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Methodology of conception of a CO₂-phile ligand for rare earth extraction using supercritical CO₂.

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Processes based on supercritical CO₂ (SCCO₂) media are attractive alternative to conventional liquid-liquid or pyrochemical processes using organic solvents for metals extraction from solid matrices, such as sludges, ores, or WEEE. SCCO₂ exhibits gas-like mass transfer rates and liquid-like solvating abilities. Its high diffusivity and low viscosity enable it to penetrate and transport solutes from porous solid matrices to the SCCO₂ phase, avoiding leaching or dissolution steps. Furthermore, its flexibility in terms of ability to adjust solvent strength by tuning operating pressure and temperature is quite interesting. Direct extraction of metal ions by SCCO₂ is inefficient due to its apolar nature and weak ionic solute-solvent interactions. Hence, organic ligands are needed in order to chelate these ions and make them soluble in SCCO₂. Such extractants must exhibit high stability, fast kinetics of complex formation with the metal to be extracted, high solubility in SC-CO₂ and high selectivity towards the targeted metal.

In order to improve their solubility, the functionalization selective molecules, based on amidophosphonates skeleton, has been initiated. The influence of linear and branched alkyl chains has been studied not only on the solubility but also on extraction capacity towards cerium. The addition of a hydrophile/CO₂-phile co-solvent has also been discussed. The most suitable operating conditions are pressure and temperature equal to (25 MPa; 313K). Moreover, the link between extractant structure to a molecular scale and macroscopic data (solubility, extraction yield) has been established using Small Angle X-Ray Scattering/SCCO₂ device. Such an analytical method allows us to elucidate formation of supramolecular aggregates and its influence on solubility and transport in SCCO₂.

This methodology will allow us to choose the most suitable extractant and operating conditions, avoiding trial and error strategy. Optimization of extractant and co-solvent amounts is also under progress with a view to pilot or industrial scale-up.