

USE OF SURFACTANT MOLECULES FOR NUCLEAR DECONTAMINATION

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ABSTRACT

This paper describes the study of a degreasing formulation based on the use of fully soluble low-foaming surfactants. The aim of the formulation is to remove Tri Butyl Phosphate from stainless steel surfaces. The efficiency of the treatment is evaluated and compared to a more conventional degreasing treatment. The results show a significant improvement in its efficiency along with a reduction in the sodium ion concentration in the solution. The feasibility of an industrial operation in the UP1 reprocessing plant at Marcoule is studied. We specifically focus on both the foaming risk during the pumping of the solution when using various pumping devices and on the handling of secondary waste effluents. A good compatibility of the new treatment is shown in both respects. Nevertheless, more work is needed. A new non-foaming formulation has been studied and the processing of secondary waste using an ozone pretreatment is now being developed.

INTRODUCTION

At a time when an increasing number of decommissioning operations have begun in France and in the USA (e.g. Brennilis, UP1 in Marcoule, Hanford), there is a need for more efficient decontamination treatments, generating less secondary liquid waste.

A great number of chemical decontamination techniques are based on the use of strong acids such as nitric acid or strong bases such as sodium hydroxide. Besides their relatively limited efficiency in many cases, the production of sodium ions due to sodium hydroxide is unwanted for it reduces resistance to leaching of the waste package.

Although surfactants are widely used for non-nuclear applications such as detergency, flottation or emulsification, they have been used very little for nuclear purposes.

Due to their amphiphile properties, surfactants show compatibility with both hydrophobic and lipophobic systems. They diffuse spontaneously at oil/water interface and very small amounts of surfactant are needed to produce a strong reduction of interfacial tension thus enhancing the following:

- stabilization of oil in water emulsions,
- stabilization of solid particle dispersion,
- solubilization of non-soluble or low soluble molecules in water,
- foam formation.

In a previous article, the use of foams for nuclear decontamination purposes was presented [1]. In this study a degreasing solution is formulated that can micellize TBP (Tri Butyl Phosphate), which is the solvent commonly used for liquid/ liquid extraction of U and Pu in reprocessing plants for burnt nuclear fuels.

LABORATORY SCALE STUDIES

Decontamination treatments of large-scale nuclear facilities such as reprocessing plants frequently involve degreasing steps with concentrated hydroxide sodium and descaling steps with concentrated nitric acid. As a representative treatment of conventional decontamination, the following one has been chosen :

- First step : nitric acid 5 mol.l⁻¹ for 1 hour at 50°C under stirring
- Second step : sodium hydroxide 5.5 mol.l⁻¹ for 2 hours at 50°C under stirring
- Third step : nitric acid 5 mol.l⁻¹ for 1 hour at 50°C under stirring

The consumption of sodium ions with this kind of treatment turns out to be very high. This leads to further complications at the vitrification step of the resulting secondary waste due to the low rate of incorporation of sodium in the glass matrix. As a consequence, the cost induced by the decontamination treatment is high.

The purpose of this study is to reduce the concentration of sodium hydroxide and to increase the efficiency of the treatment through the use of surfactants. Because on the industrial scale, stirring and heating of the solution is not always possible, a formulation efficient at room temperature (20°C+/-2°C) with no need of stirring is sought.

Selection of surfactants

In the first step, about one hundred surfactants of several chemical families are checked in aqueous solution of sodium hydroxide 0.5 mol.l⁻¹ and 1 mol.l⁻¹. The first experiments are based on very simple screening tests evaluating surfactant properties such as :

- Hydrophile Lipophile Balance (HLB)
- foamability,
- wetting power which is determined by evaluating the spreading of a drop of the solution on a stainless steel surface,
- solubility in the aqueous system.

Low foamability is considered a very important parameter since the formulation must be transferred through the different parts of the nuclear facility without excessive production of foam. Most liquid transfers in nuclear facilities are performed through the use of air-lifts or vapor ejectors which under certain conditions act as foam generators.

In the second step, a combination of two surfactants is selected for its low foaming power. The first one is a polyethoxylated alcohol of HLB 15.3 (PA) and the second one is a blockcopolymer ethoxylated and propoxylated (BC). The former is selected for its emulsifying power and the latter because it leads to a strong reduction of foamability in association with the ethoxylated alcohol due to a synergetic effect.

The rates of each surfactant in the formulation are determined as follows :

PA 0.12 % w/w
BC 0.57 % w/w

Solubilization of TBP

Solubilization of TBP in the system occurs in the hydrophobic core of the surfactant micelles. The micellization of TBP leads to the formation of a microemulsion. Contrary to emulsions, microemulsions are thermodynamically stable and a supply of dispersion energy (stirring) is not necessary [2]. This last point is an asset for in-situ decontamination purposes. Due to the non-ionic nature of the surfactant used in the formulation, the Critical Micellar Concentration of the system is very low. Thus, the formation of micelles occurs very early, increasing the solubilization capacity of the formulation.

The sodium hydroxide concentration is set at 0.5 mol.l^{-1} which is considered as an optimal value. The formulation is able to solubilize about 1.5 g.l^{-1} of TBP which is about ten times greater than the solubility of TBP in pure water.

Furthermore, the reduction factor of the sodium hydroxide concentration is greater than ten in comparison to the reference treatment.

Evaluation of degreasing efficiency on inactive samples

The degreasing power of the formulation is tested on 304 L stainless steel surfaces coated with TBP. The contact angle of water at the surface is measured during the treatment using the Wilhelmy plate method. The results show the very fast degreasing ability of this treatment. The initial wettability of the metallic surface is fully restored after less than three hours of application at room temperature and without stirring.

The efficiency of treatment is then compared with the three-step reference treatment using concentrated hydroxide sodium and nitric acid. The contact angle Θ is measured after each step in the treatments. The duration of treatment with surfactant is 3 hours. The results are shown in **figure 1**.

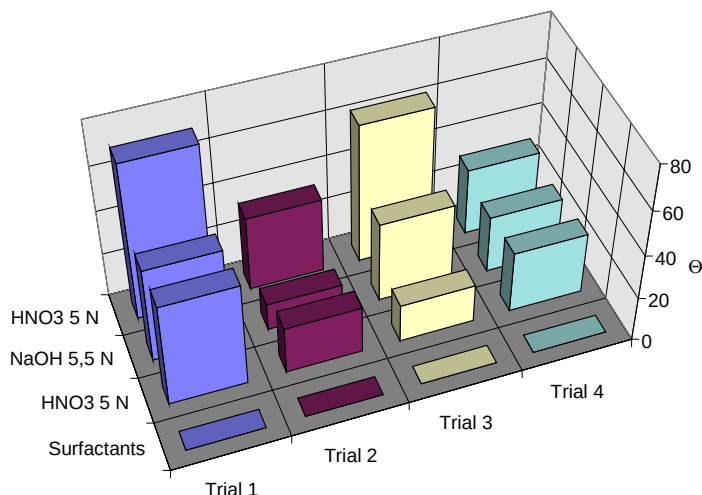


Figure 1 : Comparison of reference and surfactant treatments

The reference treatment turned out to be unable to restore the initial wettability of the metallic surface initially coated with TBP ($\Theta > 0$) whereas the new treatment, applied in one step, proved to be totally effective ($\Theta = 0$).

Optimization of the formulation

In order to reduce the impact of surfactant on liquid waste handling, the influence of the reduction of the surfactant concentration on the degreasing properties of the formulation is assessed. Thus, the time necessary to restore the wettability of a stainless steel surface (contact angle equal to zero) is measured using various formulations at various concentrations. Results are summarized in **Table 1**.

Total surfactant concentration g.l⁻¹	Degreasing time hours
7	3
3.5	6
1.4	8
0.7	40

Table 1 : Evolution of degreasing time with surfactant concentration reduction

As can be seen in **Table 1**, the smaller the concentration, the longer the degreasing time. For a concentration of 0.7 g.l⁻¹ of surfactants, the required time for total degreasing is about 40 hours. This result is quite logical and the degreasing time can be said to be compatible with an industrial operation as long as the surfactant concentration is greater than about 1 g.l⁻¹. Along with these experiments, it is shown that, although the solubilization capacity of the solution decreases when the surfactant concentration decreases, this parameter is not overly affected : only a 36% reduction of solubilization capacity is observed when the solution is diluted by a factor of 10. The major effect of concentration reduction is then essentially a kinetic one.

Decontamination efficiency assessment

The decontamination power of the formulation is assessed on real samples from the first liquid/liquid extraction cycle of the UP1 reprocessing plant in Marcoule. The samples are mainly contaminated with ¹⁰⁶Ru and to a smaller extent with ¹³⁷Cs and ¹²⁵Sb. The surface activity before and after decontamination is measured using a Germanium High Purity detector model GL 0510T - 7935/S-7 from Canberra. Geometry of the samples is taken into account for the calibration of the spectrometric apparatus using Microshield program.

Again, the efficiency of the reference treatment is compared to the treatment using surfactants. The histogram of **figure 2** illustrates a comparison of the two treatments

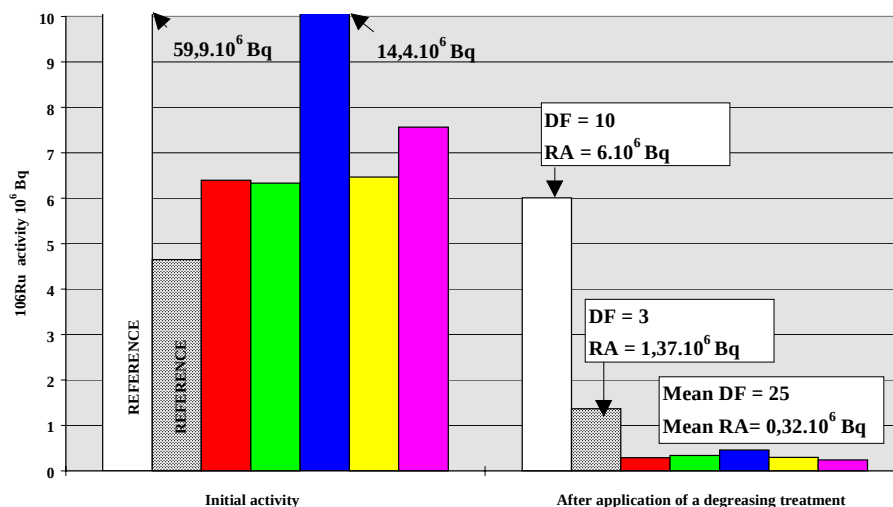


Figure 2 : Decontamination of sample using either reference treatment or surfactant treatment. “DF” stands for decontamination factor and “RA” for residual activity

The residual activities achieved with the surfactant treatment are systematically lower than those obtained using the reference treatment. The residual activity of the samples after surfactant treatment is very homogeneous and its mean value is about $0,32 \cdot 10^6$ Bq. The mean decontamination factor is about 25. Using the reference treatment, a residual activity between $1 \cdot 10^6$ Bq and $6 \cdot 10^6$ Bq is obtained and the maximum value of the decontamination factor is only 10.

The treatment using surfactants at a temperature of about 20°C appears to be significantly more efficient than the reference treatment using concentrated sodium hydroxide at 50°C.

The evaluation of decontamination efficiency in the two step treatment

Both treatments tested in the previous section are designed for the elimination of unfixed surface contamination. For dismantling purposes it is also necessary to remove fixed contamination. In this case, the aim is to eliminate the diffused radioelement in the superficial layers of the metal. For non-activated metals, the thickness of metal containing diffused activity is generally about a few micrometers. One of the most common treatments used to achieve removal of fixed contamination is a combination of Ce^{4+} ions and a strong acid such as nitric or sulfuric acid [3,4]. Cerium at valence IV is a strong oxidizing agent that can dissolve stainless steel. Another way to achieve stainless steel dissolution is to use a combination of fluorhydric acid and nitric acid. In this case, the F^- ion is the complexing agent of Fe and nitric acid is the oxidation agent enabling the dissolution of metallic iron.

Further experiments are conducted to evaluate the benefit of the following two-step treatment :

- the degreasing step using the surfactant treatment
- the de-scaling step using either the Cerium/ HNO_3 or the HF/HNO_3 treatment

The histogram of **figure 3** illustrates the results obtained with a cerium de-scaling treatment. In order to achieve a better comparison, the efficiency of a two-step treatment consisting of a reference degreasing treatment followed by a cerium de-scaling step is evaluated. The first column refers to the activity of the samples after pretreatment application with and without surfactant.

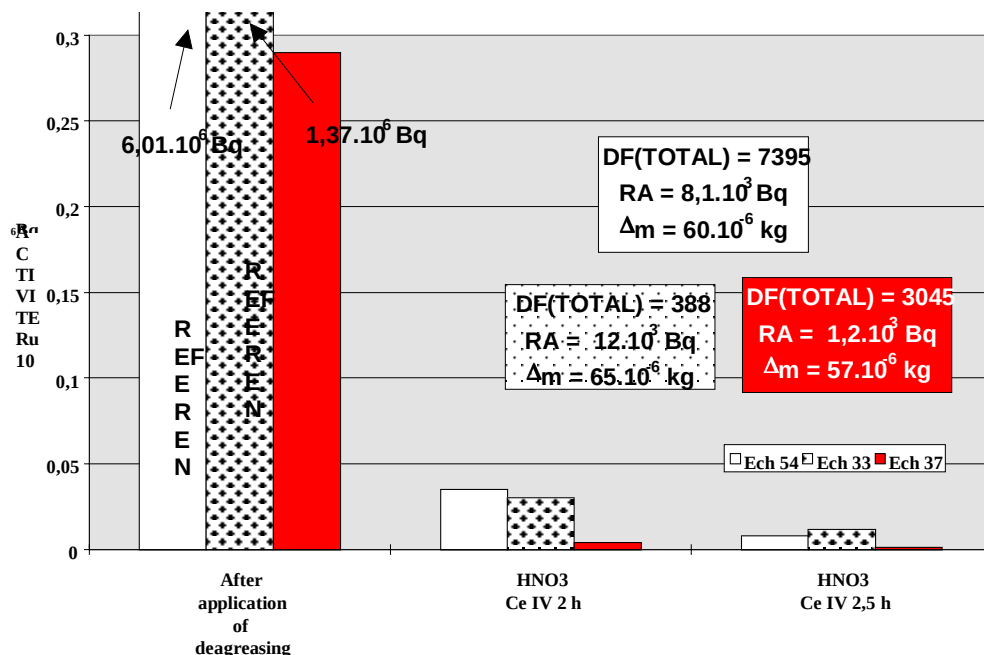


Figure 3 : Evaluation of two-step treatment consisting of a degreasing and de-scaling step

One can note that the two-step treatment including a surfactant treatment leads to a much lower residual activity. In fact, the residual activity after a succession of surfactant and cerium treatments is about ten times lesser than the residual activity after a succession of reference and cerium treatments. Two major reasons can explain this result:

- better efficiency of the first step using surfactant as seen earlier,
- better preparation of a metallic surface with surfactants thus enabling a better effect of the de-scaling treatment.

The second point is supported by the idea that the surfactant treatment restores better wettability of the metallic surface as proven during the inactive experiments. This better wettability of the surface leads to a better contact of the de-scaling solution.

Similar results are obtained with the second de-scaling treatment using fluorhydric acid.

To summarize the interest of a treatment using surfactants, it can be said that it leads to a significant reduction of steps necessary to remove unfixed radioactivity. In addition to this, the efficiency of this one-step treatment is greater in comparison to the reference treatment. Moreover, it is shown that the application of a de-scaling step after a surfactant treatment is more efficient probably because application of a surfactant solution results in a better wettability of the metallic surface.

APPLICATION ON THE INDUSTRIAL SCALE

Feasibility studies of an application on an industrial scale are being conducted at the UP1 plant in Marcoule. The study focuses on two points :

- foam formation during transfer of the surfactant solution in the plant,
- handling of the secondary liquid waste containing surfactants.

The purpose is to demonstrate the compatibility of the formulation with the existing pumping devices present in the plant and also its compatibility with the existing facilities for liquid waste handling in Marcoule. Among them, we find the evaporation/concentration step, precipitation and filtration steps, the calcination step, and the final conditioning step.

Transfer of the surfactant solution in the facility

Before any application in the plant, it is essential to demonstrate that the solution can be transferred without excessive foaming. Air-lifts, centrifugal pumps, vapor ejectors are the most commonly used devices to transfer liquid in the UP1 plant. Using industrial-scale devices, it was demonstrated that the transfer of surfactant solution through centrifugal pumps and vapor ejectors did not lead to excessive foaming. It is therefore compatible with plant operation rules.

Air-lifts proved to be a more complex problem. In fact, the transfer of liquid through air-lifts is achieved by adding gas in the liquid phase to form a biphasic system of lower density. After transfer, gas and liquid are separated in a separation tank. In our case, the apparatus can act as a foam generator. Furthermore, two categories of air-lifts can be found in the plant: atmospheric air-lifts and vacuum air-lifts. In the latter case, the elevation of the gas/liquid system is enhanced by creation of a depression in the separation tank.

Experiments were carried out on an industrial scale in collaboration with SGN France using vacuum and atmospheric air-lifts at Beaumont/La Hague. The results show no compatibility with vacuum air-lifts. This is understandable because depression causes an increase in bubble volume in the separation tank. However, due to the low number of vacuum air-lifts in the plant, this negative result is not considered to be decisive in ruling out the use of a surfactant solution.

Table 2 summarizes the results obtained with an atmospheric air-lift for various values of the gas and liquid flowrates and two values of the submergence factor defined as the ratio of the liquid pressure at air-lift entrance to the height from the air-lift entrance to separator tank expressed as the equivalent hydrostatic pressure of the liquid to be elevated. The operating conditions chosen for these experiments are representative of those used in the plant.

	Gas flowrate NL.h ⁻¹	Liquid flowrate NL.h ⁻¹	Remarks
Submergence factor = 0.3	272	108	Separator empty
	490	200	Maximal height of foam: 5 cm
	925	290	25% of separator contains foam
Submergence factor = 0.6	163	352	25% of separator contains foam
	435	710	No overflow of foam
	762	825	No overflow of foam

Table 2 : Transfer of solution containing surfactants through atmospheric air-lift

Results show that even at high value of the submergence factor there is no risk of foam overflow out of the separation tank.

For these experiments an inactive surfactant formulation containing no TBP is used. Additional experiments at the laboratory scale show that the addition of even small amounts of TBP in the solution reduces its foamability in great proportion. Due to its hydrophobic nature, TBP acts as an anti-foaming agent. Results of these further experiments are illustrated in **figure 4**. To make comparisons possible, a foaming test based on a description by Bikerman is used [5].

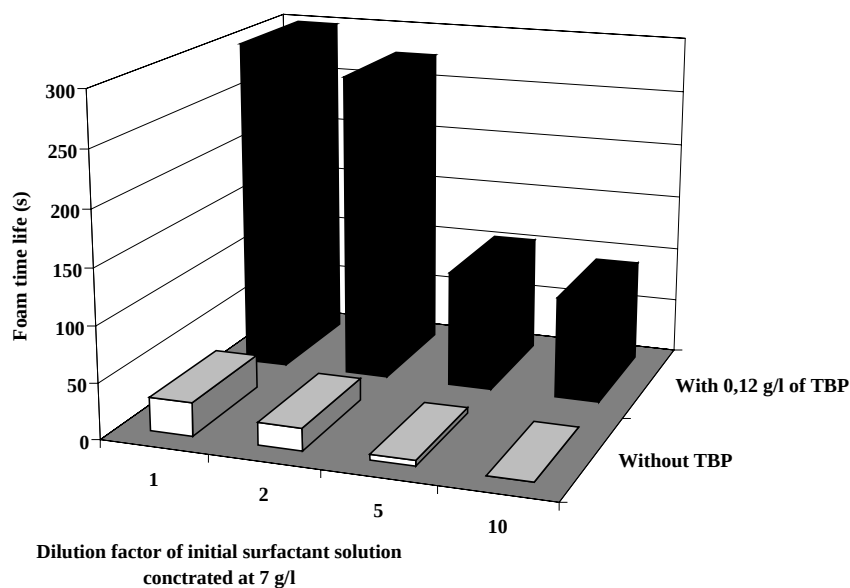


Figure 4 : Influence of surfactant concentration and TBP on foam formation

One can observe that either the addition of TBP or the reduction of surfactant concentration reduces foam production.

As a conclusion, the feasibility of the surfactant solution on an industrial scale is shown in the majority of the transfer devices present in the UP1 plant in Marcoule. Moreover,

experiments have been conducted aiming at the worst possible conditions of foam formation. In reality, the foamability will almost disappear as soon as the solution has contacted TBP which acts as an anti-foamer due to its hydrophobic nature.

Handling of the secondary waste effluent

This point is crucial in moving towards acceptance of the new treatment. The two following pathways of waste effluent handling are evaluated in this part :

1) evaporation, Chemical treatment, solid/liquid separation, conditioning in a bitumen matrix

2) evaporation, calcination, vitrification

Pathway number 1 is dedicated to low radioactive effluents whereas pathway number 2 applies to high radioactive effluents, such as those coming from reprocessing operations.

The evaporation step permits a concentration of the effluent by a factor of about ten. During the evaporation/concentration process, the salinity of the system increases by the same factor. Tests carried out in the laboratory show little compatibility of the formulation with the evaporation step due to the complex phase diagram of the solution containing organic matter. It clearly appears that the evaporation process is not the proper way of handling a liquid effluent containing significant amounts of organic matter.

In such conditions, the second pathway is eliminated considering the excessive cost of a direct calcination. Thus, it was decided to handle the effluent by applying the first series of operations omitting the evaporation step. In order to assess the influence of the presence of surfactants in the solution, both effluents with and without surfactants are handled.

No influence of the surfactants on the chemical treatment is observed. The decontamination factors are almost equal for both solutions.

The solid/liquid separation is performed on a precoat vacuum filter. The precoat is made of diatomite. A volume of 115 liters of solution is filtered. The filtrate flowrate is not affected by the surfactants nor is the volume of sludge after filtration and after a drying step of 96 hours at 105°C. No foaming problems are encountered at a surfactant concentration below 1.5 g.l⁻¹. Thus the best surfactant concentration is set at the value of 1.5 g.l⁻¹ using the two surfactants in the proportion indicated above.

Compatibility with the bitumen has been studied further.

As a conclusion, the feasibility of the handling of the secondary waste effluent is proved for conventional operations in Marcoule and for representative operating parameters : temperature, filter flowrate,...Nevertheless we also see that there is a need for more appropriate ways of handling liquid waste containing significant amounts of organic matter.

PROSPECTS

For future applications of the surfactant treatment, it will be necessary for us to improve our formulation in at least two fields :

- reduction of the foamability in vacuum air-lifts
- improved handling of the secondary waste.

New studies have been launched in both fields.

Reduction of foamability

As we have seen earlier, the foamability of the system containing surfactants is still too high for a safe transfer through vacuum air-lifts. Although the consequences of an application in UP1 are slight, the formulation has to be improved for future decontamination operations. For example, an application of the surfactant formulation is planned for the decontamination of the Marcoule Reprocessing Facility. This facility basically involves reprocessing equipment owned by the CEA used to experiment new reprocessing techniques for burnt nuclear fuel and also to reprocess non-standard burnt fuels. The majority of the pumping tools in this facility are vacuum air-lifts.

A new formulation has been worked out. A third surfactant is added which drastically reduces the foamability of the system when used in aqueous formulations containing sodium hydroxide at a concentration greater than 0.5 mol.l^{-1} . Moreover, the surfactant leads to a significant increase in the TBP solubilization capacity. This is due to its chemical nature which is close to that of the TBP molecule. However, the principal drawback of this new formulation turned out to be its very low compatibility with the existing liquid waste treatment, contrary to the first one.

Handling of the effluent

The handling of the effluent through conventional nuclear waste operation turned out to be difficult. For future decontamination operations, the adding of a pretreatment step consisting of: supercritical water, ozonation or microbiology has been considered.

For the three-component formulation mentioned earlier, the feasibility of an ozonation of an effluent containing surfactants is being studied. A combination of an ozone treatment and a conventional treatment following one of the two pathways described above, seems to be the most reasonable solution. The advantage of ozone oxidation of organic matter lies in the possibility of adding ozone to the effluent with an ozone generator outside the nuclear area thus leading to a minimization of additional costs.

Two other ways involving microbiology and thermal oxidation are now being developed in Cadarache for the handling of contaminated liquid waste containing surfactants.

CONCLUSION

A low-foaming solution, adapted to metallic degreasing purposes is formulated. The formulation is a combination of non-ionic surfactants. The anti-foaming effect is obtained only with fully soluble chemical agents. The degreasing efficiency and decontamination efficiency have been evaluated using real samples coming from the UP1 reprocessing plant in Marcoule. The treatment has been compared to a more conventional process involving concentrated sodium hydroxide. The decontamination factor reached with the new formulation is about 10 times greater for samples of equivalent initial surface activity. In addition to this, the concentration

reduction of sodium ions in the solution is approximately a factor of 10. Moreover, a subsequent application of a de-scaling treatment is enhanced when a treatment with the surfactant formulation is applied. This can be explained by a better wettability of the metallic surface after the degreasing step.

Concerning the handling of secondary waste, the feasibility of the precipitation/filtration process has been shown using dilute formulations.

As a final summary, an efficient decontamination degreasing treatment is formulated and its compatibility with the existing liquid waste processing facilities on an industrial scale is proved.

A second formulation using a third surfactant has been worked out to reduce the foamability of the system so that the solution can be transferred satisfactorily through vacuum air-lifts. This formulation will require more work before reaching full compatibility with the existing liquid waste treatment.

In the future, particular attention will be devoted to the processing of liquid waste containing surfactants. The idea is to handle any kind of surfactant effluent using the existing facilities in the nuclear industry. Additional treatments such as ozonation, microbiology and thermal oxidation are to be studied further .

REFERENCES

- [1] **Faury, M., B. Fournel, G. Boissonnet, H; Provens**, "Foams for nuclear decontamination purposes : achievements and prospects", Waste Management'98, Tucson **(1998)**
- [2] **Bourrel, M., R.S. Schechter**, "Microemulsions and related systems", Surfactant Science Series, Vol. 30, M. Dekker Ed., **(1988)**
- [3] **Bray, L.A., J.M. Seay**, "Development and Design Application of Cerium IV Decontamination Process", Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, Spectrum'88, Pasco (USA) **(1988)**
- [4] **Suwa, T., N. Kuribayashi, E. Tachikawa**, "Development of Chemical Decontamination Process with Sulfuric Acid-Cerium IV for Decommissioning", Journal of Nuclear Science and Technology, 25, pp 574-585 **(1988)**
- [5] **Bikerman, J.J.**, "Foams", Springer Verlag Berlin **(1973)**