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A topping gel for the treatment of nuclear contaminated small items

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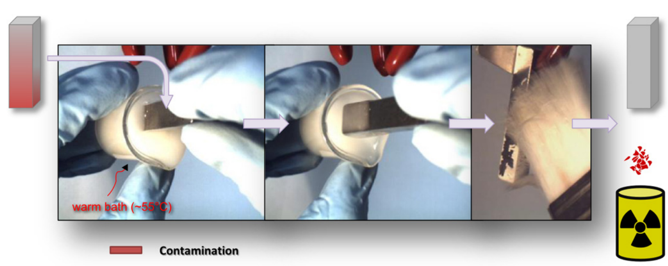
HIGHLIGHTS

- This article is an introduction towards an alternative method for small items decontamination.
- Mechanisms underlying its use are explained.
- Temperature dependent rheological behavior is investigated.
- Drying and decontamination efficiency are characterized.

GRAPHICAL ABSTRACT



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ABSTRACT

Nuclear decontamination is a key aspect of the decommissioning of facilities, can today be carried out using gelled reagents sprayed over contaminated surfaces (tens of square meters) and allows easy radionuclide retrieval. Wide ranges of formulations have been developed in our laboratory to treat several materials. The gels are formulated by adding colloidal silica particles to a reactive solution; they dry and form solid residues that are easily collected and directly conditioned. Dissemination hazards are reduced and no liquid effluent is generated or released. In order to adapt the process to the decontamination of small items, an original method involving a topping gel has been developed. A polysaccharide, carrageenan, is added to a conventional gel (silica particles + reactive solution) and by varying the temperature an abrupt sol–gel transition (around 45–50 °C) is observed. At high temperature, the low viscosity of the gel allows it to coat small parts easily, and simply removing them from the warm bath congeals the topping gel. Its decontaminating action takes place. The gel then dries and can be collected. A tradeoff has been found between the mineral mass fraction and the amount of carrageenan, and a formulation is proposed. Results on ^{60}Co contaminated black steel plates show that the decontamination factor is fully comparable to a conventional gel. Finally, drying kinetic measurements show that easily recoverable flakes are formed due to water evaporation.

1. Introduction

Monitoring nuclear facilities is an important economic and ethical issue for their operators. In 2011, in France, 125 nuclear installations are listed by the ASN (Nuclear Safety Authority), all with potential exposure to radioactive dust and wastes. "Contamination" means a deposit of atoms or molecules emitting ionizing radiations. This deposit can be a simple thin layer on a surface or sometimes species that have penetrated a few micrometers into a material. Decontamination then consists in the removal of these radionuclides allowing either maintenance or decommissioning of the installation. Various processes can be used; classical approaches consist in a physical or mechanical attack of the material

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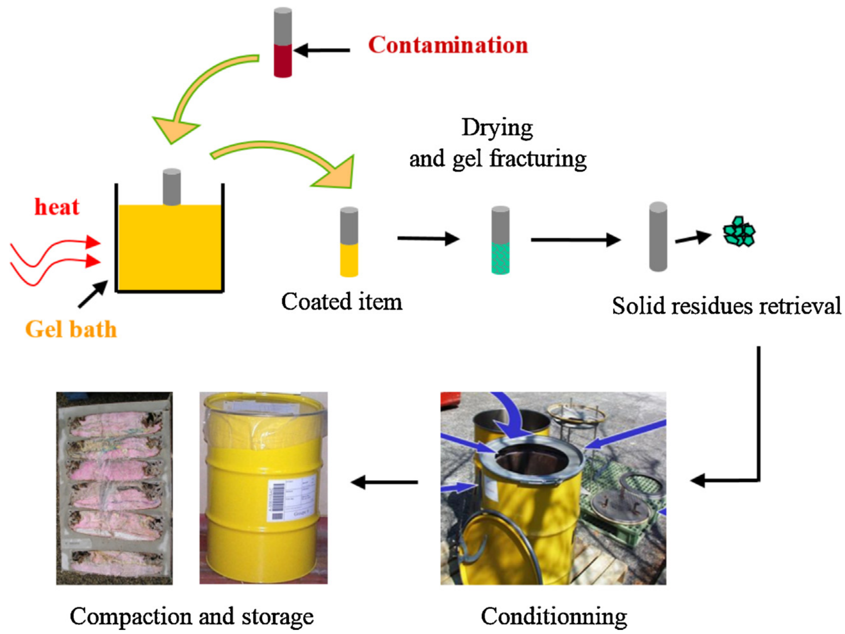

Fig. 1. Process principle.

(sanding, pressurized water, CO_2 blasting, lasers (Gillis et al., 1992; Champonnois et al., 2006), etc.) or in a chemical deterioration using acid, basic or oxidizing solutions. In order to overcome the drawbacks of these traditional methods, the CEA (French Atomic and Alternative Energies Commission), works on innovative new decontamination processes including foams (Gauchon et al., 1995) or vacuumable gels (Fournel et al., 2003; Fuentes et al., 2007).

These gels are formed by adding a mineral viscosing agent (e.g. colloidal silica) to an aggressive solution. The material is meant to be sprayed on contaminated surfaces where it dries and forms non-powder solid residues. Shear-induced viscosity changes and yield stress can be directly linked to the process requirements (sprayability, how it holds on a surface, etc.); the gel must exhibit shear-thinning or thixotropic behavior.

In order to adapt the method to the decontamination of small items measuring about 10 cm on a side, a new substrate coating method must be imagined. Spraying is not conceivable for objects with complex geometry (spring-like structures, holes or with internal surfaces). Fig. 1 shows the principle of the procedure envisaged to solve this issue (Cuer and Castellani, 2013).

The contaminated material is immersed in a heated liquid gel bath. The gel congeals and starts to attack the substrate over a thin layer of material, trapping the radionuclides by diffusion. The other steps are identical to those found in traditional sprayed gel processes, i.e. recovery of the residues and waste disposal. With this process, no liquid effluents are generated and small items can be thus treated without leakage hazards, needs little human intervention and requires only solid wastes treatment methods. Some efficient chemicals that are deprecated in the case of liquid effluent decontamination (as Ce IV) are, here, potentially usable.

Specific rheological behavior is necessary to correctly manage the decontamination of the items. The viscosity must be low enough in the bath to allow a homogeneous coating. On the other hand, the gel must adhere to the material and not flow when the item is removed from the bath. The time spent required for these steps must be short enough to avoid bath contamination.

Existing formulations do not have such behavior. Ideally, an additive sensitive to various external parameters could be suitable for this purpose and allow the final formulated material to modify its characteristics when displaced from the bath state to the coated state. For example, light-sensitive additives exist (Kuang et al., 2009; Jiang et al., 2009); the structure and rheological properties of these additives can be controlled by tuning the light power. However, the gelling kinetics in this case are relatively slow, making it difficult to use these chemicals. Magnetorheological compounds (e.g. core–shell particles of silica or hybrid gels doped with ferrofluids (Lim et al., 2004; Kornak et al., 2004; Im et al., 2005; Kroell et al., 2005)) could also work; we can imagine withdrawing the items from a liquid bath into a magnetic field, increasing the decontaminating gel viscosity. Again, this solution is tricky as the magnetic field involved here must be high (~1 Tesla) in order to obtain a sufficient rheological contrast. Solutions based on ultrasound (Naota and Koori, 2005; Paulusse et al., 2007; Piepenbrock et al., 2010) or other parameters (Gasnier et al., 2009; Gil and Hudson, 2004) could also be taken into account and investigated.

Finally, in our opinion, the simplest way to implement the process is to impose a temperature gradient between the bath and the external environment, which will modify the gel rheology. In the first part of this paper, we examine a polysaccharide, carrageenan, as a thermo-sensitive additive used in our formulations; however it is important to mention that nuclear waste treatment agencies impose a maximal of 2 wt% organic matter in such systems due to the potential release of radiolysis gas. The rheological tests are then described, followed by an assessment of the impact of different proportions of mineral/organic content on the formulated materials. Except where otherwise specified, only the results regarding a specific polysaccharide, ι-carrageenan, are discussed.

2. Materials and methods

In order to give a temperature-dependent behavior to traditional colloidal silica gels, a gelling type of carrageenan is added to the formulations. This polysaccharide exists under different forms; only ι and κ carrageenan show a sol–gel transition (i.e. a change in the polymer chains conformation that leads to different material structures and flowing properties) when the temperature is modified (Shchipunov, 2003). Their molecular structures are indicated in Fig. 2.

When the temperature decreases below a particular transition point, the chains adopt a helical structure, strengthening the material (FAO, 1990). Ions in solution can also modify the polymer network and therefore change the system viscosity by crosslinking