NEW DECONTAMINATION PROCESS USING DRYING GELS

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ABSTRACT

Within the context of nuclear plants maintenance and later dismantling, we report an attractive new decontamination technique leading to the reduction of the liquid secondary effluents volume [1]. It is based on the use of new colloidal silica gels sprayed on metallic surfaces to decontaminate and the removal of the gel containing the pollutants without water rinsing. This process is applied as following. First, the gel is sprayed onto the surface to be cleaned. Then, because the gel is able to dry at room temperature in a few hours, a thin thickness of the contaminated surface is corroded. During the drying, the gel cracks and leads to the formation of solid tiles, coming off more or less easily from the surface. Last, the final solid particles containing the pollutants are removed from the surface and recovered by vacuum cleaning or by brushing.

During the past years, different specific formulations were developed to decontaminate metals such as stainless steel, aluminium or lead.

This conference will be an overview of basic research works and application studies conducted by the CEA on this new gel decontamination technique and the first demonstrations led on Cogema sites. Main aspects of gel feature (chemical composition, rheology, drying, stability) will be developed.

INTRODUCTION

Since 1990, the studies concerning the decontamination of solid materials in the nuclear industry have been motivated by a strong reduction of the secondary wastes compared to more classical techniques based on physical methods (spraying of abrasives or high pressure water) or chemical methods involving a liquid phase and one or more reactants. These techniques usually led to large amounts of liquid wastes. Decontamination also enables radiation exposure reduction during decommissioning operations, and can potentially lead to the decategorization of waste to achieve lower disposal cost.

In 1990, CEA together with COGEMA launched a research program on gel decontamination.

The major objective of this program was the liquid volume reduction and minimization of reactants consumption for large-scale in-situ R&D operations. Properties for an efficient gel formulation have been defined and a first patent was published in 1991. It describes suited gel formulations containing silica for acid gels and alumina for alkaline gels. The basic principles involved in the formulation definition are recalled in the first part dealing with the formulation of the gel.

Based on the last gel formulation, fundamental studies have been launched since 2000 in parallel with scale one operations or demonstrations (last part of the paper). Real large scale operations appeared necessary not only to convince nuclear operators like AREVA, EDF and CEA from the benefits of the technique but also to re-route fundamental studies to take into account for specific industrial conditions. like for example gel pulverization at low pressure with a nozzle, at a distance from the pump between 1 and 15 m, at a temperature between 16 and 30 °C, and an relative humidity between 20 and 70%.

The beginning of the fundamental studies on formulation started with a new idea to improve usual formulations. The aim was to see if it was possible to prepare a gel formulation that leads, after the film pulverization with a sufficient adhesion onto the surface and after free drying, to the formation of solid tiles easily recovered by vacuum cleaning or by brushing. The aim is in this case not to reduce but avoid completely secondary liquid contaminated waste [2]

The paper is organized as follows. In first part, we describe gel formulation and preparation. In second part, we present some results of drying kinetics studies before dealing with the relationship between the drying kinetics and the efficiency of the gel in the third part. The fourth part shows preliminary results of rheology studies. Then, some words are given about cracks formation at the surface of the gel during drying. Before the conclusion summarizing the properties of our new gels, some one-scale demonstrations or real operations using these gels are described.

GEL FORMULATION

Composition

Each decontamination gel formulation can be considered as a concentrated colloidal suspension of silica or alumina in water containing suitable chemical reagent for decontamination.
The first formulations were developed in 1991 as we said before and then improved to obtain reducing gels [3]. The chemical reagent could be in general an acid, a basis, an oxidizing or reducing agent. These gels are easily prepared by mixing silica or alumina with the chemical reagent in water (See Table I).

Silica is used to prepare acid gels and alumina alkaline ones. These studies led to two commercial formulations provided by FEVDI (Fabrication Etude et Vente de Dégraissants Industriels), a company in charge of providing gels.

Table I. Mineral Gels Composition

	Oxidizing Gel **[Patent FR 2 656 949 - A]**	**Reducing Gel** **[Patent FR 2 695 839 - A]**
Viscosifier	Silica : 8 to 25% by weight	Alumina : 20 to 30% by weight
Reagent	Inorganic acid : 3 à 10 mol.L^{-1} Oxidizing agent : 0,1 à 1 mol.L^{-1}	Inorganic basis : 0,1 à 14 mol.L^{-1} Reducing agent : 0,1 à 4,5 mol.L^{-1}

These classical gel formulations could be sprayed onto the surface to decontaminate using a pump system at low (2-7 bars) or high (10-30 bars) pressure. The quantity deposited on the surface is between 0,8 to 1,2 kg/m². The corrosion measured on the surface is around 1-2 µm/h. In order to control and stop the corrosion reaction, the gel is usually rinsed with water at high pressure (150 bars) after one or two hours.

Since then, another patent have been published in 1997 concerning a gel formulation adding one organic co-viscosifier to the mineral one [4]. Two major advantages were claimed [5]:

- to reduce the silica or alumina quantity around 5% and as a consequence, the volume of the final solid waste
- to perform the thixotropic behaviour of the gel and enhance the viscosity recovery after sharing due to the stirring and the pulverization.

Table II. Organo-Mineral Gel

	Oxidizing Gel **[Patent FR 2 746 328 - A]**
Viscosifier	Silica : 4 to 6 % by weight Surfactant : 0,2 to 2% by weight
Reagent	Inorganic acid : 3 to 10 mol.L^{-1} Oxidizing agent : 0,1 to 1 mol.L^{-1}

The co-viscosifier is a hydro soluble polymer (acrylic acid or acryl amide) or a surfactant like polyoxy-ethylenic ether (Table II).

Finally, the literature describes organic gels containing for instance 10 to 13 % of a copolymer acrylic acid/acryl amide [6]. The main disadvantage to use these organic gels in the nuclear field is the need to mineralise the organic matter before conditioning the waste.

Drying Kinetics

Drying of gel films considered as a concentrated colloidal suspension have been poorly studied in literature [7,8].
The aims of this study were:

- first, to precise if a reference gel formulation containing only silica in water could dry at low temperature (15 to 40°C) to lead to solid particles of silica that can be easily removed from the surface
- to measure the drying kinetics of such a reference gel
- then to precise the influence of the temperature, the relative humidity and the airflow rate on drying kinetics.
- to determine the influence of the pH, so by measuring drying kinetics of one corrosive acid gel.
- to see, for a reference corrosive gel, if the corrosion kinetics can be controlled.
- to start the modelling of gel drying kinetics to predict efficiency profiles.

Reference Water Gel

Experimental procedure

In order to prepare the aqueous reference gel, a commercial silica provided by DEGUSSA called AEROSIL 380 with an average primary particle size of 7 nm (high specific surface of 380 g/m²) was mixed alone in water with a mechanical stirring (600 rpm).

After casting the gel on to the square stainless steel container (4 x 4 cm², height 1 or 2 mm), the weight loss of the samples, as a function of time, was recorded using a balance Mettler Toledo AX 204 S in a climatic ventilated box where relative humidity is controlled. The airflow rate U inside the ventilated box is fixed at 0,3 m/s.

Results and discussion

The drying curve of the water gel reference (thickness =1 mm) is reported on Figure 1:

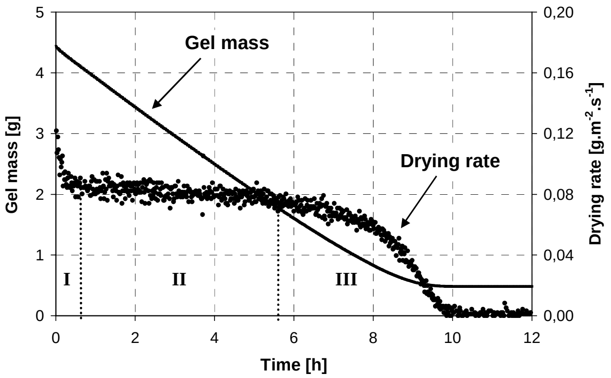

Fig. 1. The Drying Curve of One Water Gel Reference

T= 25°C, H_R = 40%, concentration (SiO_2) = 12%, U =0,3 m/s (thickness = 1 mm)

Three periods can be distinguished during the drying process.

The first one (I) lasts a few minutes and depends on the temperature and the air humidity. It corresponds to the duration needed for the film surface to reach the bulb humid temperature.

During the second one, the drying process is controlled by the evaporation process. The drying rate is constant. The resistance for the transport of water to the surface of the sample is negligible compared with the resistance at the liquid/vapour interface. This regime is evidenced for the first time in this kind of gel and is the same as the one identified by Sherwood as a general characteristic of a “very wet solid” [9].

The third period begins when the drying curve deviates from the straight line, which is called the “falling rate period” by some authors [10]. The drying process is controlled during this period by migration of water to the surface of the sample by diffusion of by capillary action.

For all these formulations, one can remove easily from the surface little solid tiles at the end of the drying. The drying time depends obviously of the thickness of the sample, the temperature and the relative humidity.

Effects of the temperature, the relative humidity and the airflow rate

In order to establish the effects of the temperature and the relative humidity on the drying kinetics of the gel, the drying kinetics were studied for different temperatures and relative humidity. The drying kinetics of the reference water gel may be described during the constant drying rate period using the equation 1 [11].

$$F_m = \frac{1}{S} \cdot \frac{dm}{dt} = U^{\alpha} \cdot \left(a + b \cdot H_R\right) \cdot \exp\left(-\frac{E}{R \cdot T}\right) \qquad \text{(Eq. 1)}$$

where F_m = 1/S .(dW/dt) is a flow describing the rate of weight loss per area unity for the water during the evaporation process. E (kJ/mol) is the activation energy for the evaporation, R (kJ/mol K) is the gas constant, T (K) the absolute temperature, t (sec.) is the time, H_R is the relative humidity, U is the airflow rate (m/s).

The activation energy of the evaporation process of the gel may be estimated from the slope of the Arrhenius plot (Ln(dm/dt) versus -1/RT).

The activation energy for the evaporation process was estimated as 31,5 ± 2 kJ/mol. The experimental value measured for the drying of a water film without silica is the same i.e. 32 kJ/mol. One find evident that during this constant drying rate period the drying process is controlled by the rate of evaporation of water from the surface of the sample.

This estimated value is by an order of magnitude lower than the value of 44 kJ/mole, given on the literature for the simple evaporation of water [11]. One hypothesis to explain this difference is that instabilities or micro-convections at the surface of the film, due to Marangony effects for a film thickness of 1-2 mm, could accelerate the evaporation kinetic. This hypothesis is under investigation by preparing optical experiments to give evidence of this phenomenon.

The effect of the relative humidity may be included in the factor (a + b.H_R) where a (kg/m²s) and b (kg/m² H_R%) are normalised constants deduced from the Figure 1 plotted F_m versus the relative humidity.

The effect of the airflow rate appears in the factor U^{α} where U is the airflow rate (m/s). To precise the value of α suspected to be around 0.8, experimentations are under preparation in a new ventilation system to allow us to change the airflow rate.

One can conclude that the drying of the silica gel containing 8 to 14 % by weight of silica involves essentially a drying step controlled by the evaporation process during the first hours at the surface and a short diffusion process controlled by the diffusion.

One can predict very accurately the drying curve during the evaporation process using an empiric model and equations developed for the evaporation period. This model is useful from the industrial point of view because it permit to predict drying kinetics of the gel as a function of operational parameters like the temperature and the relative humidity.

Another model using diffusion-controlled equations is under investigation.

Acid Formulation

In order to precise the effect of the acidity, the drying of various acid model gel formulations containing 10 % of silica and a mixture of orthophosphoric acid and nitric acid was studied. This mixture of acids is chosen because the corrosion of aluminium samples is easy to measure (see the next part Efficiency Profiles).

Even if the drying rate is obviously lower than the reference water gel, the formulations with a concentration of acid below 3M could dry in five hours at room temperature (T = 22°C) and intermediate relative humidity (H_R = 40%). This result is very interesting to prepare gels for nuclear decontamination that could be used in one day: spayed for instance onto a real contaminated surface in the morning and removed from the surface in the afternoon. If the concentration is higher than 3M, the drying time at room temperature is longer and could reach 10 to 20 hours depending on the relative humidity.

For one model formulation with an acid concentration of 3M, the third part shows the relationship between the corrosion kinetics and the drying kinetics.

EFFICIENCY PROFILES

To decontaminate the surface, the gel needs to corrode a thin thickness of the surface, between 1 or 2 µm. In general, the greater the corrosion is, the better the decontamination is.

The chemical reaction chosen as a model reaction to measure gel efficiency is the surface corrosion of aluminium samples by a mixture of two mineral acids: the nitric acid (1,5 M) and the phosphoric one (1,5 M). In this case, the efficiency of the gel film is easily measured by the weight loss of the aluminium sample. This corrosion is homogeneous, so one can deduce from the weight loss the equivalent thickness calculated in µm corroded at the surface.

Figure 2 compares at 22°C the corrosion kinetic of an aluminium sample immersed in the aqueous mixture of nitric and phosphoric acid (1,5 M/1,5 M) and the corrosion kinetic due to one gel film sprayed on the surface. Figure 2 reports also the drying kinetic (solvent weight loss) to show the relationship between the corrosion kinetic and the drying kinetic.

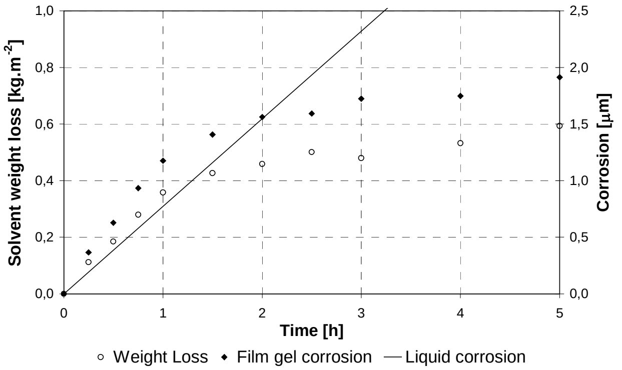

Fig. 2. The comparison between corrosion in the liquid state and in the gel state and the relationship between the corrosion kinetic and the drying kinetic – Nitric 1,5 M/Phosphoric 1,5 M Gel – T = 22°C – H_R = 40%

Three majors comments could be done:

- In the liquid state, the order of the corrosion reaction kinetic is equal to 1 and the corrosion rate is constant (0,75 µm/h).
- During the first two hours, the corrosion –i.e., the efficiency- due to the gel film is greater than the efficiency obtained in the liquid state. This result is interesting from an application point of view and shows that a gel film sprayed on the surface is more corrosive than the same liquid solution. One hypothesis advanced to explain this phenomenon is the drying of the gel. Indeed, the water weight loss induces a proton concentration in the gel which increase with time and which is responsible for the accelerated corrosion.
- Finally, one can see that the corrosion efficiency is controlled by the drying kinetic. The corrosion reaction stops when the quantity of water inside the gel is not sufficient enough to allow the mass transfer of the protons near the surface. The corrosion is than limited by diffusion. This point is pertinent because the drying time control the gel efficiency and permits to respect innocuity criteria of the sample.

RHEOLOGICAL STUDIES

The gel is composed of silica particles suspended in an aqueous acid mixture of nitric and phosphoric acid (1,5M/1,5M). Rheological studies were performed to precise the thixotropic behaviour of our formulation. In order to simulate the shearing due to the pulverization stage, one apply first to the gel a share rate of 700 s^{-1}, and then reduce suddenly the shear rate to 10 s^{-1}

in order to simulate the shearing due to the gravity on an adherent film sprayed on a vertical surface.

Figure 3 shows the viscosity as a function of time for the two different shear rates.

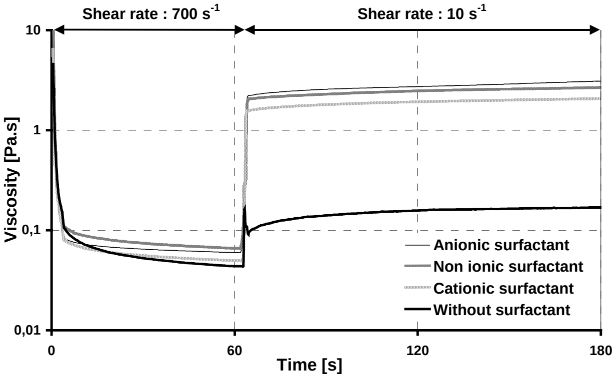

Fig. 3. Viscosity Measurements

The need to add a small quantity (< 1‰ weight) of an organic additive is clearly evidenced. In general, silica acts as a viscosifier and yields to a gel having a thixotropic behaviour which is necessary for a good spraying. The viscosity should be below 100 mPa.s under a shearing rate of 700 s^{-1} to succeed in good spraying and above 500 mPa.s under 10 s^{-1} to perform a perfect adhesion to the surface. The surfactant is a non-foaming agent, provides a good wettability on the surface and a sufficient stability in a strong acidity medium. Rheological studies showed that a few amount of surfactant was necessary to improve the gel viscosity after shearing. Adding a surfactant in the suspension had a huge effect on the viscosity. On the one hand, under a 700 s^{-1} shearing rate, the viscosity is still below 100 mPa.s, on the other hand, under 10 s^{-1}, the viscosity increases by a factor 10 compared to the gel without surfactant.

In the future, the aim is to determine the effect of the additives on the silica suspension at a microscopic scale. Additives classified according to the ionic charge present on the molecule skeleton will be studied. The researches will focus particularly on the aggregates size, on the suspension stability and on the dispersions forces that occur in the medium. The salinity and the pH of the solution will also be studied.

CRACKS FORMATION

Drying induces shrinkage in the gel that yield the formation of surface crack patterns. Figure 4 shows the geometry and the size of the solid tiles.

Fig. 4. Crack Array Obtained During the Drying Process.

The initial thickness of the gel film is 1 mm. The first cracks appear generally at the end of the drying period II and can be characterized by their spacing, their opening and their depth.

We have verified the classical fact that the thicker the film is, the larger the crack opening. Another point is that the beginning of the cracking seems to be proportional to the film thickness. New studies are under investigation to confirm these preliminary results.

At the end of the drying, we always obtain little solid aggregates with a size between 1 and 3 mm for a thickness film bounded by 1 and 2 mm. For the decontamination process, this size allows to remove easily the solids by vacuum cleaning or brushing and avoid dispersion of small-contaminated particles in the air.

Demonstration Operations

In order to illustrate the advantages of this new decontamination process, real operations or demonstrations were proposed by the CEA to convince nuclear operators like AREVA and EDF from the benefits of the technique.

In 2003, for instance, a major demonstration in a non-contaminated radiological environment took place on La Hague site to prove that the pulverization of these new gels could be useful to decontaminate ventilation system of nuclear facilities which are usually not waterproof. It is necessary to avoid the use of liquid in this case. Moreover, one can encounter in ventilation system temperature from 16 and 35 °C, relative humidity between 20 and 70%, and airflow rate from 0,1 to 1 m/s that induce the drying of our formulations.

Fig. 5. Demonstration of Ventilation Decontamination System

The process developed for ventilation system uses a pump at low pressure and a nozzle for the gel pulverization at a distance between 1 to 15 m from the pumping system. The nozzle could be introduced directly inside the ventilation system to assure the homogeneous spaying of the gel on the surfaces. After the drying period, a specific device was developed to draw up the solid wastes (See Figure 5).

First one-scale demonstrations on ventilation ducts look very promising and the next step will be to find some locations inside nuclear installations to test the developed process.

CONCLUSION

We have reported new formulations of acid colloidal gels that can be used in a new decontamination process. These formulations contain a mineral viscosifier like silica at a concentration between 8 to 14 % by weight, a chemical acid like a mixture of nitric/phosphoric acids generally below 3M and a small quantity of an additive inferior to 0.1%.

A gel film can be sprayed on the surface to treat. Then, because the gel is able to dry at room temperature in a few hours, a fine thickness of the contaminated surface is corroded controlled by the drying kinetic. During the drying, the gel cracks and leads to the formation of solid tiles. These final solid particles containing the pollutants are removed from the surface by vacuum cleaning or by brushing.

This new gel decontamination process is a compromise between three cross-linked parameters:

- gel viscosity: high to adhere to the surface and low enough to avoid problem during the pulverization (depends mainly on solution composition).
- drying kinetic: high to ensure the corrosion reaction stop not to cause damage to the materials but low to obtain good decontamination efficiency.

- cracking formation: low as possible during the first stage of the drying but high to give small solid aggregates with a size around one millimetre to facilitate the removing from the surface.

We have clarified the effect of the temperature and the relative humidity on the drying kinetic of the gel. More fundamental studies are needed to enable the modelling of gel drying and efficiency kinetics. The modelling of the evaporation of a solvent from a Non-Newtonian fluid is now at stake.

First one-scale demonstrations on ventilation ducts look very promising and the next step will be to find some locations inside nuclear installations to test the developed process.

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