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Research Paper

The Effect of Seawater Use and Solution Composition on the Quality of Blackening Results

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ABSTRACT: *The study of the use of seawater and the composition of blackening solutions on the quality of blackening results is essential in increasing the efficiency of raw materials and finding an adequate formulation in the blackening process. Blackening is a black oxide coating process that aims to increase metal resistance to corrosion and wear. This study uses seawater as a solvent with blackening solution raw materials consisting of NaOH and oxidizers with varying compositions. The parameters for testing the quality of blackening results include color testing using the visual matching method, image color picker application, and corrosion resistance testing using the weight loss method. The study results showed that seawater can be used as a solvent in making blackening solutions by providing a somewhat contrasting black color and slower corrosion rate compared to solutions without seawater. NaOH with a percentage of 50%, 70%, and 80% in the corrosion test showed an increase in corrosion resistance of 10%, 30%, and 40%, respectively, after immersion for 30 minutes at a temperature of 150°C. The resulting blackening process not only provides aesthetic value through black coating but also increases protection against material surface degradation. This research is expected to provide an alternative formulation of a blackening solution that is more environmentally friendly and economically efficient, mainly by utilizing seawater as a solvent. In addition, these results are expected to be the basis for further development in blackening applications on various materials for industrial needs.*

Keywords*: Blackening; Sea Water; Solution Composition; Color Testing; Corrosion Testing*

1. INTRODUCTION

Metal coating is a process that aims to obtain specific characteristics on the surface of a workpiece. This process is expected to improve the microstructure and resistance of the object and allow for the improvement of the physical properties of the metal. [1][2][3]. One of the coating methods widely used in industry is blackening coating. Blackening or black oxide is a coating that changes iron material to black for decorative purposes so that it is more attractive. In addition, the aim is to increase corrosion and wear resistance. [4][5][6].

The black color is produced from a chemical reaction containing sodium hydroxide, sodium nitrite, sodium nitrate, or a mixture of them, which is heated at a temperature of around 100-150℃ then reacts with iron to form magnetite (Fe_3O_4) or a thin black oxide layer that sticks firmly to the iron surface. [4][7]. In addition, the blackening coating reduces light reflection on the metal surface, making it suitable for use on components that require low visibility and better wear resistance. Components such as ST-37 steel plates or cylinders, shafts, chains, gears, screws, bolts, and nuts must have good resistance to corrosion and wear [8][9].

Seawater has the potential as an electrode to enhance redox reactions in various electrochemical processes. The composition of the main components of seawater in the form of anions Cl^-, SO_2^{-4}, HCO_3, Br^-, CO_2^{-3}, $B(OH)_4$, F^- and cations Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+} in the central ocean has been proven to be constant

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[10][11]. Seawater's main components contribute to seawater's physical-chemical properties; because it is steady throughout the ocean, it is possible to treat seawater as an electrolyte solution (sea salt) [12]. The blackening process involves reactions between atomic layers and ions in a chemical solution:

$$ {}_{m}M + nA^{z-} \rightarrow M_m + A_n + nze \quad (1)$$

Key:
M = reacting metal
A = ion in solution

Generally, the reactions formed are oxidation reactions where the metal surface is immersed in a chemical solution containing sodium, nitrate, or potassium compounds, which will decompose with the metal to form black metal oxides in the case of steel and redox reactions where the oxidized metal causes the ions contained in the solution to decrease. In contrast, the metal will lose electrons due to oxidation. The following is a reaction with an alkali solution.

$$Fe + \tfrac{1}{2} O_2 + 2NaOH \rightarrow Na_2FeO_2 + H_2O \quad (2)$$

In this reaction, the black oxide layer formed provides additional protection against corrosion and wear on the metal surface. Previous studies have shown that the composition of the chemical solution, temperature, and reaction time significantly affect the quality of the resulting layer. For example, a study by Srivastava et al.; Arab et al.; Ranjan et al., showed that adding sodium nitrite to the solution can increase the corrosion resistance of the coating [13][14]. Another study by Cuang et al. found that temperature and reaction time variations affect the thickness and homogeneity of the oxide layer [15]. However, although many studies have been on optimizing the composition of blackening solutions, studies on using seawater as a solvent are still minimal. The use of seawater has excellent potential to reduce production costs and increase the sustainability of the blackening process [16][17]. In addition, by utilizing local resources such as seawater, the industry can reduce dependence on freshwater, which is increasingly limited in some regions.

This study aims to examine the effect of using seawater as a solvent in the blackening process and to evaluate variations in solution composition on the quality of the resulting layer. By optimizing the composition of the solution, it is hoped that a blackening layer can be produced that not only has high aesthetic value but also provides optimal protection for metal materials. This study's results are expected to contribute significantly to developing a more efficient, economical, and environmentally friendly blackening process. In addition, this study can also offer practical solutions for industry to reduce production costs while increasing the sustainability of its operations. Thus, this study is relevant in a technical context and has a positive impact on supporting wiser resource management. Through this innovation, it is hoped that the blackening process will become more affordable, practical, and sustainable, which can provide significant benefits for industry in Indonesia, especially in coastal areas.

In addition to technical aspects, economic and environmental considerations are essential in developing metal coating processes. The industry faces a significant challenge in reducing production costs without sacrificing product quality. In the blackening process, using freshwater as the primary solvent is often a substantial cost component, especially in areas with limited access to freshwater resources. The use of seawater as an alternative solvent offers an opportunity to reduce these costs, especially for industries located in coastal areas [18]. With the availability of abundant seawater, the cost of procuring liquid raw materials can be minimized, thus providing a competitive advantage for the industry [19][20] From an environmental perspective, seawater is also in line with the principle of sustainability. The increasingly limited availability of fresh water in various regions of the world requires a more efficient solution in resource management. In this context, using seawater as a solvent in industrial processes can help reduce the pressure on freshwater resources. In addition, seawater contains natural ions that can support chemical reactions in the blackening process, thereby reducing the need for additional certain chemicals. This reduces production costs and the potential negative environmental impact due to excessive use of chemicals [21].

In addition to cost savings and sustainability, this study also opens up opportunities to explore the effect of seawater ion composition on the blackening layer's quality. The content of ions such as chloride (Cl^-) and sulfate (SO_4^{2-}) in seawater is known to accelerate redox reactions, which have the potential to produce oxide layers with superior characteristics. However, this ion content can also affect the stability of the chemical solution during the coating process. Therefore, an in-depth study is needed to determine the optimal composition between seawater and additional chemicals to produce a layer with maximum corrosion and wear resistance [23][24][25]. This research is expected to provide technical solutions for the metal coating industry and contribute to developing more environmentally friendly technologies. By integrating local resources such as seawater into the production process, the industry can be more adaptive to global challenges related to sustainability and efficiency. In addition, the results of this study can be the basis for further development in metal coating applications, especially in coastal areas with great potential but often face limited access to advanced technology.

2. RESEARCH METHODOLOGY

The study was conducted in several stages :

Figure 1. Research Process

Preparation of ST 37 steel samples by cutting samples that resemble each other with dimensions of 4 cm x 3 cm x 2 cm (L x W x H), then cleaned with sandpaper, making blackening solutions using seawater with a concentration of 16 M NaOH solution, 2.5 M $NaNO_2$, and 2 M $NaNO_3$. Furthermore, the sample was subjected to a pickling process, namely a dipping process that removes scale on the sample's surface [9]; the sample was dipped in a 10% H_2SO_4 solution for 30 minutes. The blackening process uses variations in NaOH composition of 80%, 70%, and 50%; the composition of $NaNO_2$ and $NaNO_3$ is adjusted to the composition of NaOH, namely 10%, 15%, and 25%, respectively. The samples were immersed in each solution at 150°C for 30 minutes.

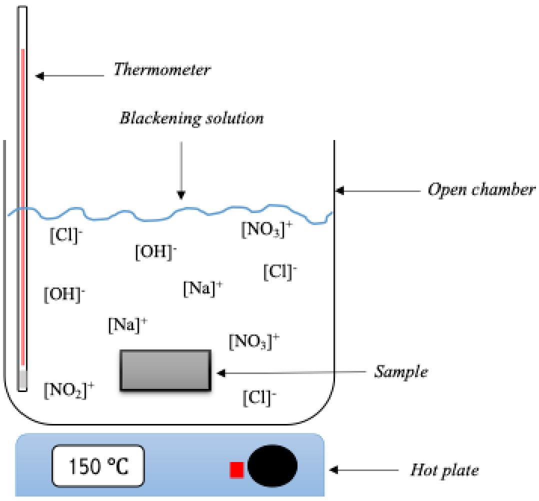


Figure 2. Blackening process scheme

Testing Method

Color difference testing using visual matching and the Image Color Picker application [5], the blackening result image is entered into the application, and then the color code will be read according to the category; the reading results will show the color difference between samples without treatment, samples with the use of seawater and samples without using seawater. Corrosion testing utilizing the weight loss method, with the following equation [25]:

$$mpy = \frac{534\ W}{D.A.T} \quad (3)$$

Note:
W = weight loss (gr)
D = density (gr/cm)
A = outside surface immersed (in^2)
T = time (hours)

3. RESULT AND DISCUSSION

3.1 Preparation of ST 37 steel samples

The ST 37 steel sample was cut and then sanded until the surface was clean and smooth; the pickling process cleaned impurities such as oxide crust. Here is the initial sample display after the pickling process.

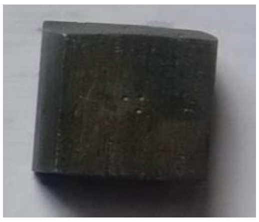
.

Figure 2. Sample after the pickling process

The cut samples have a dimensional difference of around ± 0.01 mm; the difference will significantly affect the value in determining the corrosion rate. The average sample area is around 8.06 in^2.

3.2 Preparation of blackening solution

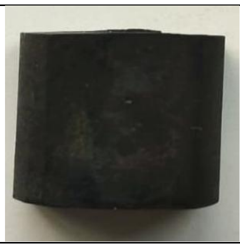
Making blackening solution by mixing NaOH 16 M, $NaNO_2$ 2.5 M, and $NaNO_3$ 2 M in 1 liter with the composition of NaOH 80%, $NaNO_2$ 10% and $NaNO_3$ 10%; NaOH 70%, $NaNO_2$ 15% and NaNO3 15%; NaOH 50%, $NaNO_2$ 25% and $NaNO_3$ 25%. NaOH solution is chosen because the large alkali concentration accelerates the hydrolysis process, thus accelerating the formation of a magnetite layer on the iron surface, increasing the reaction rate, forming a thicker layer of magnetite oxide, which functions as a protection against corrosion and provides a distinctive black color.

3.3 Color testing

Color comparison of blackening results using and without seawater with a NaOH concentration of 80%.

Table 1. Perbandingan Warna

% seawater	Display	Color Code [5]
Before blackening		CMYK 0, 2, 18, 61 RGB 100, 98, 82
100		CMYK 5, 10, 0, 92 RGB 19, 18, 20

0		CMYK 0, 0, 7, 84 RGB 42, 42, 39

Soaking using a blackening solution with 80% NaOH, 10% $NaNO_2$, and 10% $NaNO_3$. Based on the color comparison table, the sample at 100% seawater and 0% seawater gives a color display with different intensities; seawater gives a darker black color than without seawater. Seawater contains electrolyte ions such as Na + and Cl-; when they react, they form mineral salts that add alkalinity to the NaOH solution.

3.4. Corrosion resistance testing

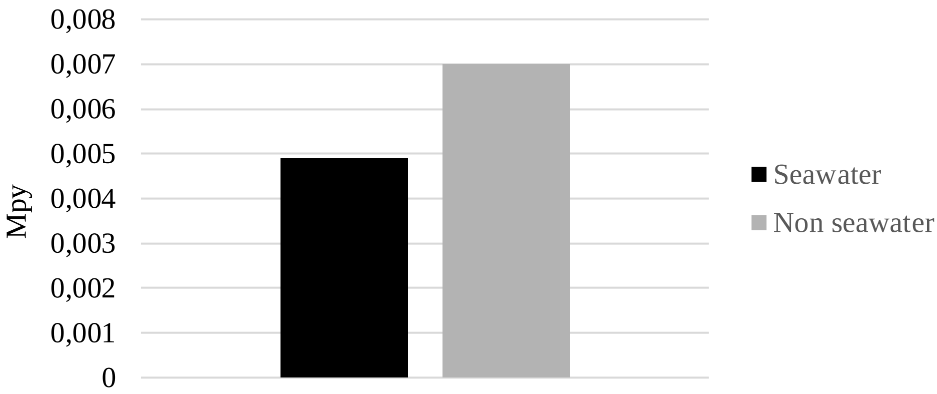


Figure 3. Corrosion rate comparison diagram using seawater and non seawater

Seawater used in the blackening process demonstrated a slower corrosion rate in comparison to the blackening process without seawater, as illustrated in Figure 2. The corrosion rate with seawater was 42.87% lower than that without seawater, indicating that the inclusion of seawater could be considered for more efficient and applicable blackening processes.

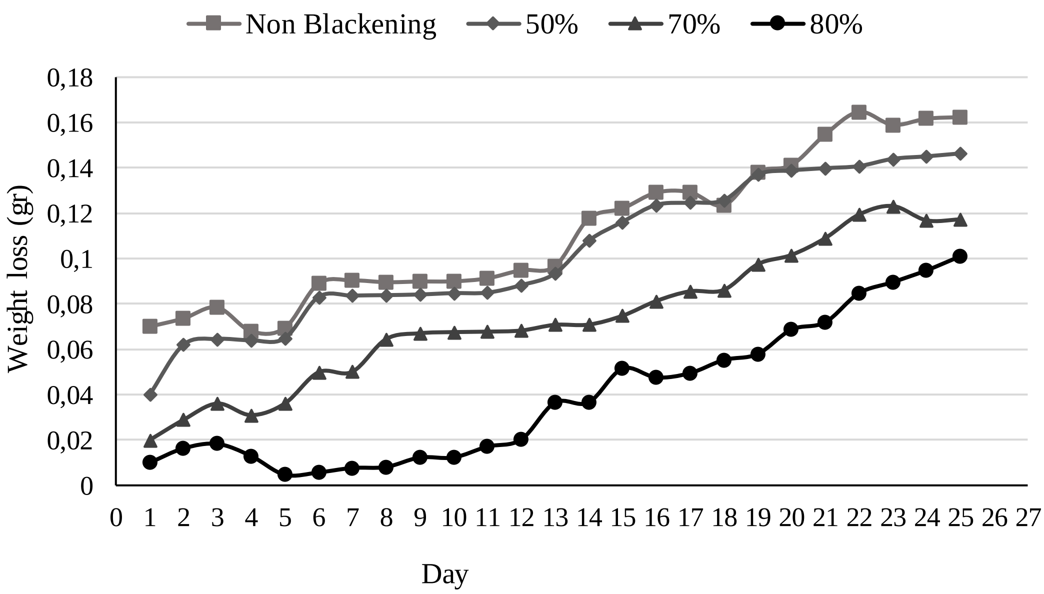


Figure 4. Graph of weight lost over 25 days

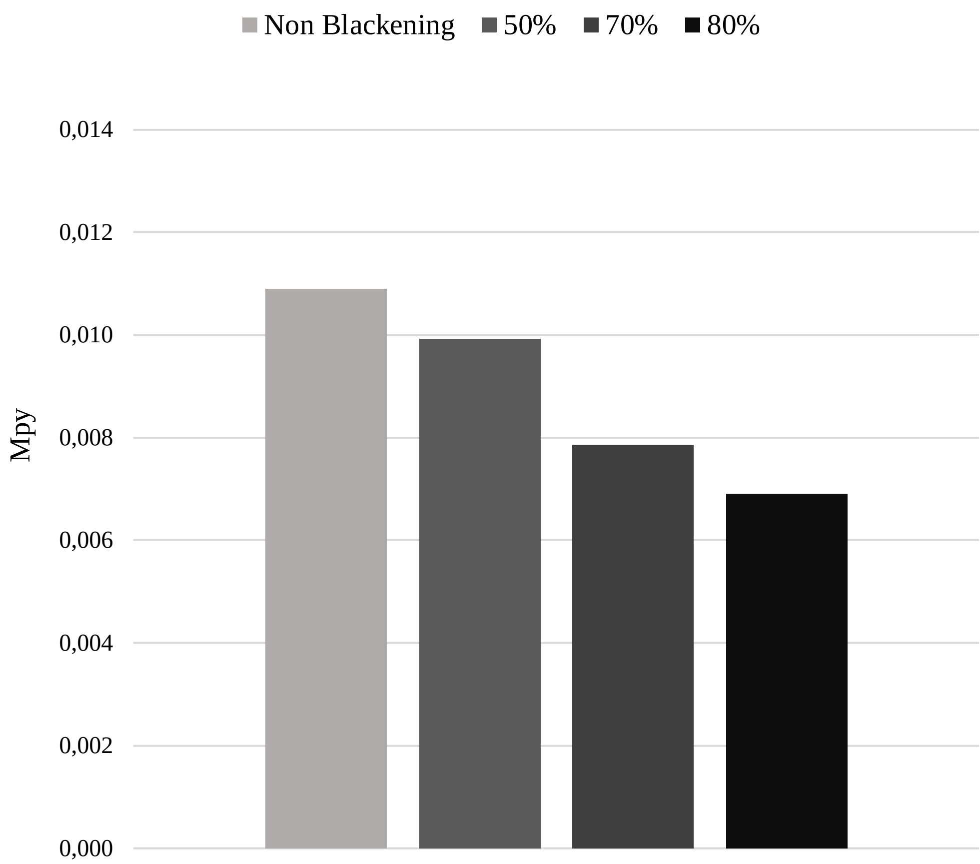


Figure 5. Corrosion rate comparison diagram

Corrosion resistance testing using the weight loss method requires a value of weight lost during the appropriate test period; the weight lost will continue to increase along with the corrosivity formed, according to Figure 4. The results of the corrosion resistance test based on Figure 5, the sample Non Blackening showed the highest corrosion rate at 0.01 mph, indicating that without treatment, the material is more susceptible to corrosion. The treatment of the NaOH composition comparison reduces the corrosion rate. Sample NaOH 50% 0.009 mpy shows a reduction in corrosion rate of 10%, Sample with NaOH 70% 0.007 mpy shows a decrease in corrosion rate of 30%, sample with NaOH 80% 0.006 mpy shows a reduction in corrosion rate of 40%. The increase in the composition of NaOH in the blackening solution shows that the composition of NaOH affects reducing the corrosion rate. Adding NaOH can inhibit the corrosion rate of certain metal alloys; some metal alloys show better corrosion resistance [26]. Using NaOH in blackening solutions shows advantages in having a lower corrosion rate than HCl solutions [26]. This information is essential to consider the effectiveness of NaOH in reducing corrosion in blackening applications.

NaOH, $NaNO_2$, and $NaNO_3$ work synergistically in blackening solution; NaOH functions as the essential component of the solution, creating strong alkaline conditions required for the iron oxidation process on the steel surface. NaOH helps in the formation of hydroxide ions (OH^-), which then interact with iron to form ferric hydroxide ($Fe(OH)_2$)[6]. The reaction that occurs is as follows:

$$Fe_{surf} + 2OHaq^- \rightarrow Fe(OH)_2 + 2e^- \quad (4)$$

$$6Fe(OH)_2 + NO_3^- + 4H^+ \rightarrow 3Fe_3O_4 + NH_4^+ + 3H_2O \quad (5)$$

$NaNO_2$ and $NaNO_3$ act as oxidizing agents in the blackening solution, assisting in the further oxidation of $Fe(OH)_2$ to magnetite (Fe_3O_4), the black protective layer on the steel surface.

4. CONCLUSION

The study results indicate that seawater can be used as an alternative solvent in manufacturing blackening solutions. The composition of the solution utilizing seawater, especially with a higher NaOH content, has proven effective in increasing the corrosion resistance of metals. The higher the concentration of NaOH, the lower the resulting corrosion rate. In addition, seawater provides a darker black color intensity compared to solutions without seawater, showing great potential for aesthetic applications and metal protection. This study also confirms that the combination of NaOH, $NaNO_2$, and $NaNO_3$ in the blackening solution plays a vital role in forming a magnetite oxide layer (Fe_3O_4), which provides optimal protection against corrosion and wear. Using seawater makes the blackening process more economical and environmentally friendly because it reduces dependence on increasingly limited fresh water. This study provides a practical solution for industry, especially in coastal areas, by integrating abundant local resources. In addition, this study contributes to developing more sustainable and efficient metal coating technology. Further research can focus on several aspects to expand the application and benefits of seawater in the blackening process. First, more in-depth studies are needed to evaluate the effect of ion variations in seawater on the quality of the resulting oxide layer. Second, the research can be expanded to explore other types of metals or alloys that can be processed using seawater-based solutions. Third, industrial-scale trials need to be conducted to measure the efficiency and consistency of this process under mass production conditions. Finally, research on the environmental impact of using seawater in the blackening process is also essential to ensure the long-term sustainability of this technology.

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REFERENCES

[1] B. Fotovvati, N. Namdari, and A. Dehghanghadikolaei, “On coating techniques for surface protection: A review,” *J. Manuf. Mater. Process.*, vol. 3, no. 28, 2019, doi: 10.3390/jmmp3010028.

[2] L. Yinghua, P. Xuelong, K. Jiacai, and D. Yingjun, “Improving the microstructure and mechanical properties of laser cladded Ni-based alloy coatings by changing their composition: A review,” *Rev. Adv. Mater. Sci.*, vol. 59, no. 1, pp. 340–351, 2020, doi: 10.1515/rams-2020-0027.

[3] X. P. Tao, S. Zhang, C. H. Zhang, C. L. Wu, J. Chen, and A. O. Abdullah, “Effect of Fe and Ni contents on microstructure and wear resistance of aluminum bronze coatings on 316 stainless steel by laser cladding,” *Surf. Coatings Technol.*, vol. 342, pp. 76–84, 2018, doi: 10.1016/j.surfcoat.2018.02.032.

[4] L. O. Gostin, “Blackening of Cast-Iron by Hydrothermal and Hot Alkaline Nitrate Treatments,” *SSRN Electron. J.*, 2022, doi: 10.2139/ssrn.4207784.

[5] A. Artesani, F. Di Turo, M. Zucchelli, and A. Traviglia, “Recent Advances in Protective Coatings for Cultural Heritage–An Overview,” *Coatings*, vol. 10, no. 217, pp. 1–36, 2020. doi:10.3390/coatings10030217

[6] E. Rudnik, “Black Nickel Coatings : From Plating Techniques to Applications,” *Coatings*, vol. 14, no. 12, pp. 1–21, 2024, doi: https://doi.org/10.3390/coatings14121588.

[7] S. B. Jonnalagadda, S. Maddila, and N. Kerru, “Chapter 4 Magnetic nanocatalysts for wastewater treatment,” in *Volume 2 Industrial Applications*, R. S. Varma and B. Banerjee, Eds., Berlin, Boston: De Gruyter, 2022, pp. 97–130. doi: doi:10.1515/9783110782165-004.

[8] T. Y. Eken and F. Oktem, “Pitting Corrosion Behaviour of St 37 Structural Steel in Several Pitting Corrosion Behaviour of St 37 Structural Steel in Several Corrosive Environments,” no. October 2019, pp. 33–48, 2016.

[9] A. H. A. Sahhal, C. T., and Karabuk, "Effect Of Severe Plastic Deformation On Mechanical Properties Of Welded St37-2 Steel," 2020. [Online]. Available: https://api.semanticscholar.org/CorpusID:216232267

[10] F. Y. Gao, P. C. Yu, and M. R. Gao, "Seawater electrolysis technologies for green hydrogen production: challenges and opportunities," *Curr. Opin. Chem. Eng.*, vol. 36, p. 100827, Jun. 2022, doi: 10.1016/J.COCHE.2022.100827.

[12] A. Srivastava, V. K. Parida, A. Majumder, B. Gupta, and A. K. Gupta, "Treatment of saline wastewater using physicochemical, biological, and hybrid processes: Insights into inhibition mechanisms, treatment efficiencies and performance enhancement," *J. Environ. Chem. Eng.*, vol. 9, no. 4, p. 105775, 2021, doi: https://doi.org/10.1016/j.jece.2021.105775.

[13] G. Kılınççeker and N. Yeşilyurt, "The Effects of Sodium Nitrite on Corrosion Resistance of Steel Reinforcement in Concrete," *Nat. Eng. Sci.*, vol. 3, no. 3, pp. 87–102, 2018.

[14] R. Ranjan, S. R. Prusty, B. Rout, R. Panigrahi, and S. Jena, "Assessing the effect of sodium nitrite as corrosion inhibitor against the corrosion of steel rebar in alkali-activated concrete," *J. Build. Eng.*, vol. 92, p. 109737, 2024, doi: https://doi.org/10.1016/j.jobe.2024.109737.

[15] C. Qiao, X. Sun, Y. Wang, L. Hao, X. Liu, and X. An, "High-temperature aging time-induced composition and thickness evolution in the native oxides film on Sn solder substrate," *J. Mater. Sci. Mater. Electron.*, vol. 32, no. 19, pp. 24209–24228, 2021, doi: 10.1007/s10854-021-06887-2.

[16] A. Fattah-alhosseini, H. Yazdani Khan, and A. Heidarpour, "Comparison of anti-corrosive properties between hot alkaline nitrate blackening and hydrothermal blackening routes," *J. Alloys Compd.*, vol. 676, pp. 474–480, 2016, doi: https://doi.org/10.1016/j.jallcom.2016.03.114.

[17] X. Hou, Y. Li, H. Zhang, P. D. Lund, J. Kwan, and S. C. E. Tsang, "Black titanium oxide: synthesis, modification, characterization, physiochemical properties, and emerging applications for energy conversion and storage, and environmental sustainability," *Chem. Soc. Rev.*, pp. 10660–10708, 2024, doi: 10.1039/d4cs00420e.

[18] I. Alameddine, R. Tarhini, and M. El-Fadel, "Household economic burden from seawater intrusion in coastal urban areas," *Water Int.*, vol. 43, no. 2, pp. 217–236, 2018, doi: 10.1080/02508060.2017.1416441.

[19] J. Chen, L. Sun, K. Wang, and Y. Zhang, "Research and applications of rechargeable seawater battery," *J. Energy Storage*, vol. 76, p. 109659, 2024, doi: https://doi.org/10.1016/j.est.2023.109659.

[20] C. H. Lee, H. J. Ho, W. S. Chen, and A. Iizuka, "Total Resource Circulation of Desalination Brine: A Review," *Adv. Sustain. Syst.*, vol. 8, no. 7, pp. 1–23, 2024, doi: 10.1002/adsu.202300460.

[21] J. N. Hahladakis, C. A. Velis, R. Weber, E. Iacovidou, and P. Purnell, "An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling," *J. Hazard. Mater.*, vol. 344, pp. 179–199, 2018, doi: 10.1016/j.jhazmat.2017.10.014.

[22] W. Pei, X. Pei, Z. Xie, and J. Wang, "Research progress of marine anti-corrosion and wear-resistant coating," *Tribol. Int.*, vol. 198, p. 109864, 2024, doi: https://doi.org/10.1016/j.triboint.2024.109864.

[23] Y. Wu, W. Zhao, and L. Wang, "State of the art and current trends on the metal corrosion and protection strategies in deep sea," *J. Mater. Sci. Technol.*, vol. 215, pp. 192–213, 2025, doi: https://doi.org/10.1016/j.jmst.2024.07.026.

[24] A. Shokri and M. Sanavi Fard, "Corrosion in seawater desalination industry: A critical analysis of impacts and mitigation strategies," *Chemosphere*, vol. 307, p. 135640, 2022, doi:

https://doi.org/10.1016/j.chemosphere.2022.135640.

[25] R. Karthikaiselvi and S. Subhashini, "Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-o-methoxy aniline)," *J. Assoc. Arab Univ. Basic Appl. Sci.*, vol. 16, pp. 74–82, 2014, doi: https://doi.org/10.1016/j.jaubas.2013.06.002.

[26] I. Hamidah *et al.*, "Corrosion of copper alloys in KOH, NaOH, NaCl, and HCl electrolyte solutions and its impact to the mechanical properties," *Alexandria Eng. J.*, vol. 60, no. 2, pp. 2235–2243, 2021, doi: https://doi.org/10.1016/j.aej.2020.12.027.