Chapter-I

INTRODUCTION

Energy is essential for economic development and quality of life for any nation. A reasonably good correlation exists between the per capita energy consumption and the quality of life, as the former is a measure of UN Human Development Index. For the past two decades, energy demand has increased roughly by 2-3\% per annum on global scale \[1\]. These figures are likely to move up with industrialization and modernization of our society. Especially in developing countries like India, where majority of the population are still out of the reach of industrialization, the energy demand is going to compound. Hence there is an urgent need to identify suitable energy resources for the future so that the required demand can be adequately met. Presently, 2/3rd of the energy demand in India is met by non-renewable sources such as coal, petroleum, natural gas etc. For a large country like India, a major fraction of energy must come from domestic resources. We have rather limited options in this regard from a long term perspective. There are environmental issues which will be inevitably associated with large-scale deployment of coal based power plants. Apart from this, a fact, which is often overlooked, is that the existing reserves of coal in our country would be inadequate to meet an enhanced rate of energy consumption, for more than a few decades. Currently lot of research and development work is going on in the fields of renewable energy sources such as solar, wind etc. However, estimates show that even under the best possible situation such energy sources may not be able to
fulfill the demand. Hence, to bridge the gap between demand and supply, nuclear energy appears to be the best solution [2].

In case of nuclear fission based technology, enormous energy can be obtained either through bombardment of fissile and/or fertile radionuclides such as $^{235}$U, $^{233}$U, $^{239}$Pu, $^{238}$U, $^{232}$Th etc., by slow or fast neutrons, which split them into lighter nuclei. India has already attained some maturity in this technology and currently $\geq 4700$ MWe electricity is being produced from 20 nuclear reactors. As far as nuclear fusion energy sources are concerned, significant R&D initiatives have been taken by the Department of Atomic Energy and other national research centres. The International Thermonuclear Experimental Reactor (ITER) is a project being developed jointly by international consortium [3].

1.1. Indian Nuclear Energy Programme

The Indian nuclear power program has been conceived bearing in mind the optimum utilization of domestic uranium and thorium reserves with the objective of providing long-term energy security to the country. One of the essential elements of the Indian strategy is to enhance the fuel utilization using a closed fuel cycle. This entails reprocessing of the spent fuel to recover fissile and fertile materials and recycle them back into the system. Considering this objective, the indigenous nuclear power program in India was initiated with Pressurized Heavy Water Reactors (PHWRs) using natural uranium and heavy water, and based on pressure tube technology. In the second stage of the Indian nuclear power program, plutonium from the natural uranium-based PHWRs will be used in Fast Breeder Reactors (FBR) for multiplying the fissile base. Considering the large thorium reserves in India, the future systems, in the third stage of the
program, will be based on natural thorium–$^{233}$U fuel cycle. A schematic diagram of closed nuclear fuel cycle is presented in figure 1.1.

1.2. Radioactive waste

Various types of nuclear waste are generated at every step of the nuclear fuel cycle. They are classified on the basis of their physical state as gaseous waste, liquid waste and solid waste. Amongst these wastes, liquid wastes need more attention due to their high volumes and mobility. Radioactive liquid waste streams are commonly classified as Exempted Waste, Low Level Waste (37-3.7×10$^6$ Bq/L), Intermediate Level Waste (3.7×10$^6$- 3.7×10$^{11}$ Bq/L) and High Level Waste (above 3.7×10$^{11}$ Bq/L) [4].

The concentrations of long lived radionuclides and tritium are also taken into account while classifying the liquid wastes. The general categorization of radioactive waste is presented in Table 1.1. Out of all radioactive wastes generated in the entire nuclear fuel cycle, high level radioactive liquid waste (HLW) contains majority (~99% of total) of the radioactivity. As major share of radioactivity belongs to the HLW, the present thesis will focus on the materials used for fixing HLW.
Figure 1.1 A schematic diagram of closed nuclear fuel cycle

<table>
<thead>
<tr>
<th>Category</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gaseous</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>&lt;2</td>
<td>&lt;3.7×10⁴</td>
<td>&lt;3.7</td>
</tr>
<tr>
<td>II</td>
<td>2-20</td>
<td>3.7×10⁴ to 3.7×10⁷</td>
<td>3.7 to 3.7×10⁴</td>
</tr>
<tr>
<td>III</td>
<td>&gt;20</td>
<td>3.7×10⁷ to 3.7×10⁹</td>
<td>&gt;3.7×10⁴</td>
</tr>
<tr>
<td>IV</td>
<td>Alpha Bearing</td>
<td>3.7×10⁹ to 3.7×10¹⁴</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td>&gt;3.7×10¹⁴</td>
</tr>
</tbody>
</table>

Table-1.1: Categorization of radioactive waste
1.3. Principles of Radioactive Liquid Waste Management

The basic principles followed in liquid waste management are

- Delay and decay for the waste having short-lived isotopes,
- Dilution and dispersion to the environment of very low level activity well below the nationally accepted levels which are in line with international practices and
- Concentration and containment of radioactivity as much as practicable.

Amongst them concentration and containment is one of the widely adopted processes for managing HLW [5].

1.4. Sources of HLW

Reprocessing of the spent fuel is the major source of HLW. Reprocessing of the spent natural uranium oxide fuel from the PHWRs and research reactors involves its dismantling and dissolution in nitric acid. The liquid thus obtained contains uranium, plutonium, fission products, corrosion products, minor actinides etc. Solvent extraction process (PUREX process) is being routinely used to recover U and Pu from this liquid using 30% tri-butyl phosphate. During this process, major stream in the form of HLW is generated from the first cycle of the extraction scheme. The high active waste (HAW) is concentrated and is termed as HLW, as it contains around 99% of radioactivity of the spent fuel.

The major components of the HLW are as follows:

a) Minor actinides such as $^{237}$Np, $^{241}$Am, $^{242,244,245}$Cm

b) Unrecovered U and Pu

c) Fission products, such as, $^{90}$Sr, $^{99}$Tc, $^{106}$Ru, $^{129}$I, $^{135,137}$Cs, $^{144}$Ce, $^{147}$Pm etc
d) Chemicals introduced in the reprocessing plant like nitric acid, sulphates, sodium nitrate, aluminum nitrate, chlorides, fluorides, traces of TBP and its degradation products,
e) Corrosion products of steel and other structural material (Fe, Ni, Cr, Mn etc),
f) Alloying elements such as Fe, Al, Si, Mo etc. in the fuel particularly when U metal is used as fuel,
g) Soluble poisons such as Gd, B and Cd.

Common radioisotopes present within HLW along with their respective half-lives are tabulated in Table 1.2. Table 1.2.B contains radionuclides which are of concern from the long term impact of the deep geological repository.

<table>
<thead>
<tr>
<th></th>
<th>A-Relatively short half life</th>
<th></th>
<th>B-Long Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium-90</td>
<td>28 yrs</td>
<td>Cerium-144</td>
<td>1.3 yrs</td>
</tr>
<tr>
<td>Ruthenium-106</td>
<td>1 yr</td>
<td>Promethium-147</td>
<td>2.3 yrs</td>
</tr>
<tr>
<td>Cesium-137</td>
<td>30 yrs</td>
<td>Curium-244</td>
<td>17.4 yrs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Technitium-99</td>
<td>$2x10^7$ yrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodine-129</td>
<td>$1.7x10^7$ yrs</td>
<td>Plutonium-240</td>
<td>6500 yrs</td>
</tr>
<tr>
<td>Neptunium-237</td>
<td>$1.6x10^8$ yrs</td>
<td>Americium-241</td>
<td>440 yrs</td>
</tr>
<tr>
<td>Plutonium-238</td>
<td>85.3 yrs</td>
<td>Americium-243</td>
<td>7300 yrs</td>
</tr>
<tr>
<td>Plutonium-239</td>
<td>24360 yrs</td>
<td>Curium-245</td>
<td>8500 yrs</td>
</tr>
</tbody>
</table>

Table 1.2: Common radioisotopes present in HLW and their half-lives ($t_{1/2}$)
1.5. Management of HLW

The HLW generated after reprocessing, requires special treatment to ensure its isolation from human environment for extended period of time. Actinides present in HLW are mostly alpha active and have very long half lives and require isolation for longer time span compared to other radioactive fission and activation products. The philosophy of ‘concentrate and contain’ is used in managing this HLW. The strategy adopted all over the world for this purpose is to convert the liquid waste into some kind of suitable solid form (immobile form) which is chemically, mechanically and thermally stable over the life time of major long lived isotopes. The solid waste form is stored in an interim storage facility in natural air circulation to allow the decay of short lived radioisotopes (Table-1.2.A) and then buried in deep geological repositories. Solidification provides improved safety during handling and shipping. Further, it minimizes the release of radioisotopes due to leaching with ground water in the deep repositories. The candidate matrix immobilizing the waste should be able to accommodate all the active and inactive components of the waste and bind them in the structure of the matrix so as to achieve the required isolation. The desirable properties of immobile matrix for fixation of high level waste forms are:

(i) Ability to incorporate a wide range of elements present in HLW.

(ii) Good chemical durability, i.e. low leachability.

(iii) Good thermal conductivity, so that the heat generated due to decay of radioactive isotopes is well dissipated.

(iv) Good thermal and radiation stability over extended periods of time.

(v) Good mechanical strength and shock resistance so that transportation to storage or disposal site is safe.
(vi) Minimum volume.

(vii) Compatibility with storage container.

(viii) Compatibility with geological repositories.

(ix) Technical and economical considerations (raw material availability, adaptability of process parameters to easily available engineering materials).

Many candidate matrices have been studied and developed for immobilization of HLW worldwide and characterized for aforesaid properties. These are briefly discussed here.

1.6. Candidate matrices for HLW

A. Glass based matrices

The most extensively studied and used waste forms are phosphate and borosilicate based glass and glass ceramics. Phosphate based glass systems were found attractive in early stages, as they can effectively incorporate molybdenum and sulphate present in the waste. The main additives of this glass form are in liquid form and formation temperatures of the system are comparatively low. However, material of construction is a major limitation in phosphate glass process because of severe corrosive conditions. Also the product, in general, is inferior from long term durability point of view.

Borosilicate based glass systems are now universally accepted as the matrix for immobilization of HLW on account of good product durability [6]. The pouring temperature is moderate being in the range of 1000 to 1100°C. However, elaborate glass forming additives are required either in the form of aqueous slurry of mixed oxides or glass frit.

Glass ceramics are obtained by controlled crystallization of the desired phases in bulk glass. In these types of matrices, the fission products and actinides of the waste can be
accommodated into a desired crystalline phase. It can be prepared by annealing the glass product at a temperature of maximum nucleation rate. Once the nuclei are formed, a second annealing step is carried out at a temperature high enough to have maximum crystal growth. The product consists of continuous glassy phase with crystals homogeneously dispersed in it. For getting the fine grained product oxides facilitating nucleation such as TiO$_2$/ZrO$_2$ are normally added into the glass matrix. With the proper composition of base glass and schedule of nucleation, the desired crystals can be generated, where the fission products and actinides can be accommodated. In general, the glass ceramics are mechanically more stable than the glass; however accommodation of particular element into a desired crystalline phase uniformly throughout the glassy phase is difficult.

B. Crystalline matrices

(i) Ceramic Waste Forms

Ceramic nuclear waste forms are attractive alternative to glass based nuclear waste form since they are thermodynamically more stable and have better chemical durability. The ceramic waste form such as supercalcine, synthetic rocks (SYNROC), sodium zirconium phosphate (NZP), sodium zirconium tungstate etc. are considered as suitable crystalline matrices for immobilization of HLW. Pyrochlores (A$_2$B$_5$O$_7$) are also being contemplated as potential ceramic waste form. Supercalcine is an alumino-silicon product of the ceramic type produced by tailored additions of Al$_2$O$_3$, SiO$_2$, CaO etc. into the liquid waste. Such types of supercalcines however have higher leaching rates than glass.

SYNROCs are titanate based crystalline forms comprising of phases like hollandite
(BaAl₂Ti₆O₁₈), perovskite (CaTiO₃), zirconolite (CaZrTi₂O₇), Ba-feldspar (BaAl₂Si₂O₈), kalsilite (KAlSiO₄), leucite (KAlSi₂O₆) etc. depending on the precursor used. Normally the precursors, such as TiO₂, CaO, ZrO₂, BaO, Al₂O₃, SiO₂ etc are used. In general, the hollandite phase accommodates the elements like Mo⁴⁺, Ru⁴⁺, Rh³⁺, Fe³⁺, Fe²⁺, Cr³⁺, Ni²⁺, K⁺, Cs⁺, Rb⁺, Na⁺ etc., the zirconolite phase accommodates the elements like U⁴⁺, Th⁴⁺, Cm³⁺, Am³⁺, Y³⁺, Ln³⁺ etc. and the perovskite phase accommodates elements like U⁴⁺, Th⁴⁺, Pu⁴⁺, Cm³⁺, Am³⁺, Y³⁺, Ln³⁺, Sr²⁺ etc [7].

C. Other matrices

Other matrices such as calcines, coated particles and metal matrix products are also potential candidates for waste immobilization. Calcines are produced by dehydration and de-nitration of the waste with no appreciable addition of other chemicals. Since the product has appreciable solubility in water, it is not considered suitable for long term disposal, but considered as intermediate product during its final solidification [8].

Coated particles are produced as a multi-barrier development concept. In this process, HLW is converted into spherical agglomerates of supercalcine powder in the form of 1-5 mm size range. Thereafter they are coated with an impervious layer of alumina and/or pyrolytic carbon for added leach resistance. This gives enhanced inertness and improvement in thermal stability, mechanical strength and leachability. In the metal matrix process, the HLW is immobilized in glass matrix and then embedded in metal matrix like lead to enhance the thermal conductivity of the final product [9]. For example, vitromet consists of waste containing glass beads encapsulated in a matrix of 99% Pb-1 % Sb alloy.
Similarly HLW can be converted to a supercalcine or to a sintered ceramic and then embedded in a metal matrix. This type of matrix will be very important for immobilization of fresh HLW, where container centerline temperature must be kept within a reasonable limit as thermal conductivity of this matrix is considerably high.

1.7. Glass – a candidate waste form for immobilization of HLW

Out of all the listed waste forms, glass has received major attention in product development as well as in long term product characterization with respect to the desired waste form characteristics. It is now the material of choice for incorporating and immobilizing the potentially hazardous radionuclides in HLW. The typical material properties, which make it superior as compared to others include (i) structural flexibility to accommodate wide range of elements (ii) simplicity in processing technique (iii) high corrosion resistance (iv) good thermal and radiation stability (v) high volume reduction during immobilization (vi) established long term integrity and (vii) inexpensive raw materials.

These characteristic properties of the glass make vitrification the focal point of systems for treatment of HLW around the world. Borosilicate based glasses have been studied in detail and have found wide acceptance in the world as one of the suitable matrices having capability to retain radioactivity for long duration. However, the glass composition varies with the composition of the respective HLW, which in turn depends on the type of reactor, burn up, off reactor cooling of spent nuclear fuel and nature of reprocessing flow sheets etc. Although the basic network is of silicon and boron oxides, other modifiers are necessary to take into account site specific variations in HLW composition [10].
1.8. Glass structure

Glass is an inorganic product of fusion (chemical reaction) which has been cooled under rigid conditions of temperatures without crystallization. It is a rigid, non crystalline (amorphous) material. The open random structure of glass is primarily responsible for achieving high waste loading and high chemical durability. The radionuclides from the nuclear waste are contained in a glass through primary and/or secondary bonding with the silicate network. This inherent property leads to the incongruent release of different elements from a waste glass. The network structure of glasses precludes the description of their composition in sample chemical formulae. The most common way of describing glass is to list relative amount of oxides derived from the raw materials used in the glass formulation even though these oxides do not exist as it is in the glass network. Another advantage of glasses over ceramic waste form is that they do not have any crystallographic limits for incorporation of waste.

According to Zachariasens’ view of atomic arrangement, the oxides involved in the glass formations can be categorized as follows [11].

a) Network formers – Oxides of elements that can produce glasses by forming chains and networks in a completely random manner. The elements of these oxides have a co-ordination number of four. The inorganic species increase the network connectivity by covalent bonds with the oxygen atoms in a silicate network. Generally network formers are acidic (e.g. SiO₂, B₂O₃ etc.) in nature.

b) Network Modifiers – Oxides of elements that can produce glasses by melting with network formers. The inorganic species interrupt the network continuity by forming ionic bonds with the oxygen or other elements in the glass network. Generally glass network modifiers are basic (e.g. Na₂O, K₂O, Li₂O, BaO, CaO) in nature.
c) **Intermediates** – These are oxides of elements that can produce glasses by fusion with network formers. The elements of these oxides have co-ordination number in between those of glass formers and glass modifiers. Intermediates can also act like network formers. In some instances, intermediates are referred to as dwellers. Generally, intermediates are amphoteric (e.g. Al₂O₃, Fe₂O₃ etc) in nature.

An oxygen atom involved in interconnecting either two network forming elements or a network forming and a network dwelling element is regarded as bridging oxygen (BO). Chemical durability of the glass increases with increase in the BO, since they help to maintain the network continuity. In general, the bridging oxygens bind covalently to both the network formers and dwellers. A non bridging oxygen (NBO) can be defined as an atom interconnecting the network forming and network modifying elements. In general the NBO’s bond covalently with formers and ionically with the modifiers. However, due to the electrostatic nature of the ionic bond, NBOs fail to retain network continuity and hence affect the glass durability adversely [12].

Hazardous constituents of the waste can be immobilized in the vitrification process either by their participation in glass formation (as network former), chemical bonding (network modifier) or encapsulation. Random network structure (two dimensional) of vitrified waste product is shown in figure 1.2.
Certain waste constituents can be immobilized by chemical bonding with the glass forming materials, particularly silica present in the wastes. The most notable chemical bonding within vitrified materials occurs, when waste constituents bond covalently with the oxygen atoms in a silica network and become part of the network. Waste constituents like U, Fe, Al etc. that interact this way, behave like network formers since they essentially replace silicon in the glass network structure. Other waste constituents can bond chemically with oxygen or other elements in the glass network. To sum up the above discussion, it is understood that ionic bonding incorporates
the material into the glass but disrupts the network continuity thereby modifying the physical and chemical properties of the vitrified materials. Materials, which interact in this fashion, are called network modifiers. Hazardous waste constituents may also be immobilized without direct chemical interaction with the glass network. Since vitrification constitutes a molten phase at some stage of the process, materials that do not interact chemically or have not completely entered the solution can be surrounded by a layer of vitrified material and thus get encapsulated, as the melt cools. This layer of vitrified material protects the capsulated constituents from the chemical attack. This structural characteristic of the glass providing three routes for immobilization of waste constituents make vitrification as the focal point of immobilization of HLW.

1.9. Glass composition for Indian nuclear reactors

In India, work on conditioning of HLW in borosilicate matrices was started in early seventies. For HLWs generated from uranium fuel cycle (PHWR), sodium borosilicate glass matrix containing TiO₂, MnO, BaO etc. are used for vitrification. On the other hand, suitable glass formulations for thorium rich HLWs, which are likely to be generated during reprocessing of spent fuel containing thorium (from AHWR), are yet to be developed [13]. The HLW from reprocessing plant at Trombay is characterized by the presence of high amounts of sulfate ions and sodium along with fission and activation products, corrosion products and actinides. Sulfate in the waste is derived from ferrous sulfamate [Fe(NH₂SO₃)₂] used as reducing agent for conversion of Pu⁴⁺ to Pu³⁺ at partitioning stage of the reprocessing and is one of the troublesome constituents with respect to vitrification in view of its limited solubility in the glass matrix. To deal with this, a barium oxide containing alkali borosilicate glass has been developed
and is routinely used for the waste immobilization [14]. The quaternary system of BaO-Na$_2$O-B$_2$O$_3$-SiO$_2$ referred to as the base glass is found to be suitable to deal the problem of sulfate ions forming a separate phase without affecting the waste oxide loading.

1.10. Radiation induced changes in nuclear waste glasses

As discussed earlier, the HLW contains most of the radioactivity generated during reactor operation. Because of the radioactive components present in the HLW, the glass experiences constant irradiation with $\alpha$, $\beta$ and $\gamma$ radiations. Numerous literature reports are available in the field of radiation induced changes in nuclear waste glass. Major work in this area has been carried out at several laboratories in the USA such as the Pacific Northwest National Laboratory by Weber and his colleagues [15], at Argonne National Laboratory [16] and Naval Research Laboratory [17]. Similar work was also initiated at CEA in France [18-20] and at the Kyushu University and Kyoto University in Japan [21]. In UK, at the University of Sheffield, radiation damage studies of nuclear waste glasses have also been carried out along with leaching studies [22-24]. Among these literature reports, a majority of the work is related to the electron beam irradiation of the waste glasses. This is understandable, because for the first few years, the $\beta$ decay plays a predominant role in radiation induced changes. Electron beam irradiations can simulate the effects of beta irradiation in the waste glasses to a great extent if not in totality. Boizot et al. have studied the electron beam irradiated French nuclear waste glasses by Raman spectroscopy and confirmed the migration of alkali metal ions in the glass [19, 25]. Similar alkali ion migration in electron beam irradiated glasses was previously also reported by Usher [26]. Ollier et al. have also studied the irradiated French waste glass to analyze the formation of molecular oxygen in it [27]. This was done by Raman depth profiling technique using micro
Raman spectroscopy. In another report the authors have investigated the microstructure evolution in the irradiated waste glasses by incorporating Cr$^{3+}$ ions as a luminescence and EPR probe [28]. The role of mixed alkali effect on the radiation damage of these glasses gave also been reported by this group [29]. Apart from trivalent chromium, many rare earth ions have been used as local structural probes to understand the beta radiation damage in the nuclear waste glasses viz the reports by Malchukova et al. where the trivalent rare earth ions, Gd$^{3+}$, Eu$^{3+}$ and Sm$^{3+}$ have been used as local structural probes to monitor the radiation damage in the glasses [30-33]. On similar lines, Ollier et al. have reported electron beam irradiation induced changes in the Yb$^{3+}$ and Sm$^{3+}$ doped waste glasses [34, 35]. In the rare earth doped glasses, it was observed that, both the oxidation states and the coordination geometries of the ions are affected by irradiation. In some cases, the formation of unusual oxidation states of the metal ions has also been observed. Several other reports suggest a modification in the borosilicate/ silicate network upon beta irradiation e.g. the reports by Buscarino et al. [36], Antonini et al. [37], Boizot et al. [38, 39] and Yang et al. [40].

Although for the first few years, the beta decay is primarily responsible for the radiation damage, in order to understand completely the damage in the glass matrix, one can not ignore the effect of gamma radiation. Further, gamma rays with higher penetrating power than the beta particles can create effects uniformly throughout the glass. Formation of defect centers along with changes in the oxidation states and coordination numbers is the main out come of the studies on gamma irradiation of the waste glasses. El Batal et al. have studied several gamma irradiated glasses in order to characterize the radiation induced changes [41, 42]. Durability and the modification in gamma irradiated borate, silicate and borosilicate glasses have also been reported by many researchers [43-47]. Like in the case of electron beam irradiated glasses,
gamma irradiated glasses incorporated with several rare earth and transition metal ions as local probes have been used to study the radiation induced changes. Baccaro et al. have reported the gamma radiation induced changes in silicate glasses incorporated with trivalent Ce, Tb and Eu [48, 49]. Gamma radiation induced changes in Sm incorporated waste glasses have been reported by Malchukova et al. [50]. Recently McGann et al. have reported an exhaustive study on the gamma radiation effects on simulated waste glasses of varying composition [51]. Apart from the gamma and beta damages occurring in the glass, the changes caused by the alpha particles and the resulting recoiled nuclei is of prime concern. In fact, majority of the atom displacements occurring in the vitreous waste form are due to recoil nuclei [52]. External heavy ion irradiation is a convenient laboratory technique for simulating the alpha damages in the borosilicate glasses from radioactive waste encapsulation point of view [53]. One can find many reports in the literature where heavy ion irradiation studies have been done on nuclear waste glasses to assess the effects of alpha decay on the structural properties of the glass matrix. There are number of reports by de Bonfils et al. on heavy ion (particularly gold) irradiated waste glasses having analogous composition to that of the French waste glass [54, 55]. In some other reports, incorporation of alpha particles in the glass matrix, either in the form of ion beam (viz $^4$He beam) or direct incorporation of actinides have been described [56-60]. Matzke had incorporated $^{244}$Cm in glass as well as SYNROC to simulate the alpha damages [61]. The same group also carried out ion implantation in the matrices at different temperatures to compare the effects [62]. Effect of different ion implantation in alkali borosilicate glasses have also been investigated by Arnold [63], who bombarded the borosilicate glasses with ‘He’, ‘Ar’ and ‘Xe’ ions and investigated the radiation induced damage. In another report ‘Kr’ ions have also been used to bombard the nuclear waste glasses and investigate the radiation damage [64]. Proton
beam irradiation of silicate glasses have been carried out by Kudo et al. [65], who used micro
fluorescence and EPR techniques to study the radiation induced damages in the glasses. Sato et
al. irradiated simulated waste glasses by electron beam, gamma rays and heavy ions to
investigate the radiation damage [66]. The change in the glass density as a function of irradiation
has been measured by the authors as a function of ion-fluence using electron microscope.
Most of these studies have shown that the nuclear waste glasses upon irradiation by high-energy
gamma rays, electron beams and heavy ions undergo changes in their structure. These changes
are caused mostly by the ionization and ballistic interaction of high-energy radiation with solid
constituents of the glass matrix, that introduce disorders in the original structure causing
formation of defect centers accompanied with volume changes, phase separation or gas
accumulation in the irradiated glasses [67-70]. It is pivotal to study these changes so as to predict
the long term leaching behavior of the vitrified waste product. Moreover, it is well known that
the optimal engineering performance of a glass is dominated by its structure. So, the knowledge
of the glass structure before and after irradiation is a prerequisite for understanding the structural
evolution of glasses under long term irradiation. In addition, these studies on the borosilicate
glasses will lead to an understanding of the nature of the damage which can further lead to
fabrication of materials in which the deleterious effects of radiation can be minimized.
Moreover, careful study of radiation induced defects can help elucidate certain structural aspects
of the glassy state which cannot be readily accessible by other means.

1.11. Spectroscopic techniques to study the radiation induced changes
Spectroscopic techniques provide non-invasive and direct methods for characterizing glass
samples before and after irradiation. Through these techniques one can obtain extensive
information with minimal sample handling. In literature one can find various spectroscopic techniques being used for these investigations. As no single spectroscopic technique is capable of answering all the questions related to the radiation damage of glasses, use of multiple techniques becomes imperative. For example, Electron Paramagnetic Resonance (EPR) can give information regarding the chemical nature of defect centers formed in the irradiated glass and quantify them. On the other hand, FTIR (Fourier Transform Infra Red) can give information about the changes in the bulk glass network. In the present set of investigations, conventional photon based techniques such as UV-Vis absorption, Photoacoustic spectroscopy (PS), Photoluminescence spectroscopy (PL), FTIR and Raman spectroscopic techniques were used along with novel techniques like positron annihilation spectroscopy (PAS) and EPR.

1.12. Motivation for the present work

As discussed above, keeping in view the high sulphate ion content in the stored HLW from Trombay reprocessing plant, a special glass formulation has been developed [14]. This alkali barium borosilicate glass formulation has been observed to tackle the problem of separate phase formation of sulphate ions quite effectively. In view of this, it is being routinely used for vitrifying the stored HLW. After vitrification, these wastes are to be stored for an interim period of 30-50 years under surveillance after which these are proposed to be buried in a deep geological repository. However, these glass matrices have not been characterized from radiation damage point of view, which is essential for predicting their long term integrity. In the present doctoral work, the alkali barium borosilicate glasses with and without dopant ions were characterized before and after irradiation. Suitable local structural probes were introduced in the
glass to monitor radiation induced structural changes in the glasses due to irradiation. Different types of radiation sources such as gamma rays, electron beam and heavy ion beam were used for the irradiation. The free volume and defect centers formed in the glass were characterized by different spectroscopic techniques. It was observed that, the bulk of the glass remains unaffected even at a high dose of $10^{11}$ Gy(J/kg).

The following issues are taken up during execution of this research work

a) Speciation studies (determination of oxidation states and coordination geometry) of different metal ions expected to be present in the waste glass. As the oxidation states predict the solubility of a particular species, these studies have direct relevance to the solubility limit of the metal ion in the glass.

b) Characterization of the waste glass after gamma irradiation in terms of various defect centers and radicals formed.

c) Use of Eu$^{3+}$ as a local probe in the glass to study radiation damage.

d) Role of ‘Fe’ in the radiation damage in glass.

e) Electron beam irradiation effects on the glass to simulate the effects of beta decay.

f) Quantification of the defects formed in the glass after radiation damage.

g) Effect of heavy ion irradiation on the glasses.
References

7. ERDA (Energy Research and Development Agency),“Alternatives for managing waste from reactors and post fission operations in the LWR fuel cycle”, 2 (1976) 14.