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REDOX REACTION MECHANISMS OF REDUCING SUGARS CONSIDERED FROM THE VIEWPOINT OF DIFFERENCES IN MOLECULAR STRUCTURES

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ABSTRACT: Although methods such as electrolytic corrosion protection are widely used to prevent rebar corrosion, they are expensive. Therefore, studies have been conducted to utilize the reducing sugar to prevent the corrosion of steel bars in concrete. However, the detailed mechanism underlying the reducing effects of various sugars is unknown, and the application conditions required for practical use are not fully understood. The magnitude of the reducing ability of various sugars was experimentally quantified in this study, and molecular orbital calculations were used to identify the molecular structures that are likely to exhibit reducing ability. The magnitude of the sugars' redox reaction was determined using Fehling's solution and Benedict's reagent. Therefore, the reducing ability of the sugars used in the experiments could be quantified to some extent, though the reactivity to various test reagents varied depending on the sugars. These two experiments revealed that fructose, which has a ketone group, exhibited the highest reactivity. The Discrete Variational-Xα method was used to search for sugars with small energy differences in the molecular orbital calculations to determine the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap. Because the high reactivity of sugars is related to their high reducing ability, sugars with high reducing abilities were identified from the calculation results. According to the calculation results, fructose exhibits a small HOMO–LUMO gap, which is consistent with the experimental results.

Keywords: Reducing sugars, DV-Xα method, Molecular orbital calculations, Corrosion

1. INTRODUCTION

In the past, numerous reinforced concrete structures were constructed on the understanding that they would be permanently sound, and a number of infrastructures have been built on this assumption. In recent years, however, it has become clear that maintaining the initial performance of reinforced concrete structures in service is difficult due to corrosion of steel in the concrete caused by salt attack [1] and carbonation [2], which leads to a decrease in structural strength, cracking, and spalling. For this reason, research on deterioration diagnosis, including the establishment of a method for measuring chloride ions in concrete, which are the cause of rebar corrosion, is being actively conducted [3].

Many methods for repairing deteriorated reinforced concrete structures have also been proposed. Various methods exist, such as mortar or adhesive press-in [4], removal of concrete around reinforcing bars and re-casting, coating with concrete containing fibers [5], and more recently, microbe-induced calcium carbonate precipitation technology [6, 7]. However, they are costly and labor-intensive. Reinforced concrete structures must have a long service life to minimize the need for repair, and an effective and economical method of steel-bar corrosion protection is required.

Therefore, we concentrated on reducing ability of the sugars. Niida et al. [8] proposed a method to reduce hexavalent chromium eluted from recycled roadbed material to harmless trivalent chromium and demonstrated the reduction of hexavalent chromium elution using sugars and polyphenols that are readily available and low-cost in previous research using reducing sugars on metals. Yamaya [9] proposed that waste syrup could be used to reduce the majority of the Cr(VI) in the solution. Therefore, numerous studies have been conducted to investigate sugar's reduction performance on Cr(VI), and sugar's reduction performance is being evaluated. Since no research has been conducted to investigate the performance of sugar on steel bars, the research was initiated to investigate the redox reaction between sugar and iron. Our previous study has investigated the electrochemical properties of sugars [10].

Iron in nature exists as iron ore in the form of iron oxide, which is refined (the loss of oxygen:

reduction) and used as iron. When iron comes into contact with water, it corrodes (combines with water and oxygen: oxidation) and tries to return to its most stable state. This phenomenon is corrosion. The phenomenon of corrosion in the presence of oxygen and water is an ionization reaction of metals caused by an electrochemical mechanism. The corrosion rate of iron decreases rapidly above pH 10 [11], and corrosion does not progress in the alkaline region above pH 12 due to the formation of a strong passive film [12]. This is precisely the pH range of steel bars in concrete. However, once the non-conductive film is destroyed by chloride contamination etc., corrosion begins, and once a macrocell corrosion circuit is formed, the corrosion rate increases at once [13]. The main problem of corrosion is not the reduction of its cross-sectional area of rebar caused by the dissolution of iron, but the formation of less soluble oxides and oxyhydroxides of Fe(II) and/or (III). The oxides adhere around the rebar and exert a compressive force on the concrete, which causes cracks in the concrete. Previous studies have reported that sugars form complexes with iron [14]. In this experiment, sugar was selected as the reducing substance because of the possibility that sugar could inhibit the formation of oxides by trapping dissolved iron.

Sugar is used as a general term for sweet seasonings, among which those called reducing sugars have functional groups (-CHO: formyl group) in their molecules that reduce other molecules. A typical example is glucose. However, these reducing sugars do not usually exhibit reducing properties because of their stable cyclic structure. In alkaline solution, the cyclic structure opens into a chain and a formyl group appears, indicating reducing properties. On the other hand, sugars with ketone can be also reducing. Ketones are generally not reducible, but ketose forms an endiol structure by keto-enol tautomerism, and this structure has been reported to be involved in redox reactions between sugars and metals [15]. Fig. 1 shows the endiolate structure of a sugar and a metal, and Fig. 2 shows the carbonyl group transfer reaction of sugar.

The purpose of this study was to elucidate the reaction mechanism of the oxidation–reduction of reducing sugars and metals. In addition to chemical experiments, the reactivity of each sugar was confirmed using molecular orbital calculations to determine the strength of the chemical bond in the transition state of the sugar molecule.

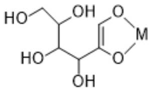


Fig. 1 The endiolate structure of sugar and metal.

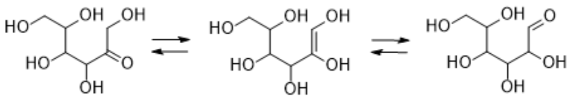


Fig. 2 Conformational changes from ketose to aldose.

2. RESEARCH SIGNIFICANCE

In recent years, the development of repair materials using waterborne epoxy-concrete composite repair materials [16] and phosphates [17] has begun, but construction costs in civil engineering are high owing to the large amounts of materials used. Therefore, inexpensive materials are required for this purpose. Sugar is an inexpensive material that is readily and widely available. As a goal, labor is reduced by mixing sugar as an admixture ingredient in concrete to extend the time it takes for the reinforcing bars to begin to corrode.

3. MAERIALS AND METHODS

3.1 Materials

3.1.1 Sugars

Based on a previous study [8-10], glucose was chosen as the reference substance. Glucose is a six-carbon monosaccharide. Monosaccharides are sugars that have not been hydrolyzed further. Monosaccharides consist of carbon, hydrogen, and oxygen. Reducing monosaccharides can have a linear structure and one of two functional groups: hydroxyl groups and aldehyde or ketone groups. Monosaccharides containing aldehyde and ketone groups are called aldoses and ketoses, respectively.

In this study, in order to examine the differences in redox reactions caused by differences in functional groups, sugars with the same structure at positions C3 to C6 were used for comparison. C=O is required for the reduction reaction, and there are two types of sugars with C=O at position C1, glucose and mannose, and only fructose has C=O at position C2. Furthermore, non-reducing sugars, there are two other sugars without C=O, sorbitol and mannitol. The above five sugars were used in this study. Table 1 depicts the structural formulae of the sugars. In the electrical resistance measurement, a commercial syrup made of high fructose corn syrup was used in addition to fructose.

3.1.2. Benedict's test

Benedict's solution, which was used in the experiment, is a commercially available clinical testing reagent (Hayashi Pure Chemical Inc., Ltd.). To prepare the reagents and experiments, distilled water was used as a solvent.

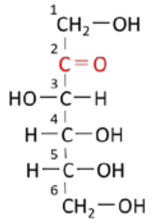
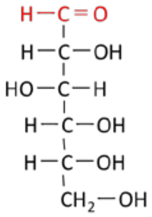
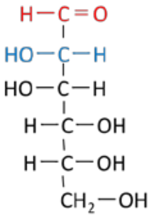
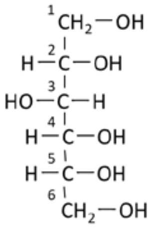
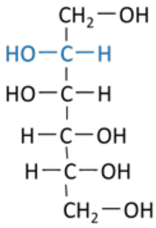
3.1.3 Fehling’s solutions

Copper(II) sulfate pentahydrate (FUJIFILM Wako Pure Chemical Corporation, guaranteed reagent) was prepared for Fehling's A solution, and potassium sodium (+)-tartrate tetrahydrate (FUJIFILM Wako Pure Chemical Corporation, Wako 1st grade) and sodium hydroxide (FUJIFILM Wako Pure Chemical Corporation, guaranteed reagent) were prepared for Fehling's B solution. Distilled water was used as the solvent for reagent preparation and experiments.

3.1.4 Electric resistance measurement

In this study, reinforced mortar (RM) were cast with ordinary Portland cement, and the diameter of the steel bars is 6 mm. NaCl was prepared to reproduce the corrosive environment.

Table 1. Fisher projections of sugars used in the experiment.

Ketose	 D-Fructose	
Aldose	 D-Glucose	 D-Mannose
Others	 D-Sorbitol	 D-Mannitol

3.2 Chemical Experiments

In order to investigate the reducing ability of sugar to iron, we examined the possibility of applying a quantitative method for the determination of reducing sugar. The Hanes method is based on the reaction in which ferricyanide (Fe(III)) is reduced by carbonyl groups to ferrocyanide (Fe(II)) under alkaline conditions. The chemical reactions of the determination in the Hanes method can be summarized as follows [18].

$$K_3Fe(CN)_6 + Reducing\ sugar \rightarrow K_4Fe(CN)_6 \quad (1)$$

$$2K_3Fe(CN)_6 + 2KI \rightarrow 2K_4Fe(CN)_6 + I_2 \quad (2)$$

$$2K_4Fe(CN)_6 + 3ZnSO_4 \rightarrow Zn_3[Fe(CN)_6]_2 \downarrow + 3K_2SO_4 \quad (3)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad (4)$$

Since cyanide compounds are highly reactive, it is difficult for the layman to handle it. We decided to conduct the experiment using copper-containing compounds as an alternative of iron. Iron has atomic number 26 and copper is 29. The outermost shells of them are N-shell, which has two electrons. Therefore, they have similar properties. Benedict reagent and Fehling's solution are widely known as reagents containing copper, and these will be used in the experiments [15, 19]. Benedict reagent and Fehling's solution contain copper ions and color is blue. When a reducing substance is added and heated, the copper is oxidized to change red copper oxide and precipitated.

3.2.1 Benedict’s test

When the sugar was dissolved in Benedict's solution, the concentration was 25 mM. Following the dissolution of the sugar in Benedict's solution, the test tubes were wrapped in Parafilm, immersed in water, and heated to 70 °C for 3, 5, and 10 min. Following that, the solution was filtered through the filter paper, which was then dried at 100 °C for 2 h, and the weight of the filter paper (No. 5C) before and after the experiment was compared to determine the amount of Cu_2O produced.

The chemical equation for the use of glucose is shown below.

$$CH_2OH \cdot (CHOH)_4 \cdot CHO + 2Cu^{2+} + 4OH^- \rightarrow CH_2OH \cdot (CHOH)_4 \cdot COOH + Cu_2O \downarrow + 2H_2O \quad (5)$$

3.2.2 Fehling’s solution

Fehling A solution was prepared by dissolving 6.92 g of copper (II) sulfate pentahydrate in 100 mL of water. To make 100 mL of Fehling's B solution, 34.6 g of potassium sodium tartrate tetrahydrate and 10.0 g of sodium hydroxide were dissolved in water.

In a test tube, sugar was dissolved to a final concentration of 25 mM. The sample solution (1.0 mL) received 0.5 mL of Fehling's A and B. The test tubes were wrapped in Parafilm and heated in a 70 °C water bath for 1, 2, 3, 4, 5, and 10 min before being filtered through filter paper (No. 5C). The filter paper was dried for 2 h at 100 °C, and the weight of the filter paper before and after the experiment was compared to determine the amount of Cu_2O produced.

The chemical equation for the use of glucose is shown below.

$$CH_2OH\cdot(CHOH)_4\cdot CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_2OH\cdot(CHOH)_4\cdot COO^- + Cu_2O\downarrow + 3H_2O \quad (6)$$

3.3 Calculation Method

3.3.1 Molecular orbital calculation

Regarding the redox reaction between metal and sugar, we refer to the redox reaction between Fehling's reagent and sugar, which has been extensively studied [15, 19]. Fehling's reagent contains copper as a metallic component. Hörner et al. elucidated the complex structures of Cu and tartaric acid in the reagent [19]. Many studies have linked the redox reaction between copper and sugar to the enediol structure, and Inoue et al. reported the transformation of sugars to the enediol structure [17].

Given that the redox reaction between iron and sugar also involves the enediol structure, the strength of the chemical bond was calculated 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.

Ellis and H. Adachi created the DV-Xα molecular orbital calculation (DV- Xα method) [20-23]. J. C. Slater proposes the electronic potential of the DV-Xα method as the "Xα potential". One advantage of the DV-Xα method is that it numerically evaluates the electronic state of a substance. Therefore, the *s* or *p*-orbitals of organic molecules can be calculated precisely. This study focuses on the intermediate transition states of sugar molecules. It is critical to accurately calculate the intermediate transition states of sugar molecules.

The chemical formula of the calculation model is $C_6H_{12}O_6$, which is a monosaccharide composed of six carbon atoms. The bond strength was calculated with reference to the second schematic on the left side of the structural changes depicted in Fig. 4. The actual model used for the calculation is shown in Fig. 5. The non-reducing sugars sorbitol and mannitol were used in the chemical experiments but were not included in the molecular orbital calculations because they do not form linear-chain structures.

The calculations were repeated until the difference in orbital populations between the iteration's initial and final states was less than 0.0005.

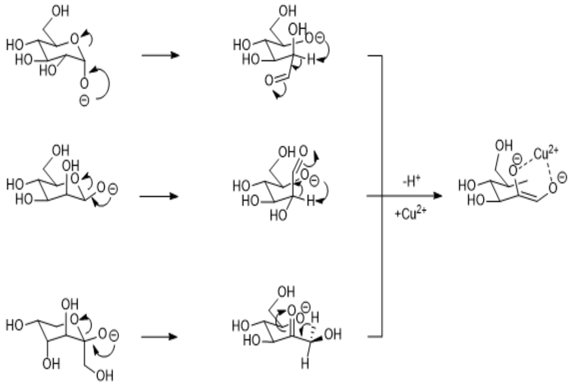


Fig. 4 Transition states to the enediol structure, from top: glucose, fructose, and mannose. [15]

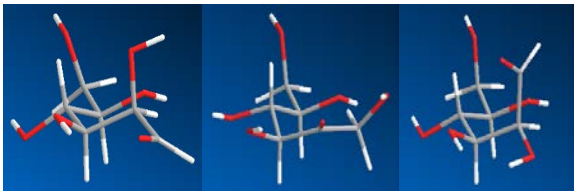


Fig. 5 Molecular models used for the calculation, from left: glucose, fructose, and mannose. Transition states were made based on the chair-shaped six-membered ring structure.

3.3.2 Highest occupied molecular orbital–lowest unoccupied molecular orbital gap

In this study, the strength of the redox reaction between copper 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 highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap was used to calculate the magnitude of the bonding strength of the redox reaction between the copper and sugar molecules.

In chemistry, HOMO and LUMO are known as frontier orbitals because they are the most reactive and characteristic orbitals. The HOMO–LUMO gap is the energy difference between the HOMO and the LUMO. It is shown in Fig. 6. Its size can be used to predict the strength and stability of transition metal complexes and the color of the solution. The larger a compound's HOMO–LUMO gap, the more stable the compound and thus the less chemically reactive it is. Conversely, the smaller the HOMO-LUMO gap, the more unstable and therefore chemically reactive the compound is. From these facts, sugars with a smaller HOMO-LUMO gap are more easily oxidized.

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. All of the five 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.

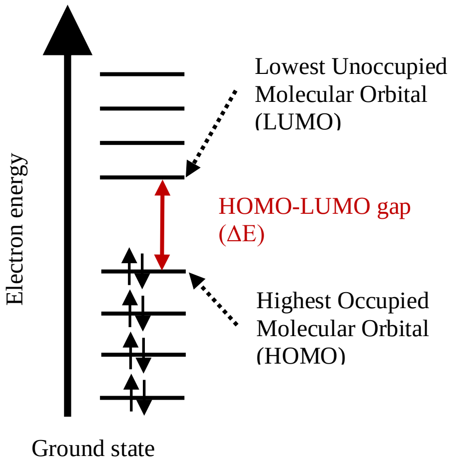


Fig.6 Illustrated of each molecular orbital and HOMO-LUMO gap.

3.4 Corrosion Rate Measurement of Steel in Mortar

RM specimens were prepared to study the effect of sugar on the corrosion protection of reinforcing bar in mortar.

The prepared RM specimens are shown in Fig. 7. The cover is 20 mm, and the steel bars exposed to the outside were coated with epoxy resin. The mortar used for the RM specimens had a water cement ratio of 0.5 and a cement to sand mass ratio of 1:3. The RM specimens were mixed with 0.16% NaCl relative to the mass of the mortar to simulate a corrosive environment. Mortar was prepared by mixing 0.5% sugar to cement and dissolving it in water. The specimens were demolded on the third day after casting and cured in air until 28 days of age. Immediately thereafter, the specimens were moistened with a wet rag and tested by iCOR [24] to measure the corrosion rate calculated from the electric resistance and polarization resistance of the mortar. Table 2 shows the display of corrosion rate values obtained by this device and an indication regarding the corrosion rate index. This time, the degree of corrosion rate is indicated by these four ranks. The corrosion rate was also measured at 40 days of age.

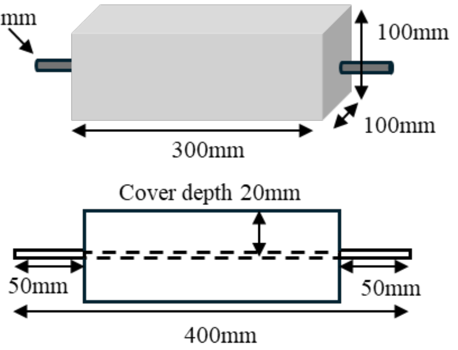


Fig. 7 Geometries of RM specimen.

Table 2. Indicators for corrosion rate.

Corrosion rate ($\mu A/cm^2$)			
very low	low	high	very high
<1.0	1-3	3-10	>10

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Benedict's Test

Fig. 8 depicts the amount of Cu_2O precipitation. Fructose was highly reactive from the start of heating, Cu_2O precipitation ended 3 min later, and Cu_2O precipitation was in a steady state. Glucose was the next most reactive. Cu_2O precipitated slowly on glucose and mannose, reaching approximately the same level as fructose precipitation after 10 min. The amount of Cu_2O precipitated at glucose and mannose was only slightly different.

Cu_2O precipitation, however, was not observed in the presence of sorbitol or mannitol. This is attributed to the fact that these two sugars are non-reducing and therefore do not undergo redox reactions.

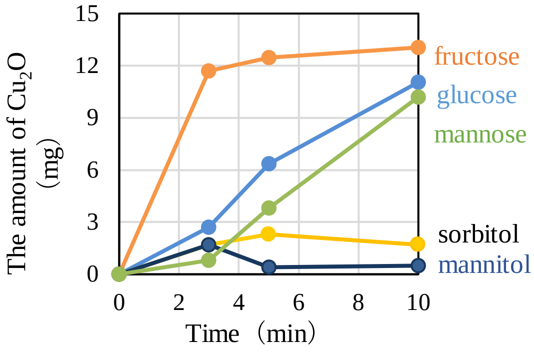


Fig.8 The amount of Cu_2O precipitation in each Benedict's solution.

Fructose is a ketose, while glucose and mannose are aldoses. As can be seen from the Fig. 8, the redox reactivity seems to be related to the functional groups. There was a difference in the reaction rate between ketose and aldose, but after enough time, all Cu^{2+} in both ketose and aldose solutions precipitated as Cu_2O.

4.2 Fehling's Solutions

The experimental results for the amount of Cu_2O precipitated in Fehling's reaction are depicted in Fig. 9. From the start of heating, fructose was highly reactive. Cu_2O precipitation ended approximately 5 min following heating, and Cu_2O precipitation was in a steady state. The next reactive was glucose; the precipitation of Cu_2O ended 3 min following heating and was in a steady state. Mannose reacted slowly, and significant precipitation was observed after 10 min. This result was identical to the one described above. In the presence of sorbitol or mannitol, no redox reactions are observed. Copper oxide is not formed because these sugars are non-reducing.

The major difference between the Fehling's reaction and the Benedict's reaction is the reactivity of mannose. In the Fehling's reaction, glucose and mannose showed similar reactivity, but in the Benedict's reaction, mannose reacted more slowly. According to [15], the low reactivity of mannose is related to steric hindrance. The initial pH is lower in the Benedict's reaction than in the Fehling's reaction, and the difference in pH suggests that the conformation of mannose in the solution is not suitable for the reaction.

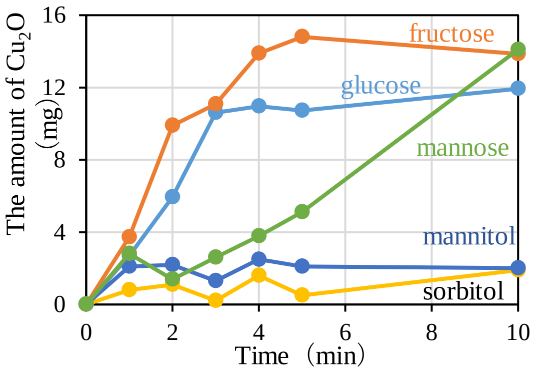


Fig. 9 The amount of Cu_2O precipitation in each Fehling solution.

From both the benedict's and fehling's reactions, it was found that fructose was the most reactive. The high-reducing ability of fructose is well known, and it is said that the reason for the high-reducing property of fructose is that the α-hydroxycarbonyl structure ($–COCH_2OH$) at positions 1 and 2 in the chain fructose molecule easily changes to a tautomer with an endiol structure in a basic aqueous solution [15]. However, although it has not been chemically proven, the authors speculate that the reason for the high reactivity of ketones is that not only 1,2-enediol but also 2,3-enediol can be obtained. Fig. 10 depicts the possible enediol structures of the ketose and the aldose. In other words, it is thought that the reaction rate increased because reaction points increased to twice.

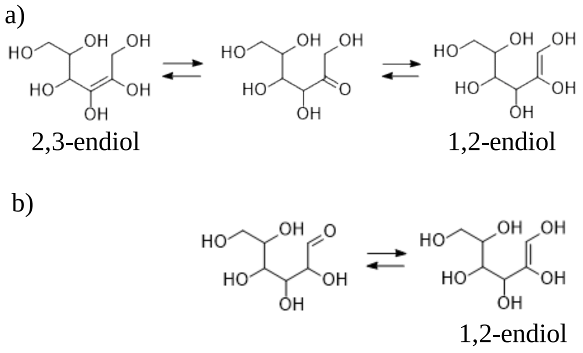


Fig. 10 Conformational changes to endiol (a: ketose, b: aldose).

4.3 Results of the DV-Xα Method

The calculated results for the HOMO–LUMO gap obtained using the DV-Xα method are listed in Table 3. The results show that fructose has the smallest energy difference in the chemical bond, which is consistent with the findings of the Fehling and Benedict reactions.

When the DV-Xα method results were compared to those of Fehling's and Benedict's reactions, it was discovered that fructose, which has a small energy difference between the HOMO and LUMO, reacts well with both Fehling's solution and Benedict's reagent and is the sugar with the highest amount of Cu_2O production. In terms of molecular orbital calculations and chemical reactions, ketose was discovered to be more reactive than aldose. Although it has not been chemically proven, it is speculated that the reason for the high reactivity of ketones is that not only 1,2-enediol but also 2,3-enediol can be obtained.

Table 3. Energy difference of the chemical bond in each sugar molecular.

Sugars	HOMO–LUMO gap (eV)
Fructose	3.5596
Glucose	3.8843
Mannose	4.0041

4.4 Corrosion Rate Measurement of Steel in Mortar

The results of the electric resistance are shown in Fig. 11. The electric resistance of the RM specimen with sugars was much lower than in the blank case without sugar. The results of the corrosion rate of the rebar are also shown in Table 4. In all cases, the corrosion rate was high at 28 days of age due to the effect of chloride admixture. On the other hand, the corrosion rates of all specimens decreased at 40 days of age. In the cases with sugars, the electrical resistivity was low, and the corrosion rate wasn't extremely high, suggesting that reducing sugar especially fructose is effective in preventing corrosion. The surface properties of RM specimens are shown in Fig. 12. It is noted that the test specimens made without sugar showed better surface condition than those with sugar, and the surface loss occurred in MS specimen with fructose.

As this study was carried out at a relatively early stage in the life of the concrete, further consideration of experimental conditions and a longer term study are needed.

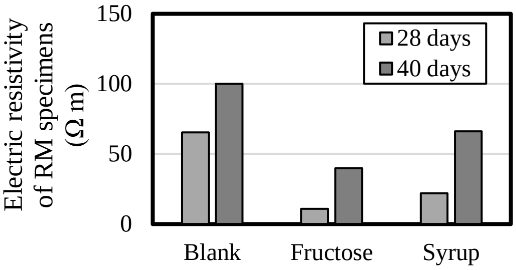


Fig. 11 Electric resistivity of RM specimen.

Fig. 12 Surface condition of RM specimens.

Table 4. Corrosion rate of the rebar in mortar measured by iCOR.

Sugars	Days 28	Days 40
Without sugar	high	low
Fructose	high	low
Syrup	very high	low

5. CONCLUSIONS

In this study, we used Benedict's and Fehling's chemical reactions to investigate the differences in the reducing ability of reducing sugars. Molecular orbital calculations were used to investigate the reactivity of various sugars in terms of the strength of their chemical bonds. Among the reducing sugars used were fructose, a ketose with a ketone group, glucose, an aldose with an aldehyde group, and mannose, an aldose. Fructose, a ketose, was the most reactive in both of Benedict's and Fehling's reaction, followed by the reductive aldoses of glucose and mannose. These results indicate differences in the reactivity of each sugar functional group. Cu_2O was not deposited on mannose at first but precipitated over time, eventually precipitating to the same extent as fructose and glucose. The reason why ketose showed the fastest reaction rate is that ketose can be 2,3-endiol as well as 1,2-endiol, which may increase the reaction rate by doubling the reaction sites. The DV-X**α** method was used to calculate the molecular orbitals. Sugar molecules were calculated using the transition states described by Inoue et al. According to the calculations, fructose exhibited the weakest bond strength, followed by glucose and mannose. These findings are of the same order as the experimental findings.

Corrosion rate experiments on rebar using mortar specimens showed that reducing sugars were effective in preventing corrosion, since the electrical resistivity was low and the corrosion rate was not extremely high. This research is a simulation of a system that cuts out the area near the rebar in concrete, but we believe it may be effective for rebar in concrete as well. However, influence of aggregate different between mortar and concrete, we plan to conduct more demonstrations.

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