Measurement of Electron Temperature and Number Density and Their Effects on Reactive Species Formation in a DC Underwater Capillary Discharge

Muhammad Waqar Ahmed\textsuperscript{a}, Md. Shabirur Rahman, Sooseok Choi\textsuperscript{a}, Ulugbek Shaislamov\textsuperscript{b}, Jong-Keun Yang\textsuperscript{a}, Rai Suresh\textsuperscript{a}, and Heon-Ju Lee\textsuperscript{a,b,*}

\textsuperscript{a}Department of Nuclear, Energy and Chemical Engineering, Jeju National University, Jeju 63243, Republic of Korea
\textsuperscript{b}Institute for Nuclear Science & Technology, Jeju National University, Jeju 63243, Republic of Korea

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Abstract The scope of this work is to determine and compare the effect of electron temperature ($T_e$) and number density ($N_e$) on the yield rate and concentration of reactive chemical species ($\cdot OH$, $H_2O_2$ and $O_3$) in an argon, air and oxygen injected negative DC (0-4 kV) capillary discharge with water flow (0.1 L/min). The discharge was created between tungsten pin-to-pin electrodes ($\Phi = 0.5$ mm) separated by a variable distance (1-2 mm) in a quartz capillary tube (2 mm inner diameter, 4 mm outer diameter), with various gas injection rates (100-800 sccm). Optical emission spectroscopy (OES) of the hydrogen Balmer lines was carried out to investigate the line shapes and intensities as functions of the discharge parameters such as the type of gas, gas injection rate and inter electrode gap distances. The intensity ratio method was used to calculate $T_e$ and Stark broadening of Balmer $\beta$ lines was adopted to determine $N_e$. The effects of $T_e$ and $N_e$ on the reactive chemical species formation were evaluated and presented. The enhancement in yield rate of reactive chemical species was revealed at the higher electron temperature, higher gas injection rates, higher discharge power and larger inter-electrode gap. The discharge with oxygen injection was the most effective one for increasing the reactive chemical species concentration. The formation of reactive chemical species was shown more directly related to $T_e$ than $N_e$ in a flowing water gas injected negative DC capillary discharge.

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Keywords: Underwater capillary discharge, Emission spectroscopy, Line ratio method, Stark broadening, Electron temperature, Electron number density, Reactive chemical species

I. Introduction

Liquid plasma plays an important role in a wide variety of industrial and environmental applications, including the sterilization of drinking water to make it free from dangerous bacteria, removal of odor from drinking water, ballast water treatment in a ship, cooling water treatment to reduce calcium carbonate precipitation and hardness, chemical applications by generating direct discharge in liquid chemicals, biological applications, medical applications and in the polymer industry [1-4]. Therefore, different kinds of applications of underwater discharge rely on the measurement of basic plasma parameters such as electron temperature ($T_e$), electron number density ($N_e$) and the yield rate of highly reactive species [5]. Due to the high dielectric constant of water, the electrical power consumption for generating the plasma in water is the most challenging issue. In the last few decades many techniques, including pulse-power technology, high frequency alternating current, and wave heating were adopted and tested to check for required input power reduction [6-8]. The information on $T_e$ and $N_e$ is often used as the first step in solving power consumption problems and suggesting an effective way of generating plasma in water. Some techniques, like the Thomson scattering and the probe method, can be used for finding $T_e$ and $N_e$, but these have some disadvantages. Thomson scattering is expensive and needs a complicated system, though it has accurate, precise spatial and temporal resolution [9]. In a Langmuir probe method, the plasma stability is altered by the probe and the results may not be so accurate and the interpretation is not easy for collision dominated discharge. When the distance of the probe tip from the plasma region changes, the calculated values alter accordingly [10]. In addition, due to the small gap and short discharge period, the measurement of such plasma characteristics by a probe method is extremely difficult and inaccurate. Generally, statistical techniques (Stark broadening, intensity ratio method) on hydrogen emission lines can be effective in determining the physical characteristics of...
plasma conveniently.

Optical emission spectroscopy (OES) is an effective technique for the determination of physical characteristics of plasma. By comparing emission intensities of hydrogen Balmer spectral lines ($H\beta = 486.127$ nm and $H\alpha = 656.285$ nm) and considering plasma approximation in local thermodynamic equilibrium (LTE) the electron temperature can be estimated [11]. The spectroscopic technique based on the relative intensities of emission lines can be used to measure $T_e$ in the plasma because the plasma temperature is directly related to the populations of each atomic energy level [12]. The Stark broadening method can be applied to determine $N_e$ using various relations available in the literature [13]. A relation from the Gig-Card theory was applied to $H\beta$ lines to determine $N_e$ [14].

Measured physical properties are correlated with the concentration of the reactive chemical species such as, OH radical, $H_2O_2$ and $O_3$ which are important for the application of under water discharge.

II. Materials and Methods

Fig. 1(a) shows a schematic diagram of the experiment set-up in this study. A visual view of the discharge is shown in Fig. 1(b). A liquid flow meter/controller (Dwyer-RM Series) was used to fix the flow rate of water at 0.1 L/min through the plasma generating quartz capillary tube having an inner diameter of 2 mm. An air compressor (CROX-RX47L) was used to provide an air stream.
controlled by an air regulator, and the flow rate of air was measured with an air flow meter (KOFLOC-1600) for different adjusted flow rates (100–800 sccm). A mass flow controller (LINE TECH M3030V), along with a mass flow control and display unit (FM-30VP), was used to control and provide the argon and oxygen flow rates for different adjusted values (100–800 sccm). An Avantes Avaspec-NIR256 miniature fiber-optic spectrometer (having spectral resolution of 0.04-20 nm, and slit size of 500 μm) was used to record the emission spectrum of Hydrogen Balmer lines under different experimental conditions. This spectrometer was also used for measuring the reactive chemical species.

Two tungsten electrodes were inserted in the quartz tube, and one electrode was connected to a negative DC power supply while the other was grounded. The inter electrode gap where the plasma was generated varied 1 and 2 mm. An injection syringe was used to inject argon, air and oxygen. The water from a small tank reservoir was allowed to enter the quartz capillary tube through a liquid flow meter that measured the flow rate of liquid. When only water exists in the capillary tube and H. V. DC is applied, the current through the water makes the boiling first, break down takes place through the water vapor and plasma is formed between the electrodes and expanded. So the conductivity of the plasma channel is high, that the current flows much, voltage drops to very low value and the discharge is stopped. Then the voltage is recovered again and the step for next pulse is started. During the underwater discharge, much of the energy is wasted for water heating and boiling. When the gas and the liquid simultaneously enter the quartz tube, the gas generates bubbles in the liquid, and these bubbles participate in breaking down the liquid at lower voltage. As reported earlier, the breakdown voltage, the time interval between the pulses and average pulse duration decrease, and the energy per pulse, average power, size of the discharge channel and radical concentration increase with the increase of gas injection [15]. The air, argon and oxygen stream in the range of 100~800 sccm, in 100 sccm intervals were injected in this study. The electrical data was measured by using a digital oscilloscope (Tektronix DPO-2024) and high current probe (Tektronix P6021), and a data storage device. The emission spectrum of hydrogen Balmer lines was recorded with a spectrometer when discharge occurred.

### III. Results and Discussion

#### 1. Electrical characteristics

Volt-Ampere characteristics were measured for two different inter-electrode distances and various gas injection rates. Fig. 2 represents a typical Volt-Ampere characteristics curve. The underwater plasma discharge follows a mechanism of bubbles and gas channels formed inside the gas-injected water and the breakdown occurs through these bubbles and gas channels. After the breakdown of the gas channel, the plasma channel implodes and discharge changed into arc and the voltage reduced down to below 100 V as shown in Fig. 2. These processes have a repeated periodic form; therefore, the discharge was pulsating [15]. At a high gas injection rate the elongation of gas channels and the increase in size of gas bubbles resulted in a high frequency of discharge pulses. Moreover, the breakdown voltage was directly related to the dielectric strength of the medium. Although the water has a high dielectric strength (65-70 kV/mm), the gas injection reduce the breakdown voltage due to the existence of gas bubbles and gas channels caused by the gas injection. Fig. 3(a, b) represents the variation of breakdown voltages under different experimental conditions. Comparing the breakdown voltage

![Figure 2. (Color online) Typical Volt-Ampere characteristics of the gas injected discharge.](image1)

![Figure 3. (Color online) Break down voltage (a) 1-mm and (b) 2-mm gap distance.](image2)
of gas-injected discharge, argon-injected discharge presented the lowest breakdown voltage, while air-injected discharge resulted in the highest breakdown voltage, and oxygen-injected discharge was positioned in the middle. It was observed that with an increase in gas injection rates, the breakdown voltage was reduced. The higher gas injection rate increased the gaseous medium in water and therefore the frequency of discharge pulses increased. In addition, the energy per pulse increased due to high gas injection rates. Both factors resulted in an increase in power of discharge pulses. The power of oxygen-injected discharge compared to argon and air was larger due to the higher energy and increased frequency of discharge pulses. At a gap distance of 2 mm, the power was higher as more intense discharge was obtained compared to 1 mm gap distance.

2. Hydrogen emission profiles

The hydrogen emission profiles were recorded as a function of gas injection rates and different inter electrode gaps. Fig. 4(a, b), fig. 5(a, b) and fig. 6(a, b) shows the typical emission spectrum of an oxygen, air and argon injected discharge respectively, at 1 mm and 2 mm inter electrode gap distances, respectively. The results demonstrate that the intensity of oxidant species generated by the discharge significantly depend upon the type of gas, gas injection rates and inter electrode gap distances. With an increase in gas injection rates and inter-electrode gap distances, the strength of discharge rises, enhancing the intensity of the spectrum. The emission intensity of the oxygen-injected discharge was proven to be higher compared to argon and air. The main factor that influenced the emission intensity was the power of the discharge pulses. The ascent in intensity of the emission spectrum with an increase in gas injection rates and the power of discharge pulses corresponded to an inflation in electron energy distribution function (EEDF). The emission intensity was highest in the oxygen-injected discharge and lowest in the argon-injected discharge, and the air-injected discharge had intermediate values in this experiment. The increase in emission intensity was due to the high electron temperature and electron number density.

3. Calculation of electron temperature ($T_e$)

Since the free electrons are responsible for the excitation of atoms and molecules, $T_e$ and $T_{mn}$ are inter-related. The emission lines intensity provides physical characteristics of plasma. If the condition of LTE for the population densities of the upper energy levels of two lines is fulfilled, then the intensity ratio method is straight forward for the determination of $T_e$ [16]. Considering the intensity of each hydrogen emission spectral line (Balmer region), the electron temperature was calculated using relation [17]:

$$T_e = \frac{\Delta E}{\ln \frac{\sum_{i} I_i \lambda_i^2 g_i}{\sum_{i} I_i \lambda_i^2 f_i}} K$$

Where $\Delta E$, $I$, $\lambda$, $g$, $K$ and $A$ are the energy difference between two levels, intensity, wavelength, statistical weighting factor, Boltzmann constant and transition.
Probability, respectively. The two hydrogen line 2s-4p transitions for Balmer-β and 2s-3p for Balmer-α were used, and the numerical values for the above relation were taken from the NIST database [18]. The intensity of these lines is obtained from the spectrum by taking integration over the respective profiles and normalizing them with the spectral response of the instrumental sensitivity.

The emission spectrum was taken after the discharge occurrence under different experimental conditions. Depending upon the experimental conditions there was a variation in the intensity and broadness of the spectral peaks. Fig. 7 represents the electron temperature, and its variation under different gas injection rates and power of discharge pulses at 1-mm and 2-mm inter-electrode gap distances. The results demonstrated that due to an increase in the gas injection rate (100-800 sccm), the power of discharge pulses, the emission intensity of the spectrum, and the electron temperature rise almost linearly.

In an oxygen-injected discharge, compared to air and argon, high electron temperature exists due to an increase in the power of discharge pulses. The presence of oxygen-related ions can effectively participate in increasing gas temperature. The expansion of discharge can reduce its temperature, but the oxygen-related ions seem to be responsible for an overall increase in gas temperature, which prevents lowering of the electron temperature due to expansion [19].

4. Calculation of electron number density ($N_e$)

Spectra of the discharge have been used to estimate the average electron density from Stark broadening. The emission spectrum of Hβ that has a probability of broadening due to various factors was used. The most dominant effects are local broadening mechanisms that include mainly Doppler broadening by thermal motion, and Pressure broadening due to collisions. The mechanism of Doppler broadening provides Gaussian profiles, while pressure broadening provides Lorentzian profiles. Doppler broadening was calculated by relation [20]:

$$\Delta \lambda_D = 7.16 \times 10^{-7} \lambda_0 \left( \frac{T_e}{M} \right),$$  

(2)

where $T_e$ = gas temperature in K, $M$ = atomic mass of emitter in atomic mass units. Pressure broadening is composed of Stark broadening and Van der Waals broadening. Van der Waals broadening was calculated by relation [21]:

$$\Delta \lambda_{de} = \frac{\lambda_0^2}{\pi} \lambda_0 = \frac{\lambda_0^2}{\pi} \left[ \frac{8 \pi \lambda_0}{\sqrt{2 \pi}} \right] = \frac{8 \pi}{\sqrt{2 \pi}} \lambda_0^2.$$
\[ \Delta \lambda_{VdW} = APT^{0.7} \]

\[ A = \text{Van der Waals coefficient having different values}\]
\[ (N_2/\text{Air} = 3.6, Ar = 5.24, O_2 = 1.32); P = \text{pressure measured} \]
\[ \text{in bar and } T_g \text{ is the gas temperature in } ^\circ \text{K}. \]

Stark broadening is the dominant component of the pressure broadening, especially for emissions from the high pressure plasma. The Stark broadening was calculated by FWHM of Balmer \( \beta \) spectral lines. Due to the Coulomb interaction between the light-emitting atoms and charged particles (mainly electrons), line broadening due to the Stark effect can occur. Mechanisms of pressure broadening, including van der Walls broadening and Stark broadening, provide Lorentzian profiles. The convolution of these two phenomena resulted in a Voigt profile, that was calculated by the following relation [22]:

\[ \Delta \lambda_{Voigt} \approx \left[ \frac{\Delta \lambda_{\text{Lorentz}}^2}{2} + \frac{\Delta \lambda_{\text{Gauss}}^2}{2} \right]^{1/2} + \frac{\Delta \lambda_{\text{Lorentz}}^2}{2}, \] (4)

The de-convolution of Lorentzian from Voigt profile provided Stark FWHM. Stark broadening (FWHM of \( H_\beta \)) having a Lorentzian profile was used in this work to find the electron number density, and the following relation was used to determine the electron density [23]:

\[ N_e = 10^{16} \chi \left[ \Delta \lambda_{\text{stark}}^{1.55} \right] \left( \text{cm}^{-3} \right), \] (5)

\( \Delta \lambda_{\text{FWHM}} \) is measured in nanometers.

After the discharge occurrence in plasma various physical and chemical processes occur simultaneously, among which ionization and recombination are the dominant processes. The most important radical (chemical oxidant specie) in water plasma is \( OH \) radical produced mostly by following the electron induced dissociation reaction, i.e. [24]:

\[ H_2O + e \rightarrow H^+ + \cdot OH + e \]

The dissociative electron recombination of water containing ions could also produce \( OH \) radical:

\[ H_3O^+ + e^- \rightarrow OH^- + H_2 \]

For non-thermal discharges with high density \( >10^{16} \text{ m}^{-3} \) and electron temperature up to 2 eV, the above chemical reaction becomes much faster than the electron impact dissociation [25]. The other secondary reactions also believed to play an important role in the production of \( OH \)-is:

Figure 8. (Color online) Electron number density under different experimental conditions and inter-electrode gap distances.
\[ H_2O + O(D^1) \rightarrow 2OH \]

First reaction occurs in the ionization phase, while the remaining two reactions occur in the recombination phase when the electron temperature is equal to the gas temperature.

Since the plasma is in water, having high density and gas injection increases the intensity of discharge that raises the chemical reactions for both recombination and ionization. It is estimated that the plasma temperature can be equal to the gas temperature. Many studies adopt other rotational bands of different molecules that can be used to obtain rotational temperatures which are mostly a good indication of the gas temperature. Especially popular is the UV emission band of \( OH \) (A-X), which is around 309 nm [26]. However, it has recently been found that the rotational population distribution is not always in equilibrium with gas temperature and this method therefore sometimes leads to overestimation [27].

Fig. 8 represents values of electron number density under different experimental conditions. At higher gas injection rates and with an increase in the power of discharge pulses the electron number density increased. The electron number density increased rapidly with the increase of the gas injection rate at first, but the increasing rate is saturated at a higher gas injection rate.

Comparing the ionization energies of three injected gasses (\( Ar = 15.7596 \) eV, \( air = 14.53 \) eV and \( O_2 = 13.6181 \) eV), the lowest ionization energy was required by oxygen, therefore, in oxygen-injected discharge, the electron collisions with oxygen effectively promoted many positive and negative ions like \( O^+ \), \( O^{2-} \), \( O^{4+} \), \( O^{3-} \), \( O^2 \), and \( O^1 \). Being an electronegative gas, oxygen’s injection in water resulted in the formation of a high density of negative ions in the plasma that caused a decrease in the plasma electron density. Since some part of oxygen exists in air also, the air-injected discharge also reduced electron number density; therefore, when compared, argon-injected underwater discharge resulted in the highest electron number density and oxygen-injected underwater discharge resulted in the lowest electron density, while air existed as an intermediate between the two other gasses. Although the power of discharge pulses was the highest in oxygen-injected discharge, the probable power consumption was in forming ions, and the excess of oxygen ions resulted in the decrease of the electron number density in oxygen bubbles containing discharge.

5. Effect of electron properties on reactive chemical species

The increase in electron temperature and number density caused an increase in the yield rate of highly-reactive chemical oxidant species \('OH, H_2O_2 and O_3\).

5.1 OH radicals

The \('OH radicals in liquid plasma, due to the highest redox potential among oxidant species (2.80 V), is a big subject of interest for environmental, medical, biological and other advanced applications. When plasma occurred in water, some chemical reactions took place that caused the generation of \('OH radicals. The dissociation of water molecules by the applied electric field, electron impact, and plasma generated shock waves, the dissociation of hydrogen peroxide and UV radiations caused the generation of \('OH radicals. Some typical chemical reactions that may take place in underwater discharge for \('OH radical generation, are given as [28]:

\[ H_2O \rightarrow H^+ + OH \]
\[ e^- + H_2O_2 \rightarrow \cdot OH + H \]
\[ H_2O + H_2O \rightarrow 2\cdot OH + H_2 + O_2 \]
\[ H_2O \rightarrow H^+ + \cdot OH \]
\[ H_2O \rightarrow H^+ + e_{aq} + \cdot OH \]
\[ e_{aq} + \cdot OH \rightarrow H_2 + \cdot OH \]
\[ e_{aq} + \cdot OH \rightarrow OH \]
\[ e_{aq} + O_2 \rightarrow HO_2 + \cdot OH \]
\[ O^+ + H^+ \rightarrow \cdot OH \]
\[ H_2O \rightarrow H^+ + \cdot OH \]
\[ HO_2^+ + H_2O \rightarrow H_2O_2 + \cdot OH \]
\[ H_2O_2 \rightarrow 2\cdot OH \]

In the case of gas injected discharge where bubbles and gas channels exist in water, the generation of \('OH radicals and their yield rate depend upon the type of gas and the gas injection rate. The life time of \('OH radicals is very short \approx 10^{-8} \) sec, therefore, a convenient method for its detection is emission spectroscopy. Fig. 9(a, b) represents the
emission spectrum of 'OH radicals ($\lambda = 309$ nm) generated by oxygen injection. In the case of argon injection, since it is a non-reactive gas, the chemical reactions are not too active. Only electric field dissociation and electron impact dissociation in water mainly participated in generating a reactive species, especially 'OH radicals. Fig. 10(a-f) represents the relative concentration of 'OH radicals, calculated by applying the Gaussian distribution function on the emission spectrum peak of 'OH radicals (at 309 nm), as a function of electron temperature and electron number density. The results show that with an increase in electron temperature and electron number density and at a long gap distance, more 'OH radicals can be induced. Compared to argon and air, a higher concentration of 'OH radicals can be induced in an oxygen injected discharge. The 'OH radicals were formed mainly due to dissociation of $\text{H}_2\text{O}_2$, which was highly influenced by nitrogen existence. Since air contains a high concentration of nitrogen (78%), the air injected discharge produced the lowest concentration of 'OH radicals among the three gases. The $\text{N}_e$ was highest in the oxygen injected discharge and as well as the concentration of 'OH radicals. While $\text{N}_e$ was highest in the argon injected discharge, an even concentration of 'OH radicals were proven to be less compared to the $\text{O}_2$ injected discharge.

5.2 Hydrogen peroxide
Hydrogen peroxide ($\text{H}_2\text{O}_2$) with a redox potential of 1.78 V is a stable and highly reactive oxidant species, which can be generated in water after plasma discharge occurrence. Unlike 'OH radicals whose life time is very short, it is stable and can be detected in water, long after plasma processing. $\text{H}_2\text{O}_2$ plays a vital role in the disinfection of water. Several methods exists for the detection of $\text{H}_2\text{O}_2$ generated in water after plasma treatment [29], but the most common method is the colorimetric method proposed by Eisenberg [30]. In this research the same photometric analysis for the determination of $\text{H}_2\text{O}_2$ generated in water was adopted after the occurrence of plasma discharge.

In this method the sample of plasma treated water, with equal amount of titanium sulfate regent, (purchased from Kanto chemicals co. Inc. Tokyo, Japan) was mixed. The hydrogen peroxide generated by water plasma reacts with titanyl ions and a yellow color complex solution of pertitanic acid was formed, under the following chemical reaction [31];

$$\text{Ti}^{4+} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O}_2 + 4\text{H}^+$$

The absorption spectrum of this yellow color complex solution was measured at 407 nm. The absorbance at this wave length corresponds to the concentration of $\text{H}_2\text{O}_2$ generated in water as a result of plasma discharge. Since the discharge was created after three different gas
injections at different gas injection rates of 100 to 800 sccm, the amount of hydrogen peroxide varies with each gas injection. Fig. 11(a-d) represents the absorption spectrum of the perltanitic acid yellow complex solution and the resulting H$_2$O$_2$ concentration at 1 mm and 2 mm inter electrode gap distances, respectively for different values of electron temperature. Fig. 12(a-c) represents the variation in concentration of H$_2$O$_2$ under different values of electron number density.

A large inter-electrode gap and higher oxygen injection rate resulted in a higher concentration of hydrogen peroxide in plasma treated water. The presence of nitrogen in water due to air injection could cause suppression of hydrogen peroxide, therefore, compared to argon and air, oxygen injected discharge yields a higher concentration of H$_2$O$_2$. Results demonstrated that with an increase in electron temperature, the concentration of H$_2$O$_2$ raised as well. The probable reason could be an increase in chemical reaction rates due to an increase in electron temperature. With an increase in electron temperature a non-linear increase in H$_2$O$_2$ concentration was observed. Effects of electron number density showed that at low density the increase of H$_2$O$_2$ concentration is slow and at a high number density the increasing rate becomes faster.

5.3 Ozone

As a result of plasma discharge occurrence in water, ozone has also been detected. The redox potential of Ozone (2.07 V) [13] is less than 'OH radicals but it can be detected in water after plasma processing. Ozone can induce 'OH radicals also after reacting with H$_2$O$_2$. Ozone formation is possible in water as well as gas ozone; therefore, in this experiment, gas bubbles generated by argon, air and oxygen exists within water so ozone can be detected in dissolved water. A common method presented by Hoigne [32] called the indigo method was used in this research for ozone measurement. Two solutions were prepared for the quantitative measurement of ozone.

Solution 1: 1 ml of phosphoric acid (H$_3$PO$_4$), (purchased from Daejung chemical and metal co. Ltd. Korea) was mixed with 620 mg of indigo reagent (purchased from Daejung chemical and metal co. Ltd. Korea) in a glass volumetric flask of 1 liter size, then the flask was filled with distilled water.

Solution 2: 28 g of sodium di-hydrogen phosphate (NaH$_2$PO$_4$), (by Sigma-Aldrich, Korea), 35 g of H$_3$PO$_4$ were mixed together in 1 liter size volumetric flask, and filled up with 1 liter of distilled water.

For reagent preparation 1 ml of each solution was taken and mixed with 12.5 ml distilled water. This gave us an indigo color liquid solution. The absorption spectrum of this solution gave us blank or reference absorbance (at 600 nm), represented by A$_1$. To determine ozone concentration, first 1 liter of plasma treated water and then 12.5 ml of this treated water sample was taken and mixed with 1 ml of each solution (solution 1 and solution 2) presented above. The addition of plasma treated water removed the indigo color from the water having 1 ml of each solution. The absorbances spectrum (at 600 nm), of this sample gave us another absorbance reference A$_2$. The differences between the two absorbencies were calculated by ∆A=A$_2$-A$_1$. The equation applied to calculate the ozone concentration is expressed as [33]:

$$O_3(\text{ppmw}) = \frac{100\Delta A}{fbV},$$

$\Delta A =$ difference in absorbance; $b =$ path length of cuvette in cm; $V =$ volume of sample; $f =$ experimentally obtained factor = 0.42.

Fig. 13(a-d) represents the typical absorption spectrum of solution and ozone concentration at 1 mm and 2 mm inter electrode gap distances, respectively.
inter electrode gaps, respectively at different electron temperatures. The results demonstrate that with increase in electron temperature and larger inter-electrode gaps, higher concentration of ozone exists. Compared to the other two gasses, oxygen proved to be a powerful ozone generating gas. Oxygen injection generated almost twice the ozone of other gasses. Fig. 14(a-c) represents the concentration of ozone dependent on electron number density. The results show that increase in electron temperature caused increase in ozone yield rate. Oxygen injected discharge generated more ozone despite having a low electron number density. The atomic oxygen reacted with water molecules and molecular oxygen to form ozone; therefore, the generation of O$_3$ can be more effective in the presence of oxygen gas bubbles in water compared to air and argon. Also the reaction rate coefficient of forming ozone through dissociation or recombination was higher in an oxygen injected discharge, compared to argon and nitrogen containing air. Moreover, the energetic electrons and UV radiations cause dissociation of oxygen molecules that cause ozone generation. Compared to oxygen, argon is a chemically inert gas; therefore, when pulsed discharges take place, argon was dissociated to excite electrons resulting in a high electron number density in a discharge containing argon bubbles. Both nitrogen and argon can have catalytic effects on the production of ozone. In the case of an air injection that contains nitrogen as a major part, such an effect is probably caused by the reactions of nitrogen atoms and electronically excited nitrogen molecules with oxygen (produced by splitting of water molecules and some concentration existing in air), that can produce additional oxygen atoms for the generation of ozone. But, at higher specific energy densities in the discharge, nitrogen existing in air can be counteracted by the quenching of oxygen atoms and the destruction of ozone. Comparison among the three gasses showed that oxygen was the best for generating ozone and, due to nitrogen, air was not too favorable.

From Fig. 10-14, the radical concentrations increased almost linearly with electron temperature which enhanced the chemical reaction. Effects of electron number density showed that at low density the increase of radical concentration is slow and at a high number density the increasing rate becomes faster. Because the electron temperature and number density couldn’t be controlled independently in the study, the fast increasing rates of radical concentration at high number density might be a result of increase in electron temperature.

**Conclusions**

The under-water capillary discharge experiment was performed. The average electron number density was observed as an order of $10^{17}$ cm$^{-3}$ by line intensity comparison, and electron temperature was 0.5-1.6 eV by Stark broadening under different experimental conditions. An increase in gas injection rate increases the power of discharge pulses, which results in an increase in electron temperature and number density. According to the high emission intensity of hydrogen Balmer lines, the electron temperature of an oxygen injected discharge is higher than those of air and argon. The electronegative characteristic of oxygen reduced the electron number density; therefore, argon represents a higher electron number density than oxygen and air. The oxidant reactive species (•OH, O$_3$, H$_2$O$_2$) has a direct relation with $T_e$, for Ar, air and O$_2$. The chemicals’ reactions that took place after discharge occurrence were affected by electron temperature more than electron number density, though both are closely correlated. The generation rate of oxidant reactive species (•OH, O$_3$, and H$_2$O$_2$) increases slowly with the electron number density increase at low number density and the increasing rates are getting faster at high number density. Oxygen injected underwater plasma discharge is most effective for generating a large amount of chemical oxidant species including O$_3$, H$_2$O$_2$, and •OH.

If we can control the electron temperature and number density independently, we can check the effect on the formation of radicals more precisely in the future.

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**References**

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