Thermoluminescence of cement

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Abstract. Cement is found to be a thermoluminescent material. The glow curves of ordinary portland cement obtained from two different sources are found to be qualitatively similar. White cement (J K Brand) exhibits intense thermoluminescence (TL) compared to Birla white brand. The emission of J K white cement seems to be mainly due to Mn impurities which enters the product through limestone, the major ingredient in the preparation of cement. The possible use of TL as a spectroscopic technique to characterize cement is discussed.

Keywords. Thermoluminescence; cement; spectroscopic characterization.

1. Introduction

Thermoluminescence (TL), the emission of light following the previous absorption of energy from radiation, is a phenomenon which is exhibited by a large number of insulating and semiconducting solids. It has found wide application in practical areas like radiation dosimetry, dating of archaeological and geological materials (Horowitz 1983; Aitken 1985; McKeever 1985). However, several novel and at first sight, unlikely applications have also appeared in literature from time to time. Amongst such attempts relevant to the present study are the possible applications of TL in quality control in industry and forensic science (Nambi 1977). Nambi (1977) gave examples of the fact that in principle TL could be used in quality control of industrial products like glass, ceramics and semiconductor. Keeping these facts in mind the TL response of cement exposed to gamma radiation has been tested.

Though the principal constituent of cement is limestone, there are a variety of cements differing in chemical characteristics which are used for specific purposes. In this investigation we have studied portland cements from only three sources viz. Hundung (Manipur), Bokajan (Assam) and Gotan (Rajasthan). The possible applications of TL of cement are discussed keeping the experimental observations of the glow curves of the material.

2. Experimental

2.1 TL recording system

All the TL curves are recorded using the commercial recording system model TL 1404 (Indotherm Instruments Pvt. Ltd., Bombay). It is a system capable of providing linear heating at any desired rate that can be varied continuously from 10°C/min to 1000°C/min. The sample can be heated up to 600°C. However, in the present case the sample is heated to a maximum of about 450°C to avoid the undesirable black body radiation. The heating rate in most cases is about 175 to 200°C/min. The glow curves are recorded on a two pen strip chart recorder.

2.2 The material

Cements from three sources are studied. They are (i) Portland Cement of the Hundung Mini Cement Plant (Ukhrul Dist., Manipur), (ii) two varieties of portland cements from the Bokajan cement factory (Assam) commercially sold as portland cement (PC) and ordinary portland cement (OPC) and (iii) white portland cement having rapid hardening properties obtained from the J K white cement works (Gotan, Dist. – Nagpur, Rajasthan) and the Birla white portland cement works (Kharia Khangar, Dist., Jodhpur).

2.3 The source of excitation

Excitation of the cements is done by irradiating it with γ -rays obtained from Co_{60} source with dose rate of 0.5675 Gy/s. In all the cases reported here the dose of radiation is 4 kGy.

3. Results and discussions

TL curves of cement irradiated with a dose of 4 kGy are shown in figure 1. The glow curve of Hundung cement exhibits four glow peaks around 120, 150, 240 and 325°C for a linear heating rate ($\beta = 200^\circ\text{C}/\text{min}$). The glow curves of two varieties of Bokajan cement also exhibit four peaks around the same temperature range. However, in the later case in one sample the 150 and 240°C peaks are highly overlapped showing a flat zone over a temperature range of 150 to 270°C (figure 1, curve b). TL curves of

Figure 1. TL curves of different varieties of cement irradiated with 4 kGy of γ -radiation ($\beta = 200^\circ\text{C}/\text{min}$). Curves a, b and c are for samples obtained from Hundung, portland cement and ordinary portland cement from Bokajan.

Figure 2. TL curves of J K white (curve a) and Birla white (curve b) cements irradiated with 4 kGy ($\beta = 180^\circ\text{C}/\text{min}$).

J K white cement and Birla white cement recorded under almost similar condition exhibit a peak in the temperature range $140\text{--}155^\circ\text{C}$ along with two peaks (figure 2). TL curve of J K white cement (curve a, figure 2) has a very intense peak at around 155°C with two weak peaks around 225 and 400°C . On the other hand Birla white cement (curve b, figure 2) shows three peaks at around 142 , 242 and 349°C in such a way that the third peak around 349°C is more intense than the first peak at 142°C . These results show that cement can be termed as a thermoluminescent material exhibiting number of TL peaks between room temperature (27°C) to 450°C . Now the question that arises is: what are the possible applications of the phenomenon of TL that is exhibited by this commonly used building material.

The first criteria required for any possible application of TL is the stability of the signal. This has been checked for the Hundung cement (as a representative of ordinary variety) and the J K white (as a representative of white variety). Figure 3 shows the effect of room temperature (27°C) fading of TL of Hundung cement. As expected the lower temperature peaks viz. 120 and 150°C peaks decrease in intensity but the higher temperature peaks viz. 240 and 325°C peaks are quite stable showing $\approx 14\%$ loss when stored for three days at room temperature (figure 3). The fading is still less ($\approx 4\%$) for the higher temperature peak in case of white cement (figure 4). In short these experiments demonstrate that the higher temperature TL peaks of cement are quite stable when stored at room temperature.

Though as early as 1938 the application of TL in the control of feldspars in ceramic product has been described (Nambi 1977), such attempts have not received attention of the industries. Recently it has been demonstrated that if properly calibrated the technique of TL can make it a simple but powerful tool for estimating the level of mixed phases in feldspar (Prescott *et al* 1990). Ordinary portland cement consists essentially of tricalcium silicate, dicalcium silicate, tricalcium aluminate; and tetracalcium aluminoferrites. Since the present work has shown that cement is thermoluminescent showing rather consistent glow pattern for samples collected from two different sources (figure 1) its TL behaviour may also find applications in estimating the mixed phases as shown in the case of feldspar. It might also be possible to ascertain whether a particular sample has come from a known source which may find application in

Figure 3. Effect of room temperature (27°C) fading of TL of Hundung cement. Curve a is a TL glow curve with no fading. Curves b and c are TL glow curves with 1 and 3 days fading ($\beta = 200^\circ\text{C}/\text{min}$).

Figure 4. Effect of room temperature (27°C) fading of high temperature TL peak of white cement irradiated with 4 kGy of gamma radiation. Curve a is with no fading and curve b is with 3 days fading (In both cases the low temperature peak has been thermally cleaned).

detecting forgery (an area of forensic science). The present preliminary study of cement is hoped to pave a way in that direction.

The glow curves of most materials are complex (McKeever 1985). In that sense the glow curves of cement, if one takes into its various constituent compounds, is rather simple. This is more so in case of white cement. Its relative high sensitivity has tempted us to investigate its glow curve in more detail. Because of the intense glow (orange-red as seen by naked eyes), it has been possible to examine the TL emission with the help of filters. It has been found that most of the emission is in the red region though emission is also found in the green and blue regions. The glow curve of white cement recorded using different filters is shown in figure 5. The TL emission of white cement occurring mostly in red region can be explained on the basis that limestone is one of the major input in cement production and its TL emission consists of a broad peak centred around 5950–6350 Å depending upon the

Figure 5. Monochromatic TL curves of white cement ($\beta = 180^\circ\text{C/min}$). Curves a, b and c correspond to TL recorded using red, green and blue filters respectively.

Mg and Mn constituents (Sankaran *et al* 1983). This emission has been attributed essentially to Mn impurity which is a well known luminescent centre in many phosphors. Therefore, the TL emission in cement most probably takes place at Mn impurity site which enters the product through the use of limestone.

Ordinary portland cement is grey in colour because of the presence of iron oxide. On the other hand white cement contains lesser amount of iron oxide. White cement is manufactured in the same way as ordinary portland cement except using China clay (Kaolin) together with limestone free from certain specified impurities. The results of the chemical analysis of the samples used in the present work is shown in table 1

Table 1. Chemical analysis of cements used.

Sample	LOI (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	CaO (%)	MgO (%)
Hundung OPC (Manipur)	2.60	19.50	4.05	6.50	61.00	1.60
Bokajan PPC (Assam)	10.35	21.07	3.90	5.10	52.72	1.70
Bokajan PPC (Assam)	4.45	21.09	4.05	5.20	58.00	2.34
J K white (Gotan, Rajasthan)	7.43	21.93	0.33	5.08	59.11	2.30
Birla white (Jodhpur)	2.57	21.87	0.31	5.24	63.99	1.17

Figure 6. Curve fitting of the most intense TL peak of white cement ($\beta = 90^\circ\text{C}/\text{min}$). ●●●●, experimental curve; ---, numerically generated curve ($E = 1.2\text{ eV}$, $s = 2.2 \times 10^{13}/\text{s}$ and $b = 2.0$); -.-, difference curve showing the existence of additional peaks.

which shows that white cement contains iron oxide though it is one order of magnitude less compared to ordinary cement. Iron is a well known quencher. Since TL of Birla white cement is less intense (one order of magnitude) than that of J K white cement though they contain similar amount of Fe_2O_3 , it is doubtful if iron impurities play any definite role in TL of cement. This is possible if iron is present in the Fe_2O_3 phase and not as an impurity.

TL of a complex system like cement is expected to be highly complex. Surprisingly this is not so (figures 1 and 4). Analysis of glow curve emitted by more than one kind of compound is of no meaning. However, if one can fit any glow peak to simple models (Randall and Wilkins 1945; Garlick and Gibson 1948; Chen 1969), one can conclude that the particular peak most probably has its origin to a specific constituent. Keeping this in mind the intense peak of white cement has been analyzed. The irradiated sample is stored for three days to allow the unstable component to decay. TL of such a sample is recorded with $\beta = 90^\circ\text{C/s}$. The intense peak occurs at 150°C (figure 6). The symmetry factor (also known as shape factor) of the peak is found to be 0.52 showing that it follows second order kinetics (Chen 1969). Curve fitting of this peak using the second order kinetics equation (Garlick and Gibson 1948) yields $E = 1.2\text{ eV}$, $s = 2.2 \times 10^{13}/\text{s}$ (figure 6). This demonstrates that this peak is elementary in nature originating from a specific constituent of cement which needs to be identified. This requires further work.

4. Conclusions

The results can be summarized as follows:

- (i) Cement is a thermoluminescent material.
- (ii) Since the TL of ordinary variety of cement obtained from two different sources are qualitatively similar, TL may be used as a spectroscopic technique to characterize the material, which may find use in quality control and forensic science.
- (iii) Mn impurity seems to be the luminescent centre. This is certain at least in the case of white cement.

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