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Hydrogen reductant waters: antioxidant characterization

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Abstract: *Nearly 21% of oxygen in the atmosphere enables all air-breathing life on Earth to produce energy from food. By oxidizing carbon compounds, active oxygen species are produced that are at risk of oxidative damage both externally and internally. 71% of the Earth's surface is covered by water, a compound of reductant (H) and oxidant (O). As hydrogen, oxygen, and water are all involved in the metabolism of redox reactions in vivo, it is not surprising that they exert a biological effect! The antioxidant, anti-inflammatory, and anti-apoptotic effects of hydrogen have recently been discovered by scientists. This study compared hydrogen therapy with three different delivery methods, including inhalation of hydrogen gas, oral hydrogen water, and injection of hydrogen saturated saline. Using magnesium hydride hydrolysis to produce hydrogen-water, the hydrogen-dissolving capacity of water can be increased by two times. Hydrogen-reduced water can be produced in-situ using this method because its antioxidant properties cannot be stored.*

Keywords: *Oral hydrogen-dissolving water, Hydrogen gas inhalation, Hydrogen-saturated saline injection*

1. Introduction

Life on earth is possible due to the existence of water. In general, hydrogen gas is hardly found in water since it is the lightest and smallest element, which causes it to disappear rapidly. A bio-mechanism to fight against oxidative damage, the anti-oxidative enzyme, was developed by life forms born in water to avoid the fatal risk. Hydrogenase is an enzyme that breaks down molecular hydrogen into active hydrogen about 3.8 billion years ago [1].

In 2007, Oshawa et al. [2] reported that inhaling only 2 % hydrogen gas can reduce oxygen-derived free radicals and improve cerebral ischemia-reperfusion injuries. Although the mechanism for hydrogen biology is not clear, the protective effects of hydrogen on oxidative stress have drawn much attention. Over 500 papers have been published on hydrogen biology since that time, covering almost every disease. Evidence shows molecular hydrogen in cells and organisms exerting antioxidant, anti-inflammatory, and anti-apoptotic effects against oxidative stress. Vitamin C and dehydroascorbic acid can be administered to treat reactive oxygen species-caused oxidative stress disease. The body maintains metabolism through the oxidation of food into energy species. To help absorb nutrients, cells produce reactive oxygen, which is unique to biological organisms. However, if overdone, tension can seriously impair physiological functions and even cause death. Traumatic injuries can also cause oxidative stress damage like a peeled apple turning brown.

At low concentrations, hydrogen does not react with beneficial reactive oxygen species, such as hydrogen peroxide and nitric oxide. By selectively neutralizing highly reactive free radicals, low concentration hydrogen is limited to destroying cytotoxic oxygen species and not all free radicals. Over 170 diseases and animal models have been shown to be treated with hydrogen, including antioxidant activity [2], [5], [6], [11], [12], [14], [15], ischemia-reperfusion injury [3], [4], [7], [10], [16], [18], Parkinson’s disease [8], [17], cancer [9], retina [10], chondrocytes [12], diabetes [13], irradiation-induced lung damage [14], mitochondrial damage [15], and cardiac [16].

The method of hydrogen applications, which has been studied in recent years by scientists in order to assess its biological effects on multiple diseases, is to resolve it in order to apply hydrogen’s antioxidant, anti-inflammatory, and anti-apoptotic functions against oxidative stress adequately [1]-[19]. Hydrogen

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molecules have been shown to have an antioxidant effect. Hydrogen molecular, however, is different from hydrogen gas. The hydrogen in hydrogen water is both atomic and molecular. The medical effects of hydrogen are constantly being studied in vivo in hydrogen bioresearch. The study emphasizes the importance of high quality hydrogen-water manufacture for clinical applications.

2. Materials and Methods

Table 1: Hydrogen delivery methods.

Administration	Delivery methods	Characteristics
Hydrogen gas	inhalation gas mixture of H_2 < 4 %	Rapid, unsafe, acute oxidative damage
Hydrogen water	oral intake H_2 water < 1.6 mg/L	low cost, safe, convenient
Hydrogen saline	Intravenous injection by saturated H_2 saline	accurate dosage
Hydrogen solution	eye drop, bath immersion	low cost, safe, convenient
Increased intestinal hydrogen amount	drug	low cost, convenient

Table 2: Three major producing hydrogen water methods.

Method	Magnesium Hydrolysis [20]	Ion-Water Electrolysis [21]	Pure-Water Electrolysis [22]
Theory	Magnesium hydrolysis	Electrolyzed water	Electrolyzed water
Purity	100%	70-98%	100%
Reaction rate	Low	Medium	Medium
Water	Tap water	Ion water	Pure water
Biproduct	Mg^{+2}, OH^{-},$Mg(OH)_2$	Cl_2, HClO, O_2, O_3	None
Safety	High	Explosion, toxicity may be possible	High
Cost	Low	Medium	High

The concentration of hydrogen molecules dissolving in tap water is only 8.65×10^{-7} mg/L at room temperature. A low level of hydrogen has no therapeutic effect in clinical applications. There is more than a million times more hydrogen in tap water than there is in saturation hydrogen atoms per one liter [20-22]. Water at room temperature contains the maximum amount of hydrogen dissolved until it reaches saturation. As hydrogen atoms become saturated, molecular hydrogen of H_2 gas is formed. At sea level, hydrogen escapes from the water surface when pressure approaches one atmosphere, which is 101.325 kilopascal. A saturation condition of hydrogen has been found to exert protective effects in biological systems [1-19]. In metabolism, hydrogen is the minimum mass gas molecule with relatively steadily reducible properties, a valuable chemical property. Because hydrogen can't directly interact with biological substances, we receive hydrogen by oral administration or injection with saturated hydrogen saline, which dissolves in water. Many trials have been performed using hydrogen inhalation medicine to treat ischemia-reperfusion injury at 1 or 2 % hydrogen concentration for 35 minutes since 2007. Research has since shown that hydrogen has therapeutic effects on a variety of diseases at a small level. Under 4 % hydrogen concentration and over 95 % hydrogen concentration, it is not flammable or explosive even in pure oxygen gas environments. In vivo hydrogen delivery methods are shown in Table 1. The following section discusses methods for producing hydrogen molecules, such as hydrolysis of metallic magnesium rods [20], electrolysis of ionic water with sodium chloride [21], and electrolysis of pure water with polymer membranes [22]. Below, we will explain and compare them in more detail.

Table 2 compares three primary methods of producing hydrogen water. Hydrogen's pureness, reaction rate, and capacity seem theoretical, but they are in fact relevant to real clinical scenarios. The water of various sources may be readily available on site or need to be transported in order to use the required amount of pure water or distilled water. Using magnesium hydrolysis, we attempt to improve conventional methods of producing hydrogen-water. In magnesium hydride hydrolysis, half of the hydrogen comes from the hydride ions and half from the water protons. When magnesium hydride is contacted with water, it produces hydrogen-water as a by-product. In practice, however, the reaction kinetics is extremely slow, and the insoluble passivation layer of magnesium hydroxide coats the outer surface to prevent water entry. At room temperature, magnesium hydride hydrolysis yields less than 1% after 30 minutes.

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3. Results and Discussion

As a catalyst in this study, citric acid activates reaction kinetics and acts as a chelating agent to inhibit magnesium hydroxide formation, which is the limiting step of magnesium hydride hydrolysis. As a result, these effects are beneficial. The method of magnesium hydrolysis initially increased the theoretical hydrogen amount by two times. This method produces hydrogen-water, which is alkaline water. Low reaction kinetics at room temperature and an insoluble layer of hydroxide on the surface prolong the reaction rate due to the low reaction kinetics. Citric acid, however, can be used as a chelating agent to activate it. Metal oxides can be dissoluble by citric acid, just like citric acid can dissolve metals. With the chemical formula $C_6H_8O_7$, citric acid is a weak organic acid. In biochemistry, critic acid is an intermediate in the tricarboxylic acid cycle, which occurs in all aerobic organisms. Higher living creatures obtain two-thirds of their energy from the citric acid cycle. As a catalyst, citric acid activates reaction kinetics and acts as a chelating agent to inhibit magnesium hydroxide formation over the entire course of the reaction, which is the limiting step in magnesium hydride hydrolysis. It is advantageous to have these effects.

Figure 1 shows a hydrogen-water production system that includes a reactor, reverse osmosis unit, valve, pump, control unit, digital display, water input, hydrogen-water output, therapeutic hydrogen-water, magnesium hydride block, and tap water input. In Figure 2, active hydrogen is produced by MgH2 hydrolysis. Hydrogen-water is converted by a weak current into active atomic hydrogen and hydrogen molecules on the platinum catalyst surface. There are also other methods of activating hydrogen-water by magnetic fields, collisions, and minerals to produce hydrogen-water containing active hydrogen.

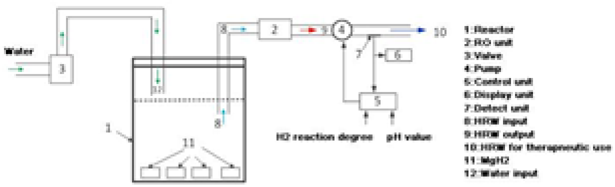

Figure 1: The method of magnesium hydride hydrolysis producing hydrogen-water.

Magnesium hydride (35x35x17 millimeter, Bio-Coke Ltd, Japan) manufactured by direct hydrogenation using a low-cost combustion synthesis [23,26]. Magnesium hydride is made from light gray crystals of magnesium iodide (99,9% purity by mass) under high pressures and temperatures of 200 bars and 500 ℃. A porous structure facilitates water molecules entering magnesium hydride to generate hydrogen.

The chemical reaction expressed below.

$$MgH_{2(s)} \rightarrow Mg^{+2}_{(aq)} + 2H^{-} \qquad (1)$$

Magnesium hydride hydrolysis follows a similar qualitative process. The water molecule reacts with magnesium hydride to release magnesium ions and negative hydrogen ions at the beginning of the response. As a result, negative hydrogen ions continuously split water molecules, releasing hydrogen gas and hydroxide ions. The pH value increases steeply as a result.

$$2H^{-} + 2H_2O_{(l)} \rightarrow H_{2(aq)} + 2OH^{-} \qquad (2)$$

As the reaction reached equilibrium at pH 11.0, magnesium hydroxide precipitated on the outer surface of magnesium hydride from the initially supersaturated solutions state. This value is in excellent agreement with what is observed in the literature for a saturated magnesium hydroxide solution [25-26].

$$Mg^{+2}_{(aq)} + 2OH^{-} \rightarrow Mg(OH)_{2(s)} \qquad (3)$$

The supersaturated solution state won't occur in the solution if the pH in the hydrolysis reaction is less than 11 with magnesium ions concentration less than 0.007 mol/L. A layer of insoluble magnesium hydroxide will not form on the surface to impede hydrolysis. Hydrogen-saturated magnesium hydride splits extremely slowly (0.0008 M). Magnesium hydride's hydrolysis behavior seems to be pH dependent. Additionally, a small amount of citric acid solution is repeatedly injected before supersaturation occurs. By chelating magnesium ions and hydroxide ions with citric acid, magnesium citrate is effectively generated.

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$$3MgH_{2(s)}+2C_3H_4(OH)(COOH)_{3(aq)}\rightarrow 6H_{2(aq)}+ Mg_3[C_3H_4(OH)(COO)_3]_{2(aq)} \quad (4)$$

The reaction percentage was calculated by

$$\text{Reaction degree in \%} = H_2/H_2 \text{ (theoretical value in Eq. (4))}. \quad (5)$$

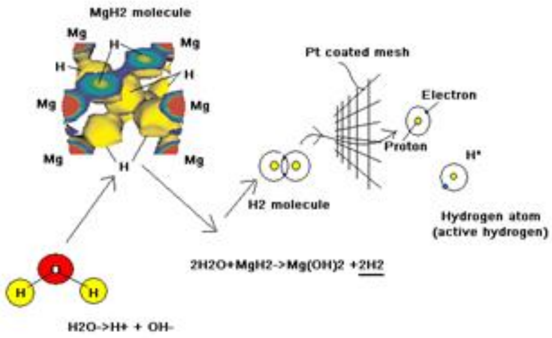

Figure 2: Magnesium hydride hydrolysis producing active hydrogen-water.

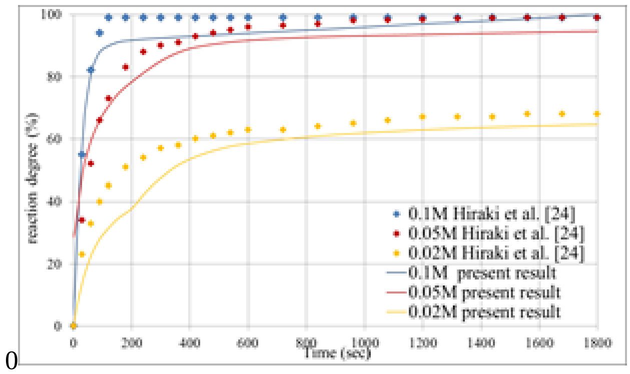

Figure 3: Reaction degree measured in the present result.

Our experiments with a stoichiometric amount of citric acid also confirmed the above behavior. A small amount of citric acid solution is injected multiple times using various steps in the system for applications. Citric acid and magnesium hydride must be mixed at a mole ratio of 2:3 in order to overcome the insoluble passivation layer. The mass of citric acid must be five times that of magnesium hydride. As shown in Figure 3, 0.02, 0.05, and 0.1 moles citric acid per one liter of pure water resulted in different degrees of magnesium hydride hydrolysis. Hiraki et al. [24] also compared these data to their literature. Molecular hydrogen could be used continuously for 30 minutes after dissolving, as shown in the Figure 4 and Figure 5.

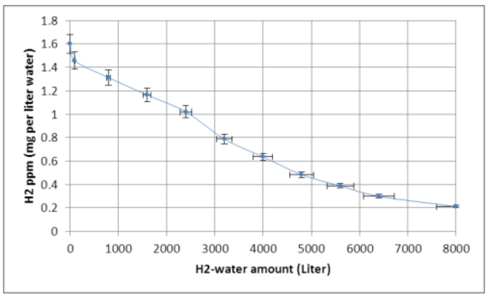

Figure 4: H2 ppm vs. H2-water amount (liters) measured in the present result.

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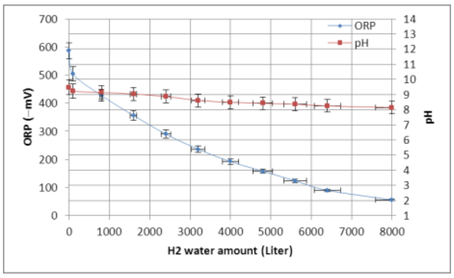

Figure 5: ORP (-mV) & pH vs. H2-water amount (liters) measured in the present result.

4. Conclusions

Due to its cheap price, non-toxic nature, and long shelf life, magnesium hydride hydrolysis offers twice the storage capacity of metallic magnesium of saturated hydrogen water. Magnesium hydride hydrolysis with water, however, is extremely slow and incomplete. After half an hour at room temperature, hydrogen yield is less than 1%. Adding citric acid solution increases the reaction kinetics and hydrogen yield significantly. Acids can adjust the pH of the solution in order to alter the kinetics and yield. By avoiding magnesium combustion in oxygen, this technology can serve as a superior replacement for magnesium hydrolysis. In comparison with other methods of generating hydrogen-water, it also results in a significant weight reduction. A small amount of molecular hydrogen, however, only partially explains oxidative stress by neutralizing reactive oxygen species. In recent years, more and more evidence has been accumulated that challenges its validity. A clinical trial is required in the future as well as evidence of the hydrogen molecular mechanism, medical effects, and biological effects.

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