Sustainable recovery of metals from intermediate products

Održivo izdvajanje metala iz međuprodukata

Srecko Stopic[1,*], Dimitrije Anđić[2], Aleksandar Jovanović[2], Marija Simić[2], Miroslav Sokić[2], Željko Kamberović[3], Bernd Friedrich[1]

[1]*Institute for Process Metallurgy and Metal Recycling, RWTH Aachen University, Inzestrasse 3, Aachen, Germany*

[2]*Institute for Technology of nuclear and other mineral raw materials, Bulevar Franš D' Eperea 86, Belgrade, Serbia*

[3]*University of Belgrade, Faculty of Technology and Metallurgy,University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

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[*]*sstopic@ime-aachen.de*

Abstract

Fast industrialization and modern life have increased the demand for critical metals such as titanium and rare earth elements. On the other hand, high-grade ore natural reserves are just mosly used and their quantity is decreased. Therefore, alternative sources of valuabled metals such as intermediate products need to be considered and investigated. Massive amounts of industrial wastes are being generated annually in production of aluminium oxide and titanium oxides. The majority is sent to landfills, which eventually poses environmental challenges such as ecological contamination and health hazards to living beings. Such industrial wastes contain various major elements (Fe, Na, Ca, Si, Al, and Ti), whose improper disposal leads to adverse effects to human being and the environment. As a result, hydrometallurgical and pyrometallurgical operations such as leaching, filtration, precipitation, solvent extraction, crystallization and metal winning have received much attention due to the fact that they improve cost effectiveness over time and enable the metal recovery businesses to thrive profitably. This paper provides a state of art review on the current technologies existing for the recovery of titanium from industrial wastes streams to analyse the sustainability. Among the wastes, red mud, electric furnace dust and fly ash are some of the largest metallurgical generated wastes. Various metal recovery processes involve wastes from aluminium and titanium industry aiming separation and extraction of target metals. The current challenges of hydrogen reduction in pyrometallurgy, sustainable hydrometallurgy other advanced technologies such as ultrasonic spray pyrolysis are partially metnioned in this paper. The hydrometallurgical method, which involves dissolving and leaching, is aproven and successful process for recovering metals from ores and concentrates. The limitations placed on waste disposal and stringent environmental legislation require environmental-friendly metal recovery technologies. This review paper provides critical information that enables researchers to identify a proper research strategy for metal recovery from different industrial intermediate products.

Keywords: *titanium; recovery; metals; reduction; hidrometallurgy; pyrometallurgy; intermediate*

Izvod

Brza industrijalizacija i savremeni život povećali su potražnju za kritičnim metalima kao što su titan i elememti retkih zemalja. S druge strane, prirodne rezerve visokokvalitetnih ruda se uglavnom koriste, a njihova količina se smanjuje. Stoga, potrebno je razmotriti i istražiti alternativne izvore vrednih metala, kao što su međuproizvodi. Ogromne količine industrijskog otpada se godišnje stvaraju u proizvodnji aluminijum oksida i titanijum oksida. Većina se šalje na deponije, što na kraju *predstavlja ekološke izazove kao što su ekološka kontaminacija i opasnost po zdravlje živih bića. Takav industrijski otpad sadrži različite glavne elemente (Fe, Na, Ca, Si, Al i Ti), čije nepravilno odlaganje dovodi do negativnih efekata na ljude i životnu sredinu. Kao rezultat toga, hidrometalurške i pirometalurške operacije kao što su luženje, filtracija, taloženje, ekstrakcija rastvaračima, kristalizacija i dobijanje metala dobile su veliku pažnju zbog činjenice da vremenom poboljšavaju isplativost i omogućavaju preduzećima izdvajanje metala da profitabilno napreduju. Ovaj rad pruža pregled najsavremenijih istraživanja, koje postoje za dobijanje titana iz tokova industrijskog otpada kako bi se analizirala održivost. Među otpadima, crveni mulj, prašina iz elektrolučnih peći i leteći pepeo su neki od najvećih otpada koji nastaju u metalurškoj industriji. Različiti procesi dobijanja metala uključuju otpad iz industrije aluminijuma i titana sa ciljem odvajanja i ekstrakcije ciljnih metala. U ovom radu su delimično predstavljeni trenutni izazovi uključivanja redukcije vodonikom u pirometalurgiji, održivoj hidrometalurgiji i drugim naprednim tehnologijama kao što je raspršivanje rastvora u ultrazvučnom polju. Hidrometalurška metoda, koja uključuje rastvaranje i separaciju, je dokazan i uspešan proces za dobijanje metala iz ruda i koncentrata. Ograničenja koja se postavljaju u pogledu odlaganja otpada i strogi propisi o zaštiti životne sredine zahtevaju ekološki prihvatljive tehnologije izdvajanja metala. Ovaj rad pruža ključne informacije koje omogućavaju istraživačima da identifikuju odgovarajuću istraživačku strategiju za dobijanje metala iz različitih industrijskih međuprodukata.*

Ključne reči: *titan; izdvanje; metal; redukcija; hidrometalurgija; pirometalurgija; međuproizvod*

Introduction

The industrial production of aluminium oxide and titanium dioxide is associated with the generation of massive volumes of industrial residues that present both environmental challenges and opportunities for resource recovery. Among these, bauxite residues or red mud by-product of alumina production through the Bayer process, and tionite, a residue from titanium dioxide (TiO_2) manufacturing from ilmenite via the sulfate process, represent two of the most significant metallurgical wastes [1]. Their safe disposal remains a pressing global issue, yet their chemical composition and mineralogy also make them promising secondary resources for metal recovery and other industrial applications [2].

Red mud is generated in quantities ranging from 0.5 to 2.0 tons per ton of alumina produced, with global stockpiles estimated to exceed 5 billion tons as of 2020. Its characteristic red color derives from a high iron oxide content, but it also contains residual alumina, silica, titanium dioxide, and alkali oxides. The material is highly alkaline (pH 9–13), which poses serious risks of soil and groundwater pollution, corrosion of infrastructure, and toxicity to ecosystems [3]. Furthermore, its fine particle size makes dusting a challenge in dry storage. Traditionally managed by slurry disposal, dry stacking, or solar drying, red mud continues to be classified as a hazardous material due to its composition and handling requirements. Nevertheless, extensive research has highlighted its potential utilization in applications such as stabilization materials, adsorbents, catalysts, ceramics, pigments, cements, and particularly in the recovery of valuable metals such as iron, aluminum, and titanium [4–5].

Tionite, on the other hand, originates mainly from the sulfate process of TiO_2 production, where undissolved ore residues are separated after leaching, as shown at Figure 1:

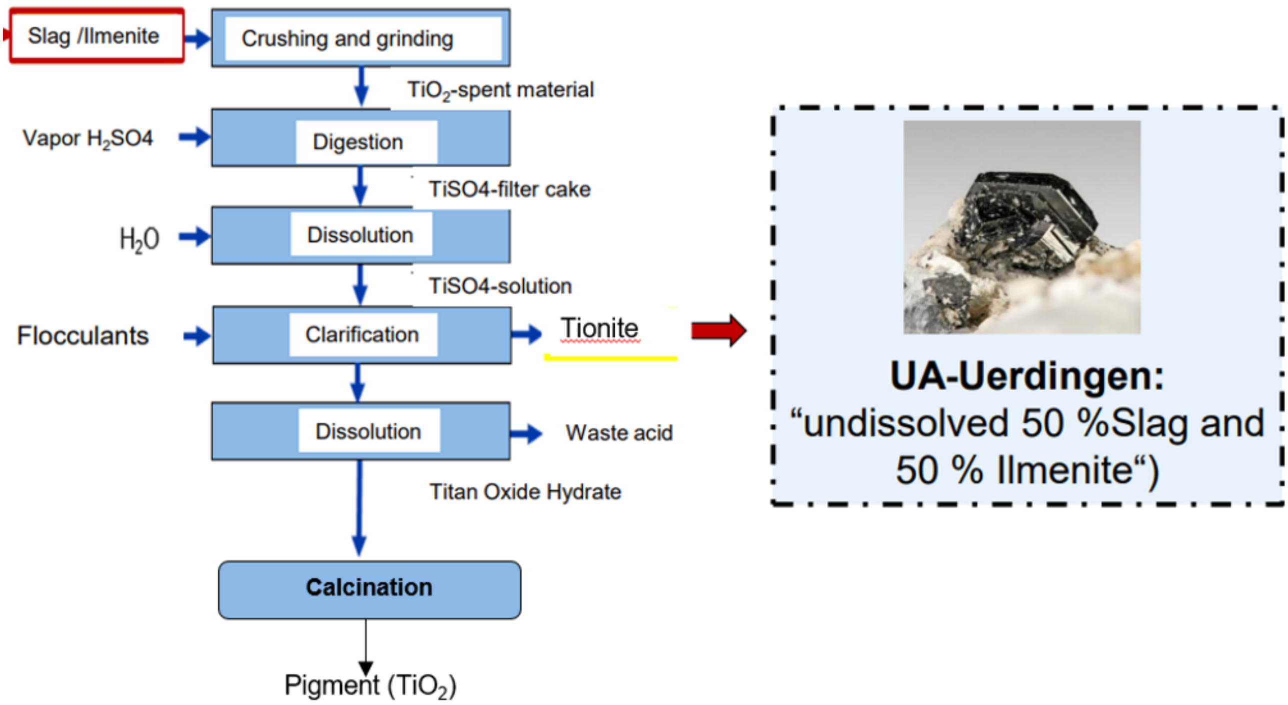

Figure 1. *Formation of tionite during production of titanium oxide using sulphate process.*

These residues are complex, consisting of unreacted titanium compounds, iron oxides, other metal oxides, and often entrapped sulfuric acid. This combination makes tionite both environmentally problematic and difficult to process. While the chloride process also generates titanium-bearing residues, tionite from the sulfate route is particularly abundant. Due to its high TiO_2 content and rutile-dominated mineralogy, tionite represents a potential secondary resource, though its stability makes direct utilization challenging. Approaches investigated for tionite valorization include hydrometallurgical leaching for titanium recovery, pyrometallurgical conversion into titanium-rich slags, reintegration into TiO_2 production, and applications in environmental remediation, construction materials, or catalyst production. Despite these efforts, large-scale solutions remain underdeveloped, and innovative strategies are required to both mitigate environmental risks and unlock its resource potential [6].

A promising pathway for the simultaneous valorization of red mud and tionite is carbothermal reduction [7]. This process enables selective reduction and separation of iron, addressing one of the key obstacles for their utilization. In the case of tionite, the addition of calcium oxide not only acts as a fluxing agent to facilitate reduction but also promotes the formation of calcium titanate, thereby disrupting the stable rutile structure and preparing the residue for downstream processing. For both residues, the reduction step serves as a preparatory stage for subsequent leaching, allowing recovery of valuable metal components while stabilizing the remaining slag.

Our general study focuses on the combined treatment of red mud and tionite using hydrometallurgical and pyrometallurgical method aiming to: (i) remove iron efficiently, (ii) destabilize the stable titanium phases in tionite, and (iii) prepare a leachable slag suitable for further resource recovery such as ultrasonic spray pyrolysis and titanium winning using molten salt electrolysis or aluminothermic reduction, as shown at Figure 2.

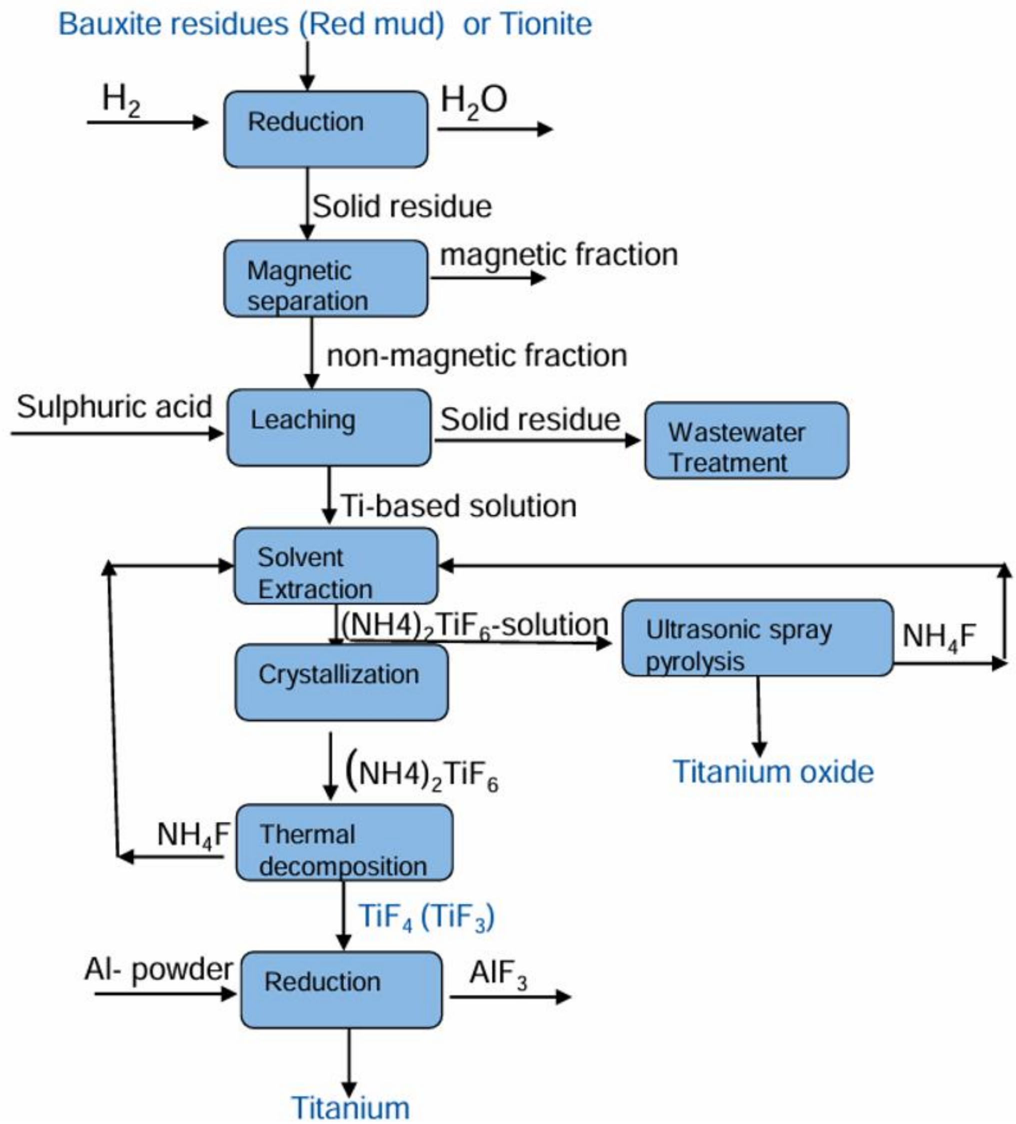

Figure 2. *Sustainable recovery of metals from intermediate products.*

In our previous work [8] dissolution of red mud and tionite was performed using high pressure leaching conditions, what is very expensive prosess. Because of all this, new investigations were carried out at low temperatures and atmospheric pressure in a glass reactor and are presented here. This paper will be focused on hydrometallurgical treatment of the intermediate from aluminium and titanium industry after pyrometallurgical treatment aiming the transfer of titanium in solution.

Experimental

Material

Different types of materials were used for the leaching under an atmospheric pressure at 90 °C: 1. Tionite (solid residue from Sulfate process for production of titanium oxide) ; 2. MAG.TION.-sample obtained after hydrogen reduction of tionite at 920°C (magnetic fraction); 3. EAF (TION)- tionite after reduction in an electric arc furnace at 1460°C , 4. red mud (dried solid residues after leaching of bauxite with sodium hydroxide in an autoclave in Nova Alumina Zvornik) and 5. Pure titanium oxide produced by VENATOR, Germany. Some used samples were shown at Figure 3.

Figure 3. *The mostly used samples for leaching experiments.*

The chemical analysis of all samples is shown in Table 1.

Table 1. Chemical analysis of samples for leaching under an atmospheric pressure

Elements (%)	Mg	Fe	Ca	Ti	Si	Al
Tionite UA	1.78	5.90	1.95	29.42	25.96	3.06
Magnetic fraction after H_2 reduction (MAG.TION)	1.74	6.10	2.16	27.36	25.43	2.94
Slag after smelting of tionite in an electric arc furnace EAF(TION)	1.41	0.75	13.43	22..68	23.95	2.44
Red mud	0.38	34.50	5.88	2.75	4.90	3.18
Titanium oxide				60		

Stopic et al. [3,5] reported that XRD-analysis of red mud confirms mostly the presence hematite and other very stable oxides such as perovskite, calcite, diaspore, boehmite, anhydride.The sample of tionite shows the presence of dominant phases which are rutile, Mg-Ti oxide, and kennedyite (iron titanium magnesium oxide). Rutile appears to be the dominant phase. The presence of Mg-Ti oxide suggests the formation of a complex phase that could influence the reactivity of titanium during leaching. Kennedyite which is a less common phase is also detected.

Experimenal Setup

The experiments were performed using leaching glass reactor with connected thermostat for the regulation temperature in an acidic solution, as shown at Figure 4. Different leaching agents such as sulphuric acid, hydrochloric acid, sodium hydroxide, and metasulfonic acid (MSA) are used at room temperature, 50°C and 90 °C using different solid/liquid ratio in duration of 4 and 6 hours.

Figure 4. *Experimental setup for the leaching experiments.*

After leaching experiments the suspension was filtrated using the equipment, as shown at Figure 5.

Figure 5. *Experimental setup for the filtration experiments.*

ICP-OES Agilent 5000 ICP-OES equipped with advanced features for enhanced performance was used for analysis of solid and liquid. This system is very efficient and known for high sensitivity and wide dynamic range, detecting and quantificating not just major but also trace elements. Advanced optics and detector technology ensure reliable and reproducible results for almost every element. EDS analysis was performed using an Octane Plus-A detector by Ametek-EDAX. This detector is very popular and has high-resolution capabilities and sensitivity, making it suitable for detailed elemental analysis.

Experimental parameters

Two experimental set were performed and presented in Table 2 and 3. The influence of concentration of leaching agent and reaction temperature on the leaching efficiency of different samples was analysed in first set of experiment. In the second set of experiment the influences of solid/liquid ratio was additionally analyzed in order to improve the leaching efficiency.

Table 2. First set experiments performed using 50 g in 1L solution in 6 hours

Exp. Number	Sample	Concentration of leaching agent (mol/L)	T (°C)
1.	EAF (TION)	2.5 H_2SO_4	90
2.	EAF (TION)	2.5 HNO_3	90
3.	EAF (TION)	5.0 NaOH	90
4.	EAF (TION)	2.5 MSA	25
5.	TiO_2	2.5 H_2SO_4	90
6.	MAG.TION.	2.5 H_2SO_4	50
7.	MAG.TION.	2.5 HNO_3	50
8.	MAG.TION.	2.5 MSA	90
9.	TIONITE	2.5 H_2SO_4	90
10.	TIONITE	2.5 HNO_3	90
11.	TIONITE	2.5 MSA	90
12.	MAG.TION.	3.0 HNO_3	90
13.	TiO_2	1.0 M HCl	90

Table 3. Second set experiments performed at 90 °C in 6 hours

Exp. Number	Sample	Concentration of leaching agent (mol/L)	Mass of sample (g)
1.	EAF (TION)	1.0 HCL	50
2.	EAF (TION)	1 H_2SO_4	50
3.	EAF (TION)	1 H_2SO_4	25
4.	MAG.TION.	1 H_2SO_4	50
5.	TIONITE	1 H_2SO_4	50
6.	MAG.TION	2.5 H_2SO_4	25
7.	EAF (TION)	2.5 HCl	50
8.	MAG.TION	2.5 HCL	50
9.	TIONITE	2.5 HCl	50
10.	EAF (TION)	2.5 HCl	25
11.	MAG.TION	2.5 HCl	6

Results and Discussion

The obtained results for leaching efficiency of different samples were presented at Figure 6.

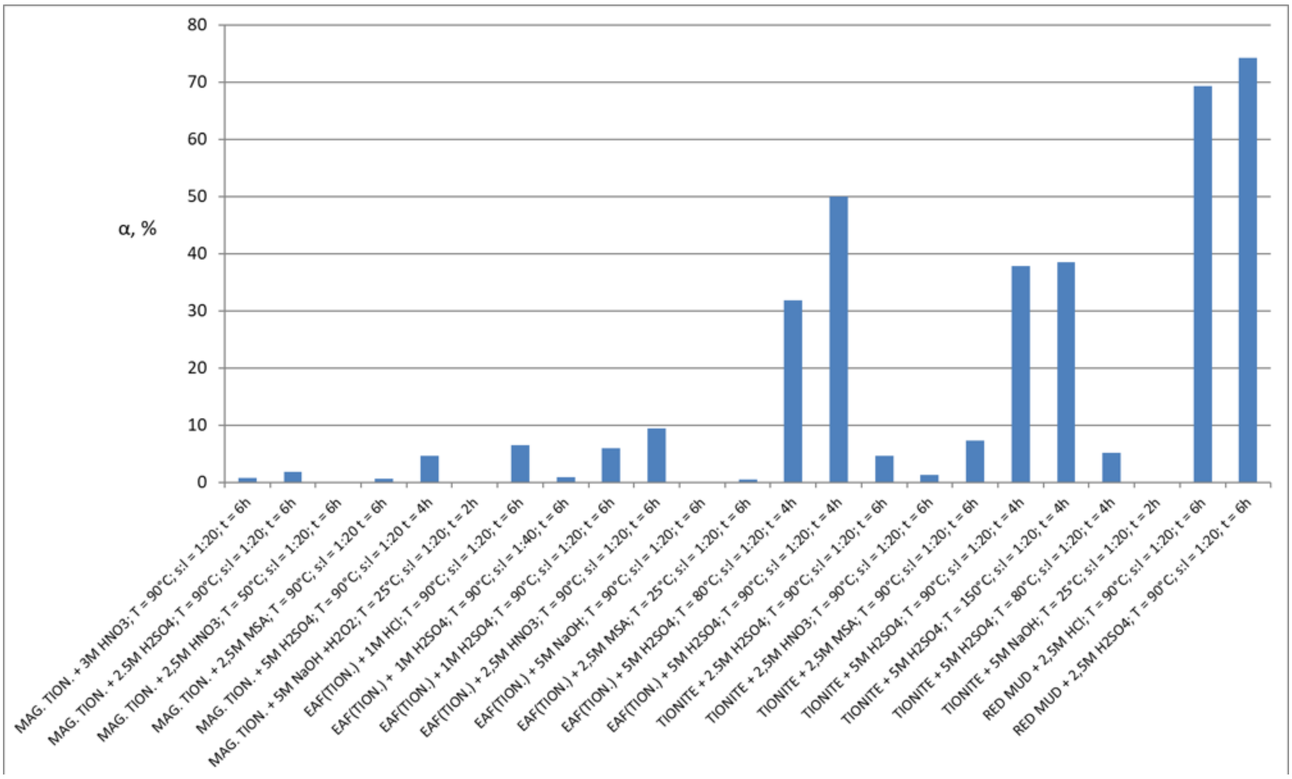

Figure 6. *Leaching efficiency of titanium for different samples.*

Based on the obtained results of leaching of the initial samples in the specified systems, tiitanium oxide is not soluble under an atmospheric pressure at room temperature and 90 °C. The best titanium leaching results were achieved during the leaching of red mud in HCl (69.3%) and H_2SO_4 (74.3%) at 90 °C in 6 hours. Lower, yet still significant titanium leaching results were achieved under the following conditions:

- EAF (TION) + 5M H_2SO_4; T = 90 °C; s:l = 1:20; t = 4h (49.9%);
- TIONITE + 5M H_2SO_4; T = 150 °C; s:l = 1:20; t = 4h (38.5%);
- TIONITE + 5M H_2SO_4; T = 90 °C; s:l = 1:20; t = 4h (37.8%);
- EAF (TION) + 5M H_2SO_4; T = 80 °C; s:l = 1:20; t = 4h (31.8%)

It was observed that temperature significantly affects the leaching degree, as confirmed by the presented results. The presence of very stable titanium oxide (rutile) in tionite is main reason for unsufficient leaching efficiency. Formation of new Ti-bearing phases (pseudobrookite, perovskite, titanite) demonstrates the impact of CaO and reduction in altering the rutile structure, what is suitable for the leaching process [5]. The use of methanesulfonic acid and sodium hydroxide showed poor dissolution of titanium from the samples. The most optimal solid/liquid ratio for dissolution is 1:20.

Conclusion

The obtained results confirm that the best dissolution of red mud is by cutting sulfuric acid to 90% in 6 hours. The LEAST dissolution is for pure titanium oxide. The conversion of titanium oxide during reduction processes leads to an increase in the efficiency of extraction due to the conversion of titanium into soluble forms. However, these results are lower than those obtained due to high pressures in the autoclave at 150°C. In general, the use of sulfuric acid gives the best results of dissolving titanium and various samples in relation to the use of hydrochloric acid, nitric, and metasulfonic acid.

By integrating metallurgical and environmental considerations, this work contributes to the development of sustainable strategies for the utilization of these major industrial intermediate products.

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