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Life cycle assessment comparison of emerging and traditional Titanium dioxide manufacturing processes

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ABSTRACT

Titanium dioxide (TiO_2) is used as pigment in a wide variety of domestic and industrial applications, and is becoming an increasingly valuable nanomaterial. TiO_2 is manufactured by the traditional sulfate process or high temperature chloride process. Several hydrometallurgical processes for manufacturing TiO_2 have recently emerged to reduce the environmental impact of TiO_2 production. A new process is reported that features alkaline roasting of titania slag (ARTS), with subsequent washing, leaching, solvent extraction, hydrolysis, and calcination stages, and implements the recycling and regeneration of alkaline and acid process streams to minimize waste generation. A virtual ARTS processing plant is described in detail and is used to conduct an LCA comparison with the sulfate, chloride, and Altairnano processes. The cumulative energy demand (CED) and total CO_2 emissions for the ARTS process are 92.6 MJ/kg TiO_2 and 7.47 kg CO_2/kg TiO_2, respectively, which compares favorably with the traditional and Altairnano processes.

1. Introduction

Titanium dioxide (TiO_2) has been commercially available as a whitening agent since the early 20th century. TiO_2 has the highest refractive index (2.4–2.7) of any other inorganic pigment, imparting a high level of opacity to other materials to which it is added (Khataee and Mansoori, 2012). It has been a critical additive in numerous domestic and industrial applications, including paint, paper, plastics (Gambogi, 2014), sunscreen (Yuan et al., 2005), cosmetics, and even as a food additive (Meacock et al., 1997). TiO_2 nanoparticles have also been used in numerous emerging technologies such as photovoltaic cells (Grätzel, 2001), biomedical devices (Yang et al., 2009), air-purification (Asadi et al., 2014), water purification (Nabi et al., 2009; Xu et al., 2010), and even cancer treatment (Lagopati et al., 2010). The world production of titanium mineral concentrates was 7.6 million metric tons in 2013, a 4% increase from the previous year. Surprisingly, 95% of concentrates are consumed for titanium dioxide pigment production, with the remainder used in welding-rod coatings, chemicals, and metal production (Gambogi, 2014). Titanium dioxide is traditionally produced by two distinct methods: the sulfate process and the chloride process (Gásquez et al., 2014).

1.1. Traditional TiO_2 manufacturing processes

The sulfate process involves digesting ilmenite (45–65% TiO_2) or titania slag (75–90% TiO_2) with concentrated sulfuric acid to produce titanium sulfate which is hydrolyzed to precipitate a hydrous titanium oxide compound. This compound can be calcined at 650–1000 °C to form either anatase or rutile-type titanium dioxide. This process accounts for roughly 40% of the total TiO_2 pigment produced world-wide (European Commission, 2007). The chloride process involves reacting natural or synthetic rutile (92–95% TiO_2) or titania slag with petroleum coke and chlorine gas at high temperatures, forming a titanium tetrachloride ($TiCl_4$) vapor. The vapor is distilled and then oxidized at > 1500 °C with oxygen and $AlCl_3$. The resulting product of these reactions is a purified rutile pigment, and the chlorine is recovered and recycled. The key reactions for this process are shown in Eq. (1) and Eq. (2).

$$TiO_{2\,(impure)} + C + 2Cl_2 \rightarrow TiCl_4 + CO_2 \quad (1)$$

$$TiCl_4 + O_2 \rightarrow TiO_{2\,(pure)} + 2\,Cl_2 \quad (2)$$

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1.2. Emerging hydrometallurgical processes

As the global reserves of high grade natural rutile become increasingly scarce, numerous alternative methods of producing TiO_2 that are able to directly use lower grade feed stocks have been investigated (Zhang et al., 2011). Most of these processes involve direct acid leaching of ilmenite or other low grade feed stocks. An improved sulfate process that reuses the raffinate from a solvent extraction step as the lixiviant for the initial leaching step has been developed by Roche et al. (2004), resulting in a reduction in acidic effluents and solid waste neutralization products. A direct leaching method of low-grade ilmenite using chloride media (20% HCl, 150–300 g/L $MgCl_2$) has been developed by Lakshmanan et al. (2010) and licensed to Argex Titanium Inc. Iron and magnesium impurities are removed from the leach solution by solvent extraction using TBP and recovered as oxides through pyrohydrolysis, which also regenerates HCl acid for leaching. The Altair process (Verhulst et al., 2002) involves directly leaching ilmenite with concentrated HCl (>360 g/L), bulk iron removal through $FeCl_2$ crystallization, and two stage solvent extraction to produce a purified titanium chloride solution, which is hydrolyzed in a spray dryer and calcined to produce TiO_2 nanoparticles. This process also uses pyrohydrolysis to regenerate acid. While these processes reduce the generation of acidic wastes, the pyrohydrolysis procedure can be quite energy intensive, as the regeneration of HCl from spent steel pickling solution via spray roasting of ferrous chloride acidic solution requires 2.5–5.0 MJ/dm^3 of treated solution (Ferreira and Mansura, 2011; Demopolous, 2008; Karner and Hofkirchner, 1996).

Alternatively, other investigators have used alkaline roasting to upgrade titanium slag. Lasheen (2008) as well as Dong et al. (2012) roasted titanium slags with soda ash at 850–900 °C with subsequent water and acid (or NaOH) leaching to produce synthetic rutile. Nayl et al. (2009) decomposed an ilmenite slag with a concentrated ammonium hydroxide paste to make a synthetic anatase product. Various investigators at the Chinese Academy of Sciences have roasted high grade titania slag (~90% TiO_2) with concentrated NaOH (Xue et al., 2009; Feng et al., 2009; Zhang et al., 2009), KOH (Qi et al., 2005; Tong et al., 2007) and NaOH–KOH (Wang et al., 2013) to form an alkaline titanate intermediate, which upon subsequent leaching, precipitation, and calcination with appropriate dopants, has produced a pigment quality rutile (Wang et al., 2011). A pilot plant utilizing this technology has been constructed in Shandong Province, and features regeneration of the reagent streams for minimal process waste emission (Wang et al., 2013). These methods indicate that alkaline roasting methods can yield high decomposition rates at medium temperatures and atmospheric pressure. Such conditions will conceivably lead to lower energy consumption than traditional manufacturing processes (Zhang et al., 2011).

1.3. New alkaline roasting of titanium slag (ARTS) process

A new TiO_2 manufacturing method has been reported by the authors (Fang et al., 2011; Middlemas et al., 2013) that utilizes the benefits of alkaline roasting of titanium slag (ARTS), solution purification by solvent extraction, and recycle/regeneration of process reagents. A simplified flow sheet for the new ARTS process is shown in Fig. 1. Titanium slag is roasted with NaOH and washed to remove soluble impurities. The products of roasting and washing are dissolved in HCl acid, mixed with an amine extractant and phase-separated to preferentially extract iron, resulting in a virtually iron-free titanium solution. The solution is heated and stirred to precipitate metatitanic acid, $TiO(OH)_2$. The precipitate is calcined to drive off chemically bound water and complete crystalline transformation to anatase or rutile TiO_2. The alkaline and acid streams will be recycled and regenerated in the process, reducing the amount of waste produced by the production of TiO_2 pigment. The impurities removed during solvent extraction can be precipitated as hydrated oxides and stored as tailings. A comparison of the key characteristics of traditional and emerging TiO_2 processes is given in Table 1.

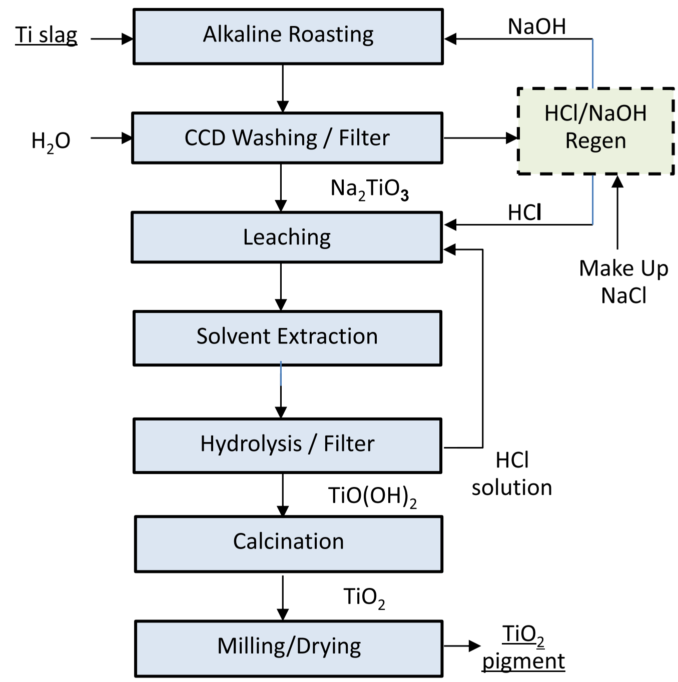

Fig. 1. Simplified process flow sheet of the alkaline roasting of titanium slag (ARTS) process.

The ultimate goal of the new ARTS method is to produce commercial purity TiO_2 pigment while reducing the energy consumption and carbon footprint of the current commercial methods. This goal is facilitated in part by avoiding the energy intensive production of $TiCl_4$ that results in direct CO_2 emission, as shown in Eq. (1). Based on the stoichiometry of this reaction, one mole of CO_2 is directly generated for every mole of TiO_2 produced, which equates to 550 kg CO_2 per ton TiO_2 produced. The world production capacity of titanium dioxide pigment by the chloride process is an estimated 3.9 million metric tons per year (60% of total world production), resulting in over 2 million tons per year of CO_2 as a byproduct of this reaction alone. With the growing global concern over climate change and rising governmental pressures on manufacturing industries to lower greenhouse emissions, cleaner and more energy efficient methods of materials manufacturing and metals production have been a topic of intense interest and research (Norgate et al., 2007; Fang et al., 2013).

The objective of the present work is to calculate the cradle-to-gate energy requirements and CO_2 emissions of the new ARTS process of manufacturing TiO_2 pigment. The results will be compared to the sulfate and chloride processes as well as the Altairnano process of manufacturing TiO_2 nanoparticles. The present work will contribute to the field of TiO_2 production by providing a life-cycle assessment (LCA) comparison of emerging TiO_2 manufacturing processes with traditional methods, and will help to evaluate if the emerging processes indeed have potential for energy savings and reduction in CO_2 emissions at an industrially significant scale.

This article is organized into five major sections. The second section includes a background on previous TiO_2 LCA studies,