Metal recovery using supercritical CO_2

Course: KE2185 Separation Processes

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Date of Submission: 2024-02-27

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Abstract

This project aims to investigate the past and present developments of extracting metals with supercritical CO_2 ($scCO_2$). The report primarily focuses on the principles behind $scCO_2$ and its ability to extract metals from coal fly ash (CFA), ores, and batteries. Supercritical fluid extraction is a growing field because of its environmental benefits compared to other extraction methods. The metals concerned are primarily rare earth elements (REEs) and heavy metals. REEs is extracted from ores, batteries, and CFA and aim to increase the reusage because of scarcity and high prices. Heavy metals are imposing an environmental hazard and $scCO_2$ is an environmentally friendly method of extraction for this purpose. The results show potential for moving from a laboratory scale to an industrial one. For CFA, an extraction efficiency up to 52% for some heavy metals and 62% for some REEs is observed. A posing problem is that not all metals are extractable since they are trapped in the coal matrix. For ores, recovery rates were around 55 % for some REEs, and for uranium, a recovery rate of around 97 % was observed. For REEs in end-of-life batteries, very high recovery rates around 90% were observed, however, the trade-off between selectivity and sensitivity in pretreatment processes remains a challenge to an industrial application of the technology. All things considered, the TRL (technology readiness level) of $scCO_2$ extraction of valuable metals was assessed as TRL 4.

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1. Introduction

The aim of this report is to study the perspectives and opportunities of a wider usage of metal extraction with the help of supercritical CO_2. This promising technique is based on exploiting the low viscosity of a gas and high density of a liquid characterizing the supercritical fluid state. This state is relatively easily accessible for CO_2, not requiring much energy or any complex equipment.

Main positive aspects of this technique include the ability to maneuver the temperature and pressure to easily affect solvation capacities, diffusivity, viscosity, density and many others. Indeed, higher temperature decreases fluid density, and higher pressure means higher density, so higher solute solubility. Also, $scCO_2$ has good heat transfer coefficient. Finally, the solvent is eco-friendly and safe (Knez *et al.*, 2019).

Up to now, technology of metal extraction with supercritical CO_2 is only present on laboratory scale. Researchers around the world are investigating the potential of $scCO_2$ in extraction of metal from ores, used electronic equipment, fly ash, industrial waste, used nuclear fuel, contaminated soil and others (Lin *et al.*, 2014). Industrially, $ScCO_2$ is used to decaffeinate coffee. With a co-solvent (water or ethanol), caffeine can be dissolved in $scCO_2$ from the beans, and then used in food and medical industry. This is a large-scale, sustainable, safe and efficient method (Zabot, 2020). It is also useful when preparing cosmetics products. Its role is to extract, often from plants, components such as waxes, colorants, fragrances, thickeners. It can enable the desired quality and purity (Zorić *et al.*, 2022). Information has also been found about using $scCO_2$ to remove pesticides and metals from agricultural crops (Cui, Wang and Shen, 2001;Tolcha *et al.*, 2020). Among these, the extraction of metals from fly ash, metal ores, and electrodes in lithium-ion batteries (LIBs) will be examined in detail in this report.

Should also be briefly mentioned the major industrial methods that are most popular, and up to now more efficient than $scCO_2$: hydrometallurgy and pyrometallurgy. They are current extraction techniques to extract indium, lithium, platinum and others from coal, phosphogypsum, fly ash, bauxite slag, and electronic waste.

Pyrometallurgy involves very high temperature reactions, where metals can be in liquid or even gas phase. It is well known but energy intensive. Hydrometallurgy involves lower temperatures. It has more applications, and is more diverse, but still consumes energy and generates waste too. The three steps include leaching (adding aqueous solution and chelating agents to the ore), followed by solution concentration (removal of impurities through precipitation, solvent extraction, ion exchange, electrowinning) and metal recovery. Leaching can be made more specific and efficient by varying pH, concentration, addition of microorganisms, calcination, electric field, microwave heating and others (Wu, Liu and Qu, 2022).

The other major alternative to $scCO_2$ are organic solvents. They could have higher solubility and are less pH-dependent (CO_2 prefers acidic solutions for high extractions), but are often toxic, require purification, and are more expensive.

Main disadvantages of $scCO_2$ include necessity of special pressurized extraction units, apolar nature of CO_2 and insufficient solubility of metal ions in it. To mitigate these downsides, various co-solvents, adducts, chelating agents, and modifiers are added. However, these substances are often themselves organic and don't respect green chemistry principles. They will be studied later in detail.

It will then be concluded in which areas $scCO_2$ extraction has the highest potential of developing into an industrial technique. Strengths, weaknesses, opportunities and threats of scaling-up $scCO_2$ technology will also be discussed.

2. Theoretical Background

2.1. Properties of $scCO_2$ useful for extraction

Supercritical point of CO_2 is achieved at relatively low temperatures and pressures: 31.1 °C and 73.8 bar. This makes this gas a good option for industrial use, without high energy needs. Its density can be easily changed as a function of temperature and pressure. This impacts the solubility of compounds in it and leads to higher extraction selectivity toward different masses, polarities, boiling points. Low viscosity favours mass transport, as a result high diffusivity and extraction speed. Low surface tension decreases surface area, therefore equipment size. Other benefits of $scCO_2$ include: chemical inertness, low cost, easy removal (just depressurize), non-toxicity, non-flammability, absence of corrosive effects, miscibility with both fluorous and organic solvents (Budisa and Schulze-Makuch, 2014). It is also easy to recover the solvent and separate it from CO_2 very easily.

2.2. Technical mechanism of supercritical fluid extraction

A scheme of $scCO_2$ extraction is presented in Figure 1. CO_2 is pumped as a liquid at around 5°C and 50 bar. It is then pressurized and heated. Then, in the extraction vessel, it is ejected onto the metal-containing material. Using solid samples leads to higher efficiency than liquid ones due to higher density and faster diffusivity. The $scCO_2$-metal mixture is then sent to the separator, where pressure is lowered. This sharply decreases metal solubility in the fluid, and it precipitates and gets collected. CO_2 can be sent to the atmosphere or recycled. The extraction itself can be controlled either by the diffusion rate (transport of metal ions towards the surface and the fluid), or the rate of dissolution in the fluid (solubility). The former can be improved by raising temperature, adding modifiers and decreasing particle size, and the latter by raising flow rate of $scCO_2$, so higher pressure, or, also, through modifiers addition like alcohols, which add polarity.

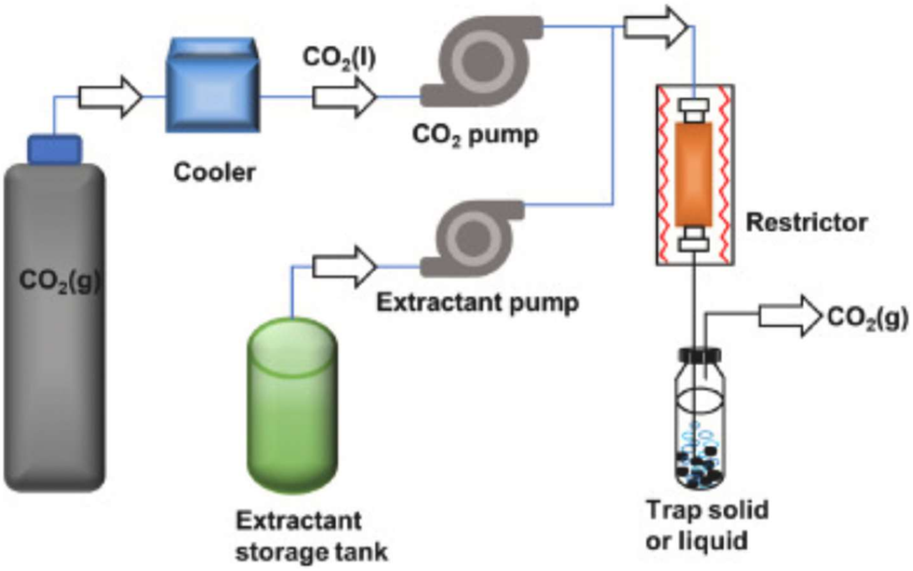

Figure 1. Components of a $scCO_2$ extraction pilot plant (Song *et al.*, 2021).

The general process described above can however be divided into static and dynamic extraction. In static extraction, $scCO_2$ dissolves the metal until equilibrium in a vessel without continuous flow for a long time. This is a simpler way and helps if diffusivity is low. However, it can be very slow. In dynamic extraction, it is the continuous renewal of solvent that helps metals get absorbed by CO_2. This is fast but only efficient if the dissolution kinetics are good.

2.3. Chemistry of $scCO_2$ extraction

The chemical side of the process can be summarized in 3 steps: coagulation, complexation and extraction. It is convenient to study this process, for example by studying extraction from acid mine drainage (Song *et al.*, 2021). Most often, the feed stream is a liquid containing rare-earth metal ions dissolved in it. It is necessary to precipitate them to form a solid phase, to obtain a higher concentration. This is done during the first phase, coagulation. A coagulant is often added, for example sodium aluminate, and a specific pH is required. The second step is complexation. Metal gets dissolved into ions surrounded by organic complexes. It is essential to form neutral complexes with the metals so that they can be easily dissolved by the non-polar CO_2. To form such complexes, it is first required to filter the mixture. Then, special complexation agents are needed, as well as an acidic environment. More details and examples of such agents are provided below. Once the agents are added, an organic phase forms with the metal complexes. Finally, the extraction step terminates the procedure. It is here that $scCO_2$ enters, so pressure and temperature requirements are particularly important. Figure 2 shows an example of such a process (Song *et al.*, 2021).

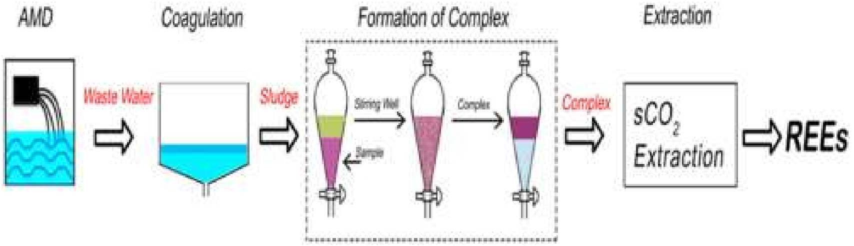

Figure 2. process of extraction with $scCO_2$ (Song *et al.*, 2021).

2.4. Altering physical parameters

The simplest ways of improving efficiency of $scCO_2$ extraction is by varying pressure and temperature. Generally high pressure increases solubility of the compound. In such cases, organic solvents may not be needed at all. Therefore, in most cases pressure is steadily increased throughout the extraction process. However, it was noticed that too high pressures decrease mass transport of CO_2 (Essien, Young and Baroutian, 2020).

Temperature rise leads to lower density of CO_2 and lower solubility. It also increases the volatility of additives: a negative phenomenon. On the other hand, complexation is faster at higher temperatures. This means that metals form neutral complexes faster, and get dissolved in CO_2. Another benefit is that high temperatures enables solvent to easier enter the solid metal-containing sample by decreasing the viscosity of the CO_2 and letting the organic solvent dissolve the solute (Wu, Liu and Qu, 2022). So, density of CO_2 has 2 aspects: low concentration lowers extraction rates, but it increases the reaction of complexation. We can then suggest that in case of a weak chelating agent, temperature could be increased, and the rate could be determined by defined flow level of CO_2. (Erkey, 2000)

2.5. Additives to enhance recovery

By addition of various chemicals, it is possible to change parameters of the extraction. The problem of greatest interest is the solubility of metal ions in supercritical CO_2. Below will be examined the main chemical additives used to enhance extraction.

First of all, an important parameter is acidity. CO_2, in presence of water, can dissolve to carbonic acid H_2CO_3 that has a pH of around 2.95 (Smart *et al.*, 1997). During the extraction, an equilibrium is formed between metal complex in supercritical phase and metal ions (K_{ex} in equation 1 below). Equation 1 shows this relationship. [MAn] is the concentration of the metal ions complexed with the ligands, [H+] is the acid concentration, [M+] the non-bound (or non-chelated) metal ions concentration and [HA] that of the protonated ligands. Extraction constant is higher in higher acidity, as seen on Figure 3. Thus, we often see that sulfuric or nitric acid is added to the extractors to enhance solubility.

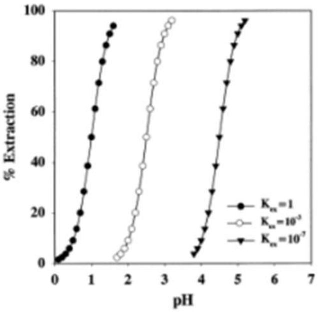

Figure 3. Dependency on pH (Erkey, 2000)

$$K_{ex} = \frac{[\overline{\mathrm{MA_n}}][\mathrm{H}^+]^n}{[\mathrm{M}^{+n}][\overline{\mathrm{HA}}]^n} \tag{1}$$

Equation 1: extraction equilibrium (Erkey, 2000)

Another group of additives are extractants or adducts. These form ligands, replacing water, around metal ions to make them soluble in CO_2. Most common examples are organophosphates, amongst which the best are the small molecules of tri-ethyl/butyl-phosphate (Zhang, Anawati and Azimi, 2022). These adducts are first dissolved in CO_2 itself (Baek *et al.*, 2016).

Another group are co-solvents, entrainers or modifiers. These are organic solvents that make metal ions more soluble, but unlike extractants, they also increase polarity of CO_2, especially if they are polar, like alcohols. Most often liquids of low polarity are used: small hydrocarbons, alcohols, and organic acids (maleic, citric). Water tends to be avoided as co-solvent (Wu, Liu and Qu, 2022).

Finally, chelating agents help create a ring-shaped ligand around the metal ion during complexation. These serves the same goal as adducts. Examples include crown ethers, dithiocarbamates, diketones. The latter two are particularly effective in the typical pH of 2-5 in extractants (Bailar and Trotman-Dickenson, 1973). However, chelators can be very specific to different metals and have low mass transport and solubility properties. This problem can be solved by adding fluorinated alkyls or ethers. The more flour atoms, the better for the dissolution of the metal chelate complex. Number of ligands also impacts: a higher number shields the metal better and improves solubility (Erkey, 2000).

Although the additives and physical transformations described above do help improve extraction, they have limitations, concerning waste and byproduct generation, as described above.

3. Applications

3.1. Coal Fly Ash

When extracting metals with $scCO_2$, one way is to extract it from coal fly ash (CFA). CFA is a fine powder that is created when combusting coal. With an increasing energy demand, coal is commonly used to generate energy in thermal power plants. The CFA consists of both oxides from iron, silicon, calcium, and magnesium as well as toxic elements from beryllium, arsenic, lead, and mercury. Most commonly, CFA is disposed of in landfills which leads to both environmental pollution and a health hazard (Naqvi, Ramkumar and Kar, 2022). Furthermore, CFA has recently shown to be a potential source for REEs (Zhu, Wang and Jun, 2023). The need for REEs is prominent in our modern society since they are used in technological products humans have adapted to needing in everyday life. Because of scarcity, new green alternatives are constantly sought after to extracting and reusing REEs and one of these may be using $scCO_2$ (Zhu, Wang and Jun, 2023).

Kersch *et al.* (2000) investigated the possibility of extracting heavy metals from CFA and sand with the help of ligands and $scCO_2$. Metals are in the form of ions in fly ash and to enable $scCO_2$ to extract heavy metals they need to be in neutral complexes. For these reasons, the authors used ligands and formed organic complexes with the ions, before using $scCO_2$. The ligands should show high complexation with the metals and at the same time be soluble in $scCO_2$. The ligands used in this article are presented in table 1 together with the yielded extraction efficiencies for different metals.

Table 1. The ligands and their effect on extracting efficiency from Kersch *et al.* (2000) at *10 wt% humidity, p=160 bar, T=45°C, t=10/30 min (10 min extraction, 30 min dynamic extraction).*

Ligands	**Recovered metals and Extraction Efficiency [%]**	
Cyanex 302 (Bis(2,4,4-trimethylpentyl)monothiophosphinic acid)	Cr	10
	Sb	9
	V	6
	Mo	12
D_2EHTPA (Bis(2-ethylhexyl)monothiophosphoric acid)	Cr	17
	Sb	12
	V	13
	Mo	18

NaDDC sodium diethyldithiocarbamate	Cr	9
	Sb	1
	V	6
	Mo	5
Cyanex 923 (Mixture of tertiary octyl- and hexylphosphine oxides)	Cr	9
	Sb	4
	V	5
	Mo	9

The extraction efficiency is defined in this article as:

$$\%\, extraction = \left(1 - \frac{metal\ on\ treated\ fly\ ash}{metal\ on\ untreated\ fly\ ash}\right) \times 100 \tag{2}$$

The results of the study showed that an average extraction efficiency of 10% for fly ash was obtained. The best results are seen with the ligand D_2EHTPA. The reason for the overall extraction efficiency being so low is that only a small number of metals are leachable since most heavy metal particles are bound to the core of the fly ash making them harder to extract. This implies that only a small fraction of the heavy metals is extractable with $scCO_2$ (Kersch *et al.*, 2000).

Zhu, Wang and Jun (2023) investigated the supercritical fluids (SCFs) $scCO_2$, scAir and scN_2 for extracting REEs from CFA. CFA has extremely low concentrations of REEs (<0.2%) whilst it contains about 90% of other impurities. When extracting the REEs it is also prominent to separate them from other metals in the CFA. Since tributyl phosphate-nitric acid (TBP-HNO_3) previously had been successful in selectively extracting REEs from other impurities, they decided to use it together with SCFs in this article. TBP-HNO_3 enables metal ions to leach out of the CFA and react with HNO_3 to form metal nitrates which more easily can be extractable with SCFs. The study shows that around 70% of the REEs were leachable from CFA. They used a multistage stripping to improve the purity of REEs and after the sixth stripping step with $scCO_2$ the results showed a general purity of REEs as 6.26%. The purity was calculated by adding up all the concentrations of the REEs in the stripping solution, and then dividing it with the total concentration of all elements in the stripping solution. The authors state that they collected 31.2% of the REEs available from CFA, which is still very little because of the low available concentrations. However, the article states that because of the large quantity of CFA produced every year, this could still be seen as a possible source of REE extraction. Furthermore, it is seen as a success compared to other extraction methods of REEs from CFA. The study was also successful in stripping away a lot of impurities where the extraction efficiency for the heavy metals Cr, Cu, Mn, and Zn where 11.9%, 9.0%, 30.9%, and 62.0%, respectively. This is compared to the average extraction efficiency of 10% using ligands by Kersch *et al.* (2000) showed much greater success for especially zinc.

Furthermore, Kersch et al. (2002) aimed at developing a method of continuously removing heavy metals from fly ash in a large-scale process of 12 dm^3. The metals investigated in this study were Zn^{2+}, Pb^{2+}, Cu^{2+}, Sb^{2+}, Ni^{2+}, and Cd^{2+} in terms of extraction efficiency defined in equation (2). Three different experiments with varying concentrations of the complexing-agent Cyanex 302 and extraction time were performed and compared. Later, one more experiment was performed to compare Cyanex 302 with the complexing agent D_2EHPA. The results showed that using 0.02g Cyanex 302/g CO_2 yielded the highest extraction efficiency for Zn^{2+}, Pb^{2+}, Cu^{2+}, and Cd^{2+} at around 21%, 12%, 46%, and 52% respectively. Using 0.005 g D_2EHPA/g CO_2 yielded the highest extraction efficiency for Sb^{2+} and Ni^{2+} at 11% and 21% respectively. The extraction time was 95 min for Cyanex 302 and 135 min for D_2EHPA at a pressure of 20 MPa and a temperature of 40°C. The results indicate that $scCO_2$ is usable when extracting metals from CFA in a larger scale and that the extraction efficiency does not depend on the amount of complexing agent, but the distribution of complexing agent over time.

The articles demonstrate the feasibility of scaling up extraction of metals from fly ash with $scCO_2$. However, a challenge it faces is the availability to extract metals from the coal when they are embedded in the matrix. The applicability in extracting REEs needs to be investigated further, but it can be seen as beneficial to use this method for heavy metals since it lowers the amounts of metals in the fly ash in an environmentally friendly way. Still, more research is needed to achieve an efficiency that can compete with other extraction methods where very high efficiencies are possible (Sahoo et al., 2016).

3.2. Ores

Another application where $scCO_2$ can be used for extraction is from ores which can contain high-valuable metals as REEs and uranium. Normally hydrometallurgy is the preferable alternative for extraction of REEs from rare-earth-containing ores due to its relatively low energy consumption and adaptability of resource scale. However, there are drawbacks to the technique, as it is reagent intensive, and strong acids, and organic solvents are often required. It is therefore desired for extraction of REEs from ores to have a process that requires low energy consumption and small waste generation that yields high extraction values. Zhang *et al.* (2020) performed a study about the extraction of REEs from a Canadian ore using $scCO_2$. The ore was a Nechalaco ore deposit located in Northwest Territories), and the drill core samples were first crushed, blended and a composite sample was made, which was then finely grounded. The chelating agent complex that was used was the TBP-HNO_3 and was prepared by mixing TBP with 70 wt% HNO_3. They tested five operating parameters: temperature, pressure, residence time, agitation rate, and solid-to-chelating agent ratio. The run with the observed highest extraction of 55 % had the conditions: 60 °C, 3000 psi pressure, 2 hours residence time, 750 rpm agitation time, and a solid-to-chelating ratio of 0,2. The extraction efficiencies were the following:

Na: 41.7 % **Al**: 35.6 % **K**: 42.2 % **Ca**: 63.9 % **Fe**: 45.4 % **Y**: 49.4 %
Zr: 91.2 % **La**: 58.1 % **Ce**: 57.3 % **Pr**: 57.4 % **Nd**: 56.8 % **Sm**: 55.9 %
Gd: 54.5% **Tb**: 52.5 % **Dy**: 47 % **Ho**: 49.3 % **Er**: 49 % **Yb**: 44.7%.

Superfluid extraction from this study showed to be a potentially viable alternative to recover REEs from primary resources. However, the authors suggest that future work should focus on improving extraction efficiency (Zhang *et al.*, 2020).

An additional extraction using $scCO_2$ is uranium from natural ores, which was studied by Leybros *et al.* (2017), and the authors mentioned that when writing, there were insufficient studies on the extraction of uranium from actual natural ores where $scCO_2$ is used. In the study, they used either commercial extractants such as the organophosphoric acids PC88A and Cyanex 301, or an amidophosphonate molecule named DEHCNPB. The extraction yield was optimal at the test's lowest temperature of 40 °C and highest pressure of 25 MPa. A high uranium yield of the extraction up to 97 % was achieved when DEHCNPB was used (Leybros *et al.*, 2017).

3.3. Batteries

Yao, Farac and Azimi (2017) reported the successful extraction of REEs from the active material on the negative electrode of an end-of-life nickel metal hydride (NiMH) from a Toyota Prius using $scCO_2$ with TBP-HNO3. The sample acquired from the negative electrode was ground using a mortar and a pestle to the mean particle size of 11.7 µm. The authors reported 86 % La, 86 % Ce, 88 % Pr, and 90 % Nd were recovered from the sample at the optimum conditions and highlighted minimal hazardous waste generation and low energy consumption of the process.

Zhang and Azimi (2022) demonstrated that a similar SCFE process can extract Li, Ni, Mn, and Co from the active material in the $Li(Ni_{0.40}Mn_{0.35}Co_{0.25})O_2$ (NMC) electrode of a lithium-ion battery. A lithium polymer cell was manually disassembled from a 40-Ah 36-cell module that was in end-of-life state after over 500 discharge/charge cycles, and 90 % extraction efficiency for Li, Co, Mn, and Ni was achieved by the process.

Bertuol et al. (2016) investigated recovering cobalt from $LiCoO_2$ (LCO) electrodes in spent lithium-ion batteries using $scCO_2$. Like in the previous study, the active material was manually separated from a batch of batteries of the same manufacturer. They reported their method enables similar recovery of cobalt (95.5 %) in a shorter reaction time (4 min) and less H_2O_2 (4 %) compared to leaching at atmospheric pressure (98 %, 60 min, 8%). However, although the authors refer to their leaching process as a modified $scCO_2$ process, Zhang and Azimi (2022) pointed out that it is more of a supercritical fluid assisted extraction, rather than a standalone scCO$_2$ process, because the polar acid solution does not dissolve in nonpolar CO$_2$.

Table 2 summarizes the REEs recovered from batteries in the studies above with more detailed process conditions including S:CA ratio (solvent and chelating agent ratio), CA (chelating agent), and RA (reducing agent).

Table 2. Studies on scCO$_2$ extraction of REEs from batteries.

Reference	**Extracted metals and recovery [wt%]**		**Type of LIB**	**Operating condition of SCFE**
Yao, Farac and Azimi (2017)	La	86	NiMH	31 MPa, 35 °C, 2 h
	Ce	86		S:CA ratio of 1:10
	Pr	88		CA: TBP-HNO$_3$(H$_2$O)
	Nd	90		RA: 2 mol% MeOH
Zhang and Azimi (2022)	Li	89	NMC	31 MPa, 60 °C, 30 min, 750 rpm
	Ni	90		S:CA ratio of 5 mL/g
	Mn	90		CA: TBP-HNO$_3$
	Co	89		RA: 4 % (v/v) H$_2$O$_2$
Bertuol *et al.* (2016)	Co	95.5	LCO	75 bar, 75 °C, 5 min
				2M H$_2$SO$_4$
				RA: H$_2$O$_2$

Reviewing the three studies, it is evident that scCO$_2$ extraction of REEs from batteries is a promising technology with great potential to help close the supply chain by significantly improving waste recovery, from both chemical and economical perspectives. The technology is also very relevant today with increasing demand for batteries for electric vehicles as well as geopolitical and ethical concerns around mining REEs.

However, the most prominent challenge in scaling up the technology to an industrial level lies not in the scCO$_2$ extraction process itself, but in the rigorous and highly sensitive pretreatment processes required before it. The structure and composition of electrode materials of batteries vary greatly by their application and manufacturer and often are not fully disclosed. In addition, no other method than manual disassembly has been successfully employed for separating the active materials from the electrodes in these studies.

Some studies investigated mechanical pretreatment methods, such as shredding (Thompson et al., 2020) and crushing and sieving by particle size differences (Porvali et al., 2019). However, the simplicity of these processes comes at a cost of low selectivity, which then mandates more extensive separation processes in downstream. Therefore, development of more robust, selective, and economical pretreatment processes is crucial for an industrial application of the process.

On the other hand, introducing legislations to enforce transparency of chemical structure and composition of key components of batteries may be suggested to facilitate pretreatment of the active materials, although this is likely to be initially met with hesitancy of the manufacturers.

4. Conclusion

Strengths of $scCO_2$ extraction clearly include its eco-friendliness, mild temperature and pressure, ease-to-modify physical and chemical parameters, safety, and other benefits, as mentioned above. Scaling up this method to replace, for example, pyrometallurgy and hydrometallurgy, will enable considerable energy savings and provide significant atom economy.

Amongst the weaknesses in scaling up $scCO_2$ extraction, we can highlight the difficulty to use CO_2 on its own to extract free metal ions. As CO_2 is apolar, it cannot dissolve polar elements. Therefore, to achieve good yields it is obligatory to add co-solvents, entrainers, complexing agents and other additives, as well as some acids. All this makes the process much less eco-friendly and waste-free. Moreover, these additives are often expensive to produce.

Another weakness would be to maintain similar temperature and pressure within the extraction column, to have uniform levels of extraction. If the substance is extracted from is a solid, batch reactors are preferred. In liquid extraction, counter-current continuous reactor is used (Machado *et al.*, 2013). In any case, adequate convection and diffusion levels are required to avoid mass transport problems. Although not a big problem for $scCO_2$ itself, it does cause challenges related to maintaining, everywhere, the appropriate conditions to avoid exiting the supercritical state. As studied before, small changes in temperature and especially pressure can largely influence solubility. So, special instruments and control equipment are needed to monitor these parameters. In large scale extraction, an extraction column will be used. This means that the pressure drop between the top and bottom must be compensated.

As shown on figure 1, the major components of a $scCO_2$ extraction facility are: CO_2 and extraction tanks, a cooler, an extraction column, pumps, and a separator. A recycle stream for CO_2 can be installed too. Most of these instruments require external energy to operate, and scaling them up leads to consecutive increase in energy demands.

Finally, a weakness is the transport of CO_2 towards the units of extraction. If it is planned to install many small-scale plants to recycle metals, it will take an entire infrastructure to bring CO_2 to it. It will have to be decided if CO_2 will be transported in solid, liquid or gas form. Moreover, the acquisition of pure CO_2 is also a problem: we can suggest it originating from industrial waste streams or from carbon capture. The first requires more logistics and the second is not very popular of a technique yet.

Opportunities of $scCO_2$ in metal extraction are related to the growth of electronic industry and the shortage of precious metals expected to grow in the coming years. Another promising aspect is that usage of $scCO_2$ is already existent now, on a large scale, in industries such as food, pharma, agriculture, polymers and others. Further research into chemical additives to help dissolution of metals will help adapt existing larger scale technologies to metal extraction.

Finally, threats of the studied technology derive from the competition with the main established metal extraction techniques: pyrometallurgy and especially hydrometallurgy. These large-scale methods are adapted to a much wider range of components and have much more financial possibilities to improve their yields further. These industries themselves constantly evolve, learn to re-use their waste and become more efficient.

We can see that $scCO_2$ extraction of metals seems like a promising technique but has a number of obvious limitations, making it not as attractive in relation to traditional methods as from the first site. The examples studied in part 3 of this report could help us conclude that the highest potential of this method is in the waste electronic equipment field. Indeed, LIB is a growing industry and traditional extraction techniques are not yet widely applied to it. Currently, used dead batteries are sent to landfill very often. $scCO_2$ extraction can be a solution, especially considering that the volumes extracted can be kept modest, in comparison to metal ores where huge amounts must be treated in one area, corresponding to the metallurgical plant. Extraction efficiencies for the batteries are also among the highest. For CFA, efficiencies are high for extraction of heavy metals but only at a small scale, which is inapplicable in industrial conditions. Furthermore, the extraction efficiency is not nearly as good as for other existing techniques meaning that a lot of more research is needed before working commercially.

To evaluate the technology readiness level (TRL) of this technique, we can underline that it is currently located somewhere in between applied research and development stages. This lets us assess it as level 4, depending on the industries it is planned to be used for. The technology concept has been formulated, proof of concept conducted, process mechanism is clear, with all its steps. The concept has been successful in laboratory environment with high yields reached. Various research groups have experimented with different additives, solvents and physical conditions to improve efficiency. We now can tell which molecules are the best at enhancing the extraction of metals. Moreover, recycle streams have also been designed. The key step necessary to reach TRL 5 is to develop a miniplant. It would also be good to be clearer with the thermodynamic and kinetic data of the process. We can argue that some of the research projects mentioned in the report have used constructions that can be considered already as miniplants. So, we can say that TRL 4 is achieved and TRL 5 is undergoing implementation currently. Considering the interest of some industries in this research field, it is possible to suggest that soon we will see reports of pilot plants for metal extraction.

As a result, we can, with cautious optimism, conclude that $scCO_2$ extraction could be scaled up to an industrial technique, in priority in the field of reusing metals from batteries. For that, current knowledge in chemistry of metal extraction, as well as the experience of existing industrial applications of $scCO_2$ for non-metal components, needs to be used. Another option would be to merge the technology into some existing industrial processes like hydrometallurgy, which would reduce initial investment costs.

5. References

Baek, D.L. *et al.* (2016) 'Extraction of Rare Earth Oxides Using Supercritical Carbon Dioxide Modified with Tri-n-Butyl Phosphate–Nitric Acid Adducts'. *Industrial & Engineering Chemistry Research,* 55 (26), pp. 7154-7163. https://doi.org/10.1021/acs.iecr.6b00554.

Bailar, J.C. and Trotman-Dickenson, A.F. (1973) *Comprehensive inorganic chemistry.* 1. edn. Oxford: Pergamon P.

Bertuol, D.A. *et al.* (2016) 'Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction'. *Waste Manag,* 51 245-251. https://doi.org/10.1016/j.wasman.2016.03.009.

Birloaga, I. and Veglio, F. (2022) 'An innovative hybrid hydrometallurgical approach for precious metals recovery from secondary resources'. *J Environ Manage,* 307 114567. https://doi.org/10.1016/j.jenvman.2022.114567.

Budisa, N. and Schulze-Makuch, D. (2014) 'Supercritical carbon dioxide and its potential as a life-sustaining solvent in a planetary environment'. *Life (Basel),* 4 (3), pp. 331-340. https://doi.org/10.3390/life4030331.

Cui, H., Wang, T. and Shen, Z. (2001) 'Removal of Trace Heavy Metals from a Natural Medicine Material by Supercritical CO2 Chelating Extraction'. *Industrial & Engineering Chemistry Research,* 40 (16), pp. 3659-3663. https://doi.org/10.1021/ie001124n.

Erkey, C. (2000) 'Supercritical carbon dioxide extraction of metals from aqueous solutions: a review'. *The Journal of Supercritical Fluids,* 17 (3), pp. 259-287. https://doi.org/10.1016/s0896-8446(99)00047-9.

Essien, S.O., Young, B. and Baroutian, S. (2020) 'Recent advances in subcritical water and supercritical carbon dioxide extraction of bioactive compounds from plant materials'. *Trends in Food Science & Technology,* 97 156-169. https://doi.org/10.1016/j.tifs.2020.01.014.

Kersch, C. *et al.* (2002) 'Municipal waste incinerator fly ash: supercritical fluid extraction of metals'. *Journal of Chemical Technology & Biotechnology,* 77 (3), pp. 256-259. https://doi.org/10.1002/jctb.589.

Kersch, C. *et al.* (2000) 'Extraction of Heavy Metals from Fly Ash and Sand with Ligands and Supercritical Carbon Dioxide'. *Industrial & Engineering Chemistry Research,* 39 (12), pp. 4670-4672. https://doi.org/10.1021/ie0002226.

Knez, Ž. *et al.* (2019) 'Are supercritical fluids solvents for the future?'. *Chemical Engineering and Processing - Process Intensification,* 141. https://doi.org/10.1016/j.cep.2019.107532.

Leybros, A. *et al.* (2017) 'Supercritical CO 2 extraction of uranium from natural ore using organophosphorus extractants'. *Chemical Engineering Journal,* 316 196-203. https://doi.org/10.1016/j.cej.2017.01.101.

Lin, F. *et al.* (2014) 'Recent Progress in Heavy Metal Extraction by Supercritical CO2 Fluids'. *Industrial & Engineering Chemistry Research,* 53 (5), pp. 1866-1877. https://doi.org/10.1021/ie4035708.

Machado, B.A.S. *et al.* (2013) 'Supercritical Fluid Extraction Using CO2: Main Applications and Future Perspectives'. *Separation Science and Technology,* 48 (18), pp. 2741-2760. https://doi.org/10.1080/01496395.2013.811422.

Naqvi, S.Z., Ramkumar, J. and Kar, K.K. (2022) 'Coal-based fly ash'. *Handbook of Fly Ash.* pp. 3-33.

Porvali, A. *et al.* (2019) 'Mechanical and hydrometallurgical processes in HCl media for the recycling of valuable metals from Li-ion battery waste'. *Resources, Conservation and Recycling,* 142 257-266. https://doi.org/10.1016/j.resconrec.2018.11.023.

Sahoo, P.K. *et al.* (2016) 'Recovery of metals and other beneficial products from coal fly ash: a sustainable approach for fly ash management'. *International Journal of Coal Science & Technology,* 3 (3), pp. 267-283. https://doi.org/10.1007/s40789-016-0141-2.

Smart, N.G. *et al.* (1997) 'Solubility of chelating agents and metal-containing compounds in supercritical fluid carbon dioxide'. *Talanta,* 44 (2), pp. 137-150. https://doi.org/10.1016/s0039-9140(96)02008-5.

Song, G. *et al.* (2021) 'Extraction of selected rare earth elements from anthracite acid mine drainage using supercritical CO2 via coagulation and complexation'. *Journal of Rare Earths,* 39 (1), pp. 83-89. https://doi.org/10.1016/j.jre.2020.02.007.

Thompson, D.L. *et al.* (2020) 'The importance of design in lithium ion battery recycling – a critical review'. *Green Chemistry,* 22 (22), pp. 7585-7603. https://doi.org/10.1039/d0gc02745f.

Tolcha, T. *et al.* (2020) 'High Density Supercritical Carbon Dioxide for the Extraction of Pesticide Residues in Onion with Multivariate Response Surface Methodology'. *Molecules,* 25 (4), pp. https://doi.org/10.3390/molecules25041012.

Wu, F., Liu, X. and Qu, G. (2022) 'High value-added resource utilization of solid waste: Review of prospects for supercritical CO2 extraction of valuable metals'. *Journal of Cleaner Production,* 372. https://doi.org/10.1016/j.jclepro.2022.133813.

Yao, Y., Farac, N.F. and Azimi, G. (2017) 'Supercritical Fluid Extraction of Rare Earth Elements from Nickel Metal Hydride Battery'. *ACS Sustainable Chemistry & Engineering,* 6 (1), pp. 1417-1426. https://doi.org/10.1021/acssuschemeng.7b03803.

Zabot, G.L. (2020) 'Decaffeination using supercritical carbon dioxide'. *Green Sustainable Process for Chemical and Environmental Engineering and Science.* pp. 255-278.

Zhang, J., Anawati, J. and Azimi, G. (2022) 'Urban mining of terbium, europium, and yttrium from real fluorescent lamp waste using supercritical fluid extraction: Process development and mechanistic investigation'. *Waste Manag,* 139 168-178. https://doi.org/10.1016/j.wasman.2021.12.033.

Zhang, J. and Azimi, G. (2022) 'Recycling of lithium, cobalt, nickel, and manganese from end-of-life lithium-ion battery of an electric vehicle using supercritical carbon dioxide'. *Resources, Conservation and Recycling,* 187. https://doi.org/10.1016/j.resconrec.2022.106628.

Zhang, J. *et al.* (2020) 'Supercritical Fluid Extraction of Rare-Earth Elements from a Canadian Ore'. 2020 Cham. Springer International Publishing, pp.107-118.

Zhu, Y., Wang, G. and Jun, Y.-S. (2023) 'Supercritical carbon dioxide/nitrogen/air extraction with multistage stripping enables selective recovery of rare earth elements from coal fly ashes'. *RSC Sustainability,* 1 (2), pp. 251-260. https://doi.org/10.1039/d2su00033d.

Zorić, M. *et al.* (2022) 'Supercritical CO2 extracts in cosmetic industry: Current status and future perspectives'. *Sustainable Chemistry and Pharmacy,* 27. https://doi.org/10.1016/j.scp.2022.100688.