Magnesium Phosphates Binding Systems for Immobilizing Solvent Radioactive Wastes

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The immobilization process of radioactive solvent wastes produced during nuclear power plants operation tends to be safe and technically feasible perhaps its most important advantage from the safety point of view is the low chamber temperature and lower explosion risk. Radioactive solvent wastes resulted from Cernavoda NPP decontamination operations consist of miscellaneous acetone, toluene, methanol, chloroform, trichloroethan, white spirit, ethylene glycol and water. Magnesium phosphate binding systems are new cement-materials which could be used for the immobilization of radioactive wastes for the set-retarding effect of solvent radioactive waste in other matrices (Portland cement, composite cement). The paper presents the influence of mineral additive on the properties of solvent waste form, mainly the setting time and the leach rate of tritium. Results of the experiments have shown that using magnesium phosphate binding systems-mineral additive, could do the solidification of solvent radioactive wastes by better results. It can thus be anticipated that the level of expectation towards magnesium phosphate binding systems will remain high and probably increase for the other organic radioactive wastes (oils, scintillation liquids).

Keywords: magnesium phosphates binding systems; radioactive solvent wastes; tritium leachability

A range of organic solvents are used for cleaning and degreasing in decontamination operation at Cernavoda Nuclear Power Plant. Solvent radioactive wastes consist of miscellaneous acetone, toluene, methanol, chloroform, trichloroethan, white spirit, ethylene glycol and water is often very heterogeneous in nature. These are normally *LLW*[1] containing only relatively small quantities of beta/gamma emitting radionuclide and varying amounts of tritium with activity below 1.5 E+08Bq/L. Management of solvent radioactive wastes should take full account of volatility, combustibility, thermal, chemical and radiolysis instability. Solvent waste immobilization has become an important step in the field of radioactive waste management. This step, *immobilize*[2] the solvent radioactive waste, is the conversion into a *conditioned waste form*[3] via solidification, embedding or fixation which minimizes the probability of radionuclides release to the environment during interim storage, transportation and final disposal [1, 2].

The practice of immobilizing radioactive waste with ordinary Portland cement began during the early years of the nuclear industry. This was primarily due to its low cost, availability and compatibility with aqueous radioactive waste [3, 4]. It was soon realized, however, that the organic radioactive wastes interact with the cement components to inhibit or retard the hydration reaction [4].

Since that time new developments have been reported for the processing and immobilization of organic radioactive waste. Many reports have been published by the *International Atomic Energy Agency (IAEA)* on various technical aspects of organic radioactive waste. There are a variety of matrix materials and techniques available for immobilizing and conditioning waste [5-8]. To overcome the hydration reaction effect inhibition one or more selected additives were added to Portland cement mixtures. Several of the more successful mixtures have been commercialized and are the lime, sodium silicate, pozzolana and blast furnace slag. The chemical compatibility of the organic radioactive wastes with hydraulic cements is poor but may be good with emulsifying agents.

As part of our previous work [9-11] we developed a solidification technology by cementation organic radioactive wastes using several formulas, different cement types and a variety of emulsifying agents: fatty acids salt (e.g., aluminium stearate - $Al(OH)(C_{18}H_{35}O_2)_2$), Nonylphenol Ethoxylates and fatty alcohols (e.g., stearyl or cetyl alcohol).

At the same time, it is recognized that other matrices are being researched as possible for future options. Included in these options are new *binders*[4] with hardening at normal temperature. There is a wide range of potential matrix materials available for conditioning radioactive wastes. Previous work at *Argonne National Laboratory (USA)* [12] and that of others [13-15] on the development of the new binder with hardening at normal temperature demonstrates the inherent favourable properties of these materials for containment of *mixed wastes*[5]. Magnesium phosphate binders are formed by reaction between magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4) in solution, governed by the reaction (1):

$$MgO + KH_2PO_4 + 5H_2O \longrightarrow MgKPO_4.6H_2O \qquad (1)$$

[1] *LLW - LLW-Low and Intermediate Level Waste according to its dose rate [1];*

[2] *Immobilization - Conversion of waste into a waste form by solidification, embedding or encapsulation. See also Conditioning [1];*

[3] *Waste form- Waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging. The waste form is a component of the waste package [1,2];*

[4] *The binder is used in this report to describe inorganic materials that have the ability to react with water at ambient conditions to form a hardened mass [16];*

[5] *Mixed waste means the presence of more than one physical state, with at least one being predominantly organic [1];*

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The MgO is also completely calcined to reduce its reactivity. The reaction produces KH_2PO_4 that is hydrated by six moles of water. Fly ash is routinely added to the binders and waste to increase waste form strength and integrity. Under most conditions, heat from the reaction causes a temperature increase up to less than 80^0C, until the waste form starts cooling upon curing. The final waste forms routinely have compressive strengths greater than 2,000 psi[6] and porosities ~50% less than those fabricated of cement. The density of the new waste form (~1.8 g/cm^3) is also routinely less than that of a cement form (~2.4 g/cm^3) [15].

Many previous studies developed by the University Politehnica Bucharest Romania, on magnesium phosphate binders [16-20] bring information about the possibility of use of such binder for emergency repair of some concrete structures, which may be taken out of service, only for short periods of time (airfield pavements, national high ways). Such binders may have a controlled hardening rate and develop early good mechanical strengths and a good chemical stability. They used a wide variety of techniques (x-ray diffraction, thermal analysis) to obtained information about the hydrates which are formed by hardening of the binders.

The object of this work is to establish if the magnesium phosphate binders may be used to immobilize the radioactive solvent. Criteria that might be applied in the selection of immobilization process and of waste storage and/or disposal are: the complexity of the technology and equipment, the regulatory requirements. Typical properties and limits of waste forms could meet the Waste Acceptance Criteria of the disposal site, in this case Baita–Bihor National Repository, are described in Refs [21].

Experiments parts

As given by the equation (1), has been studied the effect of increase content of solvent wastes on some properties of the magnesium phosphate binders. Laboratory tests are performed with inactive and active products, twelve formulas are tested.

As magnesium constituent was utilised MgO powder, calcined al 1550^0C, with MgO content of 96. 2%.The phosphate constituent was reagent potassium dihydrogen phosphate (MERCK)-KH_2PO_4.

The mineral aggregate, sand of Aghires, STAS 3965-74, sort M (50)03 was used. Laboratory tests are performed with active products, solvent radioactive from Cernavoda NPP was used. The tritium activity of the waste was 7.941 Bq/ml.

The qualification covers mixing properties (workability), hardening process (setting time), density and tritium *leach test*[7]. The specimens were prepared in laboratory according to flow sheet in figure 1.

To compare the property of the specimen were made five compositions. There were selected for conditioned radioactive solvent three matrices except mineral aggregate (sample 1, 2, 3) and two with sand of Aghires

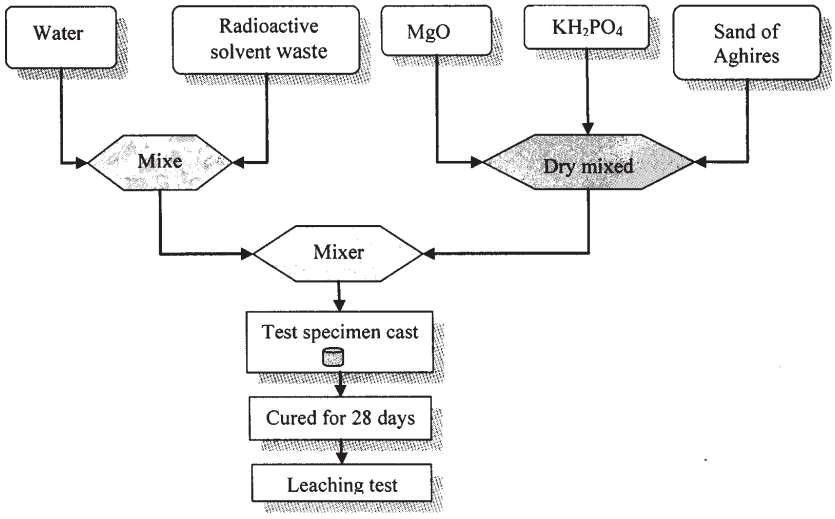

Fig. 1 Flow sheet to obtain the solvent radioactive waste specimens

Table 1
MIX PROPORTION OF IMMOBILIZING SOLVENT RADIACTIVE WASTE IN THE BINDING PASTES AND MORTARS

Sample	*MgO* [%]	*KH_2PO_4* [%]	*H_2O* [%]	Sand of Aghireş [%]	Radioactive solvent [%]
1	15	51	34	-	-
2	13.90	47.27	31.51	-	7.32
3	13.66	46.45	30.97	-	8.93
4	13.07	44.43	29.62	-	12.89
11	8.70	29.57	29.57	19.13	13.04
12	8.33	28.33	28.33	18.33	16.67

[6] *1 psi=703.06kg/m^2; 1 psi= 6.894757 kPa;*

[7] *A test conducted to determine the leach rate of a waste form. The test results may be used for judging and comparing different types of waste forms, or may serve as input data for a long term safety assessment of a repository [1];*

(sample 11, 12). The water to solid ratio in the pastes and mortars was 0.51L. The mortar composition (11, 12) was prepared with binder/sand ratio=2. The addition of solvent waste was 7.32 to 12.89% and 13 to16.67% in weight in the binding paste and respectively in the binding mortars according to table1.

Important properties are apparent density and setting time (with Vicat device) according to SR EN 12350-6 / 2005"Testing fresh concrete-Part 6: Density" and SR EN 480-2/2005 "Admixture for concrete, mortar and grout-Test methods-Part 2: Determination of setting time".

Tritium leachability from the test specimens was investigated by subjecting them to leaching in demineralized water, in accordance with a static leach test SR ISO-6961/1998,"Long term leach testing of solidified radioactive waste". The method is to place the specimen into deionized water for different times. Its renewal schedule was after the first day, third day and seventh day, once a week in the second week and third week, and once a month for the next three months. The leachant samples are analyzed to measure *p*H and conductivity. After the samples are distillate to diminish salt content salt in accordance with STAS 12293-83 "Determined tritium content", its is analyzed for tritium and carbon content with liquid scintillation method which the Liquid scintillation analyzer, type Packard, model TRI-CARB 2100 TR .

Two expressions of leach rate behaviour are used in this report. The first is leach rate (R_n, kg/m^2.s), according to SR ISO-6961/1998:

$$R_n = \frac{a_n}{A_0 \cdot F \cdot t_n}, \quad (2)$$

where:

R_n is leach rate of tritium, kg/m^2.s;

a_n - Tritium activity released in each renewal period, Bq;

A_0 – Tritium activity in the sample at time t=0, Bq/kg;

F – Surface area of specimen, m^2;

T_n - Contact time of leachant and specimen, s.

The second expression for *leach rate*[8] behaviour is requirement for the solidified waste should meet the Waste Acceptance Criteria of the disposal sites, in this case Baita–Bihor National Radioactive Waste Repository [21].

Sample	Radioactive solvent [%]	Setting time [min.]	Density [g/cm^3]
1	0	7	1.192
2	7.32	8	1.192
3	8.92	8	1.184
4	12.89	8	1.135
11	13.04	10	1.323
12	16.66	15	1.274

Table 2
SETTING TIME AND DENSITY OF THE BINDING PASTES AND MORTARS

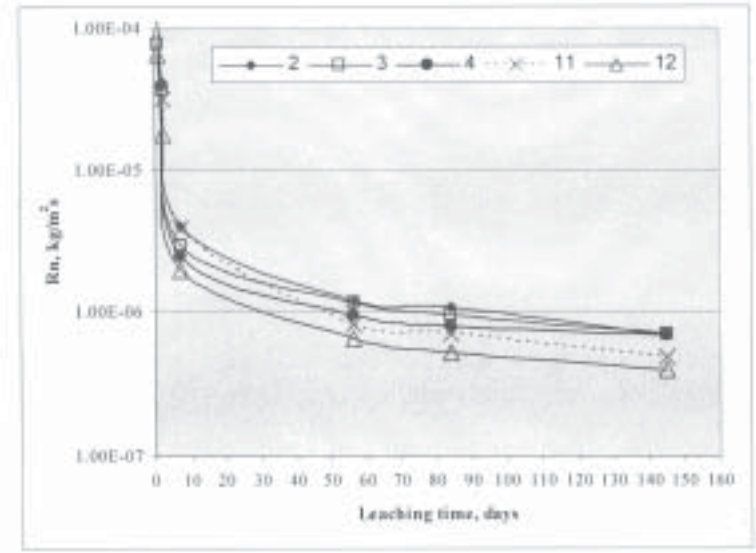

Fig. 2 Leach rates [kg/m^2.s] of immobilizing radioactive solvent wastes matrices function on leach time

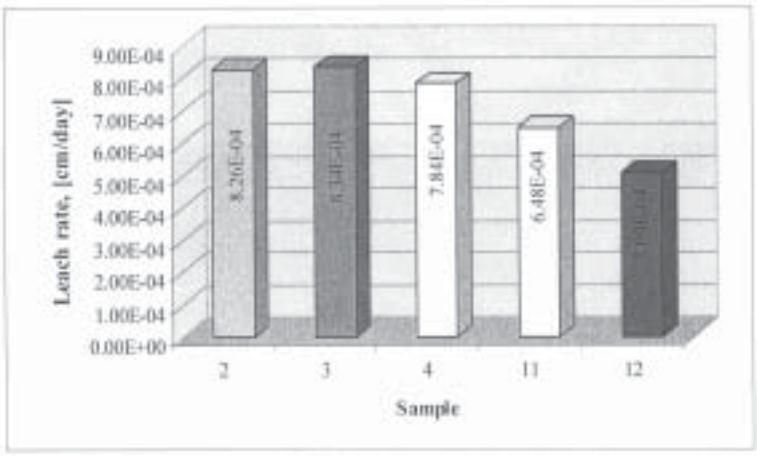

Fig. 3 Leach rates [cm/day] of immobilizing radioactive solvent wastes matrices at 145 days test

[8] *The binder is used in this report to describe inorganic materials that have the ability to react with water at ambient conditions to form a hardened mass [16].*

The leach rate (R_m, cm/day) is given by formula (3):

$$R_m = \frac{A_t \cdot V}{A_0 \cdot M \cdot S \cdot t}, \quad (3)$$

where:

R_m is leach rate of tritium, cm/s;
A_t- Tritium activity released in each renewal period, Bq;
A_0 – Activity of tritium 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.

Results and discussions

The research works presented in this paper took into consideration the correlations between composition and properties. According to this target, the defining properties were assessed. The setting time and density of the binding pastes and mortars is shown in table 2.

The pastes and the mortars had a good plasticity and some of them, swelling phenomena was observed (especially for sample 3 and 4). The setting period of time is short, increases with about 50% the setting time with presence of the sand of Aghires in magnesium phosphate binding pastes. It may be observed that the mortars prepared with sand of Aghires condoned greater percent of solvent in the matrices, about 16.66%. The density of mortars (sample 11-12) is higher than of pastes (sample 1-4).

The leach test is decisive for selection of immobilizing matrices. Figure 2 lists the tritium leach rate as equation (2) of five immobilizing matrices for 145 days. The tritium leach rate decrease in order 2>3>4>11>12, that is to say, matrix 12 exhibit the lowest leaching rate while the matrix 2 was the highest at any time. The reason may be from the addition of the sand of Aghires into magnesium phosphate binding (sample 11, 12).

The leaching rates for tritium are less 10^{-3}cm/day for immobilized radioactive solvent waste after 145 days tests, calculate of Formula 3, plotted in figure 3 indicate that all matrices tested satisfy the requirement for storage.

Conclusions

The continuing evolution in binder material, as well as the performance of matrices is constantly creating new challenges for conditioning the radioactive wastes. The comparative research work that was carried out allows conclusion, motivating to study this matrix. The new immobilizing matrix for immobilizing radioactive solvent waste exhibits the lowest leach rate of tritium. The results revealed that the addition of sand of Aghires into matrices would greatly enhance the density and the setting time and lower leaching rate of tritium.

Because of the high chemical complexity of solvent radioactive waste, further progress in magnesium phosphate binding will require the investigation of cementations systems, i.e. binder wastes interaction and mechanical strength. Such investigations must be designed to elucidate at the fundamental level, interaction involving organic wastes with magnesium phosphate binding. Results from these investigations will then support the development and optimization of the conditioning of organic radioactive waste technology.

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