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COMPARISON OF REDUCING SUGARS AS AGENT TO RETARD CORROSION RATES

* Yoko Sakakihara[1], Yoshishige Motobayashi[2], Tomoko Takashita[3], Shinichiro Okazaki[4], Tomohiko Ishii[4], and Hidenori Yoshida[4]

[1]Graduate School of Engineering, Kagawa University, Japan;
[2]Daiwa Construction Co., Ltd., Japan;
[3]Graduate School of Science for Creative Emergence, Kagawa University, Japan;
[4]Faculty of Engineering and Design, Kagawa University, Japan

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ABSTRACT: This study reports the effect of adding sugars to prevent the corrosion of reinforcing bars. Various types of sugars, including reducing sugar aldose (sugar with an aldehyde group), ketose (sugar with a ketone group), and syrup with an expiration date, were used in experiments. These sugars exhibit remarkably similar skeletal structures and identical hydroxyl groups and hydrogen positions at carbon numbers 4–6. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Tafel extrapolation were performed to reveal the effects of the sugars and their reductive abilities. ICP-AES showed that the concentration of dissolved iron in the fructose solution was about 1/270 of that observed in the blank, the lowest concentration of dissolved iron in this experiment, followed by waste syrup (WS). This demonstrated the reducibility of rebar by sugars. The ICP-AES results are consistent with the experimental results obtained using Fehling's solution and Benedict's reagent, as reported in a previous study conducted in 2021. The results of Tafel extrapolation showed no significant differences in corrosion rate. However, the current measurement methods are not optimal. Furthermore, molecular orbital calculations performed to evaluate the binding energies of the transition states of sugars to enediol structures confirmed that ketose was more reductive than aldose.

Keywords: Reducing sugars, Waste syrup, Tafel extrapolation, Corrosion

1. INTRODUCTION

In the past, it was believed that the performance of reinforced concrete (RC) structures could be maintained permanently; however, in recent years, it has become evident that the initial performance of RC structures cannot be maintained because the corrosion of the steel in the concrete, due to salt damage and neutralization [1,2], causes a decrease in the structural strength, as well as the cracking and spalling of the concrete. Therefore, maintaining the initial performance has become a major issue. Many repair methods have been proposed to bring the performance of deteriorated structures as close to their initial condition as possible through repair [3-7].

One of these is the cathodic protection system [8]. This is a method of preventing steel corrosion by continuously applying a DC current to the steel from the outside that is sufficient to overcome the corrosion current that is trying to flow out of the steel into the electrolyte. It provides long-term corrosion protection. However, the installation of electrodes, piping materials, and power supply equipment is required to control the energization status. Corrosion inhibitors are also often used to prevent corrosion. One well-known compound is nitrite [9]. Calcium nitrite and lithium nitrite are currently used. Other methods also exist, such as zinc phosphate or epoxy resin [10] applied directly to the rebar or silicate or silane-based impregnating materials that are applied over the concrete surface to prevent corrosion of the rebar. The disadvantages of these methods are that the application is labor intensive and the cost of materials is not inexpensive.

Since repair, after deterioration has occurred, is time-consuming and labor-intensive, there is a need to develop inexpensive corrosion inhibitors that can be mixed in during concrete mixing. Therefore, we focused on reducing sugars. In previous research, Niida et al. [11] proposed a method to reduce Cr(VI) leached from recycled roadbed material into harmless Cr(III) via the utilization of reducing sugars on metals. They found that leached Cr(VI) could be reduced using easily available and inexpensive sugars and polyphenols. Yamaya [12] found that most Cr(VI) in aqueous solutions can be reduced using syrup, which is a waste product in the food industry. If hexavalent chromium can be reduced to chromium oxide by reducing sugar, we thought that a similar chemical reaction might occur with iron. However, the reduction performance of reducing sugar on iron has not been investigated.

Generally, iron provided as an industrial material is chemically unstable and tries to stabilize as an oxide by reacting with oxygen. The raw material for iron, steelite, exists in nature as stable iron oxide. Steelmaking is the process of removing oxygen from iron ore so that it can be used as steel materials. Since unoxidized iron is unstable, it tries to take up oxygen again in an attempt to break out of its unstable state and return to its original state. Rust is the result of this process. The mechanism of rust formation is that water adheres to the surface of iron and the iron reacts with the dissolved oxygen in the water, causing iron ions to dissolve from the iron. The iron oxide formed by this reaction with oxygen and iron is rust. The chemical equation for the formation of rust is as follows.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$
$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (2)$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$
$$2Fe(OH)_2 + H_2O + 1/2O_2 \rightarrow Fe(OH)_3 \quad (4)$$

Therefore, reducing iron is a reaction to maintain the more unstable state. To convert iron oxide back to metallic iron, it is necessary to use a strong reducing agent such as nitrite.

In this study, it is aimed to inhibit the oxidation of iron by reducing sugar and delay the formation of rust as much as possible. And we focused on a cost-effective waste syrup (WS) derived from recycled food waste referring to Yamaya's study and conducted experiments to verify the reduction performance of the WS on steel bars. Furthermore, we sought to determine the feasibility of utilizing the WS as a novel corrosion prevention technology.

2. RESEARCH SIGNIFICANCE

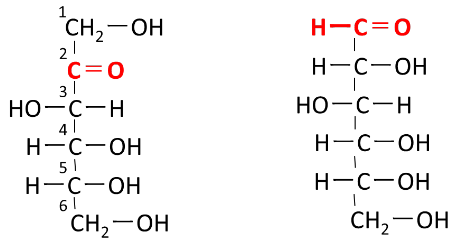
The WS is a food product that is typically fit for consumption but is discarded. In Japan, syrup is removed from distribution channels when it becomes discolored or expires. Moreover, the disposal of WS incurs significant costs and is a burden to companies. This study focuses on the reusage of substantial volumes of the expired WS in the engineering field [12, 13]. We will contribute to the creation of a system that can sustain the 3Rs; reduce, reuse and recycle, of Goal 12 of the Sustainable Development Goals (SDGs).

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Sugars

Glucose was selected as the reference substance based on a previous study [13]. The main component of the WS used in these experiments was glucose, constituting approximately 40 % of the WS. Fructose was the next most abundant component, constituting approximately 30 %. Glucose and fructose, a saccharide with six carbon atoms, were used as in previous study. Glucose is similar to fructose, in which the OH and H groups at carbon atoms from three to six are sterically in the same position. Fig. 1 shows the structural formulas of the sugars.



D-Fructose (aldose) D-Glucose (ketose)

Fig. 1 Fisher projection of fructose and glucose.

3.1.2 Rebar

A deformed steel bar (G-40 D13) was used in the experiment. It cut into 4.0 cm using a precision cutting machine, leaving only one side of the cut surface exposed with all other sides covered with epoxy resin. A sample of the rebar is shown in Fig 2.

Fig. 2 The photograph of the cut surface of rebar coated with epoxy resin.

3.2 Measurement of Corrosion Amount of Rebar Immersed in Sugar Solutions

The corrosion inhibition effect of reducing sugars on steel bars was examined. Sugar was mixed with 30 ml of distilled water to make 5% sugar solution. The concentration of sugar was set at 5.0 % because it enabled a more accurate measurement of the difference in the corrosion inhibitory effect of each sugar. The three sugars used were glucose, fructose, and WS. In addition to these three types of sugar solutions, blanks were used in the experiment. The rebar shown in Fig. 2 was prepared, and after polishing the measurement surface with water-resistant abrasive paper, iron powder was washed off with distilled water, surface oil was cleaned with ethanol and at last washed the surface with distilled water again. The rebars were immersed in conical tube containing the previously prepared sugar and blank solutions, with the surface of the rebar facing upward, and put in a constant-temperature chamber at 20 °C for one week. Fig. 3 shows the photograph of the experiment setup. After curing, the rebar was removed while brushing off any suspended matter on the surface.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), which is suitable for quantitative analysis of solution samples, was used to measure the amount of corrosion. 20 ml of the solution after curing was measured while the suspension was stirred, and 2 ml of concentrated nitric acid was added and heated for 30 minutes. After confirming that the precipitate had dissolved, it was filtered through a filter paper and the volume of the filtrate was measured. The evaporation volume was determined from the volume, and distilled water was added to make the concentration of nitric acid 0.1 mol / L, which is the same concentration as that of the ICP standard solution.

Fig. 3 Experimental setup for the measurement of corrosion amount of rebar immersed in sugar solutions. From left to right: Control Sample, Glucose, Fructose, and WS.

3.3 Measurement of Rebar Corrosion Rate in Sugar Solutions

The corrosion rate of the rebar in the sugar solution was measured to verify the effect of the reducing sugar on the corrosion rate of the rebar. Sodium chloride was added to the sugar solution because electrolytes were necessary for the measurement. As in the previous experiments, three types of sugars were used: glucose, fructose, and WS. Tafel extrapolation, an electrochemical technique, was used to measure the corrosion rate. The corrosion rate was the average of the multiple values measured for each sugar.

In the Tafel extrapolation method, the corrosion current density i_{corr} is obtained from the intersection of the extrapolated straight-line portions of the polarization curves obtained by varying the electrode potential. The process of reducing the electrode potential is called cathodic polarization, while increasing the electrode potential is called anodic polarization.

The corrosion current density (i_{corr}) obtained from the polarization curve was substituted into Eq. (5) to calculate the corrosion rate, v_{corr}. The unit mdd (mg / dm^2/day) is defined as the mass of metal that is corroded and leached per dm^2 (10 × 10 cm) per day.

$$v_{corr} = 8.594 \times M/n \times i_{corr} \quad (5)$$

v_{corr}= corrosion rate [mdd]
i_{corr}= corrosion current density [A/m^2]
M= molecular weight (Fe= 55.85 g/mol)
n= electron valence when metal dissolves

Next, 100 ml of a 5 wt% sodium chloride solution was added to 1.0 g of sugar, and the resulting solution was used as the sample solution. After the cut surface of the rebar was polished with a water-resistant abrasive paper and washed with distilled water, the rebar and the counter electrode were immersed in the sample solution, and the reference electrode was immersed in a saturated potassium chloride solution. The two containers were connected using a salt bridge, and the tip of the Luggin capillary was placed close to the measurement surface of the rebar. Each electrode was connected to a potentiostat for measurements. Fig. 4 shows a photograph of the experimental apparatus. The Luggin capillary was placed as close to the rebar as possible because the Tafel extrapolation requires observation of changes on the rebar surface.

Fig. 4 Experimental setup for Tafel extrapolation.

Table 1 lists the measurement conditions used in the Tafel extrapolation. The natural potential was measured. After the potential stabilized, it was polarized to -750 mV in the cathodic direction at a rate of 20 mV/min. Next, the rebar was removed, and the measurement surface was polished with a water-resistant abrasive paper, rinsed with distilled water, and immersed again. After standing for 5 min to allow the electrode potential to return to its natural value, it was polarized to -350 mV at a rate of 20 mV/min in the anode direction.

Table 1 Measuring conditions of Tafel extrapolation.

Items	x	Units
first and final potential	-750	mV
second and final potential	-350	mV
Scan speed	20	mV/min
Rest time	5	min

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Changes in Appearance

Fig. 5 shows the change in the appearance of the rebar after one week of immersion in the sugar solution. The order of rust formation was blank, followed by glucose, and as can be seen from the photograph, a large amount of iron was eluted in the blank. The orange color indicates that the iron is expected to have changed to iron oxyhydroxide. This chemical reaction is shown as follows.

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad (3)$$

$$\mathbf{4Fe(OH)_2 + O_2 \rightarrow 4FeO(OH) + 2H_2O} \quad (6)$$

It can be seen that the volume of the rebar in the blank is increased by iron oxide. The increase in volume due to rust causes cracks in the concrete. Cracks allow water and chlorides to penetrate into the concrete, causing further rusting.

On the other hand, almost no rust was formed on fructose or WS. The images of the rebar removed from the sugar solution are shown in Fig. 6. As in Fig. 6, rust was observed in the control sample and glucose, but the surface of the rebar in fructose and WS still showed metallic luster. Since the main component of WS is fructose, the rust inhibiting effect was similar to that of fructose.

Fig. 5 Surface of rebars immersed in various solutions for one week. From left to right: Control Sample, Glucose, Fructose, and WS.

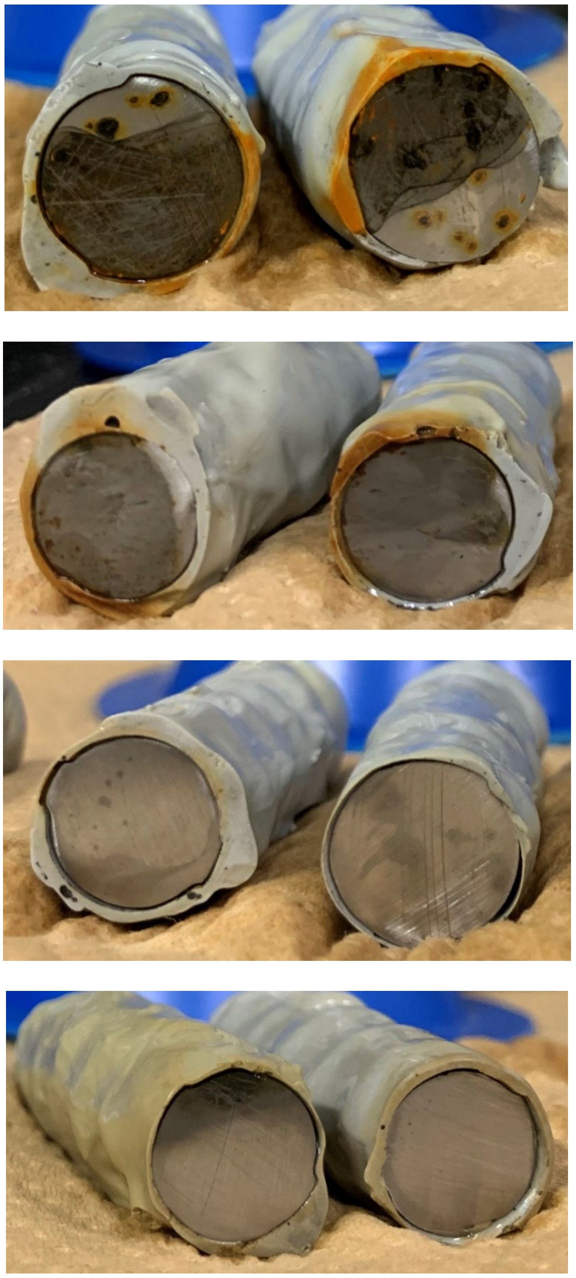


Fig. 6 The photographs of rebar extracted from sugar solution, from top: Control sample, Glucose, Fructose, WS.

4.2 Measurement of Corrosion Volume by ICP-AES

The results of the ICP-AES measurements are shown in Fig. 7. Compared with the blank, the concentration of dissolved iron in the glucose solution was slightly lower, and rust prevention was not very effective. The concentration of dissolved iron in the fructose solution was approximately 1 / 270 of the concentration observed in the blank, which was the lowest concentration of dissolved iron in this experiment. In previous studies, experiments were conducted on the redox reactions of copper and sugars. The results obtained in this study were consistent with those of the previous study [13]. Niida et al. [11] conducted experiments on the reduction of hexavalent chromium using sugars, and in their experiments, fructose was found to have a high reducing effect, which is consistent with the results of the present experiments.

As shown in Fig. 7, neither fructose nor the WS showed visible rust formation, but ICP-AES showed rust formation in WS. WS slowed rust progression to some extent, but not to the same extent as fructose.

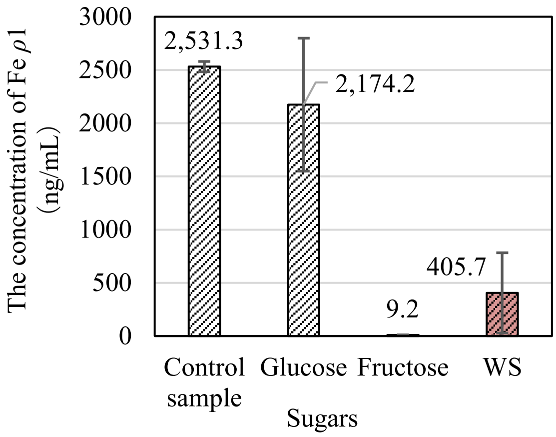


Fig. 7 Concentration of dissolved Fe in solutions.

4.3 Tafel Extrapolation

One of the Tafel curves obtained from each sugar measurement is shown in Fig. 8, and the corrosion rates calculated from the measurement results and Eq. (1) are shown in Fig. 9.

The Tafel extrapolation showed a slight suppression in the corrosion rate of the rebar immersed in the WS, but the difference was not as pronounced as that observed during the ICP-AES measurements. However, the current measurement methods are not optimal. Because the corrosion rate of the rebar was measured immediately after the rebar was immersed in the sugar solution.

In an experiment by Niida et al. [11], they investigated the reduction of hexavalent chromium up tp 4 days after immersion, and stated that the longer the immersion time, the greater the reduction effect of hexavalent chromium. and Sobhy et al. [14] investigated the corrosion rate of reinforced concrete mixed with nanofibers at different ages (30, 90, and 180) days. It has been reported that the improvements in corrosion rate and inhibition efficiency at later ages were more than at early age. As these experimental results indicate, long-term investigations should be carried out when investigating the corrosion rate of reinforcing steel.

We are planning to develop a new apparatus by changing the distance between the Luggin capillary and the electrode, pH, etc and measure the corrosion rate over longer term.

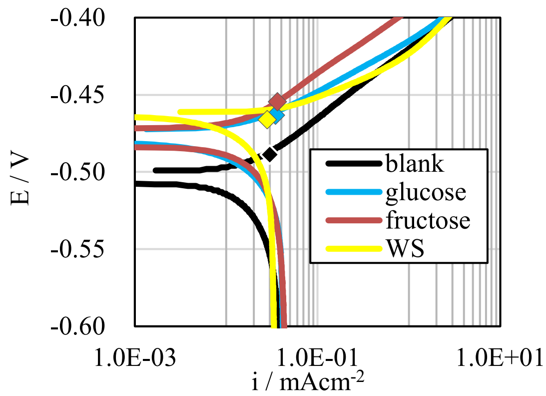


Fig. 8 Tafel extrapolation.

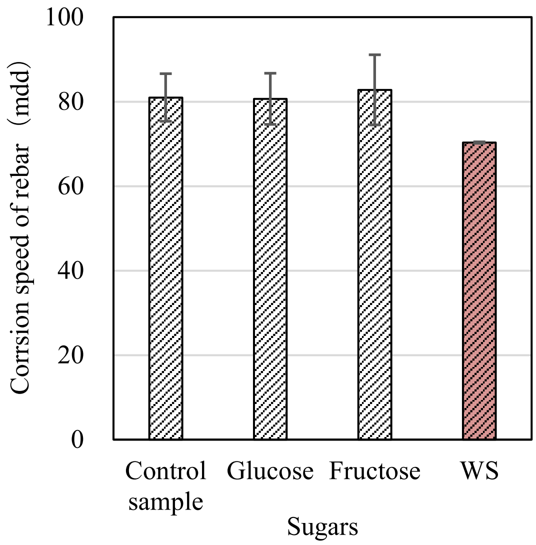


Fig. 9 Rebar corrosion rates of in sugar solutions.

5. MOLECULAR ORBITAL CALCULATION

5.1 Calculation Method

In consideration of the redox reaction between iron and sugar, we referred to the extensively studied redox reaction between Fehling's reagent and sugar. Fehling's reagent contains copper as a metallic component. The complex structure of copper and tartaric acid in the reagent was elucidated by Horner et al. [15]. In many studies, the redox reaction between copper and sugar has been related to an enediol structure, and Inoue et al. reported the transformation of the sugars into the enediol structure [16].

Since the redox reaction between iron and sugar also involves the enediol structure, the strength of the chemical bond was evaluated using the Discrete Variational-Xα (DV-Xα) molecular orbital calculation method based on the transition state diagram described in the paper by Inoue et al. [16]

The DV-Xα molecular orbital calculation method was developed by D. E. Ellis and H. Adachi [17-20]. The electronic potential of the DV-Xα method is proposed as "Xα potential" by J. C. Slater. It is one of the advantages that the DV-Xα method has numerically evaluated a substance's electronic state. Therefore, the *s* or *p*-orbitals of molecular can be accurately calculated. This study focuses on the intermediate transition state of sugar molecules. The accurate calculation of the intermediate transition state of sugar molecules is critical.

$C_6H_{12}O_6$, a monosaccharide composed of six carbon atoms, was used in the calculation model. The bond strength was calculated with reference to the second schematic on the left side of the structural changes shown in Fig. 10. The actual model used for the calculation is shown in Fig. 11. The transition from the transition state to the enediol structure is caused by oxygen withdrawing hydrogen, therefore oxygen and hydrogen atoms were simulated by writing a temporary bond. The structure was assumed to be similar to a chain structure. The calculations are performed self-consistently until the difference in orbital populations between the initial and final states of the iteration is less than 0.0005 electrons.

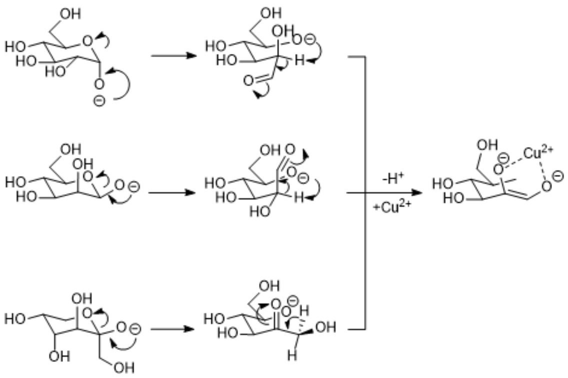


Fig. 10 Transition states to the enediol structure, from top: glucose, mannose, and fructose. [16]

5.2 Highest Occupied Molecular Orbital–Lowest Unoccupied Molecular Orbital Gap

In chemistry, the highest occupied molecular orbital is called HOMO by its initials, and lowest unoccupied molecular orbital is called LUMO. HOMO and LUMO are called frontier orbitals and are considered highly reflective and characteristic orbitals. The energy difference between the HOMO and the LUMO is the HOMO-LUMO gap. It is shown in Fig. 12. Its size can be used to predict the strength and stability of the transition metal complexes and colors produced in the solution. The compounds larger HOMO-LUMO gaps tend to be more stable and thus the less chemically reactive it is. Conversely, the smaller the HOMO-LUMO gap, the more unstable. A schematic diagram is shown in Fig. 13. The magnitude of the energy difference in the HOMO-LUMO gap has no meaning when compared between completely different substances, but when compared between similar compounds, the chemical stability of the molecules can be discussed. These two sugars used in this experiment consist of the same molecular formula, $C_6H_{12}O_6$, and have similar structures. The steric conformations of OH and H groups at No. 3-6 carbon atoms are also the same. The HOMO-LUMO gap can be compared because of their similar structures.

In this study, the strength of the redox reaction between iron and sugar molecules was examined by calculating the bond strength from the transition state of the sugar to the enediol structure in Fehling's solution. The magnitude of the bonding strength of the redox reaction between the iron and sugar molecules was evaluated by calculating the HOMO-LUMO gap.

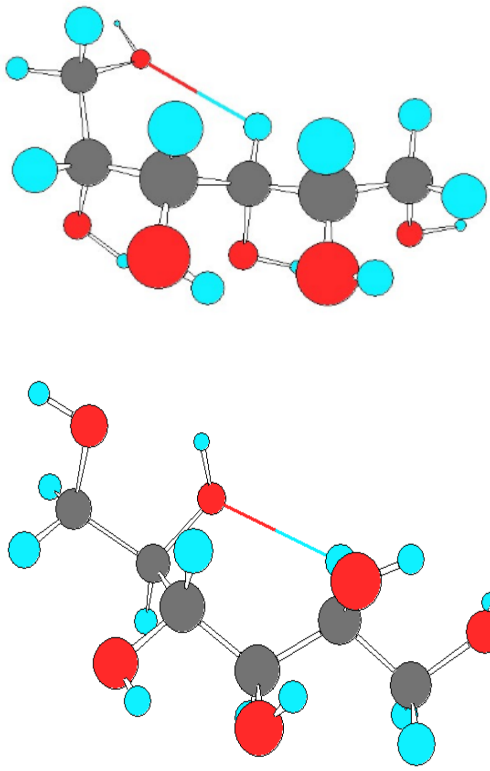


Fig. 11 The molecular models used for the calculation, from top: Glucose, Fructose. The red and blue lines are temporary bonds.

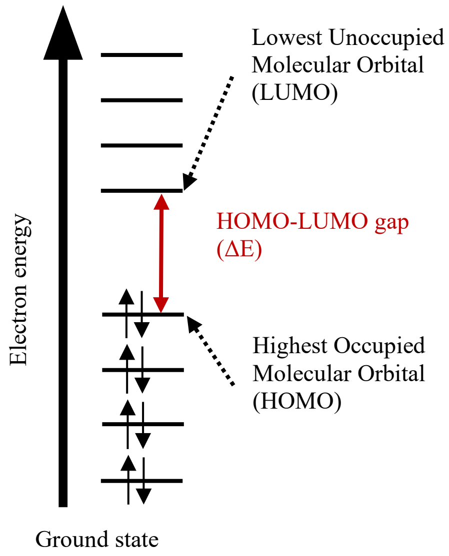


Fig. 12 Illustrated of each molecular orbital and HOMO-LUMO gap.

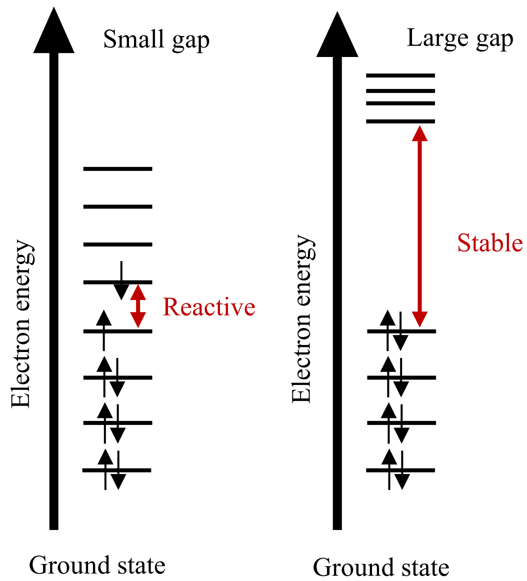


Fig. 13 The figure shows the relationship between the size of the HOMO-LUMO gap and energy stability.

5.3 Results of DV-Xα Method

Table 2 lists the calculated HOMO–LUMO gaps in the sugar transition states. The same method was repeated 10 times for each sugar, and the average value was calculated.

The HOMO-LUMO gap was smaller for fructose than for glucose. This result was consistent with our previous experimental results. Although only two types of sugars were analyzed in this study, the reactivity of the redox reactions can be determined by increasing the number of sugar types.

Table 2 HOMO-LUMO gap in the transition states of sugars.

Sugars	HOMO-LUMO gap (eV)
Fructose	3.9862
Glucose	4.2468

6. CONCLUSIONS

In this study, the corrosion rate of reinforcing bars in concrete was examined to determine whether the corrosion rate can be suppressed by sugars, particularly WS. This effect was verified by examining on the redox reactions of iron and the sugars. The rebar was immersed in a sugar solution for a certain period, and the amount of dissolved iron was measured using ICP-AES. The experimental results showed that there was no significant difference between the blank and glucose; however, fructose and the WS delayed rust formation. The concentration of dissolved iron in the fructose solution was about 1/270 of that observed in the blank, the lowest concentration of dissolved iron in this experiment, and followed by WS. These results suggest that even the WS, which is a waste product, exhibits sufficient reduction potential and effectiveness. This outcome can be attributed to the presence of fructose as the primary component in WS.

The corrosion rate of the rebar was measured using Tafel extrapolation. However, the rate did not exhibit significant changes compared to the results obtained from ICP-AES. The experimental setup requires some improvements, such as the shortening of the distance between the Luggin capillary and measurement surface and adjustment of the pH.

The bond strength was calculated using molecular orbital calculations. The transition state of sugar to enediol was used for this calculation. Fructose is unstable than glucose, indicating that fructose is more likely to undergo redox reactions.

It has long been known that mixing sugars with concrete causes cohesion inhibition. When conducting corrosion protection experiments on reinforced concrete specimens using WS, it is necessary to confirm the extent to which the cohesion inhibition is affected and how the specimen strength is changed.

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