4.0 ATTACHMENT A

Review of the Russian Experience on Inorganic Binders for Waste Treatment and Tank Closure - Final Report

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Designing-Constructing and Industrial-Inculcating Enterprise

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THE REPORT
" The Review of the Russian Experience on Inorganic Binders for Waste Treatment and Tank Closures "

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Summary.

Keywords: radioactive wastes, tanks for waste storage, radiation - dangerous objects, cementation of radioactive wastes, portland cement mixtures, radiation stability, radiolysis, radiolytical gases release, durability of the cement compositions, leaching of radionuclides, large scale experience.

In this report it is given the review of results of researches carried out in Radium Institute and in number of other Russian enterprises directed on elaboration of high-performance concrete - conserving agents designed for solidification of liquid radioactive wastes and for transfer into ecological - safe state of HAW storage tanks and decommissioned radiation - hazardous objects of nuclear power engineering. The existing Russian practical experience in the indicated area is also briefly described.

CONTENT.

INTRODUCTION.

The present review is prepared in accordance with subcontract No 8D6266-EE/2001-01 concluded with corporation " American Russian Environmental Services, Inc." The subcontract goal is to prepare a technical report on Russian experience with the use of inorganic binders for treatment of radioactive waste and for closing of waste tanks. For reflection of the Russian experience on use of cement grouts for waste treatment and tanks closure the following major subjects were determined, which should be reflected in the report:

- research of influencing of portland cement grouts composition on the mechanical strength and radiation stability of the solidified cement mixtures;
- studies of influencing of cement grouts composition on an yield of radiolytic hydrogen at high radiation doses of compositions;
- estimation of capability to improve cement grouts at their contact with groundwater due to introducing in them of the special additives;
- estimation of capability to decrease radionuclides leaching from cement grouts due to addition of the components, which can decrease migration rate of impurities in cement matrixes;
- practical experience on application of grouting methods for decommissioning of objects of nuclear power engineering and Navy nuclear radiation hazardous facilities;
- key technical problems regarding of improvement of cement grouts properties that might be resolved through an analytical and experimental research program during the potential next stage of the project;
- filled in survey of enhanced grout needs for tank closure provided by the SRTS customer.

The compositions on the basis of ordinary portland cement (OPC) and some other inorganic binders (blast furnaces slag (BPS) and pulverized fuel ash (PFA) are broad applying for solidification of low active liquid radioactive waste (1). In Russia and in USA cement grouts are applied also to conservation of radwaste tanks and other radiation - dangerous objects. The important direction of cement grouts usage is their application as construction materials and biological protection in containers and dry storages designed for long-term storage of burned up nuclear fuels.

For effective utilization in the mentioned above directions cement grouts should have a series of particular properties:

- high radiation stability that is especially important at usage of cement mixtures for decommissioning of objects with high level of irradiation (reactor compartments of nuclear powered vessels, burned up nuclear fuel storage);
- the structure of the cured grout should provide release of radiolytic gases without disturbance of monolith integrity;
- the structure of the cured grout should have low water permeability to ensure low leaching rate of radionuclides from the object in environment for all time of its long-term storage.

The special cement mixtures suitable for solidification of the liquid radwaste should have a following complex of properties:

- high radiation stability, that will allow to solidify radwastes with enough high level of activity;
- the structure of the cured cement mixture should have low water permeability to reduce to minimum release of the radionuclides from solidified radwastes in environment for all time of their long-term storage;
- the cured cement compositions should have high frost resistance;
- the cured cement mixtures should have low speed of leaching of the basic components of cement to provide high stability of the cured cement grout at contact with groundwater;
- the composition of cement grouts used for radwaste solidification should provide enough high mechanical strength at the high contents of soluble salts in cemented waste.

The primary goal which was put at realization of researches of cement mixtures with reference to treatment of liquid radwaste and decommissioning of radiation - hazardous objects including waste tanks was concluded in elaboration of cement mixture compositions which in the most degree satisfy to the presented above requirements.

Previously the literature on structure and properties of cured cement mixtures was studied with the purpose of selection of rational paths for looking up of cement mixtures composition possessing a given complex of properties.

The main features of structure and properties of hardening cement mixtures with reference to problems of radwaste treatment and radiation-hazardous objects decommissioning.

The term "cement" usually implies portland cement or materials containing portland cement. The cement produces by high temperature calcination with a partial melting of materials having high content of calcium oxide. The obtained product (clinker) is crushed up to rather high specific surface (approximately 4000 cm^2/g) to activate cement. The cement hardening begins when this powder is mixed with water. At preparation of hardening cement mixtures the water-cement weight ratio is usually selected within the limits of 0.25-0.6; the mixtures with smaller water-cement ratio become rigid and lose plasticity whereas at the greater ratio mixtures can be stratified and liberate water. The prepared mixtures must be used within 1-2 hours then their setting starts. The development of strength becomes noticeable only in 1-2 days. Then the strength fast accrues.

In general all processes of cementation have a" window" 1-2 hours, during which the prepared mixture should be used. In further it is necessary to allow to cement to hydrate chemically without mechanical effects. The decelerators and boosters of cement setting are known, but their long-time influencing on properties of cement especially in conditions of irradiation is not enough well established and their applying for cemetnation of radiation - dangerous objects can not be recommended and therefore it is necessary to work with cement mixtures in the mentioned above period (I).

Internal structure of cured cement mixtures.

In structure of the cured cement it is possible to mark three characteristic features: a matrix of solid phases, both crystaline and amorphous, system of pores of the different size and form and aqueous phase located in pores. The model of a microstructure of cured cement is shown) on fig. 1.

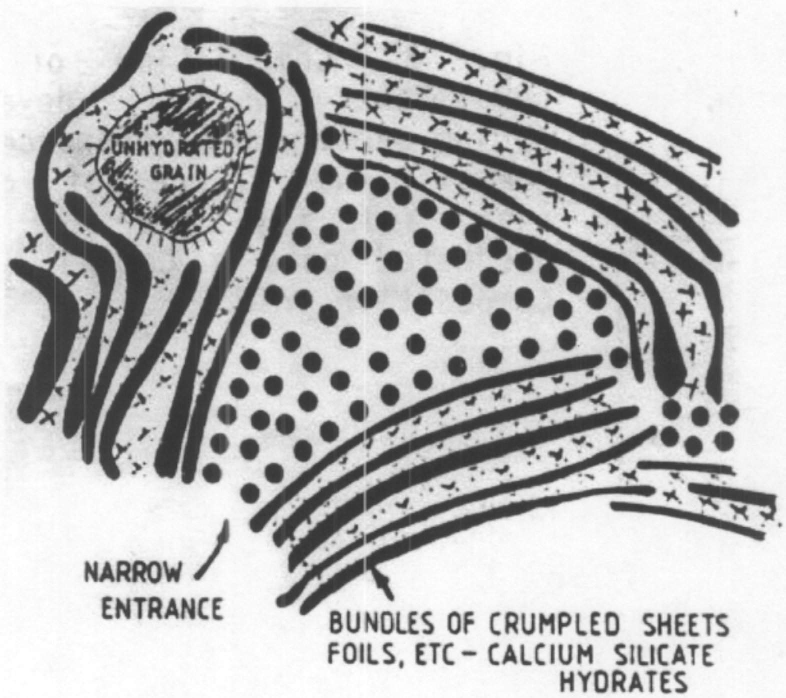

Fig. 1. Model of a microstructure of cured cement.

The gel of calcium hydrosilicate (C-S-H) is the most important component of solid phase of cured cement mixture as it contains main part of micropores. C-S-H phase is almost amorphous. As it can be seen from fig. 1, the phase of C-S-H gel consists from elements, the centers of which are grains of cement surrounded with products of its hydratation. Each element has flaky structure; the random packaging of these units creates a grid of micropores. It is not surprised that the most part of sorbtion potential of the cured cement is determined with micropores of C-S-H gel. The conducted researches show, that normally prepared samples of concrete, as a rule, do not contain pores with size > 1 micron and the main part of pores has the size < 0.1 microns. These pores determine the diffusion characteristics of cement mixtures in relation to radioactive ions therefore measured for them diffusion constants are not property of cement matrix, but concern to system pores - matrix. It is necessary to mark that in cured cement mixtures there are also other kinds of pores. In space between hydrated and not hydrated fragments of cement so-called capillary pores are formed. These pores have large sizes than pores of C-S-H gel. Common and capillary porosity is reduced with growth of degree of cement hydration, gel porosity increases a little because the volume of C-S-H gel (2) is augmented.

C-S-H gel acts as a main factor controlling pH of cement mixtures at the greater cure period. The Ca/Si ratio in C-S-H gel varies within the limits 1.8-0.9. At Ca/Si ratio 1.8. where C-S-H gel coexists with $Ca(OH)_2$, the equilibrium pH value practically equal to pH of saturated solution of calcium hydroxide. At decreasing of this ratio concentration of calcium in aqueous phase and pH are descended. The same decrease will be obtained as a result of leaching, as the cement will lose the most soluble calcium compounds. The pH of aqueous phase in pores of concrete has high importance for it properties as material for conservation of radiation-hazardous objects, since the high pH value promotes a decrease of solubility of a number of radionuclides, in particular, of most dangerous long-lived α-emitters (3) and favours to decrease of corrosion of carbon steel.

Usage of the additions for modification of properties of cement mixtures.

Addition of different components for modification of properties of cement mixtures is widely used in practice. In the table I some materials frequently added in cement are presented and the effects which are obtained with addition of such component are shown too (I).

Table I.

Materials adding in cement mixtures for improvement of their properties.

Material.	Effect from the component.
Fly ash from coal combustion.	Decrease permeability, increase mixture fluidity, lower initial heat evolution.

Ground granulated blast furnaces slag.	Decrease permeability, lover internal E_h and initial heat evolution and increase mixture fluidity.
Natural puzzolans.	Increase of sorption.
Microsilica. Superplasticizers.	Decrease permeability, increase sorption. Reduce water content and permeability.
$Ca(OH)_2$, NaOH	Condition borate waste and ensure set.
Sodium silicate .	Precipitate heavy metals, decrease permeability.
Miscellaneous getters: chemical and structural.	Reduce solubility of specific radwaste species e.g. Ag^+ for iodine conditioning.
Organic polymers.	Decrease permeability, getter for tritium.

It is possible to divide materials adding in cement into three groups. One group including natural puzzolane materials, ash, microsilica and slag can be called puzzolanic because these materials are activited with cement, react with water and cement and become the integrated part of cement matrix. The size of particles of these materials are usually less a little than size of cement particles, so the formed matrix have a little more dense packing of fragments than cement matrix and provides smaller permeability. The siliceous fly ashes and slags have a high content of glass, which concerns to main puzzolanic components (4, 5). In the short term materials of this group are enough inert and more active part of mixture (cement or $Ca(OH)_2$) determine properties of mixtures in this period.

Other materials in the table I are mainly modifying agents for matrix. The cement is usually mixed with quantity of water which is sufficient to receive fluidity of mixture appropriate to the application. But such fluidity usually receives at excess of water over that is required for a chemical hydration, it leads to porous and permeable matrix. Critical water-cement ratio indispensable for full hydration of portland cement is equal approximately 0.24, but such mixture is too hard for practical usage. The demanded fluidity can be reached at low water content by adding of superplasicizers, which are the high-molecular polar organic compounds (for example sulphonated melamin, naphthalene formaldegyde polymers or lignosulfonates(6). As usual 0.2-2 % of plasticizer, depending on it type, is diluted in mixing water. It enables to receive normal fluidity of mixtures at low water content that give possibility to obtain less permeable product. The final destiny of plasticizers in cement is not completely known. Probably initially they are fast sorbed on the products of cement hydration with the subsequent desorption and partial irreversible precipitation.

Calcium and sodium hydroxides are used for acid wastes neutralization and to condition borates which have negative influence on cement setting and even can make it impossible; addition of hydroxides reduces borates influencing.

The applying of sodium silicate is described in the literature (7), but it is not used widely in practice. This compound is soluble in water and precipitates a wide range of metallic ions from solution usually in the amorphous form, however nature of precipitations in cured cement matrixes is poorly known.

Particular getters it is offered to use to reduce leaching components of the radwastes badly sorbed by cement, for example of cesium and iodine (8). For an iodine it is offered to use addition of silver or barium (9, 10). As getter for cesium it is possible to use zeolites (II). However capacity of such components is limited because of chemical reaction between cement and zeolites. Besides the zeolite capacity is decreased because of competition of K^+ and Na^+ ions presented in cement (12). The final result of it is the necessity to add in cement of high quantity of zeolite to lower Cs^+ leaching. It results in a number of disadvanages: the mixture has high consumption of water and low compression strength. Thus the getters application is rather specific and demands special consideration in each particular case.

The organic polymers also can be used for modification of cement matrixes. In general it is necessary to concern with caution impregnation of cement matrixes with organic polymers as the diffusion coefficients in polymers are rather high and long-term stability of polymers to irradiation and degradation under an environmental stress is either unsatisfactory or unknown. The possible advantage of polymeric -cement matrixes can be improvement of immobilization of tritium (13) .

Effect of elevated temperature and radiation.

As it was noticed above, major component determining long-term properties of cured cement mixtures is C-S-H gel, which at ordinary temperatures is metastable, but exists long, natural samples of such phase with age $20*10^5$ years (I) are known. At temperature 170-180 ^{0}C this phase crystallize in autoclave during 16-24 hours. In result of gel crystallization pH of pore liquid is decreased on 1-2 units in comparison with C-S-H gel having equivalent composition, besides a considerable change of this phase volume can take place in result of crystallization. In the literature practically there are no data on rate of crystallization of C-S-H gel at temperature below 100 ^{0}C, but it is possible to suppose that the considerable temperature rise inside of curing cement mixture is extremely undesirable because of hazard of C-S-H gel crystallization.

The information, available in the literature, demonstrates that even the high doses of absorbed γ- radiation have not negative influence on the properties of dry cement (14). The effect of irradiation on cured cement mixture is appeared basically through radiolysis of water presented in it.

Main result of water radiolysis is release of gases and, first of all, of hydrogen. Irradiation of cement mixture can also modify structure of it and increases degree of it crystallinity (15)

The yield of hydrogen at radiolysis of water in cement mixtures depends on their composition, in particular, from compos ition of binders, which was used at their preparation. So it was noticed that trend of hydrogen yield for mixtures in which as binders were used ordinary portland cement (OPC) and its mixture with blast furnace slag (BPS/OPC) and fly ash (PFA/OPC) is: :BPS/OPC > OPC> PFA/OPC.

This in part may be attributed to differences of composition of aqueous solutions in pores (16).

Presented above literature information on structure and properties of cured cement mixtures allows to dedicate following main directions in elaboration of optimal composition of cement mixtures designed for radwastes treating and conservation of radiation-hazardous objects:

- usage of superplasticizers with the purpose to decrease quantity of water which is necessary for obtaining cement mixtures with demanded fluidity and low permeability;
- looking up of the addition components and filling materials ensuring to cured mixtures a gas permeability enough for deleting of radiolytical gases at preservation of their high water tightness;
- looking up of mixtures composition with a low yield of radiolytical hydrogen;
- research of possibility of using of the components sorbing radionuclides for decrease their leaching from cement mixtures.

In this report the results of experimental researches carried out in these directions are presented.

2. EXPERIMENTAL ENVESTIGATION OF PROPERT IES OF SPECIAL CEMENT MIXTURES.

The main results of the carried out researches are reviewed below. In the given section of the report the techniques of experimental researches are briefly shown also. It is necessary to mark that during preliminary researches 22 cement mixtures of different composition were tested. The mixtures possessing the most favourable combination of properties were selected for further researches. The compositions of these mixtures are shown in the table 2.

Table 2.

Composition of investigated cement mixtures.

No of mixture	Main components of Mixture		Modifying Components.		Water : solid Ratio (W/S)
	Material	Content, % vol.	Material.	Content, % vol.	
1.	Cement Shungizit filling	66.0 33.7	S-3 SDO	0.7 0.05	0.24

	material				
2.	Cement Shungizit filling material Shungizit sand	40.0 20.0 40.0	S-3 SDO	0.7 0.05	0.35
3.	Cement Shungizit filling material Mordernite sand	40.0 20.0 40.0	S-3 SDO	0.7 0.05	0.30
9.	Cement Quartz sand	40.0 60.0			0.38
21.	Cement Shungizit sand Clinoptilo-lite Sand Microsilica	38.0 37.0 5.0 7.0	S-3	0.9	0.32

2.1. Experimental techniques.

2.1.1. Irradiation of cement mixtures.

2.1.1.1 The characteristics of the gamma -irradiation installation.

Irradiation of investigated cement mixtures was carried out on gamma - irradiaton installation of V. G. Khlopin Radium Institute, which had following basic parameters:

- Source of a gamma-radiation - Co - 60;
- Sizes of irradiation chamber:
  - height - 200 mm;
  - diameter -120 mm;
- Calculated dose rate of gamma-radiation - 150 rad / sek.

The real dose rate in the irradiation chamber was measured with usage of chemical dosimetry method based on radiation oxidation of divalent iron ions in sulphate media saturated oxygen of air, so-called Frank's dosimeter (17) .

2.1.1.2. Technique of cement mixtures irradiation.

Samples of cement mixtures were placed in glass cylindrical vessels with inner diameter and height 21-22 mm and wall thickness I mm or in glass ampoules with diameter 15 mm and length 90 mm with the same wall thickness. Vessels with samples of mixtures destined for research of composition and quantity of radiolytic gases were placed in titanium hermetic capsule with wall thickness 0.5 mm.

2.1.1.3. Tests of mechanical properties of cured cement mixtures.

The determination of compressive strength were carried out according to GOST 10180-90. The hydraulic press PD-10 (GOST 8905-73) was applied to tests. The inaccuracy of measurements of load did not exceed 2 % rel. Compressive strength (Rcom) of samples was calculated according to:

$$Rcom = F/A$$

Where: F - destructive load;
A – cross section area of sample.

The mechanical tests irradiated and not irradiated samples of the same composition were done simultaneously.

2.1.1.4. Test of cement mixtures air permeability.

The device AGAMA-2R was used for evaluation of cement mixtures air permeability. This device gave possibility to measure time which was necessary to definite volume of air pass through testing sample into evacuated chamber. As all tested samples had the identical geometrical sizes for comparison of their air permeability the value of rate of air accumulation in vacuum chamber was used.

2.1.1.5. Test of waterproof of cement mixtures.

Testing of waterproof of cured cement mixture samples was done in according to GOST 12730.5-84 on which the measure of waterproof is the water pressure (W) at which on a surface of test cylindrical sample there is no yet wet spot. The increase of water pressure was made by steps 0.2 MPa during 1-5 min After each step the stop during 16 hours was made.

2.1.1.6. Research of cement mixtures structure changes at irradiation.

For research of influencing of irradiation on structure of cement mixtures the methods X-ray phase analysis and differential thermal analysis were used.

X-ray phase analysis.

For identification of crystalline phases in investigated samples the powder method permitting to receive the information on chemical composition and structure was used . For obtaining diffraction pictures the X-ray diffractometer DRON-1,5 was used with copper anode X-ray tube at anode V = 30 kV and I = 25 mA. CuK α – radiation was filtered through Ni – foil.

The identification of crystalline phases was made by comparison of data obtained from diffractograms, with data presented in catalogue 1CPD5 issued by Integrated Committee of the Powder Diffraction Standards (USA).

Differential thermal analysis of cement mixtures.

The differential thermal analysis (DTA) of cured cement mixtures was carried out with help of derivatograph Q 1500 D of the Hungarian production.

During DTA it was fixed weight changes of grinded specimen of investigated mixtures at controlling heating from 20 to 1000 ^{0}C.

2.1.1.7. Research of quantity and composition of gases which are evolving at irradiation of cement mixtures.

The chemical analysis of gas phase accumulating in capsules and ampoules during irradiation of cement mixtures was made with gas chromatographic method. The gas chromatograph "Tsvet-100" was used for gas analysis. The conditions of chromatography and system of detecting were selected recognizing that the main anticipated components of gas phase evolving at cement mixtures irradiarion are: O_2, H_2, CH_4, CO_2. The accuracy of definition of the contents of these components in samples of gas was 5-10 %.

2.1.1.8. Research of leaching of radionuclides from cured cement mixtures.

Raduonuclides (Pu-239, Am-241, Cs-137, Sr-90) were added in water used for cement mixtures preparation as nitrates. Before beginning of leaching experiments all specimens of cement mixtures were cured during 28 days.

The technique of experiments on definition of speed of leaching of radionuclides from hardening compositions on the basis of cement corresponded to the guidelines of IAEA (18) and GOST 2914-91 (19). The distilled water was used as leaching liquid.

The concentration of radionuclides in samples of leaching water was determined radiometrically on α-radiation for Pu-239 and Am-241, on β-radiation for Sr-90 and on γ-radiation for Cs-137. The accuracy of activity measurement of samples was 5-10 % rel.

2.2. RESULTS AND THEIR DISCUSSION.

Influencing of gamma-radiation on mechanical properties, air permeability and waterproof of cement grouts of different compositions.

As it was already marked in the introduction, primary goal of researches, the results of which are reviewed in this report, is looking up of cement mixtures (concrete) compositions which properties meet to demands to concrete - conserving agents used for conservation (closing) of radiation - hazardous objects, including waste tanks. In this connection influencing of gamma-irradiation on a mechanical strength, air permeability and waterproof of concrete of different compositions was studied. The obtained results are shown in the table 2.2.1

The table 2.2.1.

Influencing of gamma-radiation on mechanical properties, air permeability and waterproof of concrete of different compositions.

No of concrete compo-sition	Time of curing, days	Dose of Gamma -radia-tion, Mrad.	Compre-ssive strength, MPa.	Air perme-ability, Cm^3/sec.	Water-proof W, tm.
1	28	266	43.5	0.037	12
	90	855	41.6		
	180	1710	56.0		
	270	2565	45.9		
	690	6000	40.2		
1c	28		27.5	0.022	12
	90		25.0		
	180		20.1		
	270		29.7		

2	28	266	25.4	0.263	10
	90	855	25.0		
	180	1710	28.0		
	270	2565	26.7		
	690	6000	33.9		
2c	28		16.0	0.04	2
	90		16.8		
	180		14.7		
	270		17.4		
3	28	266	20.5	0.11	2
	90	855	21.0		
	180	1710	21.1		
	270	2565	23.8		
	690	6000	19.4		
3c	28		15.5	0.322	2
	90		15.0		
	180		13.7		
	270		16.3		
21	28	266	31.3	0.029	> 12
	90	855	34.9		
	180	1710	39.5		
	270	2565	38.8		
21c	28		37.5	0.03	> 12
	90		35.0		
	180		39.2		
	270		39.0		

As it is visible from the data of table 2.2.1., irradiation of compositions 1-3 at their curing during 28-690 day (the absorbed dose 266-6000 (Mrad) results in increase of compressive strength in comparison with control samples of cement grouts curing in normal conditions (1c-3c). For composition N 21 some decrease of strength marked at curing period 28-180 days under effect of gamma-radiation, however at the greater curing period strength of sample hardening in normal conditions and under irradiation are equalized. The obtained results allow to draw a conclusion that the gamma-irradiation of investigated compositions on the basis of portland cement with dose up to 3000 - 6000 MRad will not render negative effect on mechanical strength of the cured compositions.

Evolution of radiolytical gases at gamma-irradiation of cement mixtures.

For definition of conditions ensuring safe long-term storage of decommissioned radiation - hazardous objects, the knowledge of composition and quantity of gases evolved at irradiation of cement mixtures used at their closure is necessary.

With this purpose two series of experiments were conducted, the goal of the first of which was estimation of composition of gases released at gamma-irradiation of cement mixtures, and the goal of the second series was determination of quantity of hydrogen evolved at irradiation of mixtures of different compositions.

The results of analysis of gas phase in titanium capsules are shown in the table 2.2.2.

The table 2.2.2.

Composition of gas phase in capsules at different radiation time.

Time, days.	Dose of Gamma-radiation, Mrad.	No of concrete compo-sition	Composition of gas phase in capsule, % vol.			
			H_2	O_2	CO_2	CH_4
0	0	1	< 0.0001	78.1	0.03	-
0	0	2	< 0.0001	78.0	0.02	-
0	0	3	< 0.0001	77.9	0.03	-
28	266.1	1	3.3	10.0	0.01	< 0.1
		2	0.1	18.6	0.1	0.02
		3	12.0	13.1	0.01	0.2
36	342.1	2	0.1	18.6	0.1	0.02
64	608.2	1	1.2	14.4	0.06	0.15
		2	0.5	11.1	0.02	0.16
		3	8.5	15.6	0.03	1.1

The results of the analysis of gas phase composition in capsules have shown that at irradiation of cement mixtures that evolution of hydrogen and small amounts of methane take place. Evolution of hydrogen is connected with radiolysis of water containing in cement mixtures. Methane evolution is the result of radiolysis of organic components (superplasticizer S-3 and component SDO), added in mixtures during their preparation. Literature data show that methane is one of the main products of radiolysis of complex organic compounds (20). Apparently that at estimation of safety of long-term storage of radiation - hazardous objects filled with cement mixtures, it is possible to consider only hydrogen release, since quantity of other fire hazard gas - methane is insignificant.

For more reliable determination of hydrogen quantity released at gamma-irradiation of cement mixtures, the experiments on their irradiation in soldered glass ampoules were done that eliminated a capability of leakage of gases during irradiation. The obtained results are shown in table 2.2.3.

The table 2.2.3.

Evolution of radiolytic hydrogen at irradiation cement mixtures in glass ampoules.

No of concrete composition	Irradiation time, days.	Dose of Gamma-radiation, Mrad.	Hydrogen evolution rate, l/m^3 of mixture per hour.
1	5	47.5	0.018
	15	142.6	0.106
	29	275.6	0.064
2	5	47.5	0.034
	15	142.6	0.012
	29	275.6	0.058
9	5	47.5	0.025
	15	142.6	0.01
	29	275.6	0.01

As it is visible from the data of the table 2.2.3. the rate of hydrogen evolution does not exceed 0.11 l / m^3 of mixture per hour at dose rate 110 rad / sek. Apparently that the evolution of radiolytiical hydrogen is necessary to take into account as the dangerous factor only at conservation with the help of cement mixtures of objects with high radiation level.

Research of influencing of addition of boron carbide on release of radiolytical hydrogen from cement mixture at irradiation.

At concreting of the objects containing fissile materials for maintenance of nuclear safety it can be necessary to add in cement mixtures used for their conservation matters – neutron poisons. One of the most known matters of such type is the carbide of boron - SiC. In this connection the experiments on influencing of addition of SiC in mixture No 2 on radiolytical hydrogen release were made. With this purpose the irradiation of mixture No 2 with addition of SiC in soldered ampoules was made. The powder of SiC in quantity 50 g/kg of cement mixture was added in dry mixture of components of composition No 2 before mixing with water.

The results of determination of quantity of radiolytical hydrogen evoluted at irradiation of composition No 2 without and with addition of SiC presented in table 2.2.4.

The table 2.2.4.

Influencing of addition of SiC on evolution of hydrogen at irradiation of composition No 2.

Irradiated Composition	Weight of composition in ampoule, g.	Irradiation time, days.	Dose of Gamma-radiation, Mrad.	Hydrogen Evolution rate, L/m^3 of mixture per hour.
No2	12.3	5	47.5	0.034
	14.6	15	142.6	0.012
	10.0	29	275.6	0.052
No2 + SiC	10.7	7	66.5	0.028
	12.5	28	266.1	0.051
	12.7	70	665.3	0.053

As it is visible from the data of the table 2.2.4, the introducing of SiC in composition of cement mixture practically has not effect on rate of hydrogen evolution at gamma-irradiation of mixture.

Determination of quantity of radiolytical hydrogen which is held back by concrete.

At irradiation of compositions on the basis of cement radiolytic hydrogen is generating inside cement mixture and than goes out from mixture by diffusion through a system of cement mixture pores. It was possible to expect that the part of radiolytical hydrogen will remain in mixture phase. In this connection the research of content of hydrogen in samples of the irradiated cement mixtures was carry out.

The results of experiments on definition of hydrogen contents in samples of mixtures having compositions No 1, 2 and 3, irradiated 90 days (gamma-radiation dose 855 Mrad), are presented in the table 2.2.5.

Table 2.2.5.

The residual contents of hydrogen in samples of irradiated compositions.

Temperature of Mixture Heating, ^{0}C.	No of composition					
	1		2		3	
	Quantity of H_2		Quantity of H_2		Quantity of H_2	
	% from common.	l/t of mixture.	% from common.	l/t of mixture.	% from common.	l/t of mixture.
200	1.0	0.3	3.0	1.4	-	-
250	-	-	-	-	3.0	0.4
400	67.0	18.3	65.0	31.4	-	-
500	99.0	26.9	100.0	48.4	37.0	5.3
700	100.0	27.1	-	-	96.0	13.9
900	-	-	-	-	100.0	14.5

From the data, presented in the table 2.2.5, it is visible that all studied samples of the irradiated mixtures are containing significant amounts of hydrogen, and at heating the output of the main quantity of hydrogen is occurred at temperature 400 -500 ^{0}C for mixtures I and 2 and 500-700 ^{0}C for mixture 3. The fact that at temperature 200-250 ^{0}C the output of hydrogen is a little indicates that the binding strength of hydrogen with cement matrix is higher than at it physical adsorption. The data of the table 2.2.5 allow to suppose that the main part of hydrogen leaves from mixture at temperature at which destruction of crystallohydrates obtained at hydration of cement takes place. These crystallohydrates can retain hydrogen by formation of solid solutions similarly to chalkstone (21). Probably also holding of hydrogen by samples because of it including into closed micropores (22).

Research of influencing of the additives on leaching rate of radionuclides.

The results of experiments on influencing of addition into cement mixtures of matters which are capable to sorb radionuclides, on rate of their leaching are shown in the table 2.2.6.

The table 2.2.6.

Influencing of the addition of sorbents on leaching rate of Cs-137 and Sr-90 from cement mixtures.

Leaching time, days.	Total fraction of a leached radionuclide, % from initial quantity.							
	Composition I		Composition II		Composition III		Composition IV	
	Cs-137	Sr-90	Cs-137	Sr-90	Cs-137	Sr-90	Cs-137	Sr-90
1	0.05	<0.01	<0.01	0.15	0.26	<0.01	<0.01	0.11
4	0.18	<0.01	0.05	0.15	0.75	0.44	0.08	0.15
7	0.24	<0.01	0.12	0.28	0.92	0.72	0.08	0.19
13	0.50	<0.01	0.16	0.28	1.29	0.80	0.08	0.27
26	0.80	<0.01	0.16	0.28	2.28	0.84	0.08	0.33

The matters added to cement mixtures were:

- composition I – without addition;
- composition II – natural zeolite – clinoptilolite;
- composition III- antimony phosphate;
- composition IV- tin phosphate.

The selection of these inorganic sorbents was determined by that they are capable effectively to sorb radionuclides from solutions of miscellaneous compositions, including solutions, close on composition to pore solutions of cured cement mixtures (23, 24, 25).

As it is visible from the data of the table 2.2.6, the addition in cement mixture of the mentioned above components has essential influencing on leaching rates of Cs-137 and Sr-90.

The introducing in cement mixture of 10 % of clinoptilolite and tin phosphate results in decrease of fraction Cs-137 leached during 26 day in 5 and 10 times accordingly. The addition of antimony phosphate lead to increase of Cs-137 leaching.

In the case of Sr-90 the minimum leaching rate is watched for cement mixture without any additives, the introducing in a structure of composition any of the tested components results in increase of leaching rate, which is most significant in case of addition of antimony phosphate.

The results of the carried out researches have shown that the addition in cement mixtures of matters which are capable to sorb radionuclides, can reduce their leaching. However, the influencing of such components on properties of cured cement mixtures has complex nature and in some cases can result not in decrease, but even in increase of leaching rate which can be connected with negative effect of additives on structure of cured cement mixtures.

The results of done researches have shown that the composition of portland cement mixtures has high influence on properties of these mixtures. Changing composition of cement mixtures it is possible to obtain mixtures possessing complex of properties in the most degree adequate to areas of their applying.

In the present review we consider two fields of application of portland cement mixtures:

- conservation (closure) of radiation - hazardous objects of atomic engineering, in particular of waste tanks, reactor compartments of vessels with nuclear energy installations etc.;
- solidification and preparing for long-term storage of the liquid radwastes.

The optimal complex of properties of cement mixtures designed for applying in each of introduced above areas can be various.

So at usage of these mixtures for conservation of radiation - hazardous objects with high radiation level the important value has a high gas permeability of using mixtures because that allows to ensure going out of radiolytical gases without disturbance of concrete monolith integrity. For cement mixtures intended for solidification of the liquid radwastes middle and low level of activity the requirements of low leaching rate of radionuclides and high stability of mixture at affect of groundwater and other factors of environment of radwastes storage are going on the foreground.

Considering from these positions results of researches of portland cement mixtures it is possible to make following conclusions.

For conservation (closure) of radiation-hazardous objects with high level of radiation for which the release of significant amount of radiolytical hydrogen is possible, the most favourable combination of properties has the composition No 2, as it has a high gas permeability, that provides output of hydrogen from massive of the cured composition without disturbance of it integrity.

For conservation of radiation-hazardous objects with low radiation level, for which quantity of emanation of radiolytical hydrogen is insignificant, and for solidification of the liquid radwastes the preference is necessary to give to composition No 21, which has a low permeability, low rate of radionuclides leaching and highest stability to affect of groundwater from studied compositions on the basis of portland cement

Evaluation of service time of the cured cement mixtures at long-term storage under affect of gamma-radiation and factors of environment.

The different factors of an environment of storage act on the cured compositions utilized for conservation of radiation-hazardous objects or for cementation of radwastes prepared to long-term storage. These factors cause corrosion of cement mixtures that results in decreasing of their durability. As the cured compositions should ensure safe long-term storage of radiation-hazardous objects and cemented radwastes it is important to have a capability of the evaluation of durability of cement mixtures in conditions of their storage.

For estimation of demanded service time of the cured cement mixtures which is necessary for ecological safe handling with conservated (closed) radiation-hazardous objects and cemented radwastes it is possible to start with following reasons.

The radionuclides which can be contained in radiation-hazardous objects and radwastes can be divided into three groups

- short-lived nuclides with a half-life up to 2-3 years;
- the long-lived fission products, basic of which are Cs-137 and Sr-90, having a half-life about 30 years;
- superlong-lived nuclides (actinides, Pd-107, Tc-99, I-129) the half-life of which reaches hundreds thousand and even millions years.

For nuclides of the first group for their practically full disintegration it is enough several tens years and the reliability of cement mixtures on this period does not cause doubts.