VI.1 PROLOGUE

The discovery of electret effect has opened a new way of studying the mechanism of polarisation and absorption changes in amorphous crystalline di-electrics. The application of electrets depends on their surface charge characteristics. The properties of electrets depend upon the nature of material and the conditions they are subjected to while they are in making process. The electrets have received an enthusiastic attention for being a source of electric field. Electret is more popular due to its small size, weight and due to the very long time of surface charge (several years).

An electret is a di-electric slab exhibiting a permanent electric field, which is not neutralized by ionizing surroundings. Heaviside is amongst the first investigators, who propounded the idea of the electret as a permanently polarised di-electric. Eguchi (1919, 1922) followed the lead and prepared first electret from Carbuna wax, beeswax and rosin. He reported the conservation of polarisation in such a mixture for several years. Since then, many investigators prepared electrets from different substance under various conditions.

The material under investigation is mostly melted and high electric field applied so that the doublets orient
themselves with their axis in their direction of the electric field and when the material is allowed to solidify, it retains the orientation of doublets, which was in a molten state under the applied field. In this way (Eguch, 1925), a permanent electric polarisation is induced in the substance.

There are, however, number of methods to prepare an electret. Some of the types of electrets prepared by various methods are listed below:

a) **THERMO ELECTRET**:
Those are prepared by simultaneous application of thermal treatment and high electric field.

b) **ELECTRO ELECTRET**:
An electret prepared at room temperature by the application of high electric field.

c) **PHOTO ELECTRET**:
Simultaneous application of illumination and electric field on a specimen gives rise to photoelectret.

d) **THERMO PHOTO ELECTRET**:
This type can be prepared by simultaneous application of electric field, heat and suitable high energy radiation.

e) **RADIO ELECTRET**:
The electrets prepared by simultaneous action of penetrating radiations and electric field are known as radio electrets (Murphy, P.V., 1963).
f) **MAGNETO ELECTRET**: 
Bhatnagar (1964, 1965, 1966) introduced this term, which represents for an electret, which has been prepared by simultaneous action of thermal effects and magnetic field.

g) **BIO ELECTRET**:
Since many biological materials show an electret effect, they will be known as bio electrets.

There is a quite good analogy between an electret and a magnet, which encouraged Eguchi to name the electret as a counterpart of the magnet. As a magnet, if an electret is cut into pieces, it retains its polarity at the two ends, i.e., all the pieces are complete electrets. For maintaining the permanency of an electret, it must be kept with its faces short circuited. Reheating destroys the electret completely. Electret effect is destroyed once it is irradiated by X-rays but changes once again appear as the irradiation is removed. Magnet, however, is found in nature, whereas electret is not. Magnets can be used in open air but humidity destroys the electrification of the electret. Growth, decay and change reversal are the peculiar phenomena of the electrets, which are found in magnets.

The electrets are widely effected by parameters such as humidity (Wieder et al., 1953), pressure (Gemant, 1935), thickness (Khanna, 1967) of the material.

Whereas with the increase of humidity, the electret effect is decreased, its efficiency increases with the increase of pressure.
VI.2 THEORIES OF ELECTRETS:

Adams (1927) was the first, who put forward the hypothesis explaining the electret mechanism. He proposed that the heterocharges appearing on the substance are due to the orientation of dipoles, which have a long relaxation time and homocharges are the real charges, which compensate that heterocharges. Gemant (1935) raised an objection and observed that this does not explain all the observed behaviours in electrets. He suggested that the electrets heterocharge is due to the displacement of ions, which forms the space charges near the electrodes. A symmetrical distribution of charge between the anode and the cathode has been observed by Gemant. This was due to the difference in mobilities of the hydrogen ions and heavy organic anions. He assumed that normally, disordered crystallites attain an orientation in the field. Hermann et al. (1936), Winkel and Thiessen concluded that polarization has two components, which may be called as internal and external. The heterocharge is due to the internal polarization caused by ionic displacement and homocharge is due to external polarization in the interface between the di-electric and electrode.

Gross (1940, 1944, 1945, 1950) extended further the ideas of above named investigators on two different mechanism of thermo electret formation. According to him, heterocharge is formed by the various processes of charge absorption in
di-electrics, while homocharge is due to breakdown at the di-electric - electrode interface. The change from hetero to homocharge is due to gradual decay of the internal polarisation with the retention of the surface charge received by the thermo electret from its electrodes. Gross actually demonstrated the co-existence of the hetercharge and homocharge. Gross proposed that in polar substances, the dipole orientation under the influence of the field produce a heterocharge. By applying a sufficiently high field, conduction current penetrate in the interface and as such, the ions or electrons are fed into the di-electric or extracted from its surface and transferred to the electrodes. The field, then becomes weak, which decreases the conduction currents. The interpretation of electret on the proposed two charge systems explains most of the observed facts and his views were further substantiated by most of the recent investigators and it is most accepted theory for the electret phenomenon.

Although, characteristics of wax electrets have been extensively studied, relatively low attention has been given towards the high polymers (PVC and SR vinyl electrets). Very recently, these substances were extensively studied (Jain et al., 1968, 1969) and Nair, 1976). They concluded that the surface charge density almost remains constant after about twelve days. Both these samples give surface charge of opposite sign as in the case of a typical electret. The same authors
studied a plant material named "Bosewellia Glabra". It was concluded that charge formation characteristics of white (Bosewellia Glabra), especially, for low polarizing fields, are quite different from those for other electret-forming materials. Both the anode and cathode surfaces show the same sign of charges. In all the cases, it was concluded that the polarizing field is most essential for maintaining the best efficiency of the electrets.

More recently, attention has been drawn to the possibility of electrical polarization storage in materials of biological importance. The presence of such storage has been reported for bone, blood vessel walled materials, keratin and cellulose (Mascarenhas, 1974). Applications of the electret concept to biomaterials have also been made in the field of anti-thrombogenic surfaces by Murphy and Merchang and spinelli and colleagues. It has been observed that the electrical state is a universal property of biopolymers in general because it has so far been found to be present in collagen, geltin, artificial, polypeptides, Keratin, DNA, cellulose and chitin, the source of polarization or charge storage in the macromolecules are dipoles or ionic space charge that can be clearly identified in thermal stimulated depolarization spectra (SDS) of electret. Water bound to biopolymers can also give the electret state, which indicates the presence of dipole energy levels and structured phase that serves as another compartment for polarization storage in the "wet" state of biopolymers.
In case of bone it has been pointed out that mineral component of bone does not show electret behaviour owing to the fact that it does not show piezoelectric behaviour. The data on bone electret, reported so far seem to have been pertaining to different conditions and they are expected to differ. In the present investigation an attempt is made to study all the three materials (bone its two major components) after subjecting them to different treatments and then study their charge decay characteristics. A particular aspect of interest is the behaviour of apatite and the long term existence of electret state in all the three materials. While studying the Hall effect in bone and its components, some anomalous behaviour for apatite was observed (Behari and Andrabi, 1979). It seems then interesting to see its behaviour for the important solid state property also. As pointed out earlier, the electret phenomena was been observed in a large number of organic compounds under a given set of conditions, (Natarajan, 1972; Jain, 1970). A similar methodology is adopted in the present work so as to have some comparison with these materials. This approach is also expected to be helpful in seeking some information regarding the mechanism involved in such processes. In case of bone thermo electret the studies are carried out in the region of moderately high electric field and is the temperature range where some other data on bone are also available (Behari et al., 1974 and 1975).
Fig. VI.1: Experimental set up for studies on bone electret.
Electro electrets and magneto electrets are being formed in an identical way and their characteristic pattern is reported.

VI.2 MATERIALS AND METHODS

Tibia bone samples were obtained from freshly sacrificed rabbit and goats. The details regarding the treatment of bone and recovery of collagen and apatite remains the same as mentioned in Chapter II.

The specimens of rectangular shape were sandwiched by pasting colloidal silver paste in amyl acetate and mounted on an electret holder. The connections were taken with 40 gauge enamelled copper wire placed on the two sides of the specimen. The battery connections are shown in Fig. VI.1. All the connections were performed with grounded shielded wires and the various voltage and currents were measured with a high input impedance 616 Keithley electrometer.

VI.2.1 A measurement of total polarisation (charge/cm²) was obtained by calculating the area under the current versus time curve in the usual manner.

About twenty samples of each of the three materials bone, collagen and apatite were studied. Observations on the samples were repeated only after they lost the electret effect.
6.2.1 Thermo electret:

This type of electret was prepared by placing the electret holder in a temperature-controlled chamber. The temperature of this chamber was allowed to stabilize for at least one hour before taking the readings. The specimens were subjected to a particular field strength at a desired temperature for thirty minutes before the saturation currents were recorded. The field was then switched off and the fall of current with time was recorded till it became almost constant.

In the second set of experiments the temperature was varied and the entire procedure repeated. In this way the samples were polarized at three temperatures viz. 35°C, 45°C and 65°C at different field strengths namely 1 Kv/cm, 3 Kv/cm, 4 Kv/cm and 5 Kv/cm.

From these observations charge/cm² vs time graph was obtained in the usual manner.

6.2.2 Electro electret:

This type of electret was prepared by applying a high electric field across the specimen sandwich for about thirty minutes and then putting off the field. The charge/cm² vs time graph was obtained for different electric fields as stated in the proceedings sections.
Fig. VI.2: Charge of area vs Time plot for Bone, Collagen and Apatite at 35°C and at indicated field (thermo electret).
VI.2.3 Magneto electret:

In this case the polarization was carried out by placing the sample between the two pole pieces of an electromagnet. A weak electric field and a high magnetic field of ~16K-Gauss was applied across the specimen sandwich. At the end of ten minutes both electric and magnetic fields were switched off and the charge/cm$^2$ vs time graph was plotted.

A similar method of observation was adopted for collagen and apatite.

The data for electroelectrets and magnetoelectrets presented here correspond to room temperature and normal humidity, level, and their variation was within five per cent during the course of experiments.

VI.3 RESULTS AND DISCUSSION

For thermoelectrets the fall of charge/cm$^2$ with time in case of bone, collagen and apatite is plotted (Figs. VI.2-VI.4) at indicated temperature and electric field.

Figure (VI.5-VI.6) represent the fall of charge/cm$^2$ with time in case of bone, collagen and apatite for electroelectrets and magnets electrets respectively at indicated electric and magnetic field.

It can generally be seem that the fall of charge with time is fast in first ten seconds, after the electric field
Fig. VI.3: Charge/area vs Time plot for Bone, Collagen and Apatite at 45°C, and at indicated field.
is put off in case of thermo electrets as compared to the other two cases when the treatments are withdrawn. The charge then also continues to decrease, but rather slowly for about ten minutes and then rate of fall further declines and almost ceases after about thirty minutes. All the three materials (viz. bone, collagen and apatite) show the electret state and are able to store large amounts of polarization ($\sim 10^{-6}$ col/cm$^2 - 10^{-8}$ col/cm$^2$) in the region of fields under study. This value is comparable to the polarization storage obtained with good electret (Jain, 1970). A comparison of figures (VI.2 - VI.4) with (VI.5 - VI.6) bring out a point that electroelectret is more efficient in terms of storage of charge. A comparison with magneto electret suggest that even for a high magnetic field ($\sim 16$K-gauss) produces an electret effect which is significantly less in magnitude for a sample of almost identical dimensions. This emphasis the well known fact that magnetic field by itself are less important in controlling and effecting the biological processes. It may be further mentioned that with the help of figures (VI.2-VI.4) that at the same temperature the charge storage capacity increases sharply for a moderate increase in electric field.

The electrets prepared in this way were found to retain charge even after a lapse of seven days and in case of thermo-
Fig. VI. 4: Charge/area vs Time plot for Bone, Collagen and Apatite at 65°C, and at indicated field.
Fig. VI.5: Charge/area vs Time plot for Bone, Collagen and Apatite at indicated magnetic and electric field.
electrets charge would increase manifold once the temperature is increased.

It was further observed that the samples retained the charge when it was measured each month upto five months though the magnitude of charge was diminished by one to two orders of magnitude. The efficiency of retaining charge for apatite was found to be comparable with bone and collagen when preserved tested under identical conditions. The bone electret which was put in position for about twenty four hours at freezing temperature was found to have lost the electret effect but immediately recovered it once the temperature was increased. This is suggestive of the fact that at lower temperature the mobile charge are in a state of "Freeze" in an ordered arrangement, such that they produce no net electric field but at higher temperature, the packed arrangement is broken resulting in a net polarization charge. This shows an increasingly important role of bound water in such processes. It may be suggested that the source of electric field are dipoles (Mascasenhas, 1974) ionic space charge and phenomena of protonic conduction (H⁺-vacancy migration). On switching off the electric field, change in alignment takes place and that accounts for the decay of charge with time. A similar mechanism may be assumed to prevail in collagen and apatite. The behaviour observed here is similar to that reported for other dielectrics (Jain and Pillai, 1969; Nair, 1976).
Results on apatite are at variance with the findings of other workers (Mascarenhas, 1974) in the sense that we observed electret state in apatite also, some similarity in behaviour of all the three materials was found to be present in the Hall effect measurements (Chapter III) but even there, apatite showed some peculiar behaviour. The electret behaviour of apatite may be attributed to the asymmetry in the crystal structure produced during its extraction from full bone and some inherent lattice defects.

Although, it is difficult in practice to measure such effects in physiologically moist bone with a high water content and the effect as yet has not been demonstrated to occur in living bone in vivo, such a method of charge storage could here important consequence for the understanding of mineralization as well as the induction of new bone by external electric fields as the growth (Alhenstaedt, 1974) of all animal and plant structures occur from the positive to negative pole of existing polarization. The electrical energy storage is an important parameter at the physiologic level and specifically at the level of macroscopic gross behaviour of tissues (Mascarenhas, 1974). As suggested by some authors the electret effect in vivo may arise due to the phase change such as solidification and precipitation from a solution or from the vapour. The presence of interface potentials may be sufficient to provide electric polarization as most of insulators require a lesser field
Fig. VI.6: Charge/area vs Time plot for bone, Collagen and Apatite at indicated electric field.
of polarization. This vary then double layer into which the electret field effectively penetrates, may be of paramount importance in control and growth processes. Further, experiments performed by Yasuda in 1977 and Shiro et al. (1977) in the same year, showed that a charged teflon either wrapped or laid near the rabbit femur gives rise to callus formation and the amount was more in case of former as compared to the latter. This clearly shows that electrets can play a leading role in callus formation. Since the body temperature does not change significantly and the self electric field generated by the body will induce a charge capacity in the bone hence, this may stimulate the electric activities taking place in and around the bone. The effect so induced may be of vital importance for control and growth processes in bone.