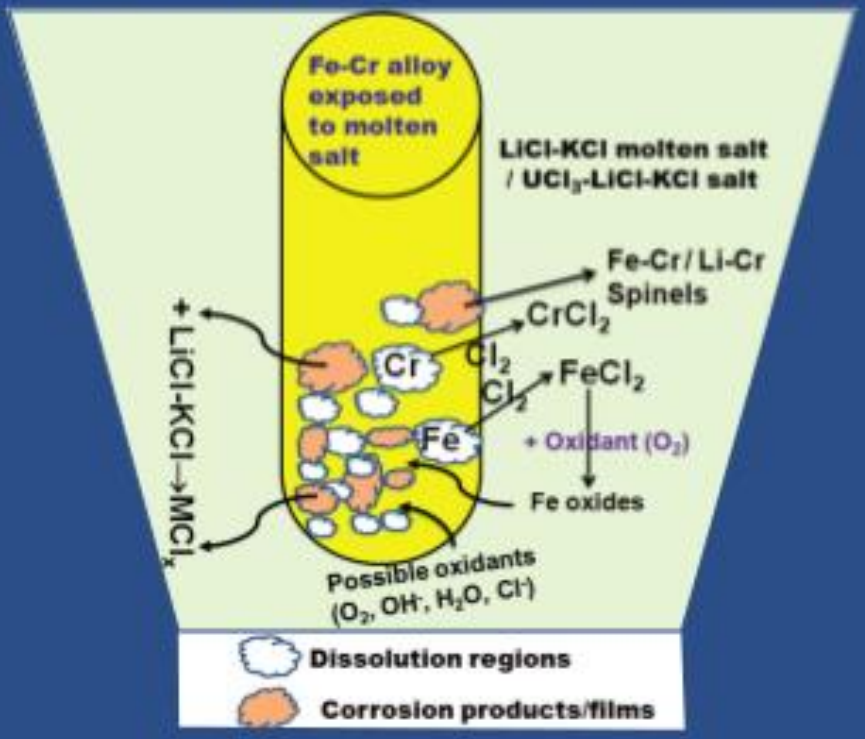
IANCAS Bulletin

Corrosion Control and Mitigation Strategies in Nuclear Power Plants



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Corrosion Control and Mitigation Strategies in Nuclear Power Plants

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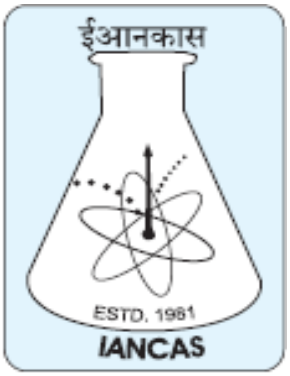

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Editor, IANCAS

Corrosion Control and Mitigation Strategies in Nuclear Power Plants

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FOCUS

It is with great pleasure that I present this volume on "*Corrosion Control and Mitigation Strategies in Nuclear Power Plants*". The bulletin brings together the challenges faced in the conventional side of various types of nuclear reactors and ensuing support streams in the nuclear industry.

The nuclear industry makes a substantial contribution towards meeting the ever increasing demand for power in a vibrant economy like India. Corrosion of structural materials is inevitable in any process stream. At the design stage of a nuclear plant, every effort is made to foresee the corrosion challenges and address them. Most of the corrosion issues faced by the plant, barring a few, fall under the category of anticipated challenges. Efforts are always on to improve and improvise the acquired knowledge to effectively tackle these issues. Critically evaluated operational experience augmented by improved materials and methodologies, the outcomes of directed research, have proven to be very effective in mitigating the corrosion issues.

The topics cover issues encountered in both secondary and tertiary side of Pressurised Heavy Water Reactors. The issues include both corrosion and bio-fouling, where an interdisciplinary approach often yields tangible benefits. Water chemistry control in these circuits plays a major role in ensuring that the intended design life and even beyond is achieved. The efficacy and viability of improved technologies in addressing the issues are highlighted. In addition, an entirely different aspect, like corrosion of structural materials in the fast reactor and associated reprocessing streams is discussed. This collection is a collage of corrosion issues faced by the nuclear industry.

I compliment the Guest Editors and all contributing authors for their sustained efforts in compiling this volume including the team of IANCAS for publishing this bulletin. I am confident that it will serve as a ready reference for operators, researchers and students engaged in the corrosion aspects of nuclear structural materials.

From Editor's Desk

Studies on corrosion mechanism of structural materials and its control in reactor operating conditions are main focus towards safe, reliable, and economic operation of nuclear power plants. Corrosion, fouling and materials degradation pose significant challenges in operation of water-cooled nuclear power plants. It is necessary for continuous R&D work in corrosion studies and control mechanisms utilizing important corrosion products. The current issue of the IANCAS bulletin is focused on bringing out a comprehensive account of these challenges and mitigation strategies through a mix of articles that are focussed on fundamentals and operational experiences.

The contributions highlight how sustained operational feedback, advances in materials science, and rigorous control of environmental parameters, water chemistry in particular, enable power plant operators in evolving effective strategies towards reducing the down time and maintaining the structural material integrity through the operational years. While PHWR is currently the main stay of Indian nuclear power program, the inclusion of PWRs and FBRs and advanced fuel cycle environments broaden the perspective to future technologies of our requirements. Taken together, this bulletin underlines the need for a sound understanding of environment-material interactions and for practical mitigation strategies based on experience and targeted research. It is hoped that this bulletin will be useful to NPP operators, researchers, and research students alike. This issue of the IANCAS bulletin on "*Corrosion Control and Mitigation Strategies in Nuclear Power Plants*" presents a well-curated collection of seven articles that reflect the current challenges and evolving nature of corrosion management practices in the nuclear industry.

On behalf of IANCAS, I thank all the authors for sharing their exhaustive research and development works for making this bulletin an important one. On behalf of IANCAS, I would like to sincerely thank the Guest Editors of this issue Dr. Veena Subramanian, SO/H, and Dr. Anupkumar, B., SO/H, WSCD, BARC-Kalpakkam in bringing out this important issue of IANCAS bulletin. I am very much thankful to Dr. T. V. Krishna Mohan, OS, & Head, WSCD, BARC and Facility Director, BARCF-Kalpakkam, for his support and encouragement, and also for his message under FOCUS. Sincere thanks to all other EC members including Dr. S. K. Sharma, Secretary, IANCAS for the continued support & time to time suggestions to bring out such type of thematic bulletins relevant for DAE, Industry and Society.

We sincerely thank Dr. A. K. Mohanty, Chairman, AEC & Secretary, DAE, and Shri Vivek Bhasin, Director, BARC, for their continued support towards IANCAS activities and IANCAS Publications. On-Behalf of IANCAS, sincere thanks and acknowledgement to Board of Research in Nuclear Sciences (BRNS), DAE; Chairman, BRNS, and Scientific Secretary & Head, BRNS for their support and granting the funds towards IANCAS publications of such relevant thematic bulletins.

Dr. Raghunath Acharya
Editor, IANCAS
OS & Head, IRAD, RC&IG, BARC

President's Message

Dear Friends,

Greetings for a Happy and Prosperous 2026!

I am happy to learn that the first volume of the IANCAS Bulletin for 2026 is being brought out on the very important topic which is quite relevant for the DAE, i.e., "*Corrosion Control and Mitigation in Nuclear Power Plants*".

This present bulletin is focussed on various aspects of corrosion related issues in Nuclear Power plants and its mitigation strategies. It offers an in-depth overview of different types of corrosion occurring in different components of the Nuclear Power plants. Corrosion mitigation strategies used for efficient operation for longer time of different components of the Nuclear reactors are also discussed in greater detail.

This thematic bulletin consists of seven articles having contributions from the experts in the field. Also, as the experts on this topic are from the Water and Steam Chemistry Division, BARC, Kalpakkam it is only apt that the guest editors, Dr. Veena Subramanian and Dr. Anupkumar B., are from that Division. I am thankful to the Guest Editors for their excellent editorial job by choosing the appropriate length of the articles with suitable contents and relevant information. I also appreciate the contributions of all those involved in preparing this valuable and informative volume.

A special thank you goes to the members of the IANCAS Executive Committee, particularly the Vice-President (HQ), Secretary, and Editor, for their dedicated efforts. The team acknowledges the financial support of BRNS, DAE.

Dr. P. K. Mohapatra
Former Director, RC&IG, BARC
President, IANCAS

From Secretary's Desk

Indian Association of Nuclear Chemists and Allied Scientists (IANCAS) was founded in the year 1981 with an objective of popularizing nuclear and radiochemistry, applications of radioisotopes, and nuclear techniques among the scientific community in India. For this purpose, IANCAS is continuously organizing seminars, National workshops and publishing periodic thematic bulletins focused on fundamentals of nuclear and radiochemistry, and applications of radioisotopes in education, research, agriculture, medicine and industry. With active participations of the life-members, IANCAS has become one of the leading scientific associations for popularizing the subject of nuclear and radiochemistry across the country.

IANCAS through its various outreach programmes motivate the young researchers and scientists to apply nuclear and radiochemistry based methods in their respective research field. In addition, IANCAS life-members through IANCAS activities motivate students to pursue a career in the field of nuclear science. For the promotion of nuclear science among the researchers, IANCAS has instituted three Awards; (i) Dr. M. V. Ramaniah Memorial Award, (ii) Dr. Tarun Datta Memorial Award, and (iii) Prof. H. J. Arnikar Best Thesis Award. All these three Awards are conferred annually. The details of these Awards are available at the IANCAS website (www.iancas.org.in).

IANCAS conducts national workshops and outreach programmes at Indian universities and colleges. IANCAS also regularly publishes thematic bulletins on the topics directly related to the nuclear science and technology with the financial support from BRNS, DAE. These bulletins are made available to all the IANCAS life-members, and are freely available at IANCAS website (www.iancas.org.in) for download.

In the series of IANCAS bulletins, the present bulletin titled "*Corrosion Control and Mitigation Strategies in Nuclear Power Plants*" aims at giving details of different types of corrosion faced by structural components of nuclear reactors and their different mitigation strategies. IANCAS thanks to all contributors/authors of the articles for sparing their valuable time and in making such an important bulletin possible. I sincerely thank, Dr. R. Acharya, Editor, IANCAS, and the Guest Editors Dr. Veena Subramanian, SO/H, and Dr. Anupkumar B., SO/H, WSCD, BARC facility, Kalpakkam, Tamil Nadu for their efforts in bringing out this important thematic bulletin.

Dr. Sandeep Kumar Sharma
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Preface from Guest Editors

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Corrosion and fouling continue to pose significant challenges for safe and reliable operation of water-cooled nuclear power plants. Corrosion, fouling, and materials degradation, often subtle in their early manifestation, can progressively weaken structural materials, heat transfer efficiency, and ultimately plant availability. The current issue of this bulletin is focused on bringing out a comprehensive account of these challenges and mitigation strategies through a mix of articles that focus on fundamentals and operational experiences.

The issue begins with articles addressing corrosion phenomena in the *secondary side of water-cooled reactors*, with particular relevance to Indian PHWRs. The secondary circuit, though non-radioactive, due to its role as a critical safety barrier and heat transfer pathway, demands stringent control over corrosion and transport of oxides (corrosion products). The contributions in this section bring out the fact that chemistry-control is as important as material selection and hydraulic design in preventing secondary side degradation through flow accelerated corrosion, deposition, and localised corrosion attacks. Further, these articles reinforce the importance of devising optimum water chemistry conditions and their effective implementation in protecting steam generator integrity, thereby enhancing overall plant reliability.

Extending this discussion, the bulletin moves to the challenges encountered in *tertiary cooling water systems*, which are particularly relevant to coastal nuclear power stations in India. Tertiary systems face additional complexities, including biofouling, microbiologically influenced corrosion, and accelerated material degradation under highly variable environmental conditions present in seawater and fresh water sources. The articles in this section highlight how corrosion and fouling of seawater intake structures and cooling system components can have cascading effects on maintenance requirements and plants' performance. The adoption of advanced antifouling and corrosion-control coatings, as discussed here, demonstrates a pragmatic approach derived from cumulative operational experiences and targeted research towards mitigating these issues.

The final set of articles shifts the focus toward *fast reactors and advanced fuel cycle environments*, an area of strategic importance for India's three-stage nuclear programme. Materials in fast reactor systems are subjected to environments that differ fundamentally from those in water-cooled reactors, including high-temperature liquid metals, molten salts, and aggressive reprocessing chemistries. The discussions on corrosion in molten salt media and pyrochemical reprocessing environments underline the necessity of developing advanced structural materials and protective coatings capable of withstanding such extreme conditions. These contributions reflect ongoing R&D efforts within DAE laboratories aimed at enabling safe, reliable, and sustainable operation of fast reactors and closed fuel cycle technologies.

Effective corrosion management requires a deep understanding of environment-material interactions, proactive monitoring, and adoption of prudent mitigation strategies tailored to each system. It is hoped that this compilation will not only serve as a technical reference for practitioners but also stimulate cross-disciplinary thinking, encouraging lessons learned in one domain to provide solutions in another.

We express our gratitude to IANCAS for facilitating this volume. We thank the authors for their valuable and timely contributions, which made this issue possible.

Corrosion and Its Control in Secondary Systems of Water–Cooled Reactors

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Abstract

The secondary coolant systems of water-cooled nuclear reactors play a critical role in heat transfer and power generation while serving as a safety barrier between the radioactive primary circuit and the non-radioactive conventional side. Owing to the use of carbon steel and the presence of both single-phase and two-phase flow regimes, these systems are susceptible to a variety of corrosion and degradation mechanisms. This article provides an overview of the major corrosion processes affecting secondary systems, with particular emphasis on steam generators in Pressurized Heavy Water Reactors. Key degradation modes such as flow-accelerated corrosion, pitting and crevice corrosion, and stress corrosion cracking are discussed in terms of their mechanisms, influencing factors, and consequences for system integrity. The role of secondary-side water chemistry, including pH control, dissolved oxygen, and impurity minimization is highlighted as the primary means of corrosion control. Conventional mitigation strategies such as all-volatile treatment (AVT), high-AVT, and oxygenated treatment (OT) are discussed in brief, along with emerging approaches based on film-forming amines, especially octadecylamine. The benefits, limitations, and practical considerations associated with these treatments are mentioned. Overall, the article emphasises the importance of optimized chemistry control, material selection, and evolving corrosion-inhibition strategies to enhance the reliability, safety, and longevity of secondary coolant systems in water-cooled nuclear reactors.

Keywords: *Steam Generator, Flow Accelerated Corrosion, All Volatile Treatment, Octadecylamine*

1. Introduction

The secondary coolant system of water cooled reactors is essentially non-radioactive and its main purpose is to receive heat from primary coolant in a heat exchanger, typically called as Steam Generator (SG). Subsequently the water boils into steam that drives the turbine and then condenses back into water to repeat the cycle. Hence secondary system consists of steam generators, condensers and feed water loops.

As they form the safety barrier between the radioactive primary side and the non-radioactive secondary side, any degradation mechanism, which impairs this barrier function, is a significant safety concern. In this article some of the corrosion processes that are of importance to secondary coolant systems will be explained in brief.

There are mainly three types of water cooled nuclear reactors namely, Pressurized Water Reactors (PWR), Pressurized Heavy Water Reactors (PHWR) or CANDU type of reactors, and Boiling Water reactors (BWR). Out of these PWRs and PHWRs have a separate secondary coolant system. The components of the secondary coolant system of these two types of reactors are similar consisting of steam generators, turbines, condensers, feed water heaters, and associated piping, though their layouts can be different. In this article most of the discussions are limited to SGs of PHWR system. Figure 1 gives a simplified schematic diagram of secondary circuit. The steam produced in the steam generator is fed to turbine to produce electricity. The steam then will be condensed, preheated and sent back as the boiler feed water. It can be observed that throughout the circuit, there will be presence of both steam phase and water phase. In PHWR, in the boiler, where the boiling takes place in the secondary feed water, the materials of construction are carbon steel 106 grade B (CS) at the

secondary side and Incoloy 800 at the primary side. In addition, most of the other structures in the secondary side are made of carbon steel. Hence, it becomes the major structural material of construction and the corrosion control of the secondary system is mostly based on properties of CS under both single and two phase environment. In Indian PHWR's secondary circuit the coolant temperature ranges from 40 °C in the condensate to 150–170 °C in feed water. The pH is adjusted in the range of 8.8–9.3 using ethanolamine [1, 2]

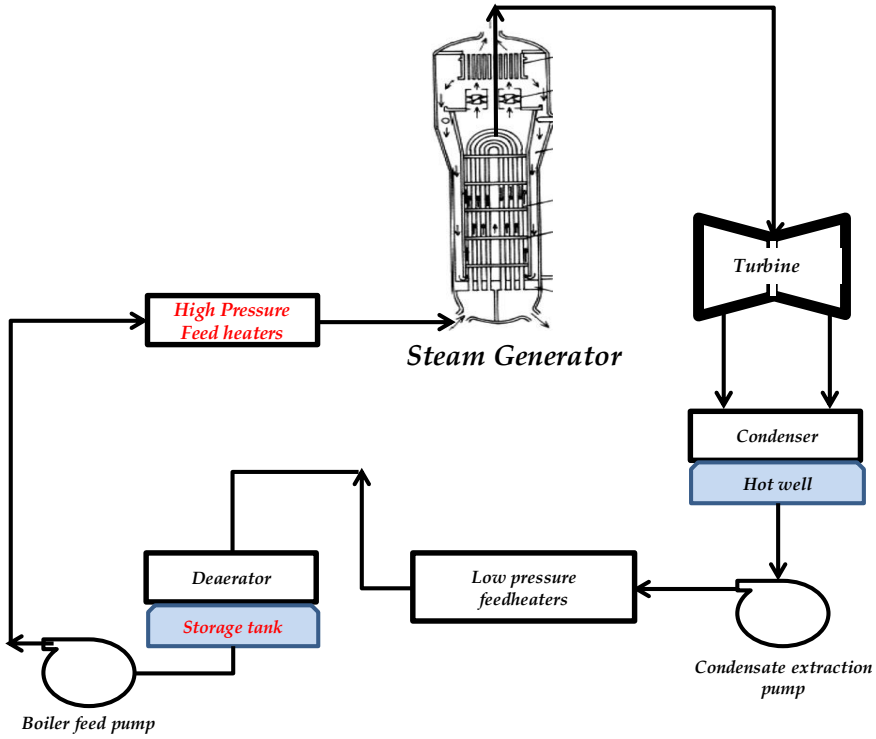

Figure 1. Simplified schematic diagram of secondary coolant system.

2. Overview of Secondary System Chemistry

The primary objective of maintaining appropriate water chemistry conditions in the secondary system is to minimize corrosion and corrosion-product release, prevent corrosion-product deposition, and limit impurity concentrations that may promote under-deposit corrosion. Since plant design and structural materials are fixed parameters, water chemistry remains the only variable that can be optimized to achieve these goals. The most critical water chemistry parameters to control throughout the steam–water cycle are pH and dissolved oxygen (DO).

As noted earlier, most structural components are constructed from carbon steel. Copper and copper alloys are commonly used in heat-exchanger tubing, while stainless steels and titanium are typically employed for condenser materials. Ideally, pH should be maintained at a level that minimizes corrosion across all materials i.e. approximately pH 10 is optimal for carbon steel. However, challenges arise due to the presence of copper alloys, which experience minimal corrosion at around pH 8.8 and are highly susceptible to localized corrosion in the presence of dissolved oxygen [1,3].

As the secondary system includes both single-phase and two-phase flow regions, volatile alkalizing agents must be used so that the chemical environment is effectively controlled throughout the cycle. This approach is employed in All-Volatile Treatment (AVT), where amines which are weak bases, are added. Achieving pH 10 using minimal amine concentration is difficult, and therefore a compromise pH range of 8.5–9.5 is typically adopted in operating systems [2,4]. Considering the wide temperature variation across the secondary circuit (from ~40 °C in condensate lines to ~180 °C in feed water systems), the required amine concentration

must be carefully defined. The desirable amine concentration is generally described as the minimum concentration in the final feed water that ensures the pH_T remains at least one unit above the neutral point at all locations.

3. Types and Mechanisms of Corrosion

Corrosion product transport to steam generator can inhibit heat transfer on SG tubes and harbour impurities on tube sheet crevices resulting in generation of potential sites for under deposit corrosion, pitting etc. In addition to these the SG tubes can undergo Stress Corrosion Cracking (SCC) under specific conditions. Flow Accelerated Corrosion (FAC) is known to be one of the main modes of failure for carbon steel pipes [5].

3.1. Flow Accelerated Corrosion

Carbon steel exhibits enhanced corrosion due to the dissolution of normally protective magnetite layer in fast flowing water that is unsaturated in dissolved Fe, which is known as Flow Accelerated corrosion or FAC. This kind of corrosion typically leads to thinning of the pipes eventually leading to rupture (Fig. 2a). Hence FAC sometimes results in catastrophic failures of components. In fact, this is the only mechanism that leads to larger leaks in the secondary circuit piping. The material surface subjected to single phase FAC is characterized by an overlapping horse shoe or orange peel pattern (Fig. 2 b,c). If steam phase also is involved, the surface of the material shows "tiger stripe" appearance (Fig. 2d). The rate of FAC primarily depends upon four factors:

(1) *Hydrodynamics and the piping configuration:* The failure due to this mechanism is more severe in the places where flow disturbances will give raise to higher velocity and higher shear stress like in elbows, tees, reducers, orifices and pump outlets.

(2) *Water Chemistry:* Magnetite forms on carbon steel piping under the prevailing de-oxygenated conditions in the secondary system. The driving force for its enhanced dissolution under flow conditions is the concentration gradient between the dissolved iron in the flowing coolant and the solubility of magnetite at the operating temperature. So, this is primarily a chemical dissolution accelerated by mass transfer and not a mechanical process like erosion.

As presence of water is essential to remove oxide film, FAC does not occur in pipes carrying dry steam. Hence pH of the solution plays an important role. Figure 3 shows how solubility decreases with increasing pH at temperature range corresponding to feed water [6–8]. Higher pH in feed water (typically $pH_{25°C}$: 8.8–9.8) lowers FAC rates of carbon steel significantly. In addition, FAC rate decreases with increasing dissolved oxygen (DO), because the presence of slightly higher DO will promote formation of hematite instead of magnetite. Hematite resists FAC as it is about 1000 times less soluble than the magnetite [5,6,9]. And for the same reason, under reducing conditions FAC rates will increase.

(3) *Material composition:* FAC commonly occurs in mild steels, and several instances of carbon steel pipe failures have been reported [7,10]. There is also clear evidence that the presence of even small amounts of chromium in the alloy can significantly reduce or prevent FAC [11,12].

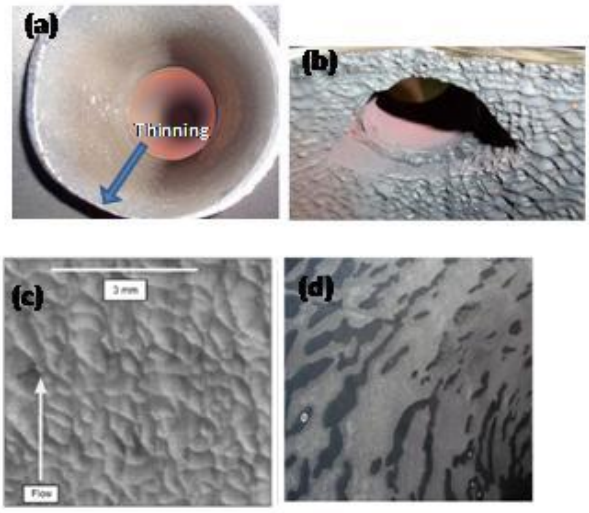

Figure 2. (a) HP heater drain pipe which has undergone FAC (b) Single phase FAC damage in a header showing scallops (c) typical dimension of scallops and (d) Tiger stripes typical of two-phase FAC (Reproduced with permission from publisher [6,7].

(4) *Temperature:* Under secondary side chemistry conditions FAC rate for carbon and

mild steels was found to have bell shaped dependence on temperature and is highest at ~150 °C at pH 7. Figure 4 shows that the temperature effect becomes prominent at higher flows [5,6,13].

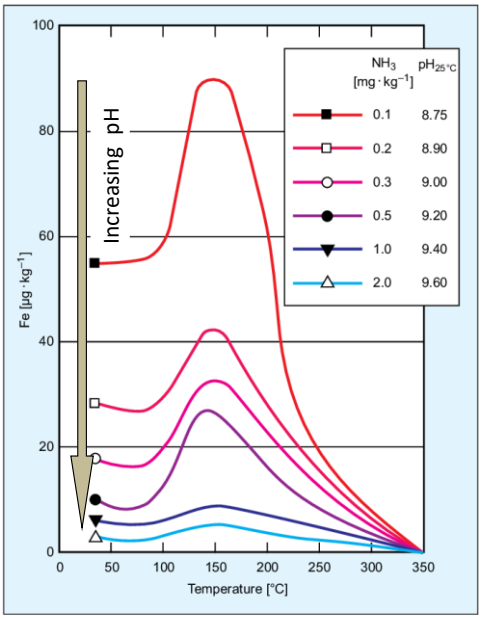

Figure 3. Variation of Solubility of Magnetite as a function pH and temperature (Reproduced with permission from author [6]).

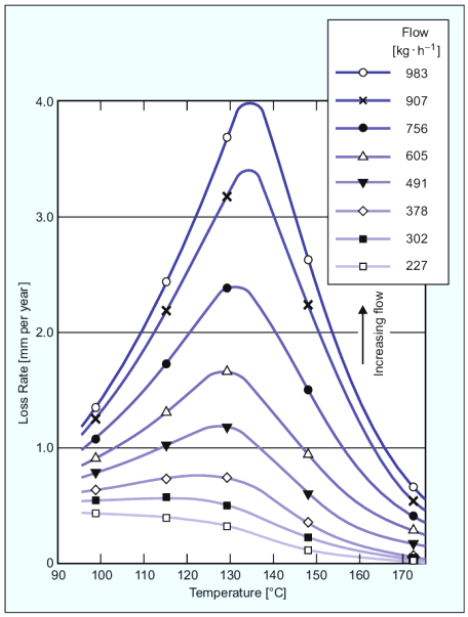

Figure 4. Effect of flow and temperature at $pH_{25°C}$ ~9 with Ammonia (Reproduced with permission from author [6, 13]).

3.2. Pitting and Crevice Corrosion

3.2.1. Pitting Corrosion

Pitting corrosion is a type of localised corrosion where certain areas will get preferentially corroded in alloys, leading to the development of holes or cavities in those areas while majority of the surface remains free from attack under aggressive environment. Pitting corrosion is characterized by the appearance of tiny perforations or holes on the SG surface (Fig. 5). It has an effect on passive alloys like stainless steel, aluminium, titanium etc. which forms an oxide that protects themselves from general corrosion.

Mechanism:

Pitting corrosion initiates via the formation of a differential aeration cell when a localized anodic site forms at a breakdown in the passive film, while the surrounding surface acts as a cathode. At the anode the metal dissolution takes place ($M \rightarrow M^{n+} + ne^-$) and is balanced by the cathodic oxygen reduction reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$). Continuous metal dissolution leads to a build-up of metal ions in the pit, driving the migration of aggressive anions such as chloride and sulphide if present in the bulk solution into the anodic region to maintain electroneutrality, forming metal chlorides. Subsequent hydrolysis of these metal chlorides produces acidic species ($MCl + H_2O \rightarrow MOH + HCl$), resulting in localized acidification within the pit. This autocatalytic generation of HCl sustains and accelerates metal dissolution, creating a self-propagating process of rapid localized corrosion that continues until the metal is ultimately perforated [14,15]. The mechanism of pitting is schematically depicted in Figure 5a [16].

Pitting corrosion may take months or years to become visible, though once initiated it can progress rapidly [15–18]. It commonly develops on upward-facing surfaces due to the trapping of corrosive solutions in pits, and is promoted by surface defects such as halide or sulphide inclusions and material heterogeneity [19]. Additional factors influencing pitting include surface finish, fluid velocity, environmental contamination, and temperature conditions. In nuclear power plants, pitting can lead to frequent shutdowns, eddy current inspections, tube repairs, and

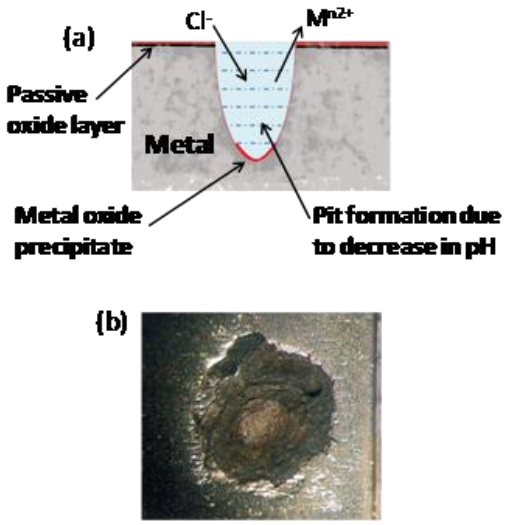

Figure 5. (a) A diagram illustrating mechanism of pitting [16] and (b) pitting on SG tube (Reproduced with permission from publisher from ref. 17).

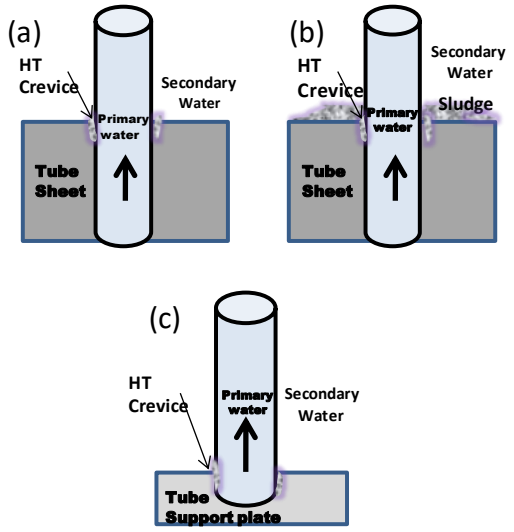

Figure 6. Illustration of crevices formed in tubes of nuclear SGs (a) at the top of tube-sheet (b) at the sludge on the TTS (c) at tube support plates [22, 26].

tube removal in steam generators. The likelihood of pitting increases under oxidizing conditions as well as while using AVT chemistry due to inadequate buffering and impurity accumulation [1,20,21]. Increased hydrazine levels help reduce pitting by minimizing oxidizing conditions.

3.2.2. Crevice Corrosion

Crevice corrosion is a form of localized corrosion that develops within narrow crevices or shielded regions (Fig. 6) [22] formed at metal–metal or metal–nonmetal interfaces, where stagnant electrolyte becomes trapped and micro-environmental conditions differ significantly from the bulk solution. In power plant systems, seawater is commonly used as a heat sink in the tertiary circuit, and any leakage into the feed water system can introduce chloride and other aggressive impurities. These contaminants accumulate within confined crevice gaps, where limited mass transport leads to progressive concentration of species by factors of 10^5 to 10^6, resulting in highly aggressive local chemistries [23,24]. The accumulation of impurities during reactor operation is referred to as hideout, while their release back into the bulk water during shutdown is termed hideout return [25]. Initiation of crevice corrosion essentially occurs due to the formation of differential aeration cell, with crevice mouth being deficient in oxygen act as anode and the rest of the surface act as cathode. Crevice corrosion can propagate rapidly and may severely compromise the structural integrity of engineering materials, often leading to unpredictable and premature failures [27].

Passivating alloys such as stainless steels, aluminium, titanium, and nickel-based alloys are particularly susceptible to crevice corrosion. Although both pitting and crevice corrosion arise from differential aeration cells, pitting does not require a specific geometric constraint and can initiate spontaneously, whereas crevice corrosion specifically develops in shielded or confined geometries [15]. Once initiated, crevice corrosion can accelerate and subsequently trigger secondary degradation mechanisms such as stress corrosion cracking (SCC), intergranular stress corrosion cracking (IGSCC), denting, atmospheric-induced SCC (AISCC), and intergranular attack (IGA) [22].

The fouling of steam generators (SGs) is partially mitigated through secondary water chemistry treatments, including all-volatile treatment (AVT). However, these approaches are often insufficient to prevent rapid degradation associated with denting and under-deposit corrosion that occurs in heated

crevice regions of SG tube-to-support or tube-to-tube interfaces [26]. Effective mitigation of crevice corrosion requires a combination of strategies, including appropriate material selection, design modifications to eliminate crevice-forming geometries, and avoidance of metal–metal or metal–nonmetal contact interfaces. Additional practices include rigorous inspection programmes, stringent control of water chemistry (e.g. hydrazine addition to reduce dissolved oxygen) [26], the use of molybdenum rich alloys, application of cathodic protection where feasible, preference for welded over riveted, lapped, or bolted joints, removal of sharp corners and stagnant flow zones, and frequent removal of deposits [14,15].

3.3. Stress Corrosion Cracking (SCC)

SCC is a major degradation mechanism in the secondary coolant systems of water-cooled reactors in both PWRs and PHWRs, particularly affecting components made of austenitic stainless steels, nickel-based alloys, and sensitized weld heat-affected zones (HAZ). SCC occurs due to the combined influence of tensile and residual stresses, corrosive chemical environments, and susceptible (sensitive) materials [28,29]. In secondary systems, impurities such as chlorides, sulphates, and caustic environments, under deposits contribute significantly to SCC initiation and propagation. Oxygen ingress, condenser leakages (especially seawater ingress), and cyclic loading can further accelerate cracking in areas such as steam generator tubing, feed water heaters, moisture separator drains, and turbine components [30].

Intergranular Stress Corrosion Cracking (IGSCC) is observed to be more prevalent than transgranular SCC (TGSCC). This is mainly because the materials commonly used in secondary system, such as sensitized austenitic stainless steels and nickel-based alloys (especially Alloy 600) tend to develop chromium depletion at grain boundaries during welding or thermal exposure by the process known as sensitization. This makes grain boundaries preferential sites for *crack initiation* when exposed to aggressive impurities such as chlorides, caustic species, and sulphates, particularly under tensile stresses and crevice or deposit environments. Thus, these boundaries provide a path of least resistance due to their weakened passive film. As a result, cracks typically propagate in an *intergranular fashion*. Transgranular SCC *can* occur, particularly in high-strength alloys or under caustic environments, but it is generally less common than IGSCC in nuclear secondary water systems [15,22,29,31]. Figure 7a,b presents some of the examples of SCC in SG tubes and figure 7c illustrates the probable locations of failure in SG components due to the SCC mechanism [31].

4. Corrosion Control and Mitigation Strategies

Corrosion and the transport of corrosion products must be strictly controlled to ensure the integrity of secondary-side components. Preventive measures include avoiding contamination and leakage into condensers, eliminating copper-bearing materials from secondary systems, maintaining proper water chemistry, and performing regular blowdown to remove accumulated sludge and deposits. In addition, the corrosion resistance of structural materials can be enhanced through alloying with elements such as Mo, Re, Ag, and Ni [18]. Overall, effective prevention relies on maintaining high-purity water chemistry, operating at higher pH with low dissolved oxygen to minimize the formation of aggressive ions, and preventing crevice and deposit formation through efficient filtration and controlled blowdown [1,3]. These preventive strategies are summarized as follows:

4.1. Water chemistry Control

High-All Volatile Treatment (H-AVT) is a water-chemistry regime used in the steam–water cycle to maintain a higher feed water pH using only volatile amines targeted mainly to counter FAC. This elevated pH_{25}> 9.8 significantly reduces the solubility of magnetite and thereby minimizes FAC in carbon steel components. In general H-AVT uses NH_3 and Hydrazine as reducing agent. An addition of about 100 µg/kg of hydrazine serves as oxygen scavenger and produces NH_3 again on thermal decomposition ($2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$) thus playing a role in both corrosion reduction and pH increase. It is known from plant experience that by applying H-AVT a final feedwater concentration of Fe

below 1 µg/kg was achievable. As a result, in addition, High-AVT lowers corrosion-product transport to the steam generator, helps maintain cleaner heat transfer surfaces, and reduces the risk of under deposit corrosion. Even though this method is quite simple to apply and quite effective, a prerequisite for this treatment is the absence of any copper alloys in the system. Moreover, maintaining a lower pH (~9.2) using only NH_3 addition in secondary systems has been found to be ineffective in preventing FAC, as evidenced by the Mihama accident [32]. So, in such cases alternative amines such as morpholine, Ethanolamine (ETA), Dimethyl amine (DMA) and Methyl propanolamine (MPA) are used [3]. Figure 8a,b give the dissociation constants and distribution coefficients of these amines as a function of temperature [33]. Some of these amines possess higher dissociation constant and a better distribution coefficient between steam and water phase and hence can give better protection against FAC as compared to NH_3.

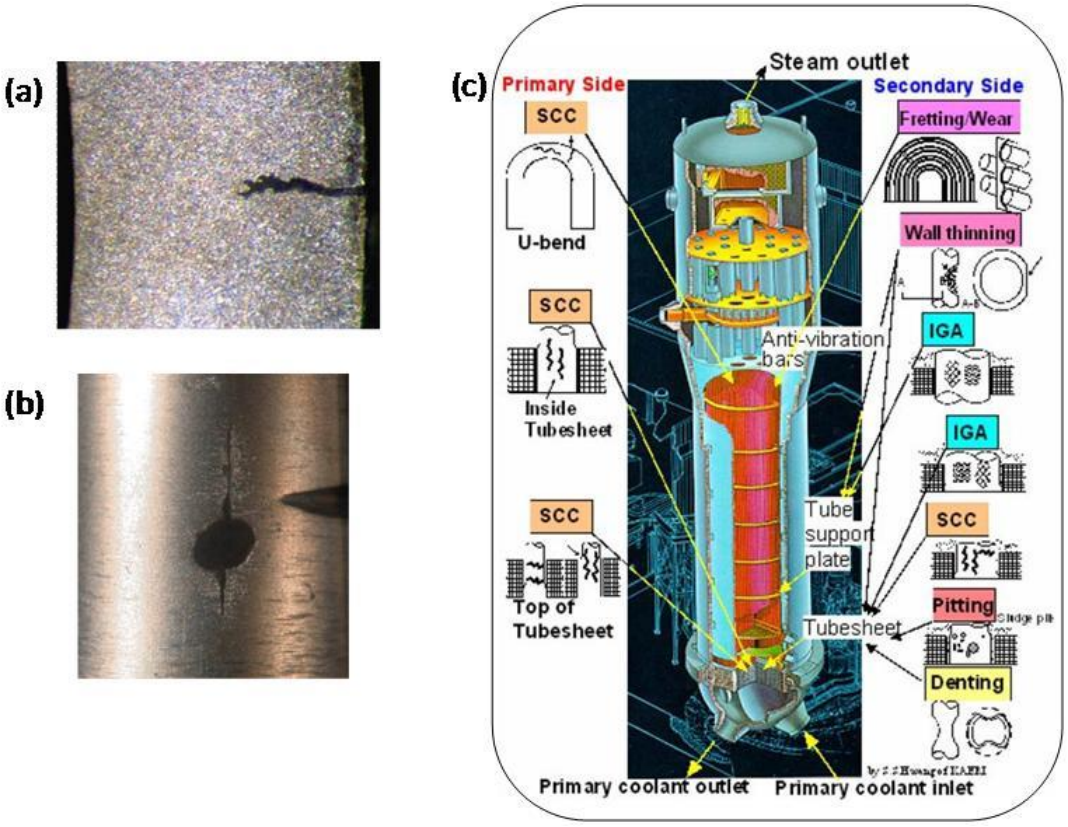

Figure 7. (a) SCC on (b) SCC associated with pitting on South Ukraine NPP tube and (c) Degradation mechanisms of SG components and the most probable location of failure (Reproduced with permission from publisher [31]).

Ethanolamine (ETA) has become the most widely used alkalizing amine in power-plant steam–water cycles. Advantages of ETA are:

- High dissociation constant
- Has moderate volatility with distribution coefficient (K_d) < 1
- Low concentration of organic acids produced on thermal decomposition
- Environment friendly

High basicity gives same pH_T with lower concentration of amine. K_d < 1 helps to maintain elevated pH even in the steam and condensate return lines where carbon steel is most vulnerable. ETA has comparatively good thermal stability, so its decomposition into organic acids is limited. Compared to morpholine, ETA produces fewer organic acids, resulting in lower cationic conductivity.

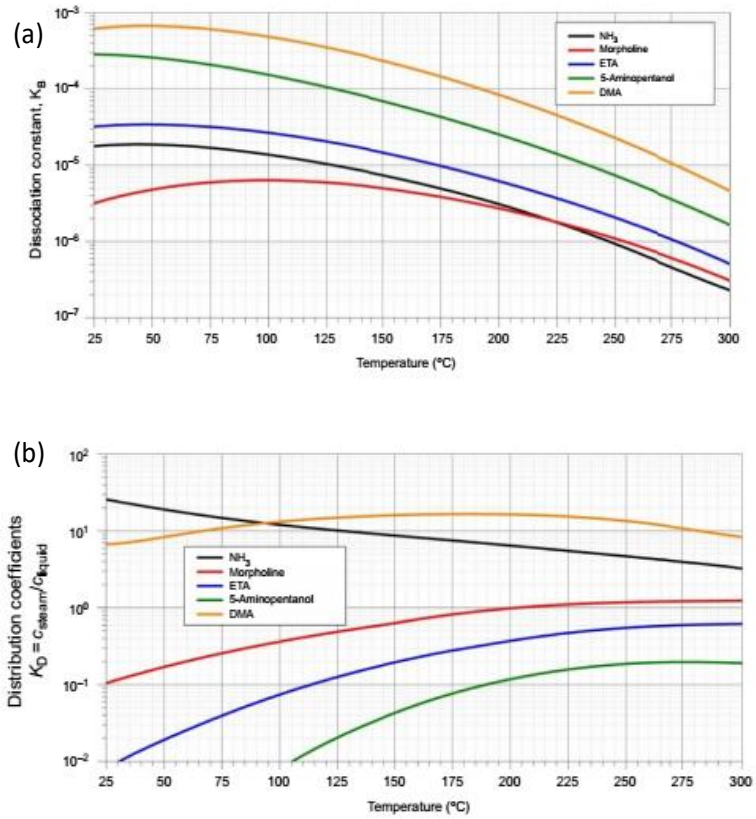

Figure 8. (a) Dissociation and (b) Distribution coefficients for the alkalizing amines (Reproduced with permission from publisher [33]).

4.2. Oxygenated Treatment (OT)

Oxygenated Treatment is used mainly to reduce FAC in carbon-steel components. In OT, a small controlled amount of dissolved oxygen is intentionally maintained in the feed water just upstream of the SG, which promotes the formation of a less soluble, protective hematite (Fe_2O_3) layer instead of the more soluble magnetite (Fe_3O_4). This dense hematite film greatly suppresses FAC rates, leading to lower corrosion-product transport and improved integrity of feed water piping, heaters, and steam-generator internals. OT is particularly effective in plants with all-ferrous feed water systems where maintaining a protective oxidizing environment is feasible.

4.3. Emerging approaches to contain corrosion

Use of Film-forming amines (FFA) or film-forming products (FFP)

FFAs constitute an important class of corrosion inhibitors used in the secondary side of power plants, particularly in condensate and feed water systems. These long-chain aliphatic amines possess a polar amine head group which enables them to adsorb strongly on carbon steel and magnetite surfaces and a hydrophobic hydrocarbon tail (Fig. 9) [6].

The general formula of FFA is $R_1 - [- NH - R_2 -]_n - NH_2$, where n is an integer between 0 to 7, R_1 is an un-branched aliphatic chain with carbon atom between 8 and 22. R_2 is a shorter hydrocarbon chain with 1 to 4 carbon atom [34]. Upon adsorption, FFAs form a thin, water-repellent film that acts as a barrier to corrosive species thereby reducing general corrosion and single phase FAC to some extent. Their effectiveness is influenced by molecular structure, chain length, water chemistry, temperature, and hydrodynamic conditions. In high-temperature secondary systems, FFAs are especially attractive because they can provide protection in both single-phase and two-phase regions where

conventional alkalizing treatments alone may be insufficient [3,35]. Octadecylamine (ODA)

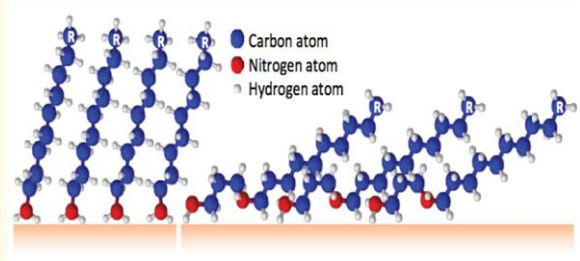

Figure 9. Schematic representations of FFA films: monoamine (left), polyamine (right) (Reproduced with permission from author [6]).

has been the most widely studied and applied FFA in power plant secondary circuits [34] ODA forms a compact and adherent film through physical adsorption and/or partial chemisorption on metal and metal oxide, with film stability improving at elevated temperatures typical of feed water and steam generator inlet conditions. At temperatures around 120–180 °C, ODA shows enhanced affinity for oxide surfaces, leading to significant reductions in corrosion rates when properly dosed. The performance of ODA is strongly dependent on its method of application; because of its low water solubility, it is commonly injected as an emulsion or dispersion [36].

In secondary-side chemistry regimes, ODA is often used as a complement to AVT or oxygenated treatment, rather than a replacement. When optimized, ODA-based treatments can improve surface hydrophobicity, reduce iron transport, and extend component life without adversely affecting heat transfer or steam generator performance. In fact, the experience has shown improved heat transfer efficiency after ODA treatment. ODACON® is a commercial film forming amine based on ODA. This is a proprietary chemical by REICON, Germany. Many of the PWRs and PHWRs have been recently using this chemical and found this effective. Figure 10 illustrate the benefits of this ODA-based formulation [36].

Some of the known benefits of ODA can be listed as:

- It reduces corrosion and corrosion product transport.
- Improved readiness after shutdown due to improved feed water quality.
- Improved SG performance.
- Minimization of hydrazine usage for wet layup.
- It does not affect the existing oxide layer.
- On thermal decomposition it does not give rise to organic acids that raise conductivity and induce corrosion.*

Owing to these factors, ODA treatment saves cost during long shutdowns.

Some of the limitations can be listed as follows:

- Known to form sticky gunk balls when used in excess quantity – Hence it is very important to optimize the concentration.
- Its interaction with IX resins not very well known – few studies are there on how it impacts Condensate polishing unit or blowdown IX [37].
- Fouling of online probes.
- During application, accurate estimation is difficult as it gets adsorbed on all surfaces.

Research has suggested that octadecylamine can mitigate FAC in single-phase flow but are less effective in two-phase environments [38].

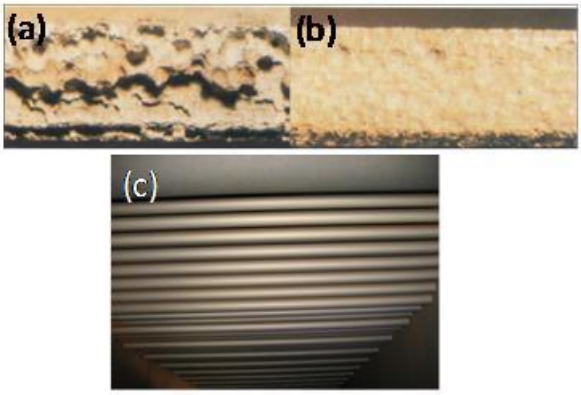

Figure 10. (a) Stereomicroscopic view of a carbon steel (ST38) exposed to water: without ODACON and (b) with ODACON and (c) a photograph showing a hydrophobic surface after treatment with ODACON (Reproduced with permission from author[36]).

*In general, thermal degradation of FFAs results in the formation of low molecular weight organic acids that increase conductivity. In addition, these acids, which usually exist as negatively charged ions in water, are known to accelerate metal corrosion. Because of this, maintaining FFA protection in the water–steam circuit is challenging. However, in the case of ODA, its decomposition occurs between 80 to 450 °C with complete decomposition occurring around 480 °C. The decomposition products of ODA are known to be NH_3(in traces), H_2, CO, CH_4, hydrocarbons and additionally di and tri-ODA.)

In summary, even though FFAs are quite beneficial, careful control of dosing, and compatibility with system materials is essential to avoid deposition or fouling. As a result, ongoing research and operational experience continue to refine the application of ODA and other FFAs as effective corrosion mitigation tools in high-temperature power plant environments.

5. Conclusions and future Outlook

Corrosion of the secondary systems of water-cooled reactors remains a significant challenge due to the combined effects of high temperature, complex flow conditions, diverse materials, and stringent safety requirements. Among the various degradation mechanisms, flow-accelerated corrosion of carbon steel continues to be the most critical, with the potential for rapid wall thinning and catastrophic failures if not adequately controlled. Localized corrosion processes such as pitting, crevice corrosion, and stress corrosion cracking further pose problems for the integrity of steam generators and associated components, particularly under conditions of impurity ingress, under deposit formation, and unfavourable aggressive micro-environments.

Effective corrosion mitigation in secondary systems depends predominantly on optimized water-chemistry control, as plant design and material choices are largely fixed once a reactor is in operation. High-AVT and oxygenated treatment have proven effective in reducing FAC when properly implemented and when system material compatibility permits (like all ferrous alloy system). The increasing application of ethanolamine has enabled improved pH control across the steam–water cycle. In recent years, film-forming amines such as octadecylamine have emerged as promising supplements to conventional chemistry regimes, offering additional protection through the formation of hydrophobic surface films that significantly reduced corrosion-product transport.

While operational experience has demonstrated appreciable benefits from FFA-based treatments, their successful deployment requires careful optimization of dosing, monitoring of surface interactions, and assessment of compatibility with condensate polishing systems and online instrumentation. Continued research, coupled with feedback from plant experience, is therefore essential to refine these approaches. In conclusion, a strategy integrating robust chemistry control, informed use of inhibitors in the form of film forming amines, vigilant monitoring, and periodic inspection is essential for ensuring the long-term reliability and safety of secondary coolant systems in nuclear power plants.

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Copper Corrosion Control in the Turbogenerator Stator Water System of MAPS

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Abstract

In the large turbogenerators, direct cooling of the stator is adopted with the coolant directly led to and discharged from the hollow conductors at the extremes of the end windings. Water is the obvious choice in view of its low electrical conductivity, low viscosity, freedom from fire or toxic risk and the simple requirements it places on external heat exchangers. For the 264 MVA two-pole BHEL made turbogenerators in Madras Atomic Power Station (MAPS), the generator stator windings are cooled by demineralized water passing through the hollow conductors. Chemistry management of water cooled turbogenerators with hollow copper conductors plays a pivotal role to avoid possible re-deposition of released copper oxides on stator windings, which otherwise may cause flow restrictions by partial plugging of conductors and may impair the cooling. The phenomenon which is of more concern is not strictly of corrosion failure, but the consequences caused by the re-deposition of copper oxides that were formed by reaction of copper with oxygen. Technical literature reported instances of Copper oxide fouling in the stator water system resulting in shut down/off-line of power plants [1].

A mixed bed polisher (IX column) is provided in the stator water system of MAPS with a part flow allowed through it to ensure requisite chemistry control and maintain copper releases as low as possible. On sensing high conductivity (>20 µS/cm) of stator water, Turbine unloading and Turbine trips happen with some time delay. Thus, periodically the ion exchange resins of the polisher are replaced with fresh resins to ensure requisite chemistry control and to avoid unintended breakthrough and associated concerns during the smooth operation of the unit. Chemistry management of stator water systems in both the units of MAPS was constantly reviewed by way of routine monitoring of chemistry parameters and also by detailed chemical analyses of the spent resins from the IX polisher in various campaigns spread across several years. The experimental studies indicated reasonably low levels of copper release rates against the theoretical estimations, thus highlighting the effectiveness of the adopted chemistry control practices.

Keywords: *Turbogenerators, Hallow conductors, Stator water system, Copper deposition, Copper corrosion, Spent resins, Turbine trip.*

1. Introduction

Madras Atomic Power Station is twin type 220 MWe Pressurised Heavy Water Reactor (PHWR). The turbine generator stator windings are of Copper material and cooled by demineralized water (DM water) passing through the hollow conductors.

The chemistry regime employed is neutral water pH with Dissolved Oxygen (DO) content maintained between 1000–2000 µg/L. So, no chemical additives are used in the system. A part of the stator water is continuously passed through a mixed bed Ion Exchange (IX) polisher to remove any soluble ionic contaminants so as to maintain the purity of system water and control the copper corrosion to as low as possible to avoid potential concerns associated with re-deposition of released copper oxides on stator windings. As per the standard literature, the expected corrosion rate under the given chemistry conditions of neutral pH and high dissolved oxygen (1000–2000 µg/L) is ~25 mg $Cu/m^2/d$.

2. Factors that influence Copper corrosion in the stator water system

Copper oxidizes rapidly in water under certain conditions of DO, pH and temperature. Two oxides of copper are formed, namely (a) Copper (I) oxide or Cuprous oxide Cu_2O (red in colour) and (b) Copper (II) oxide or Cupric oxide CuO (black in colour). In stator, a mix of these oxides is generally observed, predominantly Cu_2O with low concentrations of dissolved oxygen (<100 µg/L) and CuO with higher levels of dissolved oxygen (1000–2000 µg/L). Either of these oxide forms a stable layer. However, altering either the pH or dissolved oxygen or both result in a mixture of oxides, resulting in instability of the layer. This causes the oxide to lose its adherence to the metal surface, resulting in migration and re-deposition elsewhere in the system water circuit [2].

Variations of solubility of copper ions throughout the system is an important factor causing copper transport in the system and re-deposition at the hollow conductors and insulation hoses (PTFE) causing flow restriction at the inlet. Copper will be released the most where copper solubility is highest, and re-deposited where the solubility is lowest. Provision of mixed bed ion exchange polisher before the inlet removes all dissolved copper ions, thus avoiding deposition of copper oxides at the inlet of hollow conductors and insulation hoses (PTFE).

It is mentioned in the literature that the corrosion rate of copper is maximum between 100–1000 µg/L with a peak value between 200–400 µg/L. 'Low oxygen' and 'high oxygen' operating regimes are defined relative to this maximum. (Fig. 1)

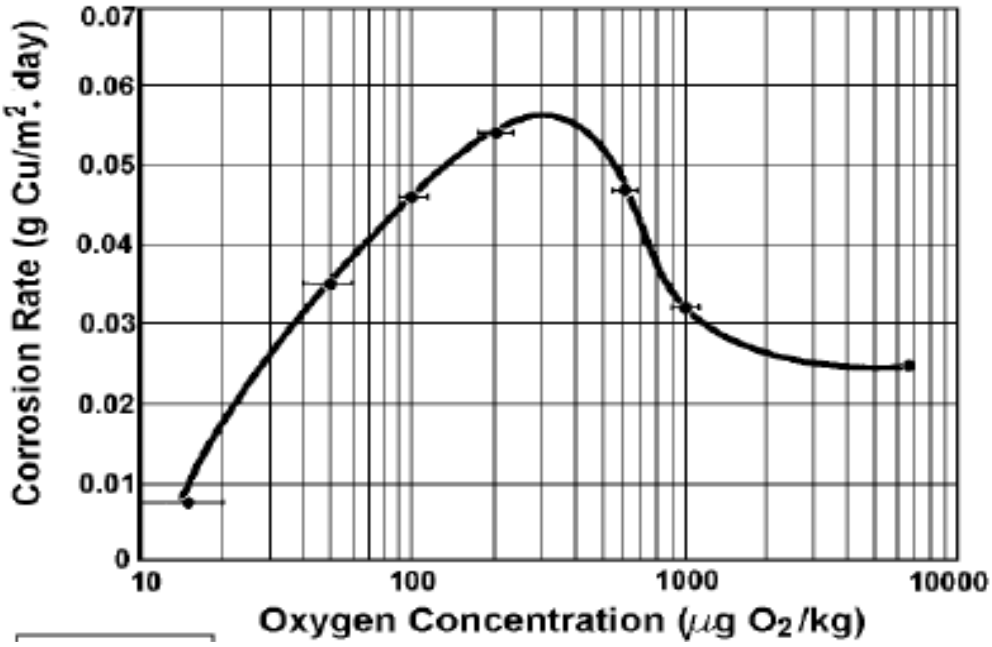

Figure.1 Corrosion rate against Oxygen concentration (reproduced with permission from [3]).

The recommended treatment regimes for stator cooling water can be categorized by their levels of dissolved oxygen and pH. There are four treatment regimes available. The options are:

- Low dissolved oxygen (<10 µg/L) and neutral pH
- High dissolved oxygen (1000–2000 µg/L) and neutral pH
- Low dissolved oxygen (<10 µg/L) and alkaline pH (8–9)
- High dissolved oxygen (1000–2000 µg/L) and alkaline pH (8–9)

Though there are four options available, only the first three are generally recommended by treatment experts or turbine manufacturers. The fourth option i.e. High Dissolved Oxygen and alkaline pH is generally not adopted as it leads to high corrosion. Any of the other three recommended options practised in operating power plants are generally plant and design specific. At MAPS, based on the given design and manufacturer recommendations, higher oxygen concentration (1000–2000 µg/L) and neutral pH (~7.0) treatment methodology is adopted. In this treatment regime, CuO is formed on the copper which is expected to firmly adhere to the surfaces and create a passive layer on the metal. This layer tends to be thicker than the Cu_2O formed under low-oxygen conditions. However, the following are some key factors that have the potential to influence and enhance the copper corrosion from the system material:

Low dissolved Oxygen (<10 µg/L) & neutral pH	**High dissolved Oxygen (1000–2000 µg/L) & neutral pH**
Low dissolved Oxygen (<10 µg/L) & alkaline pH 8–9	**High dissolved Oxygen (1000–2000 µg/L) & alkaline pH 8–9 (generally not preferred)**

(a) pH

Low levels of system water pH increases corrosion and hence enhances copper removal from the system material. The source for low pH could be poor quality make up water (DM water), as carbon dioxide entry into the makeup water drops the pH levels to more acidic and enhances the corrosion rate of copper.

(b) Sp. Conductivity

Higher levels of conductivity are an indication of presence of more ionic impurities which can result higher rates of corrosion. The sources could be (i) poor quality makeup water (DM water) (ii) exhausted ion exchange polishers (iii) incorrect practices while preparing the polishers with new resins (iv) prolonged usage of polishers etc.

(c) Dissolved Oxygen

Copper forms cuprous oxide (Cu_2O) under reducing (low-oxygen) conditions and cupric oxide (CuO) under higher oxygen levels. Either of these oxides can be stable and create a passive oxide layer on the surface of the stator bars. However, the CuO layer tends to be thicker than the Cu_2O formed under low-oxygen conditions. The Cu_2O layer is stable under low oxygen conditions and any transient oxygen spikes will have profound effect on the corrosion rate of copper. If the oxygen levels increase from ~10 µg/L to say ~500 µg/L, then the expected corrosion rate is higher than its rate at low oxygen conditions. In case of high oxygen and neutral water chemistry, CuO is formed on the copper bars. This layer tightly adheres to the surface and creates a passive layer on the metal. This layer tends to be thicker than the Cu_2O formed under low-oxygen conditions. Under this treatment, the transient oxygen spikes are expected to have less significant effect on the corrosion rate.

(d) Vacuum levels in the expansion tank

Maintaining adequate vacuum levels in the stator cooling water expansion tank would exercise an effective control on dissolved oxygen levels in the system water. Thus the vacuum levels in the Stator water expansion tank are to be adjusted in such a way that the dissolved oxygen levels are controlled between 1000–2000 ppb. Any transient changes in vacuum levels would introduce spikes in the oxygen levels and hence enhance the copper corrosion rates accordingly.

(e) Frequent make up of system water

Frequent makeup of the system with fresh DM water introduces shots of dissolved oxygen. This may cause frequent variations in the oxygen levels which could disturb the stability of the protective oxide layer and release the oxides into the system thereby enhancing the copper corrosion rate.

(f) Periodical performance monitoring of online instruments:

Periodical performance monitoring of online instruments like regular calibration or

performance checks of system conductivity meter, vacuum gauge of the expansion tank, temperature monitors would provide trends and indications and help in improving the system performance.

3. Some simple but significant measures practiced at MAPS

In MAPS, the chemistry across the mixed bed ion exchange polisher is monitored on regular basis to ensure requisite chemistry control of the Stator water system. Apart from monitoring chemistry parameters of the system, the vacuum in the stator water expansion tank is also regularly monitored and corrected for better control on dissolved oxygen levels in the system.

Some of the simple but significant measures practiced by the station are:

- Every day monitoring and trending of system water conductivity by online analyzer.
- Periodical monitoring of system water and IX outlet water for pH, conductivity by grab sampling.
- Regular monitoring and trending of system water for dissolved oxygen levels.
- Everyday monitoring of vacuum levels in the stator water expansion tank and ensuring the vacuum at requisite levels.
- Ensuring availability and performance of online conductivity meter and vacuum gauge.

4. Experimental studies and the methodology adopted

Studies were taken up with the spent resin extracted from the used IX polisher on periodical basis and subjected to chemical analysis and estimation of total copper trapped in the spent cation resin. These studies were carried out in various campaigns in both the units of MAPS, spread across several years and the results obtained were critically reviewed and analyzed.

5. Results of the studies and discussions

The spent resin samples were collected in various campaigns from both the units and the spent cation resins were subjected to chemical analysis after separation of resins. The spent resin service life varied from ~2 to 4 years. The observations and results were as below:

- The spent cation resin was observed to be faintly greenish in color indicating the presence of ionic Copper retained by the resin.
- Based on the quantity of copper retained by the cation resins, in the different campaigns conducted in both the units, the observations indicated that the copper release rates in both the units are more or less similar and in the same order.
- The general acceptable corrosion rate of copper, as mentioned in the available literature is ~25 mg/m^2/d under neutral pH and controlled aerated conditions with Dissolved oxygen levels between 1000–2000 µg/L.
- Considering the total inside surface area of all the hollow copper conductors through which stator cooling water is flowing, the corrosion rate of copper was noted to be about 18 to 22 mg/m^2/d, as observed in the several campaigns conducted in both the units of MAPS, thus within the acceptable corrosion rate of ~25 mg/m^2/d.

6. Conclusions and future Outlook

Chemistry management of Stator water system of MAPS units was reviewed to understand its effectiveness, principally focussing on the copper release rates from the system material. Detailed chemical analyses of the spent resins collected from the polishing unit of both the units were carried out in various campaigns. The studies indicated that the average copper corrosion rate is about 18–22 mg/m^2/d, which is lower than the theoretical estimation of ~25 mg/m^2/d, for the given chemistry conditions of neutral water pH and dissolved oxygen levels of 1000–2000 µg/L therefore indicating the effective chemistry management of Stator water system in both the units. Thus the studies highlighted that adherence to good chemistry practices would ensure lower corrosion rate and effective control on copper release from the Stator water system.

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Microbial Corrosion Issues in Power and Process Industries: An Overview

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Abstract

Significant corrosion losses in various industries worldwide are being attributed to microorganisms. Microbes thrive in the conducive environment of cooling water conduits and pipelines, which support their adhesion and growth through biofilms. The disparate colonisation of microorganisms on the metal surface can generate corrosion potentials almost as large as that generated between incompatible metals. As the corrosion process advances, attached microflora propagates and infests the entire cooling system. Commonly, five categories of corrosion causing bacteria are recognized viz., iron oxidising, sulphate reducing, sulphur oxidising, nitrate reducing and the exopolymer (slime) producing bacteria. Sulphate reducing bacteria are the single most common causative organism of corrosion in power and process industries, constituting 50% of all instances of biocorrosion failures. This review dwells some of the important characteristics of the bacteria, algae and fungi that are involved in promoting corrosion. Some case studies of iron, stainless steel, brass and titanium corrosion are detailed with plausible mechanism of microbial corrosion.

Keywords*: cooling water, bacteria, carbon steel, brass, stainless steel, titanium, corrosion.*

1. Microbes and Corrosion

Microorganisms which promote corrosion generally include not only bacteria but algae and fungi also. Five categories of corrosion causing bacteria are commonly recognized; they are the iron oxidising, sulphate reducing, sulphur oxidising nitrate reducing and the exopolymer producing bacteria. Sulphate Reducing Bacteria (SRB) like *Desulfovibrio*speciesare involved in the reduction of sulphate to sulphide. IOB and SRB are typical examples of the aerobic and anaerobic synergistic interaction which is most frequent in microbial corrosion of steel and its alloys used in industrial distribution systems. Additionally, some fungi and actinomyces have the potential to act as opportunistic pathogens or allergens for certain risk groups in the population. The following are some important groups of microorganisms of industrial relevance [1,2].

a) Algae

Algae are ubiquitous in distribution and are eukaryotic organism. They are present in various sizes, shapes and range from unicellular to multi-cellular forms. Algae are autotrophic and derive their energy from carbon dioxide, water and sunlight. The general classification of the algae is based partly upon the nature of the chlorophylls and accessory pigments [Chlorophyta (green algae); Rhodophyta (red algae) and Phaeophyta (brown & other pigmented algae)] present in the photosynthetic membranes. In industrial unit's algae generally flourish on wetted, well-lit surfaces such as cooling towers and distribution systems surfaces. Due to their capability to generate oxygen, organic acids and nutrients for other organisms, thus, algae play an indirect role in microbial corrosion. Algal growth in storage water systems can alter the water quality, algal metabolites and degrading products can facilitate corrosion by variation in pH, ionic concentration cells as well as by generating differential aeration cells due to adhesion to metal surfaces [3]. Fig. 1 illustrates the different algae species isolated from cooling tower.

b) Fungi

Fungi are among the most common microorganisms found in the air, soil, and on live and dead wood material. Most fungi are also capable of producing organic acids and are implicated in the corrosion of steels and aluminium especially in aircraft fuel tanks. In

addition, fungal growth/colonisation produces anaerobic sites for growth of SRB and also produce metabolic by-products that are useful for growth of various bacteria. Among the fungi, the important ones are the moulds and yeasts. Fungi deteriorate cooling tower wood and some like *Cladosporium resinae* [Fig. 2] are involved in the corrosion of aluminium alloys. It is also reported that *Cladosporium resinae* produces a bio-surfactant that degrades fuel by allowing water to partially mix with it and creating an emulsion, this affects the combustive qualities of the fuel ultimately resulting in the failure of the aircraft engine [4].

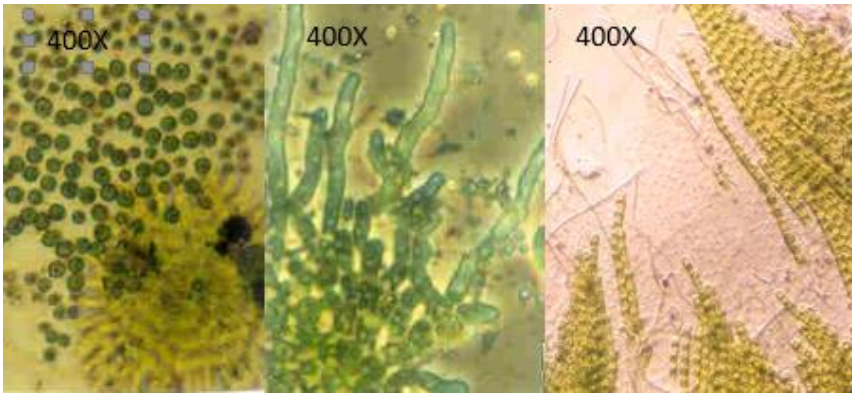

Figure 1. Algae (*Micrococcus* sp, Cyanobacteria and filamentous algae).

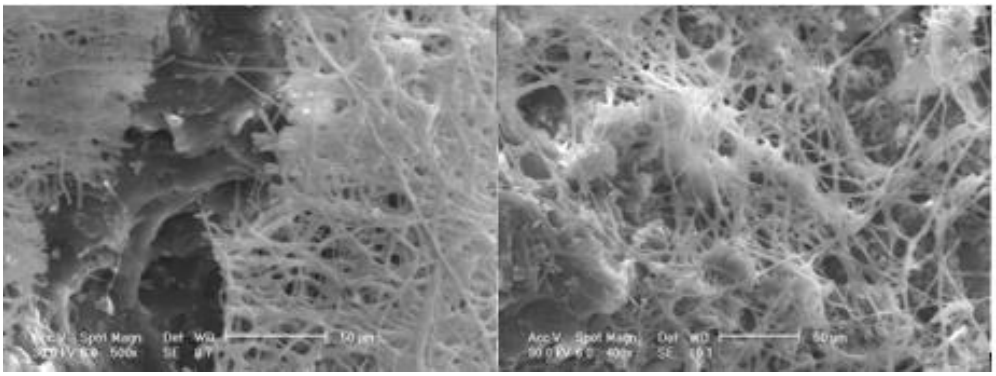

Figure 2. Fungal mycelium SEM image on ebonite surface (*Cladosporium* sp).

c) Nitrate Reducing Bacteria

Nitrate reducing bacteria constitute up to 50% of the bulk of the microbes present in aquatic systems. Nitrate reduction takes place in waters enriched with organic matter and nitrate, commonly, *Achromobacter, Bacillus, Corynebacterium, Micrococcus denitrificans, Pseudomonas, Serratia* and *Vibrio* species are examples of extremely active nitrate reducers. Since nitrate serves as an electron acceptor the growth rate of denitrifiers depends on nitrate concentration. Denitrifying bacteria require an electron donor to carry out denitrification process, which is served by organic matter. A possible mechanism of ammonia formation by denitrification process involves four stages viz.; reduction of nitrate to ammonia via nitrite, hyponitrite, and hydroxyl amine. Nitrate reduction is driven by nitrate and nitrite reductase (eq. 1 to 4). Ammonia produced due to nitrate reduction is toxic to copper alloys. Ammonia levels beyond 1 ppm induce stress corrosion cracking (SCC) in copper alloys [5].

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O \quad (1)$$

$$2NO_2^- + 4H^+ + 2e \rightarrow N_2O_2^- + 2H_2O \quad (2)$$

$$N_2O_2^- + 6H^+ + 4e \rightarrow 2NH_2OH \quad (3)$$

$$NH_2OH + 2H^+ + 2e \rightarrow NH_3 + H_2O \quad (4)$$

d) Exopolymer (Slime) Producing Bacteria

Aerobic slime formers are a diverse group of aerobic bacteria that produce extracellular polymers. The slime forming bacterial genus include *Pseudomonas, Bacillus, Flavobacterium* and *Aerobacter*. Most of the slime formers that colonise metal surfaces produce polymers and form a gel matrix on the metal. Aerobic slime formers are important mainly because "slime" complexes metal ions and promote corrosion. Slime formers are "scrubbers" of oxygen, they create an ideal site for growth of anaerobic bacteria. The exopolymers are actually a sophisticated network of sticky strands that bind the cells to the surface (Fig. 3). Apart from aiding in adhesion, the exopolymers also protect the bacteria from grazing by protozoans or bacterivores. The exopolymer network gives quasi structural stability to the biofilm [1].

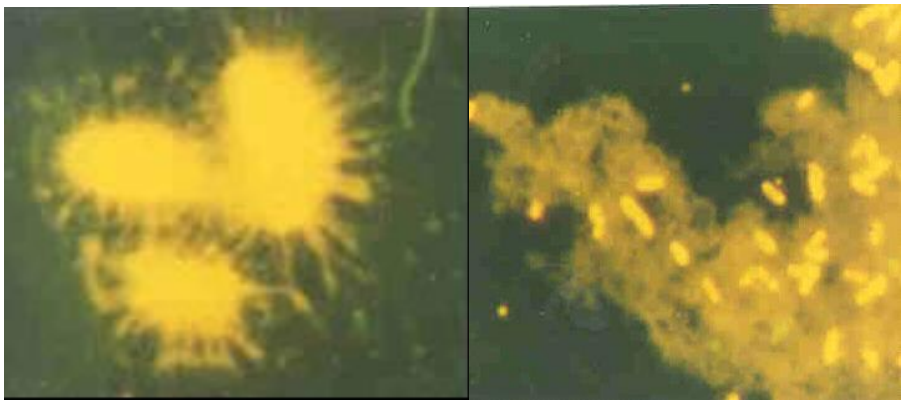

Figure 3. Exopolymer producing bacteria (Pseudomonas sp).

e) Iron Oxidizing Bacteria

The common iron oxidizing bacteria viz. Gallionella, Sphaerotilus, Crenothrix, and Leptothrix species. Theyoxidize ferrous ions to ferric state to obtain their energy and deposit ferric oxide on carbon steel pipelines and promote tubercle formation. The most common iron oxidizing bacteria are found in long filamentous sheaths and these filaments are easily seen under the microscope and have a characteristics pattern. Iron bacteria's ability to oxidize iron and then forming a low-density hydrated iron oxide in the tubercles is the key factor for corrosion of steel. Filamentous iron bacteria (Fig. 4) are "omnipresent" in carbon steel and iron distribution system pipelines. These bacteria are commonly reported in deposits associated with tuberculation [6].

f) Sulphate Reducing Bacteria [SRB]

SRB are environmentally important microorganisms, their predominance can be divided into ecological processes and economic effects. Development of SRB in biofilms can be expected whenever environmental conditions such as redox potential or oxygen tension and nutrients are available for growth. In anaerobic micro-niches, micro layers exist in the biofilms due to depletion of oxygen by aerobic microbial activity. The most significant aspect of SRB metabolism is the production of hydrogen sulphide (H_2S) which being a very strong reducing agent and able to inhibit the growth of most aerobic bacteria. Conversely, H_2S plays an important role in the natural environment as it functions as an electron donor for the growth of some species of sulphur bacteria. H_2S also affects by suppressing the growth of some aerobic organisms. This factor (H_2S) makes SRB extremely important microorganism in the oil industry where their growth and subsequent corrosion can cause great economic problems. SRB induces pitting in the form of large radial growth patterns, which are shallow in nature (Fig. 5) [7,8].

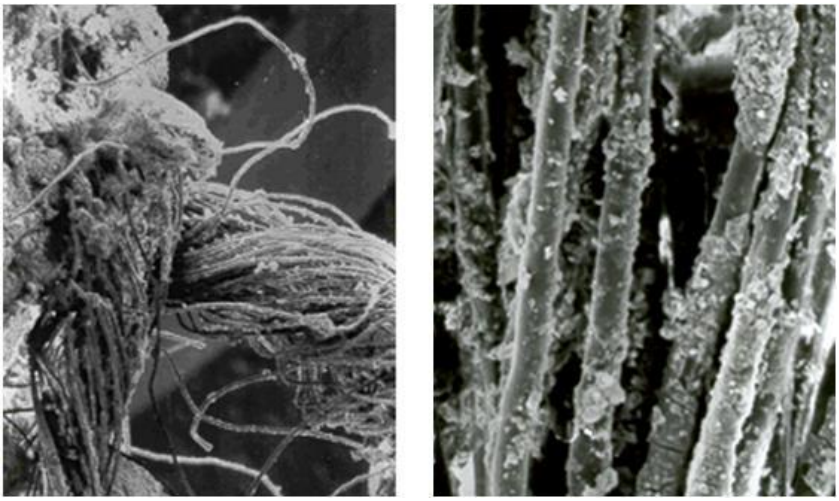

Figure 4. Iron oxidizing bacteria filaments (*Leptothrix* Sp.) a SEM image.

2. Case Studies

- **Corrosion of Carbon Steel by Iron Oxidising & Sulphate Reducing Bacteria**

The failure of carbon steel pipelines was studied in a test reactor service water system. The cooling system is of the open recirculating type with an induced draft cooling tower. The service water system is designed to provide cooling water to critical plant components such as fuel pits, coolers, containment recirculating system, pump oil, gear box and seal condenser. The structural material for the service water system mainly constitutes carbon steel (CS). Soon after commissioning of the test reactor, the service water system had problems such as flow blockage, pipe punctures and relatively high corrosion rates of carbon steel [9]. In order to understand the causes of the problems and formulate appropriate control strategy detailed water quality and microbiological analyses were carried out. The iron bacteria species isolated from the carbon steel coupons exposed in the test reactor cooling circuit was identified as *Leptothrix* sp; other bacteria identified are *Pseudomonas aeruginosa* and SRB isolate *Desulfovibrio* sp. The iron bacteria in water have not shown much variation during the course of this study (10^4 to 10^5 cfu ml^{-1}). The iron bacteria population showed peaks during summer and NE monsoon months. There were variations in SRB numbers on the CS coupons and cooling water, the SRB counts varied from 7×10^2 to 9×10^3 cfu cm^{-2} during a year. SRB population in the cooling water ranged from 10 to 35 cfu ml^{-1}. The culturable aerobic heterotrophic bacteria (CAHB) of the source water (open reservoir) and the test reactor cooling water ranged from 10^5 to 10^8 cfu ml^{-1}. To address the problems of microbial corrosion a series of experiments were carried out to understand the mechanism of CS corrosion. The corrosion rates ranged from 3–3.5 mpy. Carbon steel coupons exposed in sterile conditions (no bacterial growth) showed corrosion rates in the ~1.75 ± 0.62 mpy. The X-ray diffraction pattern (Fig. 6) of the carbon steel corrosion product gives qualitative information about the possible phases present. XRD data to the patterns in the ICDD database, revealed that $Fe(PO_3)_3$ is the predominant phase. The other phases identified are γ-Fe_2O_3, Fe_2PO_5 and $BaFeO_{3-x}$. Apart from peaks corresponding to various crystalline phases, features corresponding to poorly crystallized phase are also observed.

Iron bacteria form filamentous sheaths and layers of oxides. According to Rao et al., (2000), the oxides consist of 70% hydrated iron oxide, 20 to 25% silica (silt) and 5 to 10% other oxides. Sulphur content was less than 1%.

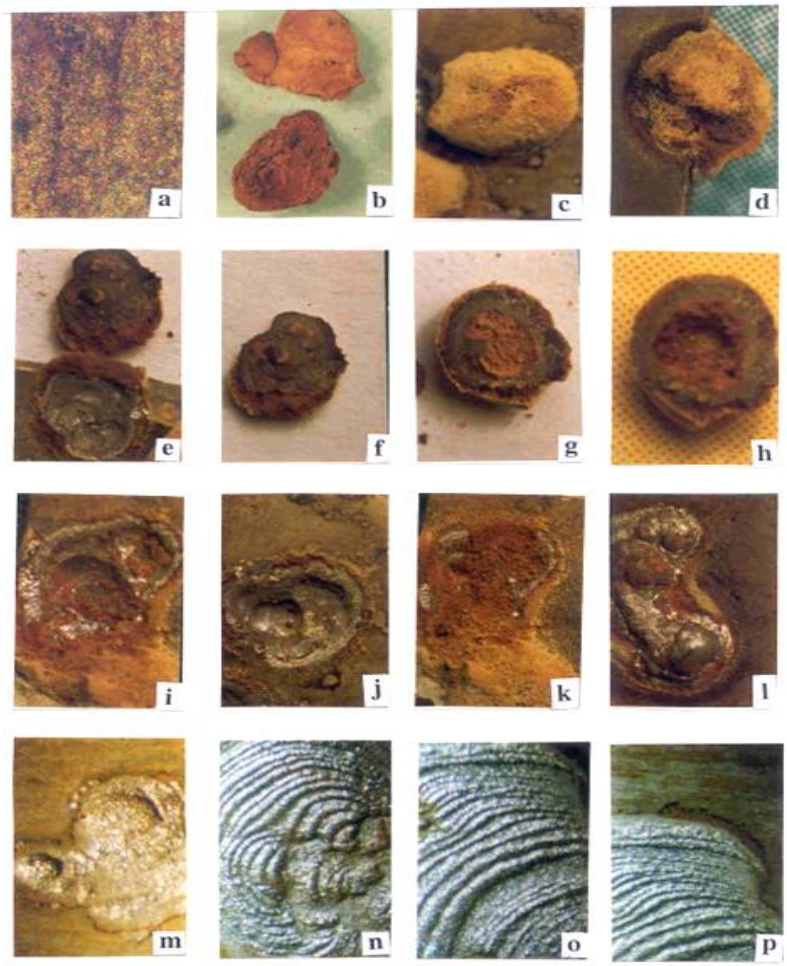

Figure5 (a–p). Multiple images showing carbon steel corrosion. The images describe; (a) Typical tubercle on carbon steel specimen (b-d) A section of tubercle showing the iron corrosion products (e-h) Bottom of the tubercle showing black corrosion deposit characteristic of iron sulphide and magnetite, (i-m) Stereo zoom image of pitting corrosion of carbon steel with corrosion products, (n–p) Typical concentric ring pattern on carbon steel induced by SRB growth

The presence of $FePS_3$ compound could be due to two possible reasons: (1) It is reported that SRB produced colloidal iron phosphate, Seed [10] confirmed that phosphate increased the rate of corrosion of carbon steel in the presence of SRB. Because reduced phosphorus is highly reactive and it could contribute to corrosion of iron. Furthermore, in an environment of sulphide the iron phosphorus formed could have reacted with sulphide to form the $FePS_3$ compound; (2) It is well known that ferrous sulphide layer is formed on metal surface by Fe^{2+} reacting with hydrogen sulphide produced by SRB. The phosphate-based water treatment programme at the test reactor could have resulted in the phosphorus ions reacting with the iron sulfide, thereby leading to the formation of the $FePS_3$ compound. Studies revealed that There is no one complete solution to control iron bacteria. Studies have revealed the mechanism of carbon corrosion once the system is infested with it. Steel corrosion is not a simple process but a combination of several factors which chiefly include bacteria. Based on the observations from this study it may conclude that the presence of *Leptothrix sp* and *Desulfovibrio sp.* is responsible for carbon steel corrosion [11].

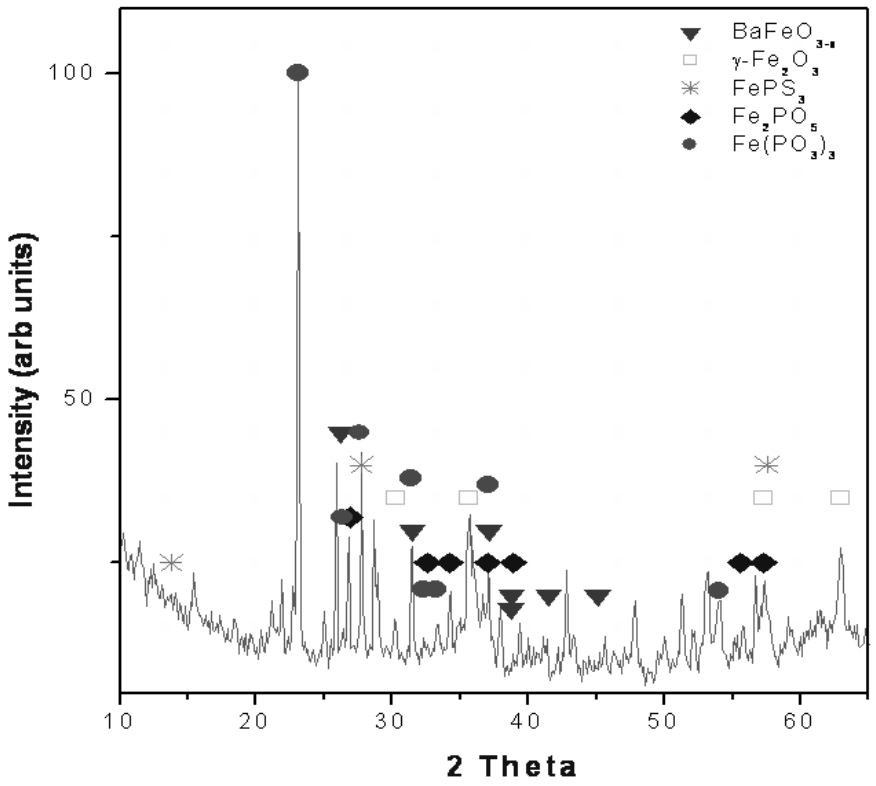

Figure 6. XRD spectrums of the carbon steel corrosion deposits.

- **Microbiologically Influenced Corrosion of Copper alloys**

Copper and its alloys are most commonly used in the fabrication of heat exchangers in cooling water systems. The alloys depend on their natural oxide for corrosion resistance. This oxide film (Cu_2O) is a defective film with vacancies in the cuprous oxide lattice into which cuprous ions can migrate. Cu_2O protective film can be disrupted by a variety of cooling water parameters which include pH, water velocity, chlorides, ammonia and biofouling. Addition of such elements as aluminium, zinc, tin, iron and nickel to copper have been successfully used to modify the cuprous oxide film to make it more corrosion resistant.

The problem of condenser tube (admiralty brass) failure at Rajasthan Atomic Power Station (RAPS) unit-II, Kota, Rajasthan, was investigated. About 2500 tubes have been replaced in a span of 6 years. The failure of the condenser tubes leads to the leakage of cooling water into the boiler, thereby violating the boiler water technical specifications. The leak rate of cooling water ranged between 300 and 2100 L $hour^{-1}$. Earlier metallurgical analyses of the failed tubes have revealed that the tubes were damaged due to stress corrosion cracking (SCC). A detailed study was carried out to look into the environmental conditions / or causative agent, which could have led to the failure of condenser tubes. Comprehensive water quality analysis of the Ranapratap Sagar Lake, which is being used as cooling medium for RAPS, was carried out. In addition, biofilms developed on perspex and metallic coupons were also characterised for various physical, chemical, biochemical and biological parameters in a time series study to

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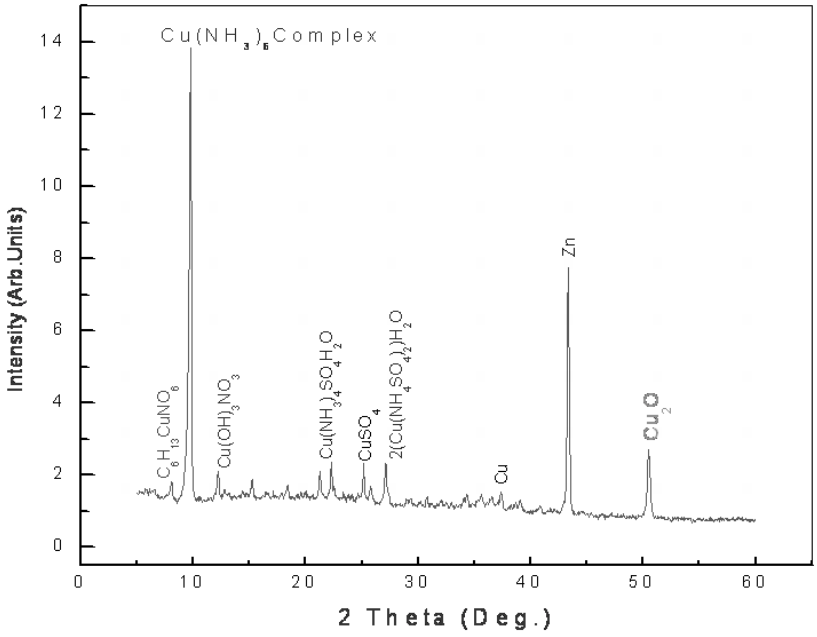

Figure 7. XRD spectrum of admiralty brass corrosion products.

understand the biofilm parameters which could have contributed to the failure [12].

Results of the water quality analyses data between the intake and outfall showed increase in dissolved oxygen (DO), chlorine demand, ammonia, nitrite and decrease in nitrate values, Total dissolved solids (TDS) from intake to outfall water showed variation while passing through the cooling system indicating a quality change.

The observed increase in pH from intake to outfall could possibly be due to the formation of ammonia in the cooling system. Similarly, the reduction in TDS from intake to outfall indicated that a large number of bacteria are thriving inside the cooling system, and dissolved salts are consumed by the bacteria, thereby reducing the TDS content in the outfall water. Moreover, relatively high values of nitrate reducing bacteria were found in the lake water (10^4 CFU/ml). This is added evidence in support of the view that nitrate is reduced to nitrite in the condenser circuit. The presence of SRB in the intake water and their increasing number in the outfall water is again a notable feature as it is also known that SRB can reduce nitrate to ammonia. SCC is initiated due to the formation of active corrosion agent, Cu $(NH_3)_4(OH)_2$ (tetra amino copper (II) hydroxide). There is a possibility of developing relatively high concentration cells of ammonia at the metal biofilm interface on account of the biofilm matrix which can locally shield ammonia levels, thereby preventing diffusion into the flowing water. When the oxide layer depleted metal surface comes in contact with ammonical environment the anodic reaction triggers, because the copper ions produced are known to complex with ammonia to form the highly soluble $Cu(NH_3)_2^+$ ions. Earlier EDAX analysis of failed brass tubes at intergranular region and at the bottom of the pit showed evidence of dezincification, complete loss of zinc was also observed in the cervices. In the present study XRD analysis of the admiralty brass corrosion products revealed the presence of copper ammonium complexes major peak a (Fig. 7) along with copper ammonium sulphate, copper, zinc, copper nitrate, and copper (II) oxide has major and minor peaks. The presence of copper ammonium complex indicates that the active corrosion agent was formed on the admiralty brass surface. Such studies will result in devising better control measures which are prudent in combating MIC. So far, to our knowledge this study is the first report of experimental evidence showing

the role of nitrate reducers in inducing SCC in admiralty brass [13,14].

- **SRB Induced Pitting Corrosion of Stainless Steel**

SRB are one of the principal corrosion causing bacteria implicated in many instances of MIC. Since SRB grow beneath the biofilm, the presence of high levels of dissolved oxygen in the bulk water does not affect their growth. SRB presence is often considered as a marker for biocorrosion, just as *Escherichia coli* is used as an indicator for potable water contamination. Till date, qualitative demonstrations regarding the presence of SRB have yielded little useful information. However, the quantitative association of SRB with industrial corrosion problems has not been addressed in detail and such information is warranted. Since many cooling circuit failures of stainless steel are being implicated due to SRB activity, the finer details of SRB growth and hydrogen sulphide in initiating corrosion of stainless steels [15]. The SEM pictures of the SS 304 specimen after exposure to SRB culture are illustrated in Fig. 8. The electron micrographs showed SRB cells embedded in the corrosion deposits and in the pits. The pits had significant SRB population and were in hemispherical shape. The pitting ratio was 5 cm^{-2} at 300 and 13.33 cm^{-2} for the exposure time of 600 h.

The pits observed in SS 304 coupons exposed to SRB were hemispherical in nature. A mechanism of microbial pitting in stainless steel has been recently published confirming the effect of sulfur compounds other than sulfides on the corrosion behaviour of iron. Studies reported elsewhere indicated that the decrease in pitting potential was associated with the total concentration of sulphide generated by SRB. Thus, bacterial growth could promote a decrease in the passive film resistance probably by producing acidic metabolites and complexing substances. Therefore, the above said conditions could have contributed to the rapid decay of passive film plausibly by sulphide activity of SRB. This has favoured the initiation of localized corrosion process such as pitting as was observed in the 304 stainless steels [16].

Figure 8. (a–b) SEM pictures of SRB growth on stainless steel–304 and pitting corrosion [magnification (a) 1725 ×; (b) 120 ×].

- **Microbial Corrosion of Titanium by Sulphate Reducing Bacteria**

Among the various industrial materials, titanium shows remarkable corrosion resistance by virtue of its tenacious oxide film. There are scarce reports on the stability of the titanium dioxide (TiO_2) layer in an obligate anaerobic milieu of SRB. With increasing use of titanium in various industrial systems and its vulnerability to bio-growth, the potential significance of SRB induced corrosion of titanium should be of concern to process engineers and material scientists. ASTM grade 2 titanium obtained in plate form (2 mm thick), specimens (2.0 × 1.5 cm) were polished on progressively finer silicon carbide papers to a final grit size of 1000. The SRB medium used for the study did not contain any chloride ion. Filter sterilised dithiothreitol was added to reduce the redox potential of the medium below -200 mV to aid the growth of obligate anaerobe SRB [8]. The medium was not

purged with inert gas. The SRB strain used for the study was isolated from a fresh water-cooled service water system of a test reactor at Kalpakkam. Prior to incubation (at room temperature) the flasks were inoculated with 10 mL of log phase SRB culture (3×10^5 cfu mL^{-1}). A semi-continuous mode of SRB growth was used for this study i.e., 75 % of the culture broth is drained and replaced with equal amount of fresh medium every four days to maintain SRB growth rate in log phase throughout the study period. A four-day replacement frequency was chosen based on the SRB growth curve, wherein the culture enters the senescence phase after 96 h. Culture purity was determined by standard aerobic and anaerobic culture plating methods every four days. A control set of titanium coupons exposed to sterilized SRB medium was also observed for a similar period of time [17].

The SRB isolate used in the study was categorized as *D. vulgaris* after carrying out various biochemical tests, including the desulfoviridin test. The growth curve and sulphide production by *D. vulgaris* are presented in Fig. 9 illustrating multiple images. The SRB growth curve showed a lag phase of up to 12 h, followed by exponential phase up to 50 h and thereafter the culture entered the stationary phase, which was observed up to 70 h. The decline phase was monitored up to 96 h. Sulphide production was noticed in the early lag phase. The SRB count on titanium coupons ranged from 10^4 to 10^5 cfu cm^{-2}. The sulphide production in the log phase was rapid and continued through the stationary phase. The semi-continuous culture kept the SRB growth in the log phase throughout the experimental period and the sulphide concentration was 0.2 to 0.4 mM. Fig. 9 also illustrates a CSLM image of the corroded titanium specimen, the image shows base metal along with several micro pits and a pit with ~50 µm diameter.

The most significant aspect of SRB metabolism is the production of H_2S, which is a very strong reducing agent and also inhibits the growth of most aerobic bacteria. The SRB strain *D. vulgaris* produced sulphide in the range of 0.2 to 0.4 mM. SRB are associated with two corrosive mechanisms: 1) they create a biofilm having a crevice like geometry on the metal surface, and 2) produce H_2S as well as Phosphine (PH_3). H_2S enhances the corrosion reactions; anodic dissolution and cathodic hydrogen evolution [18]. Confocal scanning laser microscopy (CSLM) was used to observe the pitting corrosion of the titanium specimen. Compared to a common microscope, a confocal microscope projects only light coming from focal lens. CSLM can optically section the specimen in depth, generating stacks of images successively. Later the stack of images can be used to reconstruct a 3D image of the specimen. A 3D image showing pitting corrosion of titanium specimen exposed to SRB culture. The area of the specimen scanned was 200 × 200 µm wherein a pit of 50 µm diameter and 25 µm deep was observed, along with numerous micro pits which are ~5 µm in diameter.

Pitting corrosion is a complex but important problem, which is the root cause of many corrosion failures. Majority of MIC is seen as pitting type corrosion, the microbes at the metal / biofilm interface create conditions in which, incipient pitting leads to localised corrosion is driven principally by microbiological activities. Generally, microbial colonization promotes a decrease in the passive film resistance by producing acidic metabolites and complexing substances. Hence, rapid decay of the passive film favours the initiation of localized corrosion process such as pitting. The anodic and cathodic reactions that comprise corrosion, separate spatially during pitting. The anodic sites are not inhibited, thereby triggering the metal to corrode. Generally, sulphide is cathodic to the metal and sulphide ions could have reacted with titanium ions (Ti^{2+}/ Ti^{4+}) released at the anode to form titanium sulphide [19].

New developments in microbial corrosion focus on understanding of extracellular electron transfer (EET) mechanisms, using microbes for biocontrol, integrating nanotechnology, studying complex mixed microbial communities, and developing better detection/mitigation tools. We need to move from just sulphate-reducing bacteria to other broader microbial communities, and explore the biomineralization processes for self-healing/protection of materials, highlighting both destructive and protective roles of biofilms.

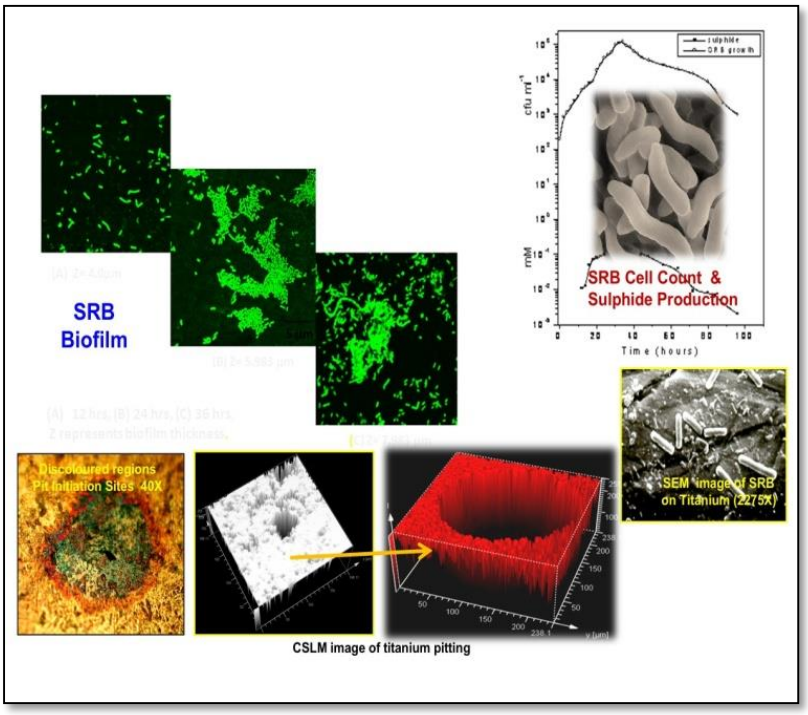

Figure 9. Multiple images showing the SRB growth curve and sulphide production, SRB biofilm on titanium and SEM and CSLM images describing the SRB and micro-pitting in titanium.

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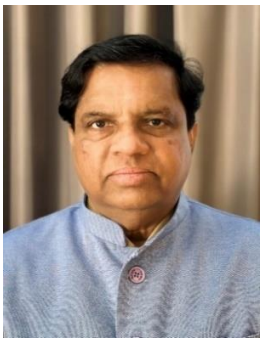
About the Author



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Contemporary Approach for Corrosion and Fouling Control of Marine Water System Screens

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Abstract

Marine structures like jetties, platforms and seawater intake system components suffer corrosion and massive fouling which may impair the intended performance of seawater cooled systems thus may affect the smooth operation of the industries and power plants thereby causing large penalties to them. In Madras Atomic Power Station (MAPS), the seawater intake system screens, which act as barriers for the entry of marine organisms into the seawater cooling systems of the plant, persistently experience severe corrosion and fouling. To overcome the corrosion and biofouling oriented challenges in the intake seawater system of MAPS and to protect the marine structures from these influences, one of the contemporary technologies of application of corrosion and fouling control coating is employed to the intake water system screens. The performance of coated screens was observed to be significantly superior with effective control on corrosion and bio-fouling of these screensthus highlighted the effectiveness of the coating applied on these screens. Due to the inherent self-polishing nature of the coating, the surfaces remained smooth thus controlling corrosion due to seawater conditions and also microbiologically induced corrosion by avoiding further attachment of bio-organisms. This has resulted in extended life of the screens with superior integrity thereby satisfying the intended objectives of these screens in the intake seawater system of MAPS for longer periods.

Keywords: *Marine structures, Intake seawater system, Application of coatings, Corrosion and Biofouling control*

1. Introduction

Corrosion and Biofouling of seawater intake system components have been a common concern for coastal power plants and also for the Madras Atomic Power Station (MAPS). The seawater for the cooling requirements of tertiary systems of both the units of MAPS is drawn from the Bay of Bengal through seawater intake, 16 meter in dia, to the pump house located about 450 meter away from the onshore. The seawater intake system screens, which are provided as the barrier for entry of marine organisms and foreign debris into the seawater cooling systems of MAPS, recurrently suffer from severe corrosion and biofouling.

In the intake system, there are 16 openings each of about 2.9 m × 1.76 m in size, through which seawater enters the sub-sea bed tunnel. Each opening has screens called trash racks. These trash racks experience severe corrosion and biofouling thus affect the inflow of water and cause variation in the water levels in the on-shore pump house which. This has a direct influence on the plant operation. Thus, it necessitates recurrent cleaning and maintenance works on these screens. These works include, physical lifting-up of heavy structures, laborious manual cleaning and maintenance on a rotation basis.

Several years of experience indicated that coal-tar epoxy coating renders temporary protection and the screens recurrently suffer massive corrosion and fouling.

To overcome the concerns associated with the corrosion and biofouling of the intake seawater system of MAPS, the contemporary technology of application of coating is employed to these screens, based on various experimental studies.

2. Corrosion and Fouling protection technologies

Biofouling, due to the decomposition products generated by the organisms involved as part of their life cycle, could generate corrosive

environment leading to what is called as Microbiologically Induced (or Influenced) Corrosion (MIC) [1]. Control of MIC is the major objective of development of efficient coatings capable of inhibiting biofouling. Growth of marine organisms would start immediately when the surface is exposed to seawater. To keep the surfaces fouling-free requires periodic cleaning with high pressure water washing (HPWW) or mechanical hard brush cleaning.

The intensity of cleaning required might be higher thus there lies a potential for damaging the surfaces and increasing the roughness of the surfaces due to repeated washing. This would increase the likelihood of recurrent fouling and loss of integrity of the surfaces and structures. Fouling protection technologies provide fouling-free surfaces. One of the contemporary technologies employed for protection of surfaces of seawater system structures is application of Corrosion and fouling control coating.

2.1. Corrosion and fouling control coating

The coating contains active chemical ingredients which is released steadily with the water inflow/impact and provides fouling-free surfaces.

Self-polishing hydrolyzing type foul control coating forms partly hydrophobic surface. When surface is exposed to seawater, the chemical constituents leach out at a controlled rate from the foul-control coating film and provide fouling protection at the surface. This is a continuous process and always fresh layer of coating gets exposed for fouling protection. Foul-control coatings make a valuable contribution to the sustained operational efficient seawater systems, achieved by the release of active ingredients (or biocides) which prevent the settlement of marine fouling organisms. The success of this process depends on the nature of chemical ingredients used, its release mechanism and the polishing and smoothing action of the employed coating.

Figure 1. (a) Corrosion & foul control applied screens and (b) Coal-tar epoxy coated screen.

Figure 2. Corrosion and foul control coated screens (a) before and (b) after water jet cleaning.

Figure 3. Coal-tar epoxy coated gates (a) before and (b) after water jet cleaning.

3. Application of corrosion and foul control coating to the seawater intake system screens

A commercial corrosion and foul control coating was considered based on the encouraging results obtained through several pilot scale studies. This coating falls under self-polishing Copolymer (SPC) group where the acrylic copolymers are with hydrolysable pendant groups like, silyl acrylate, zinc or copper acrylate polymers. Hydrolysis of the pendant groups and the dissolution of the hydrolysed polymer release the incorporated biocides and lead to a self-polishing surface which is self-smoothing [2].

Accordingly, some newly fabricated screens were applied with this coating and a few other screens were applied with the regular coal-tar epoxy coating and these gates were exposed to seawater in the intake seawater system for several years.

During the periodical inspections, it was noted that the coal-tar epoxy coated gates were getting massively corroded and fouled with dense population of bio-organisms adhering to the metal structure. They were also hard to get removed by mechanical cleaning wherein the Corrosion and foul coating applied gates were scarcely fouled and were loosely held onto the metal structure and easily getting dislodged by gentle pressure. The typical photographs of these corrosion & foul control coated screens and epoxy coated screens were as below: (Fig. 1 to Fig. 3)

4. Results and Discussions

Major results and observations with the application of corrosion & foul control coating applied to the screens of intake seawater system are as given below:

- The performance of Corrosion & foul control coated screens was significantly superior than coal-tar epoxy coated screens with remarkably effective control on corrosion and biofouling on these screens thereby ensuring intended inflow of seawater to the plant operational requirements.
- The corrosion & foul control coated screens had considerably lower density and population of bio-organisms and foreign debris over them and were loosely held.
- With gentle pressure, the fouling on the corrosion & foul control coated screens got dislodged wherein for the epoxy coated screens higher pressure or metallic scrapping was to be employed to dislodge the fouling adhering onto them.
- The mechanical methods of cleaning adopted for epoxy coated screens were resulting in loss of coating and physical damage of the screens which were consequently becoming weaker sites for further degradation and damage or corrosion of the screens. Thus, for these gates within one year reapplication of coal-tar epoxy coating was done to extend their life span wherein such requirement did not arise with the corrosion & foul control coated screens.
- The ease of cleaning of corrosion & foul control coated screens was much simpler. Post cleaning, the gates were looking fresh due to the inherent self-polishing nature of the coating.
- The anti-corrosion life of corrosion & foul control coated screen is observed to be more than ~7–8 years wherein for the epoxy coated gate, it was ~2–3 years with periodical reapplication of coal tar epoxy coating.

5. Conclusions and future Outlook

To overcome the severe corrosion and biofouling associated concerns in the intake seawater system of MAPS, one of the contemporary technologies of application of corrosion & foul control coating was employed to the intake water system screens which highlighted its effectiveness in exercising control on corrosion and biofouling of these screens thereby ensuring intended inflow of seawater to the plant operational requirements.

The corrosion & foul control coatedscreens performance was significantly superior with less dense and very low population of bio-organisms on the screens highlighting very effective corrosion and bio-fouling control.

Due to the inherent self-polishing nature of the coating, the surfaces remained smooth thus controlling further bio-attachments. The low level attachments were easily getting detached. All these resulted in extended life of the intake screens with better integrity to

satisfy the intended objectives of these screens in the intake seawater system for longer periods.

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Integrated Antifouling Strategies for Industrial Seawater Cooling Systems

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Abstract

Biofouling of surfaces is imminent in once-through seawater cooled systems. Biofouling loading on surfaces in coastal waters along the East Coast of India ranges from 65–75 kg/m^2 and 4–14 kg/m^2 inside the cooling water systems (CWS) with a biocidal regime in vogue. Most of the rocky shores along the Indian East and West Coasts comprise high biofouling pressure sites due to their high biodiversity. Oxidizing biocides, such as chlorine and bromine, have been the mainstay in large once-through CWS, with chlorine dioxide being used in smaller CWS. Marine invertebrate larvae settle from day one on surfaces, colonize, and grow into adults. Macrofouling of surfaces is a major problem in once-through CWS, which needs to be prevented during the initial settlement stages, as once established, it is hard to remove these calcareous shell forming organisms from the surface. Adequate knowledge of the toxicity of biocides in preventing the settlement of marine invertebrate larvae is a prerequisite for controlling macrofouling of surfaces in the CWS. There is no uniform prescription for a biocidal regime, and it has to be tailor made taking into consideration the type and density of organisms & their reproductive cycles for a given geographical location. Hard shell fouling by barnacles, tubeworms, green mussels, coelenterate hydroids, Bryozoans, and Ascidians comprises the majority of the fouling community in tropical Indian coastal waters. The discharge of biocides at marine outfalls is again capped to 0.2±0.1 ppm TRO (Total Residual Oxidant). Hence, for effective fouling control, recent strategies advocate the use of surface protection in the form of antifouling coatings as an effective strategy to combat the problem. Since biofouling is a surface associated phenomenon use of antifouling coatings helps in reducing the amount of biocide to be dosed to keep the CWS clean.

Keywords: *Cooling Water Systems; Biofouling; Biocides; Antifouling Coatings; Chlorination; Bromination; Chlorine dioxide, FRC.*

1. Introduction

The problem of biofouling is profound in industries drawing seawater for condenser cooling purposes like nuclear and thermal power plants, oil refineries, paper and pulp manufacturing industries. These industries abstract large quantities of seawater for condenser cooling purposes and reject the waste heat back into the environment. For example, a typical 2000 MWe power plant abstracts seawater around 65 m^3/s at velocities of 1.5–3 m/s across the cooling water system (CWS) [1]. These velocities are usually maintained to prevent sedimentation in the CWS. Generally, velocities around 1.4 m/s are maintained across the shell and tube heat exchangers. Marine invertebrate larval forms have been shown to attach even at velocities of 3.0 m/s inside the CWS [2]. The sequence of events at the surface results in conditioning layer formation followed by biofilm (microfouling) development which facilitates macrofouling organism to settle (Fig. 1).

Industrial cooling water system comprises of an offshore submerged or a subsurface/inter-tidal intake system which transported seawater through a submerged tunnel or

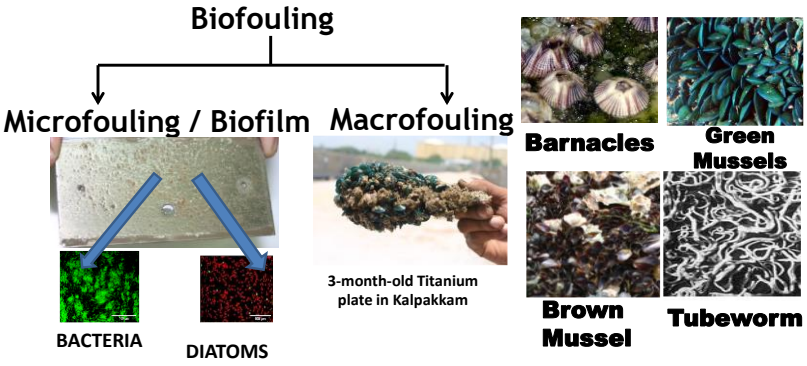


Figure 1. Biofouling of surfaces and dominant biofouling organisms in CWS of Indian power plants.

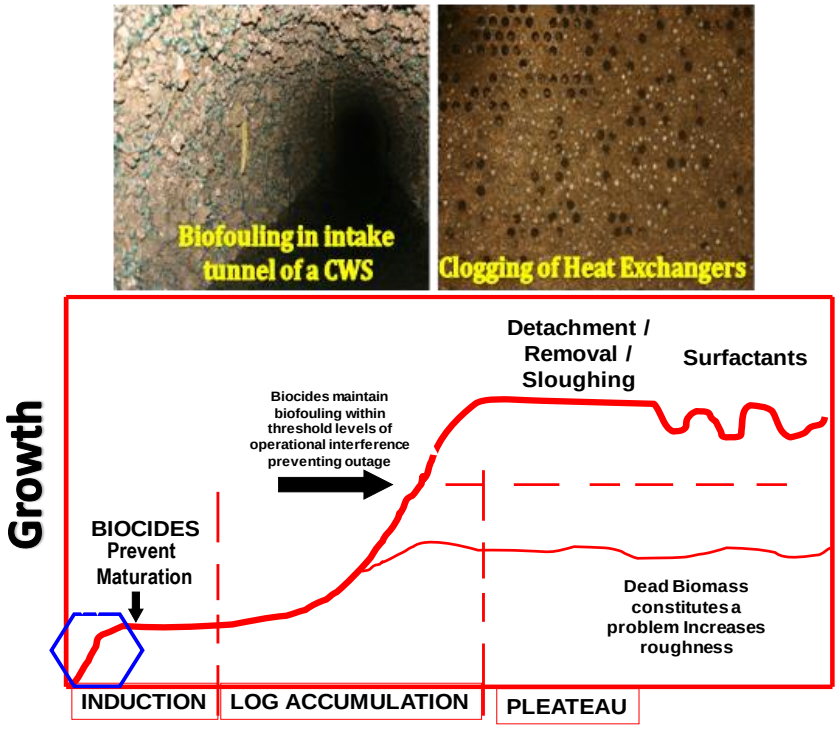


Figure 2. Biofouling growth on surfaces follows an Asymptotic model. Current strategy of biocidal dosing in tropical cooling water system relies on keeping the biofouling within the threshold levels of operational interference as cost, cleanliness and environment is to be taken into consideration.

pipeline to the shore. The pump house is generally located near shore and feeds the condensers. After passage through the condensers the seawater is returned to the natural source through a shore based outfall. The pre condenser section from the pump house experiences high fouling in the CWS.

The pre condenser section usually comprises of concrete tunnels and mild steel pipelines of varying sizes and geometries. In tropical conditions like India the pre condenser section experience very high biofouling pressure in spite of velocities ranging from 1.5–2.5 m/s. In comparison the shell and tube heat exchangers experience severe biofilm formation of condenser tubes and flow blockage due to growth of biofouling organisms and impingement of dead shells (Fig. 2).

Biofouling pressure is dependent on a number of factors like geographical location and availability of larval forms. The constant flow

of fresh seawater brings with it oxygen and nutrient and flush out excretory products which make the CWS environment favourable for settlement and growth of fouling organisms [3]. In addition, biofouling in industrial cooling water system is governed by physical and chemical heterogeneities like hydrodynamic forces, shear stress, substratum roughness, free energy and chemistry. The ionic strength of the aqueous medium also determines the development of the initial conditioning film favouring the adhesion of bacteria, diatoms producing exopolysaccharides which make the biofilm anionic. The cues emanating from the biofilms inducing marine invertebrate larvae to settle on the surfaces. For a detailed review on bifouling in cooling water systems refer to [4] and for industrial Biofouling refer to [5].

2. Economic Impact of Biofouling in Power Plant Cooling Water Systems

Biofilm formation and biofouling in shell and tube heat exchangers in once through seawater systems experience reduced heat transfer due to thermal resistance of biofilms. The thermal resistance of biofilms on heat exchanger tubes is 1/5 of a carbonate scale and a 1 mm thick biofilm has the insulating properties of a 5 mm carbonate scale. Theoretically a 1.5 mm biofilm on heat exchanger surface is known to decrease the flow area by 40%. A 1 mm loss in condenser efficiency amounts to a 1million dollar loss per anum [6]. In general, during the design of heat exchangers for seawater system a fouling factor of 0.0002 $Wm^{-2}K^{-1}$ is provided which increases the surface area by 25–45% to take care of biofouling associated losses. On the other hand, over design of heat exchangers results in increased cost of operation and thermal pollution. The presence of biofilms on condenser tubes results in formation of hot spots leading to under deposit corrosion and failure of the tubes resulting in plugging of the heat exchanger tubes. In addition, the shell and tube heat exchangers often encounter flow blockage from the detached shells upstream in the precondenser section as well as fouling growth by barnacles. To combat the problem physical antifouling methods like sponge ball cleaning have been incorporated in shell and tube heat exchangers to clean the biofilm (microbial slime) in-situ thus aiding in minimizing the downtime for offline manual cleaning.

Compared to biofilm formation macrofouling in the sea water intake tunnels results in 1) pressure drop 2) heat loss in the pump house, 3) accelerated corrosion [3]. The precondenser section of the cooling water system experiences high biofouling loads by barnacles, green mussels, bryozoans, ascidians etc. in spite of a biocidal regime in vogue. Earlier reports on economic impact of biofouling problems in a 235 MWe coastal power station is estimated to be about 40 lakh rupees [7]. In regions of heavy mussel fouling about 300 tons of mussels were removed from the intake tunnel of the Madras Atomic Power Station (MAPS) after shock chlorination [8].

Biofilm accumulation on heat exchanger tubes increases with decrease in water velocity. A study by Rubio et al. [9], demonstrated that a decrease in velocity from 2.1 to 1.3 m^3s^{-1} resulted in an increase in fouling factor by 3.5 times. In once through seawater cooled system the condenser tubes comprise chiefly of cupro-nickel 90:10 and aluminium brass 70:30 to withstand fouling and corrosion, however, these tubes have been shown to be prone to punctures. Titanium grade I has been recently used to combat the problem of corrosion. However, it has been shown that titanium is a passive material and highly prone to biofouling.

3. Biofouling Control Methods in Once-Through Seawater-Cooled Systems

3.1. Physical methods

3.1.1. Flow

In once through seawater systems, marine invertebrate larval forms have been influenced by velocity of water. Larval forms are capable of settling at high velocities up to 3.0 m^{-1} (Table 1). Once settled and metamorphosed into juveniles the adult organisms are able to withstand water velocities > 4.0 m^{-1} [10].

In large sea water cooling systems having intake tunnels / pipelines ranging from 1–3 meters in diameter the water velocity must be measured close to the wall surface compared to the mean water velocity as settling invertebrate larvae experience this velocity

and shear stress at the surface near the boundary layer. In general, it has been shown that marine invertebrate larvae settle up to water velocities up to 4 ms^{-1}. The high water velocities above 4 ms^{-1} the shear stress exceeds the shear strength of most of these organisms and hence they do not settle. Barnacles, green mussels, brown mussels have all been shown to settle at water velocities up to 3.0 ms^{-1}. Once settled and metamorphosed to adults the hard shelled surfaces of these organisms offer further sites for further favourable colonization and the fouling biomass increases in size. Hence it is of importance to adopt a chemical control strategy as flow alone cannot be used to prevent settlement of organisms in cooling water systems.

In comparison to macrofouling of cooling water conduits microfouling organisms like bacteria and diatoms are a major issue on heat exchanger tubes. Ideally water velocities across tubes in shell and tube heat exchangers are maintained around 0.5–1.4 ms^{-1} for optimum efficiency. Higher velocities than 1.4 ms^{-1} have been shown to elicit biofilm formation. Only difference is the species diversity differs. Bacterial biofilms formed at 1.4 ms^{-1} are highly compact and have been found to adhere strongly to the surface and are difficult to remove. Use of protective antifouling coatings is another strategy which is being implemented in the cooling water conduits of power station.

Table 1. Water velocity on settlement of marine invertebrate organisms.

Velocity ($m\ s^{-1}$)	**Settlement of organisms in CWS**	**Ref.**
0.3	Favours Asiatic clam settlement	[3]
Less than 0.9	Favours sedimentation and microfouling to occur	[3]
> 0.1 - 1.5	Favours mussel settlement in *Branchidontesvariablis*, *B. striatulus*and *Modiolusphilippinarum*	[11]
>3.0	Does not detach mussels	[12]
Above 2.0	Inhibits Zebra mussel larval settlement	[13]
1.8–2.2	Allows settlement of mussels, barnacles, hydroids in circular conduits	[3]
Up to 1.4	Allows mussel, barnacle, hydroid settlementin large rectangular conduits of (5–11 m^2)	[3]
>4	Preventing erosion corrosion of metal structures	[3]

3.1.2. Temperature

In general sizing of the cooling water system and the heat exchangers are done based on the process requirements and the upper thermal limits of discharges. In tropical country like India the upper thermal limits of discharge has been restricted to 7-10 ˚C for plants constructed before the year 2000. Subsequently the discharge limit has been reduced to 7 ˚C. Recently in the year 2025 the discharge limit has been further reduced to 5 ˚C considering the climate change scenario. Currently the heat exchangers and the cooling water systems have become large to meet the environmental discharge limits in the tropics. Several power plants in temperate countries have incorporated the thermal back washing strategy in their cooling water systems. The organisms living in temperate waters are acclimatized to water temperatures ranging from 15-22 ˚C and an elevated temperature results in their mortality. In comparison organisms in the tropics are acclimatized to temperatures ranging 27-30 ˚C being the

annual fluctuations of seawater temperature. These organisms are already living in their upper thermal maxima and any further increase in temperature results in their mortality.

The effect of temperature as an antifouling method is dependent on the exposure time and elevated temperatures experienced by the organism compared to the acclimatization (ambient) temperature of the organism. Different species in CWS have different tolerance to temperatures and the thermal tolerance and susceptibility needs to be ascertained for the given endemic species before arriving at the regime for thermal backwashing. The rate of acclimation also influences the thermal tolerance. In general thermal backwashing in CWS is generally administered from 3-6 h in a day (Table 2).

The McMohan [14] description of LT_{50} and LT_{100} mortality of fouling organisms is given in the following formulae, which can be used for assessing the upper lethal temperatures.

LT_{50} = 34.5–0.035+0.14 (°C acclimation temp)

LT_{100} = 36.1–0.040+0.14(°C acclimation temp)

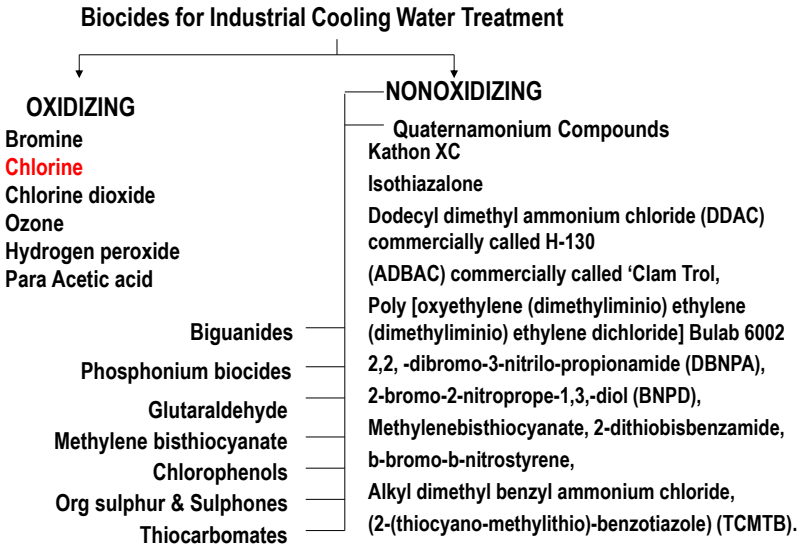
However thermal backwashing of CWS has a drawback in that the thermal shock treatments with regard to meeting the environmental limits of thermal discharges.

Table 2. Effect of temperature on the mortality of marine invertebrate organisms.

Temp. (°C)	Effect on fouling organisms	Ref.
35–37	Kills most macrofouling organisms	[15]
37 for 30 min; 38 for15 min; 39 for 5 min	Causes 100% mortality in the mussel *Mytilusedulis*	[16]
35–47	Causes 100% mortality for barnacle*M. tintinabulum*	[17]
39 for 30 h; 43 for 30 min; >45	Tolerates; 100% mortality within 2.15 h; 100% mortality immediately for *B. striatulus*	[18]
43 for 30 min	Causes 100% mortality in the greenmussel *Pernaviridis*	[18]

3.1.3. Mechanical Cleaning

Cooling water systems (CWS) in general have two lines of physical defense for the ingress of large fish and marine debris. The first line of defense is at the intake point with two types of sluices gates of different grating to prevent ingress of large fishes etc. The marine organisms are subjected to impingement on the sluice gate and the structure needs to withstand the impact. At the pump house the second level of defense in the form of travelling water screen
removes large organisms and marine debris from the system. The most vital component of the CWS is the heat exchangers where biofilm formation impacts heat transfer. To address this system HX have a sponge rubber ball system which circulates in the HX system wiping the inner side of the heat exchanger tubes periodically to prevent increase in biofilm formation. Ceramic and sponge rubber balls have been often used for online cleaning. Offline methods use taking one of the heat exchangers offline periodically and then resorting to hydrolazing (a high pressure water jet cleaning) with a pressure of 10-20,000 psi. Other off-line methods include use of mechanical cleaning using sprially wound indented plastic or iron brushes for cleaning of silt deposits. Other mechanical methods include compressed air driven devices.



Biocide	Chlorine	HOCl	OCl^-	ClO_2	O_3	H_2O_2	Br_2
Oxid Pot	1.36	1.49	0.89	1.50	2.07	1.77	1.07
Cost Rs/L	10 -12	---	---	100 - 150	150 - 200	15 - 50	75 -110

Figure 3. Oxidizing and Non oxidizing biocides for treating cooling water system.

3.1.4. Chemical Methods

In large once through seawater cooled system oxidizing biocides have been the preferred choice for application (Fig. 3). Biofouling control and environment are two sides of a coin which needs to be considered in devising an effective biocidal regime. The most common oxidizing biocides used in CWS based on their efficiency are chlorine dioxide > Chlorine > bromine > hypochlorous acid > hypobromous acid > chloramines > paraacetic acid. The classification in terms of volatility is ozone > chlorine > chlorine dioxide > chloramines > hypochlorous acid > hypobromous acid. Ozonation of seawater cooling system is not generally practised due the high cost involved and its volatility.

Chlorine has been the preferred biocide in large once through seawater cooled systems due to its cheap cost, known breakdown products, ease of handling, and availability. However, the active biocide hypochlorous acid quickly disassociates into H^+ and OCl^- at high seawater pH of 8.2. In addition, chlorine reacts with organics to form chloramines and trihalomethanes which again reduces the biocidal activity. Even with this reduced biocidal activity chlorine has been shown to reduce biofouling loads in cooling water systems from 75 kgm^2yr^{-1} to 14 kgm^2yr^{-1}. Some of these disadvantages of chlorine has led to power plant operators to switch to a safer biocide viz. chlorine dioxide (ClO_2). Chlorine dioxide is now being increasingly adopted at different power stations which require high amount of cleanliness and to meet discharge limits criteria. Chlorine dioxide does not react with organics present in seawater and produces chlorite ion as a by-product. Chlorine dioxide is a stronger oxidant and is able to penetrate effectively the biofilm matrix and able to disinfect the underlying bacteria in microbial biofilms on heat exchanger surfaces. In general half the concentrations of chlorine is required when chlorine dioxide is used. Bromination is also a preferred practice in seawater systems either by dosing bromine chloride or the use of brominated salts and activation using chlorine which is already a baseline biocide to the system. Targeted bromination is of heat exchangers usually practised in seawater systems encountering high biofouling pressure on an intermittent dosage. Chlorine dioxide and bromination is also adopted for shock targeted dose of heat exchangers to improve cleanliness and meet discharge norms.

4. Biocidal Discharge Limits at Marine Outfalls

Biocide discharge at marine outfall is regulated in many countries. In temperate countries where thereinsights into the structural material degradation inflowing molten sodium.is less biodiversity discharge of biocides at total residual oxidants (TRO) is limited from 0.01–0.1 mg/L whereas in tropical countries with high biofouling pressure and loading it is limited to 0.2 ± 0.1 mg/L. In tropical countries shock dosing is permitted to 0.4 ± 0.1 mg/L for 8 hours in a day to combat the biofouling settlement and to overcome seasonal spikes in settlement of organisms during the breeding seasons.

In CWS with heavy mussel infestation a practice called Pulse Chlorination® is adopted which relies on the opening and closing of mussel valves as an indicator for dosing of the biocide. This saves inventory of biocide and offers an effective solution for killing of adult mussels infesting the CWS.

5. Surface Protective Antifouling Coating

Since biofouling is a surface associated phenomenon and the invertebrate larvae sense the substratum and attach and settle on the substratum. It is important that surface protection in the form of antifouling coatings is applied to the cooling water systems. Currently, Polydimethylsiloxane (PDMS) based foul release coatings, which rely on the principle of low surface energy, have been in vogue. A cohesive failure of the bio-adhesives produced by biofouling organism occurs at the coating surface when exposed to flowing seawater due to shear forces exerted at the surfaces. This principle helps in keeping the surface of the antifouling coating free of fouling organisms. However, these coatings have been shown to accumulate microbial biofilms and have not been shown to be effective in preventing bacterial and diatom adhesion. Another drawback of this coating is that it also fails to prevent biofouling of surfaces under static conditions. Field trials with commercial antifouling coatings in Kalpakkam coastal waters have shown excellent foul release properties both in the coastal waters and as well as inside the cooling water system (Fig. 4,5).

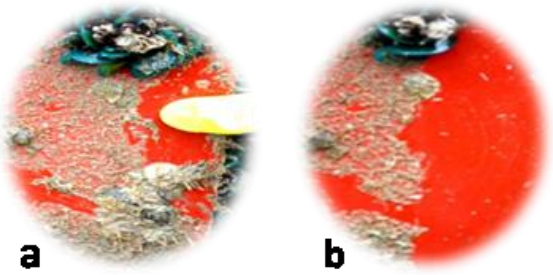


Figure 4. AF coating performance in coastal waters (a) A 100 days old AF coated panel. (b) The fouling layer was dislodged by wiping with finger.

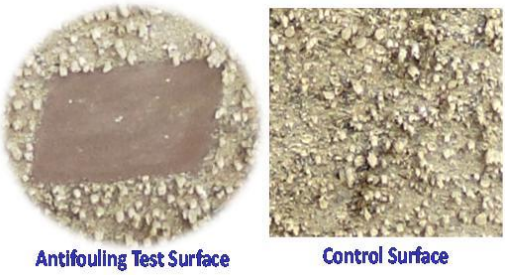


Figure 5. KKNPP Seawater Intake Conduit Antifouling Coating Performance (4 Jul 2017 – 12 Oct 2018). Dense barnacle infestation can be seen on the conduit walls. No biofouling on the test AF coated surface.

6. Conclusion and future Outlook

In tropical conditions with high biofouling pressure once once-through seawater systems are prone to heavy biofouling. It is imperative to understand that all surfaces foul and to combat fouling biocide addition is imminent. The biocidal regime (concentrations & time) is dependent on the severity of biofouling at a given site. In general, in tropical conditions, the upper limit of biocidal discharge in marine outfalls is capped to less than 0.2 mg/L of TRO, which makes the plant operators stay put with certain levels of fouling in the system. Continuous low dose biocidal addition helps to keep the fouling under control within the threshold limits such that it does not interfere with the operation of the system.

Several strategies like low dose chlorination, shock dose chlorination and targeted chlorination have been practised for combating the biofouling problem. However,

it is inevitable in the long run for biofouling build up to reach the threshold levels where shutdown of the power plant becomes imminent, and the CWS has to be taken offline to mechanically clean the conduits and pipelines.

However, the use of antifouling coatings in CWS has ameliorated the problem of biofouling of the conduits and pipelines and has improved the time interval between two successive shut down for manual cleaning. An integrated strategy of using physical deterrent methods like sluice gates, travelling water screens, antifouling coatings for the conduits and pipelines, online sponge rubber ball cleaning of heat exchangers, helps to reduce the biocidal dosings and improve the effectiveness of the biocide, as well as extending the downtime and maximizing power output.

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About the Author

Dr. P. Sriyutha Murthy did his masters in Zoology, from Loyola College, Chennai and his PhD in Zoology from the University of Madras and specialized in Biofouling and its control in cooling water systems of Nuclear Power plants. He has 30 years of experience in Biofouling control in power plants. His area of specialization involves Biofilms and Biofouling control, Ecotoxicology studies on marine organisms, Invertebrate larval biology, Ocean Acidification, Antifouling Coatings, and Superhydrophobic surfaces. He worked at the National Institute of Ocean Technology on the Ocean Thermal Energy Conversion Power Plant and later worked on developing poly dimethyl siloxane antifouling coatings along with the University of Chemical Technology, Sofia, Bulgaria which has resulted in a patent and product development. Dr. Murthy has carried out many sea cruises to study the physicochemical & biological parameters along the East & West Coast of India and has completed many Environmental Impact Assessment (EIA) studies. He was also a visiting scientist at the SWIRE Institute of Marine Science, University of Hong Kong. He joined Bhabha Atomic Research Center (BARC) Kalpakkam to work on Biofouling control for heat exchangers. He is currently working on the topics of Biomimetic approaches to create superhydrophobic antimicrobial & antifouling surfaces and exploring the diversity of microbes in the deep-sea environment.

Corrosion Issues of Structural Materials in Fast Reactor and Associated Spent Nuclear Fuels Reprocessing Plant Environments

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Abstract

The major issue limiting the service life of components in reactors and associated nuclear reprocessing plants is material degradation. However, structural components and materials suffered failures due to corrosion, resulting in significant economic losses from shutdowns, repairs, inspections, and replacements of these components, which directly impact reactor life, longevity, safety, and the economic operation of nuclear power plants and associated reprocessing plants. The paper provides an overview on the corrosion issues related to fast breeder reactors (FBRs) and associated fuel cycles, research and development activities carried out within our corrosion lab at IGCAR focusing on the development of high-temperature structural and advanced materials and novel durable coatings for corrosion protection as well as assessing the corrosion performance in different environments like: molten sodium, Pb (LBE), molten salts and steam-water, seawater, nitric acid, MIC, and concrete corrosion, steam oxidation, etc. Understanding these corrosion degradation processes in various corrosive environments is crucial for designing advanced materials and coatings that enhance component lifetimes and improve the overall safety and sustainability of current and next-generation nuclear technologies. The comprehensive strategies adopted for the development of advanced and novel materials and coating technologies to handle highly hostile and corrosive environments, for FBRs and their associated fuel cycle facilities, are also briefly highlighted.

Keywords: *Fast reactor; sodium corrosion; molten metals; molten salts corrosion; reprocessing; coatings; nitric acid corrosion*

1. Introduction

FBRs are of critical importance to India because they enable the country to overcome its limited uranium resources and transition toward long-term, self-sustaining nuclear energy. The deterioration and corrosion of materials utilized in nuclear power plants (NPP) pose significant problems to the safety, dependability, and long-term viability of nuclear systems [1]. Some major corrosion issues of structural components in fast reactor and spent fuel reprocessing environments are listed in Table 1. In FBRs, the structural materials are exposed to high temperatures, aggressive coolants, and intense irradiation, leading to unique corrosion challenges.

In sodium systems**,** the primary issues include leaching, *decarburization,* c*arburization*, and *mass transfer*, driven by carbon activity gradients between structural steels and sodium-exposed components [2,3], Lead cooled fast reactors (LFRs) offer significant safety and chemical inertness advantages over SFRs, making them an attractive option for next-generation fast reactor development. Issues such as liquid-metal embrittlement, flow-assisted erosion-corrosion, and microstructural instability exacerbate the corrosion problem of structural materials [4]. Furthermore, environment-assisted cracking (EAC) is a significant concern for the structural integrity of NPPs operating under certain conditions leading to accelerated crack initiation and growth in reactor components, which can compromise the safety and reliability of FBRs [5]. Microbiologically influenced corrosion (MIC) is a significant corrosion degradation mechanism that affects condenser and

pipeline materials through the metabolic activity of microorganisms [6,7]. A detailed understanding of these degradation processes is crucial for designing advanced materials, enhancing component lifetimes, and improving the overall safety and sustainability of current and next-generation fast reactor nuclear technologies.

Table 1. Major corrosion issues of structural components in fast reactor and spent fuel reprocessing environment.

System	Dominant Environment	Main Corrosion Modes	Affected Materials
Fast Reactor Primary	Liquid Na (500–550 °C)	Leaching, carburization and decarburization, mass transfer, ferrite layer and degraded layer, etc.	304LN, 316LN, D9, HT9, 316FR SS and 316H SS
Steam Generator	Water/steam	Oxidation and SCC	P91, 9Cr–1Mo steel
Reactor Core	Irradiation + Na	RIS, swelling, FCCI, Radiation Embrittlement (DBTT), toughness, helium embrittlement, etc.	D9, IFAC-1, F/M steels, ODS alloys
PUREX	HNO_3+ oxidizers	Uniform corrosion, active corrosion, tunnel corrosion, IGC, SCC, transpassive corrosion, galvanic, vapour phase, etc.	304L, 304ULC, NAG SS, URANUS 65, 310, URANUS S1N, Ti-Gr2, Ti-5Ta, and Zr-4
Decladding	HF, fluorides	Pitting and intergranular attack	SS, Ti alloys
Pyroprocessing	Molten salts – LiCl-KCl, NaCl-KCl, LiCl-KCl-$L_{i2}O$	Active dissolution, redox corrosion, selective dissolution, pitting, SCC, etc.	Fe/Ni alloys, graphite, Ceramic
HLW	Nitric acid + nuclear waste	Uniform, MIC, galvanic, SCC and pitting corrosion	Steel, Cu alloys, SS304L, SS 316L, Ni alloys, Zr, waste form (glass and ceramic), Ti alloys, etc.

Aqueous-based PUREX reprocessing is the deployed, globally and industrially mature method for spent nuclear fuel reprocessing, used on a commercial scale. The PUREX environment is highly aggressive for plant materials, characterized by a combination of hot and boiling conditions, concentrated nitric acid, strong oxidizing and redox species (Fe^{3+}, Cr^{6+}, Ce^{4+}, NO_2^+, NO_3^+, and nitrous acid), high radiation fields, and dissolved metal/redox ions, resulting in complex degradation mechanisms [8]. Type 304L SS is the main workhorse material for reprocessing facilities, owing to its desirable corrosion resistance in dilute to moderate concentrations (<6-8 M HNO_3) at ambient to moderate temperatures (< 80-90 °C). Nitric acid grade (NAG) stainless steels were specifically developed for high nitric acid corrosion resistance, particularly where Type 304L SS fails [8]. Titanium and zirconium-based alloys remain the preferred choice for spent fuel dissolvers, particularly in environments where boiling and high-concentration nitric acid is used. Zr exhibits exceptional corrosion resistance in all three phases (liquid, vapour, and condensate phases) at high temperatures and nitric acid concentrations, making it suitable for critical components. In contrast, Ti usage has a limit in condensate phase nitric acid applications

[8]. Furthermore, bulk metallic glasses (BMG) and refractory high-entropy alloys offer improved corrosion resistance in a nuclear reprocessing environment. Pyrochemical reprocessing is considered a promising future technology for metallic fuel fast reactors with high burn-up and closed fuel cycle sustainability [9]. The extreme operating conditions demand advanced materials, such as high-Ni alloys, refractory metals, and protective coatings (ceramic, HDG, pyrolytic graphite, nitride, carbides, etc.), to ensure the long-term durability of pyroprocessing systems. This article aims to highlight recent research, reviews, and view points on the corrosion-related degradation of materials in fast nuclear reactor systems, as well as comprehensive strategies for advanced novel materials and coating techniques that address corrosion issues in nuclear fuel reprocessing cycles in fast reactor systems.

2. Materials and Test Methods

The major materials, coating and characterization methods reported in this article are listed below:

2.1. Materials

316LN SS base and weld, 304L SS, Modified 9Cr-1Mo steel, Ti (grade 2), Carbon steel, Ceramic coating, BMG, HDG, Pyrolytic graphite (PyG), yttria stabilized zirconia (YSZ), titania stabilized zirconia (TSZ), alumina, yttria, lanthanum zirconate (LZ), magnesium aluminate spinel (MAS), and yttrium aluminium monoclinic (YAM), etc.

(i) APS coating and CVD for Pyrolytic Graphite coating

APS ceramic coatings ~300 μm thick were deposited on a 316L SS substrate with an 80–100 μm NiCrAlY bond coat.

(ii) SHP surface by coating

- The anodized and graphene oxide (GO) coated Ti was treated with a silane solution under ambient conditions before being dried in an oven.
- Using dip coating, a composite coating of nanoparticles (ZrO_2) and GO flakes was applied to carbon steel substrates.

(iii) Slow strain rate tests (SSRT)

- For evaluating the stress corrosion cracking (SCC) susceptibility of materials.

(iv) Tribocorrosion–combined wear and corrosion degradation process evaluation.

(v) Arc melting and the melt spinning method for the preparation of bulk metallic glasses alloys.

(vi) Molten salt corrosion facility for corrosion evaluation of pyrolytic graphite coating for pyrochemical reprocessing application.

(vii) Corrosion testing in corrosive environmental conditions

- Molten salt: LiCl-KCl + 5 wt.% UCl_3
- Liquid molten sodium
- Liquid molten Pb
- Acidified chloride
- Seawater
- Nitric acid of simulated reprocessing condition.

2.2. Characterization methods

Optical, FE-SEM, Water contact angle, Raman spectroscopy, XRD, Epifluorescence microscopy; Huey test (nitric acid corrosion), Electrochemical methods, etc.

3. Overview of Corrosion Issues

3.1 Corrosion of type 316LN SS and Mod. 9Cr-1Mo steel in Molten Sodium

In the fast breeder reactor (FBR), the intermediate heat exchanger (IHX) is a critical component made of 316LN SS, as the wall thickness of the IHX tubes is only 0.8 mm. The sodium corrosion of 316LN SS used in IHX is significant, as the loss in ductility due to sodium corrosion lead to premature failure of the IHX tubes. The steam generator (SG), which is of Mod. 9Cr-1Mo steel, is another critical component in the secondary circuit of FBRs, as it separates sodium from steam. The integrity of the SG tube is important, as the reaction between sodium and water is highly exothermic in nature. To mitigate the failure of IHX and SG tubes and extend the life of critical components, long-term evaluation of sodium corrosion is crucial. Thus, by subjecting the samples to flowing molten sodium at 550 °C in a Bi-metallic (BIM) loop intended to mimic the secondary circuit of an FBR, the long-term sodium corrosion behaviour and its impact on the mechanical strength of type 316LN SS and Mod. 9Cr-1Mo steel is investigated [2,3]. The dynamic BIM loop schematic diagram is shown in Fig. 1.

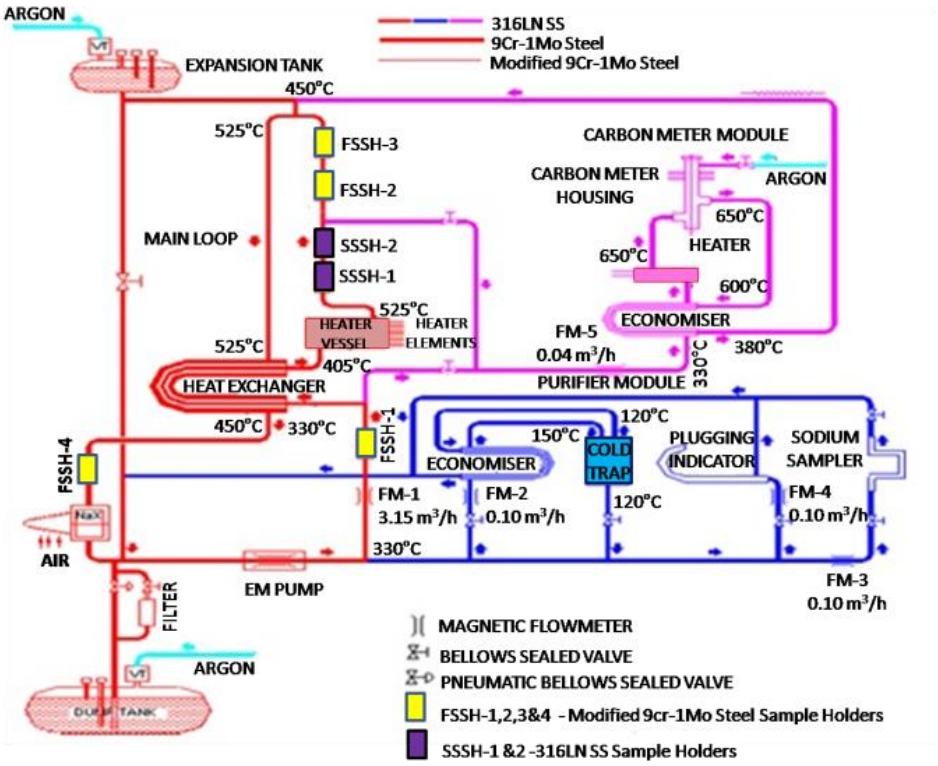

Figure 1. Schematic drawing of dynamic bimetallic loop.

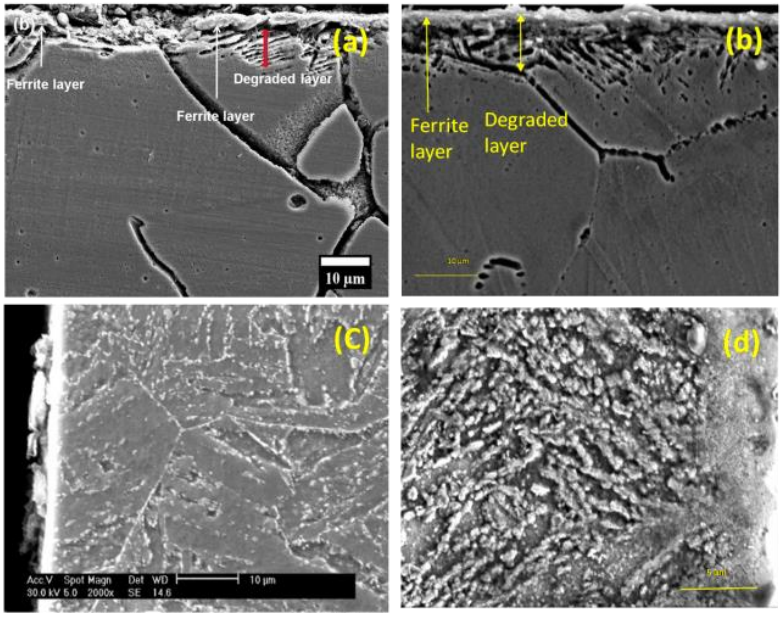

Figure 2. SEM micrographs of samples exposed to sodium for (a) 316LN SS 30000 h, (b) 316LN SS 50000 h (c) Modified 9Cr-1Mo steel 30000 h, and (d) Modified 9Cr-1Mo steel 50000 h [2,3].

The SEM cross-section micrographs of long-term corrosion tests of 316LN SS and Mod. 9Cr-1Mo steel for 30,000 and 50,000 h is displayed in Fig. 2. Ni, being an austenite stabilizer, was preferentially leached in 316LN SS, resulting in the ferrite layer

formation, as evident in the SEM micrographs (Fig. 2a and 2b). The modified austenitic layer was observed below the ferrite layer, a characteristic feature of sodium corrosion [2]. Sodium-exposed Mod. 9Cr-1Mo steel revealed no major changes in microstructural (Fig. 2c,d), microchemical and mechanical properties. However, in 316LN SS, a loss in ductility and increased surface hardness attributable to carburization [3]. A decrease in % total elongation by 40% was observed for 316LN SS after 50000 h exposure, compared to the thermally aged sample. The long-term corrosion studies provided valuable insights into the structural material degradation in flowing molten sodium.

3.2. Liquid Sodium Compatibility of Ceramic Coatings for FBRs

The liquid sodium compatibility of atmospheric plasma spray (APS)-coated ceramics in a sealed stainless-steel vessel, holding sodium and isothermally maintained at 400 °C for different durations, ranging from 100 h to 1000 h are evaluated. APS ceramic materials examined include YSZ, TSZ, alumina, yttria, LZ,MAS, and YAM [11]. At the end of 1000 h of exposure to liquid sodium, APS YSZ coating exhibited sequential disintegration in the coating thickness and showed complete removal of YSZ (Fig. 3a,b).

YSZ APS coatings are expected to fail in liquid-sodium settings due to erosion caused by liquid sodium penetration into the porous structures and decohesion at lamellae splat borders [10]. Concomitantly, APS alumina coatings failed in liquid sodium due to delamination of the intermittently deposited topcoat layers (Fig. 3c,d). The chemical reaction between sodium and alumina APS coating results in stress growth with the reaction products (Na-Al oxides) in the intermittent layers, accompanied by volume expansion at localized sites, which leads to delamination and buckling of the topcoat layers. APS yttria coatings exhibited partial thickness loss of ~20% and 30% after 500 h and 1000 h in liquid sodium, attributed to partial decohesion and erosion effects (Fig. 3 e,f).

Magnesium aluminate spinel exhibited neither thickness loss nor dissolution in long-term exposure to liquid sodium, demonstrating satisfactory performance, except for a mild surface attack (Fig. 3g, h). Extensive topcoat erosion was observed in titania-stabilized zirconia coatings, which is expected given intergranular attack and loss of cohesiveness between inter splat borders. Dislodgements were observed in lanthanum zirconate coatings, attributed to topcoat layer erosion and spallation resulting from parallel delamination cracks in the topcoat (Fig. 3i,j). YAM coatings exhibited markedly improved behaviour in liquid sodium, primarily due to their resistance to grain-boundary attack and stronger cohesion across neighbouring splat boundaries (Fig. 3k,l) [11]. From the experimental results, the coatings can be ranked in order of performance in high-temperature liquid sodium as follows: YAM/Spinel>Yttria> Alumina > LZ >TiSZ>YSZ [10, 11].

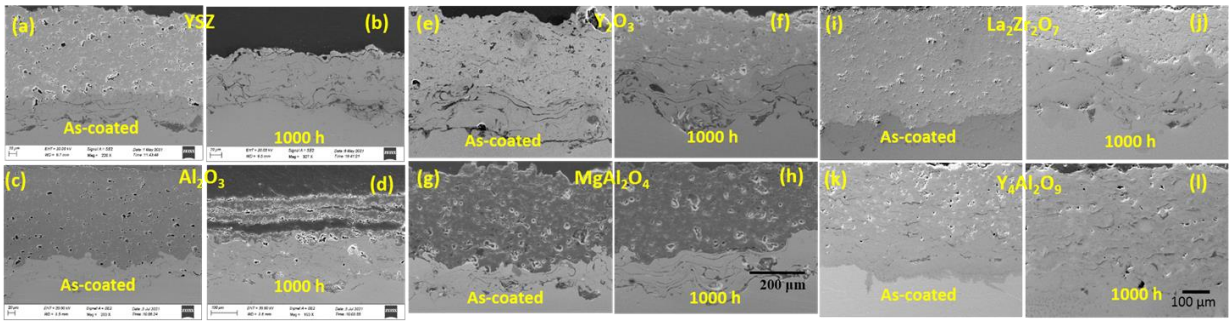

Figure 3. SEM cross-section images of as-coated and post sodium exposure for 1000 h: (a,b) YSZ; (c,d) Al_2O_3; (e,f) Y_2O_3; (g,h) $MgAl_2O_4$; (i,j) $La_2Zr_2O_7$; (k,l) $Y_4Al_2O_9$ [10, 11].

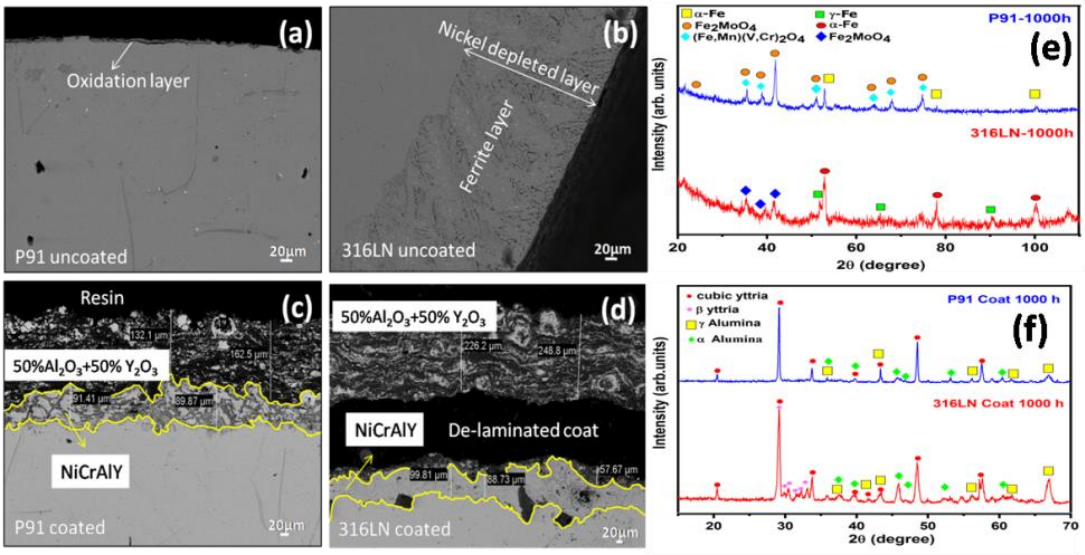

Figure 4. SEM cross-section images (a-d) after 1000 h lead exposure (a) uncoated P-91 steel (b) uncoated 316LN SS (c) coated P-91 steel (d) coated 316LN SS, (e-f) XRD analysis (e) P-91 steel and 316LN SS and (f) ceramic-coated P-91 steel and type 316LN SS [12].

3.3. Molten lead corrosion mitigation on 316LN SS and P-91 steel by ceramic composite coating approach

Molten lead corrosion poses a significant challenge to the long-term reliability of structural materials in lead-cooled fast reactors (LFRs). At elevated temperatures, molten Pb actively dissolves key alloying elements, such as Fe, Cr, and Ni, leading to rapid surface degradation and loss of mechanical integrity [12]. The work focuses on implementing protective surface ceramic composite coatings to mitigate metal dissolution and high-temperature oxidation of 316LN SS and P-91 steel. The degradation of P-91 steel is primarily uniform dissolution and associated oxidation without any phase transformation (Fig. 4a), whereas 316LN SS experienced dissolution-driven phase changes resulting in ferritization (Fig. 4b). The APS Al_2O_3-Y_2O_3 coating significantly improved the corrosion resistance of P91 in molten lead (Fig. 4c). However, the same coating on 316LN SS suffered from cracking and delamination, attributed to CTE mismatch between the ceramic layer and 316LN SS substrate (Fig. 4d) [12].

The XRD analysis confirmed the oxidation and surface transformation to ferrite in P-91 and SS316LN (Fig. 4e), and the coated material characterization remained unchanged after exposure to lead (Fig. 4f). Understanding these corrosion mechanisms is crucial for designing materials that ensure structural durability in sustained molten lead environments.

3.4. Environmental Assisted Cracking of FBR Structural Materials

Environmental-assisted cracking and aging are major concerns for the long-term viability of NPPs [5]. The Stress-Life (S-N) approach, using the Wöhler curve, was adopted to evaluate the corrosion fatigue of type 316LN SS containing 0.07 wt.% N in various conditions, including as-welded, thermally aged, and solution-annealed states, in 5 M NaCl+0.15 M Na_2SO_4 environment (Fig.5a). The study revealed that environmental factors, such as chloride-induced dissolution, significantly reduces fatigue resistance, especially at higher stress amplitudes. Where passive film breakdown accelerates surface dissolution.

Aging-induced precipitates, such as Cr_2N and $M_{23}C_6$, deplete chromium in the matrix, leading to enhanced crack propagation along chromium-depleted zones. The microstructural inhomogeneity in the weld region, particularly the transformation of delta ferrite into brittle intermetallic phases, further compromises corrosion fatigue resistance. The SCC susceptibility of materials is evaluated using slow strain rate tests

(SSRT) by assessing the ratio of per cent total elongation (%TE) to ultimate tensile strength (UTS) in chloride and inert environments [5]. The SCC Susceptibility Index (I_{SCC}) is calculated to quantify susceptibility, with an I_{SCC} value of zero indicating no susceptibility to SCC, and an I_{SCC} value < 1 to SCC susceptibility. The I_{SCC} and the ratios of UTS and %TE were determined by analyzing load-elongation curves obtained in an inert atmosphere and in a boiling 45% $MgCl_2$ solution using equation (1). The results demonstrate that elevating the nitrogen concentration enhances the SCC resistance of Type 316LN SS. Moreover, the assessment was conducted using the I_{SCC} (1) [13], which further supports the conclusion that a higher nitrogen content enhances SCC resistance in type 316LN SS, as shown in Fig. 5b.

$$SCC\ Susceptibility\ Index, I_{SCC} = 1 - \frac{\sigma_{UTS} * \%Elongation\ in\ Chloride\ Environment}{\sigma_{UTS} * \%\ Elongation\ in\ inert\ Environment} \quad (1)$$

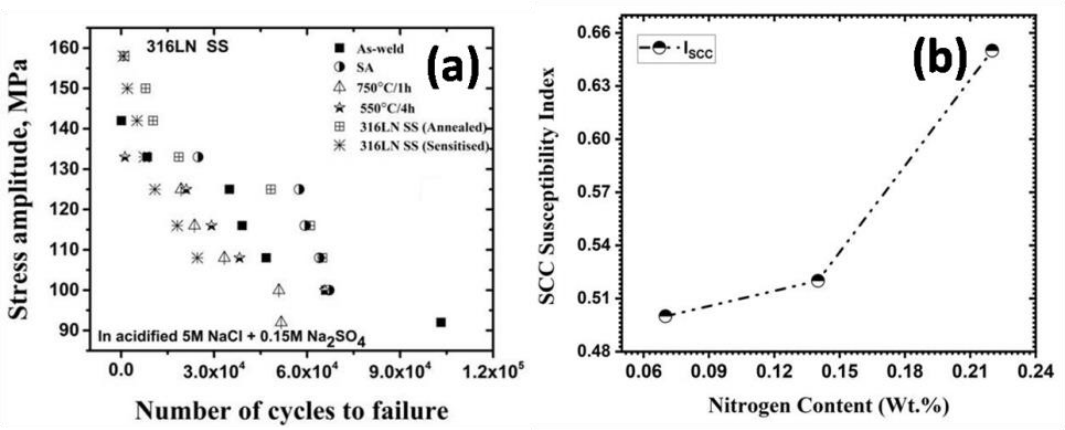

Figure. 5. (a) S-N curve of type SS316LN and weldment, and (b) SCC susceptibility index (I_{SCC}) of different nitrogen content316LN SS on its SCC resistance [5,13].

3.5. Advanced functional coatings for enhancing corrosion and biofouling resistance of condenser and pipeline materials

3.5.1. Superhydrophobic surface modification of titanium

Titanium serves as condenser tubes in the seawater-cooled NPP at Kalpakkam, India, owing to its excellent resistance to seawater corrosion. However, despite this strong corrosion performance, titanium remains susceptible to biofouling-the attachment of macro and microorganisms to its surface. Build-up of these impairs heat transfer efficiency and power output on condenser tubes. To counter this, a robust superhydrophobic (SHP) coating was developed on titanium by incorporating graphene oxide (GO) and silica nanoparticles into a silane matrix, aiming for enhanced super hydrophobicity and antifouling capabilities [7]. The SGA surfaces show a water contact angle of 173° with a negligible zero tilting angle, indicating excellent self-cleaning potential. Samples coated with silane-graphene oxide demonstrated reductions in bacterial adhesion of 3 to 5 orders of magnitude for both Gram-negative Pseudomonas sp. and Gram-positive *Bacillus sp.* compared to uncoated controls. Epifluorescence micrographs of control polished and SHP-coated titanium surfaces exposed to *Bacillus sp.* are presented in Fig. 6 (a & b). The coating also enhanced water droplet bouncing on the surface, a characteristic beneficial for self-cleaning applications.

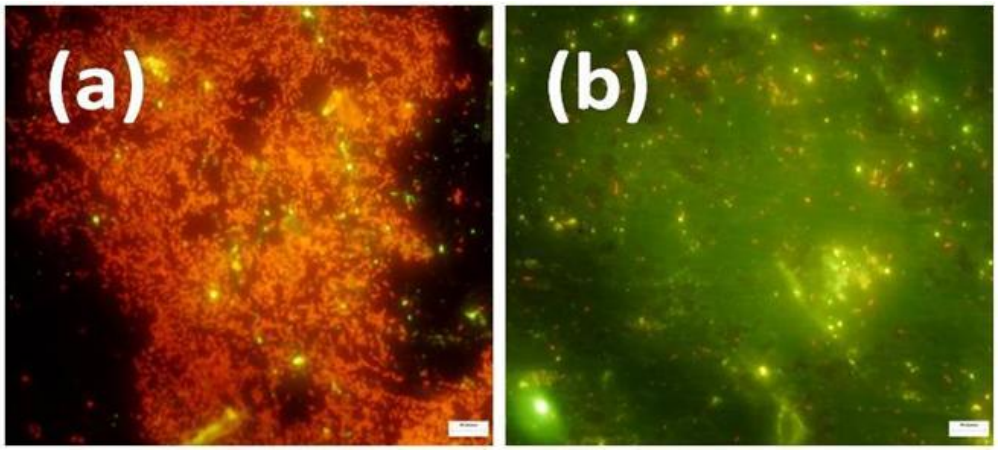

Figure 6. Epifluorescence micrographs of (a) polished titanium and (b) silica-silane coated over GO of titanium anodized and annealed in Gram-positive (*Bacillus* sp.) culture for 6 h, (20 μm scale) [7].

3.5.2. Superhydrophobic coatings on carbon steel

Microbial biofilms MIC pose a significant risk to carbon steel pipelines responsible for conveying freshwater in service and firewater systems of NPPs [14,15]. This work aims to create an SHP coating on carbon steel to provide protection against corrosive environments. Dip-coating carbon steel substrates with a composite of GO flakes, ZrO_2 nanoparticles, and silane yielded a WCA of 169±1°. The dense superhydrophobic layer formed on these samples created a superior ohmic barrier against corrosion processes, thereby improving corrosion resistance.

Silanes reduced the coating surface energy, minimizing bacterial attachment, while sharp-edged GO sheets inflicted mechanical harm to bacterial cells. ZrO_2 nanoparticles generated reactive oxygen species (ROS), inducing oxidation and bacterial cell death [14].

The combined action of these three constituents markedly decreased bacterial adhesion on superhydrophobic carbon steel substrates. Fig. 7a illustrates the characteristic beaded water droplets on SHP surfaces, and Fig. 7b depicts their self-cleaning behaviour.

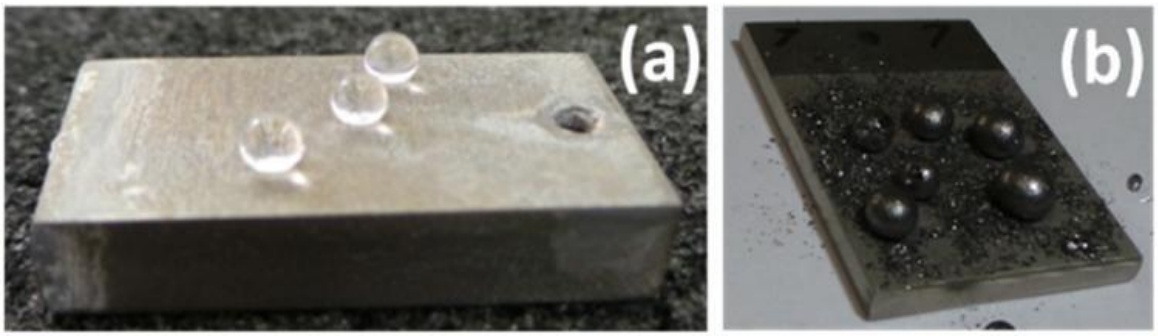

Figure 7. Photographs showing (a) water droplets on the SHP-coated carbon steel, and (b) self-cleaning property exhibited by the SHP titanium [14].

3.6. Corrosion of Aqueous Reprocessing Materials

3.6.1. Tribocorrosion behaviour of 304L SS and its weld metal in simulated reprocessing nitric acid environment

Type AISI 304L SS is protected by a stable passive layer in nitric acid, making it suitable for the majority of equipment in a reprocessing plant. In a reprocessing plant, a condition exists where continuous mechanical actions or operations lead to vibrations that can damage the passive film of 304L SS, resulting in material loss due to the combined action of mechanical wear and corrosion [16]. The combined effect of mechanical and corrosion leading to this kind of material degradation is termed tribo-corrosion. The tests were performed in 8 M HNO_3 with 9.8 N load and a 60 rpm rotational speed, respectively, using a pin-on-disc stand. The tribo-corrosion behaviour of 304L SS base and weld metal in a simulated reprocessing nitric acid environment is shown in Fig. 8. Once sliding was initiated, a cathodic shift of the OCP resulted due to the regular and intermittent passive layer removal in the contact area, and the underlying bare metal was in direct contact with the corrosive nitric acid medium. The OCP drop is in the range of ~235 and 236 mV for 8 M HNO_3 and 8 M HNO_3 containing oxidizing ions for 304L SS (Fig. 8a). However, the higher OCP drop was noted for weld metal in the range of ~284 mV and ~347 mV for 8 M HNO_3 and 8 M oxidizing ion HNO_3 (Fig. 8b). Increased dissolution in the weld active wear track area is the reason for the larger OCP reduction with weld metal compared to base metal. The measured coefficient of friction (COF) during sliding indicated that the value of COF is lower in oxidising ion-containing HNO_3, due to the more extensive oxidation of the surface, which induces a lubricating effect that reduces friction. From the (Fig. 8c) it is clearly evident that the weld metal exhibited more wear volume loss than the base metal. Delta ferrite present in the weld metal adversely affected the tribo-corrosion performance in nitric acid environments. Additionally, the oxidising ions in HNO_3 accelerated the wear volume loss observed in both the base and the weld metal, indicating a corrosion-induced wear phenomenon. The worn surface profilometry results also substantiated the wear volume loss of the materials (Fig. 8d). Thus, corrosion-accelerated wear could be a dominant factor in the greater volume loss of the weld compared to the base metal.

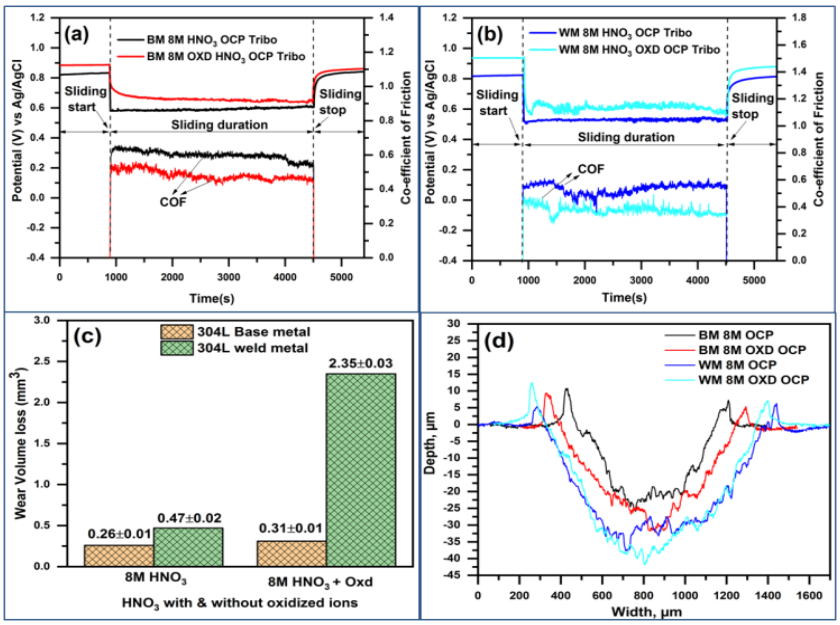

Figure 8. Tribocorrosion behaviour of 304L SS (a) OCP& COF of base metal, (b) OCP &COF weld metal, (c) wear volume loss and (d) worn profile.

3.6.2. Corrosion of $Ni_{60}Nb_{30}Ta_{10}$BMG and partially crystallized BMG alloy in nitric acid

Ni-based bulk metallic glasses (BMGs) are emerging candidates for corrosion-critical components in nuclear spent-fuel reprocessing due to their unique amorphous structure and exceptional chemical stability [17]. The corrosion resistance of $Ni_{60}Nb_{30}Ta_{10}$BMG and its partially crystallized BMG alloy in 11.5 M HNO_3 are shown in Fig. 9. The potentiodynamic polarization results (Fig. 9a) revealed nobler corrosion potential (E_{corr}) and lower passive current density (i_{pass}), indicating high corrosion resistance for metallic glass (E_{corr}0.910 V vs Ag/AgCl; i_{pass} 5 $nAcm^{-2}$) than crystallized samples (E_{corr} 0.780 V vs Ag/AgCl; i_{pass} 260 $nAcm^{-2}$) with enhanced passivation in both the samples. The wider passive region is related to the enhanced passive film stability for the metallic glass sample. The Nyquist plots (Fig. 9b) showed a larger impedance, indicating higher polarisation resistance and passive film stability for the metallic glass sample compared to the crystallised sample. The Mott-Schottky test for analyzing the semiconducting nature of the passive film, and the representative plots are shown in (Fig. 9c). Space charge capacitance measurements at the applied potential revealed a higher flat-band potential for metallic glass compared to the crystallized sample at both frequencies (1 kHz and 3 kHz). Both samples displayed n-type and p-type film behaviour; however, n-type film persisted up to 1.68 V (Ag/AgCl) and 1.4 V (Ag/AgCl), specifically for the metallic glasses and crystallized structures of the samples, respectively and then transformed into p-type semi conductivity. The passive film consisting of Nb_2O_5 and Ta_2O_5 is attributed to the n-type semi conductivity, while the Ni-oxide under layer is governed by p-type semi conductivity [17]. The semiconducting
film on the BMG exhibited lower defect densities, indicating greater passive film stability compared to that on the crystallized sample. Consequently, the reduced corrosion resistance of the crystallized sample stemmed from its more defective passive layer, which facilitated increased permeability to electroactive species.

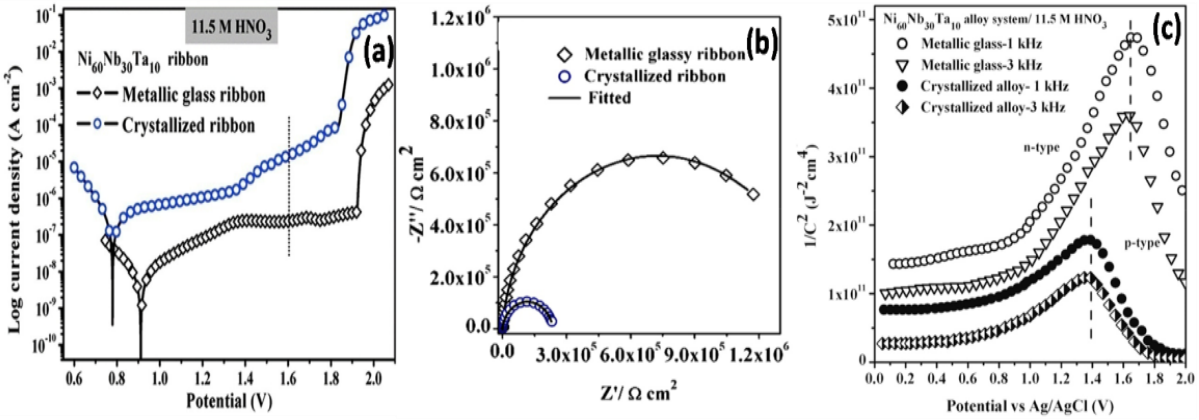

Figure 9. Electrochemical behaviour of $Ni_{60}Nb_{30}Ta_{10}$ for BMG and crystallized BMG conditions in 11.5 M HNO_3 (a) Potentiodynamic polarization, (b) EIS Nyquist plots, and (c) Mott-Schottky analysis [17].

3.7. Molten Salt Corrosion of Pyrolytic Graphite Coating for Pyrochemical Reprocessing

The primary separation process, or electrorefining of spent metallic fuels in the pyrochemical reprocessing, is performed in a molten salt electrolyte composed of a eutectic mixture of LiCl-KCl with 5–6 wt% UCl_3 at temperatures between 500-600 °C in an argon environment. The molten salt corrosion experiments are devised to examine the PyG in eutectic LiCl-KCl+5 wt.% UCl_3salt at 600 °C by static immersion for durations up to 2000 h, and to understand the chemical stability and corrosion attack/mechanism, if any, before its proposal and qualification for

pyrochemical reprocessing applications. The SEM micrographs of the as-coated and 2000 h molten salt-exposed PyG-coated surface at two different length scales (1000× and 10,000× magnification) are displayed in Fig. 10a,b. The respective area elemental dispersive spectroscopy (EDS) is shown as an inset in Fig. 10c,d, which reveals only X-ray peaks for carbon and the absence of salt phase constituent elements of Li, K, and Cl, indicating no salt remnants or corrosion products in PyG surface. The absence of additional peaks corresponding to corrosion products in XRD Fig. 10e and isotropic peaks of graphite, along with no shifting of the (002) peaks in XRD, confirms the chemical inertness and structural stability of PyG. However, a clear peak broadening of the (002) peak is evident, with the FWHM increasing from 0.48° to 0.80°, indicating disorder or strain introduced into the graphitic arrangements after molten salt exposure. Similarly, in LRS analysis (Fig. 10e, the ID/IG ratio increased from 0.2 for the as-deposited state to 0.8 after molten salt exposure, indicating in-plane disorder introduced upon molten salt exposure. Both XRD and LRS indicate disorder, as a result of the introduction of point defects, such as vacancies and broken bonds, at the PyG surface upon interaction with molten salts. However, the molten salt attack appears to be limited to an atomistic length scale and has not progressed to microstructural length scales. Thus, it can be concluded that the molten salt corrosion on PyG in LiCl-KCl-UCl3 at 600 °C for 2000 h exhibited good chemical inertness or corrosion resistance, as evident in the microstructural analysis [18].

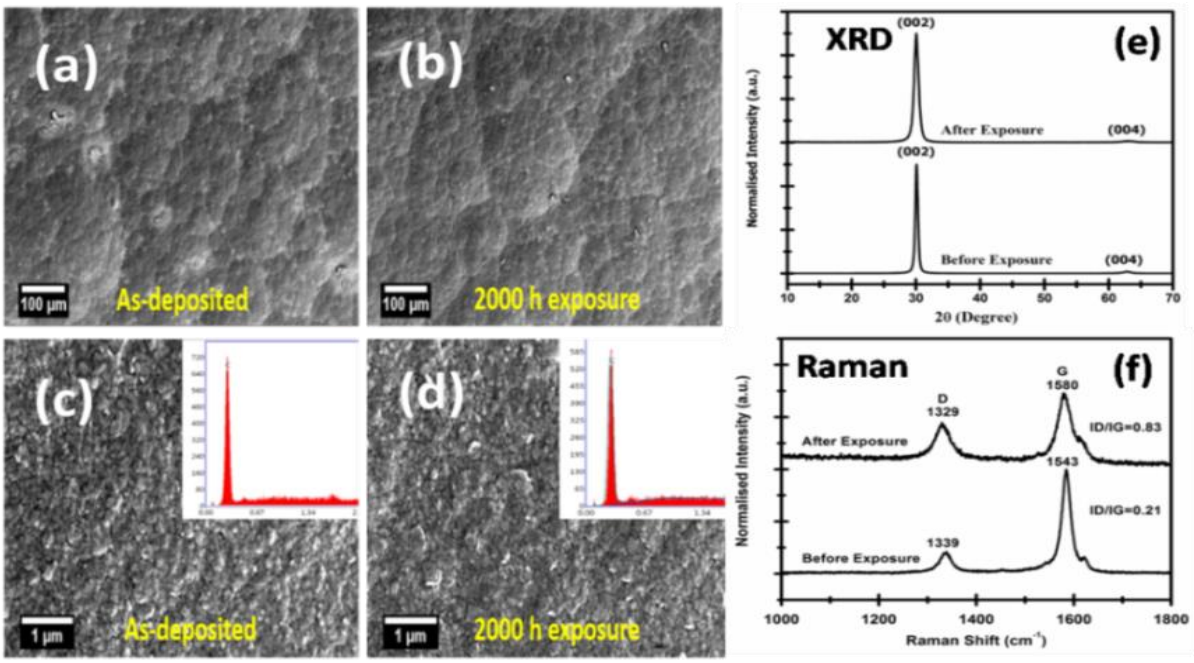

Figure 10. PyG coated (a) SEM of as-deposited 1000 ×, (b) SEM of 2000 h molten salt exposed 1000 ×, (c) SEM of as-deposited 10,000 ×, (d) SEM of 2000 h molten salt exposed 10,000 ×, (e) XRD analysis, and (f) LRS analysis [18].

4. Conclusions and Future Outlook

Based on the research overview and inputs, brief conclusions can be drawn as follows:

- The long-term sodium corrosion studies demonstrated that type 316LN SS undergoes ferrite layer formation due to nickel leaching, increasing surface hardness and a reduction in ductility due to carburization. However, Mod.9Cr-1Mo steel showed no such changes in its properties.
- Based on the liquid sodium compatibility studies, the APS ceramic coatings' performance can be ranked from good to worse as follows: YAM/Spinel >Yttria> Alumina > LZ >TiSZ> YSZ.
- The ceramic composite (50% Al_2O_3 + 50% Y_2O_3) coating is more stable on P-91 steel than SS 316LN in molten Pb.
- Environment-assisted cracking studies revealed that the inferior corrosion fatigue resistance in the as-welded condition is attributed to the transformation of delta ferrite into brittle intermetallic phases. The SCC resistance improved with nitrogen content in type 316 LN SS.
- The chemical-based graphene oxide/silane-based SHP coatings on CP-Ti and carbon steel provided resistance to MIC, biofouling, and general corrosion, making them suitable for condenser and freshwater pipeline applications.
- For PUREX reprocessing applications, the weld metal microstructure and the oxidizing ions in nitric acid have influenced the tribo-corrosion resistance of 304L SS and $Ni_{60}Nb_{30}Ta_{10}$-based BMG, which provided superior corrosion resistance in 11.5 M HNO_3.
- The pyrolytic graphite exhibited microstructural stability in the molten salt LiCl-KCl+5 wt.% UCl_3 salt at 600 °C for pyrochemical reprocessing application.

Future research focuses on:

- *Advanced Alloys:* Developing new ferritic-martensitic steels, ODS alloys, and refractory high entropy alloys for higher temperature and dose tolerance. Developing corrosion-resistant materials for use in aggressive molten salts at high temperatures.
- *Coatings and Surface Modifications:* Applying protective layers to mitigate corrosion and liquid metal embrittlement.
- *Modelling and Lifespan Prediction:* Using advanced computational tools to predict long-term material degradation.

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Overview of High Temperature Molten Salt Corrosion for Pyrochemical Reprocessing Applications

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Abstract

India's future sodium-cooled Fast breeder reactors would be fuelled with metallic fuels due to several advantages over oxide fuels. The reprocessing of these metallic fuels is proposed to be carried out using the pyrochemical reprocessing route. Pyrochemical reprocessing comprises multiple unit operations conducted under varied atmospheres and temperatures from 500 to 1500 °C. The vital step in pyrochemical reprocessing is electrorefining, which utilizes LiCl-KCl eutectic salt in molten state at 500 °C as the electrolyte under inert atmosphere to separate fuel constituents from the spent fuel. Molten salts are extremely corrosive at elevated temperatures, which warrants the use of exceptional corrosion resistant structural materials for salt-handling equipments. Several studies have evaluated materials such as stainless steels, Ni-based alloys, Cr-Mo steels, and various graphitic materials in molten salt environments. Different mitigation strategies and protocols for testing of molten salt corrosion have also been explored. Thermal-spray ceramic coatings have emerged as effective chemical barriers, significantly enhancing the structural materials corrosion resistance. This article provides an overview of high-temperature molten salt corrosion of various structural materials, its mechanism, and various mitigation strategies to avoid and minimize corrosion and also discusses about the way forward for molten salt corrosion studies to identify better materials.

Keywords*: Pyrochemical reprocessing, Molten salts, Corrosion, Corrosion mitigation*

1. Pyrochemical Reprocessing

Presently, the spent nuclear fuel (oxide fuel) from the existing pressurised heavy water reactors (PHWRs) in India is being reprocessed through the aqueous reprocessing route, namely the Plutonium Uranium Redox Extraction (PUREX) process [1,2]. Tributyl phosphate (TBP) with dodecane is used as the solvent to extract both U and Pu in PUREX process. Both carbide and oxide fuels from the Fast Breeder Test Reactor were also processed through PUREX process. In the future, metallic based spent nuclear fuels of India's Fast Breeder Reactors would be reprocessed using non-aqueous reprocessing, namely Pyrochemical reprocessing.

As the name suggests, pyrochemical reprocessing is performed at high temperatures from 500 to 1500 °C. Pyrochemical reprocessing comprises several unit operations, primarily including purification of LiCl-KCl salt, electrorefining of spent nuclear fuel, cathode deposit processing, and injection casting using induction melting of the desired fuel. A simple flow chart of the pyrochemical reprocessing is shown in Figure 1 [3]. The basic separation process of pyrochemical reprocessing is electrorefining. The electrorefining method comprise redox reactions of fuel and fission product elements in molten salt to refine uranium and plutonium, from other fission products. The variation in volatilities and thermodynamic stabilities of actinide and fission product compounds are key parameters for achieving separation. Chopping of the spent metallic fuel pins carried out first, followed by the removal of sodium by distillation. The chopped fuel pins will be taken in a perforated anode basket for electrorefining process. A eutectic mixture of LiCl-KCl salt is used as the electrolyte, with 5-6 wt.% of UCl_3, for improved electro transport during electrorefining. The molten LiCl-KCl salt will be purified first by vacuum drying, followed by chlorination, which involves passing chlorine gas into the salt at high

temperatures. Solid stainless steel and liquid cadmium cathodes are used to deposit both uranium and plutonium in electrorefining.

After electrorefining, the entrapped molten salt from the cathode deposits will be distilled off and the consolidation of the electrodeposited actinides will be carried out in cathode processing step. The obtained pure metals U and Pu are further used to make the fuel rods through injection casting in an induction furnace.

Pyrochemical reprocessing offers several advantages than aqueous based purex process, which includes (i) shorter cooling times and refining of spent fuels (U-Pu-Zr alloy) in a single step, (ii) less unit steps with no fuel transport (iii) small/compact systems, and economical, (iv) recycling of transuranics (TRUs) – Reduces High Level Waste (HLW), also in the solid form, (v)actinides can be recovered and (vii)proliferation-resistance (no product purification) [4–6]. As seen, electrorefining uses eutectic LiCl-KCl (44.5:55.5 wt.% or 58.5:41.5 mol%) salt containing 5–6 wt.% UCl_3 in molten state as the electrolyte at 500 °C under Ar gas atmosphere in glove boxes or hot cells. Hence, the structural materials in the form of crucibles, vessels, etc., for handling molten salts at high temperatures, should exhibit structural & mechanical integrity, thermal stability, and especially better corrosion resistance. Pyrochemical reprocessing is a batch process; therefore, structural materials must be used repeatedly for several batches before being discarded as waste to minimise radioactive waste generation during reprocessing. Selecting structural materials for nuclear fuel reprocessing requires consideration of several parameters, including availability, cost-effectiveness, corrosion resistance, and mechanical properties [3].

2. Molten salt corrosion

The degradation or deterioration of materials upon exposure to high temperature molten salts is known as molten salt corrosion. This occurs as the oxide layers over the materials dissolve in the molten salts, leading to further degradation of the material. Different types of molten salts, including molten chlorides, fluorides, nitrates, sulphates, and carbonates,

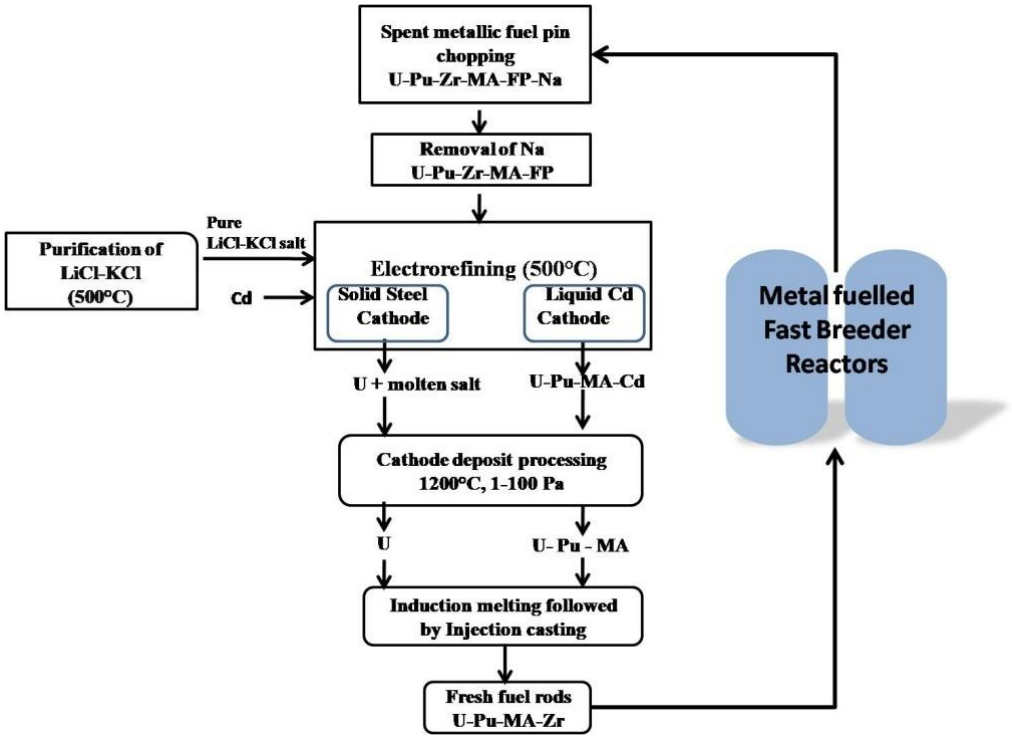

Figure 1. Flow chart of pyrochemical reprocessing.

are utilised for various purposes in concentrated solar power plants, batteries, fuel cells, and the nuclear industry, among others [8–10]. Molten salts have become essential components of the energy sector, being used for the storage and production of energy [11]. Especially in nuclear power generation, molten salts are used as coolants and as liquid fuels in molten salt reactors [12–14]. Molten salts are also used for the pyrochemical reprocessing of spent metallic fuels [4].

Material performance is key to the success of any operation/process. Corrosion plays a vital role in determining the structural material used for a particular application, especially for handling molten salts. In general, from the thermodynamic stabilities of various metal chlorides, 1st and 2nd group (alkali and alkaline earth) metals form stable chlorides than transition metals. Most of the alloying elements of structural materials are transition metals. Therefore, if an alloy is exposed to molten LiCl-KCl salt, it is expected to exhibit no reaction between the alloying elements and the salt, as the salt is more stable. Hence, structural materials are not theoretically corroded by the molten LiCl-KCl salt during exposure; however, in practice, due to the presence of oxidising impurities, the structural materials undergo severe corrosion in molten salts [15,16]. Molten salt corrosion occurs due to the presence of oxidising agents in the form of impurities, such as moisture, oxygen, metal ions, OH^-, and H^+. These impurities may originate from the synthesis of the salt, from storage in the container materials, or during the purification process. If moisture enters the salts through any means, it converts into HCl, leading to severe corrosion of materials that handle molten salts.

Molten salt corrosion is a complex process driven by several factors, including the nature of the salt, impurities, temperature gradients, and the redox properties of the salt. Hence, it is very important to have a close control of the salt chemistry, purity [17] and the experimental conditions at which the salt would be used for the said application. Generally, LiCl-KCl salt is purified by different ways [7], such as drying the salt in vacuum oven, vacuum drying subsequently chlorine gas purging in molten state, drying followed by carbochlorination process, and storing under inert gas atmospheres. Dehydration of salt is generally carried out by passing HCl gas or Cl_2 gas at below its melting point.

3. Mechanism of corrosion by molten salts

The degradation or deterioration of materials when exposed to various environments is generally known as corrosion. Corrosion is primarily an electrochemical process involving the oxidation and reduction of metals and oxidants. Molten salt corrosion is fundamentally electrochemical in nature, occurring through the oxidation (dissolution) of the specific alloying elements and simultaneous consumption of electrons by various oxidants present in the molten salts as cathodic reactions [18]. The molten salt may contain several oxidants, such as foreign metal ions, actinides and fission products from spent metallic fuel, moisture, oxygen and hydroxide ions (OH^-). The anodic dissolution or corrosion of the alloy is completely supported by the extent of cathodic reactions involving the oxidants present in the melt. If the oxidants are very less or minimal, the alloy is supposed to undergo less or minimal corrosion. The redox reactions involved in the molten salt corrosion of alloys are provided in Equations 1 to 3.

$$M \rightarrow M^{n+} + ne^- \quad (1)$$

$$Ox + ne^- \rightarrow Red \quad (2)$$

$$M + Ox \rightarrow M^{n+} + Red \quad (3)$$

where M, Ox and Red are the metal from the alloys like Fe, Ni, Cr, etc., oxidant and reductant, respectively.

The material's corrosion in a given environment is directly correlated to the extent of cathodic reactions that support the oxidation of the material, leading to corrosion. Which can be understood from thermodynamic parameters. In general, the negative Gibbs energy change of a reaction indicates the spontaneity of the reaction. The relation which relates the thermodynamic parameter, especially Gibbs energy change (ΔG) with the electrochemical parameter, potential (E) is given in equation 4.

$$\Delta G = -nFE \quad (4)$$

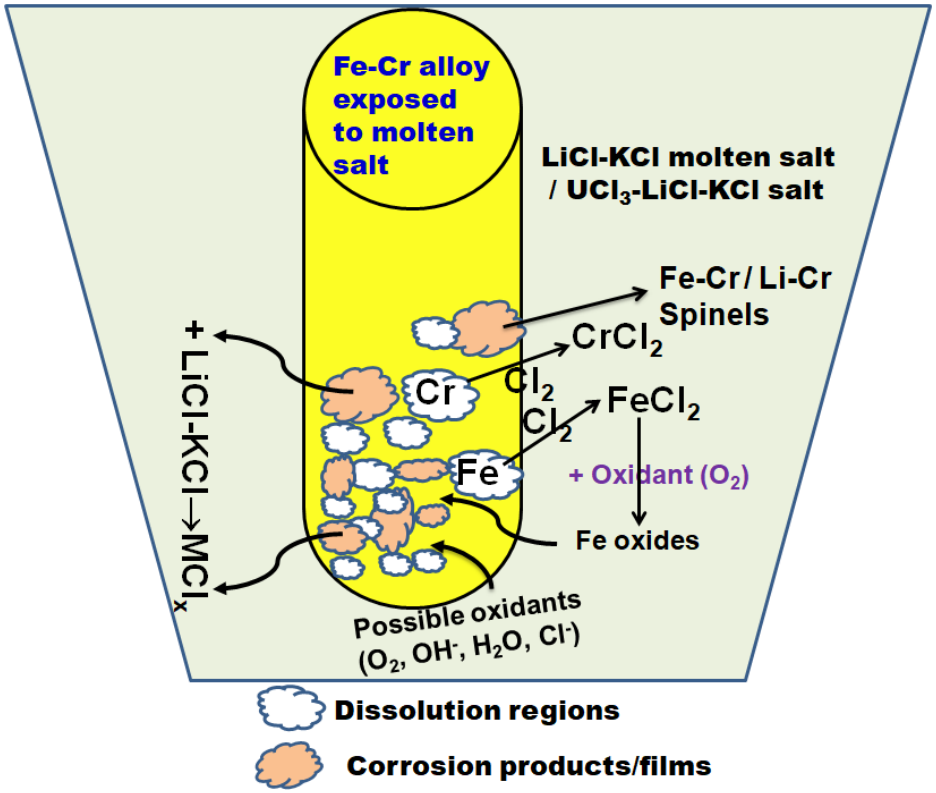

Figure 2. General corrosion mechanism expected in molten chloride salts, LiCl-KCl [7].

Here, F is the Faraday constant, and n is the number of electrons involved in the reaction. The cell potential, E is the actual potential difference of the cathodic and anodic half reactions (E_c-E_a). If E is positive for the cell in which metal/alloy is exposed to molten salt or electrolyte, then ΔG is negative and hence, the corrosion of the material occurs. For the E should be positive, the cathodic reduction potentials (E_c) should be more positive than the anodic potential (E_a). So, when we have more positive cathodic reduction potentials, the metal would undergo corrosion. It is the cathodic reactions in molten salt corrosion controls the overall corrosion of the metal/alloy exposed to molten salts. The reduction potentials of the M/M^{n+} decided the degree the of corrosion in molten salts. The oxidants (for instance foreign metal ions in the salt, impurities) reduction potentials are more (more +ve or less –ve potentials) than the exposed metal, then the exposed metal undergoes corrosion.

So in general, the molten salt corrosion of metals happens with dissolution of metals in to the molten salt, especially selective leaching of less noble metal in case of alloys [19] or alloying elements oxidation and further segregation and formation of metal oxides/hydroxides on the exposed alloys surface. The formation of oxide films or salt films are observed, however, those films are found to be not complete and stable as they easily fluxed (dissolved) by the molten chloride salts. An illustrative of molten salt corrosion mechanism is shown in Figure 2. As mentioned earlier, the molten salt purity plays a key role during corrosion. In pyrochemical reprocessing the molten salts, eutectic LiCl-KCl, prepared by purification of individual salts, LiCl and KCl by drying under vacuum at 200–300 °C for about 36 to 48 h subsequently chlorination for about an hour. After purification, the salt mixture is stored in inert atmosphere glove boxes for future use. Impurities can enter the salt during storage, transportation, and other handling processes. These impurities can lead to the aggressive corrosion of materials during exposure to molten salts.

Hence, for electrorefining applications, the LiCl-KCl eutectic salt is handled inside Ar atmosphere glove boxes or in hot cells with a purity of less than 20–50 ppm of oxygen and moisture. In addition to impurities such as moisture, oxygen, and other metal ions, fission products from spent nuclear fuel will also enter into the salt during the electrorefining process leading to further corrosion of materials.

Temperature also plays critical role in the corrosion of materials, higher temperatures led to higher corrosion rates. As the conductivity of the molten salt would increase at higher temperatures leading to faster electrochemical processes results in higher corrosion. If there exists thermal gradient within the molten salt during exposure of the material, corrosion occurs by mass transport of the less noble alloying elements, as they dissolve from high temperature regions and transport to lower temperature regions and gets segregation. The preferential dissolution and segregation of the alloying elements can lead to failure of the system in molten salt circulation systems [20].

In molten chlorides, the availability of O_2 and moisture can led to the generation of Cl_2 and HCl gas, respectively as per equations 5 and 6.

$$4Cl^-(l) + O_2(g) \leftrightarrow 2Cl_2(g) + 2O^{2-}(l) \quad (5)$$

$$H_2O(g) + Cl^-(l) \rightarrow HCl(g) + OH^-(l) \quad (6)$$

The presence of O^{2-} ions in the molten melt can support the formation of metal oxides from the metal impurities, which enhances the rate of reaction 5. This leads to higher corrosion due to the availability of more Cl_2. If the metals present in the salt as impurities can easily form stable metal hydroxides with the OH^-, then rate of reaction 6 would be higher leading to the formation of more HCl. Hence, the presence of Cl_2, HCl and metal hydroxides enhance the corrosion rate of alloys exposed to molten salts. This warrants the purification and handling of molten salt with caution to avoid molten salt corrosion.

In molten chloride salts, LiCl-KCl melt, during corrosion, the metal chlorides of the alloying elements were observed. Many of the observed metal chlorides are being volatile at 500 °C, operating temperature of the electrorefining process [21], and hence, they leaves the salt leading to higher corrosion rates. There is also another competing reaction to the metal chlorides formation occurs in molten salts corrosion, i.e. formation of the oxides. This occurs even when meager amount of oxygen presents in the melt. So one process, metal chlorides formation during corrosion leads to the weight loss of the alloy and the other process, the formation of metal oxides, results in weight gain in the alloy. Hence, on the basis of chemistry and nature of the molten chloride salt, weight gain or loss are observed during corrosion in molten salts[22]. Another important issue during molten salt corrosion is that if metal oxides forms during corrosion due oxygen availability in the melt, these oxides are not stable and not protect the alloy completely as they fluxed (dissolved) by the aggressive molten salts.

Hence, the investigation of molten salt corrosion and understanding the corrosion mechanism is necessary for the success of processes that use molten salts. It is essential to conduct corrosion studies in molten salts by replicating the actual process conditions present in pyrochemical reprocessing. There are various methods for evaluating molten salt corrosion of structural materials, including immersion experiments that record the in situ weight loss of alloys using thermogravimetric balances, as well as ex situ weight measurements and in situ monitoring of corrosion using transient electrochemical techniques. The corrosion in molten salts are also being evaluated by applying a paste of salt to the surface and heating it in a furnace to the required test temperature.

The corrosion evaluation of different structural materials including alloys, graphite in molten salt environments for the applications in pyro-reprocessing is discussed here. The research and development of several ceramic coatings on the structural materials as a corrosion barrier layers in molten salt applications is also included in the discussion.

4. Corrosion studies in molten chloride salt

A simple search in the Scopus search engine using the term “Molten salt corrosion in LiCl-KCl” yielded more than 100 articles, with the majority of research activity occurring over the last two decades. The Corrosion Science

and Technology Division at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, has emerged as a leading laboratory, as evidenced by the numerous search articles that have carried out extensive evaluations of molten salt corrosion on structural materials and developed protective ceramic coatings for molten salt applications. Some of the works conducted in our laboratory are discussed below, along with some notable other studies.

Raiman and Lee [23] correlated a large amount of data from 1960 to 2016 on the corrosion studies in both molten chloride and fluoride salts. It was reported that most corrosion rates are affected by the salt purity, type of experiment, and type of salt (chloride vs. fluoride). Jagadeeswara Rao et.al., [7] reviewed the various corrosion studies carried out in chloride molten salt especially LiCl-KCl for pyrochemical reprocessing applications. The review also discussed salt purification methodologies, corrosion mechanisms in molten chloride salts, corrosion studies of various structural materials available in the literature, corrosion mitigation strategies, and the ceramic coatings developed for molten salt corrosion resistance. Guo et. al., [18] reviewed the corrosion evaluation of various materials both in molten fluoride and chloride salts for nuclear applications. The review includes corrosion data from the 1950s, corrosion mechanisms, corrosion problems, metallurgical factors that influence corrosion, and the molten salt corrosion-resistant alloys development. There are several other studies related of molten salt corrosion by LiCl-KCl salt are available in the literature[24–28].

Over the last two decades, extensive studies on corrosion evaluation and the development of protective ceramic coatings for corrosion protection against molten salt corrosion have been carried out at our laboratory. Ravi Shankar et. al. [29] studied the corrosion behavior of various alloys, Cr-Mo steels, Ni-based alloys, and partially yttria stabilized zirconia (PSZ/YSZ) coatings in LiCl-KCl salt at 600 °C under Ar atmosphere. The corrosion resistance of different materials found to be followed the order 2.25Cr-1Mo < 9Cr-1 Mo < Ni-based alloys < PSZ coating. The corrosion behavior of SS316L and YSZ coated 316L has been tested in LiCl-KCl salt by Ravi Shankar et.al. [30, 31]. Type 316L undergone severe corrosion during immersion studies, corrosion on the surface was appeared to be having two separate regions, one was corrosion product region with Cr enrichment and the other one was attacked region with Cr depletion. The corrosion evaluation of electroformed nickel (EF Ni), EF Ni with nickel-tungsten coating, 316L, and Inconel 625 alloy in molten LiCl-KCl salt at different temperatures in an air atmosphere was reported by Ravi Shakar et al. [32] and reported that superior corrosion resistance of Inconel 625 among all the alloys studied.

Jagadeesh Sure et al. examined the corrosion behaviour of different carbon materials in eutectic LiCl-KCl salt [33,34]. Both pyrolytic carbon and glassy carbon were found to perform well against molten salt corrosion than high density and low density graphitic materials when exposed for approximately 2000 hours at 600 °C. The corrosion studies in molten salts were also conducted using thermogravimetry, where the weight gain or loss was measured in situ during molten salts exposure at high temperatures. Jagadeeswara Rao et. al [35] studied the corrosion of SS 410, alloy 600 and 9Cr-1Mo steel exposed to eutectic LiCl-KCl molten salt in inert Ar and Ar + 10% O_2 (reactive) atmospheres at different temperatures. Alloy 600 exhibited higher weight gain in both atmospheres than others at 600 °C, and minor weight changes were observed for all the alloys at 500°C under both atmospheres. Chromium segregation with Cr-rich and Cr-depleted regions was observed, and the outward diffusion of Cr resulted in the atmospheres. Chromium segregation with Cr-rich and Cr-depleted regions was observed, and the outward diffusion of Cr resulted in the formation of a less protective $LiCrO_2$ layer, as evidenced by Raman spectroscopic studies.

UCl_3-LiCl-KCl molten salt is being used in the electrorefining process as electrolyte to enhance electrotransport during the electrorefining process. To investigate the effect of UCl_3 on the molten salt corrosion of structural materials, Jagadeeswara Rao et al. studied the corrosion of different materials exposed to a UCl_3-LiCl-KCl molten salt using thermogravimetric analysis [22,36].

Chromoly steels, and SS 410 are being tested in a UCl_3-LiCl-KCl salt at different temperatures for varying durations in

different atmospheres. Marginal weight gains were reported, with the following order: SS410 > 9Cr-1Mo > 2.25Cr-1Mo for the 500 °C study, and 9Cr-1Mo > 2.25Cr-1Mo > SS410 at 600 °C for a 6 h exposure in reactive atmospheres and for a 24 h duration exposure under both inert and active atmospheres. Post-characterisations of the samples revealed the formation of α-Fe_2O_3, γ-Fe_2O_3, and Fe_3O_4, in addition to the enrichment of Mo and depletion of Cr. It was also reported that the attack was higher for 24-hour exposure than for 6-hour exposure in the UCl_3-LiCl-KCl molten salt. Madhura et. al. [37] reported the exceptional corrosion resistance of pyrolytic graphite in UCl_3-LiCl-KCl molten salt at 600 °C for up to 2000 h exposure under UHP argon.

Transient electrochemical techniques are found to the most promising tools to monitor and understand the material's corrosion behaviour in-situ during exposer to molten salts. Several research activities have been used electrochemical techniques to understand and explore the corrosion nature of materials in molten salts [38–42]. Electrochemical transient techniques, such as open-circuit potential (OCP) measurement, linear polarisation resistance (LPR) measurement, electrochemical impedance spectroscopy (EIS) measurements, and cyclic voltammetry (CV) measurements, are employed to investigate the corrosion of materials. Nishikata et al. [43] is summarized the theory electrochemical techniques used to evaluate the corrosion behaviour of materials exposed to various molten salts.

Jagadeeswara Rao et. al. [44–46] studied the corrosion of 9Cr-1Mo steel, 2.25Cr-1Mo, and Sanicro-25 in molten LiCl-KCl salt using electrochemical techniques. During the corrosion of 9Cr-1Mo steel [46] in LiCl-KCl molten salt under inert atmosphere, the OCP was found to move towards the anodic direction with intermittent shifts towards the cathodic direction. Polarisation resistance (Rp) obtained from the LPR studies increased with exposure time. EIS studies and post-characterisation of the sample revealed the existence of an intermittent oxide film over the exposed surface of 9Cr-1Mo steel. Segregation and enrichment of Cr and Mo were revealed during surface characterization using scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS).

In the case of 2.25Cr-1Mo steel [45] immersed into LiCl-KCl salt, the OCP was moved towards noble direction with exposure duration indicating the oxide layer existence. LPR, EIS studies and post characterization revealed the presence of non-protective oxide films. The corrosion behaviour of Sanicro-25 (22Cr25NiWCoCu) [44] steel in molten LiCl-KCl salt was studied using electrochemical techniques at 500 °C for about 100 h by measuring OCP, LPR, EIS at regular intervals during exposure. The change in OCP was observed towards noble potentials, with an intermittent drop in potential towards the active side. The R_p was found to be decreasing with an increase of exposure to molten salt. The oxide layer was found to be consists of Fe_3O_4, Cr_2O_3, iron hydroxide, and spinels by post examination. The EIS studies revealed three-time constant phenomenon (shown in Figure 3) considering the existence of non-protective oxide film over the surface. Akshyata et. al. [47] evaluated the corrosion behaviour of SS316L in molten LiCl-KCl salt containing $CeCl_3$ for about 98 h using electrochemical techniques. It was reported that the formation of a porous $CeCl_3$ salt layer occurred during corrosion, and simultaneously, the alloy showed dissolution of Fe, Ni, and Cr, as evidenced by cyclic voltammetry. As seen from the LiCl-KCl molten salt corrosion studies discussed above, most of the alloys attacked by the salts by dissolution of the less noble alloying elements. The segregation or dissolution of alloying elements and enrichment of the alloying elements was found to be the common among all the studied alloys. It was also observed that the formation of oxide films or corrosion products over the surface during exposure. However, owing to the aggressive nature of the LiCl-KCl, the oxide films do not effectively provide protection to the alloy from corrosion. The oxide films are found to be reactive with the chloride based molten salts and fluxed by the salt. Hence, intermittent, in-complete oxide films were observed over the surface of the alloys during post-examination of the alloys.

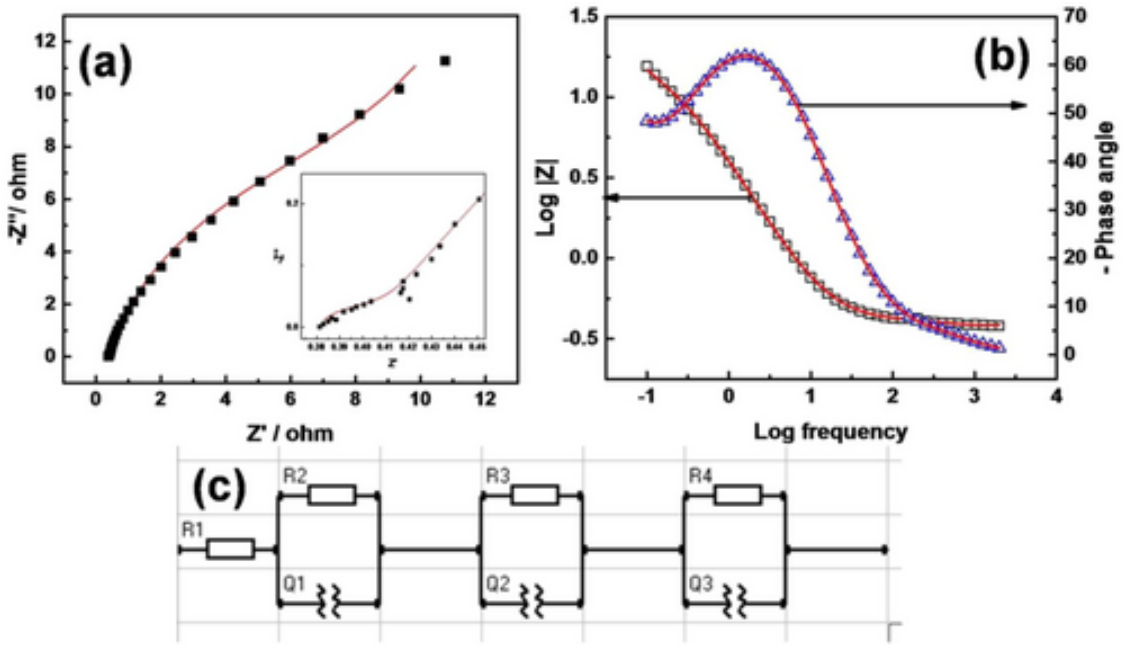

Figure 3. EIS data along with the fitting of Sanicro-25 during corrosion test in molten LiCl-KCl salt. Symbols are the experimental data and solid lines are the fit data. (a) Nyquist plot with fitting, (b) Bode modulus and phase angle plots with fitting, and (c) the equivalent circuit used for fitting [44] (Reproduced with permission from Wiley).

5. Addressing molten salt corrosion issues

The key strategies for addressing molten salt corrosion issues includes, controlling the molten salt purity, proper selection of structural materials, development of protective coatings, reducing the operating temperature to the extent possible, and early detection of corrosion. Molten salt corrosion can be reduced by using salts with highest purity. Molten chloride salts with the highest purity can be obtained through various purification methods, including vacuum drying followed by the passage of Cl_2 gas, electrolysis for removing residual metal impurities, and storing and handling the purified salt under inert atmosphere glove boxes with very low amounts of both moisture and oxygen. Galvanic corrosion of alloys exposed to molten salts can be addressed by avoiding use of different alloys in contact. The reduction potentials of the molten salts can be controlled to prevent corrosion through various methods, such as purging the molten salt with an inert gas or adding redox species like Li. By providing barrier ceramic coatings over the alloys, molten salt corrosion can also be mitigated. Thermal spray coatings are thoroughly used for molten salt corrosion resistance applications [48–53]. The research and development of several ceramic coatings for molten salt corrosion mitigation are reviewed below.

Atmospheric plasma spray (APS), one of the thermal spray technique, is commonly used to develop thick and dense thermal barrier coatings for several key applications. Various plasma spray coatings have been developed for molten salt and molten metal handling in pyrochemical reprocessing using the in-house APS facility at CSTD, IGCAR, India. Yttria stabilized zirconia (YSZ) coatings have been evaluated extensively for molten chloride salt applications. The good corrosion resistance of YSZ coatings on 316L in molten LiCl-KCl salt at 600 °C for approximately 500 hours has been reported by Ravi Shankar et al. [31]. Ravi shankar et al. also evaluated YSZ coatings developed on chromoly steels, Alloy 600, Alloy 625, and Alloy 690 in LiCl-KCl medium and reported better corrosion resistance of the YSZ coating than uncoated samples [29]. Jagadeesh Sure et. al. [54–56] studied the alumina, alumina-40% titania and YSZ coatings developed on graphite materials for

both molten salts and molten uranium applications. YSZ and alumina-40% titania coatings exhibited superior corrosion resistance in molten salt media. Laser melting of the coatings have been attempted to have less porous coatings for molten salt applications.

Jagadeeswara Rao et. al. [51,57] deposited YSZ coatings with NiCrAlY bond coat on 9Cr-1Mo steel by APS and evaluated its corrosion behaviour in UCl_3-LiCl-KCl salt for pyrochemical applications at 600 °C for up to 2000 h duration. Uncoated 9Cr-1Mo steel undergone severe corrosion and the rate of corrosion increased with time of exposure showing dissolution and corrosion product regions (Figure 4). No failure of the coating, no deterioration or no thickness loss of the coating was reported without any much surface morphology changes even for 2000 h immersion into molten salt. The surface after corrosion test appeared as lamellar morphology similar to the as-sprayed plasma spray ceramic coatings. However, some amount of UO_2 was occluded on the coating surface due to presence of moisture during the corrosion test. Similarly, Jagadeeswara Rao et. al.,[58] also studied the development of YSZ coatings without and with SiC bond coatings on high density graphite rods for molten salt handling.

The SiC bond coated YSZ coating has performed well up to 3500 h in molten salt and the YSZ coating without SiC bond coat found to have performed well without any damage up to 2000 h duration. The corrosion tested cross-section SEM images of samples with coatings without bond coat are shown in Figure 5. There is no deterioration or delamination of the coating observed. Recently, studies on the corrosion evaluation of alloys in LiCl-KCl molten salt with the addition of $EuCl_3$ and $CeCl_3$ are being carried out at our lab.

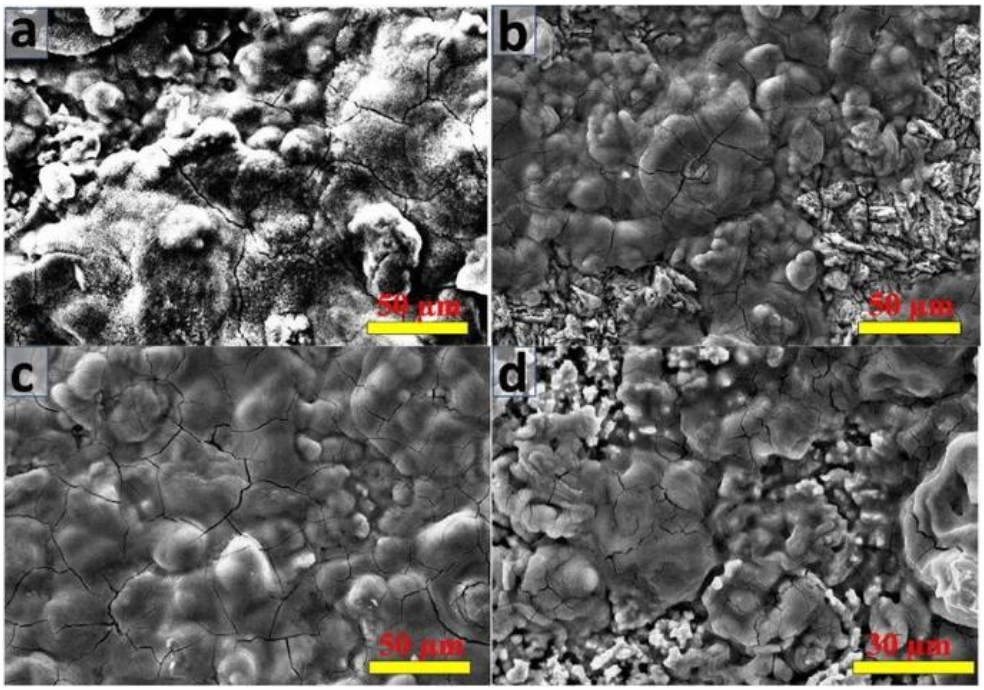

Figure 4. SEM images of molten salt, LiCl–KCl–UCl_3, corrosion tested 9Cr–1Mo steel for different durations **a.** 100 h, **b.** 250 h, **c.** 500 h and **d.** 1000 h showing both dissolution and corrosion product regions [57](Reproduced with permission from Springer Nature).

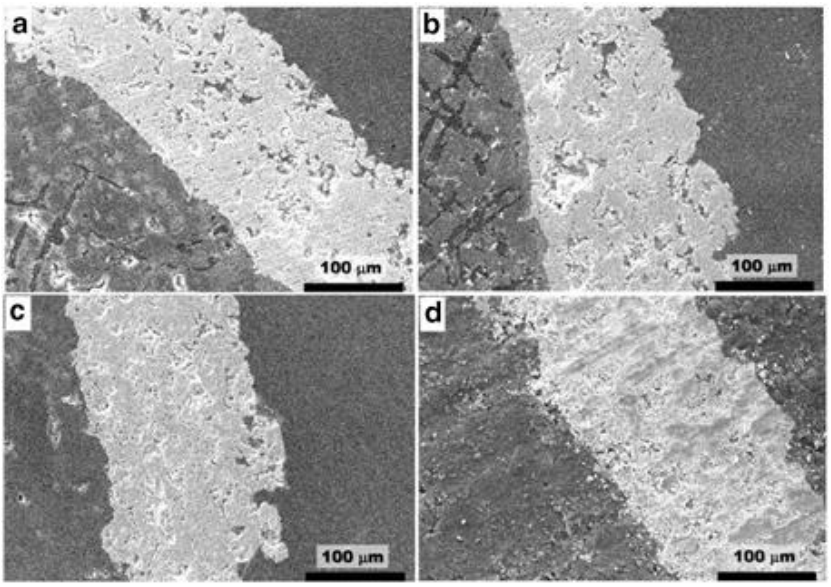

Figure 5. The cross-section images of the YSZ coatings on HDG without bond coat after molten LiCl-KCl salt corrosion test for different durations, **a.** 50h, **b.** 250 h, **c.** 1000 h and **d.** 2000 h[58](Reproduced with permission from Springer Nature).

6. Future approach of molten salt corrosion research

As discussed, molten salt corrosion is inevitable at high temperatures. However, with the proper selection of alloys, salt chemistry, and suitable corrosion-resistant coatings, molten salt corrosion can be mitigated. The research on finding better

The future R&D related to molten salt corrosion studies should focus on shifting away from traditional alloys to more specific, novel high-performance materials that can withstand the aggressive conditions. Refractory metals and alloys, including metals such as Mo, Ta, and W, as well as their alloys, exhibit superior corrosion resistance in molten chlorides. Advanced nickel based alloys also will also perform well in molten chloride environments. However, Ni-based alloys are avoided for electrorefining applications, where Cd used in the electro refiner would aggravate the corrosion of Ni. Mostly ceramics and cermets provide better corrosion resistance towards molten salt corrosion; however, their mechanical strength and long-term stability should be insufficient, and it needs to be improved.

Coatings and barrier layers should also be researched for molten salt applications, considering better ceramic coatings with improved adhesion and integrity over longer exposures. Alloys that can form in situ protective layers, which are not degraded by the molten salts, can also be considered for extensive research. Of course, as discussed earlier, the salt chemistry and the redox potential of the salt bath plays a crucial role in molten salt corrosion resistance of materials. Hence, future research should focus on controlling salt chemistry in terms of purity, impurities, and the removal of impurities by different routes, such as electrolysis, and on controlling the redox potential by introducing redox agents and buffers into the salt.

In order to predict and understand the corrosion behaviour of materials while exposed to molten salts, computational modelling and advanced characterization techniques can be used. The future research should also focus on developing online monitoring tools for molten salt applications, developing advanced electrochemical sensors, spectroscopic techniques to in situ monitoring of the salt chemistry.

Materials for handling molten chloride salts in various applications, especially for pyrochemical reprocessing, should focus on the following aspects, as shown in Figure 6: advanced corrosion-resistant materials, protective coatings, salt chemistry and redox potential control, advanced modelling, and advanced characterisation tools.

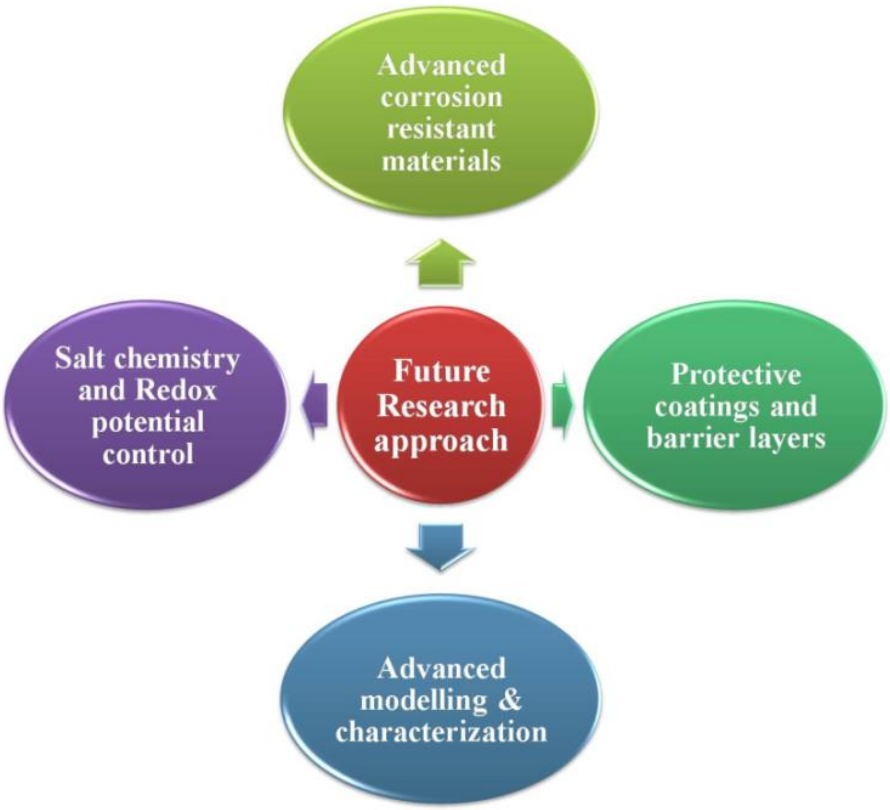

Figure 6. Pictorial depiction of the future approach of molten salt corrosion research.

7. Conclusions and future Outlook

Molten salts are increasingly utilized across emerging scientific and technological domains due to their low vapour pressure, high thermal stability, and excellent electrical conductivity. In particular, chloride-based molten salts, such as the LiCl-KCl eutectic, serve as effective solvents in the nuclear industry especially for the pyrochemical reprocessing of spent metallic fuels.

However, due to the aggressive nature of molten salts, especially chlorides at elevated temperatures due to the presence of uncontrolled impurities, poses significant challenges related to the corrosion of structural materials. This review presents the corrosion behaviour of various candidate structural materials exposed to a LiCl-KCl eutectic solution with the addition of UCl_3, $EuCl_3$, and $CeCl_3$ salts under high-temperature conditions, along with strategies for corrosion mitigation.

Experimental results indicate that corrosion rates vary depending on several factors, including alloy composition, the presence of specific alloying elements, atmospheric conditions, operating temperature, the nature of the molten salt, and the purity of the molten salt. Among various mitigation approaches, high-temperature ceramic coatings that act as chemical barriers have emerged as one of the most effective solutions for protecting structural materials in molten chloride environments during pyrochemical reprocessing.

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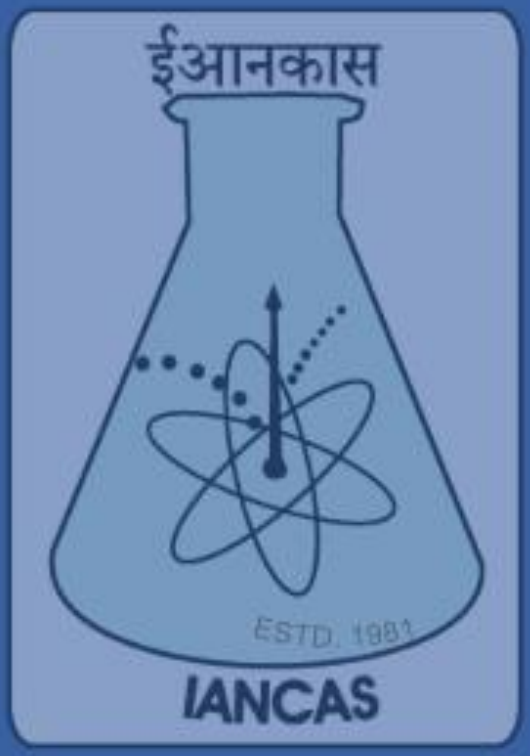

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