




Hydrometallurgical Recycling of Rare Earth Metal–Cerium from Bio-processed Residual Waste of Exhausted Automobile Catalysts

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The hydrometallurgical recycling of cerium from a secondary residue of exhausted auto-catalyst was investigated. Cerium dissolution was significantly improved up to 96% when HF was additionally introduced into a 2.0 mol/L H₂SO₄ solution. The activation energy (E_a , 31.8 kJ/mol) indicated the diffusion-controlled mechanism prevailed in cerium leaching. Subsequently, the leach liquor containing 4.2 g/L cerium was equilibrated with Cyanex 923 for solvating the post-extraction species $[\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{P}=\text{O}) \cdot \text{HSO}_4^-]_{org}$ into the organic phase. Thermodynamic properties revealed that the affinity of Cyanex 923 toward cerium was spontaneous ($\Delta G^\circ_{298\text{K}}$, -6.58 kJ/mol) and exhibited *outer-sphere* coordination for the exothermic process (ΔH° , -21.42 kJ/mol). Furthermore, cerium was quantitatively stripped (> 98%) from the loaded organic using the strippant mixture of 1.0 mol/L H₂SO₄ + 0.5 mol/L H₂O₂. Eventually, high-purity Ce₂(C₂O₄)₃·10H₂O was precipitated by adding oxalic acid at an optimized dosage of Ce³⁺:H₂C₂O₄ = 1:5.

INTRODUCTION

Three-way catalytic converters are needed in modern vehicles as they control gaseous emissions by transforming carbon monoxide to carbon dioxide (CO → CO₂), nitrogen oxides to nitrogen (NO_x → N₂), and unburnt hydrocarbon to carbon dioxide and water (HC → CO₂ + H₂O).^{1,2} Catalytic converters usually consist of platinum group metals (PGMs) as the active components with wash-coated γ -Al₂O₃ on the cordierite ceramic support.^{3,4} Owing to the excellent oxygen storage capacity of cerium, CeO₂ is additionally fabricated to promote the oxygen stability during the conversion of CO to CO₂.⁵ After exhausting the catalytic activity of converters, the current recycling practices are limited to PGMs' recovery because of the high economic

value of precious metals. In general, PGM-depleted residual mass is sent to landfills, which causes the loss of rare earth metal (cerium). Less attention is paid to cerium recovery, although the spent catalyst contains a higher weight fraction of ceria (CeO₂, up to 4 wt.%) than that of PGMs' weight.⁶ In contrast, cerium compounds are not only used in catalytic converters but also have widespread applications in diesel fuel additives, alloys, nuclear chemistry, petroleum refining, polishing agents, and low-energy fluorescence bulbs, etc..⁷ Although the soaring demand for cerium is predicted to grow with a compounded annual growth rate of 8%,⁸ the trade dispute between China and the rest of the world over the unrestricted supply of rare earth metals has put immense pressure on the associated mining, metallurgy, and chemical industries.⁹ Henceforth, the exploitation of alternative resources, such as exhausted/spent catalytic converters, is urgently required to mitigate the supply crunch for cerium.

A few pyro- and hydro-metallurgical recycling techniques have been reported for cerium recovery from exhausted catalytic converters.^{6,10} The refractory nature of ceria has been identified as the primary challenge to hydrometallurgical recycling of cerium from spent catalysts.^{11,12} It makes cerium difficult to leach in acid solutions under ordinary conditions. Pretreatment comprising concentrated H_2SO_4 baking of the spent catalyst sample has been suggested to break the refractory structure of ceria, dissolving 85% cerium.¹³ Using $\text{HCl} + \text{H}_2\text{O}_2$ leaching, the recovery of cerium through double-salt precipitation has been reported; however, the experimental details are missing.¹⁴ As an alternative to acid dissolutions, an alkali fusion of spent catalyst has been suggested for cerium recovery, although it is difficult to achieve high purity of the final product.^{15,16}

With this in mind, the present study considered the resource recovery of cerium under the concept of a circular economy (see the schematic in Fig. 1). Herein, the bio-cyanide leach residue obtained after the selective extraction of PGMs from exhausted catalyst was used as the feed material for cerium recovery. Acid (H_2SO_4) leaching in the presence of HF was investigated to improve cerium dissolution, while parameters such as the HF mixing dosage, temperature, and time were optimized. Furthermore, cerium was selectively extracted from the leach liquor while using a liquid mixture of phosphine oxides as the organic extractant. The quantitative extraction was optimized by varying the parameters such as concentrations of extractant and acid, temperature, and organic-to-aqueous (O/A) phase ratio. Finally, the reductive stripping of cerium in the presence of hydrogen peroxide followed by precipitation as a function of oxalic acid dosage was examined to achieve the quantitative recovery of a high-purity cerium salt.

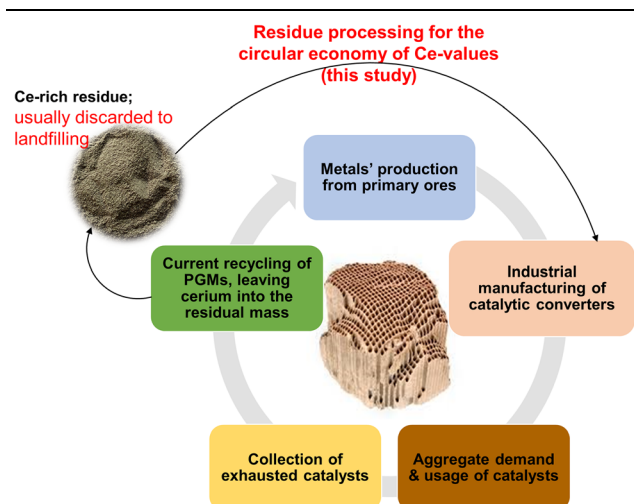


Fig. 1. Lifecycle of catalytic converters and recycling scheme to establish the circular economy of cerium from exhausted catalysts.

MATERIALS AND METHODS

Materials

The sample used in this study was obtained through the bio-cyanidation processing of exhausted auto catalysts (see the supplementary information file). The PGM-depleted residue was analyzed to be 26.47% Al, 4.35% Ce, 7.94% Si, and 2.72% Mg. The XRD analysis (not shown for the sake of brevity) of the sample indicated cordierite ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) and ceria (CeO_2) as the main compounds present in the sample.

Hydrochloric acid (HCl ; 30%, Merck), nitric acid (HNO_3 , 65%, Sigma-Aldrich), sulfuric acid (H_2SO_4 ; 95%, Daejung), and hydrofluoric acid (HF ; 40%, Merck Millipore) were used as leaching reagents. The liquid mixture of 4 tri-alkyl phosphine oxides (Cyanex 923; 93%, Cytec Canada Inc.) and distilled kerosene (Junsei Chemical Co.) were used as the organic extractant and diluent, respectively. Hydrogen peroxide (H_2O_2 ; 30%, Merck) was used as a stripping additive, while oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$; 90.03%, Junsei Chemical Co.) was used as a precipitating reagent. All the reagents were used without further purification.

Leaching Study

A 15 g sample was charged with 150 mL acid solution of a desired concentration into a 250-mL Teflon beaker. The slurry was stirred at a fixed speed of 250 rpm using the magnetic paddle. All leaching studies were conducted in a closed system for 4 h at an elevated temperature of 60°C , otherwise specified in the respective section. Addition of the calculated amount of HF was done with H_2SO_4 solution by maintaining the pulp density unchanged at 10%. After completion of leach time, the slurry was filtered in the hot condition and passed through a carbon column to remove any colloidal particles. The thus obtained clear solution was analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 7400 Duo, Thermo Scientific). The leaching efficiency of cerium was determined as:

$$\% \text{ Leaching} = \left(\frac{\text{Ce}_{\text{LL}}}{\text{Ce}_{\text{IS}}} \right) * 100 \quad (1)$$

where Ce_{IS} and Ce_{LL} are cerium contents in the input mass of the sample and output volume of the leach liquor, respectively.

Solvent Extraction

A prior treatment of leach liquor (containing 4.2 g/L Ce, 8.6 g/L Al, 0.34 g/L Mg, and 0.43 g/L Si) was conducted with 0.02 mol/L KMnO_4 to keep all cerium in its higher valance state of Ce^{4+} . Thereafter, the treated solution was used as the aqueous feed for solvent extraction (SX) studies. Unless specified, all experiments were performed at

an O/A phase ratio of 1 by taking a 30-mL volume of each phase into a 100-mL separating funnel, while maintaining the contact time (5 min), temperature ($25 \pm 2^\circ\text{C}$), and settling time (10 min) unchanged. To study the effect of acid concentrations, the synthetic solutions containing a similar composition of metal ions as the leach liquor were equilibrated with a constant feed of organic extractant. The raffinate collected after extraction was appropriately diluted with 5 vol.% HCl for analyzing the cerium content into the solution. Furthermore, the percentage extraction and distribution coefficient (D) were calculated by Eqs. (2) and (3), respectively.

$$\text{Extraction, \%} = \frac{C_{e_{in}} - C_{e_{raff}}}{C_{e_{in}}} * 100 \quad (2)$$

$$D = \frac{C_{e_{in}} - C_{e_{raff}}}{C_{e_{raff}}} \quad (3)$$

where $C_{e_{in}}$ and $C_{e_{raff}}$ represent the initial and final concentration of cerium into the aqueous feed and raffinate solution, respectively.

Cerium stripping from loaded organic obtained after the counter-current extraction (CCE) was properly washed with distilled water (at O/A, 2/1) before contacting the stripping solution. Different concentrations of H_2SO_4 were used as the stripping solutions, while the effect of an additional dosage of H_2O_2 was monitored. The percentage stripping was calculated by Eq. (4), as below:

$$\text{Stripping, \%} = \frac{C_{e_{strip}}}{C_{e_{lo}}} * 100 \quad (4)$$

where $C_{e_{strip}}$ and $C_{e_{lo}}$ represent the cerium concentration into the stripped solution and loaded organic solution, respectively.

Precipitation of Cerium Oxalate

A 50-mL Ce-bearing stripped solution in a 100-mL glass beaker was pre-heated at $90 (\pm 2)^\circ\text{C}$ under an agitation of 150 rpm (using a hot plate *cum* magnetic stirrer, SciLab, Korea). The pH of the solution was pre-adjusted at $1.5 (\pm 0.2)$ by adding 20 vol.% NaOH and maintained for 15 min of precipitation reaction by adding a predetermined concentration of oxalic acid. Thereafter, the slurry was allowed to settle for 1 h and filtered to collect the precipitates and filtrate separately. The precipitates were washed with 25 mL distilled water and characterized after overnight drying in a vacuum dryer. The filtrate was analyzed to calculate the percentage precipitation using Eq. (5), as:

$$\text{Precipitation, \%} = \frac{C_{e_{strip}} - C_{e_{flt}}}{C_{e_{strip}}} * 100 \quad (5)$$

where $C_{e_{strip}}$ and $C_{e_{flt}}$ represent the cerium concentration into the Ce-bearing stripped liquor and Ce-depleted filtrate solution, respectively.

RESULTS AND DISCUSSION

Studies on Acid Leaching

Effect of Acid Media, Concentration, and HF Addition

The leaching efficiency of cerium was first investigated using three different mineral acids, HCl, H_2SO_4 , and HNO_3 , at various concentrations ranging from 1.0 mol/L to 6.0 mol/L acid. Figure 2a revealed that no acid media could dissolve > 33% cerium from the catalyst sample. This can be directly associated with the acid resistance property of CeO_2 .¹⁷ However, using > 3.0 mol/L H_2SO_4 led to a slight decrease in cerium dissolution that might be linked to the precipitation of cerium sulfate in the presence of a higher sulfate solution.¹⁸ As the leaching efficiency did not differ much with the change of acid media, H_2SO_4 was selected to investigate the impact of the acid mixture on cerium dissolution from the catalyst sample. Furthermore, the improvement in cerium leaching was optimized by adding 0.25–2.0 mol/L HF into 2.0 mol/L H_2SO_4 solution, while keeping the other parameters constant. Figure 2a shows significant progress in cerium leaching with an increasing concentration of HF into the acid mixture compared to H_2SO_4 alone. Although HF is a weaker acid than H_2SO_4 , the F^- ions of hydrogen-bonded ion pairs ($\text{H}_3\text{O}^+\text{F}^-$ in a dilute solution) actively attack cerium, causing its dissolution into the acid solution. Thereafter, the leftover protons acquire the place that F^- ions have just cleaved from the ceria matrix.¹⁹ Cerium leaching improved significantly from 30.6% to 95.6% when the concentration of HF in the acid mixture was added from 0 mol/L to 2.0 mol/L. However, above 1.0 mol/L HF addition into the acid mixture did not show much improvement in the leaching

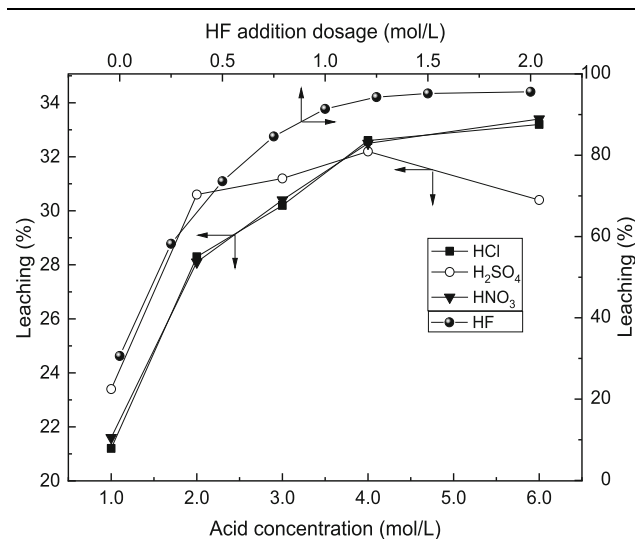


Fig. 2. Leaching behavior of cerium with different acids as a function of acid concentration (on the primary axis) and as a function of HF addition dosage with 2.0 mol/L H_2SO_4 solution (on the secondary axis).

efficiency (increased from 91.4% to only 95.6% cerium); hence, the lixiviant containing an acid mixture of 1.0 mol/L HF and 2.0 mol/L H₂SO₄ was optimized and maintained in the next sets of experiments.

The improvement in cerium leaching in the presence of HF could be possible because of the dissolution of the refractory cordierite matrix and/or destabilization of the CeO₂ structure. The dissolved concentration of Al (8.6 g/L and 8.23 g/L), Mg (0.34 g/L and 0.33 g/L), and Si (0.43 g/L and 0.38 g/L) analyzed in the leach liquor (with and without HF, respectively) ruled out the role of cordierite dissolution. A significant amount of Al in the leach liquor can be understood as the dissolution of the wash-coat γ -Al₂O₃ layer and certainly not as the dissolving of the cordierite into acid solutions. Furthermore, XRD analysis of solid samples (supplementary Figure S-1) also supported that the attack of a dilute HF solution on the cordierite matrix was not significantly different from H₂SO₄ alone; however, the peaks of CeO₂ prominently disappeared while using HF mixed H₂SO₄ solution. Additionally, this was supported by the SEM-EDX analysis of solid samples (supplementary Figure S-2). It can be seen that the surface of the initial sample (see supplementary Figure S-2a) was changed a little because of dissolution of the wash-coat layer (see supplementary Figure S-2b) and additive ceria (see supplementary Figure S-2c), although the support matrix was not attacked by the acid solutions and did not show any damage to the cordierite. Hence, an influential role of HF was found in destabilizing the oxide structure of ceria instead of breaking the cordierite structure.

Effect of Temperature and Time

Temperature and time often show a positive influence on solid-liquid mass transfer by enhancing the reaction rate; therefore, leaching was examined at different temperatures (40–80°C) under time variation from 30 min to 240 min. Results presented in Fig. 3 reveal a positive effect of temperature on leaching efficiency, and the process of cerium dissolution was significant with respect to elapsed time. As can be seen, at 40°C, leaching was very low (28.3%) until the initial 30 min but improved up to 63.7% after 240 min duration. Improvement in leaching was remarkable at 60°C, wherein cerium dissolution was found to be > 90% at 240 min, which was only 44.4% at 30 min of initial leaching. With a further elevation of the temperature at 80°C, approximately 98% leaching was achieved in 240 min, and the influence of temperature was clearly visible from the initial 30 min with > 54% leaching efficiency.

To underpin the cerium dissolution into the acid mixture, the experimental data of time and temperature variation were used to evaluate the apparent activation energy (E_a) in relative terms, as follows:²⁰

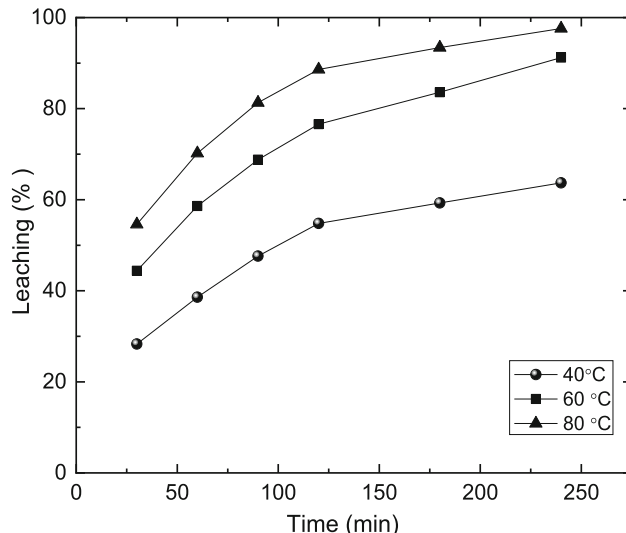


Fig. 3. Leaching behavior of cerium in acid mixture solution (2.0 mol/L H₂SO₄ + 1.0 mol/L HF) as a function of time at different temperatures.

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (6)$$

where the roasting at temperatures T_1 (40°C) and T_2 (80°C) for time t_1 (120 min) and t_2 (30 min) was considered (in which the leaching efficiency of cerium was approximately the same) to determine the E_a value. Thus, the calculated apparent activation energy was determined to be 31.8 kJ/mol, which indicated that the leaching process follows the diffusion-controlled model.²¹

Studies on Solvent Extraction using the Phosphine Oxides

Effect of Extractant Concentration

To examine the extraction behavior of cerium (as Ce⁴⁺) with a liquid mixture of 4 tri-alkyl phosphine oxides, experiments were conducted in the concentration range of 2.0 – 20.0 vol.% at an O/A phase ratio of 1. Figure 4 shows that the extraction of Ce⁴⁺ increased with more active molecules of phosphine oxides (P = O) in the organic solution. This indicates the shifting of the distribution curve with the availability of more extraction sites during the contact of two immiscible phases.^{22,23} The extraction efficiency of Ce⁴⁺ was improved from 14.4% to 90% with increasing concentration of extractant from 2.0 vol.% to 16.0 vol.%, respectively. Finally, the extraction efficiency could reach ~ 93% with 20.0 vol.% of Cyanex 923 into the organic phase. Slow progress in extraction with a higher extractant concentration can be ascribed by the increased hydration of extractant molecules.^{23,24} Notably, the co-extraction of substrate metals (Al, Mg, and Si from leach liquor) was not observed within the experimental range of this study. Furthermore, the

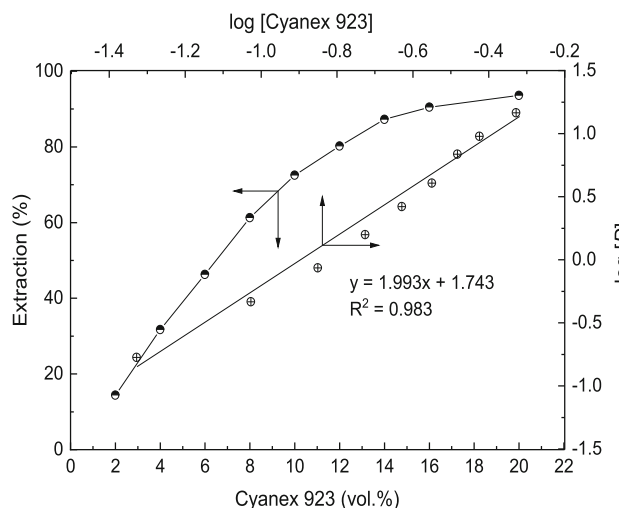


Fig. 4. Extraction of Ce^{4+} as a function of extractant concentration into the organic phase (on the primary axis) and the log–log plot of distribution coefficient versus Cyanex 923 concentration (on the secondary axis).

stoichiometric requirement of $\text{P} = \text{O}$ molecules that participate in the extraction process was evaluated by the slope analysis method. The plot of $\log[D]$ versus $\log[\text{Cyanex 923}]$ gives a straight line with a regression coefficient (R^2) value of 0.98 and slope value of 1.993 (see Fig. 4). This indicates the involvement of two moles of active $\text{P} = \text{O}$ molecules to complex with one mole of Ce^{4+} into the organic phase.

Effect of Acid Concentration

The influence of acid concentration on cerium extraction was investigated in the range from 0.25 mol/L to 2.0 mol/L, while maintaining an O/A ratio of 1 and using 20 vol.% Cyanex 923 into the organic phase. Figure 5 shows a decreasing trend for Ce^{4+} extraction with increasing concentration of acid into the aqueous feed. Extraction efficiency was found to decrease from 95% to 86% when the acid concentration was changed from 0.25 mol/L to 2.0 mol/L. This behavior can be correlated to the possible competition between metal species and bisulfate ions, which increases with higher acid concentration.^{25,26} Notably, the increasing concentration of H_2SO_4 decreases the ratio of HF with H_2SO_4 in the aqueous solution, which has been reported to be a favorable condition for metal extraction with Cyanex 923.^{26,27} In contrast, a decline in Ce^{4+} extraction with a lower HF- H_2SO_4 ratio in the present study exhibited a different phenomenon. The presence of Al^{3+} ions in leach liquor acts to scrub the fluorinated species extracted into the organic phase. This assumption was supported by the FTIR analysis (not shown for the sake of brevity). No vibrational peak was observed for the HF compound close to 1210 cm^{-1} ; however, the characteristic peaks for sulfate species HSO_4^- and SO_4^{2-} were found at 559 cm^{-1} and 1020 cm^{-1} ,

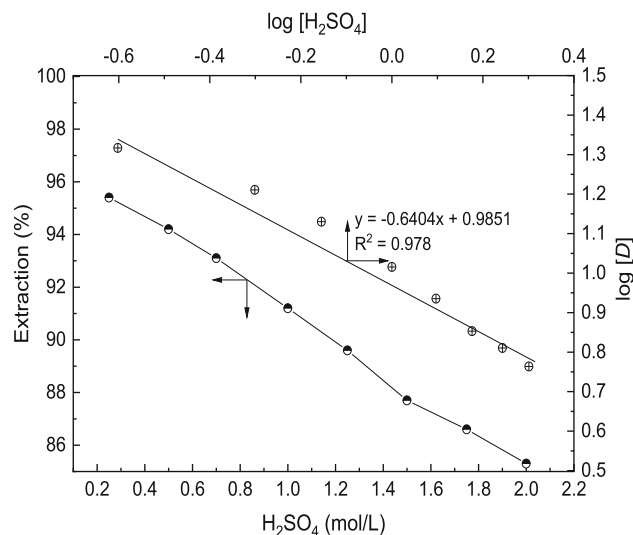
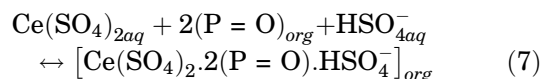


Fig. 5. Extraction of Ce^{4+} as a function of H_2SO_4 concentration in aqueous feed (on the primary axis) and the log–log plot of the distribution coefficient versus H_2SO_4 concentration (on the secondary axis).

which confirms the extraction of Ce^{4+} as its sulfate species.^{25,26} Furthermore, the log–log plot of $[D]$ versus H_2SO_4 concentration gives a straight line with R^2 value 0.97 (see Fig. 5). The obtained slope value (0.64) revealed the requirement of acid species in metal complexation at the unit mole ratio. As sulfuric acid dissociates as bisulfate ions (pka value, 1.99), the extraction reaction in line with the FTIR analysis (presence of HSO_4^-) can be written as:



Effect of Temperature and Extraction Thermodynamics

The extraction behavior of Ce^{4+} with Cyanex 923 was examined at different temperatures between 25°C and 55°C while contacting the two phases at an O/A phase ratio of 1. Figure 6 shows a declined extraction from 93% to 86% with respect to increasing temperature from 25°C to 55°C . This behavior indicates the destroyed ability of metal-binding sites with increasing temperature.²³ Furthermore, the thermodynamic properties for Ce^{4+} extraction with Cyanex 923 were determined using the van't Hoff equation, as below:

$$\log[D] = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (8)$$

The plot of $\log[D]$ versus $1/T$ yielded a straight line with R^2 value > 0.98 (see Fig. 6), where the slope and intercept values represent the apparent enthalpy change (ΔH°) and entropy change (ΔS°), respectively. The determined value of ΔH° ,

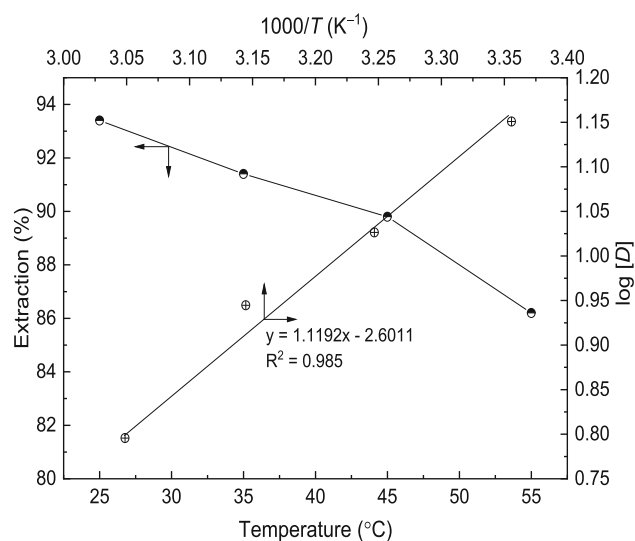


Fig. 6. Extraction of Ce^{4+} as a function of temperature (on the primary axis) and the van't Hoff plot of $\log[D]$ versus $1/T$ (on the secondary axis).

–21.42 kJ/mol, indicates the exothermic extraction process exhibiting *outer* sphere coordination between the phosphine oxides and cerium species into the organic phase.²⁸ The negative ΔS° value (–49.80 kJ/mol) indicates the increased orderliness of extracted species into the organic phase. Furthermore, ΔH° and ΔS° values were used to calculate the Gibbs free energy (ΔG°) by Eq. (9). The negative ΔG° values (at 298 K) were obtained to be –6.58 kJ/mol, which indicates the spontaneity of Ce^{4+} extraction with Cyanex 923.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

Effect of Organic-to-Aqueous Phase Ratio

The effect of the phase ratio on Ce^{4+} extraction was investigated by contacting the two phases at different volume phase ratios in the range from 1/4 to 4/1. The results showed that the extraction efficiency increased from ~ 30% to 99% within the range of O/A variations in a single contact. Using the experimental data, the extraction isotherm was determined by plotting the McCabe–Thiele diagram (as shown in Fig. 7a). This reveals that a quantitative extraction of 4.2 g/L Ce^{4+} would require a two-stage counter-current extraction (CCE) at an O/A ratio of 1. Furthermore, a batch simulation study under CCE at O/A of 1/1.2 was conducted until reaching the steady state. The 4.1 g/L Ce^{4+} yielded in the loaded organic solution was in good agreement with the predicted data, validating the plot of the extraction isotherm.

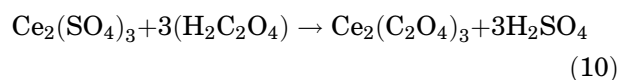
Reductive Stripping from Loaded Organic

Insufficient stripping of Ce^{4+} (~ 21%) was found to be challenging for recovery purposes and

regeneration of the organic phase as well. Hence, the stripping was investigated as a function of H_2O_2 dosage into the stripping solution containing 4.0 mol/L H_2SO_4 . The stripping behavior (shown in Fig. 7b) revealed that back-extraction of Ce^{4+} from loaded organic in its reduced form (as Ce^{3+}) increased with more H_2O_2 addition. The efficiency of Ce^{3+} stripping could increase from 21.4% to –98% by increasing the addition of H_2O_2 from 0 mol/L to 0.5 mol/L, respectively. Thereafter, the reductive stripping was also investigated as a function of H_2SO_4 concentration. Figure 7b revealed that the back-extraction process of cerium was independent of acid concentration while using ≥ 1.0 mol/L H_2SO_4 , contrary to the extraction process (see Fig. 5), which declined with increasing concentrations of acid into the aqueous feed. This clearly showed the advantage of the unique aqueous chemistry of cerium because of its existence in two oxidation states. The electronic configuration of $4f^1 5d^1 6s^2$ has a tendency to form stable Ce^{4+} along with the common losing of two 6s and one 5d electron, which form the cerous ions (Ce^{3+}),²⁹ whereas the presence of acid in the stripping solution offers the acidic environment required to avoid the formation of any insoluble at a higher pH, which may cause solvent loss.

Studies on Oxalate Salt Precipitation from Stripped Solution

Cerium oxalate has a lower solubility with a K_{sp} value of $1 \times 10^{-28.6}$. Hence, the oxalate precipitation of cerium is a simple process for recovering the high-pure precursor compound by following the reaction below:



The thermodynamic data showed that the formation of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ is possible at a wider range of pH in between 0 and 5.0. Therefore, the solution pH was maintained at 1.0 (± 0.2) while varying the oxalic acid dosage ($\text{Ce}^{3+}:\text{H}_2\text{C}_2\text{O}_4$) in the range from 1:0.5 to 1:5.

Figure 8 shows that precipitation requires more oxalic acid than the stoichiometric requirement possibly because of the need of more oxalate ions to provide the nucleation growth to the metal-oxalate compound. The precipitation efficiency of $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ improved from 18.6% to 54% with changing stoichiometric dosage from 1:0.5 to 1:2 of $\text{Ce}^{3+}:\text{H}_2\text{C}_2\text{O}_4$. A further increase in precipitant dosage as $\text{Ce}^{3+}:\text{H}_2\text{C}_2\text{O}_4 = 1:5$ could achieve > 99% recovery. To characterize the product formation, the vacuum-dried precipitates were analyzed using an XRD technique, which confirmed the formation of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (JCPDS card no. 20-0268) as the pattern shown in the inset in Fig. 8. The purity of the oxalate product was analyzed to be > 99.6%,

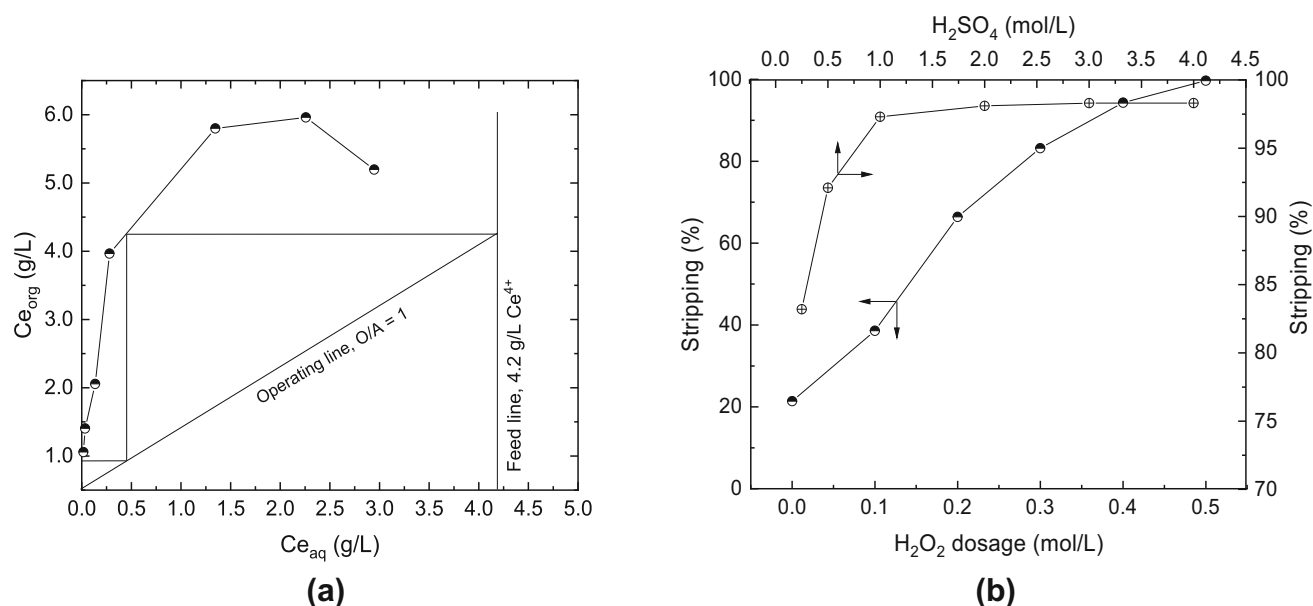


Fig. 7. (a) Extraction isotherm for Ce^{4+} by plotting the McCabe–Thiele diagram using 20 vol.% Cyanex 923 in kerosene and 4.2 g/L Ce^{4+} in the aqueous feed. (b) Stripping of Ce^{4+} from the loaded organic while contacting 4.0 mol/L H_2SO_4 as a function of H_2O_2 dosage (in the primary axis) and of H_2SO_4 with a constant 0.5 mol/L H_2O_2 (in the secondary axis).

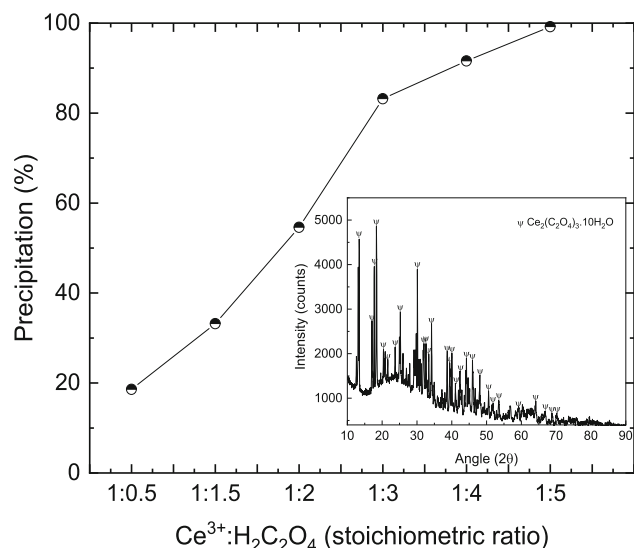


Fig. 8. Cerium precipitation from the stripped solution containing 4.1 g/L Ce^{3+} while contacting oxalic acid as a function of the $\text{Ce}:\text{H}_2\text{C}_2\text{O}_4$ stoichiometric ratio and XRD pattern of the precipitated product (in inset).

which demonstrates the potential of the present study.

CONCLUSION

In the present study, cerium was efficiently recovered from the secondary waste of bio-cyanide processed automobile catalysts using a purely hydrometallurgical recycling route that comprised leaching, solvent extraction, and precipitation techniques. Leaching of cerium was very poor (< 34%) in HCl , H_2SO_4 , and HNO_3 solutions, which could be

improved up to 95% when HF was added to 2.0 mol/L H_2SO_4 solution. Temperature and time played a vital role in cerium leaching that yielded > 97% efficiency at 80°C . The activation energy was determined to be 31.8 kJ/mol, which revealed that leaching follows the diffusion-controlled mechanism. Thereafter, cerium from leach liquor was selectively extracted over Al, Mg, and Si using Cyanex 923 by forming $[\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{P}=\text{O}) \cdot \text{HSO}_4^-]_{org}$ species into the organic phase. Quantitative extraction of 4.2 g/L Ce^{4+} was achieved using 20 vol.% extractant under two-stage CCE at an O/A ratio of 1. Tetra-valence cerium (Ce^{4+}) extracted into loaded organic phase was subsequently stripped in its reduced form (Ce^{3+}) by contacting ≥ 1.0 H_2SO_4 solution in the presence of 0.5 mol/L H_2O_2 . In the latter step, high-purity cerium was recovered as $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ by precipitating with oxalic acid at an optimal dosage of $\text{Ce}^{3+}:\text{H}_2\text{C}_2\text{O}_4$, 1:5. The demonstrated process is simple to operate and can potentially contribute to the circular economy of cerium value from the secondary waste obtained via bio-cyanide processing of exhausted automobile catalysts.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ELECTRONIC SUPPLEMENTARY MATERIAL

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