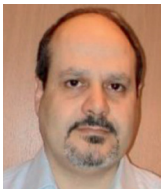
SOLIDIFICATION OF RADIOACTIVE EVAPORATOR RESIDUES WITH HIGH BORATE CONTENT







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Keywords: cementation, radioactive waste treatment, mix design development

https://doi.org/10.32970/CS.2022.1.4

1. INTRODUCTION

The Paks Nuclear Power Plant established a new cementation technology to solidify its untreatable liquid radioactive waste; therefore, CHEMCOMEX Praha a.s. company was entrusted with the task. The work involved the development of the mix design and the installation and turn operation of the technology. Using cementation technology, cement paste made using liquid radioactive waste is poured onto solid radioactive waste stored in steel barrels placed in a reinforced steel container. The qualified so-called compact waste package (CWP) will be disposed of in the National Radioactive Waste Repository in Bátaapáti (Hungary), replacing the currently used concrete container solution. These regulations are consistent with International Atomic Energy Agency (IAEA) standards (IAEA, 1990; IAEA, 1996) and the international practice (Spence et al., 2005, Ojovan et al., 2011; Bart et al. 2013; Abdel Rahman et al., 2015).

During the mix design development, the contractual conditions imposed on the cement paste, the Waste Acceptance Criteria (WAC, Radioaktív Hulladékokat Kezelő Kft., 2018), and the technological conditions had to be taken into account. During the optimisation of the mix proportions, the economic aspects had to be kept in mind, i.e. the liquid radioactive waste content of the cement paste had to be maximised while strictly adhering to the requirements.

2. THE REQUIREMENTS FOR THE CEMENT PASTE

During the mix design of cement paste development, primary attention had to be paid to safety aspects, which primarily meant reducing the leaching properties of the various radionuclides. These must also comply with the WAC of the National Radioactive Waste Repository (NRWR).

The further requirements of the mix design development are the following:

- the cement paste must be made of Hungarian cement,
- the mix must be as simple as it can be with the least number of supplementary cementing materials (SCMs) and admixtures,
- with the selected cement type, it must be processed in a wide concentration range of the characteristic composition of the given waste type,
- the mix design must allow all liquid radioactive waste type procession with the planned technological equipment.

3. THE WASTE ACCEPTANCE CRITERIA (WAC)

The final disposal conception of radioactive waste is based on the multi-barrier approach, a combination of technical barriers and protection provided by the geological environment. The technological barrier system aims to allow only a small amount of radioisotopes over a long period. This purpose can be achieved with low leachable waste form (hardened cement paste) waste isolation by its durable container and infilling any free space around the packages. The space-filling restricts the movement of water and other solutions and can provide appropriate chemical conditions and have adsorption properties for leached radioactive isotopes (Chapman, 2003; Nős et al., 2010; Ojovan, 2011).

The WAC prescribes detailed physico-chemical requirements for depositable waste:

- organic matter content and gas formulation (max. 0.5 bar),
- waste with gas content (max. 1,5 bar at 20 ºC),
- heat evaluation (max. 2 kW/m^3),
- dust content (max. 1 %m/m),
- cavity volume (max. 5 cm, max.10 %V/V)
- free liquid content (max. 1 %V/V)
- content of corrosive substances and complexing agent (max. 1 %m/m)
- hazardous material (it must not contain flammable, explosive, oxidising, infectious and corrosive substances)
- flammability (combustible, compressible waste must be compacted with a compression force of 500 kN. The empty space around combustible, uncompacted waste must be cast with cement paste or cement mortar.),
- compressive strength (min. 10 MPa),
- chemical stability and homogeneity,
- the value of diffusion coefficient (max. 10^{-7} cm^2/s)
- radioactive isotope and nuclear material content

Cementation technology meets both the free liquid content and the cavity volume requirement for waste. However, the criteria for the compressive strength and leaching properties of cement paste, which a testing laboratory will control, must also be met (Baranyi and Kopecskó, 2021).

4. TECHNOLOGY REQUIREMENTS

One of the most important requirements for cementation technology is to ensure the highest space-filling of the compact waste package with the highest water/binder (w/b) ratio and, at the same time, provide that the waste package complies with the WAC. However, the high water content causes porosity to increase due to the growth of capillaries (Lian et al., 2011; Chen et al., 2013; Kondraivendhan et al., 2016). Multiple capillaries cause a larger surface area, and water penetrates more easily into the open pores, making it easier for radioactive isotopes to leach out (Carde et al., 1999). A high w/b ratio can also cause sedimentation and bleeding of cement paste. For bleeding, the requirement is max. 1 %V/ V. About 35 - 40 %m/m of water can be incorporated into the hardened cement paste; this corresponds to a w/c ratio of 0.35 to 0.40. If the concrete is made with more water, the water will evaporate from the surface of the cement paste even in its plastic state. As a result, it begins to shrink (early or plastic shrinkage), and capillary pores of the cement stone will form (Powers, 1958; Nehme, 2004). In addition to the above, cement stone may contain air bubbles from mixing and casting. The strength of the solidified cement paste depends on the strength and porosity assumed to be non-porous cement paste.

The strength function according to Powers:

$$R_{c,\square} = R_{c,max}\left(1 - \frac{p}{100}\right)^{n},$$

where $R_{c, max}$ is the cube strength of assumed to be non-porous cement paste (cc. 200 MPa), p is the porosity, and n is an exponent (kb. 4,7) (Balázs, 1994). The leaching properties of hardened cement paste can also be deduced by measuring the compressive strength.

The thermal stress due to the high hydration heat can create cracks in the compact waste package. The requirement can reduce this if the heat of hydration of the cement paste should not reach 80 ºC in the middle of the container (Amin et al., 2009; Batog et al. 2017).

The mix design must also ensure the proper consistency of the cement pastes, which allows the free cavity volume between the solid waste in the barrels to be filled. At the same time, it must meet that requirement to minimise the amount of cement paste remaining in the mixer. For cement paste to meet these criteria, the Suttard consistency must be in the range of 150 to 200 mm. It is an essential technological requirement that the value of the consistency does not fluctuate significantly during mixing and draining.

The expected time of container filling is approx. 3 - 5 hours depending on the empty cavity of the barrels. It is undesirable for the cement paste prepared at the beginning of the filling process to begin to solidify before the last batch of cement paste is drained, as the bonding of the cement paste during the vibration of the container will be damaged. Therefore, the initial set of the cement paste should not be less than 3 hours, but the too-long setting time prevents the waste package from being moved. Particular attention should be paid to this phenomenon, as the borates in the solution retard the hydration of the cement (Cseténi and Glasser, 1995; Coumes, 2003; Davraz, 2010; Han et al., 2010; Sun et al., 2011; Kratochvíl et al., 2014; Li et al., 2019).

5. PROPERTIES OF RADIOACTIVE EVAPORATOR RESIDUES (CONCENTRATES)

The wastewater generated in the Paks NPP is evaporated to be stored in a smaller volume. The pH of the evaporated solution was adjusted at 12 with sodium hydroxide (NaOH) to increase the solubility of the borates. The resulting evaporation residues (concentrates) contain boric acid (borates) in a concentration of 180 – 200 g/dm^3; mainly, this causes the high (200 – 400 g/dm^3) dry matter content of the solution, which must be taken into account when embedding waste in cement.

The evaporator residues are stored in 17 TW-labelled tanks containing significant amounts of nitrates in addition to borates (*Table 1*). The bottom of the tanks also contains different amounts of sludge, which may consist of unknown amounts of undissolved borate crystals in addition to the insoluble phase. The molar ratio of Na:B ≈ 1 in the solutions indicates that boric acid is present in the form of sodium metaborate ($NaBO_2$) in the evaporator residues (Blansdae, 1939; Pungor, 1987).

Concerning the composition of the evaporator, residues differ in each storage tank and may even vary in the different parts of the given tank (400 – 500 m^3), so the concentrates must be homogenised in the first step. Therefore, the pre-homogenisation step takes place already in the storage tank, and after the liquid waste transportation, it is mixed in the homogeniser tank of the cementation plant.

Table 1. Composition of the various evaporator residues (MVM Paks NPP, 2019)

pH	Nitrate [g/dm^3]	Boric acid [g/dm^3]	Molar ratio ($NaOH/H_3BO_3$)
12	5 - 72	110 - 203	0.95 – 1.21
Oxidizable [g/dm^3]		Density [kg/dm^3]	Dry matter [g/dm^3]
1.3 – 52.1		1.15 –1.27	206 - 435

The cementation mix design thus had to cover the evaporation residues for approx. 230 g/dm^3 dry matter and ca. 90 g/dm^3 boric acid concentration difference. During the experiments, the mixtures were designed to its water/cement ratio (w/c) of 0.5.

6. MIX DESIGN DEVELOPMENT

The followed logic was applied during the process of the mix design development:

1. laboratory experiment with model (surrogate) solutions,
2. determination of the composition of liquid radioactive waste,
3. laboratory cementation experiments with model solutions,
4. investigation of laboratory cementation with radioactive evaporator residues,
5. pilot cementation tests.

The basic condition for the development of a cementation mix design is the knowledge of the parameters of the liquid radioactive waste to be cemented that have a significant effect on the formulation. Hence, we determined the density, pH, free alkaline (NaOH), nitrate (NO_3^-), dry matter, and boric acid (borate) content of the concentrate. Knowing these data,

we prepared inactive model solutions to simulate the radioactive evaporator residues embedded in the cement matrix.

In the first step of the mix development, the compliance of the cement paste with the technological requirements (consistency, bleeding, initial setting time, rheological behaviour, effect of vibration, early compressive strength) was investigated. In the case of appropriate mixtures, we modified the constituens based on the experience gained during the experiments to improve the cement paste's technological parameters and the properties of the final product. The measurements that need a longer time or a particular device (e.g. heat evaluation, leach test) will only be performed on mixes that already meet the requirements in their other parameters.

6.1 Materials used for the experiments

Cement types available on the Hungarian market were used for the experiments: CEM I 52.5 N (DDC), CEM I 42.5 N (DDC), CEM I 32.5 N-LH (DDC), CEM III/B 32.5 N-S (DDC), and CEM III/B 32.5 N-LH/SR (Lafarge). Two types of metakaolin were tested during the experiments: Metakaolin KM60 (KERAMOST) and Metakaolin METAVER N (NEWCHEM), which composition can be seen in *Table 2*.

Table 2. Composition of metakaolins used

	Metakaolin KM60	Metakaolin METAVER N
SiO_2	50 - 55%	52 - 53%
Al_2O_3	min. 40%	43 - 44%
Fe_2O_3	max. 1.45%	< 1%
TiO_2	max. 0.8%	< 1%
K_2O	-	< 1%
CaO	0.05 – 0.5%	< 0.5%
MgO	0.20 – 0.45%	< 0.4%
Na_2O	-	< 1%
$K_2O + Na_2O$	max. 1.5%	-

KEMA (KEMA MORAVA) microsilica was also used for experimental purposes (*Table 3*).

Table 3. Composition of KEMA microsilica used

SiO_2	~ 90%
CaO	~ 0.8%
MgO	< 1.5%
Al_2O_3	< 1%
Na_2O	~ 0.5%

Three types of plasticiser, available in the Hungarian and European markets were used: Sika ViscoCrete 21, Sika ViscoCrete 1035, Sika ViscoCrete 4035.

6.2 Test methods for cement paste

Consistency

The consistency of the fresh cement paste was measured according to the Suttard method (Macijauskas, 2013). The Suttard type viscometer is a 50 mm internal diameter and 100 mm height stainless steel cylinder placed on a horizontal smooth, scaled base plate. The cylinder must be filled to the top with cement paste. Then lift the mould and let the cement paste flow and spread on the base plate for 15 seconds,

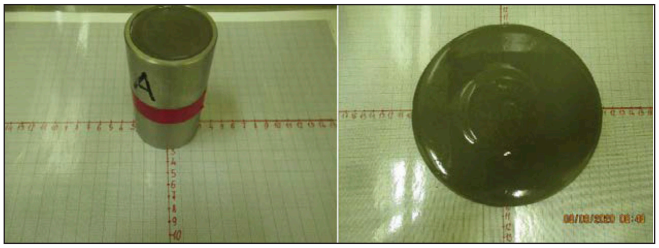

Fig. 1. Consistency measurement with Suttard method Bleeding

then measure the maximum of the cement paste spread in the two directions after 30 seconds (*Fig. 1*). The diameter of the spreading paste is calculated from the average of these two measurements.

Bleeding

Samples of cement paste of known volume are filled in a sealed sampling bottle, and the amount of water appearing on the surface is examined after 24 and 48 hours. After determining the extent of bleeding, the liquid is poured back to the surface of the sample and sealed until the subsequent measurement. The amount of bleeding is given as a %V/V of the total volume of fresh cement paste (*Fig. 2*).

Fig. 2. Bleeding and shrinkage measurement

Initial setting time (IST)

The initial setting time (IST) of the cement paste was measured with manual Vicat apparatus according to the EN 196-3 standard.

Measurement of heat evolution

The kinetics of heat of hydration was determined by pouring the cement paste into a 1 L plastic beaker and then placing it in a 300×400×300 mm polystyrene insulated box with at least 10 cm thickness. Close the calorimeter and immerse the thermocouple in the centre of the sample (*Fig. 3*), using another sensor to record the room temperature using a Comet M1200 temperature data logger (Kopecskó and Baranyi, 2022).

6.3 Test methods of hardened cement paste

Compressive strength measurement

The compressive strength of the cemented product was determined partly according to EN 196-1 and partly according to EN 12390-3 standards using a Controls DigiMax semi-au-

Fig. 3. Measurement of heat evolution

tomatic console with a compression frame with a maximum capacity of 500 kN and a 3000 kN.

Determination of rebound number

The rebound number of the solidified cement paste was measured to estimate the compressive strength of the product. The determination was performed according to EN 12504-2 with a Proceq SilverSchmidt digital Schmidt hammer.

Leaching test

The measurement method for calculating the diffusion coefficient was performed according to the ASTM C1308-08 standard. During the test, a cylindrical specimen 28 mm in diameter and 56 - 69 mm high was immersed in deionised water tempered at 20 ± 1 °C (*Fig. 4*).

The volume of the leaching water is ten times the surface of the cylinder, which must be changed to fresh (clean) water after 2, 7, 24 hours, and daily for the next 10 days by transferring the specimen. Each leaching water was sampled and examined with a gamma spectrometer. The diffusion coefficients of each component were calculated according to Fick's second law using the following equation:

$$D = \pi \left[\frac{a_n/A_0}{(\Delta t)_n}\right]^2 \left[\frac{V}{S}\right]^2 \left[\frac{1}{2}\left(\sqrt{t_n} + \sqrt{t_{n-1}}\right)\right]^2,$$

where a_n/A_0 is the cumulative leached fraction, $(Dt)_n$: $t_{n-1} - t_n$ [s] time interval, V is the volume of the specimen [cm^3], S is the surface of the specimen [cm^2].

6.4 Cementation experiments with model solutions

The first experiments were performed with CEM I 32.5 N-LH and CEM I 52.5 N cement, for which a model solution was added with a w/c ratio of 0.5. However, the cement pastes thus prepared showed a high degree of thixotropic behaviour, which would not have allowed the plant mixer to be emptied and was not suitable to fill the free space of the solid radioactive waste.

Fig. 4. The specimens stored in a climate chamber and the hanging leaching test specimen

At low salt concentrations, thixotropic behaviour of the cement paste was also observed. At high salinity, although the cement paste's consistency improved, at 0.5 w/c we experienced bleeding, initial set retardation (> 24 hours), and inappropriate compressive strength of the product made of CEM I 32.5-LH type cement.

Attempts were made to reduce the retarding effect of boric acid binding with lime hydrate ($Ca(OH)_2$), which increased the early compressive strength of the specimens by 2 to 5 MPa and minimised bleeding. Due to the early thixotropic effect of the lime hydrate and the need to solidify concentrates in a wide boric acid concentration range with only one type of cement, further experiments are required.

Mixtures made of blast furnace slag cement had better leaching properties than the Portland cement; therefore, CEM III/B 32.5 N-S cement experiments were also performed. This type of cement can be used for the solidification of evaporator residues with model solutions and lime hydrate admixture. The requirements for compressive strength, setting time and bleeding properties for these mixtures meet the specified conditions when more than 2% lime is added. Suitable consistency can only be achieved with a low boric acid content (100 g/dm^3) by using vibration. The results show that CEM III/B 32.5 N-S type cement is appropriate for solidifying the model solution with a boric acid concentration of 250 g/dm^3 at a lime hydrate addition of 1.3 - 5.4%.

Based on these results and conclusions, the effect of boric acid concentration and lime hydrate ratio on the properties and technological parameters of the solidified product was investigated. We performed the experiments with three model solutions of different boric acid concentration (80, 140, 200 g/dm^3) with a nitrate content of 42.5 g/dm^3 and a constant w/c ratio of 0.5.

Table 4. Influence of boric acid and lime hydrate on the technological parameters of the cement paste

Boric acid conc. [g/dm^3]	Suttard [mm]	IST [h]	Compressive strength[2] [MPa]
80 (0.5 – 2.5%)[1]	60 – 95	50 - 60	33 - 37
140 (0.9 – 4.6%)[1]	50	0.3 – 0.6	20 - 26
200 (1.4 – 6.9%)[1]	110 – 175	0.4 – 0.7	29 - 34

[1] Lime hydrate concentration given in cement %m/m, [2]at 28 days of age.

It can be seen from the results of *Table 4* the technological parameters studied depend on the boric acid concentration. Still, the addition of lime hydrate has practically no effect on them. All tested parameters reach the minimum expected value at medium (140 g/dm^3) boric acid concentration; therefore, further studies were performed to investigate the effect of $Ca(OH)_2$ concentration with lime hydrate-free mixtures.

Table 5. Properties of the mixtures without lime hydrate

Boric acid [g/dm^3]	Suttard [mm]	IST [h]	Compressive strength [MPa]	
			7 days	28 days
80	85	48	28.39	38.09
140	50	< 15	21.31	24.20
200	195	< 15	22.37	30.15

Our studies confirmed that the addition of lime hydrate has a negligible effect on the final properties of the solidified evaporation residue (*Table 5*). These parameters depend mainly on the concentration of boric acid in the evaporation residue.

6.5 Investigation of the kinetics of hydration heat

The kinetics of the hydration heat evolution of a cement paste prepared using a model solution with a boric acid concentration of 150 g/dm^3 can be seen in *Fig. 5*. It can state that the maximum temperature (62 °C) of CEM I 52.5 N cement paste does not exceed the limit of 80 °C.

6.6 Solidification possibilities of evaporator residues with CEM III/B 32,5 N-LH/SR type cement

The leaching properties of the hardened cement paste can be improved by reducing the porosity, which can be achieved mainly by using materials with pozzolanic properties (e.g. slag, microsilica, metakaolin) and by reducing the w/c ratio (Poon et al., 2001). By decreasing the w/c, the cement paste's viscosity is increased; at the same time, the porosity and the

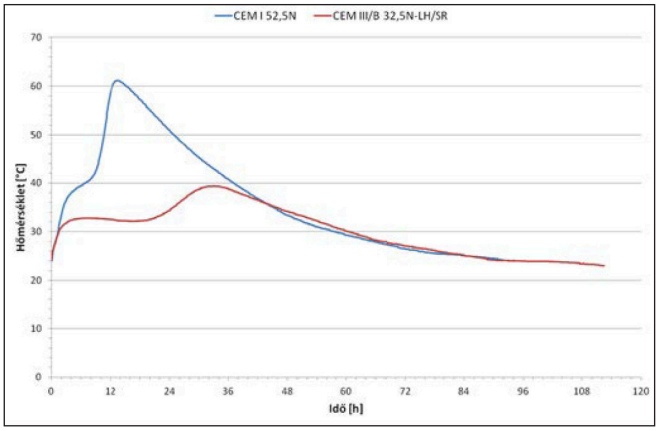

Fig. 5. Heat of hydration comparison of cement paste by using the model solution with CEM I 52.5 N and CEM III/B 32.5 N-LH/SR type cement

diffusivity are also reduced, as well as the bleeding of the cement paste but, which means a higher consistency. Therefore, in addition to the change of cement type, we also examined the effect of w/c factors on technological parameters. At the same time, we studied whether the conditions for the preparation of cement paste and the results of the experiments with pure CEM I 42.5 N Portland cement can be used to apply CEM III/B 32.5 N LH/SR cement. These experiments were also performed with evaporation residue model solutions containing 120 g/dm^3, and 210 g/dm^3 boric acid in the presence of 1.25 %V/V nitric acid (HNO_3). The rheological properties (densifying) of the cement paste can be affected by the decrease in pH, thus the optimal volume of the nitric acid was determined in previous examinations.

Based on the results shown in *Table 6*, the w/c ratio should be reduced below 0.54 to achieve better bleeding and compressive strength values.

Table 6. Parameters of mixtures made using 120 g/dm^3 boric acid concentration model solution and CEM III/B 32.5N LH/SR type cement

w/c		0.54	0.56	0.58
IST [h]		18	24 – 48	24 – 48
Suttard consistency [mm]		128	143	150
Bleeding after 24 hours [%]		0.7	0.9	1.1
Compressive strength [MPa]	7 days	4.92	4.05	3.45
	14 days	9.03	8.06	7.78
	28 days	19.96	20.55	18.24

Table 7. Parameters of mixtures made using 210 g/dm^3 boric acid concentration model solution and CEM III/B 32.5N LH/SR type cement

w/c		0.46	0.48	0.50
IST [h]		< 15	< 15	< 15
Suttard consistency [mm]		120	135	140
Bleeding after 24 hours [%]		0	0.90	0.88
Compressive strength [MPa]	7 days	8.87	8.28	8.32
	14 days	14.23	12.88	13.95
	28 days	26.67	22.66	20.09

The best parameters were shown in the sample with a boric acid concentration of 210 g/dm^3 and a w/c ratio of 0.46 (*Table 7*), but early thixotropic behaviour was also observed in this case. Increasing the w/c ratio to 0.47 could improve these properties but would increase the certainty of cement paste bleeding.

6.7 Cement pastes with the addition of metakaolin and microsilica

Henceforth, experiments were performed to improve the properties of the mixture using CEM I 42.5 N using metakaolin and microsilica at a constant nitric acid content of 1.43 %V/V (*Table 8 – 11*).

Table 8. *The main properties of cement paste made using 120 g/dm³ boric acid and metakaolin KM60 (w/c = 0.50)*

Metakaolin KM60 [%]		0	5	10
Suttard [mm]		170	150	125
IST [h]		3 – 4.5	2.5 – 3	2.5 – 3
Bleeding after 24 hours [%]		0.4	0.3	0
Bleeding after 48 hours [%]		0	0	0
Compressive strength [MPa]	7 days	24.81	18.07	27,47
	14 days	28.95	27.27	37.95
	28 days	35.78	30.70	39.49

Table 9. *The main properties of cement paste made using 210 g/dm³ boric acid and metakaolin KM60 (w/c = 0.48)*

Metakaolin KM60 [%]		0	5	10
Suttard [mm]		170	150	125
IST [h]		3 – 4.5	2.5 – 3	2.5 – 3
Bleeding after 24 hours [%]		0.4	0.3	0
Bleeding after 48 hours [%]		0	0	0
Compressive strength [MPa]	7 days	24.81	18.07	27.47
	14 days	28.95	27.27	37,95
	28 days	35.78	30.70	39.49

Table 10. *The main properties of cement paste made using 120 g/dm³ boric acid and KEMA microsilica (w/c = 0.50)*

Microsilica [%]		0	5	10
Suttard [mm]		170	145	113
IST [h]		3 – 4.5	1.42	2
Bleeding after 24 hours [%]		0.4	0	0
Bleeding after 48 hours [%]		0	0	0
Compressive strength [MPa]	7 days	24.81	22.17	19.68
	14 days	28.95	24.14	28.26
	28 days	35.78	32.07	31.47

Table 11. *The main properties of cement paste made using 210 g/dm³ boric acid and KEMA microsilica (w/c = 0.48)*

Microsilica [%]		0	5	10
Suttard [mm]		180	155	120
IST [h]		1.5	2 – 3	2 – 3
Bleeding after 24 hours [%]		0.50	0	0
Bleeding after 48 hours [%]		0.37	0	0
Compressive strength [MPa]	7 days	24.76	19.02	17.01
	14 days	31.30	26.14	24.45
	28 days	36.14	30.57	35.40

It can be seen from the data in Table 11 that the addition of microsilica and metakaolin increase the consistency of the cement paste, while these SCMs reduce the bleeding tendency. There is a slight decrease in compressive strength for both materials; however, even at 7 days of age, these values exceed the required 10 MPa.

6.8 Leaching tests of cement paste made of model solution containing ^{137}Cs tracer

The cementation experiments were performed with ^{137}Cs-labelled model solutions, which showed the efficiency of replacing part of PC with SCMs to improve the leaching properties of the final cemented product. The experiments were implemented at Nuclear Research Institute (Ústav jaderného výzkumu Řež u Prahy). The leaching test was performed according to standard ASTM C1308-08. During the specimen preparation CEM I 42.5 N, CEM III/B 32.5 N-LH/SR type cement, metakaolin, and microsilica were used with ^{137}Cs-labelled, 120 and 210 g/dm³ boric acid concentration model solution. The results showed that the diffusion coefficient of ^{137}Cs corresponded with the defined value in the WAC (10^{-7} cm²/s) even without SCMs; but using these materials, the diffusion coefficient can be reduced by an order of magnitude.

6.9 Experiments with evaporator residues

Based on observations of cementation experiments with model solutions, test mixtures were performed using different evaporation residues, which showed similar results to the inactive model solutions; therefore, further optimisation experiments were performed using CEM I 52.5 N and supplementary cementing materials (SCMs).

Table 13 shows that we achieved better results for all technological parameters using CEM 42.5 N cement.

Table 12. *The main properties of cement paste made using type CEM I 42.5 N cement and evaporation residue from the tank 02TW10B003*

w/c	0.43	0.49
pH (concentrate)	11.5	11.7
Suttard [mm]	125	160
IST [h]	25.5 - 40	28 - 40
Bleeding after 24 hours [%]	0	0.4
Compressive strength [MPa]	26.75	24.82

Table 13. *The main properties of cement paste made using two types of cement and evaporation residue from the tank 02TW10B003 (w/c = 0.49, pH = 11.8)*

Cement type	CEM I 52.5 N	CEM 42.5 N
Suttard [mm]	125	160
Suttard after 30 min. [mm]	118	155
IST [h]	48	28 - 40
Bleeding after 24 hours [%]	0	0.4

6.10 Experiences with cementation of evaporation residues from tank 02TW80B003

The concentrate to be processed for the first time with the current cementation technology is located in tank 02TW80B003, which contains a high-salt, alpha-emitting (trans-uranium-containing) solution generated during a malfunction at the Paks Nuclear Power Plant in 2003 (*Table 14*).

Table 14. Composition of evaporator residue in tank 02TW80B003 (550 m³) (MVM Paks NPP, 2019)

Molar ratio ($NaOH/H_3BO_3$)	Density [kg/dm³]	Dry matter [g/dm³]
1.08	1.232	362.60
pH	**Nitrate [g/dm³]**	**Boric acid [g/dm³]**
12	22.59	184.54

During the further mix design development, we tried to increase the waste content, so the concentrate/bonding ratio of the cement paste also ruled out the importance of using other admixtures such as superplasticiser or nitric acid. Finally, the cementation results have shown that the optimal mix proportions of the evaporator residue from the 02TW80B003 tank was achieved using 0.61 w/b (w/c = 0.44) and 25% KM60 type metakaolin. Thus the desired mixing ratio was as follows: concentrate : cement (CEM I 42.5 N) : metakaolin (Keramost KM 60) = 1 : 1.32 : 0.33. During the laboratory experiments, compressive strength tests were performed on 40×40×40 mm specimens, and then during the pilot tests, we also performed on standard specimens with an edge length of 150 mm. The results are summarised in *Table 15*, which are the averages of three parallel measurements.

Table 15. Compressive strength results of solidified cement paste made using evaporation residue from tank 02TW80B003

Exp.	Specimen type	KM60 [%]	Compressive strength [MPa]		
			7 days	14 days	28 days
Lab.	40 mm	11	6.30	38.65	48.16
	40 mm	25	22.96	50.80	55.38
Pilot	40 mm	25	1.47	18.56	40.28
	150 mm	25	n.a.	n.a.	36.96

It should be noted that the 7-day demoulding of the specimens was problematic in some cases, on the one hand, due to the slow setting of the cement paste; on the other hand, due to the adhesion of the cement paste to the mould. Another critical parameter for a cemented product is the leaching property of each isotope, i.e. the value of the diffusion coefficient. Measurements were performed according to ASTM C1308-08, previously described in *Chapter 6.2*. In our experience, the ^{60}Co isotope is only slightly, while the ^{137}Cs isotope is more soluble from the specimens. However, its diffusion coefficient is still two orders of magnitude lower ($4 \cdot 10^9$ cm²/s) than the 10^{-7} cm²/s as prescribed in the WAC.

7. CONCLUSIONS

In this study we summarised the inactive and radioactive laboratory experiments of the cementation mix design of different types of liquid radioactive waste; we presented the used materials and test methods.

The first step of the mix design development was to determine the composition of the evaporator residues, which followed by the cementation of inactive model (surrogate) solutions with CEM I 32.5 N-LH, CEM I 52.5 N, CEM III/B 32.5 N-S and CEM III/B 32.5 N-LH/SR types of cement. Henceforth, attempts were performed to reduce the set retardation effect of boric acid with lime hydrate. The measurements show that the lime hydrate has a negligible impact on the final parameters of the hardened cement paste, but the boric acid content has a great effect on it. During the further experiments, supplementary cementing materials (SCMs) were added to the cement paste to decrease the porosity and improve the leaching properties. For this purpose microsilica and metakaolin were used, but in order to decrease of diffusion coefficient, the w/c ratio of the cement paste must be reduced. During these measurements, the effect of nitric acid (1.25 – 1.43 %V/V) on the rheological properties were observed. Since the most important property of the cement paste is the low diffusion coefficient, thus the w/c and porosity must be reduced. Finally, CEM I 42.5 N type Portland cement and 20 %m/m Keramost KM60 type metakaolin was used, and with this mix design all technological parameter of the cement paste was provided.

In the case of evaporation residues, the composition can vary from tank to tank, a protocol for the development of proper and applicable mix design was also determined. As a result of the inactive laboratory experiments, all studied radioactive evaporator residues can be solidified, and the properties of the fresh and hardened cement paste meets the WAC and all technological requirements.

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