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# A BRIEF REVIEW ON RECOVERY OF CERIUM FROM GLASS POLISHING WASTE

Chenna Rao BORRA<sup>1</sup>, Thijs J.H. VLUGT<sup>2</sup>, Yongxiang YANG<sup>1</sup>, S. Erik OFFERMAN<sup>1</sup>

<sup>1</sup> Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD Delft, The Netherlands

<sup>2</sup> Process & Energy Department, Delft University of Technology, Leeghwaterstraat 39, 2628CB, Delft, The Netherlands

*c.r.borra@tudelft.nl, t.j.h.vlugt@tudelft.nl, y.yang@tudelft.nl, s.e.offerma@tudelft.nl*

## Introduction

Cerium is the most abundant element out of the 17 rare-earth elements (REEs). The current production of CeO<sub>2</sub> 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 applications<sup>1</sup>. Cerium dioxide is the main component (40 – 99%) in glass polishing powders<sup>2-4</sup>. It is also used for polishing silicon wafers and ceramics. The CeO<sub>2</sub> 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 (CeO<sub>2</sub>: 8-80%)<sup>5,6</sup> ends up in landfills<sup>3</sup>. 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 flotation<sup>7</sup>. Liang *et al.* (2009) applied flotation using sodium dodecylsulfate as a collector<sup>8</sup>. 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 $\text{CeO}_2$ by removing contaminants

Kato *et al.* removed most of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  from glass polishing waste by treating it with 4 mol/kg of NaOH at 50-60°C for 1 hour<sup>3</sup>. Kim *et al.* removed the remaining glass in the waste after a flotation treatment by NaOH leaching with a pH level of 11.5<sup>7</sup>. Removal of glass particles by sieving, flotation and/or alkali leaching can increase the lifespan of polishing powder to some extent<sup>6</sup>. 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 $\text{CeO}_2$

#### *Direct leaching*

Cerium dioxide is sparingly soluble in most of the acids at ambient conditions<sup>6</sup>. Therefore, leaching needs to be carried out in concentrated acid solutions and/or at elevated temperatures. Different acids like HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  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  $\text{CeO}_2$ <sup>7</sup>. 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 cerium<sup>9</sup>. In the first stage, they treated the mixture with 2 mol/dm<sup>3</sup> 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/dm<sup>3</sup> 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/m<sup>3</sup> HCl at 55°C<sup>8</sup>. 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<sub>2</sub> is difficult. Therefore, the use of a reductant can help in decreasing the required acid concentration and leaching temperature. Potassium iodide<sup>10</sup> and H<sub>2</sub>O<sub>2</sub><sup>5,6,11,12</sup> are used as reductants during acid leaching of glass polishing waste so far. Poscher *et al.* leached the polishing waste with HCl and H<sub>2</sub>O<sub>2</sub>. More than 97% of cerium was recovered by using concentrated acid<sup>12</sup>. An Industrial process was developed by HYDROMETAL in Belgium for the reductive leaching of CeO<sub>2</sub> in the glass polishing powder with nitric acid together with H<sub>2</sub>O<sub>2</sub><sup>5</sup>. 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 ~60% CeO<sub>2</sub>) in nitric acid and H<sub>2</sub>O<sub>2</sub> solution without any external heating because of the exothermic nature of the reaction<sup>6</sup>. However, with low cerium content (~9%) the external heating is necessary to maintain the temperature (65-70°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 iodide<sup>10</sup>. They added 15-35% HCl together with 10-20% excess of potassium iodide. They claimed that the leaching of cerium was complete within 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 acid<sup>12</sup>. 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<sub>2</sub>O<sub>2</sub> or potassium permanganate. However, oxidants other than H<sub>2</sub>O<sub>2</sub> may contaminate the product<sup>7,12</sup>. 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<sub>2</sub> and NH<sub>3</sub><sup>6</sup>. Kim *et al.* removed other REEs from cerium by double sulfate precipitation with sodium sulfate at 50°C and 90 min<sup>7</sup>. Yamada *et al.* extracted cerium preferentially over lanthanum using D2EHPA and PC-88A reagents through solvent extraction<sup>8</sup>.

### **Other processes**

Ozaki *et al.* separated cerium and other REEs from glass polishing waste by chemical transport method<sup>13</sup>. After chloride conversion, RE chlorides were exposed to Al<sub>2</sub>Cl<sub>6</sub> gas to form low volatile (LnAl<sub>3</sub>Cl<sub>12</sub>) complexes. At temperatures of 457-947°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<sup>6,9</sup>. 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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