Investigating the Lifetime of Bromine-Quenched G.M. Counters with Temperature

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Abstract

The amount of halogen quench gas as a percentage of the total fill gas contained within a gas-filled Geiger-Müller detector is directly linked to its operational characteristics. Preserving this halogen gas will help maintain the operating lifetime of the detectors. Such halogen gases are highly corrosive and the small quantities within a gas-filled detector can deplete rapidly via interactions with surrounding materials. The rate of interactions is thought to be proportional to not only temperature, but also to the current initiated by ionization events associated with the formation of each signal pulse. As all pulses are of similar magnitudes, GM detector operational lifetimes are quantified in accumulated counts rather than a given operating time. We have studied three different types of corrosion-resistant mechanisms to protect the bromine halogen gas from any interactions with 446 stainless steel detector components of ZP1200 Geiger-Müller tubes at temperatures up to 125 °C. Three types of surface treatments for these detectors used were labeled as “raw” using only an oxygen-plasma-bombardment process, “passivated” using a combination of nitric acid passivation followed by an oxygen plasma-bombardment process, and thirdly plating with a few micron thickness of chromium followed by an oxygen plasma-bombardment process. 32 detector samples were irradiated at room temperature with a Caesium-137 source at dose rates of approximately 1.3 mSv/hr up to 5.7×10^{10} accumulated counts; another 32 detector samples were aged to 3.3×10^{10} counts at 125 °C. At room temperature, the chromium-plated samples exhibited an initial rise in their starting voltage readings. All other detector performance characteristics, for all detector types, did not change significantly during the ageing process, and the surface morphology of the detector cathodes was unaffected. At 125 °C, the chromium-based plating produced the most stable long-term response. These chromium-plated samples showed no evidence of bromine deposits on the cathode samples investigated via Energy-Dispersive X-ray Spectroscopy. The raw and passivated samples, however, did show traces of bromine independent of the age of the detector. Preliminary investigations we have carried out at 175 °C highlight the importance of the chromium plating layer in preserving long-term detector performances at elevated temperatures.

1. Introduction

The gas-filled Geiger-Müller (GM) detector has long been used for radiation monitoring applications. One industry of particular interest in the development of GM detectors is the oil and gas industry. Carrying out gamma ray logging in deep-well drilling operations can subject monitoring devices to extreme conditions. The majority of oil wells have temperatures below 125 °C, as mentioned in (1). It is for this purpose that the detectors must operate at temperatures up to 125 °C. While a GM detector with an infinite operational lifetime would be ideal, due to their design, such timespans cannot be achieved without compromise. One main reason for the limitations in a GM detector's functional lifetime is due to the necessary implementation of an effective quenching mechanism; this helps to re-establish the electric field necessary for further discharges and counts to occur.

After the fill gas of a detector is ionised by incident radiation, any positive ions formed will drift towards the negative cathode wall. Upon reaching the cathode, the ions will then interact with the cathode wall and return to their neutral state by acquiring an electron. Such a process often leaves the atom in an excited state. In this state, the atom can emit a photon having sufficient energy to cause further gas ionisations; this will result in constant spurious counts being detected. The quenching mechanism, however, interrupts the emission of any secondary photons to reduce the likelihood of spurious counting occurring to a negligible level. This concept is explored further in (2).

The introduction of an additional gas component (passive quenching) or the use of an external circuit (active quenching) can be implemented to produce the required effect. For more information on the operating mechanism governing each method, along with their benefits and disadvantages, refer to (2). Due to design practicality and efficiency in higher radiation environments, a halogen gas-based quencher is more commonly used in the manufacture of GM radiation detectors.

In gas-filled GM detectors, the depletion of the quenching gas governs the lifetime of the counter. Organic gases have a limited long-term quenching ability due to each molecule dissociating irreversibly after quenching. Halogen molecules have the ability to recombine after each quench event; for this reason, they are favoured over their organic counterparts. The drawback in using halogen quench gases is that, because of their very high activity when dissociated, they might deplete through interactions with surrounding materials or

contamination, as mentioned in (2). The selection of detector materials thus becomes essential in determining the most halogen-resistant construction. The compositions of GM detector components exposed to the quench gas are carefully selected to contain high quantities of chromium [approx. 28% by weight]; the trade name of such steels is Type 446. Chromium is a common alloying element in steels due to the corresponding mixture producing a highly corrosion-resistant oxide layer, as discussed in (3). The loss of quench gas is thought to be a function of the number of energetic species produced per detection event, which relates to the measured pulse height of each count, as mentioned in (4). It is for this reason that detector lifetimes are expressed in terms of accumulated counts.

Another factor to consider in GM design is the surface conditioning of detector components exposed to the halogen. The main detector performance characteristics to consider, discussed in more detail in (5), are the detector starting voltage (Vs), the length of the Geiger plateau, the plateau gradient, the detector's sensitivity, and the background count rate. Background count rates are measured in the absence of a source and high values can signify the presence of undesirable spurious counts.

Liebson and Friedman, (6), have shown that a GM detector's Vs will drop with less quench gas and can be used to estimate the extent of losses in the detector quench gas. It has also been shown in (4) that Energy-Dispersive X-ray (EDX) analysis is suitable for investigating any halogen quench gas attack on the internal Geiger components with increasing age at temperatures up to 200 °C. In (4), it has also been suggested that quench gas interactions can occur with other components, such as the anode pins or the glass seal of the detectors in addition to the large cathode surface of the detector. However, this paper will focus on three cathode surface protection processes, which are compared in terms of their effectiveness in maintaining the operational Geiger-Müller parameters by reducing the depletion of halogen quench gases at different temperatures.

2. Materials and Methods

To carry out these investigations, Centronic Ltd.'s ZP1200 Geiger-Müller counter was selected; the halogen quench gas used is high-purity bromine. The minimum protection process considered, referred to as an oxygen bombardment, was the forced formation of a chromium oxide layer by exposing the internal surfaces of the 446 stainless steel to pure oxygen plasma. Detectors produced using this technique are labelled as 'raw samples'.

The second protective technique considered is a nitric passivation process. Such a procedure is commonly used to cleanse stainless steel surfaces of impurities and eliminate any potential corrosion sites, as shown in (7). This is possible due to the highly oxidising nature of nitric acid. After the nitric passivation, the oxygen bombardment technique was carried out. By using both techniques, it is expected that the internal surfaces will be free from any traces of contamination and also have the protective chromium oxide layer. This dual-protective process is used to produce detectors labelled as ‘passivated detectors’.

The third protective process investigated was chromium plating the internal surface of the detectors. Chromium plating is a common industrial process used to produce corrosion-resistant materials, as shown in (8). The deposition of a pure chromium layer that is several micrometres thick along the inner detector surfaces will yield a purer chromium oxide. In addition to the deposition of chromium on the internal cathode surfaces, these detector samples also undergo the oxygen bombardment process to form a chromium oxide layer before filling. Such detectors are labelled as ‘plated detectors’. All samples for all detector types have been filled with identical gas mixtures and to the same fill pressure.

Fifty-four detectors were processed for each of the three protective processes. Two separate ageing jigs with thirty-two positions were manufactured, one for each temperature, using the recommended circuit for this type of GM detector described in (5) and illustrated in **figure 2.1**. Each jig was loaded with ten plated detectors, eleven passivated detectors and eleven raw detectors. The room temperature jig was positioned 60 cm from a 6 GBq Caesium-137 gamma source. The high temperature jig was placed within an environmental chamber set to a temperature of 125 °C also situated 60 cm from the same Caesium-137 gamma source.

Figure 2.1: Circuit diagram for two detectors on each jig. All anode resistors, R_a , were in direct contact with the detector anode pins and chosen to have the Centronic recommended 10 M Ω resistances. The cathode or measuring resistors, R_m , were selected to have resistances of 56 k Ω to produce a 1 V output pulse.

The majority of the test equipment has been developed in-house at Centronic Ltd.. A variable power supply produced a variable voltage of (0 to 800 $\pm$ 2) volts across each jig. A multi-channel PicoLog 1216 data logger was then connected to the setup to monitor the output voltage pulse for each tube. The output was also connected to a scaler-timer to measure the count rate of each detector; this equipment was designed to count all input pulses above a set threshold of 100 mV. A switch-box was manufactured to isolate the signal from each GM counter.

The recommended 500 V ZP1200 operating voltage was applied during the ageing process. The initial average count rate for the detectors at room temperature was found to be (2572 $\pm$ 50) counts per second (cps) with a standard deviation of 110 counts and (1954 $\pm$ 45) cps with a standard deviation of 144 counts for the high temperature jig. Since the radiation is emitted uniformly in all directions, this difference is due to the environmental chamber attenuating some of the incident radiation.

All detector samples were exposed to the source for twenty-four hours a day. The V_s value, which is defined as the lowest applied voltage that produces a 1 V pulse across the anode resistor, for each detector was measured using the PicoLog every few weeks to capture any potential changes.

Count rate measurements for 1 second at fixed dose rate as a function of applied voltage, are typically acquired between 0 and 750 V resulting in the characteristic Geiger Plateau plots. For this purpose, the detector samples were removed from the set up and placed at a distance of 1 cm from a significantly weaker 0.6 GBq Caesium-137 gamma source at room temperature; this produced a count rate of approximately 450 cps.

At different ageing intervals, an internal cathode surface of each detector type was analysed. The samples were carefully cut open and studied under a Hitachi S3200N Scanning Electron Microscope (SEM) with the accelerating voltage set to 20 kV. Several regions of each cathode sample were studied. An energy dispersive x-ray (EDX) attachment was then used to obtain the elemental constituents at each region of interest. The aim of this EDX

analysis was to determine whether the halogen quench gas had reacted with the cathode. For a set of regions of interest per sample, the elemental compositions were recorded and averaged.

3. Starting Voltage Measurements

The detector sensitivity values and background counts for each sample remained constant with age. The starting voltage, or V_s , values as a function of the counts accumulated for the GM detector samples were recorded with a measurement uncertainty of ± 2 V and are shown in **figures 3.1**.

Figures 3.1: Detector starting voltage values as a function of the accumulated counts. (a) – at room temperature. (b) – at 125 °C. *Note: incomplete plot lines represent detectors that have been removed for surface analysis.*

The plated detectors held at room temperature showed a gradual increase in the V_s reading, which then appeared to become constant as the total accumulated counts increased. The average change for the V_s values was found to be an increase of (13.2 ± 0.7) V, with a standard deviation of 5 V, for 5.7×10^{10} accumulated counts.

The passivated and raw detectors held at room temperature gave V_s measurements that remained constant within the uncertainty. The average changes in their corresponding V_s values were calculated to be a drop of (1.8 ± 0.3) V, with a standard deviation of 1 volt, and an increase of (2.1 ± 0.7) V, with a standard deviation of 2 volts, respectively, these changes are within the spread of initial starting voltage values for nominally equal devices.

At 125 °C, the plated detectors exhibited constant V_s values after an initial rise, even as the total accumulated counts increased up to 3.3×10^{10} counts. The average change in the detectors' V_s was found to be an increase of only (3.3 ± 0.7) V, with a standard deviation of 2 volts. The average change in V_s for the passivated and raw detectors at this temperature is

more noticeable, decreasing by (11.0 ± 1.3) V, with a standard deviation of 4 V, and (4.9 ± 0.7) V, with a standard deviation of 2 V, respectively.

Preliminary investigations at 175 °C indicate even larger V_s drops for the un-plated samples of up to 21 V over a shorter ageing period of 1.0×10^{10} accumulated counts.

4. Plateau Plots

Different collections of plateau plots at different ageing statuses are shown in **figures 4.1**.

Figures 4.1: Plateau plots for the detector samples. (a) – at room temperature after accumulating 1.4×10^{10} counts. (b) – at room temperature after accumulating 5.7×10^{10} counts. (c) – at 125 °C after accumulating 1.1×10^{10} counts. (d) – at 125 °C after accumulating 3.3×10^{10} counts.

The lowest voltage value where the count rate passes 0 cps correlates with a detector's V_s value; however, the two are not identical due to the V_s measurement's set pulse-height threshold.

The plateau plots acquired for the room temperature detectors showed no significant changes in their gradients with age. The average gradient between 400 and 750 V was calculated to be (0.20 ± 0.02) cps/V, with a standard deviation of 0.06 cps/V.

At the elevated temperature, the majority of the detector plateaus maintained a consistent plateau shape where the average plateau slope was calculated as (0.25 ± 0.03) cps per volt,

with a standard deviation of 0.10 cps per volt. Two of the aged passivated detectors (25% of the sample size) did exhibit an increase in their plateau slopes; their final slope values were calculated as 0.46 cps per volt and 0.62 cps per volt. This was not found to be the case for their corresponding Vs measurements, which suffered a similar drop to all other passivated samples investigated.

5. Scanning Electron Microscope (SEM) Surface Analysis

The surfaces of the different detector types at different ageing stages were monitored with the SEM. The images shown in **figures 5.1** demonstrate that all the different detector types exhibited different internal cathode surface finishes.

Figures 5.1: SEM images of the internal cathode surface. (a) – for an un-aged plated detector. (b) – for a plated detector that has accumulated 4.3×10^{10} counts at room temperature. (c) – for a plated detector that has accumulated 2.1×10^{10} counts at 125 °C. (d) – for an un-aged passivated detector. (e) – for a passivated detector that has accumulated 4.3×10^{10} counts at room temperature. (f) – for a passivated detector that has accumulated 2.1×10^{10} counts at 125 °C. (g) – for an un-aged raw detector. (h) – for a raw detector that has accumulated 4.3×10^{10} counts at room temperature. (i) – for a raw detector that has accumulated 2.1×10^{10} counts at 125 °C.

The plated detectors have a smooth, yet heavily cracked surface. There is a possibility for such cracks to result in some trapped quench gas, or even traces of processing

contaminants, being released from the plating layer. This may explain the rise in plated starting voltages with age that have been observed. The passivated and raw detectors both had rough surfaces with numerous topographical features. The appearance of the surfaces for all samples did not seem to change as the total accumulated counts increased. Several regions were explored for each sample and similar features were observed everywhere.

6. Energy Dispersive X-Ray (EDX) Compositional Analysis

For each detector type, one cathode sample corresponding to each different ageing interval was analysed. Different areas of each cathode were highlighted and the resulting elemental constituents were recorded.

The plated detectors showed high average quantities of chromium ($85.6 \pm 0.8\%$) and oxygen ($10.7 \pm 0.8\%$); lesser quantities ($< 2\%$) of manganese, iron and carbon were present on the surface. These percentages were to be expected due to the presence of the chromium plating and the resulting chromium oxide formed. No bromine was detected across the plated cathodes at either temperature. This suggests that, within detection limits, the chromium plating layer resisted any interactions with the halogen quench gas.

The passivated and raw samples contained relatively high average amounts of chromium ($28.2 \pm 0.1\%$), iron ($62.2 \pm 0.5\%$) and oxygen ($5.9 \pm 0.5\%$); lower amounts ($< 2\%$) of carbon, silicon, manganese and bromine were also detected. Such percentages are to be expected for the type of stainless steel used and the formation of the metal oxide across the cathode surface. Silicon is often present as an alloying element in the steel used to construct the detectors; however, the only possible source of bromine is the halogen quench gas used. The elemental percentages recorded for all samples remained relatively consistent throughout the aging process. The presence of bromine was not related to the age or temperature at which the detectors were held, as shown in **figures 6.1**.

Figures 6.1: Bromine concentration across the GM cathode surface. (a) – at room temperature. (b) – at 125 °C.

When studying the oxygen content of the samples, the plated cathode surfaces were found to contain approximately 11% by weight when compared with the passivated and raw samples containing approximately 7% by weight, as shown in **figures 6.2**.

Figures 6.2: Oxygen concentration across the GM cathode surface. (a) – at room temperature. (b) – at 125 °C.

This increase is thought to be due to trapped oxygen within the micro-cracks of the plating layer. This also agrees with the rising starting voltage values only witnessed for the plated detector samples; oxygen is highly electronegative and will attract the electrons produced through radiation-induced detection events. This will act as an extra quenching mechanism. Greater voltages will thus be required to give the electrons enough energy to overcome this effect. Some studies, such as (9), have highlighted this effect by attempting to use oxygen as the primary GM quench gas.

Other surface techniques were explored to identify potential halogen quench gas interactions with the detector components. The X-Ray Photoelectron Spectroscopy (XPS) technique has been trialed; while the presence of the chromium oxide layers was confirmed, no bromine deposits were observed.

7. Conclusions

The effect of accumulated counts on GM detectors' operational parameters under constant irradiation at two different temperatures has been studied.

The raw and passivated detectors performed consistently with age at room temperature, whereas at 125 °C, both un-plated detector types suffered a drop in V_s with age. The plated

surfaces, however, were able to resist any significant performance deterioration at both room temperature and 125 °C, with the Vs remaining constant after an initial rise.

The plated ZP1200 detectors were found to produce consistent Geiger plateaus up to ages of 5.7×10^{10} accumulated counts at room temperature and 3.3×10^{10} accumulated counts at 125 °C. The only noticeable change in the performance of the plated samples was an initial increase in the measured starting voltages. This is thought to be as a result of trapped oxygen within the micro-cracks of the plating layer. The cathode surface morphology for all tubes remained constant with age at both temperatures.

No trace of bromine could be found across the surface of the plated cathode samples. The raw and passivated cathode samples showed minimal quantities of bromine. Liebson and Friedman have shown in (6) that less quench gas will produce detectors with lower Vs values. A lack of change in the bromine concentration with detector age did not match what was expected from the changes in the corresponding Vs values. This is thought to be due to the minimal amount of depletion of the quench gas, which is not yet detectable within the EDX's resolution capabilities.

The ZP1200 GM samples used for the research discussed in this paper have been designed to operate at relatively low voltages with minimal amounts of bromine. The investigations in (4) show measurable evidence of reactions between the quench gas and the detector components for Vs changes greater than 100 V. The samples used in (4), however, contained significantly higher quantities of bromine, a platinum-based protective coating and were aged at a higher temperature of 200 °C. These factors are thought to have contributed to the larger changes they observed.

When comparing the different detector types, all three protective mechanisms produced long-term stable detectors at room temperature. Under such conditions, all processes were found to be effective methods of restricting halogen corrosion; GM detectors can thus be manufactured using any of these processes.

At 125 °C, the plated detectors had superior long-term performance characteristics after an initial Vs conditioning phase. It is for this reason that chromium plating is recommended as the most effective protective process when operating GM detectors at elevated

temperatures. Over the temperature range studied, the main factors affecting the performance parameters of these detectors seemed to be related to the surface quality and an initial short-term oxygen outgassing process when in use.

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