Summary

This paper relates to the method of exploration for hydrocarbons in particular by using thermoluminescence analysis methods. Thermoluminescence is the phenomenon of emission of light caused by thermal activation of trapped charge and recombination of detrapped charge carriers with their counterpart. Thermoluminescence emission from the material depends on defects present in the material. A method for determining the potential for a source rock to have oil, gas or other hydrocarbons, comprising, analyzing a rock sample from said source rock using thermoluminescence techniques to firstly determine TL glow peak intensities, and secondly, relating the TL intensities to TL intensities of reference samples having known characteristics indicative of the proximity of the sample to a petroleum deposit. Hydrocarbon can also be explored by using artificial dosimeters by measuring radioactive dosage and comparing values from known oil producer wells, known dry holes, and related areas. Now a day’s Geophysical way of exploration is used worldwide. Thermoluminescence analysis can complement the exploration by geophysical prospecting and can add certainty to locate the zone of interest. This paper explains basics of luminescence with qualitative as well as quantitative description of thermoluminescence. This also describes methodology of using thermoluminescence for petroleum exploration.

Keywords: Thermoluminescence, petroleum exploration

Introduction

Over the past two to three decades an extensive research has been carried out on usage of various methods to explore oil, gas and minerals hidden inside the subsurface earth. The primary way of exploration in use nowadays in hydrocarbon industry is through geophysical surveys. In this process mainly we do seismic surveys and based on their travel time an approximate image of the subsurface is generated. It is well known that hydrocarbons, as they seep up toward the surface, affect the near-surface soil causing certain defects in the soil’s molecular structure. EMPIRE OIL & GAS Company of Nedlands, Western Australia claimed and reported to detect and measure the hydrocarbon associated molecular defects using thermoluminescence (TL) analysis in 2007. They perform TL analysis in 7 promising fields, all in Western Australia. Here is a brief field-by-field summary extracted from the final report published online by EMPIRE OIL & GAS Company [1]:

1 Parrot Hill East (Bee-Eater)
A strong TL anomaly, indicative of a substantial hydrocarbon presence, has been detected at a very close proximity to the planned Bee Eater-1 well.

2 Lake MacLeod
A strong TL anomaly confirmed a heavy hydrocarbon presence. The pool boundaries were outlined. The TL readings showed that the pool is larger than previously thought expanding 2 km North-West of the originally projected boundary. The optimal drilling site was identified.

3 Nabulgee Area
The TL readings were generally low. This suggests no hydrocarbon accumulations in the test area.

4 East Paterson Area
This site showed some anomalous TL readings pointing at the hydrocarbon presence in the Southeastern corner of the tested area.
5 Whitelock Dam Area
A strong TL anomaly, indicative of the hydrocarbon, was detected in the Southeastern corner of the sampled area. A good possible drilling location was identified. Testing of additional samples was suggested to a client in order to identify the very best position for an exploration well.

6 Sandalwood
A TL anomaly was detected, getting larger along the southwestern side of the tested area. Collection of additional samples was suggested in order to determine the pool boundaries and the optimal well location.

7 Midway Area
Small TL anomalies were detected in the Southern triangle portion within the sampled area. This is the case when the pool’s size and boundaries are difficult to identify. At present, the available TL data does not support drilling.

The above studies show that TL anomaly strongly related with the presence of hydrocarbons. This paper explained the basic principles of thermoluminescence and describes its use for petroleum exploration.

Basics of Luminescence
Luminescence is the emission of light from a material following the initial absorption of energy from an external source e.g. ultraviolet, x-rays, γ-rays or high-energy radiation [2]. The emission can be categorized as either fluorescence or phosphorescence, depending upon the characteristic lifetime between absorption of the excitation energy and emission of the luminescence. If the characteristic time \( \tau_c \) is less than \( 10^{-8} \) sec, then it is known as Fluorescence and if the characteristics time \( \tau_c \) is greater than that of \( 10^{-8} \) sec, then it is known as Phosphorescence. This is best explained by the family tree of luminescence phenomena shown in figure 1.

Role of Imperfections on the Luminescent Properties of Materials
Luminescence properties of materials are strongly controlled by the imperfections/defects of the crystalline solid state [3]. The lattice defects may be either structural defects arising out of the presence of inherent impurities/deliberately doped foreign atoms/ions or radiation induced stabilized defects. Due to lattice defects, there arise localized energy levels in the energy band gap of the material. These metastable levels are responsible for luminescence properties are called traps. All these processes greatly depend on the method, the mechanism and the temperature of the defect formation.

Some defects can be induced into the lattice by incident ionizing radiations such as X-rays or γ-rays on the material. Such irradiation produces e- and h+, which get trapped by the corresponding traps, their release followed by recombination caused by any means results in luminescent emission.

TRAPS
Some impurities centers possess metastable energy levels localized in the band gap of the host material known as traps. If they lie near to conduction band, an electron moving in conduction band has all probability to be trapped in these levels. To get liberated from them, the electron needs extra energy. If they lie closer to valence band, they have greater probability to trap holes, for whose release too, extra energy needs to be, supplied (Figure 2).
Figure 2: Representation of Traps.

**Thermally Stimulated Luminescence**

Thermoluminescence (TL), more appropriately called Thermally Stimulated Luminescence (TSL), is the emission of light from an insulator or semiconductor when it is heated. But it must have absorbed high energy radiation prior to its stimulation by heat [4]. Thus three essential conditions necessary for the production of Thermoluminescence are:

a) The material must be an insulator or a semiconductor (metals do not exhibit luminescent properties)

b) The materials must have at some stage absorbed energy during exposure to radiation.

c) The luminescence emission is triggered by heating the materials

Thermoluminescence is the phenomenon of luminescent emission after removal of the excitation under the condition of increasing temperature. The pattern of luminescence output vs temperature is called thermoluminescence glow curve. The intensity of luminescence vs wavelength at any particular temperature during the heating is called thermoluminescence emission spectrum. Both the curves contain many peaks depending upon the nature of the TL material. These peaks are designated as glow peaks and spectral emission peaks respectively. The TL glow curve and spectral emission curves will help in understanding the mechanism of the emission process. TL glow peaks give information such as activation energy or trap depth (E), order of kinetics (b) and the frequency factor (s) about the traps while the TL emission peaks give information about the charge recombination sites (luminescence centre).

The Thermoluminescence from the material is very sensitive to:

a) The amount and nature of impurity,

b) Thermal history,

c) Pre-thermal, mechanical and radiation effect,

d) Size of material particle,

e) Crystallization history and

f) Defect pattern present in the material.

**Qualitative Description**

The phenomenon of thermoluminescence can be explained on the basis of band theory of solids [4]. According to band theory of solids, the energy band diagram of each solid can be represented by valence and conduction band separated by a forbidden energy gap. This forbidden energy gap contains many localized levels corresponding to various defects present in the crystal such as vacant lattice sites, interstitial atoms and impurity atoms.

When photons of the incident radiation having energy greater than the forbidden energy interact with the electron in the valence band, they transfer some of the electrons from the valence band to the conduction band. Most of these excited electrons return to the valence band after a very short time (~10^{-8} sec), which give rise to luminescence and can be observed during the irradiation of the sample. This is known as the Fluorescence. Some of these excited electrons in the conduction band get trapped at the localized levels (electron traps) within the forbidden band. Similarly holes of the valence band also get trapped at the localized levels (hole traps). In this way a large number of electron and hole traps are filled during irradiation Figure 3(a).

When the crystal is heated either the electron or hole which is trapped with less energy will be thermally ejected out of the trap and excited to the conduction/valence band, move in the crystal and finally recombines with a trapped charge carrier of opposite sign. The place where recombination takes place is called recombination center and if recombination is radiative, luminescence will occur Figure 3(b) & 3(c).

It may also be possible that the detrapped electrons and holes recombine with their counterpart at an entirely new site (luminescence centre) other than the electron and hole traps Figure 3(d).

In general, a detrapped charge carrier may become retrapped from which it again excites into the
conduction/valence band by absorbing energy $E$ (activation energy) and then recombines with their counterpart, so the luminescence emission is delayed and in this case the shape of the glow curve will be different to the case when retrapping does not occur Figure 3(e).

It is also possible that a detrapped charge carrier recombines directly with their counterpart without exciting into conduction/valence band. This type of recombination is called tunneling Figure 3(f).

Quantitative Description

The probability ($p$) per unit time for thermal excitation from the trap is exponentially dependent upon temperature according to the relation [5]:

$$p = s \exp\left( \frac{-E}{kT} \right)$$  \hspace{1cm} (1.1)

where ‘$E$’ is activation energy, ‘$s$’ is a constant known as frequency factor with dimensions of reciprocal time and ‘$k$’ is Boltzmann constant.

The simple scheme of one trap/one-center model is shown if Figure 4.

The TL intensity expression for one-trap/one-center model is given as [4, 5]:

$$I = n_0 s \exp \left( \frac{-E}{kT} \right) \left[ 1 - \frac{(N-n)\sigma_n}{(N-n)\sigma_n + m\sigma_{mn}} \right]$$  \hspace{1cm} (1.2)

Equations (1.2) is known as the “General One Trap” (GOT) expression for TL emission [5]. In equation (1.2), the term in square brackets is the probability that the thermally released electrons will not be retrapped and the ratio $\frac{m\sigma_{mn}}{(N-n)\sigma_n}$ is the ratio of the retrapping probability to the recombination probability. The exact equations of the TL process depend on the mechanism of recombination of detrapped charge carriers with their counterpart. On the basis of this, thermoluminescence phenomena can be studied under the following three types of kinetics:

First Order Kinetics (Slow Retrapping)

When the recombination probability of detrapped charge carrier with their counterpart has a constant value with time then the process is called first order or monomolecular process and is described by the first order kinetics equation as

$$I = n_0 s \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{(s/q)\exp\left(-E/kT\right)}{dT} dt\right]$$  \hspace{1cm} (1.3)

where ‘$n_0$’ is the initial value of $n$ at $t=0$ and ‘$q$’ is heating rate. The properties of this equation are illustrated in Figure 5, (a) Variation of TL intensity ($I$) with $n_0$, for
constant $E$ and $q$. (b) Variation of $I$ with $E$, for constant $n_o$ and $q$. (c) Variation of $I$ with $q$, for constant $E$ and $n_o$ [5].

In Figure 5(a), the peak height varies with $n_o$ as this parameter changes from 2 to 8 arbitrary units. It is to be noted that peak position remains same, while the height of the peak (directly proportional to the area) scales with $n_o$. This is an important characteristic of all first order TL glow peaks. The other characteristic property is the asymmetry of the peak, it become wider on the low temperature side than on the high temperature side. In Figure 5(b), the shift of the peak towards higher temperatures, along with a decrease in the height and increase in the width (keeping the area constant) as $E$ varies from 0.8 eV to 1.2 eV. In Figure 5(c), the peak shifts to higher temperatures and the size of the peak increases as $q$ varies from 0.25 to 4.0 K/s.

Figure 5: Variation of Randall-Wilkins first order TL intensity equation (a) with $n_o$, (b) with $E$, (c) with $q$ [Ref. 5].

Second Order Kinetics (Fast Retrapping)

When the recombination probability for the detrapped charge carriers change with time and the recombination rate is proportional to both the concentration of the excited electrons and that of vacant impurity levels or positive holes in the valence band then the process is called second order kinetics. Garlick & Gibson [12], derived expression for ‘second order kinetics’ is given by:

$$I = n_o^2 s \ e^{E/kT} \frac{(1 + n_0 (s'/q) \int e^{E/kT} \,dT)}{T_o} \tag{1.4}$$

The important characteristics of second order TL glow peak are that it is wider and more symmetric than a first order TL glow peak. This can be understood from a consideration of the fact that in a second order reaction, significant concentrations of released electrons are retrapped before they recombine, in this way giving rise to a delay in the luminescence emission and a spreading out of the emission over a wider temperature range. Figure 6(a) shows the variation in the height of the second order TL glow peak with $n_o$. Figures 6(b) and 6(c) show the variation in the size and position of a second order TL glow peak as a function of $E$ and $q$, respectively. Note that the peak height in (b) and (c) is no longer directly proportional to the peak area, although the deviation is small [5].

Figure 6: Variation of Garlick-Gibson second order TL intensity equation with $n_o$, (b) with $E$, (c) with $q$ [Ref. 5].
General Order Kinetics

The general order kinetics equation was given by May & Partridge [13] to describe nearly all the experimental TL glow peaks. May and Partridge developed this kinetics equation:

\[ I = \frac{a}{(1 - e^{-\alpha t})^b} = s' e^{-\alpha t} \]

where \( b \) is the kinetic order, which can have values other than 1 or 2 and \( s' = s/n_0^{1-b} \).

Hence, the basic TL glow curves may alter in shape and intensity as a function of temperature. When it is known precisely how differing temperature affect the TL glow curve within a sedimentary sequence, then such can be used to indicate past sediment temperatures. Since petroleum matures in a narrow temperature window (100° to 180°C) a knowledge of the past temperatures is obvious useful in petroleum exploration.

Petroleum Exploration Using Thermoluminescence (TL) Analysis

Firstly, by comparing TL properties of samples from source rocks:

A method of petroleum exploration using TL analysis of a crystalline sample comprises first irradiating the sample with γ-radiation, significantly filling the crystal lattice traps within the sample, heating the sample from an ambient temperature to an elevated temperature, measuring the intensity of luminescent radiation at a plurality of glow peak temperatures and relating the TL intensities to TL intensities of reference samples having known characteristics indicative of the proximity of the sample to a petroleum deposit. The sample may be treated to remove unwanted accessory minerals such as Feldspar and Zircon and may be shielded from direct light to allow phosphorescence and radioluminescence to decay to insignificant levels. Generally quartz, carbonates (calcite and dolomite) and the feldspar groups determine thermoluminescent properties [15, 16]. Since intensity of TL emission depends on initial concentration of trapped electrons. This is related to the defects and impurities present in solids. Several factors, associated with the presence of hydrocarbons, cause the molecular defects resulting in the elevated TL intensity. Some of these factors are: Organo-Metallic Compounds, Oxidized Metallic Porphyrins, Uranium and Thorium, Vanadium Salts, Potassium – 40, Radon etc.

For TL analysis of rock samples, sampling points will be selected from the potentially hydrocarbon-containing structure areas. Soil samples will be excavated from these sampling points. The extracted samples will be irradiated with ionizing radiation in the laboratory at one or a plurality-of dosages. The sample will then heated and luminescent intensities being measured at a plurality of glow peak temperatures and wavelengths. The luminescent intensities can then be related to the luminescent intensity of reference samples wherein the reference samples have been subjected to a known and/or derived degree of external physical effect. Each sample will be re-tested at least 5 times in order to assure the best accuracy.

In some cases, the elevated TL intensity points towards pool boundaries. The difference between the “positive” and “negative” sets of ranges in most cases is high, permitting for outlining the gas/oil anomaly edge with a great degree of certainty.

Secondly, by using artificial TL dosimeters [17]:

The exploration of hydrocarbon using artificial dosimeters based on the assumptions that uranium in formational waters is precipitated when it enters the reducing environment of an oil trap. Further, the daughter products especially radon isotopes \( ^{222}\text{Rn}, ^{220}\text{Rn}, \) and \( ^{219}\text{Rn} \) generated midway through the decay chain of \( ^{238}\text{U}, ^{232}\text{Th}, \) and \( ^{235}\text{U} \). \( ^{222}\text{Rn} \), with a 3.8-day half-life, can migrate vertically, through the rock column overlying an oil trap by water or natural gas. In theory, if an anticlinal structure is being evaluated, low TL intensity values can be expected where the trap is sealed by secondary deposits (carbonate, sulfate, sulfur) which are not as permeable to gas escape compared to lateral areas. This results in higher TL value measurements away from a trap where the seal is missing or breached by strain fractures.

Stratigraphic or fault traps give a linear anomaly pattern that locates the edge of a trap. Offset anomalies can result from fault or fracture systems in the strata overlying a hydrocarbon trap so that knowing the geology is essential to interpret surface or near-surface radioactivity fields.

Hence, artificial TL dosimeters like LiF (Ti,Mg) can be used to measure radioactivity dosage of 200°C as petroleum matures in a narrow range of 100 to 180°C. The interpretation is done by comparing values from known oil producer wells, known dry holes, and related areas.
Conclusions

Thermoluminescence is the phenomenon of emission of light caused by thermal activation of trapped electrons and recombination of detrapped charge carriers with their counterpart. Thermoluminescence from the material depends on various factors such as amount and nature of impurity present in material, thermal history of material, pre-thermal, mechanical and radiation effect, size of material particle, crystallization history and defect pattern present in the material.

The presence of hydrocarbons, cause the molecular defects resulting in the elevated TL intensity. This is the basis for application of TL technique to determine proximity of a core sample to a hydrocarbon reserve. Artificial TL dosimeters like LiF (Ti,Mg) can also be used in hydrocarbon exploration by measuring radioactivity dosage. The advantage of using thermoluminescence after geophysical exploration is to pinpoint the exact location of hydrocarbon reserve. This technique can be used as a complimentary measure in petroleum exploration and it will be more advantageous in a widespread area with very thick overlying rock formations.

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