ROLE OF METALLURGICAL UNIT OPERATIONS IN MINERAL PROCESSING

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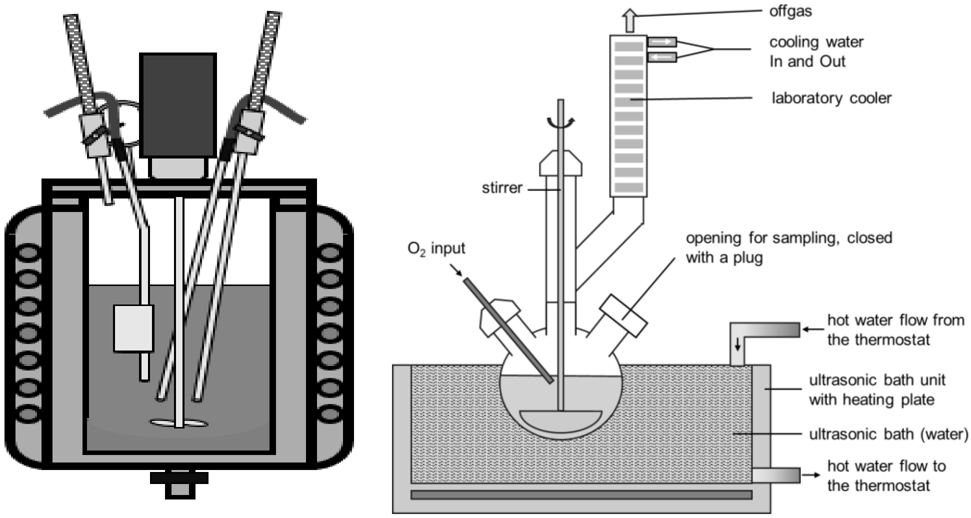
Abstract: *Unit operations in non-ferrous extractive metallurgy have high importance for mineral processing and environmental protection containing three categories: (1) hydrometallurgy (leaching under atmospheric and high pressure conditions in an autoclave, ultrasound assisted leaching; mixing of solution with gas and mechanical parts, neutralization of solution, precipitation and cementation of metals from solution aiming purification, and compound productions during crystallization), (2) pyrometallurgy (roasting, smelting, refining), and (3) electrometallurgy (aqueous electrolysis and molten salt electrolysis). The high demand for critical metals in modern life, such as rare earth elements (REE), indium, scandium, titanium and gallium has highly increased the need for an advance in understanding of an application of the unit operations in non-ferrous metallurgy regarding to mineral processing in environmental friendly processes. Treatment of eudialyte and bauxite residues will be presented in order to explain a role of metallurgical unit operations in mineral processing aiming recovery of rare earth elements and titanium! Additionally a role of hydrogen in reduction processess will be mentioned as part of one research strateg for titanium recovery from a bauxite residue!*

Key words: NON-FERROUS METALLURGY, UNIT OPERATIONS, MINERAL PROCESSING, ENVIRONMENTAL PROTECTION, CARBONATION

INTRODUCTION

Advances in understanding of a role of the unit operations in non-ferrous metallurgy have high significance in mineral processing. Unit operations in metallurgy are used in hydrometallurgical and pyrometallurgical treatment of different minerals, ores and concentrates. In hydrometallurgy, the aimed metal is first transferred from ores and concentrates to an acidic solution using a selective dissolution (leaching and dry digestion) under an atmospheric pressure below 100 °C and under a high pressure (40-50 bar) and high temperature (below 270°C) in an stirred reactor, autoclave (as shown at Figure 1, a) and tube reactor [1-5]. Ultrasound assisted leaching process was used to improve leaching efficiency of metals, as shown at Figure 1, b) [6].



a) *b)*

Figure 1, a) Sketch of an autoclave for high pressure leaching and b) Ultrasound assisted leaching

The purification of the obtained solution was performed using neutralization agents such as NaOH and $CaCO_3$ or more selective precipitation agents (sodium carbonate and oxalic acid) [7,8], as shown at Figure 2.

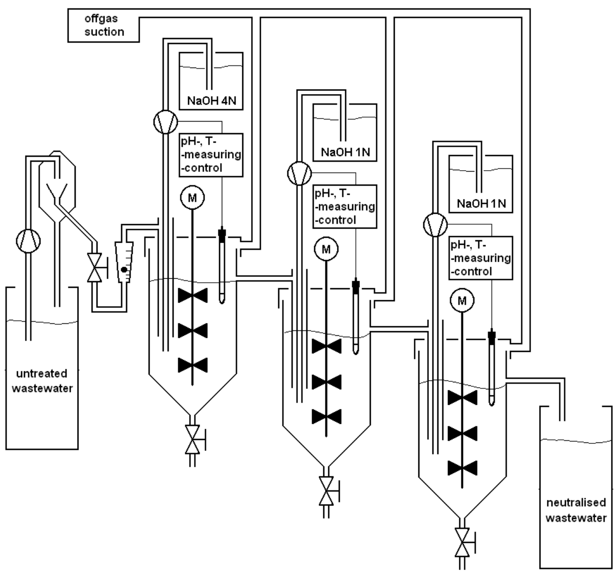


Figure 2, Continous precipitation of metals in cascade line

Purification of heavy metals such as Fe, Cu and Ni from wastewater solution is possible in different pH-value ranges using sodium hydroxide in one continuous process!

The separation of metals is possible using liquid/liquid process (solvent extraction in mixer-settler) and solid-liquid (filtration using a filter-press under high pressure (approx. 5-6 bar) [9-10]. Crystallization is the process by which a metallic compound is converted from a liquid into a solid crystalline state via a supersaturated solution [11]. The final step is metal production using electrochemical reduction process (aqueous electrolysis for basic metals such as copper, zinc, silver and molten salt electrolysis for rare earth elements and aluminum) [12-15]. Advanced process, such as ultrasonic spray pyrolysis [16-18] can be combined with reduction processes in order to produce metallic powders, as shown at Figure 3:

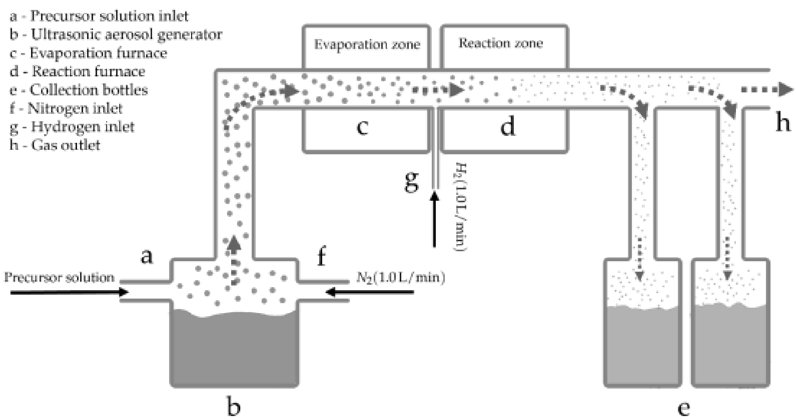


Figure 3, Production of metallic powders using ultrasonic spray pyrolysis and H_2-reduction

As shown at Figure 3 the most imortant part of process are: production of aerosol in an ultrasonic atomizer, transport of an aerosol to the furnace with a carrier gas, evaporation of water solution and precipitation with chemical reduction and final collection of powder in an electrostatic precipitator or wet scruber. The unit operation in nonferrous metallurgy are used for treatment of different minerals, ores and concentrats, what will be presented in this paper!

RECOVERY OF RARE EARTH ELEMENTS (REE) FROM EUDIALYTE

This study was a small part of the EURARE project (financed by EU Commission 2013-2017) concerned with the processing of eudialyte concentrates from Greenland and Norra Kärr, Sweden. Eudialyte ($Na_{16}Ca_6Fe_2Zr_3Si_{26}O_{73}Cl_2$) is a potential rare earth elements (REE) primary resource due to its good solubility in acid, low radioactivity and relatively high REE content. The main challenge is avoiding the formation of silica gel, which is non-filterable when using acid to extract REE. Some methods have been studied to address this issue and, based on previous research, this paper examined a complete hydrometallurgical treatment of eudialyte concentrate (1.6 % of REE) to the production of REE carbonate as a preliminary product. Dry digestion with concentrated hydrochloric acid (10 M) and subsequent water leaching of the treated eudialyte concentrate resulted in high REE extraction while avoiding gel formation. Experiments were performed at a small scale to obtain the optimal parameters. After the first two stages, 88.8% REE was leached under the optimal conditions (HCl:concentrate ratio 1.25:1, digestion time 40 min, water:concentrate ratio 2:1, leaching temperature 20–25°C and leaching time 30 min). After obtaining the pregnant leach solution, preliminary removal of impurities by a precipitation method was examined as well. When adjusting the pH to ~4.0 using calcium carbonate, zirconium, aluminium and iron were removed at 99.1%, 90.0% and 53.1%, respectively, with a REE loss of 2.1%. Finally, a pilot plant test was performed to demonstrate the feasibility and recovery performance under optimal parameters [19], as shown at Figure 4.

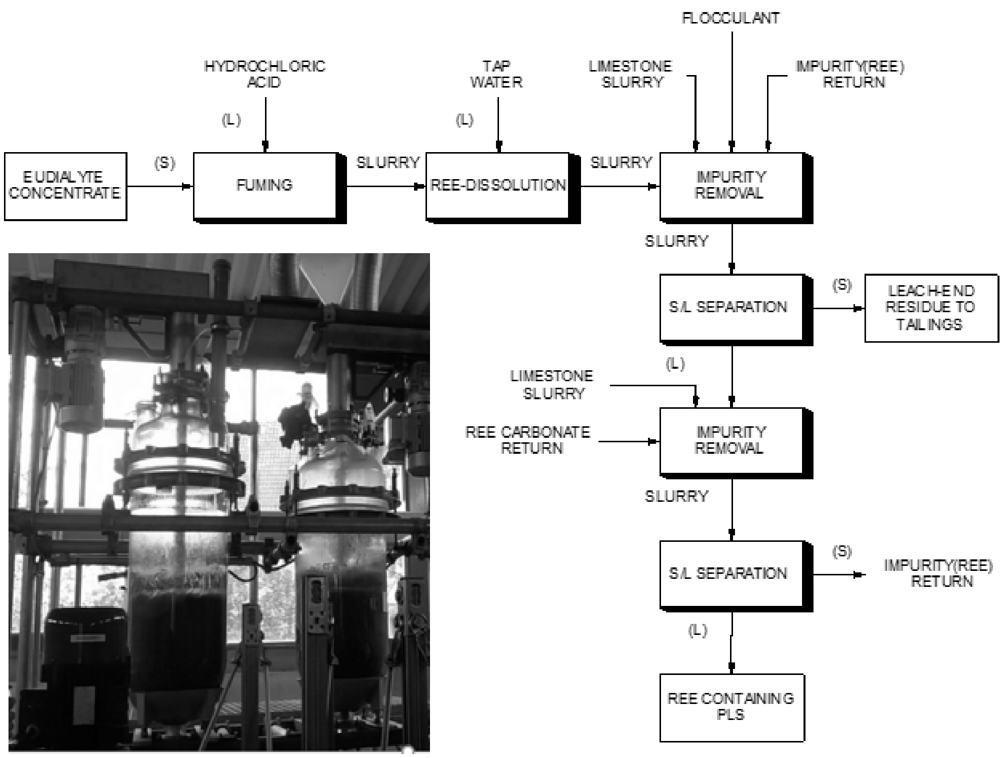


Figure 4, Flowchart of a Treatment of Eudialyte with a picture of the fuming process (dry digestion)

The material balance in the upscaling test was also calculated to offer some references for future industrial application. A REE carbonate containing 30.0% total REE was finally produced, with an overall REE recovery yield of 85.5%.

After this European project the development of a modular reactor for the dry digestion of high-silicate ores and concentrates to avoid gel formation using eudialyte ores as an example is being carried out by the Institute for Process Metallurgy and Metal Recycling at RWTH Aachen University and the konzept GmbH, Engineering Services, Düren, realized together. In this study financed by Federal Ministry for Economic Affairs and Climate Action, (No: ZF4098024SU, Acronyme: MAREKO), a new reactor is developed for a process that has already been confirmed on a laboratory scale to avoid gelling (dry digestion) during leaching. Up to 75 kg scale (100 liters) is possible to inject in reactor shown at Figure 5.

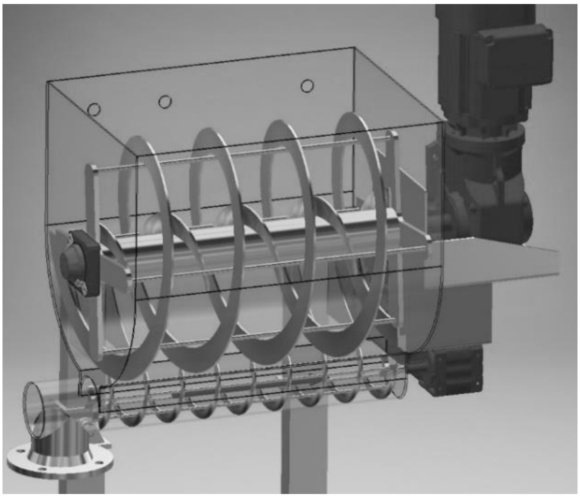


Figure 5, Dry digestion reactor with new mixing system

Special nozzle systems were used for acid injection aiming leaching of metals and water injection for a dilution of suspension and additional leaching [20]. Furthermore, it should be proven that the modular system technology is robust in terms of chemical resistance and reproducibility of the results achieved. The innovation compared to process alternatives lies in the complete avoidance of external and cost-intensive heating energy as well as the previously impossible implementation of the dry digestion process in large solution volumes. Before a gel formation, it is possible to convert the silicate components into crystals, which are filterable and stable. These results enable the cost-effective dissolution of silicate based ores and final production of rare earth oxides.

New dry digestor reactor shown at Figure 5 was used for hydrometallurgical treatment of eudalyte ore at room temperature using high concentrated sulphuric acid (12 mol/l). The tested experimental parameters for a treatment of eudialyte ore are shown in Table 1. The obtained results have shown the high leaching efficiency (higher than 90%) for rare earth elements (Nd, Y, Ce and La). At the same time the leaching efficiency for aluminium and iron amounted 10% and 25%, respectively. Minimal extraction was for silicon (about 0.2%). This is main reason that silica gel formation was prevented. The leaching efficiency for titanium, zirconium and magnesium amounted between 45 and 65%. The further application, sales and distribution of marketable mineral products is the challenge for the development of a circular economy. At the other side the production of rare earth oxides from solution after purification, precipitation and thermal decomposition is real option in this case!

Table 1, Experimental parameters for hydrometallurgical treatment in dry digestor reactor

Parameter	Unit	Value
Initial Material	kg	20
Used acid	%	96 (H_2SO_4)
Concentration	mol/L	12
Duration of dry digestion	min	120
Solid /liquid in dry digestion (H_2SO_4)	-	1:2
Solid/liquid in leaching (H_2O)	-	1:5
Duration of leaching	min	60

The obtained results under mentioned conditions are shown at Figure 6.

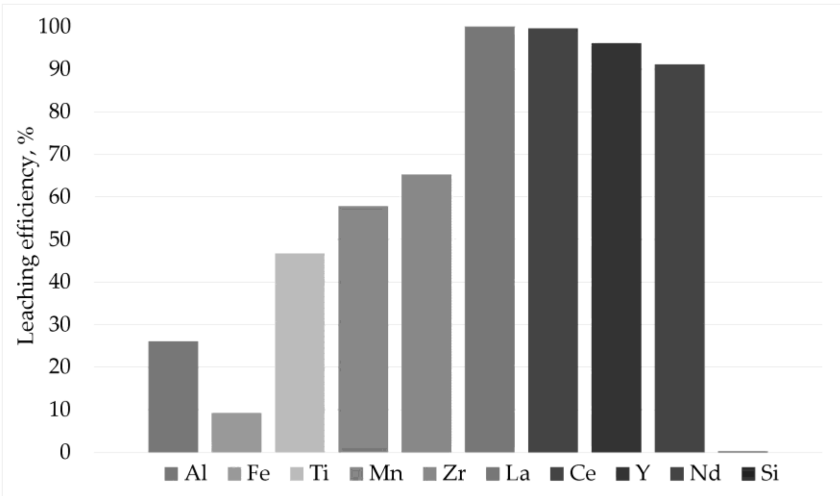


Figure 6, Leaching efficiency after treatment of an eudialyte in dry digestion reactor

RECOVERY OF REE UND TITANIUM OXIDE FROM BAUXITE RESIDUES

The Bayer Process is the traditional industrial method to produce alumina from bauxite ore. The chemical quality of precipitated aluminum hydroxide, and consequently the final alumina product in the Bayer process directly depends of the level of impurities in a refinery's Bayer liquor. Under optimal reaction parameters (temperature and time) it is possible to remove iron, zinc and copper from Bayer liquor using precipitation agent such as calcium hydroxide with an efficiency of more than 90%, in such a way that the treated solution is still economically usable in the following stages of processing while obtaining different types of aluminum trihydrate. [21]. Due to its properties such as high alkalinity, bauxite residue can be used as an input material in various neutralization processes [22] and recovery of critical metals. Three different types of bauxite residue were mostly studied, as shown in Table 2.

Table 2, Chemical Composition of BR [22]

Percent (%)	**Fe_2O_3**	**Al_2O_3**	**CaO**	**SiO_2**	**TiO_2**	**Na_2O**	**Cr_2O_3**	**Sc (ppm)**
Germany	35.3	15.7	6.7	14.0	11.4	8.9	0.2	86
Greece	44.0	23.0	10.2	5.5	5.6	1.8	0.3	122
Zvornik	49.3	12.0	8.2	10.5	4.6	2.5	0.13	76

This table shows that the bauxite residue from Zvornik, Bosnia and Hercegovina contains mostly Iron oxide. The Greek Bauxite residue contains more scandium, aluminium oxide, and chromium oxide but smaller content of sodium oxide, than the German and Zvornik one. Bauxite residue from Germany is highly alkaline due to presence of the sodium hydroxide from the Bayer process.In Europe, alumina refineries operate in Bosnia and Herzegovina (Alumina, Zvornik), France, Hungary, Germany, Greece, Ireland (AAL), Romania (ALUM), Spain and Ukraine, while significant BR deposits from refineries that have stopped their operations (legacy sites) exist in former Yugoslavia (Podgorica, Kidricevo, Mostar, Obrovac), Italy, France (RT), Germany, Hungary and other countries. The current BR production level in the EU is 6.8 million tonnes per year; while the cumulative stockpiled level is a staggering >250 million tonnes (dry matter). The bauxite residues contain scandium and gallium (Approx. 50-150 ppm) and up to an order of magnitude higher for elements such as: vanadium and rare earths elements (0.05-0.5 %). MYTILINEOS, Greece since 1991 has been pioneering research on BR handling and reuse, focusing initially on massive low value applications such as use as a raw material for geopolymer bricks, cement clinker production, iron production, bricks and tile production, soil remediation (vegetation), extraction of rare earth elements and road substrate [22]. Hydrometallurgical treatment of greek bauxite residue under mentioned conditions in new constructed dry digestion reactor leads to silica gel prevention and high leaching efficiency of REE, as shown at Figure 7!

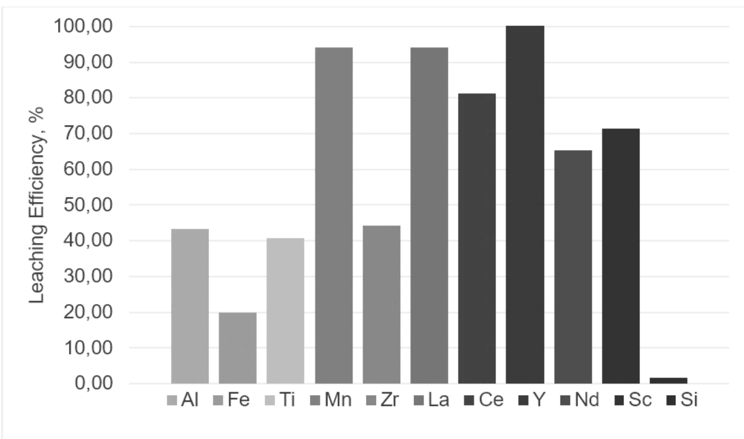


Figure 7, Leaching efficiency after treatment of Greek bauxite residue in dry digestion reactor

The obtained leaching efficiency is maximal for Y and La (more than 90 %). Unfortunately leaching of titanium is smaller than 50 %, what is also obtained from hydrometallurgical treatment of an eudialyte.

New Bauxite residue was provided from Alumina D.O, Zvornik, Bosnia and Herzegovina, as the starting raw material for our study. The factory Alumina has been in continuous production mode since October 6, 1978 and continuously processes bauxite and produces alumina, hydrates, zeolites and other related aluminosilicate products. The company Alumina currently has about 1500 employees, which is about 25 % of all employees in Zvornik. Alumina owns a red mud disposal site located about 5 km from the factory. Transportation of the red mud suspension from the factory to the landfill is carried out by suitable pumps. The area of the red sludge landfill is about 1 km^2, as shown at Figure 8.

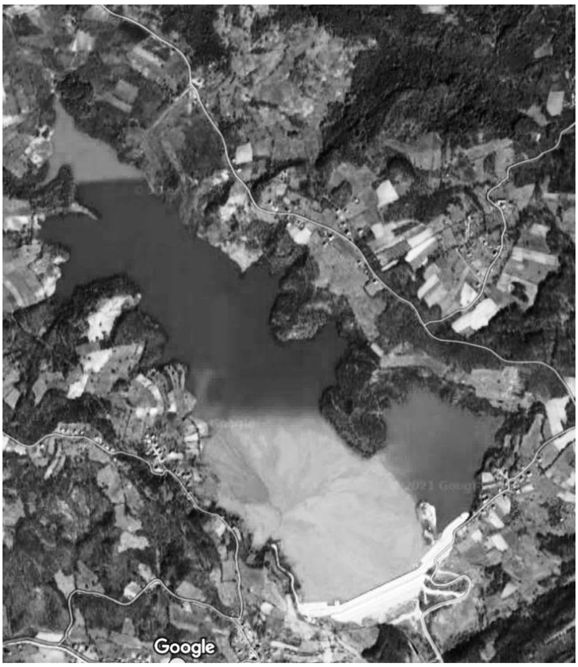


Figure 8, The area of accumulated Bauxite residue in Zvornik, Bosnia and Hercegovina

During the operation of the company Alumina doo, about 19.4 x 106 m^3 of BR suspension was disposed of. The company Alumina doo from Zvornik uses bauxite with a silicon dioxide modulus between 8.5 and 12. Accordingly, the amount of BR that is separated and disposed of at the landfill is about 1.0 - 1.2 t per ton of Al2O3 produced, or approximately 400,000 t per year. The installed technical-technological equipment at the clearing plant is of a continuous nature, where there are five installed autoclave batteries of 11-12 interconnected autoclaves in series (each autoclave has 50 m^3). The bauxite residue from Alumina was filtrated, washed and dried at 105 °C for 24 h [23].The chemical composition of BR is shown in Table 3.

Table 3, Chemical composition of BR, Zvornik

Compounds	%	Compounds	%
Ignition loss at 1000°C	8,32	Ga_2O_3	0,225
SiO_2	10,52	CuO	0,007
Fe_2O_3	49,29	K_2O	0,159
Na_2O	2,45	Tl_2O_3	0,088
TiO_2	4,59	MnO	0,145
CaO	8,23	MgO	0,627
Al_2O_3	12,03	NiO	0,034
Ag_2O	0,001	PbO	0,019
BaO	0,014	P_2O_5	0,930
Cr_2O_3	0,133	ZnO	0,016
Sc_2O_3	0,011	V_2O_5	0,135
Co_2O_3	0,012	SrO	0,075

One additional elemental ICP -OES analysis was performed in order to establish the content of rare earth elements (REE) presented in Table 4:

Table 4, Content of rare earth elements in BR, Zvornik

Content	Pr	Sc	Y	La	Ce	Nd	Sm	Tb	total
ppm	12	76	133	114	250	96	11	8	700

Regarding an unsufficient leaching efficiency one new strategy is proposed for treatment of bauxite residue! The proposed strtaegy representing decarbonizing technology combining pyrometallurgical and hydrometallurgical method (EURO-Titan Project financed by European commission; 2023-2027), as shown at Figure 9.

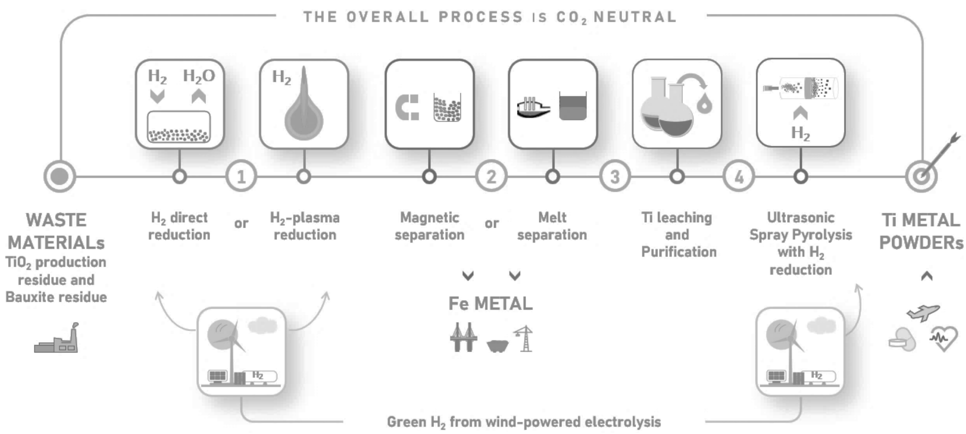


Figure 9, Research Strategy for decarbonizing technologie for Ti-recovery from bauxite residue

The main steps in this research strategy:

1. Pyrometallurgical treatment of bauxite residues by hydrogen producing iron and slag containing titanium and rare earth elements
2. Leaching of slag using conventional leaching, and intensified processes such as high pressure leaching in an sutoclave, and ultrasound assisted leaching
3. Purfication of leaching solution using solvent extraction and precipitation
4. Ultrasonic spray pyrolysis of purificated solution based on titanium with hydrogen reduction

Future research will be focused for the study of the mentioned single working steps in order to find optimal parameters for maximal titan extraction (more than 90 %) and production of metallic titanium!

CONCLUSION

Different hydrometallurgical operations are used for the recovery of crtitical elementts such as rare earth elements and titanium from eudialyte concentrate and bauxite residue! Using dry digestion process of eudialyte concentrate (1.6 % REE) at room temperature is possible to prevent silica gel formation and reach high leaching efficiency leading to a production od REE-carbonate with 30 % of REE as final product! A new dry digestion reactor was succesfully used for the treatment of eudialyte concentrate and Bauxite residues showing the high leaching efficiency for rare earth elements (more than 90 %) and titanium (smaller than 50 %). In order to increase a leaching efficiency of titanium the bauxite residue ist firstly treated in reduction process producing iron and slag! The separated slag was leached with sulphuric acid to transfer titanium in solution using conventional unit operations and intensified leaching operations! The final step is production of titanium based powders from pure titanium-based solutions using ultrasonic spray pyrolysis and hydrogen reduction!

ACKNOWLEDGEMENT

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