GERRI – Potentials and opportunities for German raw material actors

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Introduction

In 2015 leading German research institutions in the raw materials, founded the virtual institute GERRI – German Resource Research Institute. The goal of GERRI is to strengthen transdisciplinary research along the entire value chain of mineral and metalliferous raw materials and – being an independent group of experts – support industry in the development of innovative solutions for complex problems. In Germany GERRI has become a central nucleus interlinking policy, industry and research, outside the country GERRI is representing Germany's research competence and acting as "ambassador" of the German resource researcher community. In 2018 the GERRI network has founded an association thus taking the next step to further promote the bundling of raw material expertise from science and industry for the German economy. Partners are the TU Bergakademie Freiberg, RWTH Aachen University, Clausthal University of Technology, Fraunhofer project group for recycling and resource management IWKS at Fraunhofer ISC and the Helmholtz-Institute Freiberg for Resource Technology (HIF) at Helmholtz-Zentrum Dresden-Rossendorf (HZDR) and the TH Nuremberg. The Federal Institute for Geosciences and Natural Resources (BGR) and the Federal Institute for Materials Research and Testing (BAM) joined as associated partners. New members from research and public institutions are to follow.

Competences along the material value chain

Via its broad partnership and spectrum of competencies GERRI follows the vision to catalyse the supply of metal-containing and mineral resources to turn a technologically advanced and efficient circular economy into reality. The platform covers those fields of expertise and disciplines that are crucial for sustainable raw material research: Socially acceptable and non-invasive exploration of new deposits and sustainable extraction of methods, processing of minerals and "anthropogenic ores" contained in end-of-life goods. Recovering of metals and recycling of end-of-life goods (EOL) by hydrometallurgical and pyro-metallurgical methods. GERRI members are as well involved in waste management, material development, modelling and special analytical methods for material characterisation (see Figure 1). With the admission of new partners, the existing fields of competence are to be expanded (this includes as well social and economic sciences) to fully complete this platform.

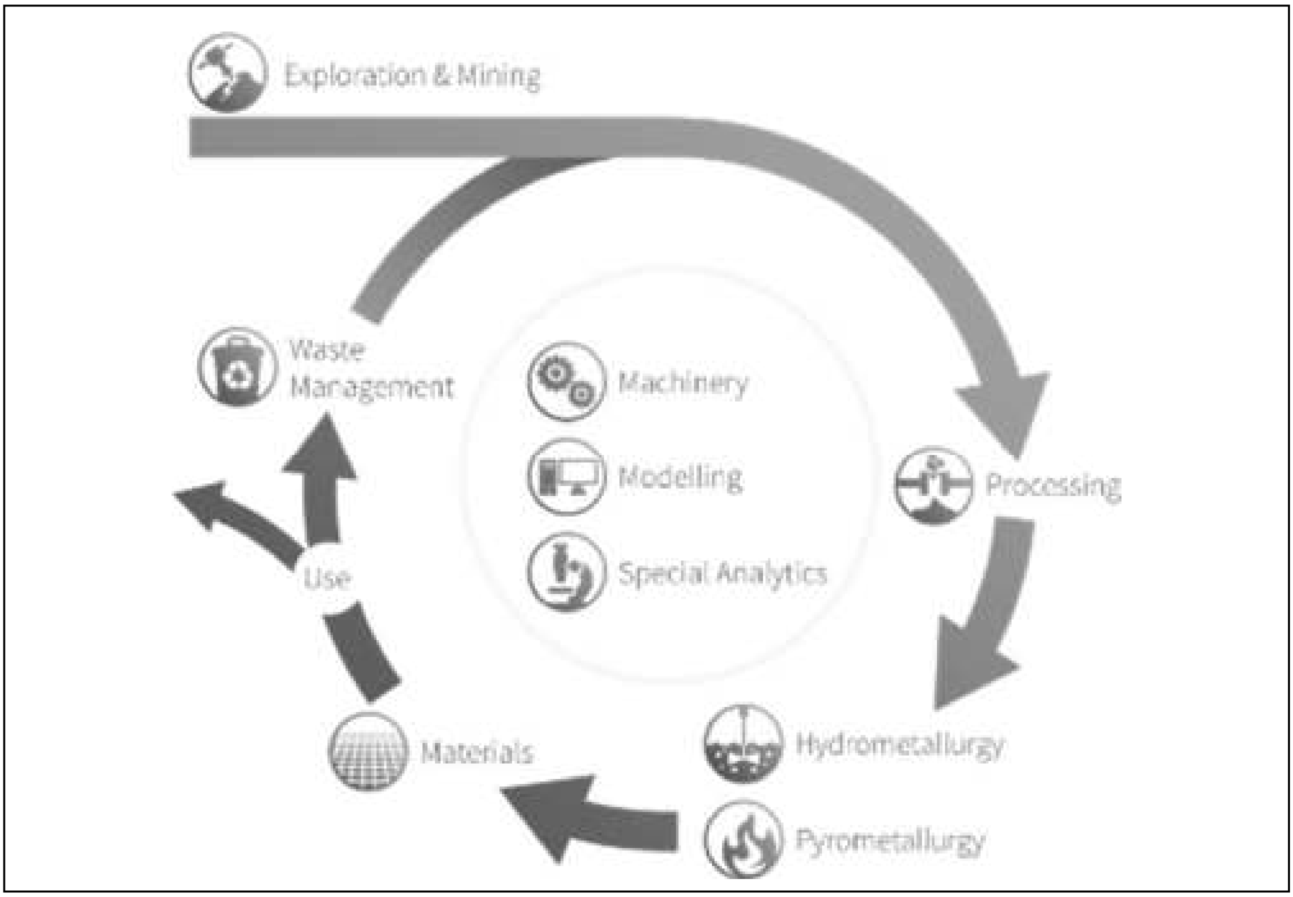

Figure 1: GERRI - Competences along the raw materials life cycle

As it will be illustrated in this article GERRI gathers partners and build projects which are tackling the complexity of raw materials supply by initiating and leading projects covering the whole value chain of raw materials. A good example for this is the winning of rare-earth elements (REE) from primary and secondary sources.

Along the value chain – REE from Brazil

With approx. 22 mt rare-earth oxide (REO) equivalent, Brazil possesses the second largest reserves of rare-earth elements (REE) in the world, together with Vietnam, only behind China [1] (Figure 2). Despite this huge potential, at the moment, no production of REEs takes place at an industrial scale, although in 2017 Brazil produced 2,000 t of REO. Motivated by price developments since 2010 and the desire to establish a complete value chain from ore up to REE containing products, especially NdFeB magnets and catalysts, several REE projects have been initiated in recent years [2].

Figure 2: The CMOC Brasil (Niobras) Boa Vista mine close to Catalão, which contains REE bearing minerals

Multiple GERRI partners are part of two Projects (MoCa & REGINA) in Brazil, dealing with the front and back end of the value chain for REE-Magnets (Figure 3). The projects are part of the CLIENT II funding program of the Federal Ministry of Education and Research of Germany, which focusses on cooperation of German and foreign scientist and companies to develop the global REE market, secure the availability of REE sources for the German economy and to lower the dependency from other countries. As third Client II funded project with a REE topic, the CaMona project consortium intends to develop a process for rare earth-bearing gypsum tailings from the fertilizer industry to provide usable REE-concentrates. In this project, only one of the GERRI partners is involved and will be therefore not considered any further in this article.

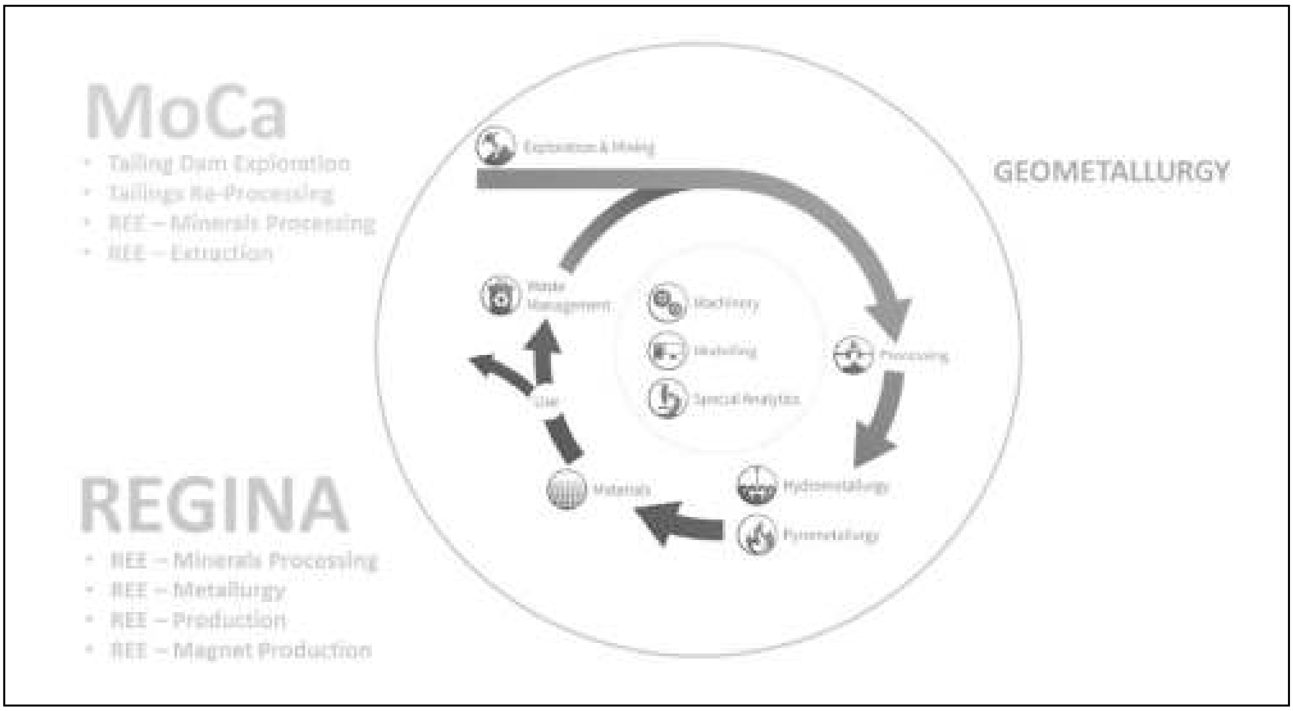

Figure 3: GERRI Competences – Projects MoCa and REGINA

The overall scheme of the projects along the value chain is shown in Figure 4. The overall objective is to develop a process chain going from mining, mineral processing, production of RE-oxide concentrates, material production up to the manufacturing of products.

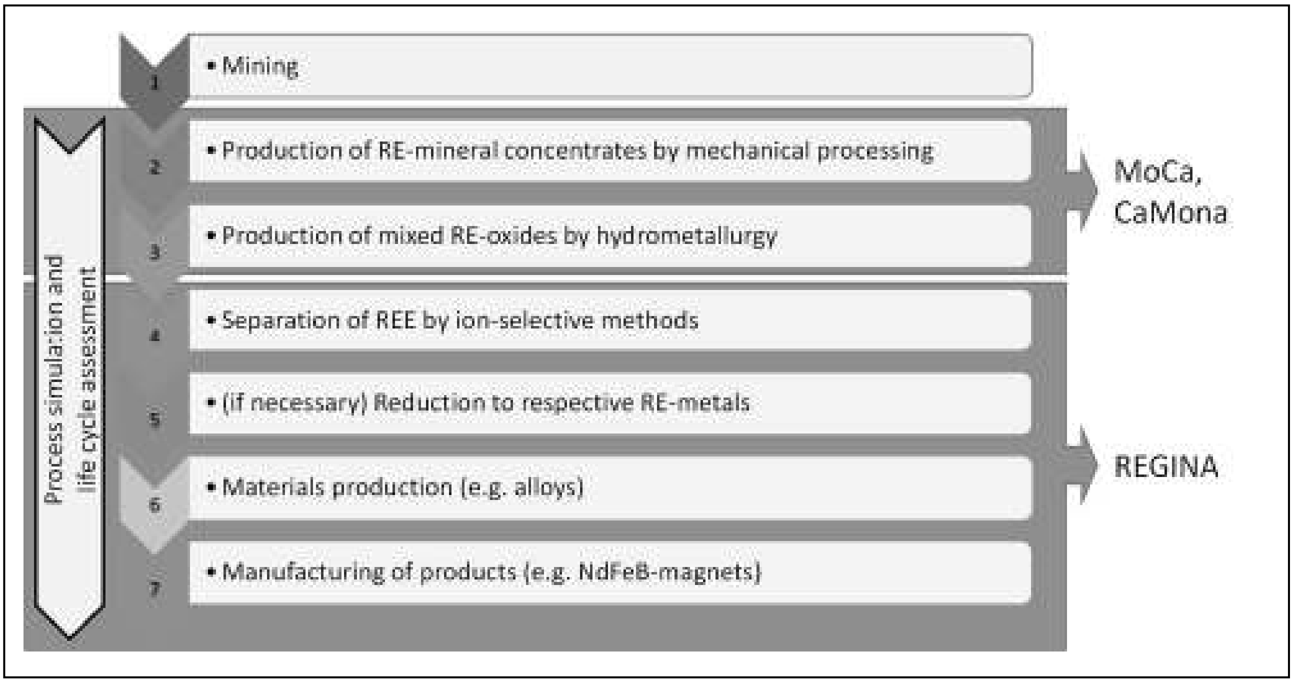

Figure 4: Overview of the Brazilian-German projects funded within CLIENT II

The Monazite Catalão (MoCa) Project

One of the most important deposits of phosphate bearing ores in Brazil is the partly weathered ultramafic alkaline-carbonatite complex Catalão in the Federal State of Goiás hosting beside phosphate (apatite) and niobium (mainly pyrochlore) bearing minerals also the REE phosphate mineral monazite. Other major components are anatase (TiO_2) and vermiculite crystallizations (sheet silicates) [3]. Currently, the deposit is mined by CMOC International Brasil and Vale due to its apatite and pyrochlore content to produce fertilizers and ferroniobium. The REE bearing minerals are lost to the tailings (Figure 5). In the current complex mineral processing, mainly magnetic separation and multi-stage flotation processes are applied for the enrichment and recovery of niobium and phosphate bearing target minerals.

The MoCa project, short for „Development of a production chain for rare earth elements from tailings of the ultramafic alkaline-carbonatite complex Catalão/Goiás" is developing processes to regain the valuable materials.

Figure 5: The Tailing Storage Facilities (TSF) of CMOC Brasil (Niobras) in Catalão

Mineral processing development of REE bearing minerals

Despite a potential of at least 25 kt REO/year and remarkable low thorium and uranium contents [4] [5] [6], so far, no emphasis was put on the recovery of the monazite. Reasons for this situation were the low REE prices prior to 2010 and the processing challenges caused by the fine grained and finely disseminated monazite crystals. The monazite occurs as microcrystalline aggregates, sometimes presenting colloidal textures, which are frequently associated with iron oxide-hydroxides and quartz.

Since these aggregates are extremely friable, the monazite crystallites are supposed to occur mainly in the ultra-fine fractions in mineral processing. Due to this nature, mineral processing poses a particular challenge and applicable unit operations are limited. Hence, to this day, only few studies have been published on the processing of monazite from the Catalão complex. The attained recoveries of REEs for the applied physical concentration processes were usually below 30 % with REO grades rarely reaching 20 %. Direct hydrometallurgical studies were also economically unfeasible, but showed that the monazite presents unusually high dissolution rates in diluted sulfuric acid at low temperatures [3] [7] [8] [9] [10] [11]. Typically, monazite requires digestion using concentrated sulfuric acid or caustic soda at high temperatures [12].

To achieve significant progress in the processing of this type of REE bearing minerals, an interdisciplinary approach is needed including the use of sophisticated technologies for the processing of ultra-fine grained minerals, especially pneumatic flotation, column flotation and centrifugal concentrators, which have not been applied to the ore up to now as well as the development of tailored flotation reagents. The process development needs to be supported by modern analytical in-situ methods combined with X-ray diffraction (XRD) as well as economic and ecological assessment of the processes. As these technologies and methods are only partly available in Brazil, a Brazilian-German collaboration is key to develop a Brazilian REE industry (e.g. plants from BV FR, Figure 6). Expected benefits for Germany are the broadening of the REE supply for the German industry, business opportunities as well as an expansion of the REE expertise of the involved partners.

Figure 6: The Boa Vista Fresh Rock (BV FR) Processing Plant of CMOC Brasil (Niobras) in Catalão

TSF Exploration

Beside the processing experiments for the development of a REE production line in combination with the existing process for the fresh rock and weathered material from the CMOC mines, the old tailing ponds are bearing still huge amounts of REE minerals like Monazite or REE rich carbonates also. To explore the REE potential of tailing ponds and to do feasibility studies for their reprocessing, a cheap and fast method is needed, to characterize the mineral composition, distribution of the REE minerals and the structure of the pond. Existing methods are working with expensive Mineral Liberation Analyses (MLA) on liner samples from tailing pond drill cores [13]. Within the MoCa project, the GERRI partners will develop this method further, using cheaper hyperspectral drill core scanning and direct push XRF data from a System developed by the FUGRO Land GmbH. A new directs push cone will be developed here, which is able to measure the REE content of the material insitu. In the end, a cheap and reliable tailing pond characterization method will be the result. This method can be used for the evaluation of other anthropogenic deposits (like tailing ponds).

Objectives of the research project MoCa

The overall objective of the project is the determination of the REE production potential of the Catalão complex considering REE grade, occurrence of the REEs in minerals with respect to their processability, competitiveness and sustainability. To achieve this, the following sub objectives will be addressed:

- Evaluation of the REE recovery potential of the current phosphate and niobium production of CMOC Brasil by chemical and mineralogical characterization of the different tailing streams.
- Evaluation of the REE recovery potential of deposited tailings by the exploration of one selected tailing dam including chemical and mineralogical characterization as well as 3-D modelling.
- Development of an advanced mineral processing route to recover the ultra-fine grained monazite crystals from selected tailing streams reaching at least 40 % REO grade in the REO concentrate to enable an economically and ecologically feasible chemical processing.
- Development of a chemical or combined biological / chemical process for the REO concentrate to extract and refine the REEs as well as to recover phosphate as by-product for the fertilizer industry.
- Economic assessment of the developed process routes to identify optimization potentials and to support the development of competitive solutions.
- Ecological assessment of the process routes including validation of available life cycle assessment (LCA) data for REEs and optimization of the data especially with regard to the production of REEs from different deposit types.

The further processing of the mixed REOs by separation and reduction to the metals will be addressed in the REGINA project.

REGINA project

The REGINA project (Rare Earth Global Industry and New Applications), funded by the federal ministry of education and research by 2,9 m. €, has been founded in 2017 with the aim to develop a process chain from tailings to a green magnet. It is a cooperation between Brazilian and German research institutions and companies. The individual competencies range from the treatment of ores to the synthesis of metal, up to the manufacturing of magnet alloys and magnets themselves. In addition to that, process simulations, life cycle assessments, and market analyses are done.

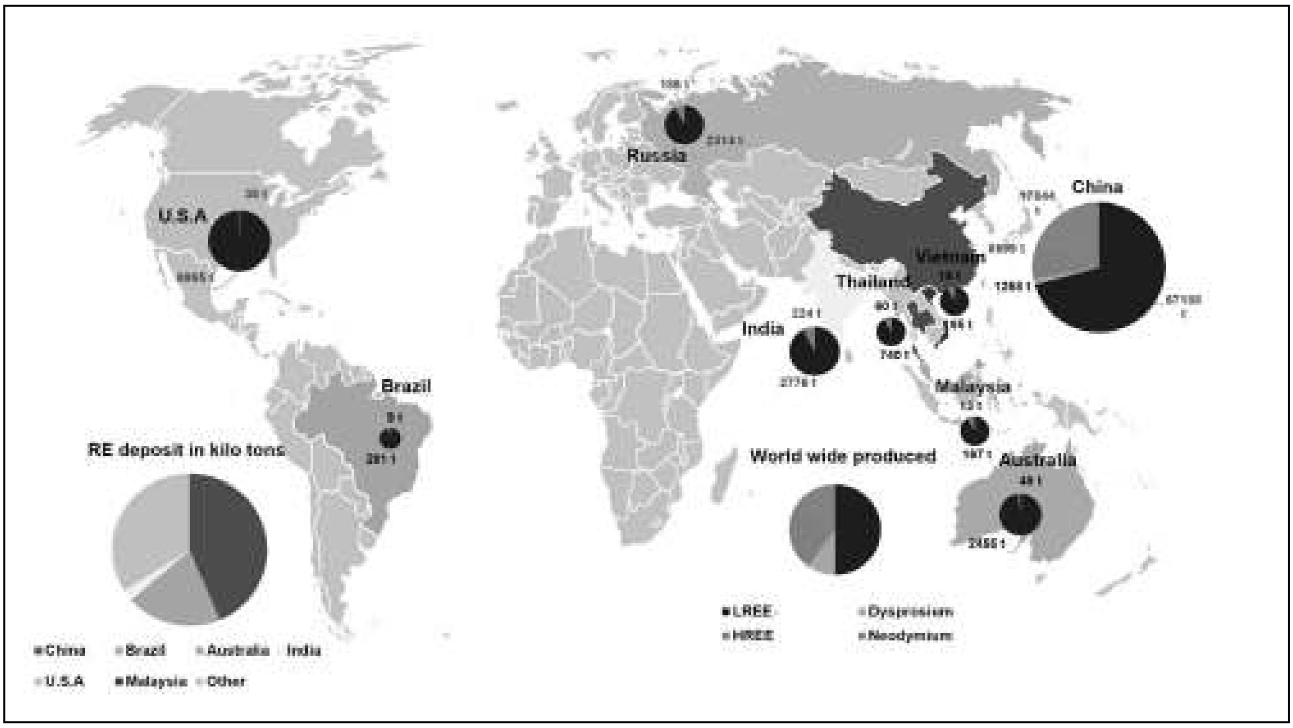

Figure 7: Deposit distribution and global production of RE (2013) [14]

Due to the large rare-earth-ores reserves, Brazil has the potential to become the second largest producer of rare earth products, which is quite a challenge with regards to China's rare earth monopoly (Figure 7). In this situation, REGINA provides different bilateral projects along the value chain, related to the production costs, as well as the environmental influence. In the end, the product will be a "green magnet" consisting of the alloy Nd / Pr-Fe-B, which is environmentally and socially acceptable and has at least comparable properties, to a market leading product.

In the following, the work packages are introduced briefly:

WP 0: The Helmholtz Institute Freiberg for Resource Technology (HZDR) and Outotec GmbH & Co. KG will create a process simulation and a life cycle assessment to analyze the market and competitive ability for the environmentally compatible magnets.
Data from literature research, as well as those of each project partner, are used in the process simulation model HSC Sim 9. With this simulation tool, it is possible to calculate the energy and water consumption for each process step.

WP 1: The Institute of Mineral and Waste Processing, Waste Disposal and Geomechanics of the TU Clausthal will develop a new separation process, which will a rare earth concentrate, won by tailings from Companhia Brasileira de Metalurgia e Mineração (CBMM) with the aim of being economically and ecologically superior to the current best available technology.

WP 2: The cooperation of the Institute for Process Metallurgy and Metal Recycling (IME, RWTH Aachen University) and the Instituto de Pesquisas Tecnológicas (IPT) will develop and optimize a molten salt electrolysis for the production of didymium, a metal mixture of neodymium and praseodymium. A large improvement is expected regarding the environmental compatibility, by using an automatization that controls the process by measuring the off-gas of the system continuously. With that advancement, it is expected that especially the amount of formed perfluorocarbons (PFCs) which are highly polluting is decreased. In a vacuum induction furnace, the master alloy is created for the magnets, together with iron and boron. To prevent a separation of that alloy, the melt will be cast on a rotating water-cooled copper plate. The flakes that are made by this process should meet the requirements to be processed to magnets. The rotating copper plate is developed with the company KME Germany GmbH & Co. KG.

WP 3: The Technische Universität Darmstadt (TUD) will define the required purity of the raw materials. The result of this step will be a definition of the magnet alloy with a requested purity, a desired composition and a custom-made structure for magnet production. This will be done in lab scale first in different furnaces to homogenize the material and afterwards in a strip caster to cast the alloy with a specific cooling rate. This performance will be investigated by the Brazilian Instituto de Pesquisas Tecnológicas (IPT) and Universidade de São Paulo (USP). The expertise from the Deutsche Magnetwerke GmbH (GMB) is used to estimate the solidification performance of the magnets, especially in terms of the interaction of the melt with the material of the crucible under different atmospheres.

WP 4: The Fraunhofer Project Group Materials Recycling and Resource Strategies (IWKS) will implement an optimization of established sintering process, with the aim to use that for the Di-Fe-B alloy. The challenge will be to adapt the right parameters for the powder synthetizing and annealing process due to the new Didymium alloy to create competitive magnets. Metal flakes have to be embrittled to monocrystalline metal powder by hydration, which is used to create the green bodies for magnets. The magnets which are created in this process chain are characterized chemically and magnetically in the community laboratory "Magnetismus" of TUD and IWKS. The Universidade Federal de Santa Catarina (UFSC), which has a long-term expertise in the field of surface treatment will investigate the process of sawing and grinding of the magnets as well as the prevention from corrosion. An additional step will be the up-scaling process, which will be implemented with the knowledge of the Fundação Centros de Referência em Tecnologias Inovadoras (CERTI).

WP 5: The aim of the DMT-Gesellschaft für Lehre und Bildung mbH; Technische Hochschule Georg Agricola (THGA) is to identify the competitive situation for REEs and the final product magnet by analysing the market, making empirical market research and SWOT analyses. The THGA develops concrete recommendations to create a win-win situation for Brazil as well as for the German economy through sustainability. The results are applied in a precise business model, which guarantees high chances of success and considers ecological, economic and social effects.

Research approach IME – Molten Salt Electrolysis

The molten salt electrolysis is investigated in Aachen at the IME with the aim to synthesize a mixture of Neodymium and Praseodymium in one process step. For this purpose an electrolyte, based on Neodymium fluoride (NdF_3), Praseodymium fluoride (PrF_3) and Lithium fluoride (LiF), was chosen because of the reaction and solubility potential of the fed material, which consists of Neodymium oxide (Nd_2O_3) and Praseodymium oxide (Pr_6O_{11}). During this process polluting off-gases like CO, CF_4 and C_2F_6 are formed. Those gases are measured online by a Gasmet DX4000 Fourier transformation infrared spectrometer (FTIR, Ansyco), meaning this device takes a gas sample every five seconds and detects its composition. This setup allows the possibility to react to different output values by adjusting several parameters.

The process parameters for a molten salt electrolysis are based on literature research and thermochemical calculations with the simulation software FactSage®, which allows simulating certain chemical reactions, like the decomposition potential or the solubility potential of oxides in the system, as well as phase diagrams for example. It was found out, that the best parameters for the process are a temperature of 1050°C, a cell potential of 9 – 11 V and an anodic current density of 1,0 – 1,25 A/cm^2.

The results of the thermochemical reactions were calculated by using the data bases FactPS® and FTLite® under the conditions of 1050 °C, one bar pressure and the activity of one, shown in table 1. The estimated building potentials are listed on the right side of the table. A change in the cell potential results in the reaching of another building potentials, for example CF_4 is first formed at 2,798 V and C_2F_6 at 2,976V. The ambition to reduce the formation of climate-damaging greenhouse gases like CO_2, CF_4 and C_2F_6 is immense. The global warming potential of perfluorocarbon (PFC) gases have a much higher influence. One gram of CF_4 makes the same amount of damage like 6630 grams of CO_2, whereas C_2F_6 is equivalent to 11100 g. [15].

Table 1: Building potentials of several reactions

2 Nd_2O_3		→	4 Nd	+ 3 O_2	2.481 V
2 Pr_6O_{11}		→	12 Pr	+ 11 O_2	2.038 V
4 NdF_3	+ 3 C	→	4 Nd	+ 3CF_4	2.798 V
4 PrF_3	+ 3 C	→	4 Pr	+ 3 CF_4	2.832 V
4 LiF	+ C	→	4 Li	+ CF_4	3.309 V
2 NdF_3	+ 2 C	→	2 Nd	+ C_2F_6	2.976 V
2 PrF_3	+ 2 C	→	2 Pr	+ C_2F_6	3,055 V
6 LiF	+ 2 C	→	6 Li	+ C_2F_6	3.487 V

To prevent the formation of environmental harmful gases, an electrolysis cell was designed and built at the IME. The cell, shown in Figure 8, is made of steel, with several Swagelok connections in the lid, through which the electrodes and other measurement devices, like the thermocouple, can be inserted. The cell has a graphite crucible, where the electrolyte is placed, a graphite anode, here a ring anode for a better current efficiency, and a tungsten cathode in the middle of the graphite ring. The displayed feeding system is gas-tight, too. Because the whole system is likely to react with oxygen, argon is constantly flushed into the cell during the trial. The electrolyte's components are dried for 24 hours at 250 °C before they are mixed and molten in a vacuum induction furnace under argon atmosphere at about 1800 mbar. The fluorides are heated up to 1100 °C and are then poured in a graphite crucible inside of the furnace. To prepare the oxides, they are also dried at 250 °C for 24 hours, are then pressed, crushed and sieved to get a grain size distribution between 0,75 mm and 2 mm.

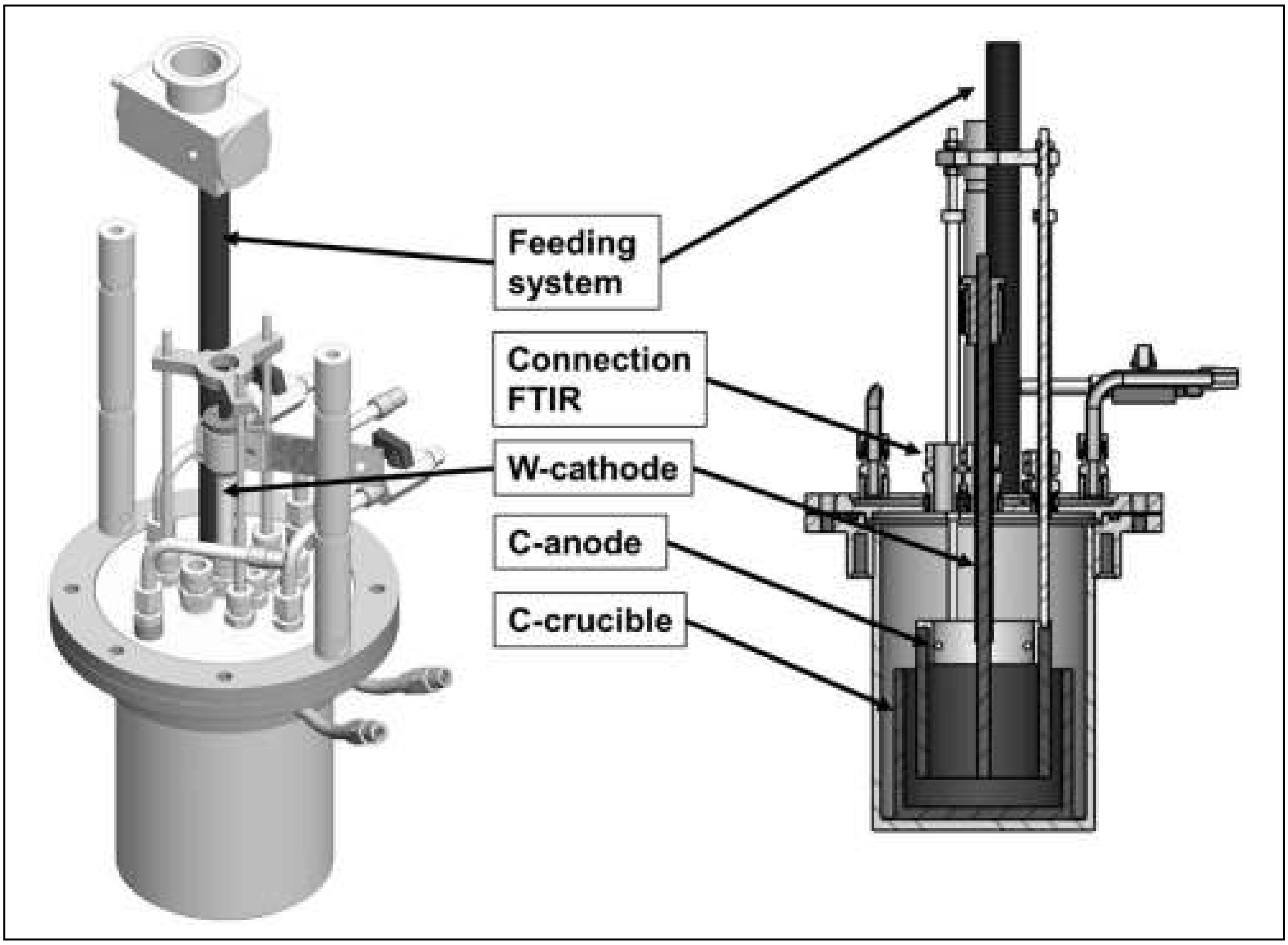

Figure 8: Electrolysis cell setup

After feeding the REE-oxides and waiting for approximately twenty minutes for them to dissolve, the process is started by applying a currency of 40 A to the system. The arising cell potential is dependent on the resistance of the system, mainly the resistance of the electrolyte which is changing over the time, shown in the upper diagram of Figure 9. At the beginning of the trial the cell potential is beneath 5 V, while after 30 minutes it is above this value. The slow increase of the cell potential results from the ongoing reactions of the ions. While in the beginning of the trial enough reactants are available in front of the electrodes, the concentration of ions decreases and with it the conductivity of the electrolyte which results in a higher cell potential, seen in Figure 9.

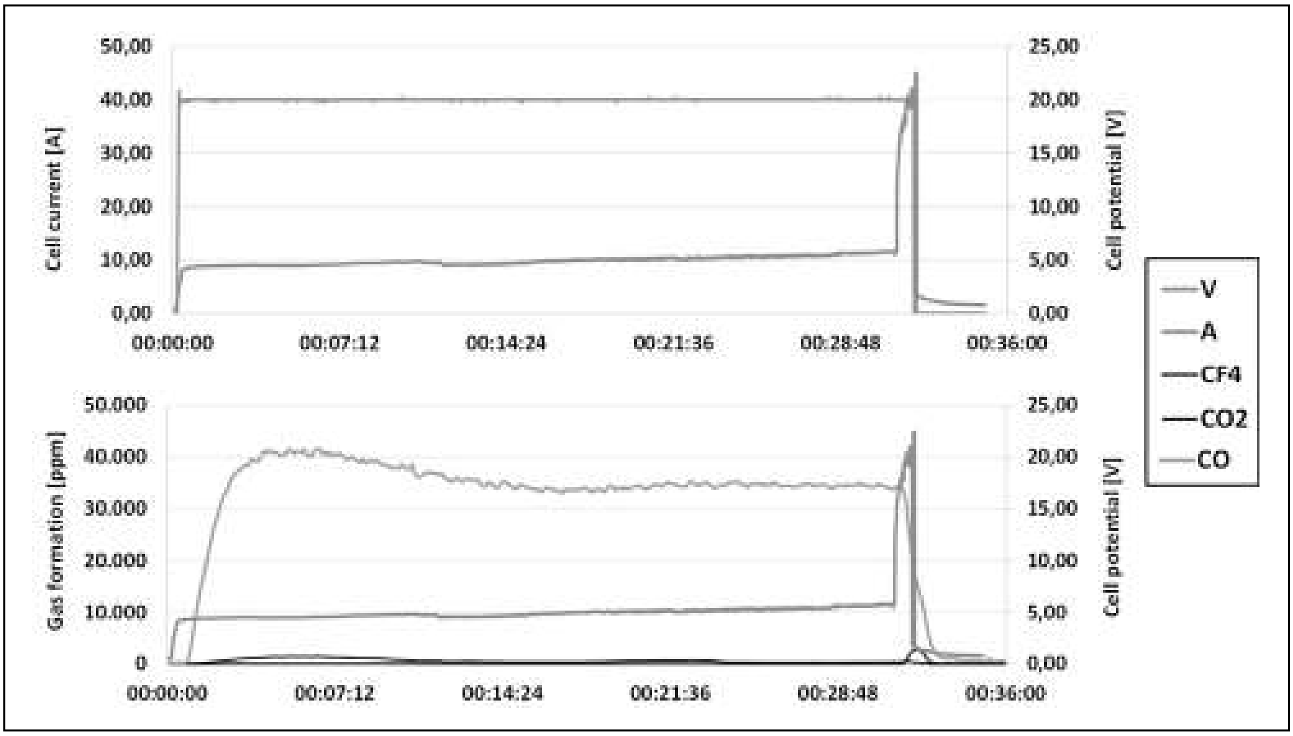

Figure 9: Upper diagram: current and potential over the time, lower diagram: potential and gas formation over the time

In the end of the trial a spontaneous increase of the potential is observed, while the current remains at 40 A. From that behaviour it can be deduced that the cell resistance has raised suddenly, which is due to the lack of reactants. With the increasing cell potential the chemical reactions at the anode are shifted from the formation of CO and CO_2 to a formation of CF_4 which can be seen in the lower diagram of Figure 9. While in the beginning the value of CO is between 32.000 ppm and 40.000 ppm the formation of CO stops by an arising anode effect and formation of CF_4 begins. At this point the trial is stopped.

Future prospective

The next step will be the introduction of automatization to avoid the formation of CF_4 gas, thus reducing unnecessary environmental impact. The concept for this automatization is the connection of the online off-gas measurement with an automatic feeding device. The process controller records the data from the FTIR and detects when certain parameters are above or below a set point, for example a certain potential, current or a gas value. When such a case occurs, the process controller triggers the feeding device which is attached to the cell and fresh oxides are brought into the system to improve the reactions. On the one hand, previous experiments have shown, that the amount of metal oxides have a great influence on the formation of PFCs [16], on the other hand the solubility limit of the oxides must not be exceeded. If the concentration of oxides in the electrolyte is too high the unsolved oxide disposes on the ground. The setup for this procedure is displayed in Figure 10. The off-gases of the molten salt electrolysis, which takes place in the presented steel cell, placed in an electric resistance furnace, are measured and analysed in the FTIR on the left side. The controller in the upper right evaluates those data and starts the feeding device if it is necessary.

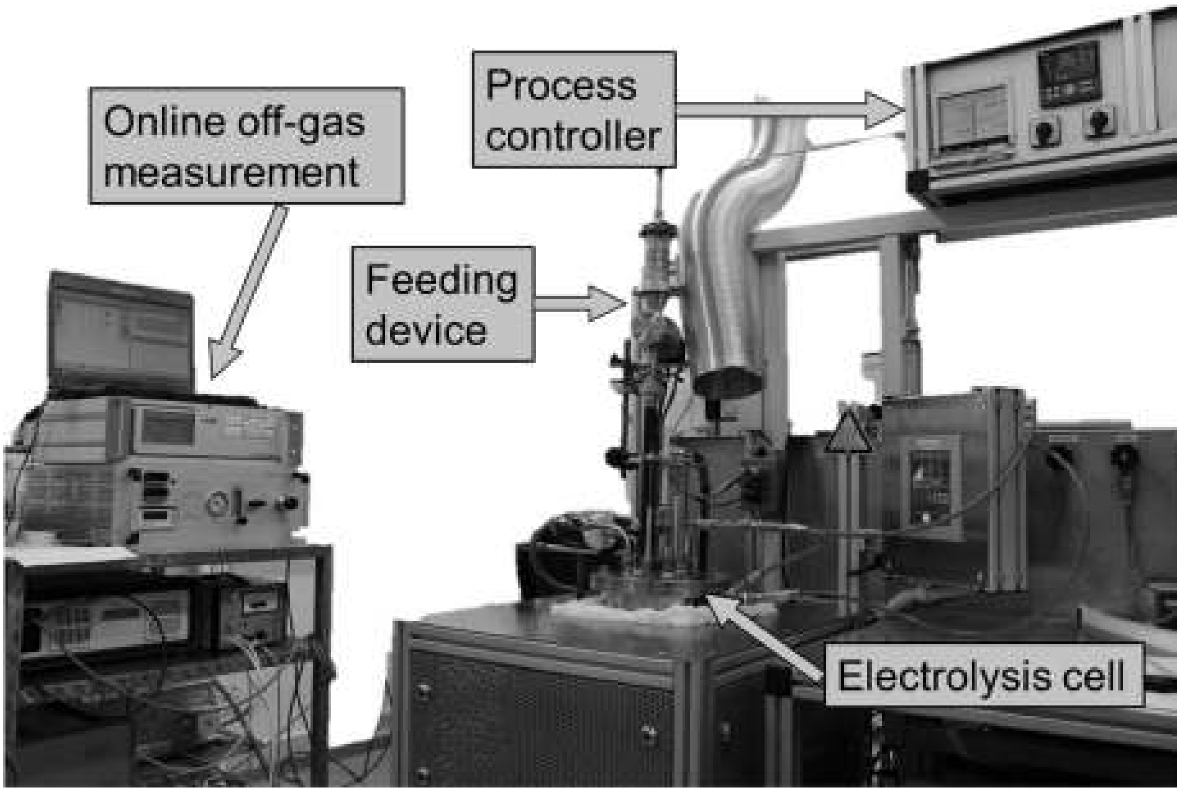

Figure 10: Experimental setup

First experiments using this setup have shown that the formation of PFCs can be reduced significantly if the controller is provided with the optimized process parameters. These parameters have to be evaluated. Right now trails are done, changing the amount and frequency of the feeding intervals, to find out, whether less oxides dosages in a higher frequency are more likely to show better results, or vice versa.

Conclusion

To reduce the environmental harmful PFC gases during the neodymium and praseodymium molten salt electrolysis, an automatization will be implemented, which is able to detect certain process parameters and will react by feeding fresh Nd/Pr-oxides into the system. Previous trails have shown, that the right metal oxide concentration and thus metal ion concentration lead to a mostly PFCs free process.

Outlook

The here presented projects are a good example of interlinked projects along the value chain concerning a specific demand, in this case the secure supply and development of REE containing materials.

Building on its technical knowledge and infrastructures and following its multidisciplinary approach as illustrated in this article, GERRI offers its expertise to politics and society thus actively engaging in legislation and regulation processes on national and European level. GERRI will approach political decision makers to elucidate that in order to realise a Circular Economy in Europe, a very specific know-how covering the whole value chain and related infrastructure is required. In particular it will be stressed that the recovery of metals and other materials from any type of EoL is a highly challenging process and requires specific expertise on how to treat the complex combinations of materials. Therefore, especially processing and metallurgy and related infrastructure plays a key role to safeguard raw materials supply, developing and operating circular cities, renewable energies and to reach a fully sustainable mobility in Europe.

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