Vacuumable gels for NRBC surface decontamination: an application to post-event remediation.

A. LUDWIG[1], F. GOETTMANN[1], F. FRANCES[1], C. LE GOFF[2], V. TANCHOU[2], M.S. CHARVOLIN[3]

[1]CEA, DEN, DTCD/SPDE, Marcoule, 30207 Bagnols-sur-Cèze cedex, France

[2]CEA, DSV, iBEB/SBTN/LDCAE, Marcoule, 30207 Bagnols-sur-Cèze cedex, France

[3]NBC-Sys, 8 rue Bonnevialle, BP 10226, 42408 Saint-Chamond, France

amelie.ludwig@cea.fr, frederic.goettmann@cea.fr, ms.charvolin@nbc-sys.com

Résumé – Depuis quelques années, la décontamination des infrastructures et des personnes contaminées par des agents radiologiques, biologiques et chimiques suscite beaucoup d'intérêt, notamment à travers le renforcement des politiques de sécurité intérieure. La plupart des techniques de décontamination sont développées sur mesure en fonction des scénarios envisagés. En se basant sur notre expérience de la formulation de gels de décontamination pour l'industrie du démantèlement dans le nucléaire, nous avons travaillé au développement de gels inorganiques pour traiter des matériaux de construction et des infrastructures civiles dans le cadre d'une intervention NRBC post-évènementielle. Notre but est de développer une formulation multifonction, de mise en œuvre aisée, pulvérisable et aspirable, générant une quantité limitée de déchets solides directement conditionnables.

Abstract – The decontamination of radiological, biological or chemical warfare agents from structures, environmental media and personnel has become an area of particular interest in recent years, especially because of increased homeland security concerns. Most suggested decontamination techniques rely on tailor made decontamination solutions. Basing on our own experience in the formulation of nuclear decontamination gels, we investigated the use of inorganic gels to treat building materials or civil infrastructures in the frame of NRBC post-event remediation. Our aim is to develop an easily deployable multitask formulation, which would be sprayable and vacuumable and would generate limited amounts of easy-to-handle waste.

1. Introduction

In the context of nuclear decommissioning, numerous techniques have been developed to enable the decontamination of building materials, large and small metallic pieces, etc. Such decontamination steps aim at reducing the residual radioactivity of the treated materials to a degree suited for their handling as standard or low activity waste. As such, decontamination considerably reduces the costs of decommissioning operations. However, improvements to these techniques were prompted by other concerns, such as the reduction of exposure time for the operating personnel or the minimization of the volumes of secondary waste. Among these improvements the development of vacuumable gels was a giant step [1-2]. Indeed, this technique employs corrosive colloidal inorganic gels as surface decontamination agents, which features several advantages:

- The employed formulations behave like sols under strain and are therefore easily sprayable on surfaces. At low strain, they undergo a sol-gel transition and thus form non flowing layers on the surfaces they were sprayed on.
- These formulations dry within the decontamination time and enable the chemical attack of the surfaces to treat, in order to solubilize the radioelements present in several tens of microns of the material.
- After drying, the gel cracks to yield non pulverulent flakes that can easily be removed from the surface by vacuum. This process considerably reduces the intervention time.
- The formed flakes concentrate the radioactivity and are compatible with most waste storage matrices without generating any liquid effluent.

Basing on this know-how, we undertook to adapt the formulation of such gels to the very case of post-NRBC attack remediation in public places.

2. Base principles of decontamination gels

As previously mentioned, vacuumable decontamination gels are already employed in nuclear decommissioning, on a daily basis. A typical example of such gels is the so-called ASPIGEL 100E [1, 2]. This gel is based on an acidic, cerium IV containing, formulation and is well suited for the removal of fixed contamination on metallic surfaces. Indeed, cerium IV enables the chemical attack of the metallic surfaces in order to solubilize the radioelements present in several tens of microns of the material. Another example is the ASPIGEL 400 which is a basic formulation for aluminum alloy materials decontamination.

In lab scale tests (Fig. 1), the gel is deposited by doctor blading on the desired substrate. There, it forms a homogeneous layer of the desired thickness (0.5-1mm). The decontamination process takes place within the drying time (2 to 48 hours depending on the formulation and on the climatic conditions). Drying results in the shrinkage of the gel and, thus, in cracks formation. The formed flakes are non pulverulent but can easily be removed, for example by brushing.

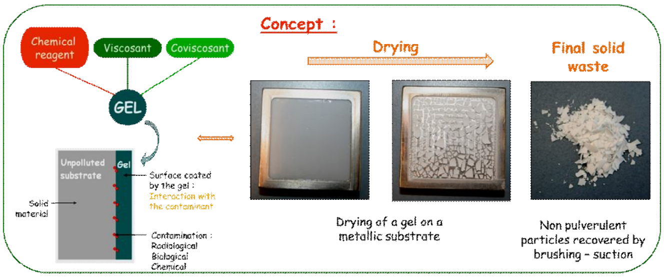

FIG. 1: Lab scale test of a vacuumable decontamination gel

In real life application, the operating mode remains largely the same (Fig. 2). The gel can be sprayed on the contaminated surface. Using suited equipment, the operator can cover up to 4m² of surface per minute. During the drying process, the presence of the operator is not required in the room. After drying, the dry gel entraps the contaminants and can be removed by vacuum cleaning. The whole process considerably limits personal exposure and the formed secondary waste is easy to handle and to store (no secondary liquid effluent).

FIG. 2: Application of a decontamination gel under real conditions

This innovative technology is now adapted to NRBC concerns in the frame of a collaboration between the French Atomic Energy and Alternative Energies Commission (CEA) and the company NBC-Sys. The corresponding project is named GIFT-RBC. Using the synergism between the two companies, different vacuumable gels are developed to handle NRBC decontamination on various materials using the adequate spraying and suction techniques.

3. Results and discussion

3.1 Design of a biocide gel

In order to adapt vacuumable gels to biological decontamination in public places, numerous factors have to be taken into account:

- The new formulation has to efficiently destroy a large spectrum of pathogens from bacteria to viruses (*Bacillus anthracis*, *Yersinia pestis*, *Francisella tularensis*, and hemorrhagic fever viruses) [6] and especially resistant forms of bacteria (i.e. spores).
- The new formulation has to be adapted to surfaces present in public places (concrete walls, porcelain tiles, glass, plastics, metallic surfaces… (Fig. 3)) and should not alter the mechanical properties or the integrity of the materials.
- The spraying techniques are to be adapted to post-event intervention conditions.

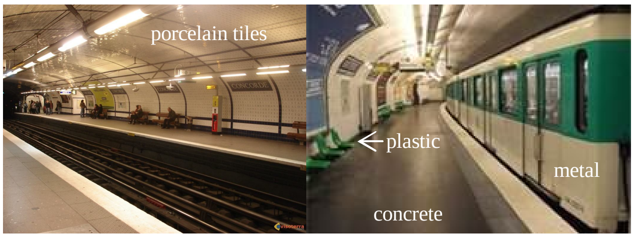

FIG. 3: Example of a sensitive public place: the Parisian underground.

For doing so, as a first draft, an alkaline biocide gel has been developed by the Atomic Energy and Alternative Energies Commission (CEA) [3]. Indeed, strong bases are known as effective media to destroy biological warfare agents [3-4-5]. Currently, an optimized biocide basic gel formulation has been designed, by adding a biocide agent to the previous formulation, so that the resulting gel efficiency and working life correspond to industrial requirements for NRBC post-event remediation.

To be employable in real conditions, vacuumable gels have to feature numerous physicochemical properties (concerning their rheology, drying times, crack formation, etc.). The new alkaline formulation thus had to behave similarly to the previously known acidic gels in the nuclear industry.

At first, classical physicochemical properties of vacuumable gels as drying kinetics, flakes size distributions and gel rheology, were tested. Figure 4 represents the drying kinetic for a biocide gel formulation and shows that this gel typically dries within five hours for a gel thickness of 0.5mm, under controlled conditions (25°C and 50% of relative humidity). This drying time fits with reasonable decontamination time of the biocide agents. Moreover, compared to the commercialized nuclear decontamination gels Aspigel 100E and Aspigel 400, the biocide gel has a similar drying time order of magnitude (the mass losses are different due to the gel compositions that are variable).

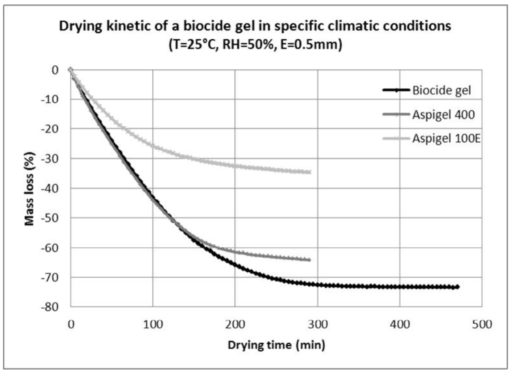

FIG. 4: Drying kinetic of a typical biological decontamination gel compared to nuclear decontamination gels

To check if the drying process yields non-pulverulent solid slices, flakes were measured showing millimetric slices well suited for the application we aimed at (Fig. 5).

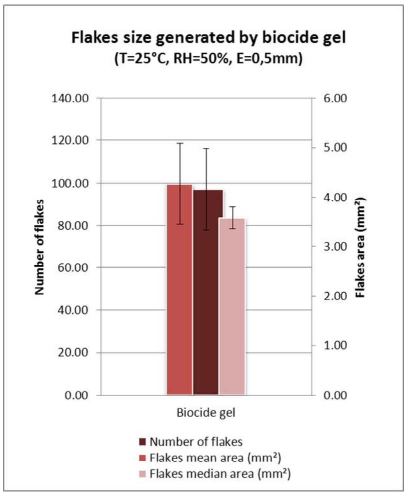

FIG. 5: Flakes size generated by a typical biological decontamination gel

Furthermore, gel viscosity was measured (Fig. 6) to show the shear thinning and the thixotropic behavior that are essential for the gel to be pulverized.

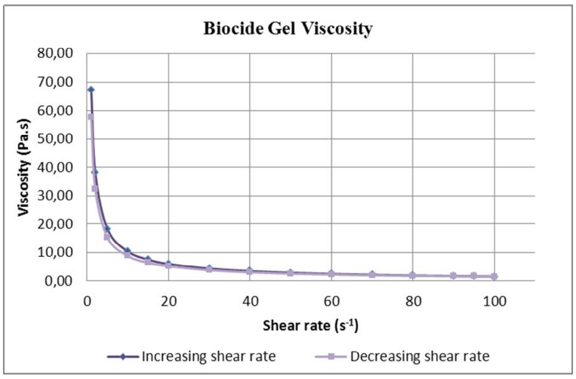

FIG. 6: Viscosity of one of the biocide gel formulation for low shear rates

Concurrently, the biocide effectiveness of this new formulation was tested on *Bacillus thuringiensis* spores (a surrogate of anthrax) and on the ricin toxin thanks to the help of biological laboratories (CEA – Mrs. V. Tanchou and C. Le Goff: DSV/iBEB/SBTN/LDCAE in Marcoule and Mr. D. Gillet: DSV/iBITEC-S/SIMOPRO in Saclay).

In fact, different substrates were contaminated with about 2x10^7 spores of *Bacillus thuringiensis* on glass, stainless steel, porcelain tile and mortar, and 2x10^6 spores on PVC and PVDF. After the application of 0.5-1mm of biocide gel and the drying step, no living spores were detected on the smooth surfaces (stainless steel and porcelain tile) and neither in the flakes on the different substrates showing that the decontamination factor is at least of 6-7 decades. On the other substrates, the decontamination factor approaches 5 decades (Fig. 7).

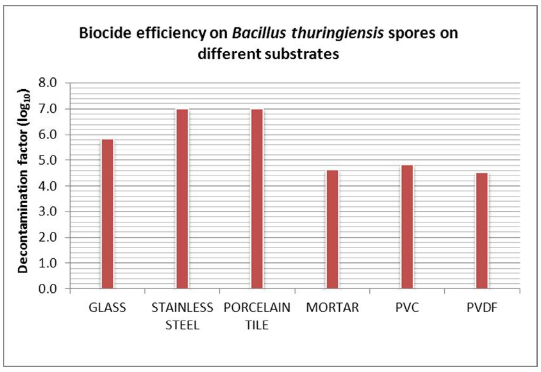

FIG. 7: Efficiency of the biocide gel on *Bacillus thuringiensis* spores

A similar formulation was tested on glass slides contaminated by 1µL of ricin solutions of increasing concentration. Cytotoxicity tests were performed on Vero cells as means to detect the activity of ricin with or without biocide gel application (Fig. 8). Without decontamination (graph on the top in dark) at ricin concentration as low as 10^{-10}M, all cells died. After decontamination with the biocide gel (graph on the bottom in red), the initial ricin concentration hardly affects cell survival and the only mortality is caused by the gel itself (as evidenced on the top graph, red dots). This evidences that our gel is able to effectively inhibit ricin on glass substrate (at least with a factor of 1000).

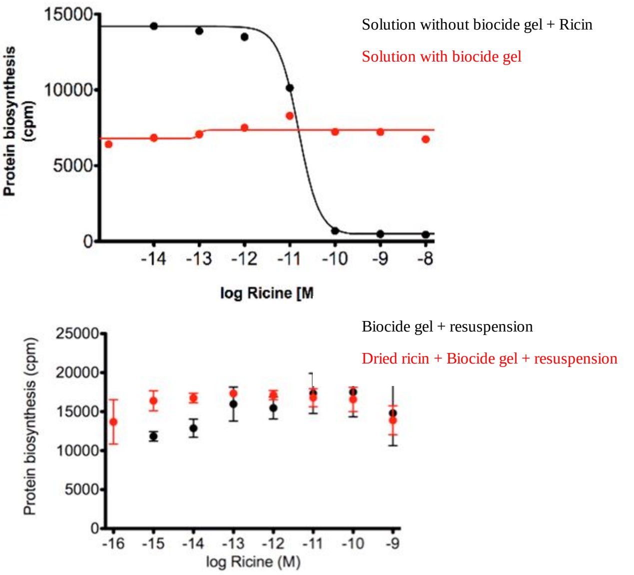

FIG. 8: Cytotoxicity tests after glass substrate contamination with ricin (upper graph: no decontamination; lower graph: decontamination using biocide gel)

Finally, NBC-Sys tested the large-scale deployability of this biocide formulation with various spraying apparatus on $3m^2$ tile covered surfaces (Fig. 9), giving very promising results: controlled thickness (0,5-1mm), uniform and regular coating, no tear.

FIG. 9: Large-scale spraying test of the biocide gel

3.2 Chemical and Radiological concerns

Concurrently to this work on the biological decontamination gel, we are working on chemical and radiological decontamination using the same gel.

Some preliminary tests have been done as concept evidence before working on the optimization of this gel.

3.2.1 Chemical decontamination

Based on the same concept than the biocide gel, to rehabilitate surfaces contaminated by chemical warfare agents (CWA), the vacuumable gel has to be in contact with the contaminant and to degrade the CWA into harmless molecules by hydrolysis or oxidation [8]. The targeted CWA are organophosphorous molecules (sarin, soman, tabun, VX) and blister agents (yperite, lewisite) [6].

In a preliminary test, a porcelain tile has been tainted by oil red (Fig. 10). The chemical decontamination gel is applied on the right side of the tile (for comparison purpose, one droplet wasn't treated at all (in the middle) and one droplet was treated with an inactive water based alumina gel (on the left)). After 3-5 minutes, the color of the red drop under the active gel faded. Afterwards, as the gel is totally dry, the flakes are removed, uncovering the clean tile. This quick experiment shows that the contact between the gel and the contaminant is good and will probably give promising results in upcoming experiments on CWA surrogates [8-9-10].

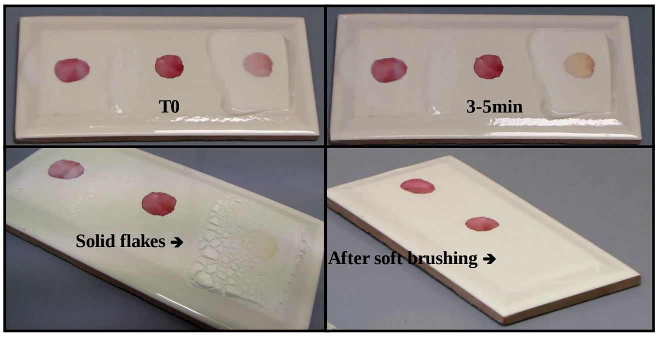

FIG. 10: Concept evidence for chemical decontamination using a vacuumable gel on a tainted tile

3.2.2 Radiological decontamination

To complete the experimentations on these strengthened vacuumable gels formulations adapted to NRBC decontamination, preliminary tests using different gels on a disk of stainless steel contaminated with 5000Bq of Cobalt 60 will be realized soon (Cobalt 60 is an easily available radioactive source for terrorists as it is used for therapy [7]).

As this technology derived from the nuclear decommissioning industry [1-2], we are very optimistic about developing an adapted version of the gel for radiological post-event remediation.

3.3 Perspectives and Conclusion

Basing on these results, we have evidenced that:

- A new kind of RBC decontaminant in form of a gel is feasible.
- The efficiency of the biological decontamination process has been demonstrated: ongoing experiments aim at testing this biocide gel on real

pathogens (*Bacillus anthracis spores*, *Yercinia pestis* and *Vaccinia* virus).

- Preliminary tests for the chemical decontamination process are promising.
- Various pulverization means are suited for large scale application.

Currently, we are working on the optimization of our gels and of the operating modes. In order to achieve the ambitious goals pursued in the framework of this project, some tasks are still going on. The required innovations concerns both the range of toxic agents, which may be treated with one single reinforced formulation (i.e. biological but also chemical warfare agents and radionuclides) as well as the operability of the designed decontamination technique. This last point is probably the trickiest one:

- Improvement in order to ensure the quality of the operating mode (i.e. assessment of the drying degree by the operators).
- Study of the stability in storage within the spraying devices in order to ensure a fast post-event intervention.

In order to evaluate these different points and to validate this decontamination process, a large-scale pulverization trial is planned in a moth-balled station of the Parisian underground in order to simulate a real post-event remediation in a sensitive site which could be a potential target.

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