Case study

Safety-security

Skin decontamination using fuller's earth

Focus

Fuller's earth, a generic name for porous aluminum silicates, is a naturally occurring material known for its high adsorptive capacity, with many potential applications in skin decontamination. Used by the military in conflict areas, this reference product has been introduced in skin decontamination procedures for civilians in the event of accidental or criminal exposure to chemical, biological, radiological or nuclear (CBRN) agents.

Challenge:

Following the study carried out to evaluate the effectiveness of fuller's earth in skin decontamination [1], it became essential to identify the material's physicochemical characteristics as a next step to complement the supplier's data. The use of photonic techniques for its characterization was deemed relevant. Synchrotron techniques complemented conventional methods for the study of the different phases involved, the elemental analysis, the composition in metal oxides and the morphological structure. The signatures obtained and the reference criteria defined by the physicochemical characteristics of the analyzed sample of fuller's earth will make it possible to compare the different aluminum silicates. The creation of a label (or CE marking) would further guarantee its quality for skin application.

SOLEIL's solution:

The properties of synchrotron radiation [2], such as its brilliance and large spectral range, lead to enhanced signal-to-noise ratio, as well as high spectral quality and spatial resolution.

1. IR spectroscopy on the SMIS beamline, an infrared spectromicroscopy beamline operating in the 0.025 - 0.8 eV energy range (~ 1.5 - 100 µm), allows for the identification of molecular groups in amorphous or crystalline systems (their chemical functions and/or characteristic bonds) based on their specific absorptions in this spectral range.

2. Powder diffraction on the CRISTAL beamline, used for the study of single crystals and powders operating in the 4 - 30 keV energy range, allows the study of ordered-structure systems (in this case, polycrystalline). A powder diffraction pattern represents diffracted intensity of a sample versus scattering angle. Using a database, it allows identification of known crystalline phases within a mixture as well as quantitative analysis (proportion of the different phases). Structure solution (lattice parameters, atomic

Annick Roul (see interview), Erik Elkaim, Scientist on the CRISTAL beamline, Céline Lory, Officer in charge of Industrial Relations, during XRPD measurements carried out on the CRISTAL beamline.

A pillar of relief and crisis management in France, the Sécurité civile («Civil Security») aims at protecting the population, property and environment throughout the country. The Direction Générale de la Sécurité Civile et de la Gestion des crises («Directorate-General for Civil Security and Crisis Management», DGSCGC) contributes to national security and provides an effective and appropriate response to major events involving chemical, biological, radiological, nuclear or explosive (CBRNE) materials.

Annick Roul, Dr. in Pharmacy, Pharmacist, colonel within professional firefighters and Pharmacy advisor for civil safety.

I have always been very involved in CBRN risk management in the field, and more specifically in the decontamination of civilian populations due to exposure to dangerous toxic products. While conducting my PhD within the UMR 5305 joint research unit involving CNRS and University Claude Bernard Lyon 1, I chose to focus my research on the

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positions.) of an unknown phase can also be performed as well as microstructural analysis (crystallites sizes, deformation). Increased photons flux, high angular resolution and beam energy tunability are the main qualities of synchrotron radiation. High flux allows *in-situ* or operando studies while high resolution is favorable for complex structure solving and microstructure determination.

3. Scanning electron microscopy (SEM) on SOLEIL and IPANEMA's Zeiss SUPRA 55-VP-SEM, via the SE2 secondary electron detector for morphological images coupled with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis, was also used in combination with other conventional techniques (XRPD on the BRUKER D2 Phaser from SOLEIL's Chemistry Laboratory).

Obtained results

1. The high-resolution XRPD technique [3] on CRISTAL highlighted a major phase: palygorskite, also known as fibrous clay. Quartz (SiO_2) was revealed through the synchrotron analysis.

2. The IR analysis [4, 5] on the SMIS beamline confirms the presence of a major phase of palygorskite in the analyzed grains of fuller's earth, as well as the presence of additional components that will be investigated in future complementary studies. The characteristic peak at 3700 cm^{-1} (elongation of the OH bond) reveals

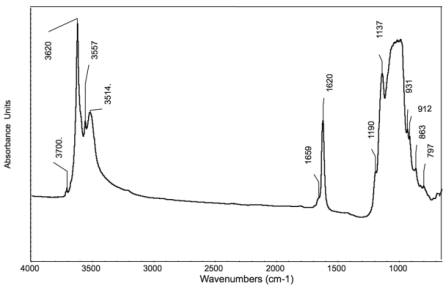

Figure 2: Infrared spectrum recorded on the SMIS beamline, in the 650 - 4000 cm-1 range.

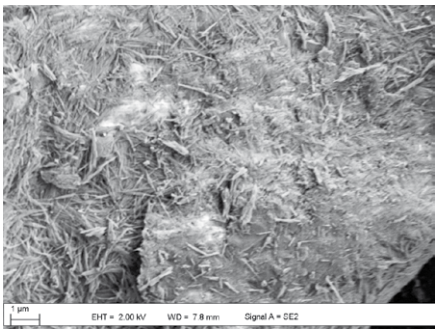

Figure 3: Image observed using SEM (SE2).

a lamellar layer structure with aluminums on the outer area.

3. The results of the SEM-SE2 analysis highlight the typical morphology of palygorskite (Figure 3).

The multimodal approach based on the use and combination of advanced and reliable techniques has allowed the characterization of the samples in their original state. Fast and discriminating visual data converge for all 3 techniques, and have led to the characteristic geological signature of palygorskite as the main component.

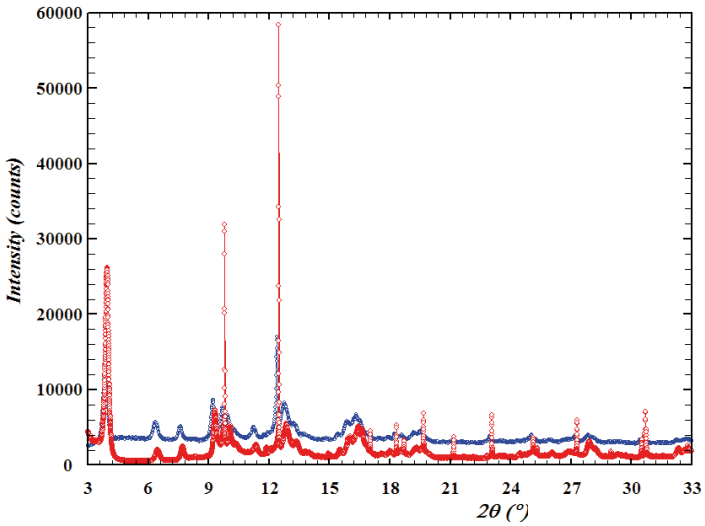

Figure 1: X-ray powder diffraction (XRPD) pattern of the sample of fuller's earth, first obtained at the Chemistry Laboratory (blue), and then on the CRISTAL beamline (red).

Focus/ follow-up

characterization of fuller's earth to obtain its geological signature and measure its effectiveness on the skin. The societal implications of the quality of skin decontamination had been identified by Paul Dumas, Researcher Emeritus and Scientific Advisor at SOLEIL, whom I met at the COBIP 2015 conference dedicated to skin biology. I immediately saw SOLEIL as a key partner due to the potential of the laboratory techniques it provides in connection with synchrotron radiation, and the expertise of its teams. The SOLEIL synchrotron facility gave me the opportunity to develop a set of fast, reliable and reproducible methods to guarantee a geological signature of this type of fuller's earth, it is a reference used to compare different types, which could be marketed. Following this first study, we have several projects moving forward: comparing different batches of fuller's earth, evaluating the equivalence of new powders with respect of its standard like in this study, and confirming its effectiveness and safety in decontamination procedures based on the study of the interactions between this type of fuller's earth and healthy or injured skin.

Acknowledgments: Erik Elkaim, CRISTAL's scientist, Paul Dumas, Distinguished Investigator of SOLEIL, Stéphanie Blanchandin, Head of the Chemistry Laboratory and Karine Chaouchi, Assistant Engineer of the Chemistry Laboratory, François Nicolas, Assistant Engineer of the Surfaces Laboratory.

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