Research Proposal

EXTRACTION OF TiO_2 FROM ILMENITE FOUND IN AVUWAKKALU RED EARTH

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Abstract

The Red Earth (RE) deposits along the northwest coastal belt of Sri Lanka, particularly in the Aruwakkalu region, are geologically significant due to their high content of heavy minerals, including ilmenite. The RE contains 8–10% ilmenite, with iron (Fe) and aluminum (Al) as surface impurities, and is characterized by high concentrations of heavy minerals and rare earth elements. Hence, this study aims to extract titanium dioxide (TiO_2) from ilmenite found in the red earth of the Aruwakkalu area. Initially, RE samples will be collected from the limestone quarry site of INSEE Cement Lanka Ltd. near Aruwakkalu in Puttalam. Physical separation including Humphrey Spiral Separation, Shaking Table Separation, and Electromagnetic Separation, will be employed to isolate ilmenite from the RE. Nevertheless, traditional TiO_2 extraction require high temperatures and the hazardous chemicals, resulting in high operational costs and significant environmental harm. Therefore, this study proposes HCl acid leaching in the presence of a metallic iron (Fe) reductant and magnesium sulfate ($MgSO_4$) additive, which has been shown to enhance Fe dissolution and reduce Ti recovery. In addition to this, NaOH alkaline leaching will be applied to remove aluminum impurities, and EDTA will be used for selective iron removal. The study will use optical microscopy, X-ray fluorescence (XRF), and X-ray diffraction (XRD) for sample characterization to assess the purity of the extracted TiO_2. By optimizing both physical and chemical separation techniques, this research aims to develop a more environmentally sustainable and cost-effective method for extracting high-purity TiO_2 from ilmenite in Sri Lankan red earth.

Keywords: Red Earth, Ilmenite, Titanium dioxide

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Section 1
Introduction

Ilmenite, iron-black, heavy, metallic oxide mineral, composed of iron and titanium oxide ($FeTiO_3$), that is used as the major source of titanium. It forms solid-solution series with geikielite and pyrophanite in which magnesium and manganese, respectively, replace iron in the crystal structure [1]. With the intention of advancing the economy, government-owned Sri Lanka Mineral Sands Ltd. has begun the rapid removal of ilmenite from the coastal regions of Mullaitivu District's Kokkulai, Kokkuthoduvai, Nayaru, Muhathuvaram, puttalam, and Chemmalai. Ilmenite is of great importance in making solar cells, marble for flooring and paint. This natural resource, which is not processed in factories in Sri Lanka, is exported to Australia and China at great environmental cost [2].

The Red earth (RE) deposit that exists along the northwest coastal belt of Sri Lanka is a significant geological formation. Fine-grained sand coated with iron-aluminum oxides brings the characteristic reddish color and the presence of important heavy minerals such as magnetite, ilmenite, and rutile enhance its economic importance [4]. A layer of red soil had been clearly observed in the mining of limestone in Aruwakkalu area. The RE contains 8-10 percent of ilmenite [3] with impurities such as Fe and Al in its surface. The results indicate two types of clustering of RE in the two regions; moderately sorted (σ = 0.8) RE in Puttalam region. Rounded quartz grains with bulbous edges and disc-shaped concavities resemble the features of dune sand in Puttalam RE. Significantly higher amounts of heavy minerals, clay minerals (kaolinite) and lighter rare earth elements (La, Ce, Pr, Nd, Sm) are found in Puttalam RE than in Mannar RE [4].

Sulfate and Chloride processes are two main techniques that have been used in extracting TiO_2 from ilmenite. Both of these conventional methods involve high temperatures that go up to 1000 ºC and usage of highly hazardous concentrated sulfuric and hydrochloric acids. Therefore, both the operational cost and environmental impact of these processes are remarkably high [5-6]. The problem faced in the use of ilmenite is its complex mineral structure which causes difficulties at the processing stage [7] and to remove surface impurities minerals such as Fe and Al.

Therefore, in this study, the synthesis of TiO2 from ilmenite in Aruwakkalu using, the methods such as alkaline leaching and EDTA selective iron removal.

Section 2
Literature Review

Ilmenite is a common accessory mineral in igneous rocks, sediments, and sedimentary rocks in many parts of the world. Apollo astronauts found abundant ilmenite in lunar rocks and the lunar regolith. Ilmenite is a black iron-titanium oxide with a chemical composition of $FeTiO3$ [8]. Ilmenite is the primary ore of titanium [8], a metal needed to make a variety of high-performance alloys. Most of the ilmenite mined worldwide is used to manufacture titanium dioxide, $TiO2$, an important pigment, whiting, and polishing abrasive.

Ilmenite is the primary ore of titanium metal. Small amounts of titanium combined with certain metals will produce durable, high-strength, lightweight alloys. These alloys are used to manufacture a wide variety high-performance parts and tools. Examples include: aircraft parts, artificial joints for humans, and sporting equipment such as bicycle frames. About 5% of the ilmenite mined is used to produce titanium metal. Some ilmenite is also used to produce synthetic rutile [8] a form of titanium dioxide used to produce white, highly reflective pigments. Ilmenite is the main source of mineral feedstock for titanium dioxide which is used in paints, paper, toothpaste, sunscreen and even food colouring [9]. The global ilmenite market size was estimated at USD 11.48 billion in 2022 and is expected to expand at a compound annual growth rate (CAGR) of 3.9% from 2023 to 2030 [10]. The growing use of titanium dioxide products in several industries such as paints & coatings, paper & pulp, plastics, and cosmetics has created a strong demand for ilmenite.

Statistical data reveal that 98% [11] of manufacturers in China use the sulphate process for the production of $TiO2$. The process can be categorized into four main stages, namely, acid digestion, hydrolysis, calcination and post-treatment. In short, the initial step of the process involves converting the raw material, ilmenite, into titanium-sulphate through acid digestion. The resulting compound is then hydrolysed to yield hydrous titania, $TiO2{\cdot}H2O$. Finally, the hydrated form is subjected to calcination to form $TiO2$. Based on statistical data from the industry, the chloride process accounts for 60% of worldwide $TiO2$ production [12].

The major steps involved in the chloride process, which is a continuous process and utilizes higher-grade rutile as the starting material to produce TiO2. These stages include chlorination, purification (condensation), oxidation and post-treatment. Because of the high sensitivity of TiCl4 vapour to moisture, it is crucial to maintain an extremely dry environment in the reaction chamber. The key feature which differentiates the hydrochloride process from the sulphate process is the use of concentrated hydrochloric acid to digest the ilmenite raw material where it has been estimated that 80% of titanium and iron in ilmenite can be dissolved [11].

The main advantage of the sulphate process is the feasibility of isolating TiO_2 either in the anatase or rutile crystalline phase, depending on the calcination temperature [11]. In chloride process titanium dioxide can be obtained through the chloride process with a higher purity only in the rutile phase without anatase contaminants [11]. In hydrochloride process It is also reported that HCl is more advantageous than other acids for the digestion process because it can be retrieved from liquid effluent through pyro-hydrolysis.

The main drawback is the environmental damage caused by the waste of the sulphate process. For instance, highly concentrated (98%) sulphuric acid is used to collapse the ore material. Furthermore, the use of water in the hydrolysis step consequently generates a huge amount diluted sulphuric acid with a lower concentration of approximately 20% [11] [5]. Since the chloride process is able to produce only the rutile form of TiO_2, the industries which require the pure anatase form will not be benefited from this extraction process. Furthermore, the raw material of this process should be higher grade natural or synthetic rutile, with low contents of MgO and CaO, which is more expensive and rarely available compared to ilmenite [**12**]. The use of concentrated acid in hydrochloride process is still problematic as in the sulphate process. As the other major drawback, the nitric acid oxidation and TOA solvent extraction steps make the overall process more complex [11].

Aruwakkalu fossil bed is a part of Sri Lanka's Jaffna limestone, which underlies the whole of Jaffna Peninsula and extends southwards mostly along the west coast. Previous authors have suggested that Aruwakkalu contains a rich assemblage of vertebrate and invertebrate fossils. We sought to confirm the Burdigalian age of this northwestern Miocene deposit at Aruwakkalu on the basis of the foraminifer

Pseudotaberina malabarica, an index fossil of the Burdigalian stage [13]. Fine-grained sand coated with iron-aluminum oxides brings the characteristic reddish color and the presence of important heavy minerals such as magnetite, ilmenite, and rutile enhance its economic importance. The results indicate clustering of RE, moderately sorted (σ = 0.8) RE [4] in Puttalam region Rounded quartz grains with bulbous edges and disc-shaped concavities resemble the features of dune sand in Puttalam RE. Magnetite and ilmenite are found as the most abundant heavy minerals in this regions. However, significantly higher amounts of heavy minerals, clay minerals (kaolinite) and lighter rare earth elements (La, Ce, Pr, Nd, Sm) are found in Puttalam RE. Therefore, though the Sri Lankan RE is considered as a single unit, it has spatial variation in geochemistry, mineralogy and texture [4] [14].

Geochemical results showed the enrichment of TiO_2, Fe_2O_3, Al_2O_3, and trace elements, and depletion of other major oxides such as Na_2O, K_2O, MnO, MgO, CaO, and P_2O_5. Consequently, it suggests the abundance of ilmenite, leucoxene, rutile, sillimanite, garnet, and rare earth element (REE)-bearing heavy minerals in potential placer deposits [15].

Spiral separation is a common gravity separation technique used to separate heavier minerals from lighter ones based on their different specific gravities. Initially, sample slurry will be prepared by adding water to the fine particle of red earth. Shaking table separation is another gravity-based technique, similar to spiral separation, used to concentrate heavier minerals from lighter ones based on their density differences. Electromagnetic separation utilizes the magnetic properties of minerals to separate them from nonmagnetic minerals. Here, ore mixture is passing through a magnetic field created by electromagnets and the field selectively attracts magnetic or weakly magnetic minerals, separating them from non-magnetic minerals. Ilmenite is a weakly magnetic mineral and it can be separated from other available non-magnetic minerals in red earth.

The presence of ilmenite in red earth deposits presents an economic opportunity for the Aruwakkalu region, since that being said, there are currently no efficient technologies for extraction and purification of red earth. A practical and cost-effective technique has to be created in order to extract and purify ilmenite from these deposits. That is the challenge of the moment In order to improve the effectiveness of ilmenite extraction, its complex mineral structure which causes difficulties at the processing stage [7] and to remove surface impurities minerals such as Fe and Al.

Section 3
Research Objectives

Major objective

To extract titanium dioxide (TiO_2) from ilmenite present in Sri Lankan red earth in Aruwakkalu region Sri Lanka.

Other Objectives

- To employ and optimize the physical separation technique to obtain ilmenite while minimizing other contaminants.
- To evaluate and optimize a chemical extraction method for titanium dioxide (TiO_2) by minimizing the Fe and Al contamination.

Section 4
Research Methodology

4.1 Sample Collection and Preparation

Red earth samples will be collected from the limestone quarry site belongs to INCEE cement lanka ltd near Aruwakkaru in Puttalam, Sri Lanka [3], where naturally occurring ilmenite-rich red earth are abundant.

4.2 Physical Separation of Ilmenite

The collected samples will be thoroughly washed to remove surface impurities and organic matter prior to the physical separation process.

4.2.1 Humphrey Spiral Separation Method

Spiral separation is a common gravity separation technique used to separate heavier minerals from lighter ones based on their different specific gravities [22]. Initially, sample slurry will be prepared by adding water to the fine particle of red earth. Then feed slurry will be introduced to the spiral separation and concentrated and concentrate and middling fractions will be collected. To obtain a good result the process will be repeated for several time.

This spiral separation will be conducted by using an industrial-scale Humphrey spiral installed at Uva Wellassa University of Sri Lanka. The spiral separation is effective gravity separation technique that enable preliminary separation of the lighter and heavier minerals based on their specific gravity. Hence, the clay fraction can be effectively removed. Finally, the concentrate and middling residuals will be mixed thoroughly and dried for three hours at 120 0C.

4.2.2 Shaking Table Separation

Shaking table separation is another gravity-based technique, similar to spiral separation, used to concentrate heavier minerals from lighter ones based on their density differences. The concentrated heavy fraction after spiral separation will be subjected to shaking table separation to further isolate the desired minerals, enhancing the purity of ilmenite and other valuable minerals from gangue materials. The middling fraction with ilmenite will be collected and dried for three hours 120 0C.

4.2.3. Electromagnetic Separation Method

Electromagnetic separation utilizes the magnetic properties of minerals to separate them from nonmagnetic minerals. Here, ore mixture is passing through a magnetic field created by electromagnets and the field selectively attracts magnetic or weakly magnetic minerals, separating them from non-magnetic minerals. Ilmenite is a weakly magnetic mineral and it can be separated from other available non-magnetic minerals in red earth.

The dried samples after shaking table will be subjected to the electromagnetic separation and the magnetic fraction that composed with ilmenite will be collected.

4.3 Titanium dioxide extraction from ilmenite

The separated magnetic fraction will be ensured for the ilmenite content and will be subjected for ball milling.

4.3.1 Removal of Al_2O_3 Contamination

Two chemical methods will be applied in order to evaluate the effective removal of Al_2O_3

4.3.1.1. Alkaline leaching

Alkaline leaching method will be used to remove aluminum contamination from ilmenite. The effective concentration of the NaOH for the removal of Al_2O_3 will be determined by the concentration series of NaOH such as 30, 40 and 50%. >53 μm powered sample of ilmenite will be treated with NaOH at 200 °C for 1 hour [16].

Al2O3+2NaOH→2NaAlO2+H2O

4.3.1.2 EDTA (Ethylene diamine tetraacetic acid) Selective Iron Removal

>53 μm powered sample of ilmenite will be added a solution of EDTA, reaching 94.8% at a solution pH of 1.68 and a hydrolysis time of 150 min., to enhance the chelating action. Under the experimental conditions, the hydrolysis of Fe^{3+} was restrained by EDTA addition into the solution. The TiO_2 content of the product rose an increase of the EDTA/Fe^{3+} molar ratio, yielding a purity of 99.9% TiO_2 as the ratio increased to 3. EDTA addition reduced the initiation of TiO^{2+} hydrolysis and the required amount of deionized washing water because larger meta-titanic acid grains

were produced which were easily filtrated and washed [17].

4.4 Extraction of TiO_2 using sulfate process

In the sulfate process, ilmenite (FeTiO3), is used. It is treated with concentrated sulfuric acid (H2SO4) and the titanium oxygen sulfate (TiOSO4) is selectively extracted and converted into titanium dioxide [18].

The process can be categorized into four main stages, namely, acid digestion, hydrolysis, calcination and post-treatment. In short, the initial step of the process involves converting the raw material, ilmenite, into titanium-sulphate through acid digestion. The resulting compound is then hydrolysed to yield hydrous titania, TiO2·H2O. Finally, the hydrated form is subjected to calcination to form TiO2 [11].

4.5 Characterization

4.5.1 Optical Microscopic Analysis.

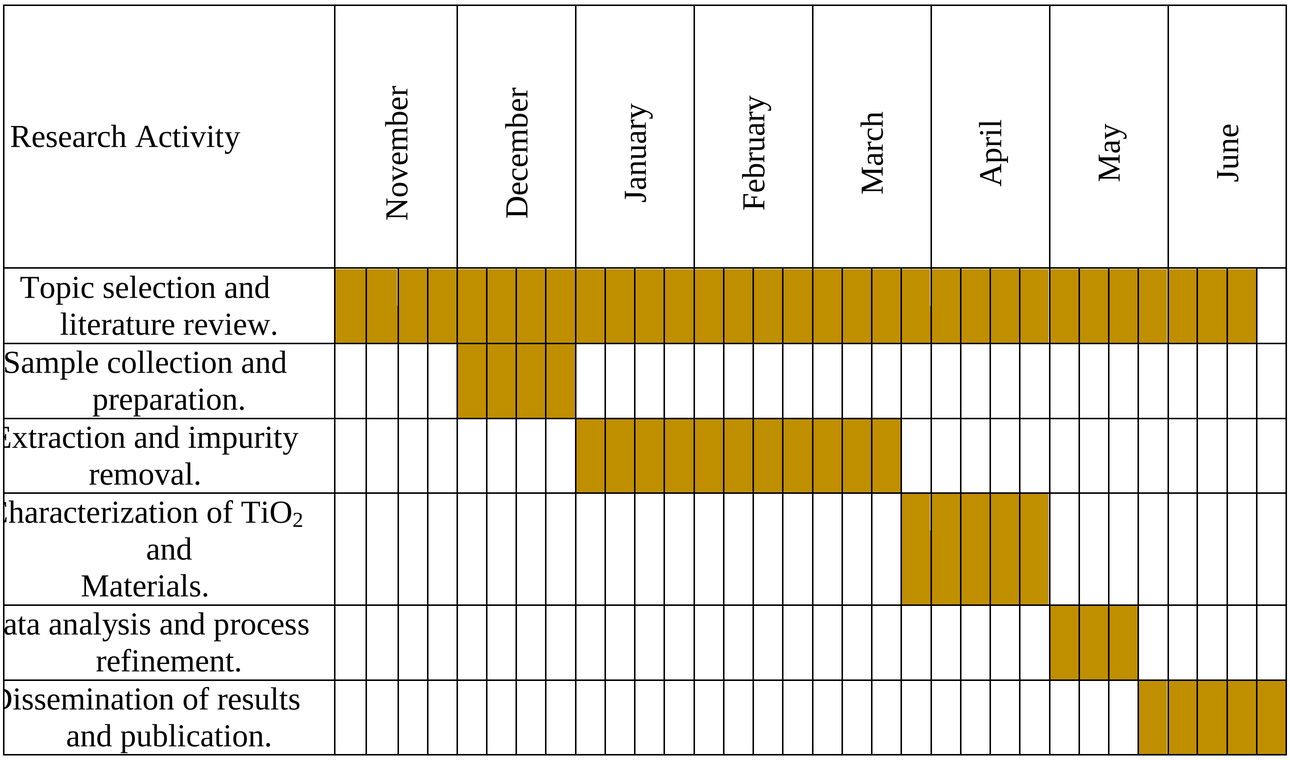
All the samples before and after the electromagnetic separation will be analyzed by Optical Microscope. The ilmenite and other nonmagnetic minerals will be identified and the results will be demonstrating the efficacy of the electromagnetic separation. Further, removal of clay fraction and the contamination level of Fe-Al coating can be observed.

4.5.2 X-ray fluorescence (XRF) Analysis

X-ray fluorescence (XRF) analysis will be conducted to determine the chemical composition the samples. Samples before and after the electromagnetic separation, after the Al_2O_3 removal treatment and after TiO_2 extraction will be analyzed with the XRF analysis.

4.5.3. X-ray diffraction (XRD) Analysis

X-ray diffraction (XRD) Analysis is used to explain the crystallinity and the different mineral phases. Hence, samples before and after the electromagnetic separation, after the Al_2O_3 removal treatment and after TiO_2 extraction will be analyzed with the XRD analysis.


Research Activity
November
December
January
February
March
April
May
June
Topic selection and literature review.
Sample collection and preparation.
Extraction and impurity removal.
Characterization of TiO_2 and Materials.
Data analysis and process refinement.
Dissemination of results and publication.

Section 6
Conclusion

The extraction of titanium dioxide from ilmenite in red earth (RE) of Aruwakkalu, Sri Lanka, may offers promising industrial potential due to the high demand of the titanium dioxide. This study focuses on developing an efficient method for TiO_2 extraction, overcoming disturbance from iron and aluminum oxide surface coating and the challenges of traditional processes that involve high temperatures and hazardous chemicals. Gravity and magnetic separation techniques will be used to separate ilmenite from red earth. The extracted TiO_2 will be evaluated for iron and aluminium contamination to ensure high purity. This study aims to increase the value of Sri Lanka's northwest coastal belt red earth deposits by improving the extraction process.

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