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Recovery of Yttrium Oxide from Titanium-Aluminium based wastes

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Abstract

Yttrium belongs to the rare earth elements and critical metals. Yttrium oxide is mostly used in fluoroscent lamps, production of electrodes, in electronic filters, lasers, superconductors and as additives in various titanium-aluminium materials to improve their properties. Recovery of yttrium oxide from secondary sources such as red mud, coatings from ceramic industry and phosphors is extremely important. The main aim of this study is to examine the selective recovery of yttrium oxide from Al-Ti based secondary materials using one combined method based mostly on leaching for selective recovery of yttrium containing: crashing and grinding of materials, sieving, leaching of chosen fine fraction with hydrochloric acid, precipitation with oxalic acid in order to produce a pure yttrium oxalate, filtration and a final thermal decomposition of yttrium oxalate. The present study summarized mostly the influence of different reaction parameters such as leaching temperature, time and concentration of hydrochloric acid on yttrium dissolution from Al-Ti based secondary materials. An increase of dissolution time and temperature increases yttrium dissolution. An increase of pressure from an atmospheric pressure to 0.5 MPa at 150°C leads to the maximum dissolution of yttrium (about 98.6 %). The final produced yttrium oxide after thermal decomposition of yttrium oxalate was analyzed using SEM and EDS-analysis.

1. INTRODUCTION

Rising numbers of assignment and a greater application range lead to an increase in demand for rare earths in the close future. As many experts predict, this tendency is continuing to an even stronger extent in the following two years 2016 and 2017. To meet this requirement increase, solely the extraction of primary raw materials will not be sufficient in the long run. The rising world population and new fields of application entail intensive research concerning recycling of rare earths and, especially, the recovery of yttrium oxide from titanium-aluminium based wastes.

However, not only the rising demand should give occasion for developing suitable recycling processes. Also, the quasi-monopoly of China concerning the extraction of rare earths and thus the extraction of yttrium oxide are a reason to reduce the dependence of numerous import countries and to take the first step to the raw-material self-sufficiency. Events like in 2010 have shown that China is, due to its impact on the international market for rare earths, capable of determining the prices of raw materials at will. As the main exporter of the valuable metals, the People's Republic decides on the fact which price other countries must pay for the rare earths. So the price of yttrium or yttrium oxide quadrupled as a result of the export restriction of China during the years from 2010 to 2011. The import countries which had discontinued their production were faced with deciding whether to pay this extremely high price or to renounce progressive technological developments in their country. Also, the shortage prediction by researchers of critical rare earths leads to the conclusion that a profitable and efficient recycling is indispensable. Nevertheless, such is not developed yet. Therefore, a great motivation stands to the recycling of yttrium oxide from ceramic molds. This work discusses the dissolution of yttrium from destroyed titanium-aluminium based wastes. To find the optimal parameters, the most important influences on the leaching process under atmospheric and high pressure are investigated and discussed.

2. CURRENT RESEARCH ON RECYCLING OF RARE EARTH FROM SECONDARY RAW MATERIALS

The topic of the rare earth recycling has only appeared recently. With the incidents at the worldwide market by the export restriction of China in 2010, a perceptible signal went through the hitherto existing importers, particularly in Europe. The difficulty gained popularity from that moment, so that first research projects came up. Nevertheless, so far no process has been developed which promises efficient, profitable and commercially as well as economically usable recycling of rare earth metals in the industrial scale. In general, the recycling can be distinguished in scrap metals which appear during the production or actual value-added chain and the scrap metals which result after the phase of utilization at the consumer and therefore at the end of their life cycle (Michelis, et al. 2011; Junk-Miler, 2015). A full process for the recovery of rare earth elements from a composite ore containing rare earth elements, including a monazite mineral group and an apatite mineral, contains the pre-leaching of the composite ore with an acid in order to substantially dissolve the apatite mineral into the leach liquor and precipitate rare earth elements from the pre-leach liquor by others (Mackowski et al., 2009). Kuzmin et al., (2012), have offered an analysis of a combined hydro-pyrometallurgical route for the processing of ores resulting in the production of rare earth elements. This was investigated using the Chuktukon ores in East Siberia in Russia. The main aim of this work by Kuzmin was to develop methods of unlocking rare earth elements in refractory ores and to study some methods for their further chemical processing. The precipitation of a cleaned solution with oxalic acid and the thermal decomposition of a formed metal oxalate after filtration with its previous drying represent the final steps in the production of rare earth oxides by (Ibrahim and El-Hussaini, 2007). The importance of yttrium and other rare earth elements is increasing in the transition to green economy because of their essential role in permanent magnets, lamp phosphors, catalysts, rechargeable batteries, etc. Because China presently produces more than 90 % of the global REE output and has an increasingly tight export quota, the rest of the world is in the risk of lacking REE supply. Because of the absence of economic and/or operational primary deposits on their territories, many European countries have to be included into the recycling of REEs from pre-consumer scrap, industrial residues, and REE-containing End-of-Life products. Despite a considerable, mostly lab-scale research effort to recycle REEs, less than 1% of REEs were recycled by 2011. This is mainly due to the inefficient collection, technological problems and, especially, a lack of incentives. A drastic improvement in the recycling of REEs is, therefore, an absolute demand. This can only be realized by developing efficient, fully integrated recycling routes, which can take advantage of the rich REE recycling literature. Secondary materials for REEs are listed by (Binnemans et al., 2013)

One of the major challenges in the processing of used phosphors for the extraction of rare earths lies in a large number of different compounds and their individual chemical properties such as solubility in an aqueous phase by (Poscher et al., 2013). The summary of this work showed that the hydrochloric leaching of a screened luminophore powder followed by the precipitation of a contaminated RE oxalate, converting the mixture into their oxides and subsequent raffination in order to dissolve most of the alkali metal oxides leads to a rare earth concentrate which could be applied as a new raw material for the subsequent process steps of refining. (Stopic et al., 2013) have studied a mechanism and kinetics of yttrium dissolution from ceramic waste dust containing about 1 wt.% yttrium under atmospheric and high pressure. The influence of different process parameters such as leaching temperature and time, the concentration of different acids and operating pressure were analyzed. In this work a new strategy for the dissolution of yttrium from titanium-aluminium based wastes was studied. After crashing, grinding, and a sieving, the fine fraction below 250 µm was leached with hydrochloric acid to reach a selective leaching. The main aim of this work is to establish the optimal parameters for maximal recovery of yttrium from ceramic waste materials.

Within the scope of this work, first, a wet-chemical process will be developed, including mechanical processing to extract yttrium from used titanium-aluminium based wastes in the laboratory scale. Afterward, this setup is transferred with optimal parameters to a technical scale. The most important objective is the development of a new hydrometallurgical recycling route for the extraction of a highly pure oxide of suitable grain size for the re-use in Ti-Al casting. Since side elements such as iron, titanium or silicon are inevitably dissolved during leaching, a selective precipitation of those impurities by calcium carbonate is tested as the next step.

3. THEORETICAL BACKGROUND OF SELECTIVE YTTRIUM LEACHING

The leaching tests in this work are based on the same mechanism, in which an acidic chemical extraction takes place. The objective is to bring the yttrium, contained in the ceramic molds, selectively into solution, while by-elements collect in solid form in the leaching residue. Not by any means, is this process suitable only for the leaching of yttrium. This is the most commonly used technology applied for most rare earth elements as it shows a high chemical extraction and separation percentage. As leaching liquor concentrated hydrochloric acid is used. This leaching agent is expected to bring the yttrium oxide into its ionic form in accordance with the following reaction equation:

$$Y_2O_3 + 6HCl \rightarrow 2Y^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_2O \qquad (1)$$

For the validation of this reaction equation, a Pourbaix diagram can be taken into account. In Figure 1 such a diagram is given for the system Y-Cl-H_2O at a temperature of 70 °C, which has been constructed with the software *Factsage*. The chart offers information about equilibria or chemical stability areas of the respective systems at defined temperatures, pH-values, and redox potentials. Therefore, the existence of several substance mixtures in certain constellations can be predicted. The diagram reveals that the desired reaction is accessible with pH-values lower than 5.8 and potentials highter than 0.8 V at a temperature of 70 °C because here triply positively charged yttrium ions are stable. By an increase of the pH-value or a decrease of the potential, however, the process parameters are in the stability range of the $Y(OH)_3$ or the YH_3. Nevertheless, besides the dissolution of the yttrium oxide, the treatment with concentrated HCl leads to other side reactions, so that other by elements dissolve as well and are present in their ionic form in the lye. These undesirable side reactions can be shown at the example of aluminum or iron according to the following reaction equation:

$$(Al,Fe)_2O_3 + 6HCl \rightarrow 2(Al,Fe)^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_2O \qquad (2)$$

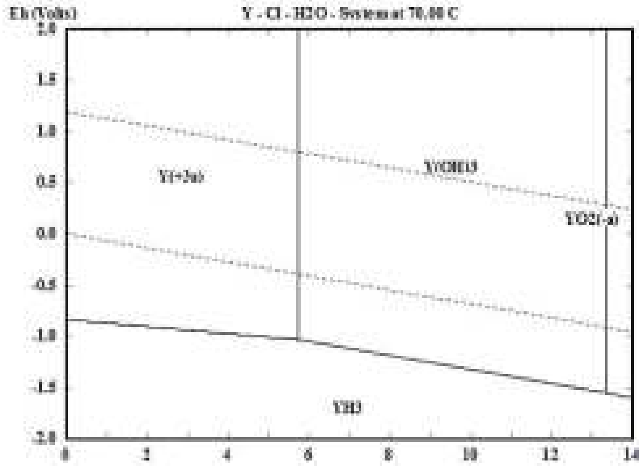

Figure 1. Pourbaix diagram of the system Y-Cl-H_2O at 70 °C

Because these dissolved by-elements have mostly a negative influence on the properties of the end product, their later presence and therefore the above mentioned reaction should be avoided. To a certain extent, other elements are inevitably dissolving so that neutralization precipitation aiming at the removal of the unwanted by-elements from the lye is tested out after the leaching.

4. EXPERIMENTAL

4.1. Material and analytical methods

The initial material, which consists of more than 90 % of Al_2O_3, also contains the yttrium oxide layer used on the casting component side, which should be separated by the subsequent very selective wet-chemical extraction processes from the rest of the ceramics. The still adhesive slurry layer of Y_2O_3 in the ceramic leftovers of different molds is recognizable by its brownish coloring. The molds (considering the full grain size spectrum) were investigated for the concentration in yttrium as well as probable adhesive impurities with the help of a planet sphere mill that broke down a representative sample of a grain size smaller 90 µm which was then handed over to the chemical department. By an ICP analysis, the concentration in yttrium and by elements were ascertained. As shown in Table 1. our RFA-WROXI analysis, the fraction of remaining elements was ascertained. As shown in Table 1. our initial material consists mainly of Al_2O^3, which serves as a back-up layer in the process of the investment casting at Access e.V in Aachen. Aluminum oxide is consequently the matrix of the studied sample. However, the concentration in yttrium with a fraction of 6.83% shows a mentionable recycling potential that should be investigated in this work. Other by- elements in oxidic form are silicon, titanium, iron, and manganese. Except for iron with 2.09%, theyaltogether make up less than 1%, but, nevertheless, should be dissolved as little as possible during the later leaching tests and be precipitated in the best way possible in the subsequent neutralization, as they could influence the cleanness of the end product, as well as the later material properties negatively. For the following leaching tests, a grain size less than 250 µm is used. The chemical department did the analysis of the yttrium concentration and other impurities carried along by the process by the RFA, plus, for controlling reasons, the WROXI 250. The analysis processes showed no serious deviations of the proportional weight distributions of the investigated elements so that for this group the following composition was determined (Table 2).

Table 1. Chemical composition of the molds in wt.-% (Y measured by ICP, remaining elements by RFA)

Element	Y	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O_4	Th
Content in wt.-%	6.83	0.26 0.15	0.17 0.13	Matrix	2.09	0.37	<0.01

Table 2. Chemical composition of the target group <250 µm, measured by RFA - Omnian 27 - overview analysis

Element	Y_2O_3	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	
content in wt.-%	18.1	7.78	0.74	Matrix	0.18	

It is to mention that the target group has an yttrium oxide concentration of 18.1 wt.-% and consequently an yttrium concentration of 14.25 wt.-%. The yttrium concentration could be increased by the classification or separation of both grain size distributions from 6.83 wt.-% to 14.25 wt.-%. Therefore, the first goal to increase the yttrium concentration of the groups before leaching by a mechanical pretreatment is achieved. Also, a clearly lower iron oxide percentage is represented in the target material while the percentage of SiO_2 has strongly and that of TiO2 has slightly risen. Analytical grade HCl, and distilled water were used for the experiments in the laboratory, and commercial grade HCl (31%), and tap water without further purification were used at the pilot plant. The compositions of solid residue were analyzed by XRF and the elements in the solution were analyzed by ICP-OES (Peculiarity Optima 5300DV, Perkin Elmer). Scanning electron microscope JEOL JSM-7000F (2006) with field emission cathode with Lateral resolution 1.2 nm at 30 kV, 3.0 nm at 1 kV was used for characterization of powder. Combined EDX/EBSD-System EDAX Pegasus was applied for elemental chemical analysis.

4.2. Leaching Tests

To recover the yttrium from the ground molds of the investment casting, the powder obtained from the sieving with a grain size smaller than 250 µm was first leached in the leaching agent. Here, special interest is in selectively dissolving the valuable rare earth metal in order to separate them from impurities and by-elements such as Al_2O_3, Fe_2O_3, and TiO_2.

4.3. Test Plan and Parameter

Reaction parameters were chosen regarding ~~to~~ our previous hydrometallurgical treatment of different samples for yttrium dissolution, as shown in our previous works. The choice of temperature and time in particular had an important significance in order to transfer our results from a laboratory to scale up conditions. A total of, 16 leaching tests with hydrochloric acid were carried out within the scope of this work to be able to ascertain the effects of different test parameters. In all the tests, the same input material was used. On this occasion, the focus was on the following parameters:

- leaching temperature
- leaching time
- ratio solid / liquid
- concentration of the hydrochloric acid
- scale enlargement / scale-up

To be able to quantify the effects of these factors in the best way possible, the test plan shown in Table 3. was worked out for the leeching. Although the smaller fractions (under 100 μm) have offered better leaching efficiency in comparison to the chosen fraction of 250 μm, the better filterability was considered. At the other side this fraction of 250 μm was mostly present in a product after grinding. The performed tests can be divided into the following classes: leaching under atmospheric pressure, pressure leaching, 24-hours test, large scale test. The revolutions per minute were varied from 125 to 300. The respective leaching temperatures were 70 °C, 90 °C, and 150 °C max together with the pressure leaching. Also, the ratio between solid and hydrochloric acid was changed (1:10, 2:10 and 3:10) to find the optimal ratio resulting in the highest yttrium yield. The molarity of the hydrochloric acid ranged from 0.5 molL^{-1} over 1 molL^{-1}, up to 2 molL^{-1}. Also changes by altering the leaching time were investigated by setting the duration to 2h, 5h or even 24h. Finally, the leaching tests 15 and 16 were developed to test the recovery of the yttrium from the used ceramic scrap metal in the pilot-plant scale. To approximate industrial scales or ratios, 10 kg at a time of input material were leached in 100 liters with hydrochloric acid. To approximate industrial scales or ratios, 10 kg at a time of input material were leached in 100 liters with hydrochloric acid.

Table 3. Test plan for leaching of the fraction group <250 μm

Test	rpm	T (°C)	Sample (g)	Volumes HCl (L)	Ratio s/l	Concentration HCl (molL^{-1})	Duration (h)
LV 1	125	70	150	1.5	1:10	1	5
LV 2	125	90	150	1.5	1:10	1	5
LV 3	125	70	300	1.5	2:10	1	5
LV 4	125	90	300	1.5	2:10	1	5
LV 5	125	70	450	1.5	3:10	1	5
LV 6	125	90	450	1.5	3:10	1	5
LV 7 D	300	150	100	1	1:10	1	2
LV 8	125	70	150	1.5	1:10	2	5
LV 9	125	70	300	1.5	2:10	2	5
LV 10	125	70	450	1.5	3:10	2	5
LV 11 D	300	150	100	1	1:10	2	2
LV 12 D	300	150	200	1	2:10	1	2
LV 13	175	70	150	1.5	1:10	1	24
LV 14 D	300	150	100	1	1:10	0.5	2
LV 15 Scale-up	250	70	10	100	1:10	1	2
LV 16 Scale-up	250	70	10	100	1:10	1	2

4.4. Leaching

For leaching tests under atmospheric pressure, the aggregate was used for the leaching of rare earth elements at the IME, RWTH Aachen University (Ma, et al. 2018). Thus, for such leaching processes specifically manufactured construction, consists of a double-walled glass vessel with a capacity of 2 liters. Thanks to this construction, the temperature of the leach is adjustable by circulating partially very hot water between those walls without coming into direct contact with the reaction chamber. The mobile heating device allows temperatures of up to 120 °C. The glass vessel is placed on a height adjustable stage that guarantees an optimal alignment and tight connection to minimize possible leakage and resulting evaporation losses height adjustable mixing device with a removable anchor stirrer and the separate motor can be set at the desired rpm lower than 250.

With two setscrews and a ring seal, the precise lid can be placed on the glass vessel and the reactor space can be sealed. The lid features three closeable openings for a mobile thermal sensor, a pH electrode and the sampling via pipette or dosage of the feed substances. Also, it has a cooling coil so that evaporated leach condenses and is returned to the reaction space. On account of possible leakage during the mixing and temporary openings in the lid for sampling, an aspiration above the test apparatus should always be installed so gasses of concentrated HCl cannot be inhaled accidentally as these gasses can be very harmful to the respiratory tract. The leaching tests at a temperature of 150 °C were carried out in a high-pressure autoclave. The aggregate used was made by Autoclave Engineers from the USA and consists of Cr-Ni-Mo-steel. It is used primarily to leach ores and dust. The reactor chamber is heatable from outside up to 300 °C and has a capacity of 2 liters. Inside the apparatus a Ti-reaction vessel, a thermal sensor, and an electric heating coil to heat up the input materials on the desired temperature. A propeller stirrer rotates during the test with up to 2500 rpm and enables a very homogeneous temperature and material distribution. A shell isolates the reaction chamber from the atmosphere. For overpressure protection, an explosion diaphragm is installed right on the same shell, while gas (particularly air, Ar, N_2) is supplied, if needed, via two gas valves and can be fed into the device. All parameters for tests in the autoclave can be controlled by an external operating console behind the shatterproof glass surrounding. An exact logging of the temperature and pressure profiles over the time is also possible from the control console. A sampling from the reactor chamber is possible without interrupting the leaching. This is enabled by a sampling space installed beyond the shell that is equipped with three valves which allow a safe sampling of 25 mL. To withstand the high pressures and temperatures of a test and guarantee optimum impermeability, the lid is solidly sealed by eight screws via a torque key. A schematic illustration of the pilot-plant, as well as the high-pressure autoclave at the IME are listed.

4.5. Influence of the Leaching Temperature

For the evaluation of the influence of the temperature on the leaching process, Figure 2 shows the temporal profile of the leaching tests LV 3, LV 4 and LV 12 D. All three tests were carried out with a ratio of the powder to the hydrochloric acid of 2:10, as well as with unimolar HCl. Nevertheless, the respective temperatures for the leaching were very different. Thus, the stir leaching test LV 3 was performed at 70 °C, the leaching test LV 4 at 90 °C and the pressure leaching test LV 12 D at 150 °C, cf. Table 3. It is particulary conspicuous on this occasion, is that the dissolution rate of the target element yttrium rises with increasing temperature. While leaching below 70 °C leads to a dissolution of yttrium of 3.15 gL^{-1} yttrium after 15 minutes, the leaching under the same circumstances but at 90 °C leads to a dissolution of 7.78 gL^{-1}. Nevertheless, the dissolved amount of yttrium at a temperature of 150 °C after 15 minutes corresponds with 29.4 gL^{-1} almost to the tenfold of LV 3. Particularly during the first 15 minutes after the test beginning, the influence of the temperature seems to be extremely significant. Whereas the dissolved amounts of the rare earth element show no mentionable increase for the pressure leaching test up to the test end after two hours with a maximum solubility of 31.5 gL^{-1}, the straight lines of the leaching rounds at 70 °C and 90 °C rise even further. After two hours of leaching for the test LV 3 approx. 14.6 gL^{-1} yttrium dissolved while LV 4 can show 24.8 gL^{-1}. However, the amount of the dissolved yttrium at 70 °C and 90 °C is still less than the amount dissolved in the pressure leaching. Because the leaching tests were scheduled for a duration of five hours, more time was available in these series of experiments for the dissolution of the input material. Thus, it could be determined that the test LV 4 operated at 90 °C can reach a maximum from 30.8 gL^{-1} and is just slightly below the test result of LV 12 D at 150 °C with 31.5 gL^{-1}. Also, the final concentration of the leaching test LV 3 has risen to a value of 23.8 gL^{-1} yttrium.

Therefore, one can state that a rise in temperature, especially during the first 15 min of leaching, affects the dissolution of yttrium considerably. While at 150 °C already after 15 min no further significant increase of dissolved yttrium is detectable, the values of the solubility at lower temperatures rise further. With a working temperature of 150 °C, more yttrium can be dissolved within one hour than at 90 °C within five hours.

Consequently, a raised temperature is accompanied by a considerably shortened leaching time as a result of quicker solution reactions and optimized kinetic conditions.

As shown in Figure 3. the leaching efficiency increases in the first 30 min reaching a leaching degree of 97%. Because of the hydrolysis of yttrium, the leaching efficiency decreased during the following 90 min.

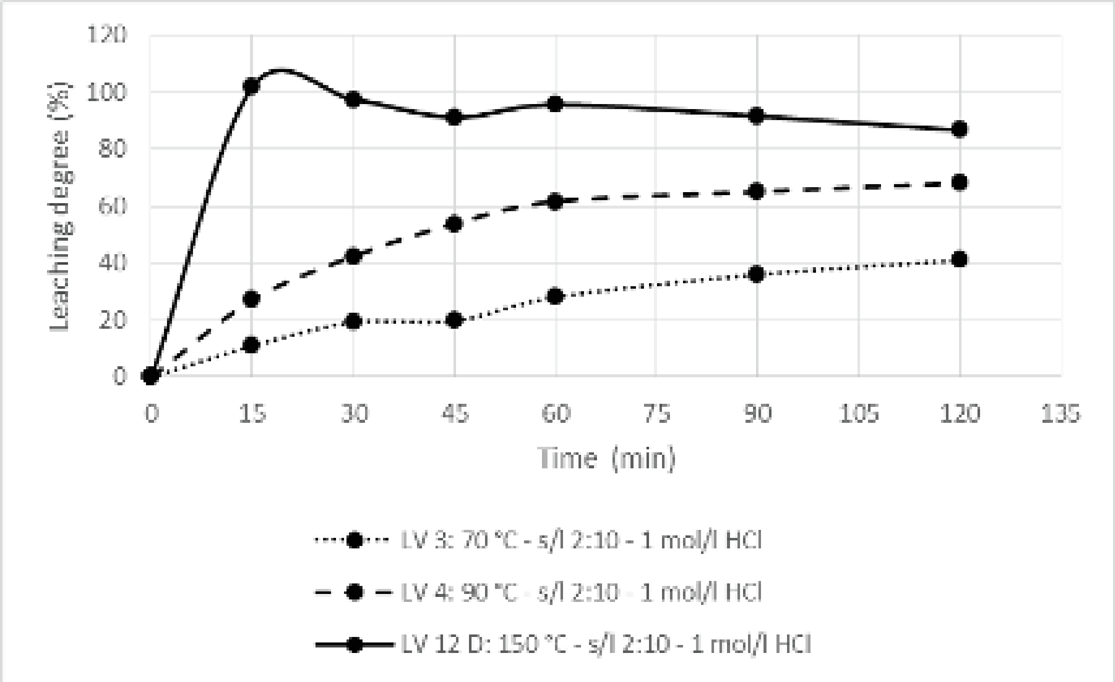

Figure 2. Temporal progression of the dissolved yttrium at 70 °C, 90 °C, and 150 °C

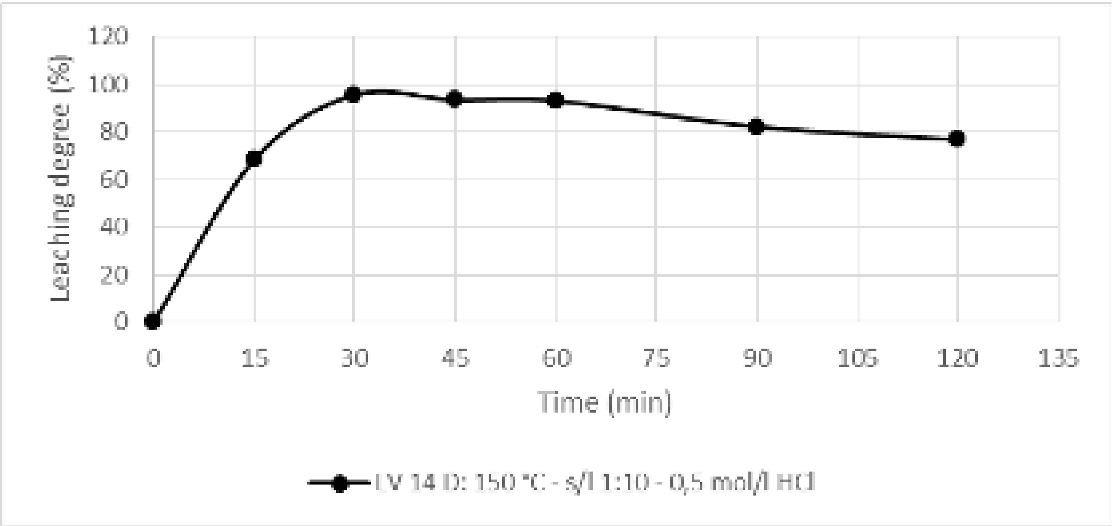

Figure 3. Leaching Efficiency in the autoclave at 150 °C

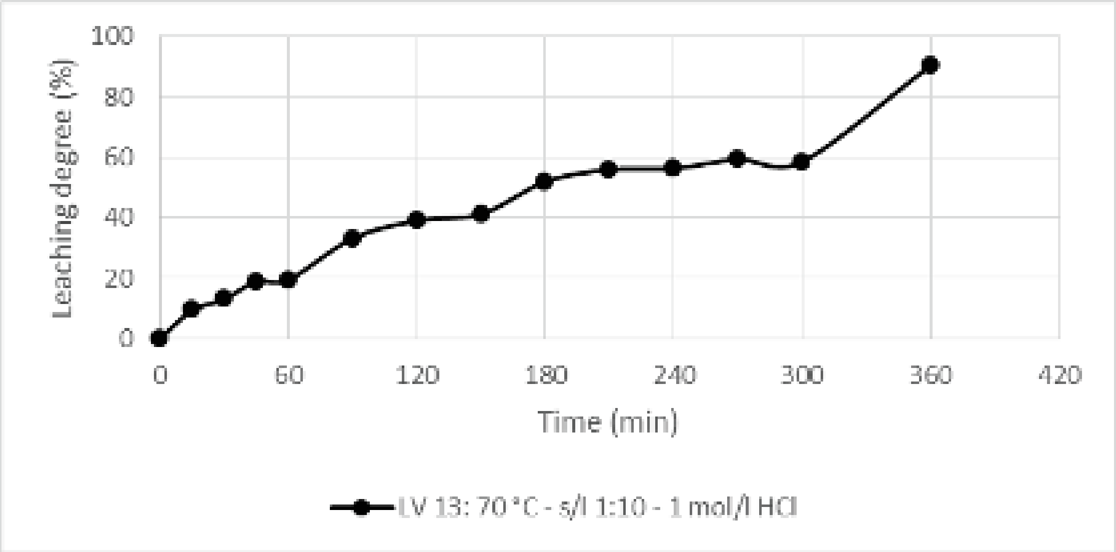

Figure 4. Temporal progression of the dissolved yttrium for the leaching – 24 hours test

4.6. Influence of the Leaching Time

To evaluate the influence of the leaching time on the success of the dissolution of the target metal, also a 24 hours test was run. The dissolved amounts of yttrium for the time this leaching test LV 13 was carried out 70 °C, a ratio solid to leach of 1:10 and a hydrochloric acid of 1 molL^{-1} are shown in Figure 6. At first, the graph shows a steady increase of the leaching degree of yttrium during the first five hours. Here the value rises to 13.2 gL^{-1}, and the graph shows still no stagnant behavior or flattening after five hours. A sampling after a leaching time of 24 hours shows that the concentration of 13.2 gL^{-1} has risen by approx. 62.88% and has adjusted to a dissolved amount of yttrium of 21.5 gL^{-1} in the lye. Consequently, the leaching is still not terminated after 5 hours, so that an extended leaching time at atmospheric pressure at 70 °C positively affects the yield. This kind of rising profile within the first five hours of leaching can be transferred to nearly all leaching tests.

The tests which were carried out in the autoclave behave differently (as shown in Figure. 2 and Figure. 3). As already stated, leaching rounds show a different profile about dissolved yttrium at raised pressure, as well as at 150 °C. This should be shown in the following tests LV 7 D, LV 11 D, LV 12 D and LV 14 D, which have all different test parameters, however, they show the same trend concerning the dissolution profile of yttrium. For all the tests it is recognizable that a value near the maximum of the dissolved yttrium is reached after 15 to 30 minutes of the leaching. Therefore, no significant increase of the yttrium concentration in the leach is to be shown after half an hour. Consequently, an extended leaching process in the autoclave does not turn out as sensibly. Extremely good results are achieved, in contrast to the tests of the leaching, after less than 30 minutes.

4.7. Influence of the Ratio of Powder to Hydrochloric Acid (s/l)

Figure 5 shows the influence of different amounts of target material under almost identical conditions. The leaching tests LV 1, LV 3 and LV 5 were performed at a temperature of 70 °C and unimolar hydrochloric acid. The ratio solid/leach varied between 1:10 in LV 1, 2:10 in LV 3 and 3:10 in LV 5. According to this increase in leached powder behave the straight lines in Figure 5. All lines show a clear increase with the time and signal an increasing amount in dissolved yttrium in the lye. In the beginning, with raised ratio of solid to liquid, the respective profiles also show a higher gradient. After a leaching time of five hours, the test LV 1 which was driven by the smallest quantity of powder of 150 grams in 1.5 liters HCl shows an yttrium concentration of 17.9 gL^{-1}. Though a doubling of the input material on 300 grams per 1.5 liters HCl does not lead to a doubling of the dissolved amount, however, the value rises on 23.8 gL^{-1} and therefore to an increase of 32.96%. Clear increase of the dissolved amount of yttrium in comparison to the tests LV 1 and LV 3, leaching test LV 5 has to offer which contains the largest amount of input material with a ratio of 3:10. This test reaches at the end of the leaching a concentration of 28.3 gL^{-1}.

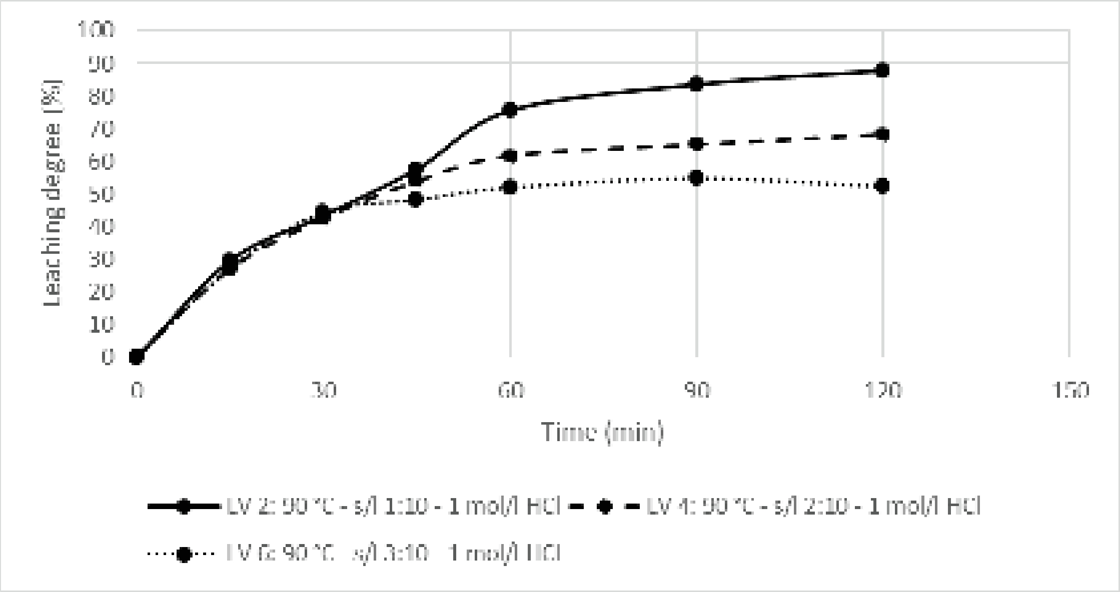

Figure 5. Temporal progression of dissolution of yttrium for the leaching – variation of the ratio of powder to hydrochloric acid

Consequently, tripling of the input material leads to an yttrium concentration raised to 58.10 % in the leach solution. Similar relations are also revealed for the tests in the high-pressure autoclave. As seen from Figure 5, the final concentration of dissolved yttrium rises with increasing the amount of input material. While with a solid/liquid ratio of 1:10 an yttrium concentration of 17.6 gL^{-1} is to be found, this value decreases with a solid/liquid ratio of 2:10 to 31.5 gL^{-1} after two hours of leaching time. The concentration of yttrium could be raised by the increase of the input material by 78.98%. It should be noted that with a rise of the ratio of used solid to leaching agent a clear increase of the dissolved yttrium goes along. This tendency is independent of the leaching procedure. However, its degree differs. A doubling of the used powder leads at high pressures to a bigger increase of the dissolved yttrium than it is the case in comparison to a stir leaching.

4.8. Influence of the Concentration of the Hydrochloric Acid

For the investigation of the leaching procedure, the concentration of the hydrochloric acid was of interest, as well. For this analysis, a series of experiments with varying molarities of the lye were carried out.

In Figure 6. the temporal progression of the leaching is shown - once for the test LV 5 and once for LV 10. Both were performed at a temperature of 70 °C, as well as a solid/liquid ratio of 3:10 while the concentrations of the hydrochloric acid were 1 $molL^{-1}$ in LV 5 and 2 $molL^{-1}$ in LV 10. The chart shows that in a more concentrated lye the dissolution is quicker altogether, and the final amount of dissolved yttrium is recognizably higher. Therefore, after five hours of leaching time, LV 5 reaches a concentration of 28.3 gL^{-1} in the lye, LV 10, however, with a doubling of the hydrochloric acid concentration reaches a maximum of 43.9 gL^{-1}. Here an improvement of the dissolution process could be achieved by a doubling of the concentration of the leaching agent by 55.12%. Also for leaching in the autoclave at high pressures a raised concentration of the hydrochloric acid results in an improved dissolution of the rare earth metal. The concentration of yttrium rises with increasing molarity of the lye. Indeed, this increase is not as strong as it is in the stirring leaching.

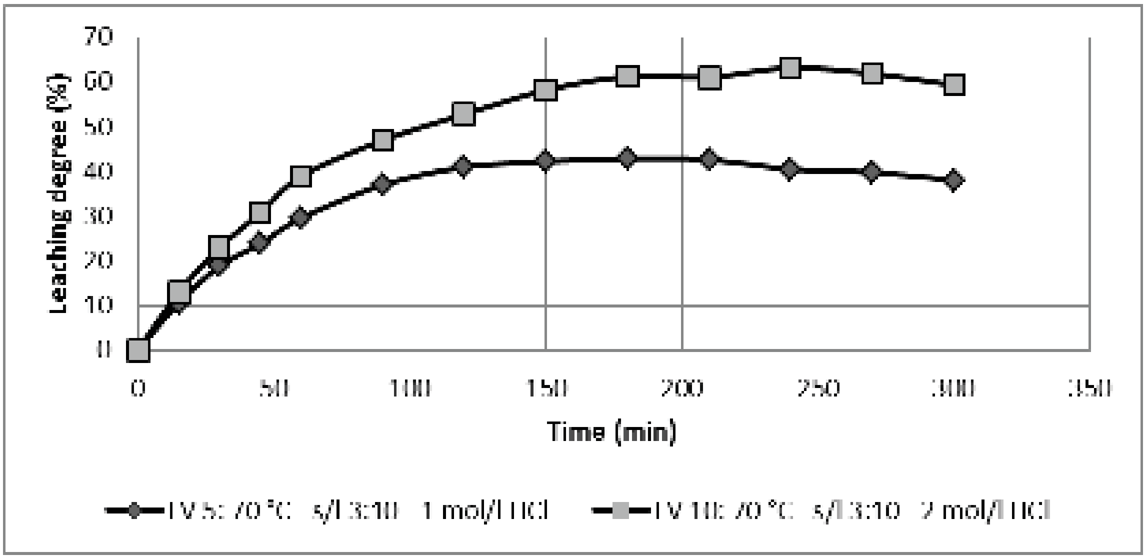

Figure 6. Temporal progression of the dissolved yttrium for the leaching - variation of the hydrochloric acid concentration

Because the leaching process nearly finishes for the tests at high pressure and a temperature of 150 °C after half an hour and no more significant change is to be recognized, a comparison of the concentrations should occur at this point. After 30 minutes of leaching with a hydrochloric acid of 0.5 $molL^{-1}$, approx. 14.1 gL^{-1} yttrium were dissolved. A doubling of the molarity to 1 $molL^{-1}$ leads to an increase of this value to 17.6 gL^{-1}. If the concentration of the lye is 2 mol/l as in LV 11 D, even 19.5 gL^{-1} are achievable. These values show once again that a rise in concentration leads to a rise of dissolved yttrium.

4.9. Final yttrium oxide powder obtained using our strategy

After filtration, neutralization of solution and precipitation with oxalic acid, the white powder of yttrium oxalate was produced. Selective precipitation with oxalic acid at fixed pH-value after leaching and phase separation are crucial for scale up. The values of solubility product are presented in Table 4.

Table 4. Solubility Product, pK_L for different compounds

Compound	Formula	pK_L
Calcium oxalate	CaC_2O_4	8.63
Magnesium oxalate	MgC_2O_4	5.32
Yttrium oxalate	$Y_2(C_2O_4)_3$	29.29
Aluminum oxalate	$Al_2(C_2O_4)_3$	2.47
Iron (II) oxalate	FeC_2O_4	6.50
Yttrium hydroxide	$Y(OH)_3$	24.5

Comparison of the values of solubility product for different compounds shown that the yttrium oxalate $Y_2(C_2O_4)_3$ has the highest value (29.29). It means that the formation of yttrium oxalate was preferred. The phase separation was performed using chamber filter press Andritz, Cologne, Germany which is not shown in this study. Yttrium oxide was finally formed after thermal decomposition of yttrium oxalate at 850 °C in 1 hour in a muffle furnace.

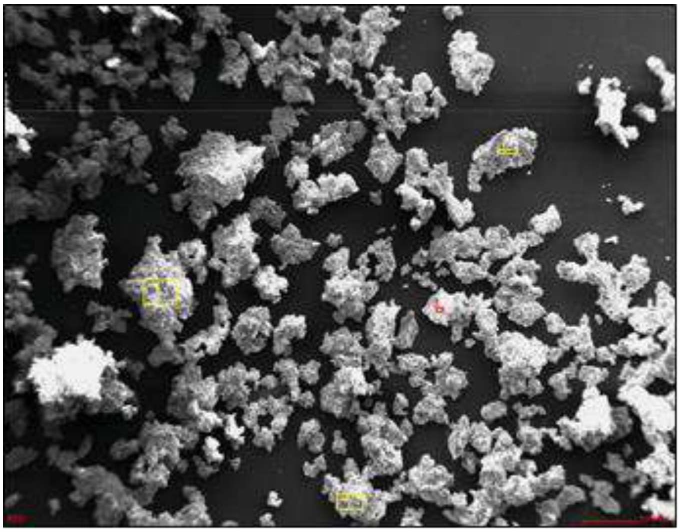

Figure 7. Typical SEM analysis of produced yttrium oxide powder

The obtained powder contains 99.69% Y_2O3, and remaining oxides in the fololowing weight percentages (%): 0.031 Fe_2O_3, 0.001 TiO_2, 0.023 SiO_2, and remaining CaO, which is sufficient purity for the new application in the ceramic parts.

5. CONCLUSION

A target fraction rich in yttrium with a grain size < 250 µm was obtained after the grinding and sieving of the primary fraction with 14.25% of the target element yttrium. This target fraction became the input material for the following tests to the very selective leaching of yttrium involving dissolution under an atmospheric pressure as well as pressure leaching in the autoclave. For a comprehensive investigation of the influence of various parameters on the leaching of broken ceramic molds, a total of 16 series of experiments was carried out, in which parameters like leaching time, temperature, concentration of the hydrochloric acid and the ratio solid to hydrochloric acid were varied. By the change of these basic conditions, it turned out that the course of the leaching tests could be influenced by a sensible choice of external parameters. Probably the most important factor to the leaching of ground molds, turns out to be the leaching temperature. At process temperatures of 150 °C, concentrations of dissolved yttrium could be registered after 30 minutes that could not be reached at 70 °C or even 90 °C after 5 hours of leaching time. Particularly during the first 15 minutes, this temperature influence is strongly perceivable. In this period, a temperature of 150 °C leads to an yttrium concentration in the leaching solution which corresponds to the tenfold of the simultaneous value at 70 °C. The leaching time, however, is unique for the leaching under atmospheric pressure and pressure leaching in an autoclave. While during leaching the yttrium concentration rises further after 5 hours of leaching, the process in the autoclave is almost finished after less than 30 minutes. No notable increase of the gradient occurs between minutes 15 to 30 as the maximum values are already reached after less than half an hour. A rise of the ratio of solid to leaching agent also leads to a different yield. Thus, a doubling of the input amount can cause an increase of the dissolved yttrium in the leaching solution by up to 78.98%. A doubling of the hydrochloric acid concentration from 1 $molL^{-1}$ to 2 mol/l also improves the leaching process. The final produced yttrium oxide using leaching (described in this work), precipitation with oxalic acid, filtration and thermal decomposition has a sufficient purity for the application in a production of titanium-aluminium parts. Using of hydrogen peroxide will be considered in the future work in order to ensure totally oxidation of Fe (II) to Fe (III) aiming at a complete precipitation of iron hydroxide.

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