1. INTRODUCTION

1.1. Sources of Radioactive Liquid Wastes:

There are two main sources of radioactive liquid wastes. The first, where wastes are generated due to activities related to nuclear fuel cycle steps such as mining milling, uranium conversation, fuel fabrication, nuclear power plants and fuel reprocessing. The second source of liquid wastes is the non fuel cycle, where they are generated from hospitals, and research institutes **(International Atomic Energy Agency 1964)**.

1.1.1. Fuel Cycle Wastes:

The nuclear fuel cycle produces ten thousand m^3/y of Intermediate Liquid Waste (ILW) and Low Liquid Waste (LLW) **(International Atomic Energy Agency 1978)**. Materials and equipment (from nuclear operations) which are contaminated and for which there is no an expected further use are called radioactive wastes. The fuel cycle is divided into two parts each one include number of steps.

The first part is called the Front End of the Nuclear Fuel Cycle which includes:

- Uranium extrapolation, mining, milling and refining
- Uranium enrichment
- Fuel element fabrication

The second part is called the Back End of the Nuclear Fuel Cycle which includes:

- Reprocessing

1.1.1.1. Mining and milling:

The uranium content in the ore is often between only 0.1% and

0.2% therefore, large amounts of ore have to be mined to get at the uranium Wastes water arising from these operations(mining and milling) vary with the type of mine or extraction operation. These liquids arising contain very small amounts of natural α-activity from the uranium ore.

Residual wastes from the milling operation contain the remaining radioactive materials from the ore, such as radium.

1.1.1.2. Uranium enrichment:

Uranium conversation from U_3O_8 to UF_6 for enrichment generates liquid wastes containing 0.03 % of the material processed including uranium, (U^{235} and U^{238} radium, Ra^{226} and thorium, Th^{230} and their daughter products. Turning uranium oxide concentrate into a useable fuel has no effect on levels of radioactivity and does not produce significant wastes. Enrichment plant produces small amounts of liquid waste (from equipment clean-up) as well as slightly radioactive sludge's **(Ginnis 1979)**.

1.1.1.3. Fuel fabrication:

When uranium is used in the reactors that significant quantities of highly radioactive wastes are generated. Fuel fabrication plants also generate some waste oils and solvents. These wastes contain natural α-emitters and large amounts of nitrates, fluorides.....etc and usually discharged to a disposal pond **(Alexander and Blomeke 1979)**.

1.1.1.4. Fuel reprocessing:

Fuel reprocessing plants can be assumed to be the main source of radioactive wastes . More than 99% of the total radioactivity generated nuclear technology appears in wastes from reprocessing plants, most of it is the high level waste (HLW). A 1400 MT/y reprocessing plant produces about 1500 m^3/y liquid concentrate with activity less than $2x10^3$ Ci/m^3, 3000 m^3/y radiated water with activity less than 200 Ci/m^3, 800 m^3/y non combustible and ash solid waste with activity less than one Ci/m^3 and about 2 m^3/y krypton gas with activity less than $8x10^6$ Ci/m^3 **(International Atomic Energy Agency 1980).**

1.1.2. Non-fuel Cycle Wastes:

Non-fuel cycle waste arises from industrial applications, institutional researches, medical treatments,..... etc. For one year, quantities of low level liquid waste (LLLW) and intermediate level liquid waste (ILLW) raised were about $3.25x10^3$ m^3 **(Philips 1979).**

1.1.2.1. Research and development wastes:

Large volume radioactive waste streams come from research and development activities connected to nuclear energy programs and from the use of radioisotopes in research and industry. Such wastes originate from large numbers of installations. The wastes resulting from the use of radioisotopes in industry are generally large in volume, nearly neutral, and have low solid contents. Their activity level is about 400 times greater than permitted for discharge. Liquid wastes may include process solution, chemical solution used for regeneration ion exchange resins, decontamination solutions, contaminated oils and ...... etc .

1.1.2.2. Radioisotope production wastes:

More than 200 different radioisotopes were being produced for use in research and industry in one year. Two types of wastes arise from the production and use of radioisotopes. The first consists of spent radioisotope sealed sources, for the most part, such sources are already packaged, and their disposal is required only after they have decayed beyond the point of usefulness .

The second is the wastes which result from the chemical process used for the production of radioisotopes from the fission products . The starting material for radioisotope production is usually an aqueous solution from which uranium and plutonium have been removed. The resulting solution, which has a composition very similar to that of neutralized purex waste, is treated for recovery of specific fission products. In general, precipitation, solvent extraction and ion exchange procedures are used for radioisotope recovery.

1.1.2.3. Pharmaceuticals and hospitals wastes:

In hospitals liquid wastes are very closely connected to the kind of radiotherapeutic and diagnostic nuclear medicine techniques that are applied. Most of the radioisotopes used are short-lived ones . Therefore, in most cases, the only treatment performed is the storage of these liquids in decay tanks before they can be released to the environment. The total volume of low level waste and intermediate level waste associated with medical uses, including diagnostic, therapeutic, teaching, and research applications, that shipped to commercial burial grounds amounts to about $1.4 \times 10^4 - 1.8 \times 10^4$ m^3 / y **(Lamb 1958)**.

1.2. Types of Radioactive Wastes:

Three types of radioactive wastes are to be considered namely liquid, solid, and gaseous wastes.

1.2.1. Radioactive liquid wastes:

Radioactive liquid waste is generated during research reactor operations and in other operations involving the application of radioisotopes. In many nuclear power plants, one of the largest sources of liquid wastes is the demineralizer regenerates. Types of radioactive liquid waste produced, depends upon the particular operation being conducted which can vary extensively in both chemical and radionuclides content **(International Atomic Energy Agency 1993)**. Preferred option for processing this type of waste is direct conditioning, generally with cement

1.2.2. Radioactive solid wastes:

Radioactive solid wastes can be segregated in two main groups, combustible solid waste and non-combustible solid waste **(International Atomic Energy Agency 1992)**. Sometimes they are segregated for compaction. Each of these classes are characterized as alpha bearing and non-alpha bearing wastes. The largest volume of solid waste is in general rubbish, which includes protective clothing, plastic sheets and bags, rubber gloves, mats, shoe covers, paper wipes, rags, towels, metal and glass **(International Atomic Energy Agency 1994)**.

1.2.3. Radioactive gaseous wastes:

Nuclear power reactors are the main sources of radioactive gaseous wastes, gases quantities depend largely on the type of reactor. The range of activity is restricted and methods of treatment are few, but nevertheless, there still exist some differences in activity levels, and composition of gaseous effluents that justify the classification of gaseous wastes **(International Atomic Energy Agency 2000)**.

1.3. Classification of Radioactive Wastes:

The principal waste classes include, low, intermediate and high level waste.

1.3.1. Low-level radioactive liquid waste:

Low-level waste is generated from hospitals, laboratories and industry, as well as the nuclear fuel cycle. It comprises paper, rags, tools, clothing, filters……. etc. which contains small amounts of mostly short-lived radioactivity. It is not dangerous to handle, but must be disposed of more carefully than normal garbage. Usually it is buried in shallow landfill sites. To reduce its volume, it is often compacted or incinerated (in a closed container) before disposal. Worldwide it comprises 90 % of the volume but only 1 % of the radioactivity of all radwaste **(International Atomic Energy Agency 1994)**. There is an incinerator with filters, it had a capacity of 15kg/h. It is in the Nuclear Research Center/Atomic Energy Authority at Inchas, Egypt.

1.3.2. Intermediate-level radioactive liquid waste:

Intermediate-level waste contains higher amounts of radioactivity and may require special shielding. It typically comprises resins, chemical sludges and reactor components, as well as contaminated materials from reactor decommissioning. Worldwide it makes up to 7 % of the volume and has 4 % of the radioactivity of all radwaste. It may be solidified in concrete or bitumen for disposal. Generally short-lived waste (mainly from reactors) is buried, but long-lived waste (from reprocessing of nuclear fuel) is disposed of deep underground **(International Atomic Energy Agency 1970)**.

1.3.3. High-level radioactive liquid waste:

High-level waste may be the spent fuel itself, or the principal waste from reprocessing of the spent fuel. While it is only 3 % of the volume of all radwaste, it holds 95 % of the radioactivity. It contains the highly-radioactive fission products and some heavy elements with long-lived radioactivity. It generates a considerable amount of heat and requires cooling, as well as special shielding during handling and transport. If the spent fuel is reprocessed, the separated waste is vitrified by incorporating it into borosilicate (Pyrex) glass which is sealed inside stainless steel canisters for eventual disposal deep underground .

On the other hand, if spent reactor fuel is not reprocessed, all the highly-radioactive isotopes remain in it, and so the whole fuel assemblies are treated as high-level waste. This spent fuel takes up about nine times the volume of equivalent vitrified high-level waste which results from reprocessing and is encapsulated ready for disposal. Both high-level waste and spent fuel are very radioactive and people handling them must be protected from their radiation. Such materials are shipped in special containers which prevent the radiation leakage out and do not rupture in an accident. Whether reprocessed or not, the volume of high-level waste is modest, - about 3 cubic metres per year of vitrified waste or 25-30 tonnes of spent fuel for a typical large nuclear reactor. The relatively small amount involves various classification systems could be used to categorize radioactive wastes **(International Atomic Energy Agency 1982)**.

Classifications were based on specific activities, dose-rates or radiotoxicities .

Other classification criteria followed the origins of waste, physico-chemical natures or types of radiation and half-lives of the radionuclides. Each of these classifications may have its advantages and disadvantages depending on the purposes of the classification. The International Atomic Energy Agency (IAEA) suggested a classification system based upon specific activity **(International Atomic Energy Agency 1970)**. The specific activities defining high, intermediate- and low-level are often different in various countries and are even different in various establishments of the same country.

1.4. Industrial Solid Wastes:

Increased industrialization over the last years in Egypt has resulted in an increased and uncontrolled generation of industrial wastes. Consequently, no systems for handling or disposing these industrial wastes, in general, and hazardous industrial wastes, in specific exist. Egypt like several other developing nations, is undergoing unprecedented process of designing and implementing environmental polices and strategies. In 1992, National Environmental Action Plan (EAP, May, 1992) was formulated by the Egyptian Environmental Affairs Agency (EEAA).

In 1993, a base line report was formulated to assess the overall problem of industrial waste management in Egypt. Consequently, recommendations for priority actions were identified and the main components of a national hazardous waste system under the provision of law 4/1994 were presented. This work provides an updated review of this report in light of the proposed technical, legal and institutional guide lines to help in the realization of such needed waste management in Egypt **(El Dars 1993).**

Undoubtedly, the increase in industrial activities over last years in Egypt has contributed significantly to the deterioration of environmental conditions in urban conglomerates and localities nationwide. As anticipated, the increase in activity was accompanied by an increase in ambient pollutant levels and the generation of large amounts of wastes.

The EAP indicated that the total amount of industrial waste generated (solid and sludge) from the various industrial activities in Egypt (hazardous and non-hazardous) to be between 0.2-1.0 million ton/year, with an approximate 50,000 ton/year being regarded as hazardous in nature. Today, with the national industrial base reaching over 22000 units and with the strict enforcement of air and waste water treatment options, this amount is expected to increase dramatically. With the current industrial practices and the irregularities observed in waste management on the local and national levels, the problem of industrial waste management in Egypt is becoming a rather complex issue. To tackle this problem systematically, the base line report was formulated to provide a preliminary assessment of the industrial waste management situation within the current technical, legal and industrial framework. In Egypt, and up till now, most of the solid wastes generated by different processes are disposed by landfill.

1.5. Problem of Industrial Solid Wastes:

The increasing amounts of wastes and the simultaneous decrease of the waste disposal space as well as the problems associated with contamination from hazardous and toxic elements are challenges with the human kind nowadays **(Boccaccini 1996)**.

Therefore, the different types of wastes must be exactly categorized and defined in order to determine the most suitable way for their disposal. According to material science view point, the waste can be described as the material by-products after fabrication or consumption and have no further value, especially within affluent developed economic and among richer citizens of developing countries. It is possible; however, to distinguish between several broad categories of waste within the total waste stream of developed economic. It may come from one of the following sources: agriculture, mineral waste industry, sewerage, municipal including household, commercial and medical, construction, nuclear, petrochemical, or dredged spoil waste..........etc.

The problem of industrial wastes encountered due to the presence of different types of wastes include worker injuries, equipment and property damage and environmental contamination. Improper management of any type of waste can result in injuries to workers in waste management operations. Such workers include refuse collectors, materials recovery facility sorters, and equipment operators at material recovery facilities, transfer stations, waste to energy facilities, and landfills. As recycling operations expand in solid waste management, there will be increased sorting and handling of waste materials; correspondingly, workers will have increased exposure to hazardous waste in the solid waste stream.

The national solid waste management association has documented a variety of worker injuries due to disposal of hazardous waste in the solid waste stream. Exposure to hazardous waste has resulted from spills, spraying (e.g., from packer trucks during compaction), touching fumes, fires, and explosions. Injuries had included burns (acid, caustic, and thermal), blinding, eye irritation, respiratory problems, rashes, nausea, and unknown chronic problems. Hazardous wastes disposed in refuse also can cause equipment and property damage **(Nikolaev et al 1998)**. The most common incidents involve fire in refuse collection trucks or transfer trailers. Virtually every company or municipal agency that collects refuse has experienced a vehicle fire due to improperly disposed hazardous wastes. Waste processing facilities have also experienced damage due to hazardous waste disposed in the waste stream.

The most serious incidents reported have been shredder explosion. Most of the problems to date have occurred in refuse derived fuel (RDF) processing plants. The current lack of management of the solid waste in some developing countries as Egypt has established a situation where large parts of the land (especially industrial areas) are covered by un-planned dumps of industrial wastes. This is not the only problem, but is, because of the character of the dumped materials, also is problem that affects the whole area and its population.

On the other hand, the use of different recycling processes may cause dangerous effects on the surroundings. For example, the environmental concerns associated with incineration emissions and the related problem of the increasing quantities of toxic wastes in waste streams grew rapidly in the late 1970s **(Depart Of Environment 1992)**.

1.6. Sorbent Materials:

Certain industrial solid wastes generated in large quantities from the Egyptian factories were used in the present study. Homra, fly ash, silica fume, ceramic and window glass represent the most important waste materials of choice. These studies were carried out to show the possibility of using Egyptian industrial wastes in managing the radioactive liquid waste and enhancing immobilization properties.

1.6.1. Homra:

Homra (crushed clay bricks) is a solid waste material, which is constituted mainly of silica quartz, aluminosilicate, anhydrite, and hematite. Therefore, it acts as a pozzolanic material **(Heikal and El-Didamony 1999).**

1.6.2. Ceramic:

Ceramic materials are inorganic materials that usually consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds. The chemical compositions of ceramic materials vary considerably from simple compou nds to bonded mixtures of many complex phases **(David 1999).**

The variation in properties of ceramic materials is large because of differences in bonding and structure. In general, ceramics are hard brittle, with low toughness and essentially no ductility at room temperature. Ceramics normally have relatively high melting temperatures and are chemically stable in many hostile environments due to the stability of their strong bonds. Although we use ceramic materials are used for many applications it is convenient to divided them into two groups, traditional ceramics and technical ceramics. Traditional ceramics were made from three basic components clay, silica, and feldspar that are mined from naturally occurring deposits. Clay is basically a hydrated aluminum silicate mineral with a very fine sized plate like structure. These platelets provide plasticity for wet forming a swell as strength after drying and firing for many traditional ceramic products, such as bricks, tile, porcelains, sanitary ware, and more. Silica (SiO_2) is also an important material for traditional ceramics it was used in glass, white ware, ceramics, various bricks and abrasives.

1.6.3. Glasses:

Glasses are a ceramic material made from inorganic materials at high temperatures. Glasses are distinguished from other ceramics because they are vitreous or amorphous, that is, they are not crystalline. Glass, in fact, is defined as an inorganic material that has been cooled to a solid state without crystalization. The amorphous structure of glass is more like that of a liquid with only short-range order of the atomic bonds.

Glasses are produced from inorganic oxides of which silica, or sand, is the most important constituent. These glasses are actually mixtures of oxides, have not definite chemical compounds.The waste glass used in this study is window glass, typical soda lime glass,. Although the silica content of glass is higher than fly ash, the equivalent reactive components ($SiO_2 + Al_2O_3 + Fe_2O_3$) are relatively low in glass. The glass satisfies the basic chemical requirements for a pozzolan .

Soda-lime glass, which is concerned in the present worke, is the most commonly produced glass, accounting for about 90% of all glass produced. In this glass, the basic composition is 71 - 73 % SiO_2, 12 - 14 % Na_2O, and 10 - 12 % CaO. The Na_2O and CaO materials decrease the softening point from 1600 ^{0}C, which makes the soda-lime glass and an addition of 0.5-1.5% Al_2O_3 is used to increase durability. Soda - lime glasss is used as flat glass (windows........ etc.), containers, and ligthing products **(Nevill et al 1995)**.

1.6.4. Fly Ash:

Fly ash generated during the combusion of coal for energy production is an industrial by-product **(Manz and Stewart 1997)** and is recognized as an environmental pollutant. Because of the environmental problem of fly ash; a good deal of work and applications on the utilization of fly ash have been undertaken in our work.

Fly ash is a fine textured material which is primarily composed of spherical non-crystalline silicate, aluminium and iron oxides compounded with some microcrystalline material, free lime and unburned carbon . It has the potential to provide multivalent cations (Ca^{2+}, Al^{3+}...... etc.) under ionized conditions, which would promote flocculation of dispersed clay particles by cation exchange **(Wang 1997)**. Fly ash generally exhibits a wide range in chemical and physical properties. These properties determine the effectiveness of the fly ash for use in soil . The characteristics of a particular fly ash are dependent on its source **(Dube 1997)**.

1.6.5. Silica Fume:

Silica Fume is a by-product of the production of silicon metal or some ferrosilicon alloy. It consistes of fine spherical grain with mean particle size ranging between 0.1 and 0.2 Mm. It a largely amorphous material composed of glass particles resulting from rapid condensation of a gaseous SiO, which oxidizes rapidly as it comes into contact with air in the cool part of the furnace which is used for the production of silicon metal or some ferrosilicon alloys **(Jumana 1997)**. The SiO_2 content of silica fume commonly used in cement-based systems is between 85 and 98 percent.

The beneficial influence of silica fume in concret is often du to a combination of various factors such as physical and pozzolanic effects. The fine silica fume particles reduce the initial porosity of the cement paste by partially occupying spaces between cement grains **(Khayat et al 1997)**.

1.7. Radioactive Waste Management:

The use of nuclear fuel cycle and radioisotopes in many purposes generates a variety of low- and intermediate- level radioactive wastes. These waste materials contain quantities of radionuclides sufficient to cause healthy risks to people when the wastes are not managed. Waste management involves a series of steps from the generation of the wastes to the safe disposal. These steps concern with treatment and conditioning, packing, transport, and disposal. Liquid wastes contain large volumes of diluted solutions containing dissolved and/or finely divided contaminated materials **(International Atomic Energy Agency 1984)**.

The processes used for decontamination of liquid wastes are ion-exchange, filtration, membrane separation, chemical treatment, and evaporation. The purified liquids resulting from these processes are decontaminated sufficiently and can be used in many purposes, while the residues contained in the ion-exchange media require conditioning to be immobilized. Matrix material that have been used are cement, bitumen, polymers, glasses and ceramics. Fuel reprocessing generates a large variety of wastes which arising within the plant are treated internally at the plant before control release to the environment. Because reprocessing plants vary considerably, the amounts of wastes produced differ also, especially for the intermediate and low level liquid wastes categories. The high level liquid waste contains 66.5 % of the filling products (FP) in 1M HNO_3 . Before it is pumped to the storage tanks, it is concentrated to various final volumes depending on the cooling time and burn-up fuel. For 1 y reprocessing it may contain 35 g FP/L while for a 10y cooling time it may be 0.2 m^3/tu (180g FP/L) contains up to 0.2 % of the uranium and plutonium processed **(International Atomic Energy Agency 1992).**

The radioactivity is usually < 1 Ci L^{-1} . The solutions may also contain appreciable amounts of solids (e.g. $NaNO_3$, iron........ etc.). The waste may be neutralised and is stored in steel tanks at the reprocessing site. The nuclides of main concern ^{90}Sr, ^{137}Cs, ^{106}Ru, ^{3}H, and the actinides. The high level nuclear waste produced in the world 10 y from now is expected to reach an amount of 10^4 t annually with a radioactivity of 7x10^4 MCi. It contains large and potentially valuable sources of metals and radiation. Since the extraction and utilization of some of the fission products or actinides will probably not be economic after the waste has been vitrified and placed in permanent geologic storage. The nuclear fuel reprocessing scheme must therefore be designed for by- product extraction.

Presently the most interesting products in the waste are the platinum group metals (due to their metal values) and ^{90}Sr, ^{137}Cs, ^{85}Kr, ^{238}Pu and ^{241}Am (due to their radiation properties). The waste contains considerable amounts of Ru, Rh and Pb, which are of scarce abundance on the earth. These elements are used as catalysts in chemical industry and as corrosion resistant materials **(Hayahi 1982).**

1.8. Liquid Waste Treatment Technologies:

1.8.1. Chemical precipitation:

The objective of a chemical precipitation process is to remove radionuclides from a liquid waste by the use of an insoluble finely divided solid material, so the radionuclides are removed from the solution by one or more of the following mechanisms **(Cross and Hooper 1987).**

- Co-precipitation with a carrier.
- Sorption onto particulates present in the waste stream.
- Sorption onto the floc (ion exchange, chemisorptions........ etc.).

The use of these processes concentrates the radioactivity present in liquid waste stream into a small volume of wet a solid that can be separated from the bulk liquid component. Chemical precipitation processes are well established methods for the removal of radioactivity from low and intermediate level wastes and are in a regular use at fuel reprocessing facilities, research establishments and some power stations **(Coste 1991).** The majority of precipitation methods is to use metal hydroxide flocs under neutral or alkaline conditions to remove the radionuclides. With this general process, a number of the radionuclides will be extensively hydrolyzed and likely to be either co-precipitated or sorbed onto the floc. Other treatments can be applied for specific radionuclides, for example, precipitation of barium sulphate for strontium removal, or nickel hexacyanoferrate for cesium removal. The process may be affected by the presence of other components of the waste stream such as complexants, trace organics or particulates. In these cases, a pre-treatment may need to be added to the main process. When the waste stream composition is variable in nature, either in its radioactive or in its non-radioactive content, a single chemical precipitation process may be in adequate. A combination of specific treatments is frequently necessary to achieve the best overall decontamination factor (DF) for total alpha and/or total beta-gamma activity of the liquid waste. Combinations of processes can be used as a multistage batch process or as a continuous precipitation process that produces one or several sludges for further conditioning and disposal.

The sludge usually has low solid contents and requires further dewatering in order to reduce the final volume of the immobilized waste. The selection of a sludge treatment process must consider both chemical and radiation stability of the sludge. This treatment is sometimes associated with solidification of the sludges which confers on them mechanical resistance and long term stability to allow their disposal.

Precipitation processes are particularly suitable for treatment of large volumes of liquid waste which contains relatively low concentrations of radioactive elements. These processes are fairly versatile and may be used to treat a wide variety of different waste streams, including those containing particulates or high concentrations of salts. The processes are economically attractive but achieve relatively low decontamination factors compared to other treatment methods, e.g. evaporation .

1.8.2. Evaporation:

Evaporation is a proven method for the treatment of medium level radioactive wastes providing both good decontamination and high concentration. The technique is well developed and both its advantages and limitations are well understood **(International Atomic Energy Agency 1968).** With nitrate systems, evaporation is usually continued to a salt a concentration of up to 400 g/l . At the Paks Nuclear Power Plant in Hungary, concentration of boric acid up to 200 g/l was achieved with a volume reduction factor of 40 to 50 and a DF of 10^5 . The formation of splids during evaporation is generally avoided as these tend to cause problems; evaporator/dryer and wiped film evaporators are, however, designed to operate in presence of solids, and the concentration may continue until a 50 wt % salt content is obtained.

In spite of high operating costs, evaporation is at present almost invariably chosen when high decontamination factors are required ($> 10^3$) or when very low radioactivity discharge is necessary in order to meet regulatory discharge requirements. The presence of volatile nuclides such as tritium and some forms of iodine and ruthenium, particularly at high nitric acid concentration, reduces the overall DF. By adding alkali to the feed solution, the volatility of iodine and ruthenium may be reduced but tritium was not affected. Operation at low evaporation temperature under a reduced pressure decreases the volatility of ruthenium **(Keys et al 1987).**

The condensate resulting from evaporation is an almost salt free solution of very low activity which may be subsequently "polished" by ion exchange, reverse osmosis, or simply fed to another stage of evaporation, befor it is discharged or recycled for use in the plant. The concentrate containing the radionuclides can be directly incorporated into a suitable matrix (e.g. cement, bitumen or plastics) or be dried to produce a salt cake for compaction into pellet form before immobilization. Corrosion may be a severe problem in evaporators, mainly because of the elevated heat transfer surface temperature employed. Severe corrosion of stainless steel at a liquid-vapour interface has been encountered in a nitric acid solution containing substantial amounts of nitrate salts. Corrosion of stainless steel, even at high nitric acid concentration, has been mitigated by using low temperature boiling under reduced pressure conditions. Scaling is caused by the formation of solid deposits on the inner surface of the evaporator, praticularly on the heat transfer surface, reducing the heat transefer efficiency and making it more expensive to operate; it may enhance corrosion .

1.8.3. Ion exchange :

The principle of ion exchange has been known for many years, and its application in water treatment processes was well developed befor its use in the nuclear industry **(Kikuchi et al 1982).** Ion Exchange processes are currently employed in a number of stages throughout the nuclear fuel cycle, from initial extraction of uranium from leach liquors arising from mining operations to the separation of actinides and treatment of wastes arising from fuel reprocessing.

For convenience, ion exchange processes are considered in two groups:

i) Those using organic exchange resins.

ii) Those employing inorganic sorbents.

1.8.3.1. Organic ion exchangers:

Organic exchange resins have been well developed, and a wide range of both anion and cation exchangers is available. The resins are mainly based on polystyrene and phenol formaldehyde onto which active groups are added. The types available are strong acid, weak acid, strong based and weak base materials. By careful selection of the functional group on the resins it is sometimes possible to achive a certain degree of selectivity for various ions. They are widely used in spent fuel storage pond water treatment. The resins are used either in bead form in a packed bed arrangement or as a powder in conjunction with a filter.

The packed bed processes usually involve elution of sorbed radionuclides into a smaller volume of solution followed by reuse of the exchangers, Where as the finely divided resin is used as a filter precoat on a once through basis. The latter method has the advantages of providing removal of both ionic and colloidal material as well as avoiding pretreatment of the waste stream to remove any particulate material that could clog a packed bed. Organic ion exchangers are prone to both thermal and radiation degradation, and certain chemical conditions can also cause degradation. The immobilization of organic resins for deposal can be achieved but there is some concern over the long term stability of the waste form and over the possibility that their presence, even in very low amounts, in a repository may be introduce a potential source of organic ligands that could enhance the mobility of radionuclides and affect the long term safety of the disposal.

1.8.3.2. Inorganic ion exchangers:

The use of inorganic sorbents for treatment of variety of aqueous radioactive wastes was originally made on the basis of their resistance to radiation, generally good resistance to chemical attack and their compatibility with potential immobilization matrices. Inorganic ion exchangers may be either naturally occuring minerals or synthetic materials. They perform the same basic exchange operations as those involved for organic exchangers. The naturally occurring materials comprise aluminosilicate material such as zeolites, clays, feldspars **(Carley-Macauly 1981).** The advantage of naturally occuring materials is their low cost but their industrial use is often difficult (impurities, bad physical properties for packed bed operations) and they sometimes need a chemical or thermal pretreatment.

Inorganic exchangers can be prepared as granular materials but they can also be used as finely divided powders in chemical precipitation processes to enhance the decontamination factor for some nuclides. Inorganic ion exchange is used at certain radio nuclear plants but its application is usually confined to the removal of fission products, e.g. cesium and strontium, from waste effluents. During the past few years, a wider application of inorganic ion exchangers in liquid waste treatment has been investigated for fission and activation product elimination and for alpha emitter removal. The use of small amounts of inorganic ion exchange materials in conjunction with ultrafiltration has been shown to be a very effective decontamination process. A wide range of exchangers exists, so the proper selection of an appropriate inorganic exchanger could lead to a good decontamination for the actinides, fission and activation products.

Many inorganic ion exchangers have shown to exhibit good thermal and radiation stability, and for this reason considerable interest in these materials has arisen in recent years, particulary in nuclear energy field. Although the large majority of recent work on the ion exchange properties of inorganic materials has been conducted with a view towards their possible use in this field, many inorganic ion exchangers possess other advantage over the organic resins which suggest that they could prove useful for applications other than Radiochemicall ones.

Many inorganic ion exchangers are much more selective for certain ions or groups of ions, and most are more easily and are more cheap than the resins. They undergo little or no swelling, which is suffered by their organic counter parts. The resistance of many inorganic ion exchangers to strong oxidising agents **(International Atomic Energy Agency 1984)** offers also an advantage over the organic resins, for the sorption of strongly oxidising ions, or for use under oxidising conditions. Further more, many inorganic exchangers are white solids, thus permitting easy location of bands due to coloured ion on columns. The major disadvantages of inorganic ion exchangers compared with their organic resin counterparts are their generally lower capacities and their lower resistance towards attack by acids and bases. Secondly, the large scale use of granular forms of inorganic exchangers might be difficult, because of poor mechanical stability.

1.8.4. Membrane processes:

These processes enable radioactive contamination to be separated from a waste stream by selective passage of certain components of that stream through a membrane. The pressure driven transfer of material across a membrane is known as either reverse osmosis (RO), ultrafiltration (UF) or microfiltration (MF), depending on the pore size in the membrane.

Radioactive waste treatment applications have been reported for the laundry wastes in nuclear power plants, of mixed laboratory wastes, and for clean up of boric acid solutions for recycle. Good decontamination and high volume reduction are being achieved using ultrafiltration to separate the floc and liquid **(Gutman 1986).** The high DFs from pilot plants were achieved by addition of a small quantity of titanium (IV) solution to form hydrous titanium oxide which is a good absorber for alpha activity during precipitation of ferric floc. The pilot plant was successfully operated to give a volume reduction of about 200 and produce a concentrate containing about 1 wt % solids.

1.9. Immobilization of Radioactive Waste:

An important treatment preliminary to the disposal of radioactive waste is its immobilization (solidification) corporation into a stable medium from which the radioactive components can not readily be leached by any medium which may come in contact with waste after disposal. The development of processes for immobilizing radioactive wastes by mixing them with various substances to give solid products of good properties severely limit the mobility of the radioactive materials has produced the possibility of safe and cheap storage or disposal of the wastes. There are different processes for immobilization of radioactive waste in a matrix material. Cementation and bituminisation processes are used throughout the world for many years.

1.9.1. Cementation processes:

For several years in different countries **(Christensen 1979)** the cementation processes for nuclear waste immobilization with and without additives have been used. Basically, the process consists of mixing the cement with the radioactive waste (solution, slurry or solids) in containers. The cement mixture is then allowed to set and various cementation processes were applied.

1.9.2. Modified cementation processes:

To gain a better quality of the cement waste forms the cementation processes were modified by introducing impregnation procedures. The basic idea is to fill or to cover the pores and thus lower the leach rate. This polymer-impregnated concrete (PIC) is essentially impermeable with improved strength, durability and resistance to chemical attack **(Management of Low- and Intermediate-Level Radioactive Wastes 1970).**

1.9.3. Bituminization processes:

For several years in different countries the bituminization process for nuclear waste immobilization has been used. Basically the process consists of mixing solutions, sludges or solids with bitumen at elevated temperatures. The water contained in the waste is evaporated and the residual particles are uniformly coated with a thin layer of bitumen **(International Atomic Energy Agency 1983).** The bitumen mixture is released in suitable containers where it cools down and solidifies. The properties of the bitumen waste form are affected by the radwaste constituents, e.g. nitrates, borates……… etc.

1.9.4. Polymer processes:

Immobilization of radioactive waste into polymeric agents is relatively new immobilization process compared to incorporation in cement or bitumen. The immobilization with polymer can take place either at ambient temperature or with hot liquid up to 60 °C . All the polymer processes are essentially batch processes where a catalyst is generally mixed with the wastes and polymer either in a pre-mixer vessel or in the receptacle itself. The polymeric processes do not really solidify the wastes, the long chained molecules of the organic polymer are linked together to form a porous sponge that traps the radioactive waste.

1.9.5. Vitrification (immobilization in glass):

Radioactive wastes are evaporated and then mixed with glass-forming materials melted and poured into stainless steel canisters which are then sealed by welding **(Glasser 1985).**

1.9.6. Synroc:

A more sophisticated method of immobilising radioactive wastes has been develiped called 'Synroc' (syntheticrock). The radioactive wastes are incorporated in the crystal lattices of the naturally-stable minerals in a synthetic rock. In other words, copying what happened in nature.

1.10. Properties of Immobilized Waste Forms:

The properties that are usually considered for the safety and economics of solidified low and intermediate level wastes management are:

- long-time chemical stability (leachability)
- Mechanical strength, thermostability and radiation resistance
- Compatibility with container.

Low leachability is generally considered as one of the most important properties in the evaluation of the immobilized waste form, where it represents the first barrier to the release of radionuclides to the environment over long periods.

Mechanical strength is desirable, especially during transport, to reduce the probability of waste forms breaking into smaller pieces.

Compatibility between the solidified waste form and the container is necessary since in most cases, corrosion from the outside should for out weight corrosion from the inside.

A knowledge of many physical, chemical, physico-chemical and Radiochemicall properties of the solidified waste forms is required for understanding the immobilization process for packaging, transport, storage and disposal of the immobilized waste form **(Lefillatre 1976).**

1.10.1. Chemical and physico-chemical properties:

A knowledge of the flammability of an immobilized waste form is important to safety in handling and is also necessary in meeting the criteria of the various regulatory bodies that govern its transportation **(Lerch 1977).**

The leaching rate of immobilized wastes can be measured by several methods. Four main methods have been generally accepted:

1- A rapid leaching test carried out with laboratory samples using an extractor of the soxhlet type (72-h residence time, at 100 °C, according to ISO recommendations).

2- A long-term leaching method carried out with laboratory samples according to IAEA recommendations **(International Atomic Energy Agency 1971).**

3- A long-term method (not yet standardized) carried out with a full scale waste form without container following the IAEA recommendations as far as the leaching water renewal frequency is concerned.

4- A static leaching test using laboratory samples has been proposed by the materials characterization center (MCC) in the united above in that it neither circulates nor replaces the leaching water.

1.10.2. Radiochemical properties:

The physical or chemical characteristics of immobilized waste forms can change as a result of alpha, beta, gamma radiation. When the absorbed radiation doses are high the solidified waste form undergo significant changes. Experimental results have shown that, in general most low and intermediate level radioactive wastes immobilized in any matrix materials (i.e. cement, bitumen, polymer and epoxy resins) can withstand such radiation doses under the conditions for storage and disposal **(Auboium et al 1980).**

1.10.3. Physical properties:

The changes in external condition (e.g. temperature, pressure and climate during storage, transport and disposal) may lead to changes in physical properties. Therefore the physical properties of an immobilized waste form should always be considered in the selection of the disposal system **(Donato 1976).**

1.10.3.1. Waste / matrix ratio:

It is necessary to know the relative loading of the waste in the final waste forms for comparing the physical properties.

Generally the amount of solid, dry waste incorporated in a matrix is in the range 10-15% by volume.

1.10.3.2. Density:

The useful value for the density of a product in case of deep –sea dumping, was more than $1.2 g/cm^3$. Higher density is also required.

1.10.3.3. Porosity and permeability:

Residual porosity in the solidified waste form affects the mechanical and physico-chemical properties. Cement matrices contain inter connected porosity that leads to high internal surface areas if the water/cement ratio is high.

1.10.3.4. Mechanical properties:

The mechanical properties of the final waste form is determined by its resistance to the ionizing radiation and the external environment (temperature or pressure). If an immobilized waste form is exposed to an accident or long term stresses during handling, storage, transport and final disposal, certain minimum values for range of mechanical properties are required.

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Treatment of low level radioactive liquid waste containing cesium-137, cobalt-60 and europium-(152+154).

Reffat (1999) studied the sorption capacity of ^{134}Cs, ^{60}Co and $^{(152+154)}$Eu presented in waste solutions by thre e prepared polymers: polyacrylic acid (PAA), polyacrylamide-acrylic acid (PAM-AA) and polyacrylamid-N-vinyl-2-pyralidon (PAM-NVP) as ion-exchangers. Results showed that, the uptake % of radioisotopes ^{134}Cs, ^{60}Co and $^{(152+154)}$Eu by the investigated polymer (PAA) amounted to about 18-85% and the time of equilibration was attained after 1, 2, 2.5 hours, respectively. In case of (PAM-AA), the uptake of radioisotopes ^{134}Cs, ^{60}Co and $^{(152+154)}$Eu reached about 43, 35, 74% and the equilibrium was attained after 2, 2, 3.5 hours, respectively. In case of (PAM-NVP), the uptake % of radioisotopes ^{134}Cs, ^{60}Co and $^{(152+154)}$Eu reached about 25, 15, 20% and the equilibration time was attained after 3.5, 3, 3.5 hours respectively. With respect to the effect of pH it was found that, the uptake of the studied radioactive isotopes increases by increasing the pH until it reaches the maximum value at pH 7.5.

Mohamed (1999) studied the possibility of decontamination of radioactive waste solutions containing ^{60}Co and $^{(152+154)}$Eu using natural sorbents like humic acid, clay and pottery. He found that the sequence of increasing uptake as related to the kind of sorbent follows the order pottery < black pottery < brown pottery < raw pottery < clay. Results also showed that the sequence of increasing uptake as related to the metal ions is found,

$Co^{2+} < Eu^{3+}$. The release of Eu^{3+} increased with increasing the pottery weight to a maximum value of 5.7%.

El-Dessouky et al (2000) used natural inorganic exchangers to remove cesium-137, cobalt-60 and europium-(152+154) using zinc sulphate as a coagulant and also different clay minerals. These clays include, feldspar, aswanly, bentonite, haematite, mud, calcite, basalt, magnetite, kaoline, sandstone, limonite and sand. The factors affecting removal process which are pH, partcle size, temperature and weight of the clay have been studied. Highest removal for Cs-137, Co-60 and Eu-(152+154) was achieved by aswanly and bentonite. Sandstone is more effective than the others. Solidified cement products have been evaluated to determine the optimum conditions of mixing most sludges containing clay by testing mechanical strength and leaching rates of the waste products.

Mohamed (2001) used some local environmental materials include sand soil, red brick and basalt stone in treatment of low level liquid wastes containing the radioactive isotopes Co-60 and Cs-137. The results indicated that, using a mixture of selected three materials, sand soil, red brick and basalt stone with ratio of 1:2:1 respectively, led to remove 95% of the radioactive materials by adsorbing it at their surface at pH 7.5, he deduced that these natural materials can be used for treatment of radioactive liquid wastes. The efficiency of these materials in the sorption of radioactive elements was studied. They found that red brick was the most suitable adsorbent as it is not affected by acids and can be used several times after treatment with 5N HCl.

Apak et al (1995) tested the use of red muds (Bauxite wastes of alumina manufacture) for radio cesium removal from water. Fractionation of the sorbent with respect to apparent grain size did not produce significant differences in the sorption efficiency. The distribution coefficients versus the respective equilibrium activity in solution showed a maximum with Cs. The traced solution activity against the adsorption data were fitted the B.E.T. (essentially types IV-V) isotherms for Cs. Desorption, temperature, PH and ionic strength-dependence tests revealed that the primary mode Cs sorption is specific adsorption while the secondary mode is ion exchange process. A rise in pH favors the ion exchange sorption of Cs is negatively affected. Competitive adsorption of an inert electrolyte, i.e. NaCl, was found severely hinders Cs sorption.

Sobolev et al (1998) showed that glass-based materials for immobilize various liquid and solid radioactive wastes generated at nuclear power plants (NPP) were designed. Glassy waste forms could be produced using electric melting including a cold crucible melting. Leach rate of cesium was 10^{-5}-10^{-6} g/(cm^2.day) (IAEA technique). Volume reduction factor after vitrification reached 4-5. Various technologies for NPP waste vitrification were developed. Direct vitrification means feeding of source waste into the melter with formation of glassy waste form for disposal. Joule heated ceramic melter, and cold crucible were tested. Process variables at treatment of Kursk, Chernobyl (RBMK), Kalinin, Novovoronezh (VVER) NPP wastes were determined. The most promising melter was the cold crucible. Pilot plant based on the cold crucibles has been designed and constructed. Solid burnable NPP wastes are incinerated and slags are incorporated in glass.

Schmidt and Chrubasik (1999) showed the volume reduction of the low level liquid (LLLW) by means of selective sorbents. Evaporator concentrates from the main LLLW stream, generated in operating nuclear power plants. The specific activity, (mainly for cesium and cobalt) was in the range between 10^6 and 10^7 Bq. The treatment methods usually used are cementation or bituminization if a matrix is necessary. In both cases the achievable volume reduction factor was 4. The cost for intermediate term and final storage, respectively has increased continuously in the recent years. So it is very advantageous to reach high volume reduction factors. With international co-operation a new process for treatment of evaporator concentrates has been developed and tested at pilot scale using evaporator contentrates generated in Kalinin NPP, Kola NPP and Khmelnitskij NPP. The results showed a volume reduction factor for the waste stored is of the order of 30 to 50. After separation of the radio cesium and cobalt the evaporator concentrates can be treated as a chemical waste.

Separation of Cs from high level waste by the inorganic exchangers has received much attention during the last three decades. In this concern granular mixed and complex inorganic exchangers with acid salts as one of the components have been developed and tested for the suitability of these exchangers to column operations and specificity in removing Cs from high level fission products acidic wastes. Decontamination factors and volume reduction factors at 1% break through values for Cs from different types of simulated acidic fission products waste solutions containing high salt concentrations.

El-Dessouky et al (2001) investigated fossil fuel fly ash (F.A.) and fumed silica (F.S.) as possible sorbents in treatment of liquid radioactive wastes. For the sorption studies, the original fly ash was activated at first by heat treatment at the different temperatures: 200 and 500 °C. Fumed silica was used as-received, where it was washed only by different solvents: water and dilute mineral acids. Heat treatment had no influence on its sorption tendency. Characterization for the original fly ash indicated the presence of some metal cations and non metal anions in addition to lower concentrations of organic matter. Differential thermal analyses (DTA) of the original fly ash indicated a phase transformation at 482.4 °C, this result was confirmed by its X-ray diffractograms. Photomicrographs, obtained from a scanning electron microscope (SEM) for the investigated materials had proven their porous and amorphous nature.

2.2 Solidification of radioisotopes in ordinary portland cement .

El-Dessouky et al, (1997) added fly ash to different radioactive waste sludges and solidified it in cement matrix. The studies showed that, the treated fly ash (TFA) enhanced the properties of the waste package and reduce the leach out of the radionuclides Cs-137, Co-60 and Eu-152,154 more than neat cement and waste sludge.

Hoyle and Grutzeck (1989) showed that the leach behavior of cesium from a series of cement-based waste forms modeled in terms of pore solution concentration and phase formation data. Cement-based materials enriched in alumina and silica, and compositionally related glasses, were hydrated in the presence of cesium hydroxide to gauge the degree of partitioning of cesium by the developing hydrates. The compositions of the pore solutions extracted from the cement-based waste forms were compared with corresponding leach data for companion samples. In both pore solution and leachantes, the retention of cesium was found directly related to the bulk composition of the waste form; the degree of partitioning of cesium by the hydrated phases increased as more alumina and/or silica were added to the formulation, suggesting that cesium-containing phases were formed. Additionally, the leachante concentration of cesium for any given composition was also found related to the pore solution concentration. This observation led to the development of a leaching model for cement-based waste forms in which the concentration of cesium in the leachate could be described in terms of pore solution concentration, diffusion, dissolution, and development of cesium host phases.

Khalil (1994) showed that ion exchange materials loaded with radioactive isotopes are generated in several processes along the nuclear fuel cycle. He investigated the possibility of solidifying ion exchanger in water glass to replace cement. Ion exchange powder was loaded with radioactive Cs-137 solidified in sodium water glasses, hardened with AIPO sub 4 and leached in water and Q-brine at 50 °C. control samples were made of high alumina cement under similar conditions. Tolerance of solidified matrix to water was quite adequate. Samples maintained their shape and dimensions to the end of the experiments. In Q-brine, samples were cracked or broken to small pieces within the first week. The fraction of ^{137}Cs leached into Q-brine was 70-90 % and not more than 14 % in water. Sodium water-glass was shown to be superior phase in water, while cement behaved better in Q-brine.

Abotsi (1996) evaluated the final forms that have been proposed for radioactive-containing solid wastes to determine their application for solid wastes that result from the treatment of newly generated liquid low-level waste (NGLLLW) and Melton Valley Storage Tank (MVST) supernate at the Oak Ridge National Laboratory (ORNL). Since cesium is the predominant radionuclides in NGLLLW and MVST supernate, he focused on the stabilization and solidification of solid wastes containing this radionuclides in cement, glass, and polymeric materials. The principal waste forms were tested with these types of wastes. Several studies showed that cesium is leached by distilled water from the solidified cement. The situation is exacerbated by the presence of sulfates in the solution, as manifested by cracking of the grout . Additives such as bentonite, blast-furance slag, fly ash, montmorillonite, pottery clay, and silica generally decrease the cesium release rate. Longer cement curing times (> 28 d) and high ionic strengths of the leaches, such as those that occur in seawater, also decrease Cs leach rate. Lower cesium leach rates were observed from vitrified wastes than from grout waste forms. However, significant quantities of cesium were volatilized due to the elevated temperatures required to vitrify the waste . Hence, vitrification generally requires the use of cleanup systems for the off-gases to prevent their release into atmosphere.

El-Dessouky et al, (1993) investigated the suitability of cement matrices for use as a solidifying agent for low and intermediate level radioactive wastes. The leachability of Cs-137 from simulated radioactive liquid waste solidified with portland cement, blast-furance slag cement and 50/50 portland/slag cement was investigated using the standard leach test. The solidification process was carried out at an optimum waste/cement ratio of 0.30 . The mechanical strength as a function of the curring time and after immersion in different leachants for one month was studied.

Sandor and Laszlo, (1997) studied the immobilization of cesium in cementitious matrices , they showed that the radioactive waste containing cesium doesn't form stable compounds therefore it can't be readily immobilized. Model matrices were prepared to map up the calcium-silicate-aluminate system considering cesium immobilization, which were of different starting compositions. To characterize cesium sorption, distribution ratios were determined. Based on the results obtained the model matrix compositions were prepared using industrial grad materials and their cesium retardation and trapping were examined by means of leaching and sorption experiments. In the light of the results obtained, it can be established that immobilization of cesium significantly depend on the starting composition of the used matrix .

El-Dessouky et al (2001) The destruction of spent TBP/Kerosene (odourless kerosene (OK)) with potassium permanganate has been investigated. Comparative studies on the immobilization of spent TBP/Kerosene and its degradation product into different matrices have been carried out. The matrices used include, ordinary portland cement, silica fume, treated fly ash, epoxy resin and cement mixed with epoxy resin. The different factors affecting solidified waste forms, such as mechanical strength, water resistance, thermal stability, chemical resistance, radiological stability and leachability have been investigated. It was found that epoxy resin and cement mixed with 5, 10, 20, and 50% of epoxy resin enhance the mechanical strength of the solidified waste forms with spent TBP/OK more than that obtained from degradation products.

The leaching rates of Eu-(152+154) from waste forms containing TBP/OK was found lower than that with degradation products.

Dellamano (1995) showed that, cement has been used around the world as the main matrix to immobilize low-and intermediate-level wastes. Cemented waste forms must comply with some requirements in order to guarantee the safe handling in the subsequent waste management steps. Silica-fume can improve the properties of the cemented waste forms. It was used as admixture in the cementation of ion-exchange resins and liquid waste from fission Mo-99 production. The behaviour of the waste forms produced were evaluated by measuring four required properties: setting time, hydration temperature of the fresh mixture, mechanical mechanical strength and leaching rate of the hydrated product.

Berson et al (1997) have been conducted a series of preliminary tests to examine the concept of reducing radionuclides leachability by controlling crack binder modifiers. Four types of cementitious materials were prepared plain mortar, cement paste with silica fume, ECC (paste) with silica fume, and ECC (mortar) with silica fume. The results showed that the optimum combinations of fiber reinforcement (such as ECC technology) and matrix modifiers (such as silica fume or clay) can significantly reduce Cs leachability. Since the current version of ECC materials were primarily developed for structural applications, further reduction in leaching of all radionuclides can be expected when careful consideration is given to matrix modification and selection of reinforcing fibers.