CONDITIONING OF SOLID RADIOACTIVE WASTE USING CEMENT MATRIX

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The article discusses solid radioactive waste conditioning using cement matrix. It considers grouting methods for the waste of different composition and fragment size. It provides cement formulations for various types of waste being cemented by mixing, impregnation and pouring. The study shows that the impregnation method can be considered as a most effective option for solid waste conditioning using cement mortars.

Keywords: *radioactive waste, cement matrix, cement compositions, solidification of solid radioactive waste.*

Introduction

Measures provided for under the Federal Target Program Nuclear and Radiation Safety in 2016—2030 involve a great deal of efforts aimed at remediation and decommissioning of nuclear legacy facilities. These inevitably result in the generation of radioactive waste (RW) of various morphological composition, including fragments of dismantled equipment, building structures and bulk materials such as construction waste and contaminated soil. Norms and rules in the field of atomic energy use [1] stipulate that the RW should be conditioned to provide its compliance with waste acceptance criteria, i.e., to provide a stable waste form, to isolate the radioactive materials and to provide the safety during waste transportation and final disposal (in RW disposal facilities, RWDF). RW available in the form of finely dispersed dusty materials, for example, ash residues, should be treated in accordance with a similar procedure. Waste from nuclear decommissioning is commonly categorized as low- and intermediate-level waste (LLW, ILW). The key LLW and ILW conditioning method provides for their inclusion into a matrix composition. Cementation of solid radioactive waste (SRW) using cement-based matrixes is considered as a most versatile and proven conditioning method. LLW and ILW cementation method is widely used globally since the resulting conditioned product meets the requirements of corresponding regulations provided quite low capital and operational costs.

Once cementation technologies were actively developed by MosNPO Radon. In 1995—2011, production units were developed to condition various groups of solid radioactive waste, performance parameters of corresponding processes and unified formulations of cement mixtures were specified allowing to produce cement compounds that would meet relevant regulatory requirements [2]. This article summarizes the main areas of cementing method application for SRW conditioning purposes.

General SRW conditioning requirements

RW processing and conditioning, in particular, when it comes to SRW, seeks to condition them into stable solid forms, to fix radioactive substances and to reduce the volume, thus, decreasing the cost of waste storage, transportation and disposal [3]. Provisions of national norms and rules in the field of atomic energy use stipulate that "RW pertaining to the first, second and third class shall be disposed of in a structurally stable waste form. The waste form and (or) the RW packaging designed for RW Class 1, 2 and 3 should preserve its physical dimensions, structure and mechanical properties under disposal conditions given the limits specified in the designs" [1]. Obviously, in this case, mechanical properties stand for the strength of the package with RW placed into a disposal facility. Thus, two options can be suggested to comply with this condition: the use of a durable container or solidification of its contents. As for the RW class 4, somewhat different regulatory requirements are applicable in this case. Therefore, such waste can be disposed of without prior cementation or without any packaging [1]. At the same time, free-flowing dusty waste requires either some treatment to provide a structurally stable waste form (cementation) or packaging [4]. Quite similar requirements for such wastes are also stipulated in [1]: "RW present in a powdery dispersible form with a high dissipating ability should be converted into a form allowing to limit its dissipating ability and (or) packed in such a way that the radiation exposure to the employees (personnel), population and the environment caused by potential release of radioactive substances from the RW package (unpackaged RW) during normal and abnormal operation of RWDF does not exceed the limits established in regulatory legal acts."

Requirements for the mechanical strength of disposal packages are viewed as main standardized indicators, since the long-term safety of RWDF largely depends on this very property of conditioned RW. Mechanical characteristics of RW packages shall comply with the conditions of transport and processing operations, including stacking, if this is provided for by the transport and processing disposal flowchart. According to engineering standards, mechanical strength of a RW package shall be not lower than the required limit established in relevant safety rules for the transportation of packages containing A-type radioactive materials, which corresponds to a compressive strength of at least 5 MPa [1]. It should be noted that these RW package requirements shall be met by combining the properties of RW packaging elements, including its radioactive content, waste form and container (packaging set) [1]. SRW containerization experience shows that the volume of voids in a container loaded with waste may amount to 40—60%. Filling of these voids with a cement mortar may prove to be efficient enough to form a cement matrix of a required quality and would result in a final product with its volume being equal to the initial bulk volume of the waste. Thus, RW conditioning option can be selected: either RW cementation resulting in a strong compound and the use of "light" and, therefore, cheaper thin-walled containers with a large useful capacity or the use of durable thick-walled containers with much lower useful capacity and much higher cost. It should be noted that the economic benefit from the use of thin-walled containers increases significantly, since the RW disposal costs are calculated based on the gross volume of the package, i.e., taking into account the container capacity.

Selection of a cementation method suggesting the use of a purposely selected cement composition depends on the waste type. For finely dispersed SRW being considered homogeneous in terms of particle size distribution, mixing methods are mainly applied either directly in a container or in a mixer. The cement compound is subject to a treatment in the container either by means of rotating the hermetically sealed container or using stirrers. The mixer treatment may be performed either in a batch or in a continuous mode.

In addition to the waste type, other parameters (simplicity and reliability of operations, performance, amount and type of secondary waste generation, minimization of radiation exposure to personnel, maintainability and the cost of equipment) affect the choice of equipment and the method of cement compound mixing. Nevertheless, the most important parameters are fail-safety, reliability and quality of cement compound mixing providing maximum waste inclusion.

Cement compound mixing in a container provides certain advantages such as simplicity of all operations, accurate control over the number of components during batch dosing, and minimum amount of secondary waste. It also has some disadvantages: the container cannot be filled completely since some free space should remain allowing the mixture to move, sampling of the cement compound to control the quality of the resulting product is quite challenging.

Batch cement compound mixing in tank mixers is characterized with the following advantages: high mixing quality, accurate control over the number of components during batch dosing, and the ease of control sampling. Relevant disadvantages mainly include possible separation of cement slurry with heterogeneous waste in the mixer due to commonly slow mixing, required application of only standard-volume containers.

Small volume of secondary waste, optimal container filling, potential application of containers having different sizes are seen as the key advantages of continuous cement mortar mixing in mixers. Corresponding disadvantages include uneven dosing of bulk components suggesting high probability of feeding equipment and mixer plugging. In addition, the composition of the compound changes when the procedure is launched and stopped.

Cementing of coarsely fragmented and compacted SRW being consolidated by pouring directly in the container is considered as the most mature method. Nevertheless, cement slurry is supplied to the surface of the SRW layer, which, under the influence of its own mass, penetrates into the voids between the waste fragments. Pouring method has some disadvantages, namely, uneven filling of voids with cement mortar, no guaranteed homogenization of the lower waste layers and potential loss of control over the quality of the cement compound; only high-flowability cement mortars can be used which can result in unsatisfactory properties of the compound, and incomplete filling of the container with waste since some free volume should remain above the SRW layer for cement mortar feeding.

Impregnation method, when the volume of the waste in the container is saturated with cement mortar using special industrial methods, is considered as the best option for SRW with small fragments and dense packing of the bulk layer. Common impregnation methods suggest either the application of a vibration impact on the container filled with waste along with simultaneous injection of high-flowability cement mortar by an injector or the use of wire mesh with waste immersed in a container with cement mortar. The advantage of the impregnation methods is seen in the guaranteed homogenization of the entire SRW volume, whereas the disadvantages include incomplete filling of the container with waste, unsatisfactory properties of the compound due to the use of high-flowability cement mortars.

The cement composition shall ensure that the quality of the cement compound complies with the requirements set for the considered production process and long-term storage. Standard regulatory requirements for cemented RW shall provide the preservation of their initial physical and chemical properties and the integrity during waste handling, transportation, storage and disposal.

Regulatory requirements [4] stipulate that "the quality indicators of the solidified SRW compound shall correspond to the quality indicators set for immobilized liquid RW in accordance with federal norms and rules in the field of atomic energy use." Table 1 shows the main quality indicators for a cement compound that should be confirmed by its testing in accordance with established procedures [5].

Table 1. Main quality indicators for cement compounds [6]

Quality indicator	Acceptable values
Water resistance (leaching rate according to ^{137}Cs and ^{90}Sr)	Not more than $1 \cdot 10^{-3}$ g/cm^2 day
Mechanical strength (ultimate compressive strength)	Not less than 50 kgf/cm^2
Radiation resistance	Mechanical strength of not less than 50 kgf/cm^2 after being exposed to a dose of 10^6 Gr
Resistance to thermal cycles	Mechanical strength: not less than 50 kgf/cm^2 after 30 freezing/thawing cycles (−40 ... +40 °C)
Water resistance	Mechanical strength: not less than 50 kgf/cm^2 after 90-day immersion in water
The volume not included into the composition of LRW cement compound	Not more than 1% by volume

There are various compositions of cement mixtures proposed for RW conditioning purposes and their choice depends on the waste type. Cement mortars suggesting the application of commonly used Portland cement (PC) with a specific surface area (S_{sp}) of 2,900—3,500 cm^2/g have proven to be good for SRW immobilization by mixing and pouring. However, these solutions are considered unsuitable for pouring close-packed or finely dispersed SRW due to significant stratification of the solution when it passes through the material layers. In this case, finely ground cements (FGC) with a specific surface of some S_{sp} = 10,000—20,000 cm^2/g can be applied. Ultra-high dispersion of cement particles provides mortars with high penetrating power comparable to the one of chemical mortars and a high strength of the bonded materials.

Soil cementing provides for the use of slag cements to increase the inclusion degree. For close-packed mixed SRW, cement mortars with high flowability and sodium silicate solutions with hardeners can be applied.

Bottom ash cementing process suggests prior preparation of dry mixtures made of bottom ash and cement and their impregnation with water or LRW.

Process parameters of SRW cementing by mixing, as well as those of cement mortar mixing for SRW solidification purposes are similar to LRW cementing parameters.

Mixing quality is considered acceptable if such mixing results in no stagnant zones of poorly mixed materials in the mixer and the cement compound has the same density throughout the mixer volume. Phase separation manifests itself in the appearance of an aqueous phase on the cement compound surface or in the deposition of heterogeneous waste. In this case, plugging of the mixer drain device may occur causing emergency shutdown of the mixer. The cement compound should not delaminate inside the container since it reduces the quality of the final product.

The setting time of the cement compound should be not less than the duration of a process cycle: the time period between the compound mixing or its pouring into the container was started and completed.

Flowability is deemed to be adequate if the cement compound flows freely from the mixer or, when mixed in a container, the quality of its mixing is considered acceptable.

Stirring method can only be used for finely dispersed SRW, such as ash residue with a homogeneous granulometric composition. A study of bottom ash cementing by stirring showed that mixing of delamination-free cement compounds of acceptable quality may involve a maximum ash content of about 30% by weight. The corresponding flowability of the compound amounted to some 100 mm. Under these conditions, such mixing is possible only within a container using a stirrer. PC is considered as a preferrable binder along with such additives as bentonite clay to reduce the leaching of radionuclides and plasticizers to increase the flowability of the cement mortar, the application of which, however, has been proven to be ineffective if the ash content exceeds 10—15 % by weight.

To identify the process parameters for SRW solidification that would provide the required quality of cement compound mixing (void-free matrix with its characteristics meeting relevant regulatory requirements), the following quality criteria have been specified. Since the grouting quality depends on the degree to which the voids between SRW fragments are filled with cement mortar throughout the entire volume, relevant criteria involve the grouting degree. The latter one is seen as a ratio between the volume of applied cement mortar and the voidness of the bulk waste volume, and the density of the cement mortar after it has filled the waste volume. This degree should correspond to a level providing the required properties of the cement compound in its upper layer.

Density of the cement mortar can be affected by the following factors, namely: size of waste fragments and voidness of the bulk layer, pressure and flow rate of the cement mortar, its flowability (viscosity) and resistance to delamination during its filtration through the waste layer, which, in turn, are influenced by solution composition and the size of particle in the cement and the additives.

Practice shows that depending on SRW type, the voidness can amount to 42—58 %. By the size of its fragments, SRW can be conditionally classified into coarsely fragmented (the size of fragments exceeds 100—150 mm and the bulk layer voidness exceeds 50 %), waste with dense packing of the bulk layer (average size of fragments amounts to some 75 mm, voidness accounts for some 50 %), finely dispersed waste (size fragments of 0.5—10 mm with the voidness level of less than 50 %).

To date, most mature and advanced SRW solidification method suggests the use of Portland cement-based compositions as a matrix material, which is due to the simplicity of the production process, its low cost, availability, guaranteed properties of Portland cement and its compatibility with the majority of RW materials.

Pouring method can be applied in case of SRW with a fragment size of more than 100—150 mm. Pouring should be followed by vibration compaction of the cement compound providing complete filling of the voids between waste fragments. It should be borne in mind that due to vibration compaction the level of the cement mortar changes. Thus, when PC is applied for solution mixing purposes, its level can decrease up to 7—8 %. In addition, vibration compaction is also characterized by another negative effect which is the segregation of up to 5—7 % (by volume) of the liquid phase on the compound surface. In practice, it is impossible to control the homogenization and the quality of the cement mortar in the lower layers of the waste, which is considered as another disadvantage of the pouring method. Effective vibration compaction suggests the use of containers with a capacity of no more than 200 liters. To improve the pouring quality, PC should be applied together with FGC additives of up to 30 %, as well as cement mortar stabilizers and plasticizers allowing to reduce the changes in the cement mortar level inside the container by 1—3 % after vibration compaction is completed.

Considering various SRW types, to increase the cementation efficiency, developed was an impregnation method based on the supply of a cement mortar under pressure through a probe to the bottom of a waste container [8]. The cement mortar rising evenly from the bottom to the top would fill the voids between the waste fragments.

The required quality of the cement compound mixing by impregnation primarily depends on the changes in the density of the cement mortar during

Table 2. Cementing parameters under a process when coarsely fragmented SRW are poured into 200 l drums [7]

Cement	Additive, % from the cement mass	Solution/cement ratio	Compressive strength after 28 days, MPa	Changed level of cement mortar after vibration compaction, % vol. (cm)	Water segregated after vibration compaction, vol. %
PC	–	0.6	27.5	7 (6)	6
	–	0.7	17.8	5 (4)	7
	Bentonite, 5	0.6	22.4	8 (7)	4
		0.7	16.4	6 (5)	6
	Stabilizer, 1 Plasticizer 0.5	0.6	23.2	7 (6)	4
		0.7	18.6	5 (4)	5
	FGC, 30	0.7	22.4	3 (2.5)	2
	Bentonite, 5 Finely ground cement, 30	0.7	20.3	2 (1.5)	1
	Bentonite, 5 Stabilizer, 1 Finely ground cement, 30	0.7	19.1	1 (1)	0
FGC	Bentonite, 5 Stabilizer, 1 Plasticizer 0.5	0.8	29	0	0

its flow through the volume of the waste, since the setting time for the solutions is much longer than the duration of the cementation cycles [2].

Density changes in the cement mortar depend on its initial characteristics, such as flowability and resistance to delamination during filtration, which in turn depend on the water-cement ratio, the size of the cement particles, the use of plasticizing, stabilizing and other additives.

Table 3 presents the composition of cement mixtures and the characteristics of production processes recommended for SRW cementation by impregnation identified based on industrial tests. FGC with S_{sp} = 10,000—12,000 cm^2/g should be applied as a binder for finely dispersed waste, whereas for close-packed and large-sized waste the preference should be given to conventional PC with FGC.

Table 3. Composition of cement mixtures and characteristics of the SRW solidification processes [7]

Parameter		Ash residue		SRW with average fragment size, mm: 75	SRW with average fragment size, mm: 100–150		Silt
		Cementation					
		Impregnation	Mixing	Impregnation	Pouring	Impregnation	Mixing
		FGC	PC				
Additive, % from the total mass of dry components	Stabilizer	1–2	–	1–2	1–2	1–2	–
	Bentonite	1–2	2–3	2–10	2–10	2–10	–
	Plasticizer	0.1–0.5	1–2	0.1–0.5	1–2	0.1–0.5	–
	FGC	–	–	20–40	10–40	10–30	–
Water-cement ratio		0.6–0.9	0.8–0.9	0.6–0.9	0.7–0.9	0.6–0.9	0.5–0.6
Flowability, mm		160–240	110–130	180–240	190–240	180–240	110–130
Max. waste inclusion, % by mass		75	30	100 % by volume			20
Process parameters for impregnation*:							
Pressure, MPa		0.02–0.1	–	0.02–0.1	–	0.02–0.05	–
Linear speed, cm / min		4–8	–	6–10	–	6–20	–
Change in the cement mortar density, %		4–6	–	2–6	–	1–4	–
Container capacity, l		100–200	100–500	Up to 3,000	200–1,000	Up to 3,000	200–500

* presented are the impregnation parameters assuming the recommended container capacities

For periodic production process suggesting SRW solidification in containers, cement mortar mixing in tank mixers under a batch mode is recommended providing the required quality of the cement mortar.

Process flowcharts and equipment were developed to cement ash residue from the combustion of combustible RW providing the cementation of close-packed and large-size SRW in containers with a volume of 0.2, 1.4, 2.7 and 3 m^3 [9—11] (Figure 1). Cement mortar with a high penetrating ability was used in this case which is specifically characterized by the application of FGC with S_{sp} of no less than 10,000 cm^2/g or PC with FGC additives as a binder depending on SRW type.

Impregnation method is recommended for the cementation of all considered SRW types. Compared to mixing, this method results in 2—2.2-fold higher inclusion of more finely-dispersed waste (for example, ash residue) into the cement compound. In addition, its application suggests that no strict requirements are imposed on the uniformity of particle sizes of the processed RW. Cementing by impregnation of close-packed and large-sized SRW provides the solidification of the bottom waste layers in the container and can be controlled by keeping track of the impregnation degree and the density of the cement mortar that has passed through the waste layer.

Two types of multicomponent compositions are proposed for the solidification of different SRW types: one is used for finely-dispersed RW cementation by impregnation method and the other is applied in case of coarsely fragmented and compacted waste by pouring. Cement composition in case of finely dispersed waste involves FGC, bentonite clay, stabilizer, plasticizer (% by weight: 96—98, 1—2, 1—2, up to 0.5, respectively). Cement composition for coarsely fragmented SRW includes PC and bentonite clay (5—10 % by weight). When it comes to the cementation of close-packed SRW, depending on the container capacity, the size and packing density of waste fragments, both compositions are mixed so that relevant ratios would provide the required process parameters.

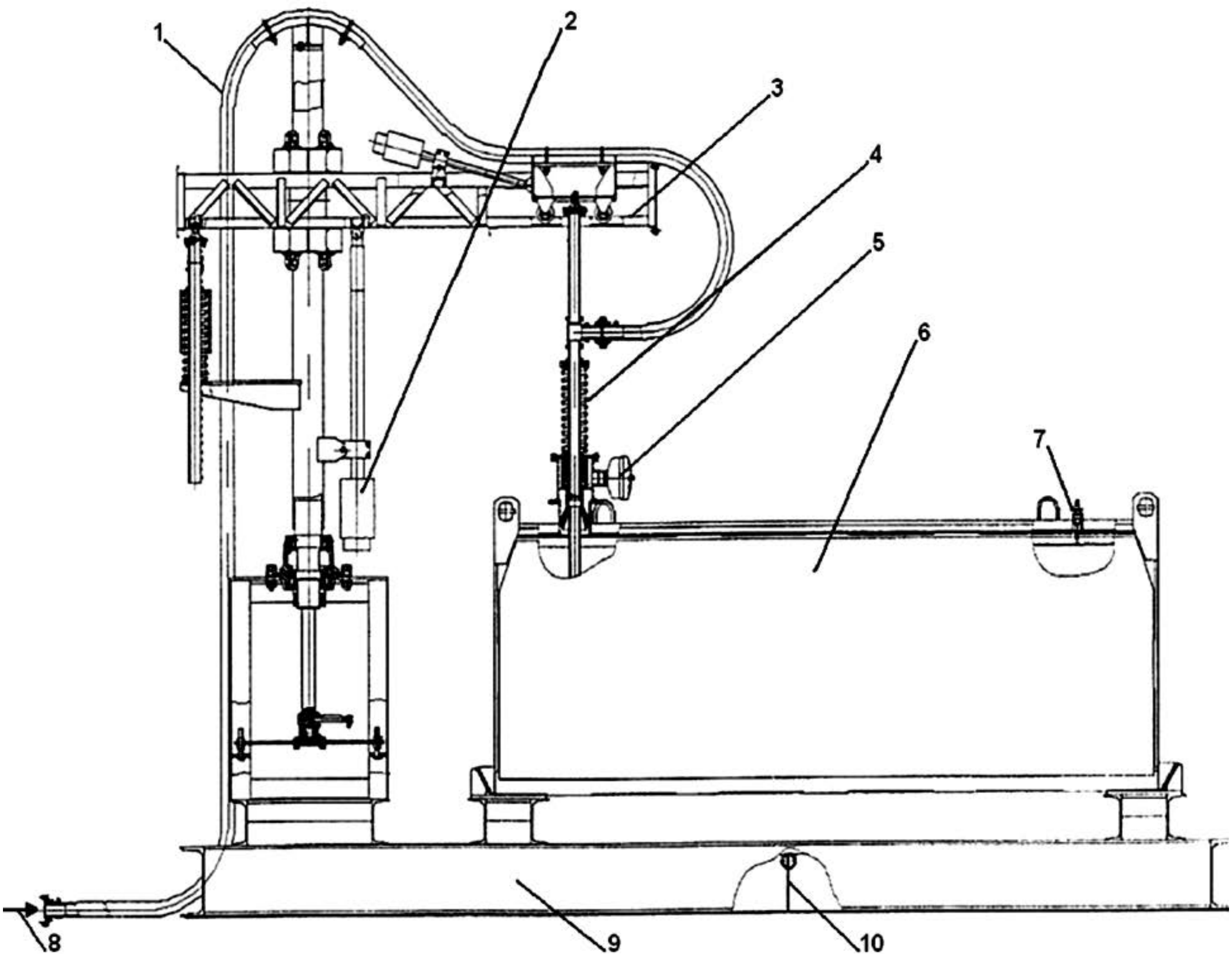

Figure 1. Layout of a unit developed for RW cementation by impregnation method:
1 — cement mortar supply pipeline; 2 — electric drive; 3 — lever; 4 — docking system; 5 — air filter; 6 — container; 7 — level sensor; 8 — cement mortar supply; 9 — bedplate; 10 — pallets

Conclusion

SRW solidification method implying the use of cement matrices to condition various types of waste is considered as a most technologically advanced one. Various binder mixture compositions are applied which allows to select most optimal methods and parameters of the process based on the composition and properties of the waste subject to processing. Waste conditioning by impregnation is viewed as a most effective method which implies an objective control over the process providing the required quality of the final product. It allows to obtain compounds with high RW content and to maximize the use of the useful container capacity.

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Bibiliographic description

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