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Review Paper

Application and Progress of Supercritical CO_2 Extraction in Metal Recovery

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Abstract. In the context of increasingly scarce resources and prominent environmental issues, typical metal-containing waste materials (such as nuclear waste, uranium tailings, spent catalysts, and spent batteries) are rich in valuable metals, including lanthanides, actinides, and transition metals. Recycling these metals is significant for both resource recovery and environmental protection. Supercritical carbon dioxide ($scCO_2$) extraction technology is a novel and environmentally friendly method characterized by its green and efficient nature. In this paper, an overview of the application of $scCO_2$ extraction technology for the recovery of metals from waste is presented, and research trends are summarized. The efficiency of metal recovery based on $scCO_2$ has been significantly improved, with the extraction rate of some valuable metals reaching over 90%. CiteSpace software was used to visualize the research status of metal recovery using $scCO_2$ extraction technology. Moreover, suggestions are proposed for future development in the field of metal recycling.

Keywords: *supercritical carbon dioxide; extraction; waste treatment; metal recycling; CiteSpace visualization*

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1 Introduction

With the acceleration of China's industrialization, the consumption of valuable metals has increased substantially, leading to the depletion of high-grade primary metal resources. Meanwhile, industrial wastes (such as nuclear waste, uranium tailings, spent catalysts, and spent batteries) contain large amounts of high-value-added metals like uranium, thorium, lithium, zinc, gold, silver, nickel, molybdenum, and cobalt. The grade of these metal elements in waste is much higher than that in natural ores, making them valuable secondary resources. Exploring technologies and methods for the renewable utilization of secondary metal resources can not only reduce environmental pollution but also effectively alleviate the depletion of mineral resources.

Current mainstream metal recovery technologies include hydrometallurgy and pyrometallurgy-hydrometallurgy combined processes. Commonly used methods are chemical precipitation, ion exchange, and solvent extraction. Chemical precipitation, typically involving sulfide or ammonium salt precipitation, often requires adding large amounts of precipitating agents, resulting in complex processes, inconvenient operation, and the generation of significant waste. Ion exchange is widely used in solution systems. For example, Berrebi et al. used ion exchange resin to separate and extract molybdenum from the alkaline leaching solution of spent catalysts; Zeng Li et al. used DP-1 chelating resin to achieve deep vanadium removal from ammonium molybdate solution. Although this method offers high selectivity for metals, its application is limited due to the small processing capacity of the resin and the difficulty of regeneration. Solvent extraction, with advantages such as high separation coefficients, simple processes, and high selectivity, has gradually become a research hotspot in the field of metal recovery in recent years. Pateli et al. dissolved and extracted metal oxides like MnO and CoO using a trifluoromethanesulfonic acid mixed system, finding that the solubility of metal oxides increased with the amount of trifluoromethanesulfonic acid added. However, traditional fluorine-containing organic solvents have disadvantages such as high toxicity and high volatility. In contrast, supercritical carbon dioxide ($scCO_2$) has advantages like high diffusivity, high solubility for metal chelates, low cost, wide availability, and no pollution, making it the most widely used supercritical fluid. $scCO_2$ extraction technology features mild and easily controllable operating conditions, avoiding the subsequent separation challenges and environmental pollution risks caused by adding excessive reagents. Its rapid mass transfer rate significantly shortens extraction time and improves efficiency, providing a more environmentally friendly and efficient solution for the metal recycling industry.

Nuclear waste and uranium tailings are rich in lanthanide and actinide metals, while spent batteries and catalysts contain large amounts of transition metals. This paper reviews the research overview of $scCO_2$ extraction technology for metal recovery in these different application scenarios, provides a visual analysis of research focus layout, analyzes the advantages and disadvantages of $scCO_2$ extraction technology, and offers suggestions for its future development.

2 Application of Supercritical CO_2 Extraction for Metals

$scCO_2$ extraction technology is a novel extraction and separation technology developed in the 1970s. Based on the non-polar, pollution-free, non-toxic, and low-cost properties of carbon dioxide, it is widely used in the extraction of organic matter in fields such as food, pharmaceuticals, and civil applications, and has matured. However, research on $scCO_2$ extraction technology for metal recovery started relatively late. In 1992, Laintz et al. first applied $scCO_2$ extraction technology to metal recovery by chelating and extracting ions like copper, mercury, and arsenic from aqueous solutions. Since then, research in the field of metal recovery has gradually emerged. This section outlines the development and research focus of $scCO_2$ extraction technology, with the separation and extraction of metals in different fields as the main line.

2.1 Recovery of Metals from Nuclear Waste Using Supercritical CO_2 Extraction

In the 1990s, to address the sharp increase in nuclear waste and resource shortages caused by the widespread use of nuclear energy, $scCO_2$ extraction technology was initially mainly used for the recovery of lanthanide and actinide metals from nuclear waste residues and wastewater. Lanthanide and actinide metals in nuclear waste mainly include La, Ce, Pr, Nd, U, Pu, etc. These metals pose significant environmental hazards but also have value in energy, resources, medicine, and the environment. Research on using $scCO_2$ technology to recover metals from nuclear waste mainly focuses on the screening of chelating agents, optimization of synergistic extractant formulations and operating conditions, and exploration of extraction mechanisms.

Common types of chelating agents include crown ethers, β-diketones, organophosphorus compounds, dithiocarbamates, and amines. Among them, organophosphorus and β-diketone compounds are the most commonly used chelating agents in the $scCO_2$ extraction of lanthanide metals. Since fluorinated β-diketones undergo structural changes and the formed chelates with lanthanide and actinide metals can further react with tributyl phosphate (TBP) to form new chelates more soluble in the $scCO_2$ system, TBP and β-diketone chelating agents are often used as combined solvents to achieve higher metal extraction efficiency. Shadrin et al. used TBP and fluorinated β-diketone as a combined solvent to remove over 95% of lanthanide elements from nuclear waste residue surfaces by adjusting the system pH. Subsequently, Tomioka et al. conducted experiments on lanthanide element extraction from nuclear wastewater using $scCO_2$ technology combined with TBP-HNO_3, achieving extraction efficiencies of 51% for Nd^{3+} and 46% for Gd^{3+}. To further optimize the extraction efficiency for lanthanide metals, researchers studied the types of β-diketones in the combined solvent. Lin et al. compared the extraction of lanthanide elements by different β-diketones in $scCO_2$ and found that using a TBP-hexafluoroacetone (hfa) chelating agent combination could achieve high extraction rates without adding modifiers.

Extraction of actinide metals mainly focuses on research concerning U. Since U in solid waste often exists in oxide form, β-diketone chelating agents and TBP cannot directly complex with UO_2 to form chelates. However, after conversion to UO_2^{2+} by adding HNO_3, it can form chelates soluble in $scCO_2$ with various ligands, including TBP and β-diketones. The neutral $UO_2(NO_3)_2 \cdot 2TBP$ chelate formed with TBP has a solubility in $scCO_2$ far higher than that of other metal chelates. Therefore, TBP-HNO_3 is commonly used as the chelating agent system for U. The $scCO_2$ fluid containing TBP-HNO_3 can replace traditional organic solvents like benzene, trichloroethylene, and triethylamine used in the PUREX method, achieving efficient extraction of UO_2^{2+}. During $scCO_2$ extraction using $TBP-HNO_3$ as the chelating agent system for actinide metals from nuclear waste, directional separation of U from other actinide metals can be achieved by controlling the $TBP-HNO_3$ ratio. Meguro et al. extracted UO_2^{2+}, Cs^+, Sr^{2+}, Ba^{2+}, Zr^{4+}, Mo^{6+}, Fe^{3+}, Ni^{2+}, and Cr^{3+} from a 3 mol/L HNO_3 solution using $scCO_2$ containing TBP. The results showed that $scCO_2$ containing TBP could effectively extract U from the solution with almost no dissolution capacity for other elements. Quach et al. found that when using a $TBP-CO_2$ system as the solvent, U and Pu could be selectively separated using $scCO_2$ when the HNO_3 concentration was below 3 mol/L.

When extracting uranyl nitrate solids using $scCO_2$ containing organophosphorus reagents-HNO_3, it was found that when the matrix is HNO_3, the extraction efficiency increases with increasing HNO_3 concentration. Under conditions of 6 mol/L HNO_3 concentration, 333.15 K temperature, and 20 MPa pressure, the extraction rate for U was as high as 99%. On the other hand, adding entrainers like methanol or ethanol can reduce the polarity of CO_2 and improve extraction efficiency. Lin et al., when extracting Th^{4+} and UO_2^{2+} using $scCO_2$ containing TBP and β-diketone, found that adding only 5% methanol to the aqueous matrix increased the extraction rate for Th^{4+} from 82% to 97% and for UO_2^{2+} from 70% to 98%.

In the $scCO_2$ extraction process, the solubility of metal chelates is a key factor determining the extraction effect, and this solubility depends on conditions such as temperature, pressure, extraction duration, and the type of entrainer. Rao et al. studied the effects of different operating temperatures, pressures, and extraction times on the extraction rate when extracting U from UO_2 powder using $scCO_2$ containing $TBP-HNO_3$. The extraction rate for U reached 99% under conditions of 323 K temperature, 15.2 MPa pressure, and 30 min extraction duration. By adjusting the concentration and type of entrainer, on one hand, the pH of the extraction environment can be changed to promote the formation of metal chelates, thereby improving extraction efficiency. For example, Toews et al. added methanol to the $TBP-HNO_3$ system, finding that the extraction rate for UO_2^{2+} increased significantly with the amount of methanol added. On the other hand, adding certain oxidants can alter the valence state of metal ions, facilitating the formation of soluble chelates. For instance, adding $FeCl_3$ oxidizes U(IV) to U(VI), forming UO_2^{2+} that complexes with TBP, thus achieving efficient U extraction.

Analyzing the reaction kinetics and thermodynamics of the extraction process helps clarify the chelation reaction-separation mechanism of the supercritical extraction process. Baek et al. conducted phase equilibrium experiments on the extraction of lanthanide metals using $TBP-H_2O$ combined with $scCO_2$. They designed a $scCO_2$ extraction device allowing visualization of the extraction state, as shown in Figure 1. The flow rates of CO_2 and the chelating agent were controlled separately by two flow meters to ensure mixing ratio. The reaction state of the chelating agent $TBP-H_2O$, $scCO_2$, and lanthanide metals was observed in real-time through the phase equilibrium view unit, and the phase equilibrium process was monitored and adjusted promptly. It was clarified that the chelate type when lanthanide metal ions reached equilibrium via $scCO_2$ extraction was $Ln(NO_3)_3(TBP)_4(H_2O)_2$, with the reaction pathway shown in equations (1) and (2); the chelate type formed when lanthanide metal oxides reached equilibrium via $scCO_2$ extraction was $Ln(NO_3)_3(TBP)_3(H_2O)_3$, with the reaction pathway shown in equations (3) and (4).

$$Ln(NO_3)_3\cdot 6H_2O + 4TBP \xrightarrow{scCO_2} Ln(NO_3)_3(TBP)_4(H_2O)_2 + 4H_2O \qquad (1)$$

$$Ln(NO_3)_3\cdot 6H_2O + 3TBP + 3H_2O \xrightarrow{scCO_2} Ln(NO_3)_3(TBP)_3(H_2O)_3 + 6H_2O \qquad (2)$$

$$6TBP(HNO_3)_{1.7}(H_2O)_{0.6} + Ln_2O_3 \xrightarrow{scCO_2} 2Ln(NO_3)_3(TBP)_3(H_2O)_3 + 0.6H_2O + 4.2HNO_3 \qquad (3)$$

$$6TBP(HNO_3)_{5.2}(H_2O)_{1.7} + Ln_2O_3 \xrightarrow{scCO_2} 2Ln(NO_3)_3(TBP)_3(H_2O)_3 + 7.2H_2O + 25.2HNO_3 \qquad (4)$$

In summary, in the field of nuclear waste treatment, effective recovery of lanthanide and actinide metals from nuclear waste has been achieved with the assistance of $scCO_2$ extraction technology, and certain progress has been made in research on optimal process operating conditions and chelation reaction-separation mechanisms. However, the currently used chelating agents are limited in type. Commonly used fluorinated β-diketone chelating agents face problems such as high cost, high toxicity, and high energy consumption. There is an urgent need to develop new types of chelating agents to break through the current technological bottlenecks.

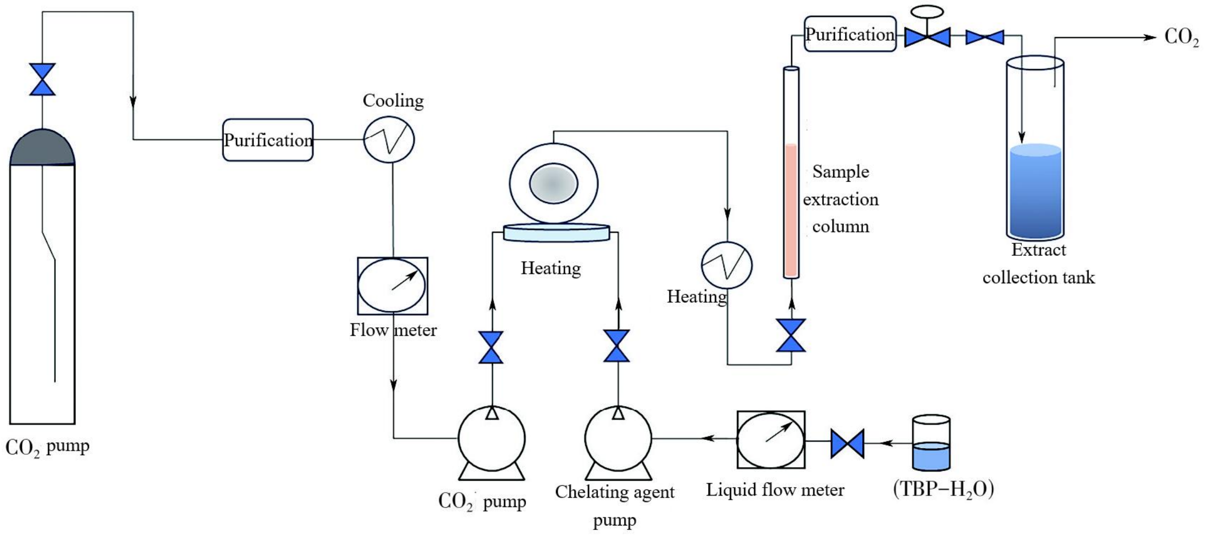

Figure 1 A scCO2 extraction device for lanthanide metal separation, capable of observing phase changes [23]

2.2 Extraction of Metals from Uranium Tailings Using Supercritical CO_2

Due to the large-scale global deployment of nuclear power and production challenges, drawing on previous experience in extracting uranium metal from nuclear waste, researchers domestically and internationally have conducted in-depth studies on the application of this technology in low-grade uranium tailing systems.

By adjusting temperature, pressure, extraction duration, synergistic extractant formulation, and extraction method, the extraction conditions for metal U from uranium tailings can be optimized. In determining the optimal extraction temperature and pressure, Kumar et al. directly mixed UO_2 and U_3O_8 mixed powder with 2 mL of TBP-HNO_3 chelating agent and performed extraction using scCO_2 at 15 MPa and 60° C. The extraction rate for U_3O_8 reached 97.05% ± 3.73%, and for UO_2 it reached 98.07% ± 4.76%. To address the issue of high reaction pressure, Li Jia et al. changed the HNO_3/TBP ratio while reducing the reaction pressure. When the HNO_3/TBP ratio was 1.4, temperature 60°C, and pressure 12 MPa, the extraction rate peaked at 94.7%. Wang Yanlong et al. added $FeCl_3$ as a reactant during scCO_2 extraction of uranium oxide. Fe^{3+}, as an oxidant, rapidly reacts with U(IV) directly in the solvent to form U(VI). Under optimal extraction pressure and time, the extraction rate reached 90% at an extraction pressure of 10 MPa. In terms of process improvement, Lin et al. adjusted the chelating agent ratio and extraction method. For UO_2^{2+} in waste liquid collected from uranium mines in the northwestern United States, they used scCO_2 fluid mixed with a 1:1 ratio of TTA and TBP for extraction, changing from 20 min dynamic extraction to 10 min static extraction, increasing the extraction efficiency from 78% ± 5% to 81% ± 4%. Zhu et al. developed a method using TBP as a chelating agent to remove uranium elements from solid particles. By changing the amount of acid in the system, separation of metal elements was achieved without damaging the matrix skeleton and structure.

The chelating agent system for extracting U from uranium tailings using scCO_2 is almost the same as that for extracting nuclear waste, generally using the TBP-HNO_3 system to directly extract U_3O_8 or UO_2 from the solid phase. Bond et al. used scCO_2 fluid containing TTA to extract standard U ore residue samples, achieving a maximum UO_2^{2+} extraction rate of 80%. Compared to extracting U from solid ore, the extraction efficiency from liquid media is generally lower because, although the liquid extraction process can shorten the extraction cycle, its pretreatment process is more complex. The process of extracting UO_2^{2+} from uranium tailing collection waste liquid using a β-diketone-TBP system is shown in Figure 2. After removing impurities, CO_2 is mixed with the chelating agent (TBP-HNO_3) and sent to the extraction vessel. After pressurization and heating to the supercritical state, it fully contacts the uranium tailings to achieve uranium extraction. The extraction phase is collected in the extract collection tank, and after steps such as washing and back-extraction, chemical precipitation, and refining (filtration, washing, calcination), high-purity uranium compound products are finally obtained. When extracting

UO_2 in a liquid environment, the type of β-diketone has a significant effect on the extraction result. Ye Shuang constructed a suitable $scCO_2$ chelation extraction system to investigate the extraction effect of combined solvents. The results showed that the optimal extraction rate for UO_2 with a single TTA solvent was 68.32%, while the extraction rate for UO_2 with a TTA+TBP combined solvent could reach 80.13%.

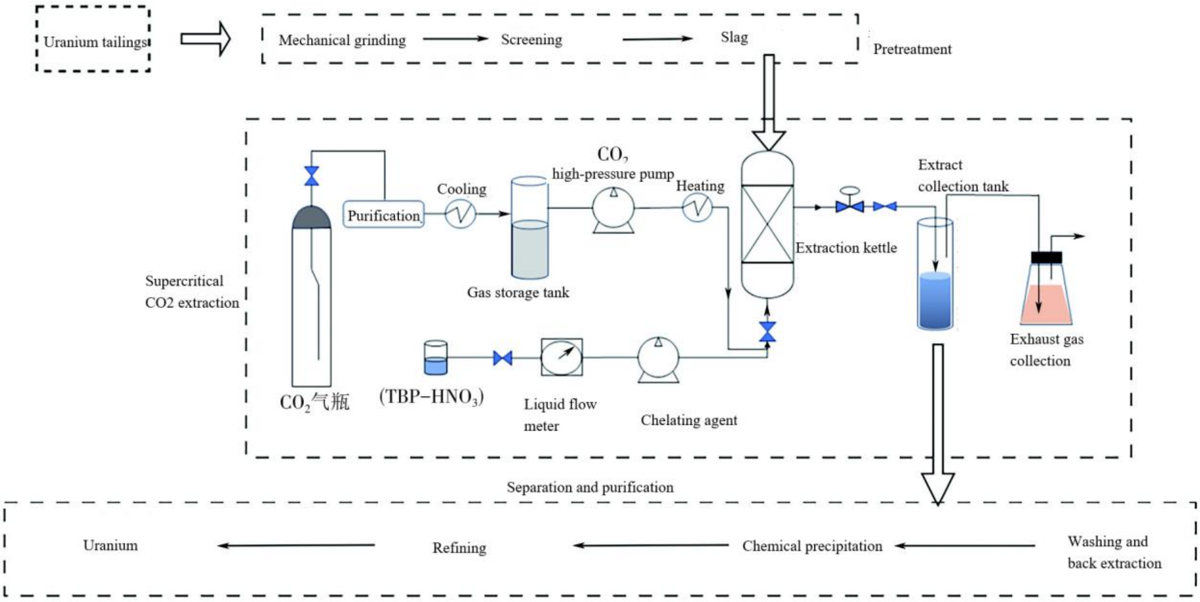

Figure 2 The scCO2 extraction process for extracting uranium from uranium tailings

Researchers have conducted some studies on the reaction mechanism of $scCO_2$ chelation extraction of metal U from uranium tailings. Yu Zhen et al. established a rapid vaporization-measurement method for chelation extracts to characterize the extraction process of U_3O_8 by $scCO_2$ containing $TBP-HNO_3$, believing that U separation can be divided into fast and slow stages. Based on the reaction pathway shown in Figure 3, Meguro et al. fitted a distribution equilibrium equation for U(VI) in the $scCO_2$ system containing $TBP-HNO_3$ using experimental data to describe the relationship between the extraction equilibrium of U(VI) in the system and the density of $scCO_2$, as shown in equation (5), where A represents a pressure-independent constant (expression in equation 6), and B represents a variable determined by the nitrate distribution equilibrium (expression in equation 7).

$$\lg D_U = (p_{U-TBP} - 2p_{TBP}) \lg \rho + A + B \qquad (5)$$

$$A = \lg K_{f,U-TBP} + (q_{U-TBP} - 2q_{TBP}) - \lg \frac{S_{U-TBP,aq}}{S^2_{TBP,aq}} \qquad (6)$$

$$B = 2\lg[NO_3^-]_{aq} + 2\lg[TBP]_{SF} \qquad (7)$$

Research on the extraction system for U in uranium ore using $scCO_2$ (including the application of fluorinated chelating agents, implementation of synergistic extraction technology, and addition of entrainers or reactants) is in-depth, and there is preliminary exploration of the chelation reaction mechanism. However, the lack of thermodynamic data leads to insufficient research on the process flow, posing certain obstacles to its industrial application.

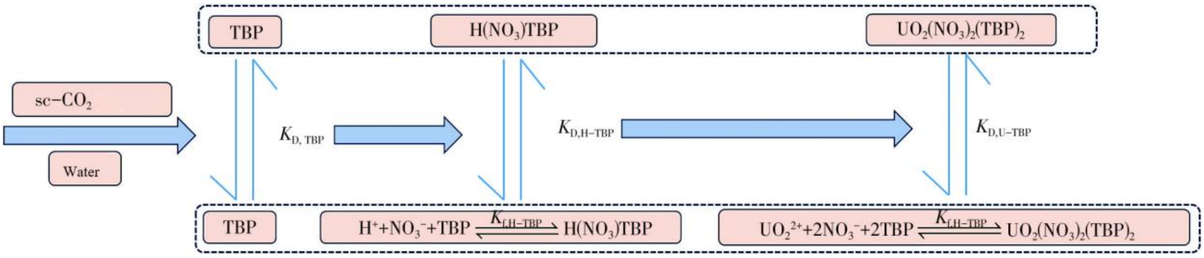

Figure 3 Mechanism of U(VI) extraction by scCO2 containing TBP-HNO3 [31]

2.3 Recovery of Metals from Spent Catalysts Using Supercritical CO₂ Extraction

Since entering the 21st century, with the rapid development of industries like petrochemicals and automobiles and the increasing prices of transition metals, research on recovering platinum group metals (PGMs) like platinum, palladium, and rhodium from spent catalysts has gradually deepened. Platinum group metals possess the attribute of scarce resources and are indispensable strategic resources in fields such as automobiles, petrochemicals, energy, and national defense equipment. However, China has low reserves of platinum group metal ores. Recovering platinum group metals is crucial for ensuring the secure supply of resources and supporting the high-quality development of related industries. Currently, research on scCO₂ extraction technology for metals from spent catalysts mainly focuses on the screening of chelating agents and optimization of operating conditions.

Since spent catalysts contain complex mixed multi-metal systems, commonly used universal chelating agents are phosphorus-based and β-diketone compounds. In recent years, many new chelating agents have also been developed. Iwao et al. compared the extraction effects of phosphinic acid, β-diketone, neutral organophosphorus compounds, etc., in scCO₂ on palladium from palladium-based catalysts. Compared to acetylacetone and TBP-HNO₃, phosphinic acid (Cyanex302) as a chelating agent had the best extraction effect. This is because the chelate formed between palladium and phosphinic acid has stronger affinity with the scCO₂ fluid than the chelates generated by acetylacetone and TBP-HNO₃. To reduce the dependence of the scCO₂ extraction process on hazardous chemicals like HNO₃, researchers developed a novel copolymer, achieving efficient recovery of palladium from spent catalysts. The extraction mechanism is shown in Figure 4. Li et al. synthesized three functionalized fluorinated polymers: PFDA-SH, P(FDA-co-DPPS), and P(FDA-co-DPPS)-SH. Among them, P(FDA-co-DPPS)-SH performed the best, achieving a 40% extraction rate for Pd from spent catalysts in scCO₂ fluid at 40° C and 25 MPa. Ruiu et al. achieved a 70% extraction rate for palladium from an aluminum-silicon-based support using pyridine-functionalized copolymer P(4VP-grad-FDA) in a scCO₂ system (40° C, 25 MPa). Subsequent optimization of extraction parameters is expected to further improve the extraction efficiency.

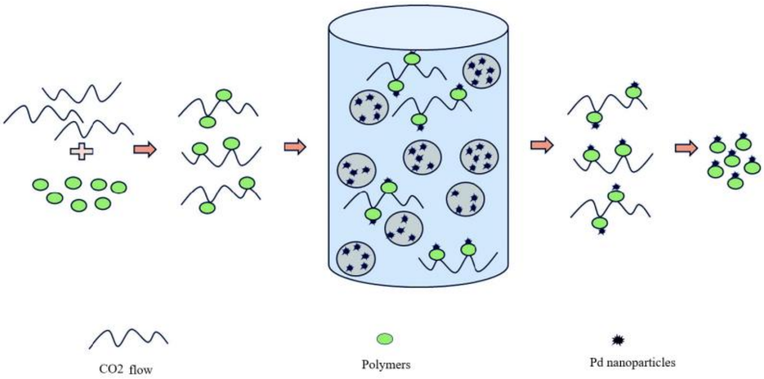

Figure 4 Mechanism of platinum group metal extraction by scCO2 combined with copolymers

By characterizing the functional group information of metal chelates, the specific chelate composition can be determined. Wang et al. built a scCO₂ extraction device that allows observation of phase changes, as shown in Figure 1, to extract Pd from spent catalysts. The oxidant and chelate in the equilibrium extraction state were taken out using a built-in needle for ultraviolet-visible spectroscopy analysis and nuclear magnetic resonance spectroscopy analysis, respectively. The optimal existing form of the oxidant in the equilibrium state was determined to be $TBP(HNO_3)_{1.0}(H_2O)_{0.4}$, and the existing state of the chelate was $Pd(hfa)_2$.

When using $scCO_2$ extraction technology to recover platinum group metals from spent catalysts, the optimal separation effect can be achieved by adjusting operating parameters such as temperature, pressure, and extraction duration. Faisal et al. used $scCO_2$ fluid with added TBP as a chelating agent to recover platinum, palladium, and rhodium metals from spent automotive exhaust catalysts, investigating the effects of factors like temperature, pressure, and extraction time on the extraction rate. It was found that after 2 hours of extraction at 60°C and 20 MPa, 95% of palladium metal could be separated. Iwao et al. used $scCO_2$ containing phosphinic acid (Cyanex302) to extract palladium-based catalysts. Under temperature range 313 – 353 K and pressure range 8 – 20 MPa, after dynamic extraction for 10 min, the extraction rate for palladium approached 100%. By adjusting the synergistic extractant formulation, efficient extraction of palladium metal can also be achieved under static extraction. Wang et al., at 40°C and 200 atm (1 atm = 101.325 kPa), selected HNO_3 existing in the form of $TBP(HNO_3)(H_2O)$ as the oxidant and hexafluoroacetone (hfa) as the chelating agent in $scCO_2$ fluid. After only 30 s of extraction reaction, energy spectrum analysis showed that 99% of the palladium metal on the support was separated.

In summary, research on the extraction conditions for platinum group precious metals from spent catalysts using $scCO_2$ is in-depth. However, due to the diverse forms and types of metals in spent catalysts, there are certain technological gaps in the directional extraction and separation processes for mixed multi-metals, and the mechanism of directional metal recovery is unclear.

2.4 Recovery of Metals from Spent Batteries Using Supercritical CO_2 Extraction

In recent years, with the rapid development of the new energy industry, the recovery of high-value-added metals like lithium, cobalt, nickel, and manganese from spent batteries has quickly become a research hotspot. These metals are core materials for manufacturing electric vehicle batteries, energy storage systems, and electronic products, holding important strategic value in the new energy and high-tech fields. The process for recovering valuable metals from spent batteries based on $scCO_2$ extraction technology is shown in Figure 5, including three stages: pretreatment, $scCO_2$ extraction separation, and purification. In the pretreatment stage, spent batteries are discharged, disassembled, and separated to obtain materials like positive and negative electrodes.

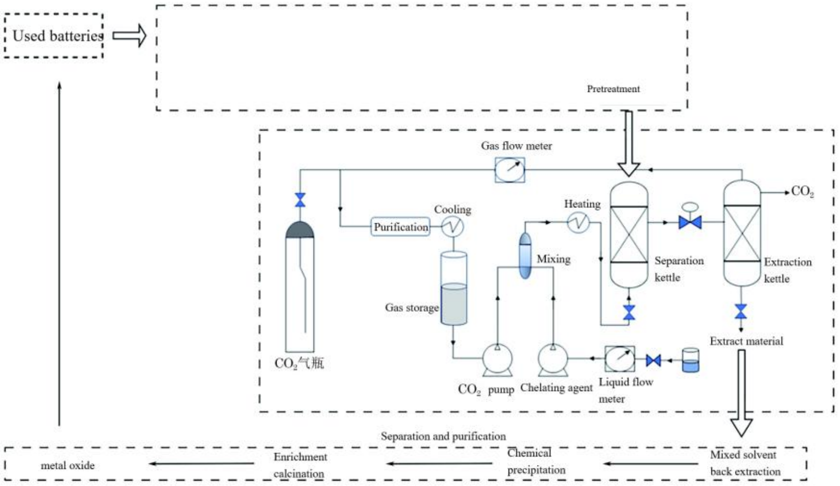

Figure 5 scCO2 extraction process for extracting lithium, cobalt, and nickel from waste batteries

In the extraction separation stage, CO_2 delivered from the gas storage tank is treated through purification devices, coolers, etc., and then mixed with the chelating agent to enter the extraction vessel for reaction. In the purification stage, the extraction phase undergoes operations such as solvent back-extraction, chemical precipitation, and enrichment calcination, finally yielding metal oxide products. Research on $scCO_2$ extraction for recovering metals from spent batteries mainly focuses on the development of new chelating agents, directional metal recovery, optimization of operating conditions, and reaction kinetics.

Spent batteries often contain multiple metals like lithium and cobalt, so currently used chelating agents mostly choose universal strong oxidizing solvent and strong acid mixed systems, as shown in Table 1. For example, Zhang et al., aiming at the low recovery rate of metal ions in traditional processes for recovering metals from spent batteries, developed a process using $scCO_2$ combined with $TBP\text{-}HNO_3$ to extract Li, Co, Mn, and Ni, with the maximum metal leaching rate reaching 90%. Compared to traditional hydrometallurgy, efficiency was improved, and reagent usage was reduced, but secondary pollution was generated. To reduce the generation of acid and alkali wastewater and achieve selective metal extraction, researchers have recently focused on developing new chelating agent systems. Vauloup et al. formulated a gradient copolymer (VBPDA-co-FD) with triple functions as a leaching agent, chelating agent, and surfactant. Based on this gradient copolymer, they developed a H_2O_2 (30 wt% aqueous solution) microemulsion system and a mixed system of H_2O_2 (30 wt% aqueous solution) and ethanol (96 vol%), achieving zero discharge of acid and alkali wastewater in the recovery process. However, due to the limited solubility of metal oxides in the copolymer during extraction, under optimal extraction conditions, the extraction rates for Co and Li were only 75%, requiring further optimization of the reducing ability of the gradient copolymer. Moreover, this developed gradient copolymer cannot achieve selective extraction of Li and Co. To solve the problem of selective metal extraction, Ruiu et al. studied new functional fluorinated gradient copolymers soluble in liquid and $scCO_2$. These functional copolymers have different types of chelating units (pyridine, triphenylphosphine, acetoacetate, thioacetate, and thiol) that can act as ligands for different metals. By adjusting extraction temperature and pressure, sequential directional recovery of Co and Li from spent lithium-ion battery cathode materials was achieved.

Table 1 Metal Extraction Rates under Optimal Conditions for Different Chelating Agents

Metal Type	Chelating Agent Type	Optimal Extraction Rate	Reference
Li	$TBP\text{-}HNO_3$	90%	[37]
Li	Acetonitrile: Propylene Carbonate3: 1	89.1% ± 3.4%	[38]
Li	$TBP\text{-}HNO_3\text{-}H_2O_2$	90%	[39]
Co	$TBP\text{-}HNO_3$	90%	[40]
Co	$TBP\text{-}HNO_3\text{-}H_2O_2$	90%	[39]
Co	4% $H_2O_2\text{-}H_2SO_4$ 4 vol% $H_2O_2\text{-}H_2SO_4$	95.5%	[41]

To obtain optimal extraction conditions, researchers typically design orthogonal experiments by adjusting temperature, pressure, time, and solid-to-liquid ratio. Zhang et al., when recovering metals from LIBs using $scCO_2$ containing $TBP\text{-}HNO_3$, studied the effects of temperature, pressure, and the ratio of adduct to sample on the extraction effect using response surface methodology. The results showed that under conditions of 60°C, 31 MPa, 30 min, 5 mL/g (adduct/sample), and 750 r/min, the extraction rates for Li, Co, Mn, and Ni could reach over 90%. Bertuel et al. used $scCO_2$ fluid combined with H_2SO_4 and 4 vol% H_2O_2 to extract Co from lithium-cobalt batteries. Under conditions of 75° C, 7.5 MPa, and 5 min, the extraction rate for Co was as high as 95.5%.

In the process of using $scCO_2$ chelation extraction for metals from spent batteries, analyzing reaction kinetics helps reveal the intrinsic mechanism of the extraction separation process fundamentally. Zhang et al. used kinetic experiments to reveal the mechanism of $scCO_2$ containing $TBP\text{-}HNO_3\text{-}H_2O_2$ extracting metals from LIBs: first, HNO_3 dissolves metal oxides into metal ions, H_2O_2 reduces the metal ions, then the metal ions form chelates with TBP ligands, and finally, the organometallic complexes are extracted and dissolved. Vauloup et al., during the extraction of Co and Li using $scCO_2$ containing gradient copolymer (VBPDA-co-FD) and H_2O_2, determined the existing form of the chelate using nuclear magnetic resonance spectroscopy and deduced its reaction pathway, as shown in equation (8).

$$2LiCoO2(s)+H2O2(aq)+6RP(O)(OH)(O-H+)(sc)=O2(sc)+\{2Co2++4RP(O)(OH)(O-)\}(sc)+\{2Li++2RP(O)(OH)(O-)\}(sc)+4H2O(aq) \qquad (8)$$

Through the above research, it is found that traditional chelating agent systems can efficiently leach metals like Li, Co, Mn, and Ni under mild conditions but cannot achieve selective separation of metals in complex multi-metal systems. Currently developed gradient copolymers are new chelating agents capable of achieving selective extraction, but further optimization is still needed to improve the metal extraction rate. In summary, $scCO_2$ extraction technology has been used for directional recovery of metals in different spent battery systems. Certain achievements have been made in the development of new chelating agent systems, and in-depth research has been conducted on extraction conditions and chelation reaction mechanisms. However, the lack of exploration in solid-liquid separation thermodynamics leads to an unclear understanding of the interaction mechanisms between chelating agents, metal chelates, and $scCO_2$ fluid.

2.5 Supercritical CO_2 Extraction of Metals from Other Secondary Resources

In addition to the aforementioned bulk wastes like nuclear waste, uranium tailings, spent catalysts, and spent batteries, $scCO_2$ extraction technology has also been used in the recovery processes of lanthanide, actinide, and transition metal elements from other secondary resources. These secondary resources contain large amounts of lanthanide and actinide metal elements such as uranium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, and ytterbium, as well as transition metal elements like cobalt, molybdenum, nickel, chromium, iron, and zinc. Research on lanthanide and actinide metals is shown in Table 2, and research on transition metals is shown in Table 3. It can be found that secondary resources containing high-value-added metals are diverse, and these resources contain various metal elements of different occurrence forms and types. The current research results of $scCO_2$ extraction metal technology in different media can provide scientific references for determining optimal operating conditions and screening chelating agents with directional separation functions for multi-metal system separation processes in different scenarios.

Table 2 Extraction of Lanthanide and Actinide Elements by $scCO_2$ Chelation

Metal	Matrix	Chelating Agent	Pressure / MPa	Temperature / °C	Reference
UO_2^{2+}	Contaminated Soil	TBP + TTA	20	80	[13]
UO_2, U_3O_8	Metal Slag	TBP-HNO_3, TOPO/TBP	15	60	[26]
La, Ce, Sm, Eu, Gd, Dy, Yb, Lu	Acidic Wastewater	TTA + TBP	35	60	[43]
La, Ce, Nd, Sm, Eu, Yb	Acidic Wastewater	TBP, DEHPA	10~25	40~60	[44]
Y, Eu, La, Ce, Tb	Simulated Waste Fluorescent Lamp Material	TBP-HNO_3	15	60	[45]
Y, La, Ce, Eu, Tb	Waste Fluorescent Lamp Phosphor	TBP-HNO_3-H_2O	15	60	[45]
La, Ce, Pr, Nd	Roasted Bastnasite	TBP-HNO_3	34	65	[46]
UO_2^{2+}	Waste Paper	TOPO+DC18C6, DEHPA+DC18C6	25	60	[47]
U(IV)	Acidic Wastewater	TBODA-HNO_3	20	40	[48]
La, Ce, Pr, Nd	Spent Battery	TBP-HNO_3-H_2O	20.7/31.0	35~55	[49]
Nd, Ho	Acidic Wastewater	TBP	17~28	60	[50]
Tb, Eu	Waste Fluorescent Lamp	TBP-HNO_3	31	40	[51]
Nd	Waste NdFeB Magnet	TBP, TBPO, TOPO	20.7	55	[52]

Table 3 Extraction of Transition Elements by $scCO_2$ Chelation

Metal	**Matrix**	**Chelating Agent**	**Pressure / MPa**	**Temperature / °C**	**Reference**
Fe	Waste NdFeB Battery	$TBP-HNO_3-H_2O$	20.7~31	35~55	[39]
Al, Ca	Waste Fluorescent Lamp	$TBP-HNO_3$	31	40	[51]
Au, Hg	Waste Paper	DCHBTC, DBBTC, BiBBBTC	20	60	[53]
Pb	Quartz Sand	FE-PBPA, FE-BPA, FE-PA, FE-DT	13.8	25	[54]
Fe	Glass Beads	HHA, OHA, PHA, PFOHA	20	60	[55]
Co	Stainless Steel	hfa, acac	40	60	[56]
As, Cr, Sb, Zn, Pb	Contaminated Soil	Cyanex 302	20	60	[57]
Ni, Zn	Electroplating Waste Liquid	hfa, tfa, acac	19.3	42	[58]
Cu, Ni, Zn, Cd, Cr, Co	Contaminated Wastewater	$FE-NH_4PPDC$	19.3	22	[59]
Na, K	Wastewater	DC18C6+HPFOA, 15-C-5+HPFOA	8~18	40	[60]
Zn, Cu, Pb, Cd, Cr	Fly Ash	Cyanex 302, DEHPA, DiOPA, NaDDC	16	45	[61]
Na, K	Wastewater	3-glyme, 4-glyme, HPFOA	10~18	40	[62]
Cr, Cu, As	Waste Wood	acac	14.7	150	[63]
$PtCl_6$	Wastewater	DTFA-PAA	15	22	[64]
Cu	Waste Paper	$PFPE-NH_4$	20.7	45	[65]
Mn, Fe	Pulp	LiFDDC	20	40	[66]
Mn	Lignocellulose	LiFDDC	20.3	40	[67]
Co, Cd, Cu, Pb, Zn	Waste Textiles	Cyanex 272/302+NaDDC, $PFPE-PO_4$	20	40	[68]
Cu, Pb, Cr, Ni	Urban Dust	tfa, NaDDC, 8-HQ	20	60	[69]
Co, Cd, Cu, Pb, Zn, Sr	Waste Paper	BDHA(BPDC), $PFOSANEt_4$	25	40	[70]
Co, Cu, Zn, Sr	Waste Paper	ROA(4-Py), $PFOSANEt_4$	20	40	[72]
Co, Cu, Zn, Mn, Ni, Fe	Waste Paper	R(BPDC)	25	40	[73]
Co, Cd, Cu, Pb, Zn, Mn, Ni, Fe	Waste Paper	FR(BPDC)	25	60	[74]
Li, Co, Ni, Mn	Spent Lithium-ion Battery	$TBP-HNO_3-H_2O_2$	31	60	[37]

3 Overview of Supercritical CO_2 Extraction for Metals and New Technologies

3.1 Overview

To conduct a macroscopic analysis of the knowledge graph visualization of the current development status of supercritical CO_2 extraction technology for metals, authoritative databases at home and abroad were selected as data sources. For domestic research, CNKI (China National Knowledge Infrastructure) was used as the data source. For foreign research, sample literature data were sourced from the core collection of the Web of Science literature database. Keyword co-occurrence analysis of related literature from 2000 to 2024 was performed based on CiteSpace software.

During data collection, clear literature screening criteria were set to ensure the scientificity, relevance, and effectiveness of the selected literature. In the CNKI database, using basic search terms like "supercritical CO_2 extraction metal" and "supercritical CO_2 metal extraction," the search results were strictly screened, excluding literature that only mentioned the technology superficially without in-depth study of the metal extraction process, as well as non-research literature such as conference notices and briefings. In Web of Science, using precise searches for "supercritical CO_2" and "metal extraction," the focus was on research results discussing metal extraction mechanisms, process optimization, and extraction of specific metals, discarding literature from other fields with low relevance to metal extraction. The minimum occurrence frequency for keywords was set to 3, and keyword data were cleaned and deduplicated. Finally, a keyword co-occurrence graph consisting of 301 keywords and 610 node connections was obtained, with a network density of 0.0125, as shown in Figure 6. In the graph, each circular node represents a keyword. From the co-occurrence graph, it can be concluded that $scCO_2$ extraction has been deeply studied in the field of metal recovery, with the extraction of radioactive metals and transition metals from nuclear waste being hot topics dominating the research field. In the $scCO_2$ metal extraction process, chelating agents and the solubility of metal chelates are key factors determining the extraction effect. Clarifying the separation mechanism of the extraction process and constructing suitable thermodynamic models can enable precise control of the extraction effect.

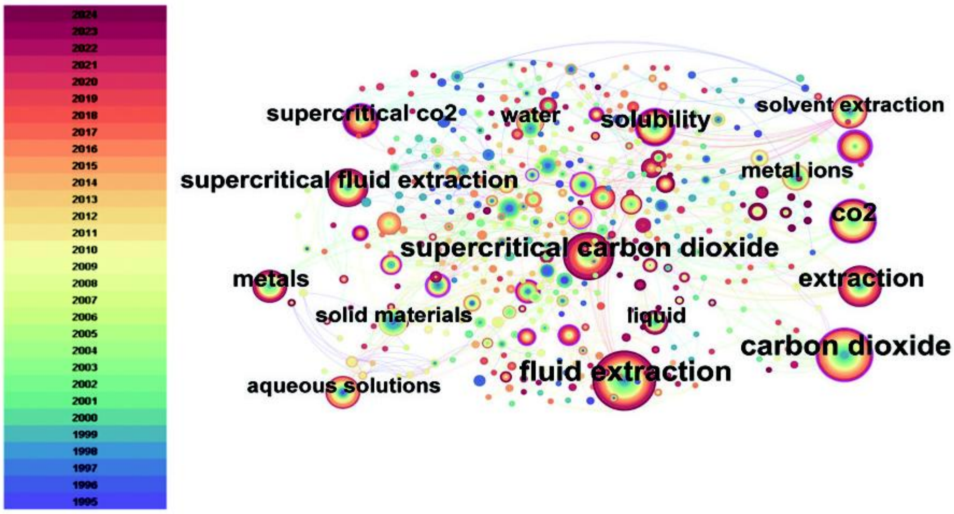

Figure 6 Keyword co-occurrence graph

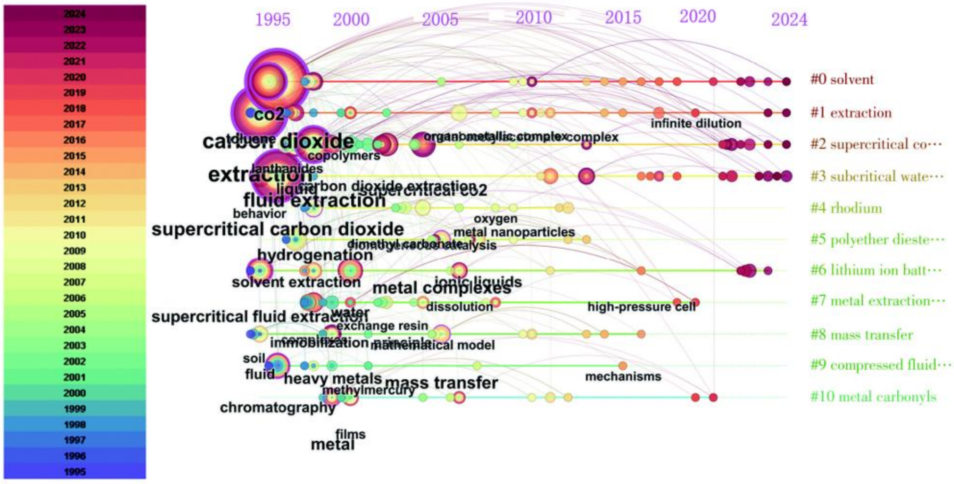

Figure 7 Keyword Timeline Graph

The keyword graph generated by CiteSpace software can be processed to form a keyword timeline, as shown in Figure 7. Keywords are presented along a timeline. The keyword timeline clearly shows the evolution process of $scCO_2$, facilitating understanding of future development trends in this field and providing relevant guidance. Studying the timeline graph reveals that $scCO_2$ extraction technology for metals has been applied in multiple fields over the past 20+ years. Interpreting the timeline, the development of supercritical CO_2 extraction technology for metals can be roughly divided into the following stages.

(1) Basic Theoretical Exploration Stage (2000–2010)

Research in this stage mainly focused on basic studies of the properties of supercritical CO_2 fluid and the mechanisms of metal extraction. Through experiments and theoretical calculations, researchers initially revealed the dissolution behavior of metal ions and chelating agents in supercritical CO_2 and the extraction mechanisms, laying a theoretical foundation for subsequent technology development.

(2) Process Optimization and Application Expansion Stage (2011–2020)

With the deepening understanding of extraction mechanisms, the research focus gradually shifted to process parameter optimization and application scenario expansion. During this period, a large number of research results emerged on improving extraction efficiency for different metal systems and optimizing process conditions. Explorations in applications such as nuclear waste treatment and electronic waste recovery also made breakthroughs.

(3) Green and Integrated Development Stage (2021–Present)

Against the backdrop of global carbon emission reduction and green chemical engineering, supercritical CO_2 extraction technology for metals has begun to deeply integrate with the concept of circular economy. Researchers are committed to developing new chelating agents based on renewable resources and constructing integrated processes with other green separation technologies like membrane separation and ionic liquid extraction to achieve more efficient and environmentally friendly metal extraction processes.

The timeline clarifies that current research on process conditions, influencing factors, and extraction mechanisms of the $scCO_2$ extraction process is relatively mature. With the deepening of global carbon emission reduction in recent years, developing new processes for $scCO_2$ metal extraction has gradually become a new research direction. However, challenging problems such as the development of new chelating agents and integration with other new green processes still need to be resolved.

3.2 New Technologies for Supercritical CO_2 Extraction of Metals

In the $scCO_2$ metal extraction process, in addition to the widely used chelation extraction technology, a $scCO_2$ reverse microemulsion system can also be constructed. This technology uses $scCO_2$ fluid mixed with surfactants and water to form a special emulsion system (Figure 8), with advantages such as high efficiency and stability, tunable physicochemical properties, and wide application systems. Hoeffling et al. synthesized surfactants like homologs of sulfosuccinate sodium, fluoroalkyl carbonates, fluoroether carbonates, and hydroxyl aluminum with high solubility in $scCO_2$. Subsequently, researchers conducted extensive studies in the field of metal extraction using $scCO_2$ microemulsion technology, achieving extraction of various transition metal ions. Liu et al. used benzoyl as a complexing agent and Triton X-100 as a surfactant, achieving a 90.52% extraction rate for Cu^{2+}. Cui et al. constructed a synergistic system of 8-hydroxyquinoline, surfactant, and modifier, achieving efficient simultaneous removal of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, and Co^{2+} from water bodies, with extraction efficiencies for each metal ion exceeding 80%. Yates et al. directly used $PFPE-NH_4$ as a surfactant to extract Cu^{2+}, achieving a single-stage extraction rate of over 99%. Cai Guilong used $scCO_2$ microemulsion to extract uranium from uranium ore, adding different concentrations of single surfactants SDBS, CTAB, OP-10, TX-100, and FSO, respectively. It was found that the fluorinated surfactant FSO had the best leaching effect, with a leaching rate of 91.75% at a concentration of 0.1 g/L.

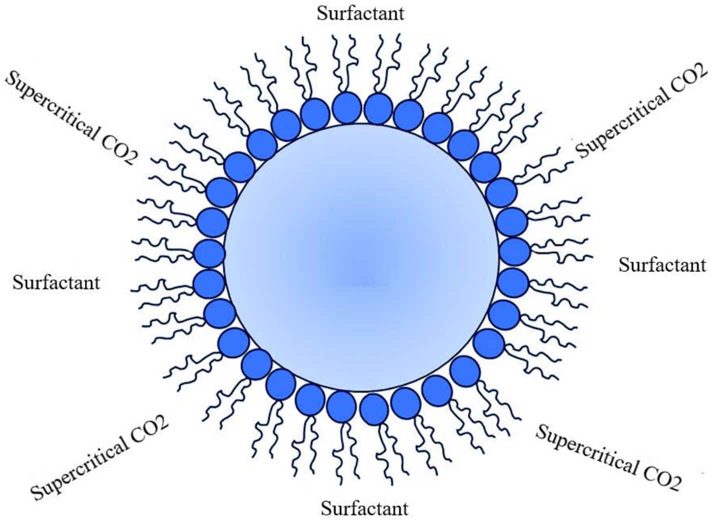

Figure 8 Microemulsion droplets

To enhance mass transfer efficiency in the $scCO_2$ extraction process, combining technologies like microwave intensification and ultrasonic intensification with $scCO_2$ extraction technology has attracted researchers' attention. Samsonova et al. achieved extraction of thorium (Th) and uranium (U) from monazite concentrate and phosphogypsum using $scCO_2$ combined with microwave intensification technology. Enokida et al. found that at 50°C and 1.52×10^7 Pa, during a 20 min dynamic extraction process, applying ultrasonic intensification effectively increased the solubility of UO_2 solid powder in $scCO_2$. The extraction rate of the $scCO_2$ extraction process with ultrasonic intensification was an order of magnitude higher than that without intensification. Lu Binbin, by combining $scCO_2$ with ultrasound, achieved complete removal of iron oxide, ferrous oxide, and magnetite from the surface of CD03 steel sheets under conditions of 33°C, 7.38 MPa, and 1200 ultrasonic cycles. Trofimov et al. introduced ultrasonic intensification into $scCO_2$ containing thenoyltrifluoroacetone (TTA) and TBP. Under conditions of 60° C, 150 atm, and ultrasonic frequency 44 – 48 kHz, the extraction rates for UO_2 and La_2O_3 exceeded 95%, while there was almost no extraction effect for ThO_2.

To achieve large-scale application of $scCO_2$ technology, modular skid-mounted design of equipment and exploration of efficient continuous extraction technology strategies are key. Currently, there is little research on skid-mounted equipment for supercritical extraction technology. Jia Wenlong et al., in the process of treating oily sludge using $scCO_2$, pointed out that skid-mounted design can improve economic efficiency. Integrating extraction equipment, pumps, valves, etc., on a movable skid-mounted platform not only facilitates transportation and installation but also reduces the equipment's footprint and construction costs. Continuous extraction technology can significantly improve extraction efficiency, reduce energy consumption and costs, thereby promoting widespread industrial application. Wang Yechen developed a device capable of continuous $scCO_2$ extraction and designed an O-ring made of polyurethane material to improve extraction sealing performance. Drawing on research results of $scCO_2$ extraction devices in other scenarios, future efforts can address large-scale application challenges in metal recovery scenarios from perspectives such as improvement of extraction vessels and continuous operation of extraction devices.

4 Conclusion

The application status of $scCO_2$ extraction technology for extracting metals from different wastes such as nuclear waste, uranium tailings, spent catalysts, and spent batteries is summarized. The development overview of $scCO_2$ extraction for metals is analyzed with the help of CiteSpace software, leading to the following main conclusions.

(1) In the field of nuclear waste and uranium tailing treatment, $scCO_2$ extraction technology has been effectively applied for lanthanide and actinide metals, with an average extraction rate exceeding 90%. Through solvent modification strategies (including the application of fluorinated chelating agents, implementation of synergistic extraction technology, and addition of entrainers or reactants), combined with precise construction of selective

extraction conditions, selective and efficient extraction of target metals has been achieved. However, this technology also faces several challenges, mainly including the high cost and biotoxicity of fluorinated β-diketone chelating agents and the high energy consumption of the extraction process.

(2) $scCO_2$ extraction technology has been extensively studied at the laboratory level for transition metal extraction, applied to the treatment of wastes like spent catalysts and spent batteries, demonstrating high feasibility. Most chelating agent systems can achieve metal extraction efficiencies over 90%. However, insufficient research on the reaction kinetics and thermodynamics of the solid-liquid separation process leads to an unclear chelation-reaction extraction mechanism.

(3) Visualization analysis using CiteSpace software indicates that existing research mainly focuses on experimental studies of extraction systems, while theoretical discussions on aspects like molecular design of chelating agents and construction of kinetic and thermodynamic models for the extraction process are relatively scarce.

Although a large number of studies have been conducted globally on extracting valuable metals from various wastes using $scCO_2$, achieving high extraction efficiencies, most are still at the laboratory exploration stage. There is insufficient research and development of new chelating agents and selective separation processes, and a lack of systematic extraction rules to guide actual industrial scale-up. To fully leverage the advantages of $scCO_2$ metal extraction and achieve its large-scale application, future research can focus on the following aspects.

(1) Develop green, economical, and recyclable new chelating agents. Future work can start from the molecular scale, deeply analyze the structure-property relationship of chelating agents, and use computer simulation and other technologies to assist in designing chelating agents with specific functional groups that are environmentally friendly, efficient, and economical. By introducing biodegradable groups into chelating agent molecules, using cheap and readily available raw materials, and developing efficient recovery technologies, their environmental friendliness and economic efficiency in industrial applications can be improved.

(2) Explore efficient and selective separation processes for complex multi-metal systems. Study the coordination characteristics between different chelating agents and metal ions to screen chelating agent combinations with high selectivity for specific metals. Simultaneously, deeply research the influence of extraction conditions such as temperature, pressure, and chelating agent concentration on metal separation effects, and establish accurate influence role models using methods like response surface optimization. Furthermore, interference from complex matrix components in actual industrial wastes on the separation process should be considered to ensure the stability and reliability of the process in industrial applications.

(3) Explore more efficient extraction and separation intensification equipment and continuous supercritical extraction strategies. Drawing on advanced reactor design concepts in the chemical engineering field, develop new internal components for extraction vessels with efficient mass transfer and mixing properties. Address the scale-up effect of extraction vessels for the needs of large-scale industrial production to ensure a smooth transition from laboratory small-scale tests to industrial production. Develop multi-stage counter-current continuous extraction processes. By rationally designing the series connection of multiple extraction units and the counter-current contact method of materials, achieve efficient continuous extraction of metals, improving production efficiency and automation levels.

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