

EXTRACTION OF LANTHANIDES FROM SPENT POLISHING AGENT

Alexander POSCHER¹, Stefan LUIDOLD², Holger SCHNIDERITSCH³ and Helmut ANTREKOWITSCH⁴

^{1,2,3,4} Chair of Nonferrous Metallurgy, University of Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria

alexander.poscher@unileoben.ac.at, stefan.luidold@unileoben.ac.at,
holger.schnideritsch@unileoben.ac.at, helmut.antrekowitsch@unileoben.ac.at

Abstract

The polishing of glass substrates or wafers requires the usage of fine grained particles based on lanthanides. During processing the sludge becomes enriched with different elements depending on the specific production program. However, concentrations of impurities can reach critical values and may influence the surface quality of the substrates in a negative way. Therefore, the polishing agents have to be removed from the system and recycled meaningfully. The paper describes ways of processing such secondary RE resources using different hydrometallurgical methods including mineral acids for the extraction. Finally, the focus was set on the evaluation of precipitation methods for the production of a rare earth concentrate.

Introduction

Polishing agents and additives used in the glass industry are estimated to represent a global demand of rare earths (RE) of approximately 10 % in terms of economic value but mainly consist of light rare earths cerium and lanthanum ^{1,2,3}. These most abundant RE have suffered from continuously falling prices (Figure 1) in the last years which makes economic recycling difficult.

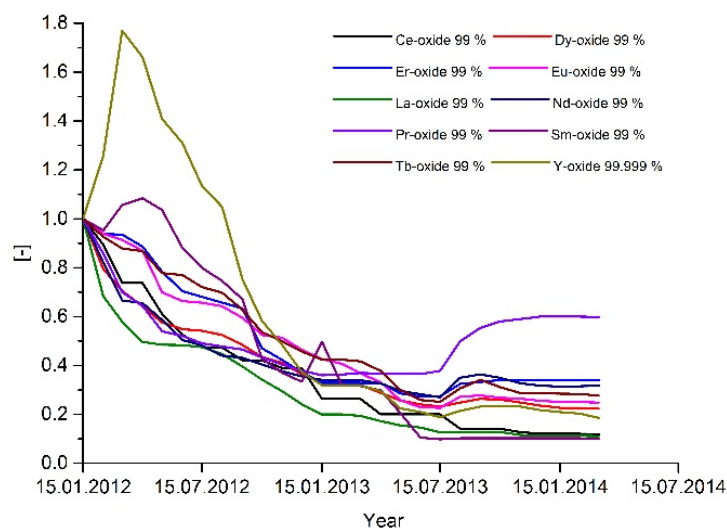


Figure 1: Relative price development of various REO from 2012 to 2014 ⁴

Based on the price level in January 2012 which was set to one, the changes in price are visualized as dimensionless values ($\text{€}_{xx/201x}/\text{€}_{01/2012}$). As can be seen from the chart the costs for many of the REOs are less than 40 % of the price at the beginning of 2012. Therefore, it seems to be of high relevance to design easy manageable, environmentally friendly and low-cost recycling processes. In contrast the strategic independence of the European Union and many other countries outside Europe from China's RE supply is a strong driving force for numerous recycling projects. Kato ⁵ suggested an alkaline treatment of spent polishing material using 4 mol/kg sodium hydroxide solution and temperatures between 50 to 60 °C. Thus, impurities such as silicon dioxide and alumina dissolve and can be separated from the solution by heating and precipitation as zeolites ⁵. Matsui ⁶ also treated abrasives with solutions of sodium hydroxide to achieve dissolution of for example SiO₂. Further processing includes a precipitation respectively a promoted settling of fine disperse cerium oxide particles with for example aluminium sulphate. Subsequent to the removal of the supernatant the precipitates are washed several times. Additionally, the pH of the resulting fraction is adjusted to low acidic or neutral in order to remove soluble impurities ⁶. An advanced process is proposed by Moon ⁷ also dealing with the removal of contaminants from a spent polishing agent by a caustic soda solution. Small amounts of sodium fluoride and sodium carbonate support the purification process ⁷.

A dry process was introduced by Ozaki ⁸ using carbo-chlorination techniques to achieve extraction of the rare earths from a material basically consisting of 38 wt.-% CeO₂, 28 wt.-% La₂O₃ and 10 wt.-% Nd₂O₃ together with alkaline earth metal oxides, silicon dioxide and fluorine. Subsequent chemical vapour deposition experiments using Al₂Cl₆ as complexing agent showed that specific temperature gradients may lead to a separation of rare earth chlorides from formed aluminium and iron chlorides. Enrichment of single rare earth chlorides can be obtained by a repeated CVT process ⁸.

Nevertheless, processes using solutions of sodium hydroxide face problems concerning the quantitative dissolution of silicon dioxide and metallic components which originate from semiconductor polishing. The application of chlorine in the process may result in the separation of the rare earths, but careful material selection of the reactor lining has to be done due to the highly corrosive media. Therefore, acidic hydrometallurgical methods seem to be favourable. One available technology is used at Hydrometal in Belgium ⁹. The rare earth compounds of spent polishing agents are dissolved by nitric acid in combination with hydrogen peroxide acting as a reducing agent for Ce(IV) in this case. The addition of oxalic acid leads to the precipitation of the RE oxalates ⁹. As it is shown later, our own experiments confirm the possibility of good cerium extraction by these chemicals, but also illustrated limited lanthanum dissolution.

Experimental

Input material

The material of interest was a typical polishing material based on lanthanides with an approximate composition according to Table 1. The major impurities which make a recycling necessary are the oxides of silicon, zinc, sodium and calcium because they may cause decreasing surface qualities of the glass substrate at critical values.

Table 1: Chemical composition of the used abrasive material

Oxide	wt.-%	Oxide	wt.-%
CeO ₂	69	SiO ₂	11
La ₂ O ₃	8	ZnO	2
Nd ₂ O ₃	1	P ₂ O ₅	2
CaO	1	Na ₂ O	1

Experimental set-up

All leaching and extraction experiments were carried out at atmospheric pressure in three-neck round-bottom flasks using a heating mantle and temperature control. Furthermore, condensers and dropping funnels were employed. The experimental set-up for the leaching tests can be seen in Figure 2. Nitric and hydrochloric acid tests were carried out under continuous agitation. Sulphuric acid experiments show onward solidification of the sludge consisting of the polishing agent and the concentrated acid at raising temperatures.

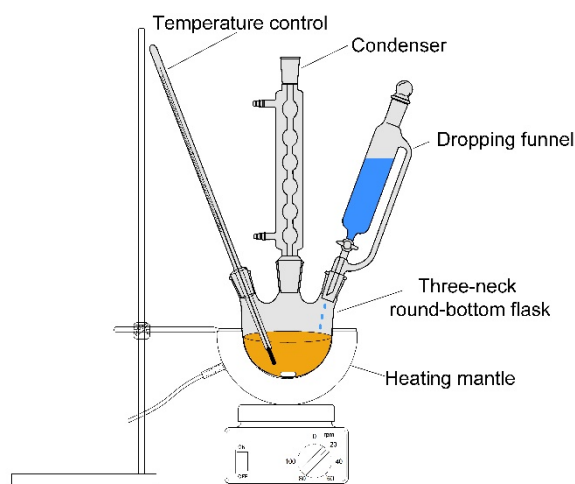


Figure 2: Experimental set-up for the extraction experiments (Figure drawn with ACD/ChemSketch)

Precipitation experiments were performed from hydrochloric and sulphuric acid solutions. These were carried out in beakers at room temperature under continuous stirring. Frits of porosity 4 (10-16 μm mesh) separated the leaching residues and precipitation products from the liquid phase. Both solid fractions were dried at 120 °C and calcined if it was assumed that the obtained compounds differ from oxides.

Nitric acid leaching

The experiments included a number of leaching experiments to determine the most important parameters. As nitric acid - an oxidizing acid - was used, hydrogen peroxide had to be added in order to reduce tetravalent cerium from CeO₂ to the cerous state. The experiments started with the addition of nitric acid to 50 g of spent polishing material. After a heating period 100 g H₂O₂ (30 wt.-%) were added. Different amounts and concentrations of nitric acid were tested and the temperature and leaching time were varied (Table 2).

Subsequently, filtration and washing of the filter cakes were done. Additionally, the solid residue was dried, the dissolved mass measured and the material was analysed by XRF.

Table 2: Basic parameters for HNO₃ experiments

Acid	Concentrations tested [wt.-%]	Additional chemicals	Temperatures tested during leaching [°C]	Leaching time [h]
HNO ₃	47, 65	H ₂ O ₂	70, 90	1, 6, 12

Hydrochloric acid leaching

Hydrochloric acid leaching tests started in the same way as the nitric acid leaching experiments. As HCl is a reducing acid, the strength of the chlorine ion was assumed to be strong enough for complete reduction of Ce⁴⁺. Therefore, the amount of hydrogen peroxide was varied as well. An overview of tested parameters in the leaching step is given in Table 3.

Table 3: Basic parameters for HCl leaching experiments

Acid	Concentrations tested [wt.-%]	Additional chemicals	Temperatures tested [°C]	Leaching time [h]
HCl	16, 21, 32	H ₂ O ₂	80, 95	4, 8

The pregnant leach solutions were adjusted to a volume of 500 ml. Subsequently, precipitation experiments using the total amount of the leaching liquor and oxalic acid were done. This step was supported by Design of Experiments which makes a statistical analysis possible. While the leaching parameters were held on a constant level (Table 4) the amounts and concentrations of oxalic acid solutions were modified. After the conversion of the precipitation product to a mixed rare earth oxide by thermal treatment at 750 °C and the XRF analysis of the product, mass balances were calculated. The yields for each element represent the raw data for the statistical analysis. As a consequence of the constant leaching parameters, the result of the statistical analysis gives accurate data about the precipitation step.

Table 4: Leaching parameters for subsequent precipitation

Pol. Agent [g]	c(acid) [wt.-%]	H ₂ O ₂ [g]	Temperature [°C]	Leaching time [h]
50	32	100	80	4

A flowsheet of the entire HCl leaching and precipitation process can be found in Figure 3.

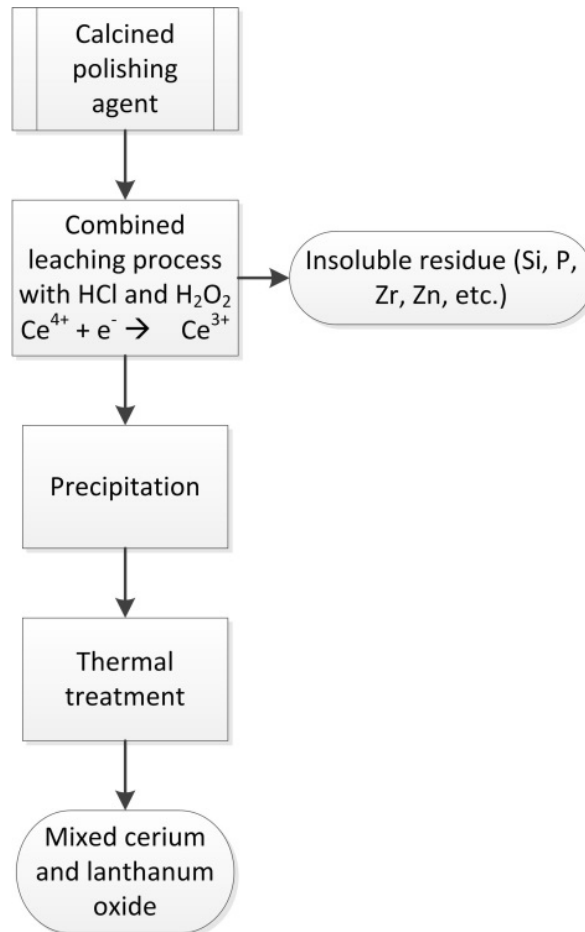


Figure 3: Process flowsheet of hydrochloric acid leaching and oxalic acid precipitation

Test execution for experiments using sulphuric acid

The experimental procedure and set-up correspond to the above described in many ways. One major difference between nitric or hydrochloric leaching experiments from the sulphuric acid process is the extraction of lanthanides in two steps including a digestion and subsequent elution of formed RE sulphates. The digestion was performed in round-bottom flasks as it was described earlier. During this process at temperatures between 100-200 °C the slurry consisting of polishing agent and concentrated sulphuric acid suffers from onward solidification. Therefore, contrary to HNO₃ and HCl experiments stirring during the entire digestion period became impossible. The digested materials were subsequently leached at room temperature with sufficient amount of water and transferred to frits. The filter cakes were washed several times, dried, calcined and finally analysed.

The pregnant red-orange leaching solutions were subsequently transferred to beakers and treated with different precipitation agents to achieve mixed RE-compounds. The universally valid process flowsheet can be seen in Figure 4.

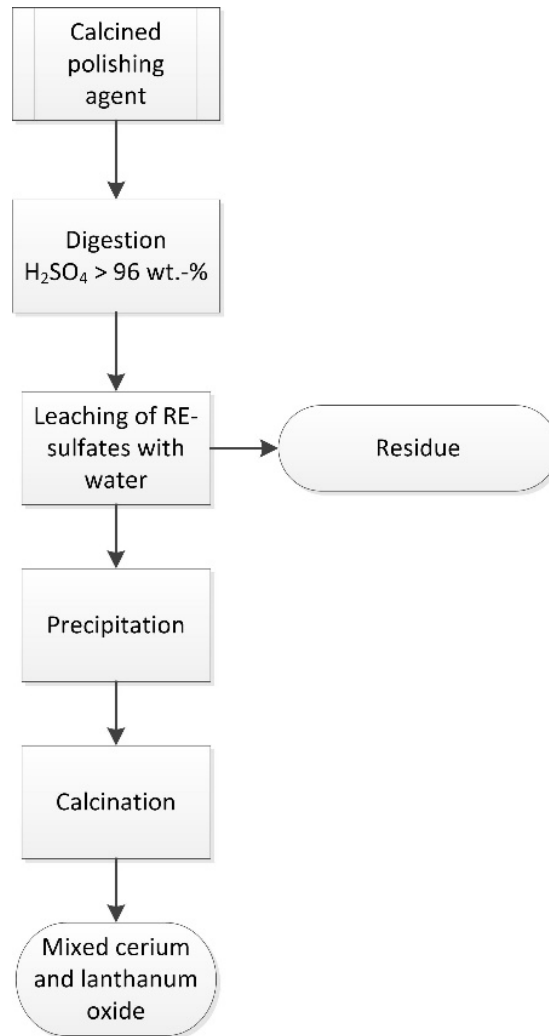


Figure 4: Sulphuric acid digestion and production of a mixed REO concentrate

Results

Nitric acid leaching experiments

Nitric acid leaching experiments showed the possibility of cerium dissolution up to 90 %. Nevertheless, it could be found that lanthanum extraction is insufficient and limited to 60-70 %. The investigations also revealed the results from Figure 5a and 5b. Decreasing solid/liquid ratios induced increasing reduction of the initial mass of the input material which correlates to the extraction of cerium and lanthanum and therefore higher extraction rates can be achieved. Figure 5b shows the effect of extended leaching periods.

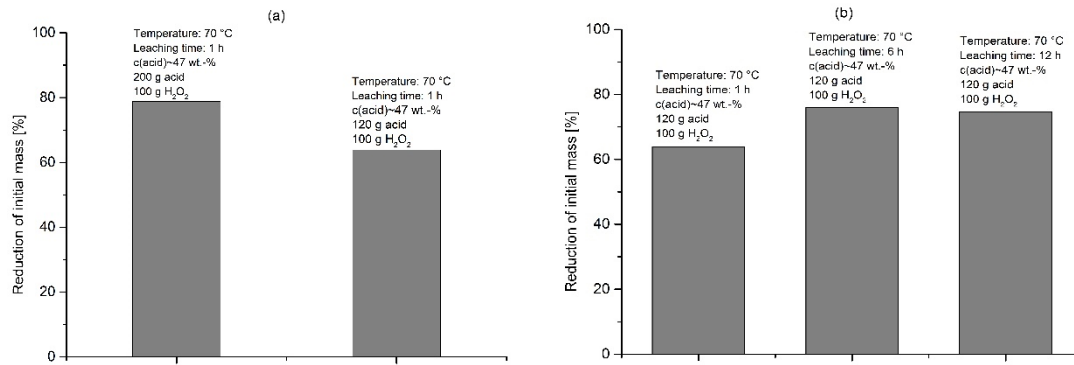


Figure 5: Influence of solid/liquid ratio and duration on the dissolution of the input material

Another comparison between the experiments visualises the effect of a change in leaching temperature. An increase in temperature from 70 to 90 °C does not lead to intensified dissolution. Moreover, an increase in acid concentration shows no effect on the extraction (Figure 6).

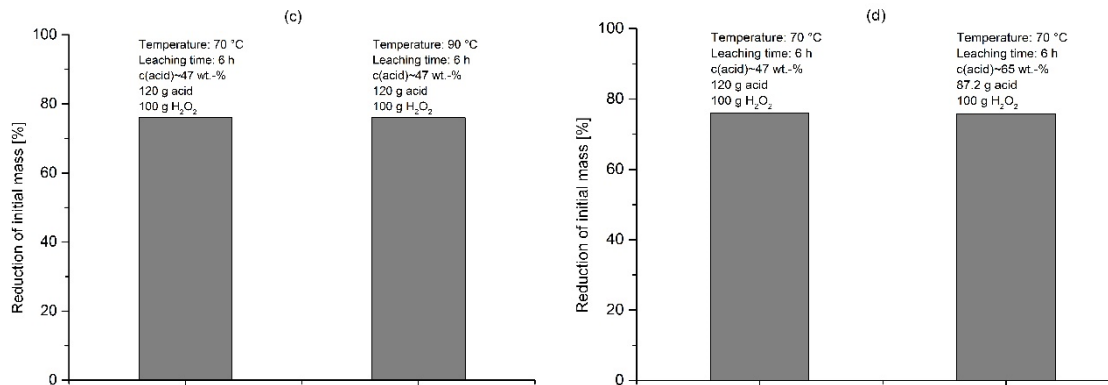


Figure 6: Influence of temperature and acid concentration on the dissolution of the input material

Hydrochloric acid leaching and precipitation experiments

Some obtained results from nitric acid leaching experiments coincide with data from HCl leaching. On the one hand, good extraction of cerium is possible under optimum leaching conditions. On the other hand the extraction of lanthanum is limited to 60-75 % as well. XRD analysis of the leaching residues revealed that mainly fluoride and phosphate compounds of lanthanum remain undissolved. Further investigations of the leaching step showed decreasing influence of H₂O₂ at larger excess and concentration of HCl. 50 % excess of acid equals a mass of 43.75 grams of HCl whereas the amount of added solutions varied depending on their concentration. As a result 50 % excess required 136.73 grams of 32 wt.-% HCl.

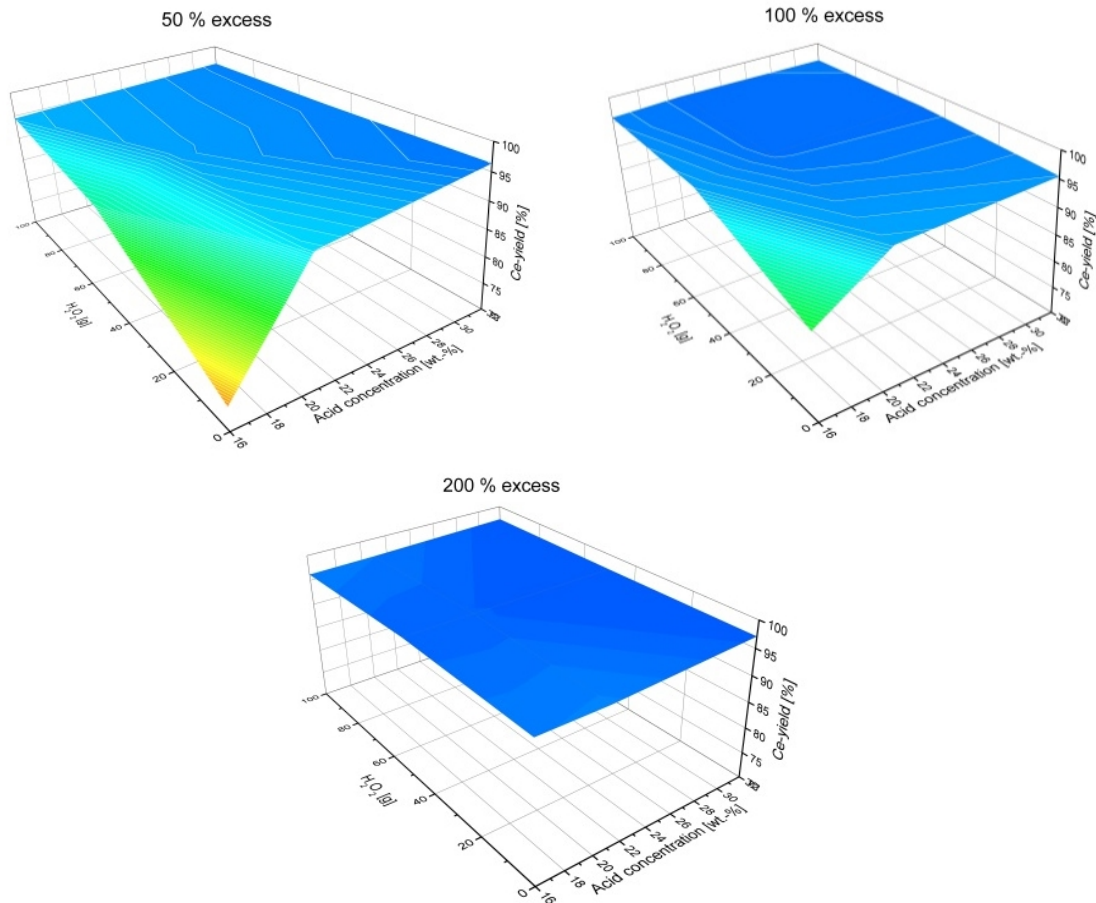


Figure 7: Ce extraction as a function of acid concentration and amount of H₂O₂

Precipitation experiments required leaching operations at constant parameters. Therefore, these tests were performed using solutions won by leaching of 50 g of polishing agent with 273.45 g HCl (32 wt.-%) which represents an excess of 200 % and 100 g H₂O₂ (30 wt.-%). After filtration the solutions were adjusted to volumes of 500 ml and transferred to oxalic acid processing. 30 to 50 g of oxalic acid were used in this process in concentrations of 50, 62.5 and 80 g/l H₂C₂O₄ corresponding to approximate excesses of the chemical of 0 to 66 %. The calculation took into account that on average 97 % of cerium, 70 % of lanthanum and 54 % of zinc present in the raw material can be extracted under the applied leaching conditions and form oxalates. Later the XRF analysis of the precipitation products showed that zinc remains in the solution. Subsequent to the above described thermal treatment and XRF analysis of the obtained mixed RE-oxide the elemental yields were determined. The result of the statistical analysis is shown in Figure 8.

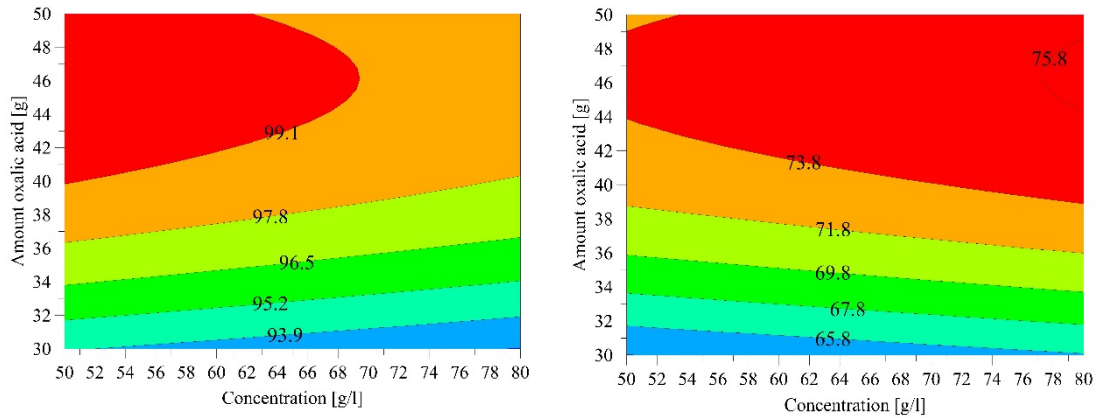


Figure 8: Prediction contour plots for cerium and lanthanum yields [10]

As can be seen from the plots above the excess of oxalic acid added to the leach liquor strongly affects the yields of Ce and La whereas there are some statistical uncertainties concerning the influence of the concentration. Nevertheless, increasing acid concentrations tend to support the formation of Ce oxalates, whereas the isolation of lanthanum decreases. The low yields for lanthanum are caused by the above mentioned limitation of the extraction. A representative chemical composition of a final product won by the described leaching and precipitation process can be found in Table 5.

Table 5: Representative XRF analysis of an oxide product

Oxide	wt.-%
CeO ₂	90.73
La ₂ O ₃	8.57
ZrO ₂	0.08
Fe ₂ O ₃	0.074
CaO	0.07
SiO ₂	0.04

Sulphuric acid leaching and precipitation experiments

The experiments revealed that sufficient sulphuric acid and temperature must be applied to the process for quantitative digestion of the spent abrasive. Furthermore, complete elution of formed sulphates requires enough water and repeated washing of the filter cakes. Optimum digestion and leaching conditions led to extraction rates of almost 99 % for Ce and 98 % for La. Figure 9 shows the filtration and washing of a digested polishing agent. However, the solutions won by this process show the disadvantage of low stability and precipitation of lanthanide salts within a couple of hours. Therefore, the further treatment with precipitation agents had to be done quickly. The products won by the application of commercial precipitation agents met the specifications for additional processing.

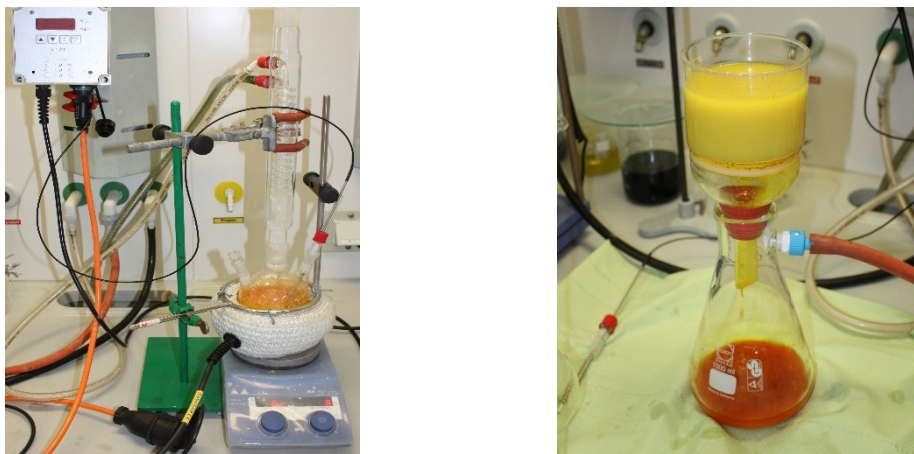


Figure 9: Digestion and elution of lanthanide compounds

Conclusions

Three ways of processing polishing materials were tested. The focus was mainly set on the extraction of lanthanides from the raw material, whereas all mineral acids of technical relevance were taken into account. Nitric and hydrochloric acid experiments showed strongly limited dissolution of lanthanum compounds. The extraction of cerium as most of it was present in its tetravalent stage necessarily requires a reducing agent in the case of HNO_3 leaching. Hydrogen peroxide was chosen as reducing agent because the resulting leach liquor is thereby not contaminated by foreign ions. Under certain conditions almost complete cerium extraction could be achieved by hydrochloric acid leaching without the use of H_2O_2 . Especially high HCl concentrations affect the dissolution of cerium in a positive way. Oxalic acid as a well-known precipitation agent for rare earth elements was chosen because of its advantage to form precipitation products at low pH values. Therefore, the contamination of the obtained products from hydrochloric solutions could be reduced. Additional experiments using concentrated sulphuric acid pointed out higher lanthanum extraction than was achieved for the previously described tests. However, digestion of the polishing material and subsequent leaching of formed water-soluble cerium and rare earth sulphates require significantly higher temperatures (up to 200 °C) and larger amounts of washing water respectively.

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