Resource Recovery of Cerium from Spent Catalytic Converter Using Aqueous Metallurgy

Sadia Ilyas, Hyunjung Kim, and Rajiv Ranjan Srivastava

Abstract Cerium recovery from a secondary waste stream generated after the extraction of Pt-group metals from spent catalytic converter has been investigated. Different mineral acids alone used as lixiviant could leach only 33% cerium; however, HF added acid mixture showed an increased leaching up to 96%. The determined value of activation energy 31.8 kJ/mol revealed that leaching progressed via diffusion-controlled mechanism. Subsequently, cerium from leach liquor was extracted using 4 tri-alkyl phosphine oxides in kerosene, which indicated the formation of extracted species to be $\left[\text{Ce}(SO_4)_2.2L.HSO_4^-\right]_{org}$. The loaded organic was quantitatively stripped back into the H_2SO_4 solution by adding an H_2O_2 dosage as a reducing agent. Thus, obtained Ce-bearing stripped solution was treated with oxalic acid to precipitate high-purity $Ce_2(C_2O_4)_3$. The process is simple and potentially dealt to recycle the critical metal values which remained less attractive until now.

Keywords Cerium · Rare earth metals · Spent automobile catalysts · HF leaching · Ce(IV) solvation · Ce(III) oxalate

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Introduction

Due to the stringent environmental regulation on automobiles' emissions, three-way catalytic converters became essential to modern automobiles for controlling the gaseous emissions [1, 2]. The catalytic converters usually consist of platinum group metals (PGMs) as the active components with wash-coated γ-Al_2O_3 on the cordierite support; however, CeO_2 acts as the structure stabilizer while promoting the catalytic activity [3, 4]. After being exhausted, the spent catalysts are usually sent to landfilling; however, certain parts are being recycled only for PGMs recovery [5]. Thus, the values of cerium are lost in residual landfilling, which is a non-sustainable practice and one of the key areas to pay the attention for recycling of this rare earth metal (REM). In contrast, cerium demands are continuously increasing in catalytic materials (including the fuel cells, auto-catalysts, and fluid-cracking catalysts), glass polishing, nuclear chemistry, semiconductor and ceramic industries, and low-energy fluorescence bulbs [6]. A compounded growth rate of cerium that is predicted to be 8% and the controlled trade of rare earths along with its reserves limited to certain geopolitical boundaries immensely pushes a need for the exploitation of alternative resources that could mitigate cerium's supply risks in the future [7, 8].

In recent times, the consumption of catalytic converters has increased proportionally with the soaring production of automobiles, therefore generating a large number of spent catalysts. The recovery of cerium from the spent catalysts can potentially contribute to the secondary supply route of this REM. Until now, numerous pyro- and hydro-metallurgical techniques have been studied for recycling of the exhausted catalytic converters [5, 9]; however, a few exist for resource recovery of cerium. Due to the refractory nature of CeO_2, it is hard to leach in dilute acid solutions [10, 11], and hence, acid baking as a pre-treatment step has been suggested to yield 85% leaching efficiency [12]. HCl leaching in the presence of H_2O_2 followed by sulfate double-salt precipitation has also been reported by Steinlechner and Antrekowitsch [13]; however, the experimental details are missing. Due to the lacking study in this context, the present study accounts for a hydro-metallurgical route to cerium recovery from a secondary generated after the PGMs' leaching from spent auto-catalysts.

Notably, the leach residue generated via the bio-cyanidation leaching of PGMs has been used as the feed material for cerium recovery in this study. Acid leaching in the presence of hydrofluoric acid (HF) has been conducted for effective dissolution of cerium, while varying the parameters like HF addition, temperature, and time. Subsequently, the extraction of cerium from leach liquor has been conducted using an organophosphorus mixture as the extractant and the influential parameters are optimized. Finally, cerium stripped from the loaded organic in the presence of hydrogen peroxide has been recovered as the high-purity oxalate precipitate.

Experimental

The sample fed in this study was obtained through the bio-cyanidation of spent auto-catalyst that containing 26.4% Al, 4.3% Ce, 2.7% Mg, and 7.9% Si. The reagents like hydrochloric acid (30%, Merck), nitric acid (65%, Sigma-Aldrich), sulfuric acid (95%, Daejung), hydrofluoric acid (40%, Merck Millipore), hydrogen peroxide (30%, Merck), oxalic acid (90%, Junsei Chemical Co.), organophosphorus organic mixture (93%, Cytec Canada Inc.), and distilled kerosene (Junsei Chemical Co.) were used without further purification. 15 g sample and 150 mL acid solutions of pre-determined concentration was taken into 250 round-bottom flask under the stirring condition (provided agitation of 250 rpm). For heating and stirring purpose, a hot plate with a magnetic stirring facility was used. Until specified, leaching studies were conducted at 60 °C for 4 h duration. When required, HF was separately added into sulfuric acid by keeping the pulp density fixed at 10%. After completion of leaching, the slurry was filtered, and the filtrate was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 7400 Duo, Thermo Scientific) for knowing the leaching efficiency. Subsequently, leach liquor containing 4.2 g/L cerium was contacted with an organic solvent of a pre-determined concentration at an O/A ratio of 1. For which, a 30-mL volume of each phase in a 100 mL separating funnel was contacted for 5 min at 25 ± 2 °C. The equilibrated solution was settled for 10 min;, thereafter, the collected raffinate was analyzed for knowing the cerium content and determining the extraction efficacy. The back-extraction of cerium was conducted using a stripping solution of 1.0 mol/L H_2SO_4 with H_2O_2. Further, the precipitation of cerium with a calculated oxalic acid was conducted using 50 mL stripped solution in 100 mL beaker, while maintaining temperature, $90(\pm 2)$ °C; agitation speed, 150 rpm; pH of the solution, $1.5(\pm 0.2)$, duration, 15 min; and settling time, 1 h. The slurry was filtered, and the filtrate was analyzed to determine the precipitation efficiency. On the other side, the precipitates were water-washed and overnight dried in a vacuum dryer for the characterization studies.

Results and Discussion

Acid Leaching

Leaching behavior of cerium in different acids was investigated at varying concentrations ranging from 1.0 to 6.0 mol/L acid. Experimental results are summarized in Fig. 1a, revealing the poor leachability for cerium (<33%) regardless of the acid media. This act can be ascribed to the acid resistance property of ceria [14]. Further, sulfuric acid was chosen due to low cost and less corrosive nature, and the change in leaching yield was investigated with the acid mixture prepared by mixing different concentrations of HF (0.25–2.0 mol/L) with 2.0 mol/L H_2SO_4. Figure 1b depicts that cerium leaching was improved with increasing concentration of HF in the
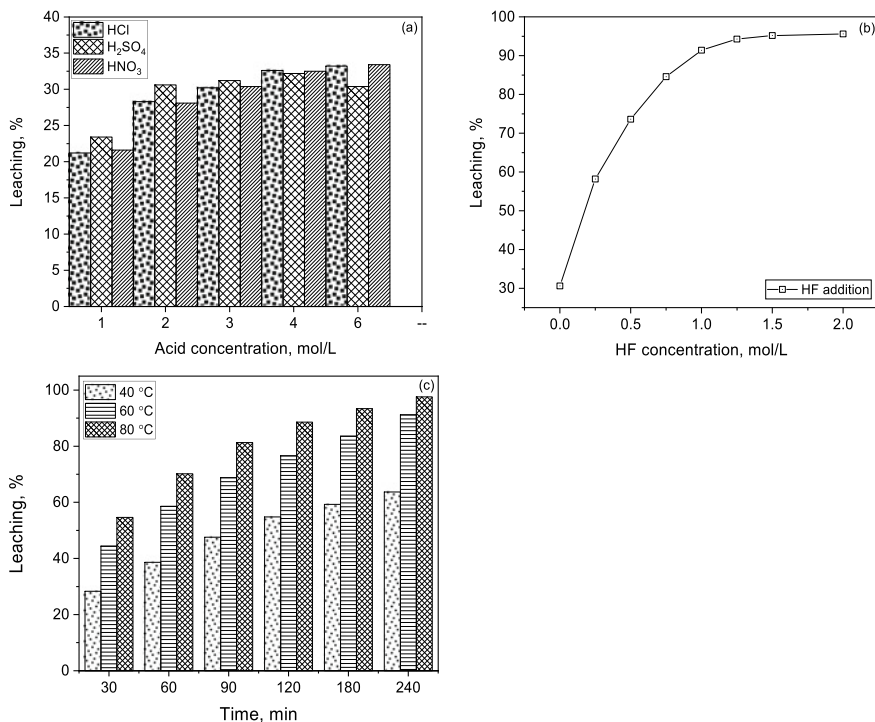
Fig. 1 Leaching behavior of cerium with different acids as a function of concentration (**a**); with acid mixture containing 2 mol/L H_2SO_4 and varied concentration of HF (**b**); and at different temperatures as a function of time (**c**)

acid mixture, indicating the influential act of fluoride ions. The leaching efficiency improved from 30.6 to 95.6% with respect to increasing concentration of HF up to 2.0 mol/L. However, not much improvement was observed above 1.0 mol/L HF in the acid mixture (increased from 91.4 to 95.6%), hence, the addition of 1.0 mol/L HF was optimized.

Further, the effect of temperature ranging from 40 to 80 °C with respect to time (up to 240 min) was investigated. Experimental results are shown in Fig. 1c depicted that at 40 °C, leaching efficiency was very low (~28% in 30 min) which could improve only to 63% in 240 min. At 60 °C, leaching was significantly improved (>90%) in 240 min which further increased up to 98% at 80 °C. To underpin the dissolution mechanism into the acid mixture, the following equation was employed to determine the apparent activation energy (E_a) [15]:

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

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) were considered (in which the leaching efficiency of cerium was approximately the same) to determine the E_a value. Thus, calculated E_a value (31.8 kJ/mol) indicated that the leaching process followed the diffusion-controlled mechanism [16].

Solvent Extraction with Organophosphorus Mixture

Cerium extraction from leach liquor was investigated with a commercially available organic mixture of 4 tri-alkyl phosphine oxides at different concentrations ranging from 2 to 20% (v/v). Experimental results are shown in Fig. 2a depicted that cerium extraction increased with increasing concentration of the organophosphorus compound, which can be corroborated to the shifting of distribution curve with more available extraction sites into the organic phase [17, 18]. The extraction improved from 14 to 90% with extractant concentration increased from 2 to 16%, and finally reached to ~93% using 20% extractant into the organic phase. The logarithmic plot for cerium distribution into both phases versus the extractant concentration yielding straight line with R^2 value 0.98 (not shown here) and slope value 1.99 could reveal that two moles of extractant are complexed with each mole of cerium extraction into the organic phase.

Further, the extraction behavior was examined as a function of acid concentration in the range of 0.25–2.0 mol/L H_2SO_4 using 20% (v/v) extractant in the organic phase. The results are shown in Fig. 2b depicted that the extraction decreased from 95 to <86% when H_2SO_4 concentration changed from 0.25 to 2.0 mol/L. This behavior can be a resultant of the competition between metal species and bisulfate ions [19, 20]. Additionally, a decline in cerium extraction with lower HF-H_2SO_4 ratio might be due to the presence of aluminum fluoride in the leach liquor which acts as a defluorinating agent to scrub the fluorinated species co-extracted into the organic phase. The logarithmic plot for cerium distribution versus H_2SO_4 concentration yielding straight line with R^2 value 0.976 (not shown here) and slope value 0.6 could reveal the requirement of one mole acid against each mole of cerium extraction. As sulfuric
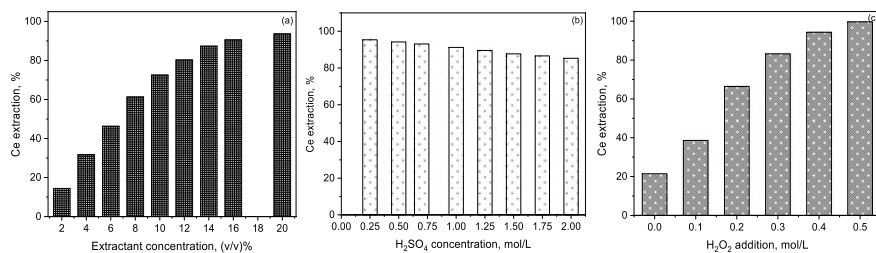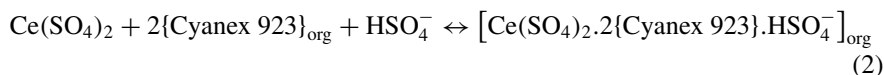

Fig. 2 Extraction behavior of cerium from leach liquor as a function of extractant concentration (**a**); acid concentration (**b**); and stripping behavior from the loaded organic as a function of H_2O_2 addition (**c**)

acid dissociates as bisulfate ions (pka value, 1.99), the stoichiometric reaction can be given as:

$$Ce(SO_4)_2 + 2\{Cyanex\ 923\}_{org} + HSO_4^- \leftrightarrow \left[Ce(SO_4)_2.2\{Cyanex\ 923\}.HSO_4^-\right]_{org} \tag{2}$$

As per the phase ratio variations at different O/A between 1/4 and 4/1, the extraction could be increased from 30 to >99%. Using the experimental data, the McCabe–Thiele diagram was drawn, which showed that the quantitative extraction of cerium can be achieved in two-stages of counter-current extraction (CCE) at an O/A ratio of 1. A batch simulation under CCE yielded 4.1 g/L cerium extraction into the organic phase, which further underwent to stripping studies. Cerium stripping from the loaded organic was examined as a function of H_2O_2 addition in 1 mol/L H_2SO_4 solution. Results are shown in Fig. 2c revealed that the stripping efficiency increased with increasing addition of H_2O_2 and reached to about 98% using 0.5 mol/L H_2O_2.

Oxalate Precipitation

Cerium form insoluble compound in the presence of oxalate ions by following the reaction below:

$$Ce_2(SO_4)_3 + 3(H_2C_2O_4) \rightarrow Ce_2(C_2O_4)_3 + 3H_2SO_4 \tag{3}$$
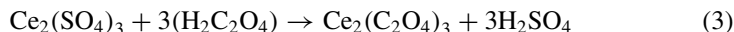
The precipitation of cerium from stripped solution after maintaining the pH at ~1.5 was investigated as a function of oxalic acid addition in the variation range of $Ce^{3+}:H_2C_2O_4 = 1:0.5–1:5$. The results are shown in Fig. 3a revealed that precipitation requires a high oxalic acid possibly due to the acceleration of nucleation
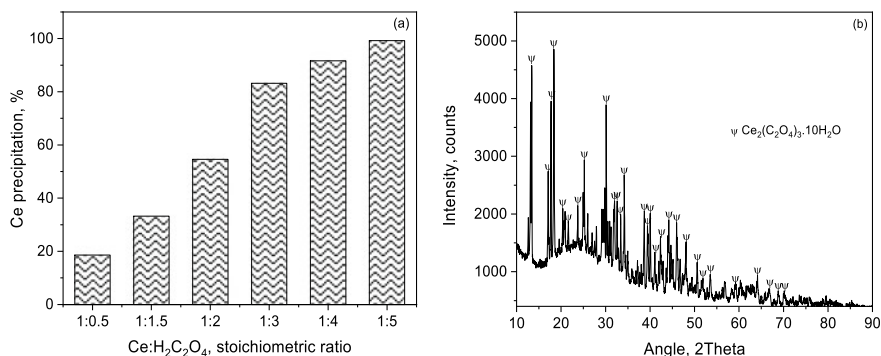

Fig. 3 Cerium precipitation from stripped liquor as a function of stoichiometric ratio with oxalic acid (**a**); and XRD patter of the oxalate precipitate (**b**)

growth in the presence of higher oxalate ions. The precipitation efficiency could be improved from 18.6 to 54% by changing addition from 1:0.5 to 1:2, which was further increased to achieve above 99% cerium recovery at 1:5. The vacuum-dried precipitate was characterized using the XRD technique, indicating the formation of $Ce_2(C_2O_4)_3.10H_2O$ (Fig. 3b). Finally, the purity of the oxalate product was analyzed to be >99.6%.

Conclusions

The efficient recovery of cerium was conducted from the secondary waste of bio-cyanide processed auto-catalysts while using the advantages of aqueous metallurgy. Due to poor leaching of cerium (<34%) in strong mineral acids, HF was introduced with 2.0 mol/L H_2SO_4 solution that could improve efficiency up to 95%. The activation energy for leaching cerium into the acid mixture was determined to be 31.8 kJ/mol, which revealed that leaching followed the diffusion-controlled mechanism. Cerium from leach liquor was subsequently extracted using an organophosphorus mixture that forming $\left[Ce(SO_4)_2.2L.HSO_4^-\right]_{org}$ species into the organic phase. Further, the quantitatively extracted cerium into the organic phase was stripped back into the aqueous phase while contacting with 1.0 mol/L H_2SO_4 + 0.5 mol/L H_2O_2. Finally, the high-purity $Ce_2(C_2O_4)_3.10H_2O$ was recovered by precipitating cerium with oxalic acid at $Ce^{3+}:H_2C_2O_4$ mole ratio = 1:5.

Conflict of Interest The authors declare that they have no conflict of interest.

References

1. Heck MR, Farrauto RJ (2001) Automobile exhausted catalyst. Appl Catal A 221:443–457
2. Kašpar J, Fornasiero P, Hickey N (2003) Automotive catalytic converters: current status and some perspective. Catal Today 77:419−449
3. Lox ES (2008) Automotive exhaust treatment. In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. WileyVCH Verlag GmbH & Co., KGaA, pp 2274–2344
4. Hickey N, Boscarato I, Kašpar J (2014) Air pollution from mobile sources: formation and effects and abatement strategies. In: Cao G, Orru R (eds) Current environmental issues and challenges. Springer, Dordrecht, pp 15–43
5. Dong H, Zhao J, Chen J, Wu J, Li B (2015) Recovery of platinum group metal from spent catalyst: a review. Int J Miner Process 145:108–113

6. Ilyas S, Kim H, Srivastava RR (2021) Extraction equilibria of cerium(IV) with Cyanex 923 followed by precipitation kinetics of cerium(III) oxalate from sulfate solution. Sep Purif Technol 254:117634

7. Hearty G (2019) Rare earths: next element in the trade war? Center for Strategic and International Studies. https://www.csis.org/analysis/rare-earths-next-element-trade-war#:~:text=With%20the%20trade%20war%20having,next%20salvo%20in%20the%20conflict.&text=A1%3A%20Rare%2Dearth%20elements%20are,which%20possess%20similar%20chemical%20properties. Accessed 14 Aug 2020

8. Cordier DJ (2009) Rare earths, metals and minerals. In: U.S. geological survey minerals yearbook

9. Ilyas S, Srivastava RR, Kim H, Cheema HA (2020) Hydrometallurgical recycling of palladium and platinum from exhausted diesel oxidation catalysts. Sep Purif Technol 248:117029

10. Lin S, Yang L, Yang X, Zhou R (2014) Redox behavior of active PdO_x species on $(Ce, Zr)_xO_2$–Al_2O_3 mixed oxides and its influence on the three-way catalytic performance. Chem Eng J 247(7):42–49

11. Morikawa A, Suzuki T, Kanazawa T, Kikuta K, Suda A, Shinjo H (2008) A new concept in high performance ceria–zirconia oxygen storage capacity material with Al_2O_3 as a diffusion barrier. Appl Catal B 78(3):210–221

12. Wu XF, Dong HG, Tong WF, Fan XX, Zhao JC, Lei Y (2015) Study on new technology for recovery of rare earth elements from used automobile catalysts. Chin Rare Earths 36(1):101–104

13. Steinlechner S, Antrekowitsch J (2015) Potential of a hydrometallurgical recycling process for catalysts to cover the demand for critical metals, like PGMs and cerium. JOM 67(2):406–411

14. Zhao Z, Qiu Z, Yang J, Ma B, Li Z, Lu S, Xu Y, Cao L, Zhang W (2019) Recovery of rare earth element cerium from spent automotive exhaust catalysts using a novel method. Waste Biomass Valori 11:4967–4976

15. Levenspiel O (1999) Chemical reaction engineering. Wiley, New York

16. Habashi F (1969) Extractive metallurgy. Gordon and Breach, Science Publishers, New York

17. Ritcey GM, Ashbrook AW (1984) Solvent extraction part I. Elsevier, Amsterdam

18. Srivastava RR, Ilyas S, Kim H, Tri NLM, Hassan N, Mudassir M, Talib N (2020) Liquid–liquid extraction and reductive stripping of chromium to valorize industrial effluent. JOM 72(2):839–846

19. Jun L, Zhenggui W, Deqian L, Gengxiang M, Zucheng J (1998) Recovery of Ce(IV) and Th(IV) from rare earths(III) with Cyanex 923. Hydrometallurgy 50:77–87

20. Liao W, Yu G, Li D (2001) Solvent extraction of cerium(IV) and fluorine(I) from sulphuric acid leaching of bastnasite by Cyanex 923. Solvent Extr Ion Exch 19:243–259