CHAPTER-1

INTRODUCTION

At present time the different environmental compartments suffer from excessive accumulation of various toxic pollutants, hazardous fallout contaminants and several naturally occurring radionuclides, including potassium-40, thorium and uranium with the natural decay series of Th and U as well as several other man-made radionuclides. It is now of common practice to regulate any uncontrolled release of hazardous wastes in different environmental compartment [1]. Toxic hazardous wastes are defined as containing chemicals posing substantial hazards to human health or to the environment when improperly treated, stored, transported, or disposed. Scientific studies show that they have toxic, carcinogenic, mutagenic, or teratogenic effects on human or other life forms. The majority of hazardous waste is generated by the chemical manufacturing, petroleum, pesticides and coal processing industries. Hazardous wastes may enter the body through ingestion, inhalation, dermal absorption, or puncture wounds [2].

1.1. Radioactivity:

Radioactivity is discovered by Henri Becquerel in 1896. It is a phenomenon in which radiation is given off by the nuclei of the elements. This radiation can be in the form of particles or electromagnetic radiation or both. The process of radioactive decay or disintegration is a statistical phenomenon. The mathematics of radioactive decay is based on the simple fact that the number of atoms disintegrating per unit time ($\Delta N/\Delta t$) is proportional to the number of radioactive atoms, (N) present. This formula can be written as [3,4]:

$$\frac{\Delta N}{\Delta t} \propto N$$

or

$$\frac{\Delta N}{\Delta t} = -\lambda N \qquad (1.1)$$

Where: λ is the decay constant. If ΔN and Δt are so small that they can be replaced by their corresponding differentials, dN and dt, then equation (1.1) becomes differential equation. The solution of this equation gives the following equation:

$$N = N_o e^{-\lambda t} \qquad (1.2)$$

Where: N_o is the initial number of radioactive atoms.

For radioactivity levels, the activity (A) of given elements is defined as the number of decays per unit time as follows:

$$A = -\lambda N \qquad (1.3)$$

and have the same exponentional behavior, where:

$$A = A_o e^{-\lambda t} \qquad (1.4)$$

Where: A is the activity remaining at time t and A_o is the initial activity at zero time.

The term half-life ($t_{1/2}$) of a radioactive isotope is defined as, the time required for either the activity or the number of radioactive atoms to decay to half of its initial value. By substituting $N/N_o = ½$ in equation (1.2) or $A/A_o = ½$ in equation (1.4), at $t = t_{1/2}$, we have [3,4]

$$t_{1/2} = \frac{0.693}{\lambda} \qquad (1.5)$$

1.1.1. Types of Radioactivity:

Radioactivity is defined as the property possessed by some elements with spontaneously emitting alpha particles (α), beta particles (β), and/or gamma radiations (γ) by the disintegration of the nuclei of atoms. Radioactivity is a naturally occurring phenomenon. It cannot stopped, and taking place since the beginning of time. The process of unstable nuclei giving off energy to reach a stable condition is called radioactive decay. Radioactivity can exist as gaseous, liquid or solid materials. Radon is a well-known example of a radioactive gas. Water often contains dissolved amounts of radon, radium and uranium. Solid radioactive waste is produced from many sources, including the uranium and rare earth mining industries, laboratory and medical facilities, and the nuclear power industry [2].

1.1.2. Units of Radiation Measurements:

Two units are used for radiation measurement. The first deals with the amount of the radioactive isotopes present in any material (e.g. contaminated scale sample). While the second deals with the exposure that, the source creates .The two are related, but the relationship is a complicated one. The amount of radioactivity in a radioactive materials, is measured in terms of Curie (Ci) in the USA and the Becquerel (Bq) in the SI system [4]. The Curie (Ci) equals to 3.7×10^{10} disintegration per second (dps or Bq), which is equal to the activity of one gram of radium (Ra-226). The subunits of Curie are milli curie (10^{-3} Ci), micro curie (10^{-6} Ci), nano curie (10^{-9} Ci) and pico curie (10^{-12} Ci). These units are given as follows:

$1mCi = 3.7\times10^{7}$ Bq, $1\mu Ci = 3.7\times10^{4}$ Bq, $1nCi = 3.7\times10^{1}$ Bq,

$1pCi = 3.7\times10^{-2}$ Bq, and $1Bq = 1dps = 2.7\times10^{-11}$Ci.

The second unit is related to radiation exposure, person's overall exposure depends on the time and concentration that an individual is exposed. Radiation exposure is measured in terms of a unit known as the roentgen equivalent man (Rem) in the USA system while Gray (Gy) or Sievert (Sv) are used in the SI system [4]. Use of Rem and Sv units are based on the physical properties of different types of radiation and their biological effectiveness. Both units are also representing exposure to a relatively large amount of radiation. It is generally measured as rate, mRem/h or μRem/h or μSv/h. The relation between the two units is given as: 1Sv=100 Rem.

1.1.3. Sources of the Environmental Radioactivity:

The radioactivity in our environment comes mainly from two sources either man-made and/or natural sources. Therefore, the radioactivity is released from various activities, such as the naturally occurring radionuclides present in our houses, air, water, foods and several industrial activities. The main sources of radioactivity are categorized as follows:

1.1.3.1. Man-made sources:

Radioisotopes are used extensively in medical facilities, biomedical research laboratories, and to a lesser extent in other types of laboratories. Clinical use of radioisotopes is expanded rapidly in such areas as cancer treatment and diagnostic testing. The lack of waste management plans at many of these

facilities results in frequent misclassification of materials as radioactive. Relatively large amounts of radioisotopes are used in clinical procedures. Most of these isotopes are strong emitters for gamma radiation, because they have short half-lives, such as technecium (Tc-99m, $t_{1/2}$ = 6h) and iodine (I-131, $t_{1/2}$ = 8.1d) [2]. The use of nuclear devices in weapons is the primary cause of radioactive fallout, although the nuclear accident at Chernobyl and various volcanic eruptions have although contributed. Tritium and several isotopes of iodine, cesium and strontium are found in the environment largely because of nuclear testing. In the United States (U.S.), most radioactive waste is a by-product of nuclear weapons production. It is estimated that 70% of U.S. radioactive waste results from defense department activities [2].

The amount of radiation to be received, which comes from man-made sources represent about one-third of the amount received from natural sources (~ 0.8 mSv/y). The largest amount of radiation exposure occurs from man-made procedures. The exposure that most people receive comes from Co-60, I-131, Tc-90m and X -ray sources, to be used therapeutically and in the diseases treatment [5].

1.1.3.2. Natural sources:

In nature, there are four naturally occurring radioactive decay series. The first series, known as thorium series, consists of a group of radionuclides related through decay in which all the mass numbers are evenly divisible by the number four (4n) series. This series has its origin radionuclides Th-232, its abundance is 100%, specific activity is 2.4×10^5 dpm/g, which undergoes α -decay with a half-life of 1.41×10^{10} y. The terminal nuclide in this decay series is the stable Pb-208, which is also known as ThD. In this series, the transformation from the original parent Th-232 to the finial product Pb-208 requires 7α and 4β -decays. The long-lived intermediate is 6.7 y for Ra-228, (Fig. (1.1)).

The second series consists of group radionuclides whose mass number when divided by 4 has a remainder 1 (4n + 1) series. This is known as the neptunium series since the longest lived, and therefore the parent is Np-237, which undergoes α -decay with half-life of 2.1×10^6 y, (Fig. (1.2)). In as much as this half-life is considerably shorter than the age of the earth, Np-237 can no longer exit on the earth, therefore, the neptunium series is not found in as

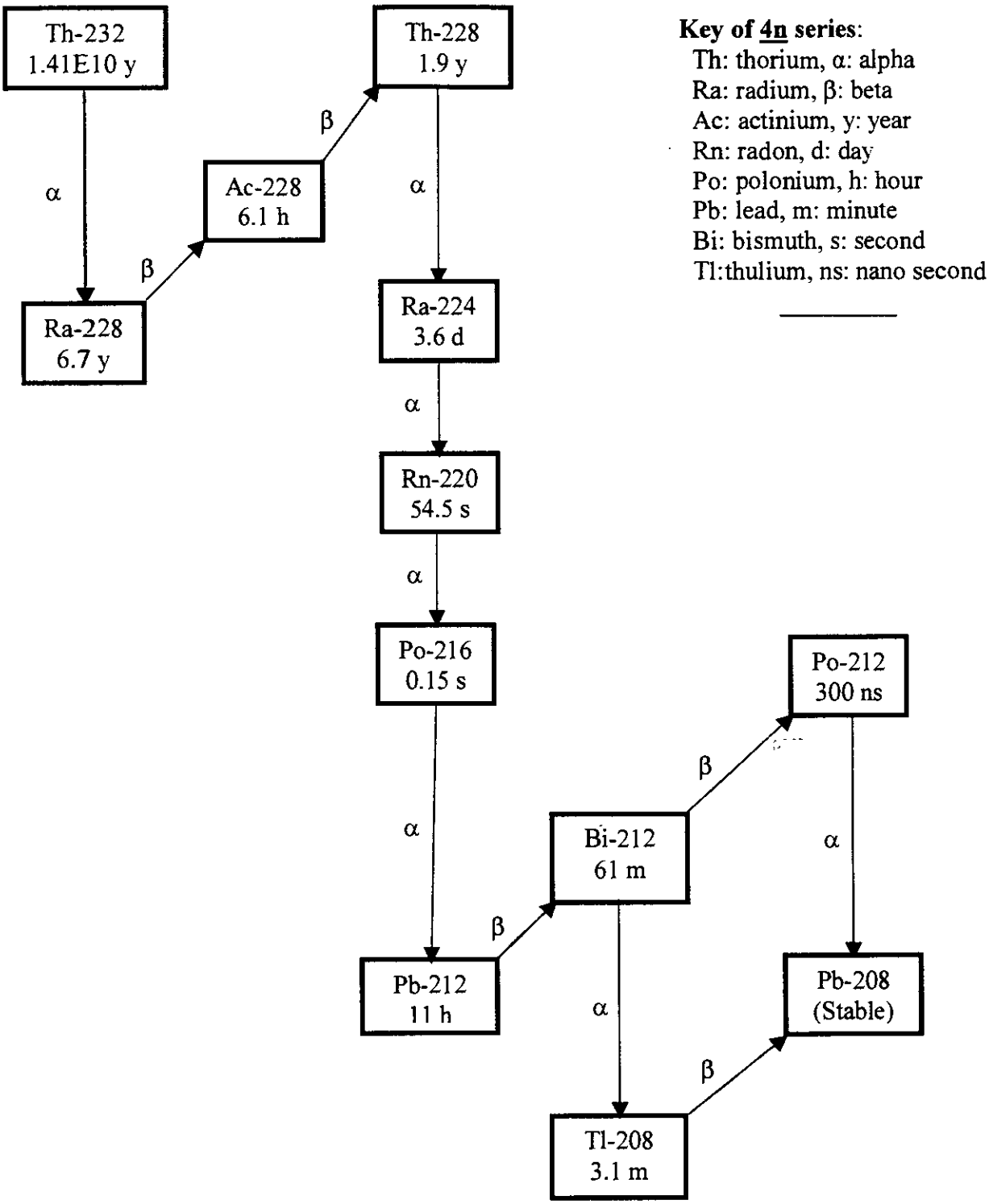

Fig. (1.1): Scheme of the thorium decay (Th-232) series.

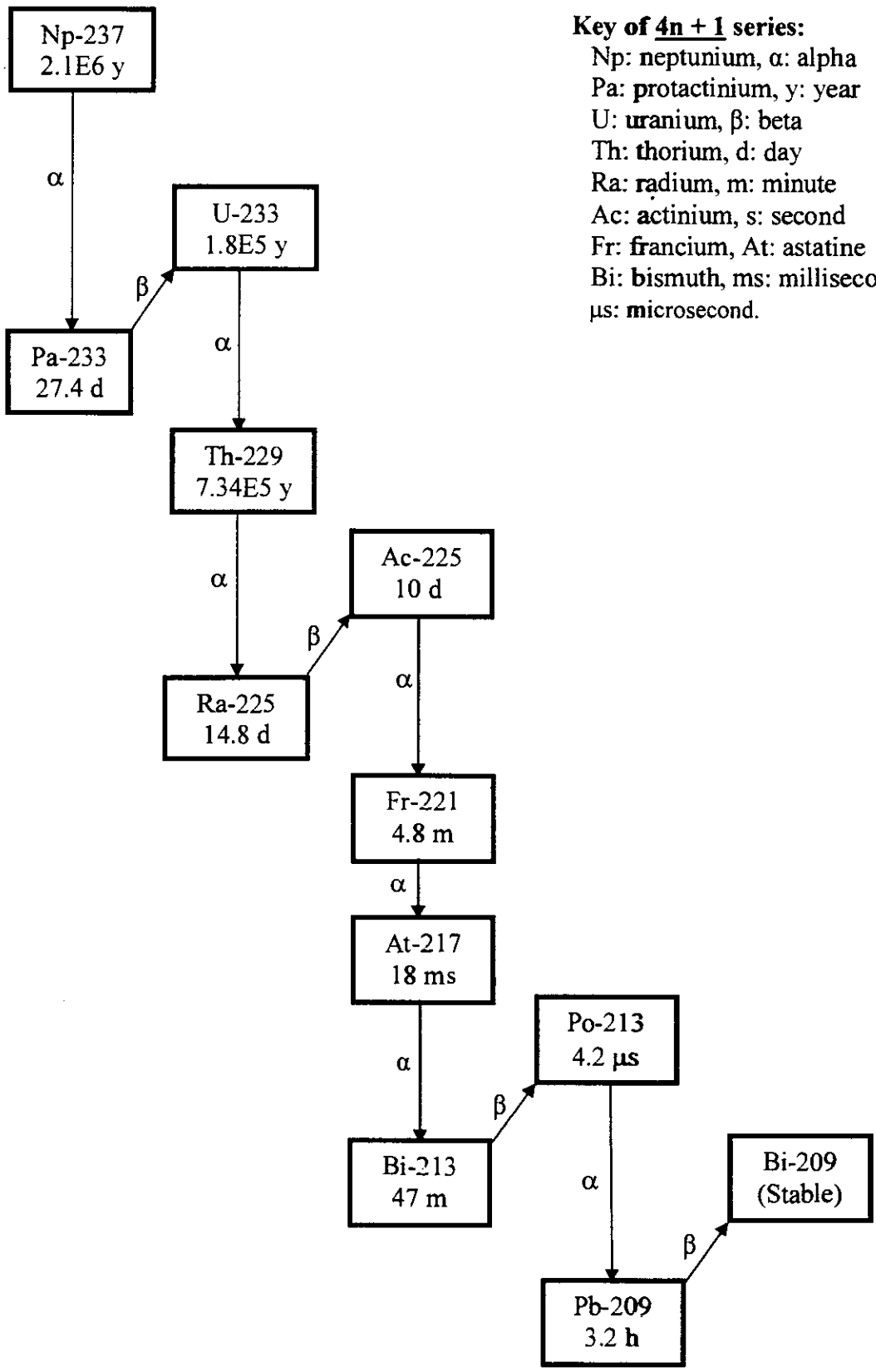

Fig. (1.2): Scheme of the neptunium (Np-237) decay series.

a natural occurrence. However it has been discovered in the spectra of some stars. The end product of neptunium series is the stable isotope Bi-209. Seven α and 4β -emission are required in the sequence of decay from the parent Np-237 to Bi-209. An important nuclide in the neptunium decay series is the uranium U-233, which has a half-life of 1.8×10^5 y, and like U-235, is fissionable by slow neutrons [3,4,6].

The third series is the uranium series, which consists of group radionuclides that, when their mass number is divided by 4 have a remainder of 2 (4n + 2) series. The parent radionuclide in this series is U-238 (abundance = 99.27 %), which undergoes α -decay with a half-life of 4.47×10^9 y. The stable product of the uranium series is Pb-206, which is reached after 8α and 6β -decay steps, (Fig. (1.3)). This is a particularly important series in nature since it provides the more important isotopes of elements Ra, Rn and Po, which can be isolated in large amounts in the processing of uranium minerals. Each ton of uranium is associated with 0.34 g of Ra-226. Radium-226 reaches radioactive equilibrium with all its daughter products to Pb-210 in several weeks. Many of the daughters emit energetic γ -rays. The fact that the radium produces radioactive gas (radon) complicates its handling. The decay of radon produces airborne radioactive atoms of Po, Bi and Pb, which may cause contamination of the surrounding.

The fourth radioactive decay series, known as actinium series, consists of a group of nuclides whose mass number divided by four leaves a remainder of 3 (4n + 3) series. The head of this series is U-235, which has an abundance of 0.72 % and a half-life of 7.1×10^8 y for α -decay. The stable end product of this series is Pb-207, which is formed after 7α and 4β -decay steps. The specific activity of U-235 is 4.8×10^6 dpm/g, (Fig. (1.4)), [4].

There are much individual radioisotopes in environment not in series, like potasium-40 ($t_{1/2}$. 1.28×10^9 y, isotopic abundance 0.0118 %), is another important, potential radioisotope found in nature. K-40 is found in plants, animals and in human bones. It is widely distributed in nature with volume concentrations ranging from 0.1 to 3.5 % in carbonates (limestones). The bones of an average human contain concentrations of ~ 17 mg of K-40. The average radiation dose received from K-40 is 0.25 mSv/y to tissue and ~ 0.36 mSv/y to bone.

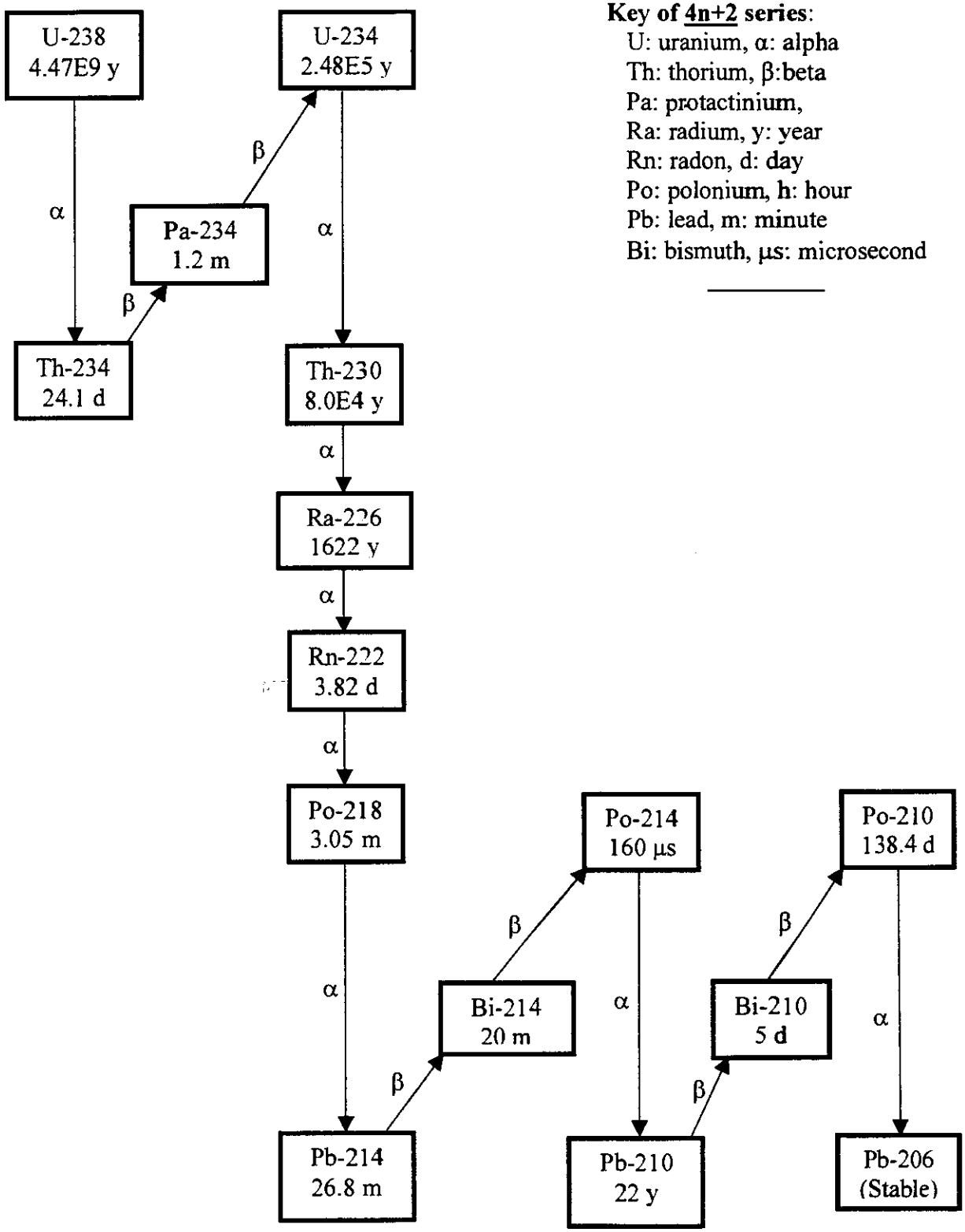

Fig. (1.3): Scheme of uranium (U-238) decay series.

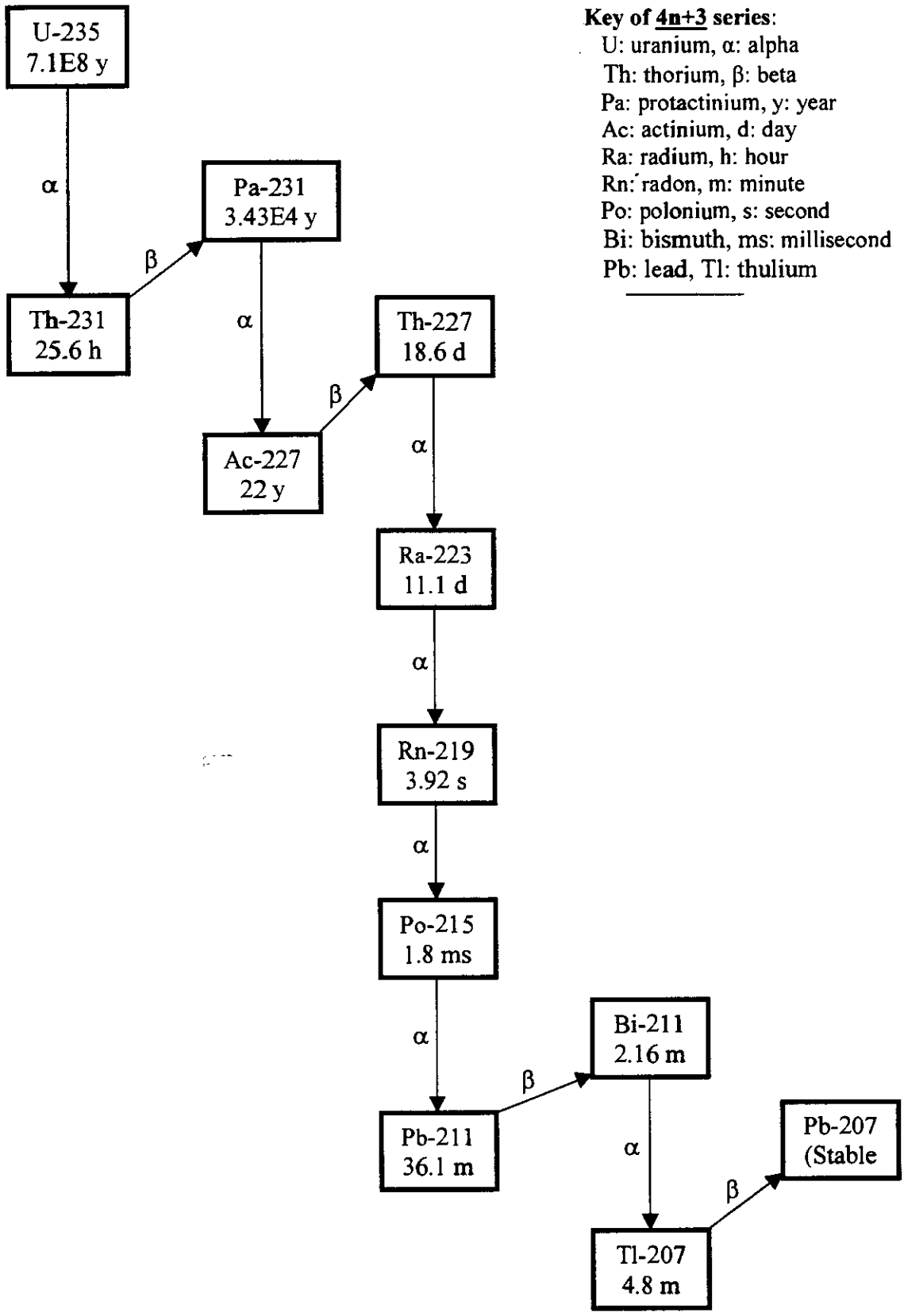

Fig. (1.4): Scheme of actinium (U-235) decay series.

The nuclear fuel cycle is defined as the activities carried out to produce energy from nuclear fuel. These activities include, mining of uranium containing ores, enrichment of uranium to fuel grade specifications, fabrication and use of fuel rods, isolation and storage of waste produced from power plants. Mining, processing, use of coal, natural gas, phosphate rock and rare earth deposits result in the concentration and release or disposal of large amounts of low-level radioactive materials. Coal fired power plants release as much radioactivity to the environment as nuclear facilities and the fly ash residue contains low level of several natural radioisotopes. Natural gas exploration is one of many radon sources in the environment. Phosphate rock has always associated with natural radioisotopes; in many cases, tailings from phosphate operation have levels above those allowed by the Nuclear Regulatory Commission (NRC) for release to the environment. Processing of rare earth containing ores produce concentrated radioactive waste can be disposed as low-level radioactive waste. If monazite ore is the rare-earth source, nearly one ton in ten must be disposed of in this manner [2]. Radioactivity in groundwater is almost due to natural deposits of uranium and/or thorium as well as potassium-40. Strict guidelines for acceptable levels of radionuclides in drinking water exist. The Environmental Protection Agency (EPA) has established maximum levels for radium to monitor for the presence of natural radionuclides. Radon is a colorless, odorless, inert and radioactive gas that escape out of the earth has been found at dangerously high level in inadequately ventilated buildings. Radon originates from the radioactive decay of uranium, thorium and/or radium. The EPA states that levels above 0.148 Bq/L should be reviewed for possible corrective actions [2].

Naturally Occurring Radioactive Materials (NORM's) are those materials that contain radioactive elements what are found naturally in the earth's environment. Examples of these radioactive elements are the U-238, U-235, Th-232 series and their respective decay daughter, as well as potassium-40. NORM's exist in soil, water, plants, animals, human, coal, lignite, petroleum, phosphate ores, geothermal wastes, wastewater...etc., in small but varying amounts almost everywhere [7].

On the other hand, nearly all the naturally occurring radioactive materials are considered in balance state. However, in several industrial processes e.g., mining of elements (U, Th, and rare earth's metals), phosphate, oil and gas

production, concentration of the natural radionuclides may be altered than its physical state, and exists in concentrations over than that exists naturally.

Wastes associated with the various industrial activities, with enhanced levels of the natural radioactivities as a result of accumulation, causes what is call, "Technological Enhanced-Naturally Occurring Radioactive Materials", to be named as acronym word **"TE-NORM"**. For instance, TE-NORM scales may build up the inside of oil field production tubing and may concentrate considerable quantities of radioactive material that has the potential to expose humans to relatively high dose of radioactivity. TE-NORM is often precipitated as sludge and scales. The human body cannot sense or detect TE-NORM, so, it can be detected and measured by specialized instrumentation [8].

1.2. Radiological Aspects:

1.2.1. Radiation Hazards:

The danger of radiation to human health was recognized during the early years of investigation on radioactive materials carried by the Curies, but little was done at that time to recommend safe handling practices. Many researchers suffered radiation burns and eventually died from radiation-induced cancers [9,10]. Radiation interacts with biological material in the same ways that, it interacts with other types of matter. In this concern, the initial effects of radiation occur at the molecules level. The ionization and excitation of the molecules of the organism may alter the chemical nature of the molecules.

The biological consequences of these ionizations depend on the identity and number of molecules that are affected. Radiation damage to protein molecules, which are the most important structural and physiological molecules in a living system, could cause immediate adverse effects in the organism's structure and/or function. It is more likely, however, that the damage is one that, would not be immediately observable, but would lead to the development of some abnormality in the future. Generally, radiation effects on the biological systems can be put into two broad classes: stochastic and non stochastic [10].

The stochastic effects are related to long-term, low-level exposures to radiation, and usually the outcome of radiation damage done initially to only a few cells. It is extremely difficult to determine accurately the effects of low level of radiation, because there are no immediate observable effects. On the

other hand, the non stochastic effects of radiations on the human are related to large radiations doses received over short period of time, where, these effects are usually seen on whole organs or body systems, rather than in only a few cells. The severity of the effects depends on the total dose, time of exposure, the irradiated part of the body, whether the dose was external or internal, and the age of the person. The most important non-stochastic effects include skin changes, alteration in the blood, gastrointestinal problems, and central nervous system changes [10].

1.2.2. Detection of Radiation:

For field detection, portable exposure survey meters are used for this purpose, to screen the different radioactive types [11]. This method is rapid and performed generally using 1"×1" NaI or NaI (T1) detector connected to an exposure rate meter, which, displays micro Roentgen or Sieverts per hour (μR/h or μSv/h). The measured radiation exposure rate represents intensity of the field radiations, to be exposed by workers, or objects. This instrument is mainly used to measure the exposure rates present in contaminated equipment. Since, this method does not have ability to discriminate the various γ-ray energies of the different radionuclide, it cannot be used to determine the specific activity concentration in any radioactive material [11].

For laboratory analysis, the main radionuclide (U, Th, Ra, Pb...etc.) in the radioactive materials is analyzed by means of different nuclear spectroscopic methods, e.g., γ or α –spectrometers, liquid scintillation systems and/or ICP-MS. In this concern, non-destructive analysis using γ -ray spectrometers equipped with Ge (Li) or HPGe detectors and connected with multichannel analyzer (MCA), are used to identify the different radionuclides in the radioactive substances and determination of their specific activity concentrations (Bq/g). This method is used in a broad spectrum to determine U-238, Th-232, Ra-228, Ra-226, Ra-224, Ra-223 and Pb-210, in the radioactive materials [12]. Also, one of the most γ -ray spectroscopic methods used for screening the different substances, employs the use of a single channel analyzer (SCA) connected with 2"×2" NaI or NaI(Tl) scintillation probe. This method is mainly used to screen materials for Ra-226 concentrations to assess secular equilibrium with Bi-214 at 609.3 keV, within energy window of 599-620 keV. When the radionuclides present in water samples, the different

radionuclides (e.g. U, Ra, and Th) are separated by suitable radiochemical methods for α -particle measurement or LSC. All the different nuclear spectroscopic instruments, used in detection, identification, and assessment of radioactivity concentrations of the TE-NORM wastes, should be related to energy and efficiency calibrations, using certified standard sources at the same geometrical condition [12].

1.2.3. Limits of Radiation Contamination and Exposure:

Human activities in different technical processes enhance the radioactive material of TE-NORM. As a result of these activities the equipment used are contaminated with TE-NORM and the waste produced can contain enhanced radioactivities. Further, human over exposures can occur. The limits of safe handling and exposure reported are given in the following sections.

1.2.3.1. Equipment:

For equipment, the criteria used to determine if a piece of equipment or pipe is subjected to regulations, is based on the amount of gamma radiation, given off by that piece of equipment [13,14]. If the measured exposure rate reading for any piece of equipment is greater than 0.5 μSv/h including background radiation levels, at any accessible point, this piece is considered contaminated. It is important to note that, this limit applies only to equipment and tubes, and does not apply to waste, which, may found in equipment itself, e.g. soil, scale, sludge, sands, slurries, barrels, drums, cutting boxes filled with TE-NORM wastes [13].

1.2.3.2. Radioactive materials:

The criteria used to determine if soils, sediments, scales, sludge, sands, slurries, contaminated with materials, are subjected to regulations, is based on the amount of Ra-226 and/or Ra-228 activities contained in the considered waste [13,14]. It is stated that, any material containing greater than 0.185 Bq/g of Ra-226 and/or Ra-228, may not be released for unrestricted use and must be controlled as being contaminated materials. On the other hand, for the aquatic systems, they become contaminated by radioactivity when, contain concentration of Ra-226 and/or Ra-228 equal to or greater than 2.22 Bq/L. Since, there is no way to equate the measured exposure rates by μSv/h (or μRem/h) on the radioactive materials to Bq/g of Ra-226 and/or Ra-228

content, a laboratory analysis must be performed on the waste to determine its specific activity levels by Bq/g [14].

1.2.3.3. Human exposure:

Limits of dose level to be exposed by human when deals with the radioactive materials are classified into three main categories:

i- If the annual dose for a worker (or, likewise, for other persons of the general public) dealing with materials containing ionizing radiation, arising from a certain practice will remain below 1mSv/y, no actions need to be taken at all. In particular, there is no need for applying the scheme of reporting and authorization.

ii- If the annual dose will be in the range between 1 and 6 mSv/y, it is generally considered adequate to apply conventional measures for good health and safety practices, thereby minimizing exposure. Health and safety practice may e.g. comprise additional ventilation at work place, where high radon levels persist (water supply stations, underground workplaces...etc.), or it may be considered to change the material composition of products to reduce the radionuclide content in the certain materials. In this case, case-by-case investigations and decisions will usually be required.

iii- If the annual dose will be above 6 mSv/y, it is usually necessary to introduce an appropriate radiation protection system. Also in this case, case-by-case investigations and decisions, which may help to reduce the exposures are usually required [15].

Generally, until now, no final decision has been reached to transform those dose levels into numerical criteria for the materials containing radioactivity. Significant exposure can occur with maintenance and cleaning of the contaminated vessel, pipes or other process equipment from the phosphate industry, the oil and gas industry and possibly also the chemical process industry where scales or precipitates are formed. Furthermore, unaware exposure to substances containing compounds in the metal scrap branch and aircraft operation may lead to significant exposure with dose up to 10 mSv/y [15].

1.3. TE-NORM Wastes Produced from Phosphate Processing:

Naturally occurring radioactive material (NORM) is present on earth in varying concentrations. Mining and mineral processing of geological materials with elevated concentrations of NORM may lead to enhanced concentrations of radionuclides in the products and wastes. In phosphate mining and fertilizer production, the problem with NORM is already recognized for more than twenty years [16]. The typical fertilizer processing plant is shown in Fig. (1.5).

Mineral phosphate fertilizers are extensively used in agriculture throughout the world for amelioration and replacement of the plant nutrient content of the soils. In the course of deposition, uranium dissolved in the form of uranyl complexes in the seawater concentrated in phosphate sediments [17]. Phosphoric acid, which used in phosphate fertilizer production, can be produce either by: (i) the electric furnace process, which use electrical energy to produce elemental phosphors (P) as a first stage, or (ii) the wet process using sulphuric acid attack. Currently, the wet process accounts for over 90% of phosphoric acid production [18]. Phosphogypsum is produced during the manufacture of phosphoric acid by treating rock phosphate (raw material) with sulphuric acid according to the following chemical reaction:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF \quad (1.6)$$

The nature and extent of radionuclides and other impurities in phosphogypsum differ with the type of raw material and the method of chemical processing [19,20]. Phosphogypsum is an acidic by-product from the phosphate fertilizer industry. Worldwide production of phosphogypsum was 120-150 million metric tones in 1980 and it is estimated that if historic trends continue, production will increase to more 300 million metric tones by the 21st century. A study in 1981 showed that of the phosphogypsum produced, 14% is reprocessed, 58% is stored and 28% is dumped into water bodies [20]. Large amounts of phosphogypsum dumped, often into water supplies through the world. The Djorf Lasfar plant in Morocco pumps 25000 tons/day of phosphogypsum into the Atlantic Ocean when operating at nominal capacity [18]. Approximately 5 tones of phosphogypsum are produced per tone of phosphoric acid [20].

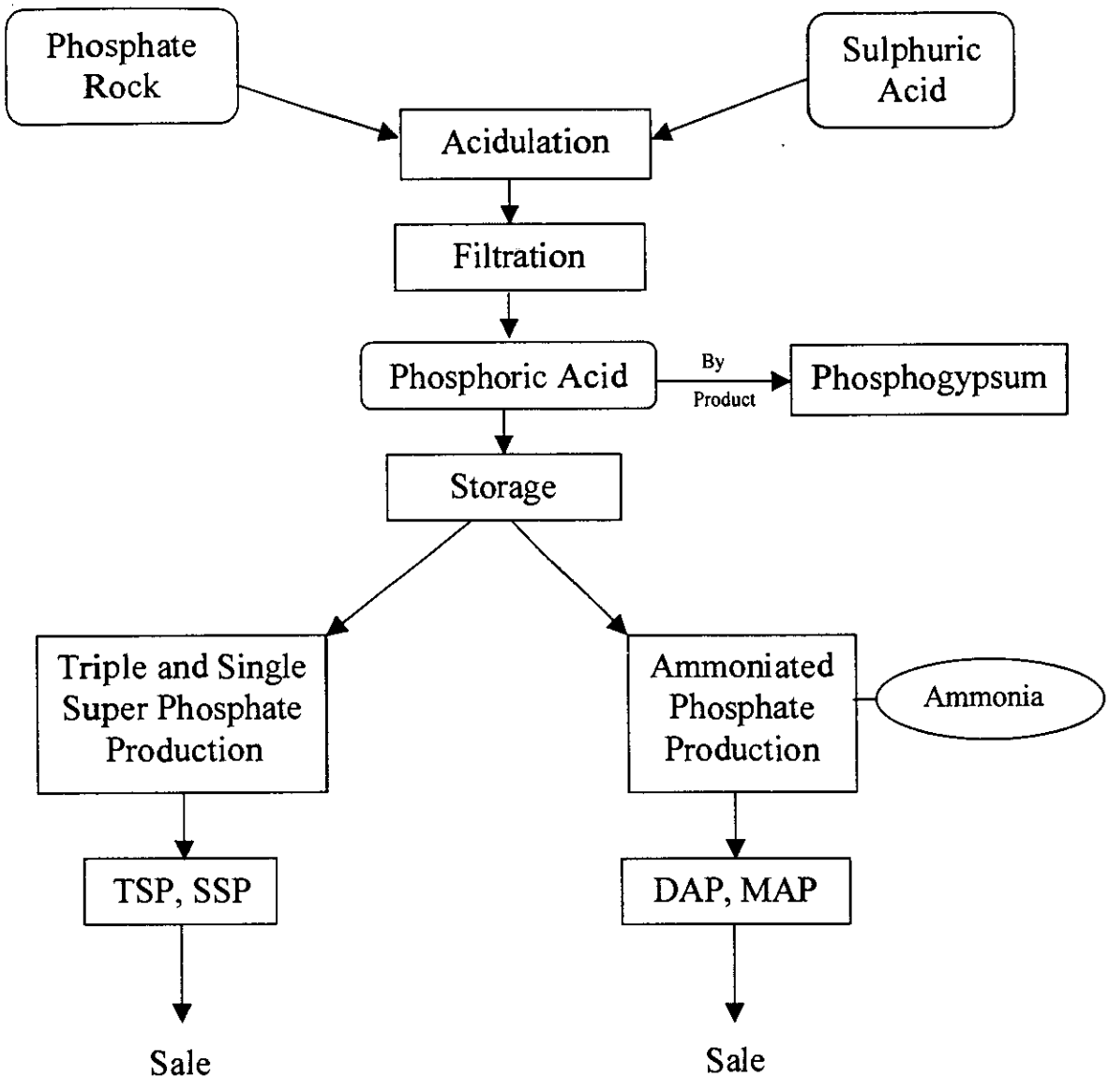

Fig. (1.5): A diagram representing wet processing of the phosphate fertilizers industry.

Notes: DAP: is the di-ammonium phosphate,
MAP: is the mono-ammonium phosphate,
SSP : is the single super phosphate, and
TSP : is the triple super phosphate.

The behavior of U-238 and Ra-226 (the principal contributors of radioactivity in phosphate rock) in the manufacture of phosphoric acid can be interpreted as follows: Ra-226 is precipitated with solid phase phosphogypsum as the insoluble radium sulphate, while U-238 remains in the liquid phase (phosphoric acid) as a uranyl complex [21]. The radioactivity present in phosphate rocks mainly caused by the disintegration products of the U-238 series. In fact, natural uranium can substitute for calcium in the phosphate rock structure and, over a period of time, accumulate in the phosphate reserves. Thus, uranium is present in fertilizers manufactured from phosphate rock. A minor contribution (5%) of radioactivity in phosphate rocks is due to the Th-232 series. In addition, these samples also contain the naturally occurring radioisotope of K-40 [21].

Phosphogypsum is composed mainly of gypsum ($CaSO_4.2H_2O$), but contains impurities of environmental concern such as fluoride (F^-), acids, trace elements, and naturally occurring radionuclides, which originate from the phosphate rock used in processing. Concentration of impurities may greatly differ between phosphogypsums, depending on the phosphate rock sources. Radium-226 is the major source of radioactivity in phosphogypsum produced from sedimentary phosphate rock [22]. The radioactivity present in these materials can enter the environment and possibly pose radiation exposure concerns through several pathways as follows: a) phosphatic fertilizer can enter agricultural lands during cultivation, b) Phosphogypsum may be used as agriculture gypsum (to deal with salinity), and c) phosphogypsum may be used as a building material. In the latter case, both internal and external exposure may occur, depending on whether Rn-222 decays in the product or diffuses into the indoor air [21]. The factors which control the shape and size of the gypsum crystals formed in the reaction slurry are: (1) the type of phosphate rock, (2) phosphate rock particle size, (3) concentration of phosphoric acid, (4) solids content in the slurry, (5) excess sulphuric acid in slurry, (6) impurities in the phosphate rock, (7) temperature, and (8) the reaction system, feed-to-volume ratios, agitation, and recirculation [18].

1.3.1. Utilization of Phosphogypsum:

Many studies have reported the effects of applications of phosphogypsum on nutrient levels and the physical and chemical properties of agriculture soils. The benefits of phosphogypsum have been documented as amendments

for: (i) highly weathered soils. with relatively low exchange capacities and/or low levels of extractable nutrients, and (ii) calcareous soils. Crop yields and quality of a variety of fruit, vegetable, grain, forage, and oil seeds have generally been found to be higher on phosphogypsum amended soils. The wide scale use of phosphogypsum appears to be restricted until concerns regarding associated natural radionuclides, F^-, heavy metals, effect on nutriaents, potential as a source of phosphorus (P) in surface water pollution, and economic considerations are more fully addressed. Despite these environmental concerns regarding phosphogypsum, some countries have made wide-scale use of the by-product as a soil amendment [23,24]. Phosphogypsum has also been used in agriculture as a feed additive for livestock [25] and as a fertilizer amendment to reduce ammonia volatilization from urea fertilizer [20].

1.3.2. Environmental Concerns Related to Storage and Uses of Phosphogypsum Wastes:

Most of phosphogypsum produced is stored in stacks [26]. A recent final ruled by the United State Environmental Protection Agency (US EPA) requires that all phosphogypsum be placed in stacks or mines [20]. Environmental contamination resulting from phosphogypsum storage may occur from: (i) atmospheric contamination with fluoride or other toxic elements, (ii) groundwater pollution with mobile anions, acidity, trace elements or radionuclides, (iii) radon gas, (iv) inhalation and/or ingestion of radioactive dust, and (v) direct exposure of gamma radiation. Other concerns with storage include surface runoff [27], and erosion and stability of the stacks. The main environmental concerns related to the storage and agricultural uses of phosphogypsm are summarized in Fig. (1.6).

1.3.2.1. Atmospheric fluoride:

Fluoride (F^-) gas emission is only a concern with operational stacks, however, transport of fine dust particles containing F^- is a potential problem for both operational and inactive stacks. Phosphate rock may contain 4% fluorine which forms HF during the acidulation process. Fluoride remains in the liquid phase but during processing gaseous of SiF_4 and HF may be formed under high temperature conditions. When phosphogypsum is sluiced to the stack some gaseous of F^- may be evolved, however, most plants use scrubbers

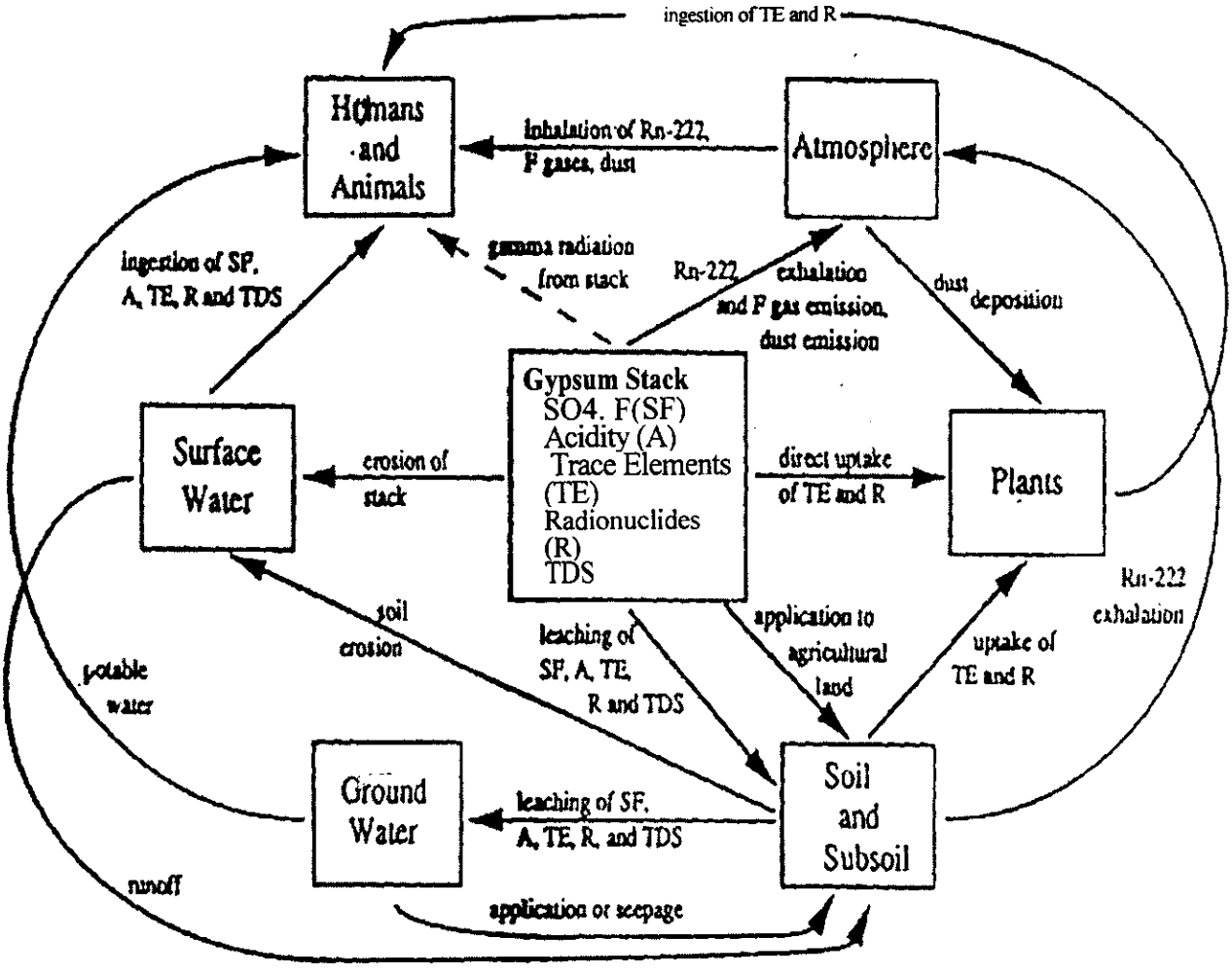

Fig. (1.6): Main environmental concerns due to the storage and agricultural use of phosphogypsum.

to remove F^-. Studies on the monitoring of F^- released from two phosphogypsum sites were investigated and discussed in Canada [28]. The results of this monitoring showed that probably only operating facilities result in elevated ambient F^- levels. The Ontario Ministry of the Environment (OME) established 35 μg/g as the upper limit of normal background concentration of F^- in foliage. During plant operation foliage sample exceeded this level as far away as 6 km from the plant site [28]. Wild grape, a plant very sensitive to F^-, showed damage in the areas surrounding the plant site.

1.3.2.2 Groundwater pollution:

Groundwater contamination may occur from process water seepage during operation of a stack or through the long-term downward leaching which occurs when rainwater infiltrates through an inactive stack. Several studies have investigated ground water pollution or the potential leachability of phosphogypsum constituents.

The results are not consistent although it is clear that the potential for groundwater pollution under a phosphogypsum stack is a concern in some situations. Acidic seepage waters may be buffered by alkaline subsoil and ground waters, thereby reducing the mobility of certain heavy metals e.g. Ni, Co, and Cu [20]. However, other chemical species such as SO_4^{2-} and F^- are not affected as much by pH changes from the stack to the subsoil. Site-specific conditions which may mitigate the impact of possible contaminants on groundwater are: (i) suitable subsurface geology, which can neutralize acidic seepage, (ii) construction of the stack on an impervious layer, and (iii) construction of interceptor wells or ditches. Other sources have reported methods of reducing seepage of contaminants from active and inactive stacks [29,30,31].

The recycled water process used to sluice phosphogypsum out to the stacks is acidic. Sulphuric, phosphoric and hydrofluoric acids reside in the phosphogypsum pores after acidulation and filtration. Consequently, elements solubilized from phosphate rock during the acidulation process may remain in solution. This water process is present in cooling ponds and also within the porosity of the phosphogypsum stack. The species solubilized during acidulation include As, Cd, Cr, Pb, Na, F^-, Mn, Fe, SO_4^{2-}, U and Th [32]. In addition to toxic elements, the water process contains high levels of total dissolved solids [33].

Studies on the groundwater at two operational Stacks (AMAX and USS) of phosphogypsum (in central Florida-USA), containing phosphatic clay deposits and a surficial sand layer were carried out. Groundwater in the area is characterized by hard calcium-magnesium bicarbonate water with low SO_4^{2-} and Cl^- concentrations. Both stacks caused slight distortion in the groundwater level which reflected recharge of water from the stack and pond areas. Significant degradation in groundwater quality was detected at the two sites. Many chemical parameters showed levels up to several of magnitude greater than natural groundwater concentrations. Relative to background concentrations, the groundwater below the two sites showed elevated concentrations of Si, Na, SO_4^{2-}, F^-, hardness, P and N. Concentrations of Cu, Mo and Zn were also elevated. Low pH was also found near the gypsum stacks and cooling ponds at the USS site. Movement of contaminants in a plume was observed at both Florida sites. Six hundreds m of groundwater from the USS stack showed sulphate concentrations which were 450 times greater than background levels. Groundwater 460 m from the AMAX stack had sulphate concentrations up to 1900 mg/L [20]. Selected members from the U-238, U-235 and Th-232 decay chains were also measured in the groundwater below the AMAX site. Radium-226 was measured below the USS site. All radionuclides, except for Ra-226 at the USS site, were within drinking water standards, however U-238 was elevated over background in some samples. At both sites elevated levels of Ra-226 were observed hundreds of meters from the stacks, indicating Ra-226 migration through the groundwater systems [20].

Rouis and Bensalah (1990) investigated the groundwater contamination below a phosphogypsum stack in Tunisia. The pH of the groundwater near the stack was less than 2. It was neutral 200 m downstream from the stack. Phosphate and F^- levels near the stack were as high as 16.3 and 8.8 g/L, respectively. Mercury and Mo levels were as high as 0.6 and 0.19 mg/L, respectively. The region of high groundwater contamination extended 100 to 400 meters downstream from the phosphogypsum stack [29]. Other studies have investigated the groundwater pollution potential of phosphogypsum, which has been used as a base for a road construction [34,35].

1.3.2.3 Radon gas and other radioactive exposure:

Pathways of radioactive exposure originating from phosphogypsum to

humans were investigated and summarized by Roessler [36]. Exposure to Rn-222 gas is one of the greatest health concerns. This section will review the studies, which have investigated the magnitude of Rn-222 gas evolution and the significance of these rates. Other forms of aerial exposure, such as radioactive dust particles and direct gamma radiation from phosphogypsum stacks, will also be included in this section. Before discussing Rn-222 it is appropriate to summarize simple dosimetry, the means by which radioactive exposure is measured.

Several terms are used to describe the health effects of radionuclides such as Rn-222 and its progeny. In terms of radon progeny concentration, Working Level (WL) of 0.001 is representative of average outdoor concentrations. Average indoor levels are 0.004 WL. The level recommended for remedial action by the U.S. National Council on Radiation Protection (NCRP) and Measurements [37] is 0.04 WL. Assuming 0.5% equilibrium between radon and its progeny, this is equivalent to a radon concentration of 300 Bq/m^3. This results in a continuous exposure rate of about 2 WLM/y [38]. In Canada, remedial measures are recommended when average indoor Rn-222 daughter concentrations exceed 0.02 WL [37].

The National Council on Radiation Protection (NCRP) (1984) recommendation for general public continuous exposure to gamma radiation above background is 10 mSv/y. Typical exposure to background gamma radiation in the US is 0.28 mSv/y (Canadian estimates are 20% lower) [39].

The effective dose equivalent, (H_E), is a measure of the total risk to the individual and is calculated by summing the dose equivalents of all the organs in the body. Both H and H_E measured in Sv. The annual effective dose equivalent for all sources of natural background radiation is approximately 2 mSv/y [20,40].

Natural background levels, determined at nine locations greater than 8 km from any phosphogypsum stack, averaged 0.0052 Bq/L. Average concentration at the base of the phosphogypsum stacks was 0.024 Bq/L, Rn-222 concentration to range between 0.011 and 0.015 Bq/L on/or close to a phosphogypsum stack. Concentrations decreased to background within 1000 m [20]. Also measured ambient Rn-222 concentrations 1-1.5 m above stacks covered with clay in Ontario. The average concentration of 0.011 Bq/L was not statistically different than background levels (0.0074 Bq/L) for the area. Radon-222 concentration above water ponds at a phosphogypsum stack in

southern Alberta averaged 0.024 Bq/L, which was not statistically different from the natural background level of 0.017 Bq/L [20].

Phosphogypsum stacks are a direct source of γ -radiation due to Ra-226 and its daughter radionuclides. Studies on the γ -radiation above 1 m of the surface of 5 phosphogypsum stacks, showed an average γ -exposure of 0.33 μSv/h. People spending long periods of time working on the stack, or living immediately adjacent to it, would be subjected to a health risk because irradiation decreases exponentially with distance [20]. The measured gross γ exposure rates averaged 0.368 μSv/h. The corresponding working year exposure would be 0.48-0.68 mSv above background. This level is low because it represents < 10% of the annual dose limit for the general public in unrestricted areas [37]. Radon daughter concentrations measured on the stack ranged between 0.0006 and 0.001 WL, while airborne Ra-226 concentration were indistinguishable from background. The individuals working on a phosphogypsum stack for a year (2000 h) would be subjected to a γ -radiation dose equivalent of 0.6 mSv. The occupational exposure limit is 50 mSv/y. Measured radon concentrations were equal to or less than 0.015 Bq/L which corresponds to < 0.004 WL. This level was equivalent to typical Florida indoor radon concentrations and 10-times less than the level set by the NCRP for remedial action [20].

1.3.2.4. Radionuclide uptake by plants and radioactive buildup in soil:

Radionuclides have been reported to be taken up by agricultural plants from soil contaminated by uranium processing wastes and mined phosphate lands, hence, there is some concern that the application of phosphogypsum to agricultural lands may result in the uptake of radionuclides by food crops. Radionuclide uptake is influenced by soil factors and the type of plant species. Root crops, leafy, vegetables and legumes tend to take up more radionuclides than fruit bearing plants [20,41].

Radium-226 and Pb-210 have been found to be significantly increased in plants grown on reclaimed phosphate mine lands. It was estimated that a person who obtained all of his or her leafy, vegetables, root vegetables, peas and beans from the phosphate mined lands would receive an effective annual dose equivalent of 0.191 mSv/y which is not considered to be a health hazard [42]. It should be noted that the NCRP guideline for restricting soil for use of

growing human food crops is a Ra-226 content of 1.5 Bq/g soils [37]. A person whose sole source of consumed grain products originating from food grown on land treated by phosphogypsum would consume approximately 1.9 Bq/d of Ra-226 and would receive a bone surface dose of 3 mSv/y and a committed effective dose equivalent (CEDE) of 0.2 mSv/y. This intake level is about 50 times greater than the typical dietary uptake and 2.5 times greater than the Federal Radiation Council guidance. The 0.2 mSv/y CEDE is 20% of NCRP recommendation for continuous exposure to an individual of the general public [20]. Recently the US EPA ruled that phosphogypsum would only be permitted for use in agriculture if the average concentration of Ra-226 in the phosphogypsum does not exceed 370 Bq/kg. This limit was set to assure that the risks due to indoor radon and direct gamma radiation in residences constructed on land previously treated with phosphogypsum do not exceed an acceptable level [20].

1.3.2.5. Non-radioactive element uptake by plants:

The potential uptake of fluoride and trace elements derived from phosphogypsum are potential environmental concerns. Phosphogypsum applications didn't result in accumulation of high fluoride concentrations in soil and plants [43]. Even if phosphogypsum application rates are large enough to cause high fluoride concentrations in the soil, some acid soil studies have shown or suggested that most of the fluoride would be adsorbed in the topsoil [44].

1.3.2.6. Other concerns:

Phosphorus contamination of surface waters as a result of land application of phosphogypsum is also a concern reading the agricultural use of phosphogypsum. The results of a laboratory rainfall simulator study suggested that application of high phosphogypsum rates may result in phosphorus being exported into waterways adjacent to the sites of application and hence it may contribute to the enhanced eutrophication of the waterways [45].

1.4. TE-NORM in Gas and Petroleum Industry:

The history of TE-NORM in oil and gas production follows closely in history of the discovery of radioactivity in the first part of 20th century. We must remember that, the discovery of radioactivity is (today) more than one hundred years old. Consequently, it is probably one of the most poorly

understood scientific phenomena to the public [46]. In 1918, a Canadian paper was published on radioactivity in natural gases. In the 1930's an elevated radium level were detected in the Russian oilfields. In 1953, the US geological society published a paper on uranium and helium in gas formations. In 1973, (EPA) performed a study on natural gases and radon (Rn-222) [46].

A number of major oil companies helped a sponsor study on radon in natural gas products that was completed in 1975. The thrust of this study was the potential effect that radon would have on the consumer of natural gas products. Radon contamination of natural gas has been known for nearly 100 years [47]. The studies conclusion stated that, radon in natural gas products does not present any hazard to the consumer. This conclusion is still very valid today for the typical customer. The study did mention, however, that radon could be a problem for the processing industry and some researches have focused on this concern [47,48].

In 1981, scale produced on offshore oil platforms in the North Sea was found to contain TE-NORM in significant quantities. These finding were presented in a 1985 offshore technology conference paper on radioactive scale formation in Houston (Texas, USA). Consequently, industry and government officials were aware of the possibility that TE-NORM scale could be present in US domestic operations [46]. In 1986, significant TE-NORM scale was found in Laurel, Mississippi (USA). Some rather alarming press headlines and feature articles followed shortly in both Mississippi and Louisiana after the presence of TE-NORM in the oil path became better known. These articles stressed the fact that, there are on current regulation, either by the state or federal governments, were specifically designed to control this radioactive waste and called for their creation and enforcement. Since TE-NORM was first re-discovered domestically, the oil and gas industry has responded progressively to TE-NORM issue by: notifying appropriate state agencies, initiating field survey and studies to characterize and locate occurrence of TE-NORM in conjunction with the American Petroleum Institute, inform other oil and gas operations, employees and contractors, and reviewing operating practices [46].

TE-NORM contamination of oil and gas industry petroleum equipment has been identified in a world wide, e.g. USA (Alaska, Gulf of Mexico region), the North Sea region, Canada, Australia, several Middle East

countries (Egypt, Saudi Arabia...etc.). Since 1918 till 1980, most researches were focused on the TE-NORM contamination of natural gas facilities, and the contamination is attributed to Ra-226 as will as Rn-222 gas and its decay products, e.g. Po-218, Pb-214, Bi-214, and Pb-210.

The presence of TE-NORM in the North Sea oil and gas production, were first discovered in 1981, and enhanced levels of radioactivity are now found in the petroleum system of several North Sea oil fields [15]. The activity concentration ranges from background level to several hundreds Bq/g (Ra-226). Doses to workers involved in handling, contaminated equipment, or waste are usually very low, and the main problem related to radioactive deposits is waste disposal [49]. The presence of TE-NORM or naturally occurring radionuclides in the product materials from oil and gas facilities, give rise to deposits with enhanced levels of these radionuclides in the processing equipment [50].

1.4.1. TE-NORM Formation:

The natural radionuclide of U-238, U-235 and Th-232, as well as the different radium-radionuclides (Ra-223, Ra-224, Ra-226, and Ra-228) and Pb-210,...etc., are brought to the surface through the extraction processes of oil and gas, they may contain levels of radioactivity above surface background [13]. As these materials are handled (e.g., stored, transported...etc.), their radioactive constituents may become separated, resulting in a concentrated TE-NORM waste [12].

The TE-NORM waste occurs though the extraction and treatment of liquid and gases hydrocarbons and is generally accompanied by the formation and accumulation of radioactive scales, sludges and films. The petroleum waste (scale or sludge) was produced by two mechanisms either incorporate or precipitate into the production equipment such as pipelines, tank storage, pumps,...etc. The TE-NORM waste as scale and sludge generated in oil and gas equipments is due to the precipitation of alkaline earth metals as sulphates, carbonates, and/or silicates [47].

Some investigations were performed concerning the composition and characterization of the formed radioactive TE-NORM waste produced during oil and gas processing. Nuclear spectroscopic analysis showed that, the main radionuclides present in these wastes are traces of U-238 and Th-232 as well as their decay daughters. The previous studies indicated that the incorporation

and co-precipitation of these natural radionuclides with alkaline earth metals (e.g., Mg, Ca, Sr, Ba) and some quantities of lead as sulphates, carbonates and/or silicates [51]. Some other studies were also performed under controlled production conditions, proved that, the factors that are greatly responsible for the formation of radioactive scale and/or sludge are water composition [12]. That, the way in which the scales are deposited is connected to the pipes, superficial features, fluid-dynamic phenomena and crystallization kinetics. They found that, variations in sulphates and carbonate solubility can give rise to scale formation, which are connected to some physical and chemical factors, e.g., temperature variation, pressure changes, pH-balance, evaporation in the gas extraction pipes and injection of incompatible sea waters. Also, the re-injected water into the reservoirs to maintain the production pressure during the field exploration seemed to be a principal cause for the scale formation [12]. Many of the physical characteristics of oil formations, high temperature pressure,..etc. tends to increase the radionuclide solubility in production fluids. Generally, uranium and thorium are relatively insoluble and remain stationary in the reservoir, while, radium is more soluble and may become mobilized in the produced water phase of the reservoir. It has been estimated that: 25000 tones of TE-NORM contaminated scale, and 225000 tones of TE-NORM contaminated sludge, are generated each year by the petroleum industry [14]. The available data indicate that, the total radium levels to extreme measurements of 15.17 kBq/g scale and 25.9 kBq/g in sludge [14].

1.4.2. Literature on the Management of TE-NORM Wastes:

As mentioned previously, when the activity level of the TE-NORM generated from petroleum industries exceeds 0.185 Bq/g, the TE-NORM becomes a radioactive waste. Different approaches for safe and low cost management of the scales, sludge, and production equipment contaminated by TE-NORM are given and these are outlined in the following:

1.4.2.1. Inhibition approaches:

The best solution to TE-NORM problem is to prevent its formation. The present technologies under development that could inhibit TE-NORM waste either, by preventing removal of radium from the source formation, or by preventing its precipitation from produced water. Houston university (USA)

and an Environmental service company developed jointly and tested a process to reduce TE-NORM contamination level in produced water by trapping TE-NORM within the subsurface formation which it originates, thereby preventing it from entering reservoir fluids that could eventually make their way into wells [13].

This in situ technology involves the use of highly selective radionuclide sorbents deposited within the reservoir matrix surrounding the well. Radionuclides that have dissolved within ground water are 'filtered' through ion exchanger and co-precipitated onto the sorbent solids as the water flows through the treated area. The process traps and reduces TE-NORM in the subsurface, which resulting in a reduction in the TE-NORM content of produced water and a reduction in the potential for scale and sludge formation in the piping [13]. Based on the very preliminary application of this technology, it is difficult to estimate its effectiveness or cost when used in the field. An economical effective way to inhibit, control, or solublize TE-NORM scale has been used. Scale inhibitors do not completely eliminate TE-NORM, since it remains dissolved in the produced water. However, they reduce the formation of the more concentrated and less hazards TE-NORM contaminated scale. Scale inhibitor by causing the scale particles to become unstable and to redissolve, leaving the radium in solution at relatively low concentration. In a study of scale formation in gas production facilities in northern Michigan (USA), phosphinopolycarboxylate and phosphate esters were found the most effective scale inhibitors [13].

Several TE-NORM scale inhibitors have been developed. Their effectiveness hasn't yet been well established [49]. Uses of these inhibitors are dependant on temperature, overall water chemistry, and barium/sulphate ratio in case of barium sulphate scale. It was suggested that, phosphinopolycarboxylate-29 (PPC-29) scale inhibitor was most effective for barium sulphate inhibition at low temperature [52]. Bishexamethylenediaminetetra (methylenephosphonic) acid (BHMDTMP) and bishexamethylenetriaminepenta (methylenephosphonic) acid (BHMTPMP) are more effective than phosphate inhibitor at higher temperature [52].

Also, there are two combined scales inhibitors, which can be used to prevent deposition of TE-NORM. Aminotrimethylenephosphonic acid (ATMP) was used to prevent deposition of calcium scale at high temperature, while, bishexamethylenetriaminetetra (methylenephosphonic) acid (BHMT-

AMP) was used for preventing formation of barium sulphate scale at relatively lower temperature [52].

1.4.2.2. Trials for treatment of TE-NORM:

1.4.2.2.1. Volume reduction:

Several companies are currently developing refining processes for reducing volumes of TE-NORM waste. The processes focus on removing the individual radioactive components from the produced solid waste. Volume reduction of TE-NORM waste was studied by two petroleum companies using two steps of physicochemical treatment [13]. The field scale pilot test is composed of:

i- Mixing 13 barrels (200 liters) of TE-NORM waste with 40 barrels of produces water. A surfactant is added to the mixture and chlorine dioxide to remove any free oil. All contents are then transferred into a large mesh screen to remove rocks and large species of debris.

ii- An average volume reduction of about 80% was obtained, with the remaining solids higher in TE-NORM contamination levels than the originally material. Using a process similar to that used in the pilot test, a full scale field trail of 3,600 barrels of TE-NORM waste achieved volume reduction of about 75% of the sand and silt fractions and the remaining, radium concentration is usually decreased [13].

Discussions with environmental service companies indicated that, this process could cost approximately $285 per barrel, $150 for processing and $135 for encapsulating the waste in casing prior to downhole placement.

1.4.2.2.2. Use of reagents:

A water-bath heaters from a gas production facility in North Sea (e.g., Netherlands and Norway), has been used as a test for equipment in laboratory aimed at the in-situ removal of TE-NORM. This is achieved by circulating an aqueous solution of commercially available scale dissolver through the contaminated equipment. For this purpose, some scale dissolvers, which are widely used within exploration, are commonly based on chelating chemistry and reportedly successfully applied in the dissolution of low specific activity scales [53].

For instance application of scale dissolver reagents resulted in the rapid and complete removal of Ra-226 and progeny containing sulphate scales as well as Pb-210 containing sulphate scales from the head internals. These studies were performed using scale dissolver consist of: 15% v/v acetic acid and 1% v/v strongly oxidant, e.g., $KMnO_4$. This reduced the total activity from 20 Bq/cm^2 to 6 Bq/cm^2, the residual activity may be removed using 0.5 M citric acid [53]. Also, scale dissolver solution 15% v/v acetic acid plus 1% v/v hydrogen peroxide was used to dissolve TE-NORM contaminated by overall activities of 2000 Bq (Ra-226)/g and 600 Bq (Pb-210)/g. This was followed by water flush. Generally, the application of a chemical scale dissolver can remove 95-99% of TE-NORM present in exploration and production facilities [53]. On the other hand, radioactive scales containing Ra-226 and its progeny as barium sulphate scales, are removed chemically using hydrochloric acid, and the residue is disposed as waste after appropriate radiometric checks [53].

1.4.2.2.3. Recycling equipment:

Qunada et al. [54], decontaminated equipment, used in extraction of crude oil and natural gas from the sea bottom, located in the North Sea, the north-eastern regions of the Atlantic Ocean. The contamination produced from accumulation of toxic materials mainly includes heavy metals such as mercury and radioactive materials of the natural origin (e.g., Ra-226, Ra-228, Pb-210,...etc.). For decontamination purpose, the contaminated equipment were taken into melting plant, especially built for this process, its annual capacity is 2000 tones of steel and metal scrap contaminated with mercury and TE-NORM. After melting, the radiological measurements showed that, the produced metal did not contain any detectable residual of TE-NORM, and can be re-used again in a steel works. About 98% of TE-NORM was bound to the slag and ~ 2% were detected in the filter dust, mainly consisting of the nuclides Pb-210 and Po-210. The secondary waste produced is ~ 13% of the total weight of the material supplied, where, it is TE-NORM waste consists of ~ 95% of slag and ~ 5% coarse dust [54].

Also, chemical separation of the radionuclide incorporated in the contaminated equipment (pipelines, tubes, pumps) is carried out by melting at 1400 °C, to further fractionation of radionuclide in melt, slag or dust. The analysis of data showed that, most of U-238 and Th-232 series are transferred from

melt (dense main component, contains only 1% of the remainder radio-activity) into the slag (light minor), component contains only 98% of the total radioactivity. All activity of Pb-210 was concentrated in the filter dust, because it is evaporated at normal melting temperature above 1300 °C, since the melting point of steel is ~ 4200 °C [55].

1.4.2.3. Subsurface injection approaches:

1.4.2.3.1. Solid TE-NORM waste:

For TE-NORM contaminated scale, sludge and soils with very low levels of radioactivity, disposal option is to spread over the ground and mixed with non-contaminated soils, to dilute the contaminated soils and reduce the radioactivity level to background level. This type of disposal is often the most cost effective [13]. Subsurface disposal option includes underground injection and down hole encapsulation. This type of disposal is widely acknowledged as one of the most environmentally sound methods of disposing TE-NORM contaminated sludge [13]. The common two forms of subsurface disposal are:

i- Underground injection, is established by mixing a TE-NORM contaminated waste with cement in slurry, then injecting the formed mixture into a deep subsurface formation.

ii- Down hole encapsulation, entail placing TE-NORM contaminated scale, sludge, tubes and other small pieces of the production equipment (e.g., valves, filters, pumps, screens,...etc.) inside the casing of a well, that is to be plugged with cement and then abandoned. Discussions with environmental service companies indicated current costs range from $230 to $270/barrel for subsurface disposal for TE-NORM sludge, depending on the volume to be disposed and the location of the disposal well. This cost includes mixing and grinding TE-NORM into slurry and pumping it down hole into the well casing [13].

1.4.2.3.2. Liquid TE-NORM waste:

TE-NORM in slurry from (e.g., waste water or solids mixed with water) can be reinvented into deep formations for disposal [13]. There are three classes for injection:

a- This option used for any liquid TE-NORM wastes. Over 90% of all produced water resulting from oil and gas operations are injected though wells into permeable disposal formation, that lie below Underground

Sources of Drinking Water (USDW), and surrounded by impermeable layers. After injection the well is closed sealed with cement and capped, effectively isolating injected materials from the surface [13]. The US EPA has estimated the cost of injecting a barrel of water in this class to ~ $0.2. Injection costs vary based on volume, depth, formation pressure, and other factor. The cost of injecting slurry could be comparable, or slightly higher.

b- Well injection, when TE-NORM concentrations prevent disposal in class (a). Therefore, the used wells in the class are deeper and are constructed to provide greater protection against potential migration of injected fluids to USDW. Disposal in class (b) well could be somewhat more expensive than class (a) injection. Transportation costs would also be higher, since a limited number of class (b) disposal wells exist [13].

c- Deep well injection, these wells consist of injecting liquid wastes contaminated by TE-NORM fluids, into the well at sufficiently high pressure to create a fracture in a permeable shale formation. After the scale/water mixture is displaced into the fracture, then, the pressure is reduced, and the fracture closes.

The scale is trapped between the fracture wells and is incapable of re-entering the well bore [13]. Deep well injection is generally regarded as an effective method for the disposal of TE-NORM waste because it dose not depend on the mechanical integrity of the well to prevent potential subsurface contamination. No published data are currently available that characterize the cost associated with the deep well injection. However, because of the greater depth and pressure involved, deep well injection would be more costly than other classes.

1.5. Assessment of Radioactivity from TE-NORM:

Nuclear spectroscopic techniques are used to identify and quantify concentrations of the natural radionuclide U-238 and Th-232 series as well as K-40 in TE-NORM wastes produced from several industrial activities. Also, the same techniques are used to identify and quantify the radioisotope in the artificial sources (e.g., Co-60, Cs-137) in different environmental samples.

These methods include α, γ -spectrometry and liquid scintillation detection. In principal, most radionuclide of uranium-series e.g., U-238, Ra-226, Pb-210, thorium-series e.g., Ra-228, Ra-224 or K-40, can be determined by γ-spectroscopy. When dealing with natural radioactive decay series of U-238

and Th-232, secular equilibrium may exist between the parent radionuclide, and their respective decay products. In the equilibrium exists, the concentration of the parent radionuclide will equal to that of each of the corresponding daughters, considering the respective decay constant in each case with the following relation:

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3. \ldots \text{etc.} \quad (1.7)$$

Where: λ is the decay constant of the radionuclide and equal to $(\ln 2)/t_{1/2}$ in seconds (s^{-1}), and N is the number of respective nuclei.

The radioactivity levels and related concentrations of the parent radionuclide can be determined in test samples through the quantitative analysis of any daughter radionuclide under squealer equilibrium condition [56,57]. For uranium-series, U-238 can be determined based on γ -energy lines of its direct daughter Th-234 at 63.3 and 92.6 keV, assuming secular equilibrium exists. Choice of these two γ -energy lines, gives a true quantity of uranium, since this represents the first decay radionuclide from U-238 through one α-decay, void from the formation of radon gas [56,58,59]. Concentration of U-238 can be determined destructively, through several radiochemical processes includes digestion of samples by mineral acids, separation, purification, followed by electrodepositing or micro co-precipitation and measurements by α -spectrometry.

Radium-226 was determined by two different ways. One based on the direct determination of Ra-226 by γ -energy line at 186.2 keV [58,60]. In case of U-235, its most probable γ -ray at 185.7 keV (57.2%) is recorded in the same peak as Ra-226 emission at 186.2 keV (3.59%). The clean U-235 photons emitted at 143.8 (10.96%), 163.4 (5.08%) and 205.3 (5.01%) keV should be avoided, as they suffer from summing in effects due to the cascades of 19.6 with 143.8 and 185.7 keV, respectively. Therefore, the peak at 186.2 keV was used in the present study, considering that:

$$C(186) = C(\text{U-235, 185.7}) + C(\text{Ra-226, 186.2}) \quad (1.8)$$

To deduce Ra-226 contribution, equilibrium with its progeny had to be ensured first by sealing the samples for a period of at least 28 days, i.e., seven half-life of Rn-222 (3.82 d). The intense γ -rays of Pb-214 and Bi-214 may be

used subsequently to determine Ra-226 activity. The clean 295.2 keV γ -ray of Pb-214 was chosen for this purpose to yield [61]:

$$C(\text{Ra - 226,186.2}) = \frac{\varepsilon(186.2) \times I(\text{Ra} - 226,186.2)}{\varepsilon(295.2) \times I(\text{Pb} - 214,295.2)} \times C(\text{Pb} - 214,295.2) \quad (1.9)$$

Also, Ra-226 was determined indirectly depending on the ingrowth of Rn-222 daughters, these are Bi-214 and Pb-214, as described by a several authors [56,62,63]. In this method, Ra-226 was determined based on the average activities of its daughters (Bi-214 and Pb-214). The determination has been performed based on different five γ -energy lines, two for Pb-214 at 295.2 and 351.9 keV, and three for Bi-214 at 609.3, 1120.3 and 1764.5 keV. Choice of these energy lines is based on their higher photon emission intensity of more than ~ 16% [54,64]. Also, Ra-226 can be determined by α -particle spectrometry, after radiochemical co-precipitation as $Ba(Ra)SO_4$ or by liquid scintillation counting of Rn-222. Lead-210 can be determined directly by its γ -energy line at 46.5 keV [65] and by radiochemical separation as lead sulphate, followed by measurement of its daughters either Bi-210 using low-background flow α/β proportional counter, or Po-210 using α -particle spectrometer, assuming that, the equilibrium exists between Pb-210 and Bi-210 [66].

For actinium-series, U-235 can be determined by γ -ray spectroscopy, directly by the γ -ray lines at 143.8, 163.4, and 205.3 keV [40], while, it can also be determined but indirectly after determination of U-238 by γ -energy lines of Th-234 at 63.3 and 92.6 keV, using the following empirical relation [57]:

$$[\text{U-235}] = (8/9) \times (1/21.7) \times [\text{U-238}]_{63.3,\ 92.6\ \text{keV}} \quad (1.10)$$

where: 8/9 is a correction factor related to energy and density of sample, and 1/21.7 is the natural ratio between U-235 and U-238. Radium-223 is determined by its γ -ray line of energy 154.3 keV with photon emission intensity of 5.6%.

For thorium-series in equilibrium, Th-232 can be directly determined based on the amount of radioactivity of Ra-228 present in the examined samples, where, Ra-228 is a direct daughter for Th-232 (Fig. (1.1)).

Therefore, determination of Ra-228 is a good representative for Th-232. Since Ra-228 is mainly β -emitter and its decay daughter Ac-228 is γ -emitter determination of Th-232 can be directly determined by the γ -rays emitter from Ac-228. From this point, Th-232 can be determined based on the three characteristic γ -energies at 338.4, 911.1 and 968.9 keV [56,58]. Ra-224 was determined indirectly based on its equilibrium with their respective decay daughters. Since there is equilibrium between Ra-224 and their products, because of the short half-live of Rn-220 ($t_{1/2}$ 55 s) [67]. Therefore, Ra-224 was determined based on different four γ -energies line of Pb-212 at 238.6 keV, Tl-208 at 583.1 and 2614.7 keV, and Bi-212 at 727.2 keV [68]. Potassium-40 is determined based on its γ -energy line at 1460 keV [56,64,69]. The photon emission intensities of several γ -emitters decayed from primordial nuclides of U-238, U-235, and Th-232, with their corresponding γ -energies are presented and given in Table (1.1).

1.6. Radiochemistry of Interested Radionuclides:

1.6.1. Radium:

The present work is mainly related to investigation on natural radioactivity produced as a result of phosphate rock processing for producing phosphoric acid and phosphate fertilizers. In this respect, radionuclides of interest are those of uranium (U), thorium (Th) and radium (Ra). Some physical properties of uranium, thorium and radium are given in Table (1.2). The naturally occurring uranium isotopes (U-238, U-235 and U-234) are given in Table (1.3). Each of these isotopes is a member of decay series, involving successive α or β -decays, accompanied with γ -radiations [4].

Radium is the element number 88 in the periodic table and it belongs to group IIA, the alkaline earth metals. Twenty-five isotopes of Ra have been identified, each with a different number of neutrons in its nucleus, all are unstable and only four are found naturally. The element radium is the heaviest of the alkaline earth group metal [71].

There are four main radium naturally occurring isotopes in the environment, namely Ra-226 belonging to the uranium series, Ra-224 and Ra-228 belonging to the thorium series and Ra-223 belonging to the actinium series. The determination of Ra-226 is more important especially from the standpoint of geochemical studies, environmental and human health effects.

Table (1.1): Photon emission intensity and γ -energies of some naturally occurring radionuclides [61,70].

Uranium (U-238)			Actinium (U-235)			Thorium (Th-232)		
nuclide	E_γ, keV	I, %	nuclide	E_γ, keV	I, %	nuclide	E_γ, keV	I, %
Pb-210	46.5	4.25	U-235	143.8	10.96	Ac-228	129.1	2.42
Th-234	63.3	4.80	U-235	163.4	5.08	Ac-228	209.25	3.89
Th-234	92.6	5.60	U-235	185.7	57.2	Pb-212	238.6	43.3
Ra-226	186.2	3.59	U-235	205.3	5.01	Ac-228	338.32	11.27
Pb-214	295.2	19.3				Ac-228	463.0	4.70
Pb-214	351.9	37.6				Tl-208	583.1	30.0
Bi-214	609.3	44.8				Bi-212	727.2	7.0
Bi-214	1120.3	14.9				Ac-228	794.9	4.9
Bi-214	1238.1	5.96				Tl-208	860.1	4.7
Bi-214	1377.7	4.15				Ac-228	911.1	29.0
Bi-214	1764.5	16.07				Ac-228	968.9	17.5
Bi-214	2204.1	5.06				Tl-208	2614.7	36.0

Notes: E_γ = Energy of γ - line in keV, and I = Intensity (%)

Table (1.2): Some physical properties of uranium, thorium and radium [71,72].

N	Z	A	electronic configuration	density, g/cm^3	m.p. °C	b.p., °C	oxidation state
U	92	238.029	[Rn] $5f^3\ 6d^1\ 7s^2$	18.90	1132	3818	3, 4, 5, 6
Th	90	232.038	[Rn] $5f^0\ 6d^2\ 7s^2$	11.70	1750	4790	4
Ra	88	226.025	[Rn] $7s^2$	6.000	700	1140	2

N = radionuclide, Z = atomic number, and A = mass number

Table (1.3): Some characteristics of the naturally occurring uranium isotopes [71].

U-isotope	$t_{1/2}$, y	abundance, %	main nuclear data		
			decay mode	energy, (Mev)	intensity, (%)
U-238	4.47×10^9	99.27	α -emitter	4.195	77.0
U-235	7.10×10^8	0.725	α -emitter	4.390	55.0
U-234	2.48×10^5	0.005	α -emitter	4.768	72.0

The well known radiotoxicity of Ra-226 results from: (a) the chemical similarity of radium to calcium, which allows a localization of Ra-226 in bone tissue, when ingested, (b) the long physical and biological (~ 45 y, bone) half-life of radium, and (c) the α -particle emission from the decay of Ra-226 and from its radioactive progenies (Rn-222, Pb-210, Po-210 and stable Pb-206). Ra-226 is present in varying concentrations in all soils, rock, and its distribution in the environment is widespread. Ra-226 is absorbed from soil by food crops and is hence incorporated into the food chain of human [73].

Some of the radium physical properties are given in Table (1.2). It has actually an atomic weight of 226.025 and its atomic number is 88, the ionic radius of radium is given as 1.40 °A (charge 2+). Its melting point is 700 °C and its boiling point is 1140 °C. Its specific gravity is 6 g/cm^3 at 20 °C. Radium is a member of the alkaline earth family and, like barium, strontium and calcium, it forms insoluble sulphate, carbonate and chromate salts. The chloride, bromide, nitrate and hydroxide salts of radium are soluble in water [74]. The relative order of solubility varies with the anion, for sulphates, the solubility decrease in the order [75].

$$Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$$

Properties of the four main radium isotopes are given in Table (1.4).

1.6.2. Radon:

Radon is one of the rare or noble gases. Its electronics configuration is [Xe] $4f^{14}\ 5d^{10}\ 4s^2\ 6p^6$. In general, the name radon refers to Rn-222, there are 27 known isotopes of radon. Other isotopes are further denoted by their common names or mass number in Table (1.5) [20,71]. Radon-222 forms from the α -decay of Ra-226 is a member of U-238 decay series. The radio-active gas has a relatively short half life, 3.82 d, and forms Po-218 by α-decay. Radon-222 is an inert, noble gas and eventually decays to form two relatively longed lived radioactive daughters, Pb-210 and Po-210 [20]. Radon can be considered as one of the most hazardous radioactive gas in the environment. The focus of health concerns related to the TE-NORM.

Table (1.4): Characteristic of some naturally occurring radium isotopes [61,71].

Ra-isotope	decay series	half life	Main nuclear data			
			α -decay mode		γ -decay mode	
			energy, Mev	intensity, %	energy, kev	intensity, %
Ra-223	U-235	11.20 **d**	5.70	50	154.3	5.6
Ra-224	Th-232	3.64 **d**	5.68	95	241	5.0
Ra-226	U-238	1622 **y**	4.78	95	186.2	3.59
Ra-228	Th-232	6.7 y	--	--	--	--

Notes: **d** = day, y = year.

Table (1.5): Naturally occurring isotopes of radon [71].

Rn-isotopes common name	Decay series	Half life	Decay mode	Energy of decay, MeV
Radon (Rn-222)	U-238	3.82 d	α	5.84
Thoron (Rn-220)	Th-232	54.5 s	α	6.28
Actinion (Rn-219)	U-235	3.92 s	α	6.82

The radiation risks associated with the handling, transport and disposal of the TE-NORM wastes contaminated with Ra-226, are primarily due to the inhalation of Rn-222, and are dependent on the rate at which Rn-222 is transported to the atmosphere or on the diffusion and subsequent emission from the TE-NORM waste matrix to the staff operators [76].

The radon gas is soluble in water, and the solubility increases with decrease in temperature. Solubility in organic liquids may be several orders of magnitude greater than in water [20]. Since the half-life of Rn-222 is far greater than the half-lives of the other radon isotopes, it is easiest to measure and hence is the isotope considered in most detail in the geochemistry of emanation. In a closed system, for a time-scale greater than one month, the geochemistry of radon is entirely the geochemistry of its parent, radium. The escape of radon from solids has been studied by numerous workers. Various terms, such as emanation power and emanation coefficient, have been applied to this phenomenon. All terms refers to the fraction of the percentage of the total generated radon that escapes from a solid [71].

1.7. Literature Survey on the Treatment of TE-NORM Wastes:

1.7.1 Treatment of Phosphogypsum Wastes:

Since phosphogypsum wastes can be used in some civil and agricultural purposes, a more attention on the treatment for removal and/or reduction of the enhanced activity levels due to Ra-226 were carried out. The available literature surveys related to remediation of radionuclides of the environmental interest content in phosphogypsum wastes are still very limited.

An extensive study was carried out on the treatment of the phospho-gypsum wastes associated with the wet-phosphatic processing in Morocco [77]. In this concern, phosphogypsum wastes were treated based on leaching using different solutions. The phosphogypsum wastes without previous pretr-eatment were treated under certain conditions using aqueous solutions within pH range of 2.1-8.84. Leaching percentages of the different radionuclides removed were found in the ranges 24.5-29.1, 23.8-26.4 and 19.8-22.8% for Ra-226, Pb-214 and Bi-214, respectively. On the other hand, phosphogypsum wastes were pretreated (calcinations at 800 °C and crushed) before leaching using various solutions under certain conditions. In this concern, the leaching % obtained for the treatment of phosphogypsum wastes (pretreated) using distilled water (DW) with stirring at the ambient temperature was 6.0, 3.2, 3.7

and 10.5% for radionuclides of Ra-226, Pb-214, Bi-214 and Th-234, respectively. At leaching using DW with boiling for one hour, the removal of radionuclides was decreased to 3.7, 2.0, 2.7 and 6.3%. The leaching % was lowered to 3.4, 0.4, 0.7 and 6.2%, when the phosphogypsum wastes were treated using DW with stirring for 6 hours at the ambient temperature. On the other hand, the pre-treated phosphogypsum wastes were treated using acidic aqueous solutions of HCl and H_3PO_4. It was observed that, removal of radionuclides using HCl solution was higher than those obtained using phosphoric acid solutions. For instance, treatment of phosphogypsum wastes using HCl solutions yield leaching % reached to 20.7, 22.1 and 25.4% for Pb-214, Bi-214 and Th-234, respectively. While the removal % was decreased to 2.4, 5.4, and 18.5% for the same radionuclides when using H_3PO_4 [77].

Treatment of the phosphogypsum waste containing Ra-226 produced from the phosphate rock processing plant in Kochi (India) was carried out using different leaching solutions. The different parameters affecting on the treatment were also investigated [19]. It was found that the actual leaching % of Ra-226 through 10-succesive leaching processes was found ~ 24 and 18% using distilled water and rainwater, respectively. Rutherford et al. [22], were found that the activity concentration of Ra-226 in the solutions produced from the treatment of phosphogypsum waste using distilled water was 0.19-0.65 Bq/L. Treatment of the by-product solid wastes produced from the phosphate fertilizers plants was also carried out in terms of batch wise and continuous leaching processes [78]. In the batch wise treatment, 10 g of phosphogypsum wastes was mixed with one liter of DW and stirred for 10 min. this process was repeated 20 times. The total activity concentration of Ra-226 remained in the solid residue of treated waste was reduced to a factor of 40%. In case of the continuous leaching, the waste was packed into column and treated with distilled water through flow rate of one ml/min. The total activity concentration of Ra-226 leached out was reduced to 16%. In a fertilizers plant at Udyogamandal (India), the phosphogypsum wastes from this plant contain mainly a mixture of calcium carbonate and calcium sulphate [79].

Leaching studies were performed on these wastes based on batch wise leaching using distilled water. It was found that, the total activity of Ra-226 removed from the phosphogypsum through ten successive treatments, was reached to 60% [79]. Polonium-210 distribution in Syrian phosphogypsum

has been studied using laboratory leaching experiments [80]. Leaching experiments using DW have shown that Po-210 is strongly bounded to phosphogypsum particles. Leaching experiments have shown that the amount of Po-210 transferred to aqueous media does not exceed 6.5 and 8.4% for batch wise and continuous leaching, respectively. The amount of dissolved Po-210 was decreased from 6.77% to 3.6% when the pH solutions used in the leaching process was increased from 3.7 to 6. Leaching using low concentration of sulphuric acid between 0.01 and 0.5 M, increased the amount of dissolved Po-210, a value of 20% was observed when sulphuric acid concentration was 0.02 M. On the other hand, the results of batch wise leaching of phosphogypsum with selective solutions were 58%, 65%, 62% and 92% by using $MgCl_2$, NH_4Ac, $NH_2OH.HCl$ in 25% of acetic acid and mixture of concentrated HNO_3 and HCl with 30% of H_2O_2, respectively [80].

1.7.2 Treatment of Sediments of Petroleum Wastes:

El-Afifi [81], studied the treatment of radioactive waste containing Ra-226 from oil and gas production, using different chemical solutions, in terms of a simple and sequential techniques based on suspending Ra-226 through the clay fraction in the waste. More than 50% of Ra-226 was removed through the treatment using moderate acids and salts solutions, while more than, 75% of Ra-226 was removed based on successive treatment or using some strong chelating reagent solutions [81].

1.8 Aim of the Present Work:

Industrial and technical activities distribute an elevated natural radioactivity due to naturally occurring radioactive materials (NORM) with subsequent concentration in their radiation hazardous. In phosphate processing for phosphoric acid and fertilizers production, large amounts of radioactive wastes are produced from this industry. These wastes contain an enhanced level of some radionuclides (e.g., Ra-226) of environmental impact that represent radiation risks to the surroundings. Therefore, the present work is directed to the following:

i- Studies on the characterization of the input and output materials accompanying the production of phosphoric acid by the wet process in Abu Zaabal Company for fertilizers and chemicals production.

ii- Studies on the treatment or decontamination of the phosphogypsum waste which produced in huge amounts as a solid waste and used in different purposes.