオゾンの水への溶解反応の速度が，酸素のそれらの反応と比較して大きいことによると考えられる．

P-11

Effects of gamma-ray irradiation and water film on corrosion rate of carbon steels

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Abstract

After the accident of 1FNPPs, the environmental condition in terms of corrosion in the PCVs has been significantly improved by nitrogen degassing and removal of chloride ions. The inner wall of the PCVs made of carbon steel is immersed in water or covered with water film, and also irradiated by gamma-ray. It is known that corrosion under water film can be accelerated because the oxygen diffusion is enhanced as the liquid film becomes thinner. Gamma-ray irradiation also accelerates corrosion due to H_2O_2 generated by water radiolysis. Corrosion behavior under the water film in gamma-ray irradiation environment is not well understood. In this study, the local corrosion rates and morphology at water line under irradiation condition are investigated with focusing the oxidant flux. In order to investigate the corrosion under the water film near water line, two specimens were prepared, (1) full immersion, and (2) partial immersion. Corrosion tests were conducted in diluted seawater at 50℃ under non-irradiation and irradiation condition(~2.76 kGy/h). It was confirmed that the corrosion at water line was accelerated by water film effect both under non-irradiation and irradiation conditions. Under irradiation condition, the corrosion rate at the water line was the highest. This is considered by the combined acceleration effects of water film and irradiation.

炭素鋼の腐食速度に及ぼすガンマ線照射および水膜の影響評価

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要　旨

福島第一原子力発電所の事故後，PCV内部の腐食に関する環境条件は窒素脱気および塩化物イオンの除去によって改善されている．炭素鋼で製造されているPCVの内壁は水中に浸漬しているか，または水膜によって覆われている．加えて，ガンマ線に照射されている．水膜が薄くなることで酸素拡散が促進されるため，水膜下における腐食は加速されることが分かっている．また，ガンマ線照射も水の放射線分解によって生成される過酸化水素によって腐食を加速させる．ガンマ線照射環境における水膜下での腐食挙動については十分な理解が行われていない．そこで，本研究では酸化剤流束に着目して照射環境下における喫水部での局所的な腐食速度および形態について調査した．喫水部近傍における水膜下での腐食を調査するために(1)全浸漬と(2)半浸漬の2種類の試験片を用意した．腐食試験は非照射環境と照射環境(~2.76 kGy/h)で50℃の希釈海水中で行われた．非照射および照射の両環境下で喫水部における腐食が水膜効果によって加速されたことを確認した．照射環境下では喫水部の腐食速度が最大であった．これは水膜と照射の加速効果が重畳したためと考えられる．

P-12

Development of Corrosion Database under Radiation Environment

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Abstract

Risk of corrosion degradation for plant materials in 1F site have been increasing with time duration and/or environmental changes by decommissioning procedure. Preventing methods for these corrosion risks are developed based on corrosion mechanism. To build a database for estimating the degradation of corrosion in irradiated condition, corrosion and radiolysis data will be accumulated. Concerning development of data set and database for radiolysis, arrangement/estimation of radiolysis existed data and preliminary radiolysis analysis were carried out. Corrosion test environment in gamma-ray irradiation was constructed in Takasaki Advanced Radiation Research Institute of National Institute for Quantum and Radiological Science and Technology (QST). In this facility, gamma-ray irradiation can be carried out in the range from ten to thousands of dose rate.

放射線環境下での腐食データベースの構築

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要　旨

福島第一原子力発電所(1F)の廃炉工程において、腐食による材料劣化に起因するリスクの増大が懸念される。このような腐食に起因するリスクへの対策は腐食メカニズムに基づき実施される必要がある。腐食反応を律速する環境要因に関しては、現状十分にデータが得られている訳ではなく、また、作業の進展に伴い時々刻々と変化し得る。よって、照射下での腐食データベース構築のために、想定される範囲を充分に包含した環境条件での腐食、およびラジオリシスデータを取得することを目指す。そのために量研ガンマ線照射施設において、ガンマ線照射下腐食試験を実施可能な環境を整備し拠点化するとともに、1F 廃炉を想定したラジオリシスデータと構造材料の腐食データを大学等と連携して取得する。

P-13

Effect of Oxygen Mass Transfer Flux on Corrosion Rate of Carbon Steel in Slurry Flow

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Abstract

In order to perform decommissioning of the Fukushima Daiichi Nuclear Power Station (1F) safely and reliably, it is necessary to predict the corrosion rate of carbon steel piping for cooling water. On the other hand, during the fuel debris retrieval operation, fine solid particles of the fuel debris, metals, and other solids may be mixed in the cooling water to form a slurry. Solid particles in cooling water may have two effects on the corrosion rate of carbon steel. The first is to accelerate the mass transfer flux of oxygen, iron ions and hydrogen ions, and the second is to scratch the surface of the carbon steel and destroy the oxide film. Therefore, the corrosion rate may be accelerated by the slurry. However, knowledge to be used for predicting corrosion rate of carbon steel in 1F slurry flow is very limited. Based on these, in this study, we conducted experiments focusing on the relationship between the corrosion rate of carbon steel and the mass transfer flux of oxygen in a slurry flow. First, the mass transfer coefficient under the slurry flow was measured using a rotating cylinder electrode. It became clear that mass transfer was promoted by the presence of solid particles. Next, corrosion tests were performed in a slurry flow and single phase flow with controlling the mass transfer flux using a rotating cylinder electrode. The mass transfer flux of oxygen was controlled by the rotational speed of the cylinder electrode and the dissolved oxygen concentration. In single phase flow, a convex relationship was obtained between the oxygen flux and the maximum corrosion rate. This is thought to be because the corrosion rate increases due to the increase in the oxidant flux, and the carbon steel is passivated when the oxidant flux exceeds the passivation limit current density. In surrly flow, corrosion rate was higher than trend obtaind in single phase flow.

固液混相流における炭素鋼腐食速度に及ぼす酸素物質移動流束の影響

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要　旨

福島第一原子力発電所（1F）の廃止措置を安全かつ確実に行うためには、冷却水用炭素鋼配管の腐食速度の予測が必要である。一方、燃料デブリ取り出し作業中に、燃料デブリや金属の切子などの微細な固体粒子が冷却水に混入してスラリーを生成する場合がある。このスラリー中の固体粒子は、炭素鋼の腐食速度に2つの影響を与える可能性がある。1つは酸素、鉄イオン、水素イオンの物質移動流束を増大させることで、2つ目は炭素鋼の表面をこすり酸化皮膜を破壊することである。そのため、スラリーによって腐食速度が増大する可能性がある。一方1Fのスラリー環境下での炭素鋼の腐食速度を予測するための知見は不足している。そこで本研究では、スラリー環境下における炭素鋼腐食速度と酸素の物質移動流束の関係性に注目して実験を実施した。まず、回転円筒電極を用いてスラリー下の物質移動係数を測定し、固体粒子の存在によって物質移動が促進されることが分かった。次に、回転円筒電極を使用して物質移動流束を制御しながら、スラリー環境と単相流下で腐食試験を実施した。酸素の物質移動流束は、円筒電極の回転速度と溶存酸素濃度によって制御した。液単相流においては、酸素流束と最大腐食速度の間に上に凸な関係が得られた。これは、酸化剤流束が増加することで腐食速度が増大し、酸化剤流束が不動態化限界電流密度以上になると炭素鋼が不動態化するためだと考えられる。スラリー下では、単相流で得られた傾向より大きな腐食速度を示した。

P-14

Propagation Continuity of Crevice Corrosion without Cathodic Reaction outside Crevice Assessed with Full-Creviced Specimen

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Abstract

In Fukushima Daiichi NPS, there is little possibility of initiation of another crevice corrosion on stainless steel, because several corrosion mitigation measures have been taken after emergency seawater injection, but it is still needed to consider propagation continuity of crevice corrosion, which once occurred after the seawater injection. In crevice corrosion of stainless steel, it is understood that cathodic reaction outside a crevice supports the anodic reaction inside the crevice. However, the cathodic reaction inside a crevice has been confirmed in recent years, and contribution of cathodic reaction inside a crevice on propagation of crevice corrosion has not been clarified. In this study, propagation continuity of crevice corrosion without cathodic reaction outside a crevice was investigated. 304L "full-creviced specimen", which has no free surface outside the crevice, and 316L "outer cathode specimen" were used to observe cathodic reaction inside or outside separately. Measurement of spontaneous potential showed that the crevice corrosion on the full-creviced specimen continued to propagate very slowly by only cathodic reaction inside the crevice until the experiment was terminated. Based on the spontaneous potential, it is considered that not only hydrogen generation but also oxygen reduction played an important role on propagation of the corrosion.

すきまのみ試験片を用いたすきま外カソード反応によらないすきま腐食の進展継続性評価

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要　旨

福島第一原子力発電所では，緊急措置として行われた海水注入の後に様々な腐食対策が行われた為，今後新たなすきま腐食が生起する可能性はほとんど無い．しかし，海水注入の直後にすきま腐食が生起したとすれば，その進展継続可能性については検討しておく必要がある．ステンレス鋼のすきま腐食において，すきま内のアノード反応はすきま外のカソード反応によって支持されていると理解されてきた．しかし一方で，近年の研究においてすきま内のカソード反応の存在が確認されており，そのすきま腐食の進展に対する寄与は明らかになっていない．本研究では，すきま内でのカソード反応のみによるすきま腐食の進展継続性について調査した．試験片は，すきま外に自由表面が無い304L鋼製「すきまのみ試験片」と，316L鋼製「外部カソード」をそれぞれ使用し，すきま内またはすきま外におけるカソード反応をそれぞれ区別して観測した．電位を測定することで，すきま内のカソード反応のみで実験の終了まですきまのみ試験片上に生起したすきま腐食がごくゆっくりと進展継続したことが分かった．また，この試験片電位より，すきま内における水素発生だけでなく酸素還元も腐食進展継続に寄与していると考えられた．

P-15

Repassivation of Crevice Corrosion on Type 316L Stainless Steel by NH_4^+ generation.

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Abstract

The effect of NO_3^- on the repassivation of crevice corrosion on Type 316L stainless steel was investigated. *In situ* monitoring of corrosion morphology inside the crevice was conducted during the crevice corrosion tests. The solution was changed from 1 M NaCl to NaCl-$NaNO_3$ in the crevice corrosion tests. Consequently, complete repassivation caused by NO_3^- was observed. Repassivation of the crevice corrosion took place in two steps. In the first step, current inside the crevice gradually decreased from *ca.* 5 mA cm^{-2} to *ca.* 5 μA cm^{-2}. After that, in the second step, the current rapidly decreased to less than 0.1 μA cm^{-2}. The first step was thought to be caused by the suppression of active dissolution by NO_3^-, since the active dissolution was suppressed in potentiodynamic polarization with acidic solutions which simulate the solution inside the crevice (pH 0.2). On the other hand, NH_4^+ was detected in the crevice solution by ion chromatography analysis after potentiostatic polarization in 2 M KNO_3. Therefore, it would be concluded that the generation of NH_4^+ results in a pH increase and the further suppression of active dissolution, which induced the second step.

NH_4^+生成に伴う 316L ステンレス鋼のすき間腐食再不働態化

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要　旨

NO_3^-が316Lステンレス鋼のすき間腐食再不働態化におよぼす影響を調査した。すき間腐食試験を行いながらすき間内部のその場観察を行った。すき間腐食試験中、試験溶液を1 M　NaCl溶液からNaCl-$NaNO_3$溶液へ変更した。その結果、NO_3^-によるすき間腐食再不働態化が観察された。NO_3^-によるすき間腐食再不働態化は二段階で生じた。一段階目では、すき間内部の電流値が約5 mAから約5 μAまで徐々に低下した。その後、二段階目で電流値は急激に0.1 μA以下まで低下した。すき間内部を模擬した低pH溶液中で測定した動電位分極曲線中でNO_3^-による活性溶解の抑制が確認されたため、一段階目はNO_3^-によるすき間内部の活性溶解の抑制によって生じたと考えられる。また、2 M KNO_3溶液中で定電位分極測定後のすき間内溶液分析の結果、NH_4^+が検出された。そのため、NH_4^+の生成がpH上昇を引き起こし、さらなる活性溶解の抑制をもたらした結果、二段階目の再不働態化が生じたと考えられる。

P-16

In-situ measurement of leaching rate of fuel debris

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Abstract

Large amounts of fuel debris are expected to be accumulated under the cooling water in the containment vessel of Fukushima Daiichi nuclear power plants. The accumulated debris is planned to be removed from the reactors in the near future. However, parts of them could be leached and dispersed into the water, and could be leaked out from the containment vessel. Therefore, the leaching behavior of fuel debris under the relevant environment should be estimated. However, it is difficult to evaluate the leaching rate of fuel debris by traditional methods, such as solution analysis of immersion liquid, because fuel debris is multiphase and heterogeneous materials. On the other hands, *in-situ* observation methods such as interferometric microscope and atomic force microscope can measure leaching rate by surface shape change in nano- and micro-meter scales.

Zircon, $ZrSiO_4$, is expected to be one of the main phases in molten core concrete interaction (MCCI) products. In this study, an *in-situ* observation method using an interferometric microscope was applied to the measurement of the leaching rate of natural zircon under the flowing aqueous solutions with pH = 0 (HCl), 7 (ultrapure water), and 14 (aq NaOH) based on the change of zircon surface. It was confirmed that the dissolution rates under different aqueous solution can be measured by the applied method. The dissolution rates of the main phases such as $(U,Zr)O_2$, can be also measured by interferometric microscope and atomic force microscope for estimating the leaching behavior of fuel debris.

その場観察技術を用いた燃料デブリの溶出速度測定に関する研究

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要　旨

事故後の福島第一原子力発電所の格納容器内には、多くの燃料デブリが冷却水中に堆積している。これらの燃料デブリは近い将来取出される計画であるが、これらの一部は冷却水中に溶出し、燃料デブリ成分の一部が水相に拡散している可能性がある。また、冷却水の一部は格納容器から環境中へ漏洩し得る。このような状況を推定・把握するためには、燃料デブリ取出し期間中の燃料デブリの溶出挙動を推定する必要がある。しかし、燃料デブリは多相系の非均質な物質であるため、その溶出速度を従来法である浸漬液の核種濃度分析から評価することは難しい。一方、干渉計や原子間力顕微鏡等のその場観察技術は、ナノからマイクロスケールの表面形状の変化を測定することで、溶出速度を測定することが可能な技術である。ジルコン($ZrSiO_4$)は溶融燃料とコンクリートの反応（MCCI）生成物の主要な生成相の一つとされており、燃料デブリ中に想定される成分の一つである。本研究では、上述のその場観察技術を用いて燃料デブリの溶出速度の測定が実施できることを検証することを目的に、pH 0 (HCl)、7（超純水）、14 (aq NaOH)の流水場中の天然ジルコンの溶解速度を、干渉計を用いた表面形状変化の測定から導出し、それぞれの溶液中での溶出速度を測定できることを確認した。この結果を踏まえ、今後は$(U, Zr)O_2$等の主要な生成相の溶出速度を干渉計や原子間力顕微鏡を用いて測定し、燃料デブリの溶出挙動を推定する計画である。

P-17

Uranium leaching from simulated fuel debris prepared from UO_2 and stainless steel

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Abstract

Fuel debris generated due to nuclear severe accidents is expected to contain a wide variety of uranium compounds. In this project, we have investigated chemical stability of simulated fuel debris containing elements from stainless steel (Fe, Cr, and Ni) against exposure to water. The simulated debris was prepared from the powders of UO_2 and SUS304 by heating the mixed powder at 1200 °C for 1 h under continuous gas flow of 2% O_2 in Ar[1]. The produced powder was characterized by XRD and SEM-EDX, Raman micro-spectroscopy, and Mössbauer spectroscopy. The series of characterization revealed that the simulated debris comprised $U(Fe,Cr)O_4$, U_3O_8, and Fe(III) oxides. Then, the simulated debris was exposed to pure water for 30 days. The same leaching test of U_3O_8 was performed for comparison. The chemical analysis of leached metals demonstrated that the U elution from the simulated debris was significantly lower than that from U_3O_8. In addition, Fe, Cr, and Ni were under quantitation limit as well. The Raman spectra showed that the exposure to water induced insignificant change in the spectra of the simulated debris, while the Raman band structure of U_3O_8 seemed to become slightly unclear after 30 days immersion.

ステンレス鋼成分を含む模擬燃料デブリからのウラン溶出

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要　旨

原子力発電所の過酷事故で生じる燃料デブリは多様なウラン化合物を包含すると考えられる。本研究ではステンレス鋼を構成する鉄、クロム、ニッケルを含む模擬燃料デブリを調製し、水中での安定性を調べた。試験に用いた模擬デブリは、二酸化ウラン粉末とSUS304ステンレス鋼粉末の混合物を2%酸素を含むアルゴン気流下において1200℃で1時間加熱して調製した[1]。得られた模擬デブリ粉末をXRD、SEM-EDX、顕微ラマン分光、メスバウアー分光により分析した結果、$U(Fe,Cr)O_4$、U_3O_8、Fe(III)酸化物の混合物であった。この模擬デブリ試料を純水に30日間浸漬し、金属元素の溶出と表面の化学状態の変化を調べた。また、比較のためU_3O_8粉末を用いた同様の浸漬試験を実施した。浸漬液の元素分析の結果、模擬デブリ試料から溶出したウランの濃度は、U_3O_8との比較において顕著に低く、また鉄、クロム、ニッケルの溶出濃度は定量下限値未満であった。顕微ラマン分光法を用いた表面分析では、U_3O_8では30日間の浸漬によりラマンスペクトルに見られるバンド構造がやや不明瞭になるのに対して、模擬デブリ試料のスペクトルには有意な変化は観測されなかった。これらの結果はステンレス鋼成分を含む模擬デブリは、ウラン酸化物と比べて、水に対して安定性が高いことを示すものである。

Reference / 参考文献

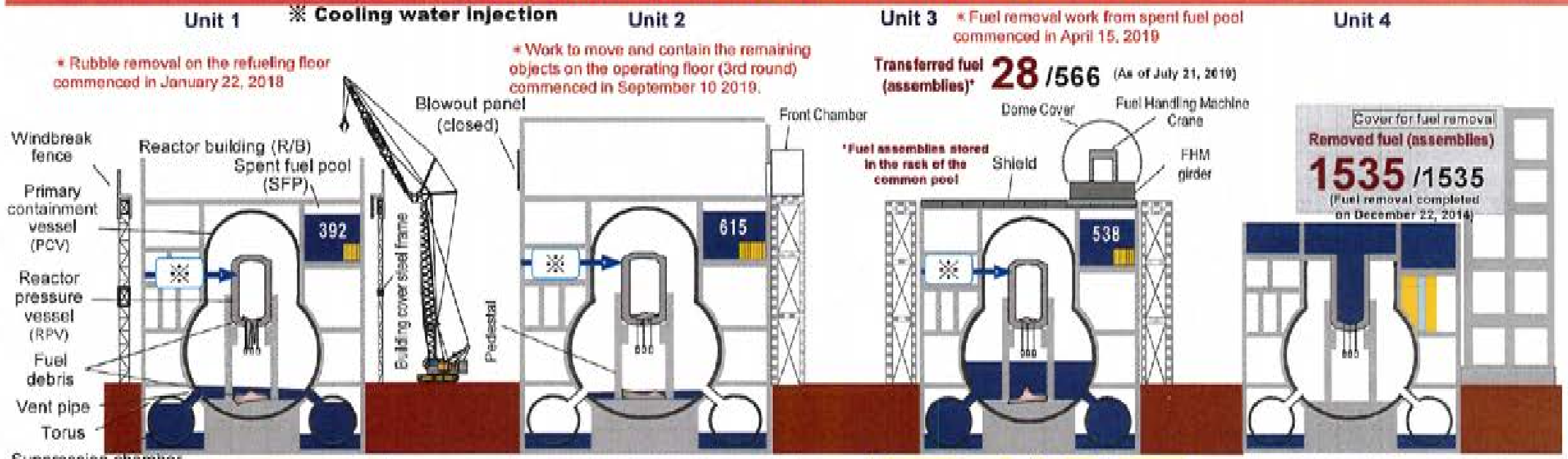
[1] D. Akiyama, H. Akiyama, A. Uehara, A. Kirishima, N. Sato, *J. Nucl. Mater.*, 520 (2019) 27-33.

附件二：TEPCO 公司提供的 1F　1~4 個機組恢復現況

TEPCO

(1) State of Units 1-4

All reactors are in cold shutdown condition



* Rubble removal on the refueling floor commenced in January 22, 2018

* Work to move and contain the remaining objects on the operating floor (3rd round) commenced in September 10 2019.

* Fuel removal work from spent fuel pool commenced in April 15, 2019

Transferred fuel (assemblies)* 28 /566 (As of July 21, 2019)

*Fuel assemblies stored in the rack of the common pool

Removed fuel (assemblies) 1535 /1535 (Fuel removal completed on December 22, 2014)

Values as of 11:00 on November 19, 2019

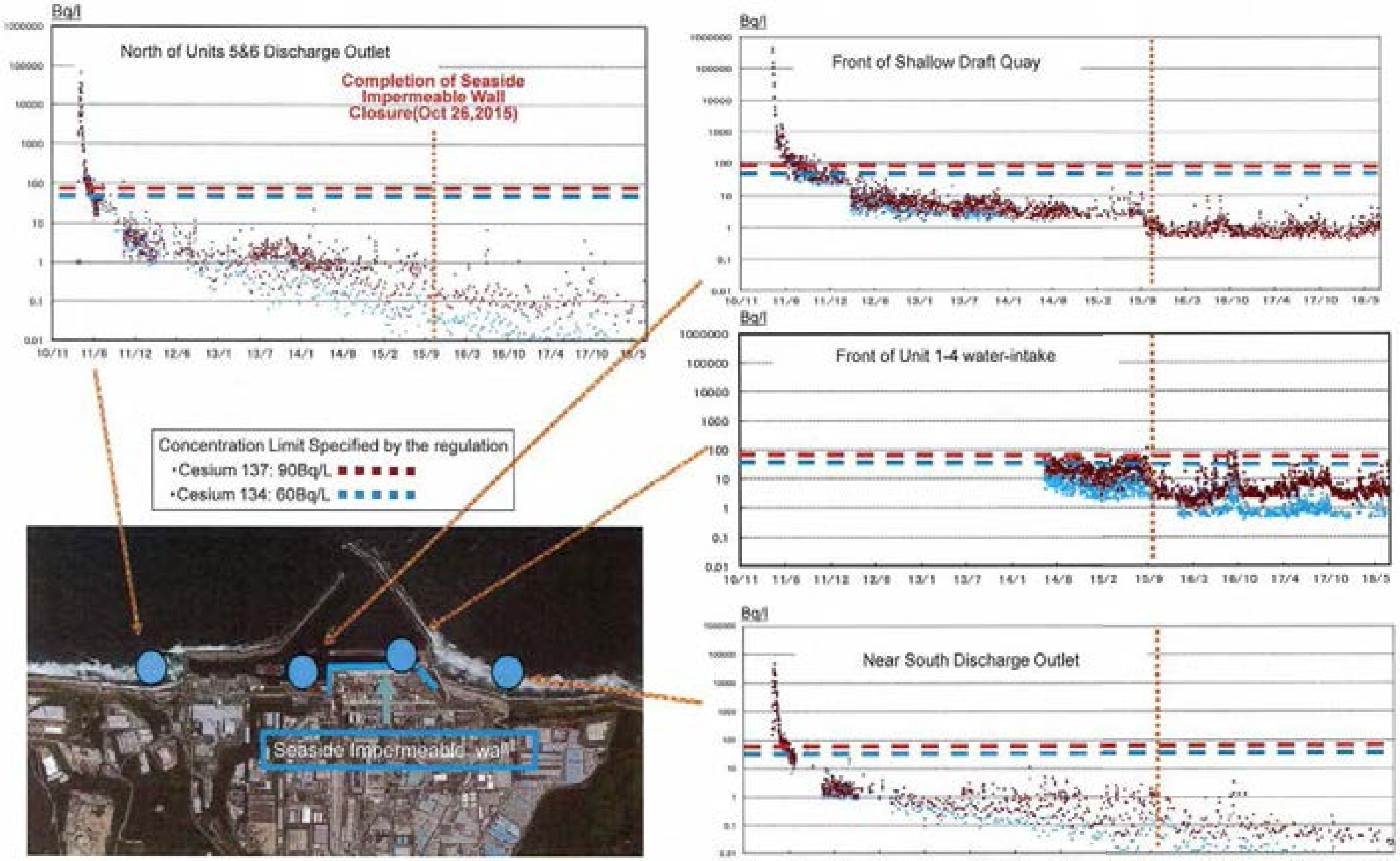
	RPV bottom temp.	PCV internal temp.	Fuel pool temp.	Water injection to the reactor
Unit 1	~23℃	~23℃	~24℃	2.8m^3/h
Unit 2	~28℃	~29℃	~24℃	2.8m^3/h
Unit 3	~27℃	~28℃	~23℃	2.9m^3/h

Plant parameters, including RPV and PCV temperatures, are monitored continuously 24 hours a day.

TEPCO

(2) Sea Area Monitoring Status

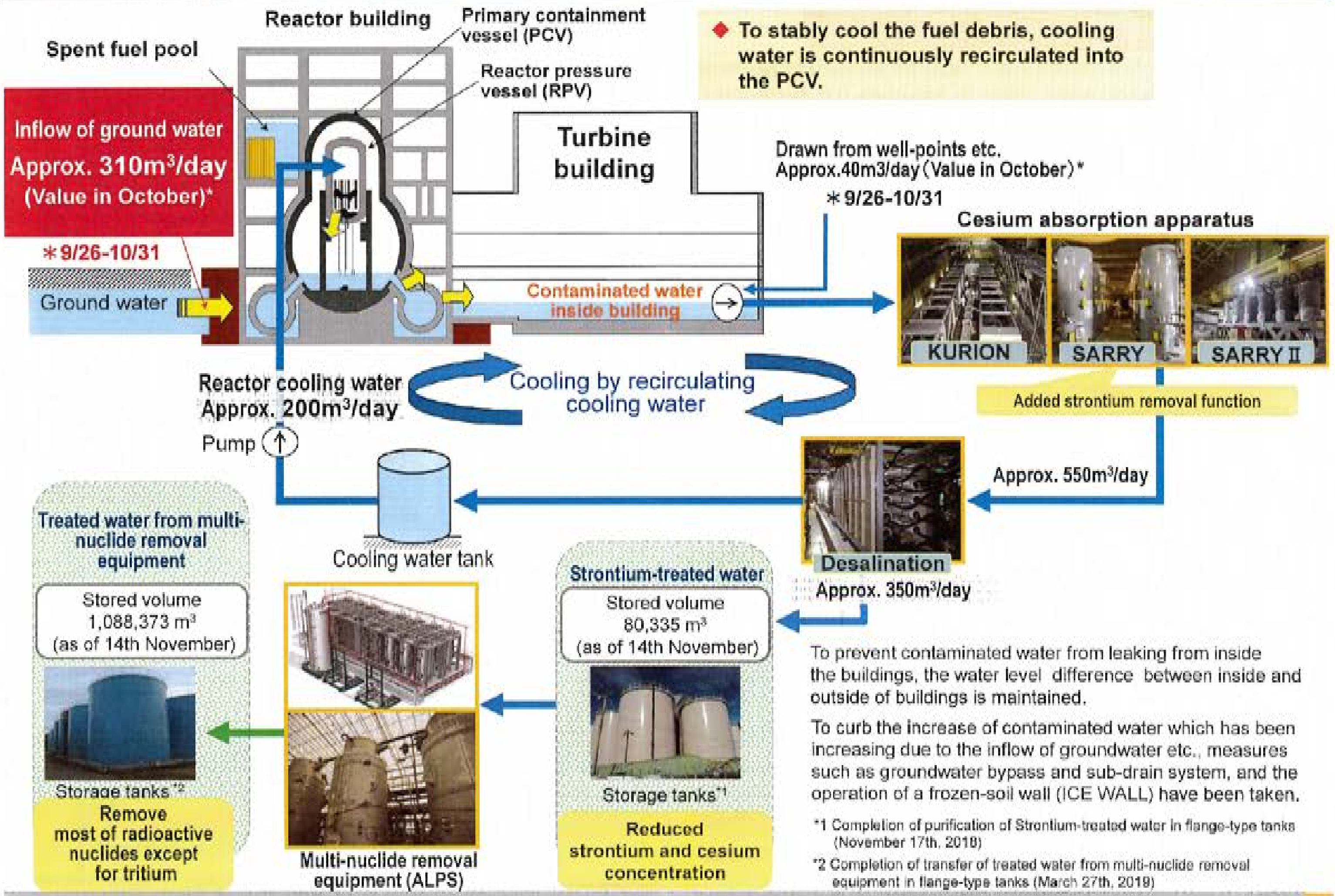
The radioactive material concentration in the port area has decreased to less than one- 1,000,000th since the accident



TEPCO

(3) Conceptional Diagram of Reactor Circulation Cooling

◆ **To stably cool the fuel debris, cooling water is continuously recirculated into the PCV.**



Reactor building

Primary containment vessel (PCV)

Reactor pressure vessel (RPV)

Spent fuel pool

Inflow of ground water
Approx. 310m³/day
(Value in October)*

＊9/26-10/31

Ground water

Turbine building

Contaminated water inside building

Drawn from well-points etc.
Approx.40m3/day (Value in October)*

＊9/26-10/31

Cesium absorption apparatus

KURION

SARRY

SARRY II

Added strontium removal function

Reactor cooling water
Approx. 200m³/day

Pump

Cooling by recirculating cooling water

Approx. 550m³/day

Desalination

Approx. 350m³/day

Cooling water tank

Treated water from multi-nuclide removal equipment

Stored volume
1,088,373 m³
(as of 14th November)

Storage tanks*2

Remove most of radioactive nuclides except for tritium

Multi-nuclide removal equipment (ALPS)

Strontium-treated water

Stored volume
80,335 m³
(as of 14th November)

Storage tanks*1

Reduced strontium and cesium concentration

To prevent contaminated water from leaking from inside the buildings, the water level difference between inside and outside of buildings is maintained.

To curb the increase of contaminated water which has been increasing due to the inflow of groundwater etc., measures such as groundwater bypass and sub-drain system, and the operation of a frozen-soil wall (ICE WALL) have been taken.

*1 Completion of purification of Strontium-treated water in flange-type tanks (November 17th, 2018)

*2 Completion of transfer of treated water from multi-nuclide removal equipment in flange-type tanks (March 27th, 2019)

TEPCO

(4) Three Policies for Contaminated Water Management

Policy 1. Remove source of contamination

① Clean up contaminated water with Multi-nuclide removal equipment (ALPS)
② Remove contaminated water in trenches (Underground tunnel with piping)

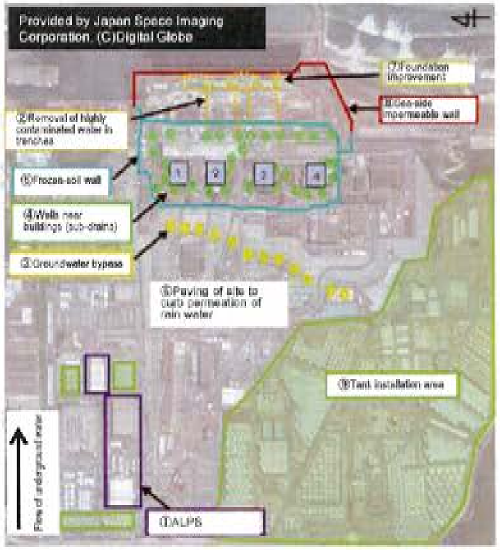
⇒①Completion of filtering highly contaminated water stored in tanks in May 2015
② Removal was completed in June 2015

Policy 2. Isolate groundwater from contamination sources

③ Pumping up groundwater through groundwater bypasses
④ Pumping up groundwater through subdrains (wells near buildings)
⑤ Installation of frozen-soil impermeable wall (Ice Wall)
⑥ Paving of site to curb permeation of rainwater into soil

⇒③ Pumping up/Drainage operation being implemented (accumulated volume is approximately 512 thousand tons [as of November 19th, 2019])
④ Pumping up/Purification and Drainage operation being implemented ＊ (809 thousand tons [as of November 18th, 2019])
⑤ Freeze work commenced in March 2016 and completed in September 2018
⑥ Paving was almost completed at the end of FY2015 (excluding Units 1-4 circumference and slope between Units 1-4 and the seaside area)

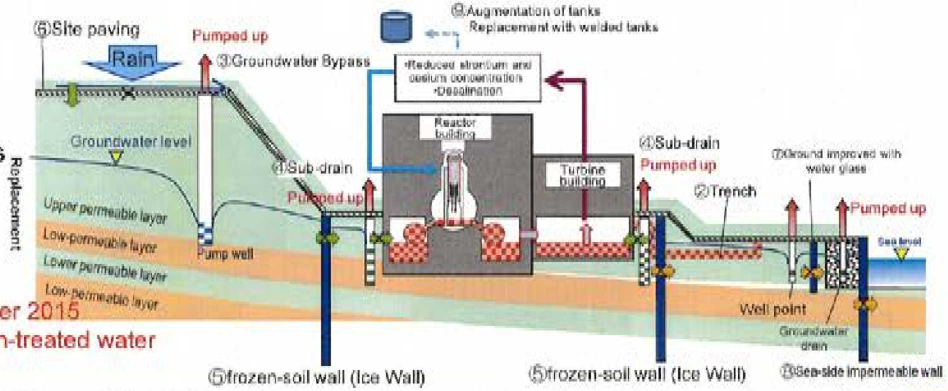
＊ temporarily stored in tanks and released after TEPCO and a third-party organization has confirmed that the water quality has met operational targets.



Policy 3. Prevent leakage of contaminated water

⑦ Ground improved with water glass
⑧ Installation of sea-side impermeable walls
⑨ Augmentation of tanks
(replacement with welded tanks etc.)

⇒⑦ Ground improvement work was completed in March 2014
⑧ Closure of Seaside Impermeable Wall in October 2015
⑨ Ongoing (completion of purification of Strontium-treated water in flange-type tanks(November 17, 2018))

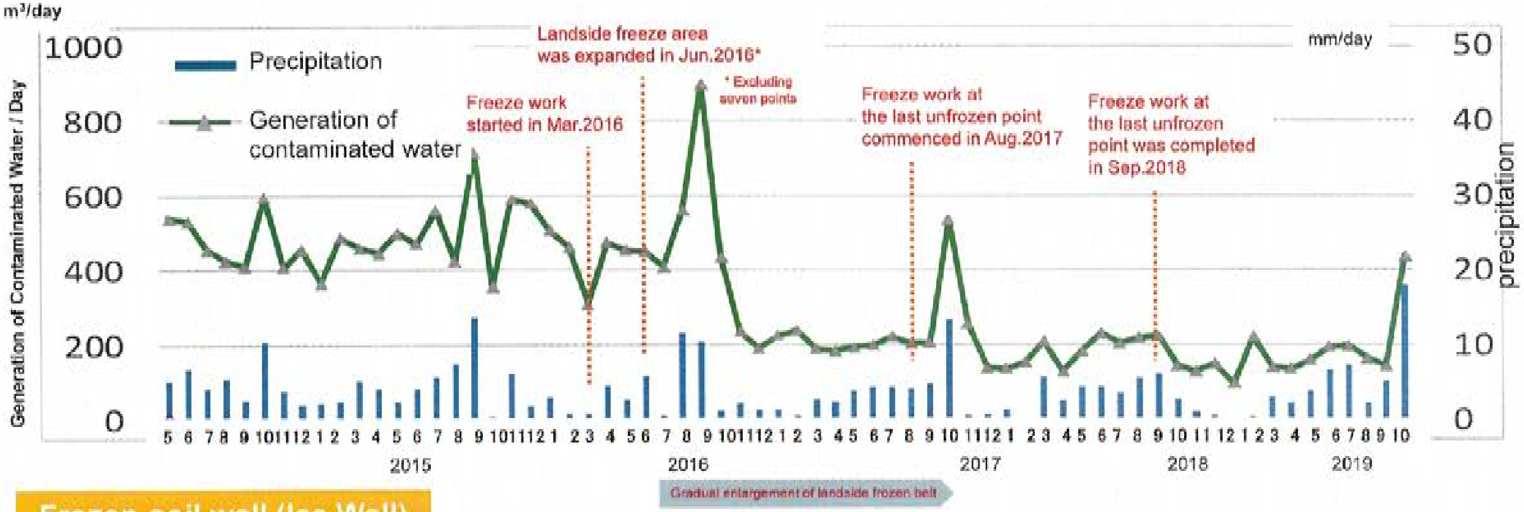


TEPCO

(5) Multilayered countermeasures to reduce contaminated water generation

Multilayered countermeasures including frozen-soil Ice Wall and sub-drains etc. taken to control underground water level

The freeze work completed at the last unfrozen point of the ice wall in Aug. 2017. Underground temperature will continue to be decline below 0℃ in almost all areas, while on the mountainside. The water level difference between the inside and outside of the wall is keeping approx. 4-5 meters. It was confirmed that Multi-layered measures including ice-wall, sub-drains and paving etc. are keeping the groundwater level stable and have contributed to the establishment of water-level management system to isolate the groundwater from the buildings. (The committee held by METI in Mar. 2018 recognized the effect of the ice wall)



Frozen-soil wall (Ice Wall)

- Freezing plant ; Refrigerator 261kW and cooling tower (30 units) to lower the temperature of antifreeze liquid (brine) to around -30 ℃
- Length ; approxi.1,500m (whole circumference)

Frozen soil wall (Ice Wall)

Image showing how to block the inflow of underground water into Units 1-4

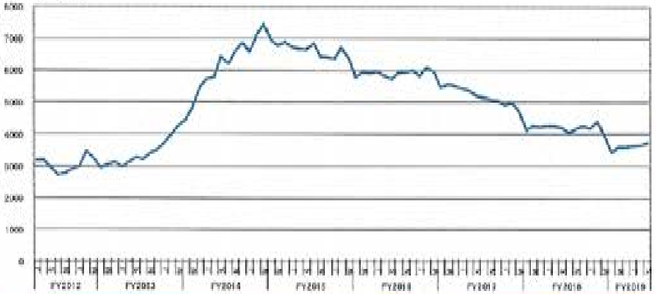
TEPCO

(6) Efforts to improve work environment

- Efforts are made to secure workers over the long term and to implement their exposure dose control. (**Currently, approximately 90% of orders are fulfilled by negotiated contracts**)
- TEPCO will continue to improve the work environment reflecting on the needs of workers.

Changes in the number of workers

- Average number of workers (TEPCO employees and contractors) per weekday is 3,790 as of October . 2019.
- The local employment ratio is approx. 60% as of October . 2019.



Improving the work environment

- Large rest house ,which provide 1,200 workers with spacious place to relax, began to operate on May 31, 2015.
- Fukushima revitalization meal service center, which serve around 2,000 hot meals a day using ingredients from Fukushima prefecture, was established on March 31 ,2015.
- Automatic driving EV bus in April, 2018 was introduced. The bus enable to move in the site of the workers with convenience effectively.

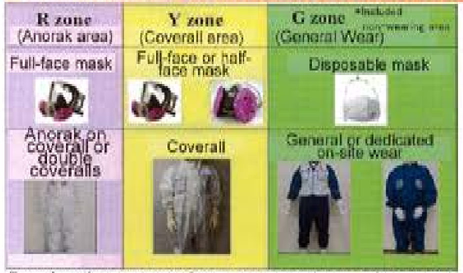
Automatic driving EV bus

Large rest house (On-Site)

Large rest house lunch room (On-site)

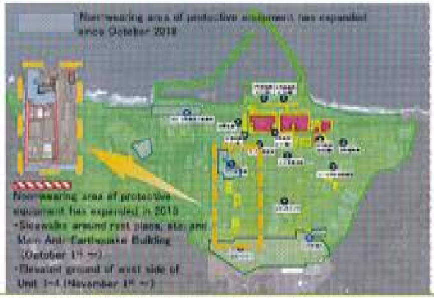
Fukushima Revitalization Meal Service Center (Okuma Town)

Optimization of radioactive protective equipment



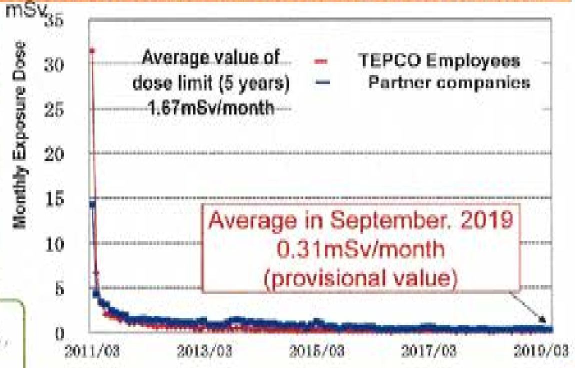
R zone (Anorak area)	**Y zone** (Coverall area)	**G zone** *Included non-wearing area (General Wear)
Full-face mask	Full-face or half-face mask	Disposable mask
Anorak on coverall or double coveralls	Coverall	General or dedicated on-site wear

Based on the progress of measures to reduce environmental dosage on site, the site was categorized into two zones: Highly contaminated area around Units 1-4 etc. and other areas to optimize protective equipment according to each category aiming at improving safety and productivity by reducing load during work.



- G-zone has expanded based on the assessment of constant dust monitors measurements (○ shows constant dust monitor).
- Circumferential roads around Unit 1-4 have been recently designated G-zone , as a result , the ratio of G-zone of the whole premise has risen to 96% in May 2018.

Monthly Transition of Exposure Dose of Workers

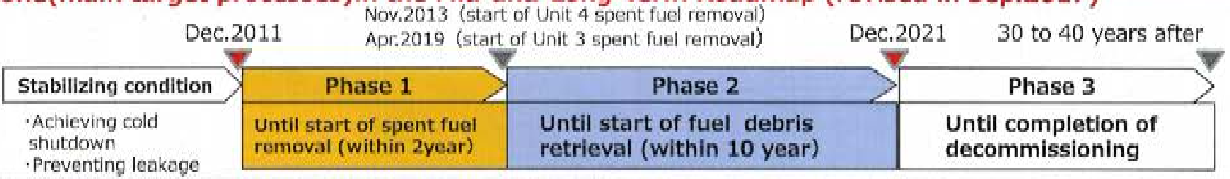


Average in September. 2019 0.31mSv/month (provisional value)

TEPCO

(7) Mid-and-Long Roadmap towards the decommissioning (Fuel debris retrieval)

Milestone(main target processes)in the Mid-and-Long-Term Roadmap (revised in Sep.2017)



Contaminated water management

①Reduction of contaminated water generation to about 150m^3/day : **Within 2020**

②All purified water by purification equipment etc. is stored in welding type tank : **Completion (March 27, 2019)**

Stagnant water treatment

①Separation of the connecting part between Units 1 and 2 and between Units 3 and 4 : **Completion (September 13, 2018)**

②Reduction of radioactive materials in stagnant water in buildings up to about one tenth of the end of FY 2014 *1

③Completion of treatment of stagnant water in buildings : **Within 2020***1

*1 At the end of FY2014, the target of reducing radioactive materials was set on the assumption that contaminated water concentrations in each building were the same. However, according the progress of contaminated water treatment, high radiation concentrations were detected in some buildings, and it was difficult to evaluate them. The treatment of radioactive materials is progressing faster than scheduled and continues to accelerate toward completion of contaminated water treatment in buildings within 2020.

Fuel removal from spent fuel pools

①Start of fuel removal from Unit1 : FY2023 (targeted year)*2

②Start of fuel removal from Unit2 : FY2023 (targeted year)

③Start of fuel removal from Unit3 : **April 15, 2019**

*2 Rubble removal on the refueling floor commenced in Jan. 2018

Fuel debris retrieval

①Determination of fuel debris retrieval methods for the first implementing unit : FY2019

②Start of fuel debris retrieval at the first implementing unit : **Within 2021**

Waste management

Technical prospects concerning processing/disposal policies and their safety : **Around FY2021**

Investigation inside the PCV vessel

Unit 1

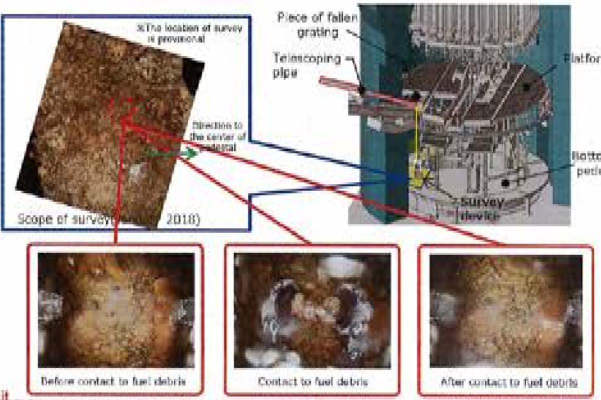
In March 2017, the investigation was conducted to investigate the spreading of fuel debris to the basement outside the pedestal. A self-propelled investigation device took images of the PCV bottom status.

Unit 3

- The inside of the PCV was investigated using a remotely operated underwater vehicle in Jul. 2017.
- Analysis of image data obtained in the investigation identified damage to multiple structures and the supposed core internals.

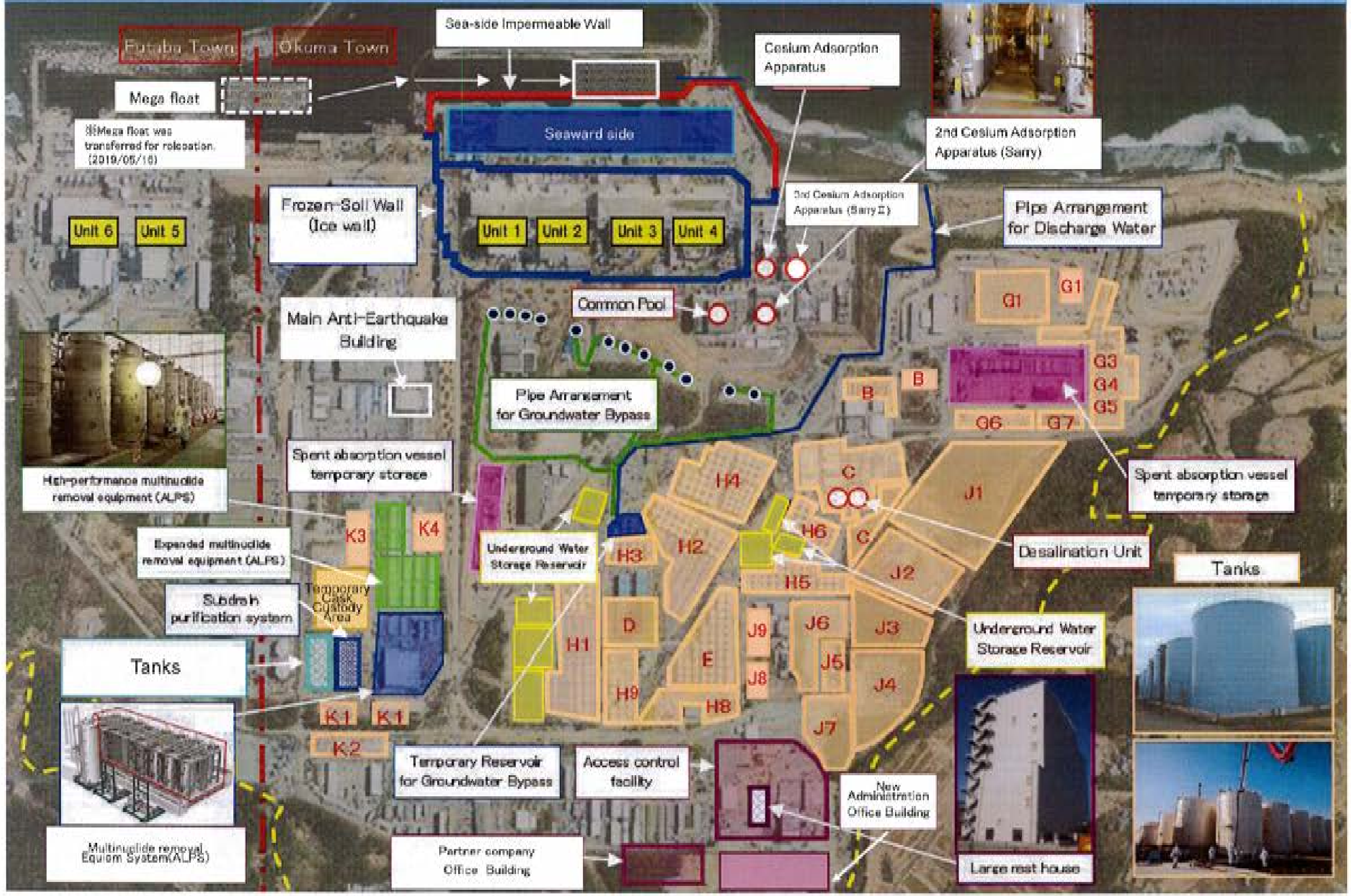
Unit 2

- The investigation inside the PCV was conducted in Jan. 2018. Deposits assumed to include fuel debris were found at the bottom of the pedestal.
- The investigation inside the PCV was conducted in February 13, 2019 in order to determine the characteristics (hardness and fragility) of deposits. Deposits of ten locations on the pedestal bottom and the platform were touched by using improved investigation device. As a result, we confirmed that pebbled deposits etc. of seven locations moved.



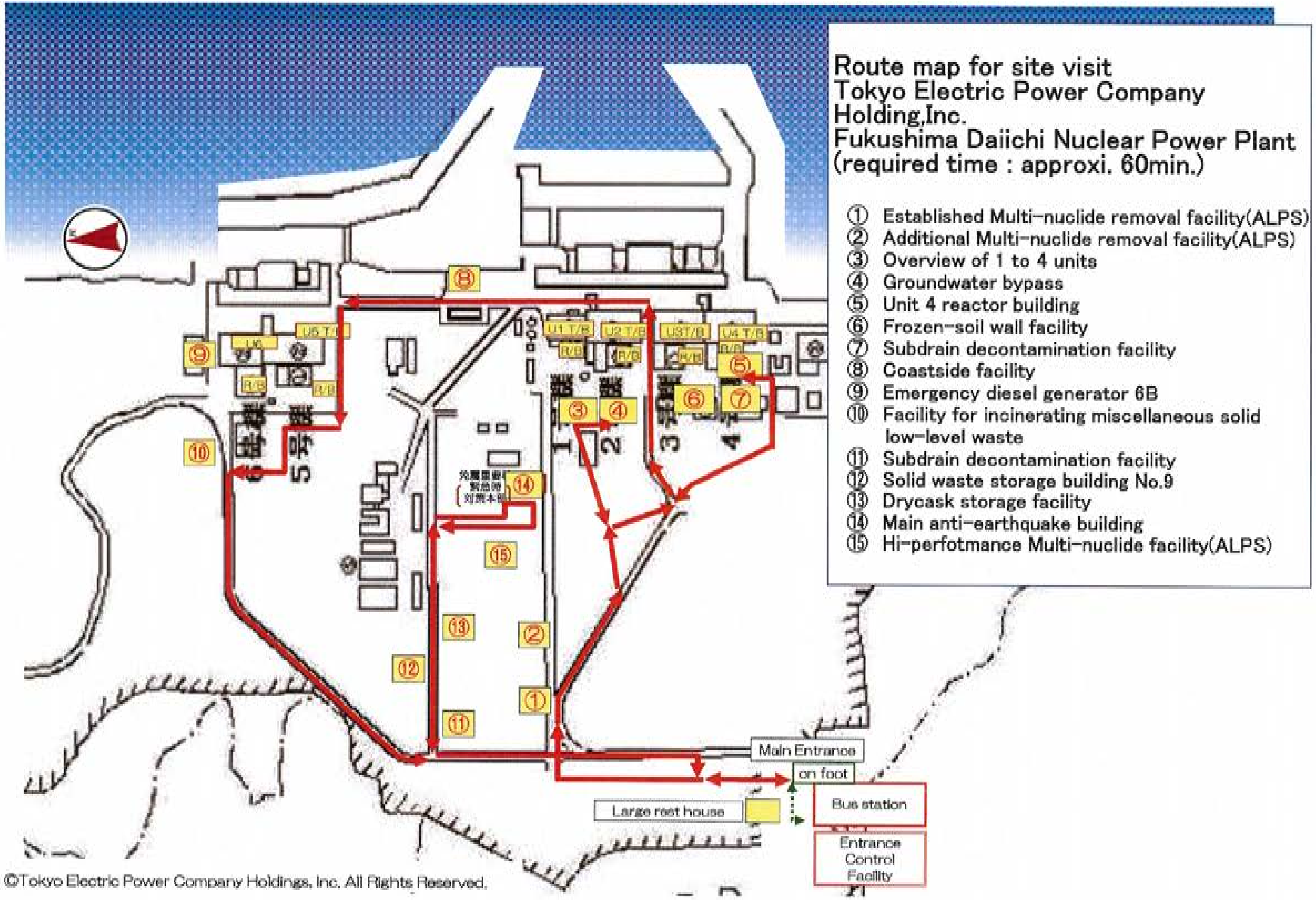
No significant change was identified in the atmospheric dose level due to investigation inside the PCV of No.1-3 Unit.

Fukushima Daiichi NPS Map



提供：日本スペースイメージング㈱, (C)DigitalGlobe

附件三：1F 電廠參觀路徑圖



Route map for site visit Tokyo Electric Power Company Holding,Inc. Fukushima Daiichi Nuclear Power Plant (required time : approxi. 60min.)

① Established Multi-nuclide removal facility(ALPS)
② Additional Multi-nuclide removal facility(ALPS)
③ Overview of 1 to 4 units
④ Groundwater bypass
⑤ Unit 4 reactor building
⑥ Frozen-soil wall facility
⑦ Subdrain decontamination facility
⑧ Coastside facility
⑨ Emergency diesel generator 6B
⑩ Facility for incinerating miscellaneous solid low-level waste
⑪ Subdrain decontamination facility
⑫ Solid waste storage building No.9
⑬ Drycask storage facility
⑭ Main anti-earthquake building
⑮ Hi-perfotmance Multi-nuclide facility(ALPS)

附件四：本所發表論文

Corrosion Behavior of A106B Carbon Steel in Still Water Environment after Decommissioning of Nuclear Power Plant

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Objectives

1. To investigate the corrosion behavior of A106B carbon steel tubing in still water environment after decommissioning of nuclear power plant.
2. To measure the corrosion rate of A106B carbon steel tubing in still water environment and prevent the leaking of decommissioned nuclear power plant.

Experimental

Table 1 Chemical composition of A 106 B

Content	Fe	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	V
Cold-drawn	Balance	0.15	0.17	0.43	0.015	0.003	0.05	0.02	0.02	0.02	0.001
Hot-rolled	Balance	0.21	0.17	0.39	0.013	0.006	0.02	0.01	0.02	0.005	0.001

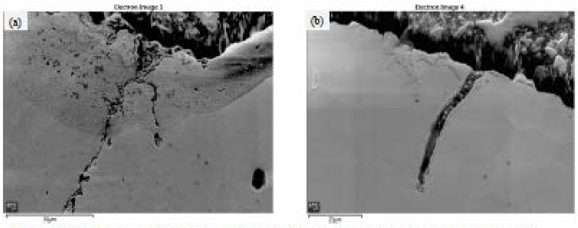

Figure 1 SEM metallographs of inner wall of the as-received (a) cold-drawn and (b) hot-rolled specimens.

Figure 2 (a) Before corrosion test specimens and after corrosion specimen (b) before cleaning (c) after cleaning

- Cold-drawn (C) and hot-rolled (H) A106 B tubing were used in this still water corrosion test . The temperature was maintained in 45 ℃ during the corrosion test.
- The lengths of the longest cracks at inner wall of as-received cold-drawn and hot-rolled specimens were about 100 μm and 50 μm, respectively.

Results and discussion

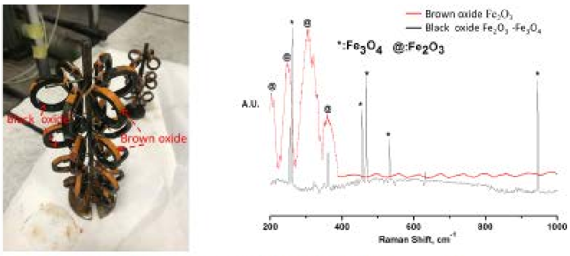

Figure 3 Raman analysis of Fe oxides produced during the corrosion test.

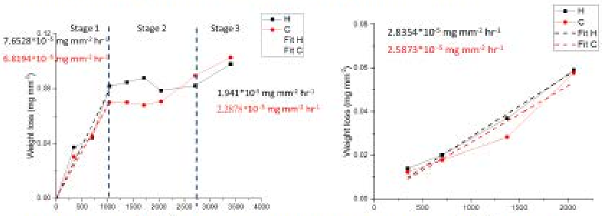

Figure 4 Weight loss of A106 B specimen immersed at (a) the beginning of the test, and (b) 1036 hours after the test.

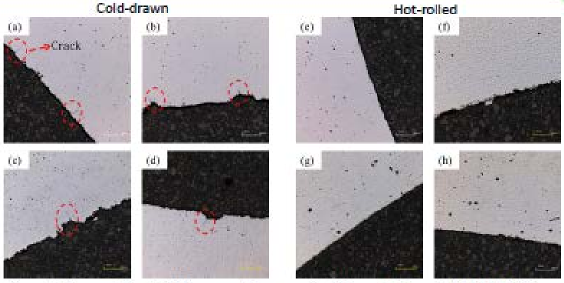

Figure 5 Cross-sectional OM images of inner wall of the cold-drawn (a) 345 (b) 698 (c) 1036 (d)1373 hours and hot-rolled (e) 345 (f) 698 (g) 1373 (h) 2040 hours.

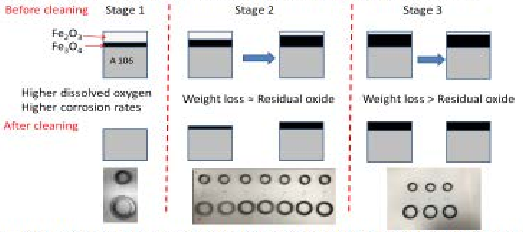

Figure 6 Illustration of the weight loss behavior in A106 B specimens during the corrosion test.

Conclusions

- ◆ The experimental results show that the corrosion rates of A106 B in still water environment at 45 ℃ are divided into three stages.
- ◆ The corrosion rates of cold-drawn and hot-rolled A106 B in Stage 1 are 8.69 * 10^{-3} μm hr^{-1} and 9.75* 10^{-3} μm hr^{-1}, and in stage 3, 2.47 * 10^{-3} μm hr^{-1} and 2.91* 10^{-3} μm hr^{-1}, respectively. The corrosion rates in Stage 1 are higher than those in Stage 3 because the dissolved oxygen level was higher in Stage 1 and the Fe_3O_4 oxide layer gradually formed in stage 3 during corrosion.
- ◆ The A106 B in still water environment at 45 ℃ was uniformly corroded and pitting was not observed.