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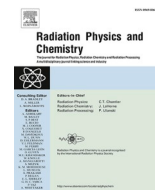
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# How septum materials affect H<sub>2</sub>O<sub>2</sub> accumulation under gamma-irradiation of water in sealed vials: A comparative study on polysiloxane rubber, PTFE, and aluminium

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## ABSTRACT

This study investigates the influence of septum materials on the radiolytic generation and steady-state concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in deionized water produced through  $\gamma$ -irradiation with a Co-60 source at a dose rate of 3 kGy/h. The experimental findings reveal that polysiloxane rubber septa significantly reduce the steady-state concentration of H<sub>2</sub>O<sub>2</sub> by up to 90 % compared to polytetrafluoroethylene (PTFE) and aluminium septa when in contact with the headspace above the solution. The suppression of H<sub>2</sub>O<sub>2</sub> accumulation was observed exclusively during irradiation. This indicates a radiation-mediated interaction between the silicone rubber and the air-saturated, closed system of the irradiated vials. A plausible explanation is that the O<sub>2</sub> in the headspace reacts with Si- and C-centered radicals formed upon irradiation of the silicone. The consumption of the O<sub>2</sub> from the head space will lead to the depletion of O<sub>2</sub> in the solution as the equilibrium between the gas phase and the liquid must be maintained. This, in turn, explains the lower H<sub>2</sub>O<sub>2</sub> concentrations in the liquid phase since O<sub>2</sub> is a precursor for H<sub>2</sub>O<sub>2</sub>. These results have implications for the design of experimental setups and the choice of materials in systems where radiolytic processes are significant.

## 1. Introduction

To explore the impact of ionizing radiation on systems and materials as well as to study radical reactions under controlled conditions, steady-state gamma irradiation is often used (Spinks and Woods, 1990). Such studies typically utilise an external gamma source, which irradiates the specimen or solution through a container. The role of the container is to keep the solution or specimen separated from the surroundings. Often, the container is sealed to maintain a controlled atmosphere inside the container. To be able to take samples for analysis without altering the conditions inside the container, different types of septa are used. The general assumption in these cases is that the septa will not affect the system under study. When studying solutions or solids immersed in liquids, the septum is usually not in direct contact with the liquid phase but only with the gaseous head space. This often further supports the assumption that the septa will not affect the system. However, in a study started several years ago, we encountered significant problems connected to reproducibility and decided to explore the reasons behind the observed problems. In that particular study, we explored

radiation-induced corrosion of various metallic materials in aqueous systems. In addition to characterising the materials prior to and after irradiation, we also monitored the concentration of H<sub>2</sub>O<sub>2</sub> in the liquid phase as a function of irradiation time. To avoid disturbing the systems, samples were taken through septa. Over the period when the experiments were conducted, the material of the septa was changed depending on availability. Hydrogen peroxide is the most stable of the primary radiolytic oxidants formed in water. For this reason, hydrogen peroxide accumulates in the system to relatively high concentrations compared to the much more reactive, and therefore short-lived, hydroxyl radical (HO•) and hydroperoxyl radical (HOO•) (Spinks and Woods, 1990). Therefore, the accumulation of H<sub>2</sub>O<sub>2</sub> often makes it one of the most important oxidants in an irradiated system. In the process of radiation-induced dissolution of UO<sub>2</sub>-based spent nuclear fuel, H<sub>2</sub>O<sub>2</sub> has been shown to be the dominating oxidant (Ekeröth et al., 2006).

In this work, we present the results of a comparative study on the effect of septa materials on H<sub>2</sub>O<sub>2</sub> concentration in gamma-irradiated glass vials containing deionized water sealed with septa. The septa materials included in the study are polysiloxane (silicone) rubber,

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polytetrafluoroethylene (PTFE), and aluminium. The investigation provides insight into how the choice of septa affects the concentration of radiolytically produced hydrogen peroxide ( $H_2O_2$ ) in  $\gamma$ -irradiated aqueous solutions.

## 2. Experimental

The presented investigations have been performed using hydrolytic glass vials (Genetec, articles 20090873, 18090864) of a nominal volume capacity of 20 ml. The investigated septa were made of 1.5 mm thick, 55° shore A, white silicone rubber and red PTFE lining (Genetec, article 18032063), 3 mm thick, 45° shore A, translucent blue silicone and white PTFE lining (Genetec, article 20030163) and 3 mm thick, 50° shore A, white silicone and aluminium foil lining (Genetec, article 20030327). For clarity, the septa will also be respectively identified in the following graphs as Septum 1, 2 and 3. The septa were respectively accommodated in 18 mm magnetic universal screw caps with a central hole and 20 mm aluminium crimp caps with a central hole. The water used for the irradiation test of the septa was type 1 ultrapure water, i.e., 18,2 M $\Omega$  cm @ 25 °C; total organic carbon (TOC)  $\leq$  5 ppb, produced with in-house equipment (Advantage A10, MilliQ) shortly before irradiation and all the samples were sealed under an ambient atmosphere. 15 ml of water was added to each vial. The irradiations were performed by placing the samples in the exposure chamber of a shielded irradiator (Gammacell 220, Atomic Energy Canada Limited) equipped with 12 GIK-7-4 type cobalt-60 sources. At the time of the experiments, the activity was 143 TBq. The doses received by the samples were tuned by varying the irradiation time, knowing the dose rate in the irradiation chamber. The  $\gamma$ -dose rate was measured to be 3 kGy/h by chemical dosimetry (Fricke dosimetry (Fricke and Morse, 1929)) in different locations of the irradiation chamber, to ensure that homogeneous irradiation of the samples was achieved. For the samples subject to multiple sampling at precise time (dose) intervals during the irradiation, 1 ml disposable syringes (disposable luer-slip two-part tuberculin syringe, Fisher Scientific) equipped with disposable 25  $\times$  0.5 mm needles (Braun) were inserted through the septa to withdraw a volume of the irradiated solution. The collected volume, between 0.1 and 0.2 ml, was transferred into a microtube (Eppendorf Snap Cap, 1 ml) and then used for  $H_2O_2$  concentration measurements. The hydrogen peroxide contents were assessed through the tri-iodide method (i.e., Ghormley method) (Allen et al., 1952). A 1 M potassium iodide solution (Sigma-Aldrich) was freshly prepared and mixed with a pH 4.65 acetate buffer (Sigma-Aldrich) solution spiked with ammonium molybdate tetrahydrate (Sigma-Aldrich) immediately before adding the sample in a volumetric ratio of 1:1:18.5. This precaution was taken to prevent ageing phenomena that could potentially alter the experimental results. For the same reason, absorbance measurements were performed in less than 10 min from their preparation. The photometric measurements were performed using a Varian Lambda-25 and a VWR UV3000 UV-Vis spectrophotometer. Absorbance measurements were performed at 350 nm in single beam mode, manually subtracting the absorbance of the blank sample before data plotting.

## 3. Results

Fig. 1 shows the hydrogen peroxide concentration measured in the aqueous solutions irradiated up to 250 kGy while contained in glass vials sealed by the three different kinds of septa assembled with both sides facing the headspace, for a total of six irradiated samples. The irradiations were limited at 250 kGy to prevent the structural failure of the polymeric septa and subsequent compromised airtightness of the vials. The irradiation of the six samples was simultaneous, and the vials were kept in the upright position for the whole duration of the experiment.

As shown in Fig. 1, the measured hydrogen peroxide content of the six samples is comparable up to a received dose of 14.8 kGy. At 250 kGy, the samples can be divided into two groups, based on their  $H_2O_2$

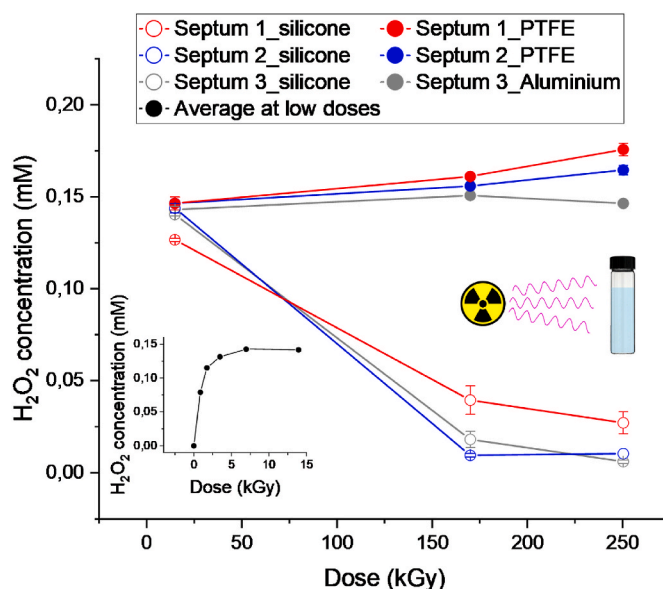


Fig. 1. Measured  $H_2O_2$  concentration versus received dose for the six irradiated samples, three for each type of septa facing the vial (septum 1, red: red PTFE/white silicone rubber, septum 2, blue: PTFE/blue silicone rubber and septum 3, grey: aluminium/white silicone rubber). Hydrogen peroxide concentration measurements were performed at 14.8, 170 and 250 kGy received dose intervals. In the inset: average  $H_2O_2$  concentration versus received dose for the six irradiated samples in the range 0–15 kGy.

concentrations. The samples equipped with Al and PTFE lining facing the headspace have an  $H_2O_2$  concentration ranging between 0.16 and 0.19 mM while the samples sealed by silicone rubber septa all have a concentration of 0.02 mM, which corresponds to values ranging from 10.5 to 12.5 % of the concentrations measured for the samples where the septa facing the headspace were lined with Al and PTFE. It is clear that the difference between the samples starts to manifest itself between 14.8 and 170 kGy, and it is not observed between 0 and 14.8 kGy. To further explore if the observed difference is merely dependent on the material or if the contact between the gaseous head space and the material has a role, the experiments were repeated but this time with the vials upside down (i.e., with the septa in direct contact with the solutions and with the headspace only contacting the glass vessel. In Fig. 2, the hydrogen peroxide concentrations measured in the second type of experiment are shown. For the whole experiment, the samples were kept in the upside-down position, forcing the contact between the septa and the water they contained.

As can be seen in Fig. 2, the difference observed in Fig. 1 is no longer present when the vials are placed upside-down and the materials are in direct contact with the solution. Hence, the effect of having silicone facing the inside of the vial is only seen when it is in contact with the head space. To explore the hydrogen peroxide reactivity towards the investigated septa materials,  $H_2O_2$  consumption was monitored in the absence of  $\gamma$ -radiation after 28 days of exposure. The results are presented in Fig. 3.

To make sure that the  $H_2O_2$  used in the experiment did not contain any stabilizer, we made use of radiolytically produced  $H_2O_2$ . As can be seen in Fig. 3, over the investigated period of 28 days, none of the septa, either kept in the upright or upside-down position, exhibited any particular reactivity towards  $H_2O_2$ . A minimal decrease in hydrogen peroxide content is expected, given the instability of  $H_2O_2$  and the lack of preservatives. Therefore, it is evident that the phenomena observed in Figs. 1 and 2 cannot be attributed to the reactivity of  $H_2O_2$ .

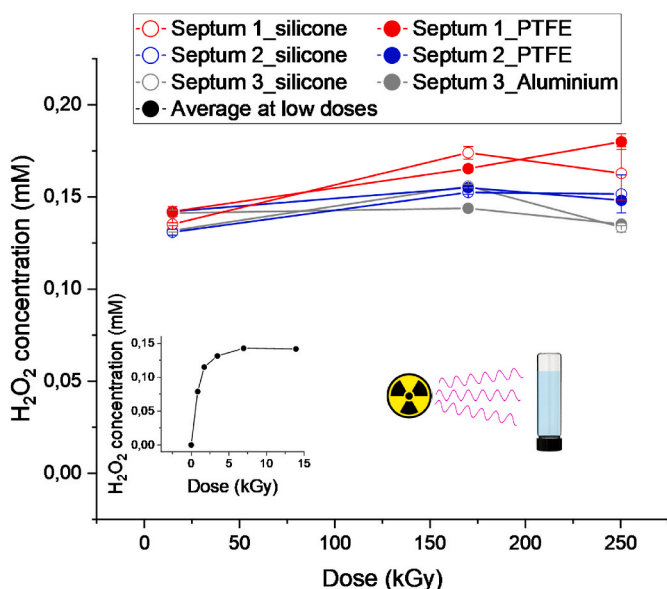


Fig. 2.  $\text{H}_2\text{O}_2$  concentration versus absorbed dose for the six irradiated samples, two for each type of septa facing the vial (septum 1, red: red PTFE/white silicone rubber, septum 2, blue: PTFE/blue silicone rubber and septum 3, grey: aluminium/white silicone rubber). Hydrogen peroxide concentration measurements were performed at 14.8, 170 and 250 kGy. Samples were kept in the upside-down position for the whole duration of the experiment. In the inset: average  $\text{H}_2\text{O}_2$  concentration versus received dose for the six irradiated samples in the range 0–15 kGy.

### 3.1. Discussion

As shown above, the discrepancy between  $\text{H}_2\text{O}_2$  concentrations in vials where silicone is facing the inside as compared to where Al or PTFE is facing the inside is only observed when silicone is in contact with the gaseous head space (Fig. 1). In addition,  $\text{H}_2\text{O}_2$  does not display any reactivity towards any of the materials used in this study (Fig. 3).

Polymers are known to undergo  $\gamma$ -radiation-induced modification (ionization and bond scission leading to radical formation, scission, cross-linking and crystallization, to name a few), resulting in alteration of chemical and mechanical properties (Clough and Shalaby, 1996). In polysiloxanes (silicone polymers), the impact of irradiation depends on the received dose rate and the availability of oxygen and water (Liu et al., 2022), (Liu et al., 2018), (Wang et al., 2020). The same parameters also affect the release of radiolytic gases in terms of relative composition and intensities (Liu et al., 2022), (Liu et al., 2018), (Wang et al., 2020). Among the radiolytic gases released by silicones, the most common are

$\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$  (Liu et al., 2022), (Liu et al., 2018), with carbon dioxide being the most abundant gaseous product if oxygen is available during irradiation (Liu et al., 2018). The proposed mechanism involves radical reactions or oxidation of the methyl group of polysiloxane, as discussed in ref. 8. According to the figure published by B. Liu et al. (2022), silicone encapsulant irradiated under a nitrogen atmosphere at a dose rate of 0.85 Gy/s mostly releases  $\text{CH}_4$  and  $\text{H}_2$ , with a gas yield of about  $0.02 \mu\text{mol s}^{-1}$  per gram of polymer, which corresponds to a surprisingly high G-value of  $20 \mu\text{mol/J}$ .

Similarly to silicone, polytetrafluoroethylene (PTFE) is strongly affected by  $\gamma$ -radiation and is known for releasing radiolytic gases such as  $\text{SiF}_4$ ,  $\text{CF}_4$ ,  $\text{C}_n\text{F}_{n+2}$ ,  $\text{C}_3\text{F}_8$  (Schnautz and Thompson, 1993), (Florin and Wall, 1961) and even HF (Schierholz et al., 1999). Aluminium is expected to be reactive towards the radiolytic oxidants and produce  $\text{Al}_2\text{O}_3$ .

The  $\text{H}_2\text{O}_2$  reactivity test presented in Fig. 3 clearly shows that direct reactions between  $\text{H}_2\text{O}_2$  and the different materials tested in this work are not the reason for the observed discrepancy. The fact that the  $\text{H}_2\text{O}_2$  concentration is more or less the same when Aluminium is facing the system (direct contact with solution or head space, Figs. 2 and 1) as when PTFE is facing the system (direct contact with solution or head space, Figs. 2 and 1) indicates that gas release from the irradiated PTFE does not affect the  $\text{H}_2\text{O}_2$  concentration up to 250 kGy. The fact that when silicone is facing the solution (Fig. 2), the  $\text{H}_2\text{O}_2$  concentration is more or less the same as when Aluminium is facing the solution or the head space (Figs. 2 and 1), implies that gas release from the irradiated silicone rubber is not the reason for the observed discrepancy when silicone is facing the head space. Gas release from both PTFE and silicone rubber should mainly be attributed to direct effects (i.e., the radiation energy is absorbed directly by the material) and be independent of whether the material is in contact with the solution or the head space.

Upon gamma-irradiation, PTFE will form radicals along the polymeric chain ( $-\text{CF}_2-\dot{\text{C}}\text{F}-\text{CF}_2-$ ,  $\text{R}\bullet$ ) and at the termination of it ( $^*\text{CF}_2-\text{CF}_2-$ ,  $\text{P}\bullet$ ) (Pinkerton and Sach, 1970). Other studies have found PTFE yields for  $\text{R}\bullet$  and  $\text{P}\bullet$  radicals in a ratio up to 10:1 (Siegel and Hedgpeth, 1967), presumably due to the recombination of the broken C–C bonds due to cage effects (Pinkerton and Sach, 1970). In presence of humid air (i.e., oxygen and water),  $\gamma$ -irradiation induces chain scissions, leading to the formation of both chain ( $-\text{CF}_2-\text{CFOO}^-\text{CF}_2-$ ) and terminal ( $-\text{CF}_2-\text{CFOO}^*$ ) peroxy radicals (Schierholz et al., 1999), (Khatipov et al., 2009), (Hoffmann et al., 2013) in a ratio close to 1:1 (Khatipov et al., 2009). Both fluoroalkyl and peroxy radicals along the main polymeric chain have been reported to be rather stable at temperatures below  $100^\circ\text{C}$  (Khatipov et al., 2009). The degree of crystallization in irradiated PTFE has been reported to increase with the received dose, limiting chain movement and therefore further stabilizing the radicals (Ormerod and Charlesby, 1963).

Upon gamma irradiation, silicones will undergo crosslinking, going

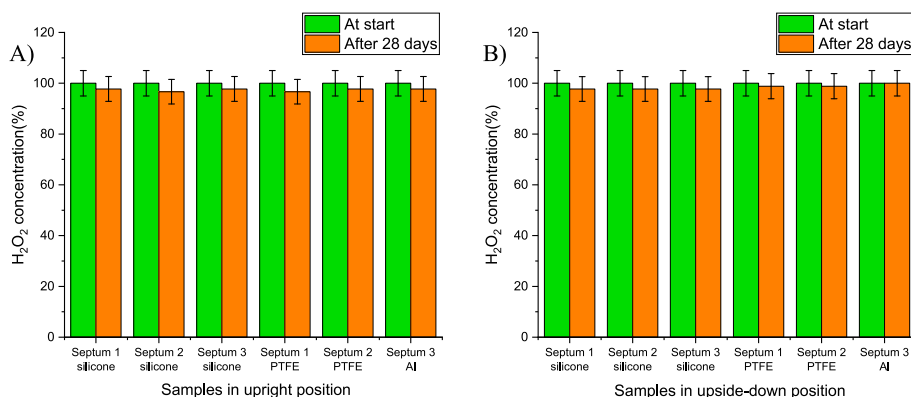


Fig. 3. A) Relative  $\text{H}_2\text{O}_2$  concentration of the six investigated samples, two for each kind of septa kept in the upright position for the entire duration of the test. B) Relative  $\text{H}_2\text{O}_2$  concentration of the six investigated samples, kept in the upside-down position for the entire duration of the test. Vials were filled with  $0.15 \text{ mM } \text{H}_2\text{O}_2$ . In green, the  $\text{H}_2\text{O}_2$  concentration was measured at the beginning of the test. In orange, the  $\text{H}_2\text{O}_2$  concentration was measured after 28 days.

through the formation of  $-\text{Si}-\text{CH}_2\bullet$ , and  $-\text{Si}\bullet$  (Ormerod and Charlesby, 1963), (Miller, 1960), (Menhofer and Heusinger, 1987), producing  $\text{H}_3\text{C}\bullet$  as well, as reported by Menhofer and Heusinger. The presence of oxygen is known to interfere heavily with the crosslinking process (Charlesby and Garratt, 1963), reducing the crosslinking yield by a factor 3 under electron irradiation (Miller, 1960). In presence of air,  $-\text{SiCH}_2\bullet$ , and  $-\text{Si}\bullet$  are expected to react with oxygen to form their peroxy derivatives, which in turn hinder the crosslinking process (Dewhurst and Pierre, 1960), (Miller, 1959). A number of studies reported that both crystallization rate and crystallinity degree are negatively affected by irradiation, with 1 MGy dose eliminating crystallization, as a result of crosslinking (Menhofer and Heusinger, 1987), (Lazurkin and Ushakov, 1958), (Palsule et al., 2008).

It is generally known that permeability, diffusivity and solubility of gases in polymers are affected by the degree of crystallinity. In fact, diffusion and permeation coefficients decrease significantly in crystallised polymers compared to amorphous ones, and oxygen solubility is reduced in crystalline regions (Jeschke and Stuart, 1961). Polymer chains are tightly and ordinally packed in crystalline regions, forming finite volumes where gas passage of molecules is hindered, therefore limiting diffusion and dissolution (Ando et al., 2020). In addition to the differences in crystallization behavior when exposed to ionizing radiation, PTFE and silicone rubber are characterised by intrinsically different oxygen permeability coefficients, with PDMS being up to  $10^2$  times more permeable than PTFE. At 35 °C, oxygen permeability values are reported as  $2.28 \times 10^{-5}$  (Pasternak et al., 1970) and  $2.68 \times 10^{-3}$  (Merkel et al., 2000) mol·m/(m<sup>2</sup>·s·Pa) for PTFE and PDMS, respectively, while their corresponding diffusivity values are  $2.2 \times 10^7$  (Pasternak et al., 1970) and  $3.4 \times 10^7$  cm<sup>2</sup>/s (Merkel et al., 2000).

As seen above, both PTFE and PDMS form radicals under irradiation that are reactive towards  $\text{O}_2$  thus enabling consumption of  $\text{O}_2$  in the headspace. While the reactivity of the radicals formed upon irradiation towards  $\text{O}_2$  is similar for both materials, the significant difference in oxygen permeability and diffusivity, both intrinsically and induced by irradiation, is responsible for the observed difference in  $\text{H}_2\text{O}_2$  evolution in the system.

In the experiments performed in this work, 15 ml of air-saturated water is irradiated with 5 ml head space of air. At room temperature, the amount of molecular oxygen ( $\text{O}_2$ ) in the head space is more than ten times higher than the amount of molecular oxygen in the solution. Given the difference in volume, the concentrations differ by a factor of 30. This implies that the rate of reaction between the radicals formed in the polymer and  $\text{O}_2$  will be much higher when the head space is in contact with the silicone rubber compared to when the aqueous solution is in contact with the silicone rubber, not including the impact of viscosity which will further enhance the difference. A more rapid consumption of  $\text{O}_2$  from the head space will lead to depletion of  $\text{O}_2$  in the solution as the equilibrium between the gas phase and the liquid must be maintained.

This, in turn, could explain the lower concentrations of radiolytically produced  $\text{H}_2\text{O}_2$  accumulated in irradiated solutions exposed to PDMS, since  $\text{O}_2$  is the most important precursor for  $\text{H}_2\text{O}_2$  formation under gamma irradiation in air-saturated aqueous solution, according to the mechanism presented in Equations (1)–(4).



Where  $\text{H}\bullet$  is one of the products of water radiolysis, which would otherwise contribute to  $\text{H}_2\text{O}_2$  degradation (Allen, 1948), as presented in Equation (5).



In oxygen-free aqueous solutions,  $\text{H}_2\text{O}_2$  is primarily formed from recombination of hydroxyl radicals in the early stages of radiolysis. The yield of this reaction is relatively low in gamma-radiolysis (Hiroki et al., 2002).

When the silicone rubber is facing the solution, as in Fig. 2, the rate of reaction between  $\text{O}_2$  and the radicals in the polymers is significantly lower (due to a lower  $\text{O}_2$  concentration and increased diffusion resistance in the aqueous phase), and the significantly larger amount of  $\text{O}_2$  in the head space will rapidly compensate for any consumption in the liquid phase. To the best of our knowledge, C-centered radicals do not display significant reactivity towards water unless the water has been activated through the formation of a complex where the bond dissociation enthalpy of the O–H bond can be significantly reduced. In fact, there are numerous studies of alkyl radical reactivity towards other solutes in aqueous solution where reactions with the solvent are not considered to be of significance. Indeed, certain alkyl radicals could be protonated in water to produce the corresponding radical cation, provided the pH is low enough. However, in our system we do not see that we have the conditions required for such reactions. Hence, reaction with  $\text{O}_2$  is the most probable reaction for C-centered radicals formed also in contact with the aqueous phase. Given reduced reaction rate with  $\text{O}_2$  present in the aqueous phase, it is plausible that cross-linking is favoured.

The experiments presented in this work have all been conducted at a constant dose rate. However, it is quite probable that the dose rate will have an impact on the radiation-induced process in the silicone rubber as well as in the PTFE. This would probably be reflected by a change in steady-state concentrations of  $\text{H}_2\text{O}_2$  in the aqueous phase. At higher dose rate, the concentration of C-centered radicals in the irradiated silicone rubber will be higher, which most probably will result in a higher fraction of radical-radical reactions compared to reactions between radicals and  $\text{O}_2$ . This would reduce the consumption of  $\text{O}_2$  at a given dose and thereby reduce the impact on  $\text{H}_2\text{O}_2$ . Given the complexity of this system, further studies would be required to clarify the possible dose rate effect as this was never the purpose of this study.

#### 4. Conclusions

The experiments performed in this work clearly show that materials in the septum of sealed glass vials can have a significant impact on the concentration of the aqueous radiolysis product  $\text{H}_2\text{O}_2$  when irradiating pure water saturated with air. This is particularly important when studying processes where  $\text{H}_2\text{O}_2$  is the dominating oxidant. The materials tested facing the inside of the vials were Aluminium, PTFE and silicone rubber. It was shown that the  $\text{H}_2\text{O}_2$  concentration dropped drastically at high doses (above 14.8 kGy) when the silicone rubber was facing the headspace. In all other cases, i.e., for aluminium and PTFE facing the headspace as well as the solution and for silicone rubber facing the solution, the  $\text{H}_2\text{O}_2$  concentration increased slightly with dose (at high dose). The rationale for this observation is argued to be a rapid reaction between  $\text{O}_2$  and Si- and C-centered radicals in the septum, leading to a depletion of  $\text{O}_2$  in the aqueous phase.  $\text{O}_2$  is a precursor for  $\text{H}_2\text{O}_2$ , and reduced  $\text{O}_2$  concentration will also lead to reduced  $\text{H}_2\text{O}_2$  concentration.

This study highlights the importance of using the right septum material when irradiating aqueous solutions to doses higher than 10 kGy.

#### CRediT authorship contribution statement

**Luca Gagliani:** Writing – original draft, Validation, Methodology, Investigation. **Christian Ekberg:** Writing – review & editing, Funding acquisition. **Mats Jonsson:** Writing – review & editing, Supervision, Funding acquisition.

#### Declaration of competing interest

The authors declare the following financial interests/personal

relationships which may be considered as potential competing interests: Luca Gagliani reports financial support was provided by Swedish Centre for Nuclear Technology (SKC). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

No data was used for the research described in the article.

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