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Effect of Sodium Benzoate Concentration on Zinc Corrosion in Marine Environment

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ABSTRACT

The growing environmental concerns have led to intensive investigations into the corrosion behaviour of metals and alloys in tropical seawater. The main aim of this study is to investigate the effect of sodium benzoate concentration on the corrosion of zinc (Zn) in seawater. The corrosion rate was determined from the weight loss measurement against immersion time. According to the finding, weight loss increases with immersion time, which means that the prolonged time causes more Zn to be eroded. Weight loss and corrosion rate show a slight decrease when the Zn is immersed in the lowest sodium benzoate concentration of 10 wt%; conversely, they increase when the concentration of sodium benzoate increases from 20 wt% to 50 wt%. These results indicate that sodium benzoate only has a corrosion-inhibitory effect on Zn at a relatively low concentration. Also, the surface morphology, as examined by a metallurgical microscope, exhibits the formation of pits and scratches on the corroded sample.

1. Introduction

The principles of electrochemistry and metallurgy that involve the reaction and subsequent deterioration of metals upon exposure to the environment are commonly referred to as corrosion. In other words, corrosion is simply the consequence of a chemical or electrochemical reactivity between a substance, typically a metal and its environment, leading to the deterioration of the material from its original properties. When corrosion takes place, metals are transformed into metallic salt compounds like hydroxides, oxides, or sulphates. A metal surface can undergo corrosive reactions when it comes into contact with contaminated substances such as moisture, chemicals, saltwater, soil, or atmospheric dust. The corrosive action begins on the metal surface and moisture in the air is often sufficient to ignite the corrosion [1-5].

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Rapid corrosion can occur due to the ease with which such thin moisture films maintain high oxygen content because of the large water/air interface area. The corrosion process of zinc in water is primarily influenced by the impurities present in the water. It is rare for naturally occurring waters to be entirely pure. For instance, seawater contains a large amount of salt, which is attributed to its high NaCl concentration. As opposed to most types of domestic or river water, sea water is unable to create a protective layer that would reduce the exposure to oxygen by the zinc surface, causing the attack to be more severe. However, it is generally accepted that the corrosion rate of zinc is low; it ranges from 0.13 µm/year in dry rural atmospheres to 0.013 mm/year in more moist atmospheres. Naturally, seawater is a mixture of salts and water that originated from the condensation of water found in the early atmosphere. Only six elements and compounds make up 99% of sea salts: chlorine (Cl^-), sodium (Na^+), sulphur ($SO_4{}^{2-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}) and potassium (K^+). The relative abundance of the major salts in seawater is constant regardless of the ocean, with the chlorine ion making up 55% of the salt [6-11].

Sodium benzoate, C_6H_5COONa (abbreviated as NaBz), is the sodium salt of benzoic acid, soluble in water and ethyl alcohol and insoluble in ethyl ether. It is a slightly alkaline and a hygroscopic product. Sodium benzoate has the potential to act as a catalyst or an inhibitor in the decomposition of metals in the presence of water, depending on the concentration used. Moreover, it has been discovered to have considerable applications as a corrosion inhibitor at low concentrations, whereas corrosion inhibition has been reported for steel, copper, copper alloys, soldered joints, aluminium and aluminium alloys. The effectiveness of this corrosion inhibitor has been reported to be positive at small concentrations [12-17]. In this study, we performed an investigation on the role of NaBz in the corrosion behaviour of zinc in natural seawater and seawater containing different NaBz concentrations using weight loss measurements and the surface microstructures were identified under a metallurgical microscope before and after Zn immersion in NaBz solution.

2. Methodology

The metal used in this study was commercially available zinc. The specimens will be cut into 25 x 25 x 3 mm^3 coupons. Before immersion, the coupons were mechanically polished using 800, 1000 and 1200 emery papers and lubricated using distilled water. The polished samples were cleaned with acetone, washed with distilled water, dried in the air and stored in a desiccator overnight before the corrosion test. The seawater solution was collected at Pulau Kambing, Kuala Terengganu, Terengganu. All the experiments will be conducted at room temperature (25 ± 0.1 ºC). The NaBz at different concentrations (10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) will be prepared in the seawater solution for the immersion of the specimens.

An electronic weight balance was used to measure the initial weight before immersion and the final weight of the specimens after immersion in the respective solutions. The specimens were immersed for a total immersion duration of 30 days and each of them was weighted for an interval of 6 days. The weight loss of every specimen was calculated by subtracting the final weight from the initial weight, since these tests are useful due to their similarity to actual conditions. Afterwards, the corrosion rate (CR) in mm/year was calculated using the following expression:

$$CR = W/DAT \tag{1}$$

where W represents weight loss (g), A denotes panel area (cm^2), D is the density (g/cm^3) and T is the immersion time (s). A metallurgical microscope (model TM-1000 Hitachi) was used to examine the surface morphology of the specimen before and after immersion in the solution. The magnification of the metallurgical microscope was set to x50 to obtain a clearer surface image. The inhibition efficiency (IE) was calculated by the following equation:

$$IE = (CR_o - CR_1) / CR_o \times 100\% \quad (2)$$

where CR_o and CR_1 are corrosion rates without and in the presence of inhibitor, respectively.

3. Results and Discussion

3.1 Weight Loss

The gravimetric approach used for analysing the corrosion is an established and trustworthy technique that exhibits a strong correlation between impedance and polarization methods [11,12]. Figure 1 illustrates the weight loss, in terms of g/cm^2, of the zinc sample immersed in purely seawater and seawater containing different concentrations of NaBz.

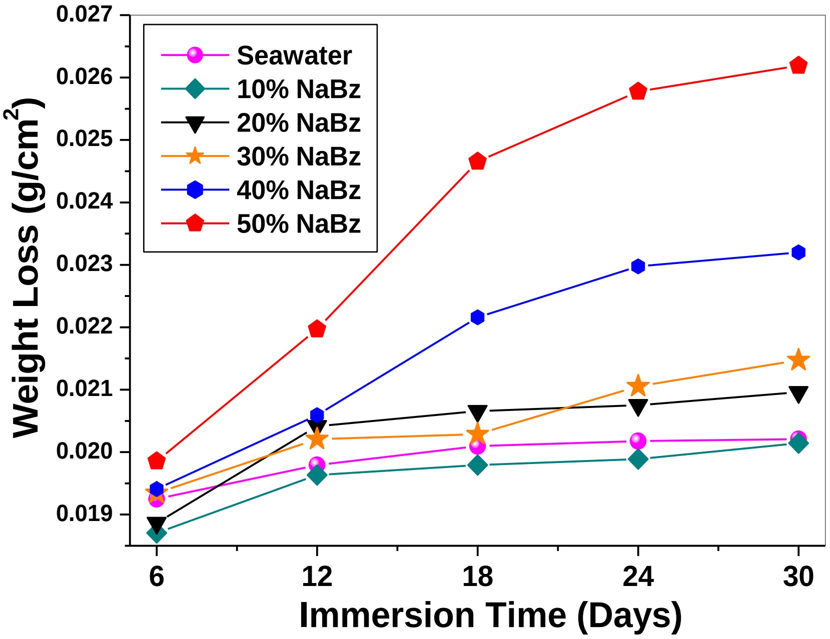

Fig. 1. Weight loss against immersion time

The results show that the weight loss for all samples increases with increasing periods of immersion. Also, higher concentrations of NaBz result in greater weight loss. The addition of 50% sodium benzoate to the seawater after thirty days is 31.87% higher than on the sixth day after immersion. This gives the highest weight loss, while for pure seawater without the presence of NaBz, the percentage difference after the sixth day and the thirtieth day is 4.98%. The addition of 10% NaBz on the thirtieth day gives the least weight loss compared to other concentrations, with a value obtained of 0.02014 g/cm2. However, after immersion of the zinc in 20% and 30% sodium benzoate, the weight loss differences increase slightly with the increment of NaBz concentration, so that the weight loss percentage differences between the 6th and 30th days for 20% and 30% NaBz are 11.13% and 11.01%, respectively. For the 40% NaBz in the seawater solution, the weight loss is higher than 30% NaBz but lower than 50% NaBz, with a 19.53% difference. For the first twelve days, the weight loss variation is significant for all the concentrations and the highest weight loss ascertained is from the immersion of zinc in 50% NaBz, with a 5.05% difference. The difference gap is increasing after the eightieth day of immersion, with 5.77% in the 50% NaBz. But after day twenty-four, the weight loss decreases to only 2.22% compared to the original weight loss and decreases to 0.80% after 30 days. With the addition of 10% of the NaBz in the seawater, the weight loss difference decreases slightly as the immersion time progresses, with the least weight loss value measured. This shows that 10% NaBz is the optimum concentration to be added to seawater for corrosion inhibition purposes.

3.2 Corrosion Rate

Figure 2 shows the corrosion rate against immersion time for zinc immersed in seawater and seawater containing different concentrations of NaBz.

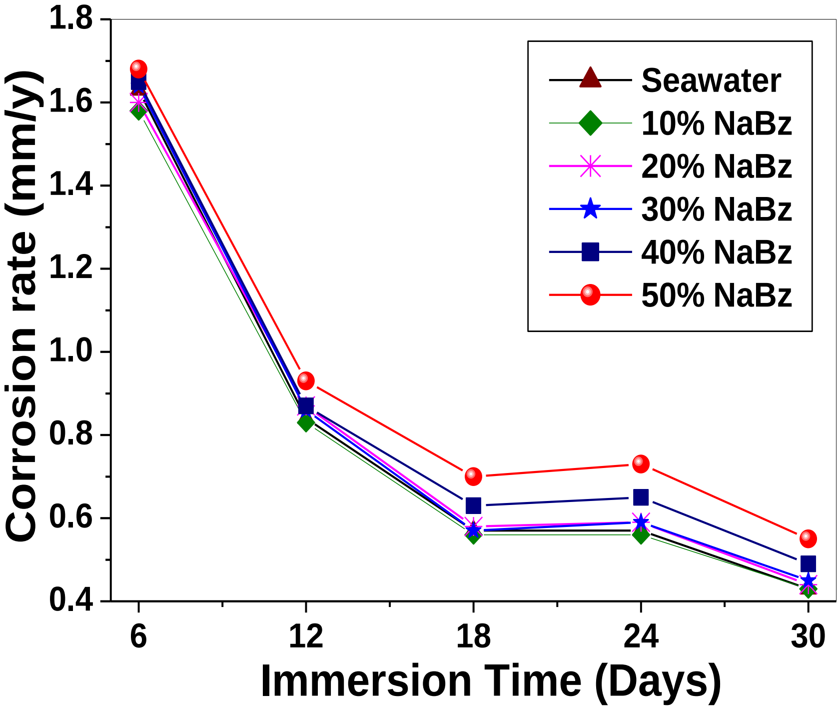

Fig. 2. Corrosion rate versus immersion time

From the results shown in Figure 2, the corrosion rates from day 6 to day 30 decrease with prolonged immersion time. This trend is due to the contamination of the seawater environment by corrosion deposits that weaken the water attack and, at the same time, reduce the chemical reactivity that was supposed to occur on the zinc surface. This tends to stifle further increases in the amount of corrosion relative to time. It is hence expected that, during the extended study period, the corrosion rate of zinc in all solutions would continue to decrease until the entire corrosion mechanism is exhausted. In the first twelve days, the corrosion rates of the samples immersed in seawater decrease with a steeper gradient, which means the samples corrode rapidly. Following a period of eighteen days of immersion in seawater, it is observed that the corrosion rate begins to decrease gradually, which is evidenced by a decline in the curve gradients. Furthermore, the corrosion rate of 50% NaBz is the highest among them from days six to thirty. Meanwhile, the samples immersed in 10% sodium benzoate show the lowest corrosion rate. For the first 12 days, the corrosion rate with time for the 50% NaBz is determined to be much higher when compared to the others. After day 24, the corrosion rate is already slowing down and is at its lowest rate compared to the measurements taken days before. With the increase in sodium benzoate solution, pitting corrosion may appear on the surface of the zinc block. According to the result, sodium benzoate may be functionalized as a film absorbed on the surface of the zinc block at a lower concentration of 10%

to inhibit the corrosion; however, this effect is negligible or reversely increases the corrosion due to the sodium benzoate becoming more acidic or alkaline at a higher concentration and these effects become stronger at increased concentration.

3.3 Surface Characterization

The picture of the present metallurgical microscope used for surface characterization is displayed in Figure 3(a). Figure 3(b) shows the image of an unexposed zinc surface prior to corrosion as captured from the metallurgical microscope. As can be seen from the figure, the surface of the metal is free of any pits and cracks, with only a few abrasions noticeable owing to the previous polishing effect. Figure 3(b-f) shows the surface morphology of zinc after being immersed in seawater and NaBz solutions at various concentrations, where these pictures were captured after 30 days of immersion. Technically, the samples were first cleaned and dried at room temperature before being monitored under the metallurgical microscope [19-21].

Subsequently, we discussed the corrosion effects one after another, as observed from these figures. Formerly, Figure 3(c) shows the formation of blisters and pinholes on the zinc surface after 30 days immersed in the solution of 90% seawater and 10% NaBz. The phenomenon of pitting corrosion is clearly visible in the specimen. Although pitting has been extensively studied, the mechanisms by which the pits are initiated, grown and repassed are not fully understood yet. Most pits are metastable and re-passivate, only a few continue to grow steadily and produce stable pitting. The actively growing pits are critically dependent on the presence of a highly concentrated solution within them [6,7,13,18,22]. In Figures 3(b–f), small pits or holes are formed. It is clear that with the increasing percentage of NaBz in seawater, the number of pits formed increases. This trend shows that the samples experienced a mild corrosion attack in forming the pits.

After 30 days immersed in seawater and NaBz solution, all the samples taken out of the solution have changed colour from bluish to brownish. The surface of the samples also shows that the corroded spots are uniformly dispersed on the surface. According to Wang *et al.,* [8], this is so-called uniform corrosion, as the corrosion takes place homogeneously over the surface of the metal by means of a chemical or electrochemical reaction. The barrier film that protects the zinc from corrosion consists of a continuous amorphous-like layer in which numerous deposited particles are imbedded. Surface analysis indicates that the film is probably a complex mixture of oxides of NaBz and zinc. Figures 3(f-g) show crazing of the coated material and flakes can be seen, which might indicate corrosion products presence like metal hydroxides and their oxides. The sodium benzoate-corroded zinc specimen probably shows salt deposition (NaBz) at the surface of the metal substrate. The specimen might be covered with the inhibitor molecules, giving protection against corrosion, where a thin layer develops on the specimen surface and eventually decreases the weight loss and corrosion rate for longer exposure times.

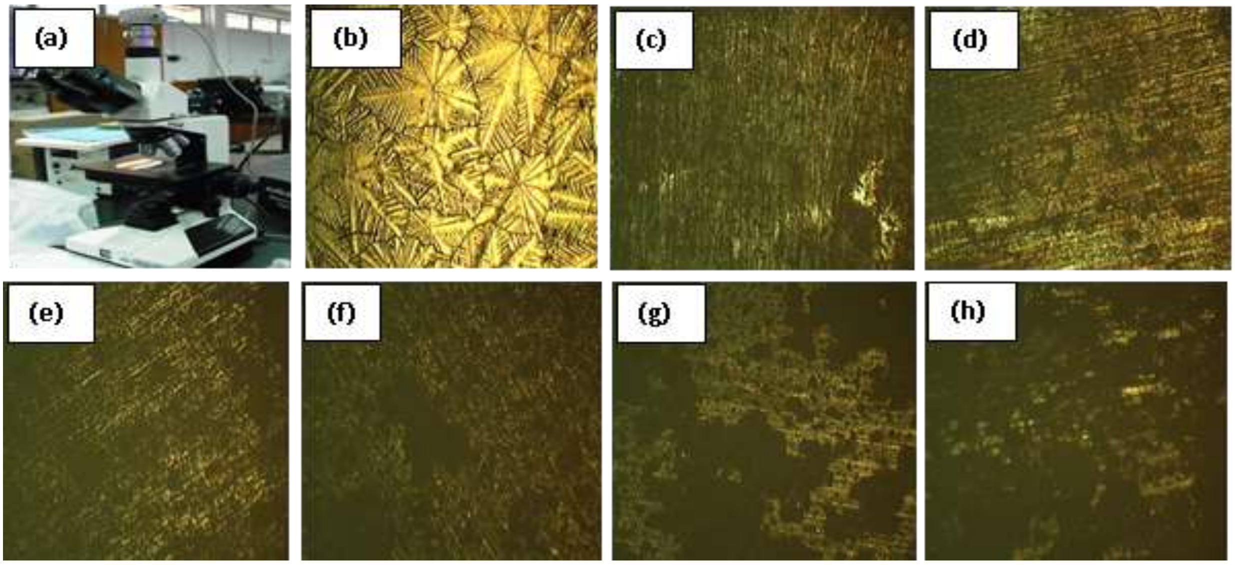

Fig. 3. (a) metallurgical microscope (b) image of the plain surface of zinc before immersion and metallurgical surface of zinc after 30 days immersed in (c) 100% seawater and in seawater containing: (d) 10% NaBz (e) 20% NaBz (f) 30% NaBz (g) 40% NaBz (h) 50% NaBz

3.4 Corrosion Inhibition Efficiency

As the presence of NaBz at a concentration of 10% has the ability to reduce both weight loss and corrosion rate to a certain extent, even if the impact is minor, it can still provide a certain level of protection for zinc. As a consequence, we can calculate the corrosion inhibition efficiency at different time intervals throughout the total immersion period. The inhibition efficiency (%) was computed using Eq. (2). The inhibition efficiency values determined are 2.45 %, 4.76 %, 12.28 %, 6.98 %, 11.76 % for the 6th, 12th, 18th, 24th and 30th days of immersion, respectively. Figure 4 illustrates the plot of inhibition efficiency in relation to the immersion duration for a 10% solution of NaBz.

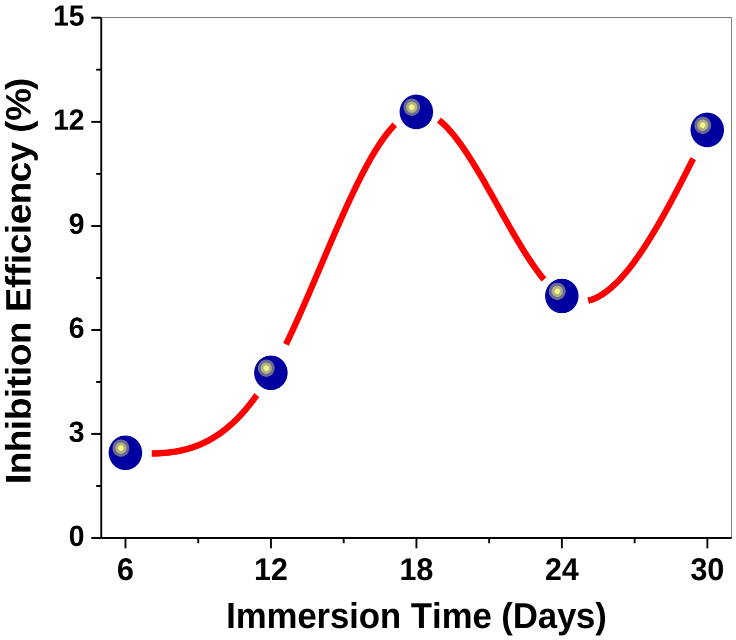

Fig. 4. Inhibition efficiency of the Zn corrosion against immersion time at 10% NaBz concentration

From this figure, the inhibition efficiency increases with time and reaches a maximum value on the 18th day for the best protection. Following this, the inhibition efficiency becomes mostly the same without any notable fluctuations. The inhibitors will interact with and eliminate the reactive corrosive substances from the surface of metal by creating a barrier between the metal and its environment, thereby diminishing the attack of chloride ions [13].

4. Conclusions

To summarize this study, we have successfully performed an investigation on the effect of sodium benzoate concentration in the range of (10–50) % on the corrosion of Zn in seawater solution for 30 days. From the results obtained, we found that the corrosion rate and weight loss were the highest in the first 12 days, after which these two parameters decreased slowly until the 30th day, due to the deposition of corrosion residues on the Zn surface. The corrosion rate of 10 wt% NaBz was lower compared to seawater, suggesting that lower NaBz concentrations can provide efficient protection to the zinc layer. However, at higher NaBz concentrations over 20%, corrosion rates and weight loss also increase, possibly attributed to the alkaline nature of NaBz, which contributes to an aggressive attack for effective corrosion.

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