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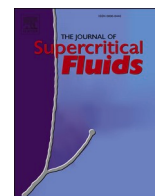
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Metals recovery by supercritical CO₂ processes: A focus on Li-ion battery metals extraction

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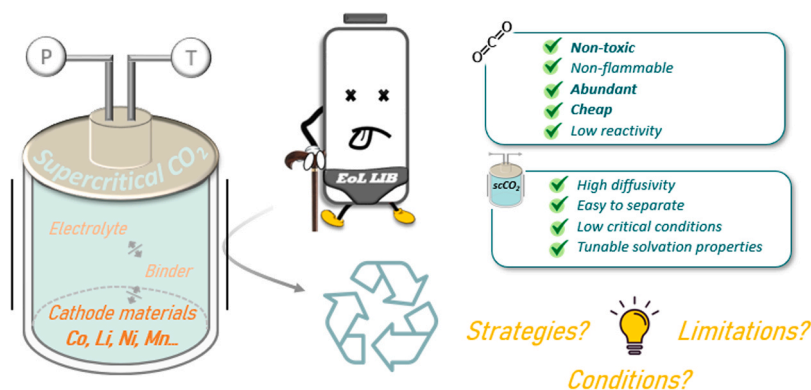
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HIGHLIGHTS

- Green recycling process using supercritical CO₂ (scCO₂).
- State of the art about the recovery of strategic metals from cathode materials for LIB recycling in the presence of scCO₂.
- Main parameters influencing metal extraction assisted by scCO₂.
- Challenges behind the use of scCO₂ as an innovative recycling process.

GRAPHICAL ABSTRACT



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ABSTRACT

As the demand for lithium-ion batteries (LIBs) continues to rise, recycling becomes essential to ensure a sustainable supply of critical raw materials while mitigating environmental impact. The European Union (EU) has set ambitious LIB recycling targets, emphasizing the need for innovative and cost-effective solutions. Although pyrometallurgical and hydrometallurgical processes currently dominate, emerging technologies such as supercritical carbon dioxide (scCO₂)-based extraction offer promising alternatives. Continued research and investment in LIB recycling infrastructures are crucial to supporting the energy transition and securing raw material independence in the coming decades. This review begins with a general overview of LIBs, their end-of-life processes, and the market and geopolitical context of LIBs and electric vehicles (EVs). It then briefly presents the interactions between CO₂ and solutes, which play a key role in determining the solubility of substances in scCO₂. In the following, the current and potential uses of scCO₂ in the field of LIBs are reviewed, with particular attention to the extraction of metal, which represents a crucial and promising application of this green technology. This focus highlights the unique features and specific challenges associated with metal recovery using scCO₂. The

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main parameters influencing metal extraction, such as pressure, temperature, co-solvents, and complexing agents, are discussed. Finally, recent advances in the extraction of the metals contained in cathode active materials using scCO_2 are presented.

1. Introduction

Over the past decades, various battery technologies have been developed to store energy through electrochemical reactions. Among them, lithium-ion batteries (LIBs) stand out as one of the most significant breakthroughs in electrochemistry. J. Goodenough, S. Whittingham, and A. Yoshino, pioneers of LIB development, received the Nobel Prize in Chemistry in 2019, and this technology has become dominant due to its efficiency and versatility. LIBs are crucial for sustainable development, particularly in the transition toward renewable energy and electric vehicles (EVs). The performance and cost of a LIB largely depend on the choice of materials used for the positive and negative electrodes, as well as the electrolyte.

The most commonly used cathode active materials (CAMs) in LIBs include lithium-containing transition metal oxides, such as LiCoO_2 (LCO), $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NMC), $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA, where $x + y + z = 1$) and LiMn_2O_4 (LMO), as well as polyanionic compounds such as LiFePO_4 (LFP) [1,2]. The choice of a CAM is essential for achieving high specific capacity, high working voltage, excellent cycle performance, enhanced safety, and cost-effectiveness [3,4].

LCO was the first CAM developed for LIBs in 1991 due to its high energy density. However, as demand for higher capacities and lower costs increased, NMC and NCA became the preferred materials for EV applications [2,5]. In 2022, NMC dominated the global EV market (60%), followed by LFP (30%) and NCA (8%) [6]. LFP, while having a lower energy density than NMC, benefits from lower production costs, greater durability, and enhanced safety [3]. The average composition of a LIB includes 2–15 wt% Co and 2–4 wt% Li for LCO and NMC, with NMC cells containing approximately 15 wt% Ni due to the use of Ni tape for cell connections [7,8].

LIBs are essential for reducing dependence on fossil fuels and

mitigating global warming. However, they also present challenges, particularly regarding hazardous waste management [9]. LIBs have a limited lifespan, estimated at approximately 10 years for EV applications, leading to concerns about the disposal and recycling of spent batteries [10].

The rapid expansion of the EV market led to a surge in LIB production [11,12], increasing from 13.8 GWh [13] in 2014–700 GWh in 2021 [14], with projections reaching 6800 GWh by 2030 [15]. At the same time, the global recycling capacity remains inadequate, with only 400 kt of recycled LIBs compared to the 1000 kt of spent LIBs expected by 2025 [16]. In Europe alone, 50 kt of spent batteries were recycled in 2023 but projections suggest that 420 kt (potential range from 200 kt to 800 kt) of end-of-life (EoL) batteries will need to be recycled in 2030, rising to 2100 kt by 2040. Initially, most LIB waste came from the consumer sector, but with the expansion of battery Gigafactories, production scrap will represent up to two-thirds of battery waste [17]. By 2035, EV batteries will be the primary source of spent LIBs requiring recycling [18].

The increasing demand for LIBs has heightened the need for critical raw materials (CRMs), particularly cobalt, lithium, nickel, manganese, aluminum, and copper. These metals are essential for the European Union (EU) energy transition goals, yet their availability is limited. For example, lithium production is concentrated in Australia (86 kt), Chile (44 kt) and China (33 kt) [19,20], while cobalt mining is dominated by the Democratic Republic of Congo, which accounts for two-thirds of the global resources [21].

To mitigate supply risks, the EU and other nations have classified certain metals as critical raw materials (CRMs, cf. Fig. 1) [22]. Lithium, cobalt, nickel, manganese, aluminum and copper are particularly vulnerable due to limited supply chains and geopolitical instability [23]. The price volatility of these metals also threatens the stability of the LIB market [24]. The demand for Li_2CO_3 is expected to rise from 116 Mt in

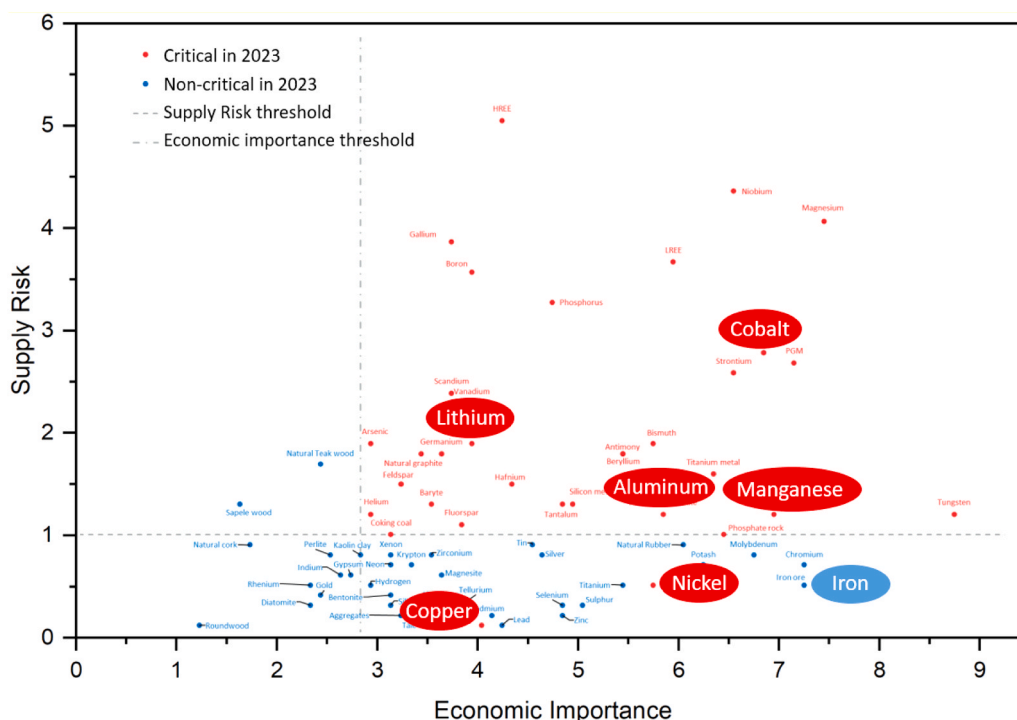


Fig. 1. Graphical representation of the EU critical raw materials list in 2023 representing the supply risk as a function of the economic importance [22].

2019–345 Mt in 2030 [25], with nearly 3/4 of the world lithium reserves located in South America [2]. This dependence on foreign sources threatens the sovereignty of countries without their own metal reserves.

Recycling spent LIBs is a crucial strategy for recovering valuable metals such as Co, Ni, Mn and Li [1], while mitigating the carbon footprint and other environmental (including biodiversity) and social burdens associated with mineral mining and refining for LIB production [26,27]. The CAMs production is the most carbon-intensive step in the LIB manufacturing process. These CAMs metals are found in LIBs at concentrations 10–1000 times higher than in natural ores [28,29]. Consequently, processing materials from LIB recycling through hydrometallurgy might lower greenhouse gas emissions from LIB production up to 50 %, depending on the region where the recycling is carried out [30]. As CAMs, where these metals are concentrated, represent the most valuable part of LIBs, recycling efforts mainly focus on their recovery [7]. Beyond addressing resource scarcity, economic and environmental assessments have shown that using recycled materials from LIBs is more beneficial than using virgin materials [31–34]. Additionally, recycling reduces the release of toxic pollutants from landfilled LIBs that contain harmful compounds, even though LIBs are considered less harmful than other battery technologies such as lead-acid and NiCd [35].

To promote sustainable LIB recycling, many countries are implementing regulations. As discussed earlier, metals from CAM are valuable resources and some countries need to improve their supply chain resilience by lowering their dependency on primary resources extraction from other regions. Depending on the resource accessibility, geopolitical situation, metals demand and economic strategies, regulations differ between countries. For example, the EU has implemented ambitious regulations targeting minimum levels of recycled materials in new batteries. The European directive (2006/66/EC), recently updated, mandated that by 2035, new batteries must contain at least 20 % recycled Co, 10 % recycled Li, and 12 % recycled Ni. Additionally, the EU aims to achieve a 65 wt% LIB recycling efficiency already by the end of 2025, with specific metal recovery rates of 95 % for Co and Ni, and 70 % for Li by 2030 [36,37]. This regulation is related to the low production capacity of the EU of lithium, cobalt and nickel, which are mainly located in Australia and Chile, Democratic Republic of Congo and Indonesia, respectively and to the volatility of their prices [38]. Regarding China and Australia, the regulations are focused on the Extended Producer Responsibility (EPR) that requires manufacturers to implement recycling proportional to their sales. China pushes traceability development, allowing an easier large-scale recycling process with a code system. In 2024, the Ministry of Industry and Information Technologies requested a recycling rate of a least 90 % for Li and 98 % for Ni and Co. In the US, although no federal law still exists, some federal programs are implemented to support the circularity of critical minerals (Battery and Critical Mineral Recycling Act of 2020 and 2021). A proposition to develop a “Battery Recycling and Second-Life Applications Program” aiming to support and award funds to the research, development, and application of advanced technologies has been made through the Infrastructure Investment and Jobs Act 2021. It should help increase the recovery rate and purity of critical minerals in EV batteries. In addition, programs for financial assistance have been implemented, such as the Inflation Reduction Act (2022), which offers tax incentives and grants to promote domestic EV battery recycling. The US Department of Energy also contributes to this promotion by funding projects with 192 million USD like the ReCell Center. Despite these funding attributions or incentives taxes, no specific recycling targets were defined by the US federal government. Unlike the EU, Japan does not have specific targets for EV battery recycling yet, but EoL LIB collection is encouraged via public campaigns, EPR is supported through the Act on the Promotion of Effective Utilization of Resources (1991) and legislation makes arrangements for hazardous waste and material treatment. South Korea supports the recycling of EoL LIB with financial rewards for companies exceeding recovery targets. India developed guidelines through its Battery Waste Management Rules in 2022 [27]. A global

harmonization of the regulation is still required as the LIBs market is built worldwide. Manufacturers and recyclers should work together to develop a common strategy to manage the traceability, the technical challenges of dismantling and optimize the required quality of the recycled products.

The European legislation is also accelerating the transition to EVs by mandating the phase-out of internal combustion engine vehicles by 2035. To achieve net-zero emissions by 2050, the International Energy Agency (IEA) estimates an EV stock of 350 million cars by 2030 [12]. Consequently, advancing LIB recycling technologies and infrastructures becomes more urgent than ever.

Inspired by the mining industry, several LIB recycling processes have been developed at the industrial scale. (i) Pyrometallurgy involves incinerating LIBs in a furnace at 1000 - 1400 °C. While Co, Ni, Cu, and Fe are recovered as alloys, Al and Li end up in the slag as oxides and are not recovered [39]. Although effective, this method does not produce battery-grade metal precursors and generates significant waste. (ii) Hydrometallurgy, a more refined process, recovers high-purity battery-grade metal precursors. It typically involves thermal pre-treatment to create the so-called black mass (BM), a mixture of metals, metal oxides and carbon. LIB cells are pyrolyzed at 500 °C to remove electrolyte, separator, binder and plastic components. During pyrolysis, the exhaust gases must be collected and neutralized to avoid environmental pollution. The pyrolyzed residue is then subjected to physical separation processes, including sieving and magnetic separation, to remove unwanted materials and to concentrate the species containing valuable metals. This metal-rich fraction, which represents the BM, is leached using aqueous solutions of inorganic acids (H₂SO₄, HCl or HNO₃), enabling the selective extraction of strategic metals via further separation steps. It must be noted that the black mass composition depends obviously on the chemistry of spent LIBs, and that in the case of CAMs with low Co concentrations, the recycling is hardly economically viable. Hydrometallurgy requires high chemical consumption but allows for the recovery of a greater range of metal precursors, which is more sustainable than extracting them from primary sources [40]. However, these two processes present several drawbacks summarized in Table 1. To support the LIB recycling industry, more sustainable alternative methods must be developed to reduce waste generation and minimize chemical usage.

One promising approach is the use of supercritical carbon dioxide (scCO₂) as a green solvent. scCO₂ is non-toxic, non-flammable [41], and easily separable after extraction processes, making it an environmentally friendly alternative to conventional solvents [42–46]. It possesses high diffusivity and adaptability, allowing efficient extraction of valuable compounds while minimizing chemical waste [47,48–50,41, 51–53]. Compared to other solvents (ethanol, T_c = 240.8 °C and P_c = 61.4 bar, or water, T_c = 374.1 °C and P_c = 221.2 bar), CO₂ has low critical conditions (T_c = 31.1 °C and P_c = 73.8 bar) demanding low energy consumption to be reached [54]. scCO₂ is also cheap due to its abundance. All these aspects make scCO₂ a suitable candidate for extraction applications.

scCO₂ has been widely used in the pharmaceutical [52], cosmetic [55,56] and food industries [57,58] for organic compound extraction (e.

Table 1
Disadvantages of current recycling technologies.

Pyrometallurgy	Hydrometallurgy
a. Li loss	a. Acidic wastewater
b. Low efficiency of Co and Ni recovery	b. High chemical consumption for selective extraction to obtain metal precursors
c. Energy-intensive	c. Toxic gas emissions from organic parts combustion during BM preparation and from leaching with inorganic acids
d. Requires hydrometallurgy to obtain battery-grade metal precursors	d. Costly process
e. Toxic gas emissions due to the combustion of organic parts	

g., decaffeination [59], cannabidiol (CBD) [60], essential oil extraction [58]). It has also been explored for soil decontamination [61,62] and sterilization [63].

However, its application in LIB metal recycling is still under investigation as metals are typically charged species that do not dissolve easily in scCO_2 . To overcome this limitation, researchers are exploring ways to complex metal cations with CO_2 -philic counter anions or use surfactants to transport CO_2 -phobic metal complexes [64]. Advantages of scCO_2 toward metals recycling will be presented later (Section 3).

Before starting the discussion, CO_2 interactions with solutes will be presented to discuss solubility in scCO_2 . Then, an overview of the scCO_2 application for LIBs will be performed. A focus on metal extraction will allow the introduction of the specificities and challenges related to this technology. The main parameters of metal extraction will be presented as well as an overview of scCO_2 extraction of metals present in LIBs.

2. CO_2 -solute interactions

To understand the solubility of ligands, metal complexes, and additives in scCO_2 , it is essential to examine their interactions with CO_2 . Solute-solvent interactions are often influenced by interrelated properties such as the polarity, polarizability and acidity. Since CO_2 is an apolar (dielectric constant between 1 and 2) and aprotic solvent, metal cations, complexing ligands (particularly ionic X-type ligands), and polarized functional groups that interact with metal cations tend to be especially CO_2 -phobic. The challenge in metal extraction using scCO_2 lies, therefore, in designing ligands with CO_2 -philic moieties that can interact favorably with CO_2 .

CO_2 -philicity, however, is not merely a function of hydrophobicity. CO_2 acts as a Lewis acid, interacting with electron-rich heteroatoms (O, N, S) and fluorine (F) due to its electron-deficient carbon [43]. Unlike apolar solvents such as alkanes, CO_2 interacts more strongly with functionalized hydrocarbons containing heteroatoms [65]. For example, CO_2 exhibits good affinity with fluorocarbons or carbonyl-based compounds due to its quadrupole moment generated by the symmetric polarization of the C=O bonds (Fig 2) [64,65]. Although CO_2 is a simple molecule, its interactions with solutes are complex and challenging to model [65].

Computational studies aimed at elucidating the nature of CO_2 -solute interactions, which are fundamental to understanding solubility behavior in scCO_2 systems. They have been well documented in the literature and key data are available in SI (cf. SI, section S2).

Predicting metal complex solubility using models remains challenging due to ligand diversity, metal nature (function, electron density), and the complex nature of the possible interactions with CO_2 . Computational works were also performed to study the factors around metal complexes that influence their solubility in scCO_2 (cf. SI, section S9 for more details about the simulation of metal complexes solubility).

To summarise literature discussions, an effective CO_2 -philic ligand

should possess heteroatoms capable of favorable Lewis acid-base interactions with CO_2 and feature groups increasing free volume (e.g., alkyl-branched chains, fluorocarbon groups) to minimize self-interactions. Metal ligand solubility in scCO_2 is moderate due to CO_2 low polarity. After complexation with a metal, the increased polarity and molecular size alter the interactions of the complex with CO_2 . Even though non-fluorinated small organic ligands can be highly soluble in CO_2 due to their low self-interactions, their solubility can significantly decrease upon metal complexation. Larger CO_2 -philic molecules may be more effective for achieving CO_2 -soluble metal complexes despite free ligand solubility limitations in scCO_2 .

CO_2 -solute interactions provide the basics for understanding extraction processes involving scCO_2 , particularly in the context of metal complexation relevant to LIB recycling. Before focusing on metal extraction, the next section reviews the current applications of scCO_2 technology in LIB recycling.

3. scCO_2 for LIBs recycling

This section highlights the general use of scCO_2 in LIB recycling, examining how this green technology can be applied to efficiently recover valuable components from spent LIBs. To date, scCO_2 has been mainly applied to electrolyte recovery and binder removal, offering a safer and more sustainable alternative to conventional processes. In contrast, the application of scCO_2 for metal recovery is limited. The challenges associated with metal extraction are discussed to shed light on the current low interest in this approach for recovering metals from CAMs.

3.1. Electrolyte recovery

To meet the European Commission target of 70 wt% recovery of spent LIBs by 2030 (cf. Introduction), all LIB components must be considered for recycling, including electrolyte and casing [66]. The electrolyte, which usually consists of a lithium salt (LiPF_6), organic carbonates (solvent, Fig. 3) and additives (Fig. 4), poses challenges due to its toxicity and flammability [67,68]. In conventional recycling processes, a thermal treatment is used to burn the organic components of the battery. This process, however, releases highly corrosive and toxic HF gas, requiring complex capture systems to protect workers [69,70]. Under these conditions, no electrolyte recovery is possible.

The electrolyte could be recovered by conventional solvent extraction, before the thermal treatment. In this case, however, multiple purification steps are necessary, increasing costs and waste generation, and eventually making the process economically unattractive [71]. A promising alternative is the use of scCO_2 , which offers a safer and more environmentally friendly approach. In 2017, Nowak *et al.* reviewed subcritical CO_2 (subCO_2) and scCO_2 technologies for LIBs electrolyte recycling [72]. These pioneering methods are summarized here, and complemented by insights from more recent studies on electrolyte extraction using scCO_2 .

Electrolyte extraction using scCO_2 under mild conditions has proven its efficiency. For instance, Grütze *et al.* [73] achieved a 73.5 ± 3.6 wt% extraction efficiency within 1 h at 40°C and 120 bar. To enhance recovery, a co-solvent can improve the solubility of electrolyte compounds in CO_2 . Additionally, adjusting pressure and temperature influences CO_2 solvation properties. The same team extracted 89.1 ± 3.4 wt% of the electrolyte with liquid CO_2 for 30 min at 25°C and 60 bar by adding acetonitrile/propylene carbonate (3:1 v/v) co-solvent mixture (0.5 mL/min, totaling 15 mL for 3 g of electrolyte) [74]. This method also extracts the electrolyte salt LiPF_6 . Liquid CO_2 outperforms scCO_2 due to its superior flow behavior, facilitating solute transport. Less polar and more volatile linear carbonates are extracted faster than cyclic ones [71,74,75]. However, the reclaimed electrolyte electrochemical properties and the possible contamination with the co-solvent have not been discussed in these publications. Rothermel *et al.* [76], also proved that

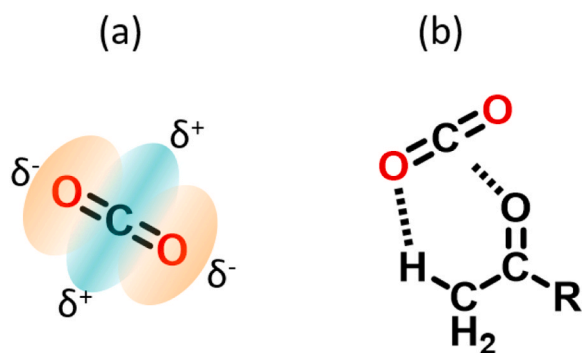


Fig. 2. Representation of the carbon dioxide quadrupole (a) and the Lewis acid-base interactions with a solute containing a ketone function (b).

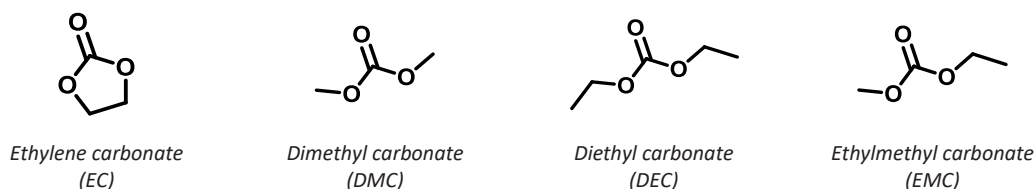


Fig. 3. The most used solvent in the electrolyte of LIBs. The solvent diversity is low because solvents need to be polar enough for dissociating Li salts and to be stable in a wide potential range (0–5.0 V vs Li^+/Li).

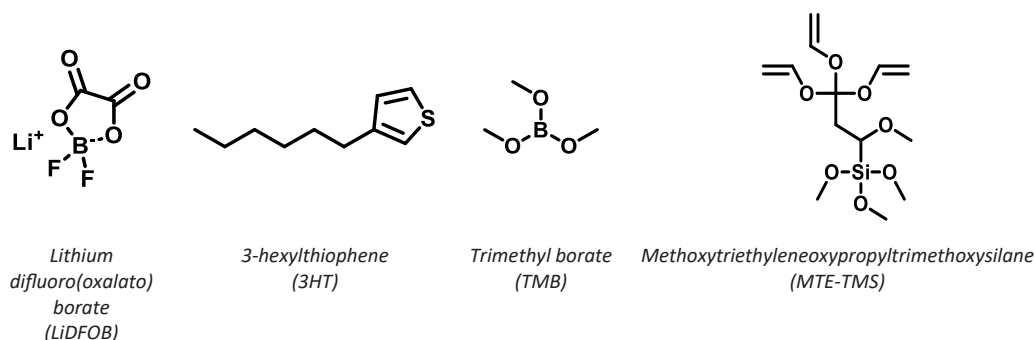


Fig. 4. Examples of additives used in the electrolyte of LIBs. Additives allow better stability in electrode/electrolyte interface and performance of LIBs.

liquid CO_2 preserves graphite crystallinity, ensuring stable electrochemical performance crucial for closed-loop LIBs recycling.

By optimizing the extraction conditions, Liu *et al.* [77] achieved an 85 % recovery yield at 40 °C, 234 bar over 45 min. Unlike Rothermel *et al.* [76], they did not study liquid CO_2 , which explains why their optimal conditions fall within the scCO_2 temperature and pressure range. Their research indicated that pressure was the most influential parameter in carbonate extraction [77]. This finding was reinforced in a more recent study by the same group, which identified CO_2 flow during dynamic extraction as the most critical factor. However, this observation applied specifically to scCO_2 . In contrast, Grütze *et al.* [74], working with liquid CO_2 , reported that pressure had little impact on extraction efficiency. Pressure modulation does not act similarly in the liquid or scCO_2 regions. Interestingly, Mu *et al.* [78] later reported similar results to Grütze *et al.* [74], showing that liquid CO_2 leads to the highest extraction efficiency. At 70 bar, temperatures exceeding 30 °C led to decreased extraction efficiency, with pressure being the major influencing factor. Liquid CO_2 offers advantages over scCO_2 , including lower energy consumption and the ability to extract LiPF_6 . Notably, without co-solvents, LiPF_6 salt is not extracted (or at least not reported) when using scCO_2 .

Liu *et al.* [71] characterized the recovered electrolyte from LIBs using scCO_2 under mild conditions (40 °C, 150 bar for 10 min, followed by a 20 min dynamic extraction). They achieved approximately 85 % extraction yield. However, water traces during extraction led to the hydrolysis of the PF_6 salt anion and the formation of HF, which can corrode electrodes and current collectors. Another byproduct, HPO_2F_2 may contaminate the recovered electrolyte. To limit the HF concentration below 50 ppm, the extracted electrolyte undergoes purification using anion exchange resin and molecular sieves. LIB performance tests compared the recovered electrolyte with commercial alternatives. At 20 °C, the ionic conductivity of the recycled electrolyte is $0.19 \text{ mS}\cdot\text{cm}^{-1}$ compared to $0.25 \text{ mS}\cdot\text{cm}^{-1}$ for the commercial one. The stability window is also slightly lowered to 5.4 V vs Li^+/Li , compared to 5.7 V vs Li^+/Li for the commercial electrolyte. Furthermore, a capacity retention of 66 % was observed after 100 cycles at 0.2 C, compared to a retention 85 % for the commercial electrolyte. This decreased performance likely results from electrolyte decomposition and the presence of HPO_2F_2 which may further hydrolyze to produce HF, phosphoric acid, and fluorinated phosphates [79]. Nonetheless, these results demonstrate that electrolyte

recycling is feasible using a low-cost solvent without the use of additional extractants, positively contributing to the development of closed-loop LIB recycling processes.

Extracting the electrolyte using subCO_2 or scCO_2 has the advantage of avoiding the degradation of CAMs. Sloop *et al.* [80] studied the re-lithiation of LCO after electrolyte extraction by scCO_2 , shredding of the electrolyte-free cells and sieving to recover the LCO mixed with carbon black, binder and graphite. The LCO, relithiated *via* a hydrothermal process in aqueous solution, provided convincing electrochemical properties. While graphite was also recovered, its electrochemical performance was however found to be suboptimal.

3.2. Binder removal

An additional advantage of subcritical and scCO_2 is its ability to remove the binder, enabling the separation of the CAM from the current collector.

The most common binder for electrode materials in LIBs is poly(vinylidene fluoride) (PVDF) [81]. This binder must be removed to facilitate the leaching of metals from CAMs, as the binder aims to retain the CAM on the current collector. Currently, this binder is burned during the already described heat treatment of conventional LIB recycling processes, leading to the production of black mass and the emission of toxic chemicals and exhaust gases (including fluorine organic compounds and HF) [82]. In addition, this method is highly energy-intensive due to the high temperature required (> 300 °C) [83]. Cryogenic grinding and ultrasonic treatments can separate CAMs from the current collector without emitting toxic compounds, but the binder remains together with the CAMs, and these processes are not yet industrialised [84]. Solvent-based methods for dissolving the binder have been developed to avoid toxic emissions, but the best solvent for PVDF is N-methyl-2-pyrrolidone (NMP), which is highly toxic. Moreover, recovering NMP requires filtration and thermal treatment steps that generate secondary pollution [69]. Recently, scCO_2 has been studied for binder removal due to the high diffusivity, low cost and solvation properties for organic compounds.

Mu *et al.* [69] successfully removed 98 wt% of active materials (LCO) from the aluminum current collector using scCO_2 at 38 °C and 100 bar for 15 min. A beneficial impact of the temperature was observed up to 38 °C. Above this temperature, binder removal is not affected, but

electrolyte extraction efficiency decreases. They also demonstrated that scCO_2 is more efficient for binder removal than traditional pyrolysis, with fewer Al impurities in the scCO_2 process.

Fu *et al.* [13] also studied scCO_2 assisted extraction of PVDF, with the addition of dimethyl sulfoxide (DMSO) as a co-solvent. 98 wt% of the binder (0.5 g initially) was dissolved at 70 °C and 80 bar for 13 min with 4 mL DMSO. At atmospheric pressure, the extracted PVDF remains in suspension in the DMSO and is then separated by centrifugation, allowing DMSO to be reused for further extraction cycles. *In situ* FT-IR spectra confirmed the dissolution of PVDF in the scCO_2 /DMSO system. Below 60 °C, however, binder removal was not efficient. To demonstrate the usefulness of scCO_2 , an experiment was performed to dissolve PVDF in DMSO at atmospheric pressure and 60 °C for 13 min, resulting in only 8 % PVDF removal.

To conclude, using scCO_2 as a solvent allows for the quick separation of CAM from organic binders and thus from the current collector due to the high diffusivity of CO_2 and its ability to solubilize/swell the PVDF binder. This process minimizes waste generation from organic solvent use and the release of toxic fluorinated compounds. The removed PVDF binder can be reused as no chemical changes are induced by scCO_2 [13].

3.3. Anode recovery

The anode materials of LIB mainly consist of graphite due to its good conductivity, high specific capacity, low working potential vs. Li^+/Li leading to high voltage in full cells, no serious volume change during cycles, stability and low-cost. Despite the abundance of carbon elements, the graphite structure production is energy-intensive and natural carbon graphite refining is mainly based in China. Consequently, carbon graphite is now considered a critical raw material by the EU [22].

Like CAMs, graphite-based electrodes are directly casted on a current collector, which is primarily a copper sheet for the anode. To ensure adhesion to the current collector, a binder is used, mainly corresponding to a styrene butadiene rubber/carboxymethyl cellulose composite [81]. Therefore, the main challenge to recover graphite is remove the binder to release the graphite powder. There is no need to leach as it is the case for CAMs that are composed of many metals. Currently, graphite is not recovered in the industrial recycling processes, $\text{C}_{(g)}$ is used as a reducing agent for some roasting processes. Consequently, it is oxidized to carbon dioxide or carbonate, which does not enable its reusability as $\text{C}_{(g)}$. The use of flotation is a promising approach to separating the graphite from the other components of a Black Mass. However, an efficient flotation requires graphite particles free from binder [85].

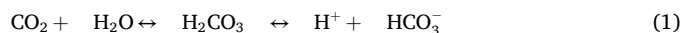
Only a few studies discussed the graphite recovery due to its low economic value. Currently, recycling processes of anode materials mainly focus on impurities removal (organic compounds and metals) and regeneration. Metals impurities are leached using concentrated inorganic acid or alkaline solutions and organic materials like binders and electrolyte are decomposed by pyrolysis. Then, the graphite is regenerated by roasting [86,87]. One study investigated the use of subCO_2 and sc-CO_2 for its recovery in comparison with a thermal treatment process. Rothermel *et al.* [76], as discussed earlier in Section 3.1, explained that subCO_2 allowed removing residual electrolyte from aged graphite obtained by shredding, which is beneficial to recover electrochemical characteristics after a thermal treatment. The authors also observed that lithium and phosphorus elements are removed during the electrolyte extraction using CO_2 . Subcritical CO_2 is preferred compared to scCO_2 as high pressure is assumed to decrease the graphite crystallinity and therefore its electrochemical properties.

3.4. Cathode active materials recycling

CAMs, which contain high-value strategic metals, are also among the LIB components studied for recycling using scCO_2 . In fact, CAMs are considered a valuable source of secondary raw materials with a high value (urban mining). Currently, to facilitate the synthesis of new CAMs,

metals must be selectively extracted to obtain battery-grade precursors. This section presents the contribution of scCO_2 to the conventional hydrometallurgical metal extraction from spent LIBs.

Bertuol *et al.* [88] developed a process combining a traditional leaching system in hydrometallurgy ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$) with scCO_2 for metals extraction from LCO. This process (Fig. 5b) does not correspond to scCO_2 extraction, as no CO_2 -soluble compounds are used to dissolve the metals or form swollen reverse micelles (water-in- CO_2 micro-emulsion) for metal transportation, and the metals remain in the aqueous phase. However, high extraction efficiency is achieved with 95.5 % of Co extracted within only 5 min. The authors highlighted the benefits of scCO_2 by comparing leaching experiments under high pressure (CO_2) and atmospheric pressure. The leaching rate is approximately 10 times faster for a system using scCO_2 , even when using a lower concentration of H_2O_2 as a reducing agent (Fig. 5a). Indeed, CO_2 acidifies the aqueous phase (Fig. 6) through the formation of carbonic acid (Eq. (1)) [89–91]. The specific influence of scCO_2 in aqueous leaching with H_2SO_4 , however, was not further discussed.



Zhang *et al.* [93] studied the extraction of Co, Ni, Mn and Li from NMC CAMs, by adding a tributylphosphate-nitric acid (TBP- HNO_3) adduct to H_2O_2 in scCO_2 . The TBP- HNO_3 adduct is a well-known system for metals extraction, and it has been largely studied for nuclear waste decontamination [94–97] and more recently for magnet recycling [98–100]. In this system, HNO_3 serves as a proton source for NMC leaching. Once leached, the generated metal cations are complexed with TBP, a Lewis base with CO_2 -philic character. TBP acts as a surfactant, aiding in the stabilization and transportation of the metal complex in scCO_2 . H_2O_2 is a reducing agent which reduces Co^{3+} and Ni^{3+} to Co^{2+} and Ni^{2+} , improving their extraction efficiency by forming stable complexes (Fig. 7b). The reduction with H_2O_2 (4 vol% in CO_2) allows increasing the extraction efficiency by 20 % (Fig. 7a), achieving maximum yields of 89 %, 90 %, 90 % and 89 % for Li, Co, Mn, and Ni, respectively, after only 10 min, significantly faster than traditional hydrometallurgical processes [101]. While no selectivity vs. a specific metal is achieved using the TBP- HNO_3 system in scCO_2 , a higher amount of HNO_3 improves the leaching efficiency, possibly through the increase in the H^+ concentration. The increase in HNO_3 concentration, however, must be accompanied by a proportional addition of TBP to stabilize the complexes.

More recently, Vauloup *et al.* developed a new strategy using a CO_2 -soluble leaching agent [102]. An easy method to synthesize such compounds is the copolymerization between a complexing monomer and a CO_2 -philic monomer. They obtained a CO_2 -philic gradient copolymer containing phosphonic diacid complexing groups (poly(vinylbenzylphosphonic diacid-co-1,1,2,2-tetrahydroperfluorodecylacrylate), p(VBPDA-co-FDA)). This system allowed the extraction of lithium and cobalt from LCO by playing a triple function: leaching agent, complexing agent and surfactant (Fig. 8). Two extraction systems were investigated with this copolymer: the first employed aqueous hydrogen peroxide as a reducing agent, while in the second, it was replaced by ethanol. Depending on scCO_2 extraction conditions such as extraction time, temperature, copolymer concentration, and the presence of additives, extraction efficiencies of up to ca. 75 % for both Li and Co were achieved at 60 °C and 250 bar.

Leclaire *et al.* also worked on metal recycling from CAMs using CO_2 but not under supercritical conditions. In this process, based on CO_2 capture technologies, compressed CO_2 gas (3 bar) reacts with amines in a ball mill to form carbamates that can then complex metals. Selective recovery of metals is possible by exploiting the differences in association properties of carbamates with metals. Two patents were filed for this process [103,104]. The principle is described in more detail in the work of Septavaux *et al.*, although it does not focus on LIBs recycling but rather on that of the $\text{La}_2\text{Ni}_9\text{Co}$ alloy [105]. Ni and Co selectivity is

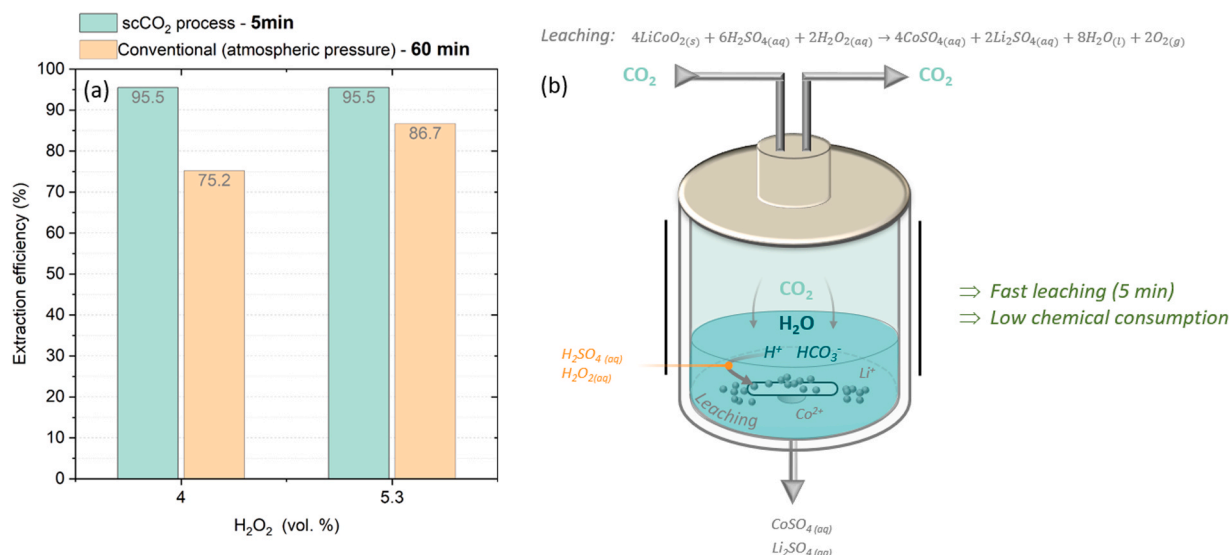


Fig. 5. (a) Cobalt extraction efficiency from LCO leaching with H₂SO₄-H₂O₂ system (assisted by scCO₂ at 75 bar (blue) and under atmospheric pressure (orange)) with different concentrations of H₂O_{2(aq)}. (2 M H₂SO₄, 75°C, solid-liquid ratio of 1/20 g.mL⁻¹). (b) Representation of the leaching/extraction process in scCO₂ using H₂SO₄-H₂O₂ aqueous system.

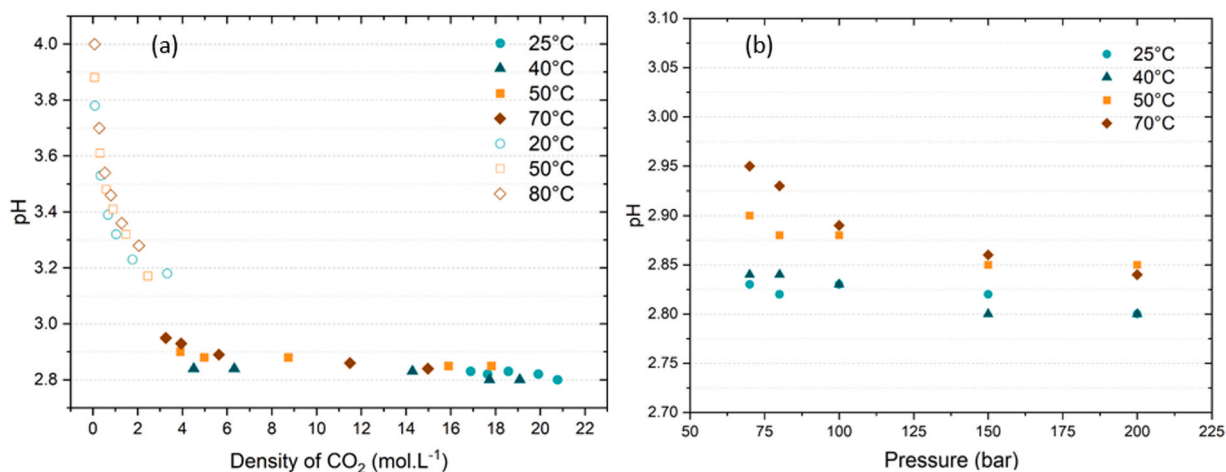


Fig. 6. pH evolution of the water in CO₂ as a function of CO₂ density (a) and pressure (b). The graphs are built with Haghi et al. [92] (hollow symbols) and Toews et al. [89] (full symbols).

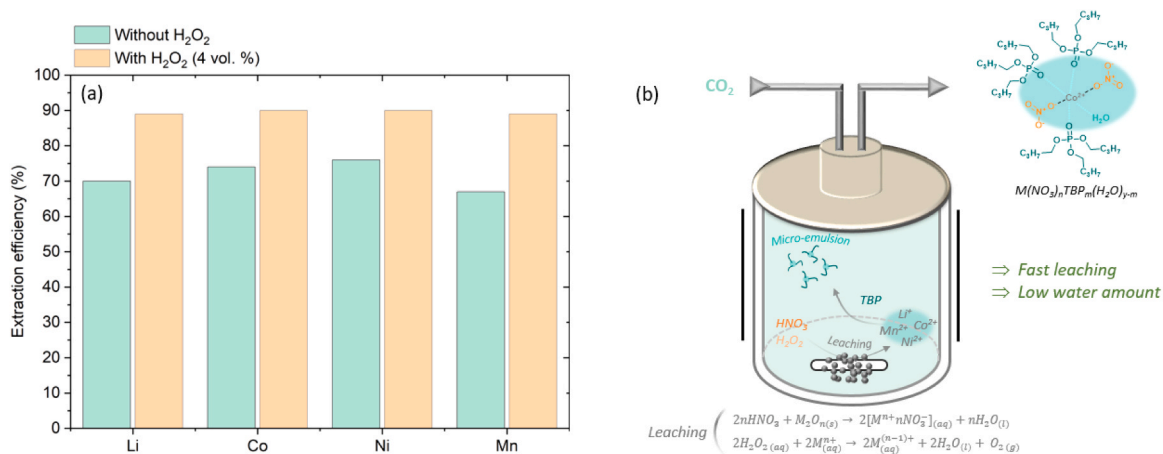


Fig. 7. (a) Metal (Li, Co, Ni, Mn) extraction efficiency from NMC leaching assisted by scCO₂ with TBP-HNO₃ system with and without H₂O₂ (60°C and 310 bar for 10 min with 5 mL.g⁻¹ (mL of TBP/HNO₃ per g of NMC)). (b) Representation of the leaching/extraction process in scCO₂ using TBP/HNO₃ + H₂O_{2(aq)}.

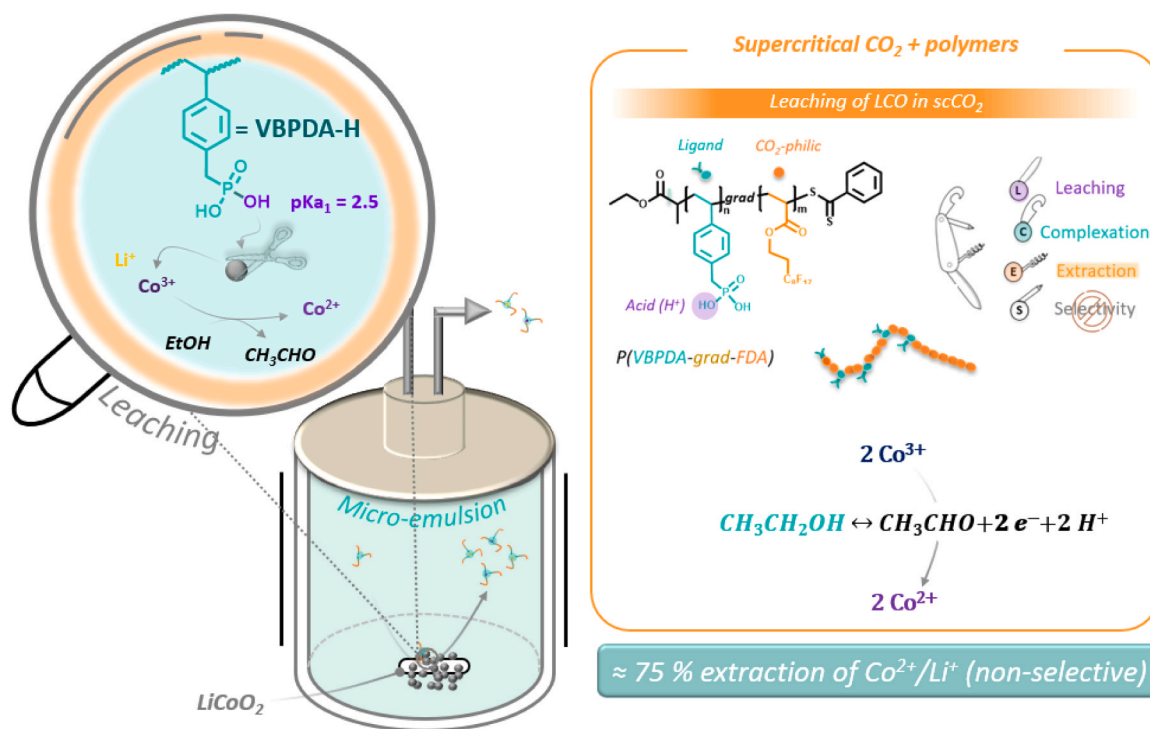


Fig. 8. Representation of the leaching/extraction process in scCO₂ using the CO₂-philic complexing copolymers p(VBPDA-co-FDA) and ethanol as a reducing agent.

highlighted when varying the amount of CO₂.

Currently, little attention has been paid to metal extraction from LIB CAMs using scCO₂. The processes involving scCO₂ combine systems developed for hydrometallurgy under atmospheric pressure and scCO₂. CAM leaching requires acidic conditions to enable both the solubilization and complexation of metal cations. Hydrometallurgy principles associated with scCO₂ properties can help limit wastewater generation and chemical consumption. However, the limited interest in scCO₂-based methods is largely due to the substantial equipment investment required compared to conventional hydrometallurgical processes. Moreover, operating with high-pressure solvents requires specialized expertise, and the stainless-steel reactors typically used under scCO₂ conditions are susceptible to corrosion.

3.5. Conclusion

So far, most studies on LIB recycling using scCO₂ technology have focused on electrolyte extraction. To date, only a few publications have dealt with the recycling of strategic metals from spent LIBs, despite many studies on the extraction of metals from CAMs using scCO₂ (cf. Section 4.3). It is noteworthy that, unlike in the case of CAMs, most metal extraction studies using scCO₂ involve metals already in their cationic form, eliminating the need for a leaching step. Nevertheless, scCO₂ can be seen as a good candidate for assisting metal leaching in the presence of water due to water acidification. This property is beneficial when scCO₂ is used to support aqueous leaching. In this case, however, scCO₂ is not a solvent.

The only systems that allow leaching in scCO₂ with CO₂-philic compounds are the TBP-HNO₃ adduct, where TBP can solubilize HNO₃ (H⁺ source), and the gradient copolymer p(VBPDA-co-FDA), where the phosphonic acid unit (H⁺ source) is solubilized by its co-monomer. So far, p(VBPDA-co-FDA) is the only CO₂-soluble X-type ligand described in the literature which is able to leach CAMs in scCO₂. A limitation that may explain this lack is that metal cation extraction with X-type CO₂-philic ligands is efficient when the ligand is deprotonated. For example, organophosphorous ligands such as Cyanex 272® are more efficient for metal extraction when a Brønsted base is added to enhance

complexation ability (cf. Section 4.2.3.4). Therefore, for X-type ligands, the conditions for efficient leaching (high concentration of H⁺) are in contrast to those needed for efficient complexation in scCO₂.

Considering the recycling of strategic metals from LIBs, scCO₂ extraction can be envisioned as a separation step after the leaching of CAMs or black mass to selectively recover metals. For example, it can be used as a green solvent to replace liquid-liquid separation steps or precipitation, thereby limiting atom consumption, waste generation, and the use of toxic compounds. Key parameters from metal extraction from CAMs may be applied to the recycling of LIBs. Adjusting solvation strength by varying operating temperature and pressure can also support the selective extraction of metals [106].

From these observations, different routes can be defined and investigated for recycling strategic metals from LIBs using scCO₂:

1. Develop CO₂-philic ligands bearing selective complexing groups and acidic functions. The goal is to replace conventional leaching in aqueous solution using a high concentration of acid, combined with a selective metal extraction due to the affinity difference between the complexing group and metals.
2. Develop CO₂-philic ligands bearing unselective complexing groups and acidic functions. The goal is to replace conventional leaching in aqueous solution using high concentrations of acid to limit wastewater generation [102].
3. Leach CAMs in aqueous solution under scCO₂ conditions as developed by Bertuol *et al.* [88].
4. Develop CO₂-philic ligands with a selective complexing group to extract previously leached metals. The goal is to replace conventional separation methods to reduce hazardous organic solvents and extractant consumption.

Supercritical water has also been investigated for CAM leaching but this supercritical fluid will not be discussed here (cf. SI, section S10 for additional information). scCO₂-based processes represent a promising technology to avoid or limit acid wastewater production, decrease chemical and organic solvent consumption, and allow easy separation of extraction reagents from the solvent by decompression. The following

sections will focus on metal extraction, providing a comprehensive overview of the factors influencing extraction efficiency. These sections are designed to complement each other, providing a deeper understanding of the challenges of metal extraction. First, various extraction systems are briefly described. Then, the key parameters and their influence on extraction efficiency will be discussed. Finally, an overview of the optimal conditions for extracting metals from CAMs will be presented.

4. Metal extraction in scCO₂ or assisted by scCO₂ and perspectives for CAM recycling

Since the second half of the 20th century, the feasibility of using

scCO₂ for metal extraction has been largely discussed in the literature, particularly in the context of nuclear waste treatment [107–114]. This extraction technology is also used for depolluting wastewater contaminated with heavy metals from various industries such as steel, mining, pigment, fertilizers, printing, and photography [108]. scCO₂ may be useful for treating incinerator fly ash [115] and recycling valuable metals from heterogeneous catalysts [116], waste from electrical and electronic equipment (WEEE) [117,118], batteries [93], and photovoltaic panels [119]. This technology has been explored for metal extraction in waste treatment due to its good diffusivity and safety features (non-toxic, non-flammable). Several reviews on metals extraction using supercritical fluids have been published [120–124]. Reviews on the supercritical extraction of metal chelates [122] and the solubility of

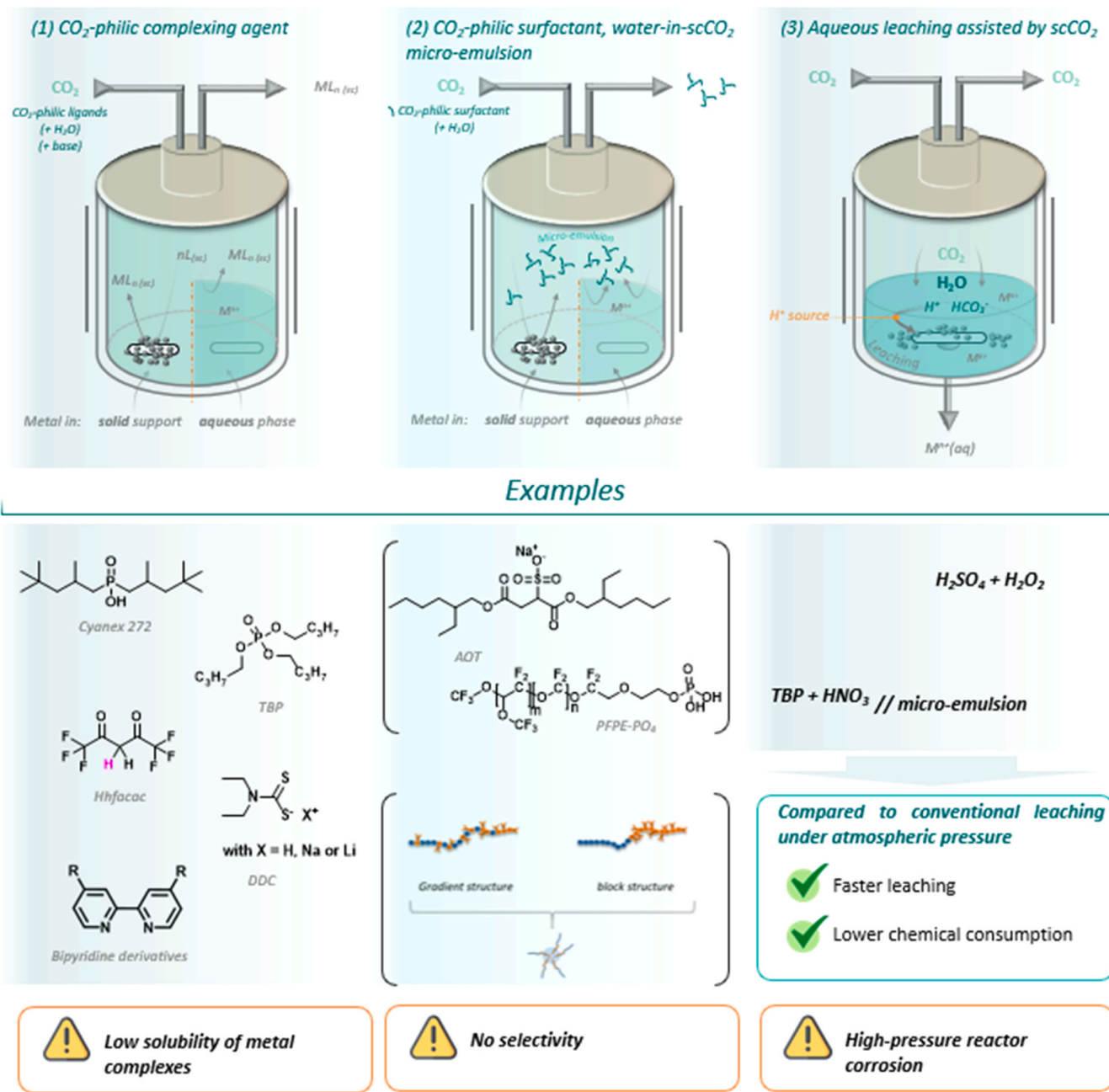


Fig. 9. Systems for the extraction of metals using scCO₂ with examples. (1) CO₂-philic complexing agents to solubilize and transport metals. (2) CO₂-philic surfactants to convey metals contained in the aqueous phase by (micro)emulsion formation. (3) scCO₂ to assist the leaching of metals in an aqueous phase. Note: TBP: Tri-n-butylphosphate, Hhfacac: Hexafluoroacetylacetone, DDC: Diethyldithiocarbamate, AOT: sodium bis(2-ethylhexyl) sulfosuccinate, PFPE-PO₄: perfluoropolyether-phosphate ester.

organometallic complexes in scCO₂ [64] are also available. More recently, Bertuol *et al.* [123] focused on WEEE, and Wu *et al.* [124] reviewed the recovery of valuable metals from solid wastes. This section summarizes the key metal extraction systems (*cf.* Section 4.1) and the parameters influencing extraction efficiency (Section 4.2), focusing on metals contained in LIBs (Li, Co, Ni, Mn, Cu and Fe). Unlike previously published reviews, an exhaustive overview mainly focused on scCO₂ extraction of metals from LIBs will be provided.

4.1. Different systems for extracting metals in scCO₂

The positive charges of metal cations make them insoluble in scCO₂, which is an apolar solvent with a low dielectric constant ($\epsilon = 1\text{--}1.52$ at 40 °C for a pressure range of 1–215 bar) [51,125]. To extract metal cations, different systems can be implemented, such as: 1) using CO₂-philic complexing agents to solubilize and transport metals; 2) introducing CO₂-philic surfactants to convey metals contained in the aqueous phase or a solid support through (micro)emulsion formation; 3) leaching in an aqueous phase assisted by scCO₂, which does not act as the solvent. These systems are represented in Fig. 9. It is noteworthy that each system has its own specificities. The extraction parameters act differently whether a micro-emulsion is used or small CO₂-soluble organic ligands are employed. The presence of an aqueous phase also influences the complexation ability due to the reactions that occur in this phase. Below is a short introduction to the different systems presented in Fig. 9. A more detailed discussion is available in the Supporting Information.

Regarding the system using CO₂-philic complexing agents to solubilize and transport metals (1), a variety of chemical species, including β -diketonates [126,127], dithiocarbamates [108,128], organophosphorous compounds [61,93,96,99,100,118,129–134], pyridine derivatives [116,135–139], carboxylic acids [48], and others have proven their efficiency. The complexing units for metal extraction in scCO₂ have already been reviewed by Ding *et al.* in 2016 [122]. An updated overview of CO₂-philic ligands classified according to the nature of their complexing functions is provided in the Supporting Information (*cf.* SI, section S4). As metal complexes using small organic ligands still present a low solubility in scCO₂, systems with micro-emulsion (2) are developed using mainly fluorinated surfactants (*cf.* SI, section S5) [140,141,111,142–146,112]. The last system (3) differs from the others as scCO₂ is not used as a solvent, but rather as a controlled atmosphere to support leaching in an aqueous phase due to water acidification, as discussed in Section 3.4 (*cf.* SI, section S6 for more details) [88,117,147–149].

There is no ideal process for recovering metals using scCO₂. The choice of the system will depend on the initial matrix of the metal to recover, as well as the purpose of the extraction: decontamination, recycling or separation. In the case of CAM recycling, a large amount of metals should be recovered to tend toward a viable recycling process. Consequently, the system (1) could be relevant as a separation step after an unselective leaching with a highly CO₂-soluble and selective ligand. The system (2) allows for performing a leaching with a low amount of water. However, the selective extraction is more challenging as metal cations can be unselectively transported in the aqueous core of the micelle. Finally, the system (3) can be perceived as an upgrade of the conventional leaching process where CO₂ allows reducing acid consumption and process time.

4.2. scCO₂ metals extraction parameters

In this section, the influence of extraction parameters on metal extraction in scCO₂ is discussed in order to identify possible general trends. These discussions are required to understand the conditions presented in Section 4.3 dealing with the extraction of metals present in LIBs. There are no universal trends for parameters to improve the metal extraction efficiency. Depending on the extraction system used (*cf.* Section 4.1), the parameters will act differently on the extraction

mechanism.

4.2.1. Temperature, pressure and CO₂ density influence on metal extraction

To illustrate the influence of pressure (P) and temperature (T) on metal extraction in scCO₂, the discussion is organized according to the three extraction systems described in Section 4.1, as their behavior may vary.

4.2.1.1. Metal extraction with CO₂-soluble ligands. In addition to the nature of the complexing agent, P and T are the two main parameters governing the extraction ability of metal complexes. Modifying P and T allows for the modulation of CO₂ density that governs solubility. For the most commonly studied pressure range, between 100 and 300 bar, the solubility of ligands and complexes generally improves when pressure increases (at constant T) [64,126]. This is explained by the increase in scCO₂ density (Fig. 10), which enhances its ability to dissolve solutes [150]. The working pressure can be determined by the apparatus limitation (P_{\max}) or chosen to limit energy consumption as the density variation is not linear with pressure and reduces at higher pressures (*e.g.*, at 40 °C, on increasing P from 75 to 150 bar, the density increases from 0.2315 to 0.7802 g.mL⁻¹, whereas from 150 to 300 bar the density only further increases to 0.9099 g.mL⁻¹).

In the case of temperature, the relationship between the solubility of metal complexes and/or extraction efficiency is not straightforward and requires a more detailed discussion. Many phenomena occur when temperature varies, and the prevalence of these phenomena depends on the working pressure as well as the extraction system (CO₂-philic ligands for complexation of metal cations in scCO₂, water-in-scCO₂ micro-emulsion, or aqueous phase assisted by scCO₂ for leaching).

For the system with CO₂-philic ligands for complexation of metal cations, when P is kept constant, increasing T lowers the CO₂ density (Fig. 10) and decreases the solubility of CO₂-philic solutes [48,136]. For example, the extraction of Co²⁺ and Ni²⁺ with pyridine derivatives with oligo-vinyl acetate (PVAc-bpy) ligands ($n = 14$, Fig. 11) at 25 °C is significantly better than at 50 °C due to the lower macro-ligand solubility at 50 °C. In fact, at 25 °C, the cloud points (*cf.* SI section S7 for cloud point definition) of OVAc-Bpy are below 220 bar, whereas it is above 300 bar at 50 °C. At 250 bar, the extraction efficiency at 25 °C is 98 % and 88 % for Ni²⁺ and Co²⁺, respectively, whereas it is less than 10 % and 20 %, respectively, at 50 °C [151].

Otherwise, increasing the temperature leads to an increase in vapor pressure saturation of the solute (ligand), which may help its dissolution. This observation is mainly confirmed for small ligand molecules, as the vapor pressure for large ligands such as PVAc-Bpy ligand is very low.

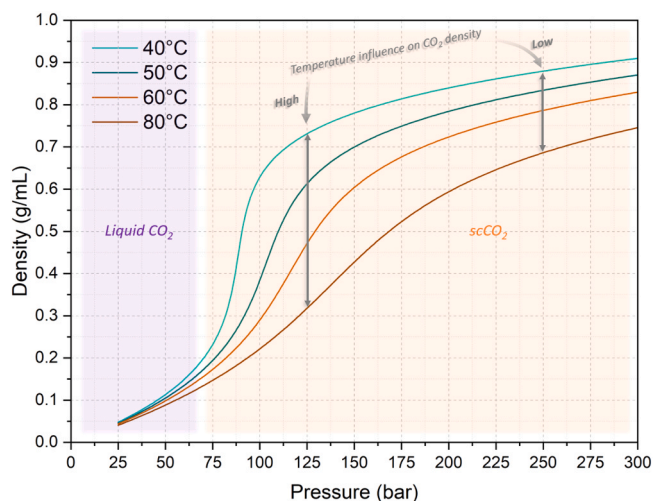


Fig. 10. CO₂ density as a function of pressure at 40, 50, 60 and 80 °C (from NIST standard reference data).

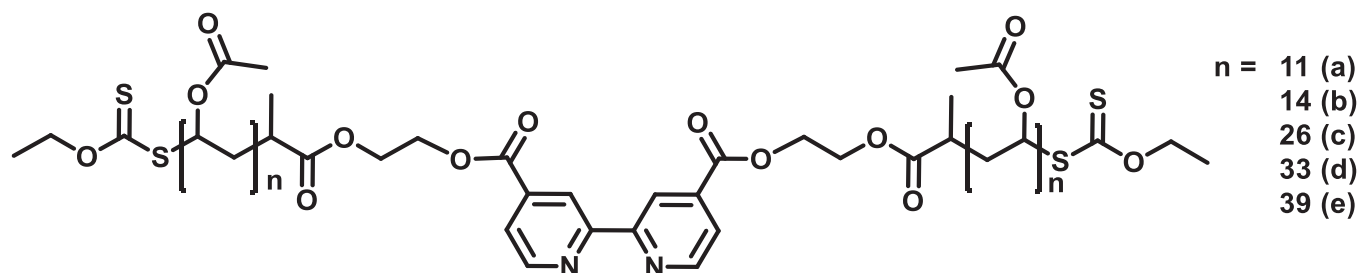


Fig. 11. Bipyridine derivatives with oligo(vinyl acetate) (PVAc-Bpy) [151].

This duality between density decrease and solute vapor pressure increase is highlighted in the work of Deepitha *et al.* where the solubility of 2-hydroxyisobutyric acid [110] and pyridine-2,6-dicarboxylic acid (PDCA) [48] in scCO_2 is improved for lower temperature at a pressure below 160 bar, but above this pressure, increasing the temperature helps to improve solute solubility. In this case, below 160 bar, the density drop caused by the temperature increase outweighs the benefits of increased vapor pressure (here, lower temperatures are beneficial). Above 160 bar, the density variation of CO_2 is less affected by T (Fig. 10) and the benefit of the increase in vapor pressure surpasses the density decrease (nevertheless, when methanol (5 mol.% in CO_2) is used as a co-solvent, this dual behavior is not present anymore: whatever the pressure, the solubility is higher for lower temperature). This dual behavior of solubility in scCO_2 was highlighted and discussed by Teoh *et al.*, who defined the pressure region where an increase in temperature negatively affects solubility as the “retrograde region”. Above this pressure region ($P > P_{\text{upper}}$, Fig. 12), a temperature increase slightly affects density (low density increase for pressures higher than 200 bar, Fig. 10) whereas the vapor pressure increase is more important [64]. Thus, for extraction systems with CO_2 -philic complexing groups, if the pressure is adjusted to be above the retrograde region, a temperature increase positively affects extraction. However, in terms of energy consumption, being inside the retrograde region (lower pressure) and applying low temperature is beneficial. In the retrograde region, therefore, lower temperatures are more appropriate ($P_{\text{lower}} < P < P_{\text{upper}}$, Fig. 12). Many studies highlighted that the better the solubility of the extractant, the higher the metal extraction efficiency [61,152], even though with a few exceptions [153].

Nevertheless, this retrograde region describing the dual behavior of solubility in scCO_2 is not sufficient to explain the relationship between

metal extraction efficiency and T and P. Indeed, increasing temperature also affects reactivity [93,126] and diffusivity. Consequently, a temperature increase may enhance the interaction between the ligand and the metal contained in a solid matrix (e.g., cotton).

Optimal conditions of temperature (40 °C) and pressure (200 bar) were observed for the metal extraction of Co^{2+} with a pyridine derivative as ligand and PFOAT as co-ligand (Fig. 13) [137]. The authors suggested that the metal complex is less stable at temperatures above 40 °C. As seen earlier, an alternative explanation could lie in the fact that a T increase leads to a vapor pressure increase and it may favor the solute solubility. However, at a certain temperature, the density of scCO_2 drops, leading to solubility and extraction decrease as the density becomes the predominant parameter. For Cu^{2+} extraction with bipyridine derivative with fluorinated chains, an optimal temperature of ~ 60 °C at 250 bar was measured [139]. A temperature of 60 °C was also found to be optimal for the extraction of Co^{2+} with hfacac at 405 bar in the presence of water (22.3 %, 78.3 % and 53.6 % for 20 °C, 60 °C and 100 °C, respectively) [126]. At 100 °C, hfacac is believed to decompose, which explains the lower efficiency.

To summarize, the presence of an optimal temperature is attributed to a compromise between four factors: (1) the saturated vapor pressure that increases with temperature, which improves the extraction at higher T (mainly for small ligands), (2) increase thermal motion enhances the mobility of complexes on the surface of the solid support (e.g., cellulose filter), also favoring higher extraction temperatures, (3) the metal complex stability as a function of the temperature, leading to worse extraction efficiency when $T > T_{\text{degradation}}$ and (4) the density of scCO_2 decreases as temperature rises, which can reduce extraction efficiency and favor lower temperature.

The optimal pressure value is explained by the dual nature of the interaction. On the one hand, density increases with pressure, thus, increasing the solvent power of scCO_2 . On the other hand, the diffusion of the metal complex is reduced by the density increase, which may hinder extraction efficiency [132]. In addition, at high pressure, competition may occur between CO_2 and the metal cation as a Lewis acid to form adducts with the ligands.

4.2.1.2. Metal extraction with a micro-emulsion system. Pressure and temperature are also important parameters for stabilizing micro-emulsions. Below the surfactant cloud point pressure (cf. SI, section S7 for the definition of cloud point), micelle aggregation occurs and the medium becomes cloudy [142]. If the temperature is increased, the pressure must also be increased to maintain a stable micro-emulsion (Fig. 14). This behavior is also observed for CO_2 -philic polymers [154, 155]. For low solute concentrations and variable temperatures, the cloud point region appears at relatively similar scCO_2 densities. When temperature increases, the density at cloud point conditions slightly decreases (Fig. 14). It can be assumed that, as temperature increases, chain-chain interactions decrease, and therefore a lower CO_2 density is required for solubilization.

For the TBP- HNO_3 system used for the extraction of Nd_2O_3 , both pressure and temperature have a positive effect (Fig. 15). The temperature acts positively as the extraction depends on the leaching of Nd_2O_3

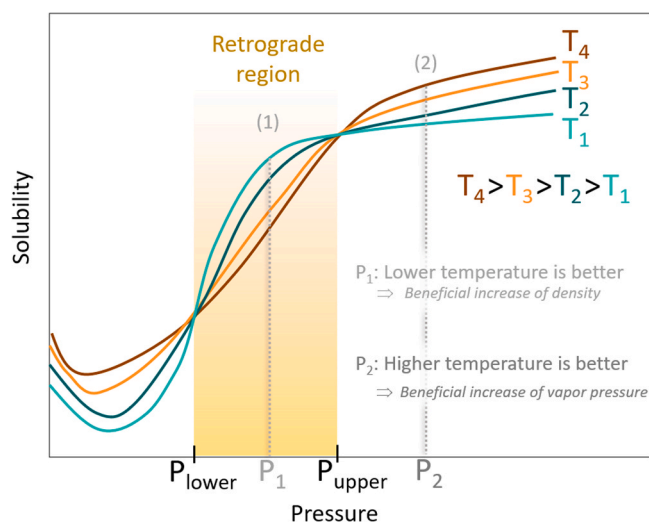


Fig. 12. Representation of the retrograde region defined by Teoh *et al.* [64]. In the retrograde region (1), the CO_2 density is the most influential factor while in (2) it is the vapor pressure of the solute.

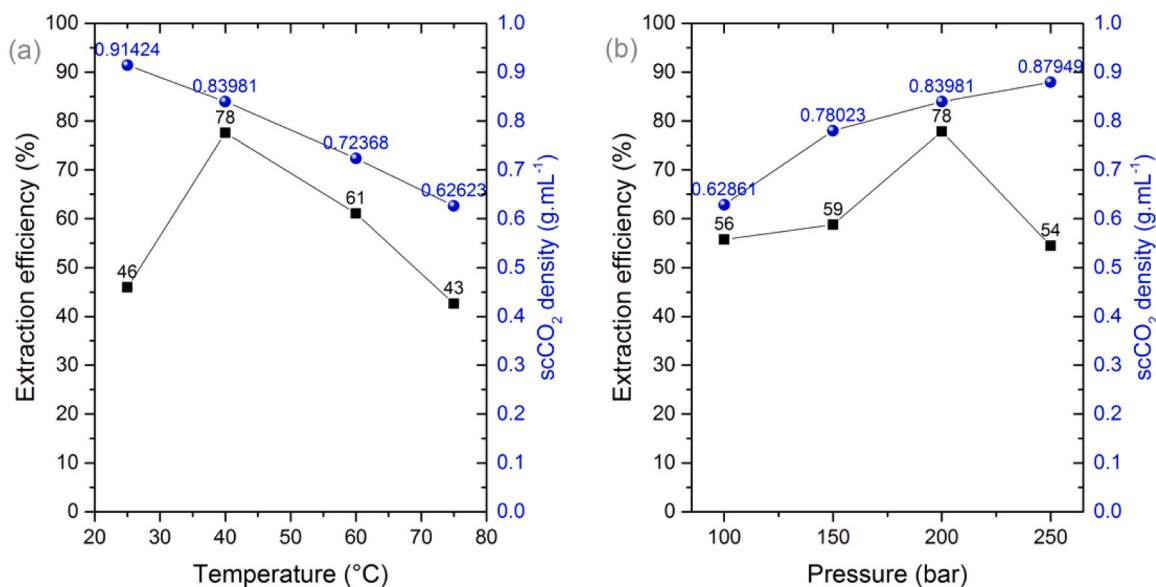


Figure 13. Co²⁺ extraction efficiency from paper filter spiked with Co(NO₃)₂. Influence of extraction temperature (a) at 200 bar and influence of extraction pressure (b) at 40 °C (30 min extraction with 200:200:1 molar ratio of co-ligand/ligand/metal).

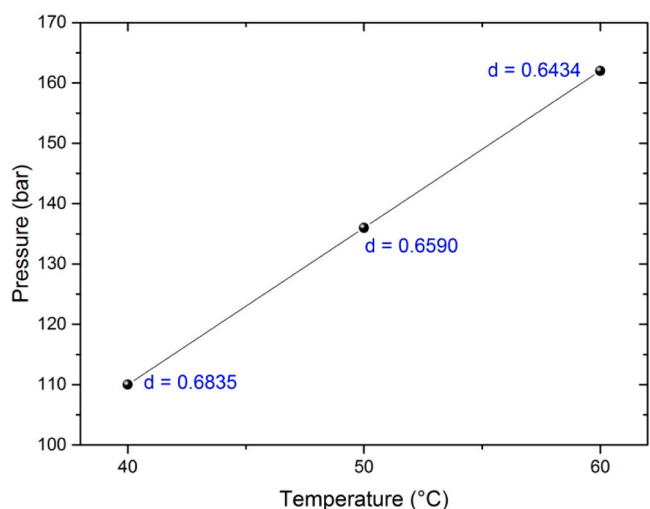


Figure 14. Cloud point conditions of TBP-HNO₃ adduct (0.03 molar fraction in CO₂) with the density value of scCO₂ for these conditions.

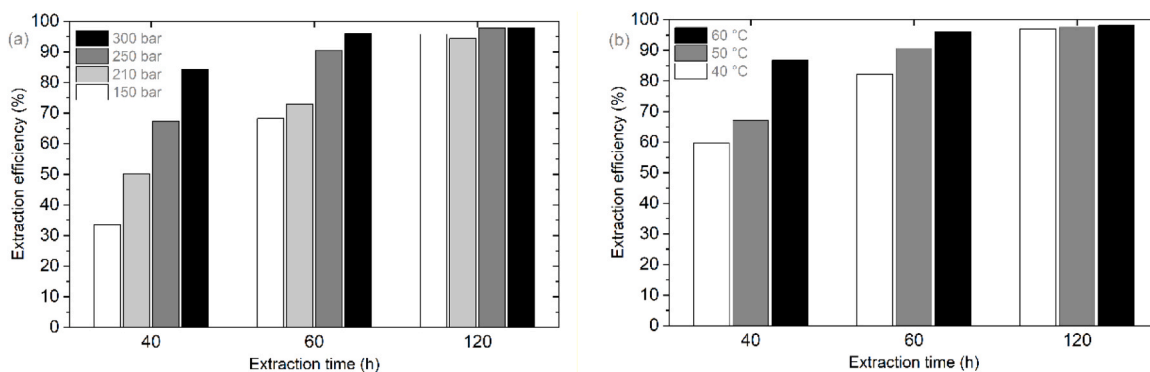


Figure 15. Extraction efficiency of Nd³⁺ from Nd₂O₃ using TBP-HNO₃ as a function of time for different pressures (a) at 50 °C and for different temperatures (b) at 210 bar.

by HNO₃, which is favored by higher temperatures [156–158].

When the pressure conditions of the extraction are above the cloud point curve and/or the extraction is already complete within the extraction duration, variations in P and T have a negligible effect on metal extraction using TBP-HNO₃ [98,159]. Zhang *et al.* confirmed this observation for NdFeB recycling using the same system [99]. However, it is noteworthy that second-order interactions show that temperature positively affects extraction when combined with a higher HNO₃ concentration. This synergistic effect is mainly due to increased reactivity caused by the high acidity.

Nevertheless, as with CO₂-soluble ligands, pressure does not only affect solubility. For example, with Triton X100 as a surfactant, the extraction of Cr(II) decreases when pressure increases, while the extraction of Au(III) increases. The ambiguous influence of pressure is related to the pH of the aqueous phase in scCO₂ (*cf.* Fig. 6). Metal solubility in solution relies on pH due to different metal speciation. Moreover, pH may affect micelles stability [144] and competition between cations and H⁺ may occur with X-type ligands.

4.2.1.3. Metal extraction by leaching assisted by scCO₂. When non-soluble ligands are used for metal leaching and extraction in an aqueous phase under scCO₂ conditions, temperature positively affects extraction efficiency. The leaching reaction in the aqueous phase is favored at high temperatures. For example, Fe and Nd recovery with an

aqueous solution of malic acid (1 M) increases from 50 % to 99 % at 60 °C and 90 °C, respectively, for a 30 min extraction at 100 bar. In such a system, the acidification of the aqueous phase is the main benefit from CO₂ and the temperature helps the leaching kinetics. A similar observation of the positive effect of temperature increase on leaching assisted by scCO₂ was made with citric acid for indium recovery [117]. As discussed with the TBP-HNO₃ system, leaching is favored at high temperatures [156–158]. A low effect of extraction pressure is also observed by an empirical model for leaching with aqueous H₂SO₄ assisted by scCO₂ [93]. This observation can be explained by: 1) leaching efficiency is minimally related to the solubility of the leaching agent in scCO₂, and 2) above 80 bar, the pH of water in CO₂ does not significantly decrease by increasing pressure (Fig. 6).

In conclusion, the influence of T and P is summarized in Fig. 16, which schematically represents the various contributing phenomena. The parameters have a complex influence that depends on the nature of the ligand, the extraction system, the specific metal involved and any potential reactions with the metal source.

4.2.2. Co-solvents

4.2.2.1. Water. The role of water in scCO₂-based metal extraction is highly system-specific, depending on the metal, its supporting matrix and the ligands involved.

In systems employing CO₂-soluble ligands, even small amounts of water can significantly affect metal extraction efficiency. For example, when using a fluorinated β-diketone, the addition of just 10 μL of water improves the efficiency by a factor of seven (0.85 μmol of Co²⁺; 100 μmol of hfacac in a 3.5 mL extraction cell at 405 bar and 60 °C) [127]. Under these conditions, this amount of water is below the solubility limit in scCO₂ (cf. SI, section S11). A similar enhancement was also observed for Cs extraction with carbamate-modified catechol as a ligand [109]. Several phenomena have been proposed to explain the beneficial effect of water: 1) it can help dissociate metal salt spiked by weakening the interaction with the solid support [160]; 2) it may stabilize the complex by hydrating it, thus occupying free coordination sites [127]; 3) it may act as a co-solvent, modifying the properties of CO₂ and enhancing its solvation ability.

The presence of liquid water, meaning above the solubility limit in scCO₂, may further enhance metal extraction by promoting the formation of micro-emulsions. For instance, when using ligands with surfactant properties such as p(VBPDA-co-FDA), the extraction efficiency of cobalt nitrate (Co(NO₃)₂) improves significantly. Without water, it is around 20 %, whereas it increases above 66 % by adding 33 mg of deionized water (160 bar and 40 °C with V_{extractor} = 8.69 mL,

1.70×10^{-7} mol Co²⁺). Under these conditions, the water is in excess with respect to its solubility in scCO₂ (cf. SI, section S11), resulting in the formation of a micro-emulsion. [112,161]. However, the excess of water in the scCO₂ extraction medium is acidified (pH = 2.8–2.9 for P > 80 bar) [89,126], affecting the metal-ligand interaction. If an X-type ligand is protonated, its ability to complex a metal cation is modified. To help complexation, a Brønsted base may be added to deprotonate the ligands (cf. Section 4.2.3.4).

In micro-emulsion systems, excess water may also destabilize micelle structure, decreasing their solubility/stability and increasing their cloud point pressure [141]. If too much water is used, the colloidal system undergoes macroscopic phase separation, forming a biphasic medium where the water phase is no longer extracted by the CO₂ flow [162]. For instance, if an excess of water or aqueous HNO₃ solution (15.5 M; 70 wt %) is added compared to the amount of ligands in the TBP-HNO₃ system, droplets of insoluble polar compounds are formed, reducing extraction efficiency [163]. This decline is attributed to the increased concentrations of both H⁺ and water, which may cause TBP-HNO₃ precipitation. Increasing the pressure can help mitigate this destabilization, by increasing CO₂ density and thus water solubility. Moreover, adding fresh TBP after a first extraction with the TBP-HNO₃ adduct helps to improve extraction by solubilizing the complex or transferring water containing the metal ion [98].

The importance of controlling water excess was also highlighted in a study on metal extraction from fly ash [129]. While some moisture in fly ash improves extraction efficiency, a water content above 15 wt% leads to a drop in efficiency. Similar observations were made for the extraction of metals spiked on a solid support [164,165].

To summarize, water plays multiple roles in scCO₂-based metal extraction systems (Fig. 17): 1) it aids in the desorption of metals cations from solid supports by competing for adsorption sites; 2) it plays the role of co-ligand to stabilize the metal complex via hydration; 3) it provides acidic protons through carbonic acid formation when dissolved in CO₂; 4) it acts as a co-solvent, enhancing the solubility and reactivity of metal complexes in CO₂; 5) it serves as a solvent in water-in-CO₂ micro-emulsions, solubilizing metal species within swollen micelles.

4.2.2.2. Alcohols. Alcohols such as methanol and ethanol are among the most common co-solvents used to enhance ligand and metal complex solubility in scCO₂. These solvents, with lower polarity than water, are miscible with scCO₂ [166] and can interact with solutes via the formation of hydrogen bonds [124,167], thus modulating the polarity of CO₂ and improving interactions at the interface between CO₂ and weakly CO₂-philic ligands/compounds [108,109,126,165]. Even small amounts of co-solvent, as low as 10 vol% relative to CO₂ can significantly

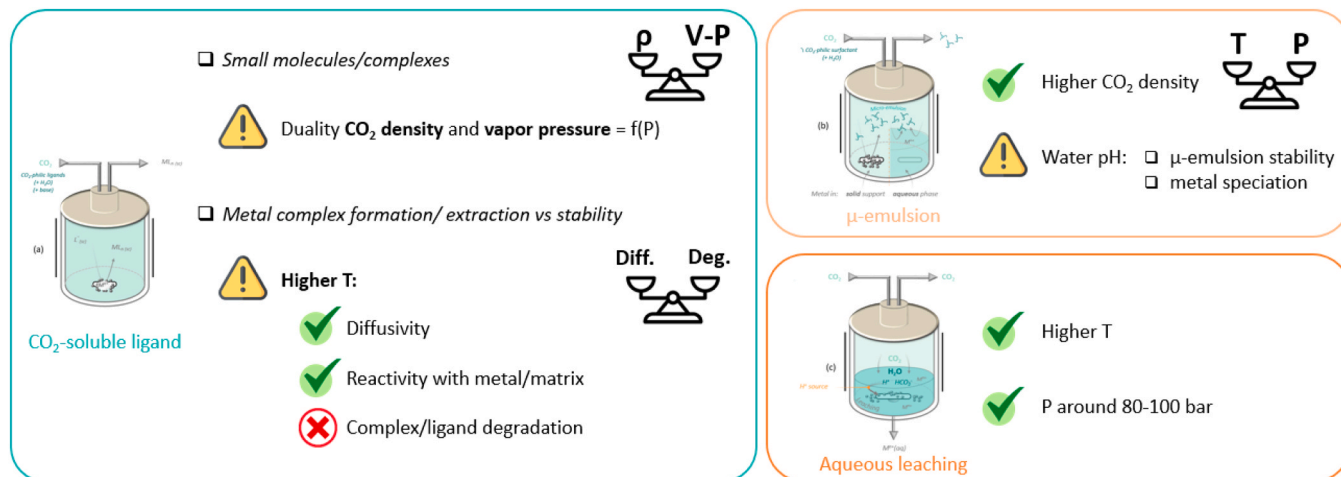


Fig. 16. Representation of the influence of the temperature and the pressure on metal extraction for the three systems.

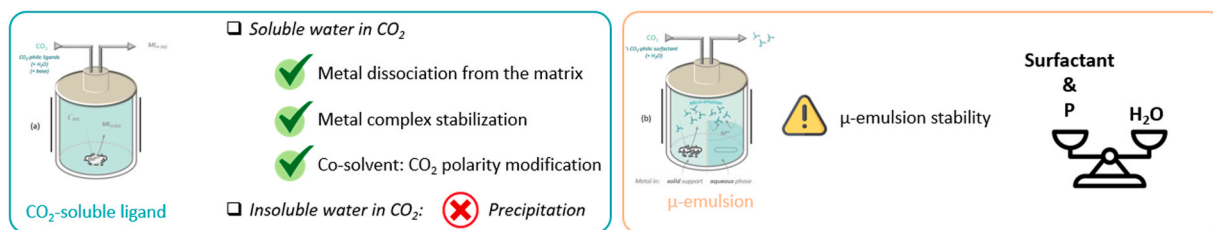


Fig. 17. Influence of water in metal extraction in $sc\text{CO}_2$.

improve solubility and extraction efficiency (Table 2) [48,126].

The addition of MeOH is also beneficial in water-in- CO_2 micro-emulsion systems. With Triton-X as a surfactant and 8-HQ derivatives as ligands, the solubility improvement helps achieve quantitative extraction [145,168]. For micro-emulsion systems using AOT as a surfactant, fluorinated surfactants such as PFPE- PO_4 can be replaced by octanol, which acts both as a surfactant and as a co-solvent for solubilizing AOT (cf. SI, Section S5). Extraction efficiencies remain comparable when using AOT + PFPE- PO_4 , 96, 95, 93, 90 and 92 %, with respect to AOT + n-octanol, 92, 88, 91, 90 and 92 %, for Co, Cd, Cu, Pb and Zn, respectively [169].

The action of co-solvents in supercritical fluid applications was discussed in more detail by Duereh *et al.* [170], who studied the Kamlet-Taft dipolarity/polarizability (π^*) of $sc\text{CO}_2$ as a function of the co-solvent nature and mole fraction. Co-solvents such as ethanol, methanol and isopropanol positively affect interactions with polar solutes due to the increase in π^* . The same team also discussed the benefits of using Hydrogen Bond Donor (HBD)–Hydrogen Bond Acceptor (HBA) solvent mixtures to modulate the solvent properties (Kamlet-Taft solvent parameters) of $sc\text{CO}_2$. HBD-HBA mixtures synergistically interact at the interface between the CO_2 -phobic solute and CO_2 , improving the solubility in $sc\text{CO}_2$ (Fig. 18) [171].

The addition of a co-solvent mixture has been shown to enhance metal extraction efficiency. For example, Bouali *et al.* [160] observed that Ce^{3+} extraction using the isobutyl amidophosphonate ligand increased up to 82 % at 250 bar and 40 °C in the presence of water and ethanol (3 $\text{mL}\cdot\text{min}^{-1}$ CO_2 and 2 $\text{mL}\cdot\text{min}^{-1}$ of 70 wt% ethanol in water). Without co-solvent addition, the extraction yield was only 12.5 % while it reached 35.9 % and 38.6 % with isopropanol (95 wt%) and ethanol (96 wt%), respectively (40 °C, 250 bar, 1 h with 3 $\text{mL}\cdot\text{min}^{-1}$ CO_2 and 2 $\text{mL}\cdot\text{min}^{-1}$ of co-solvent). The extraction efficiency increased further, reaching 72.1 % and 82.0 % when water was added to obtain an aqueous solution of isopropanol (70 wt%) and ethanol (70 wt%), respectively. Alcohol as a co-solvent may improve the affinity of water with CO_2 through a complex interface $\text{Ce}^{3+}\cdot\text{H}_2\text{O}_{(l)}\text{-Alcohol}_{(l/sc)}\text{-CO}_{2(sc)}$, in addition to promoting the formation of micelle-like structures and altering Ce^{3+} /cotton interactions.

An additional family of compounds called stabilizers lies at the interface between co-solvent and surfactant properties. Derivatives from cyclodextrin could allow a dispersion of non-soluble small molecules in $sc\text{CO}_2$ by forming inclusion complexes [172].

4.2.3. Other parameters

Other parameters can also influence metal extraction in $sc\text{CO}_2$, even if they are less frequently discussed. Among them are the partition

Table 2

Co^{2+} complexes solubility in $sc\text{CO}_2$ with acac and hfacac ligands with and without MeOH as co-solvent. Conditions: 0.5 g metal complex, 100 °C, 405 bar, 30 min static followed by 20 min dynamic extraction with 0.95 $\text{mL}\cdot\text{min}^{-1}$ CO_2 flow [126].

Compounds	Solubility (mole fraction in CO_2 ; $\times 10^8$)
$\text{Co}(\text{hfacac})_2$	27.0 \pm 4.7
$\text{Co}(\text{hfacac})_2 + 10 \text{ vol}\% \text{ MeOH}$	58.5 \pm 5.2

coefficients, the nature of the matrix that initially contains the metals, the metal speciation, and the presence of a Brønsted base.

4.2.3.1. Partition coefficients and reactions in the aqueous phase. In Section 4.2.1.1, the solubility of CO_2 -philic ligands was identified as a key factor influencing the extraction efficiency. Usually, a higher density of the CO_2 phase enhances ligand solubility and, consequently, the solubility of metal complexes in this phase. In certain cases, like binary extraction systems where a $sc\text{CO}_2$ phase (containing a metal ligand) is in contact with an aqueous phase (containing metal salts), additional factors must be considered due to reactions occurring in the aqueous phase. These systems have been examined in detail by Erkey in a dedicated review [120]. This section provides a summary of that work. Fig. 19 represents a non-exhaustive list of reactions that may occur in the aqueous phase and impact the extraction efficiency (cf. SI, section S17). The metal extraction is determined not only by the partition constants (k_{HA} and k_{MA_n}) between the aqueous and $sc\text{CO}_2$ phases, but also by:

- the dissociation constant of the ligand (HA) in water, in the case it is a cation exchanger
- the complexation constant of the metal (M^{n+}) with the dissociated ligand (nA^-) in the case it is a cation exchanger
- the pH of the aqueous phase that acts on the aforementioned constant and which is influenced by the dissolution of CO_2 in water
- the formation constant (K_x) of other metal complexes in solutions, depending on the available species (X^m)

In such systems, a cation exchange may occur between the CO_2 phase and the aqueous phase if an acidic ligand is used. This reaction is characterized by an equilibrium based on the law of mass action (Eq. 2). Metal complexation is further favored when the pKa of HA is low, as more A^- anions are generated at the same aqueous phase pH. The complexation reaction is also affected by the specificity of the aqueous phase in $sc\text{CO}_2$, which is its acidification by carbonic acid formation, as seen earlier. Therefore, the proton concentration ($[\text{H}^+]_{\text{aq}}^n$) is a complex function that also depends on this reaction. The buffering of the CO_2 phase is a challenge as carbonic acid is formed continuously [173]. In addition, even if the partitioning coefficient of a ligand is good, the extraction of a metal with this ligand can be impeded due to the hydration of the formed metal complex that presents a better affinity in the aqueous phase (Fig. 19.b and Eq. 3). Therefore, hygroscopic metal ligands that contain available empty orbitals accepting electrons are not recommended for metal extraction from an aqueous phase to $sc\text{CO}_2$. The water of hydration should be removed using an electron donor L-type ligand presenting a better affinity with the metal. An example of such a system is the formation of the adduct $\text{M}(\text{NO}_3)_n(\text{TBP})_m$ presented in the SI, section S4-1.1. It is important to note that all these reactions in the water phase also depend on the temperature; consequently, a temperature change will not only affect the CO_2 density, and thus, the ligand solubility, but also the equilibrium constants.

$$K_1 = \frac{K_c}{K_a^n} = \frac{[\text{MA}_n]_{\text{aq}} [\text{H}^+]_{\text{aq}}^n}{[\text{M}^{n+}] [\text{HA}]_{\text{aq}}^n} \quad (2)$$

$$K_1 = \frac{k_{\text{HA}}^n}{k_{\text{MA}_n}} \frac{[\text{MA}_n]_{\text{sc}} [\text{H}^+]_{\text{aq}}^n}{[\text{M}^{n+}] [\text{HA}]_{\text{sc}}^n} \text{ With } K_{\text{ex}}, \text{ the extraction constant}$$

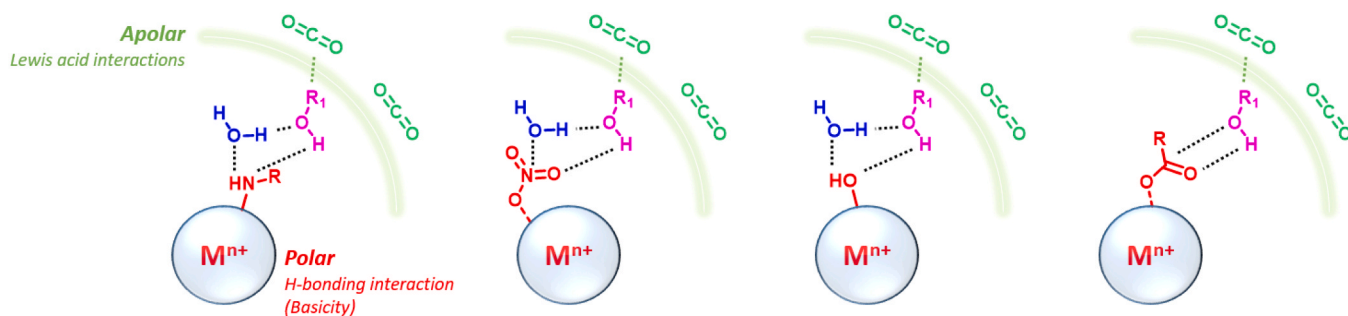


Fig. 18. Representation of the co-solvent (pink) interactions with metal complex (red) via mixed hydrogen bond donor (HBD) – hydrogen bond acceptor (HBA) with $R_1 = -CH_3$ or CH_2CH_3 .

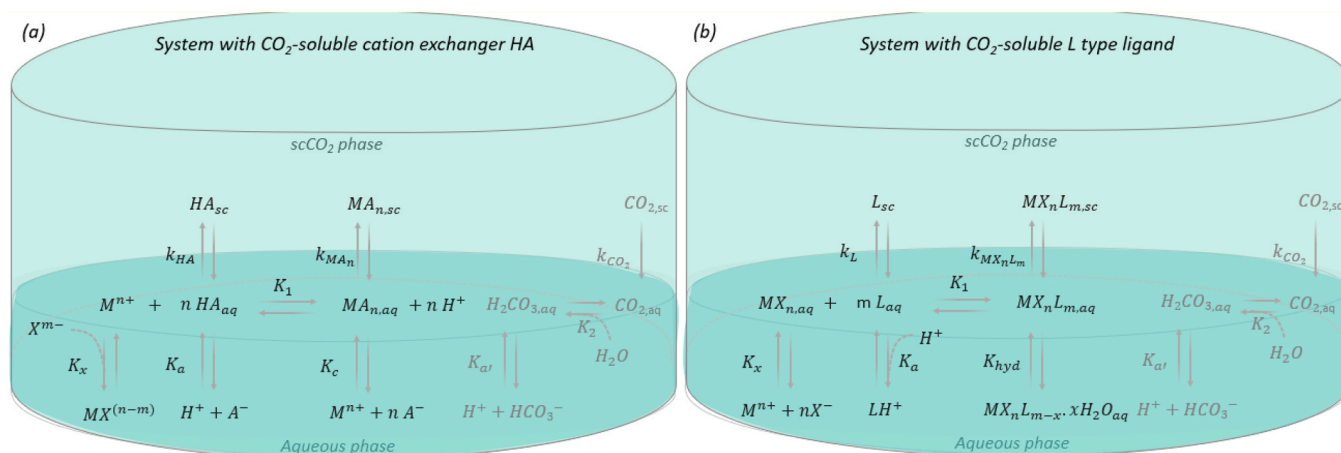


Fig. 19. Representation of the main chemical equilibria in metal extraction between an aqueous phase and $scCO_2$ using (a) a cation exchanger ligand (HA) or (b) a L-type ligand (L), both soluble in $scCO_2$. Where M is a metal, A is the conjugated base of the acid HA, X is an anionic ligand, L is an uncharged organic CO_2 -philic electron donor ligand.

$[MA_n]_{sc}$, the concentration of CO_2 -soluble metal complex in $scCO_2$

$[H^+]_{aq}$, the concentration of protons in the aqueous phase

$[M^{n+}]$, the concentration of the metal cation in the aqueous phase

$[HA]_{sc}$, the concentration of acidic CO_2 -soluble ligand in $scCO_2$

k_{MA_n} , the partition coefficient of the metal between the CO_2 phase and the aqueous phase. k_{HA} , the partition coefficient of the acid between the CO_2 phase and the aqueous phase.

k_{HA} , the partition coefficient of the acid between the CO_2 and the aqueous phases

(2)

$MX_nL_m.sc + xH_2O \rightarrow MX_nL_m.xH_2O_{aq}$

(3)

Such extraction systems might be suitable for recycling metals from LIBs, particularly when conventional leaching is previously carried out in aqueous media. An aqueous phase/ $scCO_2$ extraction process would be useful for selectively extracting metals from this solution. The challenge, therefore, lies in identifying selective ligands that are soluble in $scCO_2$.

4.2.3.2. Metal cation matrix. The targeted metals can be found in various matrices, including aqueous solutions or solid supports such as sand, cellulose or cotton [48]. The nature of the matrix significantly influences the interaction between the metal cation and the extraction system. For example, the extraction of free U and Th nitrate salts in the presence of 2-hydroxyisobutyric acid is more efficient (90 %) than U and Th spiked on a cellulose matrix (5 %) after 120 min under the same conditions. When U and Th nitrates are dissolved in an aqueous solution, the extraction is less efficient than for free nitrate salts (15 %) but works better than for metals on a solid matrix, mainly due to competing electrostatic interactions which hinder the complexation with

CO_2 -philic ligands. Similar results were obtained for the extraction of Ni^{2+} assisted by PDCA: an extraction efficiency of 89 % is obtained from aqueous solutions vs. 65 % when Ni^{2+} is spiked on sand, suggesting stronger binding of metals to solid substrates [48]. As mentioned above, the addition of a co-solvent may help to reduce such matrix effects by weakening these interactions.

In addition, the physical properties of the support material also affect extraction. For example, the particles size and structure of the matrix can be modified by pre-treatments such as ball milling, which reduce particle size, increase surface area, and induce amorphization. For instance, the extraction of rare earth elements (e.g., Y, Eu, Tb) in $scCO_2$ in an urban mining context could be significantly enhanced by introducing a ball milling pretreatment step [118].

4.2.3.3. Metal speciation. The speciation of metals on the surface of the contaminated support also influences extraction efficiency. A decrease in extraction efficiency is observed for aged metal species spiked on supports, mostly due to oxidation or hydration processes lowering their solubility [174]. For instance, Fe^{2+} forms a complex with TBP- HNO_3 that is less soluble in $scCO_2$ than the corresponding complex with Fe^{3+} ; this is attributed to Fe^{2+} coordinating only 2 TBP ligands compared to 3 TBP for Fe^{3+} , resulting in poorer charge shielding [99]. Similar trends were observed by Teoh *et al.* and others, who showed that higher oxidation states improve solubility due to enhanced shielding by the coordination of a higher number of CO_2 -philic ligands [64,175,176]. Ruiu *et al.* demonstrated that the extraction of Pd from a supported catalyst using a macro-ligand copolymer consisting of pyridine and fluorinated CO_2 -philic units (1,1,2,2-tetrahydroperfluorodecyl acrylate, FDA) (p(4VP-co-FDA)) [116] can be enhanced by a pre-treatment with

Cl₂, which causes the formation of Na₂PdCl₂, leading to a substantial improvement of the efficiency (73 %). In this case, the formation of such a Pd²⁺ chlorinated intermediate enhances the complexation with the pyridine ligands, which is less efficient when Pd is in the form of PdO.

pH also plays a critical role in determining metal speciation, and therefore, extraction efficiency in emulsion systems. For example, transition metal ions such as Co³⁺ form water-insoluble hydroxides at basic pH, whereas Cr³⁺ forms soluble Cr(H₂O)(OH)₂⁺ [144].

4.2.3.4. Brønsted base with X-type ligands. To improve extraction efficiency when using a ligand soluble in scCO₂, a base can be used to deprotonate the ligand, enhancing its interactions with the metal cation. One of the most common bases is diethylamine (DEA, pK_a = 10.98) [174,177–180]. DEA can deprotonate 8-HQ derivatives (pK_{a1} = 4.99 (NH⁺), pK_{a2} = 9.51 (PhOH) [181]) producing a negatively charged ligand that interacts more strongly with the metal cation. With DEA, Co²⁺ extraction efficiency increases from 31.8 % to 82.0 %. DEA also improves extraction when combined with Cyanex 272 (pK_a = 6.37) [177,180]. Hexamine is also used as a base to deprotonate PC-88A (phosphonic acid) [182].

Pyridine (pK_a = 5.23) was used both as a base and as a co-ligand [162]. The addition of pyridine combined with water to a fluorinated β-diketone for iron extraction from a 12Cr18Ni10Ti alloy improves extraction efficiency fivefold. However, an excess of pyridine may cause the formation of a charged complex that is poorly soluble in scCO₂. Pyridine deprotonates the β-diketone, producing the corresponding anionic β-diketonate, a chelating ligand that interacts more efficiently with metal cations [177].

4.2.3.5. Ligands or metal complex degradation. One concern about metal extraction in scCO₂ is ligand stability. Degradations of ligands or metal complexes during the process have been observed. For example, β-diketones such as Hacac and Hhfacac undergo degradation in contact with acidic water in CO₂ or at temperatures above 80 °C [127,162], leading to the formation of trifluoroacetone and trifluoroacetic acid [183]. The extraction requires a large excess of Hhfacac compared to metal cations (more than 100-fold) to overcome degradation and improve efficiency. For example, an improvement from 78 % to 91 % is observed using 100 and 350 μmol of Hhfacac, respectively, to extract 0.85 μmol of Co²⁺ [184]. Thermal degradations of metal complexes are also reported. For example, the extraction efficiency of Co²⁺ and Cu²⁺ with pyridine derivatives decreases above 40 °C due to complex degradation [137]. Some articles speculate on ligand degradation because the extraction efficiency decreases over long extraction times. For example, Yang *et al.* observed a substantial decrease in extraction efficiency for bipyridine derivatives containing fluorinated ester chains for extraction times exceeding 60 min [139]. Dithiocarbamate may also decompose into amine and carbon disulfide in acidic solution (pH < 4). Koh *et al.* followed the decomposition of NaDDC as a function of extraction time by UV-visible spectroscopy [177]. In these studies, the decomposition of the extractants does not result in an extraction efficiency decrease, but rather decomposition seems to produce a synergistic effect. NaDDC and Cyanex® 272 used alone as extractants are not efficient, but when used together, the extraction efficiency is improved. The supposition is that NaDDC decomposes into diethylamine (DEA) (Eq. 4) and the Brønsted base enhances the performance of the acidic ligand, as discussed previously [177].



4.3. Extraction of metals present in CAMs: an overview

Studies on metal extraction in scCO₂ are mainly carried out using metal salts deposited on solid supports such as cellulose filter [113,114,136,137,153,178,179], sand [48,108,126,174], lab coats [112,141,142,169,183] to simulate contaminated matrices. Metal cations, however,

can also be extracted from different matrices such as aqueous solutions, which are then directly placed in the extractor [127,128,180,182]. Realistic contaminated samples were also studied, with a primary focus on fly ash from waste incinerators [115,129,134,185]. Decontamination of activated carbon [186], soil [108,126,185], resin [187] and fireproof boards [188] has also been discussed. Compared to simulated matrices, realistic contaminated samples are more complex, influencing the interactions between the metal salts and the support, and therefore the desorption properties. Due to the various nature of the sources, direct comparison across different studies of the extraction efficiency of metals such as Co, Ni, Mn and Li is not possible. Consequently, this section provides a brief summary of the main approaches used for the recovery of Co, Ni, Mn and Li. As the different parameters and conditions were already discussed in Section 4.2, they will not be detailed further. The Supporting information presents exhaustive tables of the best extraction conditions of all mentioned studies for Co (*cf.* SI, section S12), Ni (*cf.* SI, section S13), Mn (*cf.* SI, section S14) and Li (*cf.* SI, section S15). More detail is provided for Li extraction using CO₂ as specific extraction processes were developed to recover Li from ores (*cf.* Section 4.3.4).

Only a few studies focusing on materials recycling for the recovery of valuable metals are available in the literature. In the case of cobalt, this metal is mostly extracted from spent catalysts [180] or from LIB CAMs [88].

4.3.1. Cobalt

Cobalt extraction in scCO₂ mainly focuses on Co²⁺ decontamination. Many extraction systems have proven their efficiency by extracting more than 90 % Co²⁺. Some of them are briefly described below based on different cobalt matrices.

The most efficient system for the extraction of Co²⁺ from aqueous solutions using scCO₂ is based on a phosphonic acid (PC-88A 2.5 % (v/v) in heptane), through a continuous extraction process for 80 min at 1.0 mL.min⁻¹ at 98 bar and 40 °C in a 50 mL cell filled with glass beads to favor solution contact with CO₂. The mixture of PC8–88A in heptane is introduced into the extractor at a flow rate of 0.2 mL.min⁻¹ to extract 2.5 mg of Co²⁺ from a solution of 10 wt% CoCl₂ with 90 wt% hexamine and 1 mL water. In this system, PC-88A is deprotonated by the excess of hexamine, while heptane acts as co-solvent and water helps metal complex formation with the deprotonated phosphonic acid. The most efficient temperature is 40 °C. At 70 °C and 93 bar, the extraction efficiency drops to less than 25 %, likely due to the decreased solubility of PC-88A at this temperature [182].

Another system capable of quantitatively extracting Co²⁺ from an aqueous solution, obtained by leaching of spent coal bed methane (CMB) deoxygenation catalyst, also uses a phosphonic acid (Cyanex® 272) in combination with DEA and an aliphatic tertiary amine (Alamine® 304–1) or PC-88A at 200 bar and 60 °C. Basic DEA and Alamine® 304–1 are added to deprotonate Cyanex® 272. Near-complete extraction is achieved by DEA in association with Cyanex® 272, PC-88A or D2EHPA alone [180].

For the extraction of Co²⁺ spiked on a solid matrix, efficiencies close to 95 % can be obtained. For example, Co²⁺ (3.4 × 10⁻⁷ mol) on sand is extracted at 92 % with Cyanex® 272 (5.8 × 10⁻³ mol) and DEA (3.9 × 10⁻⁷ mol) in the presence of 50 μL of water at 200 bar and 60 °C. A continuous process is used for 30 min with a 3 mL.min⁻¹ CO₂ flow [174]. Compared to the extraction of Co²⁺ in aqueous solutions with a similar system, the lower efficiency can be attributed to the difficulty of separating Co²⁺ from the solid matrix. When Co²⁺ (1.7 × 10⁻⁷ mol) is spiked on sand, 95 % is extracted using a fluorinated dithiocarbamate (LIFDDC, 1.9 × 10⁻⁵ mol) at 200 bar and 60 °C with 5 vol% methanol as co-solvent [107]. Bipyridine derivatives can also extract Co²⁺ spiked on filter paper (82–98 %) when used with a soluble water fraction in CO₂ and PFOAT as a CO₂-philic counter anion [114,139]. Finally, a water-in-CO₂ micro-emulsion system using AOT (15 mM) with PFPE-PO₄ (30 mM) with W = 15 allows the extraction efficiency of 96 % of Co²⁺ (10 μg initially spiked on a lab coat) at 200 bar 40 °C [111].

In conclusion, efficient systems have been developed for Co^{2+} extraction in scCO_2 at pressures around 200 bar and temperatures between 40 and 60 °C. Phosphonic acids combined with a Brønsted base are highly efficient. However, extractions for decontamination deal with low cobalt concentrations, and a large excess of complexing agent is used (50-to-1000-fold excess). Therefore, in terms of atom economy, progress is needed to reduce the relative amount of extractants. To the best of our knowledge, only three papers dealt with cobalt recovery from LIBs. One process does not use CO_2 -philic metal ligands as it concerns leaching from aqueous solutions under scCO_2 conditions (cf. Section 3.4 [88]). More recently, the TBP- HNO_3 system was studied for leaching and extraction of Co from NMC CAMs [93]. Finally, a system free of inorganic acid was developed with a CO_2 -philic copolymer (p(VBPDA-co-FDA)) and a reducing agent ($\text{H}_2\text{O}_{2(\text{aq})}$ or ethanol) in which the copolymer is able to leach, complex and solubilize Co^{2+} in scCO_2 [102].

4.3.2. Nickel

Nickel extraction has been less extensively studied than cobalt, partly because Ni does not present a radioactive contamination risk and has a lower market value, making it a less urgent target for recovery. Nevertheless, Ni^{2+} is a toxic metal with significant environmental and health risks, and its removal from waste streams such as fly ash remains crucial to prevent further pollution.

Using D2EHPA (2 mol.% in CO_2) as a ligand (Fig. 20), up to 98 % Ni can be extracted from fly ash without the need of a Brønsted base. In such matrices, Ni can be present in the metallic form. Consequently, the acidic conditions generated by the presence of D2EHPA may be necessary to leach Ni, and the resulting conjugated base can efficiently complex the formed Ni^{2+} (Eq. 5).



Ni^{2+} spiked on paper filters or silica gel can be extracted with efficiencies above 98 % using bipyridine derivatives in combination with PFOAT and a soluble fraction of water at 250 bar and 40–50 °C [114, 139,153]. A water-in- CO_2 micro-emulsion system using Triton X 100 with trifluoroacetic acid and methanol as a co-solvent achieves 99.8 % Ni^{2+} extraction at 200 bar and 60 °C.

In summary, Ni^{2+} extraction is very similar to the Co^{2+} one, and comparable efficiencies are obtained when utilizing the same leaching systems with comparable conditions.

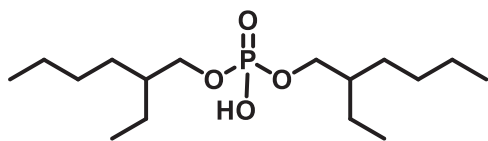
4.3.3. Manganese

As in the case of Ni, only a few publications on the extraction of Mn in scCO_2 are available in the literature. For Mn extraction from CMB catalyst using Cyanex® 272 and DEA, a complete extraction is achieved, as in the case of Co^{2+} [180]. Similarly, Mn could be extracted as effectively as Ni and Co from NMC CAMs using TBP- $\text{HNO}_3 + \text{H}_2\text{O}_{2(\text{aq})}$ [93]. However, Mn extractions with bipyridine ligands in combination with PFOAT show lower efficiency than Co and Ni extractions, with 50–70 % for Mn^{2+} compared to 82–100 % for Ni^{2+} and Co^{2+} [139,153,189].

Consequently, selective extraction of Co^{2+} and Ni^{2+} may be possible with respect to Mn^{2+} when using bipyridine derivatives.

4.3.4. Lithium

Unlike transition metal cations, lithium (Li^+) exhibits a distinct



Di-(2-ethylhexyl)phosphoric acid

Fig. 20. D2EHPA representation.

chemical behavior, and its extraction received limited attention due to its low toxicity and relatively low market value. However, the growing demand for lithium, mostly driven by its application in LIBs, has created a growing interest in developing alternative, more sustainable recovery methods. Conventional lithium extraction from ores involves inefficient and environmentally impacting processes including solar evaporation, sodium carbonate precipitation, and acid leaching after salt roasting [190]. These methods consume large amounts of water and chemicals such as H_2SO_4 , CaCO_3 , or Na_2CO_3 [191], and produce lithium carbonate (Li_2CO_3) contaminated with sulphates and heavy metals. New extraction and refining methods must therefore be implemented to limit process costs and secondary pollution emissions.

CO_2 -based processes offer a greener alternative and have been explored for lithium recovery from ores and, since 2015, also from secondary sources such as BM from spent LIBs. In these systems, lithium extraction can be carried out using subcritical CO_2 (gas and liquid) instead of scCO_2 , for producing Li carbonate. Two main processes exist: direct and indirect carbonation.

Direct carbonation involves a calcination step under a CO_2 atmosphere, where CO_2 reacts with Li (hydroxides or oxides) to form Li_2CO_3 that is then leached with water [192]. This process will not be further discussed here as it does not involve the use of liquid or scCO_2 .

Indirect carbonation, on the other hand, uses pressurized CO_2 in contact with water to leach Li from a solid matrix. CO_2 dissolves in water, forming carbonic acid, which easily leaches the lithium species poorly bound to the ore matrix or BM residue. When dealing with lithium ores, a thermal pre-treatment is required to form β -Spodumene ($\text{LiAlSi}_2\text{O}_6$) from α -Spodumene and Zinwaldite ($\text{K}(\text{Li},\text{Fe},\text{Al})(\text{AlSi}_3)\text{O}_{10}(\text{F},\text{OH})_2$). The latter represents the largest European siliceous lithium sources, but it is less concentrated in Li than Spodumene ores and contains fluorine and iron. β -Spodumene has a less compact structure, making the extraction of lithium easier [191,193]. After this thermal treatment, these ores can be treated like BM from spent LIBs. The leached lithium is solvated by carbonated species whose speciation depends on the pH, i.e., the CO_2 pressure. Depending on acid/base equilibrium, it may lead to the formation of LiHCO_3 which is highly soluble in water (solubility of 55 and 13.3 $\text{g}\cdot\text{L}^{-1}$ for LiHCO_3 and Li_2CO_3 , respectively) [192]. Other metals such as Co, Ni and Mn are not leached under these conditions; allowing for the selective recovery of lithium. The highly concentrated Li^+ solution is then thermally treated to precipitate Li_2CO_3 after water evaporation (which is energy-intensive) [192,194,195].

Chen *et al.* [193] developed a different process employing CO_2 gas instead of scCO_2 , with lithium being initially carbonated using an aqueous solution of Na_2CO_3 in an autoclave. β -Spodumene must be hydrothermally treated with a liquid-to-solid (L/S) ratio above 4 to prevent the precipitation of Li_2CO_3 on the ore surface, and with a slight excess of Na_2CO_3 compared to Li^+ (i.e., 1.2 molar excess) to improve conversion. The efficiency increases when the temperature is increased to 225 °C [193]. Water is then added to the slurry (L/S = 0.125) and a gaseous CO_2 flow is applied to solubilize Li_2CO_3 by decreasing the pH, enhancing Li recovery and removing impurities by filtration. The filtrate containing lithium bicarbonate is thermally treated at 90 °C to produce high-purity Li_2CO_3 (> 99.6 %).

The consumption of Na_2CO_3 for carbonation can be further reduced using CO_2 . For example, in recent studies, CO_2 is preferred to convert Li into LiHCO_3 . Bertau *et al.* [191] studied lithium extraction by treating β -Spodumene in water in the presence of scCO_2 (solid: liquid = 1:30, 3 h, 100 bar, 18 μm (d50), 230 °C). As previously explained, water is acidified by CO_2 dissolution, allowing Li leaching up to a concentration of 325 $\text{mg}\cdot\text{L}^{-1}$ and a recovery efficiency of 71 %. Then, an electro dialysis step concentrates the Li solution without the energy-consuming evaporation process, achieving a LiHCO_3 concentrated solution of 8.5 $\text{g}\cdot\text{L}^{-1}$ of Li^+ . The solution is then thermally treated at 90–95 °C to form Li_2CO_3 and eliminate CO_2 . The residue is filtered, resulting in purity > 99 % with an overall yield around 60 % [191]. The same research team

further developed this process to adapt it to secondary lithium resources such as BM from spent LIBs, obtaining battery-grade Li_2CO_3 (> 99.5 %) and a residue enriched in Co and Ni that can be more readily processed by a pyrometallurgical step. When ores are treated, solid residues from the filtration of Li^+ solutions, such as iron oxides, calcination by-products, SiO_2 and Al_2O_3 can be valorized [194]. Schwich *et al.* [192] and Pavon *et al.* [195] developed similar processes for BM treatment, but without the electro dialysis step. The Li^+ solution is thermally treated only to evaporate water and to form Li_2CO_3 . Schwich *et al.* explained that the alkaline pH (pH = 11–12) obtained when contacting water with BM decreases to 7–8 when water is treated with pressurized CO_2 . In the absence of CO_2 , the leaching efficiency decreases to 64 % vs. 79 % with CO_2 .

Pavon *et al.* [195] applied a design of experiments approach to study how parameters such as temperature, time and L/S ratio influence lithium recovery from BM using water in the presence of scCO_2 . This study demonstrates that higher temperatures enhance lithium leaching efficiency, while increasing the L/S ratio has a similar, though less pronounced effect. However, large volumes of water require more energy during the final evaporation step to recover Li_2CO_3 . After lithium is leached, thermal treatment of the solution enables the precipitation of high-purity Li_2CO_3 (99.8 wt%), and the remaining filtrate is recovered for further BM treatments. Other metals such as Co, Ni, Mn, Cu and Fe remain in the solid residue, highlighting the selectivity of the method. Compared to hydrometallurgical processes using inorganic and organic acids, the scCO_2 process has the advantage that Co, Ni and Mn are not leached, while the leaching efficiency of Li is virtually the same. Even though Al is also leached together with Li under these conditions, it does not precipitate in the presence of carbonates, so the purity of Li_2CO_3 is not affected.

Three papers stand out in the lithium extraction literature because they do not rely on lithium carbonation. One focuses on lithium complexation using CO_2 -soluble crown ethers (CEs) [190,196], while the others explore the recycling of NMC and LCO with the TBP- $\text{HNO}_3 + \text{H}_2\text{O}_2$ system and p(VBPDA-co-FDA) + H_2O_2 or ethanol in scCO_2 , respectively [93,102]. As the latter have been discussed previously and do not enable selective lithium extraction, only the crown ether-based approach is described here (Fig. 21).

Traditionally, CEs are used for lithium recovery in liquid-liquid systems, but their poor solubility in scCO_2 limits their direct application. To address this, Pálsdóttir *et al.* chemically modified CEs to make them soluble in CO_2 , synthesizing two new compounds (Fig. 21), 3-methylene-14-crown-4 (M14C4) and a novel fluorinated 14-crown-4 (F14C4) [190]. These L-type ligands must be used in combination with CO_2 -philic counter anions (also known as cation exchangers) such as heptadecafluorooctanesulfonic acid tetraethylammonium salt (TPFOS) and bis(2-ethylhexyl) phosphate (HDEHP) to enable lithium extraction. While TPFOS is used for its extractant abilities and solubility in scCO_2 , HDEHP, even though non-fluorinated, also shows sufficient solubility in scCO_2 . Alone, the cation exchangers show low extraction efficiency in preliminary solvent extraction tests: 3 % for HDEHP and 10 % for TPFOS, whereas combining them with CEs improves performance

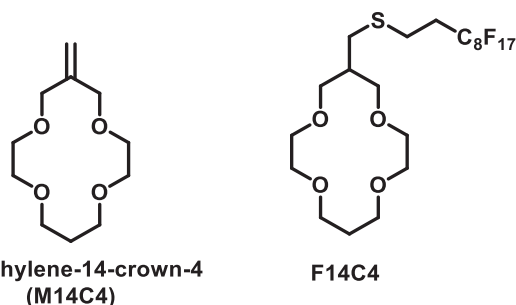


Fig. 21. Crown ether representation from the study of Pálsdóttir *et al.* [190].

to 26 % and 38 % for F14C4/HDEHP and M14C4/TPFOS, respectively. Further improvements in solution extraction tests could be obtained, but they are not discussed here because the behavior in scCO_2 is significantly different. Surprisingly, the non-fluorinated CE compound exhibits the best solubility in scCO_2 , possibly due to the lower volatility of the fluorinated CE related to its long fluorinated chain. While this observation is particularly important considering the selectivity of CEs towards lithium extraction, unfortunately, no Li^+ extraction data in scCO_2 were reported in this study.

In a previous article, the same authors tested Li^+ extractions in scCO_2 using M14C4 and F14C4 assisted by HDEHP from aqueous LiCl/NaCl mixtures ($10 \text{ mg.L}^{-1} \text{ Li}^+$ and $500 \text{ mg.L}^{-1} \text{ Na}^+$), but no selectivity between Li^+ and Na^+ was observed [196]. Moreover, a low Li^+ extraction yield of only 30 % was obtained at 60°C and 250 bar for 30 min static and 100 mL CO_2 flush at 3 mL.min^{-1} , with a 50-fold CE excess. To date, no follow-up studies have been published by this group about Li extraction in scCO_2 using CEs.

scCO_2 can also be used to extract lithium from the electrolyte (LiPF_6), although quantitative data on recovery yields are limited (cf. Section 3.1) [74]. Beyond recovery, scCO_2 -based electrolyte extraction can also be used to separate CAMs without damaging them and limit the generation of toxic by-products typically formed during the thermal treatment needed to obtain the BM (cf. Section 3.2). Once separated, the cathode powder can then be re-lithiated through hydrothermal treatment, allowing the CAMs to be reused easily without leaching steps [80].

Among current methods, indirect carbonation of lithium with CO_2 is one of the most promising technologies due to its many advantages. It allows for the selective recovery of Li with minimal energy consumption and process steps. Moreover, the same process can be used to extract Li both from primary sources (e.g., ores) and secondary sources (e.g., BM from LIBs, independently of the cathode technology). Unlike conventional methods, it does not require additional precipitation agents (e.g., NaOH and Na_2CO_3), thus avoiding the introduction of impurities such as sodium and potassium. Li_2CO_3 can be efficiently separated by precipitation, while other alkali ions remain in solution. Moreover, unreacted CO_2 can be recovered in the process through depressurization and compression, enhancing the sustainability and cost effectiveness of the method.

4.4. Conclusion and challenges

Table 3 summarizes the main systems developed for extracting metals incorporated into CAMs using scCO_2 with a yield higher than 80 %. As seen earlier, the system must be adapted as a function of the nature of the metal form. Most of the systems used a cation exchanger ligand (HA). To improve the metal complex stability/solubility in scCO_2 , a highly CO_2 -soluble species is required. For example, when using bipyridine derivatives or t-butylsalen, which are L-type ligands, PFOAT is used as a CO_2 -philic HA/surfactant. On the contrary, some HA present a lower CO_2 -philicity. In this case, a CO_2 -philic L-type ligand might be used like TBP, or a microemulsion might be implemented using a surfactant like Triton X-100. When leaching is unnecessary to obtain metal cations, complexation with a CO_2 -philic HA requires a Brønsted base to deprotonate it, facilitating A^- formation (e.g. Cyanex 272 + DEA or p(VBPDA-co-FDA) + pyridine).

The efficient extraction of valuable metals (including Co, Ni, Mn, and Li) from CAMs via scCO_2 -based systems has been successfully demonstrated in the literature. For instance, an overall 90 % recovery efficiency of these metals from NMC cathodes was achieved using TBP- $\text{HNO}_3 + \text{H}_2\text{O}_{2(\text{aq})}$ in scCO_2 . Another system, with an acidic CO_2 -philic copolymer p(VBPDA-co-FDA) + ethanol allows a 75 % recovery of Co and Li from LCO. Cobalt extraction alone reached 95 % using $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_{2(\text{aq})}$ in scCO_2 leaching, significantly reducing leaching time and reagent consumption. Additionally, selective Li extraction from BM can be obtained by carbonation using $\text{CO}_2 + \text{H}_2\text{O}$, offering a mild and selective pathway for Li recovery.

Table 3

List of the main systems explored for the extraction of metals present in CAMs using scCO₂ with a yield higher than 80 %.

System	Pressure (bar)	Temperature (°C)	Time (min)	Metals	Ref.
Extraction of metals from a solid matrix					
CO ₂ -soluble cation exchanger ligand (1) + Electron donor L-type ligand (2) - D2EHPA* (1) + TBP (2) - PFOAT (1) + t-butylsalen* (2) - PFOAT (1) + bipyridine derivatives* (2) - LiFDDC (1) - p(VBPDA-co-FDA) (1) + pyridine (2) (+ x μL of water, below the solubility limit in scCO ₂)	150–250	40–60	60–90	CoNiMn	[108,113,114,127,129,136,137,139,153,161,189]
scCO ₂ -microemulsion: CO ₂ -soluble cation exchanger surfactant (1) + Brønsted base or entrainer (2) - AOT (1) + octanol (2) - AOT* (1) + PFPE-PO ₄ (1) - p(VBPDA-co-FDA) (1) + pyridine (2)	200–250	40	60–90	CoNi	[111,141,142,161,169]
scCO ₂ -microemulsion: cation exchanger insoluble in CO ₂ (1) or L-type ligand (1') + CO ₂ -philic surfactant (2) + entrainer (3) - TFA* (1) + Triton X-100 + MeOH (3) - 8-HQ* (1') + Triton X-100 + MeOH (3)	200	60	10	CoNi	[145,168]
scCO ₂ leaching and extraction from a CAM with: cation exchanger insoluble in scCO ₂ (1) CO ₂ -soluble electron donor L-type ligand (2) + reducing agent (3) - HNO ₃ * (1) + TBP (2) + H ₂ O _{2(aq)} (3)	310	40	60	CoNiMnLi	[93]
scCO ₂ leaching and extraction from a CAM with: CO ₂ -soluble cation exchanger in scCO ₂ (1) + reducing agent (2) - p(VBPDA-co-FDA) (1) + Ethanol (2)	250	60	60	CoLi	[102]
Extraction of metals from an aqueous solution					
CO ₂ -soluble cation exchanger ligand (1) + Brønsted base (2) - Cyanex 272 (1) + DEA (2) - PC-88A (1) + hexamine (2)	200	60	n.a	CoNiMn	[174,177,180,182]
CO ₂ -soluble cation exchanger ligand (1) + entrainer (2) - β-diketone like AcAc (1) + Isopropanol (2) - PDCA ¹ (1) + MeOH (2)	100–200	25–60	15	Ni	[48,183]

¹PDCA has two carboxylic acid functions (X- ligand) but also a pyridine unit that can play the role of an L-type ligand.*Less CO₂-philic compounds of the system.

In spite of these promising results, metal recycling using scCO₂ or liquid CO₂ is still poorly studied. Most scCO₂ studies have focused on the extraction of transition metals for decontamination purposes, where its high diffusivity, non-toxicity, and easy separation from the solute by decompression are major advantages. These systems are particularly efficient for Co²⁺ and Ni²⁺ extraction, although they typically rely on a large excess of extractants. Therefore, process optimization is needed to reduce atom consumption and improve sustainability.

Another challenge when dealing with BM or CAM is the leaching step required before the metal cation extraction, which can be hindered by the presence of a Brønsted base normally used to activate X-type ligand complexation. Additionally, the reverse process, *i.e.*, the decomplexation of metals and the recycling of CO₂-philic ligands has also been poorly discussed, despite being crucial for recycling system viability (*cf.* SI, section S16). The proper recycling process of the organometallic complexes would probably merit a life cycle assessment to better evaluate the benefits. Such a back extraction/ stripping is a challenge already addressed by Erkey *et al.* in 2000 [120]. Nevertheless, no major progress has been made on this issue since then. The fact is that the better the complexation ability, the more difficult the de-complexation. If a concentrated acidic solution is required, which inherently is a productive process because it uses the same reagents as conventional leaching, the benefit of using CO₂ is lost. Other strategies should be envisioned for decomplexation by contacting CO₂ with a reagent or using a redox reaction to modify the metal oxidation state and obtain an insoluble form.

It is challenging to perform selective extraction of Co and Ni in scCO₂, as the systems capable of doing so in solution rely on the pH of the organic and aqueous phases, which is more difficult to implement in CO₂.

Several factors may explain the limited interest in scCO₂-based processes for metals recycling which are still not implemented at an industrial scale. First, the high cost and technical complexity of the

scCO₂ equipment, which require significant investments [56,57,197]. Second, the safety issues associated with high-pressure infrastructures, necessitating specific regulations. Nevertheless, scCO₂ extraction represents a cleaner alternative for metal recovery, reducing the use of hazardous chemicals and the generation of toxic aqueous effluents.

To improve economic feasibility, a recycling loop must be implemented to recover ligands without damaging them after metal extraction and reuse them, thereby limiting chemical consumption. CO₂ can also be purified and recycled. While economic analyses have been carried out for the scCO₂ extraction of natural organic compounds, where no ligands are required, the application to metal extraction remains more complex. Unlike the extraction of organic compounds, which can benefit from tunable scCO₂ polarity *via* co-solvents and temperature-pressure modulation [52,198], the extraction of metals requires the careful design of specific ligands and further process tuning.

Finally, an important potential issue is the risk of corrosion when using acids together with scCO₂. Usually, high-pressure stainless steel extractors used with scCO₂ undergo only limited corrosion by scCO₂, which is a non-oxidative medium [199]. Nevertheless, the presence of impurities in the sample to be extracted, such as soil residues, may cause corrosion when water or complexing agents are used [126]. Complexing agents may also induce the leaching of the metal oxide layer at the surface of the stainless steel vessel favoring further corrosion, as observed, for instance, when using Hhfacac together with pyridine and water [162].

5. Conclusion and perspective

The recycling of LIBs using scCO₂ is still in its early stages. Nonetheless, CO₂ is an interesting green solvent due to its ability to enable efficient and rapid extraction while limiting waste generation and toxicity. The efficient extraction of electrolytes, metals from CAMs, and binder removal has been demonstrated using scCO₂ or liquid CO₂.

Despite these advantages, interest in metal recycling using scCO₂ remains limited. This is surprising given the considerable advantages of this process:

- Low-cost, non-flammable, non-toxic and reusable solvent.
- High diffusivity of scCO₂ for improved transport and penetration.
- Simple recovery of the extracted solute through CO₂ depressurization.
- Tunable solvation properties of scCO₂ by adjusting temperature, pressure and *via* the possible addition of co-solvents.
- Selective recovery of lithium *via* carbonation in the presence of water.

However, several challenges still constrain the broad use of scCO₂ for metal recycling. These include the high initial cost and complexity of the high-pressure equipment, the need for expensive, often fluorinated CO₂-philic ligands, and the limited understanding of solute-solvent interactions in scCO₂. In particular, modelling and predicting the behavior of metal complexes in this medium remains difficult.

A deeper understanding of the stability of metal complexes in scCO₂ could significantly improve the design and optimization of scCO₂-based extraction processes. Currently, most studies on metal recovery using scCO₂ primarily focus on extraction efficiency, without providing detailed mechanistic information about the influence of key factors, such as the role of water or other additives in the mechanism. To address this problem, the development of *in situ* analytical techniques, including FTIR, Raman spectroscopy, or small-angle neutron scattering (SANS), already successfully applied in the characterization of microemulsions and self-assembled systems, could provide valuable insights into the behavior of metal complexes under varying extraction conditions. The adaptation of such *in situ* analytical tools to scCO₂ conditions, however is both technically challenging and expensive.

Different strategies for utilizing scCO₂ in the recycling of metals from spent LIBs can be proposed. A first approach involves the use of scCO₂ to assist the leaching of CAMs in an aqueous medium, which would help minimize the consumption of acid and reducing agents through water acidification. The leaching may also be carried out in scCO₂ with and without a microemulsion system by using macromolecular species to leach, complex, and, ideally, selectively extract metals from CAMs. A second strategy involves metal extraction in scCO₂ following a non-selective leaching step in aqueous solution, in a process similar to that already developed for decontamination. This approach offers a solvent-free alternative to conventional liquid-liquid separations, avoiding the use of toxic organic solvents. However, it requires the use of specifically designed CO₂-philic ligands and/or surfactants to enable efficient extraction. The extraction efficiency depends on the ability of a chemical function to both complex the target metal and remain soluble in the scCO₂ phase. This is particularly challenging as the most effective complexing functions are usually polar species, poorly soluble in scCO₂. To overcome this limitation, these ligands must be functionalised with a CO₂-philic moiety, making their design and synthesis more complex. Despite these challenges, the tunable solvation properties of CO₂, which can be adjusted by modifying pressure, temperature, ligand nature, and additives such as co-solvents, offer promising opportunities for selective metal recovery. Realizing this potential will require continued collaboration across chemistry, materials science, and process engineering to design efficient, selective, and scalable scCO₂-based recycling methods.

CRedit authorship contribution statement

Patrick Lacroix-Desmazes: Writing – review & editing, Validation, Supervision, Funding acquisition. **Nicolas Coppey:** Validation, Supervision, Project administration, Funding acquisition. **Laure Monconduit:** Writing – review & editing, Validation, Supervision, Funding acquisition. **Moulay Tahar Sougrati:** Writing – review & editing, Validation, Supervision. **Lorenzo Stievano:** Writing – review & editing,

Validation, Supervision. **Rakhi Mondal:** Writing – review & editing. **Cécile Bouilhac:** Writing – review & editing, Supervision. **Joshua Vauloup:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.supflu.2025.106794](https://doi.org/10.1016/j.supflu.2025.106794).

Data availability

No data was used for the research described in the article.

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