OBTAINING AN ALKALINE CEMENTING MATERIAL ON THE BASIS OF RADIOACTIVE SILT AND LRW OF LOW AND INTERMEDIATE ACTIVITY LEVEL

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ABSTRACT

Nowadays at Moscow SIA "RADON" the method of combined conditioning of solid radioactive wastes (SRW) and liquid radioactive wastes (LRW) is being developed. SRW represent radioactive silts of natural and artificial reservoirs. LRW represent water salt solutions of low and intermediate activity level. The developed method consists of mixing SRW with LRW and dry-weighed additives. From the resulting mixture an alkaline binding material is formed. The synthesized binding material can be used in process for hardening of other SRW and/or LRW. In this work it is shown that the developed method allows obtaining an accelerated hardening product, which has high strength characteristics and good water resistance. Its quality of does not concede to quality of a product received with use of a traditional binding material – portland cement. It is also shown that using this method it is possible to achieve a reduction in volume of the final product in comparison with the initial volume of SRW and LRW of 4-10. All secondary wastes formed during processing can be conditioned within the framework of the given technology.

INTRODUCTION

During development of a world industry the tendency of increasing quantities of various wastes is being observed. Radioactive waste quantity is increased rather considerably among other wastes, which indicates the urgency of development of ways for their processing and final disposal. Now on atomic power stations (APS) and sites for radioactive waste disposal (SRWD) in Russia the significant amount of SRW submitted is radioactive silts from natural and artificial reservoirs. At the enterprises of a nuclear industry there is also plenty of salt LRW of low and intermediate activity level.

One criterion for decisions on the problem of processing radioactive silts and LRW is to convert them to a stable condition preventing release of harmful components to the environment. For this purpose, the joint cementation method of silts and LRW can be used, i.e., embedding the silts and LRW in the greatest possible amounts in cement stone.

Radioactive wastes impose some restrictions on the process of cementation. So, the formation of cement stone with satisfactory properties is possible only at certain degrees of loading of silts to no more than 5-10 % of the general weight of cement stone. It is connected to the presence in silts of an organic component negatively influencing the final product of processing. The salt content of processed LRW also influences the properties of cement stone (1). The increased salt content of processed LRW results in reduction of the mechanical strength of cement stone and its water resistance.

To increase the percentage of silts and LRW included in cement stone, preliminary processing is possible (1, 2, 3). For silts it consists in their chemical processing with the purpose of decomposition of organic bonds negatively influencing the hardening of cement stone. Also, drying and subsequent grinding of silts is possible. The similar preliminary processing allows increasing the degree of loading of the silts, as a rule, by 10- 15 %wet of the weight of cement stone. To increase the percent of LRW included in cement stone, evaporation and cementation of concentrated still liquors can be done (2). Thus it is possible to include in cement stone up to 40%wet salts, but the mechanical strength in the resultant cement stone does not meet the desired stability requirements.

At Moscow SIA "RADON" the method of combined SRW and LRW disposal in near-surface concrete bunkers in the cement monolith form is used (1). When SRW are embedded in concrete bunkers they form a friable layer, in emptiness of which the cement mortar prepared on a basis LRW does not penetrate. Therefore the superficial waters can penetrate in deep cement monolith and erode it.

At present at Moscow SIA "RADON" the methods of combined conditioning of SRW and LRW in small containers, are under development. These methods allow preparing of the cement monolith on the basis of LRW and SRW homogeneously distributed in it. Thus the containers serve as an additional isolating barrier during storage of the solidified cement product, and besides, they are convenient for its transportation. At the same time increased water resistance of the resulting cement matrix and the content of radioactive material in it should result from application of this method. Also, application of this method should reduce the volume of the final product of processing in comparison with the initial volume of SRW and LRW (4,5).

One of the developed methods includes synthesis of an alkaline binding material from SRW (silts) and LRW (water salt solution of low and intermediate activity level). The synthesized material is used as a binding material for cementation of SRW and LRW in small containers. The method allows:

- reducing the volume of the final product in comparison with the initial volume of the silts and LRW due to combustion of an organic part present in silt and evaporation of the liquid phase present in LRW;
- receiving a final product having the required strength characteristics and leaching rate of radionuclides (in Russia the mechanical strength of cement compounds for 28 day of hardening should be not less than 5 MPa, and the leaching rate no more than 10^{-3} g/(cm^2*day));
- processing silts containing radioactive and/or toxic organic components (peat, petroleum, polymeric materials, products of vital activity of flora and fauna) in amounts up to 80 %wet of the weight initial silts;
- processing LRW low and intermediate activity level with a salt content up to 1000 g/l;
- receiving an alkaline binding material with a composition in which all radioactive materials and heavy metals are bound and which can be used for processing other radioactive or chemical waste.

WORK DESCRIPTION

The developed method of combined conditioning of SRW (silts with a content of an organic phase up to 80%wet.) and LRW (water salt solution of low and intermediate activity level with a salt content up to 1000 g/l) consists of the following. Radioactive silts are filtered by mechanical means. Filtered silts are mixed with LRW and with dry-weighed additives (CaO, Al_2O_3). The obtained raw mixture of radioactive silts, LRW and dry-weighed additives is heated up to temperatures of 700 - 850 ^oC and, aged at this temperature for 0.5 - 1 hour. The burning of a raw mixture results in the synthesis of a cement clinker, representing an alkaline binding material of a silica-alumina composition. Cement clinker is crushed into a thin powder with the specific surface area of the material not less than 2000 cm^2/g. For a drop in dusting during grinding LRW or condensate collected during synthesis of cement clinker is added to synthesized cement clinker. The resultant alkaline binding material of a silica-alumina composition is used for processing LRW. For this purpose, LRW (weight ratio of LRW and the binder material is 0.3 – 0.5) is added to the prepared alkaline binding material. The obtained cement material can be used for cementation of SRW. At present at Moscow SIA "RADON" the laboratory research on the developed method and experimental joint processing of silt and LRW on a pilot plant scale have been carried out. Total amount of jointly treated of LRW and SRW processed on pilot plant totals 750 kg.

Composition of Raw Mixture

At preparation of an alkaline binding material it was required that the raw mixture for synthesis contain two constituents: salt and mineral.

LRW of NPP with RBMK unit and LRW of SDRW of Moscow SIA "RADON" were used as salt constituent. A salt content of LRW of NPP with RBMK unit and LRW of SDRW of Moscow SIA "RADON" were 300 g/l and 500 g/l respectively. The chemical composition of dry residue of LRW was as given in Table I.

Table I.

Chemical composition of dry residue of LRW.

Place of formation LRW	Content (% wet. from a mass of dry residue)							
	Na^+	Ca^{2+}	K^+	Fe^{3+}	NO_3^-	SO_4^{2-}	CO_3^{2-}	Cl^-
NPP with RBMK unit	27.0	0.3	0.7	-	67.4	2.7	1.9	-
SDRW of Moscow SIA "RADON"	20.4	5.8	-	2.7	60.0	4.4	2.3	4.4

The silts of SDRW of Moscow SIA "RADON" and dry-weighed additives (CaO, Al_2O_3) were used as mineral constituents. Processed silts had the following characteristics:

1. Content of organic components in processed silts - 8-15 %mass.
2. Content of water in silts after filtration under vacuum - 350-400 g/kg.
3. Density of silts after filtration under vacuum - 1.35-1.50 g/cm^3.
4. Residue from filtration under vacuum and drying at 100 ^oC silts - 600-650 g/kg.
5. Residue from filtration under vacuum and heating at 1000 ^oC dry silts - 500-550 g/kg.
6. Specific activity of silts, Bq/kg: ΣCs^{137} – 1.8-9.5*10^4, ΣPu^{239} – 9.6-55.0*10^3.
7. Isotope composition of silts, Bq/kg: Cs^{137} – 1.6-9.3*10^4, Cs^{134} – 1.8-2.0*10^3, Pu^{238} – 5.0-35.0*10^3, Pu^{239} – 4.6-20.0*10^3.

The radioactive silts contained the following components in an amount indicated in Table II.

Table II.

Chemical composition of radioactive silts.

Content in initial silts, % wet					
CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O
10-12	60-62	11-13	8-10	2-3	2-4

Silts and dry-weighed additives were applied in amounts necessary to provide the basic mineral oxides (CaO, SiO_2 and Al_2O_3). At realization of the work the ratio of the salt component to the mineral component was equal to1.0-4.0 based on the dry residue.

Reception of Binder Material

The mineral constituent (silts and dry-weighed additives) and salt constituent of the raw mixture (LRW) carefully were mixed. The raw mixture was heated up to T=700-1000 ^{o}C and was maintained at this temperature for 0.5-1 hour.

The cement clinker of alkaline binding material prepared as a result of heating was ground up to a fine cement. The specific surface of the material was not less than 2000 cm^2/g. Before grinding the cement clinker was humidified by LRW and/or condensate collected during synthesis of the cement clinker. The amount of LRW and/or condensate was 3 - 5 % weight of the ground material.

Using the prepared alkaline binder material and LRW, cement samples in the form of cubes with the size (2 cm*2cm*2cm) were produced under laboratory conditions (LRW to the alkaline binder material weight ratio was 0.4). The received cement samples were tested for compressive strength and water resistance.

Processing of SRW and LRW in a pilot plant

Experimental processing of silt and LRW was executed in a pilot plant, which is shown schematically in Figure 1.

Radioactive silt is mixed with LRW and dry-weighed additives for 10-15 minutes. A device-mixer is used for preparation of raw mixtures. The ratio of LRW/SRW was equal to1.0. The raw mixture was accumulated in pallets up to 0.5-1.0 kg, and then placed on the conveyor tape of the electrical conveyor furnace. Moving the length of the furnace, the material was heated up to temperature 800-1000 ^{o}C at a speed of 5-10 ^{o}C/ minute and heated at the given temperature for 20-40 minutes.

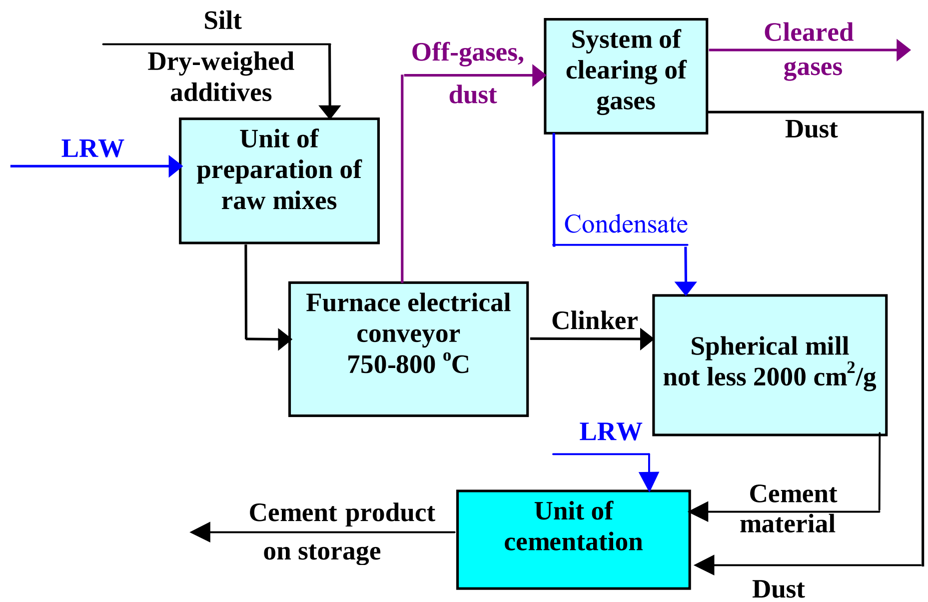

Fig.1.
The scheme of pilot plant for joint processing radioactive silts and LRW.

The gases removed from the furnace space and dust passed through a system of clearing of gases and were divided into three fractions. The first fraction - cleared gases - was sent to the atmosphere. The second fraction - condensate - acted on the grinding stage of the synthesized cement clinker for elimination of dusting. The third fraction - dust - added to the cementation stage of SRW and LRW as a radioactive waste.

Synthesized cement clinker grinding by wet mode in a spherical mill was to not less than 2000 cm^2/g. The alkaline binding material of silica-alumina composition together with dust from the system of clearing of gases was mixed with LRW using a compact cementation plant. The liquid / solid phase (L/S) ratio was 0.4.

RESULTS

The first stage of work determined the optimum temperature of synthesis of the alkaline binding material. The researched range of temperatures was 700-1000 ^{o}C. It was determined that satisfactory properties of the binding material were obtained at temperatures of 700-850. In this range of temperatures in a mixture of SRW and LRW calcination of salts occurred to form a cake of alkaline and silica-alumina composition. The content of alkaline, amphoteric and sour oxides in the cake was close to the natural minerals nepheline and jadeite.

The results of laboratory research on synthesis of an alkaline binding material with different contents in a raw mixture of a SRW and LRW and a temperature of synthesis of 700-850 ^{o}C are given in Table III and Table IV.

Table III.
Compressive strength of cement stone prepared on a basis of an alkaline binding material and LRW.

Place of formation LRW	LRW/SRW	L/S	Compressive strength of a cement stone, MPa/day		
			7	28	56
NPP with RBMK unit	1	0.4	5	24	35
	2	0.4	7	36	41
	3	0.4	4	22	31
	4	0.4	2	12	29
SDRW of Moscow SIA "RADON"	1	0.4	6	22	31
	2	0.4	9	38	44
	3	0.4	6	28	35
	4	0.4	3	17	24

Table IV.
Leaching rate from a cement stone prepared on the basis of an alkaline binding material and LRW.

Place of formation LRW	LRW/SRW	L/S	Leaching rate from a cement stone, $g/(cm^2*day)$		
			3	28	56
NPP with RBMK unit	1	0.4	$7*10^{-3}$	$4*10^{-4}$	$6*10^{-5}$
	2	0.4	$8*10^{-4}$	$2*10^{-5}$	$5*10^{-6}$
	3	0.4	$5*10^{-3}$	$2*10^{-4}$	$5*10^{-5}$
	4	0.4	$1*10^{-2}$	$8*10^{-4}$	$2*10^{-4}$
SDRW of Moscow SIA "RADON"	1	0.4	$6*10^{-3}$	$7*10^{-4}$	$1*10^{-4}$
	2	0.4	$5*10^{-4}$	$6*10^{-5}$	$2*10^{-5}$
	3	0.4	$4*10^{-3}$	$3*10^{-4}$	$6*10^{-5}$
	4	0.4	$1*10^{-2}$	$9*10^{-4}$	$1*10^{-4}$

As follows from the received results, prepared cement compounds had compressive strengths of 20-30 MPa after 28 days of hardening, and a low magnitude leaching of radionuclides. Studying the phase structure of the cement clinker and cement compound leads to the assumption of an opportunity of encapsulation of SRW and LRW components in the structure of the low solubility clinker and hydrate phases.

Depending on the structure SRW and LRW, the resulting volume of the final product of processing (cement stone) was 4-10 times less than the initial volume of radioactive components. This is because during synthesis of the alkaline binding material there was combustion of an organic part present in silt and evaporation of the liquid phase present in LRW.

The results of laboratory research were confirmed by experimental processing of silt and LRW. To the present, the total amount of LRW and SRW processed in the pilot plant is 750 kg (respectively, 500 kg (4.2 m^3) and 250 kg (1.9 m^3)). The final volume as a result of processing is 1.27 m^3 of a cement monolith. The reduction in volume of the final product in comparison with total volume of silt and LRW is 4.8.

The experience from processing has confirmed the results obtained under laboratory conditions on strength and water resistance of cement stones.

The research on off-gases during pilot processing of the prepared raw mixtures has revealed that the content of nitrogen oxides in off-gases is the following: % weight from theoretically possible: NO_x 5-10. The presence in processed silts of carbon containing substances promoted reduction formed nitrogen oxides up to elementary nitrogen. The concentration of CO in off-gases was up to 2000 mg/m^3, concentrations of NO_x, HCl and NH_3 were insignificant. Departing aerosols content, % weight from content of component in a raw mixture: Na^+ 0.4 – 0.8, Cs^+ 1.0 – 1.2, Sr^{2+} 0.1 – 0.2, Ca^{2+} 0.7 – 0.8, Cl^- 0.8 – 1.3. The concentration of radionuclides in condensate from the system of clearing of gases and in air during grinding of synthesized cement clinker was lower than the specified level. All condensate formed was used during the grinding stage of the synthesized cement clinker for elimination of dusting. Dust collected in the system of clearing of gases was added into the cementation stage of SRW and LRW in the pilot plant as a radioactive waste.

CONCLUSIONS

The carried out research has shown that use of the developed method for joint processing SRW (silts) and LRW (water salt solution of low and intermediate activity level) allows to production of a cement matrix with satisfactory strength properties and water resistance. The resultant volume of final product is less than the volume of processed materials by 4-10 times.

The combined experienced processing SRW (silts) and LRW has shown that the implementation of the developed method is rather simple, the technological process does not result in generation of secondary wastes, because all secondary wastes (condensate and dust from the system of clearing of gases) may be conditioned by the developed method.

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