Effects of radical scavengers on nanocomposite Fricke gel for heavy ion beam irradiation

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Abstract. NC-FG (nanocomposite Fricke gel) dosimeter is a 3D dosimeter for heavy ion beam without LET dependence. In this study, we evaluate the effects of silver perchlorate, a radical scavenger, on NC-FG. We find that radiological properties of NC-FG are changed by small amounts of silver perchlorate. Especially, dose response at high LET enhanced.

1. Introduction
Three-dimensional (3D) dosimetry of heavy ion beam irradiation is required in particle therapy using carbon ion beam. On the other hand, the practical application of a solid-state or gel-state dosimeter to heavy ion beam 3D dosimetry is complicated by the degradation in sensitivity as a function of linear energy transfer (LET) [1-3]. Although Fricke gel [4-8] dosimeter also shows LET dependent dose responses [9,10], the Fricke gel prepared with nano-clay under deaerated conditions (NC-FG: nanocomposite Fricke gel) shows LET-independent dose responses, and this is the only 3D dosimeter for heavy ion beam [10-12]. NC-FG show the reaction scheme with water radiolysis products as shown

\[
\text{Clay} \to \text{Fe}^{2+} + \text{OH}^{-} \rightarrow \text{Clay} \to \text{Fe}^{3+} + \text{OH}^{-}
\]

\[
\text{Clay} \to \text{Fe}^{3+} + e_{aq}^{-} \rightarrow \text{Clay} \to \text{Fe}^{2+}
\]

\[
\text{Clay} \to 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Clay} \rightarrow 2\text{Fe}^{3+} + 2\text{OH}^{-}
\]

\[G(\text{Fe}^{3+})_{\text{Clay}} \equiv G(\text{OH}) + 2G(\text{H}_2\text{O}_2) - G(e_{aq}^{-})\]

Figure 1. Reaction scheme of NC-FG
in figure 1. The reaction part of reduction of Fe\(^{3+}\) by hydrated electron is major factor for LET-independent dose responses [11]. In this paper, we investigate the effects of silver perchlorate for a radical scavenger on NC-FG for heavy ion beam irradiation, and we try to control of LET-dependence of dose response of NC-FG.

2. Material and methods

The NC-FG prepared with 2 wt% nano clay (Laponite XLG) and 1 mM ferrous sulfate ammonium base on reference [11]. Ag\(^+\) ion was added for radical scavenger. The addition of silver ion Ag\(^+\) (40% Silver Perchlorate Solution) was done in nano-clay dispersion solution while bubbling through H\(_2\) gas and mixing by magnetic stirrer (Nissin magnetic stirrer Model SW-R300) for 1 hour. After color change colorless to brown of nano-clay dispersion plus silver ion solution (0.1, 0.5 or 1 mM), we added the ferric sulfate ammonium stock solution, and mixing using same magnetic stirrer for 1 hour while bubbling through H\(_2\) gas. The obtained almost black solution after stirring was sealed into Pyrex glass tubes under a pure N\(_2\) atmosphere in a glove box. Details of the chemical compositions of NC-FGs are summarized in Table 1. The prepared Pyrex glass tubes containing NC-FG were irradiated from the bottom with a \(^{12}\)C\(^{6+}\) beam at 290 MeV/u supplied from the Biological Irradiation Port of Heavy Ion Medical Accelerator in Chiba (HIMAC) at the National Institute of Radiological Sciences (NIRS). Detailed irradiation condition is same with report [11]. A 1.5 T MRI scanner (Intera Achieva 1.5T HP Nova Dual Gradient, Philips Medical Systems, Best, The Netherlands) was used for the analysis of the NC-FG samples. The longitudinal MR relaxation rate (\(R_1 = 1/T_1\)) of the NC-FG samples was evaluated using a turbo mixed sequence. The conditions of the \(T_1\) measurements were as follows: TR = 2260 ms; TE\(_1\) = 19 ms; TE\(_2\) = 100 ms; TI = 500 ms; ETL = 6; pixel spacing = 0.8 mm.

| Table 1. Chemical composition of NC-FG |
|---------------------------------------|
| ammonium iron(II) sulfate hexahydrate (mM) | LaponiteXLG (w/w%) | silver(I) perchlorate (mM) | Bubbling |
| 1 | 1 | 2 | 0 | Deaeration |
| 2 | 1 | 2 | 0.1 | H\(_2\) |
| 3 | 1 | 2 | 0.5 | H\(_2\) |
| 4 | 1 | 2 | 1 | H\(_2\) |

3. Result

In the fig 2, Monotonically increase of \(R_1\) with dose can be observed in the experiments results of addition of Ag\(^+\) ions. On the other hand, the radiation sensitivity of NC-FG decreases with increase in Ag\(^+\) concentration. Ag\(^+\) ions have high reactivity with OH radical and also with hydrated electron [13]. Thus, it is considered that the oxidation of Fe\(^{3+}\) was suppressed by the addition of Ag\(^+\) ions. In the figure 3, Depth-\(\delta R_1\) distributions was shown, and the values of \(\delta R_1\) plotted as the normalized value at entrance surface. we can confirm that peak enhancement with increase in concertation Ag\(^+\) from the relative radiation sensitivity plot. It is means that the contribution of reduction reaction of Fe\(^{3+}\) is relatively increase by addition of Ag\(^+\) ion. If NC-FG is not prepared by using hydrogen bubbling before mixing Ag\(^+\) and Fe\(^{3+}\), rapidly oxidation before irradiation experiment was observed. The understanding of these interesting phenomena needs to the other analyzing method such as optical spectroscopy shown in literature [14]. In addition, we must also investigate dose rate effects and change over time. Enhancement of sensitivity with increase in LET value is not unique in this dosimeter but also known in Fe\(^{2+}\) + Cu\(^{2+}\) aqueous chemical dosimeter [15]. We speculate that NC-FG added Ag\(^+\) radical scavenger also has same reaction system with Fe\(^{2+}\) + Cu\(^{2+}\) aqueous chemical dosimeter.
Figure 2. The $\delta R_1$ value of the NC-FG after irradiation of $^{12}\text{C}^6+$ 290MeV/u. The symbols indicate measured values (MRI) near the entrance surface. The dashed line indicates liner fitting.

Figure 3. The relative $\delta R_1$ distribution of NC-FG after irradiation of $^{12}\text{C}^6+$ 290 MeV/u. The symbol-line show dose measured using IC (ionization chamber).

4. Conclusion
We reported that the further development of improvement radiological property of NC-FG as a function of LET. LET effect was changed using small amount of radical scavenger of Ag$^+$ ion. While LET effect enhancement by addition of Ag$^+$ ion is only phenomenological understanding, this study is clearly show NC-FG can control LET effects. It is maybe useful for development such as biological detector that has similar LET effects in the future. On the other hand, that sensitivity decrees as shown in fig 2. For more detailed characterization, it is necessary to improve the sensitivity or change the measurement system. For example, it is useful to investigate the application of a gel dosimeter using the most sensitive fluorescent probe [16-20].

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6. References
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