ASSESSMENT OF MATRIX MATERIALS AND TECHNIQUES AVAILABLE FOR CONDITIONING ALUMINUM RADIOACTIVE WASTE

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La nivel naţional, deşeurile radioactive cu aluminiu provin din dezafectarea instalaţiilor nucleare. O metodă de condiţionare a deşeurilor de aluminiu radioactiv constă într-o etapă de dizolvare a acestuia într-o soluţie alcalină cu generare de hidrogen, urmată de o etapă de amestecare a şlamului obţinut cu un liant potrivit pentru a obţine forma de deşeu condiţionat pentru depozitare. Se prezintă rezultatele unor serii de experimente, efectuate pentru a determina influenţa a două matrici asupra proprietăţilor formei de deşeu cu aluminiu condiţionat.

At national level, there are aluminum radioactive wastes produced in the decommissioning of the nuclear facilities. A method for the conditioning of aluminum radioactive wastes consists in making metallic aluminum to react with an alkali solution in order to generate hydrogen gas, and mixing the resulted liquid with a solidifying material (which contains a binding material as main component), in order to obtain a conditioned waste form for being deposited. Results of a series of experimental tests performed to determine the influence of two matrices on the properties of radioactive aluminum conditioned are presented.

Keywords: decommissioning, aluminum radioactive wastes, conditioning matrices

1. Introduction

Decommissioning of nuclear reactors invariably involves the generation of large amounts of radioactive wastes.

Subject to safety considerations, “generation of radioactive waste shall be kept to the minimum practicable”. For example, appropriate decontamination and dismantling techniques, as well as the reuse or recycling of materials, can reduce the waste inventory [1].

The implications for waste management should be considered in the options for decommissioning. Appropriate and safe waste management

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arrangements should be available, including disposal or storage routes. A waste management plan, part of the decommissioning plan, should consider the different categories of waste produced during decommissioning, and aim at the safe management of such wastes and minimizing cross-contamination, as well as secondary waste generation [1]. Guidance on predisposal management aspects for radioactive waste is given in the documents of International Atomic Energy Agency [2, 3], and in the national regulation [4,5].

A preliminary estimation of the aluminum radioactive wastes which results from decommissioning of Research Reactor is presented in Ref. [4]. In Romania, the main objective regarding the activities of radioactive waste management is to ensure reasonable achievable minimum impact over the population and environment, established by the national regulating authority [5].

Significant reductions in volumes of aluminum radioactive waste can be achieved through decontamination programs. Reuse and recycle strategies have the potential of reducing the amounts of aluminum radioactive wastes to be managed. Aluminum components have been successfully decontaminated and sold on the open market. The market value of aluminum creates a strong economic driver for decontamination of this metal [3].

The practice of conditioning radioactive waste with ordinary Portland cement began during the early years of the nuclear industry. The binding matrices composition for the radioactive waste conditioning are in a perpetual perfection, imposed both by the user and by the liability environment protection through the selection of raw materials, without negative impact over the environment. An example is the binding material with pozzolana; the world trend line now is to switch to regenerative raw materials (blast furnace slag, fuel ash, volcanic tuff, etc.) against Portland cement because during the production of this cement green house gases are liberated. In the immobilising method of the radioactive solid waste containing aluminum in Portland cement matrices, calcium hydroxide formed during hydration cement reacts with aluminum and generates hydrogen bubbles. The cement setting begins before the generation of hydrogen gas is completed. Therefore, no hardened cement matrices can be obtained and the resulting material has poor mechanical strength and insufficient properties of preventing oozing of radioactive nuclide.

New developments have been reported for the processing and immobilization of aluminum radioactive waste [6,7]. To overcome the reduction the hydration processes, one or more selected additives were added to Portland cement matrices. $LiNO_3$ addition to cement is effective to prevent hydrogen gas generation by the formation of the insoluble film ($LiH(AlO_2)25H_2O$) on aluminum surface [7].

Another method of conditioning the metallic aluminum-containing radioactive solid waste comprise the following steps: the reaction of radioactive solid waste containing metallic aluminum with an alkali solution and the generation of hydrogen gas, then mixing the resulted liquid with a solidifying material containing a latent hydraulic material, as main component to solidify it. The solidifying material containing the latent hydraulic material as main component can be obtained by mixing blast-furnace slag, converter slag and incinerator fly ash with one silica or alumina rich materials (silica fume, silica rock powder, alumina powder and ultrafine anhydrous silica). In the event that it is difficult to mix the reaction liquid and the solidifying materials because of a viscosity too high, a dispersant may be used [7].

This paper aims at comparatively examining the properties of aluminum radioactive waste forms. Radioactive aluminum forms were obtained with making aluminum react with an alkali solution and mixing the resulted liquid with commercial cement with blast furnace slag, in the attempt to find the best matrices for the solidification/stabilization of this radioactive waste. Typical properties and limits of waste forms should meet the Waste Acceptance Criteria of the disposal site, i.e. Baita–Bihor National Repository [8].

2. Experimental procedure

The first part of this work is to make radioactive metallic aluminum react with an alkali solution, in order to generate hydrogen gas, and to mix the liquid with a solidifying material containing commercial cement with blast furnace slag. A second part of this work consists in determining correlations between composition-processing-proprieties. The qualification covers mixing properties (workability), hardening process (setting time, density) and Waste Acceptance Criteria of the disposal site (compressive strength great than $5x10^6$ N/m^2 and Co-60 leach rate less to 10^{-3} cm/day).

Laboratory tests are performed with inactive and active products; twelve formulas are tested for conditioning aluminum wastes, using two type of cement:

- Portland cement EN 197-1-CEM II A-S 32.5 N-L H, with 6-20% blast furnace slag content;
- Portland cement EN 197-1-CEM II B-S 32.5 R, with 21-35% blast furnace slag content.

As mineral aggregate, sand of Aghires, sort M (50)03 was used [9].

The concentration of NaOH solution is usually in the range of 3 to 4 N. The reaction temperature is usually between 50 to 120° C, depending on the concentration of NaOH solution. The dispersant SP (0.3-1.3% polyalkylatacrilat, 1-5% glycols and utmost 97% water) [10, 11], can be used in an amount of 1 part by weight, with respect to 100 parts by weight of cement used.

Six compositions with each type of cement (A0-A11) were made in order to compare the properties of the specimen.

The water to solid ratio in the mortars was 0.4 to 0.58, depending on the treated aluminum content. The mortar composition was prepared with sand/cement ratio=0.47-0.73. The sand content decreases with the increase of the aluminum waste content. The addition of aluminum waste was 4.98 to 16.3% in weight in the binding mortars. The compositions of the aluminum radioactive waste immobilised in the binding mortars with two types of cements (CEM II/A-S and CEM II/B-S) are shown in table 1 and 2.

Table 1

The compositions of the aluminum radioactive waste immobilised in the binding mortars with cement CEM II/A-S 32.5

Samples/composition	A0	A1	A2	A3	A4	A5
Cement CEM II A-S 32.5, (%)	45.92	46.66	44.80	43.08	42.47	40.74
Sand of Aghires, (%)	33.67	34.21	29.87	25.85	22.65	19.01
Dispersant SP, (%)	0	0.47	0.45	0.43	0.42	0.41
Water, (%)	20.41	18.66	19.91	21.06	22.65	23.54
Treated aluminum wastes, (%)	0	0	4.98	9.57	11.80	16.30
water/cement ratio	0.44	0.40	0.44	0.49	0.53	0.58
sand/cement ratio	0.73	0.73	0.67	0.60	0.53	0.47

Table 2

The compositions of the aluminum radioactive waste immobilised in the binding mortars with cement CEM II/B-S 32.5

Samples/composition	A6	A7	A8	A9	A10	A11
Cement CEM II B-S 32.5, (%)	45.92	46.66	44.80	43.08	42.47	40.74
Sand of Aghires, (%)	33.67	34.21	29.87	25.85	22.65	19.01
Dispersant SP, (%)	0	0.47	0.45	0.43	0.42	0.41
Water, %	20.41	18.66	19.91	21.06	22.65	23.54
Treated aluminum wastes, (%)	0	0	4.98	9.57	11.80	16.30
water/cement ratio	0.44	0.40	0.44	0.49	0.53	0.58
sand/cement ratio	0.73	0.73	0.67	0.60	0.53	0.47

The procedure for the specimens preparation is presented in Figure 1.

The main properties assessed in this work are apparent density, setting time, and strength, according to [12, 13].

Determinations of compressive strength after 28 days were realized in accordance with [14] in 4x4x16 cm prismatic moulds. The mortar is prepared by mechanical mixing and is compacted in a mould using a vibration table.

The specimens are de moulded after 24 hours, weighed and measured.

The result of the compressive strength of the specimen, after 28-day cure, is an average of six determinations; performed on series of three prisms for each test.

The cylindrical samples of 46 mm diameter (diameter/height =1) were prepared using the selected formulas (A5 and A11, respectively). The curing time of specimens was of 28 days. The leaching test was carried out according to the method recommended by literature [14].

The method consist is in the immersion of the cylindrical specimen into demineralized water for different period of times.

The leachant was changed after 1, 3, 7 days, once a week in the first month, and once a month for the following three months.

The leachant samples are analyzed to measure pH and conductivity.

The Co-60 activity determination is performed using HPGe spectrometry system CANBERRA.

Two expressions of leach rate are used in this report. The first expression of the leach rate (Rn, kg/m2.s), according to [14, 15] is calculated with formula (1).

$$R_n = \frac{a_n}{A_0 \cdot F \cdot t_n} \qquad (1)$$

Where:

Rn is the leach rate of Co-60, kg/m^2.s;

a_n - Co-60 activity released in each renewal period, Bq;

A0 – Co-60 activity in the sample at time t=0, Bq/kg;

F – Surface area of specimen, m^2;

Tn - Contact time of leachant and specimen, s.

The second expression for the leach rate (Rm, cm/day) is calculated with formula (2) in order to meet the specific requirement for the radioactive waste forms the Waste Acceptance Criteria of the disposal site (leach rate $<10^{-3}$ cm/day) [8]:

$$R_m = \frac{A_t \cdot V}{A_0 \cdot M \cdot S \cdot t} \qquad (2)$$

Where:

Rm is the each rate of Co-60, cm/s;

At – Co-60 activity released in each renewal period, Bq;

A_0 – Activity of Co-60 in specimen, at time t=0, Bq/g;

V- Volume of the specimen, cm^3;

M – Mass of the specimen, g;

S- Surface area of specimen, cm^2;

t- Contact time of leachant and specimen, days.

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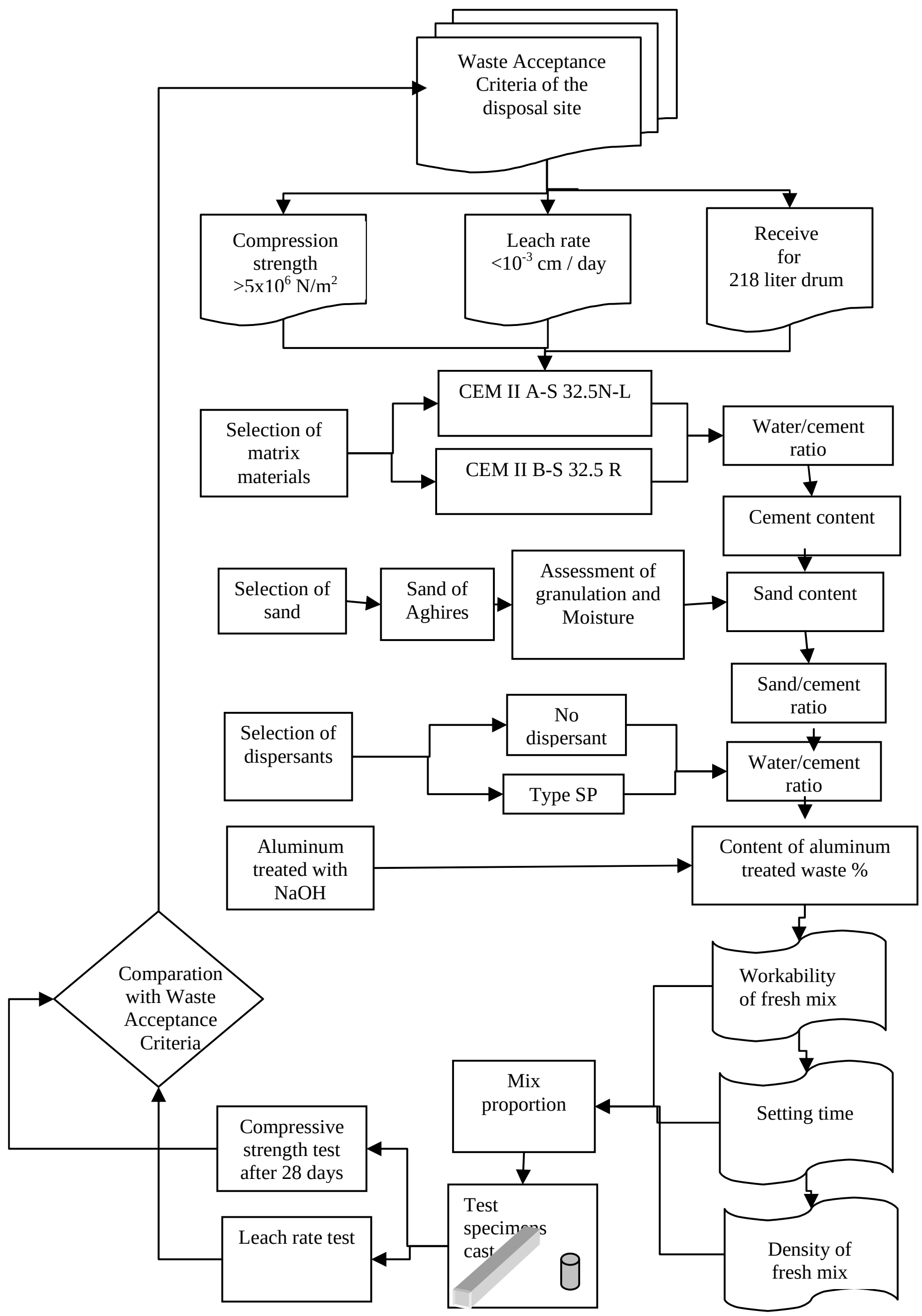

Fig. 1. Laboratory procedure for the preparation of aluminum radioactive waste specimens for their main properties assessment

3. Results and discussions

The initial and final setting time of the two types of matrices vs. the treated aluminum waste content is shown in Table 3. One may remark from both matrices used the fact that the setting time decreases with the increase of the treated aluminum waste content. The setting period of time is good for processing waste forms (A2/A8-A4/A10), but may decrease with more than 50% when the treated aluminum has more than 11.8 % in the matrices composition (A5/A11).

Table 3

Setting time of the two types of matrices vs. the treated aluminum waste content

Cement type	CEM II A-S 32.5		CEM II/B-S 32.5	
The setting time, (min.)/ Treated aluminum wastes, (%)	initial	final	initial	final
0	290	400	320	380
4.98	275	360	290	360
9.57	250	240	200	225
11.8	175	135	175	135
16.3	30	45	25	45

The important decrease of the waste forms density is due to the increase of the treated aluminum waste content (4.98 to 16 %), especially with matrices with cement CEM II A/S 32.5 (figure 2).

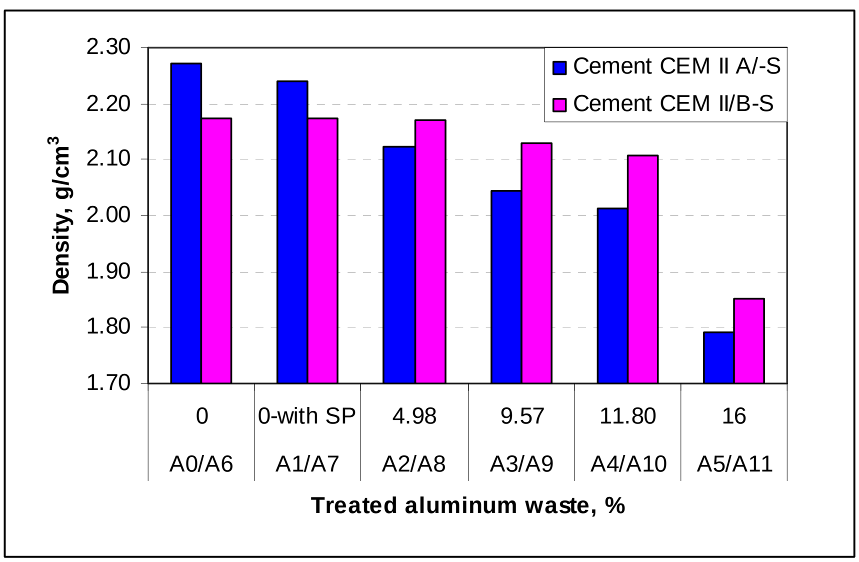

Fig. 2. Density of the two types of matrices vs. the treated aluminum waste content

The fresh mortars had a good workability and for some of them, the swelling phenomenon was observed in both matrices used, especially for the specimens with aluminum waste content more than 11.8%. The compressive strengths decrease with the increase of the aluminum waste content, as compared to matrices without aluminum waste. Compressive strengths of the samples should be more than 5 N/mm^2, according to [8], therefore the tested matrices, fulfill this requirement with maximum 11.9% treated aluminum waste content, (fig. 3).

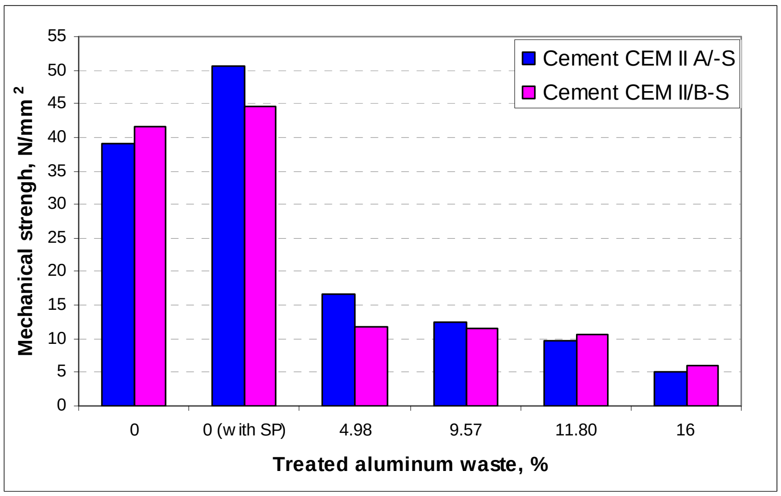

Fig. 3. The compressive strengths of the samples vs. the treated aluminum waste content

The matrices with different composition and initial activity of Co-60 have different leaching properties.

This important aspect of waste forms is illustrated in Figure 6, where there are presented the leaching rates for Co-60 for 75 days as Eq. (1) of two aluminum conditioning matrices (A5 and A11) with two initial activities (3.84x10^5 Bq/kg, 7.86x10^5 Bq/kg from A5.1, A5.2, and 4.16Ex10^5 Bq/kg, 8.64x10^5 Bq/kg from A11.1, A11.2), respectively.

One observed that the Co-60 leach rate decreases in the same way for both matrices at the same initial activity. It is shown that leach rate limit is reached at the 45th day for Co-60 (fig.4).

After 45 testing days, the obtained results for the leaching rates of Co-60 calculated by Formula (2) are less than 1x10^{-3}cm/day for immobilized radioactive aluminum waste, proving that all matrices tested satisfy the requirement for storage, especially for sample with CEM II/A-S 32.5 (fig. 5, samples A5.1 and A.5.2).

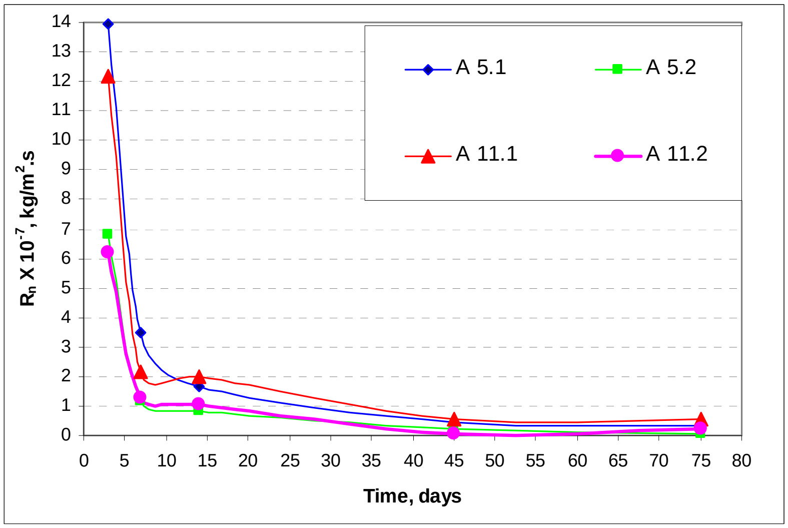

Fig. 4. Cobalt leach rates [kg/m^2.s] vs. of the two types of matrices (CEM II A/S from A 5.1 and A5.2 and CEM II B/S from A11.1 and A11.2)

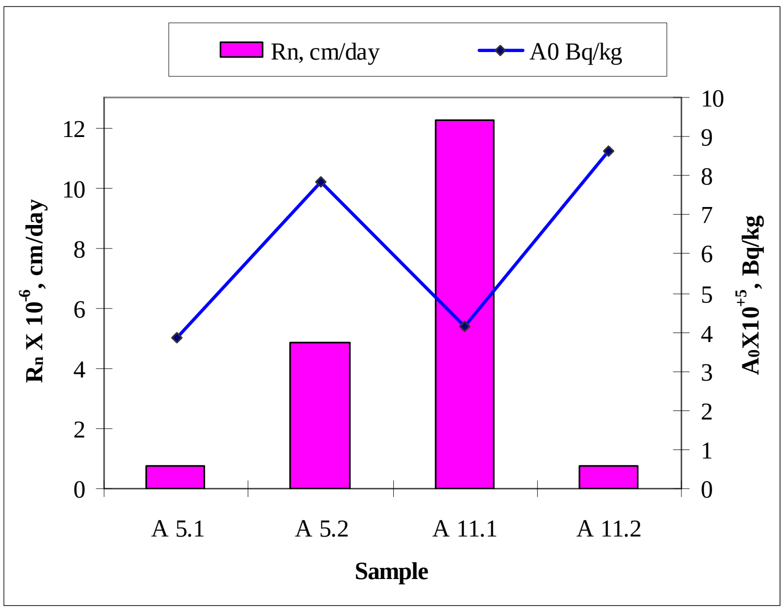

Fig. 5. Leach rates [cm/day] of aluminum radioactive wastes matrices at 45 days test function on initial activity of Co-60 in samples (3.84x10^5 Bq/kg, 7.86x10^5 Bq/kg from A5.1, A5.2 and respectively, 4.16Ex10^5Bq/kg, 8.64x10^5 Bq/kg from A11.1, A11.2)

4. Conclusions

The first step in the technology screening process for conditioning aluminum wastes is to identify potentially available binder material. The carried out research has shown that use of the cement type CEM II A-S 32.5 N-L H, with 6-20% blast furnace slag allows the production of aluminum radioactive wastes matrices with satisfactory strength properties and lowest leach rate of Co-60.

The results revealed that the addition of commercial dispersed agents SP into matrices would increase the workability of mix and the compressive strength. This report is part of an ongoing research project. Results from these investigations will then support the development and optimization of the conditioning of aluminum radioactive wastes technology.

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