

## CHAPTER II

## THEORETICAL APPROACHS

2.1 Source of Technetium-99 and Cesium-137

## 2.1.1 Technetium-99

Technetium-99,  $^{99}\text{Tc}$ , is the decay product of technetium-99m which played an important role in shaping the field of diagnostic nuclear medicine since 1960. Technetium-99m comes from its parent molybdenum-99 which has negatron emission with half-life of 66.02 hr. There are two processes for the production of high specific activity of molybdenum-99 which are mainly used for the preparation of technetium-99m, namely, 1) direct irradiation of molybdenum target such as molybdenum trioxide ( $\text{MoO}_3$ ) and 2) fission of uranium (natural or enriched) (Laohawilai, S, 1991)

2.1.1.1 Direct Irradiation of Molybdenum(III)Oxide

Pure  $\text{MoO}_3$  is irradiated at neutron fluxes exceeding  $2.1 \times 10^{13} \text{ ncm}^{-2} \text{ sec}^{-1}$  for 12 to 15 hr and then dissolved in 5.5 M NaOH.  $^{99m}\text{Tc}$  can be extracted from the alkaline solution of sodium molybdate ( $^{99}\text{Mo}$ ) by using methyl ethyl ketone (MEK). Passing the organic layer through an  $\text{Al}_2\text{O}_3$  column (pH of  $\text{Al}_2\text{O}_3$  is about 6), evaporating to dryness and redissolving with 0.9% physiological saline. The obtained technetium-99m is in the form of sodium pertechnetate ( $\text{NaTcO}_4$ )

For this study,  $^{99}\text{Tc}$  was produced by the Isotope Production Division by direct irradiation of  $\text{MoO}_3$ .

### 2.1.1.2 Fission of Uranium

Natural or enriched uranium-235 in the form of metal, U-Al alloy or uranium oxide is the target material usually employed. In a typical production, the irradiated target, uranium, is put through a separation process to recover  $^{99}\text{Mo}$  in a bed of chromatographic grade alumina. Physiological saline is then passed through the bed to elute the  $^{99\text{m}}\text{Tc}$  component.

The half-lives of  $^{99}\text{Mo}$ ,  $^{99\text{m}}\text{Tc}$  and  $^{99}\text{Tc}$ , together with the decay scheme for  $^{99}\text{Mo}$  to  $^{99\text{m}}\text{Tc}$  and  $^{99}\text{Tc}$  (IAEA, 1971) are presented as follow :

#### a) Half-lives

$^{99}\text{Mo}$ :	66.02 hr.	Recent value :	$65.98 \pm 0.10$ hr.
$^{99\text{m}}\text{Tc}$ :	6.049 hr.	Recent value :	$6.006 \pm 0.03$ hr.
$^{99}\text{Tc}$ :	$2.15 \times 10^5$ yr.	Recent value :	$2.14 \times 10^5$ yr.

#### b) Type of decay and energies

$^{99}\text{Mo}$  :

beta( $\beta^-$ )	0.250 (0.3 %)	gamma	0.018 (characteristic X-ray from technetium)
	0.445 (47.0 %)		0.021
	0.880 (1.0 %)		0.041(2.6 %), IC(e/ $\gamma$ 0.7)
	1.234 (82.0 %)		0.140(2.6 %), IC(e/ $\gamma$ 0.1)
			0.181(10.0%), IC(e/ $\gamma$ 0.13)
			0.372(1.3 %)
			0.41 (0.2 %)
			0.62 (0.1 %)
			0.74 (12.6%)
			0.78 (4.4 %)
			0.94 (0.2 %)

$^{99m}\text{Tc}$  :

IT (100 %)      gamma 0.002 (99%), IC(e/γ very large)  
 0.018 (characteristic  
 X-ray from technetium 5.7 %)  
 0.021  
 0.1405 (99%), IC(e/γ 0.11)  
 0.1426 (1%), IC(e/γ >30)

$^{99}\text{Tc}$  :

beta ( $\beta^-$ ) 0.292 (100%)

c) Decay scheme

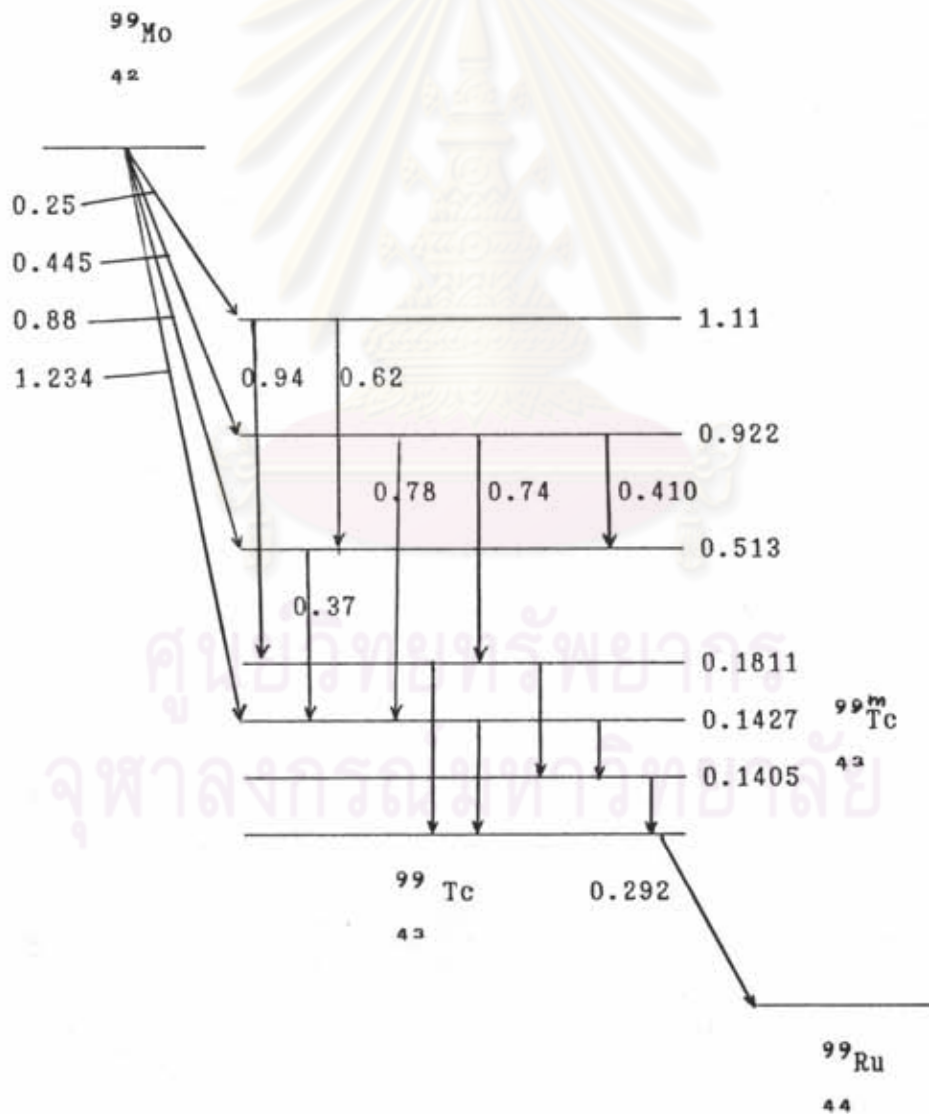


Figure 2.1 Decay Scheme for Molybdenum-99. (After: IAEA, 1971)

### 2.1.2 Cesium-137

Cesium-137 is the decay product of Xenon-137 which constitutes an important fission product in nuclear reactors. Cesium-137 emits beta and gamma decay.

There are two methods for the production of Cesium-137, as follows:

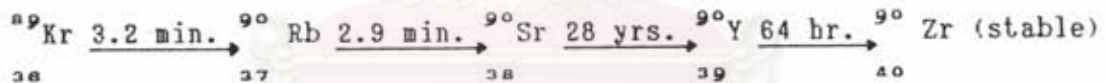
#### 2.1.2.1 Production of $^{137}\text{Cs}$ in Nuclear Explosions

Most of the radioactive nuclides released by nuclear weapons in the global fallout are produced through the process of fission. Certain heavy nuclei, such as those of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , disintegrate into two lighter nuclei. These are generally unstable and undergo further radioactive decay.

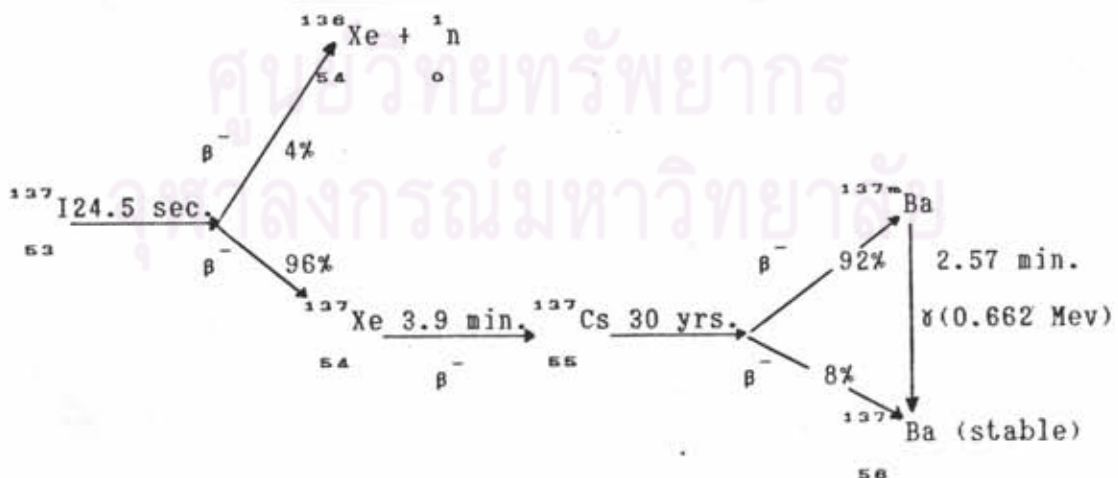
The major portion of nuclear testing has been carried out in the atmosphere. About 200 fission products are formed ranging in mass from about 70 to 170 a.m.u and in periodic number from 28 to 65. (Hasanen, 1972)

The fission reaction results in the formation of a large number of decay chains; for examples, the chains yield two long half-life nuclides which are extremely important from the point of view of radiation risk.

##### a) Chain 90:



##### b) Chain 137:



### 2.1.2.2 Production of $^{137}\text{Cs}$ from the Utility of Nuclear Energy for Peace

Nuclear energy has been used in many fields such as medicine, agriculture, industry, research, etc. Reactors has been used for research, isotope production, and electrical power. These activities produce  $^{137}\text{Cs}$ -radioactive waste among others.

The half-lives of  $^{137}\text{Xe}$ ,  $^{137}\text{Cs}$  and  $^{137}\text{Ba}$  together with their decay schemes (Kocher,1981) are as follow:

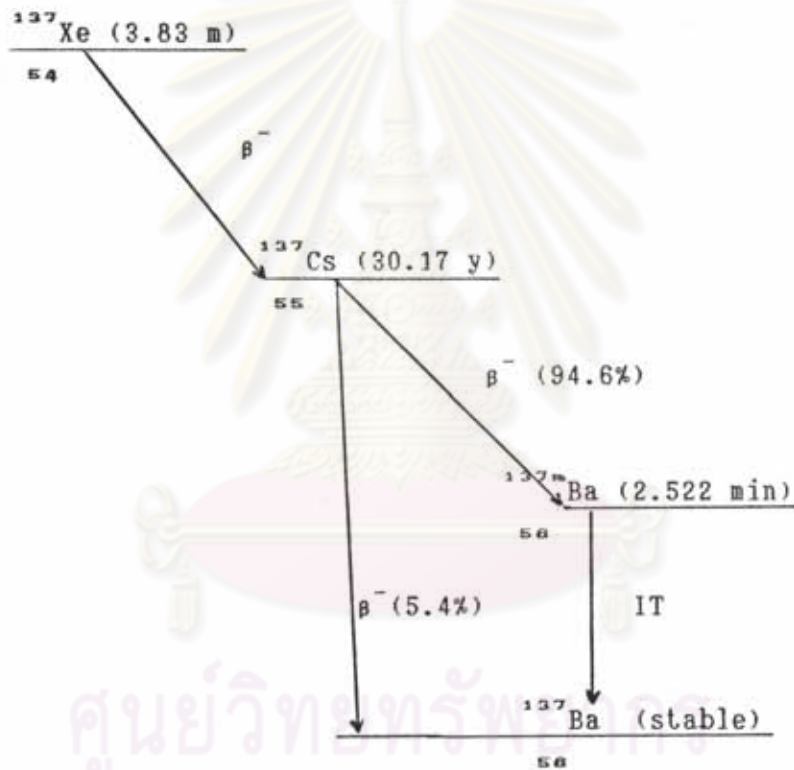


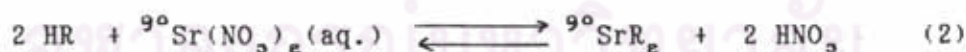
Figure 2.2 Decay Scheme for Cesium-137 (After:Kocher, 1981)

## 2.2 Principles of Ion-exchange Process

### 2.2.1. General

Ion exchange, as the name implies, is merely the exchange of ions that occurs across the boundary between a solid particle and a liquid. When certain substances are dissolved in water, they become ionized. An equal number of positively charged ions, (cations), and negatively charged ions, (anions), are formed and the solutions conduct electricity. Such substances are called electrolytes. Dissolved electrolytes, when in contact with solid ion-exchange materials, will exchange stoichiometrically equivalent amounts of ions of the same sign. Ions from the solid materials migrate from sites on the surface and even from the interior of the solid.

Materials which exchange cations with electrolytes are known as cation exchangers, those which exchange anions are called anion exchangers. Certain substances, capable of exchanging both cations and anions, are termed amphoteric ion exchangers. If it is assumed that R represents the insoluble matrix of an exchanger, typical cation-exchange reactions are: (IAEA, 1967)



Typical anion exchange reactions are:



Equation (2) describes the removal of  $^{90}\text{Sr}$  from waste by ion exchange.  $\text{H}^+$  ions from the solid exchanger HR are replaced by  $^{90}\text{Sr}^{2+}$  ions from the waste solution. Complete conversion of the HR to the  $^{90}\text{SrR}_2$  form can be accomplished by treatment of a sufficient excess of the  $^{90}\text{Sr}$  waste solution. An exchanger in this state is termed "exhausted". However, it can be "regenerated". During the regeneration process, the resulting concentrated  $^{90}\text{Sr}(\text{NO}_3)_2$  solution can be recovered for disposal, as such, or for further treatment by other techniques.

Ion exchange is often termed a 'sorption' process since in both ad- and absorption a solute becomes attached to a solid. In true sorption, however, electrolytes and non-electrolytes are collected with no release or exchange taking place. The ion-exchange process is stoichiometric. Every ion removed from solution is replaced by an equivalent amount of other ion of the same sign.

To simply illustrate the phenomenon of ion exchange, a sponge may be used as a model of an ion exchanger. The sponge itself represents the frame work held together by chemical bonds of lattice energy and carrying a surplus positive or negative charge. To achieve the required electro neutrality, assume the pore spaces are filled with a sufficient number of mobile or counter ions of a charge opposite that of the frame work. When the sponge is placed into a solution, the counter ions may float out of the pore spaces. However, no counter ion may leave unless a stoichiometrically equivalent number of ions of identical sign from the solution float into the pore space to preserve the electroneutrality. The number of counter ions available for this exchange, according to this model, is termed the ion-exchange capacity.

If the sponge is permitted to remain in the solution until all exchange ceases, a state of ion-exchange equilibrium is reached. At this time, exchanger counter ions and solution ions will be found both in the sponge pore spaces and in the solution. After the sponge has been placed in various solutions, solvent in the pore spaces may cause an increase in size of the framework, or swelling.

When the sponge is placed in the solution, it may be noted that the counter ions exchange more readily with certain solution ions than with others. This ability of the exchanger to distinguish between the various solution ions is labelled "selectivity" and it is influenced by solution ion size, valence and other interactions with the environment.

This is a description of ion exchange. An attempt will be made in the following pages to elaborate on the nature of the process with particular regard to use in treatment of radioactive waste.

### 2.2.2 Characteristics of Ion-exchange Materials

It has been determined to this point that ion exchangers are virtually insoluble materials with a framework held together by chemical bonds or lattice energy. The framework is charged by a positive or negative electric charge and electroneutrality is maintained by counter ions of the opposite sign. When placed in a solution of an electrolyte, the counter ions are free to exchange positions with electrolyte ions of the same sign. In the following paragraphs, the factors influencing this exchange will be discussed.



### 2.2.3 Ion-exchange Capacity

Elementary as the term capacity may seem, it is often misused due to a lack of appreciation of number of exchange values it can represent. When capacity is stated, total exchange capacity of a mineral is the value intended. However, it is often misunderstood as apparent capacity, breakthrough or operating capacity, sorption capacity, etc. Capacity or total exchange capacity is equal to the number of fixed ionic sites, the magnitude of the framework charge that can enter into an ion-exchange reaction. This value is a constant for a particular exchange material. On a weight basis, it is expressed as milliequivalents per millilitre. The total volume capacity of resin refers to a settled bed of fully water-swollen resin in the  $\text{Na}^+$  or  $\text{Cl}^-$  form for the strong-acid and strong-base and in the  $\text{H}^+$  and free-base form for the weak acid and weak-base resins.

### 2.2.4 Sorption Equilibria

This section deals with sorption of electrolytes and non-electrolytes. Ion exchange would normally be involved but is excluded by assuming all electrolyte ions are identical to exchanger counter ions. Sorption is a term used to describe a condition in which both adsorption and absorption reactions occur. Dissolved material is concentrated both on the surface and in the pores. Ion-exchange materials are sorbents. When in a solution of weak or non-electrolytes, sorption by ion exchangers is similar to that of nonionic adsorbents. In a solution of strong electrolytes with counter ions identical to exchanger counter ions, a sorption equilibrium results due to

the reaction with the strong electrolytes of the electrostatic forces arising from the fixed ionic groups and the counter ions of the exchanger.

#### 2.2.5 Swelling Equilibrium

The concept of swelling equilibrium will be reviewed to a limited extent since an awareness of this exchanger characteristic is essential to plant design. Pressure sufficient to burst a column develops as a resin swells. On the other hand, shrinkage of resin can result in channelling in a column.

When an ion exchanger is placed in a solution or solvent, aqueous or non-aqueous, a certain amount of sorption of solvent occurs and the exchanger expands or swells. If the exchanger is soluble in the particular solvent, swelling continues until the exchanger is completely dissolved. Normally, however, this is not the case and swelling continues only until an equilibrium is attained. With resin, for example, polar and ionic constituents tend to surround themselves with the solvent. The frame work or matrix continues to yield and stretch until its elastic forces balance the dissolution tendency.

#### 2.2.6 Ion-exchange Equilibrium: Selectivity

Ion-exchange reactions are true, reversible equilibrium reactions. At equilibrium, exchanger and electrolyte solution contain both the exchanger counter ion and the electrolyte counter ion. The distribution of these ions at equilibrium will be the same whether the reaction is approached from either end.

Assume the reactions are represented by the following equations:



(R represents the ion exchanger, E1 the electrolyte counter ion and Ex the exchanger counter ion.)

Ion-exchange equilibrium can be conveniently expressed in terms of distribution coefficients as with sorption equilibrium. The similar definition for the distribution coefficient of the counter ion is the ratio of concentrations of the counter ion in the exchanger and the solution at equilibrium. Considering ions of various valences and simplifying on the basis of trace concentrations of radioisotopes, an expression for this equilibrium distribution coefficient is  $K_d$ .

$$K_d = \frac{\text{sorbed radioisotope/g. of exchanger}}{\text{dissolved radioisotope/cm}^3 \text{ of solution}}$$

This equation is widely used in the study of mineral exchangers.

The favoured direction of either reaction (5) or (6) depends upon the relative affinity of the ion-exchanger framework or matrix for the various counter ions. This preference for one counter ion over the other also results in a different concentration ratio of counter ions within the exchanger from that in the electrolyte solution.

#### 2.2.7 Kinetics

When designing an ion-exchange processing system, it is desirable to have an appreciation of the speed at which the reaction will occur. Whether the necessary contact time is minutes or days will determine the physical size of the plant.

The ion-exchange reaction occurring when a porous exchanger and the solution of an electrolyte are in contact can be divided into five distinct successive occurrences. These are:

(1) diffusion of electrolyte ions to the surface of the exchanger

- (2) diffusion of the electrolyte ions through the exchanger-solution interface or film into the structure of the exchanger
- (3) the exchange of ions
- (4) diffusion of the exchanged ions from the structure
- (5) diffusion of the exchanged ions into the solution.

Three of these diffusional occurrences - in the solution, in the liquid interface or film, within the structure of the solid exchanger - determine the kinetics of the ion exchanger. The first process, diffusion in the solution, has little effect on rate when the general porous exchangers and relatively dilute solutions are considered. Solution strength, in fact, determines which of the two remaining processes will be the exchange rate controller. In very dilute solutions, diffusion in the interface or film will control rate of exchange. As the solution concentration is increased, both film diffusion and diffusion in the structure determine rate. With continuing increase in solution strength, a level is reached at which diffusion in the structure (solid diffusion) alone is the rate - determining process.

Actual rates of ion exchange can vary from seconds to months and a number of factors in addition to those mentioned above play important roles. Exchanger particle size is one of these. It has been shown that exchanger rates increase with diminishing size of exchanger particle under most conditions. Increasing temperatures have been found to increase the rate of exchange.

## 2.3 Ion-exchange Materials

### 2.3.1 General

A wide range of materials is available for the ion-exchange treatment of wastes. Exchangers of many sizes, shapes and forms, of wide varying capacities, costs, and chemical, thermal and mechanical stabilities, of natural or synthetic structure.

There is a great variety of ion exchange materials but they can roughly be divided into the following categories,

- inorganic exchangers (natural and synthetic)
- organic exchangers (synthetic - strong acid, weak acid, and strong base, weak base).

### 2.3.2 Historical Development of Ion-exchange Materials

The earliest systematic studies in which ion-exchange properties were described are concerned with base exchange in minerals present in the soil. Before the existence of ions in solution was demonstrated, and before the crystal structure of the solid concerned had been elucidated, it was found that when soils are treated with solutions of ammonium salts, ammonia is taken up by the soil and an equivalent quantity of calcium released. This property of "base exchange" was shown to be reversible and to involve chemically equivalent quantities of the base taken up and of that released, moreover, it was shown to hold for a number of other salts besides those of ammonia. Although many years were to elapse before the mechanism was understood—since this demands a knowledge both of the ionic nature of the solutions and of the crystal structure and composition of the clay minerals present in the soil, it was recognized as a phenomenon of considerable importance in relation to soil fertility. Some soils possess the property to a greater extent than others, and these are generally more fertile, and more capable of storing mineral fertilisers over a long period when these are applied to the soil.

Many hypotheses have been proposed to explain the phenomenon of base exchange in soils, but ultimately it was traced to two principal causes. One of these is the presence of humins and humic acids, particularly in soils rich in organic matter, when the decay of the latter produces a wide variety of organic species which possess hydroxyl or carboxyl groups which can act as ion

exchange groups in the same way as in the phenolic and carboxylic acid resin. However, in many soils of low organic content, and in soils where organic matter has been destroyed by treatment with hydrogen peroxide, a considerable ion-exchange capacity is still observed; on fractionation of the soil by removal of coarse mineral matter and careful elutriation this may be traced to the so-called "colloid fraction", which on petrographic and X-ray examination is found to consist chiefly of clay minerals. A close identification of the ion-exchange properties of soils with their clay fraction has been achieved, the gross properties of the soil depending upon the amount and types of clay minerals. Other aluminosilicates may confer ion-exchange properties in certain soils, e.g. glauconite, a ferrous aluminosilicate analogous to the zeolites, which possesses exchangeable potassium; this mineral exchanges only at the crystal surfaces, but in colloidal form possesses considerable capacity.

The first synthetic ion-exchangers were also inorganic materials; these were the synthetic zeolites or permutites developed by Gans and other workers for use in water-softening processes. They are synthetic sodium aluminosilicates in which sodium is replaced by calcium when hard water is percolated through a bed of the material; since the reaction is reversible the exchanger may be regenerated by treatment with a saturated brine solution when exhausted.

### 2.3.3 Review of Inorganic Ion Exchange Materials.

A wide range of materials is available for the ion-exchange treatment of wastes. Exchangers of many sizes, shapes and forms, of wide varying capacity, costs and chemical, thermal and mechanical stabilities, of natural or synthetic inorganic exchangers can be obtained in this section.

The basic types of inorganic ion-exchange materials may be broadly classified as show in Table 2.1.

Table 2.1 Basic Types of Inorganic Ion-exchange Materials  
(After : Amphlett, 1964)

(A) Exchangers possessing well-defined crystal structures	(i) Aluminosilicates
	(a) Two-dimensional layer-lattice structures, e.g.the clays and lamellar zeolites
	(b) Three-dimensional cage structures, e.g.the typical zeolites
	(ii) Non-siliceous materials, e.g. heteropolyacid salts
(B) Poorly crystalline and amorphous materials	(i) Hydrous oxides of polyvalent metals
	(ii) Acid salts of polyvalent metals and polybasic acids

The advantages and disadvantages of inorganic ion-exchangers, are as following:

#### Advantages

- 1) high chemical stability , inorganic exchangers are saver with strong nitric acid for elution, though some inorganics may dissolve,
- 2) high exchange capacity , for cesium synthetic zeolite can be better than organics,
- 3) selectivity, can be improved by using suitable ionic form of exchanger or by choice of eluting agents,

- 4) specificity, inorganic exchangers are known which preferentially absorb a specific ion,
- 5) thermal stability, inorganic have an advantage particularly for storage and disposal
- 6) immobilization, inorganic are compatible with or convertible to stable inorganic structures, with cement, bitument or polymers.
- 7) cost, more common inorganics are cheaper than organics, but other could be costly to prepare.



#### Disadvantages

- 1) some exchangers are pH sensitive, as hydrous oxide and oxide compounds dissolve readily at  $\text{pH} > 7$ ,
- 2) regeneration is uncertain, evidence rather thin ionorganics normally favoured for permanent absorption,
- 3) they are least useful as ion exchange column application because: a) relatively high ion exchange capacity of some exchangers as hydrous oxide and oxide compound are offset by their ease of dissolution in acids or bases and the poor filtration characteristics of the precipitates, b) relatively high swelling of some exchangers as bentonite, kaolinite and other clays.

Thereby, they are unsuitable used as column sorbents,

- 4) mechanical strength, inorganics may be brittle or soft, also may break down physically outside a certain pH range,
- 5) cost, synthetic inorganic exchangers cost relative high,
- 6) availability of inorganic exchangers are uncertain, some inorganics (e.g. hydrous titanium oxide) would have to be made primarily for the nuclear market.
- 7) handling, organic available as tough spheres, ideal for handling and transfer, inorganic generally as angular particles and may be more friable (favours non-regenerative use). Technology for moving sands can be applied for example to natural zeolites.

The following sections are described the properties of some inorganic ion-exchange materials.



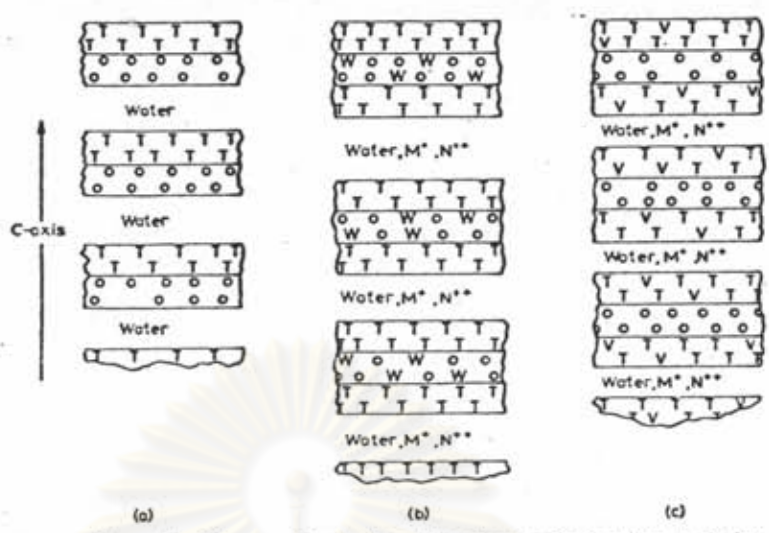
### 2.3.3.1 Natural Inorganic Materials

#### 2.3.3.1.1 The Clay Minerals

The clay minerals comprise a complex series of aluminosilicate structures in which a number of basic types shade almost imperceptibly into each other, and the structures of a number of them have been elucidated by the application of X-ray crystallography and other physical techniques. It is only necessary to consider these structures in outline in order to explain the ion-exchange properties of the clays.

Basically the aluminosilicate "backbone" of the clays is composed of alternating, parallel, two-dimension layers formed from silicate tetrahedra and aluminate octahedra (Grim, 1953)

The simplest type (Figure 2.3) is characteristic of the kaolinite clays, which are found in china clay deposits; in this type the basic unit is a double layer consisting of one silicate and one aluminate layer with negligible isomorphous substitution in either of them. Units such as these are stacked together along the c - axis of the crystal, which is perpendicular to the layer planes, at the edges and corners of which there will normally be free hydroxyl groups. The basic formula for kaolinite is  $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_6$ , although individual members of the series may depart from this ideal composition. The free hydroxyl groups may exchange with anions when immersed in a salt solution; since they are weakly acid, the hydrogen in them may also exchange with cations. As a result, the material shows a small exchange capacity which is approximately the same for both anions and cations. The cation-exchange capacities of Kaolinite is 0.02-0.10 meq/g (Amphlett, 1964)



Schematic diagram illustrating the three principal types of clay minerals. (a) Kaolinite; (b) Montmorillonite; (c) Illite. T = Tetrahedral silicate layers, O = Octahedral aluminate layers, V = Isomorphous substitution at tetrahedral sites, W = Isomorphous substitution at octahedral sites. M<sup>+</sup>, N<sup>++</sup>, balancing cations.

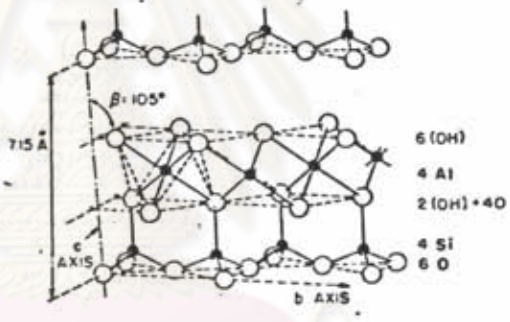


Figure 2.3 Structure of Kaolinite,  $Al_2Si_2O_5(OH)_2$ .  
 A Tetrahedral Sheet  $Si_2O_5$  linked to  
 Octahedral  $Al_2O_5(OH)_2$ . (After:IAEA, 1967)

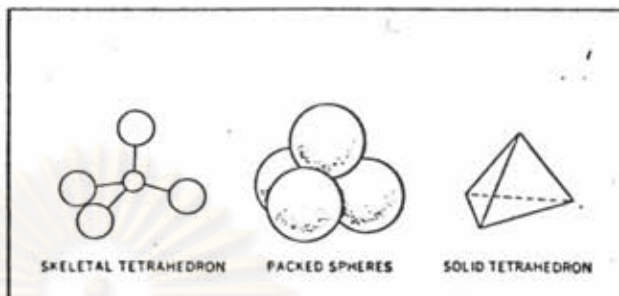
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More complex types of clay mineral are based on a repeating unit consisting of one aluminate layer sandwiched between two silicate layers, the ideal basic formula being  $\text{Si}_6\text{Al}_4\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ . As a result of isomorphous substitution however actual formula differ widely from the latter, and two well-defined and distinct types may be recognized. Such substitution may occur in either the tetrahedral or the octahedral layer, depending upon the size and co-ordination number of the substituent ion in relation to those of aluminium and silicon. For example,  $\text{Al}^{3+}$  in the octahedral layer may be replaced by  $\text{Mg}^{++}$ ,  $\text{Fe}^{++}$  and other octahedrally coordinated ions of suitable radius, and  $\text{Si}^{4+}$  in the tetrahedral layer may be replaced by  $\text{Al}^{+++}$ , since the latter can exhibit a coordination number of either 4 or 6, aluminium is found in both tetrahedral and octahedral layers in some clays.

#### 2.3.3.1.2 The Zeolites

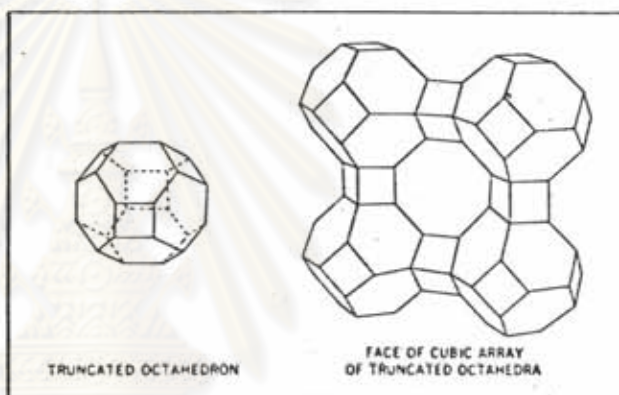
The zeolites form another group of aluminosilicate minerals, the structure of which are built up from tetrahedral groupings having the formula  $\text{AlO}_4^{5-}$  and  $\text{SiO}_4^{4-}$  in such a way that corners, edges and faces of the tetrahedra are shared to give condensed structures. Like the clays they possess well-defined crystal structures. Depending upon the structure and type of bonding, zeolites may exist as fibrous, lamellar, or rigid three-dimensional structures; the first two classes are analogous to the fibrous clays (eg. attapulgite, sepiolite) and to the typical lamellar clays and micas respectively, but the third type, with strong covalent bonding in three dimension, has no analogue in the clay series. It is this type of robust, three-dimensional network which is usually taken to represent the zeolites, and it is this type which has been extensively studied for its ion-

The structure of the zeolites consists of a rigid three-dimensional framework of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra.



The Type A Molecular Sieve has a framework composed of truncated octahedra joined in a cubic array.

This produces a central truncated cube octahedron with an internal cavity of  $11 \text{ \AA}$  in diameter. Each central cavity, termed the  $\alpha$  cage, is entered through 6 circular apertures formed by a nearly regular ring of eight oxygen atoms with a free diameter of  $4.2 \text{ \AA}$ . The cavities are thus arranged in a continuous three-dimensional pattern forming a system of unduloid-like channels with a maximum diameter of  $11 \text{ \AA}$  and a minimum of  $4.2 \text{ \AA}$ . The truncated octahedra themselves enclose a second set of smaller cavities  $6.6 \text{ \AA}$  in internal diameter ( $\beta$  cages) and connected to the larger cavities by means of a distorted ring of six oxygen atoms of  $2.2 \text{ \AA}$  free diameter.



Model of the structure of zeolite type A based on skeletal tetrahedra.

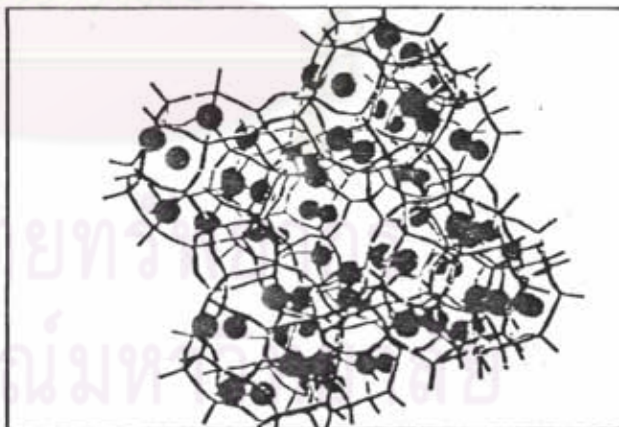


Figure 2.4 Molecular Sieve Structure of Zeolite.

(After:IAEA, 1967)

exchange properties as showed in figure 2.4. Stoichiometrically the zeolites may be regarded as being derived from the formula  $(\text{SiO}_2)_n$  by replacing silicon by aluminium to varying extents, the resulting net negative charge being balanced, as in the clay.

The clay minerals and naturally occurring zeolites, though replaced to a large extent by synthetic exchangers, continue to be used and have been applied extensively to the treatment of radioactive waste solutions. Limitations to their use include:

- (i) relatively low ion exchange capacities,
- (ii) low abrasion resistance of the zeolites,
- (iii) clay minerals tend to peptize, i.e. to form colloids in some solutions,
- (iv) these materials are partially decomposed by acids and alkalis.

#### 2.3.3.2 Synthetic Inorganic Materials (Hooper, 1984)

##### 2.3.3.2.1 Synthetic Zeolites

These materials are commercially available; they act as molecular sieves by excluding ions larger than the opening in the cryatalline matrix. Limitations to the use of synthetic zeolites are similar to those listed above for naturally occurring zeolites but the synthetic zeolites posses improved stability and a higher cation exchange capacity.

##### 2.3.3.2.2 Oxides and Hydrous Oxides

Only a few of these materials are available in commercial quantities. Many show high exchange capacity, low solubility and good radiation and thermal stability.

Cation or anion exchange sorption by oxides and hydrous oxides is known to occur predominantly by displacement of hydrogen and hydroxide ions from the sorbents provided that these have previously been washed free from impurity ions. The predominant function groups are probably metal-hydroxide bonds which can exhibit amphoteric properties favouring anion exchange at low pH and cation exchange at high pH.

Although hydrous oxides are at their most active when freshly precipitated, they are at their least useful as regards ion exchange column applications. Their relatively high ion exchange capacities are offset by their ease of dissolution in acids or bases and the poor filtration characteristics of the precipitates in general render them unsuitable for use as column sorbents.

If gelatinous precipitates of the hydrous oxides are dried they undergo considerable shrinkage to give glassy gels which break down in water to produce granular particles suitable for column applications. The structure and ion-exchange properties of these dried gels depend very much on the conditions of preparation of the precipitates and the drying procedure used to produce the granular product. During the drying stage it is probable that, apart from the removal of free water, elimination of water from  $-OH$  groups occurs to produce  $-M-O-M-$  bonds ( $M$ =metal) giving a stronger absorber material but reducing the ion-exchange capacity.

The quantitative effect of heat treatment of different oxides and hydrous oxides on their ion exchange properties varies considerably. Generally ion exchange capacities show a steady decrease with heating and at about  $200^{\circ}C$  have fallen to 20-30 % of their values for low temperature dried material. Heat treatment can improve both the selectivity and the chemical stability of these absorbers.

The use of an oxide or hydrous oxide absorber as a column material is obviously governed to a large extent by its resistance towards breakdown or dissolution when treated with various reagents. In general the insoluble acidic oxides and hydrous oxides are stable in acid solutions but dissolve readily at  $\text{pH} > 7$ . In contrast the more basic hydrous oxides such as  $\text{TiO}_2$  and  $\text{ThO}_2$  dissolve readily in mineral acids above about 0.1 M but are stable in less acid solutions.

#### 2.3.3.2.3 Acidic Salts of Multivalent Metals

A wide range of compounds of this type have been described as ion-exchangers. These salts, acting mostly as cation exchangers, are gel-like or micro-crystalline materials with the composition and properties depending on the method of preparation.

In general they are not available in commercial quantities and many are likely to be expensive to produce because of the limited availability and high cost of the materials required in their preparation.

### 2.4 Limitations of Ion-exchangers

#### 2.4.1 Limitations Applicable to All Ion exchangers

In solving chemical processing problems, existing methods are investigated and evaluated. The problem is normally well defined and the processing method providing the desired product at the lowest unit cost is selected. To evaluate the use of ion exchange for removal of radionuclides from waste solution, the capabilities and limitations of the process must be recognized and understood.

Certain characteristics of ion-exchange materials and the process itself limit its applicability and efficiency. These include:

1) Leakage. Whether column, batch, or moving bed systems are used, complete removal of a specific radionuclide is not normally possible due to leakage. In a properly designed system, leakage may be very low, but improved removals would require a considerable effort at high cost per unit improvement. This leakage may be due to:

- (a) radionuclides in colloidal size particulate form;
- (b) a portion of the radionuclide concentration, though in solution, may be in non-exchangeable or non-electrolyte form;
- (c) mechanical difficulties, e.g. channelling in columnar operation, which are difficult to protect and prevent.

2) Radionuclides in the waste must be in an exchangeable, electrolyte form. Radioelements of some of the heavy metals have hydroxide forms of low solubility. In other instances, radionuclides in solution may be sorbed by suspended matter in the waste and thereby become non-exchangeable.

3) The concentration of suspended solids in the waste solution must be very low. For most efficient and economical operation, the exchanger beds cannot be used for filtration as during column operation. In most cases, prefiltration will extend the length of ion-exchange cycles, extend the life of the exchanger, permit closer control of operation, reduce leakage and permit more efficient backwashing and regeneration.

4) The concentration of total solids in the waste solution must be relatively low. Exchange potentials of ions of similar valence become similar or decrease with increasing atomic number. Competition for exchange sites is much greater and exchange efficiency of a specific nuclide is impaired.

5) Certain radioelements, as ruthenium, are very difficult to remove from solution by ion exchange because of their chemical complexity.



6) Radionuclides which are monovalent or of low atomic number are difficult to remove by ion exchange except when exchangers specific for the element are used.

7) In certain cases, costs may be a limiting factor in consideration of the ion-exchange process. Synthetic ion-exchange resins are relatively expensive.

#### 2.4.2 Limitations Applicable to Natural Inorganic-Exchangers

The clay minerals and the zeolites, though replaced to a large extent by synthetic exchangers, continue to be used and have been applied extensively to treatment of radioactive waste solutions. Limitations in their use include:

- 1) Relatively low exchange capacities
- 2) Relatively low abrasion resistance of the zeolites
- 3) Relatively limited swelling of zeolites with restricted mobility of the exchangeable ions
- 4) Clay minerals tend to peptize
- 5) The zeolites are difficult to size mechanically
- 6) These materials are partially decomposed by acids and alkalis
- 7) Many of the clays and zeolites have only limited stability in solutions of very low silica or salt content.

Several of the naturally occurring inorganic exchange materials are treated by stabilization techniques and are available commercially, e.g. Neopermutit and Superneopermutit. With these, of course, the treatment is designed to preserve the desirable characteristics of the nature material and overcome limitations as listed above.

### 2.4.3. Limitations Applicable to Synthetic Inorganic Exchangers

Two groups of distinctly different materials, physically and chemically, comprise this category. These are the synthetic zeolites and the inorganic chemical compounds such as the exchangers prepared by combining group-IV oxides with the more acidic oxides of group V and VI. They will therefore be discussed separately.

#### 2.4.3.1. Limitations : Synthetic Zeolites

The synthetic zeolites, of which a number are commercially available, are highly specific sorbents rather than ion exchangers. They act as 'molecular sieves' by excluding particles larger than the openings in the crystalline structure. The openings are adjustable for size by converting the exchanger to other ionic forms. Limitations include:

- 1) Relatively high cost as compared to natural zeolites
- 2) Limited chemical stability in acids and bases
- 3) The presence of potassium in the waste solution seriously interferes with caesium removals. (Studies at Hanford and Brookhaven, USA demonstrated the high selectivity of the molecular sieves for caesium and strontium and their application to particular wastes.)
- 4) Limited mechanical stability. The synthetic zeolites are exact counterparts of the natural materials with some improvement in capacity and stability.



#### 2.4.3.2 Limitations: Inorganic Chemical Compounds

Few of these materials are presently available commercially due to their rather recent development. However, their outstanding characteristics - high capacity, insolubility, thermal and radiation stability - will hasten their development and result in wide commercial availability. At this stage in their acceptance, they exhibit several limitations which include:

- 1) They lose fixed ionic groups due to hydrolysis at high pH.
- 2) They are difficult to prepare in mechanically stable convenient size.



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## 2.5 Principles of Immobilizing Processes

After waste materials have been treated to achieve volume reductions and to recover valuable (active or inactive) components, they have to be conditioned for transport, storage and disposal. Conditioning is the waste-management step at which radioactive wastes are immobilized and packaged.

The immobilization processes involve the conversion of wastes to solid forms that reduce the potential for migration or dispersion of radionuclides from the wastes by natural processes during storage, transport and disposal.

The immobilization processes involve the use of various matrices, non-radioactive materials such as cement, bitumen and polymers, to fix the wastes as monoliths, usually directly in the waste containers used for subsequent handling. (IAEA, 1983)

The matrix materials must be adapted to:

- The radioactive components in the wastes (types and half-lives of radionuclides, specific activities, radiation levels, etc.)
- The chemical and physical properties of the waste materials (liquids, sludges, ion-exchangers, solids, etc.); and
- The behaviour of the package with regard to disposal conditions.

In addition, matrix materials should be relatively easy to handle and should not dilute the wastes excessively, resulting in high immobilized waste volumes relative to those of the untreated waste. Finally, the selection of the matrix materials should take into account the local, national or international industrial availability and the relevant economics.

As the matrix materials and the immobilization processes are selected, careful consideration of safety-related features must be given to identify any constraints or incompatibilities; awareness of these safety features and appropriate counter

measures will enhance the safety of routine operation of the processes and subsequent handling, transport, storage and disposal.

The setting of suitability criteria and arranging the properties in an order of importance are difficult and depend on the local circumstances and the selected methods.

Two methods have been extensively used throughout the world for many years : cementation and bituminization. Methods using polymers or other matrix materials are in the pilot-plant stage or in a stage of early industrial application.

For each matrix material several process techniques could be used in view of how the wastes are mixed with the matrix material.

This study is directed towards a cementation process for immobilizing the radioactive elements of the wastes in a cement material. The properties of cement will be described as follows.

## 2.6 Cementing Materials

A cement is a material having those adhesive and cohesive properties that make it possible to bond together mineral fragments so as to produce a continuous, self-standing monolith. There are a number of cementing materials that can be used for this purpose, including hydraulic cements, limes, gypsum plasters, asphalts, and polymers.

### 2.6.1 Elementary Composition of Cement.

The results of a routine chemical analysis of cement are customarily reported in terms of the oxides of the principal constituent elements. Table 2.2 gives summary of typical cement compositions.

Table 2.2 Typical Cement Compositions (After: IAEA, 1983)

Composition	Oxide analysis (wt%)			
	Portland cements			High alumina cement
	Type I <sup>a</sup>	Type II <sup>b</sup>	Type III <sup>c</sup>	
CaO	64	63	65	37
SiO <sub>2</sub>	21	22	20	9.6
Al <sub>2</sub> O <sub>3</sub>	6.5	5	5.5	41
Fe <sub>2</sub> O <sub>3</sub>	2.5	4	3	4.9
FeO	-	-	-	5.6
MgO	2.5	3	2.3	1.0
SO <sub>3</sub>	2.1	1.5	2.5	0.2

<sup>a</sup> Stand ARD Portland cement.

<sup>b</sup> Sulphate resistant, less reactive and slower setting.

<sup>c</sup> High early strength (very reactive, quick setting)

In addition to the determination of the oxides listed in Table 2.2, there is usually determined the loss of weight after igniting (heating to a full red heat) a sample of the cement. This check is made as an indication of possible prehydration and carbonation due to improper or prolonged storage. Normally, in a satisfactory cement the ignition losses do not exceed about 2 per cent, although a maximum value somewhat greater than this is permitted under existing specifications.

### 2.6.2 The Curing Period

The last step, and an exceedingly important one in the cementation process, is the curing. As hydration of cement takes place only in the presence of moisture and at favorable temperatures, these conditions must be maintained for a suitable time interval called the curing period.

At the time cement is mixed, sufficient water is added to give workability. The amount of mixing water actually used is ordinarily in excess of 50 percent of the weight of cement, while the amount of water required for reasonably complete hydration of the cement is considerably less than 50 percent. Therefore, if the original water can be retained, there will be more than sufficient water for curing purposes.

Specifications usually require that the surfaces of concrete be protected to prevent loss of moisture for at least 7 days where normal cement is used, and some specifications require curing for 14 days or 28 days. Where high early-strength cements are used, the curing period may be reduced by half, while for slow-hardening cements the time should be longer than for normal cements.

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## 2.7 Cementation Processes

The cementation process for nuclear waste immobilization, with and without additives, has been commonly used on an industrial scale for several years in different countries (Burns, 1971), (Christensen, 1979), (Broadbent, 1979) and (Burri, 1978)

Basically, the process consists of mixing the cement with the waste, be it as a solution, slurry or solid, within a container. The cement mix is then allowed to set. The mixing of the cement with the various radioactive wastes, i.e. sludges, resin beads etc., affects the properties of the waste form. The various cementation processes can be classified according to how this mixing is achieved (Holcomb, 1978).

### 2.7.1 The In-drum Mixing Cementation Process

In this process the cement, the waste and any additives are fed separately into a container which is also the final shipping container. A schematic diagram of this method of mixing is shown in Figure 2.5 (Holcomb, 1978). Once in the container the components are mixed until homogeneous mixture is obtained. After mixing, the cement composite is allowed to set. Finally the drum is capped with wet concrete which is also allowed to set. But the "capping" method is not used any longer for sealing a drum. It was only used during the early years of ocean dumping.

The container is monitored and quality-control checks are made on the package before it is removed for decontamination and storage.

The method of feeding the materials to the drum can vary with the preferred gravity or vibro-feeding. The mixing of cement and waste is important for the homogeneity of the final waste form. Care must be taken to avoid air entrainment as it is desirable to have the lowest possible porosity in the cured cement composite.



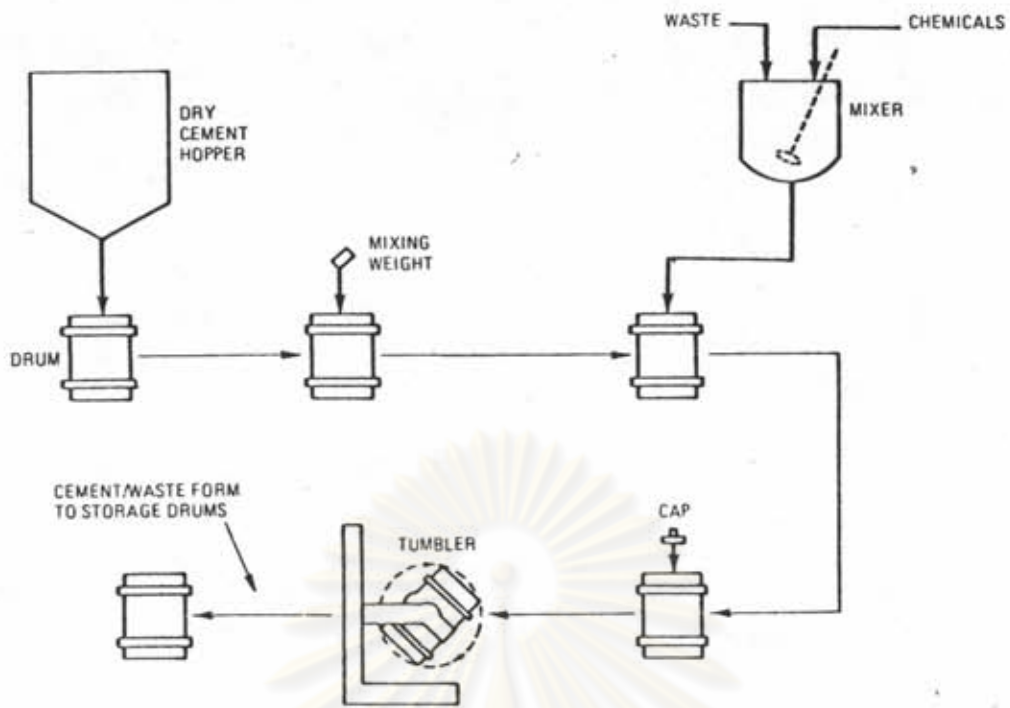


Figure 2.5 Example of In-drum Mixing Process. (After:Holcomb, 1978)

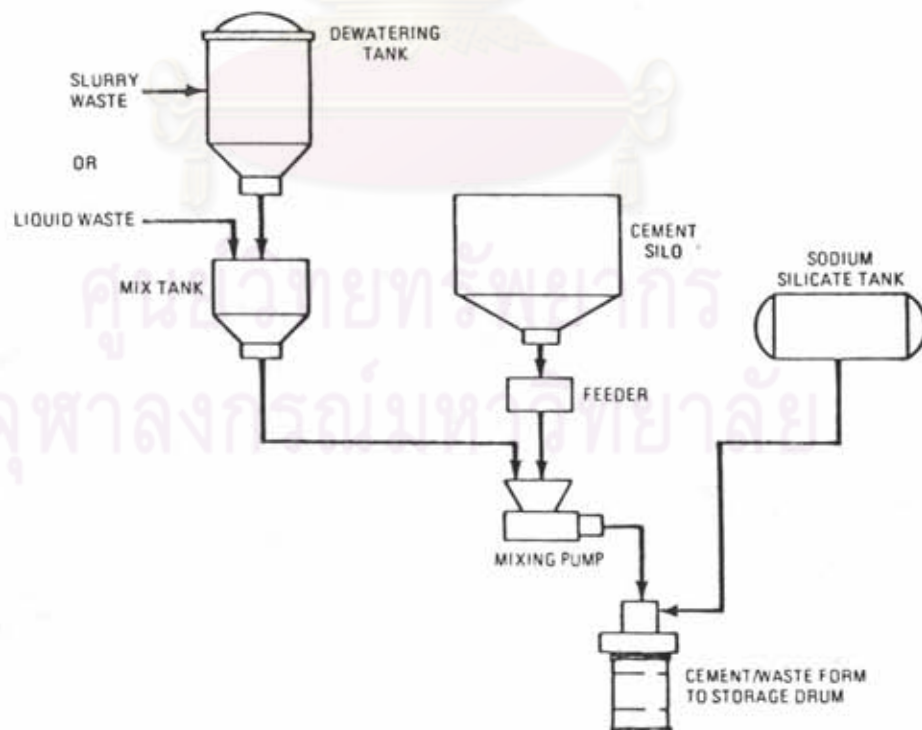


Figure 2.6 In-line Mixing Cementation Process. (After:Holcomb, 1978)

### 2.7.2 The In-line Mixing Cementation Process

In this process the cement and the waste are separately metered into one end of the mixer. The cement is fed with a screw feeder while the waste is fed with a mono-pump. The mixer is also a mono-pump. From the mixer the cement waste mixture is released directly into the storage container. The filling level in the container is monitored by both ultrasonic and contact probes. The container is then sealed, decontaminated, monitored and sent for storage. The waste tank and mixer can be flushed through after each run. If desired the rinsing water can be stored and used to prepare the feed slurry for the next run. This is done by use of a mixing blade which blends the constituents. The mixture is then drained into a container through the bottom of the mixer.

(A typical example of using in-line mixing is shown in Figure 2.6)

### 2.7.3 Mobile Cement Immobilization Plants

The waste arising annually at nuclear power plants may be immobilized within a few weeks in even a modest sized cementation plant. The plant requires trained personnel and has to be maintained continuously. As a result, considerable cost saving can be realized by building a mobile cementation plant to handle the wastes at several nuclear power stations. It is also safer to transport the plant to the waste rather than transport wet wastes considerable distances for conditioning. The plant can then have its own permanent skilled team. Several types of mobile cementation plants have been constructed. Figure 2.7 (Christ, Brunner and Kohlpoth, 1979) shows a sectioned diagram of the DEWA plant's shaped frame which contains the steel-shielded hot cell.

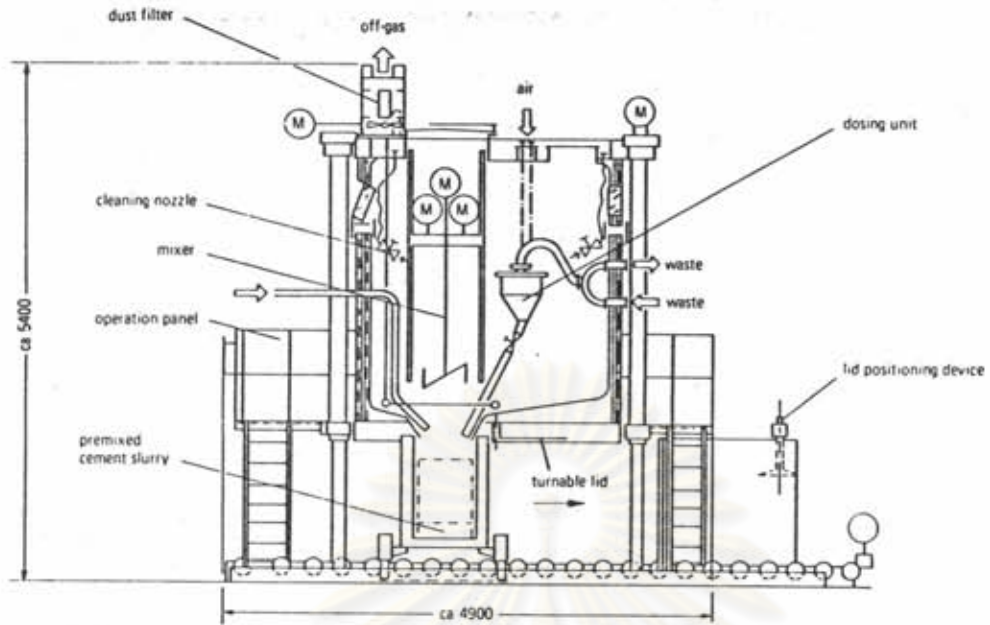


Figure 2.7 a) Mobile Cementation Plant (DEWA) Scheme  
(After: Christ, Brunner and Kohlpoth, 1979)

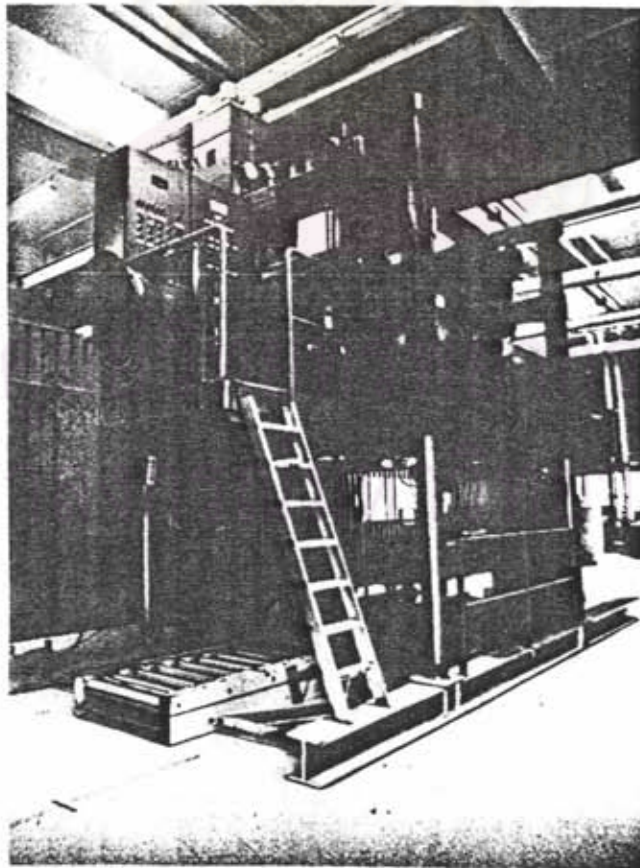


Figure 2.7 b) Mobile Cementation Plant (DEWA).  
(After: Christ, Brunner and Kohlpoth, 1979)

## 2.8 Basic Properties of Cemented Wastes

### 2.8.1. Physical and Mechanical Properties

The physical properties of an immobilized waste form should always be considered in the selection of a disposal system. For example, the requirements imposed by deep-sea dumping are different from those for shallow ground burial; the statutory requirement for transportation and interim storage are again somewhat different. Changes in external conditions, (e.g. temperature, pressure and climate during storage, transport and disposal) may lead to changes in physical properties and hence affect radionuclide release. Among the physical properties that may require consideration are waste/matrix ratio, homogeneity/heterogeneity, density, porosity, permeability, mechanical properties, thermal conductivity, swelling/shrinking and freeze/thaw cycling.

These properties and some observed effects associated with them in a range of immobilization systems are discussed below. (IAEA, 1983)

#### 2.8.1.1 Waste/Matrix Ratio

If comparisons of physical properties are to be made it is necessary to know the relative loadings of waste in the final forms. This is sometimes reported in an ill-defined way and there is uncertainty as to whether the author means volume or weight fraction, on either a wet (presence of free and/or physisorbed water) or dry waste basis. Generally, the amount of solid, dry waste incorporated in a matrix is in the range 10-15 % by volume, except in the case of conversion to ceramics where a volume reduction of the waste concentrate can be achieved.

#### 2.8.1.2 Homogeneity/Heterogeneity

In all cases the waste form under consideration consists of two or more phases, and uniformity of dispersion of either the waste or individual radio-nuclides in a matrix may affect the mechanical or physico-chemical characteristics of the final form. This property is not generally considered, except for a qualitative statement where, for example,

there is gross phase separation as in bleeding or in stratification of insoluble components (e.g.resins) because of density differences.

#### 2.8.1.3 Density

A value for density of a product is useful and, in the case of deep-sea dumping, necessary(i.e.)=  $1.2 \text{ g/cm}^3$ ). It is conceivable also that, if sufficient water was to accumulate in a shallow-land burial site, drum surfacing could occur owing to hydrostatic pressure if the product density were  $< 1.1 \text{ g/cm}^3$ .

In the case of products that are less than the theoretical density (i.e contain voids) it is necessary to describe the method of measurement and to specify bulk or apparent density.

#### 2.8.1.4 Porosity and Permeability

Residual porosity in the waste form will affect other parameters such as the mechanical and physico-chemical properties (e.g.leach rate). Porosity is usually described as interconnected (open) or closed, and a waste form may contain one or both types. Cement matrices contain intrinsic interconnected porosity that leads to high internal surface areas if the water/cement ratio is high.Such porosity can be measured directly and characterized in terms of permeability as a function of hydrostatic pressure. Ceramic final forms would ideally contain no interconnected porosity and less than 10 % closed porosity. If interconnected porosity exists the method of measuring should be reported. Premeability is not necessarily a function of porosity, and materials such as bitumen and some polymers, which are essentially pore-free solids, will permit the passage of water but to a lesser extent.

#### 2.8.1.5 Mechanical Properties

Certain minimum values for a range of mechanical properties are required if an immobilized waste form is to survive accidents or long-term stresses during handling, storage, transport and final disposal. In all waste forms the matrix is the continuous phase and will tend to determine the mechanical

properties. The incorporated waste has a detrimental or beneficial effect depending on the particular mechanical property and the proportion of waste incorporated. The mechanical properties of the final waste form will be determined by its resistance to the intrinsic ionizing radiation and the external environment, excursion of temperature and/or pressure in the event of an unpredicted occurrence.

#### 2.8.1.5.1 Compressive Strength

Among mechanical properties, cemented waste form compressive strength is of greatest significance. The measurement of the compressive strength can provide important additional information regarding the quality of the conditioned waste for disposal. The compressive strength is the criterion of quality, and working stresses are prescribed by codes in terms of percentages of the compressive strength as determined by standard tests. The usual test employs a cylindrical specimen of height equal to twice that of the diameter, moist-cured at 70 +/- 5 F for 28 days and then subjected to slow ('static') loading at a specified rate until rupture occurs; usually loading is completed within 2 or 3 min.

In this study, the minimum compressive strength value for specimens has been selected to be 15 N/mm<sup>2</sup> (~ 150 kg/cm<sup>2</sup>) as recommended by Zange, Schlenter and Laser (1982). The minimum compressive strength requirement may vary according to the different regulations in various countries e.g. a compressive strength of 2.5 N/mm<sup>2</sup> is recommended by Merz, Dyckerhoff and Odoj (1987), whereas about 5 N/mm<sup>2</sup> by Donato and Ricci (1987). But the principle is to maintain the integrity of the waste form during transportation, storage and disposal.

### 2.8.2 Release of Activity

The release of radioactivity from solidified waste products can occur by two mechanisms, each of which will be examined in detail:

- Attack by water which slowly dissolves the waste product;
- Volatilization if the temperature of the waste product rises too high (this only applies to high level waste, not for low-or intermediate waste forms ).

#### 2.8.2.1 Leaching

This is the most important single parameter in the evaluation of solidified waste products and represents the main mechanism for releasing activity to the environment over long periods of time. Considerable world-wide effort has been expended in developing solidified products that are as stable as practicable (Ewest and Levi, 1976), particularly to attack by water. However, the leaching process is time consuming and sophisticated techniques are required to measure the dissolution rates.

#### 2.8.2.2 Leaching Methods

For the past twenty years, the groups working in the field have used a variety of methods to measure leaching rates, some of which differ in many fundamental ways.

At the first meeting on waste solidification held in the USA, Thomas(1957) proposed a standard leach test utilizing a Soxhlet extractor. The method was not adopted because it was only an accelerated test. In 1969 a group of consultants called together by the IAEA made a further attempt to develop a standard test (Hespe,1971). This met with more success, and some laboratories have used techniques based on this standard test.

A further attempt is now being made by the International Standards Organization to develop a standard test which is a modified version of the IAEA test and attempt to overcome its disadvantages in application.

Leach tests generally fall into two broad groups:

- (1) Short-term tests, mainly used for short-term sorting of samples and studying the effects of variables; and
- (2) Long-term tests to simulate the actual environmental conditions in storage.

Within these two groups, many other factors have to be considered. In almost all cases, the quantity of material to be leached from the sample will be very small and may be close to the limits of detection in the leach liquor. To overcome this, various methods have been devised: sometimes glass grains are used instead of large samples in order to increase the surface-to-volume ratio being leached; in other cases, radioactive tracers of the radionuclides of interest can be incorporated in the waste form at a sufficient activity level to be measurable in the leach liquor. Obviously, this problem is not so serious in the accelerated tests carried out at elevated temperatures when the quantity leached will be two or three orders of magnitude greater than that from tests carried out at room temperature. Another difficulty with many of the standard tests proposed so far (particularly the IAEA test) is the actual preparation of the sample and, in particular the heat treatment it receives before the leaching test is carried out. Ideally, each sample should be given the heat treatment that the corresponding batch has received (or will receive), and a standard heat treatment cannot be relevant for all samples. This is one area where tests must be modified for the specific samples involved and where there is difficulty in comparing results of one laboratory with the another.



The choice of liquid used for the leaching test is also importance. In those accelerated test that use a Soxhlet extractor, the leaching liquid must be pure water. Accelerated tests carried out by suspending samples in boiling liquid could use solutions other than water. Room-temperature tests use a variety of liquids, usually ranging from distilled water to sea-water on one hand and simulated ground water on the other.

A brief description follows of various leach tests which have been widely used. (IAEA, 1979)

(A) Accelerated Leach Test

A simple accelerated leach test was developed at Battelle for rapid determination of the comparative leachability of samples (Mendel, 1970). Product samples were crushed and sieved, and the fraction passing through a 4-5 mesh seive and retained on a 60 mesh sieve was used in the test. The sample was washed with acetone to remove fines. One-gram samples were enclosed in a stainless-steel cloth bag which was equipped with a suspension wire. The sample was weighed, dried overnight in an oven at 100°C, and weighed again. It was then suspended in 130 cm<sup>3</sup> of distilled water at 95°C for three 24-hour periods. After each period the sample was removed from the water, dried overnight at 100°C, and weighed. The leached water was replaced by fresh water each day. The weight loss after each 24-hour period and the total weight loss were used as a measure of the leachability of the sample. This method was used to leach vitrified waste forms containing high level waste. It cannot be used for cement, bitument or polymers.

(B) Soxhlet Accelerated Leach Test

This test has largely replaced the one described in (A) and is fairly widely used for accelerated measurements (Mendel, 1977 and Rastogi, 1969). The sample can be either glass grains, as used in example (A), or a specially

prepared sample such as a polished disc. In this test the sample is always leached by distilled water and does not come into contact with the bulk leach liquor containing dissolved constituents. The general principal is illustrated in Figure 2.8. This test is also used for high-level waste forms.

(C) Paige Leach test

This test, developed at Idaho (Paige, 1966) and used extensively at Battelle (Mendel, 1977), is used to predict long-term leaching behaviour. It is designed to leach the sample over a period of many weeks with recirculated water at or near room temperature. Samples of known surface area are placed on a support screen (Figure 2.9), the vessel is filled with 500 cm<sup>3</sup> of distilled water which is circulated by means of a small air lift. After 24 hours, or other suitable time period, the vessel is drained and the solution analysed. A fresh supply of water is added and circulation recommenced.

(D) IAEA Standard Test

In this test (Hespe, 1971) the sample is prepared in an inert cylindrical container which is open at one end only. The container is normally 5 cm in diameter and 5 cm high, but for samples of specific activity greater than 1 Ci/ltr. the dimensions are reduced to 2.5 cm diameter and 2.5 cm height. The sample is then placed in slightly larger outer container such that the exposed face of sample is covered by at least 5 cm depth of leach fluid and the ratio:

$$\frac{\text{Volume of leach fluid}}{\text{Exposed surface area of sample}}$$

(E) BNL's Accelerated Leach Test

This test is developed by Brookhaven National Laboratory (Fuhrmann, 1990) and presented to ASTM on January 24, 1990, Las Vegas, Nevada.

BNL's Accelerated Leach Test has three components:

- 1) Semi- Dynamic leach test run at room temperature (~20°C)
- 2) Semi- Dynamic leach test run at several elevated temperatures
- 3) Computer program to calculate results and to model results.

Reference Leach Test parameters are:

- 1) 2.5 cm. diameter x 5 cm. height cylinder.
- 2) 3.0 litres distilled water (ratio of 100 x surface area of waste form ).
- 3) Temperature: 20°C and 50°C.
- 4) Triplicate Waste Forms (minimum)
- 5) Daily intervals for 11 days.

The reasons for the parameters being set as they are, is the need to maximize the quantity of water used during the experiment. This is based on : experimental evidence that leaching is often suppressed by insufficient water and the assumption that low-level waste forms are relatively leachable and there is no problem detecting elements of interest.

The "ALT" computer program, Department of Energy (DOE) needs to use data from leach tests to make predictions for performance assessment on disposal sites. Initially the program was designed to do calculations for results and to model diffusion. This was the version used for the Draft Test Method. Analysis of data generated during experimental work showed that mechanisms, other than diffusion, often control the concentrations in the leachant. Recently the program has been extensively revised.

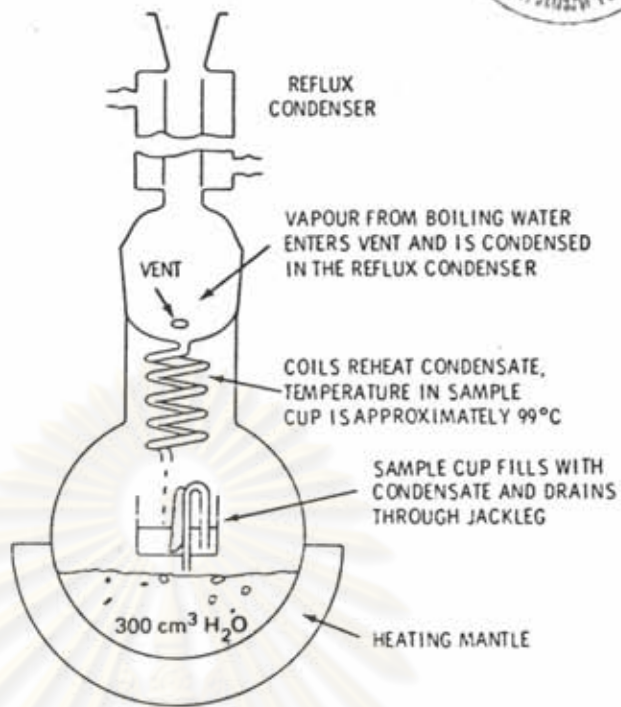


Figure 2.8 Soxhlet Leach Test Apparatus. (After: Mendel, 1977)

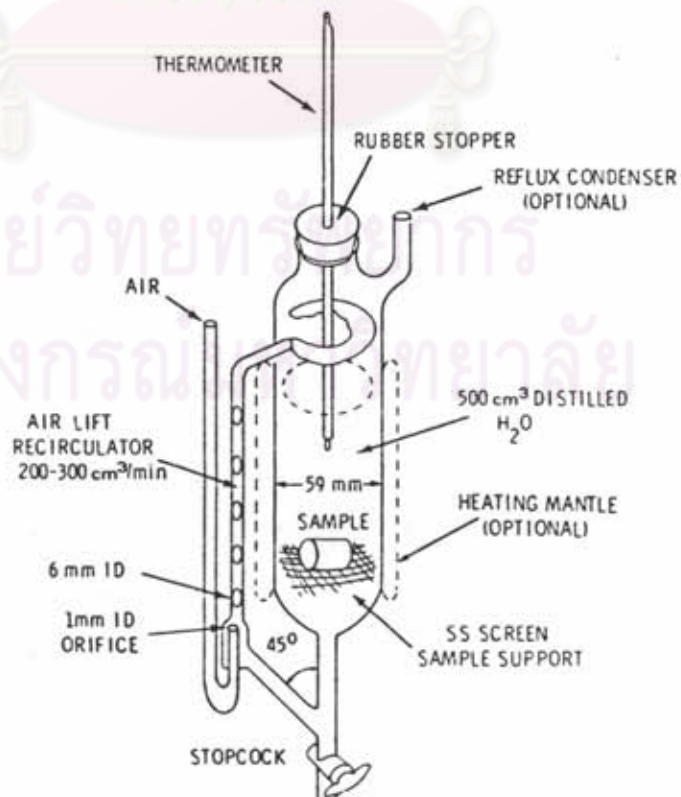


Figure 2.9 Slow Leach Test Apparatus. (After: Mendel, 1977)

### 2.8.3 Reporting of Leach Test Results

Leach rates have been reported by different groups in many different ways. For accelerated tests at 100°C, The percentage weight loss per unit time is often quoted:

$$\% \text{ weight loss} = \frac{(W_o - W_r) \times 100}{W_o}$$

where  $W_o$  = initial weight of the sample

$W_r$  = final weight of the sample

( It should be noted that this does not specify the surface area of the sample and can therefore only be used under standard test conditions for comparison purposes.)

For all tests at ambient temperature and when the weight loss is small, a leach rate is quoted:

$$\text{Leach rate, } R = \frac{A_t \cdot W_o}{A_o \cdot S \cdot t} \quad \text{g.cm}^{-2} \cdot \text{d}^{-1}$$

where  $A_t$  = amount of "A" removed in time t

$A_o$  = initial amount of "A" in sample of weight  $W_o$

S = surface area of sample ( $\text{cm}^2$ )

t = leach time (days)

" A " can be a specific isotope, an element, or the entire sample, but should be disclosed when quoting the results.

A leach factor (Hespe, 1971) has also been used according to the following:

$$\text{Leach factor, } F = \frac{A_o \cdot S}{7 \cdot A_1 \cdot V} \quad \text{week per cm or (cm. per week)}^{-1}$$

where  $A_o$  = initial amount of "A" in sample

$A_1$  = amount of "A" removed per day

S = surface area of sample ( $\text{cm}^2$ )

V = volume of sample ( $\text{cm}^3$ )

Leach rate and leach factor are simply related:

$$R = \rho / 7F$$

where  $\rho$  = density of the sample ( $\text{g.cm}^{-3}$ ). The leach factor is the reciprocal of a corrosion rate measured in cm per week.

For long-term leach data, a fractional release can also be quoted:

$$\epsilon_t A_t / A_0 \quad \text{or} \quad A_t / A_0$$

where  $t$  is a long time period. (Note: the correct SI unit for leach rate is  $\text{g.m}^{-2}.\text{s}^{-1}$ . However, since nearly all results are quoted in  $\text{g.cm}^{-2}.\text{d}^{-1}$ , this unit has been retained in the present report to avoid confusion.) (IAEA, 1979)



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย