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INNOVATIVE TECHNIQUE FOR IMPROVING THE COMPATIBILITY OF RADIOACTIVE WASTE WITH THE BLOCKING MATRIX

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INTRODUCTION

There are many types of waste produced during the operation or decommissioning of nuclear sites. This waste must be conditioned before final disposal. Conditioning it in a stable, confining, and monolithic form poses problems linked essentially to the chemical nature of the waste and its compatibility with the blocking matrix. Blocking difficulties are particularly observed with certain reactive and/or organic materials such as ion exchange resins, oils and solvents. Common matrices are based on Portland type cements.

WASTE BLOCKING ISSUES

The sustainable management of radioactive materials and waste requires conditioning of the waste for final disposal according to storage standards. The conditioning must guarantee long-term stability of the waste-matrix mixture. Waste-matrix compatibility will depend on the nature of the waste (organic, pyrophoric, reactive, etc.) and the blocking matrix (alkaline nature, etc.), to which must be added situations where the waste does not consist of a single material. Indeed, some wastes are in the form of a mixture, homogeneous or heterogeneous, of several materials with very different physico-chemical properties. For example, these mixtures can be metals (steel, aluminium, etc.), technological waste, organic compounds (oil, bitumen, etc.), ion exchange resins, ...

Cementing is the most widely used technique. The main reasons for this choice are the abundance of raw materials, the density of the material (biological protection), the mechanical resistance, the good knowledge of its long-term behaviour, the robustness of the process and the simplicity of its implementation. The waste, which has been compacted or placed in bulk, is generally placed in a basket, which in turn is placed in a metal or concrete container; it is then immobilised by a hydraulic binder (cement) to limit the risk of diffusion of radioelements to the outside and thus forms a heterogeneous mix.

Hydraulic binder is used to immobilise waste within containers or as a conditioning matrix to encapsulate intermediate level waste.

Blocking with a hydraulic binder is a low cost and easy to implement process, but it is not without its drawbacks. Interactions between the constituents of some wastes and the cementitious matrix can lead to swelling and cracking of the package, reducing its durability.

In addition to its use to block massive solid waste in containers, cementing is also used to coat waste in solution or powder form: evaporation concentrates, chemical treatment sludge, ion exchange resins, etc.

Cements combine many favourable factors for blocking waste:
- Availability,
- Low cost,
- Easy to use
- Good mechanical resistance,
- and, in general, stability over time.

The behaviour of the packages over time is very different depending on the chemical nature of the cemented waste.

INTEREST AND DESCRIPTION OF THE NuBLOCKRad MATRIX

A simple solution is to achieve the blocking of waste mainly by coating. The main objectives are to increase the rate of encapsulation and to improve the performance of the asphalt.

Indeed, cementing the waste faces two major difficulties:

- The volume of the final waste, which in general is more than twice the volume of the initial waste.

- The physical and chemical interactions between the different constituents which disrupt the implementation and the blocking operation. These interactions affect the durability of the packages.

There are several possible ways to overcome these drawbacks:

1. Reduction of the interactions between the matrix and the waste. This reduction can be achieved either by consistent pre-treatment or by neutralisation (modification of pH, surface functions, etc.) or by pre-coating (film, varnish, etc.).

2. The search for new chemistries, either by modifying existing solutions or by searching for new formulations.

The first approach, even if it can lead to viable solutions, should be discarded, except in very specific cases. The reasons are related to the presence of several wastes in a mixture and the cost of pre-treatment. Added to this is the fact that the waste approval must be validated again by demonstrating the harmlessness of the new substances introduced for the pre-treatment. Other cementing solutions have been developed for blocking specific wastes (sulpho-aluminous cement formulations). No conventional cementing solution has been developed for immobilising waste containing several materials (sludge, organic matter, etc.).

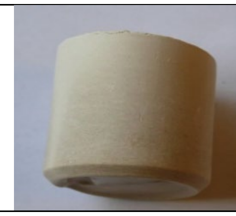
To respond to this diversity of chemical behaviour, the solution was to develop a material that contains chemical compounds in its composition to create bonds with the different wastes. The NuBLOCKRad matrix uses materials from the living environment with properties that improve the compatibility of the waste with the blocking binders.

The development of the biomaterial process has been described in the literature for several decades and is currently experiencing renewed interest, for example, in the repair of concrete structures. Processes for obtaining mineral substances using a biological process for producing mineral material and mineral carriers are known, such as those described in documents FR2723080 and FR2644475. These mineral materials are of natural or artificial origin, or part of them are of natural origin and another part of artificial origin.

The process for immobilising nuclear waste comprising the NuBlockRad matrix consists of:

- A mixing step, in which the nuclear waste is mixed with a slurry (Fig. 2) produced by mixing the mineral composition (Fig. 1) with water.

- A drying step, in which the mixture obtained in the mixing step is dried to form an immobilisation matrix (Fig. 3).

		
Fig.1 hydraulic binder NuBLOCKRad	Fig 2. NuBLOCKRad + water mixture (W/C = 0.37)	Fig.3. Mixture after drying (1 day)

The mineral composition (NuBLOCKRad binder) is obtained by a manufacturing process comprising the steps of preparing a base containing an amount of a mineral material synthesised by at least one part of a living structure selected from the plant kingdom, animal kingdom and/or micro-organisms: and transforming it into an inactivated material with a predefined texture.

The mixing of the mineral composition and water allows the mineral composition to achieve a structural arrangement leading to the creation of a three-dimensional network. The creation of this network leads to the hydrated mineral composition setting around the nuclear waste, which, after a certain drying time, results in a compact mass composed of the waste and an immobilisation matrix (fig. 3).

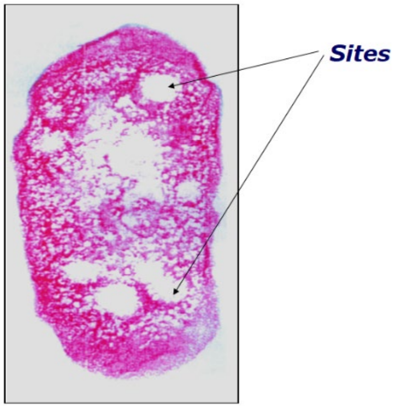
The NuBLOCKRad binder is obtained:

- From a mineralizing, mineralized or mineralizable "living structure", it is necessary to understand any cellular structure or of cellular, vegetable, animal or micro-organic origin, living and/or resulting from life and/or compounds of biological origin, crystallized or not.

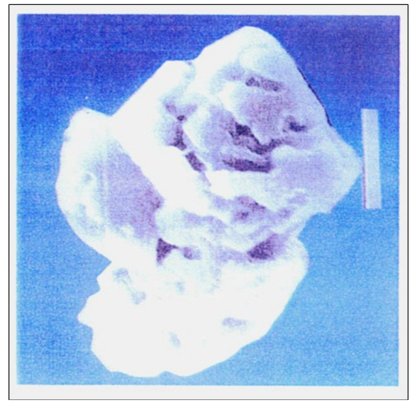
- “Inactivated material” means material devoid of any biological and/or bio-mineralising activity, of any pathogenic microbiological activity.

The preparation of the base includes a step of cultivating the living structure for a period and in a medium such that at least a part called "mineral biomass" is then produced or synthesised by this structure. After this step, a treatment phase may include a phase of inactivation of the living structure. Inactivation means obtaining an inactivated material from the living structure.

The process may include inactivation of the base to obtain the inactivated mineral substance. The composition used to obtain the biomaterial contains a living structure and a nutrient.



Mineral uptake by bacteria



Mineralized colony of bacteria after "calcification"

The described blocking product and process, called NuBLOCKRad, is an inorganic material made by microorganisms that cause crystal rearrangement based on an inorganic anchoring organisation.

The blocking principle consists of bringing NuBLOCKRad, water and waste into contact. The hydration of the binder leads to the formation of a slurry which, after drying, produces a homogeneous matrix with mechanical properties equivalent to concrete.

The incorporation of the waste can be done according to the following 2 techniques:

- By mixing the binder, the water, and the waste (valid for small-sized waste: powdery, pasty or liquid waste)
- By injecting the grout (water + NuBLOCKRad mixture) into a container containing the waste (coating).

CARACTERISATION AND COMPATIBILITY

The performance of the matrix obtained by mixing the NuBLOCKRad binder and water is that of cements with the addition of specific properties for blocking waste:

- Immobilisation of reactive metallic waste.
- Binding properties that allow waste of various types to be set in mass, such as
  - Organic,
  - Minerals,
  - Pulverulent,
  - Paste,
  - Liquids.

The general properties of this matrix are equivalent to the cementitious matrices commonly used for nuclear waste containment. The main characteristics are as follows:

- Typical grout composition: 70% NuBLOCKRad binder - 30% water;
Water/NuBLOCKRad ratio ~ 0.4 to 0.5

- pH ~ 11.5

- Mixing time for grout production: 5 - 10 min

- Practical working time (DPU - NF EN 196-3) is 6 h.

- Fluidity < 9 s (Marsh cone - NF P18-507)

- Heat of hydration (NF EN 196-9 after 41h): 178 J/g
- Loss on fire (NF EN 196-2): < 1.5%.
- Mechanical resistance to compression (NF EN 197-1): ~ 25 MPa
- Dimensional shrinkage at 1 year: < 1 mm/m

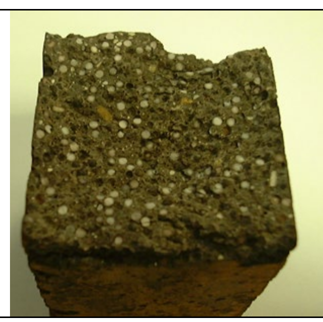
The compatibility of the matrix has been tested with various materials, including (but not limited to):

- Metallic materials: magnesium, stainless steel, aluminium, carbon steels,
- Graphite,
- Gravel, sand, soil, glass,
- Organic technological waste: plastics, ion exchange resins; bitumen, oil.

Various waste blocking tests were also carried out to demonstrate the compatibility of the immobilisation with the NuBLOCKRad matrix.

The figures below illustrate the results obtained:

		
Fig. 4: NuBLOCKRad + Aluminium	Fig. 5: NuBLOCKRad + Mg-Zr alloy (UNGG fuel cladding)	Fig. 6: NuBLOCKRad + Mg block

		
Fig. 7: NuBLOCKRad + graphite powder (23% W/W)	Fig. 8: NuBLOCKRad + Zeolites (23% W/W)	Fig 9: NuBLOCKRad + ion exchange resins (23%W/W)

The table below shows the data on the blocking tests of certain wastes and the evolution of the mechanical strength as a function of time.

Material	Incorporation rate %W/W	Penetration (bleeding)	Final density after drying	Compressive strength (MPa)			
				28 days	90 days	180 days	360 days
Graphite	23	NO	1.9	26	25	36	33
Bitumen/oil	25	NO	1.9	9	10	10	14
Zeolite	23	NO	2.0	26		27	27
Bitumen/Zeolite/oil	25	NO	2.0	28	31	27	29
Bitumen	25	NO	2.2	44	48	55	53
Ion-exchange resin	23	NO	1.7	22	26	25	24
Sludge	23	NO	2.2	41	47	46	48

SPECIAL CASE OF BITUMEN IMMOBILIZATION

Historically, wastes such as sludge or concentrates have been immobilised in bitumen.

The recovery of these wastes has been studied in two ways, by incineration and by immobilisation in a cement matrix. We studied blocking by carrying out immobilisation tests on inactive (waste-free) bitumen chips with NuBLOCKRad.

The objective was to verify the bitumen-NuBLOCKRad compatibility and the behaviour over time (mechanical resistance, shrinkage, resistance to irradiation, etc.).

Several mixtures were tested:

- Bitumen alone (mass incorporation rate TI = 25%) - Fig. 10
- Bitumen / oil 70/30 (TI = 25%) - fig. 11
- Bitumen/zeolite/oil mixture 50/30/20 (TI = 25%) - Fig. 12

The NuBLOCKRad / Bitumen specimens were irradiated with a total dose of 1300 kGy. No swelling or shrinkage was observed after irradiation. The measurement of the compressive strength before and after shows a slight increase after irradiation:

- Mechanical strength before irradiation: 43 MPa
- Mechanical strength before irradiation: 50 MPa

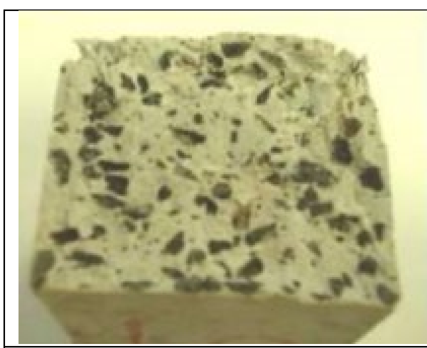


Fig 10 : NuBLOCKRad + bitume	Fig 11: NuBLOCKRad + bitumen / huile	Fig 12: NuBLOCKRad + bitumen/zéolithe/huile

CONCLUSION

The NuBLOCKRad binder used in the composition of the cementitious matrix has demonstrated its interest in obtaining an effective blocking of different materials, taken separately or in a mixture, without the need to separate these materials beforehand.

After drying, the block obtained complies with the regulations relating to the storage of waste, particularly in terms of mechanical strength, hydrogen release and leaching.

Several projects currently being studied on waste treatment in France and abroad should be able to benefit from the advances provided by NuBLOCKRad in the durability of waste packages and the security of their containment.

Nuvia is currently exploring a way of producing the binder that reduces its environmental footprint.

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