

# **SUPERCritical CO<sub>2</sub> IS A TOOL FOR NATURAL MATERIAL TREATMENTS**

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The Supercritical Fluids and Membranes Laboratory studies the SuperCritical Carbon dioxide (SC CO<sub>2</sub>) potential for both organic and/or inorganic compound extraction and permeation.

First of all, the laboratory has developed a method for extracting inorganic and organic compounds, from wood (timbers, electric poles... recycling) using SC CO<sub>2</sub>. The extracted inorganic compounds are CCA (compounds of chromium, copper and arsenic) whose extraction is rendered possible by adding a surfactant ; organic compounds extraction of PAH (Polycyclic Aromatic Hydrocarbons) has been also performed. The laboratory has developed, a new hazard-free process for cork treatment and cleaning, using SCCO<sub>2</sub>. This process allows to extract all the undesirable organic compounds (polychloroanisols are responsible of “cork taint”), maintaining all the chemical and physical properties of the cork for wine sealing bottles. SCCO<sub>2</sub> is both efficient to remove contamination in the range from 1 to 10 mg/g in wood treatment and in the lower range from 1 to 10 ng/g in cork treatment.

Secondly, SCCO<sub>2</sub> has been used for permeation on collapsed archaeological waterlogged wood. The collapses have been considered as irreversible damage, with volume loss, distortions and cracks. Several works have been done with polyethylene glycol (PEG) permeation and we have used PEG with SCCO<sub>2</sub> to decrease the viscosity. It is possible to recover a part of the initial volume by mechanical effect produced by fast compression/decompression. The laboratory has also developed an original process for leather tanning with chromium salt permeation by SCCO<sub>2</sub>. The supercritical fluid shows a high density to transport chromium to leather contact. The affinity of the chromium salts is higher for leather than CO<sub>2</sub>: this induces a successful permeation and aqueous waste-less.

SCCO<sub>2</sub> processes demonstrate today a versatility and a sustainable potential for natural product treatments.

## **I – INTRODUCTION**

SCCO<sub>2</sub> has been used for several material treatments and particularly for natural material as wood, cork, leather, textiles, etc.. The CO<sub>2</sub> ability for porous substrate used in extraction and impregnation vector has been developed from several years and numerous publications give a evidence about the interest of this way.

That is the reason why, the Laboratory of Supercritical Fluids and Membranes (LFSM/CEA–Pierrelatte) has been involved in several collaboration programs.

On wood, we have performed an original method to extract organic and inorganic compounds for recycling (timbers, electric poles...). Another topic was on impregnation of archaeological and degraded wood by SCCO<sub>2</sub> as a vector for polyethylene glycol (PEG) transport.

We have used SCCO<sub>2</sub> to perform “cork taint” (2,4,6-TriChloroAnisol: 2,4,6-TCA) elimination from cork stoppers used for wine bottle sealing.

On leather we have developed an original method to perform a chromium salts tanning without water and aqueous waste.

## **II - EQUIPMENT**

All samples of wood, cork, leather were studied in laboratory bench: with a membrane pump and 1 litre extraction autoclave or a sapphire cell of 0.015 l. and two steps of 0.3 l. cyclone separators with pressure regulation.

Measurement and characterisation have been performed in several laboratories in the CTBA (Centre Technique du Bois et de l'Ameublement) by Gas Chromatography for organic compounds and by Atomic Spectroscopy for inorganic compounds. Archeological wood has been analysed by Scanning Electron Micrograph (SEM) pictures on Nucleart Laboratory. The residual level of TCA in cork has been evaluated by SPE purification and gas chromatography / Mass Spectroscopy by SABATE laboratory. Tanning leather operations have been evaluated by ITEC (Institut TEchnique du Cuir) Laboratory and by the retraction temperature measurements.

## **III - EXPERIMENTAL PROCEDURES**

### **III-1 – SCCO<sub>2</sub> recycling wood.**

Organic compounds as Polycyclic & Aromatic Hydrocarbon (PAH) or “coal tar”: acenaphten, dibenzofuran, anthracene, triazol and other organic compounds as chlorophenols... has been removed by mild supercritical conditions, low density at 9 to 15 MPa and 313 to 323 K (from 287.5 to 682.6 kg/m<sup>3</sup>) followed by strong supercritical conditions, high density at 15 to 30 MPa and 323 to 353 K (from 682.6 to 956.7 kg/m<sup>3</sup>). On inorganic Compounds of Chromium, copper and Arsenic (CCA) has been removed by SCCO<sub>2</sub> and from 2 to 30 % of “Krytox-157-FSL<sup>®</sup>” (MW: 2500 g/mole) a polyperfluoroether (F(CF<sub>3</sub>CF<sub>2</sub>O)<sub>n</sub>CF<sub>3</sub>CF<sub>2</sub>COOH). The supercritical conditions has been similar than SCCO<sub>2</sub> organic compound extraction [1].

### **III-2 – SCCO<sub>2</sub> treatment of collapsed and archaeological wood.**

Wood samples have been treated by rapid compression / expansion pressures of SCCO<sub>2</sub> and PEG 400/4000. Conditions were several cycles with a varying pressure as a pulsation from 10 to 30 MPa and from 333 to 353 K [2].

### **III-3 – SCCO<sub>2</sub> treatment of cork.**

SCCO<sub>2</sub> was applied on cork samples to perform several density level from 378 to 777 kg/m<sup>3</sup> (from 10 to 30 MPa and 313 to 333 K). In this case, cork samples were supplemented by immersion in TCA to enhance the initial level at 5/15 ng/g before SCCO<sub>2</sub> treatment [3].

### **III-4 – SCCO<sub>2</sub> leather tanning.**

We have tested a modified chromium sulphate compound transported with SCCO<sub>2</sub> ranging from 5 to 35 MPa and from 293 to 333 K (from 800.7 to 936.1 kg/m<sup>3</sup>). Samples of leather were lightly moistly (≈ 10%) to allow the chromium salts impregnation [4][5].

## **IV - RESULTS AND DISCUSSION**

### **IV-1 – SCCO<sub>2</sub> recycling wood.**

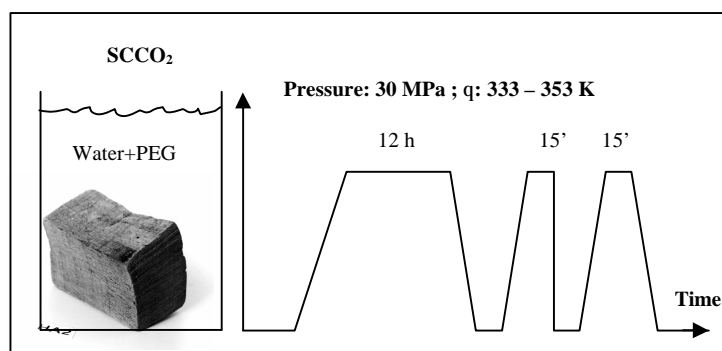
The extracted compounds are in particular inorganic pollutants as CCA whose extraction is rendered possible by adding a surfactant element (Krytox) to the SCCO<sub>2</sub>. The ratio of Krytox and water should be the preponderant factor to increase (at iso-ratio) or decrease the extraction efficiency as well as it shown in table 1.

**Table 1 : operating conditions for inorganic compounds extraction by SCCO<sub>2</sub> [1]**

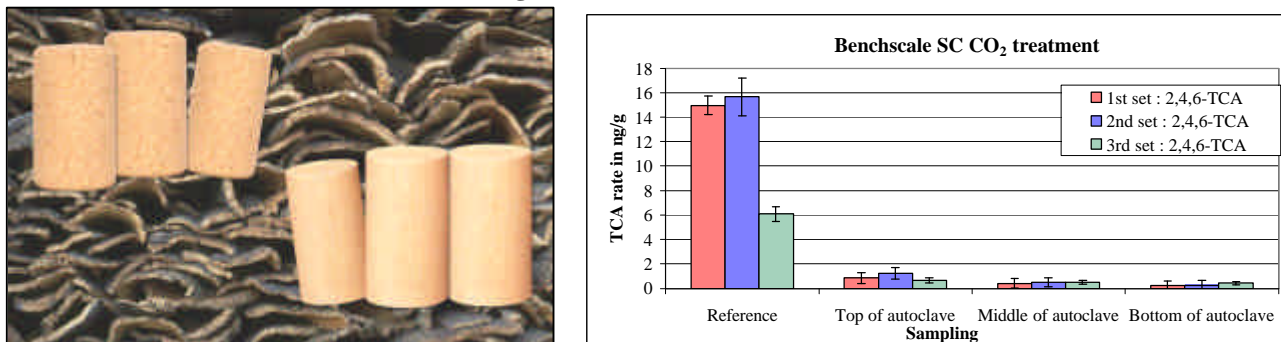
Samples	SCCO <sub>2</sub> operating conditions			Krytox/water ratio	% extraction
	Pressure	Temperature	Flow rate		
1	30.4 MPa	323 K	7 kg/h	20 / 20 (g)	55.3
2	idem	idem	idem	36 / 3.6 (g)	48.6

**IV-2 – SCCO<sub>2</sub> treatment of collapsed and archaeological wood.**

Under specific conditions and with a particular level of collapse, it is possible to achieve total or partial swelling by using rapid SCCO<sub>2</sub> decompression treatment shown in figure 1.

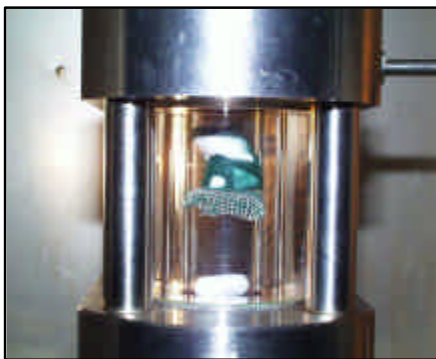
**Figure 1: SCCO<sub>2</sub> treatment of archaeological wood [2]****IV-3 – SCCO<sub>2</sub> treatment of cork.**

Once proved on lab scale, this process turned out to be very effective during scale up to bench level. Results shown in figure 2 draw up which it is possible to remove 2,4,6 TCA from  $10 \pm 5$  ng/g into the reference to residual values close to the detection limit ( $\leq 0,5$  ng/g) and a correct homogeneity on treated cork.

**Figure 2: SCCO<sub>2</sub> treatment of Cork [3]****IV-4 – SCCO<sub>2</sub> leather tanning.**

Chromium salts impregnation by SCCO<sub>2</sub> was performed successfully with 95 % of efficiency. Chromium salts present the best affinity for moistly leather than SCCO<sub>2</sub>. So, the chromium flux come from CO<sub>2</sub> toward leather. The very low viscosity and hydrophobicity of SCCO<sub>2</sub> allow chromium transfer and impregnation into a core leather as well as shown in figure 3.

**Figure 3 : Chromium salts impregnation [5]**



## **V – CONCLUSION**

SCCO<sub>2</sub> with specific properties as low viscosity ( $10^{-2}$  to  $9 \cdot 10^{-2}$  mPa/s: 30 to 100 times lower than a liquid) and high diffusivity factor ( $10^{-2}$  to  $10^{-1}$  m<sup>2</sup>/s) allows a very high penetration into core material. In all cases, the smaller supercritical fluid molecules diffuse into porous and natural material as wood, cork, leather and so on. Therefore, large molecule as surfactant, PEG, can easily diffuse into natural material. In extraction, the similar properties allow specific and very high level of removing as PAH and CCA from wood or 2,4,6-TCA from cork. The supercritical fluid update tool, with these specific properties and, natural materials, distinguished by a porous structure and from very low to low density of: 20 kg/m<sup>3</sup> for cork, 50-80 kg/m<sup>3</sup> for wood and 90 kg/m<sup>3</sup> for leather, give a couple with a quasi perfect “partnership”. So, the works performed by our laboratory was also initiated for decreasing wastes, and the using of green solvent against classical and polluting processes as leather tanning, cork cleaning and wood recycling. All works are patented by CEA in relation with industrial companies and or technical institutes [1][2][3][4][5].

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