

Article

Recovery of Titanium from Red Mud Using Carbothermic Reduction and High Pressure Leaching of the Slag in an Autoclave

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Abstract: Red mud is a by-product of alumina production, which is largely stored in landfills that can endanger the environment. Red mud, or bauxite residue, is a mixture of inorganic compounds of iron, aluminum, sodium, titanium, calcium and silicon mostly, as well as a large number of rare earth elements in small quantities. Although certain methods of using red mud already exist, none of them have been widely implemented on a large scale. This paper proposes a combination of two methods for the utilization of red mud, first by carbothermic reduction and then, by leaching under high pressure in an autoclave in order to extract useful components from it with a focus on titanium. In the first part of the work, the red mud was reduced with carbon at 1600 °C in an electric arc furnace, with the aim of removing as much iron as possible using magnetic separation. After separation, the slag is leached in an autoclave at different parameters in order to obtain the highest possible yield of titanium, aiming for the formation of titanium oxysulfate and avoiding silica gel formation. A maximal leaching efficiency of titanium of 95% was reached at 150 °C using 5 mol/L sulfuric acid with 9 bar oxygen in 2 h. We found that high-pressure conditions enabled avoiding the formation of silica gel during leaching of the slag using 5 mol/L sulfuric acid, which is a big problem at atmospheric pressure. Previously silica gel formation was prevented using the dry digestion process with 12 mol/L sulfuric acid under atmospheric pressure.

Keywords: direct reduction; leaching; titanium; slag



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1. Introduction

Red mud (RM), also known as bauxite residue, is the sludge produced during the Bayer process of alumina production from bauxite ore. This sludge is a very complex mixture of compounds. With approximately 180 million tons produced annually, red mud has become one of the largest environmentally hazardous waste products, accumulating to a staggering 4 billion tons worldwide [1,2].

RM contains a high concentration of iron compounds, which can be significantly reduced through chemical reduction processes. Additionally, it has a notable amount of titanium compounds that can be utilized for titanium production. Furthermore, red mud contains rare earth elements and a significant amount of sodium oxide (Na₂O), the latter varying based on the washing efficiency in the Bayer process [3].

Due to its alkalinity and its chemical and mineralogical properties, red mud is classified as a toxic industrial waste that must be treated before discharge. Its environmental and health impacts include land use (conventional disposal of red mud occupies large areas of

potentially productive land), groundwater contamination, soil and plant properties (it impacts soil's physical properties and has ecotoxicological effects on plants), dust generation and health risks [4].

Over the years, researchers worldwide have extensively explored various economical methods for utilizing red mud. Investigated applications include [5–9]: stabilization material, adsorbents, catalyst preparation, metal recovery (such as iron, aluminum and titanium), radiopaque materials, ceramics, construction bricks, pigments and paints and cements.

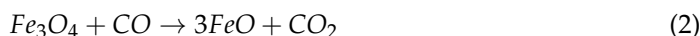
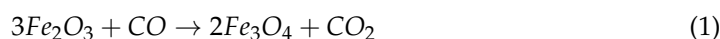
However, large quantities of red mud are never treated due to high costs and transport difficulties. For instance, it is challenging to neutralize red mud if the refinery is far from seawater or mines experiencing Acid Mine Drainage (AMD) issues. Additionally, red mud produced by refineries is unsuitable for long-distance transport, and many proposed methods for its treatment are not economical. One of the sustainable ways to utilize red mud is the recovery of titanium using reduction and leaching techniques [1,10,11].

Reduction of metallic oxides is a crucial process in metallurgy, involving the conversion of metal oxides into their respective metals. This process is vital for extracting pure metals from their ores and is achieved through various methods, primarily involving chemical reduction. The general principle of reduction involves a reducing agent that reacts with the oxygen in the metal oxide, removing the oxygen and leaving behind the pure metal [12–14].

Carbothermic reduction and hydrogen reduction are both important methods for reducing metal oxides to metals, each with distinct processes and environmental impacts.

Carbothermic reduction uses carbon as a reducing agent, typically in the form of coke, charcoal or coal. The process involves heating the metal oxide with carbon at high temperatures in a furnace. The carbon reacts with the oxygen in the metal oxide to form carbon dioxide or carbon monoxide, resulting in the extraction of pure metal. This method is widely used in the production of metals like iron, lead and zinc, and is fundamental to the steel-making industry. The advantages of carbothermic reduction include its well-established technology and efficiency for large-scale production. However, it has significant drawbacks such as high energy consumption due to the need for very high temperatures and substantial CO₂ emissions, which contribute to environmental pollution and climate change [12,15–17].

The carbothermic reduction process of RM may be represented as the following reactions [18]:



In contrast, hydrogen reduction uses hydrogen gas as the reducing agent. This method has potential applications in producing metals such as iron, copper and nickel, and is considered promising for green metallurgy and clean energy technologies. The key advantage of hydrogen reduction is its lower environmental impact, as the by-product is water instead of CO₂. It also aligns with sustainable and environmentally friendly practices. However, hydrogen reduction faces challenges such as the high cost of hydrogen gas production, which often relies on non-renewable energy sources, and the need for careful handling due to the flammability and explosiveness of hydrogen gas. Additionally, it is still in the development and optimization stage for large-scale industrial applications [19–23].

Overall, while carbothermic reduction remains the dominant method due to its established use and efficiency, hydrogen reduction offers a promising alternative that could significantly reduce environmental impacts and support sustainable development in the metallurgical industry.

Leaching is a crucial process in extractive metallurgy which is used to extract valuable metals from ores. It involves treating the ore with specific chemicals that react with the metal compounds to form soluble salts, while the impurities remain insoluble. These soluble salts can then be washed out from the ore and further processed to obtain pure

metal. The residual materials left behind after the valuable metals have been extracted are known as tailings [16,24–26].

However, leaching also has significant drawbacks, often resulting in large volumes of waste effluent and tailings. These waste products are frequently highly acidic or alkaline and can contain toxic substances, posing environmental and health risks [27,28].

Leaching processes can be applied in various ways, such as pressure leaching, atmospheric leaching and ultrasound-assisted leaching. Leaching is often performed at high temperatures to obtain better leaching efficiency. Despite its challenges, leaching remains a vital technique in the mining industry, providing a method to extract metals that might be otherwise economically or technically unfeasible to obtain through other means. Proper management and treatment of leaching effluents and tailings are essential to minimize the environmental impact and ensure the sustainability of this extraction method [28].

Several studies have explored methods for recovering valuable metals from red mud. One approach achieved high titanium (91%) and scandium (93%) recoveries through a multi-stage process involving leaching, hydrolysis and solvent extraction [29].

Another study utilized diluted sulfuric acid under atmospheric conditions, achieving a 64.5% recovery of titanium [30].

Additionally, a multi-step process involving pre-reducing-smelting and leaching achieved high recovery rates for iron (98.15%) and titanium dioxide (95.53%) with hydrochloric acid [14].

This paper presents a novel approach (Figure 1) for the utilization of red mud through the combination of carbothermic reduction and high-pressure autoclave leaching to recover valuable components, particularly titanium. By reducing red mud at 1600 °C and using magnetic separation to remove the iron, followed by optimized leaching under high-pressure conditions, the study addresses a key challenge in avoiding silica gel formation, which often hinders titanium recovery.

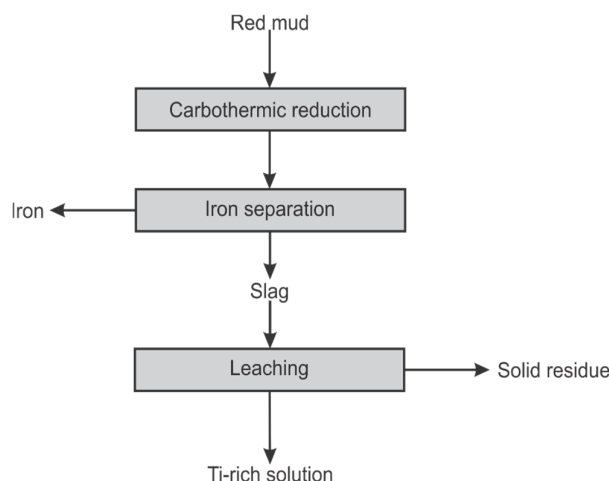


Figure 1. Design of research methodology.

Furthermore, the sustainability of this process lies in its ability to transform industrial waste into valuable raw materials. The reduction step not only removes the majority of the iron, which can be reused in the steel industry but also enriches other components like titanium, making them more accessible for further hydrometallurgical processing. Although carbothermic reduction uses high temperatures and carbon, it provides a means of significantly reducing red mud waste.

The main aim of this work is to treat our research strategy by combining the hydrometallurgical and pyrometallurgical treatment of red mud. The first step is the thermochemical modeling of carbothermic reduction in order to predict the chemical composition of produced slag, gases and metals.

2. Thermochemical Modeling

As it was already stated in the introduction part, thermodynamical modeling of the reduction of red mud is performed by the FactSageTM 8.0 software, GTT Technologies, Kohlscheid, Germany. The thermochemical modeling is performed for different temperatures and different amounts of reducing agents. All parameters of the simulations are shown in Table 1. All simulations are performed for 100 g of red mud input.

Table 1. Design of the experiments for thermochemical modeling.

Calculation No.	Temperature (°C)	Mass of C (g)	Calculation No.	Temperature (°C)	Mass of C (g)
1	1600	0	12	1700	0
2	1600	5	13	1700	5
3	1600	10	14	1700	10
4	1600	15	15	1700	15
5	1600	20	16	1700	20
6	1600	25	17	1700	25
7	1600	30	18	1700	30
8	1600	35	19	1700	35
9	1600	40	20	1700	40
10	1600	45	21	1700	45
11	1600	50	22	1700	50

As seen in Figure 2, during the reduction process, Fe_2O_3 is firstly reduced to FeO and, with the increase of reducing the agent's mass, it is further reduced to metal Fe . So, after the reduction process, there are two phases: a slag phase which is low in Fe , and the metal Fe phase. This iron metal phase can then be easily separated from the slag phase.

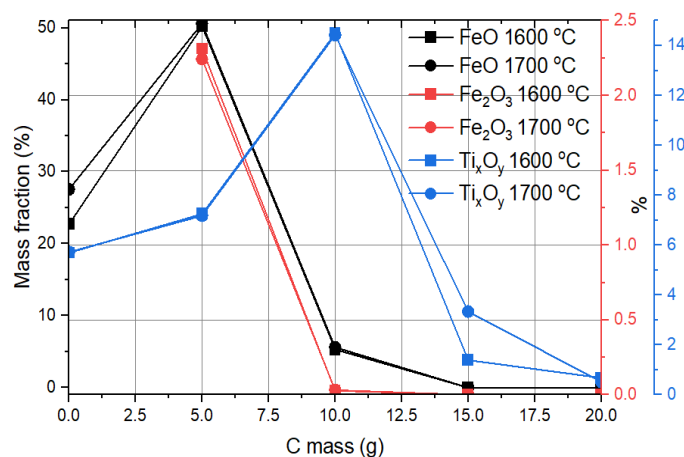


Figure 2. Dependence of the compound mass fractions on carbon content in slag.

Thermochemical modeling was essential for optimizing the carbothermic reduction of red mud. The model indicated that carbon is highly effective at reducing iron oxides, nearly to completion, as illustrated in Figure 2. However, increasing the carbon amount beyond a certain threshold leads to the reduction of titanium oxides to titanium carbide (TiC), which complicates the subsequent leaching process. Figure 2 shows that with 10 g of carbon per 100 g of red mud, the titanium oxide concentration in the slag reaches a maximum of 14.4%. Beyond this point, the concentration of titanium oxides dramatically decreases, indicating that excessive carbon leads to the formation of TiC rather than the desired titanium oxides. According to the thermochemical simulation, a carbon mass of 10 g per 100 g of red mud is optimal for the reduction process.

Figure 3 shows the different compositions of the metal phase in dependency on the mass of C . The concentration of Fe is almost 100% at a lower mass of carbon, but if the

carbon mass is increased, the Fe content decreases while other components, such as C, Si or titanium, are incorporated in the metal phase. So, the composition of the metal phase also shows that a quantity of 10 g C is suitable for the experimental trials of red mud reduction.

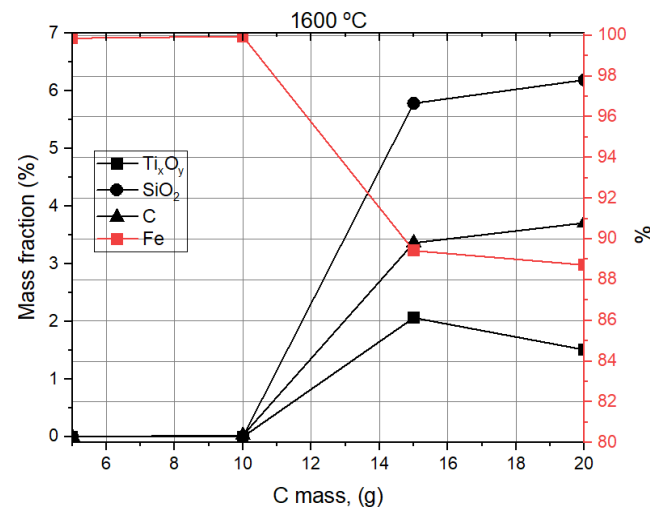


Figure 3. Composition of the metal phase depending on the reducing agent's mass.

Depending on the concentration of the reducing agent, it can be seen (Figure 4) that slag mass decreases as the mass of the reducing agent increases. The decrease can be explained because carbon is reducing the iron oxides in the red mud. The decrease is higher when the carbon mass is higher than 10 g because it also reduces the Ti oxides to TiC, which is an unwanted side product.

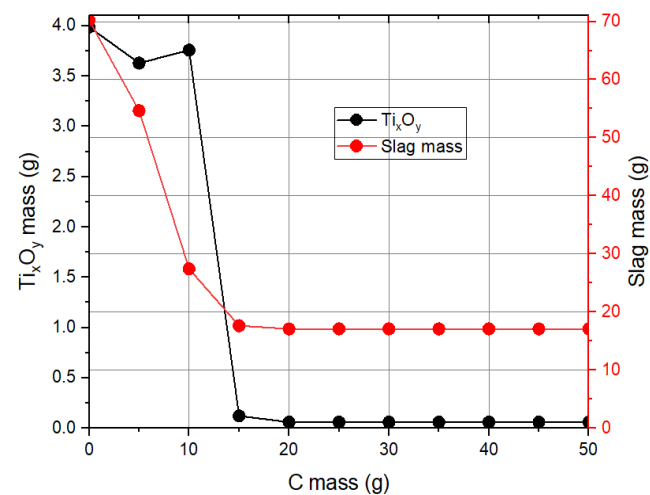


Figure 4. Dependence of slag and titanium oxide masses in the slag from reducing agent's mass.

3. Experimental Part

3.1. Material and Methods

In this work, red mud from the factory “alumina” d.o.o. was used as a raw material from Zvornik. The red mud was previously dried, ground and prepared for the reduction process. Red mud characterization was performed using an XRD analysis. The XRD analysis of red mud is shown in Figure 5.

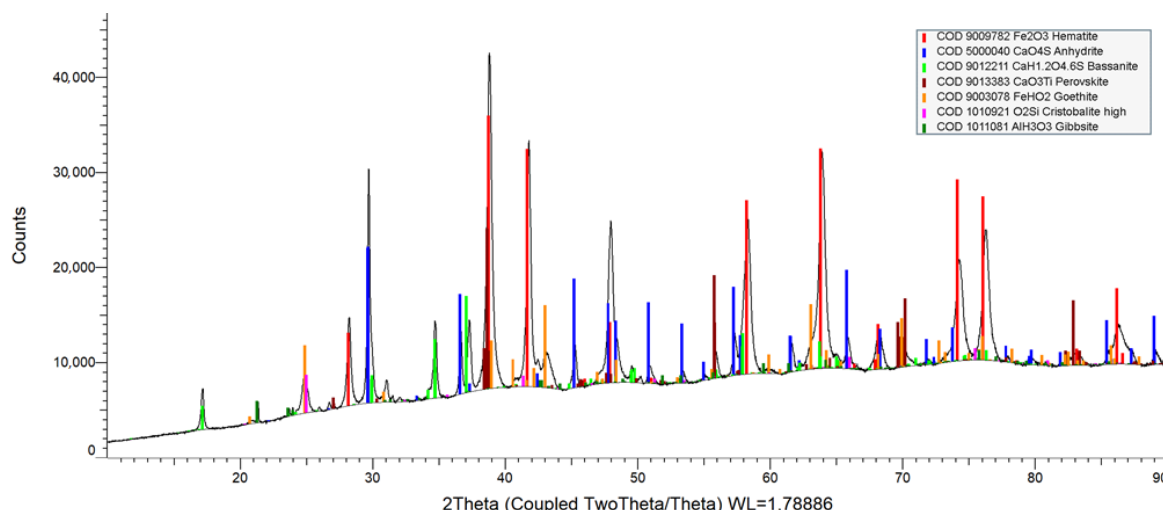


Figure 5. XRD Analysis of red mud.

As shown in Figure 5, the XRD analysis of red mud revealed the following phases: hematite, perovskite, cancrinite, ilmenite, calcite, diaspore, gibbsite and hydrogarnet. Iron is present in the structures of hematite and ilmenite. Titanium is found in the structures of perovskite and ilmenite, while aluminum is present in the structures of cancrinite, diaspore, boehmite, gibbsite and hydrogarnet. The composition of red mud is detailed in Table 2.

Table 2. Red mud composition.

Compounds	%	Compounds	%
Ignition loss at 1000 °C	8.32	Ga ₂ O ₃	0.225
SiO ₂	10.52	CuO	0.007
Fe ₂ O ₃	49.29	K ₂ O	0.159
Na ₂ O	2.45	Tl ₂ O ₃	0.088
TiO ₂	4.59	MnO	0.145
CaO	8.23	MgO	0.627
Al ₂ O ₃	12.03	NiO	0.034
Ag ₂ O	0.001	PbO	0.019
BaO	0.014	P ₂ O ₅	0.930
Cr ₂ O ₃	0.133	ZnO	0.016
Sc ₂ O ₃	0.011	V ₂ O ₅	0.135
Co ₂ O ₃	0.012	SrO	0.075

The reduction process took place in a DC electric arc furnace. Three kilograms of red mud and 10 g graphite per 100 g of red mud as the carbon-reducing agent are mixed and charged into the furnace. Because of the high viscosity of the slag after reducing the iron-oxides, the slag creates a foam. To lower the viscosity, CaO was added as a fluxing agent. The positive side effect of CaO is that the possible FeO from Fe₂SiO₄ is dissolved back into the slag with a positive change of activity of FeO. After charging, a holding time of 45 min was started to let the C react with the slag. After the holding time, the furnace was tapped to win the Fe metal phase, while the slag phase was left in the crucible.

The samples were separated mechanically using magnetic separation. The obtained products were analyzed by XRD. In Figure 6, the electric arc furnace's reduction of red mud (a) and the products of reduction (b) are shown.

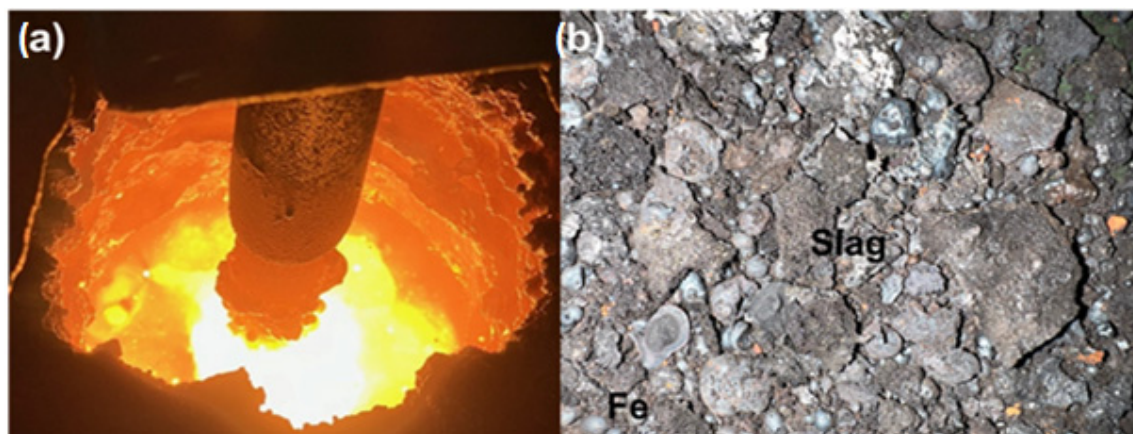


Figure 6. Electric arc furnace (a) and carbon-reduced red mud (b).

As can be clearly seen in Figure 6b, the reduction products are separated very easily, and the difference between slag and metallic iron droplets is clearly visible.

Leaching of the slag is performed in an autoclave in Buchi, Switzerland, which was designed for acid leaching (1.53 L, max pressure 200 bar, max. Temperature 270 °C) [31], as shown in Figure 7. This experimental set contains a heat exchanger with a thermostat, a mixer and probes for increasing and decreasing the pressure and also the possibility of taking a sample during the operation. The autoclave is connected to a computer and can be fully controlled by software that records all data during operation, which can later be used to process the results. Pressure in this autoclave was monitored using a manometer and digital sensors. The pressure in the system was formed from oxygen pressure (6, 9 bars) and water vapor pressure (total of 12–15 bar). The cooling of the autoclave was performed using a special system for cooling. The heating rate was 10 °C/min. The autoclave must be manually sealed with screws, and a pressure test must be performed before each operation.

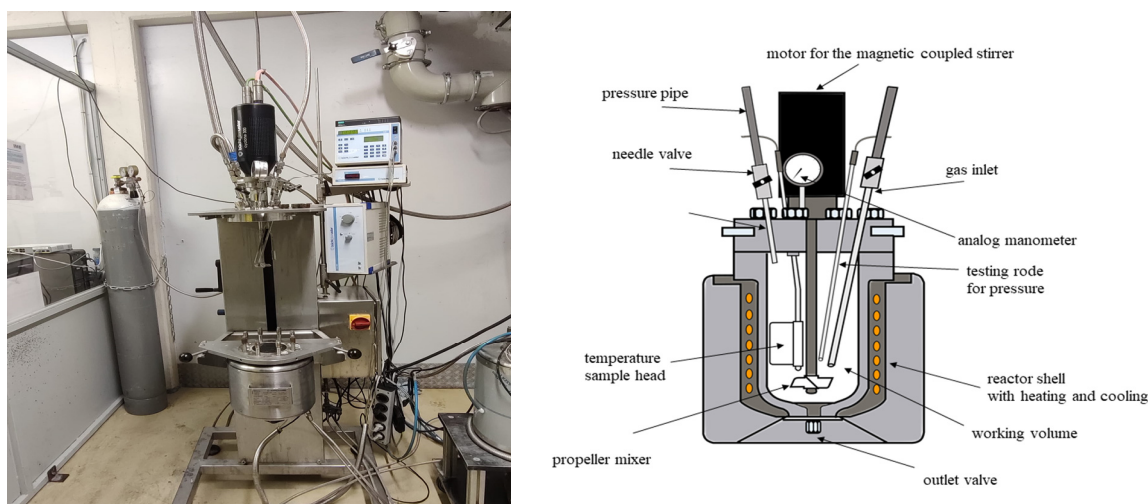


Figure 7. Experimental setup for leaching and schematic diagram of the autoclave.

The leaching process took place in an autoclave at elevated pressure and temperature. Sulfuric acid was used for leaching. The leaching process is followed by filtration, i.e., the separation of tailings from the solution. The solution was analyzed by ICP, and the solid residue with an XRD analysis. The design of the leaching is shown in Table 3.

Table 3. Design of leaching experiments.

Exp. No.	Temperature (°C)	Initial Pressure of O ₂ (bar)	Concentration of Acid (mol/dm ³)	Liquid:Solid Ratio (mL/g)	Time (min)
1	150	0 bar	0.5	10:1	30
2	150	6 bar	0.5	10:1	30
3	150	6 bar	2.5	10:1	60
4	150	6 bar	5	10:1	120
5	180	6 bar	5	10:1	120
6	150	9 bar	5	10:1	120

All experiments have been carried out in the laboratories of the IME RWTH.

In this paper, leaching is used to extract titanium from the earlier reduced slag and represents a combination of pyrometallurgical and hydrometallurgical methods of red mud processing in order to optimize and find the optimal processing process.

Pure oxygen was needed to react with titanium from the slag in order to form a dissolved form of titanium oxysulfate.

The reduced red mud powder samples were analyzed at room temperature with an X-ray powder diffraction technique using the Ultima IV Rigaku diffractometer (Rigaku, Tokyo, Japan), equipped with CuK $\alpha_{1,2}$ radiation, using a generator voltage of 40 kV and a generator current of 40 mA. The range of 10–100° 2 θ was used for all powder samples in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 1°/min, using a D/TeX Ultra-high speed detector (Rigaku, Tokyo, Japan). A glass sample carrier for sample preparation was used. The PDXL2 (Ver. 2.8.4.0) software was used to evaluate the phase composition and identification. All obtained powders were identified using the ICDD database.

An Energy-Dispersive X-Ray Spectroscopy (EDX) analysis was conducted using an Octane Plus-A system from Ametek-EDAX (2015 model, AMETEK Inc., Berwyn, PA, USA), with data analyzed through the Genesis V 6.53 software by Ametek-EDAX.

The chemical composition of the elements dissolved in the solution was determined using high-resolution inductively coupled plasma optical emission spectroscopy (ICP-OES). This technique enables the detection of elements with atomic mass numbers ranging from 7 to 250 (Li to U). The analysis was performed using a Spectro Genesis spectrometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany).

3.2. Results and Discussion

3.2.1. Carbothermic Reduction of Red Mud in an Electric Arc Furnace

As can be seen in Figure 8, thermodynamic calculations show that the experiment does not always confirm the theory. The experimentally obtained results show that less metal is obtained during reduction and that there is a greater loss of mass compared to the theory with the slag. The theoretically calculated and experimentally obtained results are close, and the differences can be because the thermodynamic calculations provide an idealized outcome based on equilibrium conditions and do not always account for kinetic factors. In reality, the reaction kinetics, including activation energy and reaction rates, could be slower, resulting in the incomplete reduction of the metallic oxide. Also, the presence of impurities in the raw materials or the reactants can lead to side reactions that are not accounted for in thermodynamic models.

In comparison to the red mud, slag shows fewer phases (Figure 9), reflecting a reduction of hematite due to the carbothermal reduction process. While perovskite and magnetite are still present, the absence of phases like hematite and gibbsite, replaced by gehlenite and more concentrated magnetite, suggests a significant transformation in the mineral composition. The slag appears more crystallized and less heterogeneous than the untreated red mud. The reduction process simplifies the mineral composition, concentrating titanium and other elements while iron-based phases are reduced or transformed.

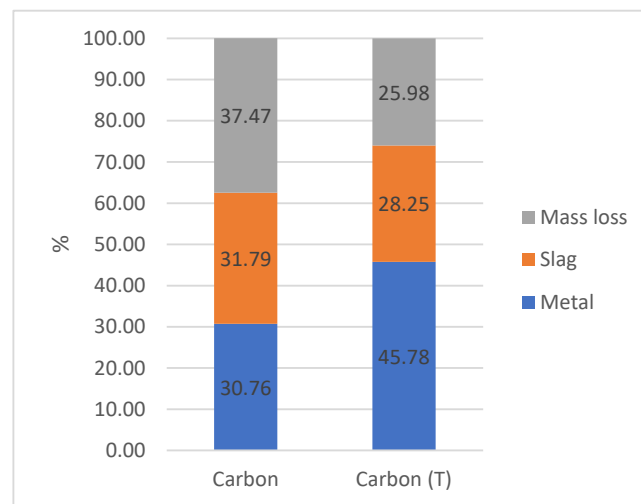


Figure 8. Thermodynamic calculation reduction of red mud (T) and experimentally obtained results.

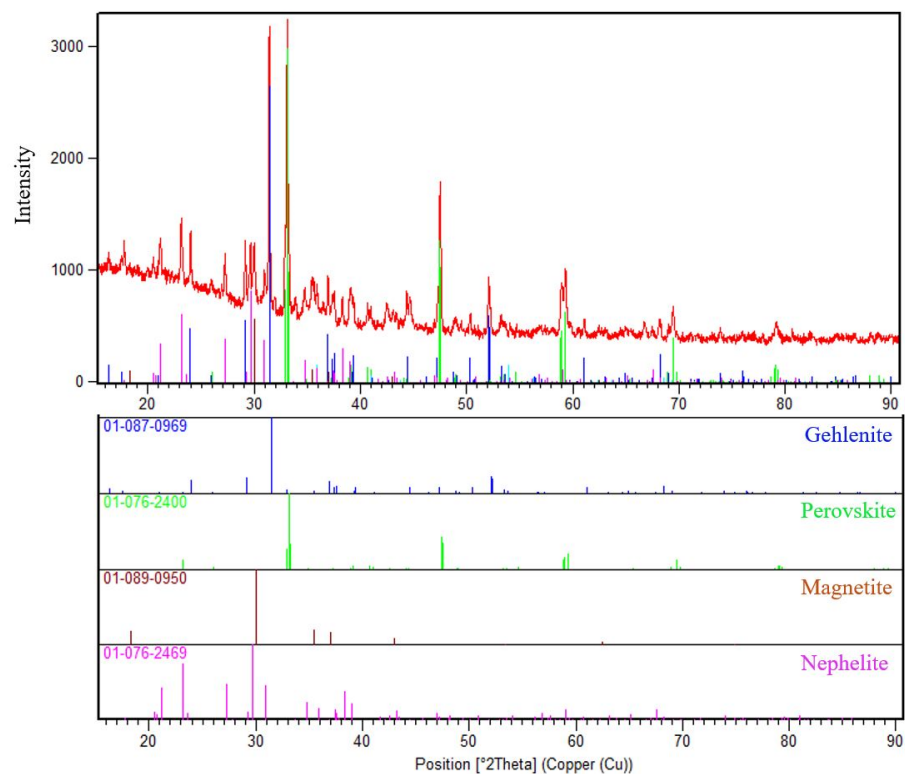
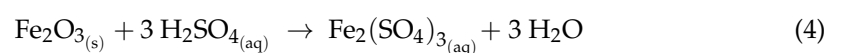
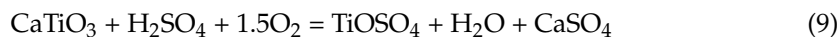
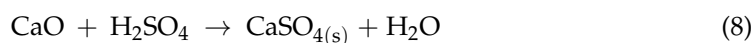
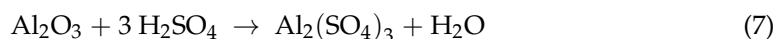


Figure 9. Diffractograms for slag reduced at 1600 °C. Identified minerals (gehlenite, perovskite and magnetite) with positions of diffraction maxima are shown in the lower part. The position of intensive diffraction maxima which do not overlap with the other maxima of the other minerals are shown in colored bands and used for comparison in mineral abundance.

3.2.2. Leaching

Leaching of slag containing mostly iron oxide is a very complex process, and its mechanism is very complicated. However, the reactions that can take place in the leaching process can be assumed as:





In Figure 10, leaching efficiency is shown for the different parameters.

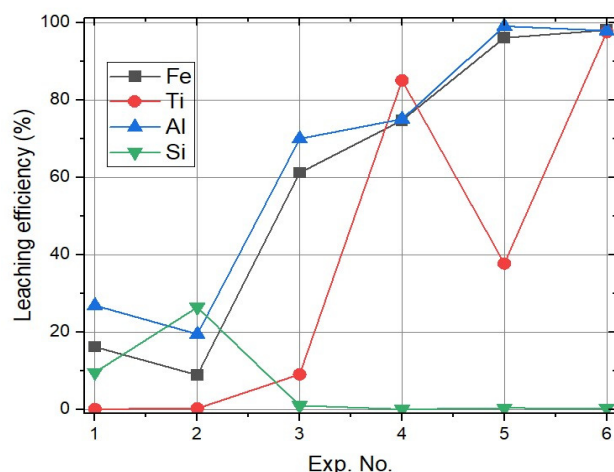


Figure 10. Leaching efficiency for different parameters (150 °C, 6–9 bar O₂, 0.5–5 mol/L H₂SO₄).

In the first three experiments, the selected parameters, such as temperature, oxygen pressure and sulfuric acid concentration, are not sufficient for the efficient leaching of titanium compounds. As the temperature increases, there is a noticeable rise in the concentrations of aluminum (Al) and iron (Fe) in the leachate, indicating enhanced leaching of these metals. However, the concentration of titanium (Ti) decreases significantly with the rise in temperature, which suggests that higher temperatures (180 °C) negatively affect the leaching efficiency of titanium under the given conditions. This indicates a possible inhibitory effect of temperature on titanium dissolution or a change in titanium's phase, making it less soluble.

On the other hand, the oxygen pressure plays a crucial role in the leaching efficiency of titanium. When the oxygen pressure is increased from 6 to 9 bars, there is a substantial improvement in titanium leaching efficiency. At an oxygen pressure of 9 bars, the leaching efficiency for titanium reaches 97.5%, demonstrating that oxygen pressure is a key parameter for optimizing the dissolution of titanium compounds. The presence of oxygen likely enhances the oxidative dissolution of titanium, making it more reactive and easier to leach in the acidic solution. Experiment number six enables the formation of titanium oxysulfate, using an increased oxygen partial pressure of 9 bar at 150 °C, using 5 mol/L of sulfuric acid, which is not present in the other mentioned experiments. The formation of titanium oxysulfate is favorable for industrial companies and the best way to recover titanium from a slag.

In addition to titanium, the leaching efficiencies for iron and aluminum are also high at increased oxygen pressures. This suggests that higher oxygen pressures not only promote the leaching of titanium but also support the dissolution of other metals like iron and aluminum, which are commonly found in similar phases within the mineral matrix.

As for silica (SiO₂), under conditions of high temperature, increased acid concentration and high oxygen pressure, the amount of leached silica is very low. This is a positive outcome because it prevents the problem of silica gelation, which can occur when too much silica is dissolved and precipitates out as a gel, causing processing difficulties. The low silica leaching under these conditions suggests that the process parameters are well-optimized to minimize silica dissolution while maximizing the leaching of target metals.

Table 4 provides the elemental analysis of the slag and solid residue from leaching experiment three (conducted at 1 h, 2.5 M H_2SO_4 , 6 bar O_2 , and a solid-to-liquid ratio of 10:1). It is evident from the data that the leaching efficiencies of all elements, especially titanium, are very low under these conditions. The low oxygen pressure (6 bars) appears to be the limiting factor, as evidenced by the much higher titanium leaching efficiency observed at 9 bars of oxygen pressure. The experiment also highlights that the other parameters, such as temperature and acid concentration, are not sufficient to achieve effective leaching without adequate oxygen pressure. This suggests that, while temperature and acid concentration play a role, oxygen pressure is the dominant factor influencing the dissolution of titanium in these experiments.

Table 4. Elemental analysis of slag and solid residue (experiment three).

Sample	Fe, %	Al, %	Si, %	Ti, %
Slag	5.27	4.14	2.72	5.59
Solid residue	4.49	3.82	2.48	5.18

Figure 11 shows the diffractogram of the solid residue after the leaching process, while Figure 5 illustrates the slag prior to leaching. A significant change in the mineralogical structure of the solid residue compared to the original slag is evident under the specified conditions (temperature of 150 °C, duration of 2 h, pressure 9 bar O_2 and 5 mol/L sulfuric acid concentration). As confirmed in Figure 11, the leaching process effectively dissolves elements such as titanium, iron and aluminum, leaving calcium, which remains in the form of calcium sulfate.

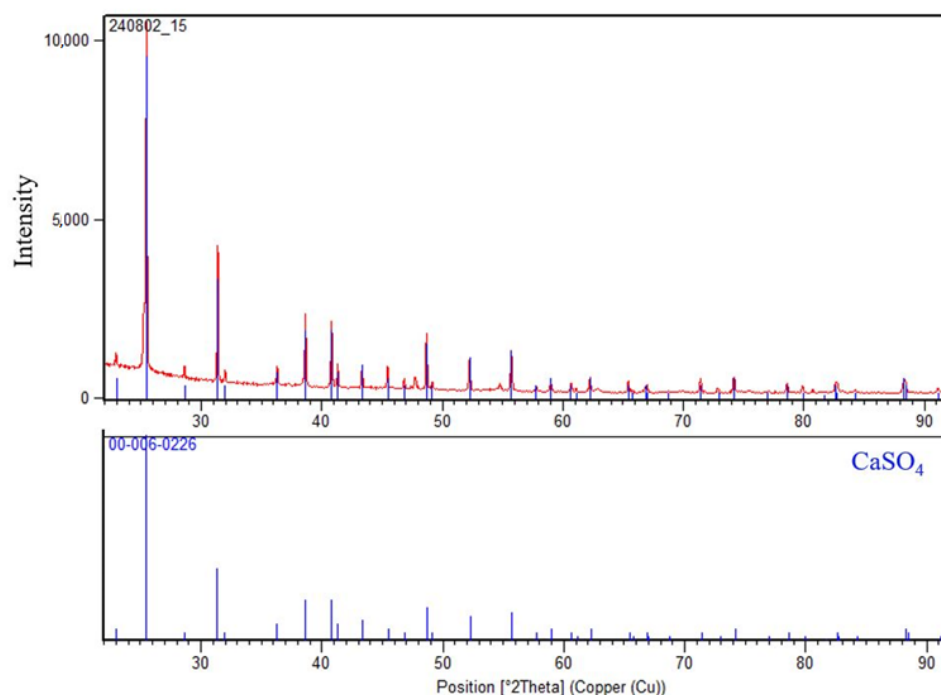


Figure 11. XRD diffractogram for solid residue after the leaching process at 150 °C, 9 bar O_2 , 2 h (experiment nine).

Figure 12 further supports the extraction of titanium from the slag, with the EDS analysis showing that only a trace amount of titanium (0.4%) remains in the residue. This confirms the effective dissolution of titanium during the leaching process. Additionally, the EDS analysis identifies elements such as aluminum, silicon and other minor components, in addition to calcium, sulfur and oxygen, suggesting the presence of an amorphous phase. Since this amorphous phase cannot be detected by XRD, it indicates

that a portion of the solid residue exists in a non-crystalline form, adding complexity to the post-leaching material and further explaining the material composition that XRD alone could not fully characterize.

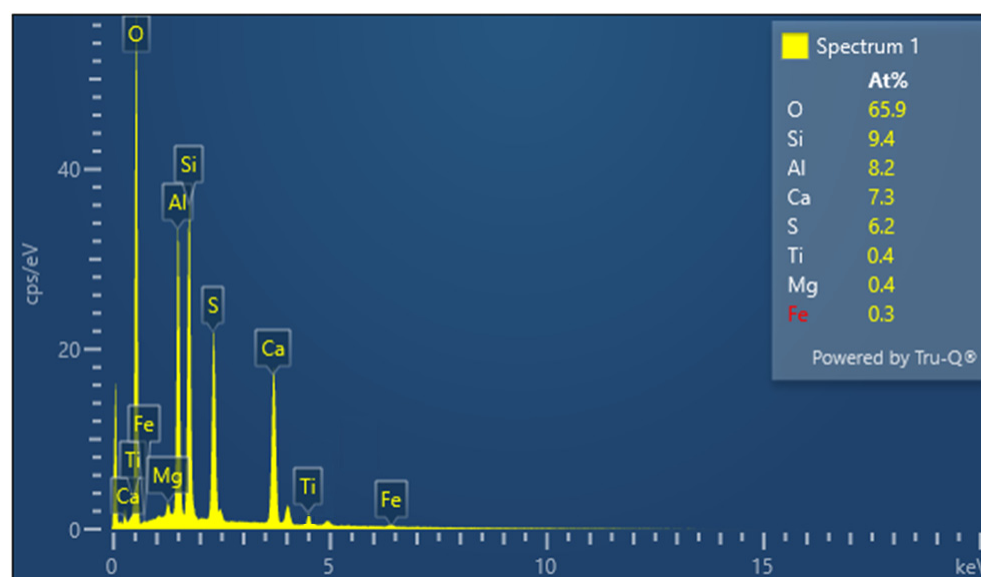


Figure 12. EDS analysis of solid residue (experiment nine).

4. Conclusions

This study successfully utilized red mud from the alumina d.o.o. factory in Zvornik as a raw material for the reduction and leaching processes. The reduction yielded easily separable products, with a clear distinction between slag and metallic iron, as evidenced in Figure 6b. Despite thermodynamic calculations predicting a certain yield, the experimental results indicated a lower metal recovery and greater mass loss during reduction, although the slag's theoretical and actual results were comparable (Figure 8).

In this study, we employ a method that first removes iron through reduction, effectively enriching the remaining components and making them easier to dissolve during subsequent leaching. The thermal treatment applied also disrupts the structural integrity of the red mud, facilitating the dissolution process. Furthermore, our approach addresses the common issue of silica gelation encountered in many other studies, ensuring a more efficient and effective leaching process.

The leaching phase, optimized for titanium recovery, revealed that increasing the oxygen pressure was crucial. At 9 bars of oxygen pressure, titanium leaching efficiency reached 97.5%. While higher temperatures improved aluminum and iron recovery, they decreased titanium extraction. This research underscores the importance of process optimization, particularly regarding oxygen pressure, to enhance the recovery of valuable metals such as titanium from red mud. The EDS and XRD analyses have confirmed the efficiency of titanium leaching. The novelty of this research lies in the innovative approach of leaching titanium in the form of oxysulfate using oxygen pressure, which significantly contributed to the high titanium recovery observed. Future investigations will explore the leaching efficiency of titanium from slag produced by plasma hydrogen reduction, aiming to compare different reduction methodologies in order to reach a maximal recovery of iron from red mud forming new slag without iron.

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