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SPURIOUS THERMOLUMINESCENCE OF SOILS

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FOOTNOTES:

1. From the Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles, California 90024.
2. These studies were supported by Contract AT (04-1) GEN-12 between the Atomic Energy Commission and the University of California.
3. The authors are indebted to Mr. Robert Mullen for determining the oxygen contamination in nitrogen and argon gases used in this study. The determinations were done with AEI MS 10 C1 mass spectrometer.

Table 1

Surface to volume glow ratios of soils unirradiated and irradiated by Co60 photons

Soil*	Unirradiated			Irradiated		
	Glow Curve Area Volume Glow** cm ²	Surface Glow*** cm ²	Surface/ Volume Glow Ratio	Glow Curve Area Volume Glow** cm ²	Surface Glow*** cm ²	Surface/ Volume Glow Ratio
Aiken	0.00	18.3	-	0.0	22.0	-
Egbert	4.33	0.20	0.05	15.23	4.64	0.30
No. 4FF	135.50	46.40	0.34	190.23	58.74	0.31
Yolo	25.23	13.20	0.52	47.97	28.26	0.59
Hanford	5.87	9.83	1.67	45.17	22.30	0.49
No. 9RDG	3.23	13.20	4.09	20.77	28.26	1.12

* Glow intensity of soil No. 4FF was measured at the lower instrument sensitivity level (9.00 + 3.0) than the other soils (950 + 3.0).

** Measured in Ar atmosphere.

*** Difference of measurements made in air and Ar.

FIGURE LEGENDS:

- FIG. 1** Block diagram of the thermoluminescence equipment.
- FIG. 2** "Natural" thermoluminescence of soils in air, nitrogen and argon atmospheres.
- FIG. 3** Thermoluminescence of soils in air, nitrogen and argon atmospheres one-half hour after exposure to Co60 gamma rays.
- FIG. 4** The amount of light output by the irradiated soils after subtracting their "natural" thermoluminescence.

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SPURIOUS THERMOLUMINESCENCE OF SOILS

H. Nishita and M. Hamilton^{1, 2, 3}

In radiation dosimetry applications, spurious thermoluminescence means any glow induced by stimuli other than ionizing radiation (8). The presence of thermoluminescence in an unirradiated solid may be caused by stimuli such as pressure, friction, chemical reaction and gas adsorption. The spurious thermoluminescence induced by pressure is designated as piezothermoluminescence and that induced by friction as tribothermoluminescence. Recently, Aitken, et al (1) have demonstrated the piezo effect with limestone after subjecting it to a pressure of 10 tons/sq. in. for 5 minutes. The pressure-induced glow was considered to be partially surface effect and partially volume effect, which are independent of one another (1, 8). The tribo effect is considered to be a surface effect. To obtain the full surface effect with LiF, both movement (by pouring or tumbling) of powder before and the presence of oxygen during readout were necessary (13). The surface effect in LiF was eliminated or greatly reduced by reading out in nitrogen (1, 2, 6-8, 13). The radiation (γ , α and β) induced glow is considered to be a volume effect, since it is not significantly affected by nitrogen (1, 8). Chemical thermoluminescence has been observed during the decomposition of sodium bicarbonate, zinc carbonate and potassium chlorate (5). Thermoluminescence resulting from the physical adsorption of gases has been discussed by Bettinali and Ferraresso (3). These investigators also outlined briefly the mechanisms giving rise to the different types of

spurious thermoluminescence. In general, most types of spurious thermoluminescence appear to arise from the presence of adsorbed oxygen on the surfaces of solid materials.

This paper gives the spurious thermoluminescence in several different kinds of soils. This study on soil thermoluminescence stems from our interest in using soil to estimate gamma ray exposure in a Cs137 radiation field established in a natural environment.

MATERIALS AND METHODS

Six soils (No. 4FF, No. 9RDG, Aiken clay loam, Hanford sandy loam, Yolo sandy loam and Egbert muck) representing widely different types were used for this study. Their chemical properties were reported previously (9). Egbert muck is a saline organic soil (32.9% O.M.). Soil No. 9RDG and Aiken clay loam are acidic, kaolinitic soils. Hanford sandy loam is a slightly acidic soil, while Yolo sandy loam is slightly basic. Illite and montmorillonite are, respectively, the predominant clay minerals. Soil No. 4FF is a non-saline calcareous soil with montmorillonite as its predominant clay mineral. The photon irradiation of the soils was done with the UCLA 10,000 curie Co60 source.

The measurements of the emitted light as a function of heating temperature (glow curve) of the thermoluminescent materials were made by the equipment shown in the block diagram (fig. 1). This equipment is a modified version of the one described previously (9). In this equipment, the two Brown recording potentiometers used in the previous system were replaced with the Hewlett-Packard X-Y recorder (Model 2D-2), so that the glow curve was obtained directly. However, the portion of the glow curve corrected for black body radiation, which was

determined as described before (9), was drawn manually. The threshold temperature for black body radiation varied somewhat with the soil used, but it usually occurred in the range of 350° to 400°C . The heating system was completely reconstructed, so that the samples were heated directly on the heater. The heater was made of stainless steel plate (2.5 mm thick) with a circular recess (17.5 mm dia. x 1.3 mm depth) for holding the sample. Also, a Hewlett-Packard temperature programmer (Model 240M) was inserted to obtain various heating rates, linear from ambient to around 500°C . All of the present results were obtained by using a heating rate of 500°C per minute. Provision also was made to maintain a continuously changing nitrogen or argon atmosphere in the sample heating chamber (flow rate: 1 l./min).. The sample was flushed for one minute before each run.

RESULTS AND DISCUSSION

Figure 2 shows the "natural" thermoluminescence of soils in air, argon (Ar) and pre-purified nitrogen (PP- N_2) atmospheres. The oxygen contamination in Ar was 149 ± 34 ppm and that in the PP- N_2 was 34 ± 6 ppm. In air, the areas under the glow curves, which represent the total light outputs by the soils, were in the following order of magnitudes: Egbert (45.3 cm^2) < Hanford (157.0 cm^2) < No. 9RDG (164.3 cm^2) < Aiken (183.0 cm^2) < Yolo (432.3 cm^2) < No. 4FF (1819.0 cm^2). Some of the causes for the differences of thermoluminescence among these soils were discussed previously (9, 10). Using air atmosphere as the basis of comparison, the relative thermoluminescence in Ar (table in fig. 2) ranged from 0.0 for Aiken to 0.96 for Egbert. In

PP-N₂, the relative thermoluminescence ranged from 0.0 for Aiken to 1.06 for Egbert. The thermoluminescence in PP-N₂ was generally greater than that in Ar. In fact, in PP-N₂ the thermoluminescence of the organic soil (Egbert) was increased over that in air for some undetermined reason. This increase, which occurred in the temperature range above 390°C, appeared to be due to the inorganic fraction of the soil, since the organic fraction (separated by the HF-HCl method (11)) showed no detectable thermoluminescence in air or PP-N₂ atmosphere. The Aiken clay loam exhibited an interesting effect in that it showed no detectable thermoluminescence in PP-N₂ or Ar atmosphere. Consequently, if the decrease of thermoluminescence in PP-N₂ or Ar relative to that in air is taken to be spurious glow and if spurious glow is assumed to be surface glow, then Aiken, unlike the other soils examined, showed no detectable amount of "natural" volume glow (the glow originating within the volume of the luminescent particles).

Figure 3 shows the glow curves obtained for the six soils in air, Ar and PP-N₂ atmospheres after exposure to 1,000 R of Co60 photons. In air, the areas under the glow curves were in the following order: Egbert (198.7 cm²) < Aiken (220.0 cm²) < No. 9RDG (439.3 cm²) < Hanford (647.7 cm²) < Yolo (762.3 cm²) < No. 4FF (2489.7 cm²). Note that this order is different from that for the "natural" glow. In addition to the gases listed above, the glow curves for these irradiated soils were obtained also in research grade nitrogen (RG-N₂), which contained < 1 ppm oxygen contamination. The glow curves obtained in RG-N₂, however, are not shown in figure 3, because they were virtually superimposed on those obtained in Ar for the corresponding soil. Using air

as the basis of comparison, the relative light output in RG-N_2 was No. 4FF, 0.77; No. 9RDG, 0.45; Aiken, 0.0; Hanford, 0.68; Yolo, 0.66; and Egbert, 0.69. Note that these relative light outputs are similar to those for the corresponding soil in Ar (table in fig. 3). Figure 3 indicates that Ar was again more effective in reducing spurious glow than PP-N_2 . This, of course, implies that RG-N_2 was more effective than PP-N_2 in reducing spurious glow. Thus, spurious thermoluminescence appeared to be related to oxygen contamination in the flush gas as observed by several previous investigators (1, 2, 6-8, 13), who worked with other materials.

In comparison to PP-N_2 , the greater apparent effectiveness of Ar in reducing spurious glow despite its relatively high oxygen contamination may be due to its lower thermal conductivity, which is about two-thirds that of air or N_2 (8). For very fine powders, the transfer of heat between the solid surfaces is negligible compared to that transmitted by the gas between the particles (4). Because of the lower thermal coupling between the heating pan and the LiF granules in Ar, Nash, Attix and Schulman (8) found a shift in the photon-induced glow peak toward a higher temperature at a relatively fast heating rate. The faster the heating rate, the greater was the lag of the phosphor temperature behind the pan temperature. With the mineral soils examined in the present study (heating rate of $500^\circ\text{C}/\text{min.}$), the lowering of the height of the glow peaks occurred, but there was no obvious shift of the peaks toward the higher temperature in argon. The glow peak for the organic soil (Egbert muck), however, showed a definite shift toward the higher temperature in PP-N_2 as well as in Ar (figs.

2 and 3). Thus, besides the relative thermal conductivity of the gases, there appeared to be other undetermined factor or factors that need to be considered.

Figure 3 also shows that the spurious thermoluminescence occurred over the entire temperature range with the major fraction of it occurring above 250°C in the relatively deep trap zone. The latter effect is qualitatively in agreement with other investigations. For example, working with LiF powder, Svarcer and Fowler (13) found that spurious glow occurred in the range of 300° to 400°C . With a sample of limestone, the spurious glow, which was considered to be from micaceous impurities, was resolved into two peaks at 420° and 530°C (1). Svarcer and Fowler (13) suggested that spurious glow was due to the states of crystal surfaces dependent on absorbed oxygen. They also suggest that since oxygen has a strong affinity for electrons and would trap electrons in a fairly strong energy bond, the formation of deep traps is consistent with expectation.

Figure 4 shows the glow curves for Co60-irradiated soils after their "natural" thermoluminescence has been subtracted. The spurious thermoluminescence has been eliminated also from these results, since the readout was done in Ar. Assuming that spurious thermoluminescence is surface glow, the results shown in figure 4 indicate the Co60-induced volume glow. It will be noted, however, that these curves represent only an approximation of the Co60-induced volume glow, because during the irradiation period, certain amounts of "healing" of defects that existed in the crystalline materials of the soil before irradiation may occur. This, of course, means that the number of the natural

defects existing before irradiation with Co60 photons may be different from that after irradiation. In any case, among the soils examined (except soil No. 4FF), the volume glow appeared to be predominantly in the low temperature range ($< 250^{\circ}\text{C}$), while the surface glow (fig. 3) occurred predominantly in the high temperature range ($> 250^{\circ}\text{C}$). In other words, the Co60-induced volume glow was due predominantly to the shallow electron (hole) traps, while the surface glow was due mostly to the deep traps. The exceptionally high volume glow shown by soil No. 4FF in the high temperature range was primarily due to its high lime content (33%). This was indicated by the fact that the thermoluminescence in the high temperature range was reduced more than 90 per cent after the soil was leached with 0.1 N HCl.

The proportion of the surface glow to the volume glow depended on the kind of soil. This is readily seen in table 1, which gives the surface/volume glow ratios for soils that have been unexposed and exposed to 1,000 R of Co60 photons. Excluding Aiken, the surface/volume glow ratios ranged from 0.05 to 4.09 for the soils that were unexposed to Co60 photons. After exposure to 1,000 R of Co60 photons, both the volume glow and the surface glow of the soils increased considerably, but their surface/volume glow ratios were approximately the same, less or greater than the ratios for the corresponding soils unexposed to Co60 radiation. Thus, the increase of the volume glow relative to the increase of the surface glow depended on the soil. These differences were consistent with expectation since the soils differed widely in their physical and chemical characteristics. The Aiken clay loam irradiated to 1,000 R showed an increase of surface glow, but for some

undetermined reason, it did not show any detectable amount of volume glow until it was irradiated to 2,000 R. This characteristic of Aiken clay loam demonstrates that it is possible to obtain an increase of surface glow on irradiation without the formation of detectable amounts of volume glow.

The mechanism for the formation of surface glow is still not well understood. Perhaps a mechanism similar to that hypothesized by Bettinali and Ferraresso (3) is applicable. Adsorption of oxygen on the solid surfaces may produce free electrons or holes which recombine with charges of opposite sign to produce an electron-hole luminescent process. The formation of spurious thermoluminescence upon irradiation might occur as follows. During irradiation, some electrons at the crystal surfaces are displaced by the incident photons. These electrons could be displaced into the volume of the crystals or ejected into the surrounding ionized air, depending on the angle of incidence of the photons. This would produce additional sites of charge imbalance or defects on the crystal surfaces. Depending on the chemical nature of the crystals, a certain fraction of these defects could be additional sites for oxygen adsorption producing the surface effect. Furthermore, the incident photons cause ionization and to some extent produce additional defects such as cation and anion vacancies within the crystal. These would be increased in number above that which was present before irradiation. This, in turn, may increase the probable number of electrons, holes and defects that could migrate to the crystal surfaces at any given temperature. The surfacing defects that produce local areas of positive charge may then constitute additional

sites for the adsorption of oxygen involved in the electron-hole thermoluminescent process.

SUMMARY

Spurious thermoluminescence of six soils differing widely in physical and chemical characteristics was examined. As observed by previous investigators working with other materials, the spurious glow of soils also appeared to be dependent on the oxygen adsorbed on the surface of the luminescent particles. The amount of "natural" spurious thermoluminescence depended on the kind of soil. Spurious (surface) glow and volume glow were increased considerably by exposing the soils to Co60 photons. The increase of the surface glow relative to that of the volume glow on irradiation depended also on the soil. One soil (Aiken clay loam) examined showed that it is possible to obtain the increase of surface glow on irradiation without the formation of detectable amounts of volume glow. Except for one soil (soil No. 4FF), the volume glow of the soils exposed to Co60 photons occurred predominantly in the low temperature range ($< 250^{\circ}\text{C}$), while the surface glow occurred predominantly in the high temperature range ($> 250^{\circ}\text{C}$). The large amount of volume glow induced in soil No. 4FF by irradiation appeared to be due to its high lime content.

FIG. 1 Block diagram of the thermoluminescence equipment.

FIG. 2 "Natural" thermoluminescence of soils in air, nitrogen and argon atmospheres.

FIG. 3 Thermoluminescence of soils in air, nitrogen and argon atmospheres one-half hour after exposure to Co60 gamma rays.

FIG. 4 The amount of light output by the irradiated soils after subtracting their "natural" thermoluminescence.