

NEW SURFACTANT LIQUID FORMULATION FOR TBP REMOVAL IN REPROCESSING PLANTS FOR DECOMMISSIONING PURPOSES

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ABSTRACT

The Commissariat à l'Énergie Atomique (CEA) and the Compagnie Générale des Matières Nucléaires (COGEMA) have developed [1] surfactant liquid solutions to remove organic matter located at the surfaces of equipment used in reprocessing facilities. This equipment may be covered with Tri Butyl Phosphate (TBP) or products resulting from TBP radiolysis like Dibutylphosphate (DBP) or Monobutylphosphate (MBP). These molecules can be combined with Uranium, Plutonium or metal ions like zirconium. Conventional treatments like sodium hydroxide usually have poor degreasing effect, so few of these products can be removed successfully.

The aim of developing new formulations is to achieve a better degreasing effect and to eliminate sodium ions from the secondary liquid wastes to ease glass formation. During the past years, low alkaline formulations have been developed (sodium content about 0,5 M to 1 M) [2]. More recently, it was decided to try to remove sodium ions completely and keep a high degreasing efficiency. A study of a degreasing formulation based on the original use of fully soluble low-foaming surfactants in nitric acid medium has been performed. A combination of two non-ionic surfactants was chosen. Non-ionic surfactants have a low Critical Micellar Concentration (CMC) which allows minimization of organic matter in the solution. The first surfactant is a polyglycolic ether fatty alcohol (FA) leading to high solubilization capability. The second is a Block Copolymer (BC) having a high wetting power. Solubilization of TBP occurs in the micelles formed above the CMC. The standard formulation has a total amount of 10 g/L surfactants. This surfactant formulation increases the maximum TBP solubilization to more than 5 g/L, about 15 times larger than the true value of TBP solubility in the acid alone.

In order to compare different treatments, the first experiments were performed on TBP and synthetic Iron-Dibutylphosphate deposits representative of deposits found in liquid/liquid extraction equipments of a reprocessing plant. Excellent decontamination factors were obtained. A specific treatment of the effluent was developed, based on hydrogen peroxide, to achieve organic matter oxidation after decontamination and before evaporation, vitrification and conditioning.

In March 2004, the Pilot Reprocessing Unit in Marcoule successfully tested this new surfactant formulation in nitric acid for liquid-liquid extraction decontamination decommissioning. The associated oxidation treatment with hydrogen peroxide also gave excellent results.

INTRODUCTION

CEA has developed [1] surfactant liquid solutions to remove organic matter located at the surfaces of components used in reprocessing facilities. These components may be covered with TBP or products resulting from TBP radiolysis like DBP or MBP. Conventional treatments used for decontamination usually have poor degreasing effect so few of these products can be removed successfully. The aim of developing these new treatments is to achieve a better degreasing effect and eliminate sodium ions from the secondary liquid wastes. In a first step, low alkaline formulations have been developed (sodium content about 0.5 M to 1 M) [2]. In a second step, sodium ions are removed completely, while retaining a high degreasing efficiency. Another advantage of sodium hydroxide free solutions avoiding plutonium (Pu) precipitation during the decontamination process.

This paper describes the study of a degreasing formulation based on the use of fully soluble low-foaming surfactants in nitric acid medium.

Laboratory Scale Experiments

The aim of the surfactant formulation is to remove TBP from stainless steel surfaces. Based on previous studies we choose a combination of two non ionic surfactants. Non ionic surfactants have a low CMC (less than 300 mg/L in water) which allows a minimization of organic matter in the solution. The first surfactant is a polyglycolic ether fatty alcohol (FA) having a high value Hydrophilic Lipophilic Balance (HLB)= 12.5 leading to high solubilization capability. The second is a BC having a high wetting power. Solubilization of TBP occurs in the micelles formed above the CMC. A standard formulation having 10 g/L surfactants, largely above the CMC to increase solubilizing capability, and a concentration ratio [FA] to [BC] equal to 4, has been further studied.

The maximum solubilizing power occurs for nitric acid solutions around 0,5-1 M with a TBP concentration of more than 5 g/L which; about 15 times larger than the true value of TBP solubility in the acid (and water) alone. For larger values of the acid concentration, solubilization of TBP decreases quickly. This can be explained by a diminution of surfactant solubility in acidic conditions. TBP solubilizing efficiency for the same surfactant formulation in alkaline conditions (sodium hydroxide) is very small. As a conclusion the studied formulation is specific to acidic medium, as expected.

The foaming power of the surfactant formulation as a function of nitric acid concentration has been further evaluated. The foaming test is of the Bikermann type; the foam half life time in a one metre high column and for fixed operating conditions is recorded. Foam life time is twice as high for low acid concentrations. Thus, foamability varies qualitatively with TBP solubilizing power.

Experiments have been performed on TBP and synthetic Iron-Dibutylphosphate deposits to compare different treatments. These deposits are considered representative of deposits that can be found in liquid/liquid extraction components of a reprocessing plant. The aim of these experiments is to determine if surfactants are able to remove solid deposits thanks to their high absorption ability at the substrate/deposit interface. Fe-DBP precipitates are deposited on stainless steel samples sizing 5 cm x 5 cm and shown with solution comparison results in Figure 1.

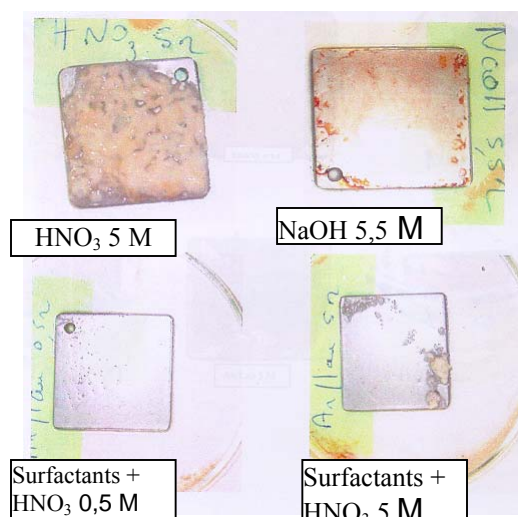


Fig. 1. Final deposits aspect of Fe-DBP deposit after 48 hours for different solutions [changed to proper format]

Surfactant formulation is compared to sodium hydroxide which has a low degreasing effect and reacts chemically with iron deposits to form iron hydroxides. Only the sample contacted with surfactants and 0,5 M nitric acid is cleaned entirely. As expected, NaOH efficiency is high due to chemical reaction with iron II but small parts of deposits remain on the sample after experiment. Moreover, iron hydroxides resulting from the chemical reaction with sodium hydroxide lead to heavy precipitates that settle to the bottom, thus potentially increasing the Pu concentration locally. Pure nitric acid has a very low organic matter removal efficiency. Surfactant efficiency decreases as nitric concentration increases as was already the case for TBP solubilization. This confirms the necessity of working at moderate values of nitric concentrations.

Higher surfactant efficiency can be explained by the strong affinity of hydrophilic head of the surfactant for the metallic surface, whereas the hydrophobic tail adsorbs preferentially at the deposit's surface. Insertion of surfactant at the metal-deposit interface facilitates deposit removal. A significant improvement of efficiency is observed for given deposit properties in the case of Iron-DBP complexes.

EXPERIMENTS ON RADIOACTIVE SAMPLES

Experiments have also been made on radioactive samples from the CEA pilot fuel reprocessing unit located in Marcoule. These samples are from the metallic cover of liquid/liquid extraction battery which have been contacted with TBP during reprocessing operations.

Table I summarizes the results attained on six different samples having an initial activity ranging from 600 Bq/cm² to 3700 Bq/cm². Surfactants are compared with sodium hydroxide and nitric acid treatments.

Table I. Results of Cover Decontamination

Sample n°	Treatment	Initial activity Bq/cm ²	Final activity Bq/cm ²	DF	Time - Temperature
1	NaOH 5,5 M	1150	640	1,8	6 h - 40°C
2	HNO ₃ 5 M	990	245	4,0	6 h - 40°C
3	Surfactants - HNO ₃ 5 M	610	100	6,1	6 h - 40°C
4	Surfactants - HNO ₃ 0,5 M	3640	245	14,9	6 h - 40°C
5	Surfactants - HNO ₃ 0,5 M	1510	600	2,5	6 h - 30°C
6	Surfactants - HNO ₃ 0,5 M	865	100	8,7	6 h - 40°C

For similar initial activity a better Decontamination Factor (DF), defined as the ratio of initial activity to final activity is obtained when using surfactants than when using pure acid. A relatively poor efficiency of sodium hydroxide is also observed. Comparing the surfactant solution at 0,5 M acidic concentration with the one at 5 M, no decisive difference is observed although maximum DF is obtained for the 0,5 M acidic concentration. There is a temperature effect (compare results with samples 5 and 4, 6). However, the working temperature is limited due to demixion of surfactant BC for high temperature, above the cloud point. This phenomenon is due to a de-hydration of hydrophilic head of the molecule at high temperature (around 40°C).

A drop spreading test was performed at the metallic surface after treatment. This is a qualitative assessment of the cleaning efficiency of the different treatments. A good spread of the water drop indicates a cleaner surface, whereas a non spreading drop indicates a poorer degreasing efficiency. The results are presented in Table II.

Table II. Results of Drop Spreading Test

Sample n°	Treatment	Observations	Time - Temperature
1	NaOH 5,5 M	Drop is not spreading	6 h - 40°C
2	HNO ₃ 5 M	Drop is not spreading	6 h - 40°C
3	Surfactants - HNO ₃ 5 M	Drop spreads	6 h - 40°C
4	Surfactants - HNO ₃ 0,5 M	Drop spreads	6 h - 40°C
5	Surfactants - HNO ₃ 0,5 M	Drop spreads poorly	6 h - 30°C
6	Surfactants - HNO ₃ 0,5 M	Drop spreads	6 h - 40°C

As expected from these results, the less efficiency, the poorer is the drop spreading which correlates well with activity measurements. Surfactants at 40°C show a better degreasing efficiency than other treatments. To summarize observations, the results obtained with active samples correlate well with non active results; degreasing, and thus decontamination, is enhanced using a surfactant formulation.

Liquid Secondary Waste Processing

After treatment, the solutions contain organic compounds from the surfactants themselves and from the removed organic solutions. High amounts of organic matter (surfactants and TBP) could lead to complex multiphase solutions along the evaporation process. A method to remove organics from the solution before sending it to evaporators has been studied. Many ways to remove organic content of the solution have been reviewed :

- Ozonation [3]
- Hydrothermal oxidation using supercritical water (which is under development for nuclear purposes)
- Microbiology
- Incineration.

A treatment based on hydrogen peroxide has been chosen and successfully developed to achieve organic matter oxidation after treatment. This gave the best combination of economic considerations and a robust process. It is based on hydrogen peroxide Fenton type oxidation of organic molecules catalyzed with a metallic ion, in this case a nickel nitrate. Large organic molecules are reduced to smaller ones during the process. Small organic acids (like acetic acid, formic acid or oxalic acid) are used as tracers to evidence the reaction progress. Preliminary tests have been made at the laboratory scale with non-radioactive solution tracers. A hot test has been performed in the ATALANTE facility, in Marcoule. The aim of these experiments was to reduce the foamability of the surfactant system, increase compatibility with evaporators, and calcinator conditions and address liquid waste vitrification needs.

A simulated surfactant solution containing HDBP) is used for the non-radioactive laboratory scale experiments. An HDBP target (simulated organic containment) was coated on a metallic sample and contacted with the surfactant solution. Initial conditions for the processing of the solution are:

- Nickel Nitrate : $4 \times 10^{-3} \text{M}$
- H_2O_2 : 2 M
- Temperature : 60°C

HDBP conversion into phosphate was very efficient with this treatment. The conversion of carbon could reach high values within an hour (up to 95%). Moreover, no oxalic acid was detected and foamability of the system has almost disappeared.

A hot test was performed in the ATALANTE facility. The Organic phase was sampled in a liquid-liquid contactor of the Pilot Reprocessing Facility in Marcoule, then contacted with the

surfactant formulation until saturation was reached. The aqueous surfactant formulation was then separated from the organic phase and treated with hydrogen peroxide. The organic phase is mainly TBP and TPH, which is an oil refining byproduct containing dodecane. Initial conditions for the processing of the solution are:

- Nickel Nitrate : $5 \times 10^{-3} \text{ M}$
- H_2O_2 : 1,6 M
- Temperature : 60°C

After three hydrogen peroxide additions and an 80-hour treatment, 94% of organic carbon was removed. A non-foaming condition is reached after the first hydrogen peroxide addition. This evolution is similar to the trial observed for the non-radioactive test although hydrogen peroxide consumption is higher in the case of the non-radioactive solution. This can be explained by a different cation composition.

Acetic and formic acids are the main carboxylic acids evolved in this process. Oxalic acid concentration is very low ($< 1,6 \times 10^{-3} \text{ M}$). These acids represent almost 100% of the identified carbon in the solution.

The radioactive solution was then be evaporated until a concentration factor of 7 was reached. No phase separation was observed. The concentrations of U and Pu were too low to allow an understanding of their behavior during the treatment, but no major problem was encountered.

Although more investigation is needed for higher Pu and U concentrations, the behavior of the surfactant system qualitatively matches the requirements for a safe industrial processing of the secondary liquid waste.

SCALE ONE EXPERIMENT

A 'scale one' experiment was scheduled for the end of February 2004 in the Pilot Reprocessing Facility in Marcoule to validate the experimental results with the nitric acid surfactant formulation. Operations consisted of testing an industrial scale process of three stages (i), (ii), (iii):

- (i) Degreasing of equipment of a chemical treatment unit (extraction cycle) of a reprocessing plant. The objective was to remove the residual organic matter (TBP and degradation products) and to recover the contamination associated with those materials. The equipment was rinsed using a surface-active solution in acidic medium (cf III),
- (ii) Mineralization of the effluents resulting from this degreasing. The objective is to destroy the organic matter (surfactant and greases) to reduce the effluent foaming capacity and to reach compatibility with the evaporation process. The effluents were oxidized by peroxide in a catalytic process (cf IV),
- (iii) Concentration of the mineralised effluent in an evaporator to reduce the volume of effluent and achieve organic matter destruction.

Degreasing

Degreasing was carried out in two mixer-settler batteries of the U/Pu partition cycle. Since its start-up in 1988 this equipment has treated 13 tons of U+Pu (1,3 tons of Pu) resulting from the reprocessing of varied fuels (EL, MOX, RNR., etc.). The end of processing occurred in 1994. Flushing of the system occurred in 1994 and acidic rinsing operations were carried out between 1998 and 1999. Since then the equipment has remained empty. At the beginning of degreasing operation the equipment contained liquid organic matter (above 350g) and solid organic matter (unknown quantity). The equipment was first degreased using the surfactant solution. In a second step the equipment is rinsed using the nitric acid solution. Figures two and three represent the organo-phosphate species (TBP, DBP) and uranium and plutonium removed during sequences of degreasing/rinsing. For each curve the cumulative evolution of the parameter, the value after each sequence and the percentage which this value represents on the whole of the operation is shown. The plateau value is compared (in the form of ratio) with the theoretical value by considering solution concentrations initially present. A value higher than the unit is due to a previous precipitate species being solubilized.

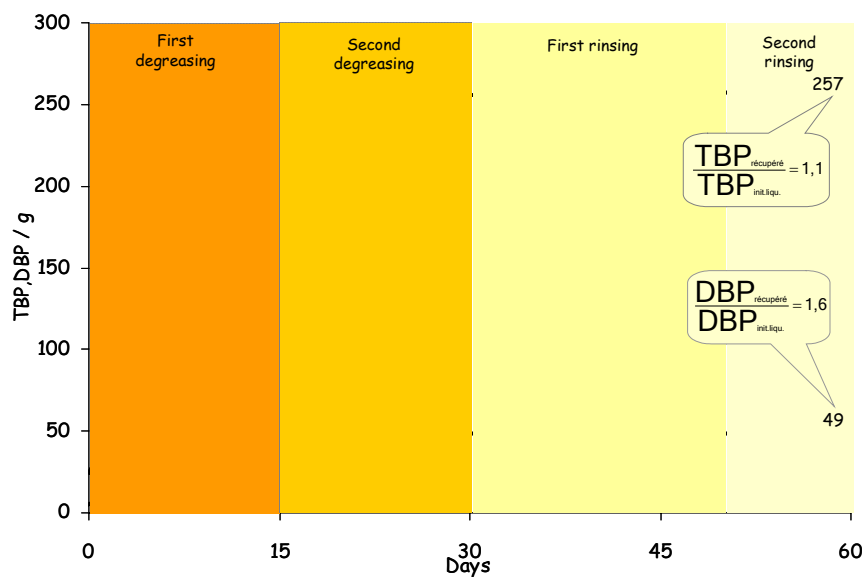


Fig. 2. Organo phosphoric species removal during degreasing/rinsing sequences [proper format inserted]

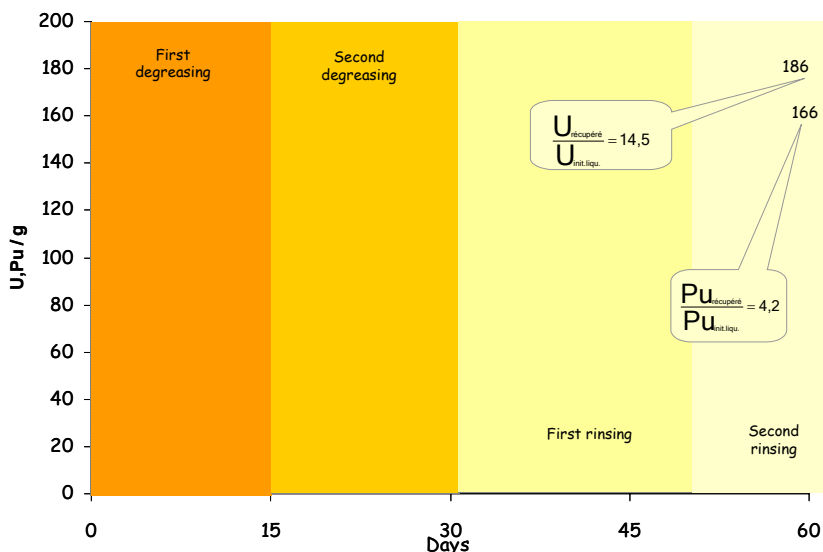


Fig. 3. Plutonium and uranium removal during degreasing/rinsing sequences [proper format inserted]

A significant quantity of DBP is extracted from the deposits (ratio equal to 1,6). These precipitate species contain radioactive elements which are dissolved during the process. Plutonium dissolution kinetics is slower. However, plutonium solubilization kinetics is four times faster during the acid rinsing than during dynamic degreasing. It would seem that surfactant adsorbed layer at the precipitate/solution interface slows the plutonium diffusion. Voltametric measurement of Pu diffusion coefficient into nitric acid and nitric acid plus surfactant solutions seems to confirm this hypothesis.

After the operation, measurements and sampling were carried out in order to estimate the plutonium and the alpha activity residual in the equipment. Table 3 presents alpha decontamination output operation.

Table III. Output of Recovery of Alpha Activity

	In liquid phase	In solid phase	Total
Act α_{initial} /Bq	$4,4 \cdot 10^8$	$6,7 \cdot 10^9$	$7,14 \cdot 10^9$
Act $\alpha_{\text{recovered}}$ /Bq	$4,4 \cdot 10^8$	$1,86 \cdot 10^9$	$2,3 \cdot 10^9$
Act $\alpha_{\text{résidual}}$	0	$4,84 \cdot 10^9$	$4,84 \cdot 10^9$
α recovery yield	100%	28%	32%

Mineralization

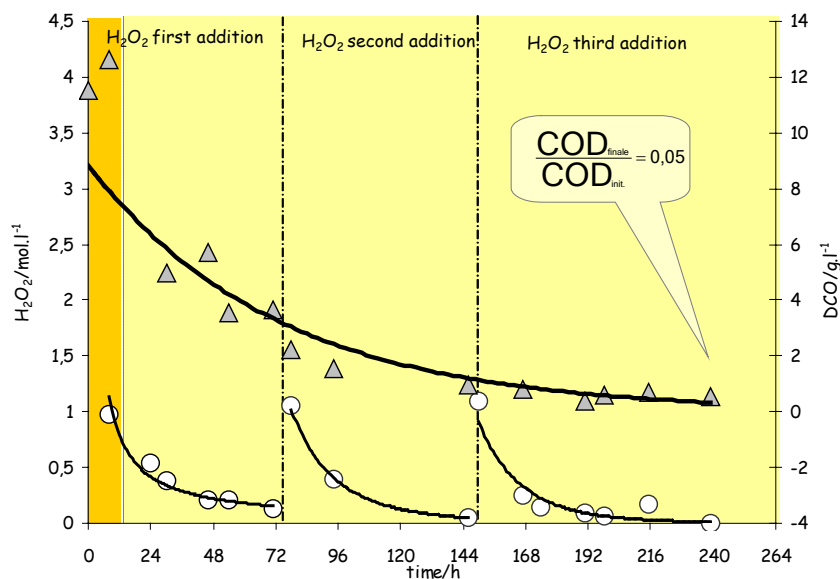


Fig. 4. COD and H₂O₂ during mineralization (second batch)

Figure 4 presents the Chemical Oxygen Demand (COD) and hydrogen peroxide evolution as a function of time during waste processing.

One notes a regular reduction in the COD and hydrogen peroxide concentration. This shows the organic species mineralization reaction. Effluent foamability decreases strongly and quickly (foaming test reached after 6 hours). The process allows a “quasi complete” mineralization. Indeed the residual organic matter is 5% of the initial organic matter. Another notable fact is the decelerating speed of consumption of hydrogen peroxide when the organic matter concentration decreases.

Table IV. Assessment of Mineralization Operations

	Batch 1	Batch 2	Batch 3
COD _{init} /g.l ⁻¹	26	11,5	0,3
H ₂ O ₂ additions	1	3	1
duration/h	46	240	120
% acétic	17	64	44
% formic	70	33	47
% glycolic	13	1	4

COD decreasing/%	70	95	NS
TOC decreasing/%	80	95	NS
TOP decreasing/%	34	95	NS

Concentration

Concentration occurred without denitration due to initial low acidity and the small concentration factor targeted (above 7). The flow of distillate was approximately 40 liters per hour. Table V shows the principal results of the operation.

Table V. Concentration Operation Results

	Volume/l	Activity /Bq	Acétic/g	Formic/g	Phosphoric/g
initial	350	$9,7 \cdot 10^8$	50,6	33,7	26
distillate	300	$1,2 \cdot 10^6$	41,5	70,7	< DL
concentrate	50	$9,6 \cdot 10^8$	< DL	< DL	23

Results

These results indicate that:

- The feasibility of industrial implementation of the three stages has been tested.
- Each stage efficiency and behaviour has been studied.
- Degreasing is effective. Most of TBP has been removed from equipment. A large amount of deposits were dissolved. The radioactive elements associated with the organics matter (liquid or deposits) were recovered. Residual deposits still contain a significant quantity of the alpha activity.
- - Mineralization of the degreasing effluents is effective, the operation significantly decreases the foaming capacity of the effluents. A thorough mineralization is possible by using several hydrogen peroxide additions.
- -Concentration of the mineralized effluents does not create a particular difficulty.

CONCLUSION

The chemical properties of a surfactant solution in a nitric acid medium have been detailed. The aim of the formulation is to remove TBP molecules from metallic surfaces. The efficiency of the treatment was evaluated on non-radioactive, and radioactive samples and compared to more conventional treatments like concentrated sodium hydroxide and pure nitric acid. A micellization of 5,3 g/L of TBP in 0,5 M nitric acid is obtained. This value is about 15 times larger than TBP solubility in the acid. The efficiency is higher than sodium hydroxide and the risk of Pu and U precipitation is eliminated in acidic conditions. Moreover, secondary liquid wastes are compatible with the vitrification unit as they contain no sodium ions. A pretreatment including oxidation with peroxide hydrogen and evaporation has been further validated. A large scale experiment was performed with success at the Pilot Reprocessing Facility in Marcoule. In the future this experiment will be examined in the context of larger scale decommissioning projects. In parallel to these industrial objectives, basic studies have been launched with Montpellier University to get a better understanding of basic phenomena involved in the TBP solubilization.

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