

Process technology for production of hydrogen-rich water and water characterizing by highly negative oxidation reduction potential

Abstract

The construction of plasma reactors and the technological process of obtaining water rich in hydrogen and characterized by a negative oxidation potential are presented in the publication. Hydrogen-rich water was obtained based on non-plasma technology and water saturation with hydrogen gas in a reactor vessel or in glass bottles. We have developed a plasma flow reactor that allows for contactless microstructuring and modifying the properties of water / aqueous solutions by resonant stochastic vibration amplification of selected chemical compounds in water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge. This water is then saturated with hydrogen gas in the reactor or in glass bottles. The water obtained in the reactor is characterized by a high concentration of hydrogen (8 ppm) and a negative oxidation-reduction potential (ORP) value (−450 mV). In this technology, the process of saturating water with hydrogen in a 1 m³ tank at a temperature of 20°C takes about 30 minutes. In the technology of obtaining water with negative ORP potential in the bottles, the process of saturating the water with hydrogen lasts only 5-10 seconds. Water obtained with such technology in the glass bottles does not contain much hydrogen gas after 24 hours, while it is characterized by a negative ORP value of about −380 mV even for a period of three months. Obtaining water with presented parameters is possible only in the case of water subjected to the influence of broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge.

Keywords: hydrogen-rich water (HRW), stochastic liquid softener system for water, hydrogen concentration in water, oxidation reduction potential (ORP)

1. Introduction

Hydrogen water is water with dissolved hydrogen gas (H₂). Hydrogen water is made by dissolving gaseous molecular hydrogen into water under pressure or by the electrolysis process of water [1]. Interest in hydrogen-rich water (HRW) has grown rapidly in the last decade [2-6]. This interest is dictated, on the one hand, by the possibility of industrial production of simple alcohols in the reaction of hydrogen gas and CO₂ in water with the use of catalysts [7-11]. It is also worth mentioning the use of hydrogen water in the alternative medicine as a pro-health factor [12-14]. The concentration of hydrogen gas (H₂) in pure water is usually low, about 8.65×10^{-7} mg/L, and such water has limited industrial use and no therapeutic value, and therefore, methods are being sought to increase hydrogen concentration in water. Testing the concentration of hydrogen gas in water is analytically difficult. The hydrogen gas in water easily penetrates plastic vessel walls and thus it is released leaking into the atmosphere [15]. Better, although more expensive choice is glass or metal bottles. Hydrogen does not react with water. It does, however, dissolve to the extent of about 0.00160 g kg⁻¹ at 20°C (297 K) and 1 atmosphere pressure [16]. It is therefore advantageous to use

water with free spaces enveloped by one of the known treatment technologies, and therefore capable of dissolving more gases. Experimental data for the phase behavior of ($\text{H}_2\text{O} + \text{H}_2$) have been reported by several authors. Wiebe *et al.* [17,18] studied the solubility of H_2 in H_2O by means of a degassing technique whereby H_2 saturated H_2O samples were expanded to low pressure and the amount of gas evolved could have been measured in a gas burette. Kling [19] studied the ($\text{H}_2\text{O} + \text{H}_2$) system temperatures between 323.15 K and 423.15 K using a synthetic variable-volume bubble-point method at pressures between 3 MPa and 15 MPa. Additional data were reported by Gillespie [20] and Rahbari [21]. Sabo [22] calculated that the most probable water cluster formed around the hydrogen molecule within the first hydration shell contains 16 water molecules, and the coordination number of H_2 in liquid water is 16. H_2 - H_2O mixtures have revealed the formation of the hydrogen clathrate hydrates. A rhombohedral hydrate with a H_2O sublattice similar to ice II is stable between 0.75 and 3.1 GPa (295 K). Above 2.3 GPa, a novel hydrate forms with the H_2O molecules in a cubic diamond structure and with a very high H_2 : H_2O stoichiometry of 1:1. The H_2 molecules occupy voids in the H_2O framework, thus improving the packing efficiency and stabilizing this hydrate to very high pressures of at least 30 GPa [23]. At low temperature (T) and high pressure (P), gas molecules can be held in ice cages to form crystalline molecular compounds that may have application for energy storage. We synthesized a hydrogen clathrate hydrate, $\text{H}_2(\text{H}_2\text{O})_2$, that holds 50 g/L hydrogen by volume or 5.3 wt %. The clathrate, synthesized at 200-300 MPa and 240-249 K, can be preserved to ambient P at 77 K. The stored hydrogen is released when the clathrate is warmed to 140 K at ambient P [24]. The H_2 gas in water solution forms clusters. The water-water hydrogen bond is reinforced when its proton donor moiety acts as the hydrogen bond acceptor with respect to the H_2 molecule and when the acceptor moiety acts as a hydrogen bond donor. On the other hand, the water-water hydrogen bond is weakened when the donor water molecule behaves as a double donor, or the acceptor water molecule as a double acceptor [25]. Clathrate hydrates belong to a group of inclusion solid state compounds in which the hydrophobic guest molecule occupies the host polyhedra cages that are formed by hydrogen bonded water molecules. One can imagine clathrate hydrates as solid solutions of water trapping hydrophobic molecules. The local structure of water around the hydrogen solute is only weakly perturbed from its bulk structure and thermodynamically resembles bulk water. In order to be of practical utility for hydrogen storage, hydrogen clathrates need to satisfy two criteria: first, they need to be synthesized under more moderate thermodynamic conditions, ideally under ambient temperature and pressure; second, at the same time they should maximize hydrogen occupancy [26]. Many scientists, especially those elaborating therapeutic purposes, link the oxidation-reduction potential (ORP) with concentration H_2 in water [27,28]. The oxidation-reduction potential (ORP) is used to determine the oxidation-reduction potential of water but such an approach needs more detailed explanation. The value of ORP is usually expressed in positive or negative millivolts as a measure of water's tendency to act either as a reducing agent (electron donor) or oxidizing agent (electron acceptor). A positive ORP indicates the presence of potential oxidizers, while a negative ORP indicates the presence of potential reducers. In case of hydrogen-rich water, the negative values of ORP are an indication of the presence of a reducing agent in form of hydrogen gas (H_2). However, a value of ORP is not a real measure of concentration of hydrogen gas in the water but it only represents redox potential from two species of hydrogen in the water: hydrogen gas (H_2) and hydrogen ions (H^+). Therefore, the pH of the solution must play a key role in this type of measurement. The values of ORP measurement are sensitive to changes in the water's pH but also insensitive to changes in dissolved hydrogen gas, especially at high concentrations of gaseous hydrogen in the water [29,30,31,32]. H_2 is an inert molecule which can scavenge the highly active oxidants as hydroxyl radical ($\cdot\text{OH}$) and peroxyxynitrite (ONOO^-) [33].

In our previous paper [34,35] we presented an industrial method of obtaining water capable of dissolving different gasses such as CO₂ and O₂, but soon after and quite unexpectedly very good results have been recorded for hydrogen gas. Its solubility in water which passed the treatment with the use of radio noise enabled a high concentration of hydrogen to become a real admixture. In this paper we describe a stable formation of hydrogen-rich water presenting industrial methods for obtaining water rich in hydrogen gas with a high ORP potential.

2. EXPERIMENTAL

For industrial scale, the water was used from our own intake (Besko, Poland) using several processes to obtain HRW. Water analysis was performed in an accredited laboratory (Oikos, Swieta Katarzyna, Poland) in accordance with the applicable standards for water analysis.

ORP-200: Waterproof Professional Series ORP/Temp Meter and RP-969 ORP Test Pen Oxidation Reduction Potential Tester were used to test the oxidation-reduction potential of liquids, with resolution of 1 mV, and with a standard measuring range of 0 to ±1999 mV. Meters were calibrated to +92 mV.

TDS-3Water Quality Tester TDS Meter was used to measurements of the Total Dissolved Solids (TDS), which are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water. TDS principle is based on conductivity and is expressed in parts per million (ppm). TDS-3Water Quality Tester has been calibrated with a NaCl 342 ppm solution.

The pH measurement was performed using a pH meter CP-505 with an EPS-1 measuring electrode (Elmetron, Poland). The electrode was calibrated using two buffer solutions (pH = 4.00 and 10.00). Calibration of the pH meter was performed at the temperature at 25°C, while the measurement of pH of water in the technological process was performed at the temperature of the process.

2.1 Determination of hydrogen concentrations

Oxidimetry determination of the hydrogen concentration was performed by a redox titration [36]. The methylene blue-platinum colloid reagent H2Blue (Aquacentrum Munich) is effective in determining the concentration of hydrogen gas in an aqueous solution. H2Blue formula is a reagent which can be used to measure the concentration of dissolved H₂ gas in hydrogen-rich water. The H2Blue reagent was added dropwise to 20 mL samples of hydrogen-rich water until the solution changed from blue to colorless. 20 mL of hydrogen water reduces one drop of the methylene blue-platinum colloid reagent, the concentration of dissolved hydrogen (DH) is 14.5 µmol/L or 0.03 ppm or each drop represents 0.10 ppm of hydrogen gas dissolved under pressure into a water state using a 6 mL sample of water.

3. RESULTS AND DISCUSSION

The demand for hydrogen-rich water increases annually. This is mainly due to the search for industrial methods of obtaining organic compounds in water rich in hydrogen and carbon dioxide [37] and the increasing use of hydrogen-rich water as an antioxidant for industrial and medical purposes [38,39,40]. The methods of obtaining hydrogen-rich water can be divided

into two groups. The first consists in desolvation process of hydrogen gas in water at reduced temperature and often under elevated pressure, and the second is to use procedures in which the water is enriched with hydrogen using electrolysis process.

The method and device for the production of antioxidant drinking water enriched with active hydrogen are known from the Polish patent application No. PL.406260 [41]. The method consists in the fact that the water taken from the source, ground by a water nozzle, is subjected to demineralization in order to achieve a uniform structure and chemical composition, and then cooled to a temperature of 2-3°C and poured into a saturation buffer tank. Hydrogen is fed to the tank through a valve, and then, through a mixing device and a dosing pump, water with hydrogen is transported to the expansion tank. A method for producing hydrogen-rich water is described in US Patent No. US10953041 [42]. The method of producing hydrogen-containing water includes the steps of: pumping water into at least one process vessel; degassing of liquids with a vacuum pump; mixing the liquid; lowering the temperature of the liquid; pumping chilled, agitated, degassed carrier liquid into a hydrogen reactor containing hydrogen gas. The concentration of hydrogen gas in the water in the hydrogen reactor vessel ranges from 3 ppm to 10 ppm.

The device for producing hydrogen-rich water with an ejector is also known from Chinese utility model No. CN209348450 [43]; it comprises a series of interconnected water tanks in which the hydrogen is dissolved in water by a series of ejectors. The method of producing hydrogen-rich water by physical method and the device for its production are known from the Chinese patent applications No. CN110482667 [44] and CN107021556 [45]. The method is carried out in a closed environment. High purity hydrogen under high pressure is fed into the water either directly or through molecular sieves.

Another method of obtaining hydrogen-rich water is method based on electrolysis [46], in which a high concentration of hydrogen in water is obtained by changing the cross-linking structure of water and creating stable hydrogen hydrates. In HRW-such water, in which the structural network of hydrogen bonds loosens, water molecules acquire additional degrees of freedom. The essence of water activation is the destruction of cluster structures to saturate water with monomolecules. The cluster of activated water contains 5-6 molecules (ordinary water: 13-16 molecules). Such water is considered more active in terms of biophysical and biological indicators. Water, activated in any way, has a high fluidity (low surface tension) and a dissolving power. The content of dissolved hydrogen in water can be from 1.6 to 10 mg/L and depends on the pressure. The ORP of water in this case is from -600 to -50 mV, but the total mineralization of water and pH do not change. The solution does not lose substantially its properties for 30 days, which allows it to be transported and stored. When the solution is sealed in glass containers, the storage life is up to one year [47,48].

In this publication, based on previous experience, we present a new technology for obtaining water rich in hydrogen. We have developed a plasma flow reactor that allows for contactless microstructuring and modifying the properties of water / aqueous solutions by resonant stochastic vibration amplification of selected chemical compounds in water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge [49]. Plasma treated water shows different gas absorption properties than pre-process water samples [34,35,36].

We present two installations for water saturation with hydrogen gas (Figs. 1 and 2). Both installations consist of three modules. The first module (UW) for obtaining water from the natural water reservoir is equipped with a set of pumps enabling water transport to the second module (MS). The tank (ZM) of the second module with a capacity of 2 m³ connected by pipes to the plasma flow devices (RS) makes it possible to obtain, after 30 minutes, 2 m³ of water with changed physicochemical parameters as a result of plasma treatment. The third module of the system is presented in two technical solutions; the first solution is intended for

obtaining water saturated with hydrogen at a temperature of 20°C in a 1 m³ tank equipped with a diffuser through which hydrogen gas is introduced under the pressure of 6 hPa. The process of water saturation with hydrogen is carried out for 30 minutes. After this time, the water from the reservoir is used technologically. The second presented technological solution is intended for the preparation of water with a stable, negative potential of ORP of water rich in hydrogen in 250 ml glass bottles (PD) (Fig. 3). At each station, water is automatically poured into the bottles after plasma treatment, and a small diffuser is introduced through which hydrogen gas is dosed for only 5-10 sec. The system enables a simultaneous process on 10 workstations.

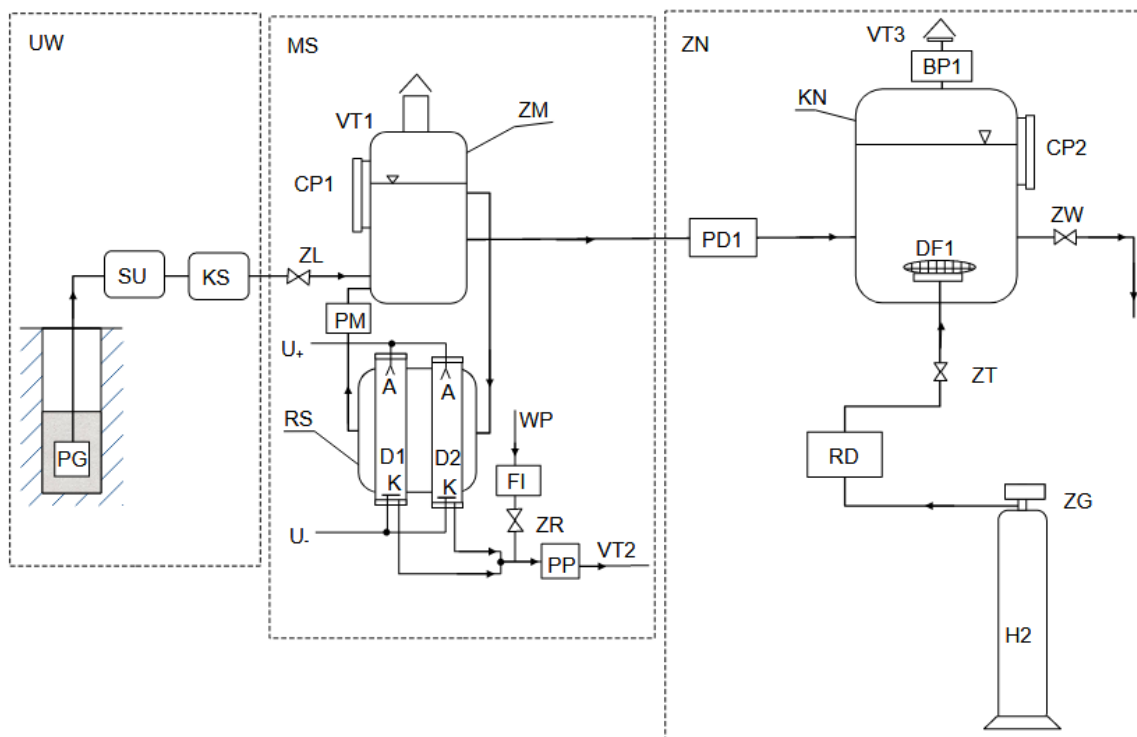


Fig.1. The scheme of the installation for the production of HRW in the plasma reactor

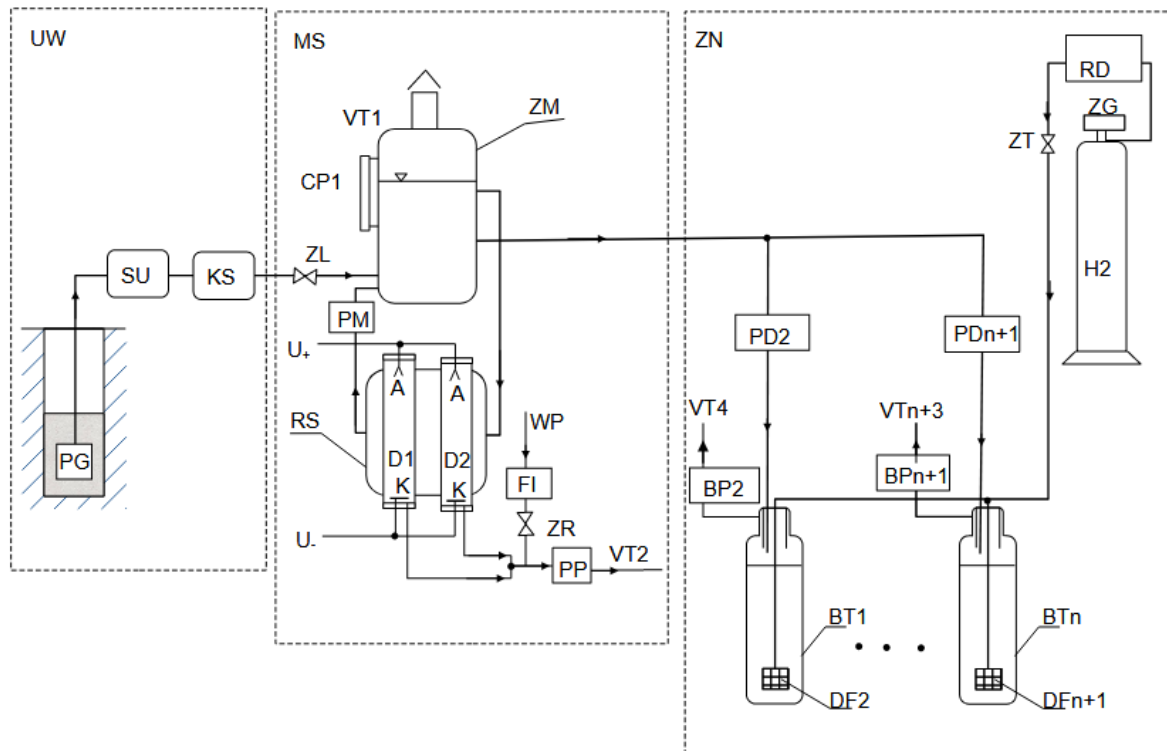


Fig.2 The scheme of the installation for the production of HRW in glass bottles

List of symbols in the drawing:

A - cavity anode

BP₁ - first back pressure regulator

BP₂ - second back pressure regulator

BT - bottle

CP1 - first water level sensor

CP2 - second water level sensor

DF – diffuser

DS₁,..., DS_n - glass noise diode

FI - air filter

H₂ - hydrogen cylinder

K - flat cold cathode

KN - hydrogen saturation chamber

KS - mineral composition corrector

MS - noise-operated microcluster

PD - dosing pump

PG - submersible pump

PM - microcluster water pump
PP - vacuum pump
RD - regulator - pressure reducer
RS – plasma reactor
SU - water treatment plant
UW - water source
VT1 - VT_n - ventillation exhaust
WP - humid ambient air inlet
ZM - microcluster tank
ZN - hydrogen infiltration unit
ZG - main gas valve
ZL – linear water flow valve
ZR - vacuum regulating valve
ZW - hydrogenated water outlet valve
ZT - three-way hydrogen valve



Fig.3. Fragment of the installation - a bottling line for filling bottles

Characteristics of the system in terms of hydrogen-rich water quality

The method of obtaining HRW is based on water taken from Besko, our own intake, which is then subjected to a unique process changing the properties of the water in a flow plasma reactor with DS1 - DS_n plasma-filled noise diodes, which have A cavity anodes and cold K cathodes supplied with pulsating DC voltage. Inside the glass bodies of the DS1 - DS_n noise diodes, a vacuum is maintained which is necessary to generate glow discharge plasma in air of natural or increased humidity. As a result of such a process, the physicochemical parameters of the water and the mineral composition in relation to the initial water do not change significantly, while the size of the dominant water clusters does change. This reduction in the size of the dominant water clusters enables a better placement of inert gases, e.g. hydrogen, in the spaces between the water structures and the formation of low-volume hydrogen hydrates. The water from the ZM tank is fed with hydrogen gas saturation in the ZN module. The physicochemical parameters of water, the mineral composition of hydrogen-rich water after saturation with hydrogen are retained; the dissolved oxygen concentration undergoes a significant change and oxidation-reduction potential (ORP). HRW is characterized by the content of hydrogen gas at the level of 10 ppm, approx. -400 eV ORP at pH = 7.22. The advantages of this technology in relation to those used so far include the possibility of obtaining the level of water saturation with hydrogen to the level of approx. 10 ppm without the need for additional water cooling and degassing before soaking. With the temperature of the water taken from the deep source of 13-15°C, the duration of the soaking process does not exceed 60 seconds. The physicochemical parameters of water during the process are presented in Table 1.

Table 1. The values of physicochemical parameters of water prior (in) and after processing

No.		Reference document	Unit	Water taken from the source	Water at the output of the module MS	HRW	
						Method 1 In the tank	Method 2 In glass bottles
1.	pH	PN-EN ISO 10523:2012	[pH]	7.1 ± 0.2	7.2 ± 0.2	7.8 ± 0.4	7.9 ± 0.4
2.	Determination of specific electrical conductivity	PN-EN-27888:1999	[μS/cm]	830 ± 91	679 ± 75	754 ± 89	764 ± 90
3.	Determination of permanganate index	PN-EN ISO 8467:2001	[mg O ₂ /dm ³]	<0.5	1.6 ± 0.1	<0.5	<0.5
4.	Determination of the magnesium – EDTA titrimetric method	PN-C-04554-4:1999	[mg Mg/dm ³]	7 ± 1	7 ± 1	6 ± 1	6 ± 1
5.	Determination of calcium content — EDTA titrimetric method	PN-ISO 6058:1999	[mg Ca/dm ³]	<5.0	<5.0	<5.0	<5.0
6.	Determination of Iron	PN-EN ISO 17294-	[mg Fe/dm ³]	0.045 ± 0.012	0.100 ± 0.012	0.100 ± 0.012	0.100 ± 0.012

		2:2016-11					
7.	Determination of Manganese	PN-EN ISO 17294-2:2016-11	[mg Mn/dm ³]	0.007±0.001	0.0032±0.0004	<0.003	<0.003
8.	Determination of dissolved oxygen - Electrochemical probe method	PN-ISO 5814:2013-04	[mg O ₂ /dm ³]	8.8±0.7	8.6±0.7	<0.1	<0.1
9.	Determination of ammonium	PN-ISO 7150-1:2002	[mg NH ₄ /dm ³]	<0.129	<0.129	<0.129	<0.129
10.	Determination of dissolved anions - nitrates	PN-EN ISO 10304-1:2009, Ac2012	[mgNO ₃ /dm ³]	7.46 ± 0.97	8.62 ± 1.12	7.11 ± 0.85	7.09± 0.67
11.	Determination of dissolved anions - chloride	PN-EN ISO 10304-1:2009, Ac2012	[mg Cl/dm ³]	33 ± 3	31 ± 3	32 ± 3	32 ± 3
12.	Determination of dissolved anions - sulfates	PN-EN ISO 10304-1:2009, Ac:2012	[mg SO ₄ /dm ³]	32 ± 5	43 ± 7	42 ± 5	43 ± 7
13.	Determination of dissolved anions- Fluoride	PN-EN ISO 10304-1:2009, Ac:2012	[mg F/dm ³]	0.251 ± 0.045	0.228 ± 0.041	0.231 ± 0.044	0.232 ± 0.042
14.	Total Dissolved Solids (TDS) [ppm]			204±5	195±5	208±5	198±5
15.	Determination of hydrogen concentrations, H ₂ Blue method		ppm			12±1	10±1
16.	Oxidation Reduction Potential (ORP) [mV]			135±3	158±4	-480±8	-502±8
17.	Temperature			13°C	15°C	20°C	20°C

Characteristics and durability of the final HRW water product with negative values of ORP

In this paper, we also undertook research on the durability of the water ORP potential and concentration of hydrogen. The values of physicochemical parameters of water in time characterized product durability shown in Table 2.

Table 2. The values of physicochemical parameters of water in time, characterized product durability

	Reference document	Unit	Water at the output of the module	Water from module MS after	HRW after 7 days in tank	Water after 7 days in glass

			MS	7 days in glass bottles	reactor	bottles
pH	PN-EN ISO 10523:2012	[pH]	7.2 ± 0.2	7.9 ± 0.4	8.1 ± 0.4	8.1 ± 0.4
Determination of specific electrical conductivity	PN-EN-27888:1999	[μS/cm]	679± 75	717 ± 78	720 ± 70	714 ± 78
Determination of permanganate index	PN-EN ISO 8467:2001	[mg O ₂ /dm ³]	1.6± 0.1	<0.5	<0.5	<0.5
Determination of the magnesium – EDTA titrimetric method	PN-C-04554-4:1999	[mg Mg/dm ³]	<5.0	<0.5	<0.5	<0.5
Determination of calcium content — EDTA titrimetric method	PN-ISO 6058:1999	[mg Ca/dm ³]	<5.0	<5.0	<5.0	<5.0
Determination of dissolved oxygen - Electrochemical probe method	PN-ISO 5814:2013-04	[mg O ₂ /dm ³]	8.6± 0.7	5.2± 0.7	<0.5	<0.5
Determination of ammonium	PN-ISO 7150-1:2002	[mg NH ₄ /dm ³]	<0.129	0.46±0.05	<0.1	<0.1
Determination of dissolved anions - nitrates	PN-EN ISO 10304-1:2009, Ac2012	[mgNO ₃ /dm ³]	8.62 ± 1.12	2.4± 0.4	2.1± 0.4	2.1± 0.4
Determination of dissolved anions - chloride	PN-EN ISO 10304-1:2009, Ac2012	[mg Cl/dm ³]	31 ± 3	32 ± 3	35 ±3	36 ±3
Determination of dissolved anions - sulfates	PN-EN ISO 10304-1:2009, Ac:2012	[mg SO ₄ /dm ³]	43 ± 7	55 ± 5	54 ± 5	54 ± 5
Determination of dissolved anions-Fluoride	PN-EN ISO 10304-1:2009, Ac:2012	[mg F/dm ³]	0.22 ± 0.04	0.26 ± 0.05	0.25 ± 0.05	0.26 ± 0.05
Determination of Iron	PN-EN ISO 17294-2:2016-11	[mg Fe/dm ³]	0.100± 0.012	<0.10	<0.10	<0.10
Determination of Manganese	PN-EN ISO 17294-2:2016-11	[mg Mn/dm ³]	0.0032± 0.0004	<0.003	<0.003	<0.003
Determination of hydrogen concentrations, H ₂ Blue method		ppm	0	0	8	0
Oxidation Reduction Potential (ORP) [mV]			158±4	123±4	-450±8	-379±8

Temperature			15°C	25°C	25°C	25°C
-------------	--	--	------	------	------	------

Detailed studies of changes in the ORP value (Fig. 4) and the concentration of hydrogen (Fig. 5) in water in tank reactor and in glass bottles over time were carried out, focusing on changes occurring up to 60 minutes and up to 7 days, also analyzing the OPR value of water after 90 days.

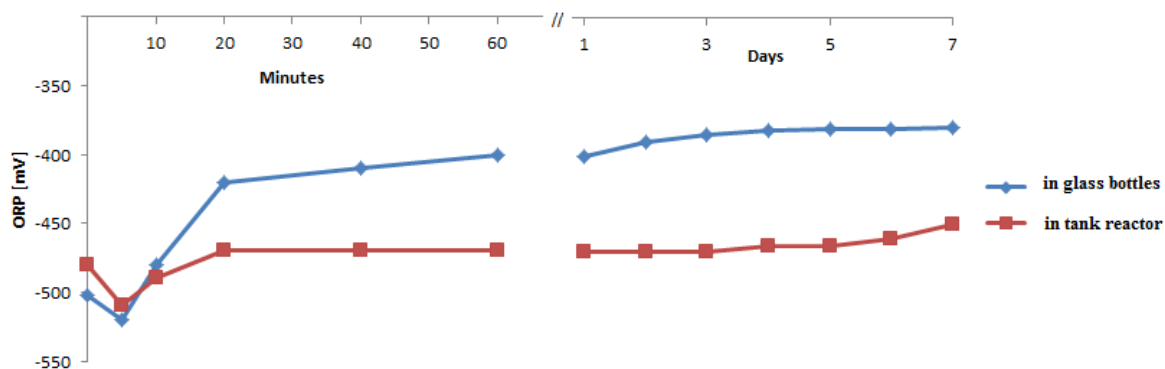


Fig. 4. The values of ORP of water at pH=8.1 in tank reactor and in glass bottles obtained after saturated of hydrogen gas

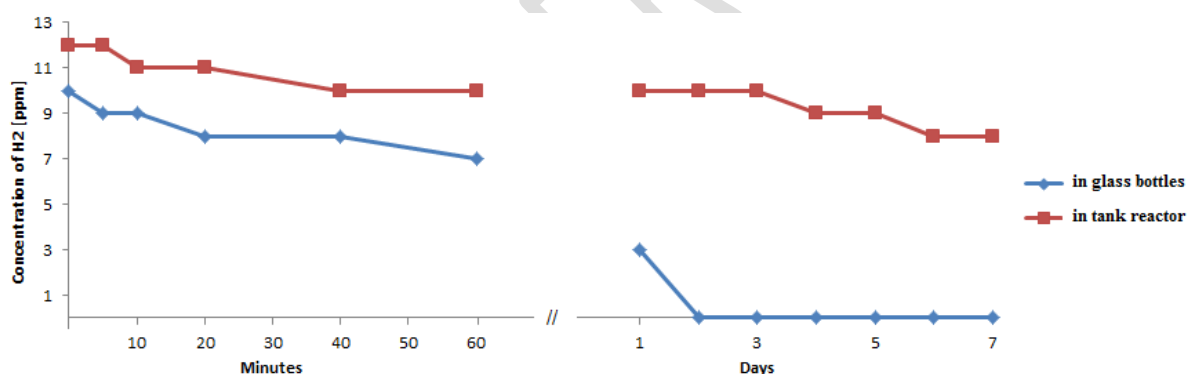


Fig. 5. The concentration of hydrogen gas in water at pH=8.1 in tank reactor and glass bottles obtained after saturated of hydrogen gas

The molecular hydrogen (H_2) is a neutral molecule which, when dissolved in water, has no influence on the water's pH. Negative ORP values of water -380 ± 20 in closed glass bottles are maintained for 90 days, while the concentration of hydrogen in water is not measurable after 24 hours. On the other hand, in PET bottles of water, after two days, the ORP values of water take positive values, while the concentration of hydrogen dissolved in water is immeasurable after 6 hours.

The influence of water temperature on the ORP value was investigated. For this purpose, water from the reactor at a temperature of $20^\circ C$ containing 8ppm of hydrogen and characterized by an ORP value of $-450mV$ was poured into an open bottle and heated to a temperature of $90-95^\circ C$. After 20 min, the water was cooled to $25^\circ C$ and the water was found

to be free of dissolved hydrogen (H₂Blue method) and the ORP value decreased by 6-10mV from the initial value. The pH value of the water did not change. The measurements were repeated three times. The presence of gaseous hydrogen dissolved in water has a slight effect on the ORP value of the water. The big influence on the ORP of water has of pH and the content of chemical compounds in the water [50].

4. CONCLUSION

Hydrogen-rich water was obtained based on plasma technology and water saturation with hydrogen gas in a reactor vessel or in the glass bottles. A plasma flow reactor that allows for contactless microstructuring and modifying the properties of water/aqueous solutions by resonant stochastic vibration amplification of selected chemical compounds in water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge was used as a first step to produce water with hydrogen gas. This water is then saturated with hydrogen gas in the reactor or in the glass bottles. The water obtained in the reactor is characterized by a high concentration of hydrogen (8 ppm) and a negative oxidation-reduction potential (ORP) value (-450 mV). In this technology, the process of saturating water with hydrogen in a 1 m³ tank takes about 30 minutes at a temperature of 20°C. In the technology of obtaining water with negative ORP potential in the bottles, the process of saturating the water with hydrogen lasts only 5-10 seconds. Water obtained with this technology in bottles does not contain hydrogen gas after 24 hours, while it is characterized by a negative ORP value of about -380 mV even for a period of 3 months. The concentration of ions present in the water during the hydrogenation process practically does not change. Hydrogen gas in water of temperature of about 20°C is not a reagent for dissolved ions enabling the oxidation-reduction reaction to take place. Obtaining water with the presented parameters is possible only in the case of water subjected to the influence of broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge.

REFERENCE

1. Kim JJ, Yu AR, Park, G.S., Park SK, Jang HD, Yang HJ, Lee MY. Development of hybrid-reduced water and its antioxidative effects. *Toxicol Environ Health Sci.* 2011;3:227–231. DOI:10.1007/s13530-011-0104-3
2. Sim M, Kim CS, Shon WJ, Lee YK, Choi EY, Shin DM. Hydrogen-rich water reduces inflammatory responses and prevents apoptosis of peripheral blood cells in healthy adults: a randomized, double-blind, controlled trial. *Sci Rep.* 2020;10:12130. DOI: 10.1038/s41598-020-68930-2
3. Ostojic SM. Hydrogen-rich water as a modulator of gut microbiota? *J Functional Foods.* 2021;78:104360. <https://doi.org/10.1016/j.jff.2021.104360>

4. An R, Luo S, Zhou H, Zhang Y, Zhang L, Hu H, Li P. Effects of hydrogen-rich water combined with vacuum precooling on the senescence and antioxidant capacity of pakchoi (*Brassica rapa* subsp. *Chinensis*), *Scientia Horticulturae*. 2021;89;110469. DOI:10.1016/j.scienta.2021.110469
5. Vazquez D, Guillen-Gosalbez G. Process design within planetary boundaries: Application to CO₂ based methanol production. *Engineering Science* 2021;246;116891. DOI: 10.1016/j.ces.2021.116891
6. Khunathorncharoenwong N, Charoensuppanimit P, Assabumrungrat S, Kim-Lohsoontorn P. Techno-economic analysis of alternative processes for alcohol-assisted methanol synthesis from carbon dioxide and hydrogen. *Ind Eng Chem Res*. 2021;46;24591-24606. DOI: 10.1016/j.ijhydene.2020.01.230
7. Lu C, Zhang Z, Zhou X, Hu J, Ge X, Xia C, et al. Effect of substrate concentration on hydrogen production by photo-fermentation in the pilot-scale baffled bioreactor. *Bioresource Technology* 2018;247;1173–1176. DOI: 10.1016/j.biortech.2017.07.122
8. Liu Y, Zhang Y, Wang T, Tsubaki N. Efficient Conversion of Carbon Dioxide to Methanol Using Copper Catalyst by a New Low-temperature Hydrogenation Process. *Chem Lett*. 2007; 36;1182–1183. DOI: 10.1246/cl.2007.1182
9. Jadhav SG, Vaidya PD, Bhanage BM, Joshi JB. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. *Chem Eng Res Des*. 2014;92;2557–2567. DOI: 10.1016/j.cherd.2014.03.005
10. Boretti A. Renewable hydrogen to recycle CO₂ to methanol, *Int. J. Hydrogen Energy*. 2013;38;1806 -1812. DOI: 10.1016/j.ijhydene.2012.11.097
11. Mao WL, Mao HK. Hydrogen storage in molecular compounds., *PNAS* 2004;101;708–710. DOI: 10.1073/pnas.0307449100
12. Timon R, Olcina G, Gonzalez-Custodio A, Camacho-Cardenosa M, Camacho-Cardenosa A, Guardado IM. Effects of 7-day intake of hydrogen-rich water on physical performance of trained and untrained subjects. *Biol Sport*. 2021;38;269–275. DOI: 10.5114/biol sport.2020.9862
13. Lapin AA, Kalayda AA, Filippov SD, Zelenkov VN. Biochemical effects of molecular hydrogen in aqueous systems *International Scientific and Practical Conference: Water Power Energy Forum 2018 IOP Conf. Series: Earth and Environmental Science* 288 (2019) 012054 IOP.
14. Shen M, Zhang H, Yu C, Wang F, Sun X. A review of experimental studies of hydrogen as a new therapeutic agent in emergency and critical care medicine, *Med Gas Res*. 2014;4;17. DOI: 10.1186/2045-9912-4-17
15. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-based hardness, temperatures and the container materials, and effects of the oral washing and drinking, *Med Gas Res* 10, 2020, 67-74. DOI: 10.4103/2045-9912.285559

16. Engineering ToolBox, Solubility of Gases in Water vs. Temperature, https://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html
17. Wiebe R, Gaddy VL. The Solubility of Hydrogen in Water at 0, 50, 75 and 100° from 25 to 1000 Atmospheres. *J Am Chem Soc.* 1934;56:76–79, <https://doi.org/10.1021/ja01316a022>
18. Wiebe R, Gaddy VL, Heins JC. Solubility of Hydrogen in Sodium Chloride Brine at High Pressures. *Ind Eng Chem.* 24 (1932) 823-825. DOI:10.1016/j.fluid.2021.113025
19. Kling G, Maurer G. The solubility of hydrogen in water and in 2-aminoethanol at temperatures between 323 K and 423 K and pressures up to 16 MPa. *J Chem Thermodyn.* 23 (1991) 531-541. DOI:10.1016/S0021-9614(05)80095-3
20. Gillespie PRC, Wilson GM. Vapor-Liquid Equilibrium Data on Water-Substitute Gas Components: N₂ - H₂O, H₂ - H₂O, CO - H₂O, H₂ - CO - H₂O, and H₂S - H₂O. GPA Research Report, 1980, pp. 1-34.
21. Rahbari A, Brenkman J, Hens R, Ramdin M, van den Broeke LJP, Schoon R, et al. Solubility of Water in Hydrogen at High Pressures: A Molecular Simulation Study. *J Chem Eng Data.* 2019;64:4103–4115. DOI: 10.1021/acs.jced.9b00513.
22. Sabo D, Rempe SB, Greathouse JA, Martin MG. Molecular studies of the structural properties of hydrogen gas in bulk water, Molecular studies of the structural properties of hydrogen gas in bulk water. *Molecular Simulation.* 2006;32:269–278. DOI: 10.1080/08927020600728621
23. Vos WL, Finger LW, Hemley RJ, Mao HK. Novel H₂-H₂O Clathrates at High Pressures. *Phys Rev Lett.* 1993;71:3150- 3153. DOI:10.1103/PhysRevLett.71.3150.
24. Mao WL, Mao HK, Hydrogen storage in molecular compounds. *PNAS.* 2004;101:708–710. doi10.1073pnas.0307449100
25. Sadlej J, Cybulski SM, Szczeniński MM. Ab Initio Study of Nonadditive Effects in the (H₂O)₂··H₂ Cluster, *Phys. Chem.* 1996;100:10875–10881. <https://doi.org/10.1021/jp952781+>
26. Sabo D, Varma S, Martin MG, Rempe SB. Studies of the thermodynamic properties of hydrogen gas in bulk water. *J Phys Chem B* 2008;112:867-876. DOI: 10.1021/jp075459v
27. Campbell DH, Wilson JT, McInnes DM. Determining dissolved hydrogen, methane, and vinyl chloride concentrations in aqueous solution on a nanomolar scale with the bubble strip method. Proceedings of the 1998 Conference on Hazardous Waste Research, <https://engg.ksu.edu/HSRC/98Proceed/15Kampbell/15kampbell.pdf>
28. Goncharuk VV, Bagrii VA, Melnik LA, Chebotareva RD, Bashtan SY. The Use of Redox Potential in Water Treatment Processes. *J Water Chem Technol.* 2010;32:1–9. DOI:10.3103/S1063455X10010017
29. Oxidation Reduction Potential (ORP) International Hydrogen Standards Association. <https://www.intlhasa.org/oxidation-reduction-potential-orp/>

30. Sharpe R. Analysis of the Relationship between Dissolved Molecular Hydrogen Gas, pH and ORP using the Nernst Equation. <https://nebula.wsimg.com/e00f13c6a421e24d28be6558ff968736?AccessKeyId=781CCB9A394A3C0D544A&disposition=0&alloworigin=1>
31. Miyahara T, Oizumi M, Nakatani T, Sato T. Effect of voltage polarity on oxidation-reduction potential by plasma in water. *AIP Advances* 2014;4;047115. <https://doi.org/10.1063/1.4871475>
32. Chang CN, Ma YS, Lo CW. Application of oxidation–reduction potential as a controlling parameter in waste activated sludge hydrolysis. *Chemical Engineering Journal* 2002;90;273–281. DOI:10.1016/S1385-8947(02)00015-3
33. Ohsawa I, Ishikawa M, Takahashi K, Watanabe M, Nishimaki K, Yamagata K, et al. Hydrogen acts as a therapeutic antioxidant by selectively reducing cytotoxic oxygen radicals. *Nat Med.* 2007;13;688–694. DOI: 10.1038/nm1577
34. Yelkin I, Reszke E, Schroeder G. Glow Discharge Plasma as a Cause of Changes in Aqueous Solutions: The Mass Spectrometry Study of Solvation Processes of Ions. *Asian J Chem.* 2021;33;220-230. DOI:10.14233/ajchem.2021.2301
35. Yelkin I, Reszke E, Binkiewicz G, Schroeder G. The Industrial Production of Water Dedicated to Absorption of Gases, *Journal of Water Resource and Protection.* 2021;13;632-653. DOI: 10.4236/jwarp.2021.138034
36. Seo T, Kurokawa R, Sato B, A convenient method for determining the concentration of hydrogen in water: use of methylene blue with colloidal platinum. *Medical Gas Research* 2012;2;1. <http://www.medicalgasresearch.com/content/2/1/1>
37. Hadjadj R, Csizmadia IG, Mizsey P, Jensen SK, Viskolcz B, Fiser B. Water enhanced mechanism for CO₂ – Methanol conversion. *Chem Phys Letters,* 2020;746;137298. DOI:10.1016/j.cplett.2020.137298
38. Davoodabadi A, . Mahmoudi A, . Ghasemi H. The potential of hydrogen hydrate as a future hydrogen storage medium. *Science.* 2021;24;101907. DOI:10.1016/j.isci.2020.101907
39. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-based hardness, temperatures and the container materials, and effects of the oral washing and drinking. *Med Gas Res.* 2020;10;67-74. DOI:10.4103/2045-9912.285559.
40. Russell G, Nenov A, Kisher H, Hancock JT. Molecular Hydrogen as Medicine: An Assessment of Administration Methods. *Hydrogen.* 2021;2;444–460. <https://doi.org/10.3390/hydrogen2040025>
41. Patent PL 405260. Method and device for antioxidant production drinking water enriched with active hydrogen
42. Patent US10953041. Hydrogen-containing composition

43. Patent CN209348450. A device for producing hydrogen-rich water with an ejector
44. Patent CN110482667. A method of producing hydrogen-rich water by physical method and a device for it production
45. Patent CN107021556. Apparatus and method of automatic production of high concentration water rich in hydrogen.
46. Kim JJ, Yu AR, Park GS, Park SK, Jang HD, Yang HJ, Lee MY. Development of hybrid-reduced water and its antioxidative effects. *Toxicol Environ Health Sci.* 2011;3;327–231. DOI;10.1007/s13530-011-0104-3
47. Lapin AA, Kalayda AA, Filippov SD, Zelenkov VN. 2019 IOP Conf. Ser.: Earth Environ Sci. 288 012054
48. Patent RF2557974. A61P43, A61K33 Hydrogen cocktail - a means to stimulate lymphatic drainage, the way it is produced.
49. Patent PL 238174. Method and device for microstructuring of liquids, including body fluids
50. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-based hardness, temperatures and the container materials, and effects of the oral washing and drinking. *Med Gas Res.* 2020;10;67-74. DOI;10.4103/2045-9912.285559