

A BRIEF REVIEW ON RECOVERY OF CERIUM FROM GLASS POLISHING WASTE

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Introduction

Cerium is the most abundant element out of the 17 rare-earth elements (REEs). The current production of CeO₂ is about 54,400 t (32% of RE oxides). About 40,000 t of RE oxides are consumed by glass industry, out of which about 16,000 tons are being used for polishing applications¹. Cerium dioxide is the main component (40 – 99%) in glass polishing powders^{2–4}. It is also used for polishing silicon wafers and ceramics. The CeO₂ particles in the slurry polish the glass with chemical-mechanical action. The waste slurry generated after glass polishing contains cerium together with other REEs (mainly lanthanum, neodymium and praseodymium), silicon, iron, aluminium, zinc, sodium *etc.* The concentration of the elements other than REEs in glass polishing waste depends on the chemical composition of the glass, additives and flocculants. The abrasive properties of polishing powder diminish due to the enrichment of the slurry with other elements with time and affect the quality of product adversely. Currently, the waste generated after polishing (CeO₂: 8-80%)^{5,6} ends up in landfills³. Recycling of this waste not only contributes to the proper utilisation of natural resources but also makes recycling of valuable REEs possible, and it also saves the disposal cost. In addition, the recovered cerium can be converted to cerium metal and used in high value aluminium and magnesium alloys and steels. This generates highly added value from waste and closes metal loops. Therefore, this paper reviews the literature on recovery of cerium from glass polishing waste.

Recovery of polishing powder (cerium compounds)

Physical separation

Silica is a major impurity in polishing waste. It can be removed by physical or physicochemical separation processes like sieving, flotation *etc.* in order to re-use the polishing powder. Kim *et al.* partially removed the glass particles from waste by flotation⁷. Liang *et al.* (2009) applied flotation using sodium dodecylsulfate as a collector⁸. The recovery was only 40% with a purity of 44% (35% in feed sample) when

they used real slurry. However, it is difficult to remove all the silica particles as the particle size is very small ($< 5 \mu\text{m}$). Therefore, chemical separation processes are required for further purification, *i.e.* for the removal of silica and/or other elements.

Chemical separation

Alkali Leaching - purification of CeO_2 by removing contaminants

Kato *et al.* removed most of Al_2O_3 and SiO_2 from glass polishing waste by treating it with 4 mol/kg of NaOH at 50-60°C for 1 hour³. Kim *et al.* removed the remaining glass in the waste after a flotation treatment by NaOH leaching with a pH level of 11.5⁷. Removal of glass particles by sieving, flotation and/or alkali leaching can increase the lifespan of polishing powder to some extent⁶. However, the removal of silica and/or alumina alone is insufficient as the increase in concentration of other elements adversely affects the product quality after several cycles. Therefore, complete removal of impurities or dissolution of cerium into a leach solution followed by cerium recovery is required.

Acid leaching – (selective) dissolution of CeO_2

Direct leaching

Cerium dioxide is sparingly soluble in most of the acids at ambient conditions⁶. Therefore, leaching needs to be carried out in concentrated acid solutions and/or at elevated temperatures. Different acids like HCl, HNO_3 and H_2SO_4 can be used for leaching of glass polishing waste. Sulfuric acid is a low-cost reagent and less corrosive. However, the solubility of RE sulfates is very low in leach solutions.

After removal of silica from glass polishing waste by flotation and after alkali leaching, Kim *et al.* performed oxidative roasting on dried samples at 600°C to convert cerium compounds to CeO_2 ⁷. Cerium was leached from the roasted mass by concentrated sulphuric acid solution at 60°C. They claimed that 10% more cerium is dissolved into the leach solution in case the roasting step is included in the processing. However, the roasting step for a small increase in cerium recovery is difficult to be justified. Um *et al.* leached a synthetic mixture with sulphuric acid in two stages for selective recovery of cerium⁹. In the first stage, they treated the mixture with 2 mol/dm³ sulphuric acid at 90°C for leaching La, Nd, Pr and Ca. In the second stage, the leach residue from the first stage was treated with 12 mol/dm³ sulphuric acid and 120°C. After leaching, the leach solution was diluted with water to dissolve $\text{Ce}(\text{SO}_4)_2$. Yamada *et al.* (2010) were able to recover cerium selectively by using 1.4 kmol/m³ HCl at 55°C⁸. The recovery of cerium is about 65% and that of lanthanum is very low. From this study, it looks that cerium can be selectively dissolved. However, the recovery of cerium or lanthanum mainly depends on the nature of different compounds in the polishing powder (mineralogy). For example, if the lanthanum is present in a phosphate or fluoride phase then it is difficult to dissolve.

Acid Leaching together with a reductant

As discussed earlier, direct acid leaching of CeO_2 is difficult. Therefore, the use of a reductant can help in decreasing the required acid concentration and leaching temperature. Potassium iodide¹⁰ and H_2O_2 ^{5,6,11,12} are used as reductants during acid leaching of glass polishing waste so far. Poscher *et al.* leached the polishing waste with HCl and H_2O_2 . More than 97% of cerium was recovered by using concentrated acid¹². An Industrial process was developed by HYDROMETAL in Belgium for the by reductive leaching of CeO_2 in the glass polishing powder with nitric acid together with H_2O_2 ⁵. They chose nitric acid lixiviant as it is selective towards silica and alumina. They used higher temperature for diffusion of acid into the silica matrix and also to enhance filtration. Janoš *et al.* are able to leach the glass polishing waste (containing a high fraction of $\sim 60\%$ CeO_2) in nitric acid and H_2O_2 solution without any external heating because of the exothermic nature of the reaction⁶. However, with low cerium content ($\sim 9\%$) the external heating is necessary to maintain the temperature ($65\text{--}70^\circ\text{C}$). The dissolution of cerium was around 70%. In another work, Janoš *et al.* studied the leaching of polishing waste with hydrochloric acid and potassium iodide¹⁰. They added 15-35% HCl together with 10-20% excess of potassium iodide. They claimed that the leaching of cerium was complete with in 15-60 min.

Recovery of cerium from leach solutions

Different methods that are used for the recovery of cerium from a leach solution include double salt precipitation, oxalate precipitation, carbonate precipitation, hydroxide precipitation and solvent extraction. Poscher *et al.* precipitated cerium and lanthanum from the solution with oxalic acid¹². The precipitated oxalates are calcined at 650°C to convert oxalates to respective oxides. They also proposed to selectively precipitate cerium (III) from solution with an oxidising treatment and pH adjustment. These oxidising agents include H_2O_2 or potassium permanganate. However, oxidants other than H_2O_2 may contaminate the product^{7,12}. After cerium removal by oxidation, lanthanum can be removed by oxalic acid treatment. Cerium was also recovered from the solution by a mixture of CO_2 and NH_3 ⁶. Kim *et al.* removed other REEs from cerium by double sulfate precipitation with sodium sulfate at 50°C and 90 min⁷. Yamada *et al.* extracted cerium preferentially over lanthanum using D2EHPA and PC-88A reagents through solvent extraction⁸.

Other processes

Ozaki *et al.* separated cerium and other REEs from glass polishing waste by chemical transport method¹³. After chloride conversion, RE chlorides were exposed to Al_2Cl_6 gas to form low volatile ($\text{LnAl}_3\text{Cl}_{12}$) complexes. At temperatures of $457\text{--}947^\circ\text{C}$ these complexes dissociate and form RE chlorides. By this process REEs were successfully separated from other elements, however it is difficult to separate individual REEs, because of their similar properties.

Applications of recovered cerium

Large quantities of cerium can be generated by treating the current glass polishing waste and waste from landfills. Hence, the recovered cerium can be used in glass polishing or other applications like redox flow batteries, oxidimetric agent, as a catalyser and in sewage treatment^{6,9}. The recovered cerium can also be used for preparing valuable Al-Ce alloys.

Conclusions

Large quantity of cerium in glass polishing waste is being lost in landfills. The life of glass polishing waste can be extended by removing silica with physical beneficiation and/or alkali leaching processes. Cerium and other REEs can be recovered from glass polishing waste by acid leaching processes followed by extraction from leach solutions. However, high acid concentration and/or temperatures or costly reagents (reductants) are required during leaching. The extracted cerium can be re-used in glass polishing or other high value-added applications.

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