CEMENT SOLIDIFICATION OF BWR AND PWR BEAD RESINS

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INTRODUCTION

The most troublesome waste categories to be solidified with cement are the bead resins generated by a BWR and a PWR unit, especially because of the swelling tendency of the beads and the retarding effect on cement setting and hardening caused by the boric acid in the PWR resins. To characterize the quality of the cement solidified product obtained from a full-scale system operating for about seven years, the following properties have been examined: the mechanical strength; the resistance to disintegration of the cement matrix depending on swelling of the granular resins; the water resistance of the solidified product; the leachability of cesium from the solidified product.

Core samples with a length of 1 m and a diameter of 0.1 m have been obtained from full-scale solidified products. They do not exhibit any change and do not show any tendency towards disintegration after being submerged in water for about 3 years. The crushing strength varies between 350-500 kg/cm^2 (5000-7000 psi) Concrete moulds split in two sections reveal a homogenous distribution of the granules in the solidified product.

The leach rate of cesium from naked specimens containing BWR and PWR resins after 50 days of leaching varies between $1.3 \times 10^{-9} - 9 \times 10^{-7}$ g/cm^2 · d depending on additives.

After 7 years of operation approximately 700 concrete moulds containing bead resins have been generated. Also 2000 moulds containing filter sludges have been produced. The moulds have been stored in a warehouse at temperatures between -20°C and 25°C (-4°F and 77°F) without any signs of deterioration or crack formation.

WASTE CATEGORIES. WASTE VOLUMES AND SPECIFIC ACTIVITY

Table I. BWR and PWR waste categories and annual generated waste volumes

BWR-wastes

Category	Source	Spec. act. Ci/m^3	Waste volume m^3	Number of concrete container	Surface dose rate (rem/h) on containers [1]
Granular resins	Reactor water cleanup system	300	12	25 70	20 (0.1) 1 (0.25)
Powder resins	Pool water cleanup system	10	3	4	0.5-1 (0.1)
Powder resin	Condensate cleanup system	0.1	25	30	< 0.1 (0.1)
Granular resin	Liq. waste system	1-10	5	10	0.1-1 (0.1)
Evaporator concentrate	Floor drain	0.1-1	No production during seven years		
				70-115	

PWR-wastes [2]

Category	Source	Spec. act. Ci/m^3	Waste volume m^3	Number of concrete container	Surface dose rate (rem/h) on containers
Granular resins	Primary systems	1000	10	60 120	4 (0.25) 2 (0.25)
Granular resins	Sec. systems	< 0.1	15	20	<< 0.1 (0.1)
				80-140	

1) Figures in parenthesis: Wall thickness (in m) of concrete container.

2) PWR-wastes. H_3BO_3: 60 g/kg waste.

PLANT DESIGN AND SYSTEM OPERATION

A flow sheet of the system is shown in Fig. 1. The prefabricated concrete moulds are transferred to the solidification position by means of a programmed and remotely controlled transport vehicle. The moulds are filled with a closely controlled mixture of partially dewatered waste, additives and cement. The mixture in the mould is homogenized with a remotely controlled mechanical stirrer which is left in the solidified waste and serves as reinforcement. The process is supervised by means of weighing, radiation monitoring and closed circuit television. Special attention has been paid to the problem of cleaning the system after operation and to prevent spread of air borne activity to the surrounding premises. When the filling and mixing operations are completed, the mould is transferred to the capping position. Here, a special type of dry concrete is mixed with a small volume of water and poured on top of the solidified waste in the concrete container. After setting of the concrete lid the block is transferred to the site storage.

PARAMETERS WHICH WILL HAVE INFLUENCE UPON THE SOLIDIFIED PRODUCT

The water-to-cement ratio and the resin concentration

To obtain an acceptable solidified product the water content of the resins - i.e. the total water content in the waste to be solidified - must be well known so that a correct and an acceptably low water-to-cement ratio ($w/c \leq 0.40$) can be obtained.

Also, the resin content of the solidified product is limited by the requirement of sufficient space between the granules.

The three component diagrams for bead resins, water and cement (in % by volume) is shown in Fig. 2 where the line I in the diagram refers to an addition of transport water corresponding to about 16 % of the resins. The line II refers to no addition of transport water, that is even level of settled resins and water. This means the waste consists of granules, void water and gel water.

During about seven years of full scale operation the solidification of bead resins has been achieved within the area B_2 B_3 C_3 C_2, where the lines B_2 B_3 and C_2 C_3 correspond to a w/c ratio of 0.40 and 0.30 respectively, i.e. the w/c ratio of the

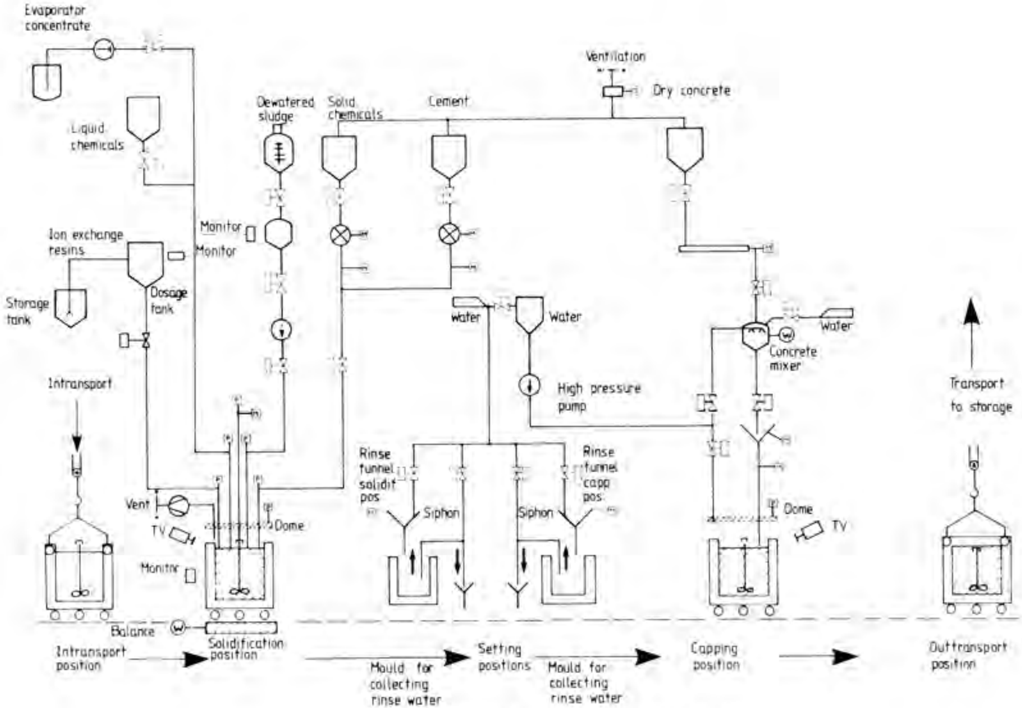

Fig 1 – Concrete Solidification System

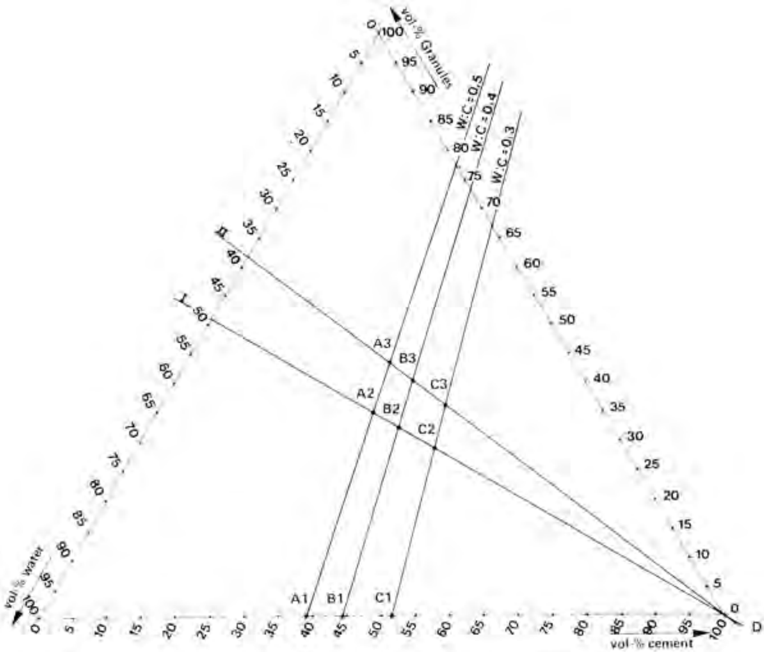

Fig. 2. Three Component Diagram (% by vol.) for the System: Water-Resins-Cement

solidified product < 0.40. It must be pointed out that swelling of the beads can take place and completely destroy the cement matrix if the w/c > 0.40, that is the line B_2 B_3 constitutes the upper limit of the w/c ratio.

The point B_2 corresponds to about 32 % by volume of resins in the solidified product. To meet the requirement of sufficient space between the granules in the solidified product the maximum amount of beads corresponds to about 40 % by volume of the product, i.e. point B_3 in the diagram. The line B_3 C_3 constitutes the upper limit of the concentration of beads in the solidified product.

To prevent water transport in the solidified product and to inhibit any tendency of swelling of the granules after solidification and to make the product resistant to frost cracking proprietary chemicals are added before mixing the waste with cement.

The influence of boric acid

As shown in Fig. 3, curve IV, boric acid is an excellent retarder of cement setting, holding up setting and hardening indefinitely [1]. This effect of boric acid is inhibited by adding a complexing agent before mixing the waste with cement.

THE SPECIFIC ACTIVITY OF THE WASTE AND SURFACE DOSE RATE ON THE CONCRETE CONTAINER

The two wall thicknesses of the prefabricated concrete pre-forms used are 0.1 m and 0.25 m respectively. The wall thickness is chosen in each case to keep the surface dose rate of the mould $\leqslant$ 1 rem/h which is regulatory requirement in Sweden. The operator therefore has to know the activity level of the waste to be solidified. As shown in Fig. 4 the surface dose rate of moulds with varying thicknesses is plotted against the specific activity of the waste. It has been assumed that cement and additives dilute the waste to about twice the original volume.

By using concrete cubic pre-forms one achieves a waste product which is easily handled and transported and therefore suitable for storage at site, awaiting final disposal in conjunction with plant decommissioning. However, it should be pointed out the use of prefabricated moulds is of course not a prerequisite for applying a concrete solidification process as described here. Any type of "container" could be utilized if

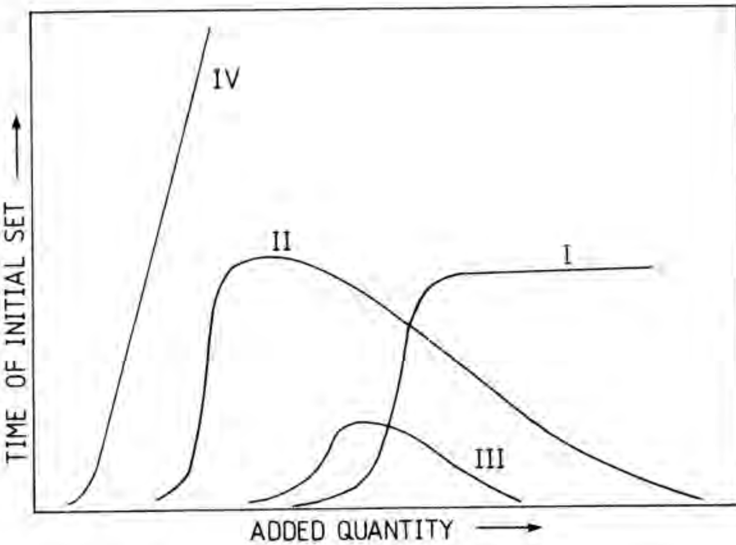

Fig. 3.- Action of various retarders

Examples of salts in the different groups

I: $CaSO_4$ $2H_2O$

II: $CaCl_2$

III: Na_2CO_3

IV: $Na_2B_4O_7$

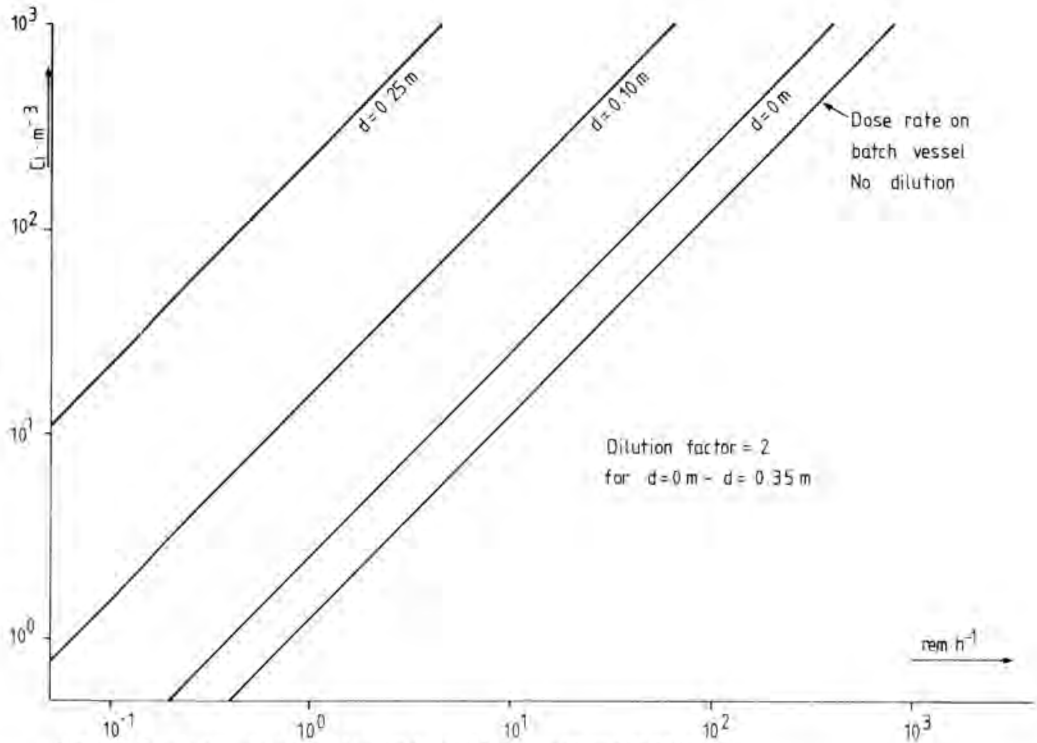

Fig.4.- Surface dose rate and activity concentration

there are no requirements on surface dose rate of the product to be stored and disposed of.

In Fig. 5 the surface dose rate on concrete containers with different wall thicknesses (d in meter) is plotted against the specific waste volume which is defined as cubic meter resins per cubic meter storage volume. In this special case the specific activity of the waste is 100 Ci/m^3. As seen from the diagram the surface dose rate on a steel container (d = 0 m) is about 45 rem/h with a dilution factor of 2. The specific waste volume is about 0.53 $m^3 \cdot m^{-3}$, i.e. when 530 liter settled resins is solidified as described above the storage volume needed will be 1 m^3.

When using a concrete container with a wall thickness of 0.1 m and the dilution factor is 2 the specific waste volume will be about 0.31 $m^3 \cdot m^{-3}$ and the surface dose rate will decrease to about 7 rem/h.

THE SOLIDIFIED PRODUCT

Core samples with a length of 1 m and a diameter of 0.1 m have been obtained from full scale solidified products. The core samples do not exhibit any change and do not show any tendency towards disintegration after being submerged in water for about three years.

The crushing strength varies between 350-500 kg/cm^2 (5000-7000 psi).

Concrete moulds split in two sections reveal a homogenous distribution of the granules into the cement gel.

Now, after seven years of operation, approximately 700 concrete moulds containing medium level waste (bead resins) have been generated. An additional 2000 moulds containing low-level waste (filter sludge) have also been produced. They have been stored in a warehouse at temperatures between -20°C and 25°C (-4°F and 77°F) without any signs of deterioration or crack formation.

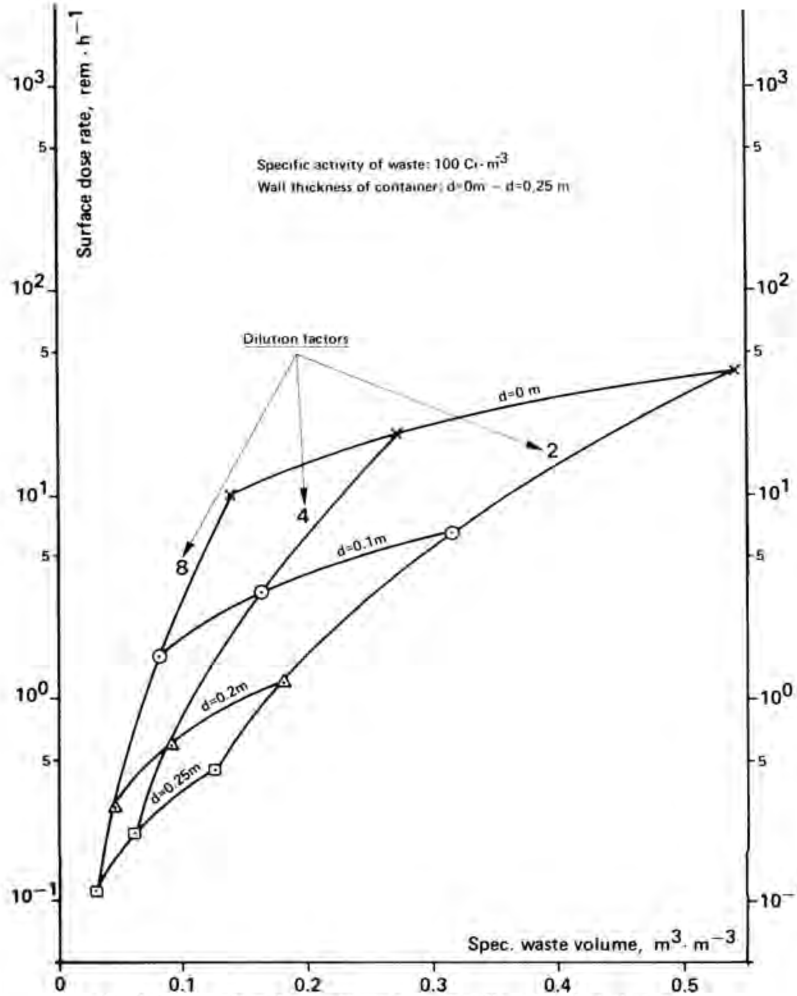

Fig. 5. Surface Dose Rate on Containers with different Wall Thicknesses versus Spec. Waste Volumes.

THE LEACHING OF ^{137}CESIUM FROM THE SOLIDIFIED BEAD RESINS

The leach rate of ^{137}cesium from naked specimen containing simulated BWR and PWR bead resins contaminated with ^{137}cesium and non radioactive CsCl has been determined after 50 days of leaching in tap water. Vermiculite or Zeolon-900 was added to some of the mixtures to test the retention efficiency on cesium leachability. The results of the leach tests are given in Table II.

The modified effective diffusivities given in Table II have been used to compute the diffusion of ^{137}cesium from bead resins solidified with cement in concrete moulds, which have an internal volume of 1 m^3 and the external dimensions of 1.2 x 1.2 x 1.2 m. The wall thickness is 0.1 m. A non radioactive concrete lid (0.1 m) is poured on top of the solidified waste. The moulds are assumed to be submerged in water containing no cesium. For long leaching times the decay of ^{137}cesium in the product and in the leachate has been taken into account. In the calculations the diffusion resistance of the concrete mould walls has also been taken into account.

For solidified BWR bead resins without any additives in the grout a comparison is made between the amounts of ^{137}cesium leached from an intact mould, a mould split in two and an intact mould containing 1 % vermiculite in the shell (Fig. 6). As seen from Fig. 6 the presence of vermiculite in the shell has some retention efficiency of the leaching of ^{137}cesium. The maximum inventory amount of ^{137}cesium in the environment leached from a mould split in two with an exposed surface area of 2 m^2 (about 20 ft^2) will be about 3 % of the initial inventory after about ten years.

For solidified BWR bead resins with 5 % Zeolon-900 in the grout a comparison is made between the amount of ^{137}cesium leached from an intact mould, a mould split in two and an intact mould containing 1 % vermiculite in the shell (Fig. 7). By comparing diagram 2 in Fig. 6 which corresponds to a mould without any additives in grout or shell with diagram 3 in Fig. 7 it is evident that the leachability of ^{137}cesium can be reduced by a factor of about 100 with additives in grout and shell.

The same reduction efficiency on ^{137}cesium leachability is obtained for cement solidified PWR bead resins.

Table II. Modified Effective Diffusivities for ^{137}Cesium Leached from Cement Solidified BWR and PWR Bead Resins

Additives	Modified Effective Diffusivities D_e			
	BWR Bead Resins		PWR Bead Resins	
	D_e (cm^2/s)	D_e (cm^2/day)	D_e (cm^2/s)	D_e (cm^2/day)
No Additives in the Grout	1.01 E-08	8.7 E-04	1.27 E-08	1.1 E-03
1 % Vermiculite in the Grout	7.29 E-09	6.3 E-04	1.08 E-08	9.3 E-04
2 % Vermiculite in the Grout	4.51 E-09	3.9 E-04	8.00 E-09	6.9 E-04
2 % Zeolon-900 in the Grout	3.00 E-10	2.6 E-05	2.08 E-10	1.8 E-05
5 % Zeolon-900 in the Grout	3.24 E-11	2.8 E-06	2.43 E-11	2.1 E-06

Remarks: The amount of additive in each Grout is based upon the amount of Cement added to obtain a w/c ratio of 0.35.

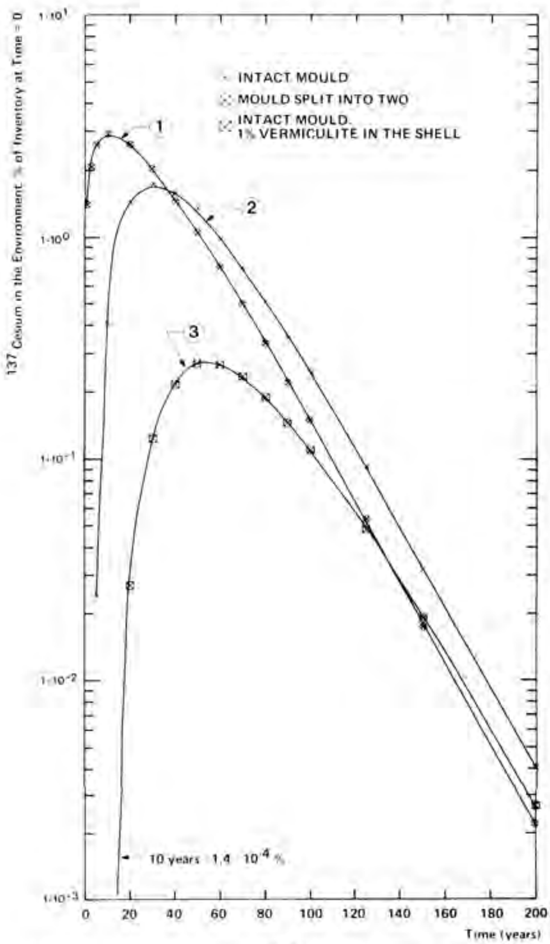

Fig. 6. Comparison between the ^{137} Cesium Inventory in the Environment Leached from an Intact Mould, a Mould Split into two and an Intact Mould with 1% Vermiculite in the Shell. Decay in Product and Decay in Leachant. Solidified BWR Bead Resins. No Additives in the Grout.

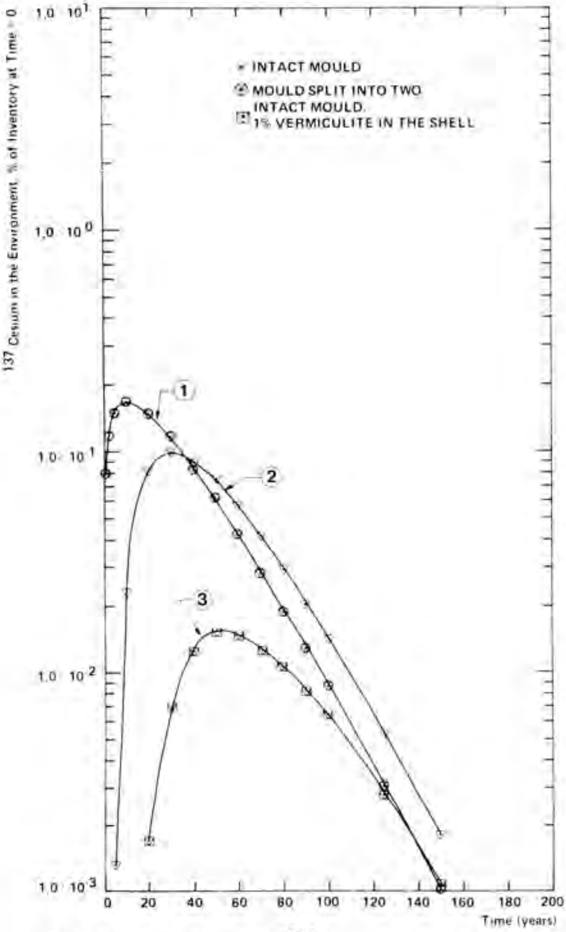

Fig.7. Comparison between the ^{137}Cesium Inventory in the Environment Leached from an Intact Mould, a Mould Split into two and an Intact Mould with 1% Vermiculite in the Shell. Decay in Product and Decay in Leachant. Solidified BWR Bead Resins. 5% Zeolon-900 in the Grout.

References

(1) Lea, F M: The Chemistry of Cement and Concrete.
Third ed. Edward Arnold (Publishers) Ltd. London 1976.