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Executive Summary

The objective of this project was to demonstrate the potential of a new process technology to reduce the energy consumption and CO₂ emission from the production of titanium dioxide (TiO₂) pigment. TiO₂ is one of the most commonly used minerals in the chemical manufacturing industry. It has been commercially processed as a pigment since the early 1900's, and has a wide variety of domestic and industrial applications. TiO₂ pigment is currently produced primarily by the use of the so called "chloride process". A key step of the chloride process relies on high temperature carbo-chlorination of TiO₂ bearing raw materials, hence producing large quantities of CO₂. The new method uses a chemical/metallurgical sequential extraction methodology to produce pigment grade TiO₂ from high-TiO₂ slag. The specific project objectives were to 1) study and prove the scientific validity of the concept, 2) understand the primary chemical reactions and the efficiency of sequential extraction schemes, 3) determine the properties of TiO₂ produced using the technology, and 4) model the energy consumptions and environmental benefits of the technology.

These objectives were successfully met and a new process for producing commercial quality TiO₂ pigment was developed and experimentally validated. The process features a unique combination of established metallurgical processes, including alkaline roasting of titania slag followed by leaching, solvent extraction, hydrolysis, and calcination. The caustic, acidic, and organic streams in the process will also be regenerated and reused in the process, greatly reducing environmental waste. The purpose and effect of each of these steps in producing purified TiO₂ is detailed in the report. The levels of impurities in our pigment meet the requirements for commercial pigment, and are nearly equivalent to those of two commercial pigments. Solvent extraction with an amine extractant proved to be extremely effective in achieving these targets.

A model plant producing 100,000 tons TiO₂ per year was designed that would employ the new method of pigment manufacture. A flow sheet was developed and a mass and energy balance was performed. A comparison of the new process and the chloride process indicate that implementation of the new process in the US would result in a 21% decrease in energy consumption, an annual energy savings of 42.7 million GJ. The new process would reduce CO₂ emissions by 21% in comparison to the chloride process, an annual reduction of 2.70 million tons of CO₂. Since the process equipment employed in the new process is well established in other industrial processes and the raw materials for the two processes are identical we believe the capital, labor and materials cost of production of pigment grade TiO₂ using the new method would be at least equivalent to that of the chloride process. Additionally, it is likely that the operating costs will be lower by using the new process because of the reduced energy consumption.

Although the new process technology is logical and feasible based on its chemistry, thermodynamic principles, and experimental results, its development and refinement through more rigorous and comprehensive research at the kilogram scale is needed to establish it as a competitive industrial process. The effect of the recycling of process streams on the final product quality should also be investigated. Further development would also help determine if the energy efficiency and the environmental benefits of the new process are indeed significantly better than current commercial methods of pigment manufacture.

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Disclaimer: Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

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1. INTRODUCTION

1.1 Scope and Objectives

The overall objective of the proposed project was to demonstrate the potential of a new process technology that reduces energy consumption and CO₂ emission from the production of titanium dioxide (TiO₂) pigment. This was accomplished by following four specific objectives

- *Study and prove the scientific validity of the concept*
- *Understand the primary chemical reactions and the efficiency of sequential extraction schemes that may affect the practical implications of the concept*
- *Determine the properties of TiO₂ produced using the technology*
- *Model energy consumptions and environmental benefits of the technology.*

This report details the results of the successful completion of these objectives throughout the course of the project.

We proposed to replace the chloride process with an integrated chemical sequential treatment and extraction process. We designed and developed a sequential extraction scheme, or a multistage method by which specifically designed thermal treatments and chemical reagents were sequentially applied to the solid mixture to achieve metal fractionation. The selected treatments and reagents (or extractants), the number of stages, and the order by which they were applied were studied and the best process parameters were chosen.

The overall sequence from feed material to pigment is shown in **Figure 1**.

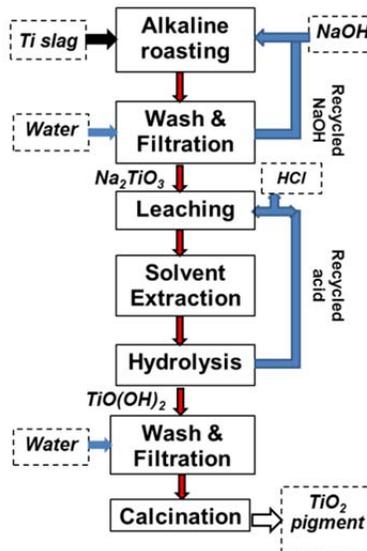


Figure 1. Flow sheet of the new process for making TiO₂ pigment

It can be seen that the chloride process is replaced by several industrially mature unit processes that are arranged in a unique and novel sequence.

1. Alkaline roasting involving the reaction of titania slag and alkaline hydroxides at moderate temperatures
2. Chemical sequential extraction and purification processes - *including acid leaching and solvent extraction* - for removing iron, silicon, and other impurities from the material
3. Hydrolysis and calcination to produce raw TiO₂ pigment

The key distinction between the developed process and the chloride process is that the chloride process is pyrometallurgical (high-temperature), while the proposed process is a hydrometallurgical process (water based). The new process avoids the high-temperature carbochlorination and oxidation steps of the chloride process, inherently reducing the required energy and eliminating direct CO₂ emission.

The key distinction from the sulfate process is that the new process uses alkaline digestion instead of acid, and recycles process reagents instead of discharging them into the local environment.

1.2 Key Challenges

Based on the experimental results and the industrial requirements for pigment products, the key Challenges to the proposed overall process scheme were:

- 1) Purity: The process had to produce a TiO₂ pigment product with iron (Fe) and other transition metal content below 50 ppm. These metals can discolor and degrade the whitening ability of the pigment. Each unit process serves to produce a purer TiO₂ product by specifically removing one or more of the discoloring impurities. As shown in our Experimental Results, the current embodiment of our procedure produces a pigment product that meets or exceeds the requirements of commercial pigments produced by the sulfate and chloride processes.
- 2) Energy: Because the process involves leaching and hydrolysis, steps that require heating large quantities of water, the process was designed to ensure that the total energy consumption was reduced by the use of waste heat recovery
- 3) Recycling: The primary goal of recycling and regeneration of reagents is to reduce process wastes. In addition to that, the energy consumption of recycling / regeneration of HCl and NaOH were accounted for in the overall energy consumption tally to ensure the entire life cycle is more energy efficient than conventional processes.

As it will be shown in the Experimental Results, we have demonstrated on the gram scale that the chemistry of the proposed process is valid and sound. High purity TiO₂ products were produced using the proposed chemistry. Before reporting the experimental results, however, the specific steps in the developed process and the experimental procedures are described in the Technical Approach section.

2. BACKGROUND

Titanium dioxide (TiO₂) is one of the most commonly used minerals in the chemical manufacturing industry. It has been commercially processed as a pigment since the early 1900's, and has a wide variety of domestic and industrial applications [1]. Due to their unique optical properties, TiO₂ nanoparticles are also becoming increasingly significant in technological applications. TiO₂ has the highest refractive index (2.4-2.7) of any other inorganic pigment, imparting a high level of opacity (and hence whiteness) to whatever material it is added [2]. The world production of titanium mineral concentrates was 6.7 million metric tons in 2011, with approximately 95% of concentrates consumed for titanium dioxide pigment production. US pigment manufacturers produced 1.4 million tons of TiO₂ in 2011 with a value of 3.8 billion USD [3]. Titanium dioxide is commercially produced by two distinct methods: the sulfate process [4] and the chloride process [5].

2.1 The sulfate process

The sulfate process involves digesting ilmenite or titania slag 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. The major advantages include low capital costs and flexibility in feed material. The major disadvantages of this process include an abundant generation of acidic and solid waste, a large consumption of energy, and a variable quality of product due to batch (as oppose to continuous) processing. This process accounts for roughly 40% of the total TiO₂ pigment produced world-wide [6].

2.2 The chloride process

The chloride process involves reacting rutile (natural or synthetic) or titania slag with petroleum coke and chlorine gas at high temperatures, forming a titanium tetrachloride (TiCl₄) vapor. The vapor is distilled and then oxidized at 1300-1800°C with oxygen and AlCl₃. The key reactions for this process are shown below.



The resulting product of these reactions is a purified TiO₂ pigment. A process flow chart is shown in **Figure 2**.

While the process does not produce the same magnitude of wastes as the sulfate method, it still has several environmental issues of its own. From the stoichiometry of Reaction 1, we can see that 1 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 3.4 million metric tons per year (60% of total world production), resulting in approximately 1.9 million tons per year of CO_2 directly emitted from this reaction alone.

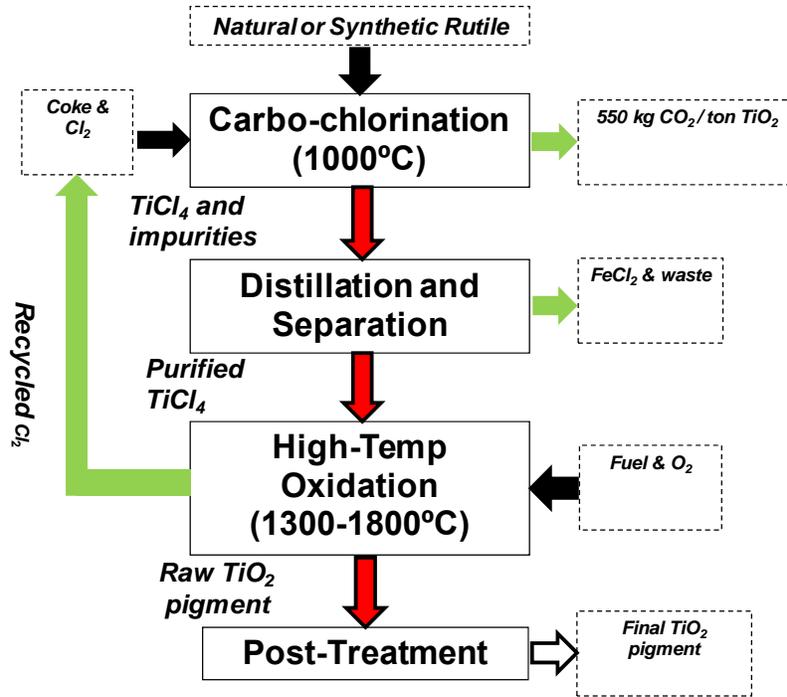


Figure 2. Flow sheet of the chloride process

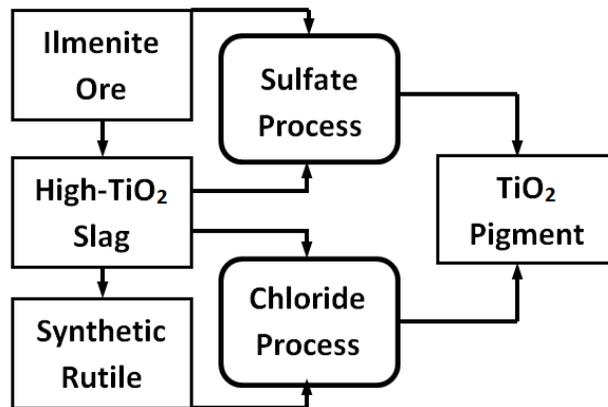


Figure 3. Schematic illustration of conventional pigment manufacturing processes from ore to pigment

2.3 Raw materials for TiO₂ pigment production

Figure 3 shows the raw material for the chloride process can be either titania slag or synthetic rutile. The most common method for producing titania slag is the smelting process which reduces iron oxides to liquid iron in large electric arc furnaces [7]. The main product of the smelting is high-TiO₂ slag containing approximately 75 to 85% TiO₂. The co-product of smelting is pig iron, which can be used as raw material for the steel industry. The smelting process is valuable because the pig iron co-product is considerably more useful and environmentally friendly than the large quantities of iron sulfate waste produced by digesting raw ilmenite in the sulfate process. Synthetic rutile can be considered a further upgraded raw material from high-TiO₂ slag (titania slag), with a TiO₂ content of 92-96%. Synthetic rutile is produced by a combination of partial reduction and acid leaching steps [8]. The energy consumed in producing either slag or synthetic rutile is roughly equivalent (35.5 and 35.0 MJ/ton TiO₂, respectively) [9]. However, the production of synthetic rutile results in a considerable amount of solid and acidic waste. For this reason, we have chosen to use titania slag as the feed material for our new process.

Overall, the use of the chloride process is preferred over the use of sulfate process. Therefore, any new process must be significantly more energy efficient and more environmentally friendly than the chloride process.

2.4 The Altair process

In addition to the two conventional commercial processes, there are other possible processes that are promising and should be noted here. Among them, the hydrometallurgical process patented by Altair Nanomaterials Inc is relevant to the proposed technology [10]. The Altair process involves digestion of ore using concentrated hydrochloric acid followed by multiple leaching, reduction, crystallization, solvent-extraction, evaporation, hydrolysis, and calcination steps. The advantages of the Altair process over that of conventional chloride or sulfate processes are that it does not need extreme high temperature and it does not produce large volumes of acidic liquid waste. Therefore, the Altair process is in the right direction. However, it is also apparent that the Altair process is very complicated, requires expensive process equipment materials to withstand concentrated acid, and is an inherently energy intensive process.

3. TECHNICAL APPROACH

The key components of the overall process for separating TiO₂ from other elements/compounds in the slag and purifying the products include the following:

- a) Alkaline roasting,
- b) Leaching using HCl solution,
- c) Solvent extraction, and
- d) Hydrolysis and calcination.

3.1 Roasting

Roasting is one of several standardized chemical metallurgy processes for upgrading metals from raw materials or intermediate products such as slag. Alkaline roasting of vanadium slags has been an established upgrading process for several years [11].

We applied this established alkaline hydroxide roasting process to titanium bearing slags in order to produce pigment grade TiO₂ (>99%) when it is combined with the subsequent purification processes. The role of the roasting process was twofold:

- 1). *Chemically separate titanium dioxide from iron oxides, silica, and other impurities through the reactions of the slag with an alkaline metal hydroxide such as NaOH.*
- 2). *Form soluble sodium-metal compounds with impurity metals so that they may be removed with water in subsequent steps*

First, the chemical separation of TiO₂ from iron oxides and other impurities are accomplished by the following reactions:



By forming Na₂TiO₃, TiO₂ is chemically separated from iron oxides and other impurities. Na₂TiO₃ will later be reacted with acid to form TiOCl₂ solution, which when hydrolyzed and calcined, will become pure TiO₂. It should be noted that Na₂TiO₃ is insoluble in water but does dissolve in HCl solutions.

Second, the other role of roasting is to prepare the impurity elements for removal. Impurities in titania slag typically include FeO, SiO₂, Al₂O₃, CaO, and MgO and so on. Alkaline salts such as NaOH react with these oxides in the slag to form various sodium-metal complexes. Impurity elements such as Al, Mn, Cr, V, and Si form water soluble complexes that can easily be washed away whereas Fe, Mg, and Ca form insoluble compounds that must be removed in

subsequent extraction stages. The success of these conversions was optimized by controlling the NaOH to slag ratio and temperature of the roasting.

Sorelslag (provided by Rio Tinto Iron and Titanium) was used as the raw material for our roasting experiments. Sorelslag has a total TiO_2 content of 78.5 % with FeO (9.75%) and MgO (5.57%) as major impurities. For initial experiments, several grams of slag were mixed with excess reagent grade NaOH in a nickel crucible and heated for four hours inside a muffle furnace. The molten mixture was removed and washed 3 times with distilled water and filtered to remove excess NaOH and remove soluble impurity compounds. A sample of washed product was dissolved in acid and analyzed using ICP. Roasted slag samples both before and after washing were analyzed using X-ray diffraction and SEM.

For subsequent roasting experiments, a cylindrical reaction vessel was fabricated from $\frac{1}{4}$ inch thick Inconel 200 pipe. A nickel based alloy was necessary due to the highly corrosive environment of using molten sodium hydroxide. The vessel had ports for an agitator and a thermocouple as well as a sampling port in which the slag and NaOH were poured in and sampled with during the experiment. The agitator was also made of nickel. The temperature was monitored with an Omega K-type thermocouple with the tip 1 mm above the bottom of the vessel. The vessel was placed inside a Xin Yoo XY1200 top loading crucible furnace and the periphery of the vessel was filled in with insulating wool. The furnace was equipped with a self-regulating temperature control unit that allowed for a constant temperature with $\pm 1^\circ \text{C}$ precision to be maintained within the reaction vessel. A diagram of the vessel and furnace setup is shown in **Figure 4**.

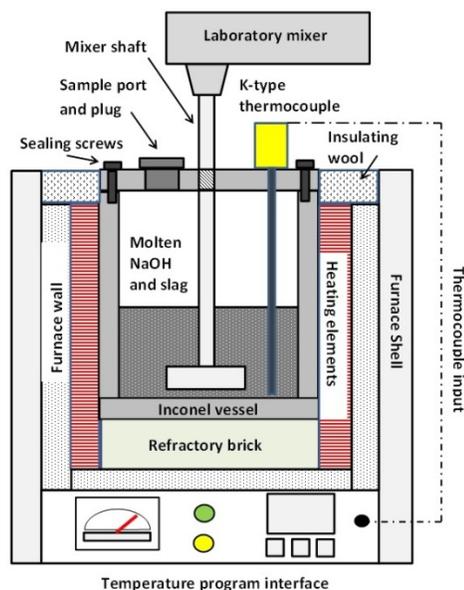


Figure 4. Experimental setup for the alkaline roasting of titania slag

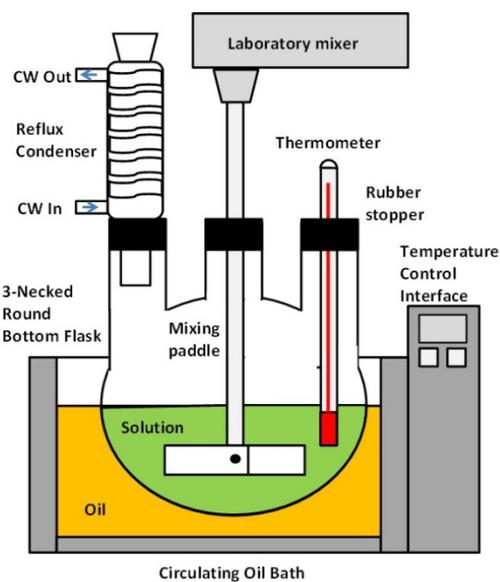


Figure 5. Experimental setup for the acid leaching of roasted slag

3.2 Leaching

As mentioned previously, trace amounts of impurity elements such as Fe have strong negative effects on the “whiteness” of TiO₂ pigments. One of the most difficult challenges is to reduce Fe and other transition metal contents to below 50 ppm. The critical steps for removing Fe and other remaining transition elements not completely removed by roasting and washing are the leaching and the solvent extraction processes prior to hydrolysis.

Leaching was performed by dissolving washed Na₂TiO₃ product with various concentrations of HCl solution in a stirred reactor at various temperatures. The Na₂TiO₃ reacts according to the following reaction:



TiO₂ also reacts with HCl according to the following:



Iron and other impurities follow similar dissolution reactions.

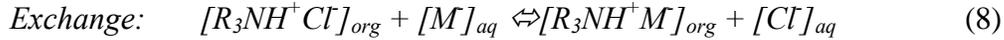
The majority of the Na₂TiO₃ will dissolved after a relatively short amount of time, leaving behind Ca and Si compounds that have limited solubility. Unfortunately, most of the Fe and other transition metals also dissolved into solution. The leach solutions were heated in a 3-necked round bottomed glass reactor submersed in a temperature controlled oil-bath. The leach solution was stirred by a polypropylene paddle attached to a standard laboratory mixer mounted above the oil bath. The leaching temperature was monitored by a standard laboratory thermometer and a reflux condenser was also used to minimize solution loss by evaporation. A diagram of the leaching apparatus is shown in **Figure 5**. The leach solutions were filtered using a Buchner funnel and filter paper. The leach liquor was diluted in 5% nitric acid and analyzed using an ICP-OES or ICP-MS analyzer.

3.3 Solvent extraction

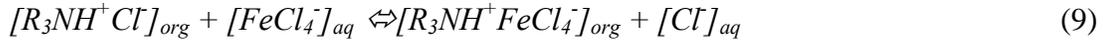
TiO₂ pigment produced in preliminary tests had a slight yellow tint. Even in very small concentrations, transition metals such as iron and chromium can act as chromophores that significantly reduce the whiteness of the pigment. Rigorous washing of the precalcined hydrate with reducing solutions such as Ti₂(SO₄)₃ proved to be insufficient in their removal of Fe and other metal impurities. Therefore, the use of an amine extractant to preferentially extract Fe in the leach solution prior to hydrolysis was investigated.

Amine extractants have been used for decades in various solution concentration and purification applications. Alamine 336 is a common amine extractant that has been used to

recover a wide variety of dissolved metals including cadmium, cobalt, iron, hafnium, tungsten, uranium and vanadium [12]. Alamine 336 is an insoluble tri-octyl/decyl amine that forms soluble salts of anionic species at low pH in organic diluents such as kerosene. It contains a basic nitrogen atom that can react with a variety of inorganic acids to form amine salts that undergo ion exchange with other anionic species. The general reaction in chloride media is shown below in two steps, protonation and exchange [13].



The extent to which a metal anionic complex, M^- , exchanges for Cl^- is dependent on the affinity of the two anions for the cation and the energy of solvation by the aqueous phase. The formation and extraction of the anionic complexes depends upon the concentration of the anion forming the anionic complex, such as chloride in iron chloro-complexes. Iron forms an anionic chloro-complex, $(FeCl_4)^-$, which exchanges with Cl^- ions in the amine salt, as shown in the following reaction.



Solvent extraction was performed by mixing filtered leach solution with the organic extractant phase for several minutes in a glass beaker and then separating the phases in a separatory funnel (aqueous and organic phases are immiscible), resulting in an organic phase “loaded” with iron and a nearly iron-free Ti aqueous solution. The organic solvent was comprised of 20 vol. % Alamine 336 diluted in kerosene with 10 vol. % dodecanol added as a modifier to prevent third phase formation. The best results were obtained when the organic solvent was mixed with the leach solution in a volume ratio of 1.33:1 and a solution temperature of 40-45° C.

3.4 Hydrolysis and calcination

Hydrolysis involves heating and stirring the titanium bearing solution to promote the formation of H_2TiO_3 , an insoluble hydrated titanium oxide compound known as metatitanic acid. The reaction proceeds according to the following equation:



Most of the soluble impurities were left in solution. Hydrolysis was conducted using the same apparatus as the leaching step, although the solution temperature was increased to 100°C. The resulting precipitate was separated from solution by centrifugation and thoroughly rinsed with dilute HCl to remove absorbed impurities. The hydrolysis solution was sampled at various times and analyzed using ICP-OES.

The metatitanic acid pulp was transferred to a small alumina crucible and heated in a muffle furnace to 650-900° C, allowing for the release of chemically bound water and the formation of TiO₂ crystals, as shown in the following equation:



The crystal type, particle size and morphology were dependent on the temperature of the calcination as well as the size and morphology of the product of hydrolysis. The resulting TiO₂ pigment was analyzed using X-ray diffraction and SEM. The purity of the pigment was analyzed by acid digestion and ICP-MS analysis.

3.5 Utilizing waste heat

Minimizing energy consumptions by utilizing waste heat is an important component of the proposed technology. The unit processes can be divided into two groups: a) those that operate at less than 100°C in aqueous solutions, such as leaching (~50°C), solvent extraction (~40°C) and hydrolysis (~100°C); and b) those that operate at above 100°C, such as NaOH roasting of titania slag (~500°C) and calcination of H₂TiO₃ (650-900°C).

The high temperature steps produce a significant amount of so-called medium-temperature (230-650°C) or high-temperature (>650°C) waste heat which can be economically utilized for the low temperature steps, thus minimizing the energy consumptions of the overall proposed process. For either of the two high temperature steps, i.e., NaOH roasting of titania slag and calcination of H₂TiO₃, one part of the waste heat is contained in the high temperature flue gas consisting of large amount of water vapor released from the reaction; the other part of waste heat is released during the cooling of the reaction product discharge, i.e., Na₂TiO₃ or TiO₂.

A common practice in the production of TiO₂ pigment using the sulfate process is to blow steam into the solution bath to offer very efficient heating for the hydrolysis step. Therefore, the waste heat from both the hot flue gas and the product discharge in the high temperature steps in the proposed process will be converted into hot steam by using the waste heat boiler as illustrated in **Figure 6**. The waste heat of hot flue gas can be directly inputted into the boiler, while the waste heat of product discharge needs to be transferred first to air passing through a cooling rotary (where the product discharge is contained for cooling down) and then inputted into the boiler. A cooling rotary is a heat exchanger commonly used for recovery of waste heat of calcinations in the sulfate process. Although experimental data for process heat recovery was

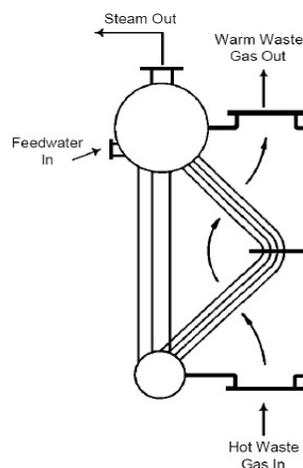


Figure 6. Schematic of a waste-heat boiler

beyond the scope of our project, the amount of recoverable heat from higher temperature reactions is estimated in the energy analysis section.

3.6 Recycling and regeneration of HCl and NaOH

Recycling and regeneration of HCl and NaOH is another critical component of the developed technology. The residual acidic or alkaline solutions must be treated and recycled. The net effect of the regeneration and recycling is that the entire proposed process for making TiO₂ will have significantly reduced waste streams, which provide an important advantage over the current processes.

In general, acid and/or alkaline waste solutions from metallurgical industries are often mixed with lime or acid to neutralize the solution. The residual solutions from TiO₂ production in the proposed process may contain low concentrations of salts (NaCl) from acid leaching and NaOH from alkaline leaching. A portion of the residual NaOH solution can be concentrated and reused in the roasting process using multiple effect evaporators. Another portion can be used to neutralize residual acid streams, which forms a residual NaCl brine solution that can be treated to produce HCl and NaOH solutions on site using electrolytic techniques. During the electrolytic process, most or all impurities in the residual solution can also be recovered and/or removed as solids.

The reactions during the regeneration of HCl and NaOH by electrolysis from the residual NaCl solutions are as follows:

Anode half-cell reaction for production of chlorine -



Cathode half-cell reaction for production of hydrogen -



Chlorine and hydrogen form HCl in the gas phase -



HCl is adsorbed by water to produce industrial grade hydrochloric acid. In the aqueous phase, Na⁺ and OH⁻ combine to form NaOH. The resulting NaOH and HCl produced by this process can be reused in the initial roasting and leaching steps of the overall process. Thus, the main process reagents can be recycled.

Some impurities will remain in the residual solutions from the process. Most impurities will be removed from the electrolysis solution prior to electrolysis. Impurity removal will be performed by first neutralizing the solution or by solvent extraction/ion exchange techniques.

Increasing the pH of the solution will cause many of the impurity metals such as Fe(II), Al(III), Cr(III), Ca(II), and Mg(II) to precipitate as hydroxide compounds. Si(IV) will convert to SiO₂. Alternatively, removal of residual impurity metals will be performed by adding a small amount of sodium sulfide. The residual metal impurity precipitates will be filtered from the residual solution prior to electrolysis. It is expected that a small amount of the impurities may remain in electrolyte solution without adversely affecting the process [14].

4. EXPERIMENTAL RESULTS

The feasibility of the proposed technology lies in the feasibility of each individual step of the process. The key reactions of the overall process, including those discussed above, were tested and validated on the gram scale in the laboratory. The results of these tests are summarized below.

4.1 Roasting with NaOH

XRD analysis confirmed that the major product of the NaOH/slag reaction is indeed Na₂TiO₃ and some free TiO₂ (see **Figure 7**). Other peaks are attributed to small amounts of unreacted slag.

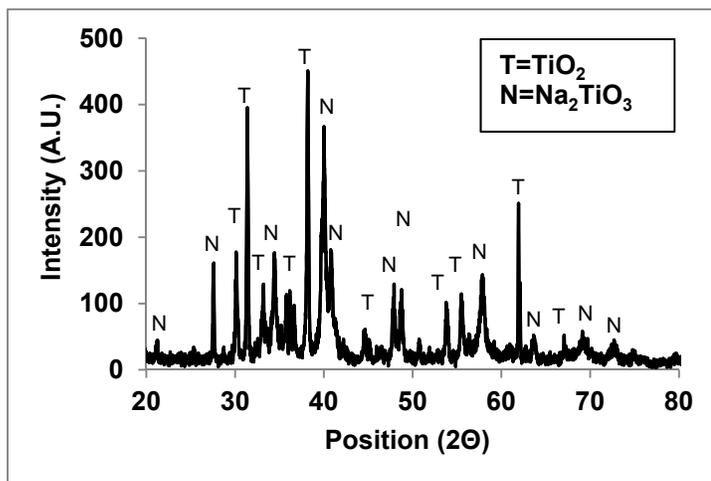


Figure 7. X-ray diffraction pattern of roasted slag

A sample of washed product was dissolved in acid and analyzed using ICP. The composition is shown in **Table I**. As we predicted, the major impurities in the insoluble after-wash solid are iron, calcium, and magnesium compounds. ICP analysis of the initial wash-water indicates that a majority of the Cr, Al, Mn, and Si were dissolved into the alkali solution, as is also shown in **Table I**. This step represents a major removal of these soluble impurities.

Table 1. Compositions of alkaline roast product and wash solution following washing

Wash Product (in wt. %)							
Ti	Na	Fe	Mg	Ca	Mn	Si	Al
35.67	11.46	6.00	2.65	0.44	0.18	0.15	0.14
Wash Solution (in ppm)							
Ti	Na	Fe	Mg	Ca	Mn	Si	Al
<1	132500	6	<1	4	<1	260	950

4.2 Leaching

The extent of leaching has strong dependence on the concentration of HCl solution. A series of leach tests were performed using HCl solutions varying from 0.75 M to 2.0 M at a pulp density of 2% by weight. The leaching was conducted at 50°C for 1 hour. Recovery is measured as the amount of each metal leached into solution divided by the total amount originally present in the solid. The leaching recoveries of the metals in the roast product are shown in **Figure 8** as a function of HCl concentration.

It is apparent that Ti recovery significantly improves with an increase in HCl concentration, whereas the recovery of Na remains relatively unchanged. After each leaching experiment, the leach solution and undissolved solids were separated by vacuum filtration. At lower concentrations, the solution was quite turbid and difficult to filter. Once the HCl concentration exceeded 1.5, the filtered solution became clearer and had less fine suspended particles, although precipitation occurred in the filtered solution after a few days. It is apparent that lower concentrations of acid are sufficient to dissolve Ti but not to keep it in solution, resulting in low temperature hydrolysis. The product of low temperature hydrolysis is a hydrated titanium oxide compound known as orthotitanic acid, Ti(OH)_4 ($\text{TiO}_2 \cdot 2\text{H}_2\text{O}$) [15]. The concentration of Ti in the residue did not vary much from sample to sample, although the amount of residue decreased with increasing acidity. The structure of the residue for each sample did not vary and showed only weak anatase and SiO_2 peaks.

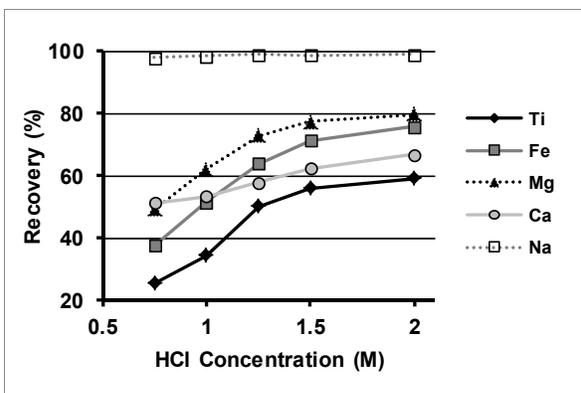


Figure 8. Leaching recovery of Ti and impurity metals as a function of HCl concentration. The leaching was performed for 1 hour at a pulp density of 9% and a temperature of 50°C

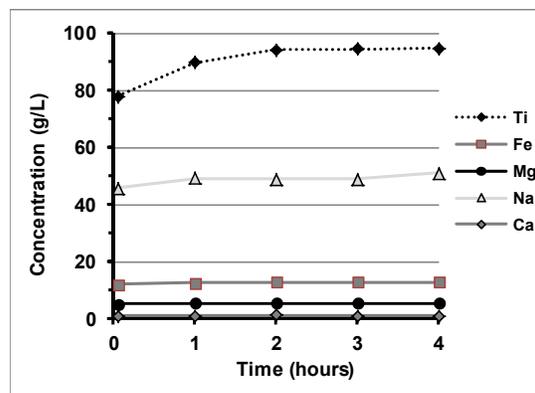


Figure 9. Leaching recovery of Ti and impurity metals as a function of time. The leaching was performed with 5 M HCl at a pulp density of 9% and a temperature of 50°C

Leaching experiments using higher concentrations of acid but at higher pulp density were also conducted. The leaching was performed with 5 M HCl at a pulp density of 9% by weight and a temperature of 50°C. The solution was sampled after 3 minutes and at each hour afterwards. The aliquots were filtered and diluted for ICP analysis. The various concentrations of metals in solution as a function of time are shown in **Figure 9**.

It is apparent that the dissolution reaction occurs very rapidly and that a substantial portion of metals have been dissolved after only a few minutes. The concentration of Ti in solution was 77.8 g/L after 3 minutes and 94.1 g/L after two hours, increasing only slightly to 94.6 g/L after 4 hours. The stability of the Ti concentration over several hours and the negligible amount of residue at the end of the experiment indicates that minimal if any low temperature hydrolysis occurred. It also appears that the leaching of most of the impurities occurs almost immediately and increases only slightly thereafter. The concentration of Fe after 3 minutes was 12.0 g/L and only increased to 13.0 g/L after 4 hours. The other impurity metals had concentrations of less than 1.0 g/L and showed little increase over time. Leaching experiments conducted at the same pulp density but with even higher concentrations of HCl (8.4 M and 12 M) appeared to increase Ti recovery only marginally.

4.3 Solvent extraction (SX)

Initially, the leach solutions were filtered, hydrolyzed, thoroughly washed, and then calcined. However this procedure failed to reduce the iron content to acceptable levels. Therefore, a solvent extraction (SX) procedure was developed to remove Fe content in the leach liquor prior to hydrolysis.

The leach solution used in the solvent extraction experiments was prepared by leaching the washed after-roast product with various concentrations of hydrochloric acid. The liquid to

solids ratio for each leaching test was 10:1. The compositions of the leach solution prepared with 5 M HCl and the raffinate after one contact are shown in **Table II**.

Table II. Composition of pregnant leach solution and raffinate

(in ppm)	Ti	Fe	Al	Mg	Mn	Ca	Si	Na
Leach Solution	94610	12970	270	5580	80	1140	620	51060
Raffinate	105270	<10	300	6160	100	1230	620	55300

It is apparent that nearly 100% of the Fe in the leach solution was removed after a single contact with the amine extractant. The reaction occurred very rapidly with equilibrium between the phases occurring in less than a minute of contact time. The level of Fe was less than the detectable limit of the ICP analyzer (0.01 ppm), which when correcting for dilution, was less than 0.01 g/L, or 10 ppm. The concentration of the other metals increase slightly due to the removal of Fe from the aqueous system. These results represent a major breakthrough in overcoming the challenge of producing sufficiently pure TiO₂ pigment by the new process.

The extraction efficiency of a particular extractant for a metal is given by the extraction coefficient, E_C . This coefficient is determined by dividing the equilibrium concentration of metal in the organic phase by the concentration in the aqueous phase. The concentration of metal within the organic phase was determined by mass balance.

Leach solutions prepared by using various concentrations of HCl acid were contacted with amine extractant under the same conditions mentioned previously. One solution was prepared by using 4.8 M HCl with 1.5 M CaCl₂ added to bring the total chloride concentration to 7.8 M. The extraction coefficients of each metal after a single contact of the solvent with each solution are shown in **Table III**.

Table III. Extraction coefficients after one contact of Alamine 336 extractant with solutions prepared at different HCl and total chloride concentrations

[Cl ⁻] (M)	[HCl] (M)	Ti	Fe	Al	Mg	Mn	Ca	Na
1.6	1.6	-	0.10	-	-	-	-	-
5	5	-	970	-	-	-	-	-
7.8	4.8	0.01	770	0.20	0.02	0.63	0.27	0.12
8.3	8.3	0.14	390	0.37	0.14	0.24	0.21	0.13
12	12	0.09	190	0.06	0.01	0.54	0.11	0.02

The highest extraction coefficient for Fe was 970 at 5 M HCl which then declined with further addition of chloride to the system. In the test with 1.6 M HCl, a considerable amount of Ti precipitated upon contact of the solvent with the leach solution, and the extraction of Fe was very poor. The 4.8 M HCl solution with added CaCl₂ showed better extraction than the solution with higher acid and chloride concentrations but not as well as the 5 M HCl solution. It is apparent that relatively high chloride concentrations are needed for appreciable extraction, however excessively high concentrations can limit extraction.

4.4 Hydrolysis

A portion of Ti solution that had undergone solvent extraction was diluted by a factor of four with distilled water, heated at 100°C for several hours and stirred at 300 rpm. The diluted solution contained 26.3 g/L Ti. Solution samples were taken after each hour and diluted for ICP analysis. The change in the concentrations of each of the metals as a percentage of initial concentrations is shown in **Figure 10**.

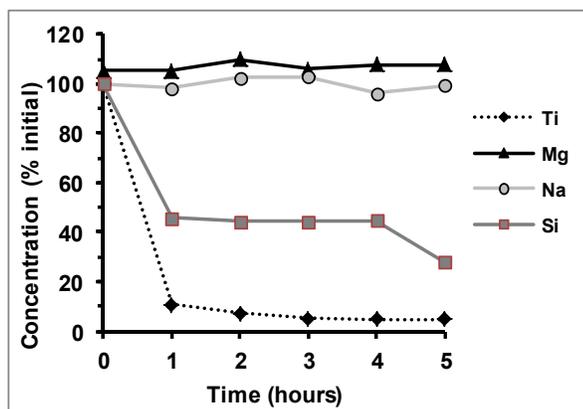


Figure 10. Concentration of dissolved Ti and other metals as a function of time during hydrolysis

Under the experimental conditions, the hydrolysis of Ti occurred rapidly as its concentration decreased nearly 90% in the first hour. The rate sharply decreased thereafter and stayed steady at 95% depletion after 3 hour. Due to the depletion of Ti in the solution, not surprisingly, the concentration of most of the impurities increased slightly above their initial concentrations. The main exception appears to be Si, which appeared to follow the trend of Ti. It is feasible that Si adsorbed onto the porous surface of the metatitanic acid particles.

4.5 Calcination and analysis of pigment purity

The morphology of pigment calcined at 650 °C for two hours was examined using SEM. As can be seen in **Figure 11**, the TiO₂ has formed clusters of spherical crystallites approximately 0.3-0.5 μm in diameter. The standard particle size for commercial pigments is 0.2-0.3 μm [16]. XRD analysis of the pigment indicates that only anatase TiO₂ is present as shown in **Figure 12**. Higher calcination temperatures will result in conversion to the rutile phase, although excessively high temperatures will sinter the particles and darken their color.

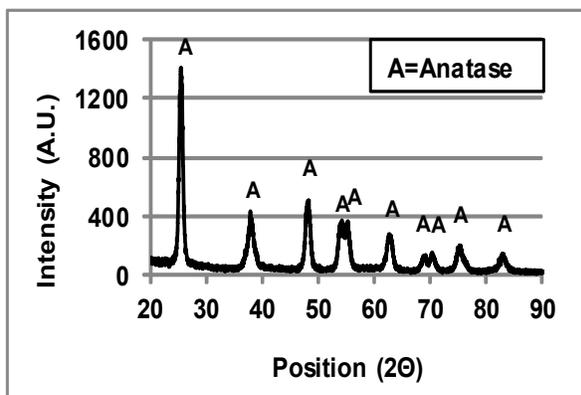
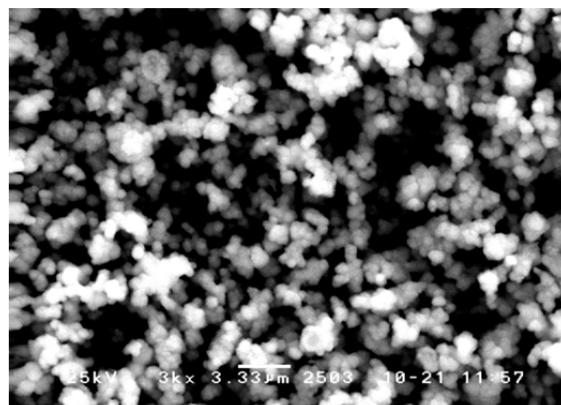


Figure 11. X-ray diffraction pattern of anatase TiO₂ pigment calcined at 650°C for 2 hours



Figures 12. SEM Image (3000x) of anatase TiO₂ pigment calcined at 650°C for 2 hours

The composition of the pigment was analyzed by digestion and ICP-MS. Two commercial pigments were also digested and analyzed for a comparison, and the compositions are shown in **Table IV**.

Table IV. Comparison of the concentration of impurities in pigment from new process and two commercial pigments

(in ppm)	Fe	Cr	Mg	Mn	Ca	Si	Na
Pigment W/O SX	962	63	492	16	290	19732	68
Pigment W/ SX	20	13	267	4	46	467	204
Company A- Anatase	<11	<63	458	<16	147	855	57
Company B- Rutile	12	<13	300	<7	112	386	110

It is apparent that the levels of impurities in our pigment meet the requirements for commercial pigment, and are nearly equivalent to those of two commercial pigments. Solvent extraction proved to be extremely effective in helping us achieve our targets

5. Energy, Environmental, and Economic Benefits

5.1 The reduction of energy consumption

A key objective of this research was to determine if the new method of TiO₂ pigment manufacture offers any benefits over current technology with regards to energy consumption. The methods of determining the answer to this question are detailed below.

5.1.1 The method for energy consumption analysis

Calculating the total energy consumption of a particular chemical product can be a challenging exercise, especially if the end product can be synthesized by a number of processes using a variety of starting materials and various methods of handling process wastes. This proves to be the case for TiO₂. Another difficulty is finding reliable data that describes the total energy input. Each analysis will consider different system boundaries, i.e., different starting and ending points to consider in the energy accounting. Some data sets only consider the process from the entry of the feed material to the production of the final pigment product. This boundary will be referred to as “**Feed to Gate**”. This analysis can only give a limited scope of the actual energy requirements and environmental impact that different processing routes produce. A more comprehensive consideration includes the energy requirements for mining, transporting and preparing the raw minerals for use as a feed stock in the particular unit processes (often referred to as beneficiation). The proper treatment of gaseous and liquid waste streams (referred to as emissions and effluents, respectively) is also important to consider. This more comprehensive analysis (sometimes referred to as Life-Cycle Assessment or LCA) will be referred to as “**Cradle to Gate**”. Judicious consideration of each of these factors is imperative for a proper comparison of the current and the proposed TiO₂ processing options. In this section, the comprehensive energy consumption analysis, i.e., “Cradle to Gate” method, is given for the chloride process, the sulfate process and the new process.

5.1.2 Defining System Boundaries

In order to make a fair comparison between the chloride process, the sulfate process and the new process, the starting and ending points for all three processes are assumed to be the same with ilmenite ore as the starting point and uncoated TiO₂ pigment as the ending point, as shown in **Figure 13**. The ilmenite smelting is an upgrading process for preparing feed material for the subsequent pigment production process.

For the sulfate process, though ilmenite can be directly used as feed material, the upgraded feed material, i.e., titania slag, is economically and environmentally more attractive, because there will be less waste disposal and most of the iron in the ilmenite will be transformed to higher-valued co-product (pig iron) during ilmenite smelting.

For the chloride process, another upgrading process (solid reduction plus acid leaching) to prepare another feed material, i.e., synthetic rutile, is also commercially used. However, as mentioned previously, the energy consumed in the production of synthetic rutile and titania slag is essentially equivalent. Therefore, it is reasonable to compare energy consumption between the different processes based on the route and the starting and ending points as **Figure 13** shows.

5.1.3 Energy consumption of the new process

A model plant producing 100,000 tons TiO₂ per year has been designed that would employ the new method of pigment manufacture. A flow sheet was developed and a mass and energy balance was performed. Process equipment was selected and sized according to data from mineral and chemical engineering equipment handbooks [17-20] and verified by professionals in the metallurgical processing industry. The energy required for roasting and calcination as well as the recoverable energy from the hot discharge products was calculated using HSC [21] thermodynamic calculations software available from Outokumpu Technologies. A heat loss of 20% was chosen for the roasting and calcination kilns, as well as a 15% loss in the waste heat boilers.

The estimated energy required for processing titania slag to uncoated pigment is 31.8 GJ/ton of TiO₂. This value includes the energy consumptions of NaOH roasting, leaching, solvent extraction, hydrolysis, calcination, milling, etc. The energy consumption of each step in the new pigment making process is shown in **Table V**. Also included are the size reduction,

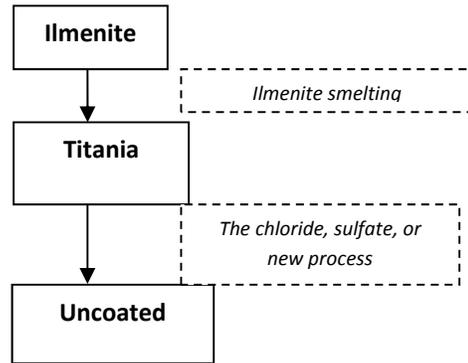


Figure 13. The system boundary of the energy consumption analysis of different processes.

solid-liquid separation, material transport, etc., associated with each step. It was assumed that the heat needed for the leaching stage would be provided by the hot recycled solution from the hydrolysis stage as well as the exothermic reaction of HCl gas with water. The processing steps from titania slag to uncoated pigment only make up roughly a quarter of the total energy consumption.

The recycling and regeneration of caustic and acid streams through the chlor-alkali electrolysis process contribute a substantial energy cost. Most of the caustic and chlorine used in the chemicals industry is produced by the chlor-alkali process, so more energy efficient methods of obtaining NaOH and HCl are not readily available. The energy requirements for the chlor-alkali process were taken from a Best Available Techniques report produced by the European Commission [14]. In order to produce sufficient fresh HCl and NaOH for the leaching and roasting processes, 53.7 GJ/ton of TiO₂ are consumed which accounts for 42.4% of the total energy requirements. This includes the energy to run the membrane technology chlor-alkali cells and the concentration of NaOH solution by evaporation.

As mentioned previously, heat recovery is also an integral aspect of the new process. It was calculated that 11.7 GJ of energy could be recovered for every ton of TiO₂ produced. This recovered heat, mostly in the form of steam, is an energy credit that results in less consumption of natural gas for lower temperature processes. Some electrical power (1.4 GJ / ton TiO₂) would be needed for pumping water through the heat exchanging tubes of the waste heat boilers and to run the cooling rotaries. A value of 39.6 GJ/ton TiO₂ for the production of titania slag from ilmenite is used for each of the three pigment making processes [22]. Thus, the total energy consumption of the new process is estimated to be 114.8 GJ/ton of TiO₂.

Table V. Energy consumption of each step in the new pigment making process

Energy (GJ/ton TiO ₂)	Energy (GJ/ton TiO ₂)		Total	% Total
	Nat Gas	Elec		
Slag Prep	9.5	30.1	39.6	31.4
Roasting	3.0	0.4	3.4	2.7
Leaching	-	0.2	0.2	0.2
Solvent Extraction	-	0.2	0.2	0.1
Hydrolysis	6.6	0.2	6.9	5.4
Calcination	17.4	3.7	21.1	16.7
Heat Recovery	-	1.4	1.4	1.1
Recyc/Regen	7.5	46.2	53.7	42.4
Total	44.0	82.4	126.4	100
Heat Recovered	11.7	-	11.7	9.2
Grand Total	32.3	82.4	114.8	

5.1.4 Energy consumption comparison between different processes

The energy consumption values for the sulfate process and the chloride process using slag as a feed material are 123.2 and 145.2 GJ/ton of TiO_2 , respectively, based on a US Bureau of Mines minerals energy consumption report prepared by Battelle Columbus Laboratories [22]. This report included a line-itemed list of the electricity and natural gas needed for each step of the sulfate and chloride processes, including those for slag preparation. The sulfate process energy tally also includes 13.8 GJ/ton TiO_2 to account for the recycle and reconcentration of spent sulfuric acid in the digestion process, which is becoming more common as environmental regulations tighten [23].

A comparison of the energy consumptions of the new pigment manufacturing process and the traditional processes is shown in **Figure 14**. Implementation of the new process would result in a 7% decrease in comparison to the sulfate process and a 21% decrease in comparison to the chloride process. Based on the annual production of 1.4 million metric tons of TiO_2 (predominantly by the chloride process) in the US according to USGS mineral commodity report [3], this means an annual energy savings of 42.7 million GJ.

The annual world production capacity of TiO_2 is approximately 6.5 million tons per year [3] with 60% of that made by the chloride process and the other 40% by the sulfate process. The total energy consumption is thus approximately 320.3 million GJ per year for the sulfate process and 566.5 million GJ per year for the chloride process, totaling 886.8 million GJ per year. If the two processes were replaced by the new process, a total of 140.8 million GJ would be saved, assuming of course that slag was the only feedstock used.

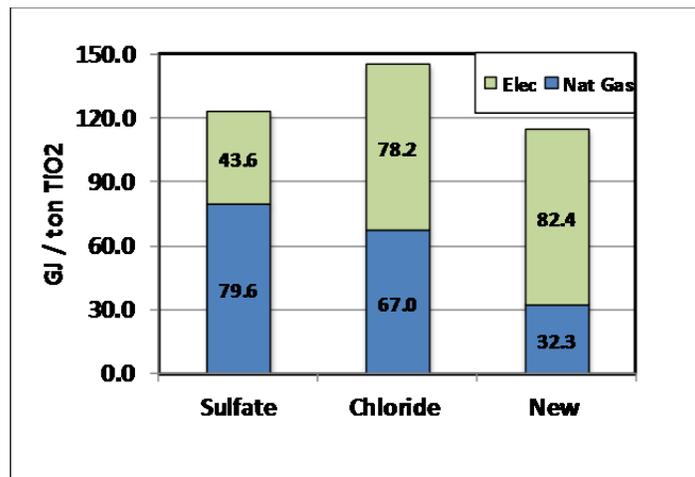


Figure 14. Energy consumption of the sulfate, chloride, and new methods of pigment manufacture, divided into contributions from electricity and natural gas

5.2 The reduction of CO₂ emission

CO₂ emission of any manufacturing processes consists of two parts: a) direct emission of CO₂ as a reaction product of the process; and b) indirect emission of CO₂ from the consumed energy of the process because producing energy will emit CO₂. While both the sulfate process and the new process have no direct CO₂ emissions, the chloride process releases a significant amount of CO₂ in the first stage of the process, i.e., carbo-chlorination step, when TiO₂ in the titania slag is converted into TiCl₄ (see Reaction 1). The reaction stoichiometry suggests that there will be 1 mol CO₂ released for every 1 mol TiO₂ produced by the chloride process, that is, approximately 550 kg of CO₂ per ton of TiO₂.

Based on the electricity and natural gas requirements reported above, it is possible to calculate the expected CO₂ emissions from each step in the new process. The calculations were made using the Greenhouse Equivalencies Calculator available on the EPA website [24]. The total kilowatt-hours and therms of natural gas consumed for each step were entered and the associated carbon footprint was returned, based on geographically averaged values. The CO₂ emitted from the carbothermic reduction of slag is included as part of the natural gas value for slag preparation. The emissions are reported as tons of CO₂ emitted per ton TiO₂ produced. The results of this analysis are shown in **Table 6**. The total CO₂ emission of the new process is 7.41 tons/ton TiO₂. As expected, the amount of CO₂ emitted is roughly proportional to the energy consumed in each step. The regeneration of process reagents is responsible for over 40% of the total carbon emissions closely followed by slag preparation. It is expected that the upgrading of ilmenite to synthetic rutile would have a similar carbon footprint.

Table VI. CO₂ emissions of each step in the new pigment making process

Emissions (Ton CO ₂ /ton TiO ₂)				
	Nat Gas	Elec	Total	%Total
Slag Prep	1.35	1.73	3.08	38.6
Roasting	0.14	0.03	0.17	2.1
Leaching		0.01	0.01	0.2
Solvent Extraction		0.01	0.01	0.1
Hydrolysis	0.31	0.01	0.33	4.1
Calcination	0.82	0.23	1.05	13.2
Heat Recovery		0.09	0.09	1.1
Reagent Recycle/Regen	0.35	2.87	3.23	40.5
Total	2.98	4.98	7.96	100
Heat Recovered	0.55		0.55	6.9
Grand Total	2.43	4.98	7.41	

The CO₂ emissions associated with the sulfate process and the chloride process have also been calculated based on the energy consumptions reported in the previous section. The total CO₂ emissions (direct and indirect) of each process are shown in Figure 15. The total CO₂ emissions of the sulfate process and the chloride process are 7.56 and 9.34 tons/ton TiO₂, respectively. Implementation of the new process would result in a 2% decrease in comparison to the sulfate process and a 21% decrease in comparison to the chloride process. Based on the annual US production of 1.4 million metric tons of TiO₂, this means an annual reduction of 2.70 million tons of CO₂. Using the world production values from the previous section, the total carbon footprint is approximately 19.7 million tons per year for the sulfate process and 36.4 million tons per year for the chloride process, totaling 56.1 million tons per year. The new process would reduce CO₂ emissions by 7.9 million tons, assuming once again that slag was the only feedstock used.

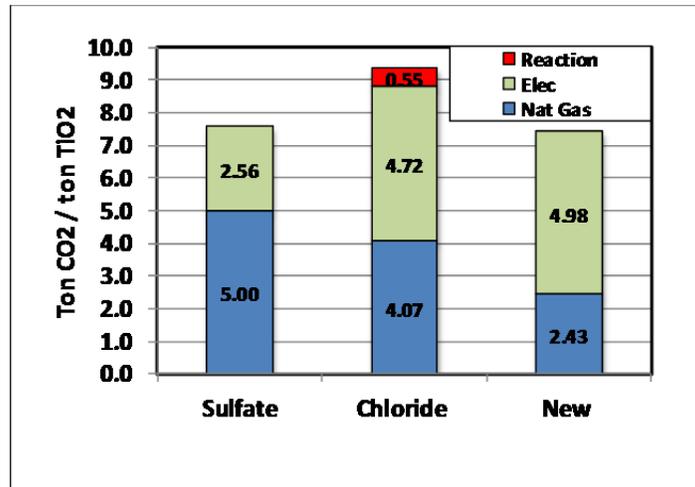


Figure 15. CO₂ emissions of the sulfate, chloride, and new methods of pigment manufacture, divided into contributions from electricity, natural gas, and direct emissions from chemical reactions

6. ACCOMPLISHMENTS

Publications:

- “A new method for production of titanium dioxide pigment”, Scott Middlemas, Z. Zak Fang, Peng Fan, *Hydrometallurgy*, 131–132 (2013), pg. 107–113.

Conference Presentations:

- “A new method of producing titanium dioxide pigment without direct CO₂ emission”, Scott Middlemas, Z. Zak Fang, Peng Fan, Energy Technologies and Carbon Dioxide Management Symposium, MS&T 2012.
- “A new method for production of titanium dioxide pigment-eliminating direct CO₂ emissions,” Scott Middlemas, Z. Zak Fang, Peng Fan, T. T. Chen Honorary Symposium, Conference Proceedings, TMS 2012

Patent Application:

- “Production of titanium dioxide pigments”, PCT/US2011/067583 Patent Application, Zak Fang, Peng Fan, Scott Middlemas

7. CONCLUSIONS

A new process for producing commercial quality TiO₂ pigment features a unique combination of established metallurgical processes, including alkaline roasting of titania slag followed by leaching, solvent extraction, hydrolysis, and calcination. Experimental validation of the process chemistry has been demonstrated. Titanium recovery was found to be highly dependent on HCl concentration as insufficient acidity resulted in low temperature hydrolysis. At a liquids-to-solids ratio of 10:1, leaching with 5 M HCl followed by solvent extraction with an Alamine 336 extractant produced a titanium chloride solution with less than 10 ppm Fe. After hydrolysis and calcination, anatase pigment containing < 20 ppm Fe was produced. The levels of impurities in our pigment meet the requirements for commercial pigment, and are nearly equivalent to those of two commercial pigments.

The potential benefits of the technology reported can be summarized in four separate categories: energy savings, reduced emissions, reduced environmental waste, and economic savings.

Energy savings: An analysis of the energy consumption of the new process indicates that it would consume 31.8 GJ/ton of TiO₂. The largest portion of the energy is consumed in recycling

and regeneration process reagents with the second largest being the preparation of the slag feed. A comparison of the new process and the chloride process indicate that implementation of the new process in the US would result in a 21% decrease in energy consumption, an annual energy savings of 42.7 million GJ (based on 1.4 million ton TiO₂ annual production.)

Reduced emissions: The total CO₂ emission of the new process is 7.41 tons/ton TiO₂, which would reduce CO₂ emissions by 21% in comparison to the chloride process, an annual reduction of 2.70 million tons of CO₂ in the US. It is believed that further process optimization could potentially yield even greater savings.

Reduced environmental waste: As shown earlier, the new process involves the recycle and regeneration of NaOH and HCl from the solutions after leaching operations. By doing so, the new process will produce significantly reduced wastes than if the roasting and leach solutions were all discharged. This is a considerable advantage over the sulfate process that is still used in many parts of the world, in which acidic waste streams are a considerable challenge. The main waste from the process would be insoluble impurity metals precipitated from the alkaline and acid streams prior to regeneration. These precipitates would be in the form of environmentally benign metal oxides and hydroxides and would be stored in tailings impoundments according to current mining regulations.

Economic benefits: At this stage of the development, we can only speculate on the potential economic benefits of the new process versus that of the chloride process. First, because the process equipment employed in the new process is well established in other industrial processes and the raw materials for the two processes are identical we believe the capital, labor and materials cost of production of pigment grade TiO₂ using the new method would be at least equivalent to that of the chloride process. Secondly, we believe that it is likely that the operating costs will be lower by using the new process because of the reduced energy consumption.

8. RECOMMENDATIONS FOR FUTURE RESEARCH

Although the new process technology is logical and feasible based on its chemistry, thermodynamic principles, and experimental results, its development and refinement through more rigorous and comprehensive research at the kilogram scale is needed to establish it as a competitive industrial process. Some critical questions to be answered by conducting a scaled-up investigation would be:

- What effects does the recycling of process streams have on the quality of the final product?
- Are there more energy efficient methods of producing hydrochloric acid than electrolytic means?

- How efficient is the heat recovery from the roasting and calcination stages?
- Would the optimized process parameters determined in a gram scale production investigation yield similar results at a kilogram scale production or pilot plant level?
- Is the energy efficiency as well as the environmental benefits of the proposed process indeed significantly better than current commercial processes?
- Would producing TiO₂ using the proposed process be indeed cost effective in the current economic climate?

We anticipate that the results of such a project would demonstrate the feasibility of the technology for commercial scale-up, so that the decision could be made regarding the future of this technology.

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