Life Cycle of Titanium Dioxide Nanoparticle Production

Impact of Emissions and Use of Resources

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Summary

Life cycle impact of emissions, energy requirements, and exergetic losses are calculated for a novel process for producing titanium dioxide nanoparticles from an ilmenite feedstock. The Altairnano hydrochloride process analyzed is tailored for the production of nanoscale particles, unlike established commercial processes. The life cycle energy requirements for the production of these particles is compared with that of traditional building materials on a per unit mass basis. The environmental impact assessment and energy analysis results both emphasize the use of nonrenewable fossil fuels in the upstream life cycle. Exergy analysis shows fuel losses to be secondary to material losses, particularly in the mining of ilmenite ore. These analyses are based on the same inventory data. The main contributions of this work are to provide life cycle inventory of a nanomanufacturing process and reveal potential insights from exergy analysis that are not available from other methods.

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Introduction

Titanium dioxide (TiO_2) has been commercially produced for use as a white pigment since the early 20th century. Its high refractive index provides a bright white color that does not fade with exposure to solar radiation. Typical rutile-phase pigment-grade TiO_2 particles are on the order of 250 nanometers (nm) to 1 micrometer (μm) in diameter. They are used in paints, plastics, coatings, and cosmetics to provide color and opacity.

In the last several years, a market has opened up for anatase-phase TiO_2 particles that fall into the nano range—in other words, particles with a diameter between 1 and 100 nm. These nanoparticles are pervasive in the cosmetics industry, used especially for sun protection in sunscreens and skin care products. Anatase nanoparticle coatings are also photocatalytic when exposed to ultraviolet light. This unique property has led to applications such as antibacterial coatings or so-called self-cleaning surfaces. These coatings have the added advantage of holding up indefinitely over long exposure to sunlight.

Currently, two mature processes exist for TiO_2 production, namely the chloride process and the sulphate process. The chloride process is better suited for processing naturally occurring rutile-phase TiO_2 deposits; the sulphate process is preferred for processing titanium-rich ilmenite ores. U.S. production of TiO_2 is primarily through the chloride process, whereas European manufacturers prefer the sulphate process. The process considered here is a third route that uses ilmenite ore as the feedstock but processes it with hydrochloric acid instead of sulfuric acid.

The importance of life cycle assessment (LCA) of emerging nanotechnologies has been recognized, and recent work is focusing in this direction. One previous life cycle assessment of TiO_2 microparticles (Reck and Richards 1999) concentrates on the current commercial processes present in industry, namely the sulphate and chloride processes. The authors calculate gross energy requirements for the two processes, considering various scenarios for feedstocks and recycling. In addition, various emissions, including sulfur oxides (SO_x) and industrial solid wastes, are calculated over the life cycle and presented. This analysis does not address nanoparticle production or questions of energy quality.

LCAs of other nanoproducts include a recent study on the life cycle implications of carbon nanofiber (CNF) production (Khanna et al. 2008). This study compares the energy consumption and environmental impact of CNFs with those of more traditional materials, such as aluminum and steel. The major finding of this study is that, on a per mass basis, CNFs are much more energy intensive, in some cases as much as 300 times more, than traditional materials. Conclusions cannot be drawn on the basis of this alone, because CNFs would never replace other materials on a one-to-one mass basis. The authors addressed this issue by comparing the life cycles of polymer nanocomposites with other materials for use as automotive body panels. This study by Khanna and Bakshi (2009) found that nanocomposites may save up to 10% energy during the life of an average car over steel.

Kushnir and Sanden (2008) studied the energy requirement data for several common processes for producing carbon nanoparticles, including carbon nanotubes and fullerenes. The processes include fluidized bed and floating catalyst chemical vapor deposition, pyrolysis, and laser ablation, among others. The authors include thermal, chemical, electrical, and solar energy sources in their calculations. They found that these processes use between two and 100 times more energy than aluminum production. Due to incomplete information about all stages of production, the authors do not draw hard conclusions, but their data lean toward chemical vapor deposition methods as the least energy intensive. Their study also acknowledges that material losses are not included.

Healy and colleagues (2008) present a traditional life cycle assessment of three processes for manufacturing single-walled carbon nanotubes. The processes are arc ablation, chemical vapor deposition, and a high-pressure carbon monoxide process. One of the problems they encounter, as in most other life cycle studies of nanomaterials, is a lack of toxicity information for the nanotubes; therefore, their analysis is limited to providing a base case for the manufacturing processes and their impacts in three categories: airborne inorganics, climate change, and

acidification potential. For the base case, it is found that the high-pressure carbon monoxide process has the lowest impacts.

The present work contributes to the existing research by providing life cycle inventory information for the hydrochloride nanomanufacturing process for producing TiO_2 nanoparticles, which is currently absent from the literature. Like the study by Khanna and colleagues (2008), this work compares the life cycle energy use of nano TiO_2 with that of conventional materials in an intensive (per unit mass) and extensive (for total production) manner. In addition to a traditional impact assessment and first law energy analysis, this work also includes an exergy analysis to account for material resource consumption in the process. This analysis is based on the same inventory and is not an idealized exergy analysis based on reversible processes. Besides the inventory data, the main contribution of this work is to report on the insight that is to be gained when one compares results from all three methods: life cycle assessment, energy, and exergy analysis. The strengths and weaknesses of each are highlighted through the case study.

This article is organized into four major sections. The second section provides background on the Altairnano hydrochloride process and on the methods of analysis used in this study, namely life cycle assessment, energy, and exergy analysis. The third section describes specifically how these methods were applied in this study, including the definition of the boundary considered. Results and a discussion for each method are presented in the fourth section, and, finally, conclusions and considerations for future work are provided.

Background

The Altair Hydrochloride Process

The Altairnano hydrochloride process is a relatively new approach for the production of TiO_2 nanoparticles. It currently exists at the pilot scale, with a larger plant under construction. A process flow diagram for the hydrochloride process is presented in figure 1. This figure and the description that follows are based on patent literature and articles from Altairnano published in the open literature (Duyvesteyn et al. 2000a, 2000b, 2000c; Verhulst et al. 2002, 2003, 2006a, 2006b). Ilmenite ore is the main feedstock, similar to the sulphate process. The ideal formula of ilmenite is $FeTiO_3$, but impurities and variations are always

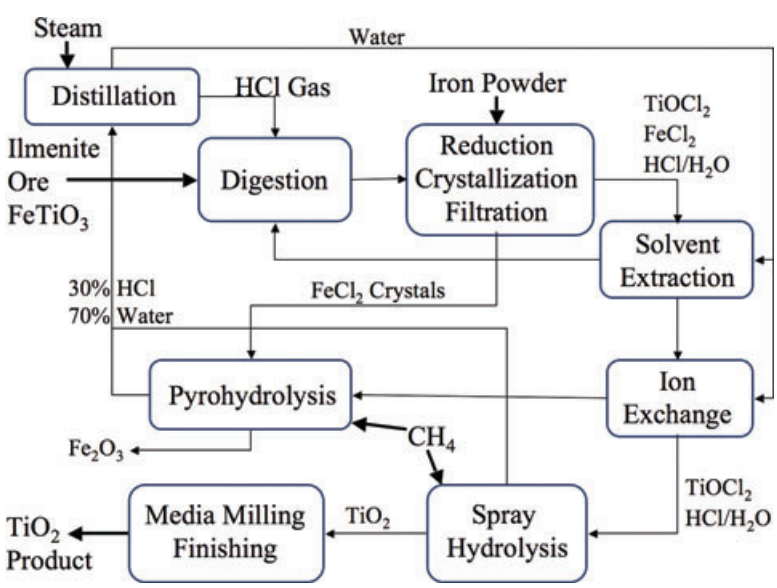

Figure 1 Process flow diagram for the local Altair hydrochloride process. HCl = hydrochloric acid; $TiOCl_2$ = titanyl chloride; $FeCl_2$ = iron chloride; H_2O = water; $FeTiO_3$ = ilmenite; Fe_2O_3 = iron oxide; CH_4 = methane; TiO_2 = titanium dioxide.

present. Although ilmenite is common in many places around the world, the largest sources of ilmenite ore from mining are Australia, South Africa, and Canada (Survey 2006).

Ilmenite is first introduced in the digestion unit, along with an excess of concentrated hydrochloric acid (HCl); this results in the following reaction:

$$2FeTiO_3 + 4HCl \rightarrow 2FeCl_2 + 2TiOCl_2 + 2H_2O + O_2 \quad (1)$$

Most of the acid is recovered in subsequent steps and recycled back into the digestion, but a small feed is required to maintain the necessary level. After digestion, the goal is to remove the iron and chloride ions before they react to form the TiO_2. The mixture is reduced with the addition of a small amount of iron powder, which ensures that all the iron is in the form of Fe^{2+}, so that it will crystallize out as iron chloride ($FeCl_2$) when the temperature is lowered to about 4°C.

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+} \quad (2)$$

The $FeCl_2$ crystals are then filtered from the product stream and sent to the pyrohydrolysis unit, which is described later.

After filtration, the product stream goes through a solvent extraction with trialkyl phosphine oxide, which removes any residual iron ions. The last separation step is an ion exchange with sodium hydroxide (NaOH) to remove the remaining chloride ions. At this point, the clean product stream is ready for the following reaction, which is carried out in a modified spray dryer.

$$TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl \quad (3)$$

A large amount of methane is burned at this stage for dehydration of the product. This is the innovative part of the hydrochloride process that allows for production of uniformly distributed nanoparticles. The spray hydrolysis reaction produces high-purity TiO_2 in the form of hollow spheres a few microns in diameter. The sphere size and thickness required for the desired particles can be controlled through variations in the temperature and flow rate in the spray hydrolysis stage. The spheres are then calcined at around 400°C to 500°C, which crystallizes the amorphous TiO_2 to anatase phase particles, which are next broken up in a wet media mill and further processed in other optional coating steps. The end product is 40-nm anatase-phase TiO_2 nanoparticles. The current pilot-scale plant produces approximately 100 kilograms per hour (kg/hr) of product from an ilmenite feed of about 210 kg/hr. The hydrochloric acid produced in this reaction is sent to distillation to be recycled.

In a parallel recycle loop, the following pyrohydrolysis reaction is used to regenerate the HCl from the $FeCl_2$ crystals.

$$2FeCl_2 + 2H_2O + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + 4HCl \quad (4)$$

Iron oxide (Fe_2O_3) is produced as a by-product, and the regenerated HCl is sent to a swing distillation unit, which breaks the water-HCl azeotrope before it is recycled back to the digestion unit. High-pressure steam is used to run the distillation.

Methods

The three methods of life cycle evaluation considered in this study are life cycle impact assessment, first-law energy analysis, and combined first-law and second-law exergy analysis. What follows is a description of each of these methods and how they were carried out in this study.

Life cycle assessment is a method for evaluating a product that takes into account the production chain not only for the product but also for everything else that contributes directly or indirectly to the product. Often, when a process is "improved," the problems are simply shifted to another area of the life cycle. The hope of life cycle assessment is that when the system boundaries are defined carefully, such oversight can be prevented.

As described by ISO 14044, life cycle assessment has four distinct parts (Guinee 1992). The first involves defining the goal and scope of the analysis. This includes defining the functional unit for the product being made and clearly defining the boundaries the analysis will cover. The second step is the life cycle inventory, in which the system is modeled and all flows into, out of, and within the system are defined. This includes not only the material and energy requirements

for the process but also the emissions and waste products.

The third step is impact assessment. In this step, all the emissions from the inventory are categorized according to their potential damage in one or more of the established categories, such as carcinogenicity, ecotoxicity, or fossil fuel use. These categories are standardized to equivalents of a common emission. For instance, global warming potential is reported in units of carbon dioxide equivalents. Other emissions that affect global warming potential are converted to this common unit according to characterization factors. This convention causes all the damage categories to have different units. To compare across categories, researchers typically normalize values against the estimated total damage for that category in the country or even the world.

The final step is interpretation. This step sometimes involves weighting the impact categories according to human preferences to achieve a single impact score that can be compared to alternative products or processes. The decisions made in earlier steps of the analysis influence what can be learned from the results. Improvement analysis is also an important part of the interpretation stage. In improvement analysis, key areas are identified as having the highest potential for positive change given a certain amount of time and capital investment. Currently, this is a relatively underdeveloped area in applying LCA to process selection, and development and will be the focus of our future work.

Energy analysis obeys the first law of thermodynamics, which states that enthalpy is conserved. For material streams, change in enthalpy is calculated as

$$\Delta H = nC_p \Delta T \tag{5}$$

where n is the number of moles, C_p is the heat capacity, and ΔT is the difference in temperature between the material stream and the ambient surroundings. Because this quantity is conserved, we can also use first-law analysis to calculate energy losses in a process or process unit as the difference between the enthalpy leaving and entering. Fossil fuels also have an enthalpy value, which is close to their heating value.

First-law methods in general are not thermodynamically complete, because they ignore issues of energy availability. For example, water at two temperatures can have the same enthalpy content, but the one at the higher temperature has a greater ability to do work. This difference is not captured in energy analysis. To combat this problem, second-law analysis calculates the potential for doing useful work and uses that as the basis for evaluation. In addition, first-law methods cannot account for the value of nonfuel material resources used or produced by a process. This is a very important distinction when the final product is a material, which usually has a very small fuel energy value.

Exergy is defined as the maximum amount of useful work that can be obtained from a material stream when it is brought to equilibrium with its surroundings (Szargut 2005). For every type of gradient with the surroundings, there is a different type of exergy. For this article, we ignore potential, kinetic, and nuclear exergy and instead focus on physical and chemical exergy.

Physical exergy is the amount of work that can be obtained when a stream's temperature and pressure are brought into equilibrium with the surroundings. It can be calculated as (Szargut 2005)

$$b_{ph} = h_{ph} - T_0 s_{ph} \tag{6}$$

where h_{ph} is enthalpy, T_0 is the reference temperature, and s_{ph} is entropy.

Chemical exergy can be thought of as the work obtainable by exploitation of concentration gradients between the material stream and the surroundings. The standard chemical exergy of a compound can be calculated as (Szargut 2005)

$$b^{o}_{ch} = \Delta_f G^{\circ} + \sum n_{el} b^{o}_{chel} \tag{7}$$

where $\Delta_f G^{\circ}$ is Gibbs's standard free energy of formation for the compound, n_{el} is the number of moles of each element per unit of compound, and b^{o}_{el} is the standard chemical exergy of the elements found in the compound. Values of $\Delta_f G^{\circ}$ can be found in the literature and in thermodynamic handbooks for most compounds (Meester et al. 2006; West et al. 2007). Standard values of b^{o}_{el} have been calculated for each element according to its standard reaction of formation and can be found in the work of Szargut (2005). The chemical exergy of fuels is a special case that we call fuel exergy. One applies a multiplier to the

heating values for the fuel to find the fuel exergy. This multiplier is usually close to unity, and more exact values can be found in the work of Szargut and colleagues (1988).

The difference between the exergetic inputs and outputs to a process is termed the irreversibility rate, $\dot{I}$, of the process (Kotas 1986).

$$\dot{I} = \sum \Delta b_{in} - \sum \Delta b_{out} \tag{8}$$

The irreversibility rate represents the sum of exergy destruction and loss in the process. If the inputs and outputs represent the raw materials and products, then the irreversibility rate is the minimum amount of work that must be done to transform the inputs into the outputs or the maximum work that can be obtained from the transformation. If other streams in the practical process, such as energy flow, are included, then the irreversibility can be used to identify the largest exergy sinks in a process and opportunities for enhancing system efficiency.

Approach

This section begins with an explanation of the boundaries chosen for the analysis. In addition, we apply the methods described in the previous section specifically to the Altair hydrochloride TiO_2 process. Finally, we consider sources of uncertainty in the analysis. Often, the type and quality of the available inventory data influence how a given process can be analyzed. In some cases, one must use aggregation or approximation to augment what is known.

Goal, Scope, and Boundaries

As mentioned before, this study was done at the life cycle scale, including all material, energy, and fuel inputs to the process and their upstream inputs and emissions. It also includes the process itself as a black box. This is a traditional boundary and is generally used in a cradle-to-gate life cycle assessment. This boundary is indicated by the dashed line in figure 2. It is important to notice that the nanoparticle product of the process is

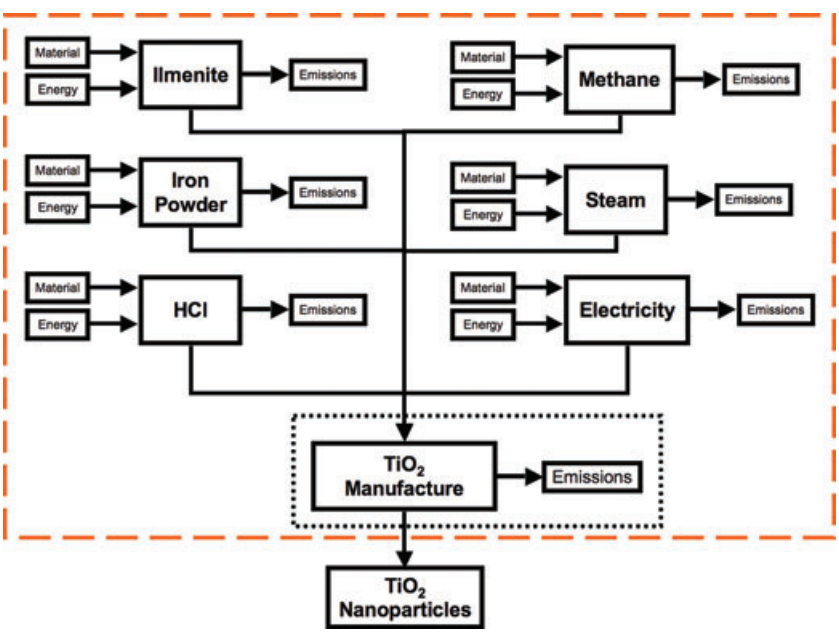

Figure 2 Life cycle scale flow diagram for the hydrochloride process. The local process shown in figure 1 is indicated by the dotted line, and the cradle-to-gate boundary used in this work is indicated by the dashed line. HCl = hydrochloric acid; TiO_2 = titanium dioxide.

outside the boundary because the exact impacts of the particles are unknown. Several ongoing studies are looking at toxicological and environmental impacts of nanoparticles, and these data could be included in the current analysis when available. Also of note, the iron oxide produced in the pyrohydrolysis stage is a low-value byproduct; therefore, no allocation schemes have been considered in the present study.

Assessing the Impact of Emissions

A traditional cradle-to-gate LCA was carried out as defined above. A functional unit of 1 kg of TiO_2 nanoparticle product was chosen. An initial material and energy inventory was compiled from Altair articles and patents (Duyvesteyn et al. 2000a, 2000b, 2000c; Verhulst et al. 2002, 2003, 2006a, 2006b). When necessary, we made approximations and estimates using sources from the open literature. Process and construction equipment was excluded in all cases.

The corresponding processes for each of the inputs were selected from the available life cycle inventory (LCI) databases. These include inventory about iron ore from mine, an aggregate sector that includes ilmenite; crude iron for the iron powder; HCl for the hydrochloric acid; natural gas for the methane; on-site steam for the steam; and electricity average for the electricity. With the values from table 1, we found the materials, fuels, and emissions associated with the upstream processing of the inputs to the local TiO_2 plant using commercial databases. Except for electricity, the rest of the data came from the Eidgenössische Technische Hochschule Zürich (ETH) and European data sets. Electricity was for the U.S. mix. For impact assessment, both midpoint and endpoint assessment methods were considered. The Eco-indicator 99 methodology is widely used for the quantification and categorization of emissions into impact categories. There are some limitations of this methodology, however. First, although Eco-indicator 99 claims to account for resource consumption, it is chiefly concerned with fossil fuel use. The method used to account for the depletion of other resources is based on surplus energy, or the additional energy that will be required to extract the resource in the future due to the depletion of the resource in the present. When compared with more rigorous thermodynamic methods, such as emergy and exergy analysis, surplus energy tends to drastically undervalue natural resources because it assumes their exergetic content to be free and only includes the additional energy that must be expended to deliver the resource in a usable form. Another drawback to the Eco-indicator 99 methodology is that it depends on subjective survey results for further aggregating the midpoint indicators to an endpoint single score. In the present study, we have tried to avoid aggregation where possible, so only the midpoint impact indicators are reported in the results. The Eco-indicator 99 endpoint score for the process can, however, be found in the Supporting Information on the Web. The relative contribution of each input's value chain to the total damage in each category is reported. These data allow for simple comparison of the inputs within a given impact category, but to compare meaningfully across categories, we have normalized the impacts. The normalized values represent the impact as a fraction of the total impact in each category recorded for the whole U.S. economy.

Table 1 Mass, energy, and exergy values of inputs needed to produce 1 kilogram (kg) of titanium dioxide nanoparticles.

Inputs	*Mass (kg/kg TiO_2)*	*Energy (MJ)*	*Exergy (MJ)*
Ilmenite	2.165	0	1.928
Iron powder	0.103	0	0.691
Hydrochloric acid	0.065	0	0.151
Methane	0.866	44.894	46.690
Steam	14.948	2.559	4.572
Electricity	–	5.443	5.443

Note: The mass of inputs was calculated from the work of Verhulst and colleagues (2002, 2003). Where necessary, energy and exergy content of inputs were calculated from equations (5) and (8), respectively. kg/kg TiO_2 = kilograms per kilogram of titanium dioxide; MJ = megajoules.

Energy and Exergy

We used the results from the LCA above to calculate the upstream energy and exergy requirements for each of the inputs to the hydrochloride

process. According to convention, the first-law energy analysis includes only nonrenewable fossil fuel inputs, namely crude oil, natural gas, and coal. The enthalpy values of the fuels were calculated as their heating values. Nuclear power was not included in the first-law analysis because it does not come from a traditional fossil fuel and is often left out of this type of analysis. Renewable resources, such as wind, hydro, and solar power, are also not included in the first-law analysis.

The six major inputs to the process and their energy and exergy values are shown in table 1. The exergy analysis was done in the same way as the first-law analysis, except that all upstream material inputs were included in addition to the nonrenewable fuels. Values for the specific chemical exergy of materials were gathered from the work of Meester and colleagues (2006) or calculated from Szargut's (2005) work according to equation (7). At this level of analysis, the physical exergy of all flows was considered to be negligible. This would not be the case in a more detailed analysis of the process, where temperature and pressure information is available. Once the values for all the flows were evaluated, we were able to calculate energy and exergy losses and efficiencies for each of the six major inputs to the process.

Uncertainty

The results of the analysis presented here represent a realistic but best case scenario due to incomplete data and other sources of uncertainty. The inventory of inputs and emissions for the Altair hydrochloride process available in the literature is not complete. Omissions from the literature include separation agents for the solvent extraction and ion exchange unit operations as well as the emissions and electricity requirements for all steps in the process. The separation agents were considered negligible in the present analysis, but emissions and electricity requirements were included on the basis of estimates from the mass and energy balances or from literature concerning similar equipment. The final source of uncertainty in this process is due to the final product, nanoparticles. The consensus is that the properties of materials at the nanoscale are different from those of their bulk counterparts. For that reason, little is known about the possible effects of nanoparticles if or when they end up in the environment. If data from such a scenario indicate that the nanoproduct has a larger life cycle impact than conventional materials, preferring the nanoproduct over the conventional product may not make sense with today's technology.

Results and Discussion

This section focuses on each method of analysis individually and then reflects on what all three can tell us together. The energy and exergy analyses direct our attention toward the largest thermodynamic losses in the process, whereas the life cycle assessment emphasizes the environmental impacts of emissions. It is not necessary that the results from these methods be in agreement. We compare the results to see what insights can be revealed. The analysis concentrates on the six external inputs to the process, which can be grouped into two categories. The material inputs comprise ilmenite ore, iron powder, and hydrochloric acid. The heat or fuel inputs are methane, steam, and electricity. We refer to these categories often in this section.

Impact Assessment

Life cycle impact assessment results for the coarse scale are shown in figures 3 and 4. The impact assessment in figure 3 shows only the relative amount of damage in each category compared to the total for all inputs. For example, ilmenite ore production represents more than 65% of the ozone depletion potential of all the inputs; however, its absolute value is very small, as shown in the normalization plot in figure 4. In general, the impact assessment shows that ilmenite mining and steam generation are the most prominent in most categories. Also, the fossil fuels category is dominated by the production of steam and methane for use in the process.

The normalization plot in figure 4 shows the amount of damage in each category as a fraction of the total damage for the United States. Fossil fuel use is by far the most significant

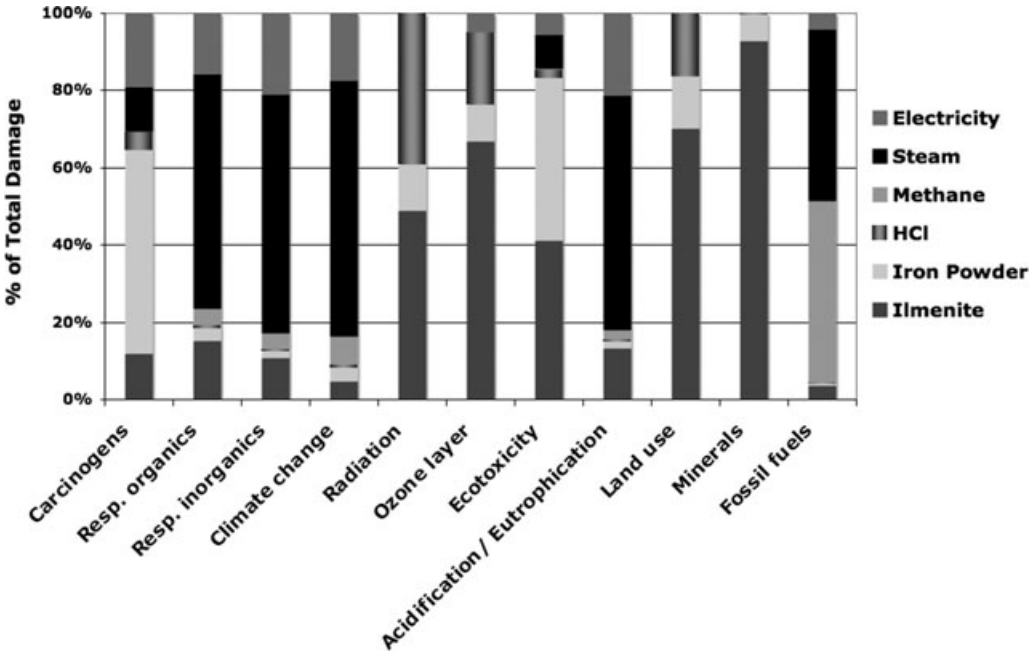

Figure 3 Impact assessment for 1 kilogram (kg) of titanium dioxide (TiO_2) produced. HCl = hydrochloric acid; Resp. = respiratory.

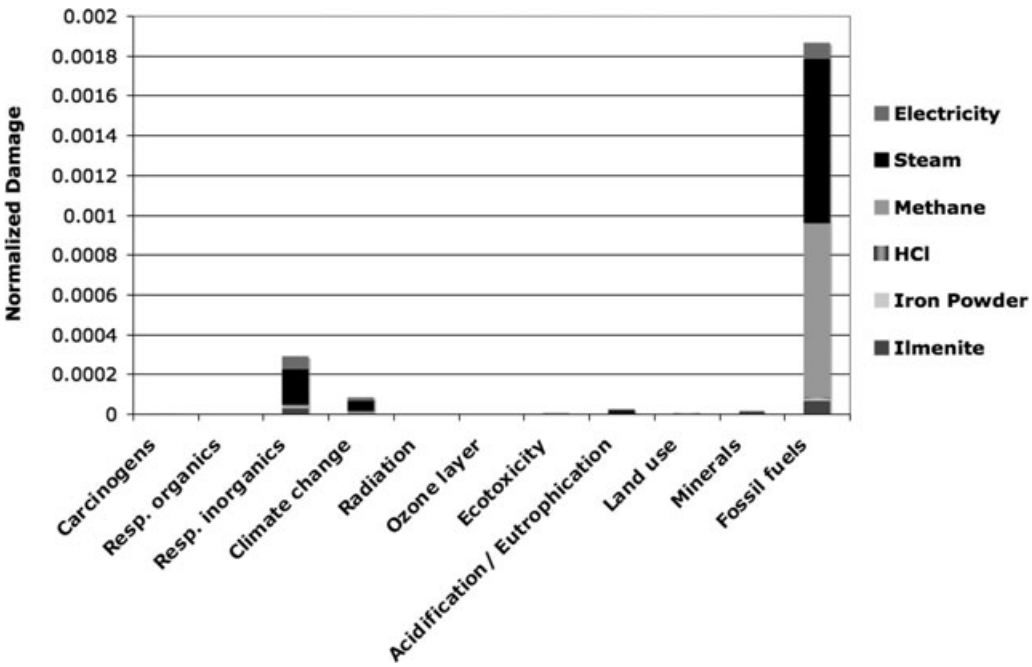

Figure 4 Normalized impacts for 1 kilogram (kg) of titanium dioxide (TiO_2) produced. HCl = hydrochloric acid; Resp. = respiratory.

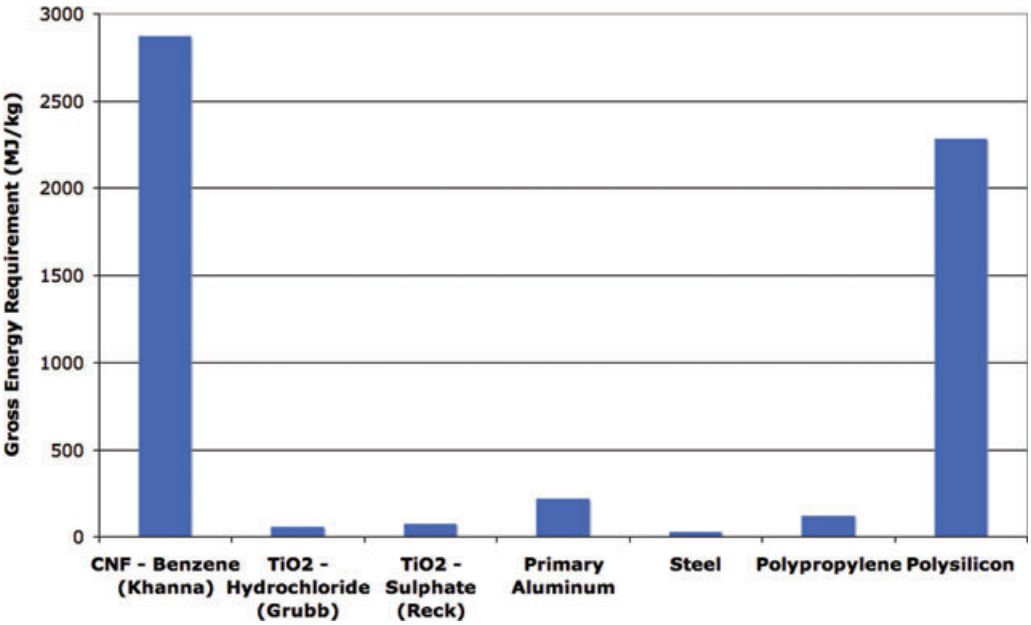

Figure 5 Comparison of the per unit mass gross energy requirement of several materials (Reck and Richards 1999; Khanna et al. 2008). MJ/kg = megajoules per kilogram; CNF = carbon nanofiber; TiO_2 = titanium dioxide.

category, dwarfing all the others. Within fossil fuel use, steam generation and methane production are again the dominant inputs. If we are concerned with reducing the fossil fuel dependency of the process, reducing the amount required of these two inputs—or reducing the fossil fuels required to produce them through some type of innovation—should be the first priority.

Energy and Exergy

To put this process into context with other nanomaterials and more conventional construction materials, figure 5 compares the gross energy requirements for several materials. This comparison has been done on an equal mass basis. Because all of the materials are used in different amounts and for very different applications, the results in figure 5 can only serve as a benchmark and cannot be used to draw concrete conclusions. The figure does show, however, that the per unit mass energy requirement for producing TiO_2 is more on the order of traditional building materials, such as steel, than carbon-based nanomaterials, such as CNFs. This implies that, unlike carbon-based nano fibers and particles, large-scale adoption of TiO_2 nanoparticles may consume significantly less energy.

An extensive comparison of these materials is possible if we multiply the per unit mass results by the total annual production volume of each material. Figure 6 shows the results of this calculation. Microscale TiO_2 was assumed to have been produced according to the Altair hydrochloride process, with the exclusion of the calcination and milling steps. Annual production of nanoscale TiO_2 was difficult to obtain, so it has been estimated as 1% of the total microscale pigmentary TiO_2 production. Even with this conservative estimate, the annual energy requirement is about an order of magnitude larger than that for CNFs, which are currently produced in very small amounts. The immense amounts of steel and aluminum produced annually puts their energy requirements a couple orders of magnitude above all other materials considered.

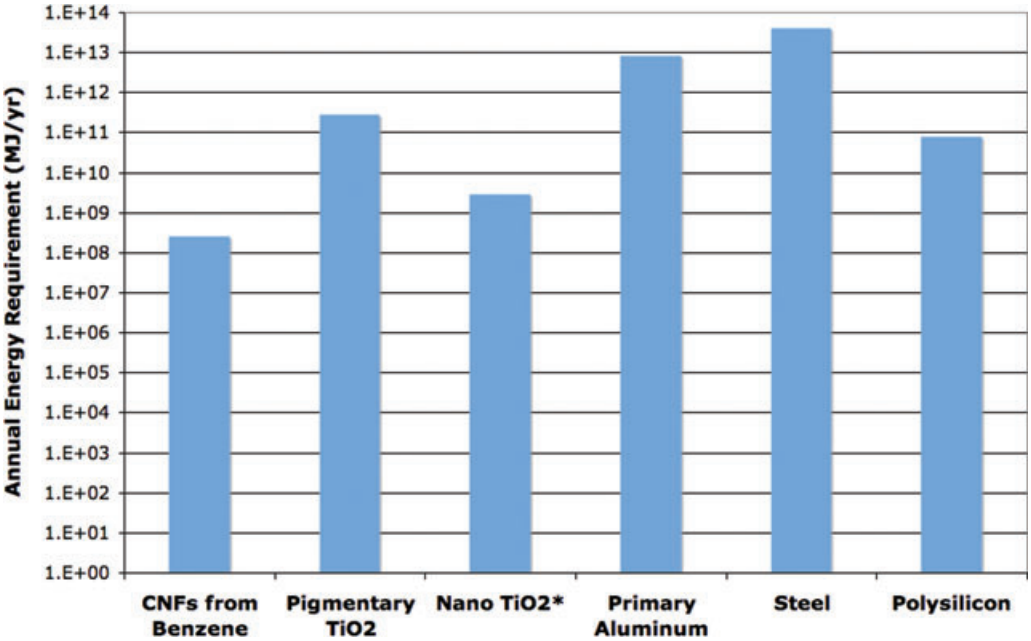

Figure 6 Comparison of the total energy requirement of several materials, calculated as the product of the per unit mass energy requirement and the total annual production volume. Asterisk indicates that production of nano titanium dioxide (TiO_2) is estimated as 1% of pigmentary production. MJ/yr = megajoules per year; CNF = carbon nanofiber.

Some might question the value of comparing energy intensity data on a mass basis, because this is not a functional comparison. For instance, 1 kg of steel is not directly comparable to 1 kg of nanoparticles, because for a given application very different amounts of each material will be required, perhaps in combination with other materials, as in the case of nanocomposites. Relative energy intensity can, however, provide a first approximation for the feasibility of a new technology in comparison to established techniques. One study in the literature compares the electricity demand of 20 different manufacturing processes (Gutowski 2009). When the data are compiled, they provide a general understanding of where emerging technologies are moving in terms of energy intensity. Furthermore, this type of data could potentially be used to predict the energy requirements of new or future processes. In his book on energy, Vaclav Smil (2008) presents data showing how the energy intensity of materials has traditionally decreased over time as technology and practices improve. Researchers anticipate that the energy requirements for carbon-based nanoparticles will go down as the technology matures; however, titanium dioxide has been commercially produced for more than 50 years, and is unlikely to see any drastic decrease in energy investment.

The first-law energy, or enthalpy, losses are shown in figure 7. These include only the nonrenewable fossil fuels—oil, gas, and coal—used in the life cycle defined for TiO_2. The natural gas required for methane production represents the largest energy input to the process, followed by the energy required to produce the steam and electricity. This seems logical because both steam and electricity are produced from burning fossil fuels, so one would anticipate a significant energy investment in the upstream stages. Comparatively, the material inputs are insignificant because they require relatively few fossil fuel resources in their value chain.

The results of the exergy analysis in figure 8 show a much different trend from the first-law analysis. The losses attributed to the fuel inputs are nearly identical to the first-law results, but the material inputs show much greater losses. The

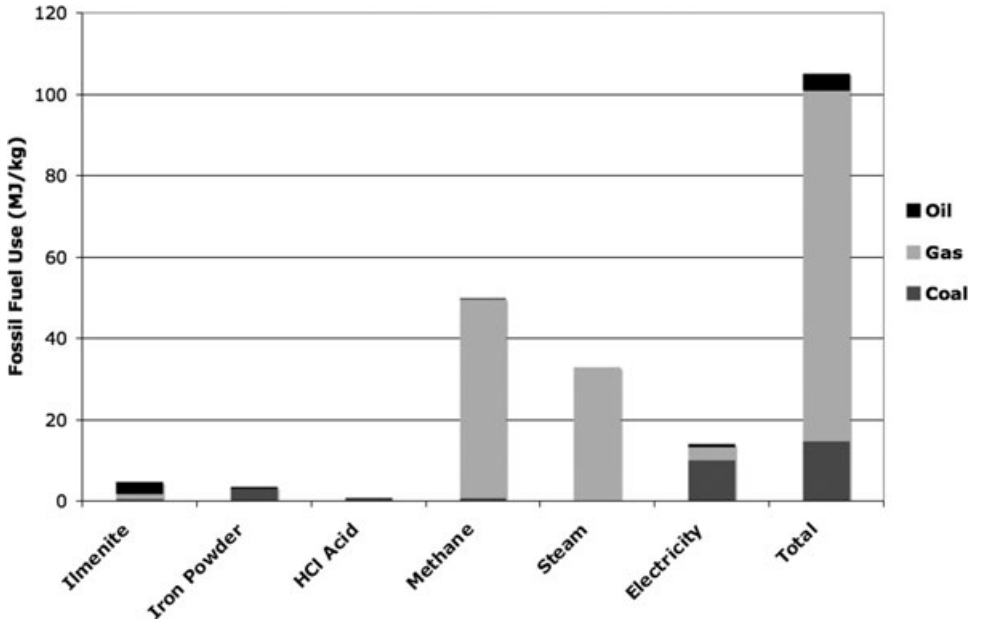

Figure 7 Energy use for 1 kilogram (kg) of titanium dioxide (TiO_2) produced, broken down by fossil fuel type: oil, gas, and coal. MJ/kg = megajoules per kilogram; HCl = hydrochloric acid.

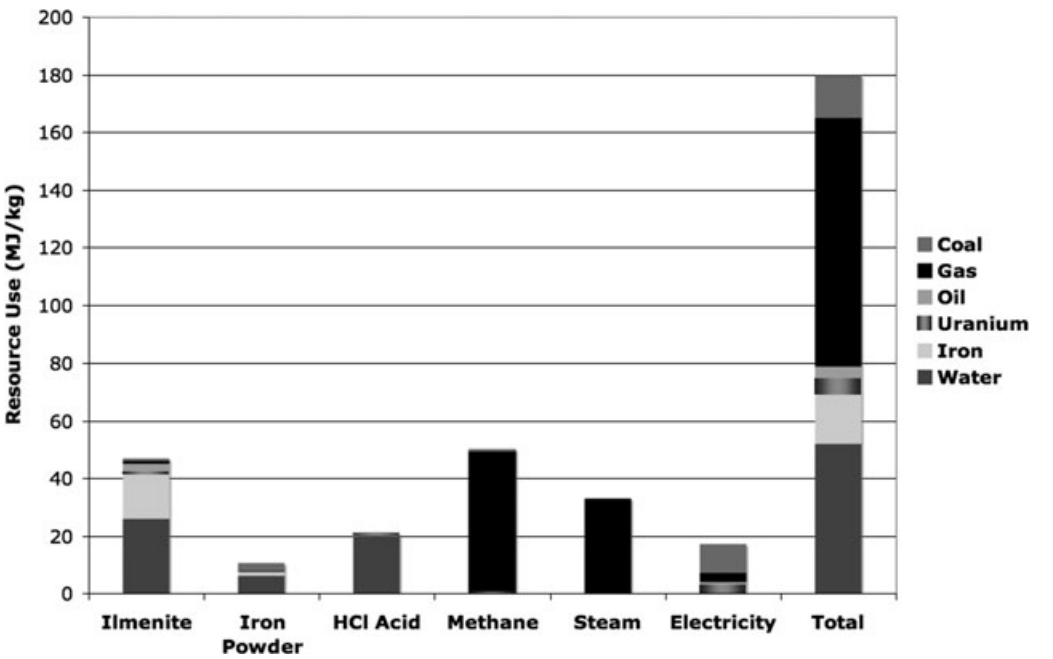

Figure 8 Irreversibility rate for 1 kilogram (kg) of titanium dioxide (TiO_2) produced, broken down by materials and fuels required for each input to the process. MJ/kg = megajoules per kilogram; HCl = hydrochloric acid.

ilmenite is especially exergy intensive because of the resources needed for mining and enriching the ore, which requires large amounts of water. The total exergy loss due to mining is 47 megajoules (MJ) for every kilogram of final product. This is more than ten times the first-law losses and very clearly illustrates the disparity between energy and exergy analysis due to the inclusion of nonfuel natural resources. When other natural resources as well as fuels are included in the exergy calculation, the production of material inputs post much higher losses. The fuel-based inputs have supply chains dominated by nonrenewable fossil fuels and have very few other material requirements, so the analysis is nearly unchanged when compared with the first-law results.

Although exergy analysis is more rigorous than first-law methods, one oversight native to exergy analysis and most other resource accounting methods is the assumption of substitutability between the resources being aggregated or compared in the value chains. When one sums the exergy of different materials, one makes an inherent assumption that there is no difference between equal quantities of exergy. For example, it is assumed that a joule of water exergy may be substituted for a joule of coal exergy, although we know intuitively that coal is of a higher quality. There are no generally accepted methods to account for this substitutability problem, but defining quality indicators in terms of economic value (Cleveland et al. 2000) or ecological cumulative exergy consumption (Hau and Bakshi 2004) or emergy (Odum 1996) seems promising (Baral and Bakshi 2010). Emergy analysis reports the amount of embedded energy or cumulatively expended energy to produce a material. These methods are outside the scope of the current study, but they could make for interesting future directions.

In summary, the results of the life cycle assessment and the first-law energy analysis both direct attention toward the fuel-based inputs, whereas exergy analysis emphasizes the material inputs, especially the ilmenite ore. This is an important result because it shows that including material resource consumption can produce results that cannot be obtained by traditional methods. Judgments of sustainability should be concerned with more than just fossil fuels, especially when one considers material-intensive processes, as in the present case study.

Conclusions and Future Work

On an equal mass basis, energy requirements for the Altair hydrochloride process for producing TiO_2 nanoparticles compare favorably to traditional materials, such as steel and aluminum, and are vastly lower than those for carbon nanofiber production. Energy requirements for this process also appear to be on the same order of magnitude as the sulphate commercial process it would replace. Although the materials being compared are not substitutes, such a comparison provides intuition about the life cycle intensity of nano TiO_2 as compared to conventional materials. Such intuition can be useful for quick calculations. A comparison of total energy requirements reveals the low production volumes of nanomaterials when compared to traditional materials, such as steel or aluminum. With increasing popularity of TiO_2 nanoparticles, however, their life cycle impact could rival that of materials such as polysilicon. Ultimately, for a fair comparison, nanoproducts using TiO_2 should be compared with products made by conventional methods for the same functional unit. The data in this article are essential for such a comparison.

The thermodynamic analysis in this article is based on the same data as those used for LCA and does not represent an ideal process. From a thermodynamic perspective, first-law analysis shows the largest losses in methane and steam production, which indicates close agreement with the conventional impact assessment in LCA. Exergy analysis, however, shows much larger losses for ilmenite mining and hydrochloric acid production. The majority of these losses are due to materials use. This seems to imply that the processing of material inputs for this manufacturing process is much more exergy intensive than for the fuel inputs. This phenomenon should hold true for other materials-based chemical processes.

Further study will look more closely at the process units identified in figure 1. An analysis similar to that presented in this work should advance understanding of losses and impacts within the

process itself. A comparison of the results from the present study with those at the local level will provide valuable insight into where improvements can be most readily achieved. Eventually, we hope to develop a general methodology for using LCA and exergy analysis as a design tool for chemical and other industrial processes.

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References

Baral, A. and B. R. Bakshi. 2010. Thermodynamic metrics for aggregation of natural resources in life cycle analysis: Insight via application to some transportation fuels. *Environmental Science and Technology* 44(2): 800–807.

Cleveland, C. J., R. K. Kaufman, and D. I. Stern . 2000. Aggregation and the role of energy in the economy. *Ecological Economics* 2: 301–317.

Duyvesteyn, W. P., T. M. Spitler, B. J. Sabacky, and J. Prochazka. 2000a. Processing aqueous titanium chloride solutions to ultrafine titanium dioxide. U.S. Patent 6440383, filed Feb. 14, 2000, and issued Aug. 27, 2002.

Duyvesteyn, W. P., B. J. Sabacky, D. E. V. Verhulst, P. G. West-Sells, T. M. Spitler, A. Vince, J. R. Burkholder, and B. J. P. M. Huls. 2000b. Processing titaniferous ore to titanium dioxide pigment. U.S. Patent 6375923, filed Feb. 7, 2000, and issued April 23, 2002.

Duyvesteyn, W. P., T. M. Spitler, B. J. Sabacky, A. Vince, and J. Prochazka. 2000c. Processing aqueous titanium solutions to titanium dioxide pigment. U.S. Patent 6548039, filed Feb. 14, 2000, and issued April 15, 2003.

Guinee, J. B. ed. 1992. *Handbook on life cycle assessment: Operational guide to the ISO standards*. Dordrecht, the Netherlands: Kluwer Academic.

Gutowski, T. G. 2009. Thermodynamic analysis of resources used in manufacturing processes. *Environmental Science and Technology* 43(5): 1584–1590.

Hau, J. L. and B. R. Bakshi. 2004. Expanding exergy analysis to account for ecosystem products and services. *Environmental Science & Technology* 38(13): 3768–3777.

Healy, M. L., L. J. Dahlben, and J. A. Isaacs. 2008. Environmental assessment of single-walled carbon nanotube processes. *Journal of Industrial Ecology* 12(3): 376–393.

Khanna, V., B. R. Bakshi, and L. J. Lee. 2008. Carbon nanofiber production: Life cycle energy consumption and environmental impact. *Journal of Industrial Ecology* 12(3): 394–421.

Khanna, V. and B. R. Bakshi. 2009. Carbon nanofiber polymer composites: Evaluation of life cycle energy use. *Environmental Science and Technology* 43(6): 2078–2084.

Kotas, T. J. 1986. Exergy method of thermal and chemical plant analysis. *Chemical Engineering Research and Design* 64: 212–229.

Kushnir, D. and B. A. Sanden. 2008. Energy requirements of carbon nanoparticle production. *Journal of Industrial Ecology* 12(3): 360–375.

Meester, B. D., J. DeWulf, A. Janssens, and H. Van Langenhove. 2006. An improved calculation of the exergy of natural resources for exergetic life cycle assessment (ELCA). *Environmental Science and Technology* 40: 6844–6851.

Odum, H. T. 1996. *Environmental Accounting: EMERGY and environmental decision making*. New York: Wiley.

Reck, E. and M. Richards. 1999. TiO_2 manufacture and life cycle analysis. *Pigment and Resin Technology* 28(3): 149–157.

Smil, V. 2008. *Energy in nature and society: General energetics of complex systems*. Cambridge, MA: MIT Press.

Szargut, J. 2005. *Exergy method: Technical and ecological applications*. Southampton, UK: WIT Press.

Szargut, J., D. R. Morris, and F. Steward. 1988. *Exergy analysis of thermal, chemical, and metallurgical processes*. Amsterdam: John Benjamins.

U.S. Geological Survey. 2006. *Titanium mineral concentrates*. Reston, VA: U.S. Geological Survey.

Verhulst, D., B. Sabacky, T. Spitler, and W. Duyvesteyn. 2002. The Altair TiO_2 pigment process and its extension to the field of nanomaterials. *CIM Bulletin* 95: 89–94.

Verhulst, D., B. Sabacky, T. Spitler, and J. Prochazka. 2003. New developments in the Altair TiO_2 hydrochloride pigment process. In *Proceedings of the 5th International Conference in Honor of Professor Ian Ritchie*.

Verhulst, D., B. Sabacky, J. Lang, and D. Ellsworth. 2006a. Iron control in the Altair hydrochloride pigment process. In *Proceedings of the 3rd International Symposium on Iron Control in Hydrometallurgy*.

Verhulst, D., B. Sabacky, R. Marganski, B. Wang, and D. Ellsworth. 2006b. Optimization of the critical steps of the Altair hydrochloride pigment process. In *Proceedings of the Sohn Symposium on Advanced Processing of Metals and Materials*. Warrendale, PA: TMS.

West, R. H., G. J. O. Beran, W. H. Green, and M. Kraft. 2007. First-principles thermochemistry for the production of TiO_2 from $TiCl_4$. *Journal of Physical Chemistry* 111: 3560–3565.

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Supporting Information

Supporting information may be found in the online version of this article:

Supporting information S1 This supporting information provides details about the calculations used in the main article, along with tables and figures containing more details about the study.

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