

Development of a new extractant system for rare earth extraction from WEEE in supercritical CO₂

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The supply of high valuable metals such as rare earths elements, indium or platinumoids from primary ores arises as a critical issue, especially because of the scarcity of geological resources or the geopolitical context. Facing this problem, Waste Electrical and Electronic Equipments (WEEE) can be considered as secondary raw materials ore, estimated at 11 Mt of valuable metals per year in Europe. In this context, the development of recycling and reuse processes will henceforward be a major industrial challenge. The current processes are based on mechanical treatment, leaching and hydrometallurgical or pyrometallurgical extraction and purification steps. An alternative to these processes consists of the implementation of supercritical fluids in a view to minimize water, chemicals and energy consumptions.

Supercritical CO₂ (SCCO₂) exhibits gas-like mass transfer rates and has liquid-like solvating abilities. Its high diffusivity and low viscosity enable it to penetrate and transport solutes from porous solid matrixes to the SCCO₂ phase. Furthermore, its flexibility in terms of solvating power by tuning operating pressure and temperature is quite interesting. Direct extraction of metal ions by SCCO₂ is inefficient due to charge neutralization requirement and weak ionic solute-solvent interactions. Hence, organic ligands are required in order to chelate these ions and make them soluble in SCCO₂.

A general methodology has been applied to study extractant/co-solvent/water system so as to extract cerium chosen as a model of rare earths elements. Extractant system must exhibit high stability, fast kinetics of complex formation with the metal to be extracted, high solubility in SCCO₂ and high selectivity towards the targeted metal cation. Homemade amidophosphonate ligands have been synthesized and studied here, replacing commercial extractants such as tributylphosphate or Cyanex.

Solubility measurements were carried out for temperatures ranging from 313 to 331 K and pressures ranging from 13 to 28 MPa. A ternary diagram considering extractant/co-solvent/CO₂ was established to determine the most suitable conditions with a view to extraction runs. By adding co-solvent (ethanol or isopropanol) and water in wise proportions, extractant solubility in SCCO₂ reaches 84.2 mmol.mol⁻¹. Thanks to this solubility increase, Ce extraction yields up to 82% were obtained using our experimental device.

Moreover, the influence of the nature of cerium deposits on cotton as a model substrate has been considered for cerium concentration ranging from 0.2 to 260 mg Ce per g of cotton. A model was created to link cerium concentration with the structure of deposits. This model was validated by SEM and SAXS measurements allowing to identify the shape and the mean thickness of Ce deposits. Highest Ce extraction yields are noticeable in the presence of Ce aggregates compared with Ce multilayers. Last but not least, rare earth extraction feasibility has been proved with quantitative extraction and collection yields and good selectivity towards cerium, neodymium, europium or gadolinium.

These promising results will be confirmed by rare earth extraction runs on primary ore or WEEE, before considering scale-up. The study of the behavior of the considered extractant system in SCCO₂ at a microscopic scale is under progress to elucidate the structure of the extractant system alone and in presence of Ce so as to explain solubility and extraction gain at a macroscopic scale. This study will help us understanding the role of co-solvent and/or water onto the structure of aggregates or "micelles" into SCCO₂, and to link this local structure to the extraction efficiency.