TOWARDS IMPROVING THE DETECTION LIMIT OF ELECTRON PARAMAGNETIC RESONANCE (EPR) DOSIMETRY OF DRYWALL (WALLBOARD)

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Abstract

The intensity of the electron paramagnetic resonance (EPR) line corresponding to the carbonate free radical (CO_3^-) in gypsum ($CaSO_4 \cdot 2H_2O$) drywall was previously shown to be proportional to absorbed dose. Heating irradiated drywall reduces the radiosensitive signal of the CO_3^- radical. The response of the CO_3^- EPR line to heat treatments is being studied in order to determine a background for an arbitrary drywall sample. Ultimately this is expected to improve the precision of dose measurements with drywall and to reduce the detection limit. Controlled heating of irradiated drywall was performed at temperatures between 50° C and 100° C. Although higher temperatures reduce the radiosensitive signal rapidly, the non-radiosensitive EPR signals are affected dramatically as well, presumably due to a phrase change from gypsum to plaster of Paris to anhydrite.

1. Introduction

Accidents or malicious use of radioactive materials may result in the exposure of individuals who are not wearing dosimeters. In such cases, it may be necessary to determine the absorbed dose using materials which are not ordinarily considered as dosimeters. One particularly attractive material that can be used as a dosimeter is drywall. In North America, drywall panels, which are composed almost entirely of gypsum ($CaSO_4 \cdot 2H_2O$), are a nearly ubiquitous construction material. Absorbed dose in drywall may be measured through electron paramagnetic resonance (EPR) dosimetry [1][2].

EPR is based on the resonant absorption of microwaves through electronic spin transitions in the presence of an external magnetic field. For example, a free electron placed in a magnetic field will occupy either a spin-up or a spin-down state, with the difference in the energy levels increasing as the external magnetic field increases (Zeeman splitting)[3]. Incident microwaves will drive transitions between the two energy states. When the different in energy states is equal to the microwave photon energy absorption is possible and a transition occurs.

In a typical EPR measurement, the external magnetic field is increased (swept) while the microwave frequency (energy) is held constant. At resonance, an increase in microwave energy absorption indicates the presence of paramagnetic centres. For experimental ease, the measured EPR spectrum is usually the first derivative of absorption.

Ionizing radiation induces the formation of paramagnetic CO_3^- free radicals in gypsum, which originate from non-paramagnetic impurities in the host gypsum [3][4][5]. The intensity of the EPR line corresponding to the CO_3^- radical was first proposed by Haskell, et al. using this EPR line to measure absorbed dose in drywall. Subsequent work by Thompson, et al. demonstrated the successful reconstruction of dose in irradiated drywall panels. Although the preliminary work reported a detection limit of less than 1 Gy, the subsequent study by Thompson, et al. suggested a detection limit of about 2.5 [1][2].

In order to accurately determine dose in drywall one needs to subtract the background (unirradiated sample) signal (Figure 1). The work by Thompson, et al. [1] used a known sample of unirradiated drywall as a "universal" background for all irradiated samples. However, the background of each drywall sample is expected to vary due to variations in the concentrations of trace impurities in the gypsum. This occurs with respect to multiple samples taken from a single drywall panel and with respect to drywall panels produced from gypsum sourced from different geographical locations.

In order to accurately determine absorbed dose and to improve the detection limit, it will be necessary to obtain an appropriate background (unirradiated sample) EPR spectrum for an arbitrary sample of drywall. The approach taken in this study is to use controlled heating to eliminate the radiation-induced CO_3^- line. Ultimately the results of this experiment will allow us to determine an appropriate heating temperature and duration suitable for removing the irradiated signal while retaining an unchanged background.

2. Methods and Materials

A JES-FA100 X-band (9.4 GHz) continuous-wave EPR spectrometer was used to perform the measurements in this study. The spectrometer was turned on at least 3 hours before usage to allow it to stabilize. All measurements were performed at room temperature using a 5 mm ID Suprasil (Wilmad LabGlass) sample tube placed in a TE_{011} cylindrical cavity. The parameters that were used to measure the CO_3^- line were 9.0 mW (power), 334±4 mT (centre field ± half-width), 0.1 mT (modulation amplitude), 1x30 s (repetitions x sweep time), 0.1 s (time constant), 140 arbitrary units (gain). All EPR spectra were normalized by aliquot mass. Spectrometer stability was confirmed through monitoring the intensity of the internal Mn^{2+} standard.

The EPR spectrum of an unirradiated, unheated aliquot served as the background for all EPR measurements. The background spectrum was aligned in magnetic field by minimizing the least-squares difference in the difference spectrum in the region of the Mn^{2+} (III) line (Figure 1). The EPR intensity of the CO_3^- line was determined as the peak-to-peak intensity in the difference spectrum.

Drywall was sampled from the interior of Sheetrock brand gypsum panels, manufactured by Canadian Gypsum Company at Hagersville, Ontario. The gypsum was crushed with an agate mortar and pestle and sieved to a grain size of 150–250 μm. A dose of 47.9±3.0 Gy was

delivered to aliquots that were approximately 100 mg in mass using the ^{60}Co source (gamma ray energies of 1.17 and 1.33 MeV) at the McMaster Nuclear Reactor.

Isochronal heating was performed on a single aliquot of irradiated drywall. The aliquot was heated at successive temperatures for 15 minutes each. Following each heating step, an EPR spectrum was obtained. The temperatures ranged from room temperature (21 °C) to 120 °C holding time constant.

Isothermal heating was performed on four aliquots of drywall. For each aliquot, the temperature was held constant (50° C, 75° C, 85° C, 100° C), and EPR measurements were performed at various times.

3. Results and Discussion

The EPR spectrum of irradiated drywall is shown in Figure 1. The sharp peak at 335.54 mT is due to the presence of CO_3^- radicals in the irradiated drywall. The remaining major features are the Mn^{2+} line at 330.45 mT [3] and the broad peak that ranges from 335.2 to 336 mT, which is likely due to MnO [6]. Following proper alignment of the background spectrum, the difference spectrum clearly shows the CO_3^- line (figure 1). The peak-to-peak intensity of this line is proportional to absorbed dose [1].

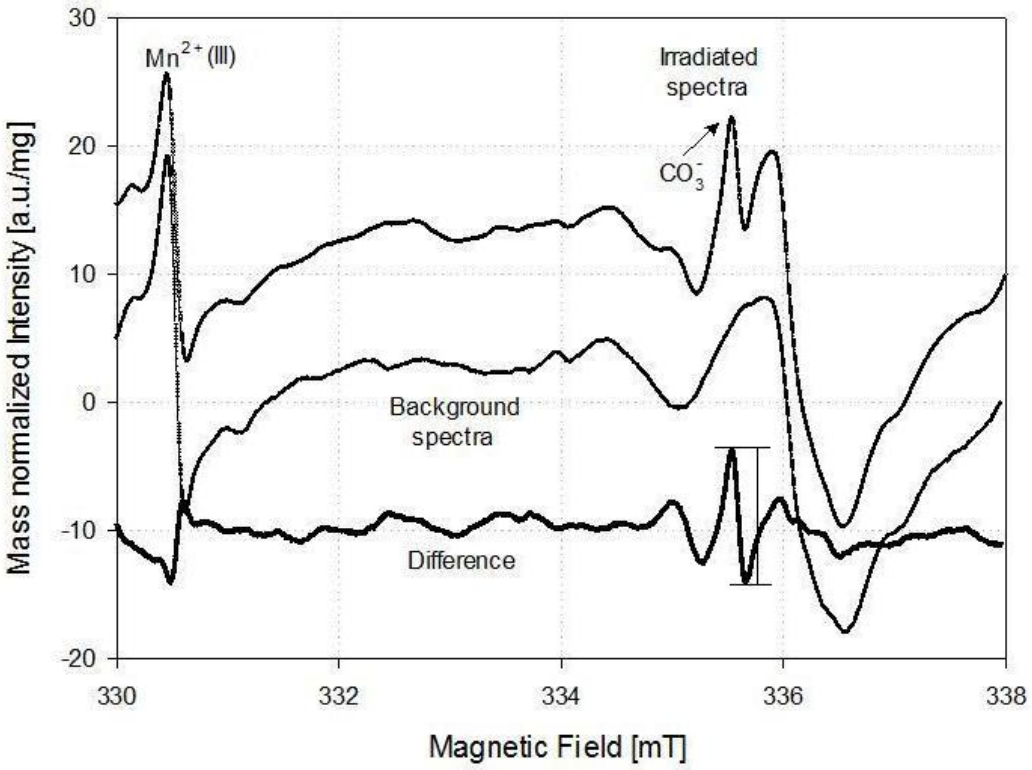

Figure 1 Stacked EPR plot of irradiated (47.9±3.0 Gy), unirradiated drywall and the difference. The EPR line of the radiation induced CO_3^- radical appears at a magnetic field of 335.54 mT. EPR scan parameters: 9 mW, 334±4 mT, 0.1 mT, 1x30 s, 0.1 s, 140 a.u.

The initial line in the difference curve (330.5 mT) is an artifact of background subtraction. This is due to the differences in signal intensity about the Mn^{2+}(III) peak from the irradiated drywall aliquot and the aliquot used for the background.

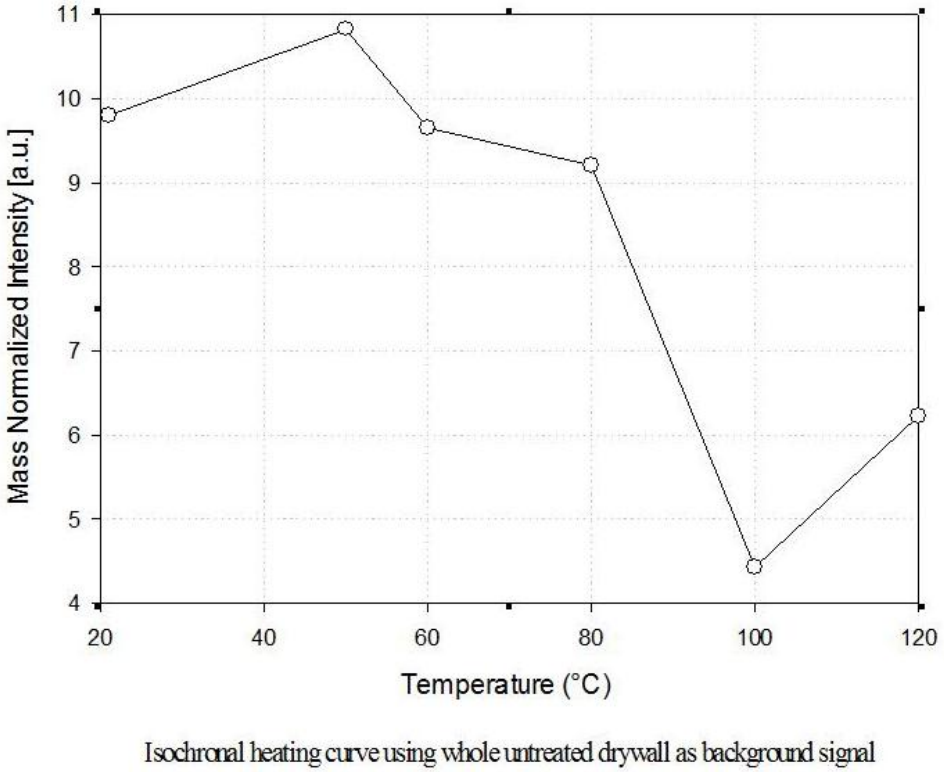

Figure 2 An irradiated aliquot (47.9±3.0 Gy) was heated to various temperatures using 15 minute intervals. The intensity decreases from 60 °C to 100 °C then rises afterwards at 120 °C. The kinetics are still not fully understood.

The isochronal heating curve is shown in figure 2. The intensity increases from room-temperature to 50° C, followed by a decrease to 100° C, and an increase at 120° C. The EPR intensity of the CO_3^- line is approximately stable to about 80° C, and rapidly decreases thereafter. The increase at 50° C is likely due to charge transfer, in which non-paramagnetic centres are converted to paramagnetic CO_3^- due to the heating [3]. The increase of intensity at 120° C is not yet understood.

A possible explanation of this increase in intensity at 120 °C could be due to the phase change. At 95 °C plaster of Paris undergoes a phase change to anhydrite due to the evaporation of water [7]. Because of this possibility it may be difficult to interpret the data when using heating temperatures at this level.

The isothermal heating curves are shown in figure 3 and 4. At 75° C, 85° C, and 100° C, the EPR intensity of the CO_3^- line decreases in an exponential fashion. The signal lifetimes at each temperature were determined to be 7883 s, 3250 s and 1186 s respectively. At 50° C, the EPR intensity has not yet decreased sufficiently in order to fit an exponential function to the data.

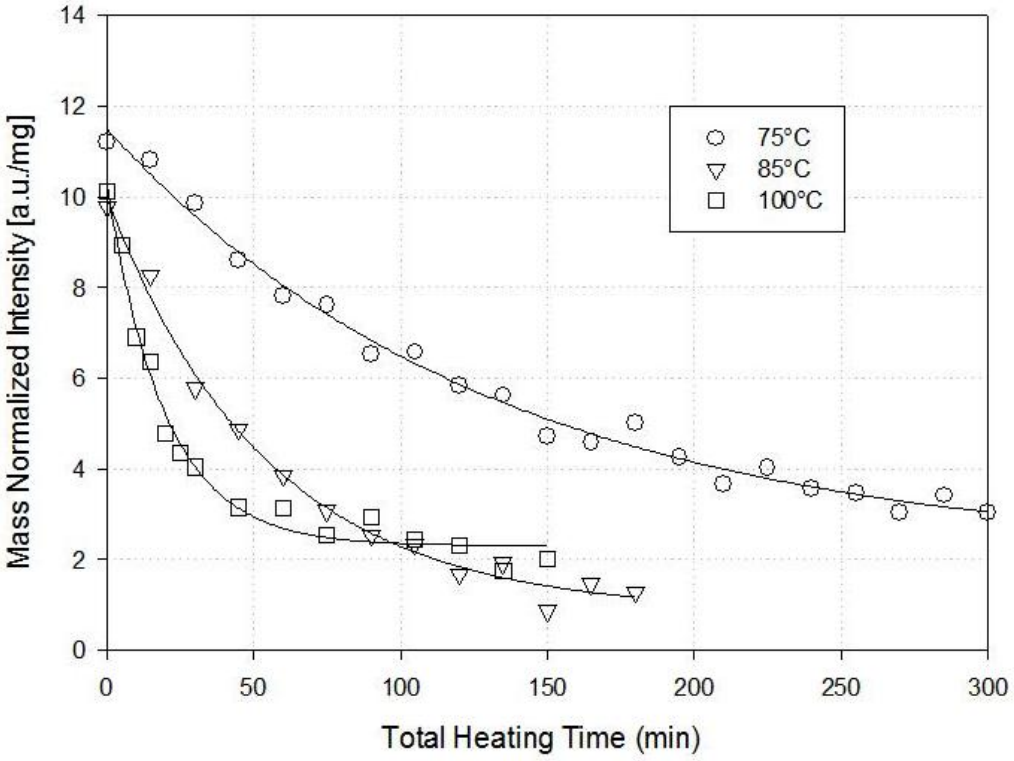

Figure 3 The decay of intensities of the carbonate EPR line from heating temperatures of 75 °C, 85 °C and 100 °C. The most rapid decay is for the 100 °C heating temperature.

As seen in the above figure the intensity of the carbonate line 100 °C decays rather rapidly. However, figure 2 shows that such a temperature is not satisfactory since any heating after that point results in an increased signal and possible changes to the background.

$$Intensity = 2.093 + 9.406e^{-7.611\times10^{-3}\times time} \quad (1)$$

$$Intensity = 8.467\times10^{-1} + 9.143e^{-1.846\times10^{-2}\times time} \quad (2)$$

$$Intensity = 2.311 + 7.98e^{-5.06\times10^{-2}\times time} \quad (3)$$

The isothermal decay curves were fit with exponential decay functions, with R^2 equal to 0.98 or greater.

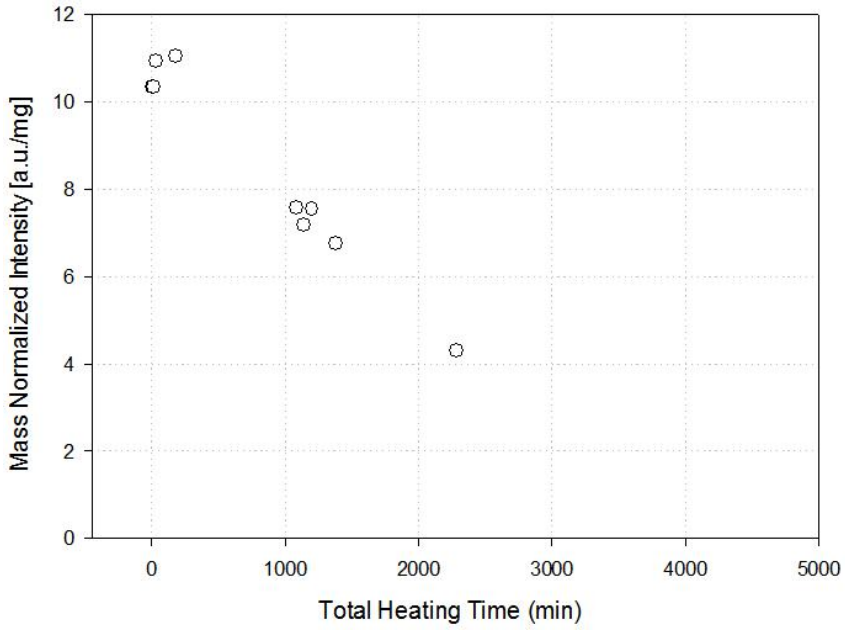

Figure 4 Shows the 50 °C isothermal heating curve for various time intervals. The long duration of heating occurred for 15 hours. The cluster of points are measurements made during that day.

The decay of the carbonate line intensity with respect to heating at 50 °C appears to linear, as seen in Figure 4. With additional heating, it is expected that this decay of intensity would also appear to be exponential or exponential-like. Although no curve fit was applied. The mean lifetime of the carbonate line was determined to be 8.211×10^4 s at 50 °C.

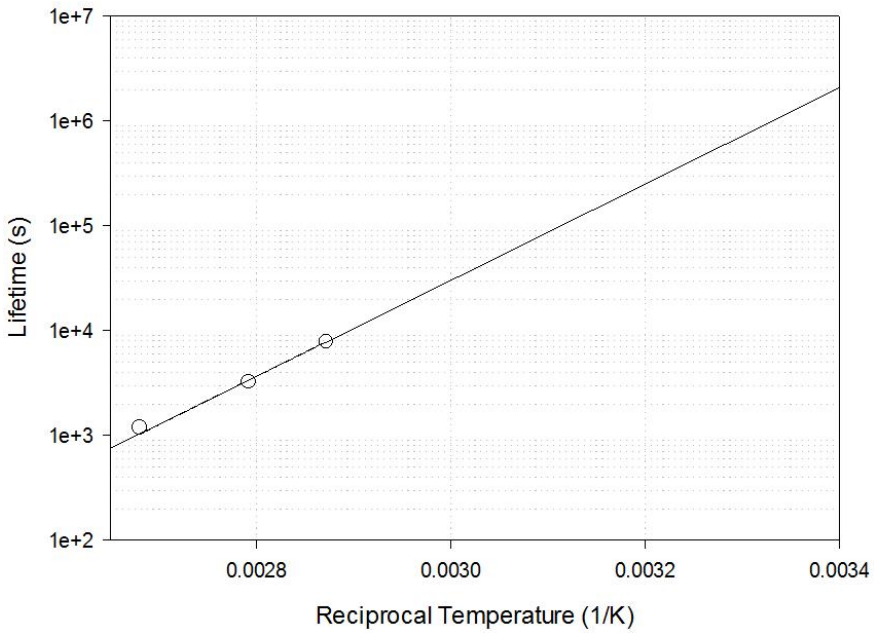

Figure 5 Lifetime in seconds is plotted versus reciprocal temperature. For first-order (exponential) decay, a linear function should be observed. A linear fit was applied and extrapolated to room temperature ($1/T=0.0034$ K^{-1}).

The lifetimes determined from the isothermal heating curves may be used to extrapolate a room-temperature lifetime of $2x10^6$ s, as seen in figure 5. This indicates that the irradiated CO_3^- centres are sufficiently stable at room temperature for drywall to be suitable as an emergency EPR dosimeter.

4. Conclusions

Obtaining an ideal background is a key factor in attaining an improved measurement of absorbed dose in drywall. Heating at high temperatures for an extended duration affects the baseline of the EPR signal rendering it ineffective for background subtraction. This phenomenon could be attributed to the phase change from gypsum to plaster of pairs to anhydrite, or to charge transfer. An appropriate protocol for heating irradiated drywall to remove the carbonate EPR line will involve heating the sample between 85° C and 100° C. Further research will be performed in order to find the ideal time and temperature.

5. Future Directions

Additional heating experiments will be performed in order to improve the understanding of the decay kinetics of the carbonate EPR line in irradiated drywall. An appropriate heating protocol will be found to allow complete removal of the carbonate EPR line intensity. Additionally, we plan to study drywall which is produced using gypsum obtained from different mines. Finally, we plan to study drywall dosimetry following neutron irradiation.

6. Acknowledgments

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7. References

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