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IMMOBILIZATION OF TRITIATED WASTE-WATER BY HYDRAULIC CEMENTS

A SURVEY OF THE STATE-OF-THE-ART



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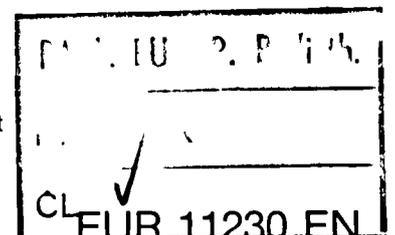
IMMOBILIZATION OF TRITIATED WASTE-WATER BY HYDRAULIC CEMENTS

A SURVEY OF THE STATE-OF-THE-ART

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ABSTRACT

An experimental research programme including as one of its major items the definition of a strategy for tritiated waste management is being prepared at the JRC-Ispra. Laboratory work will be performed in ETHEL, the European Tritium Handling Experimental Laboratory under construction at Ispra.

To provide background information needed for defining items and planning the execution of such activities, a survey of the state of the art and R&D performed in the field of tritiated water immobilization by hydraulic cements and ultimate packaging by multiple containment systems has been carried out.

Particular attention has been focused on results of tritium leach test programmes performed at various USA laboratories in order to verify the leach resistance properties of some tritium immobilization and containment options.

Problems and draw backs associated with such options are discussed. Final conclusions are presented.

CONTENTS

	page
1. Introduction and Summary	1
2. Hydraulic cements and aggregates	2
3. Cement hydration and resulting products	3
4. Proportioning of water to cement	4
5. Factors affecting tritium immobilization by cement hydration	5
5.1 Porosity	5
5.2 Evaporable water fraction	6
6. Cement additives	7
7. Mixing techniques	8
8. Additional treatments on a cement block	9
8.1 Coatings	9
8.2 Polymer impregnation	10
9. Leachability of radionuclides incorporated into a cement matrix	10
10. Results of tritium leach tests	11
10.1 Uncoated specimens	12
10.2 Coated specimens	12
10.3 Polymer impregnated specimens	16
10.4 Modified cement matrix inside burial packages	25
11. Conclusions	28
12. References	29
 Appendices :	
I. Composition of some varieties of hydraulic cements	35
II. Hydrated cement compounds	41
III. Water bonding and water mobility in set cement	43
IV. Cement additives	47
V. The polymer impregnation technique applied to tritiated concrete (PITC process)	49
VI. Parametric definition of tritium leach rate	57
VII. Burial package for tritiated liquid wastes	61

Glossary

1. Introduction and Summary

Hydraulic cements are the materials most widely investigated and practised for radwaste conditioning and disposal with the aim of minimizing the risks of radionuclide releases from the solidified waste to the environment (1-6).

The water capacity of commercially available hydraulic cements is in principle reasonably high, e.g. approximately 25 wt% for portland type cements and up to 50 wt% for high alumina cements. Theoretical values are somewhat higher since they neglect non-hydrating impurities present in commercial cements (2). However the amount of water needed to obtain a waste-cement product that would satisfy storage or disposal requirements may vary case by case according to:

- the relative amounts of individual cement constituents and the general stoichiometry of resulting hydrated and hydroxylated compounds;
- the nature and relative amount of additives eventually added to cement for various purposes (e.g. increase of the immobilized water loading or workability or resistance to compression);
- the nature and relative amount of liquid and/or solid wastes to be incorporated into cement or concrete (e.g. concentrates, sludges, ion exchange resin, inorganic sorbents, miscellaneous wastes, etc.) which often may act as water sorbents (2).

The procedure and technology related to the cement hydration process are simple and well known. A hydraulic cement mixed with water and aggregates (i.e. sand, gravel and/or wastes in various forms and sizes) reacts with water to form a paste that sets and hardens to give a final solid product referred to as concrete.

Mixing of the various components can be achieved either by in-drum or in-line techniques, e.g. the rotary mixing or the drum tumbling applied on a batch basis, as well as the screw dynamic mixing applied either on a batch or continuous basis.

In the current practice standard types of concrete have been used for several years to immobilize solid radioactive items and packaged waste. However for medium and low active liquid wastes and sludges different techniques are required and formulations of neat cement only are replacing the use of concrete (5). Inert materials such as sand and aggregates have therefore been excluded from the mix. The liquid waste and sludges can be considered as replacing the water normally used for mixing with the cement.

The use of hydraulic cements for the purpose of immobilizing tritiated aqueous wastes has been regarded as an attractive option for the following reasons:

- I. Cement is the cheapest candidate material having a considerably high water sorption capacity.
- II. Cement is an immobilizing agent already accepted and practised in many countries for incorporating and disposing of various types radioactive wastes.
- III. The shielding effect of concrete is particularly useful when gamma-emitter contaminants such as fission and/or activation products are associated with tritiated water.

The practical application of cement hydration as a tritiated water immobilization procedure requires that secondary low-level tritiated effluents arising from maintenance of water-cement mixing equipment and decontamination of operational area should be minimized or eliminated. This requirement is mandatory otherwise uncontrolled cleaning and maintenance operations could generate additional amounts of tritiated effluents having (even at a low tritium content) larger volumes than the hydration process disposes (13). For this purpose an appropriate choice of the cementation procedure and related process conditions have been performed. Mixing

and curing steps have been carried out in closed systems to prevent tritium leakage by evaporation. Blending of cement with tritiated liquid waste has been achieved even without mechanical mixing (injector technique) (17-27).

Factors of major influence in determining the degree of tritium retention in hydrated cements have been identified as mainly dealing with the porosity of the cement block, the fraction of mobile (evaporable) water held in it and the physical conditions surrounding the block such as the ambient temperature, moisture and environmental water. If not adequately controlled these factors will significantly contribute to increase the mobile fraction of the original tritiated water incorporated into the hardened cement with a simultaneous increase of its mobility hence of tritium release rate to the environment. The probability of keeping tritium release rate as low as possible will therefore depend on the close control of such factors. The total pore volume and the fraction of evaporable water present in a cement block can be controlled by a careful determination of two important process parameters, i.e. the water to cement ratio originally employed in the cement paste and the time period applied for "curing" (i.e. hydrating) the cement block.

Surface coatings, polymer impregnant as well as special containment packages based on multiple container assemblies have been utilised to trap tritium escaping from a tritiated cement block and to prevent the penetration into the block pores of moisture or water.

The tritium retention properties of some containment options resulting from the combination of these physical barriers have been demonstrated by both small laboratory and full-scale leach test programmes.

In the present report a review of the state of R&D in this field is performed with particular attention being focused on major problems encountered and significant results achieved.

The conclusions of this survey are intended to provide some background information needed to plan experimental activities to be carried out in ETHEL^(*) with the aim of defining the strategy in the field of tritiated waste management.

2. Hydraulic cements and aggregates

A hydraulic cement powder mixed with inert aggregates and water reacts with the latter to form a paste that sets and hardens to give a final solid product referred to as concrete.

Three types of hydraulic cements commonly used to make concrete have so far been applied for radioactive waste immobilization purposes. The most currently used are the "portland" varieties although "pozzolanic", "slag" and high alumina cements have also been applied.

Hydraulic cements mainly consist of calcium silicate and calcium aluminate mixed in various proportion. Their chemistry is complex but fairly well understood. Typical compositions of some varieties of such cements are shown in Appendix I.

Aggregates in a commercial concrete usually consist of natural sand, gravels, stone chippings or crushed rocks. They are added to the hydraulic cement powder with the aim of obtaining a concrete with an adequate capacity of resisting to compression (compressive strength). However, for the purpose of immobilizing radioactive waste, aggregates generally consist of the various forms of solid waste.

In the current practice standard types of concrete have been used for several years to immobilize solid radioactive items and packaged wastes. But sands are not normally used in the cementation of liquid wastes and slurries since they are inert

(*) European Tritium Handling Experimental Laboratory.

materials which do not adsorb or react with liquids in the same way as cement. The addition of sand reduces the amount of liquid waste that can be incorporated into a mix, hence its volume loading in the product (5). Sands, however, are used in grouts and concretes used in the solidification of some types of solid wastes.

Cement types differ in the amount of water required to form a paste of "suitable workability" (see next sections) and in the setting times. According to Lokken (3) a cement-water paste is considered "set" when sufficient hydration has taken place to give a mix of "friable" rigidity. To increase cement set times, through addition of set retarders and/or excess of water may be applied.

Set retarders alter the rate of hydration without affecting the nature of hydrated compounds in concrete. Retarders may be organic or inorganic. Organic retarders include derivatives of hydroxylated carboxylic acids and their salts as well as derivatives of lignin such as lignosulphonic acid and its salts. Inorganic retarders include zinc salts, phosphates, silicofluorides, boric acid and borax (3,5).

Excess of water is generally undesirable since physical properties of concrete can be adversely affected (3,7).

3. Cement hydration and resulting products

The hydration of the constituents of a cement is a necessary condition for the setting and subsequent hardening of cement paste. As a consequence of the hydration reaction various products form. A brief description of products resulting from the hydration of portland and high alumina cements is given in Appendix II. In the case of portland type cements the hydration products separate out either as crystals of microscopic size (calcium hydroxide) or apparently amorphous solid state (mainly hydrated calcium silicate, with some calcium aluminates, aluminoferrites), forming a cement gel which is primarily responsible for the mechanical strength of the set cement (7).

According to the results of X-ray and electron-microscope studies, the cement gel is to be regarded as a porous solid, composed up to 50% of an aggregation of calcium silicate hydrate ("tobermorite gel") particles. These particles are sheet-like in form and only 30-40 Angstroms thick, but extend in the two other dimensions to a hundred or more times the thickness, with one dimension going up to one or several microns (7). Their specific surface area is in the vicinity of 175 to 200 m²/g of dry paste (8).

Another product of hydration of di- and tri-calcium silicates is calcium hydroxide which may constitute 25% of cement gel and whose crystals are large enough to be visible in an optical microscope (8).

In a freshly mixed neat cement paste a water-filled space is present which is available for the formation of cement hydration products. The volume of this space is initially determined by the original water to cement ratio of the paste. As hydration proceeds this volume is progressively reduced by the formation of the hydrated cement gel which has a bulk volume larger than the unhydrated cement itself. At any time the residue of the space originally filled by water, which has not been occupied by hydration products, constitutes the capillary system of the paste. The capillary pores of this system can be considered to vary from 80 to 130,000 Angstroms in diameter (8). On the other end the hydrated cement gel is itself porous containing pores, referred as gel pores, that are smaller than capillary pores, their diameters varying in the range of 10 to 80 Angstroms. In an hardened cement paste or concrete there are also still larger pores formed by air entrapped under aggregate particles (8).

As a result of the hydrated cement setting and hardening a monolithic block is

thus obtained having inside its whole body a network of capillary and gel pores. Their total volume is dependent upon the original water to cement ratio (w/c) and the degree of hydration of the cement, and tends to increase if the original w/c ratio is increased.

As described in Appendix II aqueous tritiated wastes can react with hydraulic cements to form hydrated silicate and aluminate compounds. Portland (PC) and high alumina cements (HAC) may fix approximately 25% and 50% water by weight respectively. Because of its higher water loading and shorter curing time HAC would represent the best choice especially for immobilizing tritiated waste-waters. However, as a consequence of HAC hydration, metastable hydrates are produced (see Appendix II) which may convert to lower hydrate-forms on ageing (18).

4. Proportioning of water to cement

To form a workable cement paste and to obtain a waste cement block that might be satisfactory for radwaste storage or disposal a minimum amount of water is required. Usually this amount varies from type to type of cement depending on:

- the relative amount of individual cement constituents and the general stoichiometry of resulting hydrated and hydroxylated compounds
- the nature and relative amount of additives eventually mixed with cement powder with the aim of either increasing the proportion of the immobilized waste-water or achieving any other purpose
- the nature and relative amount of liquid and/or solid wastes to be incorporated into concrete.

It is known that minimum values of the w/c ratios applied for current radwaste cementation purposes are 0.22 and 0.25 for portland and high alumina cements respectively (2). If significantly lower ratios are applied the final product is friable and consequently cannot form a solid monolithic block. It is also known, that some waste solids (e.g. vermiculite, zeolites and ion-exchange resins) will sorb and retain large amounts of water. This water must be supplied with the solid to prevent it from sequestering the needed water from the cement paste and producing as a result a dry, unworkable mix.

Conversely an excess of water will result in a layer of free water on the surface of the solidified product.

Total water to cement weight ratios of 0.33-0.35 are currently applied for radwaste cementing purposes using an ordinary portland cement (OPC) with a maximum value of about 0.5 being attained without cement additives. With vermiculite, diatomaceous earth or similar absorbents the maximum water to cement ratio can be as high as 0.7 to 1.1 (2). Some examples of typical cement-radwaste formulations (2) are shown in Table 1.

For tritiated waste-water immobilization purposes the water to cement weight ratio must be carefully determined mainly with the aim of minimizing the amount of unbound water present in hardened cement. This is because an excess of tritiated water in an unbound state can obviously be more easily leached out or evaporated.

TABLE 1 - Current water to cement weight ratios in typical cement-radwaste formulations (2).

Waste type*	Weight ratio		Weight %		
	<u>dry waste</u> cement	<u>total water</u> cement	dry waste	cement	Total water
- 25 wt% Na ₂ SO ₄ concentrate	0.12	0.37	8	66	26
- 30 wt% NaNO ₃ concentrate	0.15	0.35	10	66	24
- 20-25 wt% water treatment sludge	0.09-0.17	0.27-0.51	7-10	73-60	20-30
- 400 g/l evaporator concentrate (+ 0.13 kg vermiculite/kg cement)	0.33	0.70	16	50	34
- bead resins (preneutralized with NaOH) (50% water)	0.25	0.56	14	55	31
- diatomaceous earth (67% water)	0.42	1.1	17	40	43
- Linde AW-500 zeolite (39% water)	1.21	1.0	38	31	31

* Slurries, sludges and solids.

5. Factors affecting the tritium immobilization by cement

When cement hydration is applied with the aim of immobilizing tritiated aqueous wastes there are two factors which have a decisive influence in determining the tritium retention efficiency of a set cement block; the porosity of the cement block and the fraction of the evaporable (i.e. mobile) water held in it. Both of these factors depend upon the w/c ratio originally applied to the cement mix as well as on the time period during which the hardened cement is "allowed to cure".

5.1 Porosity

As mentioned in section 3 the product resulting from the hydration of cement constituents and hardening of the set cement paste is a monolithic solid block having inside its whole body a network of capillary and gel pores.

Tritiated water evaporation as well as environmental water and water vapor permeation are known to occur through such pores in function of their volume, size and continuity. It is evident that the permeability of the block depends on its porosity. This will therefore play a very important role in influencing the rate of tritium release which may occur by humidity exchange or leaching phenomena.

If tritiated aqueous waste has to be immobilized by cement and being the total pore volume dependent upon the original w/c ratio applied to the cement mix, the proportion of water to cement has to be carefully calculated so that the resulting cement block will attain a sufficiently low porosity along with a still acceptable consistency.

The reduction of the yield of tritium immobilization will obviously be a consequence but it could be balanced, if it is the case, by an adequate degree of tritium enrichment applied to tritiated aqueous waste.

5.2 Evaporable water fraction

The water incorporated in a cement block is currently recognized as being held in three modes (29):

1. As water chemically combined to form all the hydrated compounds found in set and hardened cement.
2. As water adsorbed in the gel mass formed by the hydrated cement compounds.
3. As water held inside the capillary system of the concrete structure.

While in hydrated cement compounds the combined water is firmly fixed by chemical bonds, water adsorbed in the cement gel structure (by means of attractive forces of physical nature) and held inside the capillary system is weakly bound.

It is evident that depending on the nature and strength of its bonds, water held in a cement block will exhibit different degrees of mobility. Relationships between water bonding and water mobility are more deeply discussed in Appendix III.

To make a distinction, even if approximate, between physically adsorbed and chemically combined water, and also to give some indications of their mobilities, Powers and Brownyard (9) have postulated the classification of the water held in set cement into two categories, i.e. the "evaporable" water and the "non-evaporable" one. The "evaporable" fraction includes the water held inside the capillary system and that adsorbed in the gel mass of the concrete, while the "non-evaporable" one includes the water chemically combined in the structure of hydrated cement compounds.

If tritiated water is incorporated in a cement block the "evaporable" water fraction, i.e. the fraction weakly bound, is thus susceptible of being easily removed from the block. This may occur because of diffusion and exchange, if ambient moisture comes in contact with the block, or leaching, if environmental water permeates through the block, with a consequent tritium release to the environment. Obviously an excessive porosity of hardened cement will facilitate this release (see sub-section 5.1).

On the other end the hydration of cement constituents is known to continue in a cement block over long periods of time. Different periods of time are normally applied for "curing" (i.e. hydrating) the hardened cement depending on the type of cement used in the mix. (15). However the hydration of these cements is not complete after these periods as they simply represent the time required for the cement block to obtain a large fraction (~ 90%) of their ultimate strength. Thus, if the stoichiometric amount of water is added to a cement, a fraction of evaporable (hence most mobile) water will be present in the hardened cement paste in amounts which decrease with time. Even if less than the stoichiometric amount of the water needed for complete hydration is added, a fraction of evaporable water will still be present in the hardened cement after the normal curing time, its amount decreasing as the original w/c ratio decreases.

One has therefore to conclude that, if the cement hydration process is chosen as a method for immobilizing tritiated aqueous wastes the cementation procedure has to meet the following requirements:

1. Any excess of tritiated water which might be held in hardened cement as free or unbound water must be avoided in order to prevent an excess of easily removable tritiated water,
2. The porosity of the resulting tritiated cement block has to be kept sufficiently low in order to minimize its incremental effect on the rate of tritium release to the environment,
3. After hardening the cement block has to be adequately "cured" (i.e. left to stand

under controlled conditions) in order to reach in a reasonable time the maximum achievable degree of cement hydration.

Practically the above requirements can be met by performing an accurate determination and control of process parameters such as the w/c ratio and the "curing" time, the latter being dependent on the cement type.

Water to cement ratios near 0.2, allowing to obtain still workable cement mixes, have thus been applied to prepare tritiated cement specimens tested at the various laboratory for experimental studies on tritium leaching (see section 10).

Curing times of 28 days for portland cements (types I, II, IV and V, see Appendix III) and 1 day for portland type III and high alumina cements are currently applied as adequate time periods for attaining a sufficient strength in the hardened cement (15).

However, since even after an adequate curing period a fraction of tritiated evaporable water will still be present in a tritiated cement block, storage or disposal methods must be applied that prevent any possibility of contacts with external moisture and environmental water.

6. Cement additives

In the current practice of radwaste cementation some materials having a remarkable capability of sorbing water have often been added to the cement mortar with the aim of loading in the set cement larger water amounts than achievable by cement alone. The most current materials applied as cement additives in the radwaste cementation practice are briefly described in Appendix IV.

As shown in Table 1 w/c ratios as high as 0.7 to 1.1 may in practice be reached by adding to cement mortar suitable amounts of hydrated vermiculite, diatomaceous earth and zeolite (2).

However, as stressed in subsections 5.1 & 5.2, in applications where tritiated water has to be immobilized any excess of tritiated water loading has to be carefully avoided since it will negatively affect the efficiency of tritium immobilization leading to an increase of tritium release to the environment.

The option of adding water absorbent as vermiculite or diatomaceous earth to the cement mortar was experimentally evaluated on the basis of tritium leaching from the various composites. Leach data from experimental tests performed at BNL (Brookhaven National Lab.) (15) demonstrated that the addition of such absorbers to the cement mortar led to an increase of tritiated water loadings but also to an increase of tritium release rate.

This has been explained by the fact that the major fraction of the aqueous tritium immobilized in the composite was found to be held by the absorbent in an unbound state and thus readily available for both exchange and leaching. There was, of course, also an unbound tritiated water fraction associated with the hydrated cement phase, but this was a minor and progressively decreasing quantity with the continued hydration of cement compounds. Only the polymer impregnation (see subsection 8.2) applied to these composites could minimize the tritium release rate by reducing the porosity of the composite and thus preventing the intrusion of leachants. However, since during impregnation the monomer was absorbed also on the absorbent additive, a polymer depletion occurred at the composite surface resulting in a leach rate exceeding that of a typical PITC composite.

The use of silica gel as a cement additive to allow a larger tritiated water content in a PITC composite was also investigated at BNL (15) always on the basis of

leach rate measurements. A water/adsorber ratio of 0.3 was initially applied, which represents approximately two-thirds of the water necessary to completely saturate the silica gel. This because the initial water adsorbed on silica gel is known to be bound more firmly than the water subsequently added and the complete saturation could have had a negative effect on the leach properties of the composite.

The leach rate data from the preliminary formulations (15) suggested that the use of silica gel as an additive of portland III type cement did not increase tritium leachability. It was however found that the benefit of the higher tritiated water amount immobilized per volume unit of the composite is offset by the low density of the obtained composite and the high cost of silica relative to the other materials (15).

It is worth noting that so far molecular sieves seem having not been considered for testing as additive materials probably due to their relatively high cost and lower loading capacity as compared to the other materials.

Furthermore one has to point out that silica gels and molecular sieves, could be usefully employed as filling materials inside annular voids between secondary and tertiary containers. Acting thus as a barrier the particles of such materials could trap evaporable tritiated water escaping from the block.

Another option which could be investigated in terms of tritium leach rate from the resulting composite could be the addition to the cement mortar of a bitumen emulsion. This is a well known technique applied since many years at CEN-Cadarache (France) for immobilizing alpha-bearing solid wastes (4,10).

7. Mixing techniques

The immobilization of radioactive wastes by cement or concrete entails the blending of the various components of the mix (e.g. liquid waste solutions with dry cement powder, partially or completely dried waste sludges and waste concentrates with premixed water-cement, solid waste with cement grout) which can be achieved within the solidification container or in-line outside the container.

In-drum mixing techniques such as (4):

- rotary mixing in concrete lined drum or containers with the possibility of "losing" rotating blades inside the cement mixture and using them as an additional reinforcement of the solidified block;
- tumbling/rolling of drum provided or not with mixing rollers;
- gravity mixing (i.e. injection of cement grout into concrete lined containers or trenches);

are applied on a batch basis while in-line mixing techniques either on a batch or continuous basis. In the latter case cement, water and waste in various forms and sizes are simultaneously fed into the mixer (e.g. screw extruder system) at predetermined rates and the mixture is directly discharged into the immobilization container (11).

For tritium immobilization purpose available alternatives for the cement mixing and the subsequently casting operations have been evaluated. This with the consideration that the most appropriate technique must be selected, which would allow to minimize the possibility of contaminating the process equipment and operational area. Subsequent cleaning of them will in fact generate secondary tritiated wastes, that even if at a lower activity level, could have volumes larger than the process disposes. On the basis of such considerations the most viable among the above mentioned in-drum techniques undoubtedly appear to be the tumbling/rolling for liquid wastes and the gravity mixing for solid wastes. Rotary mixing appears less attractive because, to

avoid decontamination and cleaning operations, mixing blades should be disposed within the solidification container.

Three blending methods have been applied at BNL (12-20) in the framework of experimental tests on aqueous tritium immobilization based on the PITC process (see Appendix V).

The first method entails the end-over-end tumbling of the cement and water in the containing waste drum (12-16). It is a dynamic in-drum mixing technique producing a homogeneous mixture. No cleaning of equipment is required but a substantial volume of cement paste (~90 litres inside a 30 gallons drum) is to be handled (see Appendix V).

When the preparation of smaller size specimens was needed at BNL (17-19, Table 4), the required specimens size (~16 litres volume) was not compatible with in-drum tumbling technique developed for large scale PITC composites. Therefore specimens were prepared using a conventional dough type mixer which produced a final product of similar density as that obtained by the in-drum tumbling technique (see Appendix V).

The third method, i.e. the injector technique, is based on a static technique more compatible with the glove-box or hot cell operations, entailing the handling of small volumes of highly tritiated aqueous waste (17-20). This method was also successfully applied at MML (Monsanto Mound Lab.) (21-27). By such a technique an injector is used to carefully distribute the aqueous tritiated waste into the centre of the dry cement mass inside an appropriate container. Slow addition of tritiated water is mandatory and cleaning of injector could be avoided if disposable injectors are used. As suggested by the ETHEL design staff this will be needed especially when full-scale packages have to be implemented using such a technique.

For more details on all the above described methods see Appendix V.

8. Additional treatments on a cement block

In order to improve the tritium retention capacity and to reduce tritium release rate a tritiated cement block may be submitted to further treatments such as the application of surfacial coatings or impregnation of the whole body porosity by polymers.

A great variety of coatings (asphalts, beeswax, paraffine, enamel, grease, epoxy-resins and coal-tar) has been tested for this purpose (28-30).

8.1 Coatings

Coatings may be applied to cement or concrete blocks by several techniques such as dipping, painting, or casting around the block. The technique chosen should minimize handling to reduce the possibility of contamination. With proper process design, no effluent should be generated. Coating processes should be done in a closed system to prevent tritium release through evaporation.

To minimize evaporation, coating materials and processes should be selected to avoid applications necessitating high temperature (2).

Some types of coatings are, however, subject to spalling, delamination and crackings which would result in a sudden increase in the rate of tritium release equal to that for an uncoated concrete. Coatings may fail by (1) spalling or delamination of the coating resulting from hydrostatic pressure when pinholes develop in the coating, allowing environmental water to diffuse into the specimen, (2) delamination due to poor bonding or differences in thermal expansion coefficients between the coating and

the concrete, and (3) cracking or fracturing of the concrete composite in which case the coating is no longer effective.

8.2 Polymer impregnation

The polymer impregnation process allows to fill the pores and capillary voids usually present in the body of a cement block with a liquid organic monomer which is then polymerized "in situ" by heating the block itself (12-27). This treatment gives a final composite not subjected to failure by the above mechanisms and hence much more reliable as a barrier to tritium release.

The preparation of a polymer impregnated cement or concrete (PIC) normally involves the following process steps:

- a) Blending of cement (and aggregates if any) with water according to a suitable water to cement ratio.
- b) Setting, hardening and curing under heating of the resulting cement-water paste.
- c) Impregnation of dehydrated concrete with a catalysed organic monomer.
- d) Heating of impregnated material for polymerization.

The resulting composite is essentially impermeable to water and has significantly improved strength, durability and resistance to chemical attack and weathering. Water diffusion inside the concrete block as well as water penetration from outside is thus hindered.

For these reasons the polymer impregnated tritiated concrete (PITC) was regarded as an interesting option for tritium immobilization purposes.

As described in Appendix V at BNL and MML (12-27) the polymer impregnation process was associated to different cement hydration techniques in order to support experimental studies on aqueous tritium immobilization.

Nevertheless it is worth noting that the polymer impregnation of the cement specimen such as described in Appendix V is based on the soak technique that gives a non-homogeneous final product. This because the polymer loading is highest at the outer layer of the cement specimen while the water content in it is higher at the centre and decreases as the outer surface of the specimen is approached.

As pointed out in (31) a homogeneous impregnation of the whole concrete body would be preferable for tritium immobilization purposes especially if in such conditions an effective improvement of tritium retention will be experimentally demonstrated.

9. Leachability of radionuclides incorporated into a cement matrix

Leachability is considered a very important parameter in the safety evaluation of radioactive waste forms. Under normal conditions the waste forms would be contained within sealed containers in absence of any water. Leachability becomes a concern under postulated accident situations where the container is breached and water is allowed to come in direct contact with the waste form. The lower the leachability, the greater the safety by allowing more time to recover and take action on the exposed waste in the event of an accident (3).

Numerous studies have been performed on leachability of some typical fission isotopes immobilized inside neat cement or concrete waste forms. The results indicate that leachability in general varies with type of cement, type and amount of immobilized waste and cumulated leach time.

Other factors that may affect leachability include curing time, irradiation, prolonged exposure to high temperature and leachant renewal frequency (3).

The leach rate is the parameter currently used to measure the leachability of a radionuclide incorporated into a suitable matrix. As mentioned in Appendix VI results of leach rate tests may and have been differently reported due to the different modes of defining this parameter.

In order to normalize the results of various laboratory tests and to make easier their comparison, the application of a standard method (32, see also Appendix VI) has been recommended by IAEA.

Leaching of tritiated waste composites results in a tritium release to the environment due to:

- the dissolution of soluble tritiated components in the leachant;
- the removal of free or uncombined tritiated water by the leachant;
- the chemical exchange between hydrated cement compounds and fresh leaching water.

The hydration of cement is known to give compounds of relatively low solubility. Calcium hydroxide is the most soluble component of hydrated portland cements, while aluminium hydroxide resulting from hydration of high alumina cements is soluble only in alkaline media. Aluminium hydroxide will thus dissolve during leaching due to the presence of calcium hydroxide. The latter is also formed with aluminium hydroxide during the hydration of alumina cements, although to a lesser extent than in the case of portland cements. Since these hydroxides are all tritiated, their dissolution into the leachant will result in a release to the environment of a tritium fraction originally incorporated into hardened cement.

An essential contribution to the tritium release through leaching is given by the removal of free or uncombined (i.e. evaporable) water held in a tritiated cement matrix, the amount of which depends on the original w/c ratio applied to the cement mix and on curing time. As stressed in subsection 5.2 the reduction of the water directly removable by an eventual leaching can be attained by reducing the original w/c ratio and employing adequate curing times.

A further contribution to tritium release could occur as a result of chemical exchange between tritiated water combined in hydrated cement compounds, i.e. the so called non-evaporable water and leaching water. It seems however that tests concerning such exchange have not been made and consequently the extent to which such an exchange takes place is not known (31).

10. Results of tritium leach tests

Many extensive experimental studies have been carried out at BNL (12-20), MML (21-27), LASL (Los Alamos Scientific Lab.) (28) and BARC (Bhabha Atomic Research Centre, India) (29,30) in order to investigate the tritium leachability from tritiated cement matrices. A comparative evaluation of their results is unfortunately rather difficult because of lack of full experimental details on test specimens, representative of the waste composite (composition, preparation, dimensions, surface conditions and porosity, volume to surface ratio) and uncomplete reporting of leach test procedures (sample surface to leachate volume ratio, renewal frequency of leachant). Most laboratory leach tests have been performed using small volume specimens (within 100-300 ml), which apparently would allow to compare their results even if usually expressed in different measurement units. Nevertheless the differences in the specimen preparation "history" and leaching conditions do not legitimate, in principle, the direct comparison of these results.

Anyhow some of these results are presented in Tables 2 to 6. For harmonization purposes all the reported leach test results have been expressed as cumulative per cent

tritium releases referred to the total tritium amount initially present in the package, after decay correction. This was necessary because tritium leach results obtained at the various laboratories were differently expressed, namely as:

- daily (12-14) and cumulative (18-20) fraction releases at BNL;
- total and fractional permeations (or releases) at MML (21-27, 34-44);
- cumulative per cent releases at LASL and BARC (28,29).

Since the cumulative fractional release is calculated by dividing the total tritium radioactivity measured in the leach water by the total tritium radioactivity initially in the package (after correction for decay), the cumulative per cent release can be obtained by multiplying by one hundred the fractional release value.

10.1 Uncoated specimens

Cumulative per cent tritium release data measured at LASL (28) for uncoated portland type I cement specimens indicate (see Figs. 1 & 2) an initial high release of tritium which decreases rather uniformly with increasing leach time. As shown by the curves reported in Figs. 1 & 2 after the first 10 weeks of leaching cumulative releases of 32% and 39% have been measured for type T6, T16 and H1 specimens respectively (see Table 2). After 69 and 57 weeks their cumulative releases increase to 58% and 65% respectively.

Details on the specimen preparation and leach procedure are reported in Table 2. No data are however available on the volume to surface ratio which can make independent the leach results from the sample geometry and size.

At BNL (12-14) a considerably high tritium release was obtained by leach tests on uncoated portland type III (rapid hardening) cement specimens. After the first 10 days of leaching (see Table 4) a cumulative tritium release of 65.6% was measured, i.e. a value much higher than that measured at LASL. A control of other leach data reported in Table 2 of reference (14) let us anyhow conclude that someone of them would be erroneous.

As reported in Refs. (31, 33) at MML cumulative tritium releases of 2.5% after 20 weeks and 8% after 28 weeks were measured by leach tests again on portland type III cement. These values appear rather low if compared with LASL and BNL results reported in Tabs. 2 & 4. Unfortunately no information on these tests are available so that no experimental details can be given for them.

10.2 Coated specimens

Various coatings of asphalt, beeswax, paraffin and epoxy paints applied to tritiated cement specimens by dipping and painting techniques have been leach-tested at LASL (28) and BARC (29,30). These coatings act as a physical barrier capable of reducing the tritium release from the specimen. As shown in Table 2 and 3 their efficiency is evaluated in terms of reduction of tritium release rate with respect to the uncoated specimens.

After 5 weeks of leaching (see Table 2) the reduction factor remains considerably high for beeswax and paraffin ($f \sim 66$) and still acceptable for asphalt ($f = 5-9$). However as the leach time increased (e.g. after 57 weeks) both the factors decrease remaining still significant only for beeswax and paraffin ($f \sim 16$).

When thicker asphalt layers were applied to specimens by successive dippings or casting techniques still lower cumulative per cent tritium releases were measured.

Commercially available coating paints tested at BARC gave fairly comparable results. As shown in Table 3 Shalimastic HD, a cold-applied coal-tar paint appeared to be the most promising coating material.

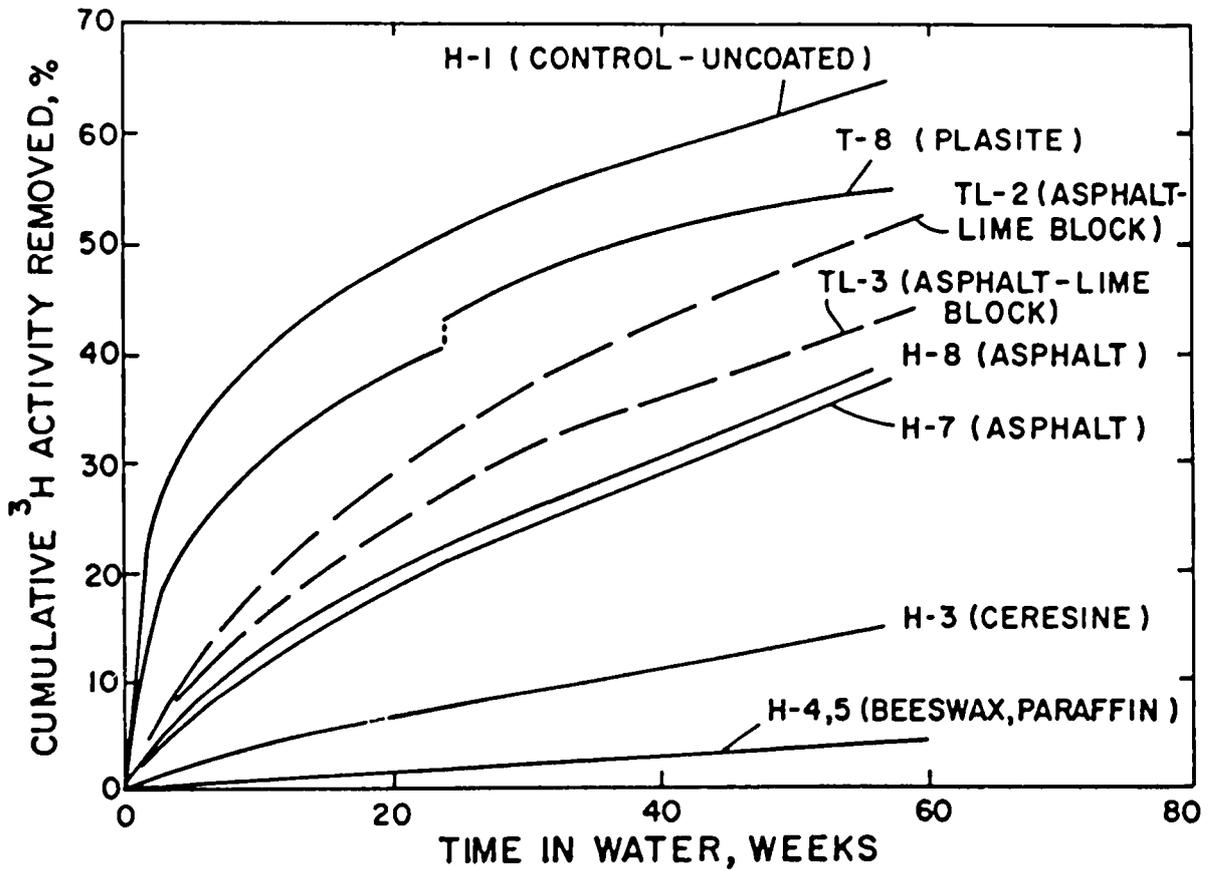


FIG. 1 - Tritium Leach Test at LASL. Comparative Release of Tritium from Coated and Uncoated Tritiated Cement Paste Blocks Immersed in Water Including Data for Two Asphalt-tritiated Lime Blocks (28).

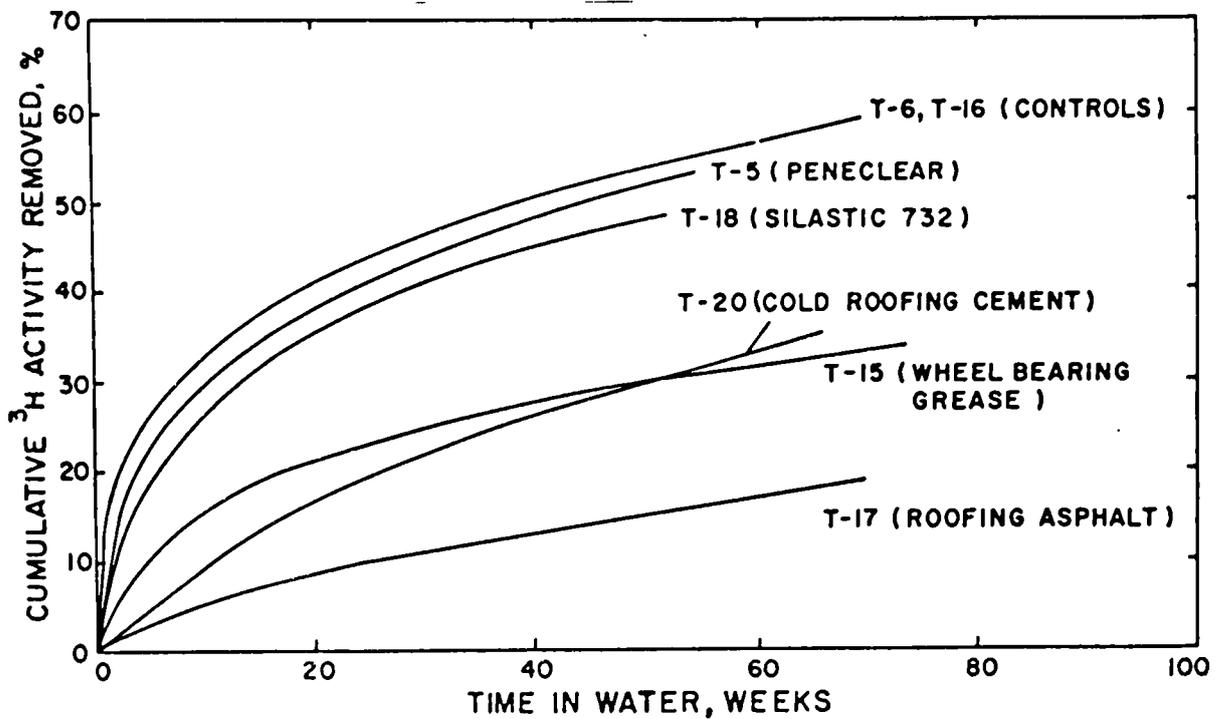


FIG. 2 - Tritium Leach Tests at LASL. Comparative Release of Tritium from Coated and Uncoated Tritiated Cement Paste Blocks Immersed in Water (28).

TABLE 2 - Results of Leach tests performed at LASL on coated tritiated concrete specimens.

SPECIMEN IDENTIFICATION						RESULTS				Ref.	
W/C ratio	Volume (litres)	Tritium MBq	Tritium mCi	Series type	Coating	Leach Time (wk)	Cumulative Per Cent Release	Leach Rate Reduction Factor			
0.3 ⁽¹⁾	~ 0.1	~ 12	~0.32	T6,T16	Uncoated	5	~26.25	1	-	-	28
				H1	Uncoated	5	~32.6	1	-	-	
		~ 12	0.32	T6,T16	Uncoated	10	~32.0	-	-	-	
				H1	Uncoated	10	~39.0	-	-	-	
		~ 12	0.32	T6,T16	Uncoated	69	~58.0	-	-	1	
				H1	Uncoated	57	~65.0	-	1	1	
		~ 12	0.32	T17	Roofing Asphalt	5	~ 3.0	-9 ⁽⁵⁾	-	-	
				T17	Roofing Asphalt	69	~19.0	-	-	-3 ⁽⁵⁾	
		~111	3.0	H7	Asphalt ⁽²⁾	5	6.3	-5 ⁽⁶⁾	-	-	
				H7	Asphalt ⁽²⁾	57	36.0	-	-1.8 ⁽⁶⁾	-	
		~111	3.0	H4-H5	Beewax, Paraffin	5	0.49	-66 ⁽⁶⁾	-	-	
				H4-H5	Beewax, Paraffin	57	~4.0	-	16 ⁽⁶⁾	-	
n.a.	n.a.	n.a.	n.a.	n.a.	Asphalt ⁽³⁾	5	0.45	-	-	-	
n.a.	n.a.	n.a.	n.a.	n.a.	Asphalt ⁽⁴⁾	4	8x10 ⁻³	-	-	-	

- (1) Portland I cement paste prepared by means of a laboratory mixer. Curing times variable from 2 days up to a year. Leachant (0.5-1 litres) changed at 1 and 4 weeks intervals.
- (2) Coating obtained by extended dipping in hot asphalt.
- (3) Thicker coatings obtained by successive short dipping steps in hot asphalt at 150°C.
- (4) Thicker coatings (0.75-1 inches thickness) obtained by a casting procedure (13).
- (5) Compare with type T uncoated samples.
- (6) Compare with type H uncoated samples; n.a. = not available

TABLE 3 - Results of tritium leach tests performed at BARC (India) on coated concrete specimens.

SPECIMEN IDENTIFICATION					RESULTS						
W/C ratio	Volume (litres)	Tritium MBq	curies (mg)	V/S (cm)	Coating	Leach Time (wk)	Cumulative Per Cent Release	Leach Rate Reduction Factor			Ref.
0.4 ⁽¹⁾	n.a.	9.5	2.5x10 ⁻⁴ (2.5x10 ⁻⁵)	n.a.	Uncoated	4.4	14.0	1	-	-	29
						9.6	18.0	-	1	-	
						-35	20.0	-	-	1	
					Epoxy ⁽²⁾	4.4	3.0	4.7	-	-	
						9.6	6.0	-	3.0	-	
						-35	16.0	-	-	1.25	
					Shalimastic HD ⁽³⁾	4.4	0.5	28	-	-	
						9.6	0.8	-	22	-	
						-35	2.0	-	-	10	
					Anticor ⁽⁴⁾	4.4	0.7	20	-	-	
						9.6	1.0	-	18	-	
						-35	4.0	-	-	5	

- (1) 100 g cement + 40 ml tritiated water + 20 g vermiculite; curing time of 28 days. After coating leaching was started at the 45th day from casting.
- (2) A two-pack-air drying paint with polyamide as hardener.
- (3) A cold-applied coal-tar paint CA50 (USA).
- (4) CNSL epoxy coal-tar pitch paint (Indian Patent); n.a. = not available

The coating procedure for Shalimastic HD (29) was the following. Three coats of primer were applied on the concrete block. The primer, Tarstill special, is a coal-tar pitch-based anticorrosive paint. Over this three successive coat of Shalimastic HD were applied, with a minimum 24 h. drying time between each coat, in dry air atmosphere.

After 4.4 weeks of leach testing a reduction factor of 28 was attained with respect to the uncoated specimen. With the increasing of the leach time the leaching reduction factor decreased as expected, remaining still significant after 35 weeks ($f = 10$)

Furthermore it was pointed out (29) that a visual observation of Shalimastic HD-coated blocks left in distilled water for two years showed that the coating retained its original form without any indication of cracking.

10.3 Polymer impregnated specimens

Extensive leach test on polymer impregnated tritiated concrete (PITC) specimens have been performed in USA at SRP (Savannah River Plant), BNL and MML. Results have been published in several progress reports (12-27, 33-38) and reviewed by McKay in the frame of a CEC contract (31). Furthermore in October 1980 in the frame of the IAEA Seminar held at Juelich (FRG) on the "Handling of Tritiated Wastes" a further critical review of these results was presented by Williamson (33).

All these results are reviewed and discussed in the following subsections.

10.3.1 Unpackaged PITC specimens

As reported in Refs. (18) to (20) four PITC samples prepared at BNL were sent to SRP and buried without containers in individual lysimeters (see Fig. 3) at four different locations.

Details on the preparation of samples are given in Appendix V.

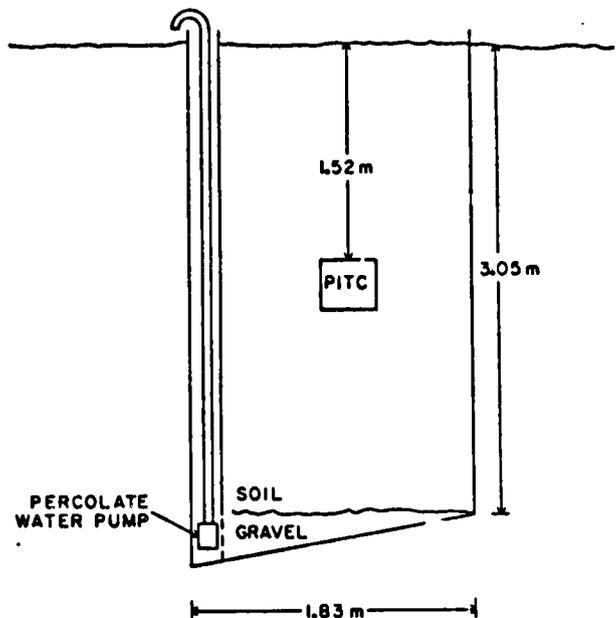


FIG. 3 - SRP test lysimeter for measurement of the rate of tritium release from polymer impregnated tritiated concrete (PITC) (19).

Percolate water could not be removed from the lysimeter before the fourteenth week from the sample burial. This because before that time, all the rainfall was still retained by the lysimeter soil. A control lysimeter was used to determine the fraction of tritium to be subtracted as a background to the tritium content measured in the percolate water of each lysimeter. Sampling was performed weekly.

As shown in Figs. 4 & 5 taken from Refs. (19,20) experimental tritium release data, averaged on the four lysimeter results, were plotted versus cumulative time since burial. Individual lysimeter results were normalized in terms of (cumulative fraction release) $\times (V/S)$, where V is the volume and S the geometric surface area of the specimen. This is in order to make the tritium release independent of the surface area effects and to allow correlations of data measured for specimens of different size and geometry.

During the initial period of percolate water collection tritium leach rate progressively increased until, after 21 weeks (140 d), it reached (see Fig. 4) an approximately linear average value (slope) of $5.26 \times 10^{-6} \text{ cm d}^{-1}$. After 36 weeks (252 d) the rate of tritium leaching still increased reaching a linear average value of $1.43 \times 10^{-4} \text{ cm d}^{-1}$ (Fig. 5). Based on experimental diagrams of Figs. 4 & 5 cumulative tritium leach data expressed as per cent values have been calculated and reported in Table 4. After a cumulative burial time of 31 weeks (217 d) the cumulative per cent release of tritium is of 0.01%, while after 62 weeks (434 d) the corresponding value is significantly higher (0.61%).

It comes out from all these figures that the leach rate of tritium, which was at beginning very low, unexpectedly increased with burial time. This behaviour was explained (19,20) as due to a partial channeling of water down the sides of the lysimeter instead of being homogeneously absorbed in the soil and consequently brought in rapid contact with the specimens.

At BNL a PITC specimen of the same dimension and formulation (19,20) as those used in lysimeter testing at SRP was submitted to a static leaching test by distilled water in order to compare results. The difference from the lysimeter specimens was due to the higher specimen density prior to impregnation (1.53 g/cm^3) which allowed a lower polymer loading (12.9%) leading to a higher composite density (1.725 g/cm^3) (see Appendix V).

Leach testing was performed by immersing the specimen (without container) in 40 litres of distilled water. The leachant was not changed and one millilitre samples were taken for analyses by liquid scintillation counting.

All the results measured during 55 weeks (385 d) of leaching are shown in Fig. 6 taken from Ref. (20). They are expressed as (cumulative fractional tritium release) $\times (V/S)$ versus the cumulative leach time. The tritium leach rate was approximately linear with a slope of $8.7 \times 10^{-5} \text{ cm d}^{-1}$ (20).

For comparison purposes some data calculated after cumulative leach times of about 12, 28, 43 & 55 weeks and expressed as cumulative per cent values have been reported in Table 4. From these data it appears that after about 30 weeks more severe leaching occurred in static than in burial leach tests. This was, however, only apparent, due to the above mentioned channeling effect of the percolate water. The cumulative per cent release after 55 weeks (0.73%) was in fact comparable with the value obtained from burial test after 62 weeks (0.61%). This because the latter value was averaged on a longer time period during which probably the water channeling disappeared and its effect on tritium release was compensated.

10.3.2 Packaged PITC specimens

At MML (21-27) small-scale samples were fabricated in the frame of a leaching test programme in order to measure and compare the release of tritium from packaged tritiated concrete with and without polystyrene impregnation. All the samples were

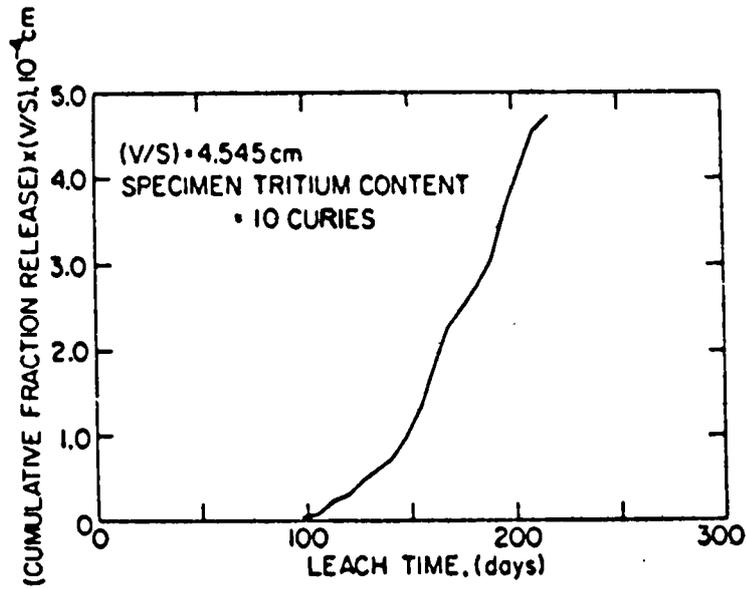


FIG. 4 - SRP lysimeter tests; (cumulative fraction tritium release) x (V/S) versus time; lysimeter specimen average (19).

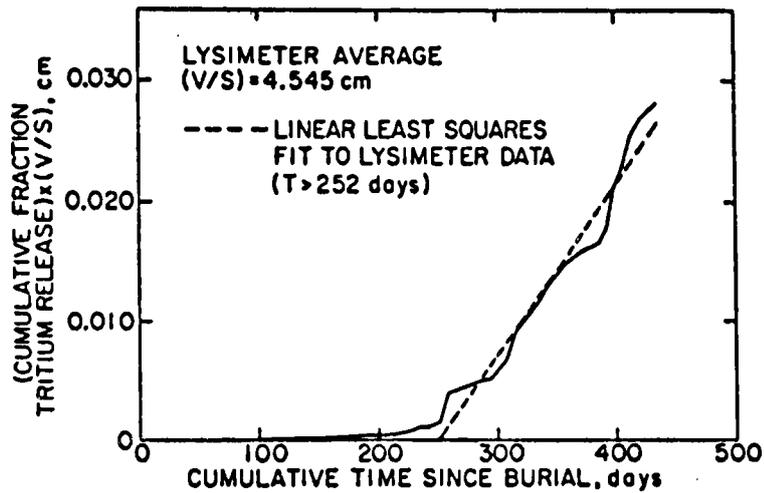


FIG. 5 - SRP lysimeter tests; (cumulative fraction tritium release) x (V/S) versus time since burial; lysimeter specimen average (20).

TABLE 4 - Results of tritium leach performed at BNL and SRP on PITC specimens.

SPECIMEN IDENTIFICATION					RESULTS				
W/C ratio	Volume (litres)	Tritium GBq	curies (mg)	V/S (cm)	Type of Containment	Leach Time (wk)	Cumulative Per Cent Release	Leach Rate Reduction Factor	Ref.
0.18 ⁽¹⁾	n.a.	3.7x10 ⁻³	10 ⁻⁴	n.a.	TC, no PI,	1.5	65.6	1	12-14
	n.a.	3.7x10 ⁻³	(10 ⁻⁵)	n.a.	PITC/16	1.5	0.1	656	
	n.a.	3.7x10 ⁻³		n.a.	PITC/16	2.0	1.21	50	
	n.a.	3.7x10 ⁻³		n.a.	PITC/16	4.5	2.66	25	
0.22 ⁽²⁾	~16	370	10	4.54	PITC/16	31	0.010 ⁽⁴⁾	-	
			(1)			62	0.61 ⁽⁴⁾	-	
0.22 ⁽³⁾	~13	370	10	4.54	PITC/13	-12	0.16	-	19-20
			(1)			-28	0.39	-	
						-43	0.56	-	
						-55	0.73	-	

- (1) Samples prepared and tested at BNL. No details available on the mixing procedure for preparing portland type III cement paste. Leachant was totally changed every day.
- (2) Lysimeter samples tested at SRP without container. Portland type III cement paste prepared at BNL by a conventional dough type mixer. Curing time of 5 days at 40°C.
- (3) Duplicate lysimeter samples prepared at BNL like samples at point (2) and leach tested at BNL without container. Leachant (40 litres) not changed and sampled (1 ml fractions) periodically for analysis.
- (4) Releases values averaged on four specimens.

n.a. = not available; TC = Tritiated Concrete; PI = Polymer Impregnated; PITC/13 or 16 = Polymer Impregnated Tritiated Concrete/13% or 16% catalyst.

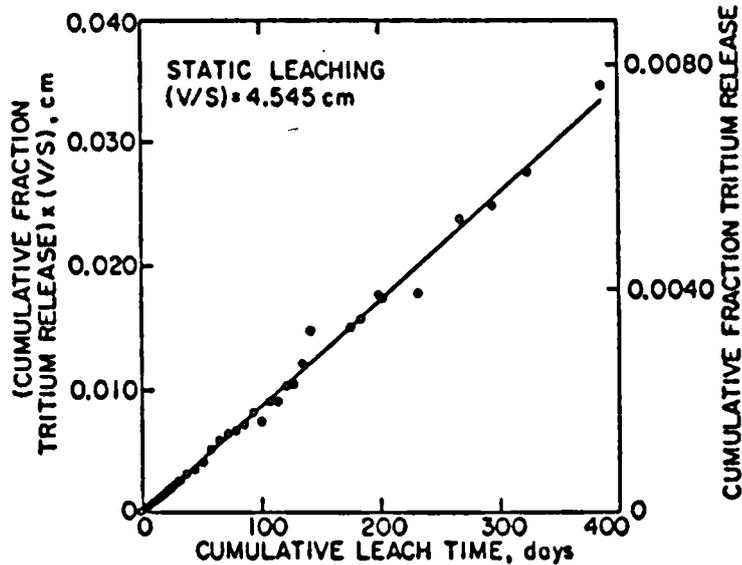


FIG. 6 - (Cumulative fraction tritium release) \times (V/S) versus leach time for static leaching of the lysimeter test duplicate specimen (20).

packaged in 500 ml linear-high-density-polyethylene bottles (27). Their preparation was done according to the procedure described in Appendix V.

The samples were then placed in a test apparatus (Fig. 7) containing 1.6 litres of distilled water for leach testing. No change of leachant was made and 10, 1 and 0.1 microlitres fractions were sampled periodically on a weekly basis (27).

The permeation data for the most significant nine test samples prepared using a portland type III cement (21-27) are given in Table 5. For comparison purposes they are expressed as cumulative per cent tritium releases. Note that PITC samples 59 and 72 (respectively 5% and 0.5% AIBN catalyst, see Appendix V) were put into the test programme with the polyethylene bottle removed out only 25 and 21 weeks after their preparation. This means that their effective leach time was 25 and 21 weeks lower than the permeation time indicated for their respective first & fourth sample groups.

As shown in Table 5 the cumulative per cent release of tritium into the water bath from samples 59 and 72 after the bottle removal was respectively 100 and 50 times greater than that diffused through the polyethylene bottle of samples 57 & 58 (first group) and 69 to 71 (fourth group). The greatly increased tritium releases from these samples were essentially attributed to the removal the polyethylene bottle. Without the polyethylene a thin layer of polystyrene was in fact the only barrier between the cement matrix and the water (26).

The effect of the catalyst amount (the higher the catalyst concentration, the higher the internal bulk temperature) would in principle be demonstrated either by comparing release data from the first and fourth sample groups or those from samples

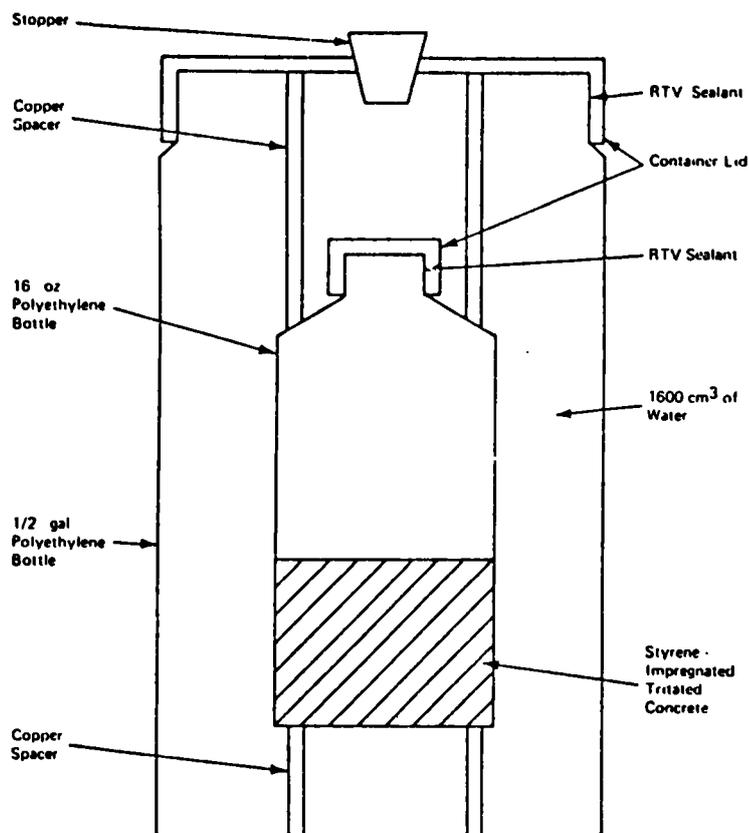


FIG. 7 - Experimental setup for PITC permeation test (26).

59 and 72. But this effect was numerically evident only for sample 59 and 72, no substantial differences having been found between data from the first and fourth packaged PITC sample groups. This was attributed to the "masking" effect of the polyethylene bottle. As shown in Table 5 the release from sample 72, using 0.5% catalyst (as recommended by the BNL) was approximately one-half the release from sample 59 using 5% catalyst (34). This difference was attributed to a lower rate of polymerization reached with 0.5% catalyst, yielding consequently a lower internal bulk temperature (24,26). The bubbles generated by the higher polymerization temperature in the 5% catalyst polystyrene were indicated (34) as being the most likely responsible for the larger tritium release of sample 59.

No significant differences were found (see Table 5) between release data from the fifth concrete sample group (which did not have styrene added) and those from first and fourth PITC sample groups. This was attributed to the barrier effect of the polyethylene bottle which was much thicker than the layer of polystyrene. Such a barrier was in fact so efficient in reducing the tritium leach rate that, when utilized, it had the capability of masking any other additional concrete conditioning.

As shown in Table 5 after approximately a year of leach time the polyethylene barrier reduced the cumulative per cent release of fourth and fifth sample groups to average values which are comparable with the target value of 0.36% per year indicated in Ref. (31) as the maximum leakage rate "likely to be acceptable over any time in a tritium immobilization scheme".

TABLE 5 - Results of tritium permeation tests performed at MML on PITC specimens.

SPECIMEN IDENTIFICATION							RESULTS						
W/C ratio	Volume (litres)	Tritium TBq	Ci (mg)	V/S (cm)	Group n°	Sample n°	Type of containment	Leach Time (wk)	Cumulative Per Cent Release	Leach Rate Reduction Factor		Ref.	
n.a.	n.a.	n.a.	n.a.	n.a.	-	-	TC no PI no PB	20 28	2.52 7.84	- 1	- -	- -	31-33
0.25 ⁽¹⁾	-0.2	14.3	386 (38.6)	1.05	1	57-58	PITC/5 + PB	6 33 65	0.10 0.50 0.66	- - -	- - -100	- - -	
					1	59	PITC/5 no PB	13 41 68	39.1 52.0 64.0	- - -	- - 1	- - 1	
					4	69-71	PITC/0.5 + PB	6 33 47 64	0.11 0.35 0.42 0.54	- - - -	- - - -60	- - -	21-27
					4	72	PITC/0.5 no PB	13 42 70 100	12.1 24.7 33.0 43.0	- - - -	- - 1	- - 2	
					5	73-74	TC + PB no PI	6 25 39 54	0.10 0.26 0.32 0.43	- -30 -	- - -	- -	

22

(1) Portland type III cement paste preparation based on the injector technique. Polymer impregnation based on the soak technique. No change of leachant and periodical sampling of 10, 1 and 0.1 microliters fractions.

(2) Effective leach times calculated by subtracting 25 and 21 weeks to the permeation time of 1st and 4th sample groups.
 n.a. = not available; TC = Tritiated concrete; PB = Polyethylene Bottle Package; PI = Polymer Impregnation; PITC/0.5 or 5 = Polymer Impregnated Tritiated Concrete, with 0.5% or 5% catalyst.

The barrier effect of polyethylene did appear more evident when also sample 70 (0.5% catalyst) and sample 74 (no impregnation) were removed from their bottles and then submerged in the same water bath already used for the previous permeation tests on bottled PITC samples (34-36). As shown in Table 6, with the polyethylene bottle removed out, the tritium release from the "nude" samples 70 and 74 to leach water began to increase markedly. After only 16 additional weeks since the bottle removal, the cumulative per cent release from sample 70 increased from 0.54% to 20% ($f \sim 40$) and that from sample 74 from 0.43% to 60% ($f \sim 140$).

Sample 70 (0.5% catalyst) showed therefore a better leach resistance than sample 74 (no polystyrene impregnation), but also than sample 59 (5% catalyst), its cumulative release (see Table 6) being at any leach time lower than that of both samples 74 and 59. The comparison with sample 74 demonstrated the beneficial effect of the polystyrene impregnation in terms of tritium leach reduction and also that this effect can be completely masked if a still more efficient barrier such as the polyethylene container is employed.

Furthermore the comparison with sample 59 (5% catalyst) demonstrated once again how the amount of catalyst (determining the internal bulk temperature due to polymerization) may negatively affect the integrity of the polystyrene barrier and consequently the tritium leach-resistance of the composite.

One has to conclude that undoubtedly the sealed polyethylene container demonstrated to be much more efficient as a tritium containment barrier than the polystyrene impregnation. The latter can properly be employed as an additional barrier in the event that all other barriers of the burial package might accidentally leak. In such event it is just the "microencapsulation" of tritiated concrete achieved by its polystyrene impregnation that will allow a control of tritium leaching by incoming ground water (34).

Finally one has to remark the discrepancy in terms of tritium release between PITC "nude" samples 59, 70 & 72 and duplicate lysimeter samples tested at BNL (see Table 4). The BNL leach test results were in fact one to two orders of magnitude lower than the MML results. Unfortunately neither laboratory did made any comments to explain this discrepancy.

It is worth noting however that significant differences can be found in the procedure applied for concrete specimen preparation, in their size and in the amount of tritium immobilized in the PITC specimens tested at BNL and MML (see Tables 4 and 5). Although tritium activity in BNL specimens was about a factor 3×10^5 lower than that of MML specimens, tritium leaching rate appears to be independent from the variation of tritium concentration in concrete specimens. Hawthorne in Ref. (48) has arrived at this conclusion after having compared some tritium in leaching results obtained by different laboratories.

To explain the above discrepancy of BNL and MML results the same author has suggested an interference with the cement hydration process by the polymer, the extent of which could depend on the PITC preparation procedure (49).

Full-scale "cold", PIC burial packages have also been prepared (26, 27, 34-38) at MML. For this purpose a DOT specification 17H 30-gal (~ 115 litres) steel drum and a 27-gal (~ 102 litres) high density polyethylene liner were used (see Appendix V). As for small scale samples the method of polymer impregnation was as similar as much as possible to the process used at BNL (12-20).

TABLE 6 - Some results of tritium permeation tests performed at MML on PITC specimens.

SPECIMEN IDENTIFICATION							RESULTS					
W/C ratio	Volume (litres)	Tritium TBq	Ci (mg)	V/S (cm)	Group n°	Sample n°	Type of containment	Leach Time (wk)	Cumulative Per Cent Release	Leach Rate Reduction Factor	Ref.	
0.25	0.2	14.3	386 (38.6)	1.05	1	59	PITC/5	68	64.0	-	1	34-36
							no PB	99	74.0	-	-	
								122	77.0	-	-	
					4	70	PITC/0.5 + PB	64	0.54	-40	-	27
						70	PITC/0.5 no PB	64+16= 80 64+46=110 64+69=133	20.0 46.0 57.0	1 - -	3 - -	34-36
						72	PITC/0.5 no PB	70 101 124	33.0 43.0 53.0	- - -	- - -	34-36
					5	74	TC, no PI + PB	54	0.43	-140	-	27
						74	TC, no PI no PB	54+16= 70 54+46=100 54+69=123	60.0 81.0 74.0	1 - -	1 - -	34-36

Major problems to overcome in scaling-up the preparation procedure were due to:

- the density of the 27-gal polyethylene liners which had to be sufficiently high to ensure an adequate resistance to the polymerization temperature and to the chemical attack of the styrene monomer;
- the thermal behaviour of the whole package system (tritiated concrete + monomer inside 27-gal polyethylene liner and 30-gal drum) which was considerably different from that of the small-scale 200 ml concrete samples. Since the polymerization reaction normally generate rather high temperatures there was indeed much more polymerization energy to dissipate in a low thermal conductivity system such as a 30-gal concrete drum.

Attempts were made at MML (27) in order to optimize the full-scale application of the PITC process. Three limitations of the process conditions were found to be essential to this end, namely:

1. The contact time between the styrene monomer and the polyethylene liner has to be kept to a minimum. The longer the contact time, the more extended the damage of the liner.
2. The temperature to which the polyethylene liner is exposed has not to exceed its melting point. The higher density polyethylene had therefore the advantage of a higher melting point of 200°C as compared to the 120°C of the low density polyethylene.
3. The maximum (center) temperature of the waste package has not to exceed 100°C otherwise water held in concrete vaporizes causing bubbles in the polystyrene bulk.

As described in Appendix V the above limitations were met by suitable variations of the experimental parameters and an adequate monitoring and control of the process conditions.

10.4 Modified cement matrix inside burial packages

In order to investigate the leach-resistance of their actual burial packages a test programme was initiated at MML in May 1975 and is still continuing (39-47). As described in Ref. (45) each test consisted of the individual immersion of representative actual burial packages in a known volume of leach water. A maximum of 27 litres of high specific activity tritiated water (37 to 74 TBq per litre) was added without agitation to a portland cement/plaster dry mix previously prepared using a maximum weight ratio of one part water to three parts dry cement-plaster mix.

The actual package of the tritiated water sorbed on the portland cement - gypsum plaster mix consisted of a inner polyethylene liner (27-gal) containing the solidified tritiated water sealed inside a 30-gal steel drum, which was in turn sealed inside a 55-gal (~ 210 litres) steel drum.

The internal and external surfaces of the 30-gal drum were coated with an asphalt layer while vermiculite and asphalt were used to fill the spaces between the drums. Further details on the package assembling are given in Appendix VII.

Permeation tests were performed inside a 83-gal (~ 318 litres) (see Fig. 8). The leach water was periodically analysed for tritium using liquid scintillation counting.

Figs. 9 and 10 taken from Ref. (44) show the results obtained after about 400 weeks (~ 8 years) of permeation time. Tritium permeation was expressed as total (in millicuries) and fractional tritium permeation (ratio of total curies permeation to total curies in the package), both as a function of time in test. Total actual radioactivity in each package were corrected for decay time since the burial package was assembled.

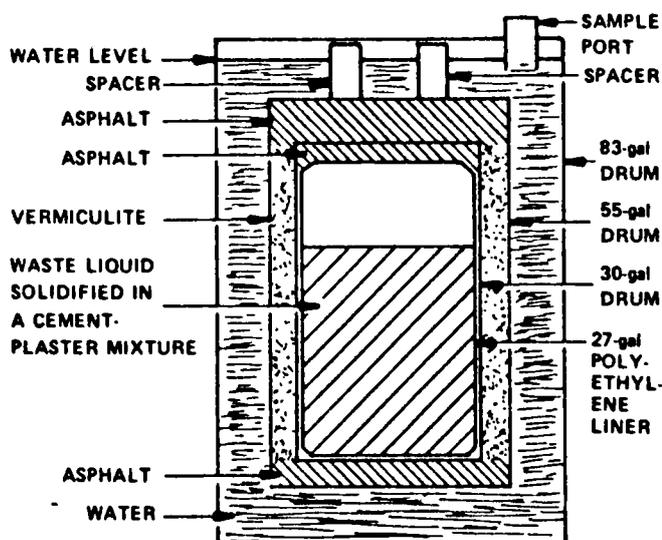


FIG. 8 - Permeation test on tritiated waste package (45).

Figs. 9 and 10 illustrates an almost constant permeation rate (slope) for the waste drum n° 205. As to the waste drum n° 318 the rate of tritium permeation appear nearly constant up to the 140th week of permeation time, then increases abruptly becoming again nearly constant after the 200th week. No explanation was found for this behaviour.

The data measured during these permeation tests indicate that even in case of the waste drum n° 318 the percentage of tritium that would be released per year to the ground water from the multi-walled container package would largely not exceed the maximum target value (0.36% per year) proposed in Ref. (31) for HTO release from packages.

In order to make comparison of permeation rates between burial packages containing PITS samples and tritiated samples of cement-plaster mix, two packages were prepared at MML in October 1979 and inserted into the permeation test programme (41-44, 46). The comparison of the permeation rates between these two drums should have to indicate any eventual additional benefits in terms of tritium release resulting from the application of the polymer impregnation process.

Last information available from MML (46) indicates that after being kept under permeation test conditions for four years cumulative tritium releases from these drums were found to be very low. Tritium activity in both the leach solutions remained still near the background levels, with practically no significant difference between the two drums. These results were unexpected essentially because the burial package of the tritiated cement-plaster was prepared using a procedure identical to that for the above waste drum n° 318. No comments were made to explain these results.

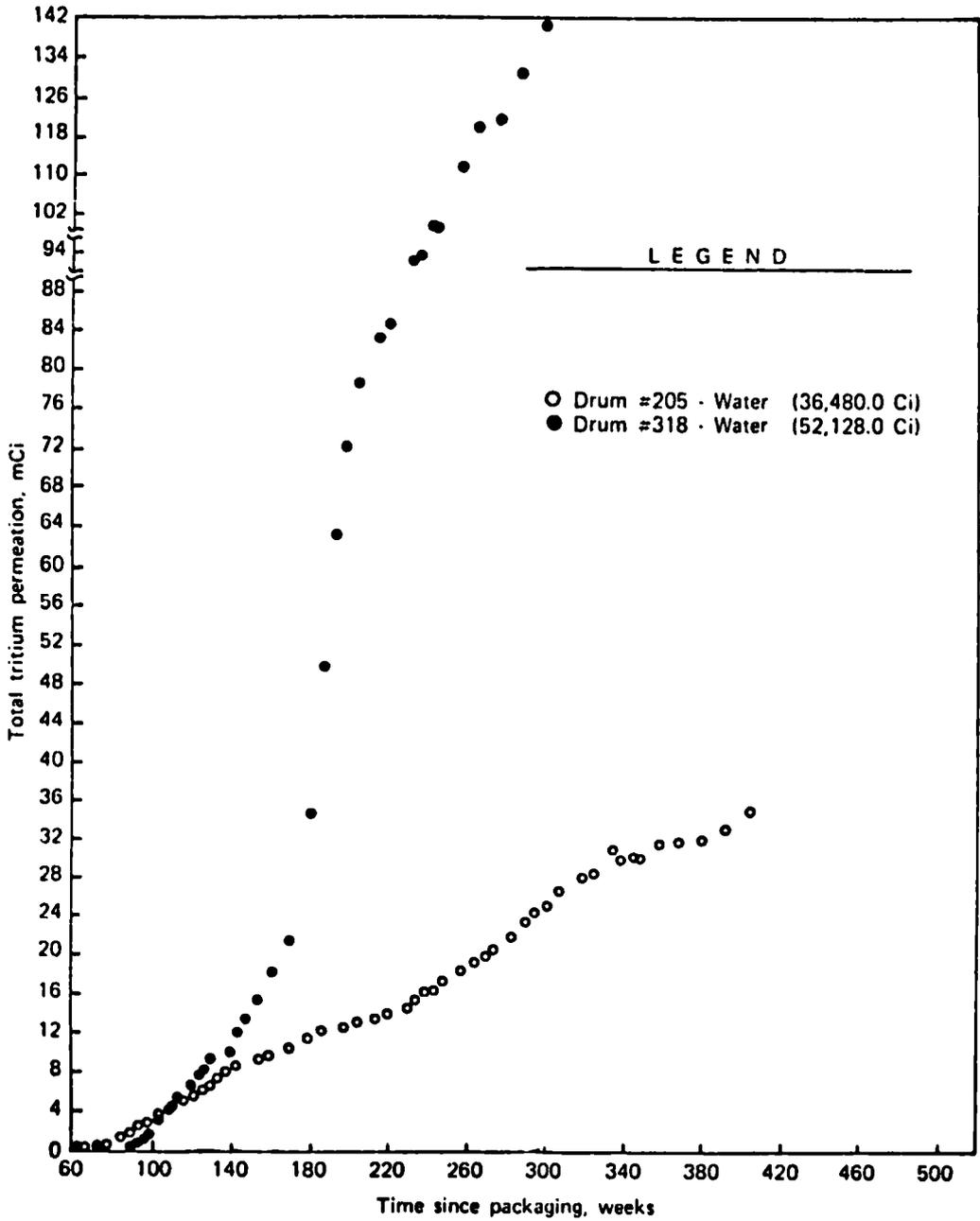


FIG. 9 - Burial package permeation tests at MML. Total tritium permeation as a function of time (44).

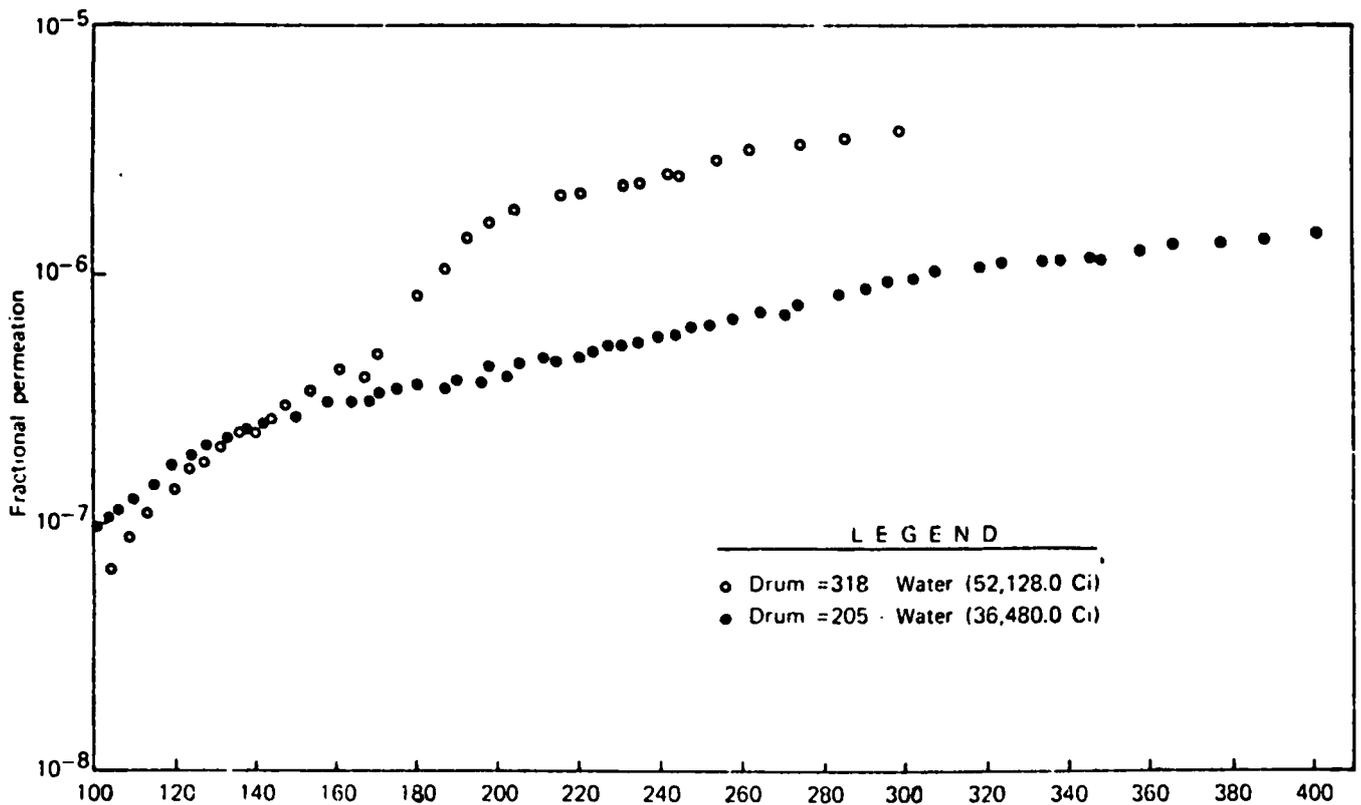


FIG. 10 - Burial package permeation tests at MML. Fractional tritium permeation for two drums of tritiated water under test (44).

11. Conclusions

Although there is some difficulty in making a close comparative evaluation of the experimental results obtained at the various laboratories, nevertheless it can be concluded that:

- The cement hydration process do not have the capability of immobilizing tritium up to the desired extent so that for a tritiated cement matrix alone a satisfactory leach-resistance property cannot be achieved. This because a considerable fraction of tritiated water held in the matrix was found to be highly mobile, hence easily evaporable and leachable. High alumina cements are capable of binding twice as much water as portland type cements. In terms of tritium immobilization this advantage is however rather limited because of the metastable hydrated compounds produced by HAC hydration which may convert to lower hydrate-forms on ageing.
- Cement additives such as water sorbents (i.e. vermiculite, diatomaceous earths) were found to allow increased tritiated water loadings but unfortunately also higher tritium release rates. However whether and to what extent the use of molecular sieves as a cement additive may improve the leach resistance of a tritiated cement block should be experimentally verified.

- To minimize the degree of tritium leachability from a tritiated cement matrix the use of additional physical barrier systems is therefore mandatory.
- Some types of coatings are capable of improving the leach-resistance property of a tritiated cement matrix but their efficiency is highly dependent upon their integrity which may become worse as time goes on, due to spalling, delamination and cracking phenomena.
- The polystyrene impregnation (PITC process) is a technique which has the capability of reducing the tritium leach rate from a tritiated cement matrix, hence the contamination hazard at the burial sites. Its most appropriate application should therefore be that of an additional barrier to tritium release especially in the event all the other containment barriers of the burial package might accidentally breach with consequent incoming of ground water into a direct contact with the tritiated waste form. However contradictory results have been reported by some laboratories concerning the extent of this reduction. Further, if applied on full-scale for encapsulating a tritiated cement matrix, the PITC process is likely to become somewhat complicated due to the need of adequate systems for monitoring and control of the polymerization process.
- The most simple laboratory-scale procedure for hydrating cement with tritiated waste-water appears to be that based on the injector technique applied to the dry cement mix vibrated inside the waste container. The use of disposable injectors for full-scale tritiated water immobilization and packaging can eliminate any source of secondary tritiated liquid wastes. Possible adverse implications in terms of tritium release, due to the presence of "lost" injectors (e.g. a possible channeling effect) inside the hardened cement body, should be investigated.
- The high density polyethylene drum liners used as primary containment of a tritiated cement matrix demonstrated to have a high efficiency as a physical barrier to tritium release, especially in case of highly tritiated specimens. Its excellent resistance to tritium permeation allows to maintain the release of tritium much below the values measured for bare tritiated cement blocks.
- The MML burial packages based on the employ of a multiple barrier system (i.e. polyethylene liner, multi-walled containers, intermediate voids filled up with vermiculite and asphalt) exhibit on full-scale testing an excellent resistance to tritium permeation, although the high amounts of tritium (3 to 5 g) immobilized in each package. Average tritium release rates which can be calculated by permeation data from such packages remain largely below the limit of 0.36% per year proposed as the maximum target value for HTO release from packages (31).

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APPENDICES

Appendix I - COMPOSITION OF SOME VARIETIES OF HYDRAULIC CEMENTS

1. Portland cements (PC)

The name "portland" was given to this cement because of the resemblance of the colour of the set cement to Portland stone (1).

Portland cement is obtained by burning at clinkering temperature a mixture of calcareous and argillaceous materials in suitable proportions and grinding the resulting clinker. Limestone and clay as well as a mixture of chalk and clay are common raw materials used for this purpose. There are various types of portland cement depending on the preparatory conditions, the fineness of grinding of the clinker and on the addition of certain additives or the restriction of the amount of various constituents. These cement types may differ one from the other in the heat of hydration, time of setting, chemical resistance, strength, etc..

Analyses of modern cements are shown in Tables 1 and 3 taken from Reference (2). The current nomenclature of cement constituents and their heats of hydration are shown in Table 2.

TABLE 1 - Composition (wt%) of some British portland cements (2).

	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	K ₂ O	SO ₃	Free CaO	C ₄ AF	C ₃ A	C ₃ S	C ₂ S
Ordinary	65.6	0.70	4.31	2.55	23.73	0.24	0.31	0.66	1.00	1.0	8	7	47	32
	65.5	1.23	5.90	1.59	22.76	0.33	0.43	0.50	1.60	1.4	5	13	41	34
	64.4	0.89	5.36	3.27	21.19	0.34	0.36	0.58	2.53	1.9	10	9	45	27
	64.6	0.56	7.64	3.30	19.09	0.34	0.25	0.57	2.19	0.6	10	15	53	15
	65.5	0.97	6.85	2.30	20.54	0.35	0.16	0.76	1.54	2.0	7	14	48	22
	63.1	0.82	6.28	3.59	20.56	0.37	0.27	0.58	2.59	1.7	11	11	39	30
Rapid-hardening	64.5	1.28	5.19	2.91	20.66	0.30	0.08	0.70	2.66	2.0	9	9	50	21
	65.4	0.51	5.00	4.31	20.04	0.42	0.48	0.78	1.47	1.4	13	6	64	9
	63.0	1.46	6.07	2.67	20.21	0.33	0.12	0.94	2.10	1.5	8	12	46	23
	64.3	1.27	4.74	2.15	22.37	0.36	0.18	0.53	1.82	2.3	7	9	42	32
Sulphate-resisting	63.8	0.92	4.07	4.65	21.09	0.28	0.13	0.67	2.56	2.9	14	3	58	17
	64.5	0.89	3.13	5.23	22.14	0.21	0.18	0.45	2.08	1.5	16	0	54	22
Low-heat	61.8	1.69	4.60	2.07	25.08	0.25	0.19	0.77	2.57	0.7	6	9	17	59
	62.0	1.59	4.54	2.06	25.80	0.23	0.20	0.65	1.87	0.9	6	9	15	63

TABLE 2 - Nomenclature and heats of hydration of cement constituents (4).

Compound	Formula	Nomenclature	Heat of Hydration (kJ/kg)
Tricalcium silicate	3CaO SiO ₂	C ₃ S	502
Dicalcium silicate	2CaO SiO ₂	C ₂ S	250
Tetracalcium aluminoferrite	4CaO Al ₂ O ₃ Fe ₂ O ₃	C ₄ AF	419
Tricalcium aluminate	3CaO Al ₂ O ₃	C ₃ A	867

TABLE 3 - Composition (wt%) of some American portland cements (2).

ASTM type	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	K ₂ O	SO ₂	Free CaO	C ₄ AF	C ₃ A	C ₃ S	C ₂ S
I	63.8	3.7	5.6	2.4	20.7	0.23	0.21	0.51	1.6	0.4	7	11	55	18
	63.1	2.5	4.7	3.0	22.1	0.21	0.06	1.30	1.7	0.2	9	7	47	28
	65.8	1.1	4.7	2.1	22.2	0.30	0.04	0.19	1.6	1.6	6	9	54	23
	62.8	1.7	6.7	2.5	21.1	0.39	0.95	0.51	1.8	2.0	8	14	33	35
II	61.4	3.1	4.8	4.8	20.8	0.21	0.06	1.30	1.8	0.9	15	5	44	26
	64.9	1.9	4.0	2.1	24.0	0.23	0.23	0.55	1.7	1.5	6	7	41	38
III	65.6	1.4	5.2	2.5	20.0	0.27	0.21	0.44	2.3	1.8	8	10	63	10
	63.3	4.3	5.1	2.0	20.3	0.21	0.19	0.28	2.5	1.9	6	10	51	19
IV	59.6	3.0	4.6	5.0	22.9	0.23	0.06	1.19	1.3	0.4	15	4	25	47
	63.6	1.1	3.7	3.1	25.2	0.19	0.33	0.01	1.9	0.4	9	5	31	49
V	64.3	1.7	3.1	3.3	24.4	0.19	0.08	0.22	1.4	0.5	10	3	45	36
	64.2	2.5	1.9	1.3	26.1	0.12	0.10	0.15	2.0	1.8	4	3	35	48
	63.3†	1.2	3.3	4.7	23.1	—	0.08	0.37	1.7	—	14	1	49	30

† Corrected for free CaO.

It is worth noting that although the amounts of the various oxides present only vary between somewhat restricted limits, the corresponding contents of the different compounds present in the cement vary much more widely. A relatively small change in the analytical composition of the cement may thus significantly change the compound content and consequently quite considerably alter the set cement properties.

Various types of portland cement have been utilised at PNL (Pacific Northwest Lab.) of Richland (WA) (3) for experimental studies on radwaste immobilization by concrete. Relative compositions of portland types I to V cements are reported in Table 4.

TABLE 4 - Typical Relative Composition of portland cements used at PNL (3).

Cement type	Composition, wt%			
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
I	45	27	11	8
II	44	31	7	13
III	53	19	10	7
IV	20	53	6	14
V	38	43	4	8

Type I portland cement is an ordinary purpose cement (OPC). Type II is a modified cement type employed to yield a lower heat of hydration (see Table 2) than type I, slower setting, and a better sulphate resistance. Type III develops a large

fraction of its ultimate strength in very few days and has a larger heat generation rate than type I. Type IV has a low heat generation rate and amount of heat. Type V is formulated to resist severe sulphate attack (SRPC).

The ordinary portland cement is the most commercially available and the cheapest variety. An ordinary portland cement can hydrate approximately 25 wt% of water.

2. Modified portland cements

2.1 Slag cements

Blast furnace slag (BFS) is a waste product generated during the iron smelting. If BFS is quenched with cold water a sandy product having a glasslike structure is obtained. Silica and lime are the main constituents of this product.

When finely ground quenched BFS shows hydraulic properties, i.e. it has the property of setting when mixed with water (4, 5). Its process of hydration is very similar to that of portland cements but the initial set and the early rate of strength development is lower (4). The chemical composition of BFS is given in Table 5 together with an ordinary portland cement (OPC), a sulphate resistant portland cement (SRPC) and a pulverised fuel ash (PFA) are also reported.

TABLE 5 - Typical Composition (wt%) of OPC, SRPC, BFS and PFA (4).

Compound	OPC	SRPC	BFS	PFA
CaO	64.5	64.5	42.5	2.0
SiO ₂	20.0	20.0	36.5	50.5
Al ₂ O ₃	7.0	4.0	11.0	30.5
FeO/Fe ₂ O ₃	2.2	5.5	0.3	8.5
MgO	1.3	1.1	7.0	1.5
MnO	---	---	0.4	---
Na ₂ O	0.4	0.2	0.5	1.1
K ₂ O	0.5	0.4	0.6	3.2
TiO ₂	0.3	---	0.5	2.3
SO ₃	2.5	2.3	0.2	0.5
Loss/gain on ignition	-1.3	-1.1	+2.4	-3.3
C	---	---	0.1	3-7

To improve the quality of BFS by increasing its CaO content up to that of OPC, ground limestone may be added to ground BFS. The mixture is then burned to a clinker (like portland cement) and subsequently very finely ground. To reduce costs a further 30% of ground BFS is mixed in. The product is sold under the name of slag cement or iron portland cement (5).

BFS is also used for the partial replacement of portland cement to obtain

BFS/OPC blends containing BFS percentages within 25 wt% to 90 wt% (4). When compared to OPC composites high BFS/OPC replacements (i.e. > 50 wt% BFS) exhibit a lower permeability to water and a lower temperature maximum reached in the composite during the early stage of hydration.

2.2 Pozzolanic cements

In several countries pozzolanas or pozzolanic cements have been or are being used for the immobilization of radioactive wastes (1). A pozzolana can be defined as a siliceous and aluminous material which is capable of reacting with lime in the presence of water at ordinary temperature to produce cementing compounds (calcium silicates) (6). Italian pozzolana, trass etc. are examples of naturally occurring pozzolanas of volcanic origin. Artificial pozzolanas can be prepared by burning at suitable temperatures certain clays, shales and diatomaceous earths containing a proportion of clay.

Pozzolanic cements are produced by grinding together a portland cement clinker and a pozzolana or by mixing together a hydrated lime and a pozzolana.

A mixture of ordinary portland cement (80 wt%) and fly-ash (SiO_2 , 20 wt%) was experimented at PNL (3) as a pozzolanic cement. Fly-ash is a pozzolanic material enhancing cementing properties of portland cements by reacting with the calcium hydroxide formed during the hydration of cement.

Pulverised fuel ash (PFA) is a waste material produced during the burning of pulverised coal in a power station and separated from the effluent gas of combustion.

As shown in Table 5 the main constituents of PFA are silica and alumina (4). Carbon is present in PFA in amounts which vary from 10 wt% to less than 3 wt%, according to the combustion efficiency at the power station. Between 2 wt% and 5 wt% of PFA is soluble in water giving an alkaline reaction. The solution contain calcium and sulphate ions.

PFA acts as a pozzolanic material (7) i.e. it contains a reactive form of silica which may react with calcium hydroxide produced during the hydration of portland cement to form calcium silicate (4).

Usually only the finer PFA fraction i.e. the fraction separated from the effluent gas at the second removal stage by electrostatic precipitation, is the material used for the partial replacement of OPC to obtain a pozzolanic cement mix.

Experiments carried out in the USSR and reported by Ref. (1) confirm that in pozzolanic cements there are substances present which have high sorption properties for radioisotopes. However, the total surface of a block formed using pozzolanic cement is normally about twice that of portland. As the leaching rate is directly related to the surface exposed there is usually no real reduction in the amounts of radioisotopes going into solution when pozzolanic cement is used. Therefore this type of cement is normally used for the grouting of solid radioactive items.

3. High-alumina cements (HAC)

High-alumina cements are obtained by fusing or sintering a mixture, in suitable proportions, of aluminous and calcareous materials and grinding the resulting product to a fine powder. Limestone and bauxite are the raw materials used for this purpose (2).

A HAC is composed essentially of roughly equal proportions of alumina and lime, both usually within the range 36-42 wt%, a proportion of iron oxides up to 20 wt%, and a small percentage of silica (4-7 wt%). The iron oxides are present in both the ferrous and ferric states, the relative proportions depending on the extent to

which an oxidizing atmosphere is maintained in the furnace during burning. Of the minor constituents titania occurs to the extent of about 2 wt%, magnesia usually 1 wt% or less, and sulphate or sulphide less than 0.5 wt%. The content of alkalis is usually less than 0.5 wt%; too high an alkali content may, in fact, be troublesome in some cements by producing undesirably quick setting. Insoluble matter may range around 2% (2).

The high-alumina cements made commercially have been classified into four types as shown in Table 6 taken from Reference (8). By far the largest proportion of world production is of type 1, red bauxite being the most widely available and cheapest source of alumina. White bauxite, as used for type 3, is much less freely available.

TABLE 6 - Types of high-alumina cement.

Type	Colour	Al ₂ O ₃ per cent	Iron oxides as per cent		SiO ₂ per cent	CaO per cent	Source of alumina	Process of manufacture
			Fe ₂ O ₃					
1	Grey to black	37-40	11-17	3-8	36-40	Red bauxite	Fusion	
2	Light grey	48-51	1-1.5	5-8	39-42	Red bauxite	Reductive fusion with removal of Fe metal	
3	Cream or light grey	51-60	1-2.5	3-6	30-40	White bauxite	Sintering Clinkering Fusion	
4	White	72-80	0-0.5	0-0.5	17-27	Alumina	Sintering Clinkering	

TABLE 7 - Typical composition (wt%) of some HAC* manufactured in different countries (9).

Country	Type of manufacture	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	FeO	TiO ₂	MgO	S''	SO ₃
England	Reverberatory furnace fusion	4-5	38-40	36-39	8-10	5-7	< 2	1	Trace	0.1
France	„	3.5-4.5	38-40	36-39	9-11	4-6	< 2	1	Trace	0.1
Spain	„	4-5	36-38	39-42	10-12	4-5	< 2	1	Trace	0.1
Yugoslavia	„	6-8	38-40	36-39	8-10	4-7	< 2	1	Trace	0.1
U.S.A.	Rotary kiln fusion	8-9	40-41	36-37	5-6	5-6	< 2	1	0.2	0.2
Germany†	Blastfurnace Reductive fusion	5-8	48-51	39-42	0.1	< 1	1.5	1	1	0.5
Czechoslovakia	Brick-kiln-type furnace sintering	6-8	40-45	37-42	12-14	Trace	< 2	1	Trace	0.5

* T. D. Robson, *High Alumina Cements and Concretes*, Contractors Record Ltd., London 1962. All cements made from red bauxite
 † Also 1 per cent metallic Fe.

The present British Standard for HAC (BS 915:1947) requires a minimum content of Al_2O_3 of 32 wt% and a ratio of Al_2O_3 to CaO, by weight, between 0.85 and 1.30.

The analysis of HAC manufactured in some european countries and in the USA are compared in Table 7 (9).

Compared to portland cements HAC can hydrate considerably higher water amounts and needs shorter curing times. During hydration HAC reacts with water to form hydrated alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$) and three differently hydrated calcium aluminates. Each of them may become the predominant final product depending on hydration temperature and curing conditions (temperature, moisture), so that HAC can fix final percentages of water approximately variable from 35 to 70 wt% (see Appendix II).

Hydrated alumina, like $\text{Ca}(\text{OH})_2$, is also a non-cementing compound but it does not contribute, as $\text{Ca}(\text{OH})_2$, to long-term detrimental effects on overall concrete stability (3).

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- (2) Lea F.M. - *The Chemistry of Cement and Concrete*, 3rd Ed. (1970), E. Arnold Publ. Ltd.
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- (7) Takemoto K., Uchikawa H. - Hydration of Pozzolan Cement, 7th Int. Congress of Chemistry of Cement, quoted in Ref. 4.
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Appendix II - HYDRATED CEMENT COMPOUNDS

1. Hydrated calcium silicate, aluminate, aluminoferrite and hydrated calcium hydroxide from hydration of portland cements (PC).

During the hydration of a portland cement the anhydrous tri- and di-calcium silicates (C_3S and C_2S , see Appendix I) react with water to form calcium hydroxide and a less basic gel of calcium silicate hydrate.

The composition of these gels changes during the period of the reaction and it also varies with the water to solid ratio of the mix and temperature. The reaction product may be generally indicated as a CSH gel without any particular composition.

More specific forms of gel have been defined (1) as CSH(I) consisting of poorly crystallized foils or platelets with a tobermorite-like structure and a $CaO:SiO_2$ molar ratio of 0.8 to 1.5 as well as CSH(II) showing a fibrous structure and a molar ratio of 1.5 to 2.

The CSH gels obtained by hydration of C_3S and C_2S appeared as very poorly crystallized products showing only a few of the X-ray diffraction lines of well crystallized tobermorites.

It was in fact for long time uncertain whether any crystalline hydrated calcium silicate was produced by action of water at ordinary temperature on the anhydrous calcium silicates. That such crystals are formed in sub-microscopic size and the nature of the gelatinous material was essentially crystalline have been demonstrated only by means of X-ray and electron microscopy examinations (2).

Anhydrous tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) rapidly react with water, the former more rapidly than the latter, due to its higher alumine content.

Both the components form hexagonal plate hydrate crystals (3) without precipitation of calcium and aluminum hydroxides (4).

A final stable isomeric compound $3 CaO \cdot Al_2O_3 \cdot 6H_2O$ (C_3AH_6) is obtained from C_3A hydration while a hydrated $4 CaO \cdot Al_2O_3 \cdot Fe_2O_3$ crystalline compound is obtained from C_4AF (4).

2. Hydrated calcium aluminate and hydrated alumina from hydration of high alumine cements (HAC)

During hydration HAC reacts with water to form cementing hydrated calcium aluminates and hydrated alumina ($Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$).

At low temperatures (5) $CaO \cdot Al_2O_3 \cdot 10H_2O$ (CAH_{10}) is formed in HAC pastes and at about 20°C a gel of $2CaO \cdot Al_2O_3 \cdot 8H_2O$ (C_2AH_8) and $Al_2O_3 \cdot 3H_2O$ (AH_3) appears. However the amount of C_2AH_8 reported by different investigators as formed by hydration at temperatures between about 20 and 23°C varies considerably (5).

It may be influenced by the alkali content of the cement as well as by the cement components (e.g. $C_{12}A_7$). At 25°C and above the initial main hydration products are C_2AH_8 and AH_3 and as the temperature is raised, $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (C_3AH_6) become the predominant product within days or weeks (5).

The compounds CAH_{10} and C_2AH_8 produced at ordinary temperatures are metastables and a prolonged ageing tends to change them into the cubic compound C_3AH_6 . At ordinary temperatures ($\leq 18^\circ C$) this change is very slow and may never

occur in concrete kept dry. On the contrary it must be expected to occur, even if very slowly, in wet concrete and rapidly at high temperature (35-40°C).

A reduction of the solid volume occurs, which is estimated to correspond to just below the half of the original volume according to reaction:



as well as to about two-thirds according to reaction (5):



HAC combine with considerably more water during hydration than does portland cements. If the initial product of hydration is a mixture of mono- and dicalcium hydroaluminates (CAH_{10} , C_2AH_8) 70 wt% of water would be required; if C_2AH_8 and AH_3 about 50 w%; and if C_3AH_6 and AH_3 about 35 w%. Such calculations are approximate since they assume a complete hydration of the alumina and silica compounds and make no allowance of the iron compounds.

References

- (1) Lea F.M. - The Chemistry of cement and concrete, 3rd Ed. (1970), E. Arnold Publ. Ltd., p. 175.
- (2) *ibid.*, p. 187 & 260.
- (3) *ibid.*, p. 261.
- (4) *ibid.*, p. 183.
- (5) *ibid.*, p. 505, 506 & 507.

Appendix III - WATER BONDING AND WATER MOBILITY IN SET CEMENT

Many attempts were so far made to study the nature of water bonds in a set cement or concrete and to divide water in categories or groups that might be as much as possible representative of the various modes of water bonding in set cement. Free water, capillary condensed water, gel adsorbed water chemically combined water are some categories so far used to diversify the various water fractions that may be held in set cement by different bonding modes.

Various divisions can be obtained by determining the amount of water remaining after drying at reduced vapor pressures (or at increasing temperatures) or alternatively the amount of water that can be frozen or removed by solvents (1).

An exemple of results obtained by some drying methods is given in Table 1 (1, 2).

TABLE 1 - Weight ratios between retained water at equilibrium and anhydrous OPC obtained on drying by different methods.

Relative humidity (p/p _s)	Drying method	Retained water / Anhydrous OPC (wt) ratio
$3 \cdot 10^{-4}$	Mg(ClO ₄) ₂ · 2·4 H ₂ O at 25°C	0.22
$2 \cdot 10^{-5}$	Ice at -79°C	0.20
$8 \cdot 10^{-7}$	P ₂ O ₅ at 25°C	0.18
-	Heating at 105°C	0.20
-	Heating at 50°C	0.26

Beside the conditions of drying, the content of water retained in a dried set cement was found to depend also on the age of specimen, the speed of hydration of cement components and the initial w/c ratio.

One has however to point out that all such methods ascribe to each group a specific reduced vapor pressure which appears somewhat arbitrary since the curve of the vapor pressure against water content for set portland cement is a continuous one, without showing any breaks like those, for instance, obtained with crystalline hydrates (Fig. 1). The gel structure of the mass of set cement and its heterogeneous nature should normally affect this curve and it is indeed surprising that any such effect might be masked. This means that practically there are no particular vapor pressures which diversify the gel water from that combined as water of hydration or indeed the gel water from the capillary water.

According to Powers and Brownyard (3) the water held in set cement should be classified into two categories, i.e. the "non-evaporable" water defined as that retained on drying to a constant weight, at 23°C "in vacuo" over Mg(ClO₄)₂ · 2H₂O-4H₂O and the "evaporable" water which is the difference between the amount of water held in the saturated surface-dry condition and the former value.

The non-evaporable water is thus considered to be a measure of the chemically combined water fraction which in principle cannot be easily removed from set cement.

But this measure can be only approximate, since at so low vapor pressures like those reported in Table 1 hydrated calcium aluminate, calcium sulphoaluminate and tobermorite are known to lose some of their crystallization water (inter layer water from the crystal lattice) (1).

On the contrary the evaporable water, being less strongly bound, is the most easily removable (hence mobile) fraction (1, 4). This water fraction is largely represented by that part of water which is condensed inside the capillary system of set cement as well as that part which is adsorbed in the gel mass by means of attractive forces of physical nature (1).

Although evaporable and non-evaporable water fractions cannot be sharply distinguished, their distinction may help in explaining the decrease with time of the water vapor pressure observed in a set cement block.

Some isothermes (see Fig. 1) obtained by Powers and Brownyard and reported by Ref. (1) well illustrate the relationship between the water content of a portland cement block and its relative vapor pressure (p/p_s) or relative humidity at 25°C.

As shown in Fig. 1 the vapor pressure over set cement remains at the saturation value ($p/p_s = 1$) as long as the free water is present. After the free water is removed and the water surface recedes into the capillary voids the relative water vapor pressure drops.

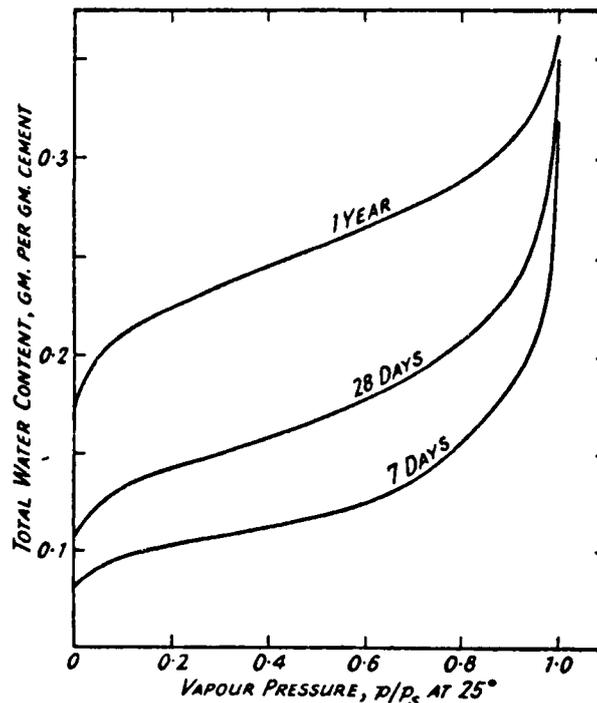


FIG. 1 - Relation between water content and vapour pressure for set cement (1, 3).

This could be explained by a progressive filling (as the hydration proceeds) of the capillary volume with cement hydration products to which correspond a simultaneous progressive diminution of the amount of evaporable water contained in the capillary voids. As reported in Ref. (1) below a relative vapor pressure estimated at 0.3 to 0.45, the capillaries of the set cement appear to be empty and all the adsorbed water distributed in the mass of the cement gel. In this case the evaporable

water content was found to depend only on the content of non-evaporable water and thus on amount of the cement gel (1).

At higher relative vapor pressures the water in the gel increases further and also starts to be held by surface adsorption or capillary condensation inside capillary pores, with the capillary condensation becoming substantial only at relative humidity values approaching 80% (1).

When a very low vapor pressure is reached the water present in set cement is practically only that defined as the non-evaporable one, which is known to increase slowly over a long period of time as the hydration of cement components proceeds. This is well illustrated in Fig. 1 where it can be seen that the w/c ratio of the specimen at point $p/ps = 0$ increases from 0,08 to 0,17 as its age (i.e. the curing time) increases from 7 to 365 days (1).

TABLE 2 - Per cent water contents in a set OPC block at different relative vapor pressures and curing times.

p/ps	0			0.4		0.6		1.0	
curing time	NEV	EV	TOT	EV	TOT	EV	TOT	EV	TOT
1y	17.0	7.5	24.5	10.0	27.0	19.3	36.3		
7d	8.0	3.0	11.0	4.0	12.0	24.5	32.5		
%	+9.0	+4.5	+13.5	+6.0	+15.0	-5.2	+3.8		

NEV = non-evaporable; EV = evaporable; TOT = total water.

Over the same period of time the total water content held at saturation ($p/ps = 1$, Fig. 1 and Table 2) increases only from 32.5% to 36.3% (+3.8%), which means that a diminution of the evaporable water fraction from 24.5% to 19.3% (-5.2%) does occur. These figures make thus evidence that the increase of the non-evaporable water fraction with time can be ascribed to a conversion of a portion of evaporable water to the non-evaporable water form.

At vapor pressures below the saturation point this is numerically not evident because the above mentioned conversion is masked by a simultaneous progressive adsorption of evaporable water.

The curves of Fig. 1 show also that a set cement block which has been allowed to stand (i.e. "cured") for 7 or 28 or 365 days, at a fixed vapor pressure may lose or gain evaporable water depending on whether its actual w/c ratio is higher or lower than the w/c value that is determined in a curve of Fig. 1 by the fixed conditions of vapor pressure and curing time.

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Appendix IV - CEMENT ADDITIVES

Burned gypsum, silica xerogels (i.e. dried out silica gels), vermiculite and diatomaceous earth may be used as additives to cement (1, 2) mainly in order to increase the amount of water that can be immobilized.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) loses 75% of its crystallization water at 128°C to give "burned" gypsum ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), an hemihydrate containing 6.2 wt% water that is capable of tacking back the lost water at ordinary temperature (2-4).

Up to the hemihydrate composition the burned gypsum binds water strongly giving a dew-point of -62°C . At higher water loadings the held water is not firmly fixed (2).

The burned gypsum used for industrial purposes (i.e. "plaster of Paris") generally contains less water than the hemihydrate but it must not be completely dehydrated otherwise it loses any capability of rehydration (4).

Silica xerogels (xeros = dry) are amorphous dehydrated gels of silica (3, 5) which, due to their highly developed internal surface have a high water capacity, being capable of loading up to about 40 wt% of water. However only at low water loadings water is strongly held and the lowest values of water vapor pressure can be attained (2).

As reported in Ref. (6) the strongly held water would not be chemically bound, but only mechanically retained inside the smallest cavities of the gel by means of capillary forces.

The artificially produced silica xerogels have the advantage over the infusorial earth that their structure can be adapted to a specific use by controlling their preparation procedure (7).

Diatomaceous (or infusorial) earth is an amorphous hydrate silicon oxide that occurs in nature in earthy form ("Kieselguhr") and consists of the remains of the silica skeleton (5) of former "infusoria" (diatoms). This material is notable for its excellent capacity for absorbing liquids.

Vermiculite is a mica-like material (i.e. a hydrated sodium-aluminium silicate) which exfoliates when heated to $600-900^\circ$. It is an excellent liquid absorbent and it can change its sodium with calcium and magnesium which may help in the uptake of other nuclides (1, 3). If intimately mixed with dry cement it allows the infiltration of cement powder into its porous structure absorbing then liquids like a sponge.

Zeolites are a class of crystalline compounds (i.e. hydrated sodium-alumino-silicates) either occurring in nature or produced synthetically on a commercial scale, which have the property of exchanging the sodium that they contain with other metals when introduced in their solutions (8). It is also characteristic of zeolites that they can lose or resorb water continuously without involving major changes in their crystal structure as it is the characteristic of most crystalline hydrates (e.g. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) (9).

Linde AW 500 zeolite mentioned in Table 1 is in particular a synthetic chabazite used for the decontamination of aqueous wastes from Cs^{137} .

Molecular sieves is a commercial name used for a special type of zeolites produced synthetically. The LINDE Company markets a dried zeolite A containing 1.5 wt.% of water as HA type molecular sieves ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 0.24\text{H}_2\text{O}$). It is worth noting that zeolite A, when fully hydrated ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.45\text{H}_2\text{O}$), contains 22 wt.% of water but when water loading diminishes to 17 wt.% ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$

$2\text{SiO}_2 \cdot 3.24\text{H}_2\text{O}$) its vapor pressure at 25°C amounts $5 \cdot 10^{-4}$ bar which is two order of magnitude lower than the vapor pressure of water at 25°C ($3 \cdot 10^{-2}$ bar).

References

- (1) USERDA - Alternative for Managing Wastes from Research and Post-Fission Operations in the LWR Fuel Cycle, ERDA-76-43 (1976) Vol. 2, part 2.
- (2) *ibid.*, Vol. 2, part 3.
- (3) Management of Tritium at Nuclear Facilities, IAEA Technical Report Series N° 234, IAEA, Vienna (1984).
- (4) Remy H. - Treatise of Inorganic Chemistry, Vol. I, Elsevier Publ. Co. (1956) p. 280.
- (5) *ibid.*, p. 487, 491
- (6) *ibid.*, p. 494.
- (7) *ibid.*, p. 496.
- (8) *ibid.*, p. 513.
- (9) *ibid.*, p. 514.

Appendix V - THE POLYMER IMPREGNATION TECHNIQUE APPLIED TO TRITIATED CONCRETES (PITC process)

In the USA the immobilization of tritiated water has been investigated since seventies at BNL and MML with particular emphasis being given to the polymer impregnation of tritiated concretes (1-14).

In the frame of the PITC process developed at BNL and MML special mixing techniques such as end-over-end tumbling and injector techniques, were developed for blending tritiated aqueous waste with cement. *

1. End-over-end tumbling technique

In this process (2-5, 7, Fig. 1) the cement was added to the mixing drum (which also becomes the casting and storage container) in a "cold" area of the disposal facility and stored until needed. Monitoring of this drum filling step was done on a weight rather than volumetric basis to ensure a proper formulation. A mixing weight, if necessary to assure adequate mixing, could also be added to the drum at that time.

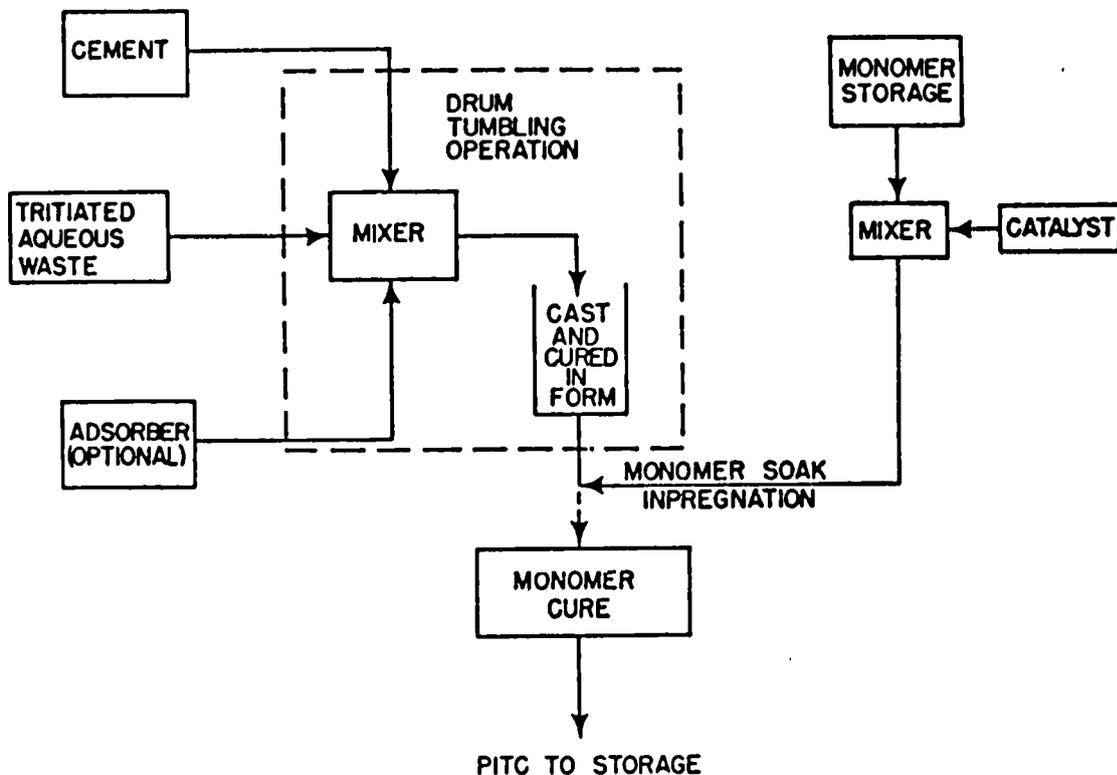


FIG. 1 - Conceptual fixation of tritiated aqueous waste in polymer impregnated concrete (PITC) by in-drum tumbling and soak impregnation techniques (3).

The mixing and casting operations simply consisted of adding the required amount of tritiated aqueous waste to the drum, closing the bung-hole, transferring the drum to the tumbler and tumbling the mix. Experiments demonstrated that a casting in excess of 2/3 of the volume of a 30-gal (~ 115 litres) drum can be thoroughly mixed by tumbling at 20 rpm for 10 minutes without a mixing weight (3).

Standard 30-gal DOT 17C mild steel drum were selected as casting containers based on consideration of exotherm temperature resulting from the heat of hydration of a water-cement mix. The dimensions of such a drum are approximately 46 cm. I.D. by 69.5 cm high. A composite occupying 80% of the nominal volume of this container will have a volume of about 90 litres. Such a 30-gal drum may also be inserted into a standard 55-gal (~ 210 litres) drum in the event of contamination, leakage or the desire to provide an additional containment barrier.

Portland type III and HA cements were selected because of their rapid curing properties. Although the production of metastable hydrated compounds (see Appendix II), HAC were selected also because of their more efficient packing properties than portland type III cement, resulting in a lower porosity, hence lower polymer loading (4).

Both types of cements were mixed with tritiated water to give a w/c ratio of about 0.2 (3). HAC can, of course, hydrate considerably more water than does portland cements (~ 50 wt.%), but a significant increase of the w/c value above that used would result in too dense cement blocks, not easily permeable by styrene monomer (4).

Mixing by the drum tumbling technique eliminates the need of equipment cleaning operations and also minimizes the possibility of contamination as mixing occurs in a closed drum. Since the drum also serves as the casting container the need of a transfert operation is eliminated.

After mixing the cement paste was cured at 40°C. For portland type III or HA cement curing required about 24 hours to induce complete hydration. The concrete, equilibrated to room temperature, was then impregnated by a soak technique. Styrene monomer, catalyzed with 5 g/kg of 2,2-[Azobis-2-methylpropionitrile] (AIBN catalyst) or benzoyl peroxide (used as a low temperature catalyst) (1-9, 14) was added to the waste container through an opening in the drum cover in the proportion of 150-200 g of styrene per kg of cement paste. Approximately 4-5 hours soaking was allowed, the time required for a complete impregnation being variable and depending on the concrete volume, density and composition but typically requiring a few hours. After the soak impregnation was completed the casting was heated to 50-70°C (depending on the catalyst used) to induce polymerization which was completed in 24 hours (7).

Catalyst-promoter systems which cure at room temperature was not applied to PITC as viscosity changes, which may occur during impregnation due to the initiation of polymerization, may impede the complete permeation of the matrix by the monomer (4, 5).

2. Conventional mixer technique

Smaller size but similar density specimens (6-9) were also produced at BNL for lysimeter tests at SRP (see subsection 10.3.1) using a conventional dough type mixer and a w/c ratio of 0.22, i.e. the same value applied with the end-over-end tumbling technique, hence well representative of this type of composite. The water necessary to give a w/c ratio of 0.22, added along with a suitable amount of tritiated water to provide a total activity of 370 GBq (10 Ci) for each specimen, was mixed until a uniform consistency was obtained.

The portland type III cement mix was transferred to a 5-gal (~ 19 litres)

polyethylene carboy, the latter being vibrated to provide proper packing of the mix. The carboy was then sealed and placed in a oven for five days at 40°C to ensure the complete curing of the cement.

After removal from the oven the casting was allowed to equilibrate at room temperature before polymer impregnation. The same soak impregnation techniques was applied as described for the above tumbling method. The specimen geometry was cylindrical with approximate dimensions of 27 cm diameter x 28 cm height for a composite volume of about 16 litres (0.566 ft³), a volume to surface ratio of 4.545 and a density before impregnation of 1.465 g/cm³ (8, 9).

In the case of lysimeter test at SRP impregnation produced PITC specimens with a density of 1.707 g/cm³ and a polymer loading of 16.5 ± 0.3% and in the case of duplicate lysimeter tests at BNL PITC specimens with a density of 1.725 g/cm³ and a polymer loading of 12.9% (8, 9).

3. Injector technique

In this process (6-14, Figs. 2-4) the 5-gal cement casting container was filled with dry portland type III cement and compacted by vibration. The injector which is simply a hollow tube containing several orifices along its length through which the aqueous waste is dispersed, was inserted into the dry cement. Tritiated aqueous waste was then introduced into the cement through the injector. Aqueous waste was added to the cement until the waste reached the external surfaces of the cement as evidenced by dampness. The injector was withdrawn and the cement casting was allowed to cure. After the casting had cured, catalyzed styrene monomer was introduced into the casting container and allowed to soak through the composite. After the casting had been completely permeated by the monomer, the monomer was thermally polymerized. Subsequent to the waste injection, the process was the same as the previously developed end-over-end drum tumbling method (9).

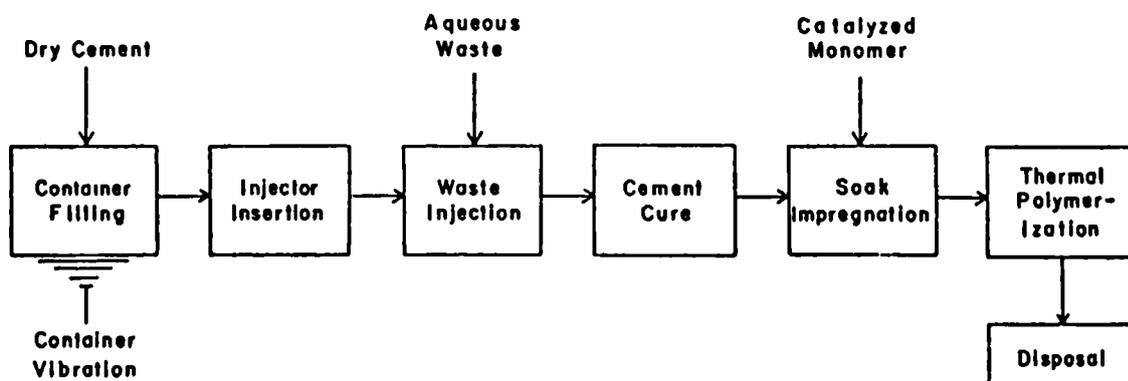


FIG. 2 - Conceptual fixation of tritiated aqueous waste in polymer impregnated concrete (PITC) by the injector and soak impregnation techniques (6, 9).

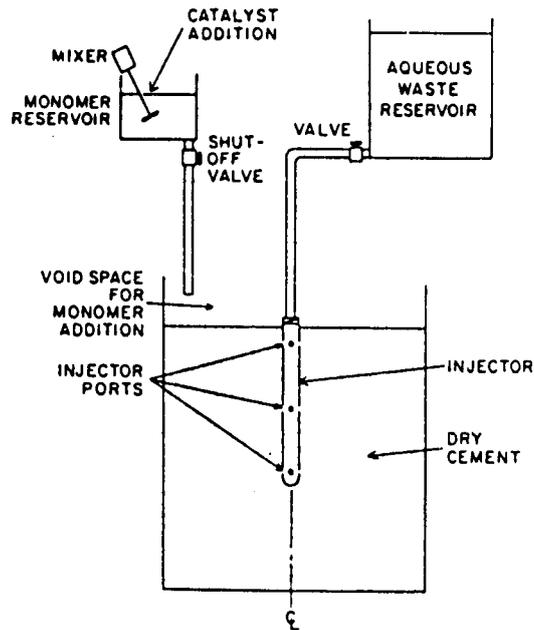


FIG. 3 - Injector technique for the fixation of aqueous wastes in polymer impregnated concrete (9).

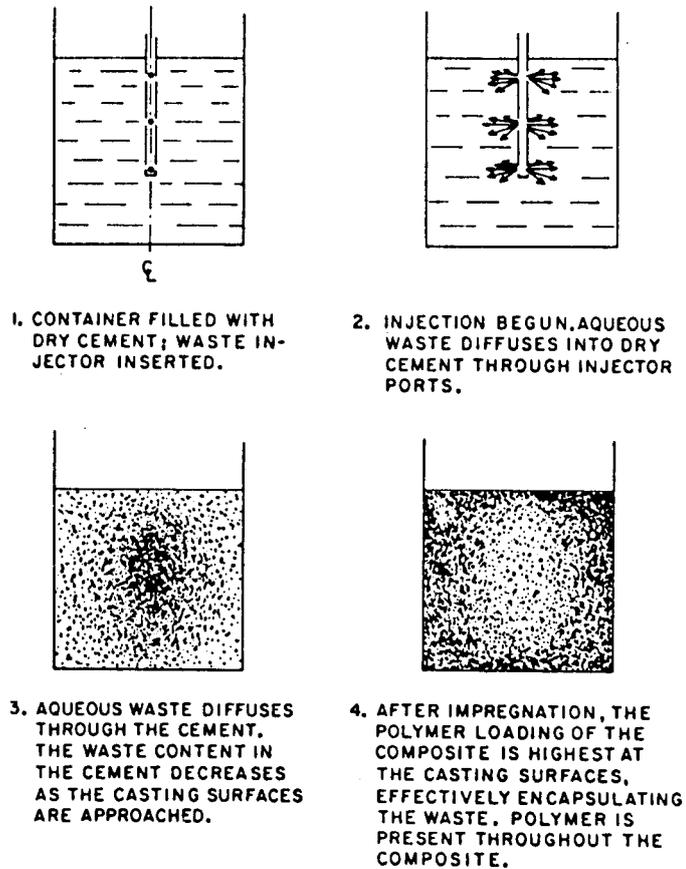


FIG. 4 - Fixation of aqueous waste in polymer impregnated concrete by the injector techniques (9).

Injector and soak impregnation techniques applied at BNL (9) produced "hot" PITC specimens with an average density of 1.783 g/cm^3 , an average polymer loading of 23.15% and a total activity of 170 GBq (4.6 Ci) for each specimen. The specimen geometry was cylindrical with approximate dimensions of 28 cm diameter x 26.3 cm height, representing a volume of about 16 litres (0.572 ft^3) and a V/S ratio of about 4.6. Unfortunately no data are available on the results of static leach tests which were foreseen for these samples.

The same injector technique was applied at MML in order to produce tritiated concrete specimens for small- and full-scale leaching tests on packaged PITC composites (10-14).

3.1 Small-scale tests

The samples were prepared (14) by filling a 500 ml linear high-density-polyethylene bottles (6.67 cm diam.) with 250 g of portland type III cement to a height of 5.79 cm, then vibrating the bottles to compact the cement. An injector was used to introduce 64 g of tritiated water containing 14.3 TBq (386 Ci) of tritium (i.e. 6 Ci of tritium per gram of water which correspond to several time the normal concentration of tritiated waste water at the Mound Facility) into the center of the cement mass at a rate of 2 ml/min. After this mixture was cured at room temperature for 5 days, 62.5 g of styrene monomer containing 0.5% and 5% of AIBN catalyst (see above) was added to the void space above the concrete and allowed to soak into the block for 5 hours. The samples were then placed in an oven at 40°C (5% catalyst) or 55°C (0.5% catalyst) for 18 hours to obtain styrene polymerization (11).

It should however be noted that assuming the above indicated dimensions as the final dimensions of the composite it results that the S/V ratio of each specimen is equal to about 0.95 cm^{-1} . This is in contradiction with the stated similarity in terms of S/V ratio (11, 14) with BNL specimens sent to SRP, having a S/V ration of 0.22 cm^{-1} (9).

3.2 Full-scale tests

The following procedure was applied at MML (14) for successfully fabricating PITC waste package utilized for full-scale tests:

1. Place a 27-gal low-density-polyethylene drum liner into a 30-gal (~ 115 litres) steel drum. Note that cross-linked high-density polyethylene is more desirable because of its superior resistance to styrene and heat damage.
2. Fill the liner with 112 kg of portland type III cement and vibrate the drum to settle cement.
3. Place the injector vertically in the axis of the drum, so that the end of the rod is in the center of the cement mass. The injection rod is 1/2 in. copper tubing with one end capped. Holes (1/8 in. diameter) are drilled: one in the cap and four groups of four holes arranged radially, which start at the end and are spaced at 2-1/2 in. intervals.
4. Insert three thermocouples for monitoring and process control at the:
 - center of cement block,
 - circumference of the cement block, and at the
 - outside surface of the steel 30-gal drum under the heaters (locations: 1, 3, and 4 or 5 on Fig. 5).
5. Inject 27 liters of water at 0.23 liter per minute, then remove the injector rod, filling the hole with cement.

6. Replace bungs on the liner and allow the cement to cure from 3-5 days at ambient temperature.
7. Install band heaters and insulation on the 30-gal (115 litres) drum and heat the package to 45°C. When the correct temperature has been established, add 24.3 kg of styrene monomer containing 3/4 wt.% (or 185.5 g) catalyst (2,2'-azobis [2-methylpropionitrile]) to the void above the cement block and allow it to soak into the cement.
8. Increase the heat when the package reaches ~ 45°C again (~ 2 hr), being careful not to exceed 110°C at the liner. Heat until 70°C is attained at the circumference of the cement block (~ 5 hr), then turn off the heaters. Polymerization should occur within approximately 7 hr.

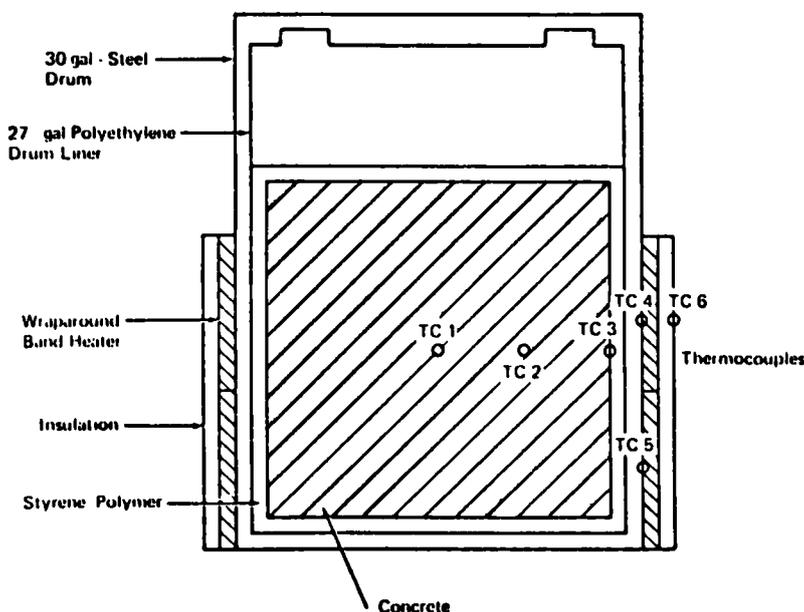


FIG. 5 - Full scale PITC waste package.

References

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- (2) As Ref. 1, PR n° 3, BNL-19981 (January-March 1975).
- (3) Colombo P. et al. - The Fixation of Aqueous Tritiated Waste in Polymer Impregnated Concrete and in Polyacetilene, BNL 20898, Conf. 750989 (1975).
- (4) As Ref. 1, PR n° 4, BNL-20421 (April-June 1975).
- (5) As Ref. 1, PR n° 5, BNL-20779 (July-September 1975).
- (6) As Ref. 1, PR n° 7, BNL-21700 (January-March 1976).

- (7) **Nellson R.M. et al.** - Immobilization of Tritiated Aqueous Waste in Polymer Impregnated Concrete, BNL-22900, Conf. 770611-21 (1977).
- (8) **As Ref. 1, PR n° 9, BNL-50625 (July-September 1976).**
- (9) **As Ref. 1, PR n° 12, BNL-50733 (April-June 1977).**
- (10) **Dauby J.J. et al.** - Tritium Waste Control Project, MLM-2451 (October 1976 - March 1977).
- (11) **As Ref. 10, MLM-2484 (April-September 1977).**
- (12) **As Ref. 10, MLM-2519 (January-March 1978).**
- (13) **As Ref. 10, MLM-2542 (July 1978).**
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Appendix VI - PARAMETRIC DEFINITION OF TRITIUM LEACH RATE

The leach rate is the parameter currently used to quantify the leachability of a radionuclides.

At PNL (1) the leach rate measured for cesium and strontium by static leaching tests and expressed by $\text{g}\cdot\text{cm}^{-2}\cdot\text{d}^{-1}$, was defined by:

$$L = \frac{I}{F A} \cdot \frac{\Delta m}{\Delta t}$$

where:

- F = weight fraction of the radionuclide in the leach specimen, i.e. initial mass of the radionuclide divided by the total mass of the leach specimen
- A = surface area of the leach specimen, (cm^2)
- Δm = mass of the radionuclide leached during time Δt , (g)
- Δt = time interval between changes of leachant, (d)

At BNL (2, 3) where a daily change of leachant was done, the bulk leach rate measured for tritium by static leaching tests and expressed by the same above dimensions was defined by:

$$L_B = F_i \frac{d \cdot V}{S \cdot t}$$

where:

- F_i = cumulative fractional release of the i^{th} radionuclide
- d = composite density, (g cm^{-3})
- v = composite volume, (cm^3)
- S = composite surface area, (cm^2)
- t = leach time, (d)

At LASL (4) where change of leachant was done after 1 to 4 weeks and MML (5) where no change of leachant was done, results of tritium leach tests were expressed respectively by cumulative percentage activity removed and cumulative fractional release as a function of time period in weeks since immersion in the leach water. Fractional release was obtained by using the leach water sample activity to calculate tritium activity in the bulk leach water and then dividing by the total tritium activity initially in the specimen, corrected for decay (5).

It is known that IAEA in 1971 (6) recommended a standard method for reporting the results of leach tests. According to this method the results shall be expressed by:

1. a plot of the cumulative fraction of radioactivity leached from the specimen as a function of the total time of leaching, i.e. by:

$$\frac{\sum a_n}{A_o} \cdot \frac{V}{S} \quad \text{versus} \quad \sum \Delta t_n \quad \text{or} \quad \frac{\sum a_n}{A_o} \quad \text{versus} \quad \sum \sqrt{\Delta t_n}$$

where:

- a_n = radioactivity leached during the leachant-renewal period n
 A_o = radioactivity initially present in specimen
 S_o = exposed surface area of specimen, (cm²)
 V = volume of specimen, (cm³)
 Δt_n = duration (d) of leachant-renewal period n.

2. A plot of the incremental leach rate, R_n as a function of leach time (d). The incremental leach rate, expressed by cmⁿd⁻¹, is defined by:

$$R_n = \frac{a_n}{A_o} \cdot \frac{V}{S} \cdot \frac{1}{\Delta t_n}$$

where:

- a_n = radioactivity leached during the leachant-renewal period n
 A_o = radioactivity initially present in the specimen
 S_o = exposed surface area of specimen, (cm²)
 V = volume of specimen, (cm³)
 t_n = cumulated number of leaching days at the end of the leachant-renewal period n
 Δt_n = duration (d) of leachant-renewal period n.

The values for R_n are averaged over $\Delta t_n = t_n - t_{n-1}$, i.e. the duration (d) of the water-renewal period n. They should therefore be plotted against the corresponding leach time value calculated by the expression:

$$t_n - (t_n - t_{n-1})/2$$

The factors a_n/A_o and $\Sigma a_n/A_o$ represent the fractional and the cumulative fractional releases of the concerned radionuclide, while the factor V/S is included to make independent the result from the sample geometry and size.

In tests involving radionuclides whose half-lives are comparable in length to that of the test, A_o has to be corrected by the factor $e^{-\lambda t}$ (where λ is the decay constant for the radionuclide).

References

- (1) Lokken R.O. - A review of Radioactive Waste Immobilization in Concrete, PNL-2654 (1978).
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- (5) **Tritium Waste Control Reports, MLM 2484 (1978), MLM 2519 (1978), MLM 2644 (1979).**
- (6) **Hespe E.D. Editor - Leach Testing of Immobilized Radioactive Waste Solids, At. Energy Rev., 2, 1 (1971) 195.**

Appendix VII - BURIAL PACKAGE FOR TRITIATED LIQUID WASTES

The description of the burial package applied at MML for tritiated liquid wastes is summarized in Table I, taken from Ref. (1).

TABLE 1 - Recommended burial package for tritiated liquid wastes.

CONTAINMENT	
Primary:	rigid polyethylene, polypropylene, or equivalent corrosion and impact resistant material, with leak-tight closure; must fit inside 30-gal (115-litres) secondary.
Secondary:	asphalt coated 30-gal (115-litres) 17H steel drum.
Tertiary:	55-gal (210-litres) 17H steel drum.
SOLIDIFICATION	
Water:	maximum weight ratio of one part water to three parts dry cement-plaster mixture.
Oil and organics:	maximum weight ratio of two parts oil or organics to one part vermiculite or three parts "Absorbal".
TRITIUM CONTENT	
Maximum of 70,000 Ci (2.59 PBq) (~ 7 g tritium) per 30-gal (115-l) drum.	

The standard primary/secondary burial package is prepared by inserting a 27-gal (100-litres) polyethylene drum^a into an asphalt-coated 30-gal (115-litres) steel drum^b. The polyethylene drum is filled with either 81 kg (~ 90 litres) of a 3-to-1 dry mixture of perlited gypsum plaster and portland cement for water or 9.5 kg (~ 90 litres) of vermiculite for organic (pump oil) wastes; 32 kg (~ 90 litres) of "Absorbal" may be substituted for packaging organic wastes. The steel drum is then connected to the bottom of an inert handling enclosure for total containment during transfer of the liquid.

After calorimetry, the liquid waste is transferred via a calibrated metering pump into the polyethylene drum; the volume transferred is verified using calibrated sight glasses on the holding tanks. A maximum of 27 litres of water or 25 litres of pump oil is transferred into the polyethylene drum. When the transfer is completed, the polyethylene drum is sealed and the inert enclosure is flushed with argon to remove residual tritium. The polyethylene drum is checked for leakage, then the drum

^a DOT Specification 2S, polyethylene, 0.0625-in. minimum wall thickness, 27-gal capacity, closures to be two 2-in. Buttress threaded fittings (1).

^b DOT Specification 17H, 18-gauge body and head, 18.25-in. i.d., 12-gauge bolted ring, drop forged lugs, all external and internal surfaces coated with 10- to 15-mil Cabot's FLEXIBLAC #3230 (1).

is removed from the bottom of the enclosure. The void volume above the polyethylene drum is filled with asphalt^c, and the steel drum lid is sealed in place using General Electric RTV sealant and a bolted clamp ring. The steel drum is then checked for leakage.

The sealed, 30-gal (115-litres) drum is centered in a 55-gal (210-litres) steel drum containing ~ 4 gal (15-litres) of asphalt. Vermiculite or Absorbal is then poured between the two drums to a level ~ 2 in. (50 mm) below the top of the 30-gal drum lid. The remaining void volume is filled with more asphalt, and the 55-gal drum lid is sealed with RTV and a bolted clamp ring. Figure 1 shows the total burial package.

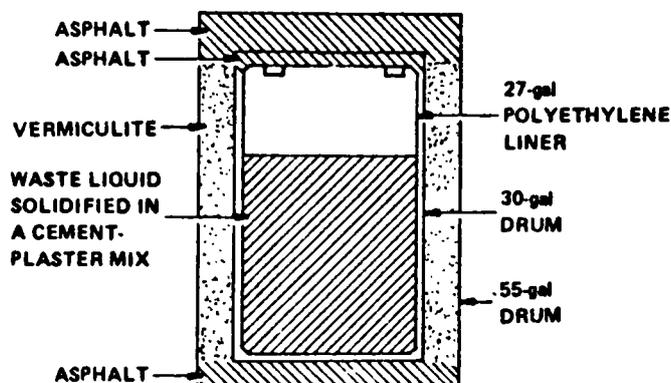


FIG. 1 - Schematic of tritiated waste package (1).

Reference

- (1) Mershad E.A. et al. - Packaging of Tritium-Contaminated Liquid Wastes, Nucl. Tech. 32 (1977) 53.

^c Bituminous coating, formulation to conform to specification MIL-C-102A-Type I (1).

GLOSSARY

ALUMINE	Aluminium Oxide (Al_2O_3)
BLAST FURNACE SLAG	A by-product generated during iron smelting in blast furnace. It is formed by the combination of the earthy constituents of the iron ores with the limestone flux.
BURNED GYPSUM	Calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) containing 6.2 wt% of water and obtained by dehydration of gypsum.
CEMENT MORTAR	A mixture of cement powder with water and sand (1-2 parts of sand for use under water or 3 parts for use in air) to give a whole of pasty consistency.
CHALK	White soft earthy limestone (CaCO_3) used for burning to lime (CaO).
CLAY	Basically $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ or $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
CLINKER	A term used to cover the partly fused or sintered ashes arising from the combustion of coal in large furnaces such as those used for steam raising at electricity power stations.
CONCRETE	A hardened mixture of cement or lime mortar with gravel or stone chippings to give an artificial conglomerate.
CURING TIME	The time required for a hardened cement block to obtain a large fraction (~ 90%) of its ultimate strength.
DIATOMACEOUS EARTH	An amorphous hydrated silicon oxide that occurs in nature in earthy form (Kieselguhr).
GYPSUM	Calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) containing about 20 wt% of water which occurs in nature and is by-product of phosphate fertiliser manufacture.
HARDENING TIME	The time required for set cement paste to develop a strong irreversible crystalline structure.
HYDRATED ALUMINE	Aluminium hydroxide, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$.
HIGH ALUMINA CEMENTS	A mixture of limestone and bauxite, which is fused (1500°C - 1600°C) or sintered (1000°C - 1200°C) and then finely ground.

HYDRAULIC CEMENT	A finely ground mixture containing a variable proportion of calcium silicates, aluminates and ferrites that has the property of setting to a very strong mass (block) when mixed into paste with water. "Hydraulic" is a term to specify the capability of hardening even under water.
LIME	Calcium oxide (CaO). Burnt lime, caustic and quick lime are synonyms.
LIME MORTAR	A mixture of powdered lime with sand and water to give a whole of pasty consistency.
LIME PASTE	Calcium hydroxide Ca(OH)_2 or $\text{CaO} \cdot \text{H}_2\text{O}$. Hydrated lime is a synonym.
LIME STONE	Kinds of rocks mainly of carbonate of calcium (CaCO_3).
PLASTER OF PARIS	A "burned" gypsum used for industrial purposes containing calcium sulfate hemihydrate usually mixed with some unchanged gypsum and some hard-burned material.
PORTLAND CEMENT	A mixture of finely divided limestone and clay burned to clinker at 1400°C and than finely ground.
POZZOLANA	A siliceous and aluminous material capable of reacting with lime in presence of water at ordinary temperature to produce cementitious compounds.
POZZOLANIC CEMENT	A finely ground mixture of portland cement and pozzolana (or fly ash) or hydrated lime and pozzolana.
SETTING TIME	The time which elapses after mixing cement with water (1) and before the paste will resist a certain arbitrary fixed pressure or, (2) before a sufficient cement hydration has taken place to give a mix of "friable" rigidity.
SLAG CEMENT	A mixture of blast furnace slag (previously quenched with water and finely ground) with ground limestone (CaCO_3) which is burned to clinker and then very finely ground. Iron portland cement is a synonym.
SILICA	Silicon Oxide (SiO_2).
SILICA XEROGELS	An amorphous dehydrated gel of silica (SiO_2) being capable of adsorbing up to about 40 wt% of water.
VERMICULITE	A mica-like material (i.e. hydrated sodium-alumino-silicate) which exfoliates when heated to $600\text{-}900^\circ\text{C}$ (expanded mica).

SLUDGE	A humid, glutinous or viscous substance or mixture such as a soft, moist and sticky earth (mud).
SLURRY	A fluid paste made by a mixture of solid material with water.
VERMICULITE	A mica-like material (i.e. hydrated sodium-alumino-silicate) which exfoliates when heated to 600-900°C (expanded mica).
ZEOLITES	A group of insoluble hydrated alumino-silicates of alkalis and alkaline earth, occurring in nature and produced synthetically. They have the properties of exchanging some of their basic constituents and losing or adsorbing water without changing their structure.

