METHODS AND PRODUCTION OF CEMENTATION MATERIALS FOR IMMOBILISATION INTO WASTE FORM. RESEARCH OF CEMENTATION PROCESSES FOR SPECIFIC LIQUID RADIOACTIVE WASTE STREAMS OF RADIOCHEMICAL PLANTS

L.P. SUKHANOV[†]

A.A. Bochvar High-Technology Research Institute of Inorganic Materials (VNIINM)
SNF and Radioactive Waste Management Centre, Moscow,
Russian Federation

Abstract

In the near future Russian Federation is planning to use industrial cementation facilities at two radiochemical combines - PA ”Mayak” and Mountain Chemical Combine. Scope of the research within the IAEA CRP contact No. 14176 included the development of cementation processes for specfic liquid radioactive waste streams that are present in these enterprisers. The research on cementation of liquid waste from spent nuclear fuel reprocessing at PA ”Mayak” allowed obtaining experimental data characterizing the technological process and basic characteristics of the produced cement compounds (e.g. mechanical strength, water resistance, frost resistance, flowability, etc.) immobilizing different streams of waste (e.g. hydrated-salt sludges, filter material pulps, mixture of hydrated salt slurries and filter material pulps, tritium liquid waste). Determined optimum technological parameters will allow industrial scale production of cement compound with required quality and higher flowability that is necessary for providing uniform filling of compartments of storage facilities at these sites. The research has been also carried out for the development of cementation technology for immobilization of pulps from storage tanks of Mountain Chemical Combine radiochemical plant. Cementation of such pulps is a difficult technological task because pulps are of complex chemical composition (e.g. hydroxides of manganese, iron, nickel, etc., as well as silicon oxide) and a relatively high activity. The research of cementation process selection for these pulps included studies of the impact of sorbing additive type and content on cement compounds leachability, flowability, impact of cement compound age to its mechanical strength, heat generation of cement compounds and others. The research results obtained allowed testing of cementation facility with a pulse type mixer on the full-scale. Use of such mixer for pulp cementation makes possible to prepare a homogeneous cement compound with the required quality. In general research performed provided better understanding of factors influencing characteristics of cement compounds during their production and use for storage and disposal. Investigations were performed using the simulated solutions and pulps, containing radionuclides. All facilities and equipment available used at A.A.Bochvar Institute.

1. INTRODUCTION

The IAEA CRP “The behaviours of cementitious materials in long term storage and disposal” has the aim to collect and disiminate experiences of scientific research of various participating organizations in estimating the properties and performance of cementitious materials used in waste conditioning systems.

The cementation (immobilization in inorganic matrix compositions) of arising and accumulated radioactive wastes (RW) is very important for safety of operating radiochemical plants. In the near future the Russian Federation is planning to use industrial cementation units at its two radiochemical

---

[†]All research was completed at A.A.Bochvar Institute. Co-authors were Zhaharova K.P., Naumenko K.P., Chimchenko O.M., Pogorelko O.N., Lebedeva A.V. (A.A.Bochvar Institute), Revenko Ju.A., Kravchenko B.A. (Mountain Chemical Combine).

combines - PA ”Mayak” and Mountain Chemical Combine. Liquid RW of these enterprisers that are envisaged for cementation includes different radioactive solutions and pulps with a complex miscellaneous content. Some of these components of liquid RW streams can significantly impact on the cementation process and on properties of produced cement compound. Therefore, it is necessary to investigate cementation process of these waste streams and to determinate factors impacting on characteristics and behaviors of cement compound in its production, as well as for storage and disposal.

The research within the IAEA CRP included the study of cementation process for specific liquid radioactive waste streams of PA ”Mayak” and Mountain Chemical Combine.

Scientific scope of this work included the broad research of cementation process and determination of properties of produced cement compounds with the major objective to provide the production of cement compounds that would satisfy national waste acceptance criteria and requirements. It was necessary to study physical and chemical processes occurring at production of cement compound and as well the impacts of some RW properties on cement compound characteristics (e.g. heat generation, loading of salts, hydroxide concentration, mixing method, liquid phase arising and others) for different waste streams. The research included studies of all main characteristics of cement compounds (e.g. mechanical stability, water resistance, frost resistance, flowability and others).

The scientific results contributed to this work are better understanding of the factors which can impact on characteristics of produced cement compounds containing different liquid radioactive waste (LRW) of radiochemical plants (hydrated-salt sludges, filter material pulps, tritium liquid waste, accumulated pulps from storage tanks and others). This knowledge should be sufficient for evaluation and determination of the behaviors of cement compound in its production stage, storage and disposal.

Main outcomes of research are:

a) selection of optimum technical parameters for cementation process,

b) obtaining data on characteristics of produced cement compounds,

c) knowledge of factors impacting characteristics of cement compounds during their production stage, storage and disposal.

Facilities used are laboratory and pilot cementation facilities; instruments and equipment for characterization of cement compounds (mechanical stability, water resistance, frost resistance, flowability and others); radiation control instruments; laboratory equipment for simulant samples of solvents and pulps preparation and characterization (mixers, scales, pH-meters and others); and computers and other techniques, used at A.A.Bochvar Institute.

Researchers and specialists of Mountain Chemical Combine took part in this work, besides specialists of A.A.Bochvar Institute.

2. RESEARCH METHOLOGY AND THE EXPERIMENTAL TECHNIQUES AND EQUIPMENT

2.1. Sample Preparation

The cement paste made by mixing of the components ,using the laboratory-scale equipment, is placed into the device designated for preparation of cement compound samples. The device represents a dismountable cartridge (cassette) consisting of several cells to allow making of cement cubes 2×2×2 cm in size. Upper surface of the cement paste is covered by a polymeric film to prevent desiccation (drying). The device is then placed in a humid-air atmosphere (i.e. in an exsiccator with water at the bottom). After being held for 28 days or for the other selected but fixed time, the samples are taken from the cells for further analyses.

2.2. Cement Paste Plasticity (flowability) Test

Plasticity of a cement paste is characterized by degree of its flowability measured by the viscosimeter using the standard testing procedure. The LRW and a binder are mixed in selected proportion for one minute and then are held for two minutes at rest. After holding, the obtained cement paste is intensively stirred and poured into the cylinder (with both ends open) placed at the centre of a horizontal glass plate with the marks on it (the marks are the concentric circles arranged with a step of 0,5 cm). The excess of the cement paste is removed from cylinder by a knife. Then the cylinder is turned upright with the result that the paste spreads over the surface. Average diameter of the resultant circle is the one, that characterizes flowability of the cement paste.

2.3. Determination of Ultimate Compressive Strength

Ultimate compressive strength is determined by means of a hydraulic press using the standard test procedure.

2.4. Determination of Frost Resistance of Cement Compounds

Frost resistance is determined by comparison of the mechanical (compressive) strength of the samples, which have been exposed to 30 cycles of alternate freezing and thawing, to the mechanical strength of the reference samples that are being held under room conditions during the test period. The selected freezing temperature was 20 degrees below zero and the thawing temperature was + 20±5°C. Frost resistance of a cement compound is considered satisfactory if the mechanical strength of the tested samples meet the requirement that is not less than 75 % of the mechanical strength of the reference samples and not less than permissible value of 50 kg/cm^2.

2.5. Immersion Tests (resistance during long stay in water)

Immersion tests are performed to assess water resistance (leachability) of a cement compound during long stay in water. Water resistance is determined by comparison of the strength of the samples held in water for 90 days to the strength of the reference samples held in the air under room conditions. Water resistance (index of leachability) of the compounds is considered satisfactory if the strength of the samples, which were held in water meet the requirement that is equal or not less than 75 % of the strength of the reference samples and not less than permissible of 50 kg/cm^2.

2.6. Long-Term Leaching Tests of Cement Compounds

Tests are performed to assess a degree of radionuclide fixation in a cement compound obtained after incorporation of nuclear waste into inorganic matrices (e.g. cement, slag portland cement, metallurgical slag). A degree of radionuclide fixation in a cement compound is determined by the rate of leaching of radionuclides and by the value of the activity that is passed into a solution from a cement compound. The samples are immersed in a distilled water at room temperature (20-25°C). The containers for leaching test are vessels provided with lids and made of polyethylene or other organic polymer.

A sample is tested to determine or to calculate the specific activity, the geometric surface and the mass.A sample is placed in the leaching container and is covered with a contact medium (water or a solution). The volume of a contact liquid should be such that the ratio of a numerical value of the contact medium volume (V, cm^3) to a numerical value of the geometric surface of the sample (S, cm^2) is in the range from 3 to 10. Furthermore, the contact medium layer should be not less than 1 cm above the sample.

After the sample is covered by the contact medium, the container is closed by the lid and is left for a predetrmined time. No contact-medium mixing or container shaking is performed. During the holding period, the test-room temperature is recorded.After predetermined periods of time (e.g. 1, 2, 3, 7, 14 and 28 days and then monthly or more, if necessary) the contact medium is changed. For this purpose, the contact medium is poured out from the container into an empty clean vessel. The container (with the sample) is rinsed with a small amount of distilled water, which is then poured out into the same vessel.

The tested sample is poured with a new contact-medium portion to continue the leaching process. The sample should not be dried out during water change.The poured-out contact medium and the sample wash water are analyzed to determine the total activity and, if necessary, the content of individual radionuclides**.**The tests are terminated if the leaching rate becomes constant or if the quantity of the radionuclides, which passed from the sample to the contact medium, reaches 20 % of their initial content in the sample.

Some equipment and devices used for testing are shoven in the ANNEX to this report.

3. CEMENT COMPOUND QUALITY REQUIREMENTS

There are two types of requirements that are specified for a cement compound:

1) The general requirements of national regulatory standards [1, 2]

This type of requirements includes determination of quantitative parameters of certain characteristics of cement compounds (mechanical strength, water resistance, frost resistance). If these requirements are satisfactory then safe transportation and long-term storage of cement compounds is considered as ensured.

2) The additional requirements that are not contained in regulatory standards

These requirements are dependant to characteristics of the waste, type of the cementation facility and the storage facility, as well as others factors. Additional requirements for cement compounds are defiend as:

- Maximum loading capacity of cement compounds, which is necessary for reducing costs of creating and operating a storage facility

- Sufficient plasticity (flowability) to ensure the cement compound discharge from a cementation facility mixer and the uniform filling of a container or the storage facility compartments (in case that such concept is chosen for PA “Mayak”).

- The heat released in the process of hydrating and hardering the matrix material should not hot up the cement compound above 90°C,

- Minimum free liquid phase should remain on the surface of the hardened cement compound

4. DESCRIPTION AND DISCUSSION OF RESEARCH RESULTS

4.1. The research of cementation process of radioactive waste from spent nuclear fuel reprocessing

At present all liquid ILW generated during spent nuclear fuel (SNF) reprocessing at radiochemical plant RT-1 of PA “Mayak” is directed without conditioning to a special open storage ponds for collection and long-term storage. Such practice does not comply with a modern safety requirements of RW management. The cementation industrial complex and cement compound storage facilities are planned to be created at PA “Mayak to addres this safety concern.

The planned new technological scheme for liquid ILW management at PA "Mayak" is to stop practice of releases of liquid RW into special open storage ponds and to perform remidial actions to shut them down in the future. Immobilization of RW into cement compound and its subsequent placement in near-surface storage (or disposal) facility is one of important steps for resolution of ecological problem at PA "Mayak".

4.1.1. Characteristics of liquid radioactive waste due for cementation

It is planned that the major portion of PA "Mayak" liquid ILW will be vitrified together with a liquid HLW. Cementation is to be applied only to such types of ILW that cannot be vitrified because of their chemical composition. The main types of liquid ILW due for cementation are shown in Table 1.

TABLE 1. CHARACTERISTICS OF PA "MAYAK" LIQUID ILW SUPPOSED TO BE CONDITIONED BY CEMENTATION

№	Liquid ILW streams	Liquid ILW characteristics
1	Ammonia solution	NH_4NO_3 = 45-60 g/l , NH_4OH= 3-10 g/l
2	Acidic decontamination solution	HNO_3 = 50 g/l , $H_2C_2O_4$ = 2 g/l NaF = less than 0,5 g/l
3	Acidic rafinate from extraction	Fe = 2-5 g/l , H_2SO_4 = 3-5 g/l , HNO_3 = 180-200 g/l
4	Concentrate resulting from membrane-sorbtion liquid LLW treatment	Saltcontent -20 g/l, i.e. $NaNO_3$ – 85-90%
5	Ion-exchange resins pulps	Solid/water ratio= 1:10
6	Manganese dioxide pulps	MnO_2 – 20 g/l
7	Filter perlyte pulps	Solid/water ratio=1:10
8	Tritium-containing LRW	Activity - till 1 Ci/l

4.1.2. Technological scheme of PA "MAYAK" liquid ILW management

Particularities of technological scheme of PO "Mayak" liquid ILW cementation are as follows.

The scheme is based on the following general provisions:

- The generated LRW would be collected separately in receiving tanks where selected types of waste could be mixed, if necessary;
- Salt solutions would be concentrated by evaporation before cementation. Nitric acid and ammonia could be distilled off to considerably reduce the volumes of cement compound and alkali consumption for neutralization of acid LRW, as well as return of the regenerated nitric acid for a new use. Besides, if ammonia is removed from alkali solutions, it will not be released from the cement compound stored;
- Evaporator concentrate would be neutralized and as results it will include the sludge of iron hydroxide;
- Containing LRW are planned to be cemented without pretreatment and separately from the other types of LRW since the cement compound needs additional protection against tritium losses during the storage period.

Particularities of technological scheme of PA "Mayak" liquid ILW cementation are as follows:

- cement compound would be placed directly into storage facility compartments (compartment volume – 380 m^3), or without a prior packaging into drums (this is option in consideration now);

- two options for cementation are considered for application: 1) separate cementation of different waste streams e.g. solutions, hydrate-salt sludge and filtering material pulps and 2) cementation of all ILW mixed waste streams (except tritium water which is planned to be solidified separately)

4.1.3. Experiments results and conclusion

4.1.3.1. General aspects

The purposes of the research were as follows:

1) Determination of basic technological parameters for cementation of liquid ILW, including salt solutions and pulps of hydroxides and filter materials,

2) Refinement of parameters for liquid RW cementation with high content of hydroxide pulp,

3) Development of the cementation process to obtain cement compounds with a higher flowability, necessary for uniform filling of storage facility compartments;

4) Determination of basic physical and chemical characteristics of obtained cement compounds (mechanical strength, water resistance, frost resistance, flowability, etc.)

5) Assessment of behaviours of obtained cement compounds under storage conditions.

The research were performed and applied to both main streams of liquid ILW generated during reprocessing of SNF: salt solutions with iron hydrated sludge and filter-material pulps. The following possible alternatives for cementation of waste streams were considered:

- Cementation of hydrated-salt sludge
- Cementation of filter-material pulps;
- Cementation of a mixture of hydrated-salt sludge and filter-material pulps
- Cementation of tritium liquid waste

4.1.3.2. Simulants used

The basic components of the hydrated-salt sludge are iron hydroxide and sodium salts of sulfuric and nitric acids. In actual conditions, the ratio of these two components in the cemented ILW is variable. Therefore, the simulates of various compositions were used.

4.1.3.3. Matrix materials

In most experiments, a mixture of portland cement (Grade PC500-D0) and bentonitic clay was used as a matrix material. The content of bentonitic clay in the matrix material in all the experiments was 10% by mass. Bentonitic clay, which was introduced from a cement compound being in contact with water, acted as a sorbent to reduce leachability of radionuclides, primarily Cs-137 [3]. The slag portland cement, a mixture of portland cement and metallurgical slag, was also used in a number of experiments.

4.1.3.4. Cementation of hydrated-salt sludges

The experiments with LRW simulates containing iron hydroxide, along with soluble salts (sodium nitrate, sodium sulfate, etc.), indicated that the quality of the produced compounds depend on many factors. The quantity of iron hydroxide in cemented LRW and the physical-chemical characteristics of pulp, which depends on the method of the pulp preparation (temperature, pH, holding time, etc.) are two variables of major importance.

4.2. Assessment of effect of a compound composition on flowability of cement paste and mechanical strength of a solid product

This series of experiments used freshly prepared simulates of hydrated-salt sludges. The sludge was mixed with the matrix material for 3 minutes. Flowability of the cement paste and mechanical strength were determined during experiments using the samples with different holding time. The results of these experiments are given in Table 2.

Findings from the experiments:

1) Within the same composition of hydrated-salt solutions with sludge, the solution/cement ratio is the key factor that influences the flowability of the cement paste and mechanical strength of obtained cement compound. With this ratio decreased, the cement paste flowability drops considerably and the mechanical strength increases. When the solution/cement ratio equals 1.47 and, respectively, the water/binder ratio equals 1.1, the mechanical strength does not reach required standardized defined value even within a year. With a smaller values of solution/cement and water/cement ratios, the samples develop necessary strength, but such process proceeds very slowly.

2) Double reduction of the iron hydroxide content in a cement compound, with other conditions being equal, results in increase of the cement-paste flowability, but is of little influence on the mechanical strength of a compound. Decrease of the water/ctement ratio to 0.5 results in notable increase of strength, but in this case the cement paste practically loses its flowability.

4.3. Assessment of effect of sludge age on quality of a cement compound

For assessing the effect of time of the hydrated-salt sludge storage from the moment of its generation till the moment of its mixing with the binder (age of sludge), the samples were prepared to contain 40% by mass of sludge of the following composition: $Fe(OH)_3$ – 30 g/l, Na_2SO_4 – 30g/l, $NaNO_3$ – 240 g/l. In all the experiments, solution/cement = 0.67, W/B = 0.5, and the loading capacity of cement compound was equal to 19 mass%. The sludge and the matrix material were mixed by a laboratory mixer for 3 minutes. The obtained results are presented in Table 3.

TABLE 2. EFFECT OF A CEMENT COMPOUND COMPOSITION ON FLOWABILITY OF CEMENT PASTE AND MECHANICAL STRENGTH OF A SOLIDIFIED PRODUCT

Composition of hydrated-salt sludge, g/l			Composition of compound, % by mass		S/C*	W/C**	Loading capacity), % by mass	Flowability of cement compound, mm	Mechanical strength of cement compound [σ_{comp}]	
$Fe(OH)_3$	Na_2SO_4	$NaNO_3$	Pulp	Binder					Time, days	[σ_{comp}], kg/cm^2
30	30	240	59.5	40.5	1.47	1.1	15.0	120	28 51 360	35 32 45
30	30	240	57.1	42.9	1.33	1.0	14.1	110	28 51 360	34 40 55
30	30	240	54.5	45.5	1.2	0.9	13.6	90	28 330	52 95
15	15	270	54.5	45.5	1.2	0.9	13.6	140	32 63 159	32 49 73
15	15	270	40	60.0	0.67	0.5	10.0	70	28 56	155 169

* S/C – the ratio of the waste in the cement compound mass to the matrix-material mass,
**W/C – the ratio of the water mass in the compound to the matrix-material mass.

Findings from the experiments:

1) With increasing age of the hydrated-salt sludge, the cement-paste fluidity drops. The mechanical strength variations does not show a clearly defined tendency. Furthermore, in all cases the mechanical strength is much higher than the standardized required value.

2) During preparation of a cement compound, the false setting effect was observed. On further mixing, this effect disappears. The false-setting start time varies depending on composition of solution, its age and the mixing conditions.

TABLE 3. EFFECT OF AGE OF HYDRATED-SALT SLUDGE ON CEMENT PASTE FLOWABILITY AND MECHANICAL STRENGTH OF A CEMENT COMPOUND

Age of sludge, days	Flowability of cement compound, mm	Mechanical strength of cement compound	
		Holding time, days	$[\sigma_{comp}]$, kg/cm^2
No holding	157	120	275
5	130	250	350
10	70	235	288
16	40	235	350

4.3.1.1. Cementation of filter material pulps

The second group of ILW, which is subject to cementation, represents a mixture of ion-exchange resins, filter perlite (FP) and a small amount of manganese dioxide. For the experiments the filter material pulps were presented as a mixture of the cation exchanger (KU-2) and the anion exchanger resins (AV-17) in the ratio of 1:1 by mass. The characteristics of the samples with the pulps of various composition are given in Table 4.

TABLE 4. COMPOSITION AND MECHANICAL STRENGTH OF SAMPLES WITH FILTER-MATERIAL PULPS

Content of ILW components in pulp			S/C	W/C	Loading capacity of cement compound, % by mass)	Mechanical strength of cement compound	
IER	FP	MnO_2				Holding time, days	$[\sigma_{comp}]$,kg/cm^2
13.2	7.3	-	0.83	0.66	9.4	42 112	129 122
13.2	7.3	-	1.13	0.90	10.9	42 112	65 102
13.2	7.3	-	1.70	1.35	13.0	28 680	25 40
7.8	4.3	0.65	0.58	0.50	4.6	31 540	250 285
6.8	3.8	0.60	0.65	0.58	4.4	29 525	240 300
6.8	3.8	0.60	0.78	0.65	6.9	29 520	240 235

Findings from the experiments:

1) During cementation of filter-material pulps, the loading capacity of a cement compound should not exceed 10% by mass of the solid components in pulp in the water/cement ratio of 0.9.

2) With smaller values of the loading capacity as well as of the water/cement ratio, the samples are developing the strength that exceeds the required standardized value already within a month. In all other cases, the strength, increase ends not later than 1-1.5 months.

3) With the loading capacity of 10.9 % and the W/C ratio of 0.9, the sample continued to develop strength on further holding after 1.5 month.

4.3.1.2. Cementation of a mixture of hydrated-salt sludge and filter-material pulps

The current plan at PA Mayak is to place the cement compound directly into the storage facility compartments, i.e. without its prior packaging. Under such circumstances, one of the most important features of the produced cement compound is its flowability, which should be sufficient to ensure uniform filling of a storage-facility compartment.

The purpose of the experiments:

- Determine the cement-paste flowability for the most complex option, i.e. for the option of cementation of a mixture of hydrated-salt sludge and filter-material pulps,

- investigate the possibility to increase the flowability by using plasticizers.

4.4. Assessment of effect of pulp alkalinity, presence of superplasticizer and method of its introduction on cement-paste flowability and cement-compound strength

It is known [4] that the efficiency of plasticizers depends on many factors including medium alkalinity and on whether a plasticizer is introduced into a cement paste or a liquid waste.

Used as a ILW simulant in the performed experiments was the pulp containing 15 g/l $Fe(OH)_3$, 19 g/l Na_2SO_4, 18.5 g/l $NaNO_3$, 66 g/l IER, and 36 g/l FP.

The superplasticizer (Crade C-3) was used to obtaine cement compound flowabiliry increase. In all experiments the solution/cement ratio equaled 1.0, while the waste loading capacity was 7% by mass. During the experiments, the pulp alkalinity and the superplasticizer introduction methods varied (Table 5).

Findings from the experiments:

Presence of a plasticizer in the pulp and a plasticizer-introduction method have no significant effect on flowability of the cement paste and on the mechanical strength of the obtained cement compound.

TABLE 5. EFFECT OF PULP LKALINITY, SUPERPLASTICIZER PRESENCE AND SUPERPLASTICIZER INTRODUCTION METHOD ON CEMENT-PASTE FLOWABILITY AND CEMENT-COMPOUND STRENGTH

Method of C-3 Introduction	Without C-3				Introduction of C-3 into Pulp				Introduction of C-3 into Cement Paste			
pH	7	8	10	12	7	8	10	12	7	8	10	12
Flowability,	103	190	180	224			178		175		175	
mm	103	190	180	205	164	220	176	-	175	200	175	-
Mechanical Strength				113								
[σ_{comp}], kg/cm^2	120	110	-	113	-	-	125	-	130	127	113	130

4.5. Assessment of effect of pulp age and pH on cement-paste flowability and cement-compound strength

The dependence of the cement-paste flowability and the compound strength on the pulp age was studied at two pH values (7 and 12). The pulp, which was used in the research, contained 28.6 g/l $Fe(OH)_3$, 24.2 g/l Na_2SO_4, 24.6 g/l $NaNO_3$, 66 g/l IER, and 36.3 g/l FP. In all the experiments the solution/cement ratio was kept to be equal to 0.85, which was equivalent of the water/binder ratio of 0.72 (Table 6).

TABLE 6. EFFECT OF AGE AND PH OF PULP ON FLOWABILITY OF CEMENT PASTE AND MECHANICAL STRENGTH OF CEMENT COMPOUND

Pulp pH	Pulp Age, days	Flowability, mm	Mechanical Strength [σ_{comp}] in 35 days, kg/cm^2
7	1	75	185
7	3	93	195
7	10	88	125
7	21	133	118
7	31	138	145
12	1	116	155
7	3	145	167
7	10	105	185
7	21	128	136
7	31	129	128

Findings from the experiments:

- With high alkalinity of the pulp (pH =12), the increased time of its holding up to one month prior to cementation does not lead to a noticeable change in the cement-paste flowability and the mechanical strength of the cement compound.

- When cementing the pulp with pH =7, the mechanical strength does not depend practically on age of the pulp, and the flowability of the cement paste with the pulp aged 10 or less days is somewhat less than that of the samples with the pulps aged 21 and 31 days.

4.6. Assessment of effect of binder type on characteristics of cement compounds

The assessment of effect of a binder type on the cement compound characteristics was made using, as an example, the pulp containing 20 g/l $Fe(OH)_3$, 20 g/l Na_2SO_4, 260 g/l $NaNO_3$, 66 g/l IER, and 36 g/l FP. During the experiments, the pulp pH and the solution/binder ratio were changed.

The obtained results are presented in Table 7.

TABLE 7. EFFECT OF BINDER TYPE ON FLOWABILITY OF CEMENT PASTE AND MECHANICAL STRENGTH OF COMPOUND

Binder Type	S/C	Pulp pH	Cement Paste Flowability, mm	Mechanical Strength [σ_{comp}] in 28 days, kg/cm^2
Portland Cement	0.9	10	165	-
Portland Cement	0.9	12	150	225
Slag Portland Cement	0.9	12	145	125
Portland Cement	1.0	12	158	-
Slag Portland Cement	1.0	12	140	130
Portland Cement	1.1	10	195	190
Slag Portland Cement	1.1	10	145	125

Findings of the experiments:

It has been demonstrated that for all options of waste streams cementation using both the portland cement and the slag portland cement as a matrix, water resistance and frost resistance of the cement compounds meets the standard requirements.

4.7. Frost resistance and water resistance of cement compounds with ILW of PA Mayak

Frost resistance and the water resistance (leachability) are the quality indicators for cement compound, regulated by the Russian standards [1, 2].

Findings from the experiments:

The investigations on the frost resistance and water resistance of the cemented ILW of PA Mayak showed that the ability of the samples to withstand multiple freezing thawing cycles was sharply dropping if the test samples failed to meet requirements of “not less than 75% of the final strength value”. Therefore, testing of the samples with 28 days holding, (as provided for by the Russian Standard), often leads to negative conclusion on applicability. In this connection, Table 8 presents the data obtained in the course of testing of the samples after their holding more than 28 days.

TABLE 8. FROST RESISTANCE AND WATER RESISTANCE OF CEMENT COMPOUNDS

Cement Compound Composition, % by mass							Frost Resistance		Water Resistance	
$Fe(OH)_3$	Na_2SO_4	$NaNO_3$	IER	FP	H_2O	Binder	$[\sigma_{comp}]_{frost}$, kg/cm^2	$[\sigma_{comp}]_{ref}$ kg/cm^2	$[\sigma_{comp}]_{water}$ kg/cm^2	$[\sigma_{comp}]_{ref}$ kg/cm^2
Portland Cement (Grade 500-DO)										
0.34	0.25	18.6	-	-	20.6	60.2	250	280	215	220
0.50	0.50	9.0	-	-	30.0	60.0	220	210	220	250
0.60	0.60	10.8	-	-	36.5	51.5	120	120	105	80
-	-	-	6.0	3.4	36.0	54.6	155	162	120	154
-	-	-	7.0	3.9	42.1	46.0	75	72	102	95
0.80	0.80	10.8	2.7	1.5	33.4	50.0	154	178	-	-
0.90	0.90	11.3	2.9	1.6	34.8	47.6	138	152	157	160
Slag Portland Cement										
0.80	0.80	10.3	2.6	1.4	31.5	52.6	225	238	170	205
0.80	0.80	10.8	2.7	1.5	33.4	50.0	196	191	120	158
0.90	0.90	11.3	2.9	1.6	34.8	47.6	103	132	146	162
0.80	0.80	10.3	2.6	1.4	31.5	52.6	162	140	168	195

* $[\sigma_{comp}]_{frost}$, $[\sigma_{comp}]_{water}$, $[\sigma_{comp}]_{ref}$ - the mechanical compressive strength of the samples tested for frost resistance, water resistance, and, respectively, of cement compound

4.7.1.1. Cementation of tritium-containing liquid RW

The following requirements [6] have been imposed on the technique of immobilization of the tritium-containing LRW into an inorganic matrix:

- The tritium release from the solidified liquid RW package should not exceed 10^{-3}% of the total tritium amount in LRW;

- The package integrity should be guaranteed for 150 years, or until tritium is decayed to a negligible level.

The experiments on the technique of tritium-containing LRW solidification were performed as follows (Table 9). Several batches of Tritium-Containing cement compound were made on the basis of three possible matrix materials - SPC, PC mixed with clinoptilolite, and magnesia cement. The amount of each sample equaled 100 cm^3. The cement compound samples were prepared in metal cells. Before being filled with the cement compound, the inner surface of the cell was coated with the waterproofing-material layer, 1 mm in thickness. Solidified cement compound was removed from the cell and the compound surface was coated with the waterproofing material (Bitumen BND 60/90) with a thickness of 5 mm.

TABLE 9. AMOUNT OF TRITIUM TRANSFERRED TO CONTACT WATER FROM CEMENT COMPOUNDS WITH WATERPROOF COAT WITHIN ONE DAY

Sample Composition, % by mass	Tritium fraction of (… $\times10^{-3}$ %) washed out from the sample within one day after different periods of cement compound hardering				
	0-1 days	1-2 days	2-3 days	3-7 days	7-14 days
SPC – 66.5, water – 33.5	2.4	1.4	0.8	0.5	0.4
PC – 28.5, clinoptilolite – 51.5, water – 20.0	4.7	2.4	1.4	0.5	0.4
MgO – 43.0, $MgSO_4$ –14.0, H_2O – 43.0	5.0	3.2	1.8	1.6	1.7

Findings from the experiments:

- In all experiments, the tritium leaching rate within the first days of contact water-cement compound was equal to 1×10^{-4} g/cm^2 day, which is equivalent of the tritium loss equal to 5×10^{-3}%. In three days, the tritium losses are close to the allowable value.

- The degree of tritium retention in the magnesia-compound-based samples is somewhat less than that when using SPC (special portland cement) and PC (portland cement).

4.8. Research of cementation of pulps with miscellaneous physical and chemical content stored in tanks of MCC.

4.8.1. Characteristics of pulps contained in MSS storage tanks

Pulp wastes were generated during previous activity of the MCC radiochemical plant. All pulps should be removed from the tanks according to radiochemical plant decommissioning program and converted to the stable form suitable for further long term storage/disposal. Pulps management technological scheme includes following stages:

Present stages:

- Removal of the liquid phase from tanks
- Dissolution of the solid phase of pulp in tanks
- Extraction of U and Pu from solutions (if it is justifiable)
- Collection of undissolved pulp residues (as a “secondary” pulp) in interim tanks

Future stages (R&D):

- Immobilization of undissolved pulp residues in cement matrix
- Long term storage/disposal of cement compound

As may be seen from the table below, special peculiarity of the MCC pulps lies in their multicomponent chemical composition and considerable content of alpha-radionuclides. Interim storage of the pulp before its conditioning (cementation) is held in the alkaline medium, therefore basic mass of the pulp’s solid phase will consist of hydrated oxides of Fe, Al, Mn, Ni and Cr which can react with cement components. Earlier publications made it known that X-ray structural analysis of the cement compound, on the basis of metallurgical slag, showed that Fe, Cr, Cu, Ni and some other components are found there in chemically combined condition and practically don’t wash out. [7].

Table 10 represents average contents of undissolved residues contained in the pulp that is subject to cementation.

TABLE 10. AVERAGE CONTENTS OF UNDISSOLVED RESIDUES CONTAINED IN THE PULP THAT IS SUBJECT TO CEMENTATION

Pulp components	Fe	Mn	Cr	Ni	Al	SiO2	Pu	U	Solid phase in the pulp	ß-activity (Sr 90)
Content of undis-solved residues in the pulp, g/l	15 ± 10	9 ± 7	1 ± 0,5	9 ± 8	2,5 ± 1	3 ± 2	0,15 ± 0,05	4 ± 1	100 ± 60	1 ± 0,5 Ci/l

4.8.2. Basis for the use of cementation technology for MCC pulps immobilization

The cementation method was chosen because of its following advantages:

- the process is low-temperature and doesn't require complicated equipment
- availability and relative inexpensiveness of matrix materials
- absence of secondary wastes
- possibility of obtaining the compound quality that meets the long term storage and disposal requirements
- cement ability to maintain alkaline condition in pore water for a long time which leads to solubility reduction of such alpha emmiting radionuclides as U and Pu [8].

Cemented pulps will be packaged in metal containers (200 l drums) and send to interim storage. Cs-137and Pu-239 are "critical" radionuclides for safety of long-term cementitious pulp storage because they are contained in pulps at relatively high concentrations. The reliability of localization of Cs-137 in the cement compound can be achieved by including sorbents into the matrix material – clay of bentonite types and zeolits (for instance, clinoptilolite) which will permit to reduce the leach rate of Cs-137 from the cement compound

The safety of long storage (eventualy qualified latter as disposal) of cement compound containing Pu-239 is based on the fact that the storage for MCC cementitious pulps will have several barriers: e.g. matrix composition, container and packaging elements, engineering part that includes building structures, buffer materials and sealing elements, massive rock materials between storage facility and the environment (storage facility is located at a depth of ~ 200 meters below the surface).

Earlier publications made it known that the use of cementation for the conditioning of liquid nuclear waste allows to fix alpha-radionuclides (U, Pu, Am) safely in the cement compound [9-13].

4.8.3. Experiments results and conclusion

The research purposes are as follows:

- Determining the basic process parameters of cementation of pulps from storage tanks of MCC,
- Optimizing the cementation process to obtain cement compound with a maximum loading capacity that meets the requirements of the regulatory documents,
- Determining the basic physical and chemical characteristics of the obtained cement compounds (mechanical strength, water resistance, frost resistance, flowability, etc.),

- Estimating the behaviors of the obtained cement compounds under storage and disposal conditions.

4.9. Selection of pulps simulates

Main components of undissolved residues of pulps are hydrates and silica. The residues of all tanks are mostly similar in a qualitative composition. The quantitative composition (ratios of certain components), however, differs for a different tanks.

In the cementation experiments, two types of pulps with different ratio of hydroxides to silica (Table 11) were used as simulates:

- Pulp simulant No.1 with a low silica content (6.3 wt %),

- Pulp simulant or No.2 with a high silica content (24.3 wt %)

As is evident from Table 11, the ratio of hydroxides to silica in the pulp simulant No.1 was equal to 1:15, while in the pulp simulant No.2 it was lower and equals to 1:3.

TABLE 11. COMPOSITIONS OF SIMULATED PULPS

Pulp component	Content of components in undissolved residue, *wt* %	
	Pulp simulator No.1 (with a low *silica* content)	Pulp simulator No.2 (with a high *silica* content)
$Al(OH)_3$	11.3	9.1
$Fe(OH)_3$	27.8	22.5
$Cr(OH)_3$	2.3	1.9
$Mn(OH)_2$	38.1	30.8
$Ni(OH)_2$	14.2	11.4
SiO_2	6.3	24.3
	100,0	100,0

The following binding materials and additives were used to prepare cement compounds:

- Portland cement PC500-D0 produced as per GOST 10178-85 by Belgorod Cement Plant,
- Slag *P*ortland cement SPC400 produced as per GOST 10178-85 by Lipetskcement Plant;
- Bentonite clay M4T1K produced as per GOST 28177-89 by Keramzit Plant,
- clinoptilolite having the following particle-size distribution: particles of more than 1 mm in size – 22.16 wt %; particles of up to 0.5 mm – 43.58 wt %; particles of up to 0.25 mm – 10.20 wt %; particles of up to 0.125 mm – 21.52 wt %, particles less than 0.125 mm – 2.54 wt %.

Various combinations and ratios of those reagents were used in the experiments.

4.9.1.1. Study of the influence of sorbing additives type and content on cement compound leachibility

Radionuclides leachability and mechanical strength are two of the most important characteristics of cement compound. Leachability can be reduced by increasing the density of cement stone by decreasing of W/C ratio, use of binding materials to make a low-porous compound, introducing to the cement matrix different sorbing additions, such as various clayey materials (vermiculite, bentonite) and ceolyte (clinoptilolite) [17, 19-20].

Experimental results presented in Tables 12 – 13 indicate:

- PC as well as SPC can be used as binding material for conditioning pulps.
- Mechanical strength of all cement compounds increases with the length of time of their storage, especially for compounds based on SPC.
- The increase of water-cement ratio from 1,0 (in most experiments) to 1,7 (test 5 in Table 12) decreases mechanical strength and frost resistance of the compounds.
- The decrease of hydroxide content in pulp (pulp simulant No 2) with a same loading capacity is conducive to the improvement of compound quality. Mechanical strength, frost resistance and water resistance of these samples is 1,2-1,5 higher.
- All compounds based on PC with 30 wt % to 70 wt % of sorbents (clinoptilolite and its mix with bentonite) are characterised by a very low caesium leachability – $3,3x10^{-5}$g/cm^{2}xday on average, which is 2 times lower than typical for a sample sized 2 x 2 x 2 cm. The total amount of activity after being in the water for 7 days did not exceed 0,07% from the starting point. High W/C did not influence the leachability of Cs-137 from the samples (Table 13).
- Exchanging bentonite with clinoptilolite does not result in the deterioration of the compound's chemical and physical properties, even if its amount is increased to 30% of the compound mass.
- Introducing pulps into the compound leads to a slowdown of hardening process so it takes 1,5 - 2 months to reach 75% mechanical strength .
- The change of hydroxide and silicon oxide relation in the pulp composition within stated limits does have an insignificant impact on the compound quality. However, compound compositions mentioned above with a satisfactory quality have a very low flowability, which leads to the necessity of finding a way for its improvement.

TABLE 12. INFLUENCE OF MATRIX MATERIAL, PULP COMPOSITION AND W/C ON THE PROPERTIES OF THE CEMENT COMPOUND

No	Matrix composition % wt	pH of pulp	S/C	W/C	Loading capacity % wt	Mechanical strength [σ_{compr}], after n days, MPa			Frost resistance		Water resistance	
						28	56	90	[σ_{compr}]$_{frost}$ after 30 cycles of freezing and thawing, MPa	[σ_{compr}] of control samples, MPa	[σ_{compr}]$_{water}$ after 90 days in water, MPa	[σ_{compr}] of control samples, MPa
	Pulp simulator No.1											
1	SPC–80 Clinoptilolite -20	6	1,1	1,0	6,4	6,2	10,6	8,8	6,9	8,8	9,1	10,1
2	SPC –80 Clinoptilolite -20	12	1,1	1,0	6,4	6,8	10,3	11,3	6,9	11,3	9,8	11,8
3	SPC–70 Clinoptilolite -30	12	1,1	1,0	6,4	7,8	10,3	11,3	11,3	11,3	10,3	10,8
4	SPC -80 Clinoptilolite -10 Bentonite-10	12	1,1	1,0	6,4	6,9	12,7	15,5	11,3	15,5	13,0	14,2
5	SPC –80 Bentonite -20	12	1,9	1,7	6,4	3,1	6,8	6,4	4,0	6,4	5,9	6,2
6	PC –70 Clinoptilolite -30	10	1,1	1,0	6,4	6,2	10,3	10,3	10,3	10,3	9,3	11,6
	Pulp simulator No.2											
7	SPC –90 Bentonite -10	10	1,4	1,2	8,8	11,8	13,7	14,5	12,3	14,5	10,8	14,5
8	SPC –90 Bentonite -10	8	1,2	1,0	7,5	12,3	14,2	12,6	13,7	12,3	15,2	12,6
9	SPC –90 Bentonite -10	8	1,0	0,9	5,7	11,3	15,3	16,7	13,1	16,7	17,6	19,6
10	SPC –85 Bentonite -15	8	1,2	1,0	8,2	12,3	14,2	16,0	11,3	16,0	14,2	10,3
11	PC–90 Bentonite -10	8	1,2	1,1	6,8	15,5	16,2	16,7	no datas	16,7	16,7	11,3

12	PC–90 Clinoptilolite -10	8	1,2	1,0	8,2	13,4	14,7	19,6	16,7	19,6	18,2	18,6

TABLE 13. SORBENT TYPE AND CONTENT INFLUENCE ON CEMENT COMPOUNDS LEACHABILITY

Matrix composition % wt	Samples activity, x1·10^4 Bq	W/C	Mechanical strength [σ_{compr}] after 28 days, MPa	Water contact time, days	Leachability rate, g/sm^2·day	Washed activity part, %
PC– 70 Clinoptilolite - 30	2,22	0,8	14,3	1	$3{,}8\cdot10^{-5}$	0,007
				2	$5{,}9\cdot10^{-6}$	0,017
				3	$6{,}9\cdot10^{-5}$	0,029
				7	$6{,}1\cdot10^{-5}$	0,073
PC– 63 Clinoptilolite – 30 Bentonite - 7	2,11	0,8	26,2	1	$5{,}1\cdot10^{-5}$	0,008
				2	$4{,}9\cdot10^{-5}$	0,016
				3	$4{,}4\cdot10^{-5}$.	0,024
				7	$3{,}3\cdot10^{-5}$	0,046
PC – 40 Clinoptilolite – 60	0,93	1,37	13,0	1	$3{,}6\cdot10^{-5}$	0,007
				2	$4{,}8\cdot10^{-5}$	0,015
				3	$8{,}2\cdot10^{-5}$	0,030
				7	$4{,}1\cdot10^{-5}$	0,060
PC – 27 Clinoptilolite – 44 Bentonite - 29	1,0	1,37	13,0	1	$2{,}5\cdot10^{-5}$	0,005
				2	$5{,}4\cdot10^{-5}$	0,016
				3	$1{,}4\cdot10^{-5}$	0,045
				7	$2{,}8\cdot10^{-5}$	0,067

4.9.1.2. Study of cement compounds flowability

Flowability is a characteristic of cement compound that is important for its preparation in the mixer and discharge into containers. The conditions under which the compound is homogeneous and fills containers without trouble determine the optimum flowability value.

Flowability values were determined in compounds with pulp imitators (their contents are shown in Table 14). Mixtures PC and SPC with a sorbing additives (bentonite or clinoptilolite) in mass correlation 9:1 were used as a matrix material in the experiments.

The results of the experiments are shown in Tables 14 – 15 and Figures 1 - 10.

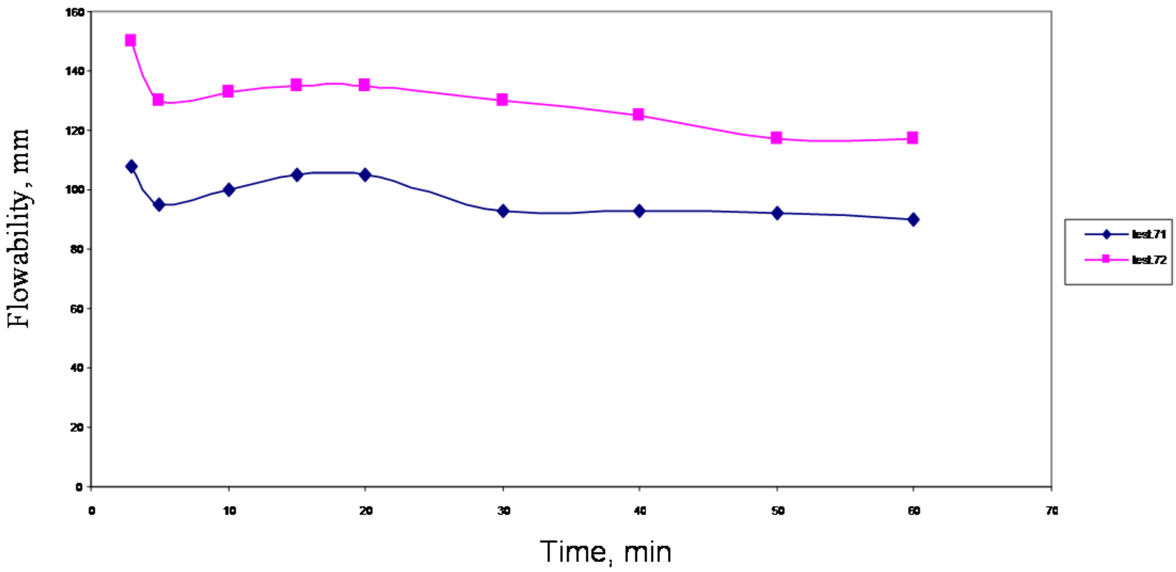

FIG. 1. Flowability of cement compound on the basis PC by W/C=0,65 (test 71) and W/C=0,70 (test 72). Loading capacity –3,0 wt % of dry undissolved pulp simulator No 1 residue.

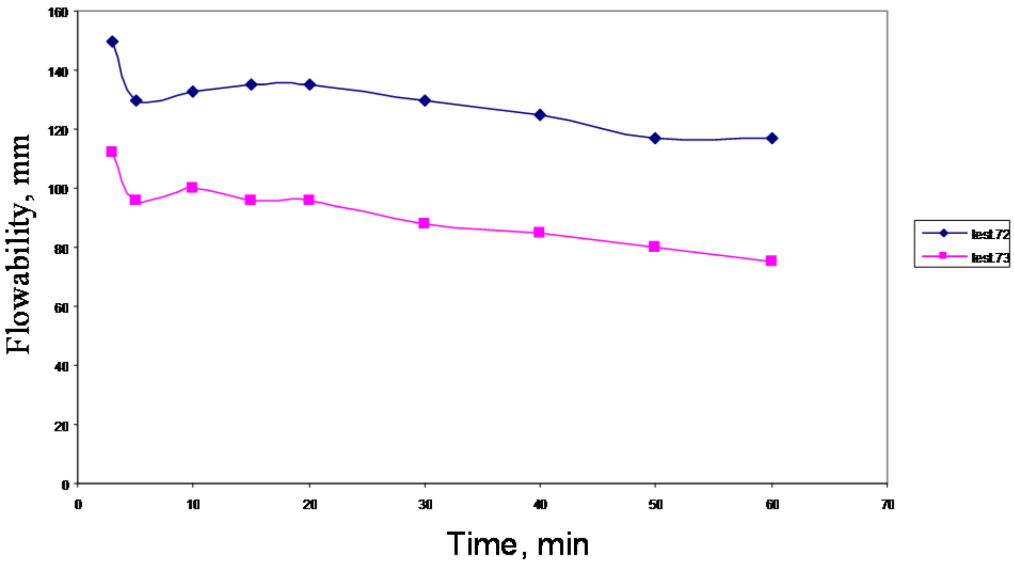

FIG. 2. Flowability of cement compound on the basis PC by W/C=0,70 (test 72, loading capacity – 3,0 wt % of dry undissolved pulp simulator No 1 residue) and W/C=0,70 (test 73 loading capacity – 5,0 wt %).

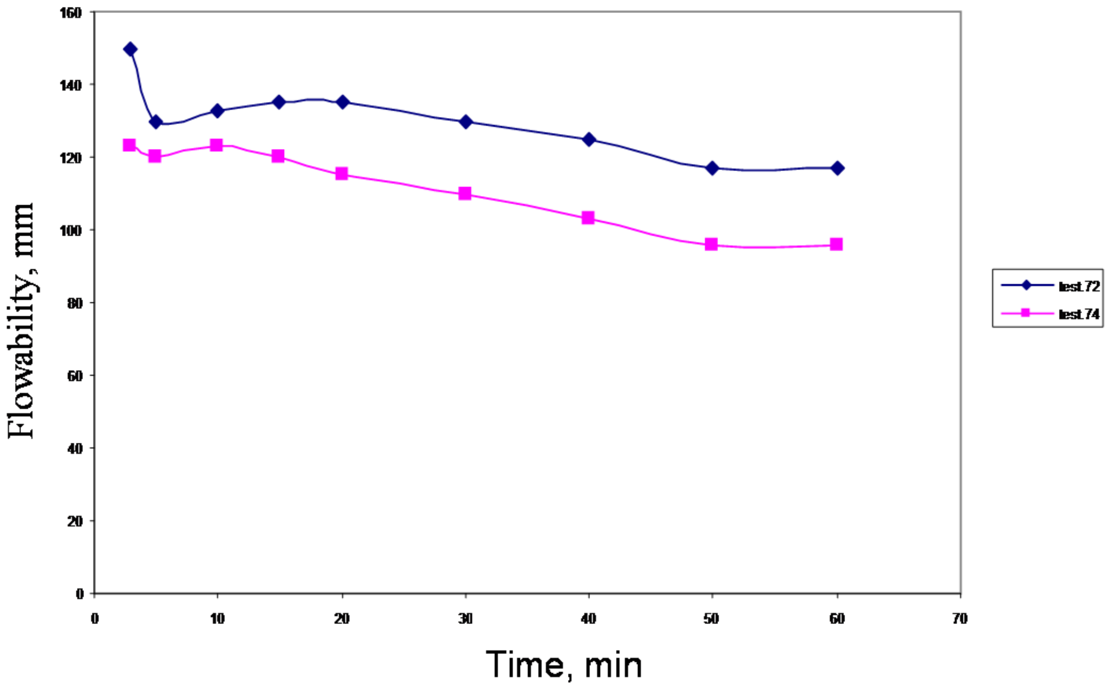

FIG. 3. Flowability of cement compound on the basis PC (test 72) and SPC (test 74) by W/C=0,70. Loading capacity of cement compound –3,0 wt % of dry undissolved pulp simulator residue No 1.

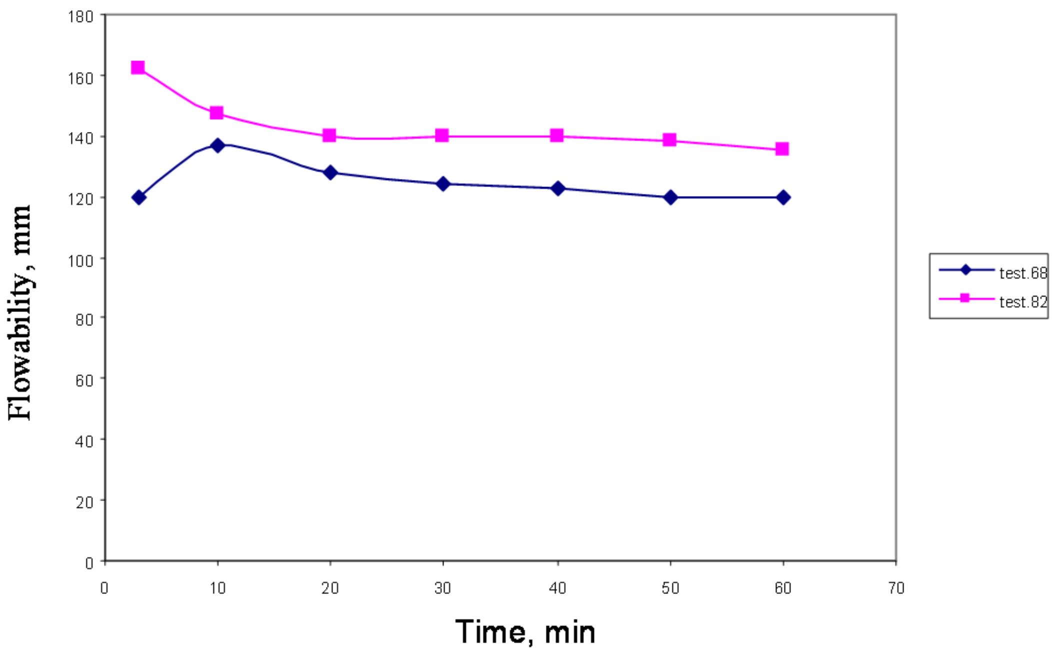

FIG. 4. Flowability of cement compound on the basis PC (test 68) and SPC (test 82) without pulp simulator (W/C=0,70).

TABLE 14. FLOWABILITY OF CEMENT COMPOUND CONTAINING PULP SIMULATOR NO 1

No	Compound composition, wt%					pH of pulp	W/C	Flowability after n minutes, mm								
	PC	SPC	Bentonite	Dry undissolved pulp residue	Water			3	5	10	15	20	30	40	50	60
71	52,9	-	5,9	3,0	38,2	7	0,65	108	95	100	105	105	93	93	92	90
72	51,3	-	5,7	3,0	40,0	7	0,70	150	130	133	135	135	130	125	117	117
73	50,3	-	5,6	5,0	39,1	7	0,70	112	96	100	96	96	88	85	80	75
74	-	51,5	5,7	3,0	39,9	10	0,70	123	120	123	120	115	110	103	96	96
68	53,1	-	5,9	-	41	-	0,70	120	-	135	130	128	124	123	120	120
82	-	53,1	5,9	-	41	-	0,70	162	145	147	145	140	140	140	138	135

TABLE 15. FLOWABILITY OF CEMENT COMPOUND, CONTAINING PULP SIMULATOR NO 2

No	Compound composition, wt%						pH of pulp	W/C	Flowability after n minutes, mm								
	PC	SPC	Bentonite	Clinopti-lolite	Dry undissolved pulp residue	Water			3	5	10	15	20	30	40	50	60
84	50,8	-	5,6	-	4	39,6	7,2	0,70	118	90	100	98	98	95	92	90	85
89	46,0	-	5,1	-	8	40,9	7,2	0,80	125	120	115	112	113	108	97	95	85
90	44,8	-	4,9	-	8	42,3	7,1	0,85	150	142	131	128	126	113	105	100	93
91	-	46,0	5,1	-	8	40,9	11,0	0,80	150	138	135	127	122	112	98	96	93
94	-	49,4	5,5	-	4	41,1	11,0	0,75	153	132	132	127	125	118	114	106	100
97	-	49,4	-	5,5	4	41,1	11,0	0,75	177	177	177	-	172	170	-	-	-
98	-	50,8	-	5,6	4	39,6	11,0	0,70	165	-	158	-	157	148	147	147	145

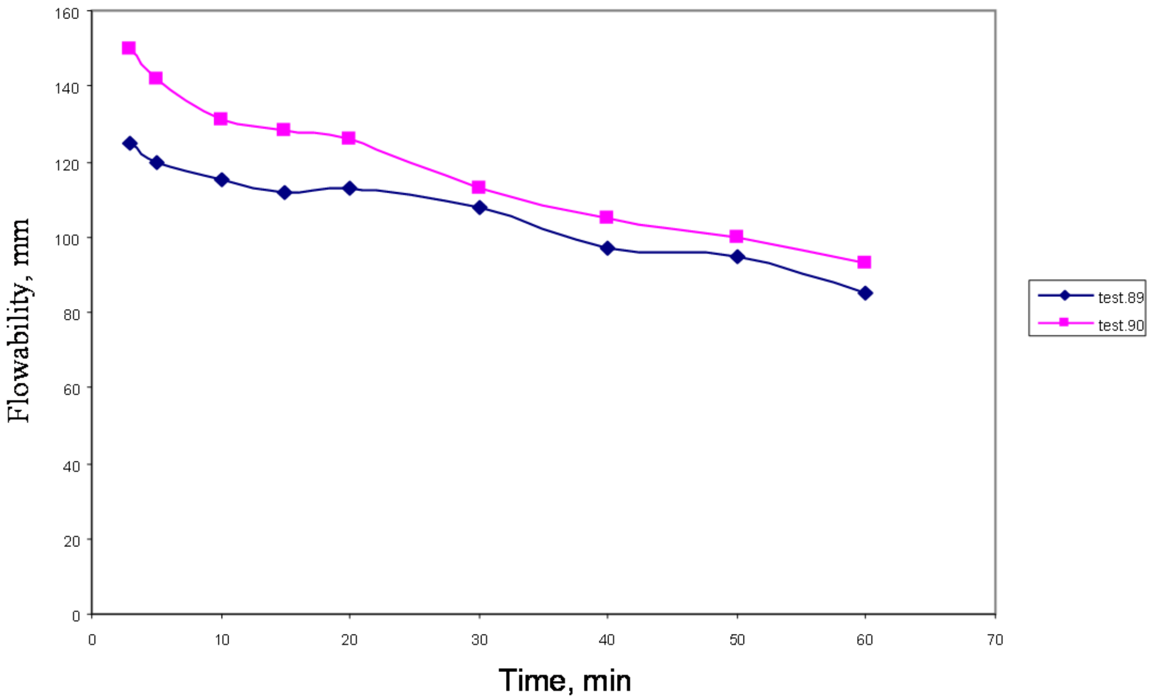

FIG. 5. Flowability of cement compounds (loading capacity of dry undissolved pulp simulator No2 residue – 8,0 wt %) on the basis of PC by W/C=0,80 (test 89) and by W/C=0,90 (test 90).

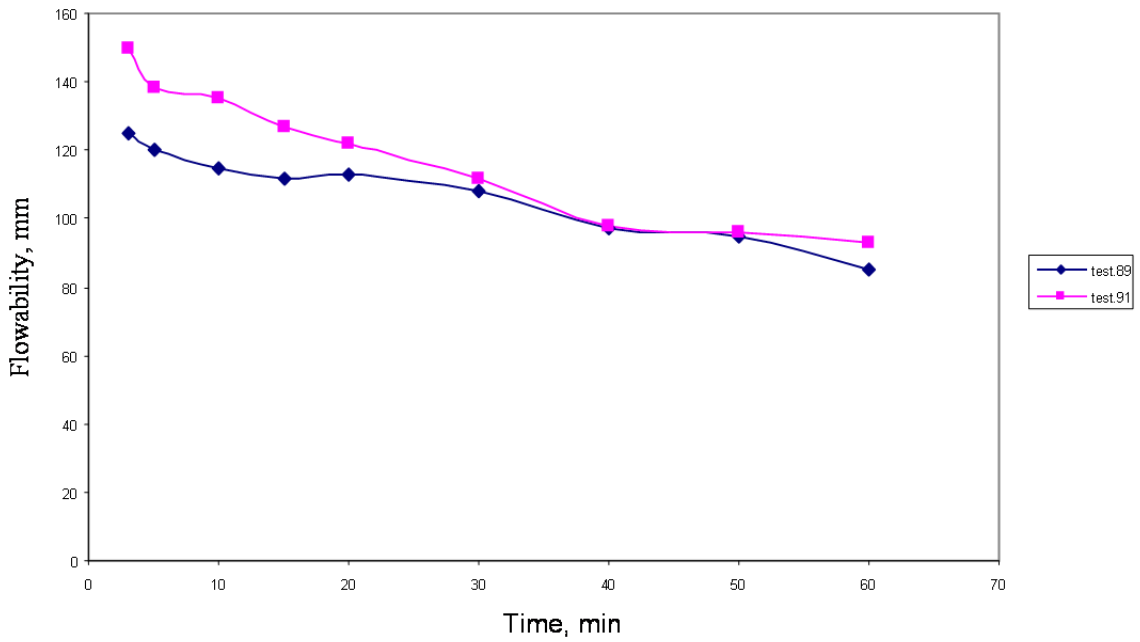

FIG. 6. Flowability of cement compounds on the basis of PC (test 89) and SPC (test 91) by W/C=0,80. Loading capacity of dry undissolved pulp simulator No2 residue – 8,0 wt %.

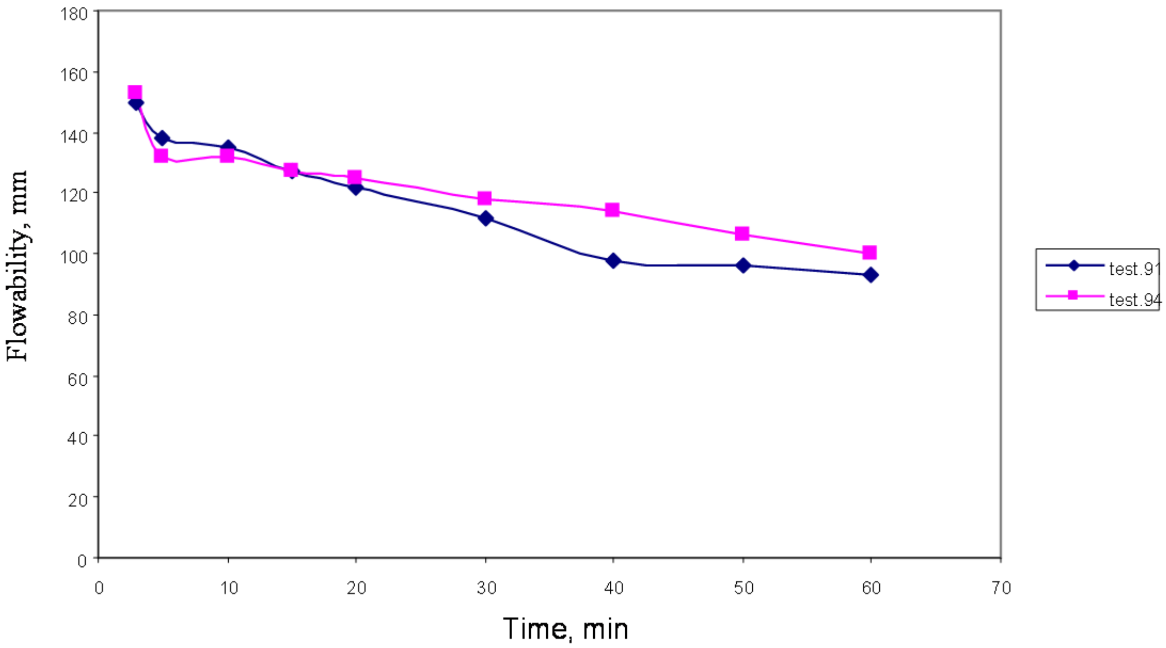

FIG. 7. Flowability of cement compounds on the basis of SPC with loading capacity of dry undissolved pulp simulator No2 residue – 4,0 wt %. In test 94 W/C=0,80 and in test 91 W/C=0,80.

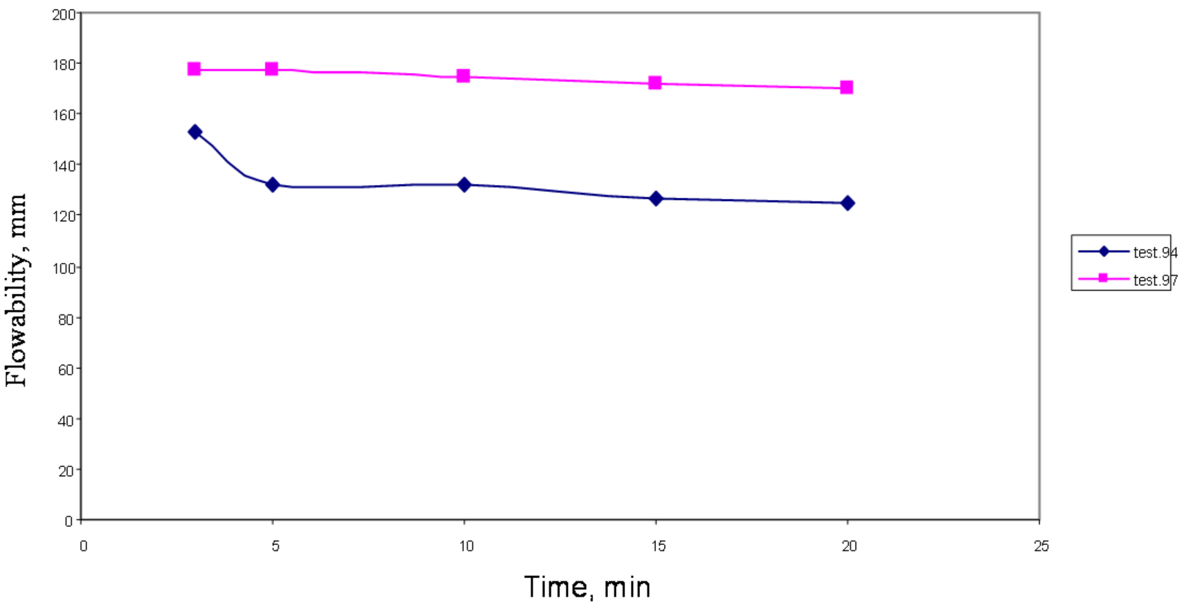

FIG. 8. The dependence of cement compound flowability from type of sorbing additives. Cement compound composition: loading capacity of dry undissolved pulp simulator No2 residue – 4,0 wt %, W/C=0,75, sorbing additives - bentonite (test 94) and clinoptilolite (test 97).

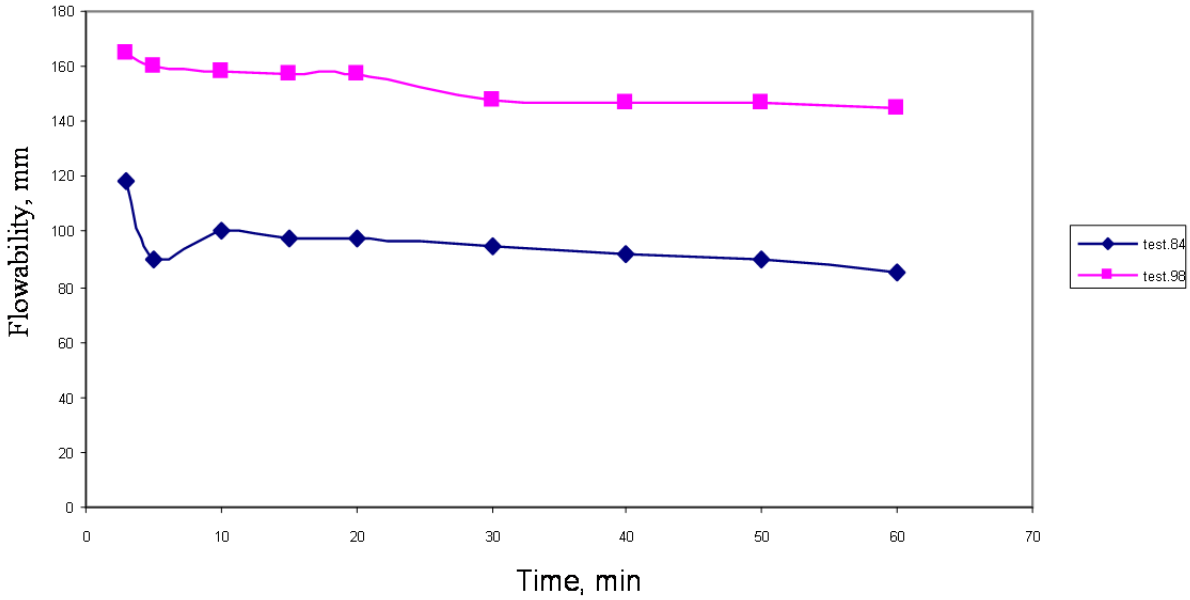

FIG. 9. Flowability of cement compound on the basis PC + bentonite (test 84) and SPC + clinoptilolite (test 98). Loading capacity of dry undissolved pulp simulator No2 residue – 4,0 wt %, W/C=0,70.

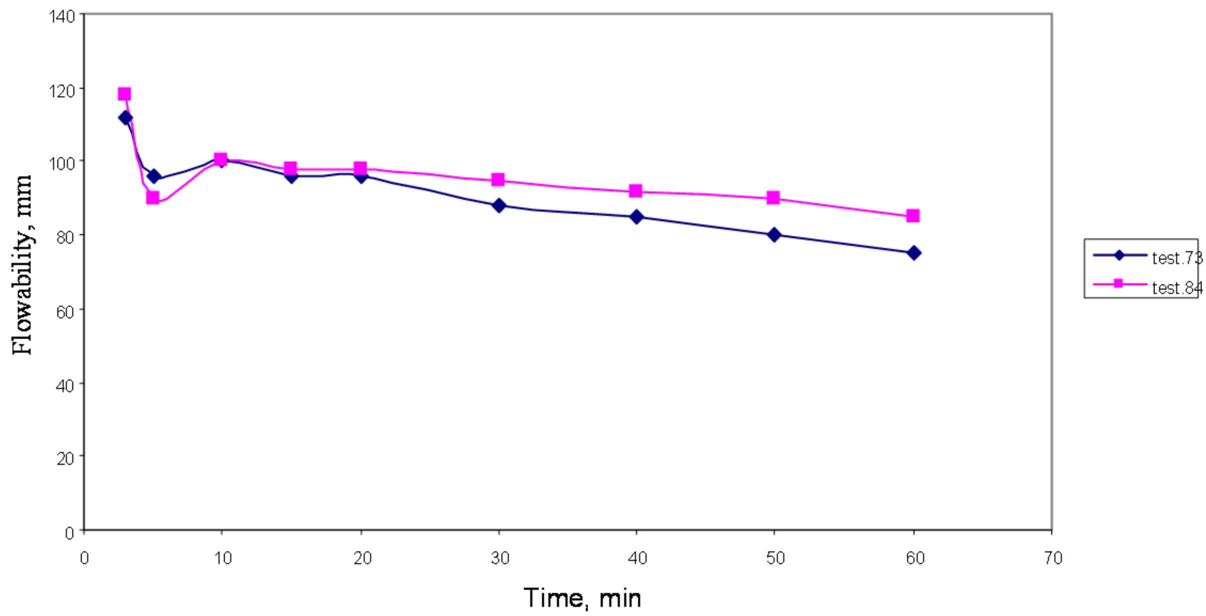

FIG. 10. Flowability of cement compounds containing pulp simulator No 1 (test 73) and pulp simulator No 2 (test 84).)

The results of experiments indicates:

- The maximum flowability with the minimum W/C characterizes the compound where the matrix material is a mixture of 90 wt % of SPC and 10 wt % of clinoptilolite. As compared to a similar compound based on the mixture of PC with bentonite the flowability increases practically twice.

- Comparison of flowability of compounds with approximately same content with pulp simulant No 1 and pulp simulant No 2 shows that pulp content change does not lead to a change in plasticity of the cement paste.

- With equal content of pulp dry undissolved residue in cement compound and with the same binding substances the higher flowability is in tests, where W/C is the highest.

- With the equal W/C ratio, flowability notably reduces when the content of pulp dry residue in the compound is increased from 3 to 5 wt %.

4.10. Influence of plasticizing additive on the cement compound flowability

The presence of hydrate pulps in cement compound considerably reduces flowability of the compound and may lead to difficulties in preparation of the compound and its discharge from the mixer.

There is no point in increasing the compound flowability by lowerering loading capacity in containers or by higher W/C ratio in compounds. The possibility to increase cement paste flowability is tested by doping it with a special plasticizing additive. Superplasticizing additive S-3 that is widely used in construction material production was used as such additive. S-3 is added to the cement paste in the end of stirring. Tables 16 and 17 give experimental results.

The results of experiments indicates:

- Flowability of cement compound with dry pulp residue is a complex phenomena depending on various factors.

- Cement compounds on the basis of SPC have a higher flowability than compounds on the basis of PC; however the impact of superplasticizing additive on the flowability of compounds on the basis of SPC is less important.

- S-3 plasticizing performance depends not only on its concentration but also on the quantity of sorbing additive and alkalinity of the medium. For example, when the matrix material contains 10% of bentonite and 0,5% of S-3 and the pulp pH increases from 8 to 12, the cement paste flowability is reduced insignificantly - from 80 to 72mm (tests 45b and 47b), and when the content of bentonite is 15% and of C-3 1%, the same pH increase leads to the flowability reduction twice - from 80 to 40 mm (tests 45v and 47v). The same drastic decrease of flowability as the alkalinity increases is observed for cement compounds without S-3 (tests 45a and 47a).

TABLE 16. THE INFLUENCE OF PLASTICIZING ADDITIVE S-3 ON FLOWABILITY OF CEMENT COMPOUND ON THE BASIS OF PC

No	Matrix composition, % wt	S-3 content in matrix composition, % wt	Loading capacity of cement compound, wt %	Pн of pulp	Flowability, mm
45a	PC-500Д0-90 Bentonite-10	0	4,4	8	70
45б	PC-500Д0-90 Bentonite-10	0,5	4,4	8	80
46a	PC-500Д0-90 Bentonite-10	0	5,0	10	40
46б	PC-500Д0-90 Bentonite-10	0,5	5,0	10	75
47a	PC-500Д0-90 Bentonite-10	0	4,4	12	40
47б	PC-500Д0-90 Bentonite-10	0,5	4,4	12	72

24	PC-500Д0-85 Bentonite-15	0	4,4	8	40
45в	PC-500Д0-85 Bentonite-15	1,0	4,3	8	80
46в	PC-500Д0-85 Bentonite-15	1,0	4,3	10	40
47в	PC-500Д0-85 Bentonite-15	1,0	4,3	12	40

TABLE 17. INFLUENCE OF PLASTICIZING ADDITIVE S-3 ON FLOWABILITY OF CEMENT COMPOUND ON THE BASIS OF SPC

No	Matrix composition, % wt	S-3 content in matrix composition, % wt	Loading capacity of cement compound, wt %	W/C	pH of pulp	Flowability, mm
37a	SPC 400 - 90 Bentonite - 10	0	4,3	0,7	8	65
20	SPC 400 - 90 Bentonite - 10	0,5	4,4	0,7	8	90
27	SPC 400 - 90 Bentonite - 10	1,0	4,4	0,7	8	110
37в	SPC 400 - 85 Bentonite - 15	1,0	4,2	0,7	8	87
38в	SPC 400 - 85 Bentonite - 15	1,0	4,2	0,7	10	40
39в	SPC 400 - 85 Bentonite - 15	1,0	4,2	0,7	12	40
50a	SPC 400 - 90 Clinoptilolite - 10	0	4,4	0,7	8	70
50б	SPC 400 - 90 Clinoptilolite - 10	1,0	4,4	0,7	8	95
50в	SPC 400 - 85 Clinoptilolite - 15	1,0	4,3	0,7	8	95
49в	SPC 400 - 85 Clinoptilolite - 15	1,0	4,3	0,7	10	105
48в	SPC 400 - 85 Clinoptilolite - 15	1,0	4,3	0,7	12	95

4.10.1.1. Study of influence of cement compound age on its mechanical strength

Experiments were carried out on cement compound samples on the basis of PC and SPC with bentonite and clinoptilolite. Their content in compounds made 4,4 wt %, W/C - 0,72. Measurements were taken in the period 28-150 days of compound samples exposure. The results of experiments are shown in Fig. 11.

The results of experiments are a follows:

- Mechanical strength of all tested samples increases during a long period of time and reaches its final value by the age of approximately 90 days (Fig. 11).

- The maximum growth of mechanical strength was recorded for cement compounds on the following mixture basis: SPC + clinoptilolite - from 110 up to 240 kg/sm^2, the minimum growth - for cement compounds on the following mixture basis: SPC+ bentonite - from 160 up to 190 kg/sm^2.

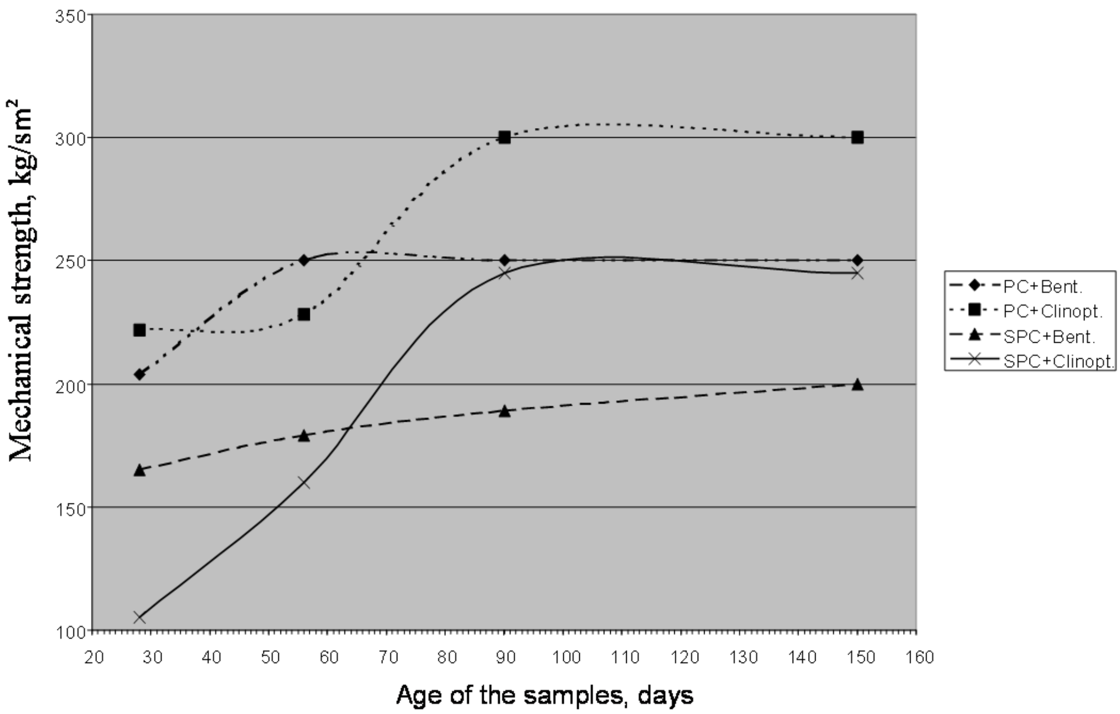

FIG. 11. Impact of cement compound age on its mechanic strength.

4.10.1.2. Study of heat generation of cement compounds

Table 17 shows compositions of the studied materials and compounds and values of specific heat release. Figures 12 – 16 show samples temperature curves. Y-axis of all curves is used for marking the mathematical difference between sample and ambient temperatures (difference of temperatures).

TABLE 17. HEAT CHARACTERISTICS OF CEMENT COMPOUNDS

No	Matrix composition, % wt				Pulp content on cement compound, wt %	W/C	Time till t_{max}, h	$t_{max}-t_o$, °C	Specific heat release till t_{max}		Specific heating capacity, Joule/(g °C) (till t_{max})
	PC	SPC	Bentonite	Clinoptilolite					Joule per g of compound	Joule per g of cement	
T4	90	-	10	-	-	0,78	12,0	8,9	43,9	83,2	5,0
T1	90	-	10	--	-	0,78	11,0	10,5	60,6	114,2	5,8
T2	90	-	10	-	-	0,74 C-3	11,5	12,1	51,4	95,4	4,2
T6	90	-	10	-	4 (pulp imitator No1)	0,74	11,5	9,0	43,5	84,5	4,8
T7	90	-	10	-	8 (pulp imitator No1)	0,73	9,5	14,5	53,5	133,8	3,7
T3		90	10	-	-	0,78 pH 11	13,0	10,4	46,0	86,9	4,4
T10	-	90	10	-	-	0,7 pH 7	12,0	11,0	51,4	97,0	4,7
T8		90	10	-	8(pulp imitator No1)	0,89 pH 11	11,0 12,0	10,0 9,0	35,6 42,8	77,4 90,7	3,6 4,7
T20	90	-	-	10	8 (pulp imitator No2)	0,7	13,0	9,0	11,0	22,7	1,2
T21	90	-	10	-	8 (pulp imitator No2)	0,7	11,0	8,9	21,1	43,2	2,4
T22	70	-	-	30	8 (pulp imitator No2)	0,7	8,0	7,0	12,4	23,6	1,8

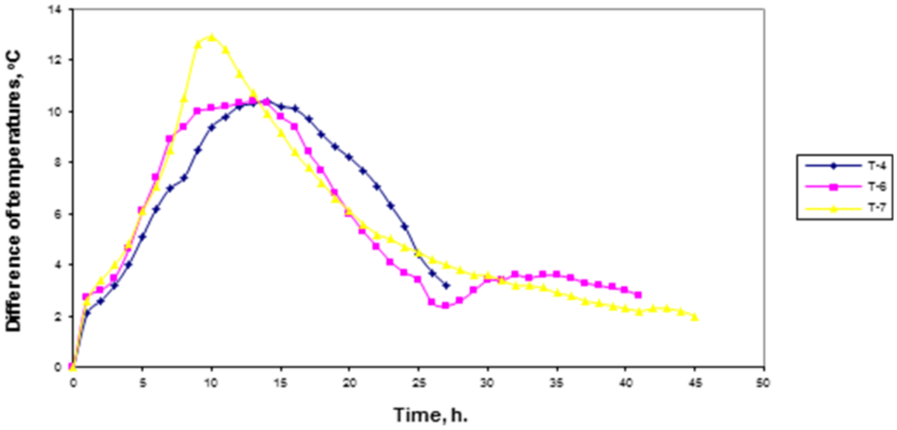

FIG. 12. The impact of pulp content in cement compounds on heat release in the process of hydration of binding substances (test T4 – cement compound without pulp, test T6 – 4 wt % of pulp, test T7 – 8 wt% of pulp).

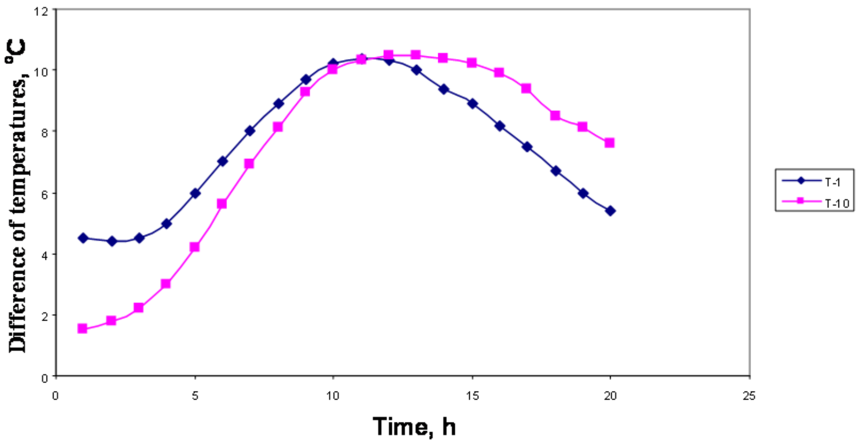

FIG. 13. The heat release in the process of hydration of binding substances in cement compounds on the basis of PC (test T4) and SPC (test T10).

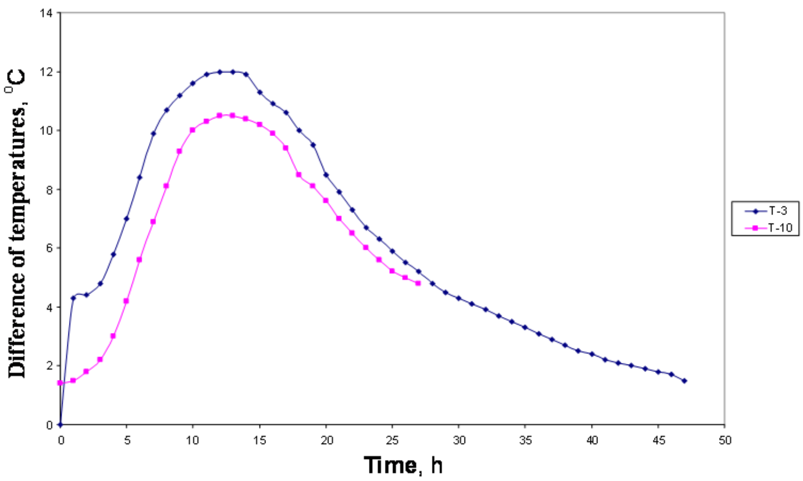

FIG. 14. The impact of alkalinity of temper liquid on heat release in the process of hydration of binding substances in cement compounds on the basis of SPC (test T3 – pH 11 and test T10 – pH 7).

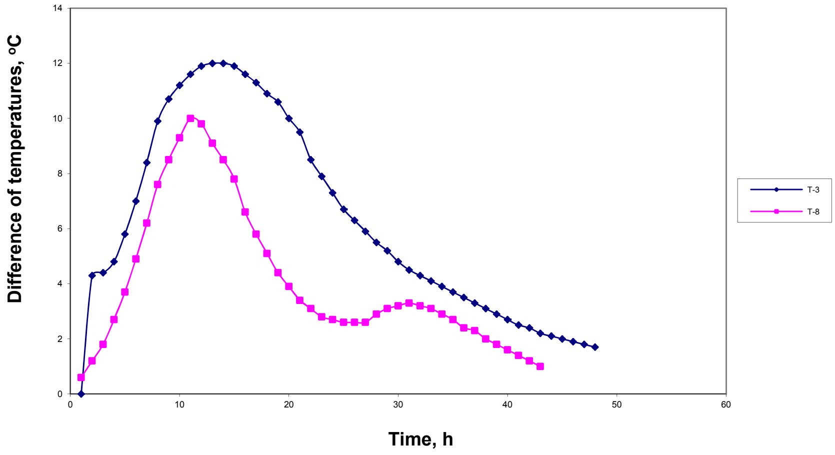

FIG. 15. The impact of pulp on heat release in the process of hydration of binding substances in cement compounds on the basis of SPC (test T3 – without pulp, test T8 - 8 wt % pulp).

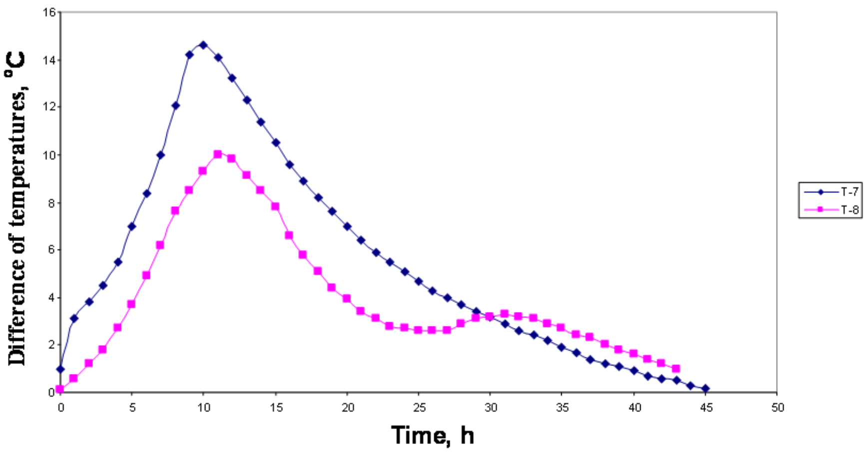

FIG. 16. The dependence of heat release from hardening of compounds with pulps on the type of the binding substance (test T7 - PS, test T8 - SPS).

The results of experiments indicates:

- Incorporation of pulp into cement compound till loading capacity is no more than 4% wt does not change the heat release from hydration in comparison with heat release from hydration of compound without pulp. However, the heat release increases if the loading capacity of compound is 8% wt.

- Substitution of SPC for PC reduces the heat release, which is most pronounced for compounds with loading capacity of 8% of dry undissolved pulp simulant residue.

- Incorporation of superplasticizing agent S-3 in the cement compound slows down the hydration process and reduces the heat release.

- The minimal heat is released from compounds where clinoplilplite is used as a sorbing additive.

4.10.1.3. Testing of pulse type mixer for pulps cementation

It is important for the cementation process to ensure that the cement compound after the mixer is homogeneous. The stirring performance of a mixer depends on its construction, of operation, and characteristics of mixing substances. Mixture viscosity and time necessary to obtain a satisfactory results are important factors. It should be noted that the period of stirring should not be too long from the beginning of hydration process by which the compound solidifies since it may lead to difficulties in discharging the compound from the mixer.

VNIINM has developed a unique cementation facility with a pulse type mixer. The facility has two advantges - there is no stirrer in it, and the cement compound is guaranteed to be discharged from the mixer. It was interesting to evaluate the possibility of its use for cementation of pulps from storage facilities of MCC. Prototype of industrial cementation facility with a pulse type mixer was tested on pulp simulates of different composition.

The objective of tests is to check the possibility to obtain homogeneous compound of a required quality using the pulse type mixer. Full-scale facility tests were only performed after large number of laboratory tests.

In the tests, samples were drawn during discharging of the cement paste from the mixer,. The quality of pulps/matrix materials mixture was checked as per two parameters: flowability and mechanical strength of the cement compound. Gradually the contents of the pulp simulates were made more complicated. The final test series were carried out with the following technological parameters: cement compound composition (wt %): PS 500-DO - 90; bentonite - 10, W/C - 0,9. the loading capacity of cement compound - 5,2 wt %

The tests were carried out as follows. The cementation facility mixer was loaded with pulp simulates and a mixture of PS 500-DO and bentonite, which was added to the mixer with permanent stirring for 20 min. After the complete loading the mixer was stirred for 5 minutes and then discharged. Three samples were drawn in the beginning, in the middle and at the end of the discharge process to determine the flowability of the compound. Table 18 shows the main parameters of the cementation mode, contents of pulp and matrix substance and the sample cement compound test results.

The results of experiments indicates:

- Samples of cement compound have a similar flowability - 120-135 mm. Compound can be easily discharged from the mixer and fills the drum evenly.

- Cement compound quality meets the standard requirements of mechanical strength, water resistance and freeze resistance.

- Several hours after the loading of the drum the cement compound gets heated (up to 100°C and more) which proves the necessity to use matrix materials with the least heat release in the compound solidification process.

From these experiments it was concluded that the use of a pulse type mixer for pulp cementation makes possible generation of a homogeneous cement compound with a high flowability suitable for the discharge of compound from the mixer into the drums.

TABLE 18. CEMENTATION PROCESS PARAMETERS BY TESTING PROTOTYPE OF INDUSTRIAL CEMENTATION FACILITY WITH A PULSE TYPE MIXER

No	Dry undissolved residue in pulp, wt %	pH of pulp	W/C	Loading capacity of cement compound, wt %	Flowability, мм in n minutes		Mechanical strength [$\sigma_{\mathbf{compr}}$], MPa after n days			Frost resistance		Water resistance	
										[$\sigma_{\mathbf{compr}}$]$_{frost}$ after30 cycles of freezing and thawing, MPa	[$\sigma_{\mathbf{compr}}$] of control samples, MPa	[$\sigma_{\mathbf{compr}}$]$_{water}$ after 90 days in water, MPa	[$\sigma_{\mathbf{compr}}$] of control samples, MPa
					0	30	28	56	90				
29	10,4	9	0,9	5,2	110	115	9,1	10,2	10,6	9,2	10,6	13,0	9,8
30	10,4	12	0,9	5,2	125	123	7,7	7,4	9,3	7,2	9,3	11,8	10,9
30*	10,4	10	0,9	5,2	130	125	9,8	12,3	10,6	9,3	10,6	15,0	11,3
					135	-	9,8	-	12,3		-	-	-
					130	130	-	11,8	10,6		12,3	-	-
									12,3				

*Test 30 was carry out in the laboratory (its results is given for comparison)

5. CONCLUSION

The immobilization of all arising and accumulated liquid radioactive waste in cement matrix compositions is very important for ecological safety of radiochemical plants. In the near future Russian Federation is planning to use industrial cementation units at its two radiochemical combines - PA ”Mayak” (Urals)and Mountain Chemical Combine (Siberia). Wastes of these enterprises that will be sent for cementation includes different radioactive solutions and pulps with complex miscellaneous content.

Scientific scope of the research within the IAEA CRP included the development of cementation processes of specific types of liquid waste streams of PA ”Mayak” and Mountain Chemical Combine. The objective was to study processes occurring at production of cement compound and as well the influence of some waste components on the cement compound quality (mechanical strength, water resistance, frost resistance, flowability, heat generation, loading of salts, limit hydroxide concentration, mixing method, liquid phase arising and others). The research included charaterizations of all the main characteristics of cement compounds. The anticipated scientific results were the understanding of the factors which can impact characteristics of produced cement compounds containing liquid waste of radiochemical plants. General research objective was to receive a new knowledge on cementation technology of radiochemical plants liquid waste.

The executed research on cementation of radioactive waste from spent nuclear fuel reprocessing gave experimental data characterizing the technological process and basic physical and chemical characteristics of produced cement compounds containing different waste (hydrated-salt sludges, filter material pulps, mixture of hydrated salt slurries and filter material pulps, tritium-liquid waste). Determined cementation process parameters will allow to produce cement compound with required quality.

The broad research has been carried out for the development of cementation technology for immobilization of pulps from storage tanks of Mountain Chemical Combine radiochemical plant. Cementation of such pulps is a difficult technological task because pulps are characterized by a complex chemical composition (hydroxides of manganese, iron, nickel, etc., as well as silicon oxide) and a relatively high activity. The research of cementation process of these pulps included the study of the impacts of sorbing additive type and content on cement compounds leachability, cement compounds flowability, influence of cement compound age on its mechanical strength, heat generation of cement compounds and others. The results allowed to state that portland cement and slag portland cement with sorbing additive (klinoptilolite or bentonite)) may be used as a matrix material for pulps immobilization. Experiments helped to determine optimal parameters for cementation process ensuring the required quality of cement compound. Testing of the full-scale cementation facility with a pulse type mixer with use of research results showed that the use of such type mixer for pulp cementation makes it possible to prepare a homogeneous cement compound with the required quality including flowability.

In general the executive research gave new knowledge of factors impacting characteristics of cement compounds during their production stage, storage and disposal. Next step should be testing of the technological regimes on the pilot facility as stage before implementation of industrial cementation facility providing the large-scale production of cement compounds with a required quality.

Investigations were performed using the simulated solutions and pulps, containing radionuclides. All facilities and equipment available including pilot cementation facilities, instruments, radiation control instruments, laboratory equipment, computers and other technique are used at A.A.Bochvar Institute.

Following specialists took part in this work: from A.A.Bochvar Institute - Sukhanov L.P., Poluektov P.P., Zakharova K.P, Naumenko N.A., Chimchenko O.M., Pogorelko O.N., Lebedeva A.V. and from Mountain Chemical Combine – Revenko Ju.A. and Kravchenko V.A.

ACKNOWLEDGEMENTS

Acknowledgements are due to following specialists from A.A.Bochvar Institute - Sukhanov L.P., Poluektov P.P., Zakharova K.P, Naumenko N.A., Chimchenko O.M., Pogorelko O.N., Lebedeva A.V. and from Mountain Chemical Combine to Revenko Ju.A. and Kravchenko V.A.

REFERENCES

[1] GOST R 51883-2002, Radioactive waste cemented. General technical requirements.

[2] NP-019-2000, Collection, treatment, storage and conditioning of liquid RW, Safety requirements.

[3] ZARHAROVA, K.P., et al.,. Radioactive waste localization. Clay influence on cement compound characteristics, Atomic Energy **79** 1 (1995) 23-26.

[4] BATRAKOV, V.G., Modified concrets, Moscow (1990).

[5] BROWN, D.J., LEE, D.J., PRICE, M.S.T., SMITH, D.L.G., Cement - based processes for immobilization of intermediate level radioactive wastes. Proceedings of the conference “Radioactive waste management», London (1985) 145-152.

[6] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Tritium at Nuclear Facilities, IAEA-TRS-234,Vienna, IAEA (1984).

[7] MALEK, R.I.A., ROY, D.M., LICASTRO, P.H., LANGTON, C.A., Slag cement-low level radioactive waste forms at Savannah River Plant, Am. Ceram. Soc. Bull. **65** 12 (1986) 1578-1583.

[8] DOLE, M.L.R., PALMER, M.J., Draft report on conditioning of alpha-bearing wastes,Vienna, November, IAEA, Vienna (1987).

[9] SCHEETZ, B.E., ROY, D.M., Candace Tanner et al. Properties of cement-solidified radioactive waste forms with high levels of loading., Am. Ceram. Soc. Bull. **64** 5 (1985) 687-690.

[10] PIERLAS, R., Conditioning of radioactive waste by concreting, “Radioactive waste management from decommissioning of spent fuel storage, Vol.2, “Waste processing and conditioning, French industrial experience” (1985)164.

[11] ATKINSON, A., EVERITT, N.M., GUPPY, R., Evolution of pH in a radwaste repository. Experimental simulation of cement leacheng. UKAFA, Harwell Lab. (UK) Materials Development Div, AERE-R-12594, DOE-RW-89025, ISBNO-7058-1499-8, March, 1987, UPC №1(64), 1990.

[12] BROWN, D.J., LEE, D.J., PRICE, M.S.T., SMITH, D.L.G., Cement-based processes for the immobilization of intermediate level radioactive waste, Proceedings of the conference "Radioactive waste management", British Nuclear Energy Society, London, 27-29 November, 1984, p.145-152.

[13] VEJMELKA, P., Solidification of liquid concentrates in cement, Management of radioactive wastes, "Interregional training course ”, IAEA, Karlsruhe, FRG, 7 Sept. – 2 Oct. 1987.

[14] KOCHER, D.C., W.LEE, D., Disposal of low-level radioactive waste on the Oak-Ridge reservation, I. Preliminary Screening analysis for identification of important radionuclides, "Radioactive waste management and the Nuclear Fuel Cycle” **16** 2 (1991) 83-99.

[15] READ, D., KROL, A.A., J.THOMPSON, B.G., A structured programme of research into the chemical aspects of radioactive waste disposal, Mat. Res. Soc. Symp **84** (1987) 343-354.

[16] ANGUS, M.J., GLASSER, F.P., The chemical environment in cement matrices, Scientific basis Nucl. Waste manag., 9-th International Symposium, 9-11 Sept., 1985.

[17] MIHARA, SASAKI, T., SHIMOJO, M., SUZUKI, K., Solidification of low-level wastes by inorganic binder, Fifth International conference on radioactive waste management and environmental remediation, vol.2 (1995) 1077-1081.

[18] ELSDEN, A.D., SILMS, J., HARDING, K., A process for the immobilization of a radioactive waste (inorganic ion-exchange material) in a cement matrix, IAEA-SM-261/30, p.167-176.

[19] GUANGRE QIAN, DARREN DELAI SUN, JOO HWA TAY, New aluminium-rich alkali slag matrix with clay minerals for immobilizing simulated radioactive Sr and Cs waste, Journal of Nuclear Materials **299** 3 (2001) 199-204.

[20] TYSON, A., Cesium-leaching from clinoptilolite/cement wasteforms, Proceedings Spectrum`90, Nuclear and Hazardous waste management, Tennessee, 30.09.-04.10.1990.

DEFINITIONS AND ABBREVIATIONS

HLW – high level radioactive waste

IER –ion-exange resins

ILW – intermediate level radioactive waste

FP – filter perlyte

LRW – liquid radioactive waste

MCC – Mountain Chemical Combine

PA“Mayak” –Production Association “Mayak”

PC – portland cement

RW – radioactive waste

SNF – spent nuclear fuel

S-3 – superplasticizer

SPC – slag portland cement

S/C – solution/cement ratio

σ_{comp} – cement compound mechanical strength (compressing) rate, кg/cm^2

VNIINM - A.A.Bochvar Hightechnological Scientific and Research Institute of Inorganic Materials

W/C – water/cement ratio

σ_{comp} – cement compound mechanical strength (compressing) rate, кg/cm^2