Study of an Innovative Nuclear Process Based on Dense CO$_2$:
Application to Decontamination and Pu Recovery – 10394

B. Fournel, I. Stoychev, T. Ribaut*, P. Lacroix-Desmazes*, JC. Ruiz, and S. Sarrade
Waste Management Department, CEA Marcoule France
*Institut Charles Gerhardt, ICG-IAM, Ecole Nationale Supérieure de Chimie de Montpellier, France

ABSTRACT

Dense CO$_2$ is an environment friendly, non-polar and non-toxic solvent, exhibiting a significant solvent power toward organic molecule. The aim of the work is to study the interaction between surfactants and supercritical CO$_2$ and to get results that evidence an enhancement of contamination extraction efficiency from solid substrates when using the dense CO$_2$ process in combination with surfactants. Firstly, a dry process essentially based on a physical removal of PuO$_2$ contamination with dense CO$_2$ has been studied. Preliminary results are also given about the possibility of separating PuO$_2$ and recovering it using a ceramic membrane. Then, the syntheses of multi-purpose gradient copolymers and their use to remove different chemical forms of cobalt are presented.

INTRODUCTION

This paper describes a process based on dense CO$_2$ for the decontamination of miscellaneous organic wastes and fabrics coming from nuclear facilities. Dense CO$_2$ is an environment friendly, non-polar and non-toxic solvent, exhibiting a significant solvent power toward organic molecules. The solvent power is enhanced in the supercritical domain (P>7,38 MPa and T > 31°C). Therefore it is a very attractive solvent for nuclear applications as it will produce no secondary wastes. Furthermore, the separation of contamination from CO$_2$ is very easily performed by lowering the pressure and is much more effective than with conventional organic liquid solvents. The first part of the paper presents the main outlines of a study devoted to the removal of PuO$_2$ particles in dry CO$_2$. Preliminary results are also given about the possibility of separating PuO$_2$ and recovering it using a ceramic membrane. The second part addresses the synthesis of new multi purposes amphiphilic macromolecules which:
- form water in a CO$_2$ microemulsion,
- are able to complex dissolved contamination
- help the removal of particulate contamination in the frame of a dry process such as presented in the first part of the paper.

REMOVAL OF CEO$_2$ (AS A SURROGATE FOR PUO$_2$) FROM ORGANIC WASTES

Basic studies

Industrial context

Mixed oxide (MOX) fabrication results in the production of secondary wastes contaminated with PuO$_2$ powder. The contaminated technological wastes mainly come from gloveboxes and are composed of gloves, textiles, metallic parts, etc. Since for criticality reason, the MOX fuels are maintained in a dry atmosphere, the PuO$_2$ contamination is weakly bound to the above mentioned solid substrates. The dominant forces are presumably Van der Waals forces or weak electrostatic forces.

Targeted contamination

The considered contamination in this study consists of solid particles of plutonium dioxide (diameter size under 10 μm). Because of the very low solubility of plutonium dioxide in aqueous solutions, strong acids and high temperatures are generally required to dissolve this molecule. This option, which leads to the production of secondary wastes has been rejected. Furthermore, the challenging option of

eliminating aqueous liquids from the process has a great value in terms of avoiding criticality issues. In this study, cerium oxide particles (CeO_2) are chosen to simulate PuO_2 contamination since the electronic configurations of PuO_2 and CeO_2 are similar.

Choice of a suitable process

The study is based on a physical process that excludes chemical reactions. The main objective is to remove mechanically the particles of CeO_2 using a stirred system. Two type of stirring systems have been addressed: mechanical stirring and ultrasonic stirring. Mechanical stirring comprises a simple rotating blade and is probably the most attractive system in the view of a future industrial application due to its simplicity. Due to the low viscosity of dense CO_2 (order of magnitude 10^{-5} Pa.s), high shear stress values are however not expected in this case. Thus, it is foreseen that a more efficient agitation technique should be studied. Ultrasonic stirring is known to generate locally high stress forces. Because of the high density of pressurized CO_2 (of the same order of magnitude as classical solvents , 200 to 900 kg.m^{-3} depending on the pressure and temperature values), it is a suitable fluid for the propagation of sound waves.

Experimental setup

A sketch of the experimental set up is given in t Figure 1. The first cell on the left is a 270 ml "stirring cell" equipped with two sapphire windows at 90° and fitted with a CCD camera. This cell is used to perform the stirring of the CeO_2 particles in order to produce a dispersion of solid particles in dense CO_2.
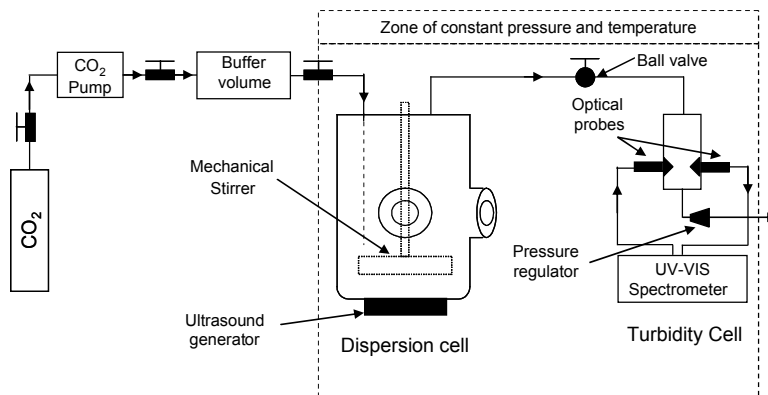
Fig. 1 : Experimental set up

The second cell on the right is a 30 ml cylindrical shaped "turbidity cell" equipped with two optical probes (at 180°) connected to an ultraviolet spectrophotometer "Lambda 40" through two optical fibers of 1 m each. The internal diameter of the cell is 20 mm. The distance from the bottom of the cell to the center of the probes is 30 mm. The distance from the center of the probes to the top of the cell is 65 mm. The distance between the optical probes (i.e., the path length) is 10 mm.

Turbidity measurements have been performed in two stages. In the first stage, 40 mg of nano-powder of CeO_2 are dispersed in the stirring cell at a given pressure and temperature. The size of the particles is 30 nm but due to attractive forces, they are likely to form aggregates as suggested by the SEM pictures presented in the figure below.
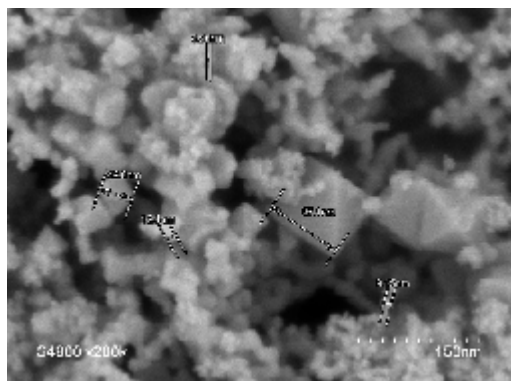
Fig. 2: SEM pictures of CeO$_2$ particles

The dispersion is created by stirring the reactor for 20 minutes with a turbine-type stirrer (d = 35 mm) fitted with four blades (45° angle). In the second stage, a part of the dispersion is transferred into the turbidity cell where the turbidity measurement takes place. During the transfer, the pressure is kept constant (15 MPa, 298 K). The transfer occurs thanks to the introduction of an additional fixed CO$_2$ volume in the stirring cell. Suspended particles/aggregates are then swept away and transferred to the turbidity measurement cell.

Results : mechanical stirring

Figure 3 presents a typical curve of turbidity evolution recorded in the second cell.
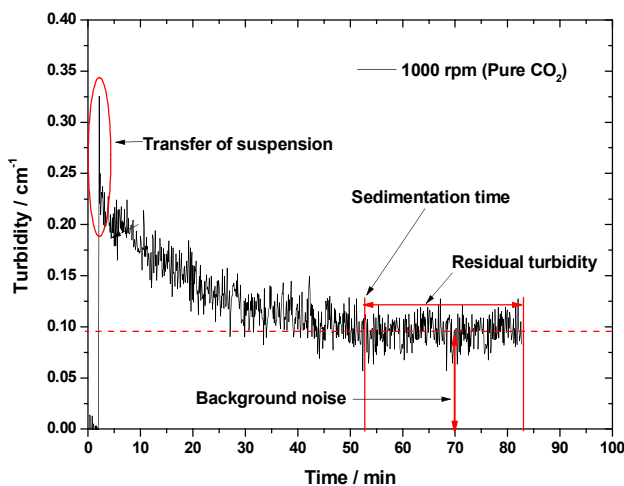

Fig. 3 : Turbidity versus time in pure CO$_2$

The initial turbidity value depends on the quality of the dispersion. A high initial turbidity indicates a large number of transferred particles or aggregates and/or a small particle size. A second remarkable figure is the time needed for the turbidity to decrease down to zero (relative value recorded in the absence of particles after calibration in pure pressurized CO$_2$). The total sedimentation time is characteristic of the smallest particle sedimentation. The size of the smallest aggregates can be derived from the Stokes equation

$$d_{agg} = \sqrt{\frac{18\eta_{CO_2} H_{sed}}{gt_{sed}(\rho_{agg} - \rho_{CO_2})}} \quad \text{(Eq. 1)}$$

t_{sed} –sedimentation time (s). H_{sed} –sedimentation height; d_{agg} – agglomerates diameter des (m) ; ρ_{agg} – agglomerates specific weight (kg.m^{-3}); g – gravity constant (9,81 m.s^{-2}) ;η_{CO2} –CO_2 viscosity (Pa.s); ρ_{CO2} –CO_2 specific weight (kg.m^{-3})

Figure 4 presents the evolution of the sedimentation time and size of the smallest aggregates calculated from the Stokes equation versus the stirring speed.
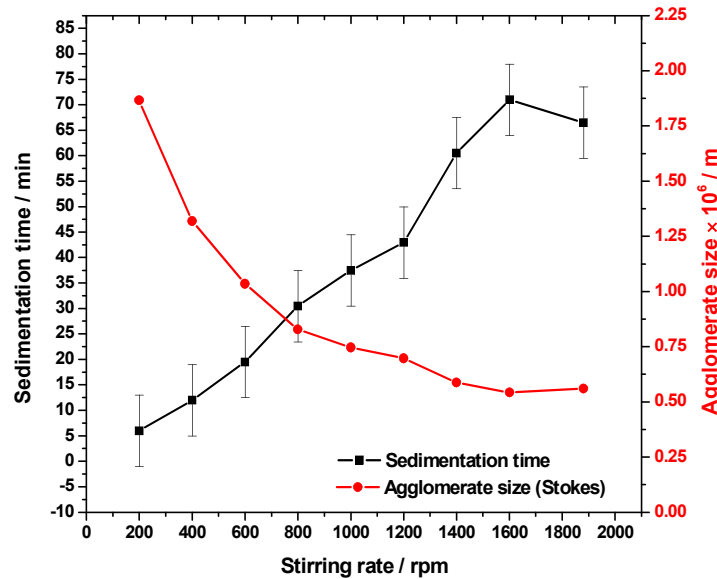

Fig. 4 : Sedimentation time and agglomerates size from Stokes Equation versus stirring rate

Sedimentation time increases as the mechanical stirring rate increases. When the stirring rate is high, the power dissipated in the CO_2/particle system increases and higher shear stresses are generated. Thus transferred aggregates are smaller as can be seen form the size evolution curve. However, under strong stirring (1880 rpm), aggregates size estimated by the Stokes equation reaches a plateau at about 600 nm and the corresponding maximal sedimentation time is about 70 min.

Results : Ultrasonic stirring

In this case, an ultrasonic probe (40 kHz, the estimated power transmitted to the fluid is 80 W) has been fitted into the first cell. The generated waves are transferred from the outer part of the reactor inside the reactor. A low mechanical stirring rate (200 rpm) is however maintained in order to homogenize the system and to enable particles/aggregates to be driven in all parts of the reactor. This ensures also that particles/aggregates receive a comparable amount of ultrasonic power as some heterogeneity may exist in the wave propagation due to the reactor geometry and probe configuration.

The first curve in Figure 5 presents the record of turbidity versus time for the case of ultrasonic stirring. For the sake of comparison, the previous result obtained under a high mechanical stirring rate (1880 rpm) has also been plotted.
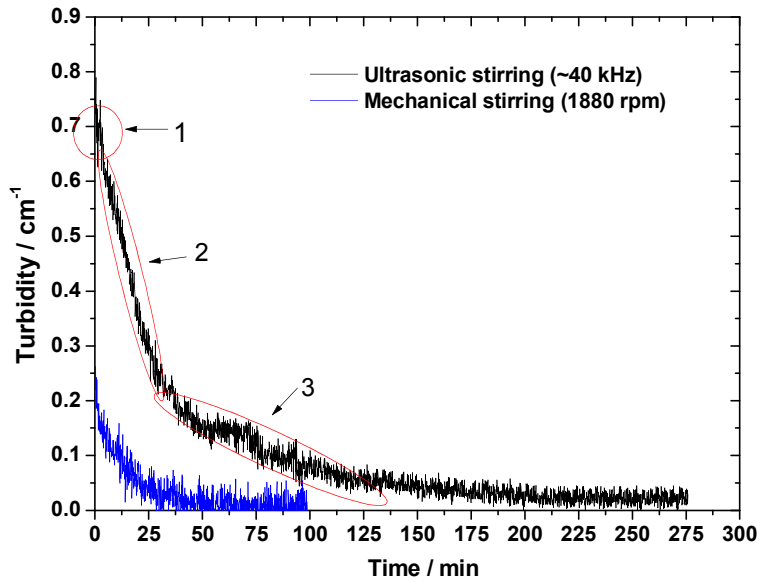
Fig. 5 : Comparison of turbidity curves : mechanical and ultrasonic stirring

One can see that the initial turbidity is much larger in the case of ultrasonic stirring (region 1). This indicates a much more efficient dispersion than in the case of mechanical stirring. The total sedimentation time has also increased. From the Stokes equation, the size reduction of the smallest aggregates is estimated to be a factor about 2 (300 nm instead of 600 nm).

The most interesting feature is that the curve shows a new regime (region 2). This regime appears during the first 25 minutes. The decrease of turbidity is very fast and almost linear. Two hypotheses can explain this phenomenon:

the size of the initial particles/aggregates is large and they settle very quickly
- rapid flocculation of particles or small aggregates occurs and the formed aggregates settle down quickly.

The first hypothesis has been ruled out by video camera records. From these records, it appears unambiguously that the size of the aggregates in the case of ultrasonic stirring is much smaller than for mechanical stirring.

In order to confirm the second hypothesis, a poly(dimethyl siloxane (PDMS) surfactant has been added to the system. Due to their amphiphilic properties, surfactants are used to enhance the interaction between nonpolar CO_2 and the polar contaminants. The phase behavior and the interfacial activity of block and graft type PDMS—PEO (poly(dimethyl siloxane)-poly(ethylene oxide)) copolymers have first been studied to assess their applicability in a dense-CO_2-decontamination-based process [1]. The copolymers having a PEO weight fraction of 40 % presented the highest potential to avoid particle aggregation and thus enhance the stabilization of the metal oxide particles. The following molecule has been chosen (Figure 6):
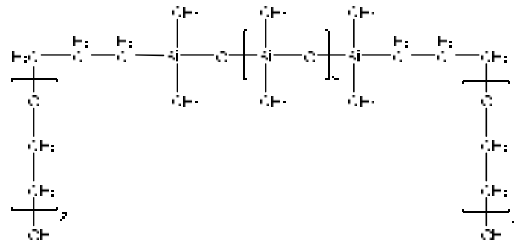
Fig. 6 : Structure of the chosen tri-block PDMS surfactant : Molecular Weight 1900 g.mol⁻¹, 41 wt% PEO

Figure 7 presents the record of turbidity versus time for two concentration values of PDMS surfactant. The curves are compared to the case where no surfactant is added.
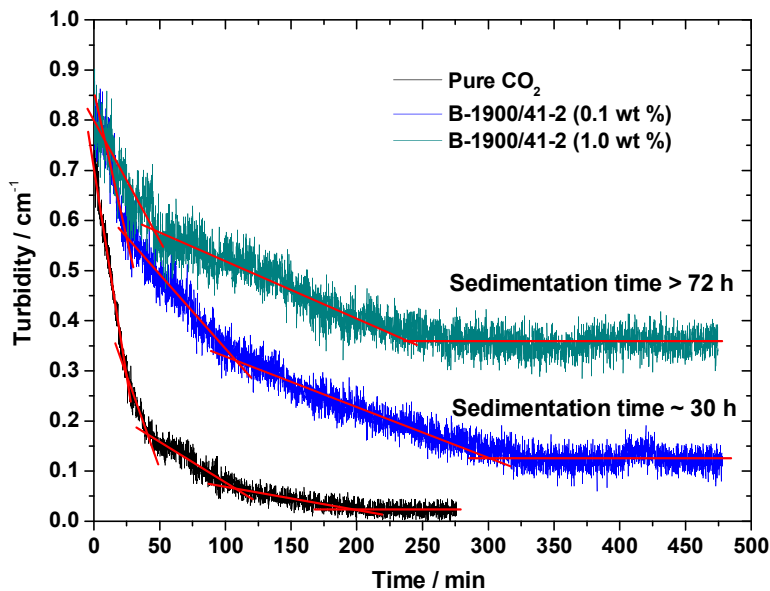
Fig. 7 : Effect of surfactant concentration on the turbidity evolution

From these curves, we notice a strong effect of surfactant addition in the system. However, the initial value of turbidity is not affected by the surfactant presence. This means that the dispersion quality is mainly dependant on the stirring process. Conversely, the second part of the curve is very much affected by the presence of surfactant. More precisely, the second regime still occurs, but the value reached by the turbidity after the fast decrease period is much higher than in the case of pure CO_2. For an increased concentration, the effect of surfactant is even stronger. It can be concluded that the surfactant prevents the sedimentation of particles/aggregates. The main hypothesis is that the surfactant adsorbs at the particle interface and builds a steric barrier that prevents particles from flocculating. As a consequence, the sedimentation time is increased. Interestingly, one can notice that after a long period of time (several tens of hours), some aggregates are still in suspension in the system as the turbidity value is not zero. This indicates that the surfactant has sterically enhanced the stabilization of some agglomerates.

As the size of the PDMS surfactant is of the order of magnitude of a few nm, we estimate that the range of aggregate sizes for which the adsorption of surfactant can effectively affect the Van der Waals interactions is between 30 nm and 100 nm [1]. These figures provide an indication of the initial size of the particles once they are introduced into the turbidity measurement cell.

From the above presented results we can conclude that the PDMS surfactant is very effective for modifying particle/particle interactions and probably preventing flocculation.

Removal efficiency from organic substrates

The above results show that mechanical and ultrasonic stirring are efficient at enhancing the dispersion of nanoparticles of CeO_2 in dense CO_2. Moreover, in the case of ultrasonic stirring, the addition of a PDMS-type surfactant provides an additional effect. Dispersion enhancement is expected to help particle removal from contaminated substrates. Another interesting feature of the surfactant molecule is expected. Due to their polarity difference, they are expected to adsorb at the contamination/matrix interface, thus enhancing the removal of particles from the substrate by reducing the adhesion forces. In the following section, we have performed experiments on artificially contaminated samples. Experiments are performed with and without surfactant and in the presence of mechanical or ultrasonic stirring.

Experiments

Trials have been performed on polyurethane samples. In this case, substrates have been contacted with a micrometric CeO_2 powder (< 5 µm) in a dry atmosphere to mimic the real contamination process. The amount of deposited CeO_2 is estimated to be 0,53+/-0,1 mg/cm². The samples have been placed in the stirred cell. Experiments have been performed in dense CO_2 (P = 15 MPa and T = 298 K). After experiment, the cell is rinsed with pure CO_2 in order to prevent particle deposition on the sample. The decontaminated sample is removed and analyzed with an inductively coupled plasma (ICP) spectrometer.

Removal efficiency with mechanical stirring

In pure CO_2 and for a mechanical rate of 1000 rpm (stirred for 1 hour), the experimental removal efficiency is 77+/-3%. In the presence of the PDMS surfactant (0,3 %w/w), the removal efficiency increases up to 98+/-0,3%.

The role played by the surfactant in this case is obvious. It is believed that the effect of the surfactant is mainly explained by the reduction of adhesion forces between particles and substrates due to the polarity difference.

Removal efficiency in the case of ultrasonic stirring

Ultrasonic stirring has been performed under the same CO_2 conditions, but the stirring time has been set to 30 minutes. In pure CO_2 the removal efficiency is 96+/-0,4%, which is much higher than in the case of mechanical stirring. This enhancement is explained by a stronger local stirring and an efficient dispersion of agglomerates in the system. In the presence of the PDMS surfactant (0,3 %w/w), the removal efficiency increases to 97,7+/-0,3%.

That better efficiency is observed in the case of surfactants can be explained by a better dispersion of the agglomerates as well as by a reduction of substrate/particle interactions. The first phenomenon is likely to be low due to the rather large particle size in this case. Thus the increase in the removal efficiency is rather small and is between 1 and 2%.

This can appear a modest result, but we have to keep in mind that experiments have been performed with surrogate samples. For real samples, higher adhesion forces are likely as well as smaller particles. Nonetheless, even a small increase in decontamination efficiency can be decisive in terms of waste decategorization.

Toward the recovery of Pu

The above results show that a process based on the association of dense CO_2 and ultrasonic stirring is certainly well adapted for the removal of dry particles contamination. Furthermore it has been demonstrated that a surfactant can bring a complementary action and can help increase the process efficiency. This increase in efficiency due to surfactant addition will be even stronger in the case of smaller particles as shown above where nanometer-size CeO_2 particles have been employed.

A further step of the process would be to separate the particles from the CO_2 flux and potentially from the surfactant in order to recover PuO_2 and reuse it.

In the next figure the general block diagram of the process is sketched. The CO_2 is recycled and an additional separation step is added in order to recover the PuO_2.
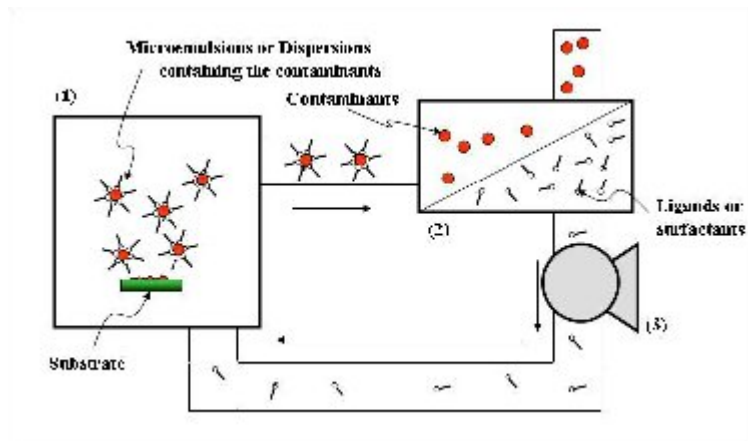
Fig. 8 : Schematic diagram of the continuous CO_2 process using separation step; (1) High pressure reactor, (2) Separator, (3) High pressure circulation pump.

A simple separation step generally consists of lowering the pressure. In a cyclone-type reactor, this enhances CO_2 particle separation. When no surfactants are present, this is probably the most effective and economical way to achieve a nearly total separation. However, in the presence of surfactant, we aim at separating surfactant molecules from contamination in order to :
- minimize the amount of surfactant in the recovered contamination
- recycle the surfactant, thus minimizing the total amount of organic matter in the secondary wastes.

Nanofiltration experiments of surfactant/CeO_2 particles separation have been performed on ZrO_2-coated alumina membranes having a porosity of 1 kD (estimated pore size 0,6 nm) to ensure a 100% CeO_2 retention. Ceramic membranes are very interesting in the view to set up a CO_2-based nuclear process as they will exhibit no interactions with dense CO_2 due to their chemical inertness. Furthermore, they will be very well suited for disposal or storage as they contain no organic parts.

The details of the experiments described above are reported elsewhere [2] while here, only the most interesting result regarding the present study will be presented.

These preliminary experiments have been performed with an hydrocarbonated block copolymer, the Pluronics PE6100 (a copolymer of ethylene oxide and propylene oxide, M.W. = 1650 g/mol), which has a molecular weight close to the above mentioned PDMS.

The aim of the study was to show that the retention of particles is effective and that the surfactant could flow across the membrane in order to recycle it.

In the following figure several experiments have been performed for various transmembrane pressures. The surfactants are initially placed in a CO_2 tank at a pressure of 25 MPa and are then allowed to flow through the membrane.
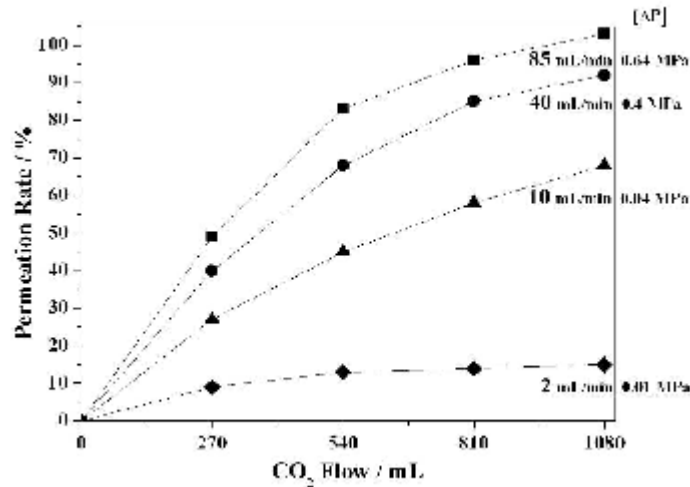
Fig. 9 : Effect of flow rate in membrane separation with 1kD (1 channel) membrane at 40 ℃ and 25 MPa.

It can be seen that the permeation of PE 6100 increases with CO_2 flux. After this transitory regime, a plateau is reached and a constant value of the permeation is observed. One can see that a value of pressure difference above 0,64 MPa ensures the total permeation of the surfactant through the membrane. The existence of a plateau for lower values of the transmembrane pressure is explained by the setup of an equilibrium of hydrodynamic forces through the pores and the adhesion forces of the surfactant adsorbed at the pore wall.

On the other hand, SEM pictures show qualitatively that CeO_2 particles are effectively stopped by the membrane (see Figure 10)
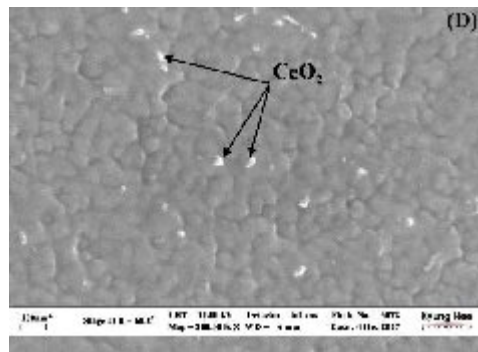
Fig. 10 : SEM pictures of CeO_2 particles at the membrane surface after experiment (here a preliminary result obtained with a 300 kD membrane is shown)

These preliminary filtration results show that the separation of surfactant/particles can be achieved using a ceramic membrane with a small porosity at reasonable pressure difference values. In fact the pressure difference necessary to achieve the separation is of the order of 1 MPa. This must be compared to values ranging from 15 MPa to 25 MPa in the CO_2 decontamination process. Addressing the future decontamination process, we can expect that the recycling of the surfactant as part of the decontamination process will be highly effective and that the recovered PuO_2 will contain only traces of surfactants due to e adsorbed molecules on the surface. A further CO_2 washing of recovered PuO_2 can be foreseen in order to eliminate the remaining traces of surfactants. As a conclusion we can expect from the separation step using standard ceramic membranes a very high recovery of PuO_2 that could potentially be re-used.

REMOVAL OF COBALT

This section presents also an approach based on the use of surfactants to remove contaminants in dense CO_2. However, in this case not only a physical effect is expected, but also a chemical effect since complexing of chemical additives will be involved in the process.

Industrial context

PuO_2 contamination is an example of non soluble contamination. Among the contaminants present in nuclear wastes, we address ^{60}Co-contaminated fabrics (clothes). Cobalt is chosen as a representative contaminant from nuclear power plants. In this case, ^{60}Co can exhibit different chemical forms having various solubilities. Ionic Co is expected in the case of wet contamination as well as the cobalt oxide forms which are far less water soluble. Moreover, cobalt hydroxide forms may occur depending on pH conditions. In the case of dry contamination, we can thus find either cobalt oxide or cobalt hydroxide particles.

Because in this case criticality is not an issue compared with the case of Pu contamination, different strategies can be proposed that address the different chemical types of contaminants encountered:
- a dry decontamination as proposed for PuO_2 to remove Co particles
- a microemulsion of water in CO_2 to remove water soluble Co contamination
- a microemulsion of chelating additives to help the solubilization of low water soluble Co chemical forms (Co oxide and Co hydroxide)

Synthesis of new additives

The use of commercial surfactants to generate a microemulsion of water in dense CO_2 has been reported in the literature. Complexing agents are often added to enhance the solubilization of the contamination [3].

The synthesis of new copolymer additives that exhibit complexing properties and amphiphilic properties to remove dry contaminants and enhance the formation of microemulsions is foreseen. More precisely, the study addresses the synthesis of gradient copolymers where the general structure and aggregation behavior is presented in Figure 11.
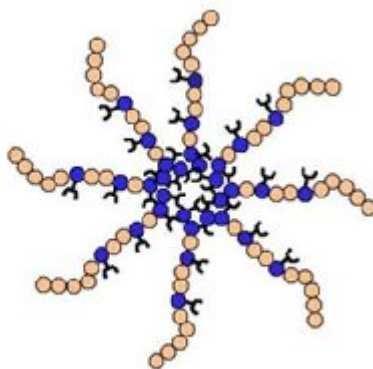
Fig. 11 : Gradient copolymers bearing complexing moities (dark points stand for CO₂ phobic units and clear points for CO₂ philic units, Y stands for complexing moities)

Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-acetoacetoxyethyl methacrylate) (poly(FDA-*co*-AAEM)), poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-vinylbenzylphosphonic acid diethylester) (poly(FDA-*co*-VBPDE)) and poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-vinylbenzylphosphonic diacid) (poly(FDA-*co*-VBPDA)) have been synthesized at CNRS Montpellier [4]. The CO_2-philic block is composed of a fluorinated molecule for which the corresponding homopolymer solubility in dense CO_2 is of the order of several tens of %, depending on pressure and temperature conditions. The CO_2-phobic part either bear an acetoacetoxy, phosphonic or phosphonic diacid structure, which exhibits a high affinity for particles as well as complexing properties toward cobalt.

Gradient copolymers appear very advantageous due to their solubility under much milder conditions of pressure and temperature when compared with block copolymers. The gradient structure implies that the complexing moieties are present along the copolymer chain. Thus a complexing efficiency is expected not only in the micelle core, but also in the transition region between the micelle core and the micelle shell.

Qualitative assessment of dry contamination removal

Turbidity experiments have been performed in the same way as described above. In this case the particles are composed of cobalt hydroxide and their size is about 300 nm. The experiments were performed with a stirring rate of 300 rpm. The pressure is 21 MPa and the temperature 313 K.

The next figure presents the results of turbidity evolution versus time for poly(FDA-*co*-AAEM) containing 27,5% mol of AAEM (acrylate-*co*-acetoacetoxyethyl methacrylate).
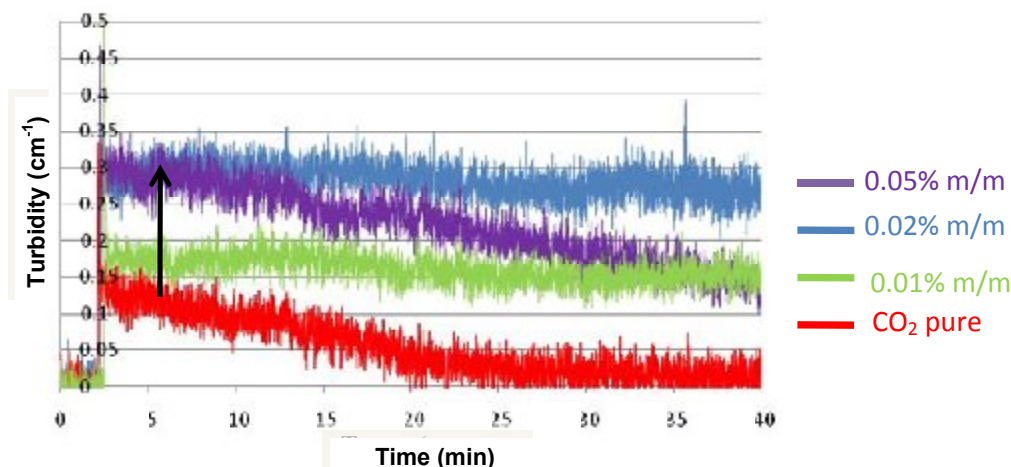
Fig. 12 : Turbidity versus time for the poly(FDA-*co*-AAEM) containing 27,5% mol of AAEM

It can be seen that the turbidity initial value as well as the sedimentation time are enhanced by the surfactant. This demonstrates that the dispersion is enhanced by surfactant adsorption at the particle surface. This case is similar to the case of CeO_2 particles discussed above. In this case we notice that the effect of concentration exhibits a maximum. This is explained by a depletion flocculation phenomenon beyond an optimal value of the ratio of surfactant to solid particles.

Assessment of complexing efficiency

For these experiments a fabric sample (cotton/polyester) contaminated with a non-radioactive cobalt nitrate solution and then dried has been used to mimic a real contamination case.

The following extraction tests have been performed in an extraction cell at 16 MPa and 313 K.

Extraction efficiency is further compared to a result already reported in the literature [5]. The most striking results are presented in Table 1.

Table 1 : Efficiency of gradient copolymer to remove cobalt from fabric sample

System	Water (mg)	Number of ligands to Co	Extraction efficiency (%)
pure CO_2	33	0	0-2
CO_2/Poly(FDA-*co*-VBPDA)	33	30	36 ± 6
Cyanex 302 (Literature)[5]	30	1930 3850	17 40

The extraction assisted with gradient copolymers has a comparable efficiency to that of Cyanex 302 (bis (2,4,4,-trimethylpentyl) monothiophosphinic acid $R_2P(S)OH$) for similar CO_2 conditions (20 MPa and 313 K) [5]. However, when the molecular ratio of ligand per mole of Co is considered, this ratio is about 120 times smaller in the case of gradient copolymers compared to Cyanex under similar conditions. These results demonstrate the benefit of using gradient copolymers instead of the classical ligand/surfactant association.

CONCLUSION AND PROSPECTS

The aim of this work was to demonstrate an enhancement of contamination extraction efficiency from solid substrates when using dense CO_2 process.

Therefore, a dry process essentially based on a physical removal of PuO_2 contamination with dense CO_2 has been studied. For this 100% waterfree process, the decontamination efficiency relies on a combined action of a highly turbulent flow generated either by mechanical stirring or by ultrasonic stirring and a PDMS-based surfactant to increase contaminant extraction. The feasibility of using a ceramic membrane to further separate the contamination from the surfactants has been further qualitatively assessed.

In order to evaluate the utility of custom-made surfactants, multi-purpose gradient copolymers have been studied. The polymers are fluorinated molecules. Whereas fluoro-based polymers exhibit high solubility in dense CO_2 when compared to siloxane-based polymers, they can be considered as a drawback for the post-treatment of secondary wastes. However, this study must be considered as a first attempt to design custom-made molecules for decontamination purposes.

In the future, we plan to study custom-made siloxinated polymers which are more compatible with nuclear industry constraints.

These encouraging results have led the CEA to plan the commissioning of a laboratory-scale pilot to perform tests with radioactive samples. It is scheduled that this unit will begin operation by 2013 at CEA Marcoule.

REFERENCES

[1] I.STOYCHEV, "Study of the dispersion of cerium oxide particles in compressed CO_2 in presence of syloxinated amphiphilic copolymers: application to nuclear decontamination", PhD Manuscript, CEA, University of Montpellier II (2009).

[2] M. KOH, B. FOURNEL, S. SARRADE, L. SCHRIVE, I. STOYCHEV, P. LACROIX-DESMAZES, T. RIBAUT, K. PARK,, "Continuous Supercritical CO_2 Process using Nanofiltration by Inorganic Membrane", Industrial & Engineering Chemistry Research, Vol. 48**,** 11**,** 5406-5414 **(** 2009).

[3] M. KOH, J. YOO, M. JU, B. JOO,K. PARK, H. KIM, H. KIM, B. FOURNEL," Surface decontamination of radioactive metal wastes using acid-in-supercritical CO_2 emulsions", Industrial & Engineering Chemistry Research, Vol. 47**,** 2,**:** 278-283 **(** 2008).

[4] T. RIBAUT, P. LACROIX-DESMAZES, B. FOURNEL, S. SARRADE, "Synthesis of Gradient Copolymers with Complexing Groups by RAFT Polymerization and Their Solubility in Supercritical CO2", Journal of Polymer Science Part A-Polymer Chemistry, Vol. 47**,** 20, 5448-5460 (2009).

[5] J.S. WANG, M. KOH, C.M. WAI, "Nuclear laundry using supercritical fluid solutions", Ind. Eng. Chem. Res., 43, 1580-1585 (2004).