Luminescence in Coal. The Effect of Mineral Matter, Air, and Swelling

Rita K. Hessley

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101

Introduction

Based on the work of Coyne et al (1), who showed that simple dehydration of clay minerals results in measurable spontaneous emmission of light, we have undertaken the investigation of spontaneous light emmission in coals (2). Coal is frequently found in regions where clay minerals are abundant. Following Coyne, our initial study (2) monitored light emission from coal when an aqueous slurry of micronized coal was subjected to dehydration over $CaSO_4$. That work showed that luminescence did occur in a coal containing relatively little inorganic material (3% ash) as well as in a coal with a substantially higher (18%) content of mineral matter.

Several questions arose from that study. In particular, because the addition of as little as 1-2% (w/w) kaolinite to a coal sample exhibited a marked increase in luminescence, it was critical to determine, if possible, whether the photon release was caused only by the mineral matter content and not by the effect of dehydration on the coal structure itself. Thus, one goal of this phase of the investigation was to look for spontaneous luminescence in ash-free coal.

A second question was whether the phenomenon was related to, or dependent upon, excitation of the oxygen or nitrogen in air. Thus, the second goal of this work was to examine samples prepared with the exclusion of air.

Finally, Coyne et al (3) have also shown that kaolinites exhibit pronounced spontaneous luminescence as they swell in a slurry prepared with various amines. Because coal, also, generally swells readily in amine solvents, several measurements were carried out to determine whether coal luminescence could be detected as a function of solvent swelling.

EXPERIMENTAL

Preparation of Samples

The coal used for this study is a Western Kentucky hvA bituminous coal obtained from the Western Kentucky University Center for Coal Science. A summary of the analysis of the coal is given in Table I.

Table I

Analysis of Coal Bank Sample #86025

Moisture(as det.)	4.07	Carbon	66.74
Ash	15.50	Hydrogen	4.59
VM	35.3	Nitrogen	1.42
fixed Carbon	49.2	Sulfur	4.55
BTU	11,012	Oxygen(diff)	6.71

A portion of the 60-mesh coal was beneficiated in $ZnCl_2$ media of specific gravity 1.30. After cleaning, the recovered coal was micronized for 2 minutes in a Union Process Model 1-S stirred ball attritor mill. This effectively reduced the average particle size of the sample to 10 microns. Unbeneficiated 60-mesh coal was subjected to exhaustive solvent extraction with refluxing Dimethylformamide (DMF) under N_2. The

residue was then washed repeatedly with refluxing methanol under N_2 before being dried in a vacuum oven. The extracted material was recovered from the DMF and was also washed, and dried in vacuo.

The ash from the same coal was obtained according to ASTM D3173. The ash analysis is shown in Table II.

Table II

Major and Minor Metal Oxides in Ash from Coal Bank Sample #86025

	Raw	Clean
% SiO_2	42.9	41.4
% Al_2O_3	16.3	19.7
% Fe_2O_3	33.3	21.2
% CaO	1.10	.61
% MgO	.51	.33
% K_2O	1.46	1.10
% MnO_2	.04	.01

Measurement of Luminescence

Spontaneous luminescence was measured as a function of time. Single photon monitoring was carried out using the Packard Model 1500 "TriCarb" liquid scintillation counter. Data were recorded as counts per minute and were printed at one minute intervals for 99 minute maximum monitoring period.

A sample slurry was prepared by direct weighing and mixing of the solid and water. Typically, a coating of about 2.5 cm was applied to the inside of a standard scintillation vial above about 1 cm of indicating $CaSO_4$. For all trials, the slurry was applied manually and it was difficult to apply precisely the same amount of sample each time. Generally, 80-120 mg samples were used which consisted of at least a water:coal ratio of 2:1. For swelling experiments, the method described by Coyne (3) was used to prepare the samples. Pyridine and DMF were used as the swelling solvents. To prepare samples in an air-free environment, a stream of argon was used to purge the vial prior to and during application of the slurry.

RESULTS AND DISCUSSION

Figure 1 shows a portion of the photon output for the dehydration of the whole coal #86025 (15.5% ash). As in our previous study, the photon count was observed to decay monotonically until spontaneous luminescence occurred at some time after initiation of drying. Figure 2 shows data for the beneficiated sample (1.25% ash). These data confirm our earlier observations that even low ash coals exhibit luminescent behavior. Figure 3 shows that extraction residue, which retains most if not all of the inorganic matter in coal, also displays spontaneous luminescence during dehydration. The traces in these figures cannot be compared directly with regards to the time required for the on-set of photon emmission nor with regards to the intensity. Our earlier work showed that time and intensity differences between samples are dependent on the sample size (thickness) and total moisture content.

Figure 4 shows the trace of counts per minute with time for the material extracted from coal with refluxing DMF. This material is essentially ash-free, and shows no spontaneous luminescence during the period monitored. This is striking evidence that ash-free coal does not exhibit luminescent behavior. Of course, the extract from additional samples needs to be studied in order to confirm this observation conclusively. Measurement of photon emmission in recovered ash (Figure 5) was difficult to measure and was not nearly as impressive in its intensity as is

observed with kaolinite (1). The ash was very granular and difficult to grind sufficiently fine to prepare a smooth paste. It may also be important that the ash obtained from the coal used in this study was brick-red and contained 33.3 % (w/w) Iron oxide and, correspondingly, a smaller quantity of aluminum and silicon oxides. For comparison, the luminescence during dehydration for a coal ash containing much less iron oxide (based on its white coloration) was recorded and is shown in Figure 6. These data suggest that photon emmission from ash may be affected by its overall composition.

All attempts to induce measurable photon emmission in either whole coal or coal extract by solvent swelling have been unsuccessful. One explanation is that the small (mg) quantities of coal being used swell rapidly enough in the two amine solvents tested that luminescence accompanying swelling may be dissipated in the time required to grind and prepare the sample (3). These experiments are being continued using other, less vigorous, swelling solvents.

Using kaolinite, there is no change observed for spontaneous luminescence in samples prepared under argon. However, there remains some question whether the sample vials are air-tight throughout the counting period. Thus, our initial trials to determine the effect of air on the presence and intensity of spontaneous luminescence in coal are incomplete.

CONCLUSIONS

It has been shown that spontaneous luminescence in coal during dehydration is dependent directly on the ash, or mineral matter content of the coal. In the absence of any ash, no photon emmission is observed. Coal extraction residue retains the property of luminescenc during dehydration; coal ash also exhibits luminescence, but appears to be affected strongly by the presence of iron oxide (or by the actual clay mineral content). Quantities of ash as small as a few percent by weight dispersed throughout the coal matrix are sufficient to cause the phenomenom to be observable. Work is continuing to explore the effects of air and solvent swelling.

REFERENCES

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2. Hessley, R. K. and L. M. Coyne, Preprints, Amer. Chem. Soc. Div. Fuel Chem., Denver, 32(1), 547 (1987).

3. Coyne, Lelia M., Glenn Pollack and Roger Kloepping, Clays Clay Miner., 32(1), 58 (1984).

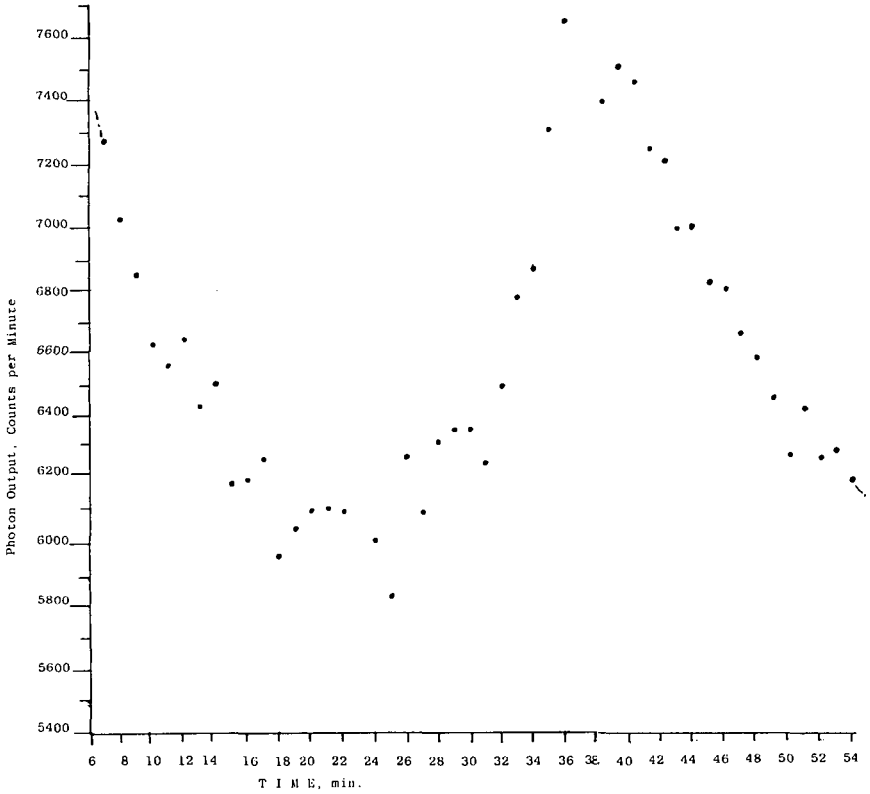

Figure 1. Photon output for Dehydration of whole coal (15.5% ash)

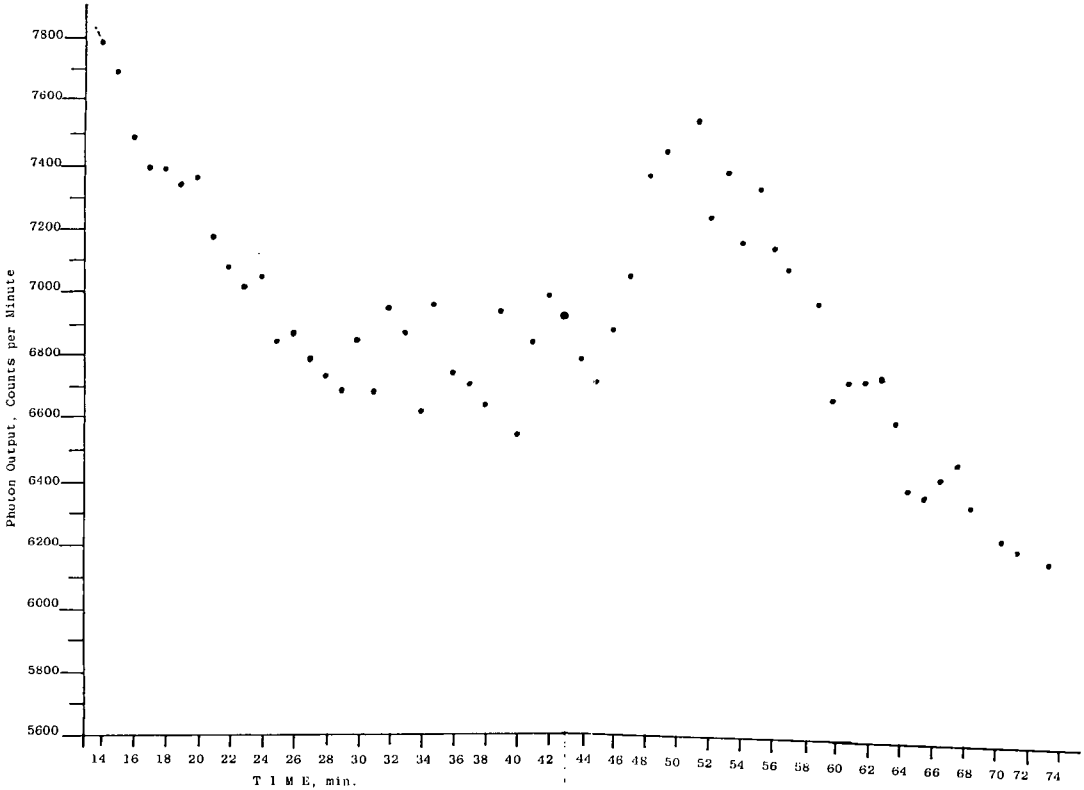

Figure 2. Photon Output for Beneficiated coal (1.25% ash).

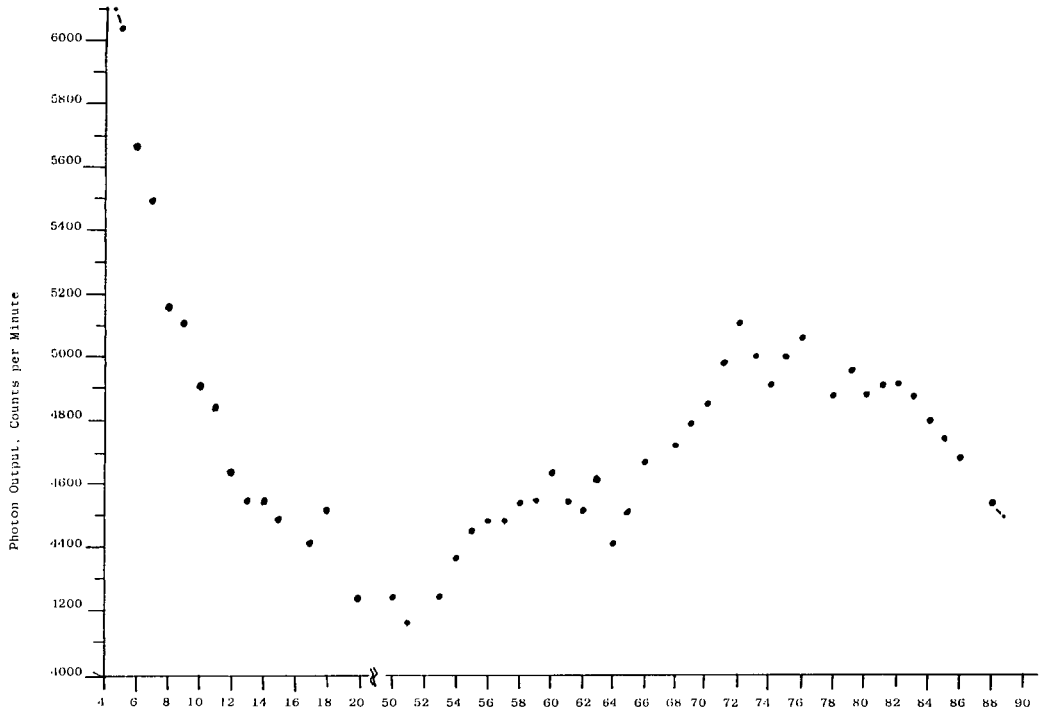

Figure 3. Photon Output on Dehydration for Coal Extraction Residue

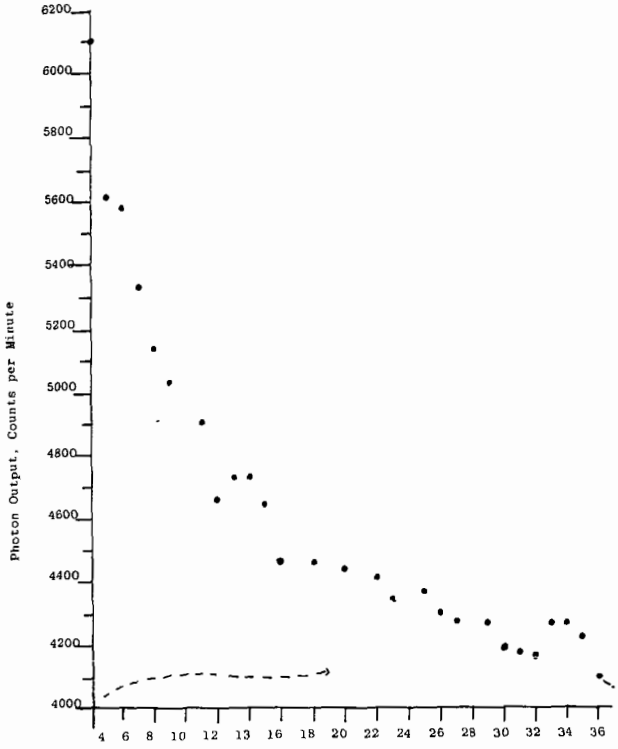

Figure 4. Photon Output for Dehydration of Whole Coal Extract

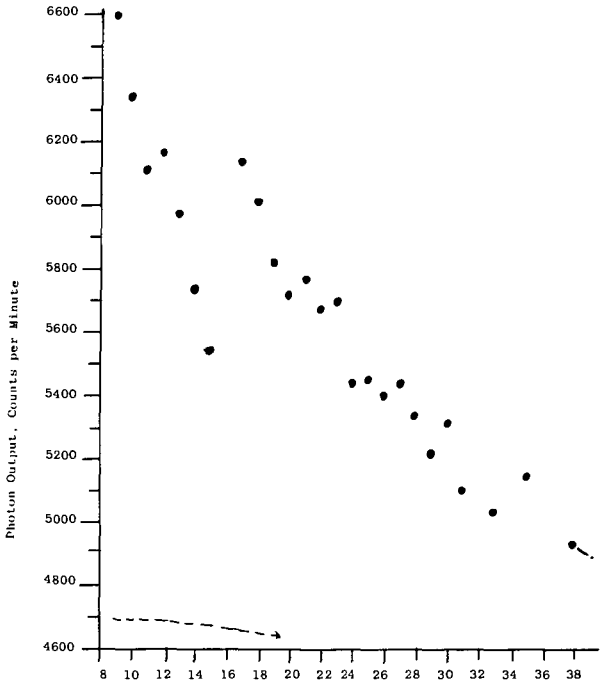

Figure 5. Photon Output for Dehydration of Recovered Coal Ash

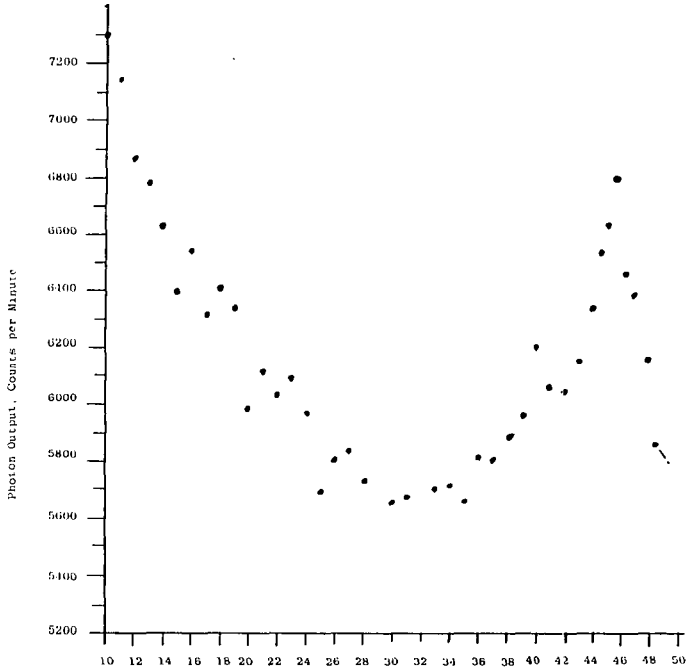

Figure 6. Photon Output for Dehydration of a Low-Iron Ash