RELIABILITY ASPECTS OF RAW TREATMENT AND STORAGE ISSUES AND TECHNOLOGY

L. Jeliazkova
Balbok Co.
Sofia, Bulgaria

ABSTRACT

The general idea of the investigation carried out for 3 years presented in this paper and the results obtained, is the multibarrier protection against radioactive waste when isolating it from environment. For a country as Bulgaria, where there aren't natural geological forms to provide a protection, research in this field is very important, because we must create this protection by ourselves.

Subject of the investigation is low and intermediate level radioactive waste with high content of boric acid from NPP-Kozloduy.

The first part of the paper treats properties of cement solidified final products: compressive strength, leachability, cold resistance, water resistance, bio resistance, stability against thermo-shocks. It's proved that loess, typical for NPP-kozloduy region is a suitable supplement of cement mixture. The practical result of the complete research is the created technology for cementing liquid radioactive waste from NPP-Kozloduy.

In the second part of the paper the created in Bulgaria container for solidified radioactive waste, tested and licensed as suitable package for storage and transportation is discussed.

INTRODUCTION

Safety long term storage of low and intermediate level radwaste is provided by a multibarrier shield. The conception, which is accepted and developed in these investigations includes achievement of high indeces for:

- the hard-set final product;
- the package of the final product.

After conditioning the radioactive waste can be placed in engineered disposal facilities - half-underground and underground type, which are designed with corresponding bioprotection and stability against earthquakes.

PROCESSING OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE WASTE

Liquid radioactive waste of NPP-Kozloduy with reactors type WWER are put to concentration by evaporation. The evaporation concentrate (bottoms)is with high contents of boric acid and radioactivity up to 1.10-3 Ci/l.

Experimental Plan

The technology of cementation has been chosen for processing of radioactive waste from NPP-Kozloduy as it is universal method for immobilization of low and intermediate level radioactive waste, it is simple and inexpensive. But regardless of universality of the method, the quality of the final product depend much on composition of waste, cement used and inert supplements.

The technology that we created secures processing of radioactive waste which contains boric acid (from reactors type WWER) up to the final product showing indices as following:

- compressive strength - above 10 MPa on the 28^{th} day;
- water penetration - none;
- waterproof - shall not change compressing strength after its 90^{th} day of staying in water;
- freezing tight - shall endure over 50 cycles of freezing and defreezing from minus 20°C to plus 20°C;
- stability against thermo-shocks - shall endure over 30 cycles of freezing and warming from minus 20°C to plus 60°C
- bioproof - shall contain bacteriocides properties;
- leachability - by Cs^{137}, Cs^{134}, Co^{60}, under 1.10^{-3} per g/cm^2;
- salt-content - over 10% weight ratio in final product.

Leachability has been defined by ISO 6961 on test samples, containing liquid RAW at department "Radiochemistry" of NPP "Kozloduy". As combining substance has been used cement with additives, securing great strength of the final product, high ratio of water/cement and poor leachability of radionuclides implied in cement matrix. RAW are used as water.

Technology and the manner of applying is for cementing liquid RAW allow a selection of adequate properties for achieving the above mentioned indices of the final product.

The technology has been worked out on the basis of performing a program - the result of two-years' broad research.

The investigations has been carried out with different composition of components and different water/cement ratio. As components of the mixture for solidification were used three sorts of cement and six kinds supplements - loess, zeolite, bentonite, kieselguhr, ash from thermo-electric power stations and micro silicious dust.

The goals of the investigations, held on this broad research program was:

- to specify several alternative compositions with good indices of the final product and salt-content to the highest degree;
- to investigate the influence of the form of the boric acid on the process of solidification of the final product.

Results And Discussion

The experiments with simulated bottoms (SB) were held in two cycles.

The first included ten different groups of compositions:

I group	- cement/loess/SB
II group	- cement/bentonite/SB
III group	- cement/zeolite/SB
IV group	- cement/loess/bentonite/SB

V group - cement/loess/zeolite/SB
VI group - cement/bentonite/zeolite/SB
VII group - cement/loess/microsilicious dust/SB
VIII group - cement/microsilicious dust/SB
IX group - cement/ash/microsilicious dust/SB
X group - cement/zeolite/microsilicious dust/SB

In these ten groups were used different kinds of SB (SB-1, SB-2, SB-3) and cement. The components ratio was different too. The following indices were measured: compressive strength, water resistance, volume density and water-content.

The three compositions (from the I, III and VII groups) that had the best rheological and physicomecanical indices in the first cycle were used in the second cycle. This cycle included a broad program of tests. That compositions had been prepared in high speed mixer. The results of the tests are given in Tables I-IV.

By experiment was proved that the inhibiting effect of boric acid on solidification process do not exist when it is in the form of natrium metaborate. The limit for absence of coming up salts on the extern serfice of the final product is 11.5% weight. The test of cyclic heating (60°C) and freezing (-20°C) is extremely severe. The periodical increasing and decreasing of the final product volume create strains that lead to disintegration of the material. Four samples were put to 50 thermic shocks. Two of them, of the II (I group) and III (III group) compositions broke up on big parts relatively on 30th and 40th cycles of heating/freezing. The rest of samples were tested after the 50th thermoshock. For the II composition (I group) the compressive strength was reduced with 19%. For the III composition (III group) the compressive strength wasn't changed.

TABLE I
Results From Compressive Strenght Test

Composition	Compressive strength on the n-th day						
	7	14	28	60	90	120	150
I (VII group	15.2	19.7	26.5	37.5	38.9	39.1	40.2
II (I group)	7.4	9.4	11.1	11.2	15.1	15.3	16.4
III (III group)	1	11.1	15.5	17.3	17.1	16.3	17.2

TABLE II
Results From Freezing-Resistance Test

Composition	10 cycles		30 cycles		50 cycles	
	Rh1	Rh2 MPa	Rh1	Rh2 MPa	Rh1	Rh2 MPa
I (VII group)	27.8	30.1	28.2	28.8	29.3	27.1
II (I group)	12.5	11.3	13.8	13.0	14.3	14.1
III (III group)	16.9	18.4	17.2	17.4	18.3	14.2

Note: Rh1 - compressive strenght of the control sample
Rh2 -compressive strenght of the sample after 10, 30 and 50 cycles freezing (-20°C) and defreezing (+20°C).

TABLE III
Results from Water-resistance Test

Composition	Rh after water immersion for n days,MPa		
	30 days	60 days	90 days
I (VII group)	33.0	30.0	29.6
II (I group)	13.6	15.7	15.0
III (III group)	17.5	17.1	20.8

TABLE IV
Results from Biodegradation-Resistance Test

Composition	Rh control sample	Rh tested sample
I (VII group)	40.2	34.5
II (I group)	16.4	16.6
III (III group)	17.2	17.5

Note: The compositions showed bactericidic properties. The samples were treated with the following strains:
Aspergillus niger (V.Tieghem)
Penicillium funiculosum (Thom)
Peacilomyces varioti (Bainir)
Trichoderma viride (Pers ex Fr)
Chaetamium globosum (Kunre)

The carried out tests confirmed the opportunity of using zeolite as supplement when processing (cementing) radioactive waste of NPP-Kozloduy and proved such opportunity for the loess. While carrying out our investigation and planning the experiments we based on previously done and discussed research works in field of structure formation in cement-loess mixtures with high water-content (1). The conclusions reached by Bulgarian and foreign authors are connected with the reactions that run in a tricalcium silicate (C3S) system. Here are the most important of them:

1. $C_3S + H_2O \dashrightarrow C_3S_2H_n$ (hydrated gel) + $Ca(OH)_2$
2. $Ca(OH)_2 \dashrightarrow Ca^{2+} + (OH)^-$
3. $Ca^{2+} + 2(OH)^- + SiO_2 \dashrightarrow CSH$
   $Ca^{2+} + 2(OH)^- + Al_2O_3 \dashrightarrow CAH$
4. $C_3S_2H_n$ (with low pH) $\dashrightarrow$ CSH + lime

Note: C - CaO calcium oxide
S - SiO_2 silicon oxide
A - Al_2O_3 aluminum oxide
H - H_2O water

The loess creates favorable conditions for cement stone solidification because of the following reasons. $C_3S_2H_n$ makes unbroken skeleton in the system and for its correct solidification the medium must be satiated with calcium hydroxide. The high content of carbonates in the clay fraction creates conditions for this (3). It's typical for Bulgarian loesses that they have high average values of pH. This reduces the opportunity for $C_3S_2H_n$ destructing - reaction 4. As regards to origin of additional cementing compounds (reaction 3) it's necessary to take into consideration the following special features in loess composition. The quartz is main mineral in the fraction over 0.05 mm. In the examined loess the mica and feldspar content are also high. This is proved by roentgenostructural analysis after heating of the loess on 1000°C. Because of this reason must be noted chemical interaction of calcium hydroxide not only with minerals of the clay fraction but also with quartzes, micas, feldspars and other minerals of the bigger fractions. It's considered that the higher compressive strength under higher humidities and intensive structural transformation are due to more intensive running of reactions 3. But under higher humidity two opposite factors act: on one side more intensive running of reactions 3 and on the other - slowing down crystallization cement stone solidification, because the presence of water lightens pre-crystallization processes and disturbs the thermodinamical resistance of the system.

Of course the real system is more complex than above discussed, but these general theoretical and experimental considerations were necessary while planning the experimental program and choosing the proportions of the components in cement composition. The results of the experiments proved that loess can be used as supplement in the cement mixture.

The additional preliminary investigations on sorbing properties of loess, zeolite and bentonite showed that they all are good sorbents of cesium and cobalt. The best sorbing properties has bentonite. This was proved by long term leach test on samples, prepared with real bottoms. The results are given in the Table V.

The general conclusion, reached on the base of presented results is that cementing is expedient for processing bottoms of NPP-Kozloduy. The final product, prepared by this technology has very good indices, assured by two alternative supplements - loess and zeolite. This technology duarants assurance of the first barrier in long-term storage of radioactive waste.

CONTAINER OF REINFORCED CONCRETE FOR STORAGE AND TRANSPORTATION OF SOLIDIFIED LIQUID RADIOACTIVE WASTE

The container is made of reinforced concrete - 1.95m per side, consisting of two parts - body and lid.

The container is designed to store and transport solid and processed indulated RAW with low activity (LSA - III) and has been classified as package type IP - III, in conformity with the Regulations for Safe Transportation of Radioactive Substances, by IAEA Safety Series No 6.

Characteristics of the container:

- mass of empty container - 6 t;

TABLE V
Leaching rate, Li [kg/cm^2.day] for Radionuclides on 150th Day

Composition	Cs-134	Cs-137	Co-60	NO_3
With bentonite	2.87-5	1.75-5	6.39-5	1.05-3
With loess	3.85-5	4.68-5	6.85-5	2.98-3
With zeolite *	6.24-5	7.61-5	4.28-5	2.87-4
With zeolite **	4.58-5	4.15-5	6.35-5	2.62-4

Note: * zeolite from Bely bair deposit
** zeolite from Bely plast deposit

- reliable mass of full container - up to 20 t;
- reinforcement is calculated and fulfilled (no welding) corrosion-proof for over 300 years;
- there are 4 hooks at the top angles of the body which serve as grippers to manipulate when its transportation and manipulation are carried out, also for precise positioning and arrangement one on the top of another;
- there are sockets at the 4 bottom angles where the hooks are inserted when arranging the containers one on the top of another;
- the lid has been shaped so as to fit tightly into the body of the container and has an opening in the middle through which the cement-radioactive mixture is poured in and prevents the outer surface from being polluted when the pouring is effected;
- after filling the container the opening is closed with concrete. The opening has the shape of "inverted cone" and prevents popping out of the "cup";
- the lid is tightly welded to the body with eight welded parts incorporated both in the body and the lid of the container;
- another metal parts are coated with anticorrosion substance.

To prove the fitness of the container a wide program of tests have been carried out, provisorily divided in two parts:

- To prove fitness for storage of RAW for a long period of time;
- To prove fitness as transportation package.

For criterion in assessing fitness of the container series of shielding tests were performed before and after the other tests. The difference in power of exposition shall not exceed 20 per cent.

As the greater part of test in the two groups coincide, to prove fitness of the container, the following program has been adopted:

The design includes requirement for corrosion proof, avoiding welds of reinforcement. The cement has been designed for a combination of use of additives, where the respective strength increases from 25 to 75 per cent (over 40 MPa on the 18-th day), while, waterproofness grows from 2 to 7 times compared with the common concrete mixtures.

The steadiness of this concrete mixtures has been proved against thermic cycles, chemical reagents and microorganisms.

Watertightness of the container has been proved. The test defines the capability of the container to keep liquids and not to allow any leakage of subsoil waters through the concrete. After the elapse of 48 hours its outer surface was checked for wetness, leakage, cracks. Its surface was dry.

Filled up containers were arranged in four levels during 48 hours. No outside damages were observed (cracks, tear-offs, etc.).

The seismic test was carried out on four full of sand containers arranged one on the top of the other. The maximum acceleration reached by the mass of one-ton oscillator acting over the base of feed-up of 0.15 g is respectively 2.5 x 0.15 = 0.375 g.

The spectrum of reaction recommended by IAEA in the Directory for Safety of Nuclear Plants No 50 SG - SI to 5 per cent of critical finding points as maximum dynamic coefficient

3.13 at 2.5 hz. The respective maximum acceleration ought to be 3.13 x 0.15 = 0.47 g. This value was accelerated the minimum down to which the group of four containers ought to be loaded.

The close observation of the containers while the tests were carried out as well as the processing of recorded accelerations showed that no danger existed with that loading for tipping over of the containers arranged one on the top of the others nor sliding at touching planes. No cracks, damages nor *frays* were noticed.

The results of the carried out dynamic test on concrete containers arranged one on the top of the other, showed that they are fit to endure the prescribed seismic impact at maximum horizontal acceleration at the base 0.15 g having a reserve of over 1.7 times according to IAEA spectrum and to 2.5 times Bulgarian Standard - 87 and demonstrating no damages, tip-over sand slidings.

Two containers were percussion and earthquake tested; one full of cement mixture: they were dropped falling on the bottom, edge, side-bottom and top. One of the two modelled real conditions of operation: full of cementing grout and the other full of equal mass sand (in order to check effect of dynamic percussion of the sand on the container side at drop).

The container full cementing grout underwent free drop on the bottom from 60 cm height, on edge, side-bottom (at emergency) and on corner from 35 cm height.

The container filled with "heavy" sand underwent free drop on edge from 60 cm height, on bottom from 60 cm height, on corner from 30 cm height and on edge from 35 cm height. No cracks were found on both containers. Tear-offs were located aground the bump-spots (at the corners) and of sizes and depth uncovering only the outer reinforcement (i.e. maximum depth up to two cm).

One container filled with cementing grout was percussion and earthquake tested. The purpose of the test was to evaluate the degree of fortuitous radiation average if one container dropped from fourth row of the repository. At free drop on the base from 6.5 m height the container filled with cementing grout and percussion and earthquake tested preserved its integrity. It got a number of vertical surface cracks and one-two horizontal volumetric cracks. The lid suffered most, but although it had many volumetric cracks it retained its integrity. It should be pointed out that the test was carried out under most unfavorable condition: not hardened cementing grout, which is in additional load to the sides (hydraulic percussion at drop), particularly to the lid, which caused the appearance of serious cracks. Despite this unfavorable condition the container proved its exceptional properties. The container was easily lifted with a help of a crane and moved away, and that proves that transportation and manipulation are possible. One can guess that with hardened cementing grout damages at free drop from the above-mentioned height will be far smaller. Results show that in a situation of average dropping of a container from the fourth row (containers will be arranged in four rows, while in storehouse) no radiation will occur.

The penetration test was carried out upon the lid of a container having undergone percussion, earthquake and drop tests from 60 cm fall on the bottom, edge and corner. The metal rod used had a diameter 3.2 cm with semi spherical end and weighed 6 kg. It was dropped six times - three times from one m height, one time from 1.5 m height and two times from 1.7 m height. At the place of impact no cracks appeared nor any damage of wholeness, with the exception of slightment compression.

A container filled with cementing grout, penetration and earthquake tested was placed in a concrete basin, containing diesel fuel which was ignited and left burning for 30 minutes. The fire was extinguished with the help of fire-extinguisher with a purpose of causing thermic shock on the container. The results of this extreme test are satisfactory, two damages incurred (a torn-off part of container's wall, deep 7 cm) are subject to elimination by applying a coating able to recover the original state of the container.

The radiation shield of the container proved its fitness for storage and transportation of RAW with law activity (LSA-III) and what is more with good shielding reserve on the one part because it has been defined by using a *point-source* without accounting its back-absorption while cementing of RAW is being carried out, and on the other, that at the point-source itself power of exposition from 1 to 2 times lower than the admissible (1-1.5 Sv/h).

The container is fit for storage and transportation of law-radioactive wastes (LSA-III) and meets the requirements of package type A, i.e. has big available reserve when used. The lack of defects, concerning its volume, with the applied local radiation shield proves in itself that the selected technology is adequate for the production of the container.

ACKNOWLEDGEMENTS

The author wishes to express her gratitude to Mr. P.Colombo, Brookhaven National Laboratory, USA (consultations). The author wish to point out the generous support which has been given to her by the Committee on the Use of Atomic Energy for Peaceful Purposes of Bulgaria. In addition, the author appreciates the dedicated assistance of hers colleagues and co-workers in this research, especially Messrs. S. Tsochev, Al. Alexiev, M. Meshulam, St. Radomirski, W. Stanchev from NPP Kozloduy and Mr. P. Abadjiev from Scientific Research Building Institute, Sofia, Bulgaria.

This research work was supported by NPP-Kozloduy under Contract No 109/89-3.

REFERENCES

Not available.