CALCIUM FLUORIDE (CaF₂) FROM OYSTER SHELL AS A RAW MATERIAL FOR THERMOLUMINESCENCE DOSIMETER

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Lyra Coloma

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Richita Rodriguez
DEDICATION

This undergraduate thesis is dedicated to the researchers' Family, Friends and Professors who served as inspiration in pursuing this research.

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ABSTRACT

This study aims to develop a Thermoluminescence Dosimeter raw material made of Calcium Fluoride from locally available seashells that is suitable for personal radiation monitoring. Oyster shells were collected and grounded as powder samples and analyzed for Calcium Fluoride (CaF₂) content using XRF & XRD Testing. Samples include pure CaF₂, pure Oyster shell, and Oyster shells treated with acid. Based from the XRF results, natural oyster shell (w/ and w/o HNO₃) had high percentage of calcium about 49.64% and 47.45%, next to the pure Calcium Fluoride of 51.08%. X-ray Diffractrogram shows that Oyster sample had the nearest desired structure of CaF₂ compared with two seashells relative to the pure CaF₂ as standard materials. Results show that all of the natural oyster samples displayed TL emission glow curves at the temperature range 200-300 °C. It was also found that pure Oyster sample has better TL response as compared to the treated ones. The researchers concluded that the Calcium Fluoride from Oyster shells (without acid and heated) is a potentially good low-cost TLD raw material and may be used as an alternative for the much more expensive LiF dosimeters.
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CHAPTER I

INTRODUCTION

Radiation is a bundle of energy some of which are in the form of electromagnetic wave (EM wave). Gamma rays, x-rays, ultraviolet rays (UV rays), infrared (IR), radio waves and microwaves are examples of radiation. Other radiation types include alpha and beta particles, electrons, protons and neutrons. These different kinds of radiation can be categorized into ionizing and non-ionizing radiation.\(^1\)

Ionizing radiation can cause atom or group of atoms to lose an electron because it has sufficient high energy to do gamma, beta, alpha, UV and x-rays fall under this type. On the other hand, non-ionizing radiation like IR, ultrasound and short high energy radio frequency are radiations that cannot cause any ionization because of its low energy.

Radiation plays a very significant role in many applications especially in medical practices nowadays. Many medical apparatus and equipments use ionizing and non-ionizing radiation for diagnostic and therapeutics purposes. Ultrasound for instance uses non-ionizing radiation. On the other hand, ionizing radiation is found in x-ray machines, linear accelerators, Computed Tomography (CT) scanners, Positron Emission Tomography (PET) and in the nuclear medicine.

The use of ionizing radiation has led to major developments in the diagnosis and treatment of patients especially those with cancer. An example of which is the detection of breast cancer at an early stage when it may be curable with the use of mammography.
Also, needle biopsies are safer, accurate and informative when guided by x-ray or other imaging technique. Radiation is used in monitoring the response of tumors to treatment and in distinguishing malignant tumor from benign ones. Another is the bone and liver scan that detect cancers.

Radiation can also be used in many other ways. Just as doctors can label substances inside human body, scientist can label substances that can pass through plants, animals, or even earth. It has also helped in a wide variety of things such as in knowing the type of soil different plants need to grow, the size of newly discovered oil fields, tracing of ocean current, finding the age of ancient object, designing and constructing new instruments and equipments, measuring air pollution, killing bacteria, preserving food without chemicals and refrigeration, processing sludge for fertilizer, locating natural resources and many others.

In industry, engineers use radiation to measure thickness of materials in a process called radiography to find hard to detect defects in many types of metals and machines and infrastructures. The Agriculture industry makes use of radiation to improve food production, by exposing plants seeds to radiation to bring about new and better types or varieties of plants. Also, radiation can be used to control insects' population, thereby decrease the use of pesticides.  

All human beings are exposed to ionizing radiation both from natural and artificial sources. Exposure to natural radiation arises from cosmic and terrestrial sources, as well as from natural radioactivity in our food and drinks. Throughout history, man has been exposed to natural radiation; however whether their exposure has been harmful or beneficial to human species is yet to be determined. In contrast, artificial radiation
sources have only been introduced in the last 100 years and many benefits have been gained from their use.

Radiation can be very beneficial as long as it is properly used. However, it could also cause harmful biological effects especially ionizing radiation. Ionizing radiation can cause structural changes in cells by breaking the electron bonds that hold molecules together. For example, radiation can damage the genetic material either directly by displacing electrons from the deoxyribonucleic acid (DNA) molecule in the cell that then interacts with DNA. A cell can be destroyed quickly or its growth or function may be altered through a change (or mutation) that may not be evident for many years. However, the possibility of this inducing a clinically significant illness or other problem is quite remote at small radiation doses.

The severity of radiation’s effects depends on many factors such as the magnitude and duration of the dose; the area of the body exposed to it; and a person’s sex, age and physical condition. A very large dose of radiation to the whole body at one time can result to death. Exposure to large doses of radiation can increase the risk of developing cancer. Because of a radiation-induced cancer is distinguishable from cancer caused by other factors, it is very difficult to pinpoint radiation as the cause of cancer in a particular individual. ⁴

For health workers who work under radiology department, nuclear medicine, radiation oncology and some laboratories that uses radiation and even for patients under examinations and treatment of radiation, exposure should be minimized to avoid biological effects of radiation. The basic framework of radiological protection is intended
to provide an appropriate standard protection against ionizing radiation without unduly limiting the beneficial practices giving rise to exposures.⁵

For this reason, a system of radiation protection has been developed to protect people from unnecessary or excessive exposures to ionizing radiation. This system is updated to ensure the best possible protection for both radiation workers and for members of the general public. In accordance with the International Atomic Energy Agency (IAEA) International Basic Safety Standards, which is based largely on the 1990 “Recommendations of the International Commission on radiological Protection” (ICRP Publication 60), doses received by individuals during occupational exposure to ionizing radiation should be monitored. In the Philippines, the Radiation Protection Services (RPS) Unit of the Philippine Nuclear Research Institute (PNRI) is the group tasked to provide monitoring system by providing Thermoluminescence Dosimeter (TLD) and film badge services authorized users of radiation and radioactive materials in the country.⁶

Unfortunately, Thermoluminescence dosimeter that is used in the country which is made of lithium fluoride (LiF) is very expensive and imported from other countries specifically from the Harshaw Company in USA. Calcium fluoride (CaF₂) also known as fluorite exhibits a strong radiation-induced thermoluminescence and after special treatment, can be used satisfactorily for radiation dosimetry purposes. For this reason, the researchers attempt to produce a raw material from different seashells particularly the mussels, white shells and oyster shells which were known to have substantial calcium (as well as calcium fluoride) content as a substitute to the presently used thermo luminescent dosimeters. The main goal of this research is to develop an effective Calcium Fluoride TLD made from the selected Philippines seashells for personal radiation monitoring.
1.1 Statement of the Problem

This study aims to develop a TLD raw material made up of Calcium Fluoride from locally available seashells that is suitable for personal radiation monitoring. Specifically, the study aims to answer the following:

1. Can CaF$_2$ synthesized from oysters be used as raw material for TLDs?

2. Is the thermoluminescent properties of the Calcium Fluoride can be used satisfactorily for personal monitoring?

3. How efficient and feasible is it to use Calcium Fluoride from seashells compared with the existing TLD-Lithium Fluoride?

1.2 Assumption

The following assumption serves as the bases of the study:

1. Natural Calcium fluoride is a thermoluminescent material, which is found to have a better sensitivity as a detector for radiation measurement. It can be used for measuring very low radiation levels and is relatively more inexpensive for dosimeter application.
1.3 Hypothesis

The following scientific guess below was defined in this research.

1. It is possible to produce a Thermoluminescence Dosimeter from Calcium Fluoride (CaF$_2$) Synthesized from natural seashells, which can be a substitute raw material for Lithium Fluoride (LiF).

2. Thermoluminescence property of CaF$_2$ synthesized from seashells is suitable for dosimeter purpose.

1.4 Significance of Study

The researchers aim is to develop a thermoluminescent dosimeter made up of Calcium Fluoride extracted from locally available seashells to be used as a substitute raw material for Lithium Fluoride-TLDs.

This study aims to benefits the following institutions:

1. For Philippine Nuclear Research Institute to develop a low-cost and effective thermoluminescence dosimeter made of locally available TL material.

2. The Polytechnic University of the Philippines, College of Science and Department of Natural Science, particularly the Bachelor of Science in Physics students and professors, as well as the other related courses can investigate the importance of thermoluminescence dosimeter made up of Calcium Fluoride for personal and environmental radiation monitoring. This research will help the academic institution in gaining knowledge and awareness in Radiation Protection and some application of thermoluminescent materials on radiation dosimetry.
3. Lastly, other future researchers who want to continue improving this study. This will be a big help and additional information in the field of Health Physics and Radiation Protection.

1.5 Scope and Limitations of the Study

This thermoluminescence dosimeter made up of Calcium Fluoride from seashells is a device used to measure radiation of exposure. The study is limited only on investigating TL properties of CaF$_2$ in oyster shell for TLD purposes.

1.6 Definition of terms

The following are the terms need to define in this research:

**Absorbed Dose** is a measure of radiation received or absorbed by the target. It is equivalent to energy per unit mass.

**Afterglow** is the ratio of the intensity measured at specified time (usually after 6ms) time to the intensity of the component.

**Alpha particle** is a particle consists of two protons and two neutrons tightly bond together, and which is ejected from the nucleus during radioactive decay.

**Background** is a quantity determined as number of luminescent pulses emitted by radioactive substance within 1 second in the bulk of scintillator with the weight of 1 kilogram.

**Beta Particle** is an electron, which is ejected from the nucleus of a radio nuclide at high speed during radioactive decay.
**Calcium Fluoride** is also known as fluorite or fluorspar. It exists in nature as mineral fluorite. Fluorites exhibit a strong radiation-induced thermoluminescence and after special treatment, can be used satisfactorily for radiation dosimetry purposes.

**Effective Dose** is the summation of the tissue equivalent dose, each multiplied by the appropriate tissue weighing factor.

**Exposure** is the amount of ionization in air produced by radiation in a particular area.

**Fading** is the apparent loss of TL signal between exposure and evaluation.

**Glow Curve** is a graph of the light emitted as a function of time or temperature.

![Glow Curve Graph](image)

*Fig. 1 shows the glow curve graph where the highest intensity occurs in 190°C.*

**Ionization** is the process of removing an electron from a target atom, thereby producing an ion pair.

**Lithium Fluoride** is another phosphor that has been studied in lithium borate. Usually Manganese activator is added to this material; this appears to be the most promising with the lithium-based phosphor.

**MDL** or **Minimum Detection Limit.** This is the minimum amount of radiation that can be detected by the TLD reader. MDL = 0.04mSv.

**Monitoring Period** is the duration of the measurement of dose related to the assessment with exposure to radiation.
Occupational Exposure, are all exposures of personal incurred in the course of their work, excluding exposure that are excluded and exempted by the International Basic Safety Standards.

Personnel is any person who works, whether full time, part time or temporarily, for an employer and who has recognized rights and duties.

Phosphorescence is the emission of light after the irradiation period. The delay time can be from a few seconds to weeks of months.

Radioactivity is the number of disintegration of a nucleus occurring per second.

Rem is the special unit of any of the quantities expressed as dose equivalent. The dose equivalent in rems is equal to the absorbed dose in rads multiplied by the quality factor (1 rem = 0.01 sievert).

Sensitivity is a measure of the effectiveness of a detector in producing an electrical signal at the peak sensitivity wavelength.

Thermoluminescence (TL) is the ability of some material to convert the energy from radiation to a radiation of a different wavelength, normally in the visible light range.

Thermoluminescence Dosimeter, this is a device is used to measure the radiation dose to which the phosphor has been exposed.

Thermoluminiscence Reader, these consist of a controlled heating element and a photomultiplier system which determines the light fluencies emitted during the heating with the dosimeter material. In most Tld readers, the integrated light intensity is measured as a function of heating temperature cycle.
Sievert is the SI unit of any of the quantities expressed as dose equivalent. The dose equivalent in sieverts is equal to the absorbed dose in grays multiplied by the quality factor (1 Sv=100 rem).

1.7 Conceptual Framework

The conceptual framework summarizes the flow of the research.

Fig. 2 The Conceptual Paradigm of the Research

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CHAPTER II

REVIEW ON RELATED LITERATURE

This chapter involves the related literatures of about Thermoluminescence and its properties, together with the different processes of thermoluminescence dosimeter. The compounds of Calcium Fluoride and the summary of the TLD property of calcium fluoride.

2.1 Related Literatures

2.1.1 TLD and its Properties

Electrons in some solids can exist in two energy states, a lower energy state called the valence band and a higher energy state called the conduction band. The difference (energy region) between the two bands is called the band gap. Electrons in the conduction band or in the band gap have more energy than the valence band electrons. Normally in a solid, no electrons exist in energy states contained in the band gap. This is a "forbidden region." In some materials, defects in the material exist or impurities are added that can trap electrons in the band gap and hold them there. These trapped electrons represent stored energy for the time that the electrons are held. (See figure 3). This energy is given up (e.g. emitted as light photons when the material is heated up) as the electron returns to the valence band. 7
In most materials, this energy is given up as heat in the surrounding material, however, in some materials a portion of energy is emitted as light photons. This property is called luminescence. (See figure 4)

Thermoluminescence has been observed for centuries, whenever certain fluorites and limestone have been heated. Sir Robert Boyle and his colleagues as early as 1660 reported on thermoluminescence could be used as radiation detector and more specifically, as a radiation dosimeter. The property of thermoluminescence (thermo means heat and lumen means light) of some materials is one method used for personnel dosimeters. Thermoluminescence (TL) is the ability of some materials to convert the energy from absorbed radiation to a
radiation of a different wavelength, normally in the visible light range. There are two categories of thermoluminescence. Fluorescence is emission of light during or immediately after irradiation (within fractions of a second) of the phosphor. This is not a particularly useful reaction for TLD use. TLDs use phosphorescence as their means of detection of radiation. Phosphorescence is the emission of light after the irradiation period. The delay time can be from a few seconds to weeks or months.  

2.1.2 Thermoluminescence Dosimeter Process

In Thermoluminescence dosimetry (TLD) this property is used to measure the radiation exposure to which the phosphor has been exposed. This is done by means of "TLD Reader", consisting a controlled heating element and a photomultiplier system which determines the light fluence emitted during the heating of the dosimeter material. In most TLD reader, the integrated light intensity is measured as a function of heating temperature cycle. The resulting graph is called a GLOW CURVE (see fig. 1). Thus, thermoluminescence dosimetry consist of two steps:

1. Radiation exposure, which leaves some excited electrons in metastable traps;
2. Read-out, which consist of controlled heating of the exposed TLD and measurement of the integrated light intensity emitted.

Heating of the TL material causes the trapped electrons to return to the valence band. When this happens, energy is emitted in the form of visible light. The light output is detected and measured by a photomultiplier tube and a (proportional) dose equivalent is then calculated. A typical basic TLD reader contains the following components: (See figure 5).
Fig. 5 shows the heater, which raises the phosphor temperature. Photomultiplier Tube measures the light output and Meter/Recorder which display and record data.

In research it is common to employ both a digital system to record pulses from the photomultiplier tube and an x-y recorder to produce glow curve.  

2.1.3 Glow Curve

A glow curve can be obtained from the heating process. The light output from TL material is not easily interpreted. Multiple peaks result as the material is heated and electrons trapped in "shallow" traps are released. This results in a peak as these traps are emptied. The light output drops off as these traps are depleted. As heating continues, the electrons in deeper traps are released. This results in additional peaks. Usually the highest peak is used to calculate the dose equivalent. The area under the curve represents the radiation energy deposited on the TLD. A simple glow curve is shown in figure 1.
After the readout is complete, the TLD is annealed at a high temperature. This process essentially zeroes the TL material by releasing all trapped electrons. The TLD is then ready for reuse.²

2.1.4 Advantages and Disadvantages of TLD
Advantages (as compared to film dosimeter badges) includes:

· More accurate and able to measure a greater range of doses
· Quicker turnaround time for readout or faster processing
· Reusable and more robust

Disadvantages:

· Each dose cannot be read out more than once
· The readout process effectively "zeroes" the TLD

TLD manufacturing differs from company to company; so specific chip arrangement and composition may vary. Most badges are lithium fluoride (LiF) and calcium fluoride (CaF₂). Lithium has two stable isotopes, ⁶Li and ⁷Li. ⁶Li is sensitive to neutrons, but ⁷Li is not. Neutrons interact in ⁶Li to give tritium (³H) and alphas via the reaction: ⁶Li(n,alpha)³H. In fact the reason that ⁶Li is a special nuclear material (SNM) is that this same reaction is used for the production of tritium for nuclear weapons.
Different types of TLD:

Ring TLD made of Lithium Fluoride

Pocket TLD made of LiF

2.1.5 Calcium Fluoride and Background

Calcium Fluoride (CaF₂) is also known as fluorite or fluorospar. It is a naturally occurring mineral that is transparent to translucent with color varying widely from intense purple, to blue green, to yellow, through to reddish oranges, pinks, white and brown. It exists in nature as the mineral fluorite. Fluorite exhibits a strong radiation-induced thermoluminescence and after special treatment, can be used satisfactorily for radiation dosimetry purposes.

Compounds of Calcium Fluoride:

- Formula as commonly written: CaF₂
- Formula weight: 78.075
- Class: Fluoride
- Synonyms: calcium(II) fluoride, calcium difluoride
- Physical properties:
  - Color: white
  - Appearance: crystalline solid
  - Melting point: 1418° C
- Boiling point: 2533 °C
- Density: 318 kg m⁻³

**Synthesis**

One way to make small amount of calcium fluoride is by the neutralization of chalk with hydrofluoric acid. \[ \text{CaCO}_3(s) + 2\text{HF} (aq) \rightarrow \text{CaF}_2(s) + \text{H}_2\text{O} (l) + \text{CO}_2 (g) \]

**2.1.6 TLD Property of Calcium Fluoride**

The first reported use of radiothermoluminescence of natural calcium fluoride occurred in 1903. This phosphor exhibits three principal peaks in the glow curve which occur at 70-100 °C, 150-190 °C and 250-300 °C. The lowest peak has shown serious fading characteristics as a function of storage time. The response of calcium fluoride as function of gamma ray exposure is linear from a few mR to about 500 R with a standard deviation of ± 2%. The response of natural phosphor to fast neutrons is negligible. However, the response to thermal neutrons is about the same as for gamma-rays per rem in tissue. By enclosing the material in a metal filter (e.g. lead), the gamma-ray response can be made constant, within ±20 to 30% over the energy range of 80 keV to 1.2 MeV. A synthetic calcium fluoride is also available. This phosphor is activated with manganese and shows only a single glow peak located at about 260 °C. The thermoluminescent spectrum shows a maximum at about 5000 Å. The response of commercial calcium fluoride dosimeters is about a factor of 10 higher at 40 keV than the response measured at \(^{60}\)Co energies (1.25 MeV). Table 1 summarizes the TLD properties of calcium fluoride. 7
Table 1: Summary of Performance of CaF₂: Mn and CaF₂: Dy

<table>
<thead>
<tr>
<th>Property</th>
<th>CaF₂: Mn (TLD-400)ᵃ</th>
<th>CaF₂: Dy (TLD-200)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.18</td>
<td>3.18</td>
</tr>
<tr>
<td>Effective Atomic Number</td>
<td>16.3</td>
<td>16.3</td>
</tr>
<tr>
<td>TL Emission Spectrum</td>
<td>4,400-6,000 Å</td>
<td>4,835-5,765 Å</td>
</tr>
<tr>
<td>Temperature of Main Peak</td>
<td>260 °C</td>
<td>180 °C</td>
</tr>
<tr>
<td>Efficiency to ⁶⁰Co Relative to LiF</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Energy response</td>
<td>~13</td>
<td>~12.5</td>
</tr>
<tr>
<td>Useful Range</td>
<td>mR -3x10⁵ R</td>
<td>10μR - 10⁶ R</td>
</tr>
<tr>
<td>Fading</td>
<td>10%, 16 hr;</td>
<td>10%, 24hr;</td>
</tr>
<tr>
<td></td>
<td>15%, 2 wks</td>
<td>16%, 2 wks</td>
</tr>
<tr>
<td>Physical Forms</td>
<td>Powder, Teflon,</td>
<td>Powder, crystals,</td>
</tr>
<tr>
<td></td>
<td>Pressed, glass encapsulated</td>
<td>glass bulbs</td>
</tr>
</tbody>
</table>

ᵃ Ratio of response at 30 keV to response at ⁶⁰Co energies.
ᵇ Commercial designation (Harshaw Chemical Company)
ᶜ Registered trademark E. I. duPont de Nemours and Company, Inc., Wilmington, DE.

2.2 Related Studies

The following foreign related studies were significantly related on the present research.

2.2.1 Radiation Monitoring with Natural Calcium Fluoride Thermoluminescent Detectors.⁹

A simple system for radiation monitoring that makes use of the thermoluminescent property of natural calcium fluoride powder is presented. It consists of a kanthal strip on which a thin layer of thermoluminescent detector is deposited by means of a resin. The exposed dosimeter is read by directly heating it by passing a 30-A electric current through it for a half minute. The thermoluminescent glow is measured and recorded with a cooled low dark-current photomultiplier tube coupled with an electrometer d.c amplifier and recorder. Integrated exposures as low as 10 mR can be read without any inert gas atmosphere during the reading. The system of dosimetry is
used for both personnel and area monitoring in reactors and processing plants. Gamma and beta exposures received by the personnel in mixed fields during operations such as irradiated fuel handling are evaluated separately and compared with reading from other monitoring instruments. This system of monitoring is also being routinely used for environmental monitoring with a view to ensuring advance indication of any trend towards harmful build-up of radiation fields in the Bhabha Atomic Research center due to normal operations carried out in its various plants and laboratories, and also to provide background information for use in radiation emergency operations. A representative set of data obtained in personnel, area and environmental monitoring is presented and compared with data obtained with conventional monitoring instruments. The problem of energy dependence, light sensitivity, thermal glow, fading, etc..., as faced by the authors, are discussed.

2.2.2 A new TL detectors develop for multiple applications.¹⁰

S. Wang et. al of Department of Radiotherapy Chinese PLA General Hospital in Beijing China studied the photo energy response. Range of linearity without supra-linearity, detector threshold, ideal glow curve with the dominant peak, photosensitivity and thermal fading effects in LiF (Mg, Cu, P) which is doped with PbO to develop new detector that would satisfy the higher demands on dosimetric detectors.

In their research, the researcher have concluded that the new detector should processes the following advantages below:

1. good and adjustable photon energy response
2. low detection threshold
3. high sensitivity
4. linear range of measurable dose without supralinearity
5. low annealing temperature
6. very small thermal fading and insensitivity to chemical solutions.

Because it can be used in a variety of shapes such as powder, glass capillary pipe full of TL powder, punched discs or cut chips and rods of various sizes, the detectors can meet the needs of applications in several different fields.

2.2.3 Comparative Studies on the thermoluminescent Properties of Sintered Pellets of Natural and Synthetic CaF$_2$ for UV Dosimetry.$^{11}$

The phototransferred thermoluminescent (PTTL) of sintered pellets of natural CaF$_2$ from Brazil is compared with that of CaF$_2$ doped with Ce$^{3+}$ and/or Dy$^{3+}$. It is shown that the excitation spectrum provides a convenient way to find an optimum condition of pre-heat treatment of sintered CaF$_2$ after UV irradiation. The sintered CaF$_2$ containing a small amount of Ce$^{3+}$ (0.2 mol %) shows a strong glow peak around 90°C after UV irradiation. On co-doping with Dy$^{3+}$ in CaF$_2$:Ce$^{3+}$, the prominent glow peak shifts to 270°C. The peak intensity shows a linear response to the UV irradiation dose. The recombination process of these main glow peaks is discussed on the basis of the TL emission and the excitation peaks caused by the relevant impurities.

2.2.4 Dosimetric Characteristics of Natural Calcium Fluoride of Iran.$^{12}$

Thermoluminescent characteristics of nine batches of fluorite (natural CaF$_2$) from seven mines in Iran were studied for radiation protection dosimetry, some preliminary
results of which are presented and discussed. The initial thermal treatment was optimised for cleaning the natural dose at 500°C for 24 h. All the batches, except two, showed the same glow curve structures with three prominent peaks of different intensities at approximately 120, 180 and 270°C (β = 3(C.s⁻¹)). One batch from one mine showed sensitivity about 8.7 times by peak area higher than that of TLD-100 (Harshaw) powder and about the same sensitivity as that of TLD-200, with a dose response linear up to 100 Gy. A thermal fading of 15% during the first day and 17% during a month reached negligible fading per month after a post-irradiation thermal treatment at 100°C for 20 min. The minimum measurable dose of this phosphor was determined to be 18 μGy.mg⁻¹.
CHAPTER III

METHODOLOGY & EXPERIMENTAL PROCEDURES

This experiment was divided into two stages. Materials preparation of calcium fluoride from oyster samples and testing of the samples to determine the TL properties.

3.1 Stage 1: Materials Preparation

In this stage, the researchers performed the following experimental procedures:


   Green mussels, white shell and oyster shell (fig. 8) were collected as initial samples for synthesis of calcium fluoride. These materials are locally abundant and contain calcium.

2. Sample preparation for X-ray Fluorescence (XRF) Analysis

   Each sample was grinded (fig. 9a), pulverized and sieved in 115-mesh (fig. 9b) grain size at Nuclear Material Science Unit (NMR). After sieving the materials, the pulverized green mussels, white shell and pure oyster shell were delivered to Applied Physics Unit for XRF Testing.

3. Removal of unnecessary product from Oyster shell

   Oyster shell in powder form materials was dissolved with 4N HNO₃ to eliminate the calcium carbonate. First it was settled and washed out to remove
excess acid and visible impurity particles. Then settled particles were dried in an oven. The oyster sample with HNO₃ was added for XRF testing. (See fig. 10a)

4. X-ray Fluorescence Testing and Analysis

Each samples weighing 5 grams were pelletized using a 6-ton hydraulic press (fig. 11) before XRF testing to determine the elemental content of the product. 5 grams of pure calcium fluoride powder was also pelletized (see figure 12) and used as the reference materials for XRF quantitative analysis of calcium. At the XRF machine, samples were initially exposed to Fe-55 source to determine the elements with low Z (fig. 13) and final exposure to Cd 109 to determine the elements at higher Z. (See fig. 14).

7. Characterization via X-ray Diffraction Analysis (XRD)

After the initial XRF tests of the samples, the materials were analyzed in XRD Machine to determine structural composition of the samples. (See fig. 15)

8. Comparison with the standard materials

Each sample were compared and analyzed according to their elemental content after XRF testing. Computations were made to determine the percentage of calcium content.

9. Calculating the Percentage of Calcium

Fluoride was not visible in XRF; however calcium content were calculated from each sample by using the area of calcium peak of the CaF₂ and the do simple ratio and proportion. (See results in table 2)

10. Selecting the oysters' powder as the final samples for TLD testing.
Oyster with HNO3 acid (called s-1) and without acid (s-2) were selected as the final samples for TLD testing. Pure CaF2 in powder form (s-3) was also used for standard reference material.

3.2 Stage 2 (Testing of materials)

Stage 2 includes the testing of samples for TLD properties using the following procedures:

1. Pre- Irradiation of the samples

Oyster with HNO3 acid (fig. 18), without acid (fig. 19), with acid powder or sieved in 115-mesh before adding HNO3 acid (fig. 20) and pure CaF2 powder were prepared for irradiation. Each sample was placed in a crucible and annealed at 400°C for 1 hour using the furnace then slow cooled in oven from 400°C to 100°C in 1 hour. After slow cooling, the furnace was then turned off and the samples were left and stored inside it for 17 hrs.

2. Assembling of Dosimeter Materials

After pre-irradiation each sample weighing 1.0914 g was pelletized using an automatic 25 tons pressure hydraulic press. (see fig. 22). Finish pellet samples were cut with a molded cutter about 7mm diameter and 1mm thickness (size were fitted with the hole of the TLD holder). After cutting, each sample was attached at the center-right of the mylar plastic about 9.5mm wide and 24.6mm length using silicon sealant. Each sample was placed and heated inside the oven at 200°C for 1 hour to test the heat resistance of the prepared dosimeter materials.
3. **Irradiation**

Each sample was placed in a TLD cardholder (see fig. 21) with barcode and exposed individually using a strontium-90 with about 200 g.u or 2mSv dose of radiation for 29 seconds. After exposure, the samples were kept and set aside for 24 hrs to stabilize the crystal structure. Before reading the samples, the TLD reader 6600 (see fig. 23) was set:

1. Start the WinREMS program and select file for new workspace.
2. Set the title of the Time Temperature Profile (TTP) setup and select the acquisition mode *Anneal Dosimeters*. Check the used box element iii. Acquire maximum temperature is 300°C for 40 seconds.

4. **Evaluation of the samples**

Exposed samples were automatically readout using TLD reader 6600 (Harshaw) with WinREM software program. (see results of glow curve in fig.24). All measurements were carried out in a purified N₂ atmosphere.
CHAPTER IV

RESULT AND ANALYSIS OF THE DATA

Upon doing the methodology, the researchers obtained the following:

4.1 Presentation of the collected samples:

Fig. 8 (From top-clockwise) shows the collected samples of oyster shell, white shells (locally known as umang) and green mussels (tahong).

Fig. 10a shows the sieved oyster sample with HNO3 acid and fig. 10b was the oyster sample without acid.
Fig. 9a shows the oyster shells pulverized using the grinding machine from PNRI-Nuclear material Science (NMR) Unit.

Fig. 9b shows the sieved powder of pulverized oyster in 115-mesh.

Fig. 11: Manual Hydraulic Press

Fig. 12 shows the pelletized CaF2 for XRF Testing.
4.2 Results of XRF Analysis exposed in Fe55 and Cd109 excitation sources:

Fig.13 XRF spectra of 3 different shells and CaF2 (XPIPS, Fe55)

The result in fig. 13 shows the peaks of calcium of different samples. Pure Calcium Fluoride (CaF$_2$) shows highest intensity of 3568 cts. at 3.65 keV. The second highest peak was the pure oyster with intensity of 3559 cts. at 3.65 keV. Third was the white shell with intensity of 3334 cts. at 3.65 keV. Fourth was the oyster sample with HNO$_3$ acid with Intensity of 3323 at 3.65 KeV. The lowest sample with intensity of 3158 cts. at 3.65 keV., was the green mussels.

Silicon at 1.74 keV. and Argon at 2.90 keV. elements were identified to be present in the XRF analysis below Z. Argon comes from the air.
Fig. 14 XRF spectra of Oyster (with or without HNO$_3$) and CaF$_2$ (XPIPS, Cd109)

The result in fig. 14 shows the spectra of Oyster (with or without HNO$_3$) and CaF$_2$ in pellet form (5 grams each). Using Cd109 excitation-source, Iron (Fe), Bromine (Br) and Strontium (Sr) were identified present elements.

**Table 2: Summary of Calculated Percentage of Calcium present in Green mussels, White shell, Oyster shell (with or without HNO$_3$) and Pure Calcium Fluoride.**

<table>
<thead>
<tr>
<th>XRF Samples</th>
<th>% Of Calcium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder green mussels</td>
<td>45.93%</td>
</tr>
<tr>
<td>Powder white shell</td>
<td>48.603%</td>
</tr>
<tr>
<td>Powder oyster shell (w/o acid)</td>
<td>49.64%</td>
</tr>
</tbody>
</table>
Table 2 shows that the pure oyster shell without acid was less than 1.44% of Calcium from the standard sample of pure calcium fluoride. 2.19% of Calcium was removed from the oyster with HNO₃. Green mussel (tahong) have the lowest percent of calcium about 45.93% among the white shell and oyster shell.

To determine the compound structure of the samples, X-ray Diffraction Analysis (XRD) was used. The result of XRD of Green mussels, white shell and oyster (all were in powder form) were compared with the standard structure of pure calcium fluoride.

4.3 Result of X-ray Diffraction Analysis of the 3 different seashells and CaF₂

Fig. 15: XRD graph of natural Oyster powder

Fig. 15 shows X-Ray Diffractogram of Natural Oyster Powder, 3476 counts is the highest intensity along with a 2θ of 29.52 degrees. The second highest intensity is 3460 counts with a 2θ of 29.54 degrees. And the third highest peak recorded appeared in 2θ of 47.64 degrees with an intensity of 1260 counts.
From the result shown in Fig. 16 appeared with a three (3) visible peaks from the sample of natural oyster treated with HNO3 run in XRD. These three (3) visible peaks appeared to be the three highest peaks throughout the XRD testing. In 29.36 in 2 (Degrees) with an intensity of 3587 cts., the second peak appeared is 47.44 with an intensity of 1216 cts. and 48.44 with an intensity of 623 cts. appeared as the third highest peak appeared from the test.

Fig. 15 and Fig. 16 had a common peak of Calcium Fluoride but natural oyster had a big difference in intensity than oyster treated in HNO3.
Figure 17 shows the superimposed X-Ray Diffractogram of 3 different seashells: Natural Oyster, White Seashell and Green Mussels plus the XRD of Pure Calcium Fluoride (CaF$_2$) powder.

It can be seen from the figure that among the three seashells the Natural Oyster has the nearest diffractogram with the Calcium Fluoride (CaF$_2$). Therefore Natural Oyster had the most abundant compound of Calcium Fluoride than to White Seashell and Green Mussels.

Based from the XRD result, Oyster shell samples was selected for the stage 2 or testing for TLD materials.
4.4 Stage 2: Irradiated samples of Oyster seashells & pure Calcium Fluoride:

Fig. 18 Oyster w/ acid heated
Fig. 19 Oyster w/o acid heated
Fig. 20 Oyster w/ acid powder heated
Fig. 21 Finished TLD material w/ cardholder
Fig. 22 Automatic Hydraulic Press
Fig. 23 TLD Reader 6600
4.5 Result of Glow curve in TLD Read-out

Figure 24.a Glow curve of Pure CaF$_2$

Figure 24.b Glow curve of Oyster w/o & w/o heat

Figure 24.c Oyster without acid & heated
Implications of the findings

Figure 24 shows the time-temperature-intensity profile of the different samples, also known as the glow curve. It illustrates the intensity profile of each of the samples as the heating temperature is increased constantly in time.

It is illustrated in the glow curves that all of the samples are thermoluminescent. Looking closely, TL response starts at approximately 200°C. Pure CaF2 is found to have a prominent peak unlike the other samples.
Most samples showed TL emission glow curve. Pure Calcium Fluoride with barcode of 623247 shows the highest collected charge of 26.70 nC. Oyster without acid and heated with barcode of 623370 shows the second highest reading of 15.61 nC followed by 13.94 nC for barcode 623368, the Oyster with acid and heated. A summary of the collected samples’ total charge readings are shown in Table 3.

Table 3: Summary of Charges of Exposed Dosimeter Materials

Table 3.1 Charges of Pure Calcium Fluoride

<table>
<thead>
<tr>
<th>TLD Barcode</th>
<th>Charge (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>623247</td>
</tr>
<tr>
<td>2</td>
<td>623243</td>
</tr>
<tr>
<td>3</td>
<td>623251</td>
</tr>
<tr>
<td>4</td>
<td>623362</td>
</tr>
<tr>
<td>5</td>
<td>Blank</td>
</tr>
</tbody>
</table>

Average Charges of Pure CaF$_2$ 11.6628

Table 3.2 Charges of Oyster without acid & without heat

<table>
<thead>
<tr>
<th>TLD Barcode</th>
<th>Charge (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>623219</td>
</tr>
<tr>
<td>2</td>
<td>623386</td>
</tr>
<tr>
<td>3</td>
<td>623387</td>
</tr>
<tr>
<td>4</td>
<td>623390</td>
</tr>
<tr>
<td>5</td>
<td>623383</td>
</tr>
</tbody>
</table>

Average Charges of Oyster w/o acid & w/o heat 4.1832
Table 3.3 Charges of Oyster without acid and Heated

<table>
<thead>
<tr>
<th>TLD Barcode</th>
<th>Charge (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 623259</td>
<td>11.38</td>
</tr>
<tr>
<td>2 623227</td>
<td>8.747</td>
</tr>
<tr>
<td>3 623370</td>
<td>15.61</td>
</tr>
<tr>
<td>4 623394</td>
<td>9.110</td>
</tr>
<tr>
<td>5 623361</td>
<td>3.476</td>
</tr>
<tr>
<td><strong>Average Charges of Oyster w/o acid &amp; heated</strong></td>
<td><strong>9.6646</strong></td>
</tr>
</tbody>
</table>

Table 3.4 Charges of Oyster w/ acid powder & Heated

<table>
<thead>
<tr>
<th>TLD Barcode</th>
<th>Charge (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 623239</td>
<td>5.306</td>
</tr>
<tr>
<td>2 623363</td>
<td>7.953</td>
</tr>
<tr>
<td>3 623263</td>
<td>5.186</td>
</tr>
<tr>
<td>4 623378</td>
<td>2.973</td>
</tr>
<tr>
<td>5 623271</td>
<td>5.820</td>
</tr>
<tr>
<td><strong>Average Charges of Oyster w/o acid &amp; w/o heat</strong></td>
<td><strong>5.4476</strong></td>
</tr>
</tbody>
</table>

Table 3.5 Charges of Oyster w/ acid powder & Heated

<table>
<thead>
<tr>
<th>TLD Barcode</th>
<th>Charge (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 623235</td>
<td>6.713</td>
</tr>
<tr>
<td>2 623396</td>
<td>4.744</td>
</tr>
<tr>
<td>3 623279</td>
<td>4.615</td>
</tr>
<tr>
<td>Name of Samples</td>
<td>Average Charge (nC)</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Average Charges of Pure CaF₂</td>
<td>11.6628</td>
</tr>
<tr>
<td>Average Charges of Oyster w/o acid &amp; w/o heat</td>
<td>4.1832</td>
</tr>
<tr>
<td>Average Charges of Oyster w/o acid &amp; heated</td>
<td>9.6646</td>
</tr>
<tr>
<td>Average Charges of Oyster w/o acid &amp; w/o heat</td>
<td>5.4476</td>
</tr>
<tr>
<td>Average Charges of Oyster w/ acid &amp; heated</td>
<td>7.2588</td>
</tr>
</tbody>
</table>

Table 4: Summary of Average Charges of Oyster seashell samples & pure CaF₂

The thermoluminescent intensity of samples are sensed by the photomultiplier tube of the TLD reader, for which the signals are converted into charges. The amounts of charges collected therefore are proportional to the TL strength and thereby to its response in absorbing radiation.

Based from the tables (and also shown in the intensities of the glow curves in Figure 24), it is shown that pure CaF₂ has the highest TL response. It is followed by pure heated oyster (w/o acid). The least response is that of the unheated oyster without acid.
CHAPTER V
SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 SUMMARY
From the 3 different seashells used for TLD materials, natural Oyster seashell with HNO₃ acid and without HNO₃ acid were selected for TLD testing for the following reasons:

1. Based from the XRF results, natural oyster shell (w/ and w/o HNO₃) had high percentage of calcium about 49.64% and 47.45%, next to the pure Calcium Fluoride of 51.08%.
2. Based from the X-ray Diffractogram results showed that natural oyster shell had the nearest desired CaF₂ structure from two seashells.
3. From the TLD tests, all of the samples were shown to have TL properties. Pure Calcium Fluoride and heated oyster samples without acid were found to have the best TL response.

5.2 CONCLUSION
The researchers conclude that the Calcium Fluoride from Oyster shells (without acid and heated) is a good substitute TLD material for lithium fluoride.
All of the samples of oyster shells tested showed TL response for absorbed radiation as illustrated in the glow curve structure and collected charges. Although the scope of the present investigation does include proportionality, fading, sensitivity and other parameters, the fact that it displayed thermoluminescence shows that it has substantial amounts of CaF2 and therefore is suitable for TLD use.

This result therefore implies that with further intensive studies, oyster shell can be used as a very low cost TLD material which could be very useful for our country’s radiation dosimeter purposes.

5.3 RECOMMENDATIONS

This research recommended the following:

1. Further studies of parameters such as sensitivity of TL materials, range of linearity, low rate of TL loss, repeatability in response for mass production of a high quality phosphor for radiation protection dosimetry.

2. Further research in natural oyster and other local shells to test for calcium fluoride content suitable for TLD materials or doped with other elements.
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