STUDIES ON IMPURITY REMOVAL IN ALTERNATIVE TITANIUM EXTRACTION PROCESSES

by

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STATEMENT OF DISSERTATION APPROVAL

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ABSTRACT

Titanium is often referred to as “wonder metal” due to its superior properties. At present, titanium is predominantly produced through Kroll’s process which is complex, expensive, and needs much higher specific energy than the thermodynamic requirement and that restricts titanium’s widespread use.

Direct reduction of titanium slag (DRTS) is an alternative process to produce titanium from titanium hydride at a lower projected cost and energy expense. In DRTS, a two-step leaching process is used to lower the aluminum, magnesium, and silicon content in titanium to meet the ASTM International (ASTM) specifications. Magnesium was leached in a mildly acidic condition while aluminum, and silicon impurities were leached under alkaline condition. The effect of varying temperature, concentration of acid or alkali, and adding certain additives to the lixiviants have been investigated for aluminum and silicon removal. Leaching at 140^{o}C for 3 h using a solution of 2 M NaOH and 2.5 g/l of sodium gluconate, and a solid-liquid ratio of 1g to 100 ml, produced titanium hydride with the desired aluminum and silicon contents. The effect of varying temperature, concentration of acid, and solid to liquid ratio have been investigated for magnesium removal. Magnesium content in titanium hydride was lowered below specification requirements by leaching with 0.05 M hydrochloric acid at 50^{o}C for 15 min using solid-liquid ratio of 1 g to 400 ml.

Another process for separating titanium from dissolved ilmenite using dihydroxybenzene (catechol) as a metal-organic precipitate was demonstrated. Titanium

(IV) was chemically bonded with catechol at a pH of 5.5 to form a precipitate containing 98.7% Ti. The results from density functional theory simulations predicted a gap of 2.914 eV between the two frontier orbital lobes (highest occupied molecular orbital and lowest unoccupied molecular orbital) suggesting stability of the metal complex. This precipitate can be reduced in a hydrogen atmosphere to form titanium hydride which again can be dehydrogenated to form titanium.

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CHAPTER 1

INTRODUCTION

Technological advances are often directly related with the ability to manufacture material that is more versatile. Metals are a unique class of materials with a diverse set of properties. These properties can be engineered by different methods according to specific requirements. Therefore, the advancement in technology for making and shaping of metals play a significant role in the development of science as illustrated by the fact that use of metals, especially steel is a widely accepted yardstick of development in society.

Titanium is a transition metal and is one of the latest additions to the list of commercially produced metals. The superior properties of titanium such as low density,[1-4] high strength to weight ratio,[1-3] high-temperature resistance,[2,3] extreme corrosion resistance,[1-3] biocompatibility,[4,5] excellent process performance1 and high reliability,[6] makes it stand out from the others.

Titanium was first extracted on a commercial scale in the United States in the 1950s as an advanced material for military aircraft.[7,8] Soon the advantages of this metal were realized and by the 1970s, about 10% (by weight) of titanium components were used for commercial aircraft.[8] By the 1980s titanium was used for a variety of other applications including construction,[2,8] marine,[9] corrosive industrial,[8] structural,[8] sports equipment,[10] biomedical implants,[4,5] and nuclear waste disposal[11] to name but a few. In spite of the

advantages in terms of physical, mechanical, and chemical properties, due to high costs associated with titanium products, they are only used for applications where cost doesn't affect the choice of material.[3,7] On weight basis, titanium is about 30 times more expensive than steel and 6 times more expensive than aluminum.[12] Titanium is the ninth most abundant element in the earth's crust and is the fourth most abundant engineering metal.[3,13,14] Yet, on a tonnage basis, titanium's production is significantly lower than other less abundant metals such as copper and manganese. The high cost of titanium is primarily due of the complexity of the conventional extraction method. Titanium production is labor intensive and requires high capital cost. The conventional method is a batch type process involving several slow steps such as by-product removal through leaching and vacuum distillation.[13]

Titanium is a highly reactive element, which has strong affinity for interstitial elements such as carbon, hydrogen, oxygen, and nitrogen.[7] It also has high solubility of other elements within itself.[7] This explains the complexity of separating titanium from other elements during the complexation process. The bulk of the total titanium produced worldwide involves the metallothermic reduction of titanium tetrachloride with either sodium or magnesium.[1-4,7,8] The specific energy consumption for titanium production through this method is much higher than the thermodynamic requirement for converting titanium ore into metallic titanium.[15]

Therefore, over the years, a number of alternative titanium extraction technologies have been proposed, all of which are aimed at the reduction of energy consumption for the process, thus reducing the cost of extraction.[16-20] Direct Reduction of Titanium Slag (DRTS) is one such technique which was recently proposed by Fang et al.[16] This proposed

technique had three major steps; (a) first the reduction of upgraded titanium slag (UGS) with magnesium into titanium hydride in a hydrogen environment; (b) separation of titanium hydride from reduced titanium slag; and (c) subsequent conversion of the titanium hydride into titanium powder by dehydrogenation. A schematic of the steps to be followed according to DRTS techniques is shown in Figure 1.1. From the process flowsheet of DRTS, it can be observed that the separation of impurities from reduced UGS is a crucial step. A part of this thesis presents methods and techniques to achieve efficient separation of aluminum and silicon impurities present in reduced upgraded titanium slag.

The process of direct reduction of titanium slag can also be applied directly to other titanium oxide resources with a grade higher than titanium slag. The process was applied on titanium dioxide (pigment), which initially contained very low impurities. The major impurities in reduced titanium dioxide to be removed to obtain titanium hydride would be magnesium bearing compounds. The optimal parameter for magnesium and salt removal from reduced titanium dioxide are also presented in this work. The results are believed to be applicable for reduced UGS with magnesium impurities and salts as well.

The DRTS method for producing titanium by dehydrogenation of titanium hydride is projected to be more economical than Kroll's process as it involves fewer steps at lower temperatures for shorter durations and also skips the elaborate leaching and refining processes. Still, this process requires upgraded titanium slag feed and also involves magnesium hydride or magnesium and hydrogen as the reducing agent. So, the economics can be improved further if extraction is made from even lower grade titanium resources and the use of magnesium could be eliminated. It has been reported that aromatics with alcoholic groups such as dihydroxybenzene can be used to selectively precipitate metal

ions out of a solution when the solution alkalinity is carefully controlled.[21-23] Also, it has been reported that dihydroxybenzene does not decompose unless high temperatures are reached.[24] In view of these observations, a new chemical route for obtaining high purity titanium powders starting with ilmenite has been evaluated. In this process, titanium is selectively precipitated as titanium catecholate from a multielement solution prepared by dissolving ilmenite in an acidic solution. The precipitate would be separated, washed, dried, and ground up before reducing it in a hydrogen atmosphere to produce titanium hydride which can be dehydrogenated to obtain titanium sponge. This study also describes the process of dissolving ilmenite into acidic solution and selective separation of titanium as titanium catecholate from a multielement bearing solution. The experimental observations are also corroborated by the results of density functional theory (DFT) simulation results which provide an improved understanding of the complexation at a molecular level.

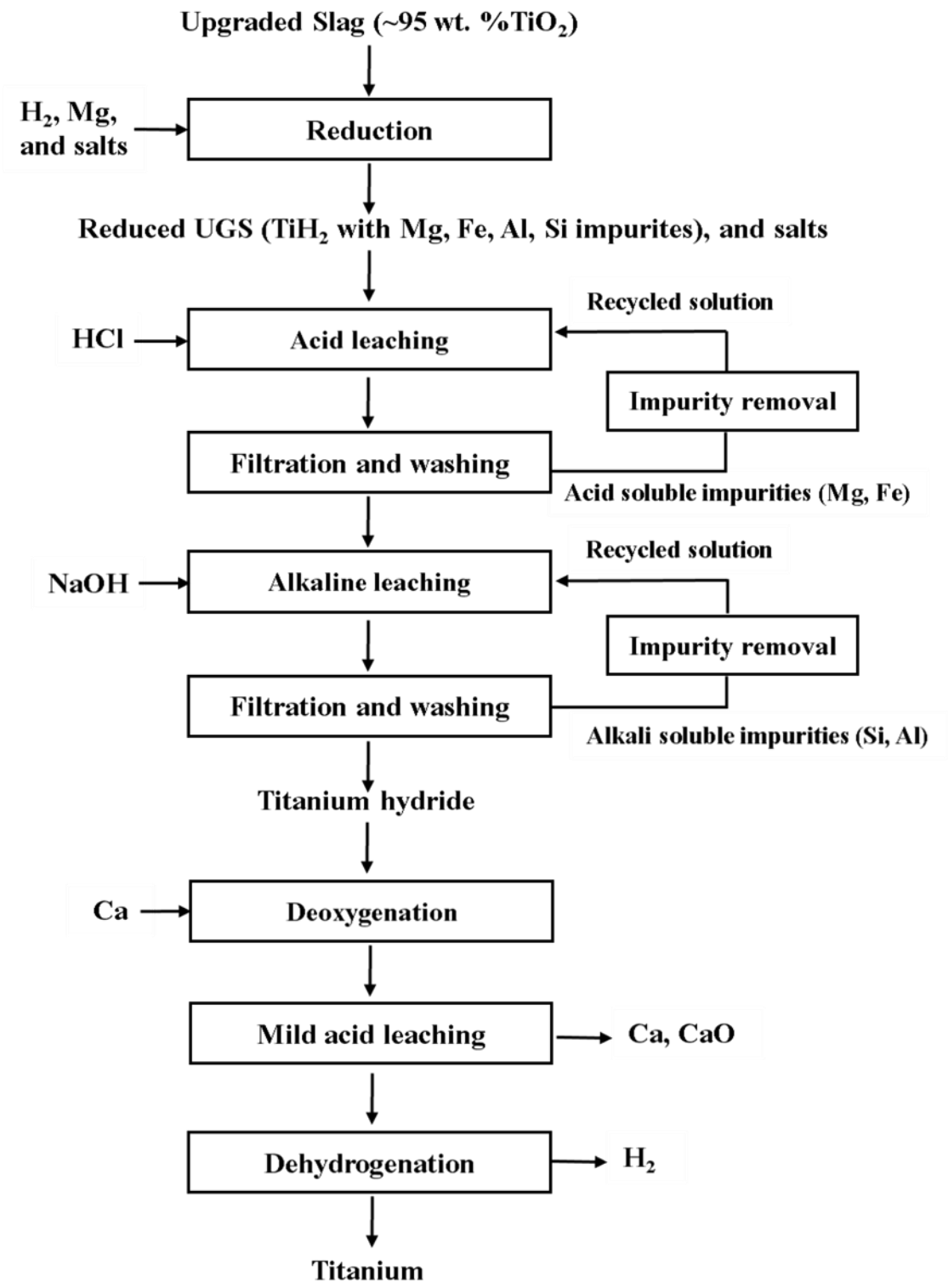


Figure 1.1 Process flowsheet of Ti extraction by direct reduction of titanium slag (DRTS) method.

CHAPTER 2

REVIEW OF LITERATURE

2.1 Titanium Sources

Titanium occurs mostly as ilmenite ($FeTiO_3$) which is a titaniferous ore containing around 50 % TiO_2.[13] Ilmenite mineral is commonly found in beach sand.[13] Weathering can sometimes result in deposits where the titanium dioxide (TiO_2) fraction in the ilmenite is found to be between 65% to 70%.[13] Leucoxene is another type of titanium ore that might contain to up to 87 % TiO_2.[13] Rutile is a naturally occurring titanium ore with more than 96% TiO_2, this is the highest grade ore but its deposits are not as common.[13] China and Australia have the largest deposits of ilmenite and rutile, respectively. In 2013, South Africa led the world in annual ilmenite production with 1,100,000 t, while Australia produced 450,000 t of rutile.[25]

The major portion of the titanium ore mined is used for manufacturing titanium dioxide pigment which is used as an industrial mineral in a variety of industries like the paint and paper industries. Only a fraction of the total titanium ore mined is used for metal production.[25]

The mined ore, in most cases, has a low grade of TiO_2, and therefore, it needs to undergo concentration operation(s) before it can be used for any further downstream metallurgical operation.[26-28] In the case of ilmenite, the traditional way of concentrating

involves the carbothermic reduction of the ore in an electric arc furnace or a rotary kiln to produce pig iron and a slag rich in titanium dioxide.[13] This slag is referred to as titania-rich slag, titanium slag, or even titania slag, in some cases. Reported assays of the mineral constituents of the titanium slags were found to vary over a range of composition.[13,27-29] The range of values for the mineral contents in titanium slag reported in different literature sources are compiled and tabulated in Table 2.1.

The grade of titanium dioxide in the titanium slag can be improved further by additional treatment to as high as 94.5% TiO_2. The process involved is called upgrading and the resultant product with a higher grade of titanium oxide is called upgraded slag or UGS. Different upgrading techniques have been reported in the literature and some of them include roast-leach, conditioning during smelting and then leaching, or slag stripping. Studies on the process of upgrading have also reported the effectiveness of various additives like sodium carbonate (Na_2CO_3) and phosphoric acid (H_3PO_4) in titanium rich slag for activation roasting at high temperature followed by leaching in dilute sulfuric acid.[30,31]

2.2 Conventional Method

On a commercial scale, titanium is mostly produced by the Kroll's process. This method involves magnesiothermic reduction of titanium tetrachloride into titanium. The first crucial step for this process is the production of titanium tetrachloride of sufficient purity so that metal of acceptable quality is produced. A combination of coke, chlorine, and titanium ore is needed to produce titanium tetrachloride. The titanium oxide grade of the ore used should preferably be as high as possible, but current practices have a certain

degree of tolerance for the presence of lower grade ores in the chlorination feed. The reaction can be performed in either a fluidized bed reactor or a shaft furnace or even in a molten salt bath in which chlorine is bubbled through, depending on the choice of setup.[13] The chemical reactions occurring during the formation of titanium tetrachloride are given by equations 2.1 and 2.2.

$$TiO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow TiCl_4(v) + 2CO(g) \qquad (2.1)$$

$$TiO_2(s) + 2Cl_2(g) + C(s) \rightarrow TiCl_4(v) + CO_2(g) \qquad (2.2)$$

The reactions are usually carried out at around 950°C and the titanium tetrachloride vapors are separated using fractional distillation.[13] The complexity of the fractional distillation process increases if the feed material has more impurity.

The magnesiothermic reduction of titanium tetrachloride is performed at around 900°C. The chemical reaction involved is given by equation 2.3.

$$TiCl_4(v) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l) \qquad (2.3)$$

This is a batch operation and is always conducted with magnesium in excess of the stoichiometric requirement. The excess magnesium ensures the complete reduction of titanium chlorides in case lower chlorides such as $TiCl_2$ and $TiCl_3$ are also formed. The excess liquid magnesium metal is tapped from the bottom of the reactor. The titanium metal is produced in the form of a sponge, and the magnesium chloride and excess magnesium can be separated in variety of ways. This separation process is crucial and it determines the

quality of the product and also the process economics.[13]

The separation can be achieved in a number of ways such as (i) acid leaching of the magnesium and the magnesium chloride, (ii) vaporization of magnesium and magnesium chloride by hot (~1000^{o}C) argon sweeps followed by condensation, and (iii) high temperature vacuum distillation of magnesium chloride and magnesium.[13]

2.3 Alternative Methods

2.3.1 Hunter Process

Some of the major alternatives to Kroll's process include Hunter, FFC Cambridge, and Armstrong processes.[3,16-20]

The Hunter process, like the Kroll's process is also a metallothermic reduction of titanium tetrachloride into titanium sponge. In this case, instead of magnesium, sodium is used as a reductant. The chemical reaction involved in Hunter process is a single step process, given by equation 2.4. [13]

$$TiCl_4(g) + 4Na(l) \rightarrow Ti(s) + 4NaCl(l) \quad (2.4)$$

On a molar basis, the sodium required for the Hunter process is twice the magnesium required for the Kroll's process. The sodium chloride obtained as a by-product is not recycled like the magnesium chloride.[13]

A two-step process for reduction of titanium tetrachloride with sodium also exists which involves two reactions given by equations 2.5 and 2.6.

$$TiCl_4(v) + 2Na(l) \rightarrow TiCl_2(s) + 2NaCl(l) \quad (2.5)$$

$$TiCl_2(s) + 2Na(l) \rightarrow Ti(s) + 2NaCl(l) \quad (2.6)$$

The first reaction is carried out under an argon atmosphere at a temperature of 232°C. The second step is carried out at 1000°C. The advantage of using the Hunter process is that by proper control of the operating variables, the purity of the titanium sponge can be higher than that obtained from the Kroll's process using vacuum-distillation of magnesium-reduced sponge.[13]

2.3.2 FFC Cambridge Process

In the FFC Cambridge process, a simple one-step electrochemical method is employed to reduce metal oxide into metal powder. This process involves an electrochemical cell where titanium oxide is used as a cathode, molten calcium chloride is chosen as the electrolyte, and a graphite as the anode. On application of a voltage either of the following reactions can occur. The calcium can react to form calcium oxide and metallic titanium either chemically or electrochemically (the calcium can deposit on the titanium oxide or the titanium dioxide may ionize), depending on the voltage applied, as shown by equations 2.7, 2.8, and 2.9. The calcium oxide is dissolved into the calcium chloride salt mixture and forms oxide anions in solution which migrate towards the graphite anode to evolve as oxygen. The oxygen also reacts with the graphite and forms a mixture of carbon monoxide, carbon dioxide, and oxygen. The reaction is carried out at around 850-950°C for several hours.[19]

$$Ca^{2+} + 2e^- \rightleftharpoons Ca \quad (2.7)$$

$$TiO_x + xCa \rightleftharpoons Ti + xCaO \quad (2.8)$$

$$TiO_x + 2xe^- \rightleftharpoons Ti + xO^{2-} \quad (2.9)$$

Although the process was developed for the production of titanium, many other elements which exists as oxide minerals such as chromium, tantalum, silicon, cobalt, molybdenum, and vanadium can also be extracted using this method. The major cost associated with this method is the fabrication of a sintered oxide mineral, which is used as electrode. The method is also fairly time consuming as a low concentration of oxygen is needed in the titanium product and the oxygen transport is diffusion controlled. Also, some greenhouse gases are evolved in the process.[19]

2.3.3 Armstrong Process

The Armstrong process is a one-step continuous process for the production of titanium metal and alloy powders. The chemistry of the Armstrong process is the same as that of the one-step Hunter process. In this method, liquid sodium is pumped in a continuous loop and controlled amounts of titanium tetrachloride are injected at a certain point in the loop, the $TiCl_4$ reacts with molten sodium to form metallic titanium and sodium chloride. The product titanium, sodium chloride and some sodium is recovered by filtration without affecting the flow. First the sodium is separated by fractional distillation and then the sodium chloride is washed out leaving behind only pure titanium powder.[20]

2.3.4 Direct Reduction of Titanium Slag Process

Like the name suggests, direct reduction of titanium slag (DRTS) involves the direct reduction of titanium slag (concentrated ore) into titanium hydride without the formation of titanium tetrachloride intermediate. The primary chemical reaction of interest in the DRTS process is given by equation 2.10. [16]

$$TiO_2(s) + 2Mg(s) + H_2(g) \xrightarrow{MgCl_2} TiH_2(s) + 2MgO(s) \quad (2.10)$$

Salts, such as magnesium chloride, are added to the reduction for improved kinetics. The purity of the titanium hydride product is directly related to the purity of the titanium oxide feed stock used. In the case where pure titanium dioxide is used, the titanium hydride needs to be simply separated from the magnesium compounds and salt. Unlike most of the hydrides, titanium hydride does not have high reactivity in water. Therefore, hydrometallurgical leaching of the impurities is an acceptable option.[32]

When UGS was used as feed stock, besides magnesium, predominant impurity elements present in reduced UGS were aluminum, iron and silicon containing impurities. On controlling the leaching parameters properly these impurities can also be removed hydrometallurgically and pure titanium hydride can be obtained. The titanium hydride can be converted into titanium powder by dehydrogenation at around 500^{o}C according to equation 2.11.[16]

$$TiH_2(s) \xrightarrow{500^oC} Ti(s) + H_2(g) \quad (2.11)$$

Aluminum in titanium alloys at low levels is present as a solid solution and it helps in alpha phase stabilization. At higher concentrations, it forms precipitates of titanium-aluminum intermetallics which can be used to improve properties. However, while designing an alloy it might be difficult if not impossible to transform the aluminum impurities in the reduced titanium slag into beneficial attributes.

Silicon is another impurity element in titanium alloys which if present in uncontrolled amount can deteriorate the high temperature performances and mechanical properties of titanium alloys. Therefore, it is of great importance to develop technology to control the content of aluminum and silicon impurities in titanium alloys within acceptable limits. Yet, there are few previous studies on aluminum and silicon removal from reduced UGS.[33] Moreover, this hydrometallurgical process can be a very cost-effective process as it requires short operating times and avoids involvement of specialized and sophisticated equipment.

2.4 Advantages of DRTS Process

The projected costs of titanium products obtained through the DRTS process are less than for other known processes. However, cost is not the only advantage of the DRTS process. In Kroll's process, titanium is first obtained as a sponge and then vacuum refined to form ingots, which are shaped into mill products.[13] This is arguably not an efficient process for subsequent manufacturing operations as there are challenges involved in forging and machining. The fact that the "buy to fly" ratio of titanium components for aerospace components is as high as 1:7 on average and can go up to 1:20 for some specific parts, demonstrates the inefficient material utilization in traditional manufacturing and

fabrication processes.[6] Near net-shape manufacturing techniques such as superplastic forming, isothermal forging, diffusion bonding, injection casting, powder metallurgy (PM) can be implemented to minimize the material loss of titanium while retaining the benefits of advantageous properties. PM practices have been reported for manufacturing both elemental titanium and titanium alloys.[6] The PM technique, for the fabrication of alloy components, can be classified as either blended element (BE) or prealloyed (PA) depending on the powder used. BE PM uses titanium powder from discarded sponge fines from ingot production, mixed with appropriate alloying elements while PA PM uses higher cost prealloyed powder blends.[6] Currently, titanium alloys such as Ti-6%Al-7%Nb are being manufactured through PM techniques and PM has potential to replace Ti-6%Al-4%V as materials for surgical implants due to lower manufacturing costs and the ability to form highly complex geometries.[34] The starting material for making titanium components though powder metallurgical techniques can be titanium sponge fines, titanium powder, or titanium hydride.[35] Due to the brittle nature of titanium hydride,[36] there exists a particle size distribution in the powder. This leads to the formation of a denser green structure, and these structures have lower shrinkage on sintering.[37] Typically, titanium hydride is obtained by hydrogenation of titanium sponge.[38] Thus, there is an added cost for converting the titanium, produced by conventional techniques, into titanium hydride. Therefore, for near-net shape manufacturing processes it would be more economical to extract titanium as hydride directly from UGS according to DRTS.[16] Titanium hydride is also less prone to oxidation unlike titanium powder, especially if present with a fine particle size, and hence, it has a much longer shelf life.

To sum up, the DRTS process not only significantly reduced the titanium cost but also

has an added advantage in storing titanium products and manufacturing of components. Moreover, this method also reduces greenhouse emissions.

2.5 Titanium Complexation Using Catechol

The overall process of selective precipitation of titanium using catechol is schematically shown in Figure 2.1. First the titanium bearing source is dissolved into a solution to produce Ti (IV) ions along with ions of other elements originating in ilmenite. Next, from this titanium bearing solution, titanium is selectively precipitated out as a complex according to equation 2.12. This precipitate was separated by filtration, washed and dried before reduction to titanium hydride. The complexing agent was also recycled along with titanium hydride production in accordance to this scheme:

$$Ti(s) \xrightarrow{dissolution} Ti(IV)(aq.)$$

$$\xrightarrow{+Catechol(in\ NH_3)} Ti(Catechol)_x(NH_3)_y \xrightarrow{+H_2} TiH_2 + xCatechol + y\ NH_3 \quad (2.12)$$

The titanium bearing source can be ilmenite, titanium dioxide, titanium slag, or other common sources as long as it can be dissolved into the solution easily and economically. The reduction step is based on previous research,[21,22] but the leaching, precipitation, and compound recycling steps are specific to this project and its team.

2.6 Impurity Removal - DRTS

Metallurgical processing involves several methods that are commonly employed for impurity removal. Depending on the nature of bonding between the impurity and the valuable fraction, the method of impurity removal is selected. Impurities that are physically

bonded can be separated by a variety of physical processes depending on the case. For chemically bonded impurities, according to the temperature of process operation the separation techniques can be broadly classified into high-temperature or pyrometallurgical processes and low-temperature or hydrometallurgical processes. In general, if the impurity to be removed is a large fraction only then high-temperature and energy intensive pyrometallurgical processes are considered to be cost effective methods.

In the cases of DRTS processing the starting material, UGS is a high grade titanium dioxide resource. Therefore, the fraction of impurities in the reduced UGS is low. This condition favors the use of low-temperature impurity removal processing. Titanium hydride, the major fraction of reduced UGS, is water insoluble and has resistance to dilute acid solutions, while it reacts with hydrofluoric acid and hot sulfuric acid.[39] This makes the application of leaching for impurity removal a possibility. TiH_2 has a possibility of reacting vigorously with oxidizing reagents.[40] Hence, the use of oxidizing acids such as nitric acid is also not a possibility. Moreover, it has been reported in literature that hydrochloric acid has a lower dissolution rate of TiH_2 compared to sulfuric acid. Therefore, hydrochloric acid was used for acid leaching process.

The principal impurities in reduced UGS contains aluminum, iron, magnesium, and silicon. These elements can be present as a variety of compounds in the reduced UGS such as oxides, intermetallic compounds, etc. Therefore, the impurities can be targeted based on the chemical behavior of the elements. The removal of impurities containing elements know to form basic compounds can be targeted in acid medium and vice-versa. The impurities can be removed even further if a chelation reaction is employed in parallel to the acid-base reaction. Therefore, the use of chelating additives in the lixiviants is an

effective way of improving the effectiveness of a leaching operation. The solution bearing the impurities, after leaching, can be treated further to form by-products from the impurities or form derivatives that can be recycled into reagents useful for the process.

2.7. Evaluation of Governing Mechanism

The overall rate of reaction is a result of the underlying rate controlling mechanisms. The mechanisms governing the kinetics of a fluid-solid reaction can be determined by fitting the conversion data over time to models deduced for different conditions. Leaching being a particular kind of fluid-solid reaction determination of governing mechanism for a particular impurity is possible by fitting the data for fraction leached over time to these models[41].

In the case of nonporous particles, the reaction rate can be controlled by

(i) diffusion of species through external boundary layer

(ii) interfacial chemical reaction

(iii) inner diffusion of species

For control under diffusion of species through external boundary layer it can be shown that

$$X = kt \tag{2.13}$$

For interfacial chemical reaction control kinetics, it can be shown that

$$1 - (1 - X)^{\frac{1}{3}} = kt \tag{2.14}$$

For inner diffusion of species, it can be shown that

$$3 - 2X - 3(1 - X)^{\frac{2}{3}} = kt \qquad (2.15)$$

where the fraction of impurities leached is X, k is a constant depending on parameters of the system and t is the time at which X is measured. The function for inner diffusion control, left hand side, of the equation 2.15 is referred to as the p(X) in the subsequent cases.

Table 2.1: Range for the mineralogical composition of typical titanium slag reported in literature.

Avg. Slag Composition	**TiO_2**	**FeO +Fe_2O_3**	**SiO_2**	**Al_2O_3**	**MgO+CaO**	**Other Impurities**
Percent by weight	77.0-92.5	1.0-10.0	1.0-5.3	0.75-3.10	0.25-5.10	1.75-2.80

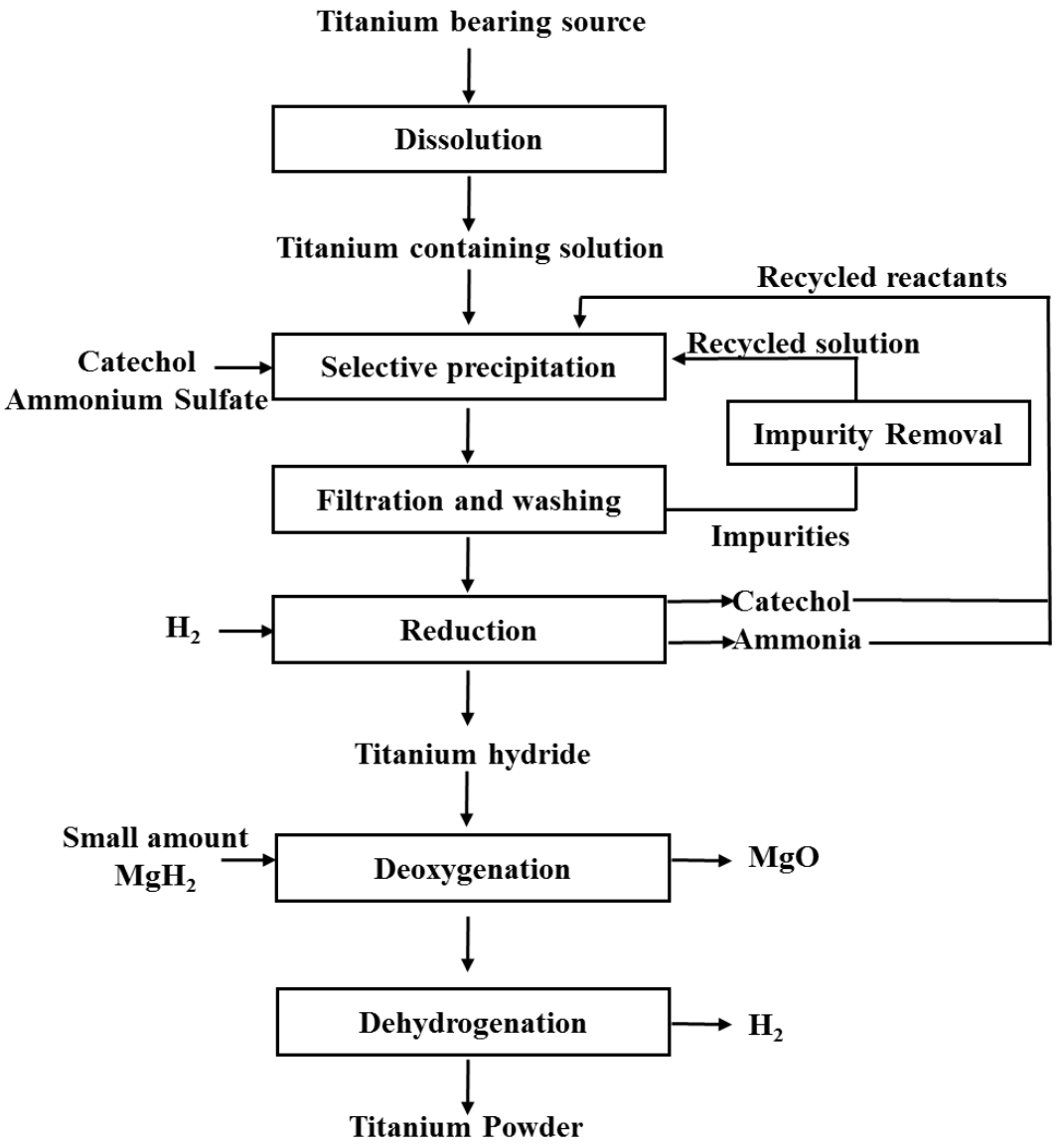


Figure 2.1. Process flow diagram for selective complexation of titanium using dihydroxybenzene (catechol) and method for subsequent processing needed to produce titanium powder.

CHAPTER 3

LEACHING BEHAVIOR OF PURE MINERALS AND SURROGATE REDUCED UGS

3.1 Materials and Methods

3.1.1 Preparation of Pure Minerals

The pure mineral compounds used for this particular study were all purchased from Sigma-Aldrich, Inc., in their pure forms and were directly used for the experiments.

3.1.2 Preparation of Surrogate-Reduced UGS

The surrogate-reduced UGS was produced by thoroughly mixing titanium hydride (TiH_2), ferric oxide (Fe_2O_3), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and magnesium oxide (MgO). These pure minerals were purchased from Sigma-Aldrich, Inc., and were mixed together directly without any further treatment, in the ratio shown in Table 3.1. This ratio is believed to represent a typical composition of reduced upgraded titanium slag (UGS).

3.1.3 Experimental Procedure

The leaching experiments were carried out in a setup using an Erlenmeyer flask, made out of polymer, that was sealed using a thermal and chemical resistant plug to prevent loss

of vapors. A thermometer was inserted through an opening drilled in the plug. This enabled the continuous measurement of temperature during the experiments. The setup was placed on a hot plate with magnetic stirring capability. Magnetic stir bars were used for mixing the slurry at a predetermined speed of 500 rpm. All the experiments were carried out with a solid-liquid ratio of 1:100 (g/ml) at 70^{o}C for 4h. Samples of residual solids and leach liquor were collected just after the completion of the experiments.

For the pure mineral tests, two leaching tests were performed to study the effectiveness of every lixiviant. In one test, the target impurity in the form of pure mineral compound was reacted with the impurity, and in the other test, pure titanium hydride (desired product) was leached with the same lixiviant under identical conditions. However, while experimenting with surrogate reduced UGS samples only one experiment was sufficient as the results were analyzed using a quantitative atomic spectroscopic technique.

3.1.4 Analysis of Results

In the case of pure mineral leaching, the fraction of solid leached was determined by tracking the change in weight of the solid sample before and after the leaching operation. The impurity removal for surrogate-reduced UGS leaching was determined by analyzing the final leach liquor using an inductively coupled plasma optical emission spectrometer (ICP-OES).

3.2 Results and Discussion

3.2.1 Pure Mineral Tests

Leaching was carried out under both acidic and alkaline conditions. In addition to simple acidic and alkaline chemistries, selected additives were added to the acidic or alkaline base solutions. This was done to study the effects of specific additives in leaching of particular impurity elements or mineral compounds under acidic or alkaline solutions. The base solution and the additives were primarily selected based on the basic knowledge of chemistry of each target impurity. Additives were also selected based on reported effectiveness on similar chemistries found in the literature.[42-48]

Based on results from a wide range of tests performed with different lixiviants, the most effective lixiviants are tabulated in Table 3.2, and have been classified according to the different targeted impurity elements (which were taken in the form of pure oxide minerals). The removal percentages of impurities are reported alongside the data for loss of pure titanium hydride with the same lixiviant.

It can be observed from results in Table 3.2 that lixiviants with the highest selectivity for silicon and aluminum impurities were alkaline solutions with certain additive compounds. While lixiviants most effective for iron were acidic with certain additive compounds. The removal of iron was always accompanied with a measurable amount of titanium loss. Magnesium compounds were found to be leached almost completely even in aqueous acidic salt solutions indicating relative ease in their removal. It is to be noted that even a small removal percentage for pure minerals in a particular lixiviant is acceptable, as long as there is very low corresponding TiH_2 loss, since the total impurity content in typical reduced UGS is less than 5wt%.

3.2.2 Surrogate-Reduced UGS Tests

The lixiviants found to be effective from the pure mineral tests (section 3.2.1) were used to leach the surrogate reduced UGS to study the effectiveness and selectivity of a lixiviant in the presence of other components. In addition, some new promising lixiviants were tested directly on surrogate-reduced UGS and the results obtained are tabulated in Table 3.3.

The results show that almost complete removal of silicon, aluminum, and magnesium impurities can be achieved with small corresponding titanium losses by properly selecting the lixiviants. Silicon removal was best under alkaline lixiviants while aluminum and magnesium removal was favored under acidic media. None of the lixiviants used in the study could selectively remove iron from surrogate reduced UGS without very high amounts of titanium losses.

There were differences in the leaching behavior between the pure minerals and the surrogate-reduced UGS. This might be due to the difference in selectivity of lixiviant towards impurity elements in the surrogate slag mixture. Selectivity of a lixiviant towards an impurity element can be affected by several factors including but not restricted to mineralogical or chemical form in which impurities are present in, crystal structure of the minerals, composition of the mixture, chemical nature of other compounds in the mixture, and operating parameters for the leaching operation.

Table 3.1: The weight fraction of the pure minerals in surrogate-reduced UGS.

Composition	**TiH_2**	**Fe_2O_3**	**SiO_2**	**Al_2O_3**	**MgO**
Weight %	94.5	2.4	1.2	1	0.9

Table 3.2: Removal fraction of an impurity, as pure mineral, with different lixiviants at 70^{o}C for 4h.

Targeted Element	**Lixiviant**	**Removal (% as oxides)**	**TiH_2 retained(%)**
Si (SiO_2)	1 M NaOH + 3g/L EDTA	~100	~100
	1 M NaOH + 3g/L Anhydroerythritol	~100	~100
	0.2 M HCl + 0.05 M H_3BO_3 + 3g/l NTA	8.20	99.62
Al (Al_2O_3)	1 M NaOH + 3g/L Sodium Gluconate	48	~100
	0.2 M HCl + 0.05M H_3BO_3 + 3g/l NTA	2.34	99.62
Mg (MgO)	1 M NH_4Cl +1M Sodium Citrate	~100	~100
	1 M NH_4Cl +1M Sodium Phosphate	86	~100
Fe (Fe_2O_3)	0.6 M HCl	10	72
	0.2 M HCl + 3g/L NTA	25	98
	0.2 M HCl + 0.05 M H_3BO_3 + 3g/l NTA	6.28	99.62

(*NTA: Nitrilo Tri-acetic Acid & EDTA: Ethelene Di-amine Tertra-acetic Acid)

Table 3.3: Removal fraction of impurities from surrogate-reduced UGS with different lixiviants at 70^{o}C for 4h.

Sample	Lixiviant	Loss(%)	Removal(%)			
		Ti	Al	Fe	Mg	Si
Synthetic Product	1 M NaOH + 3g/L Sodium Gluconate	0.76	0	0	3.96	~100
	1 M NH_4Cl + 1M Na-phosphate	0	0.73	0	~100	12.94
	1 M NaOH + 3g/L EDTA	0	0	0	3.98	~100
	1 M NaOH+ 3g/L Anhydroerythritol	0.62	0	0	0	~100
	0.6 M HCl + 15% H_2O_2	12.75	90.19	0	0	13.81
	0.2 M HCl + 0.05 M H_3BO_3 + 3g/L NTA	0.03	~100	0	~100	4.4
	1M NH_4Cl + 1M Na-Citrate	0.01	0	0	~100	23.71

(*NTA: Nitrilo Tri-acetic Acid & EDTA: Ethelene Di-amine Tertra-acetic Acid)

CHAPTER 4

LEACHING BEHAVIOR OF ALUMINUM IMPURITIES IN REDUCED UPGRADED TITANIUM SLAG

4.1 Materials and Methods

4.1.1 Preparation of Reduced Upgraded Titanium Slag and Salt Removal

The process flow diagram for the production of titanium hydride powder according to the DRTS process is presented in Figure 4.1. The as-received upgraded titanium slag (UGS) was first milled to a particle size below 40 μm and was thoroughly mixed with magnesium turnings and salts. The mixture contained UGS, Mg, and salts in the ratio of 1:1:1 by weight. The salts had two parts by weight of magnesium chloride to one part by weight of potassium chloride. This mixture was reduced under a hydrogen atmosphere at 750^{o}C for 6 h. To facilitate the reduction kinetics of UGS, magnesium was added in excess of the stoichiometric requirement. The salts were added to increase the rate and extent of reduction.[16] The resultant product was a mixture of reduced UGS (predominantly titanium hydride), magnesium compounds (magnesium oxide and unreacted magnesium), and salts. Reduced UGS was separated from the magnesium compounds and salts by washing the mixture with 4.3 M acetic acid (CH_3COOH) at a solid to liquid ratio of 1 g to 40 ml for 2 h at 70^{o}C. Vacuum filtration was used to obtain the reduced UGS as filter cakes from the slurry after leaching. These cakes were thoroughly washed with deionized water and 0.05

M hydrochloric acid to ensure complete removal of all water soluble components such as magnesium compounds and salts. Next, these cakes were dried in an oven at 70^{o}C, then pulverized into powder on drying. The pulverized powder had an average particle size of 0.1μm and the size distribution is presented in Figure 4.2 (a). The extremely fine particle size leads to the formation of aggregates as observed from the SEM image in Figure 4.2 (b). This reduced upgraded titania slag or reduced UGS powder was used as the starting material for all the leaching tests.

4.1.2 Experimental Procedure

The leaching experiments that involved operating temperatures below the boiling point of water were conducted in Erlenmeyer flasks made out of semitransparent polymer. These flasks were sealed with a temperature and chemical resistant plug to reduce the loss of lixiviants by evaporation. The operating temperature was observed using a thermometer that was inserted into the flask through an opening in the plug. A solid to liquid ratio for each of the experiments, using washed reduced UGS as starting material, were maintained at 1g to 100 ml. Typically, a combination of 2 g of salt removed reduced UGS and 200 ml of lixiviant was used. Homogenization of the leaching solution was achieved using a magnetic stir-bar revolving with a speed of 1,000 rpm. A heating mantle was used to provide the heat necessary to reach and maintain a preset, uniform temperature. On reaching the preset temperature the solution was allowed to homogenize until no fluctuation ($\pm$ 1^{o}C) in temperature was observable. Next salt removed reduced UGS (typically 2 g) was added into the flask. The experiment was conducted for four hours and samples were collected at the end of every hour of leaching to study the reaction kinetics.

In the case of leaching experiments conducted at temperatures exceeding the boiling point of water (140^{o} and 190^{o}C), a pressure reactor setup was used. The pressure reactor setup had a digital temperature controller and a motorized stirring system through which the temperature set point, heating rate, and speed of rotation could be adjusted. The heating rate was adjusted so that it took about 1 h to reach the temperature set point and then the system was held at that temperature for 3 h. Stirring speed was set at 250 rpm to ensure homogenization of the system. 100 ml of lixiviant was used for every gram of solid and usually 2 g of reduced UGS was leached using 200 ml of solution. The high-temperature experiments were carried out inside a beaker made out of Teflon, placed inside the pressure reactor. After the 3 h of holding the system was cooled down and the sample was obtained through vacuum filtration followed by thorough washing with deionized water.

4.1.3 Analysis of Results

The quantitative elemental analyses were obtained using an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) setup. The diffraction patterns were from an X-ray Diffraction (XRD) instrument. The particle size distribution was determined using a Laser Diffraction Particle Size Analyzer. A scanning electron microscope was used to observe the morphology of products.

4.2 Results and Discussion

Aluminum is an element which forms compounds with amphoteric properties. Therefore, experimental studies were conducted under both acidic and alkaline conditions to investigate the leaching behavior of aluminum in reduced titanium slag. Results from

experiments carried out under acidic and alkaline conditions are being presented separately. The objective of leaching was to lower the aluminum content in reduced titanium slag below the maximum permissible impurity limit specified by ASTM for titanium product. In Table 4.1 the typical composition of reduced UGS after washing is reported along with specifications for titanium product according to ASTM B299-2013.

It can be observed from Table 4.1 that the aluminum content needs to be decreased by about 86 wt. % to meet the ASTM B299-2013 specification. Besides controlling the operating parameters, in certain cases the effectiveness of a lixiviant was found to be increased by addition of additive compounds.[32,33,49] These compounds may facilitate the formation of chelates or simply catalyze the removal reaction. Therefore, additive compounds were also added to both acidic and alkaline solutions to determine if the efficiency of aluminum removal could be improved. Previous studies have demonstrated the effectiveness of complexing agents like sodium gluconate, EDTA and boric acid as sequestering agents in a system having compositions similar to reduced titanium slag as well for other metallic systems. [32,33,42-49] Hence, the effect of boric acid, EDTA, and sodium gluconate for this particular system were studied.

4.2.1 Acidic Leaching

It was observed that on leaching reduced UGS with acid there was a loss of titanium products that depended on the concentration of the acid being used. The dependence of titanium loss on the concentration of acid being used was studied. From the results shown in Figure 4.3, it can be seen that the loss of titanium increases rapidly with increase in the acid concentration.

From the standpoint of preserving the final product, titanium loss should be minimized. The loss of titanium would probably not be significant in terms of the overall economics of the process if it could be kept below 1- 2 wt. %. Therefore, for acidic leaching the maximum allowable acid concentration was set to be 0.1 M hydrochloric acid.

4.2.1.1 Effect of acid concentration

The effect of concentration of acid on the removal of aluminum is illustrated by Figure 4.4. It was observed that the aluminum removal increases with increase in concentration of acid from 0.05 M hydrochloric acid to 0.1 M hydrochloric acid at 90^{o}C. The corresponding titanium loss was also found to increase with increase in concentration but in both cases the loss was below 1 wt %. Therefore, at 90^{o}C, 0.1 M hydrochloric acid is the optimal concentration of acid for removing the maximum amount of aluminum impurities with less than 1% loss of titanium.

4.2.1.2 Effect of additive

Boric acid is known to have chemical affinity towards certain aluminum compounds.[43-45] Therefore, boric acid was used as an additive to improve the aluminum removal from reduced UGS in an acidic media. The boric acid was added to 0.1 M hydrochloric acid solution to further increase the aluminum removal while preventing titanium loss of more than 1wt%. From the kinetic studies as shown in Figure 4.5 it was observed that addition of boric acid helped in improving the aluminum removal with low titanium loss. Although the addition of boric acid improved aluminum removal it should be noted that at 90^{o}C the fraction of aluminum removed was only about 27% while around 86% removal was needed

to meet the specifications. Therefore, the leaching temperature was increased in order to improve the removal of aluminum.

4.2.1.3 Effect of temperature

In general, increasing the temperature of leaching increases the fraction of targeted component leached. Therefore, to achieve low levels of aluminum as specified by ASTM specifications, the reduced upgraded titanium slag was leached further with a combination of 0.1 M hydrochloric acid and 1 M boric acid (H_3BO_3) at 140^{o}C and 190^{o}C. The results were compared with reduced upgraded titanium slag leaching conducted with 0.1 M hydrochloric acid under otherwise identical conditions. It can be seen from Figure 4.6 that the removal of aluminum reaches a maximum at 140^{o}C for both 0.1 M hydrochloric acid and a combination of 0.1 M hydrochloric acid and 1 M boric acid (H_3BO_3). The increase in the percentage removal of aluminum on addition of boric acid additive seems to be almost independent of the temperature. The associated titanium loss in the case of boric acid addition is also higher but the minimum titanium is lost when the temperature is kept at 140^{o}C. Therefore, for aluminum removal from reduced upgraded titanium slag using a combination of 0.1 M hydrochloric and 1 M boric acid at 140^{o}C is suitable.

It was noted that in spite of rapid improvement in removal with increased temperature the fraction of aluminum leached from the reduced upgraded titanium slag using these solutions under best conditions was not enough to meet the aluminum specification for titanium product. Based on the trend of the curve for aluminum removal between 90 and 190^{o}C using a maximum acid concentration of 0.1 M hydrochloric acid it is unlikely that the ASTM specifications can be met.

4.2.2 Alkaline Leaching

Leaching studies in acidic medium demonstrated that removal of aluminum up to the level needed for the titanium product to be of acceptable quality is unlikely with acceptable titanium losses associated. Hence, leaching in alkaline media was performed in order to investigate if operating conditions can be adjusted to achieve desired aluminum removal.

4.2.2.1 Effect of alkali concentration

Kinetics of removal of aluminum from reduced titanium slag investigated at different levels of alkalinity at 90^{o}C is shown in Figure 4.7. Increase in alkalinity of the lixiviant leads to increase in the fraction of aluminum removed. The increase was not appreciable once the concentration of sodium hydroxide (NaOH) was increased beyond 2 M sodium hydroxide. Hence, it can be said that at 90^{o}C a 2 M sodium hydroxide solution is adequate for achieving close to maximum possible aluminum removal. It is also interesting to note that unlike acidic solutions there is a very small titanium loss even with alkaline solutions with concentrations as high as 4 M sodium hydroxide.

4.2.2.2 Effect of additive

To study the effect of additives on the kinetics of aluminum removal from reduced upgraded titanium slag, 10 g/l of the additive compounds (sodium gluconate, EDTA) was added to a 2 M sodium hydroxide solution and leaching was performed. A comparison between the aluminum removal kinetics on addition of 10 g/l of an additive compound to 2 M sodium hydroxide solution and 2 M sodium hydroxide solution, without any addition, is shown in Figure 4.8. It is observed that the aluminum removal kinetics was almost

unaltered by the addition of 10 g/l of EDTA to 2 M sodium hydroxide solution. While the addition of 10 g/l of sodium gluconate to 2 M sodium hydroxide solution increased the aluminum removal fraction considerably. Although the addition of 10 g/l of sodium gluconate to 2 M sodium hydroxide solution improved the fraction of aluminum removed, there was also a significant titanium loss.

The benefits of sodium gluconate addition to 2 M sodium hydroxide could only be realized if the associated titanium loss could be minimized. The minimization of titanium loss can either be achieved by lowering the concentration of the additive compound or by lowering the temperature of the leaching operation. Decreasing the temperature of leaching would imply that the fraction of aluminum removed would likely be lowered. The aluminum content in the residue after leaching with a lixiviant, containing 2 M sodium hydroxide and 10 g/l sodium gluconate at 90^{o}C, was higher than the ASTM specification. Therefore, the only possible way for improving the aluminum removal as well as minimizing the associated titanium loss was to control the amount of additive in the lixiviant. The change in the kinetics of aluminum removal on varying the amount of sodium gluconate in 2 M sodium hydroxide solution is depicted in Figure 4.9. If the amount of sodium gluconate added to 2 M sodium hydroxide was kept below 2.5 g/l, the corresponding titanium loss could be regulated below 2 wt. %. Although the titanium loss could be controlled, it can be seen that the addition of sodium gluconate at such levels suppresses the fraction of aluminum removed instead of facilitating aluminum removal. Hence, it seems likely that the use of 2 M sodium hydroxide solution without the addition of any additive compound would be best for removal of aluminum from reduced upgraded titanium slag.

The phenomenon of suppression of aluminum removal in an alkaline medium on addition of sodium gluconate, can be better understood on comparing results of leaching using different alkalinity and identical sodium gluconate concentration as shown in Figure 4.10. Increase in the alkalinity of the leaching solution from 0.5 M sodium hydroxide to 2 M sodium hydroxide made the phenomenon of suppression of aluminum removal more prominent. In summary, it can be stated that the suppression phenomenon is a function of both the amount of sodium gluconate added and also the alkalinity of the base solution it is added to.

4.2.2.3 Effect of temperature

From the previous section, it can be concluded that the aluminum removal from the reduced upgraded titanium slag at 90^{o}C under alkaline lixiviant was most effective when 2 M sodium hydroxide was used. Yet, the aluminum removal fraction required for meeting the ASTM specification could not be achieved by leaching at 90^{o}C. Therefore, the temperature of leaching was increased to study the effect of temperature on aluminum removal fraction. Since 2 M sodium hydroxide solution was found to be the most effective in removing aluminum impurities from reduced UGS, the leaching experiments were performed at five different temperatures. It was observed from Figure 4.11, that increase in temperature drastically increases the fraction of aluminum removed. Leaching with 2 M sodium hydroxide for 3 h at 140^{o}C resulted in around 94 % of aluminum removal which is enough to meet the ASTM specification of aluminum in titanium products. On further increasing the temperature to 190^{o}C the aluminum removal fraction was increased to 98% but the product was oxidized under the severe operating conditions. The oxidation can be

readily perceived by comparing the X-ray diffraction pattern of the product after leaching with 2 M sodium hydroxide at 190^{o}C to the X-ray diffraction pattern for the starting material as presented in Figure 4.12.

Although, a phenomenon of suppression of aluminum removal was observed on addition of sodium gluconate to alkaline solution at 90^{o}C, this was not seen from the results of high temperature (140^{o}C) leaching experiments performed with 2 M sodium hydroxide and 2.5 g/l of sodium gluconate. At 140^{o}C, both the aluminum removal and the corresponding titanium loss seemed to be unaffected by the presence of sodium gluconate. As the product after leaching at 190^{o}C was highly oxidized, as can be seen from Figure 4.12, the corresponding titanium loss was not represented in Figure 4.11, as it is a presumably a very large fraction and also not of any practical interest.

4.2.3 Studies on the Governing Mechanism for Aluminum Removal

As described in section 2.7 from the kinetic data based on the fraction of material leached over time, the governing kinetics can be identified. The removal fraction of aluminum over time was measured over time under different leaching conditions. For each of these conditions the data were fitted to the kinetic models for interfacial chemical reaction, inner diffusion controlled, and external or boundary layer diffusion control to identify the governing mechanism, and the coefficient of determination values (R^2 value) are tabulated in Table 4.2. These values can vary between zero and unity and a higher value indicates a stronger fit to the model.

From Table 4.2, it can be seen that inner diffusion control seemed to be the most probable mechanism describing leaching in both acidic and alkaline conditions. However,

the fit of the data in the alkaline leaching is poor, thus, the mechanism for alkaline leaching is not conclusive. To confirm the governing kinetic mechanism for aluminum removal under acidic conditions the kinetic data were obtained under different temperatures (70^{o}C and 80^{o}C) with a 0.1 M HCl lixiviant, the results are presented in Figure 4.13.

It can be seen from Figure 4.13 that the data had close agreement with the values predicted according to inner diffusion model. In the case of leaching with alkaline lixiviants, the kinetic data did not correlate well with any of the three kinetic models used. Although, statistically the best correlation was found for the inner diffusion control kinetics. The kinetic data for aluminum removal fitted to the inner diffusion model are presented in Figure 4.14.

The fit of the kinetic data in the case of leaching with 2.0 M NaOH + 10 g/l Sodium Gluconate and 0.5 M NaOH +2.5 g/l Sodium Gluconate were much better than other cases. This fact may indicate that there is an influence of sodium gluconate in changing the controlling mechanism, and hence facilitate the removal of impurities like aluminum. The effect is found to be dependent on sodium gluconate concentration, the alkalinity of the base solution, and the temperature at which the leaching is performed.

From the Arrhenius plot, Figure 4.15, for leaching of aluminum impurities in reduced UGS with 0.1 M HCl the activation energy was determined to be 52.924 kJ/mol. This value is low enough to suggest the possibility of an inner diffusion controlled mechanism. However, it is to be noted that the fit is only moderately good, and hence the mechanism could still be mixed controlled. Further investigation is necessary to reach a definite conclusion.

Table 4.1. Composition of reduced UGS without salt and targeted composition.

Elements	Al	Fe	Si	Mg	Ti
Typical salt-removed Reduced UGS (wt. %)	0.35	1.07	2.02	0.36	bal
ASTM specified limits (wt. %) for Mg-reduced product	0.05	0.15	0.04	0.50	bal
Typical Removal (%) needed	85.71	85.98	98.02	-	-

Table 4.2**.** The coefficient of determination values on fitting the kinetic data to the different models for different experiments.

Al Removal	**R^2**		
Experiment	**Interfacial Chemical**	**Inner diffusion controlled**	**Outer Layer diffusion control**
0.05 M HCl 90°C	0.9794	0.9384	0.9756
0.1 M HCl 90°C	0.8887	0.9984	0.8709
0.05 M HCl + 1 M Boric Acid 90°C	0.9598	0.9736	0.9498
0.1 M HCl + 1 M Boric Acid 90°C	0.8476	0.9911	0.8188
0.5 M NaOH 90°C	0.5204	0.7736	0.4989
1.0 M NaOH 90°C	0.509	0.7457	0.4852
2.0 M NaOH 90°C	0.455	0.674	0.4288
4.0 M NaOH 90°C	0.4619	0.6779	0.4328
2.0 M NaOH 2.5 g/l S.G. 90°C	0.3156	0.4502	0.3042
2.0 M NaOH 5 g/l S.G. 90°C	0.3419	0.495	0.3042
2.0 M NaOH 10 g/l S.G. 90°C	0.5219	0.7561	0.4652
2.0 M NaOH 10 g/l EDTA 90°C	0.5431	0.7976	0.5154
0.5 M NaOH 2.5 g/l S.G. 90°C	0.66	0.9139	0.6346

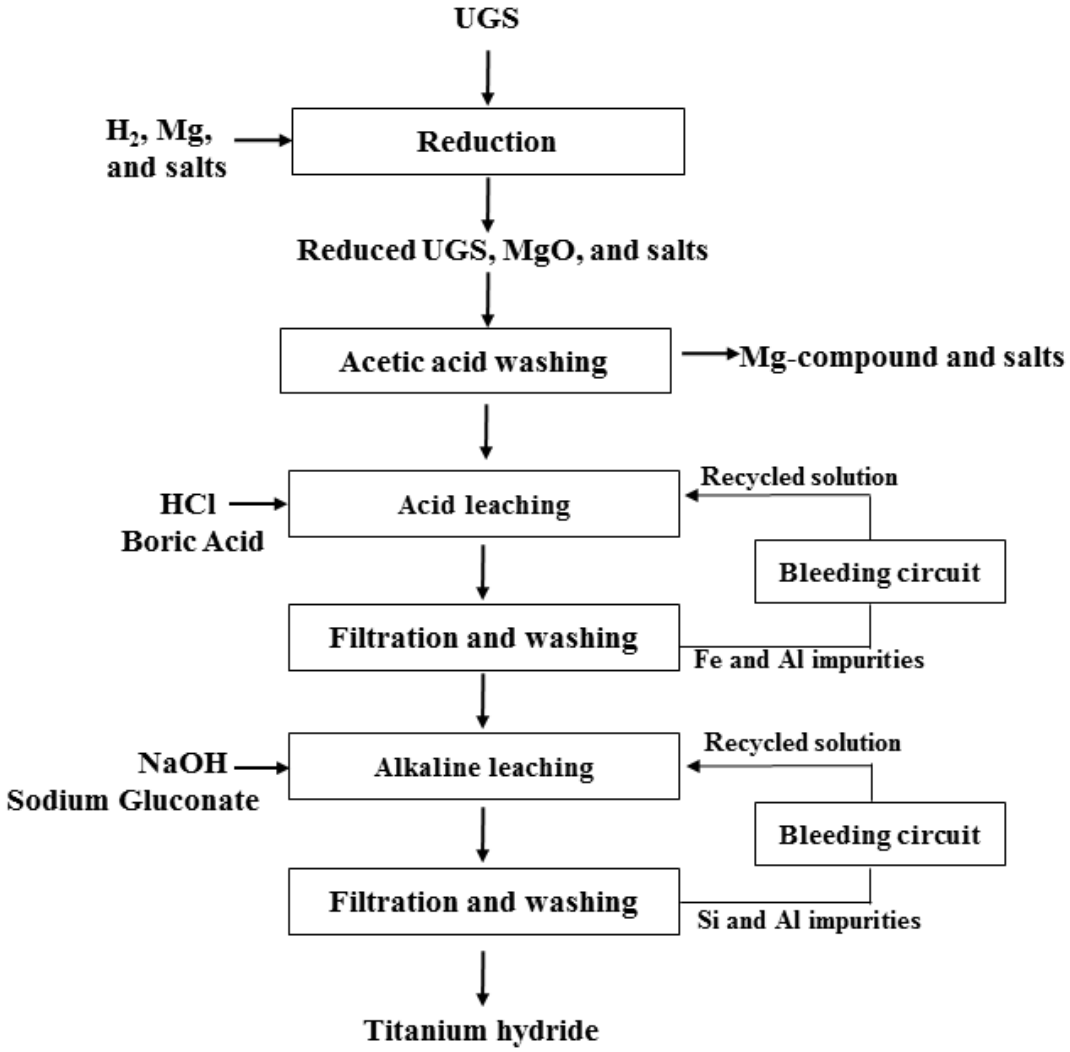
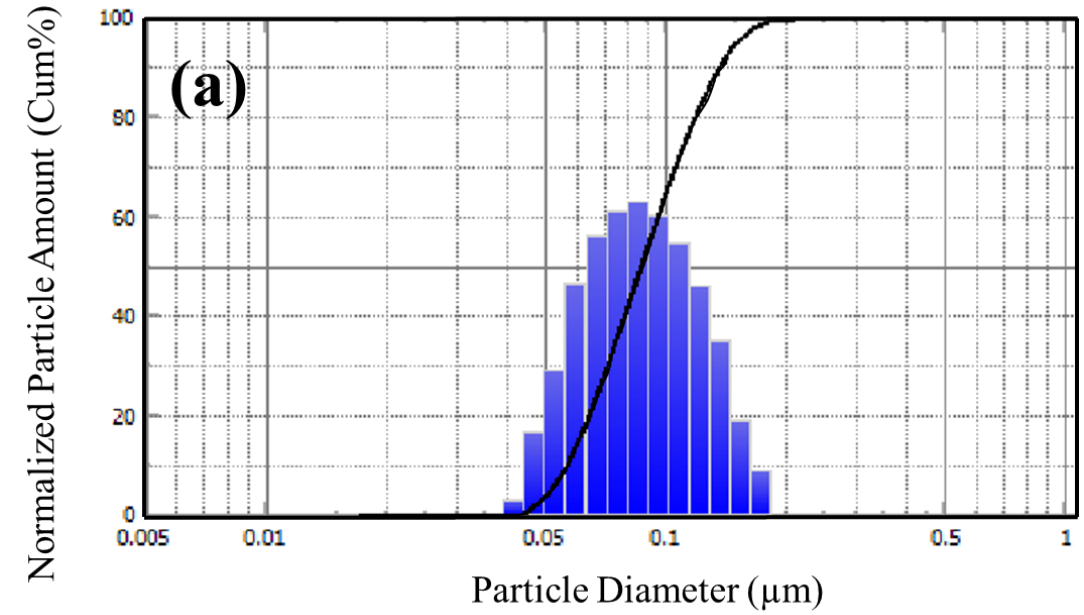


Figure 4.1: Process flow sheet for the production of titanium hydride powder according to direct reduction of titanium slag (DRTS) process.



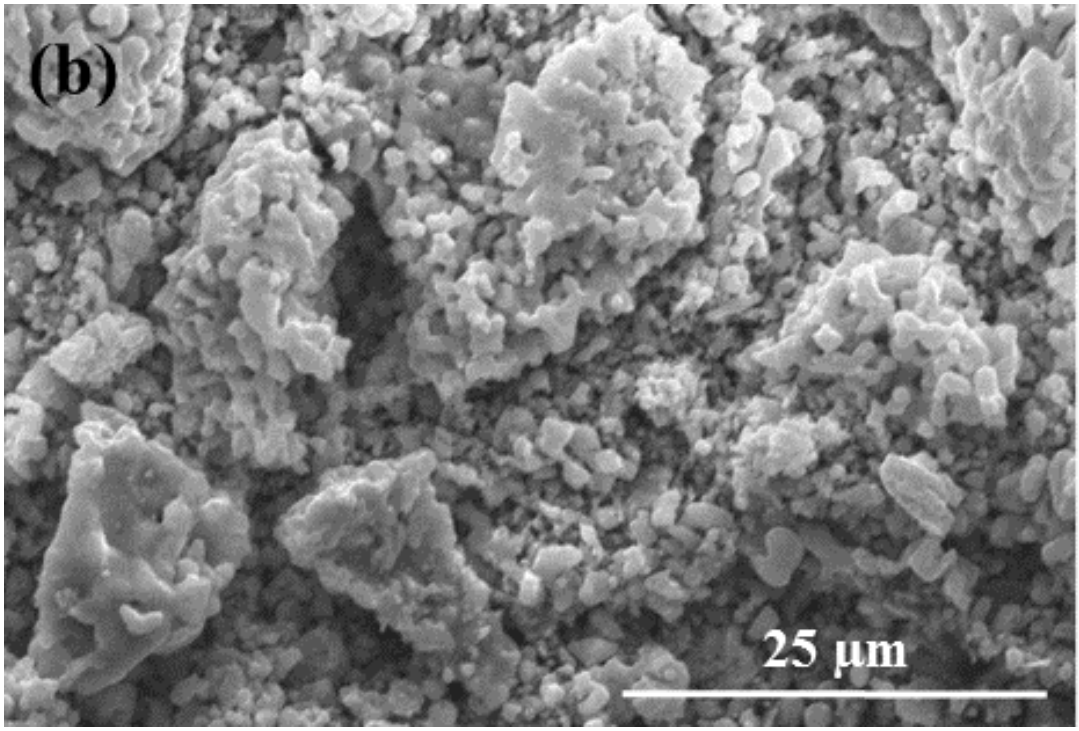


Figure 4.2. (a) Particle size distribution (b) SEM image of salt removed reduced UGS (starting material).

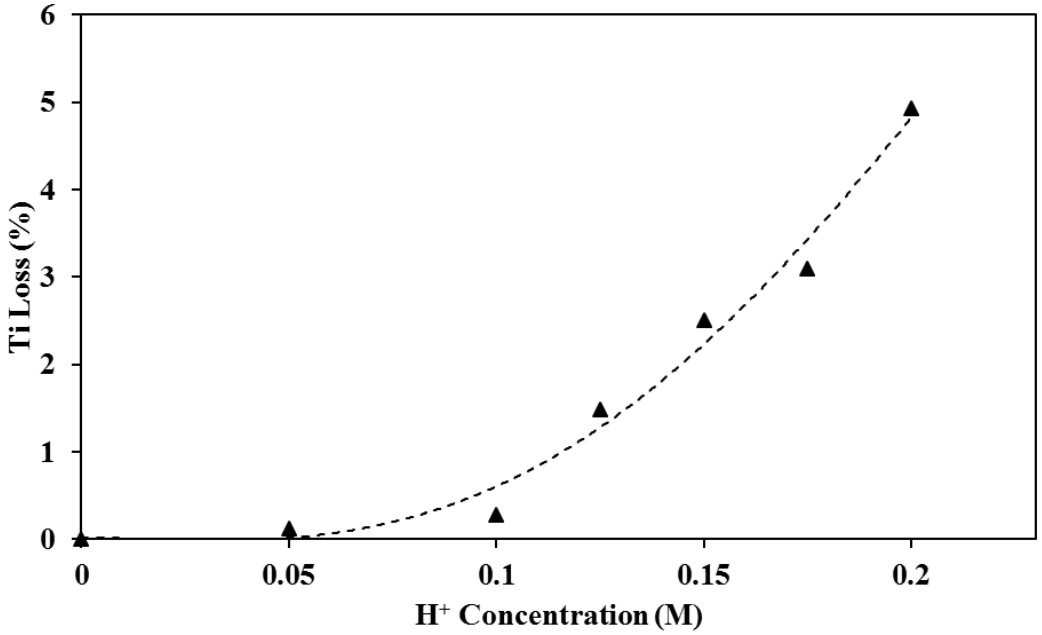


Figure 4.3. Titanium loss associated with leaching of reduced titania slag at different concentration of hydrochloric acid at 90ºC.

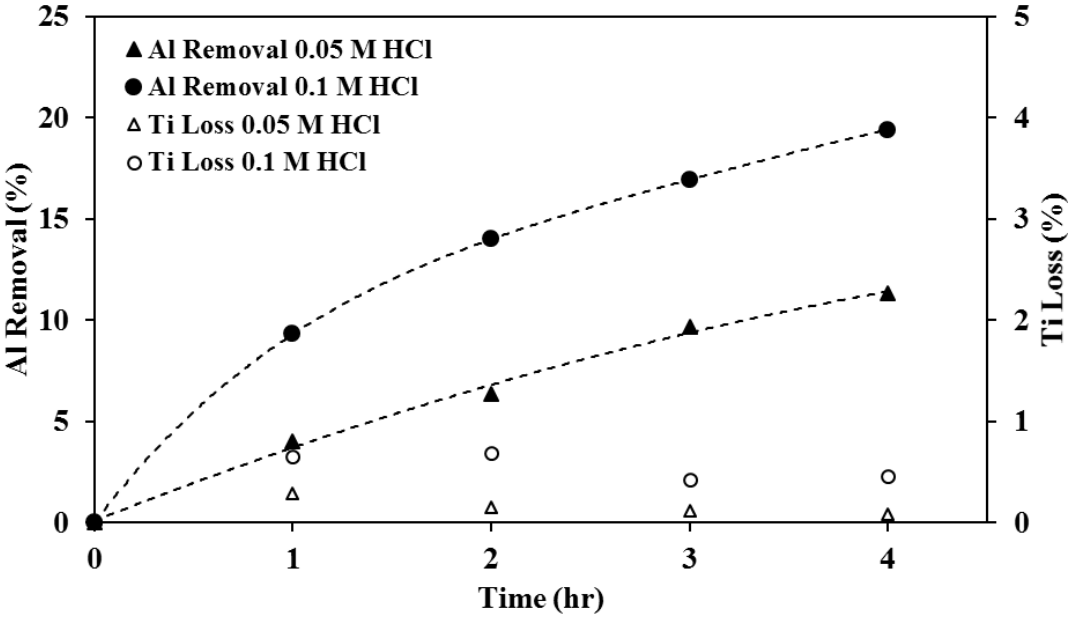


Figure 4.4. Kinetics of removal of aluminum in reduced titania slag along with corresponding titanium losses at different concentration of hydrochloric acid at 90ºC.

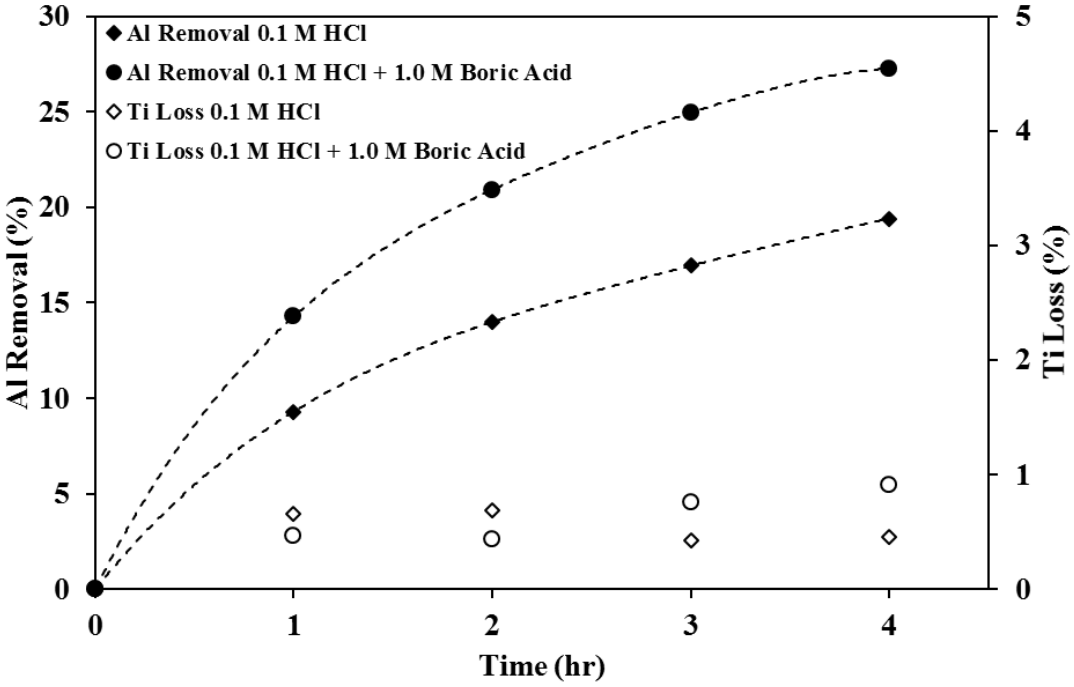


Figure 4.5. Role of boric acid on the kinetics of removal of aluminum in reduced upgraded titanium slag in acidic lixiviant and also on the corresponding titanium losses at 90^{o}C.

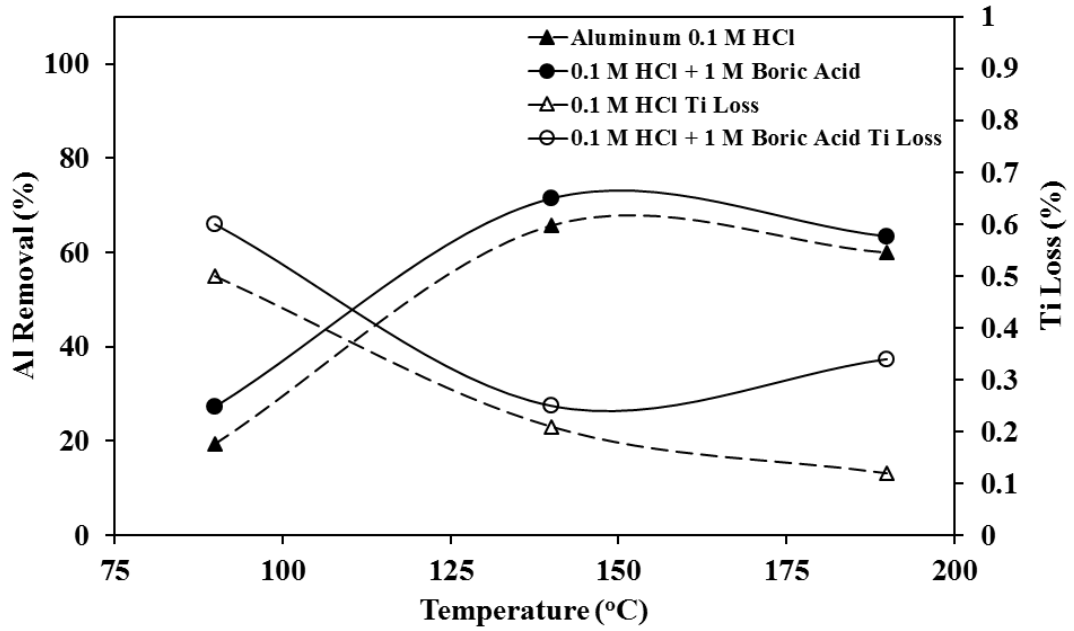


Figure 4.6. Effect of temperature on aluminum removal and corresponding titanium loss from reduced upgraded titanium slag under acidic condition with or without additive addition.

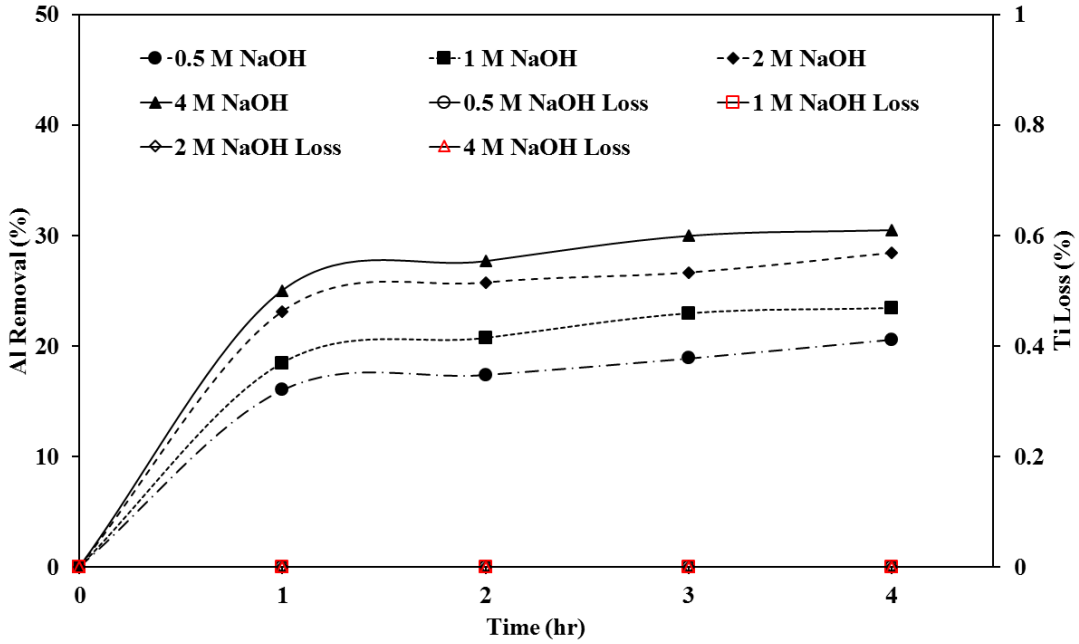


Figure 4.7. Kinetics of aluminum removal and corresponding titanium loss from reduced upgraded titanium slag at different alkali concentrations at 90ºC.

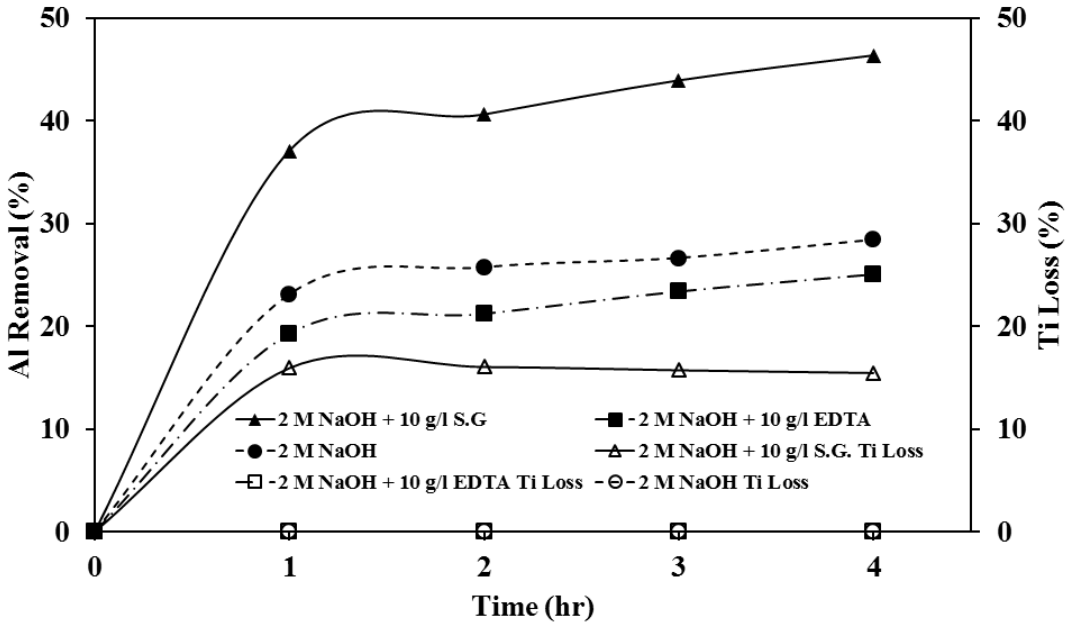


Figure 4.8. Role of sodium gluconate and EDTA on the kinetics of aluminum removal and corresponding titanium losses in 2 M sodium hydroxide solution at 90ºC.

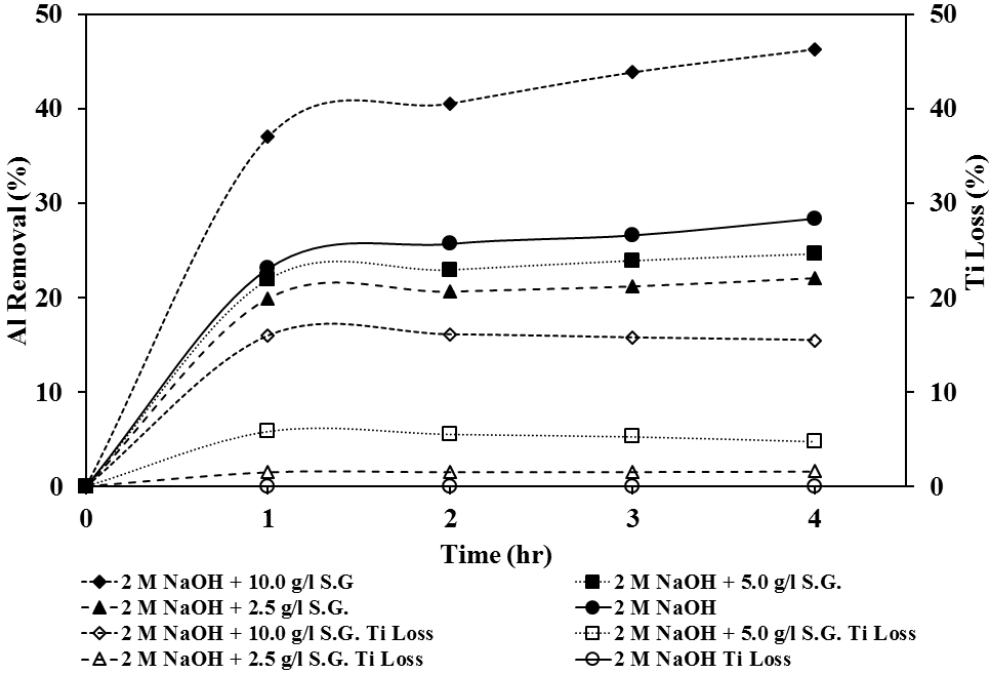


Figure 4.9. Effect of amount of sodium gluconate addition to 2 M sodium hydroxide on the kinetics of aluminum removal and corresponding titanium loss at 90^{o}C.

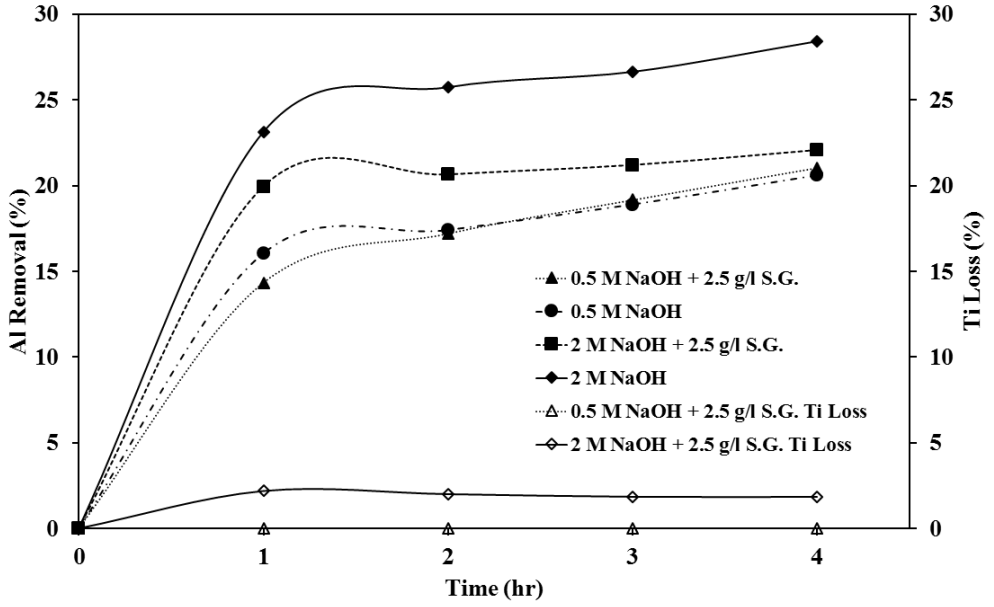


Figure 4.10. Effect of alkalinity of the base solution on the aluminum removal kinetics with or without the addition of 2.5 g/l of sodium gluconate to alkaline lixiviant at 90^{o}C.

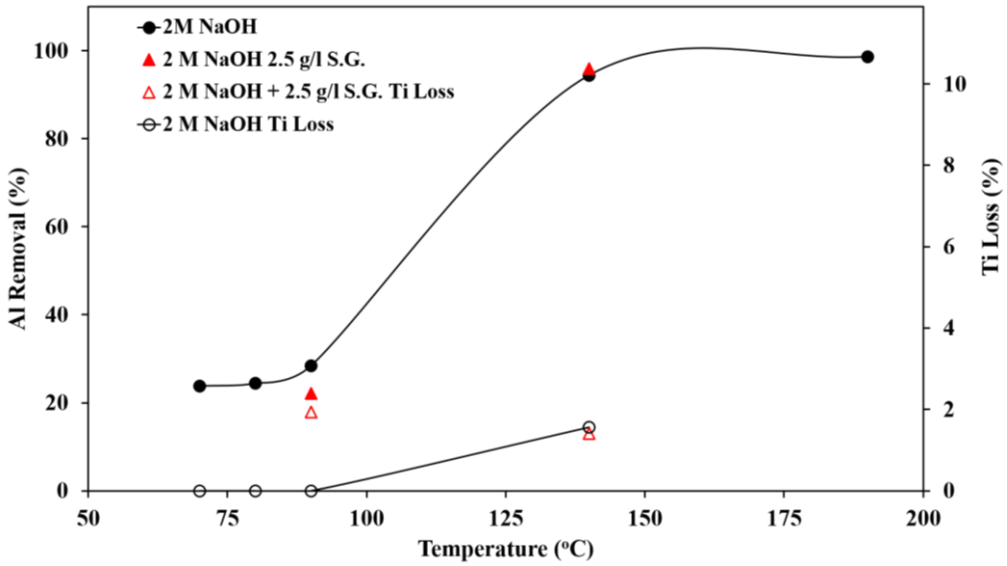


Figure 4.11. Effect of temperature on aluminum removal and corresponding titanium loss from reduced upgraded titanium slag under alkaline condition with or without additive addition.

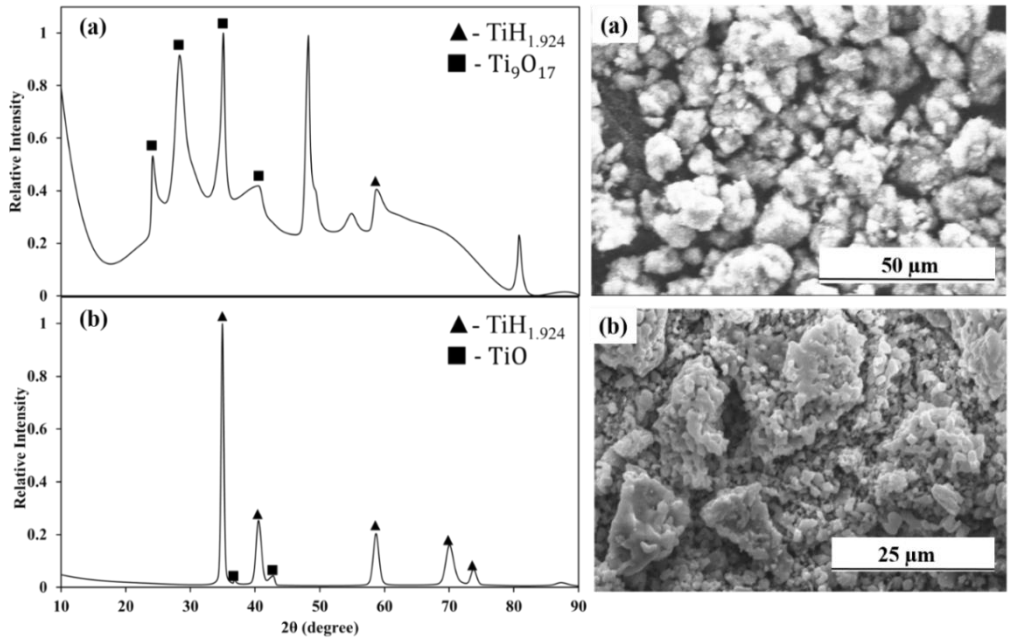


Figure 4.12. X-ray diffraction patterns and corresponding SEM images for (a) reduced upgraded titanium slag leaching with 2 M sodium hydroxide at 190ºC (b) starting material (reduced upgraded titanium slag).

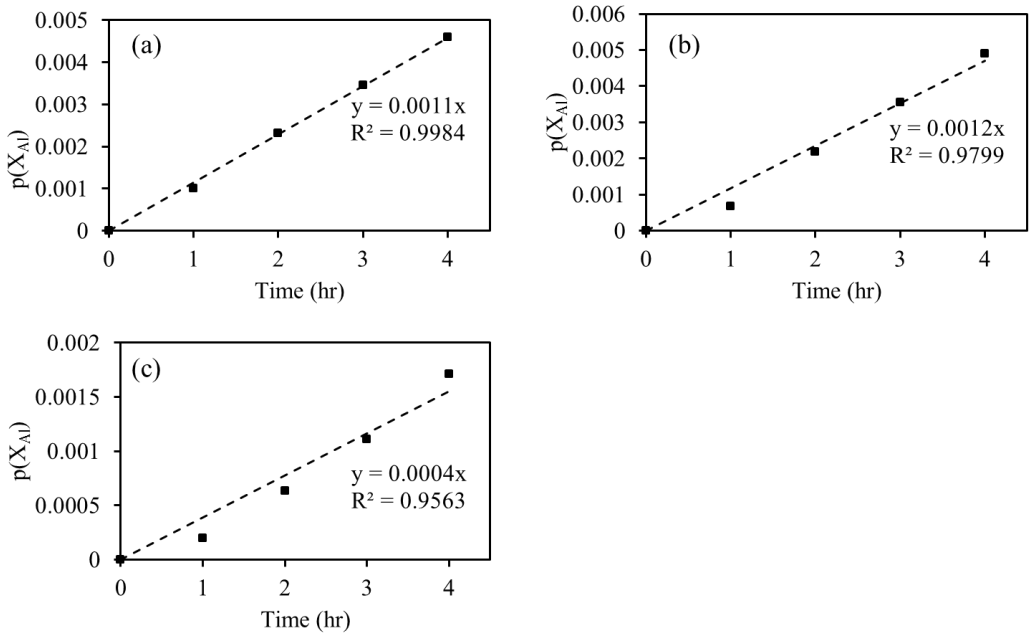


Figure 4.13. The leaching data for aluminum removed with (a) 0.1 M HCl at 90^{o}C, (b) 0.1 M HCl at 80^{o}C, (c) 0.1 M HCl at 70^{o}C were fitted to inner diffusion control kinetic model.

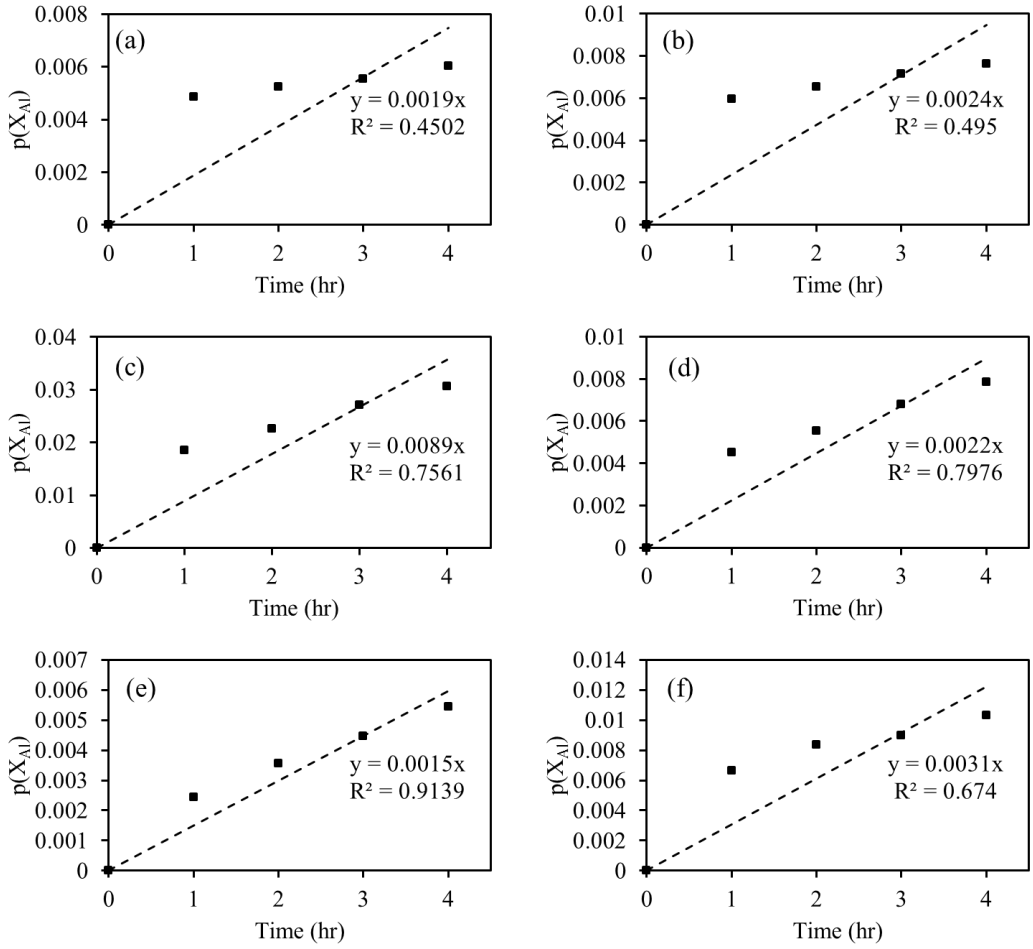


Figure 4.14. The leaching data for aluminum removed with (a) 2.0 M NaOH + 2.5 g/l S.G at 90ºC, (b) 2.0 M NaOH + 5 g/l S.G at 90ºC, (c) 2.0 M NaOH + 10 g/l S.G at 90ºC (d) 2.0 M NaOH + 10 g/l EDTA at 90ºC (e) 0.5 M NaOH + 2.5 g/l S.G at 90ºC (f) 2.0 M NaOH at 90ºC were fitted to inner diffusion control kinetic model (*S.G stands for Sodium Gluconate).

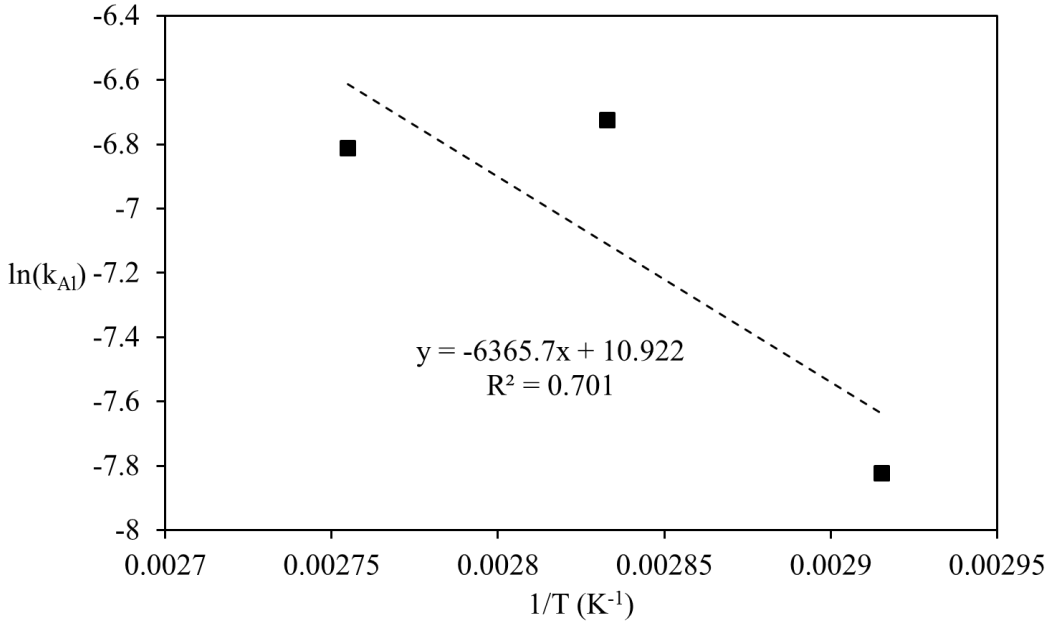


Figure 4.15. Logarithm of reaction constant versus inverse of absolute temperature for aluminum leaching from reduced UGS with 0.1 M HCl.

CHAPTER 5

LEACHING BEHAVIOR OF SILICON IMPURITIES IN REDUCED UPGRADED TITANIUM SLAG

5.1 Materials and Methods

5.1.1 Preparation of Reduced Upgraded Titanium Slag and Salt Removal

To produce reduced upgraded titanium slag, first the upgraded titanium slag (UGS) product was ground to <40 μm. Next, the pulverized UGS powder was intimately mixed with magnesium turnings and a combination of salts in the ratio of 1:1:1 by weight. The salt combination was a mixture of anhydrous magnesium chloride and potassium chloride with a weight ratio of 2:1. Next the mixture of UGS, magnesium, and salts was reduced under a hydrogen atmosphere at 750^{o}C for 6 h. To ensure the maximum extent of reduction the reductant magnesium was added in excess of stoichiometric requirement. The product obtained directly from the furnace was a mixture of reduced upgraded titanium slag, which is predominantly titanium hydride, with magnesium compounds (predominantly magnesium oxide and unreacted magnesium) and salts. The magnesium compounds and the salts were removed by washing the mixture with a 4.3 M acetic acid (CH_3COOH) solution with a solid to liquid ratio of 1 g to 40 ml for 2 h at 70^{o}C. The reduced upgraded titanium slag (UGS) was obtained as a filter cake by separating the solid residue after acetic acid washing using a vacuum filtration setup.

The cakes were thoroughly washed using 0.05 M hydrochloric acid followed by deionized water to remove any water soluble components such as magnesium compounds and salts that might still remain. Then the filter cakes were completely dried in an oven at 70^{o}C. On drying the cakes were pulverized into powder. The pulverized powder had an average particle size of 0.1μ and the size distribution is presented in Figure 4.2 (a). The extremely fine particle size leads to the formation of aggregates as observed from the SEM image in Figure 4.2 (b). The reduced upgraded titania slag or reduced UGS powder so obtained was used as feed stock for all the leaching experiments discussed in this chapter.

5.1.2 Experimental Procedure

All the leaching experiments described in the subsequent sections of this chapter were carried out in either of two setups, depending on the operating temperature of the leaching process. In the cases when the experiments were carried out at temperatures below the boiling point of water, the setup comprised of an Erlenmeyer flask made out of polymer sealed with a chemical and temperature resistant plug. The plug was used to minimize evaporative losses. A thermometer was inserted through an opening in the plug and the temperature was monitored continuously throughout the experiment. A heating mantel with magnetic stirring facility was used to provide the heat for raising and maintaining the temperature of the lixiviant at a preset, uniform temperature. The lixiviant was stirred with a magnetic stir bar at 1000 rpm to ensure homogeneity. Once the temperature was stabilized ($\pm$1^{o}C) at the preset uniform temperature, salt removed reduced UGS was added into the lixiviant in quantities so that the solid to liquid ratio was maintained at 1 g to 100 ml. Typically, a 2-g sample of salt removed reduced UGS was used in 200 ml of lixiviant. The

temperature was maintained for 4 h and the samples were taken every hour.

When the leaching temperature was above the boiling point of water (140^{o}C, 190^{o}C), a pressure reactor was used. The setup had a digital temperature controller and stirring was done with a motorized system. The sample was put into the lixiviant, contained in a Teflon beaker, maintaining a solid liquid ratio of 1g to 100 ml. The beaker was placed inside reactor and the heating rate was used such that a preset uniform temperature was reached in about an hour. After the preset temperature was reached the system was held there for a period of 3 h. Throughout the process stirring was performed at 250 rpm to ensure the homogenization of the slurry. Samples of the residual solids and the leach liquor were obtained after the pressure reactor was cooled down. The solids were separated by vacuum filtration setup followed by thorough washing with deionized water.

5.1.3 Analysis of Results

An Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) setup was used to obtain the quantitative assays of the elements. Diffraction patterns were obtained from an X-ray Diffraction (XRD) instrument and the particle size distribution was determined using a Laser Diffraction Particle Size Analyzer. Micrographs and morphology of samples were observed using a scanning electron microscope.

5.2 Results and Discussion

Silicon is an element which has been classified as a metalloid and forms a variety of oxides and intermetallic compounds. From the studied on pure minerals and surrogated reduced UGS (sections 3.2.1 and 3.2.2) it was found that the removal of silicon was

possible in both alkaline and acidic conditions. While the basic lixiviants were found to be more effective, the possibility of using an acid lixiviant could not be ruled out. Therefore, experimental studies were conducted under both acidic and alkaline conditions to investigate the leaching behavior of silicon in actual reduced upgraded titanium slag. The results from experiments carried out under acidic and alkaline conditions are being presented separately. The objective of leaching was to lower the silicon content in reduced titanium slag below the maximum permissible impurity limit specified by ASTM for titanium product. In Table 5.1 the typical composition of reduced UGS after washing is reported along with specifications for titanium product according to ASTM B299-2013.

It can be observed from Table 5.1 that about 98 wt. % of silicon removal is needed to meet the specification. Besides controlling the operating parameters, in certain cases the effectiveness of a lixiviant was found to be increased by addition of additive compounds.[32,33,49] These compounds may facilitate the formation of chelates or simply catalyze the removal reaction. Therefore, additive compounds were also added to effective leaching solutions to determine if the efficiency of silicon removal could be improved. Previous studies have demonstrated the effectiveness of complexing agents like sodium gluconate and EDTA as sequestering agents in alkaline medium for a system having compositions similar to reduced titanium slag,[33] as well for other systems containing silicon.[47-48] Hence, the effect of EDTA, and sodium gluconate in alkaline media for this particular system were studied.

5.2.1 Acidic Leaching

As reported in the section 4.2.1, on leaching reduced UGS with various concentrations of hydrochloric acid significant loss of titanium products was observed. From the study on the dependence of titanium loss on the concentration of acid presented in Figure 4.3, it can be seen that the loss of titanium increases rapidly with increase in the acid concentration.

Therefore, in order to preserve the final product, a limit was imposed on the maximum allowable titanium loss in the case of leaching with acidic lixiviants. It was decided that if the loss could be kept below 1- 2 wt. % the economics of the process would not be affected significantly. Therefore, for acidic leaching the maximum allowable acid concentration was set to be 0.1 M hydrochloric acid.

5.2.1.1 Effect of acid concentration

The effect of concentration of hydrochloric acid on the silicon removal kinetics is illustrated by Figure 5.1. It was observed that the change in fraction of silicon removed in 4 h on increasing the acid concentration in the lixiviant from 0.05 M hydrochloric acid to 0.1 M hydrochloric acid at 90^{o}C was not very large although the use of 0.1 M hydrochloric acid resulted in higher fraction of removal in shorter durations of leaching. The corresponding titanium losses were also found to increase with increase in concentration of acid but, in both cases, the loss was below 1% by weight.

5.2.1.2 Effect of temperature

It can be seen from Figure 5.1 that the fraction of silicon removed with acidic lixiviant at 90^{o}C was very small compared to the removal required to meet the titanium product

specification from ASTM. In general, on increasing the temperature of leaching the fraction of targeted impurity removed increases. Therefore, to obtain products with low levels of silicon and low Ti loss, the reduced upgraded titanium slag was leached at 140^{o}C and 190^{o}C with acidic lixiviants. A comparison between the fraction of silicon removed from reduced upgraded titanium slag on using 0.05 M hydrochloric acid and 0.1 M hydrochloric acid under otherwise identical conditions can be seen in Figure 5.2. It can be seen from Figure 5.2 that the removal of silicon reaches a maximum at 140^{o}C for both 0.05 M hydrochloric acid and 0.1 M hydrochloric acid and then the value stays put on the average. The associated titanium loss in the case of higher acid concentration was a little higher but the absolute titanium loss was kept below 1wt % for leaching at both 140^{o}C and 190^{o}C. Therefore, the best silicon removal from reduced upgraded titanium slag under acidic conditions was achieved when the concentration of acid used was 0.1 M hydrochloric acid and the temperature of operation was 140^{o}C.

Although increasing the temperature of leaching caused the silicon removal fraction to go up rapidly, even under the best conditions, with an acidic lixiviant, the ASTM specifications for silicon in titanium products could not be met by a large margin. Further, based on the trend of the curve for fraction of silicon removed over temperature, it is unlikely that the ASTM specifications can be met by going to higher temperatures.

5.2.2 Alkaline Leaching

Results from the leaching experiments in acidic medium demonstrated that removal of silicon to the extent needed to satisfy the ASTM specification of titanium products is unlikely to be achieved by acidic leaching with acceptable titanium losses associated.

Therefore, experiments with alkaline lixiviants were performed to investigate the process of silicon removal from reduced upgraded titanium slag and to find operating conditions for silicon removal.

5.2.2.1 Effect of alkali concentration

Figure 5.3 shows the kinetics of silicon removal from reduced titanium slag when leached with lixiviants of different levels of alkalinity at 90^{o}C. An increase in alkalinity of the lixiviant resulted in an increase in the fraction of silicon removed. However, the concentration of sodium hydroxide (NaOH) was increased beyond 2 M sodium hydroxide, there was no appreciable increment in silicon removal. Therefore, at 90^{o}C, a 2 M sodium hydroxide solution was found to be the optimal alkali concentration for silicon removal. Another interesting observation is that for alkaline lixiviants there is a very small associated titanium loss even with concentrations as high as 4 M sodium hydroxide.

5.2.2.2 Effect of additive

Since 2 M sodium hydroxide solution was found to be the optimal concentration for silicon removal at 90^{o}C, 10 g/l of the additive compounds (sodium gluconate, EDTA) was added to a 2 M sodium hydroxide solution was used as a lixiviant for investing kinetics of silicon removal. A comparison between the kinetics of silicon removal on addition of 10 g/l of an additive compound to 2 M sodium hydroxide solution and 2 M sodium hydroxide solution, without any addition, is shown in Figure 5.4. It is observed that the silicon removal kinetics remained almost unaltered by the addition of 10 g/l of EDTA to 2 M sodium hydroxide solution. While the addition of 10 g/l of sodium gluconate to 2 M sodium

hydroxide solution led to considerable increase in the fraction of silicon removal. However, improvement in silicon removal on the addition of 10 g/l of sodium gluconate to 2 M sodium hydroxide solution was associated with quite high titanium loss.

Sodium gluconate addition to 2 M sodium hydroxide could only be considered to be beneficial if the associated titanium loss could be minimized by controlling the amount of sodium gluconate added while improving the silicon removal. Hence, kinetic studies were performed by lowering the concentration of the additive compound added to 2 M sodium hydroxide base solution. The kinetics of silicon removal on varying the amount of sodium gluconate in 2 M sodium hydroxide solution is depicted in Figure 5.5. If the amount of sodium gluconate added to 2 M sodium hydroxide was kept below 2.5 g/l, the corresponding titanium loss was found to be below 2 wt. %. From Figure 5.6, a comparison between the kinetics of silicon removal with 2 M sodium hydroxide solution with or without the addition of 2.5 g/l of sodium gluconate can be made. It is observed that the addition of sodium gluconate in controlled amounts helps improve the fraction of silicon removed while regulating titanium losses within acceptable limits. Hence, the results indicate that the use of 2 M sodium hydroxide solution with 2.5 g/l of sodium gluconate addition would be best for removal of silicon from reduced upgraded titanium slag.

The effect of alkalinity of the base solution on the additive sodium gluconate can be better understood by comparing results of leaching kinetics of silicon using different alkalinity and identical sodium gluconate concentration as shown in Figure 5.6. Increase in the alkalinity of the leaching solution from 0.5 M sodium hydroxide to 2 M sodium hydroxide made the average increase in the fraction of silicon removed less, both in relative an absolute term. Therefore, it can be observed that the fraction of silicon removed not only

depends on the concentration of the additive used but also on the alkalinity of the base solution. Effect of additives are more prominent in base solutions with lower alkalinity.

5.2.2.3 Effect of temperature

The results for silicon removal discussed in the previous sections show that the silicon removal from the reduced upgraded titanium slag at 90^{o}C under alkaline lixiviant was most effective when a combination of 2 M sodium hydroxide with 2.5 g/l of sodium gluconate addition was used, although the ASTM specification for silicon in titanium products could not be satisfied by leaching under these conditions at 90^{o}C. Increase in temperature of leaching in general increase the fraction of target impurity leached. Therefore, the temperature of leaching was increased to improve the fraction of silicon removed. Since 2 M sodium hydroxide was found to be the most effective in lixiviant removing silicon impurities from reduced UGS, when no additives were used, it was chosen as a lixiviant. Leaching experiments were conducted at five different temperatures with 2 M sodium hydroxide solution and the results are presented in Figure 5.7. Upon increasing the temperature from 90^{o}C to 140^{o}C, the fraction of silicon removal was found to be increasing on average. When the temperature of leaching was increased further from 140^{o}C to 190^{o}C, the silicon removal was not improved any further. Instead, at 190^{o}C, there was oxidation of the reduced titanium hydride as observed from the X-ray diffraction patterns of the residue after leaching shown in Figure 5.8. Leaching with 2 M sodium hydroxide for 3 h at 140^{o}C resulted in around 95 % of silicon removal which is still not enough to meet the ASTM specification of silicon in titanium products. Therefore, leaching tests were conducted at 140^{o}C with 2 M sodium hydroxide and 2.5 g/l of sodium gluconate as a

lixiviant. Leaching under the aforementioned conditions resulted in around 99.2% silicon removal which was sufficient to meet the ASTM specification for silicon content in titanium products. It is to be noted that the titanium losses associated with the leaching of reduced upgraded titanium slag with or without additives added to a 2 M sodium hydroxide solution at 140^{o}C was similar under both conditions.

The degree of oxidation increases with increase in alkalinity of the base solution which can be readily perceived by comparing the X-ray diffraction patterns, as shown in Figure 5.8, for the residual solids after leaching reduced upgraded titanium slag with sodium hydroxide solution of different alkalinity at 190^{o}C. As the product after leaching at 190^{o}C was highly oxidized, as can be seen from Figure 5.8, the corresponding titanium loss was not represented in Figure 5.7, as it is a presumably a very large fraction and also not of any practical interest. Furthermore, the oxidation in the reduced UGS sample can be distinguished by simply looking at the micrographs, obtained from SEM analysis of the solid residue after leaching. As can be seen from the SEM images shown in Figure 5.8, the micrographs for the residue after leaching with 0.5 M sodium hydroxide solution and 1 M sodium hydroxide solution had a larger particle size and lacked sharp edges which might indicate the possibility of oxidation of the outer surface of the particles. The evidence of oxidation can be seen from the corresponding X-ray diffraction patterns shown in Figure 5.8 (b) and 5.8 (c).

5.2.3 Studies on the Governing Mechanism for Silicon Removal

The removal fraction of silicon was recorded over time for leaching with different lixiviants. This kinetic data obtained under each of these conditions were fitted to the

kinetic model for interfacial chemical reaction, inner diffusion controlled, and external or boundary layer diffusion control to identify the governing mechanism and the coefficient of determination values (R^2 value) are tabulated in Table 5.2.

The correlation values presented in Table 5.2. show a general trend for the data to have a higher degree of fit to the inner diffusion controlled model irrespective of the nature of lixiviant used. However, the fit to the inner diffusion control mechanism was much better for the kinetic data obtained for acidic lixiviants than it was with alkaline lixiviants. The exception being the cases where additives like sodium gluconate or EDTA was added to an alkaline base solution and then used as a lixiviant.

Since the kinetic data for silicon removal have the best fit to inner diffusion controlled model for leaching under acidic conditions, silicon removal kinetics with 0.1 M HCl was studied at different temperatures. The data obtained were fit into the inner diffusion controlled model and presented in Figure 5.10 It can be readily seen from Figure 5.10, that the fit to the controlling mechanism is remarkable over the chosen temperatures.

The kinetic data obtained from leaching under alkaline conditions, in general, did not fit well to any of the kinetic models under consideration, but the highest coefficients of determination were found when the data were force fitted into an inner diffusion controlled model. The plots for different alkaline leaching kinetics are shown in Figure 5.11.

It is to be noted that the fit of the kinetic data to the inner diffusion control model was quite good when the lixiviant consisted of additive compounds like sodium gluconate and EDTA in an alkaline base solution. The correlation was found to vary with the type of additive, additive concentration as well as alkalinity of the base solution. This might indicate to a change in controlling kinetic mechanism on addition of additives, which in

turn can help explain the positive effects of additive addition.

From the fitting of the kinetic data, it was found that inner diffusion control might be the predominant controlling mechanism for silicon removal from reduced UGS under acidic condition. This was supported by the activation energy calculations from the Arrhenius plots shown in Figure 5.12. The activation energy was found to be 28.154 kJ/mol which is a sufficiently low value to indicate an inner diffusion control mechanism.

Table 5.1. Composition of reduced UGS without salt and targeted composition.

Elements	Al	Fe	Si	Mg	Ti
Typical salt-removed Reduced UGS (wt. %)	0.35	1.07	2.02	0.36	bal
ASTM specified limits (wt. %) for Mg-reduced product	0.05	0.15	0.04	0.50	bal
Typical Removal (%) needed	85.71	85.98	98.02	-	-

Table 5.2. The coefficient of determination values on fitting the kinetic data to the different models for different experiments.

Si Removal	**R^2**		
Experiment	**Interfacial Chemical**	**Inner diffusion controlled**	**Outer Layer diffusion control**
0.05 M HCl 90°C	0.8805	0.9924	0.8599
0.1 M HCl 90°C	0.6737	0.9185	0.6518
0.05 M HCl + 1 M Boric Acid 90°C	0.8646	0.9956	0.8429
0.1 M HCl + 1 M Boric Acid 90°C	0.3949	0.5267	0.3844
0.5 M NaOH 90°C	0.4496	0.643	0.4121
1.0 M NaOH 90°C	0.4537	0.6479	0.4039
2.0 M NaOH 90°C	0.455	0.674	0.4288
4.0 M NaOH 90°C	0.4672	0.6459	0.3694
2.0 M NaOH 2.5 g/l S.G. 90°C	0.2966	0.3719	0.233
2.0 M NaOH 5 g/l S.G. 90°C	0.3669	0.4932	0.2894
2.0 M NaOH 10 g/l S.G. 90°C	0.9051	0.9418	0.4149
2.0 M NaOH 10 g/l EDTA 90°C	0.5099	0.7149	0.4033
0.5 M NaOH 2.5 g/l S.G. 90°C	0.6527	0.8894	0.5648

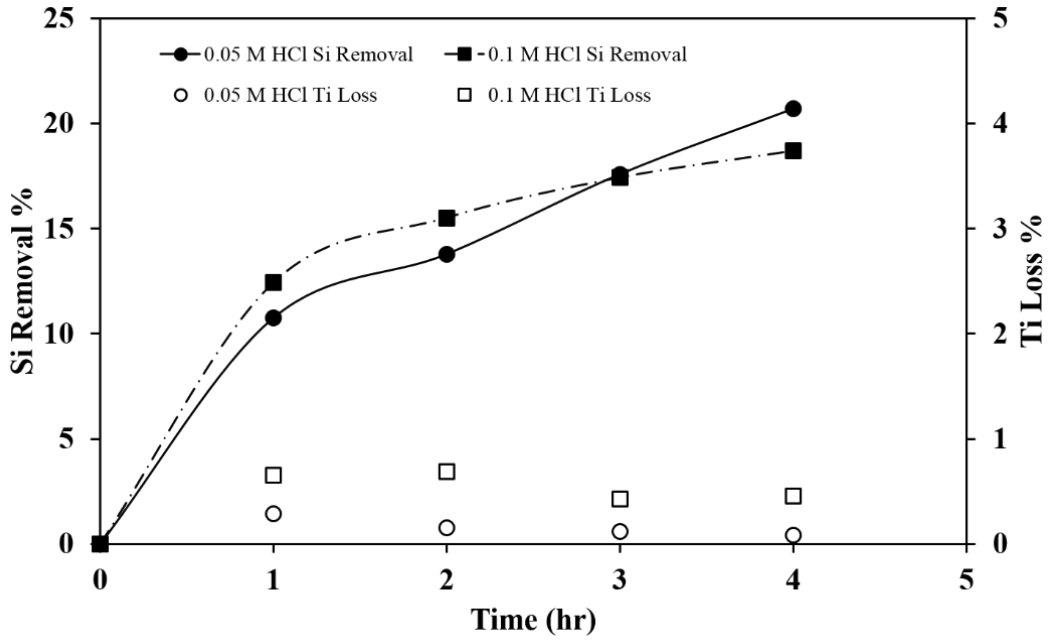


Figure 5.1. The leaching characteristics of silicon in reduced titanium slag under different concentrations of acid at 90ºC.

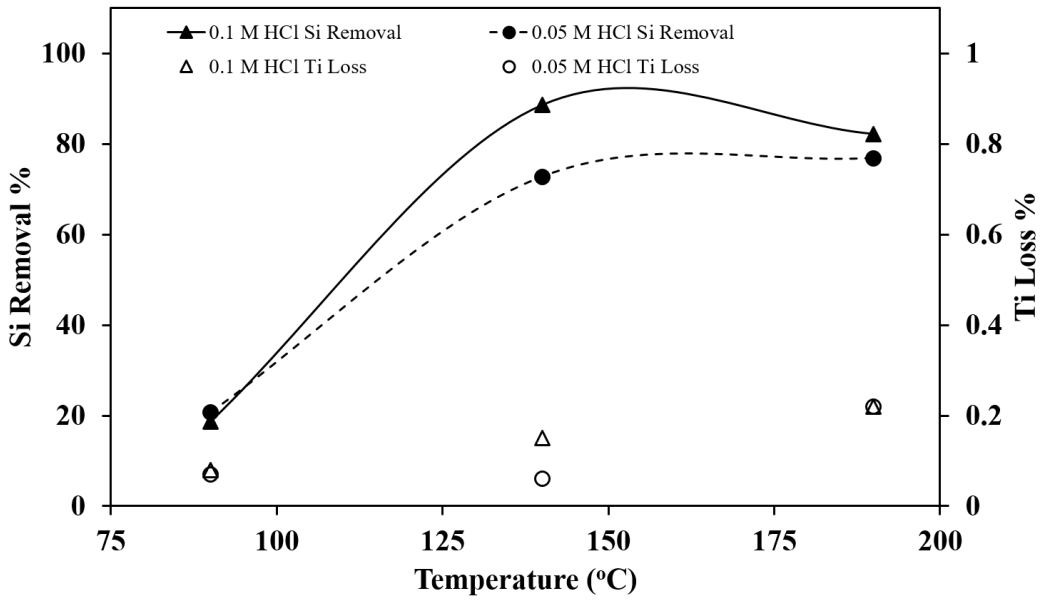


Figure 5.2. Effect of leaching temperature on silicon removal and corresponding titanium loss from reduce upgraded titanium slag under acidic condition.

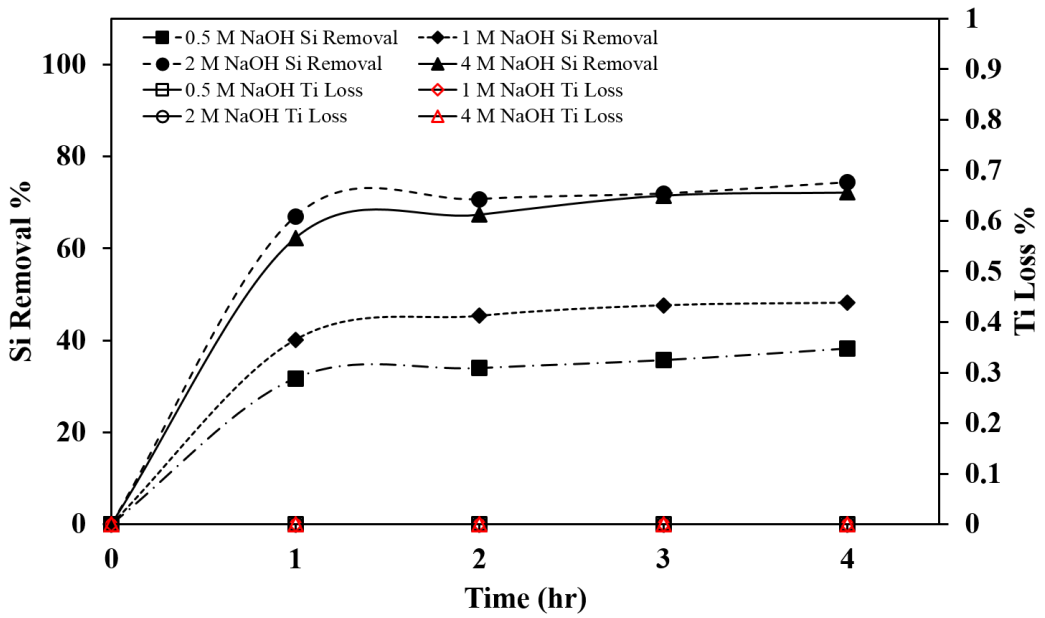


Figure 5.3. Kinetics of silicon removal and corresponding titanium loss from reduced upgraded titanium slag at different alkali concentrations at 90ºC.

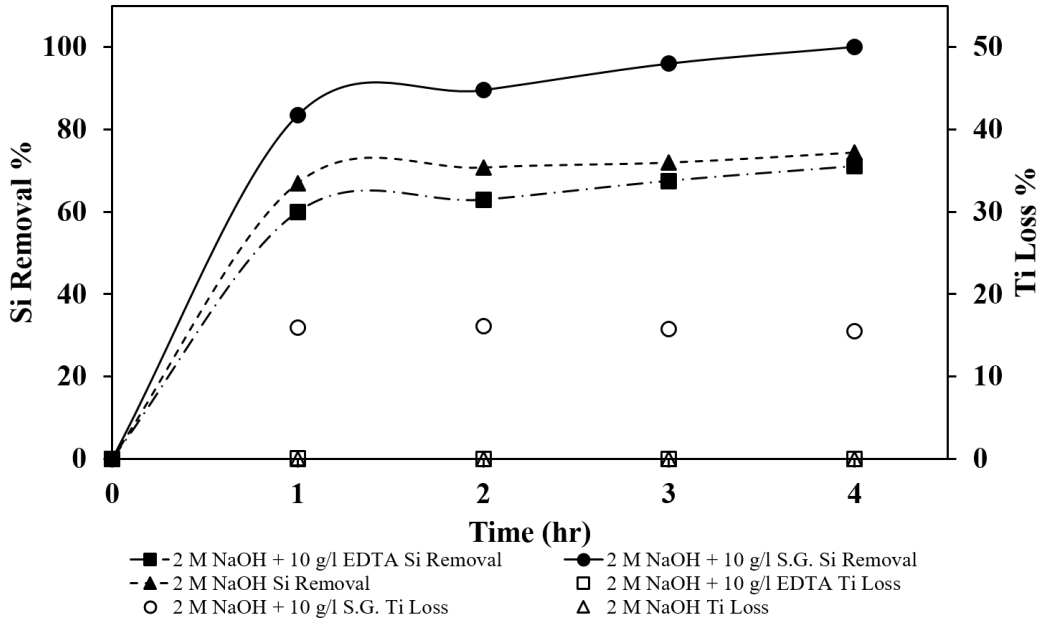


Figure 5.4. Role of sodium gluconate (S.G.) and EDTA on the kinetics of silicon removal and corresponding titanium losses in 2 M NaOH solution at 90ºC.

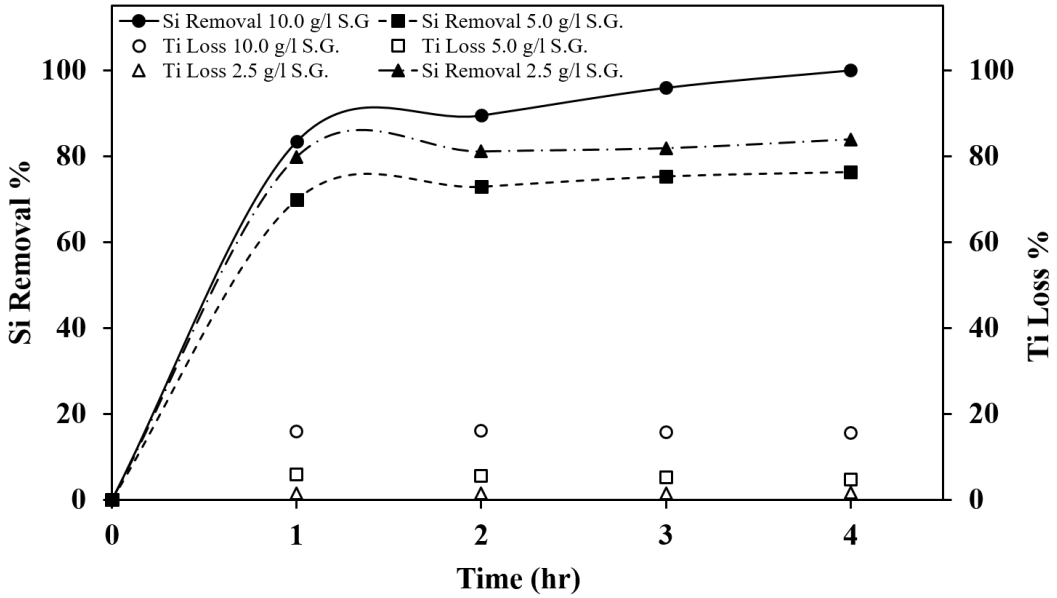


Figure 5.5. Effect of amount of sodium gluconate addition to 2 M sodium hydroxide on the kinetics of silicon removal and corresponding titanium loss at 90°C.

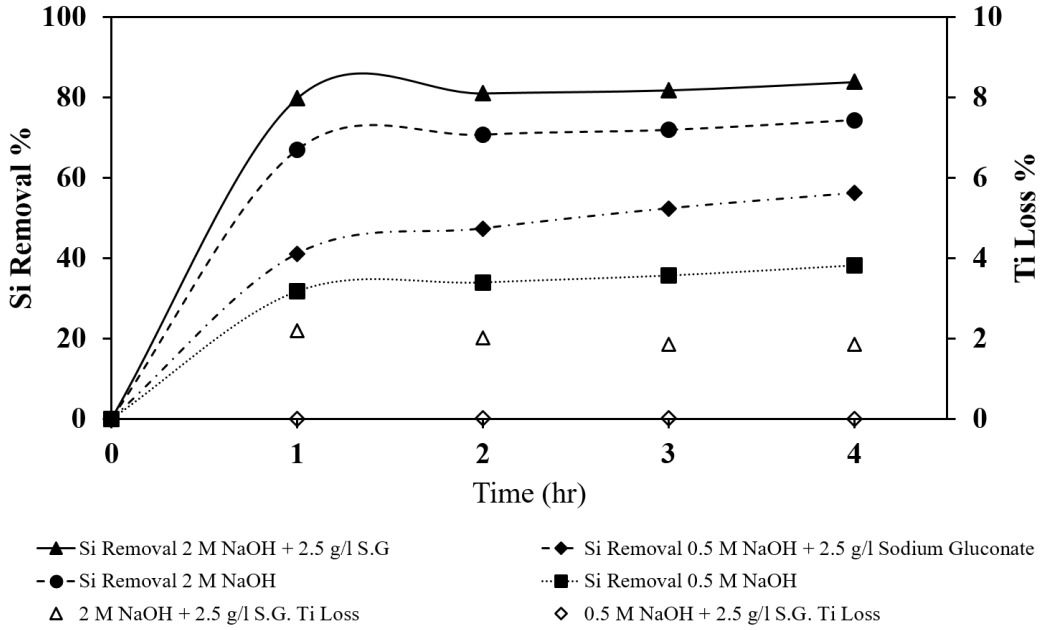


Figure 5.6. Effect of alkalinity of the base solution on the silicon removal kinetics with or without the addition of 2.5 g/l of sodium gluconate to alkaline lixiviant at 90°C.

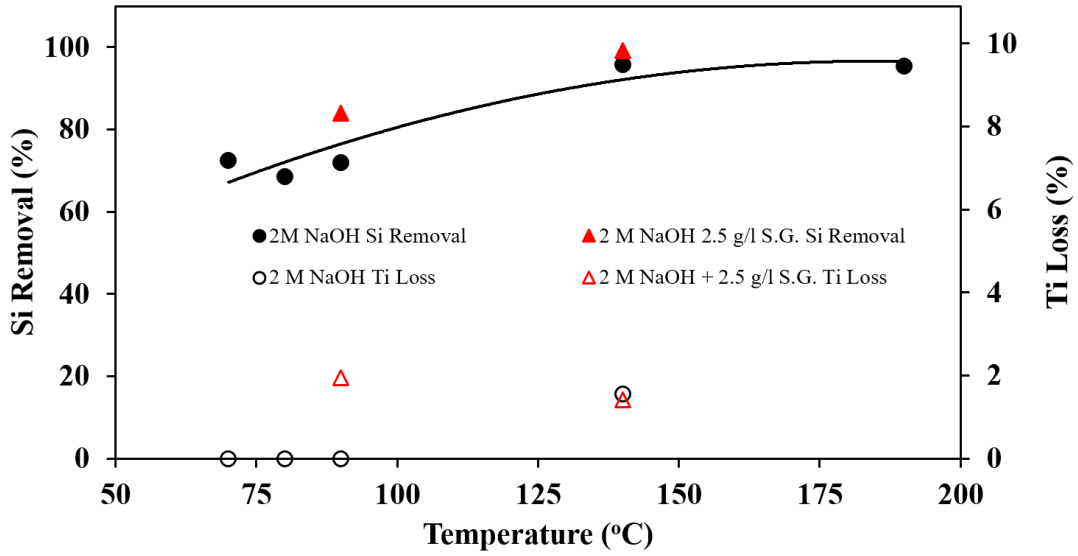


Figure 5.7. Effect of temperature on silicon removal and corresponding titanium loss from reduced upgraded titanium slag under alkaline condition with or without additive.

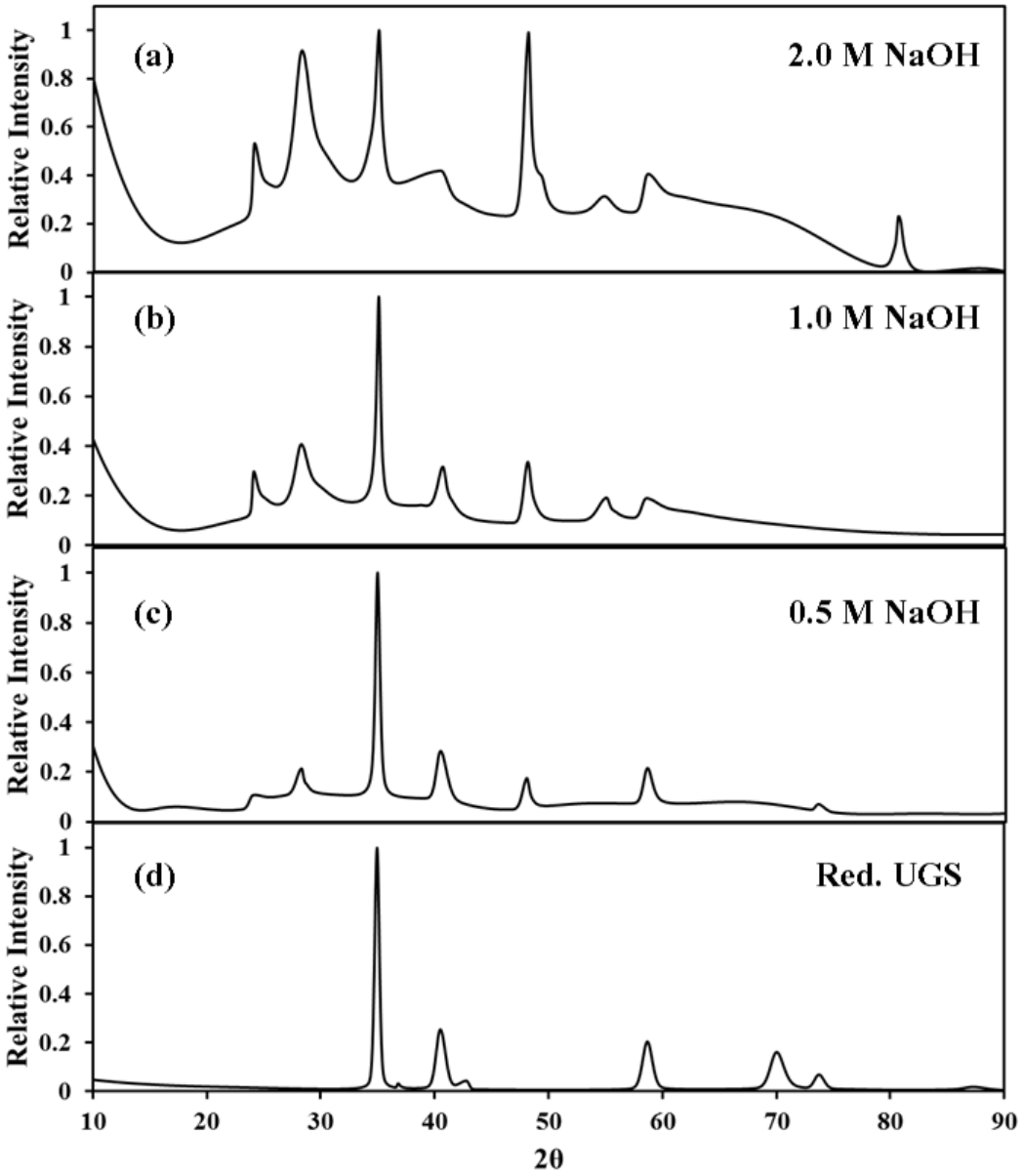


Figure 5.8. X-ray diffraction patterns for (a) reduced upgraded titanium slag leached with 2.0 M sodium hydroxide at 190^{o}C, (b) reduced upgraded titanium slag leached with 1.0 M sodium hydroxide at 190^{o}C, (c) reduced upgraded titanium slag leached with 0.5 M sodium hydroxide at 190^{o}C, (d) reduced upgraded titanium slag (starting material).

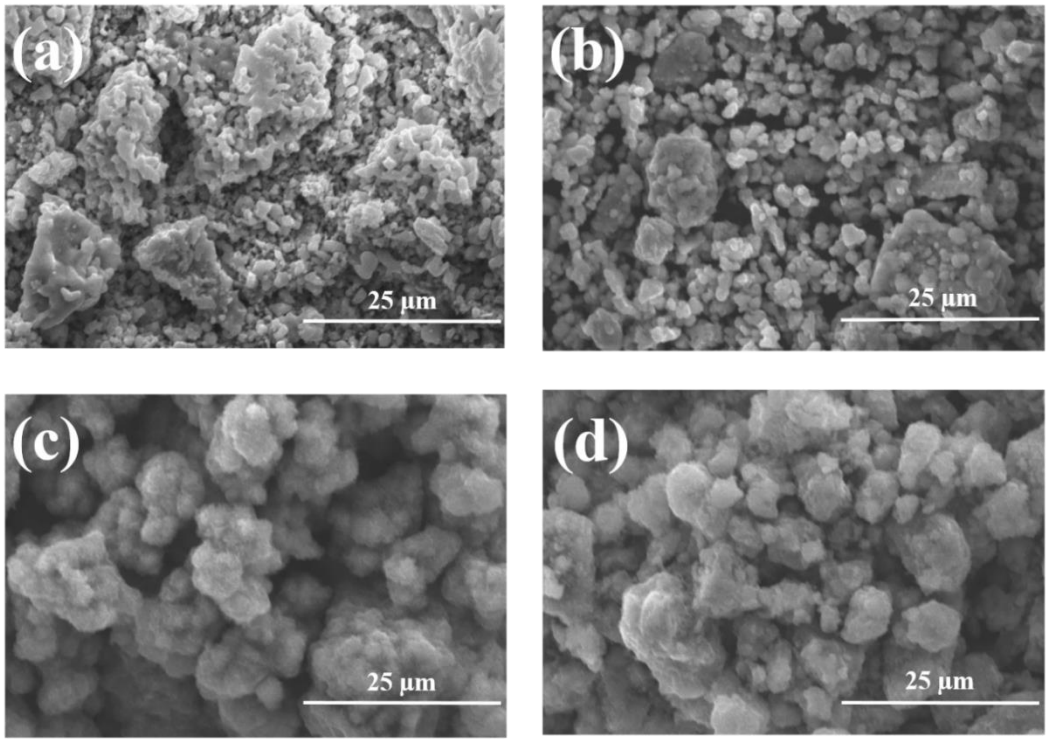


Figure 5.9. SEM micrographs for (a) reduced upgraded titanium slag (starting material), (b) reduced upgraded titanium slag leached with 2.0 M sodium hydroxide and 2.5 g/l sodium gluconate at 140^{o}C, (c) reduced upgraded titanium slag leached with 0.5 M sodium hydroxide at 190^{o}C, (d) reduced upgraded titanium slag leached with 1.0 M sodium hydroxide at 190^{o}C.

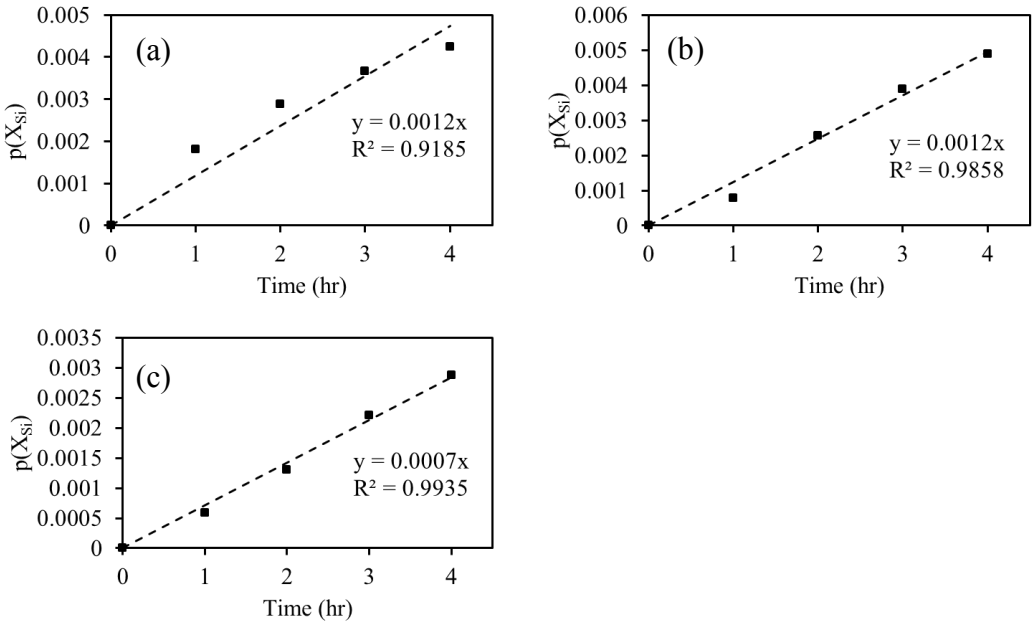


Figure 5.10. The leaching data for silicon removed with (a) 0.1 M HCl at 90°C, (b) 0.1 M HCl at 80°C, (c) 0.1 M HCl at 70°C were fitted to inner diffusion control kinetic model.

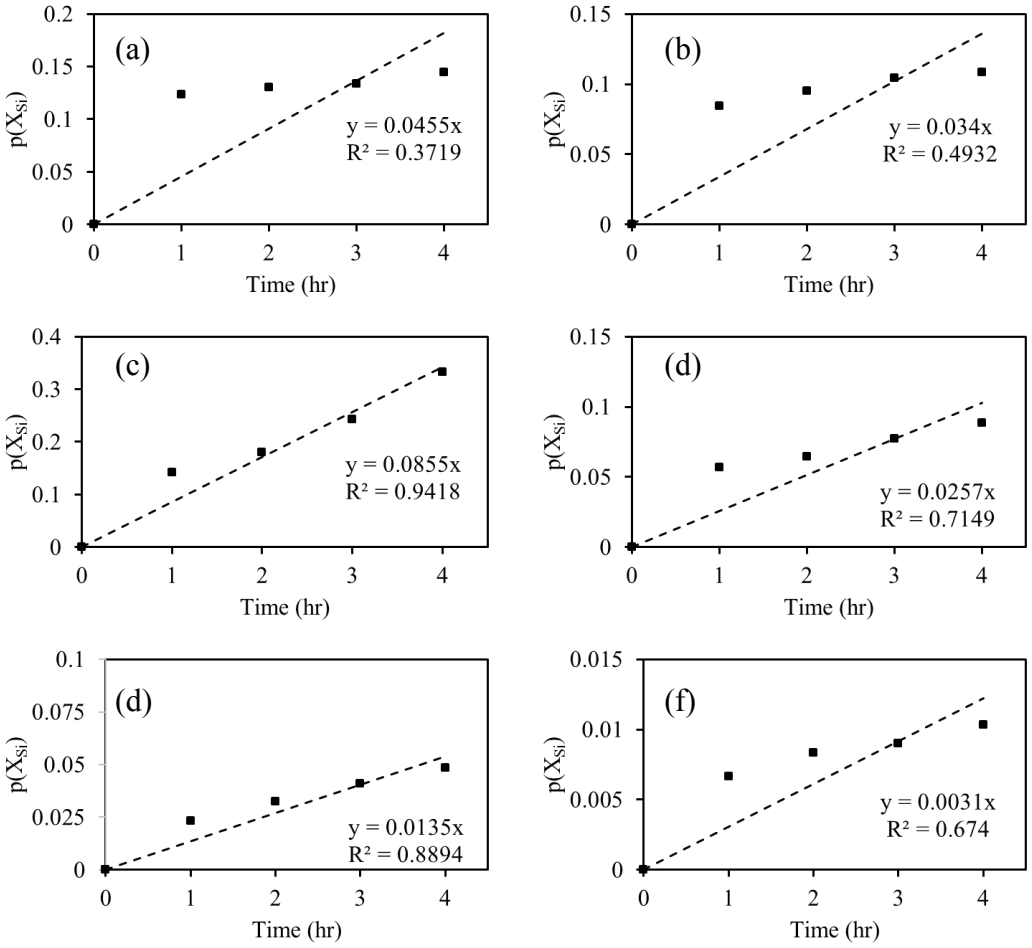


Figure 5.11. The leaching data for silicon removed with (a) 2.0 M NaOH + 2.5 g/l S.G at 90ºC, (b) 2.0 M NaOH + 5 g/l S.G at 90ºC, (c) 2.0 M NaOH + 10 g/l S.G at 90ºC (d) 2.0 M NaOH + 10 g/l EDTA at 90ºC (e) 0.5 M NaOH + 2.5 g/l S.G at 90ºC (f) 2.0 M NaOH at 90ºC were fitted to inner diffusion control kinetic model (*S.G stands for Sodium Gluconate).

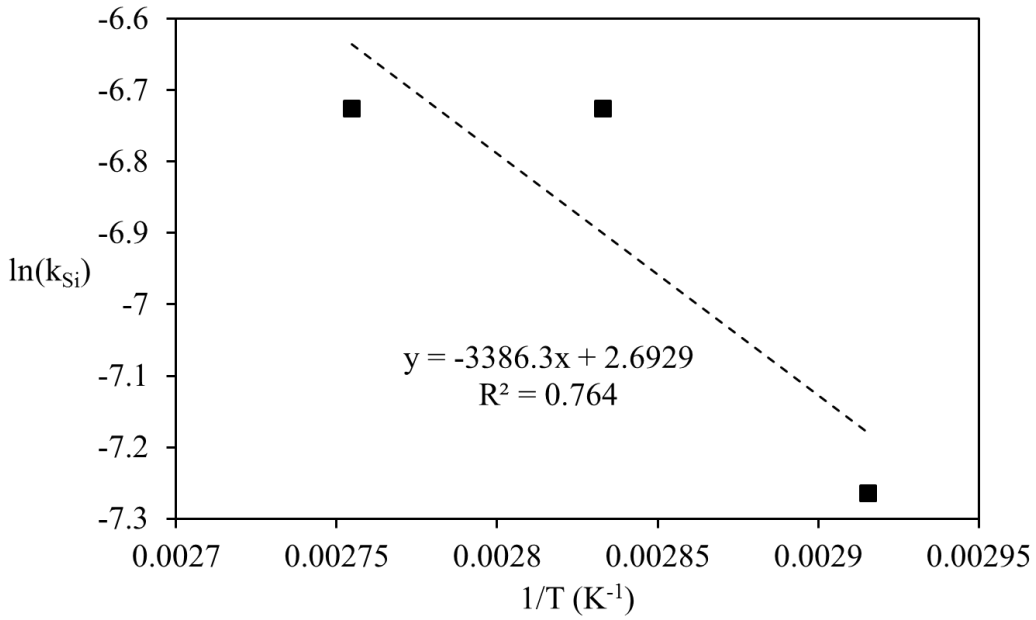


Figure 5.12. Logarithm of reaction constant versus inverse of absolute temperature for aluminum leaching from reduced UGS with 0.1 M HCl.

CHAPTER 6

LEACHING BEHAVIOR OF MAGNESIUM IMPURITIES FROM REDUCED TITANIUM DIOXIDE CONTAINING MAGNESIUM COMPOUNDS AND SALTS

6.1 Materials and Methods

6.1.1 Preparation of Reduced Upgraded Titanium Dioxide

The starting material for all the experiments described in this chapter was reduced titanium dioxide containing magnesium compounds and salts. This was obtained from the furnace immediately after the completion of the reduction of titanium dioxide with magnesium, hydrogen, and salt. In the reduction process, commercially available titanium dioxide was mixed with magnesium turnings and anhydrous magnesium chloride salt in the ratio of 3:2:1 by weight and reduction was carried out at 750^{o}C under a hydrogen environment to obtain reduced titanium dioxide (predominantly titanium hydride) along with magnesium compounds and salts. The magnesium compounds and salts present along with the reduced titanium dioxide were produced from the magnesium compounds and anhydrous magnesium chloride added to the mixture before the reduction. The reduced titanium dioxide with the magnesium compounds and salts obtained directly from the furnace contained both big lumps and some fine particles. To obtain a relatively uniform size fraction the sample was ground and sieved. The particles finer than 212 μm and coarser

than 53 μm were separated for the following experiments.

The initial material was observed under a SEM and X-ray diffraction studies were conducted to identify the structure, morphology and phases present in the starting material. Figure 6.1 and Figure 6.2 show the SEM image and the X-ray diffraction pattern of the starting material, respectively.

In the SEM image (Figure 6.1) it was observed that there are both elongated and rounded particles in the starting material with certain size distribution. The X-ray diffraction pattern showed the presence of a few magnesium bearing compounds along with titanium hydride. The major magnesium containing compounds were periclase syn. (MgO), bischofite syn. ($MgCl_2.6H_2O$), and karrooite syn. ($MgTi_2O_5$).

The magnesium and titanium contents were also evaluated for the starting material composition by elemental spectroscopic analysis using ICP-OES and their average content was found to be 28.49 and 22.31 wt. %, respectively.

6.1.2 Experimental Procedure

A sealed Erlenmeyer flask equipped with heating, stirring, and temperature measurement system was used. The slurry was homogenized by stirring with a magnetic stir-bar which was rotated at 1000 rpm. A factorial design of experiment was done where three leaching parameters- temperature, initial concentration of acid, and solid to liquid ratio were varied for the experiments while keeping all other parameters constant. In the factorial design of experiments three levels of temperature, two levels of initial acid concentration and two levels of solid to liquid ratio were used, the details of which are tabulated in Table 6.1. Sampling was done after 300 s (5 min), 900 s (15 min) and 1800 s

(30 min) after the start of each experiment to obtain the results reported below.

6.1.3 Analysis of Results

The fraction of magnesium removal was calculated using quantitative elemental analyses of the samples obtained from an inductively coupled plasma optical emission spectroscopy (ICP-OES) instrument. The structures and the phases present in of the starting material and the final residual solids after the leaching operation were observed using a scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies.

6.2 Results and Discussion

Since the magnesium bearing compounds in the reduced titanium dioxide were predominantly present in the form of periclase syn.(MgO) and bischofite syn. ($MgCl_2.6H_2O$) they could be easily dissolved in any mildly acidic aqueous solution. The bischofite syn. being a salt would probably have dissolved in the aqueous medium while the periclase syn would probably have reacted with the acid and formed a water soluble salt. The commonly used acids for this purpose are acetic acid and hydrochloric acid. The reactions of periclase syn. with acetic acid and hydrochloric acid are given by equations 6.1 and 6.2, respectively.

$$MgO + 2CH_3COOH = Mg(CH_3COO)_2 + H_2O \quad (6.1)$$

$$MgO + 2HCl = MgCl_2 + H_2O \quad (6.2)$$

$$MgCl_2 \xrightarrow{electrolysis} Mg + Cl_2 \quad (6.3)$$

The product magnesium chloride ($MgCl_2$) is recyclable while the product magnesium acetate ($Mg(CH_3COO)_2$) is not. The product magnesium chloride ($MgCl_2$) is done by electrolysis through Dow's process which produces metallic magnesium (Mg) and chlorine (Cl_2) as given by equation 6.3. Moreover, it was observed from previous experimental studies that a higher concentration of acetic acid solution was needed to remove the magnesium bearing compounds as effectively as hydrochloric acid. Therefore, from an economic standpoint, use of hydrochloric acid is preferred over acetic acid. Therefore, in the present study, the leaching of magnesium compounds was studied in a hydrochloric acid medium.

6.2.1 Effect of Acid Concentration

To observe the effect of acid concentration on the removal of magnesium compounds from reduced titanium dioxide two different acid concentrations, 0.05 M hydrochloric acid, and 0.2 M hydrochloric acid were used in the following study. Figures 6.3 through 6.8 show the differences in leaching behavior of magnesium containing impurities on using these concentrations of acids under different conditions. The effectiveness of a leaching operation was decided by taking into account both by the magnesium compound removal achieved on absolute terms, by the operation, and also by the corresponding titanium loss.

It was observed that when 0.2 M hydrochloric acid was used to leach the magnesium compounds at 25^{o}C using a solid-liquid ratio of 1 g to 800 ml magnesium compounds could be removed almost completely. This removal was also accompanied by a titanium loss of about 1 % by weight.

On decreasing the solid to liquid ratio to 1:400 it was found that at 25^{o}C complete

removal of magnesium products could not be achieved even with a 0.2 M hydrochloric acid concentration. While the titanium loss remained almost unaltered.

On increasing the temperature of the leaching solution to 50^{o}C almost complete removal of magnesium compounds could be achieved with both 0.05 M and with 0.2 M hydrochloric acid. Although, the time required to achieve close to complete removal of the magnesium compounds was more in case of 0.05 M than for 0.02 M hydrochloric acid solution. The corresponding titanium losses in both cases were below 2% (by weight).

Based on the results from experiments performed at 50^{o}C, the trend for the magnesium removal seemed to be unaffected by the decrease in solid to liquid ratio from 1 g in 800 ml to 1 g in 400 ml. However, the corresponding titanium loss was found to be a little lower in this case.

Next, on increasing the leaching temperature to 90^{o}C it was found that there was no significant difference in the behavior of magnesium leaching on changing the initial concentration of acid in lixiviant from 0.05 M hydrochloric acid to 0.2 M hydrochloric acid. Although when titanium loss is considered the use of 0.2 M hydrochloric was associated with very high titanium loss.

At 90^{o}C, the results from experiments conducted at different solid to liquid ratio did not show any significant difference in terms of kinetics of magnesium removal and titanium loss. Almost complete removal of magnesium compounds, with insignificant titanium loss, could be achieved by using 0.05 M hydrochloric acid with a solid to liquid ratio of 1 g to 400 ml.

6.2.2 Effect of Temperature

The fraction of magnesium compounds removed was found to be strongly dependent on the temperature at which leaching was performed. When a 0.05 M hydrochloric acid solution with a solid to liquid ratio of 1 g to 800 ml was used, the kinetics of leaching of magnesium compounds at different temperatures are presented in Figure 6.9. When the leaching temperature was 50^{o}C or more, near complete removal of magnesium compounds could be achieved. The kinetics of removal of magnesium was faster when a higher temperature of leaching was used. The titanium losses were found to be almost independent of temperature under these conditions.

For the case when 0.05 M hydrochloric acid at a solid to liquid ratio of 1 g to 400 ml was used at different temperatures, the leaching kinetics of the magnesium compounds are shown in Figure 6.10. The kinetics of removal was strongly dependent on temperature but the dependence was found to be more than for the case when solid to liquid ratio of 1 g to 800 ml was used. On using a temperature of 50^{o}C or more near complete removal of magnesium compounds were observed and higher temperature demonstrated a faster kinetics. The corresponding titanium losses were found to increase with increase in temperature although on absolute scale the losses were not very high.

The kinetics of leaching of magnesium bearing compounds and the corresponding titanium losses were also studied for experiments performed at different temperatures with a 0.2 M hydrochloric acid using a solid to liquid ratio of 1 g to 800 ml. It was observed from Figure 6.11 that near complete removal of magnesium could be achieved at temperatures of 25^{o}C or above. Although, the kinetics were greatly improved at elevated temperatures. The titanium loss also increased rapidly at 90^{o}C while the losses were within

the range of tolerance for leaching at 50^{o}C.

When the solid liquid ratio with 0.2 M hydrochloric acid was decreased to 1 g to 400 ml at various temperatures the kinetics of removal of magnesium compounds showed that near complete removal was achieved at 50^{o}C and beyond. The kinetics of magnesium removal seemed unaffected by the temperature beyond 50^{o}C but the corresponding titanium losses was very high in case of leaching at 90^{o}C.

6.2.3 Effect of Solid to Liquid Ratio

As observed by comparing Figure 6.9 to Figure 6.10, and Figure 6.11 to Figure 6.12, the effect of solid to liquid ratio on the kinetics of removal of magnesium bearing compounds was not very prominent except in the experiments performed at low temperatures. In most of the cases, in the experiments using a higher solid to liquid ratio the titanium losses were found to be relatively higher.

6.2.4 Analysis of Product after Leaching

From the results, it was found that a number of different conditions were suitable for near complete removal of the magnesium compounds but operating the leaching at 50^{0}C with a solid liquid ratio of 1:400 for 15 min seemed to be justified optimization from the standpoint of both energy required and time required for the operation. The product obtained after the removal of magnesium compounds was studied under the scanning electron microscope and a X-ray diffraction pattern was also obtained. The results are presented in Figure 6.13 and Figure 6.14, respectively.

The micrograph of the final product, Figure 6.13, showed more uniform particles. The

particle dimensions seemed to be a smaller on average.

From the comparison of X-ray diffraction patterns, shown in Figures 6.2 and 6.14, a reduction in the number and intensity of peaks corresponding to magnesium impurities was observed. This clearly showed the effectiveness of the leaching operation. Also, some titanium oxide peaks were observed in Figure 6.14 which might have resulted from surface oxidation or low amount of oxygen dissolved inside the particles due to its fine particle size.

Table 6.1. The values of the levels chosen in the factorial design of experiments.

Factors	**Temperature (^oC)**	**Initial H^+ conc. (M)**	**Solid to Liquid ratio (g / ml)**
Values	25	0.05	1:400
	50	0.2	1:800
	90		

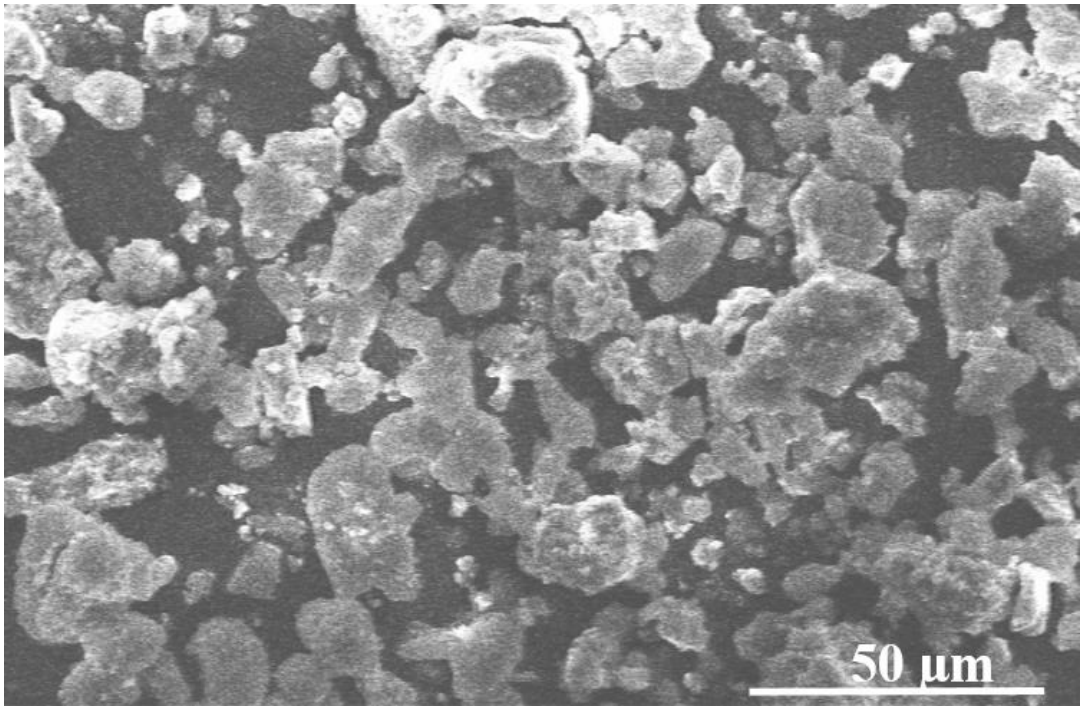


Figure 6.1. SEM image of reduced titanium dioxide along with magnesium compounds.

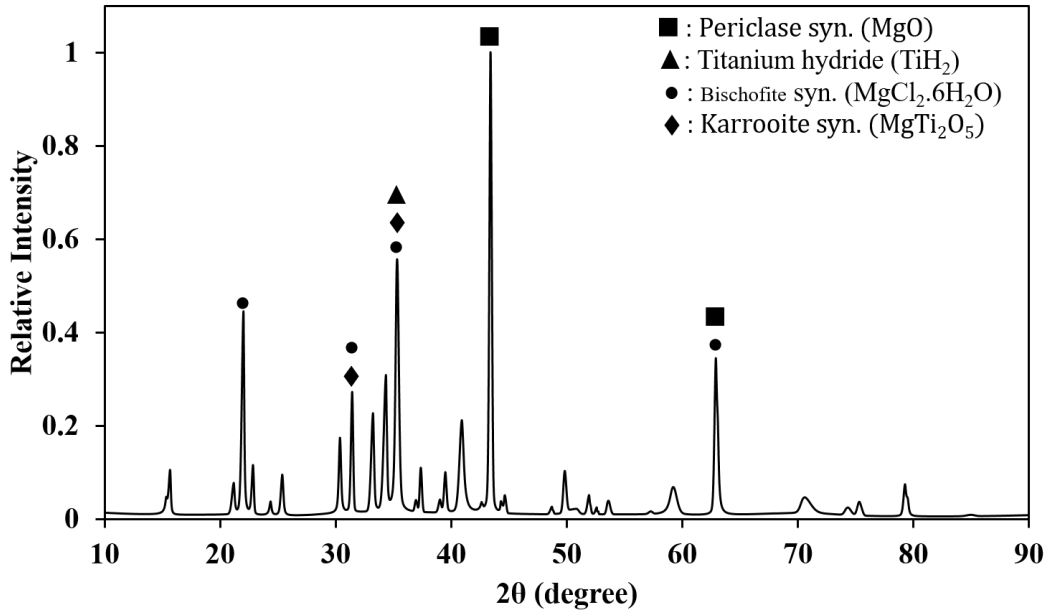


Figure 6.2. X-ray diffraction pattern of reduced titanium dioxide along with magnesium compounds.

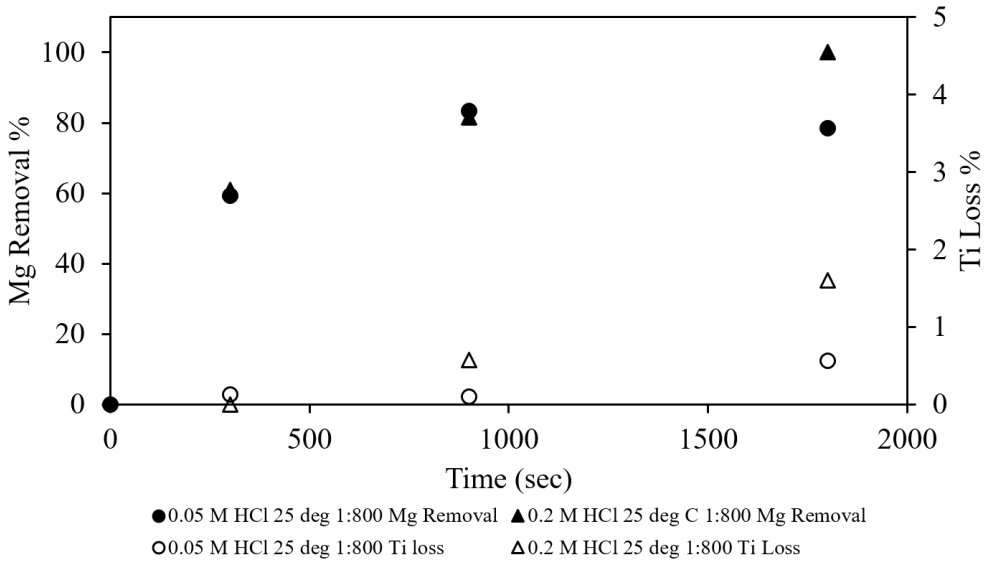


Figure 6.3. Effect of acid concentration when temperature was maintained at 25^{o}C and a solid-liquid ratio of 1 g to 800 ml was used.

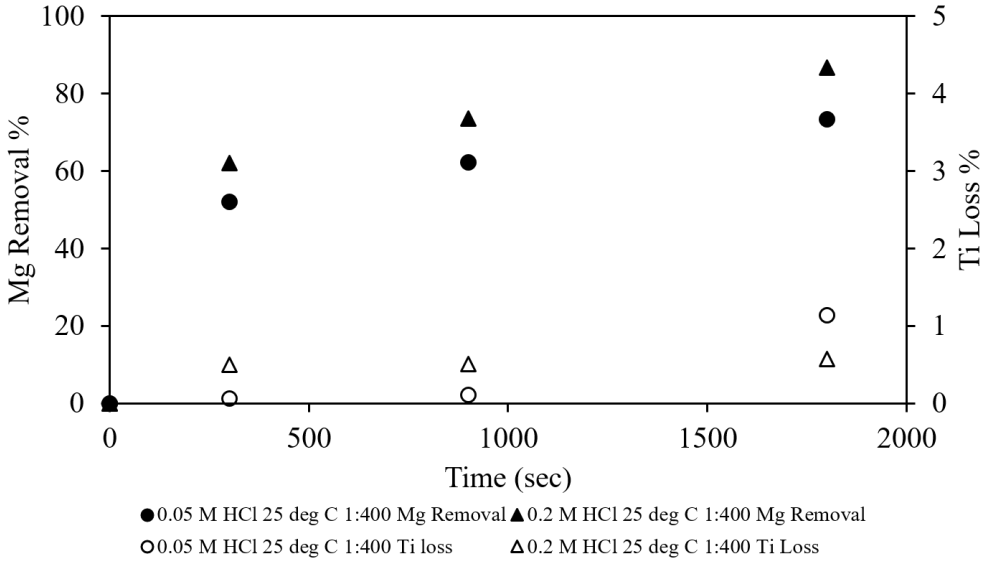


Figure 6.4. Effect of acid concentration when temperature was maintained at 25^{o}C and a solid-liquid ratio of 1 g to 400 ml was used.

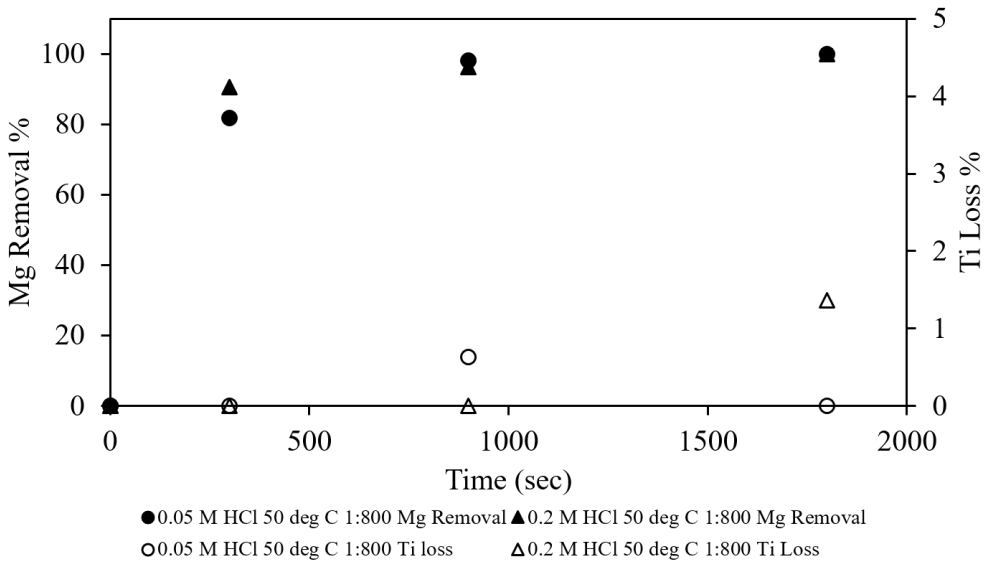


Figure 6.5. Effect of acid concentration when temperature was maintained at 50^{o}C and a solid-liquid ratio of 1 g to 800 ml was used.

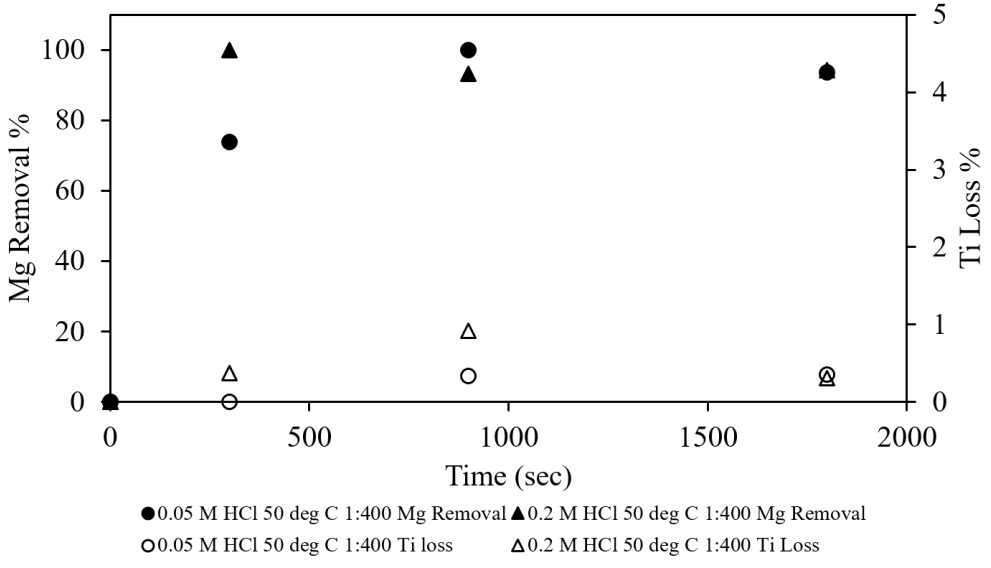


Figure 6.6. Effect of acid concentration when temperature was maintained at 50^{o}C and a solid-liquid ratio of 1 g to 400 ml was used.

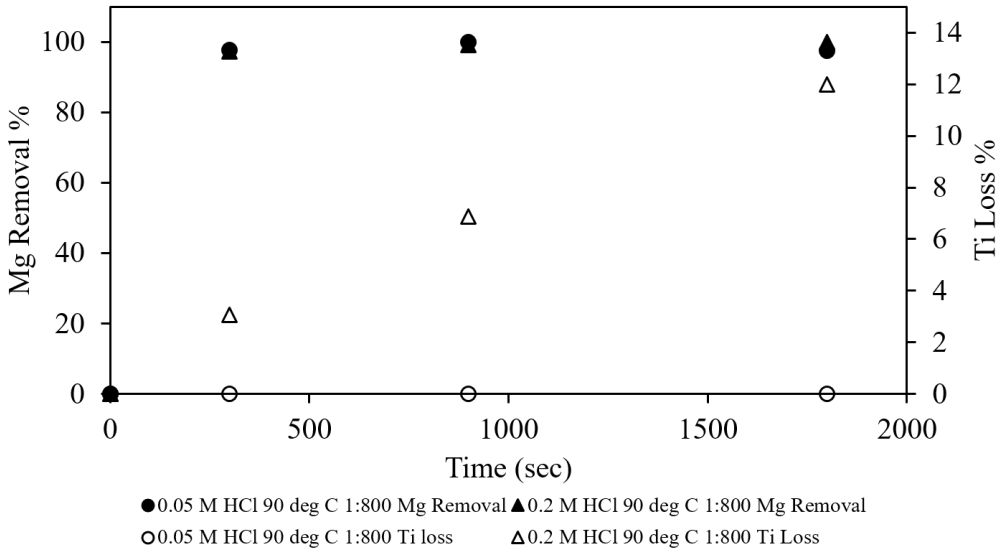


Figure 6.7. Effect of acid concentration when temperature was maintained at 90^{o}Cand a solid-liquid ratio of 1 g to 800 ml was used.

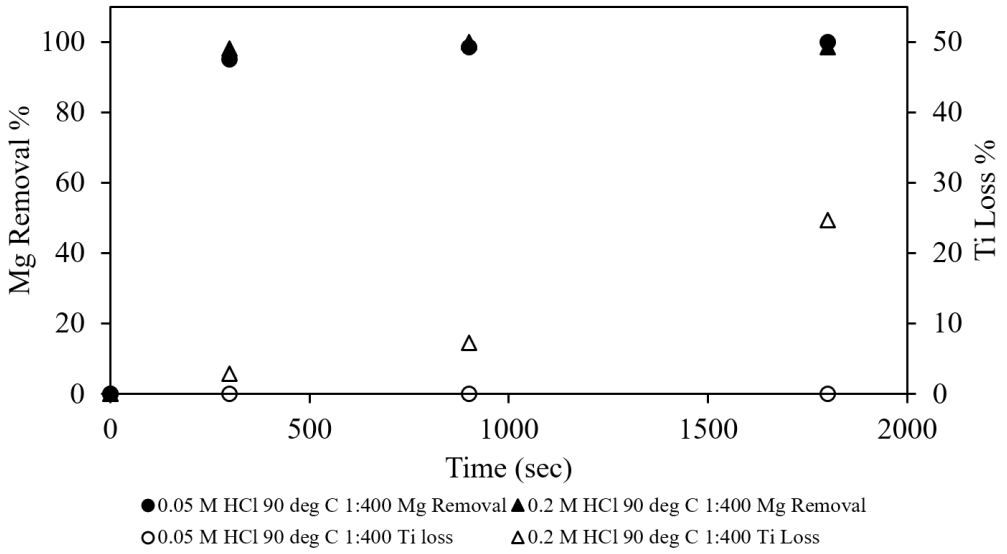


Figure 6.8. Effect of acid concentration when temperature was maintained at 90^{o}C and a solid-liquid ratio of 1 g to 400 ml was used.

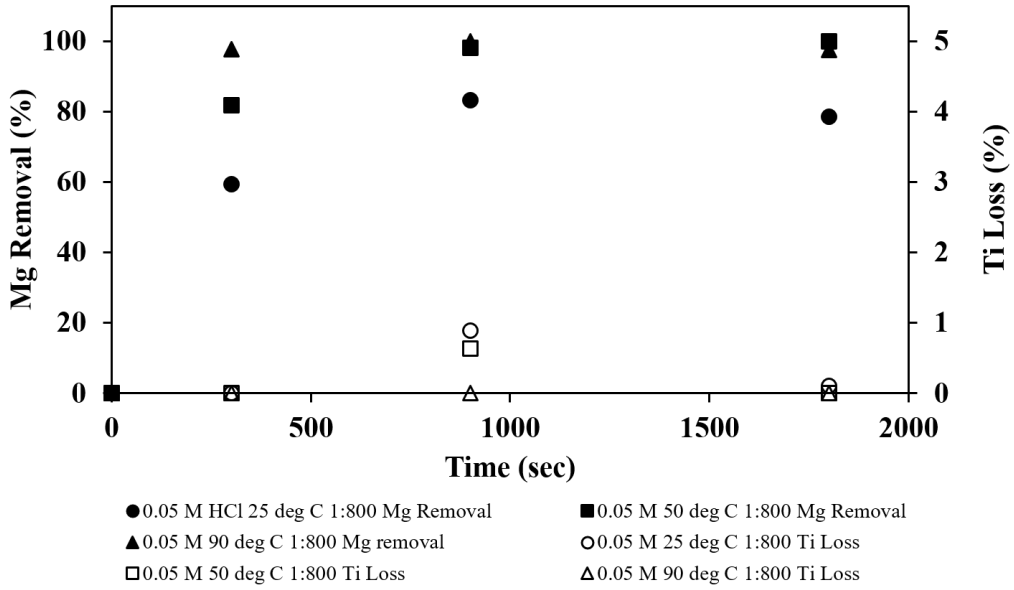


Figure 6.9. Effect of leaching temperature when lixiviant initially contained 0.05 M hydrochloric acid and a solid-liquid ratio of 1 g to 800 ml was used.

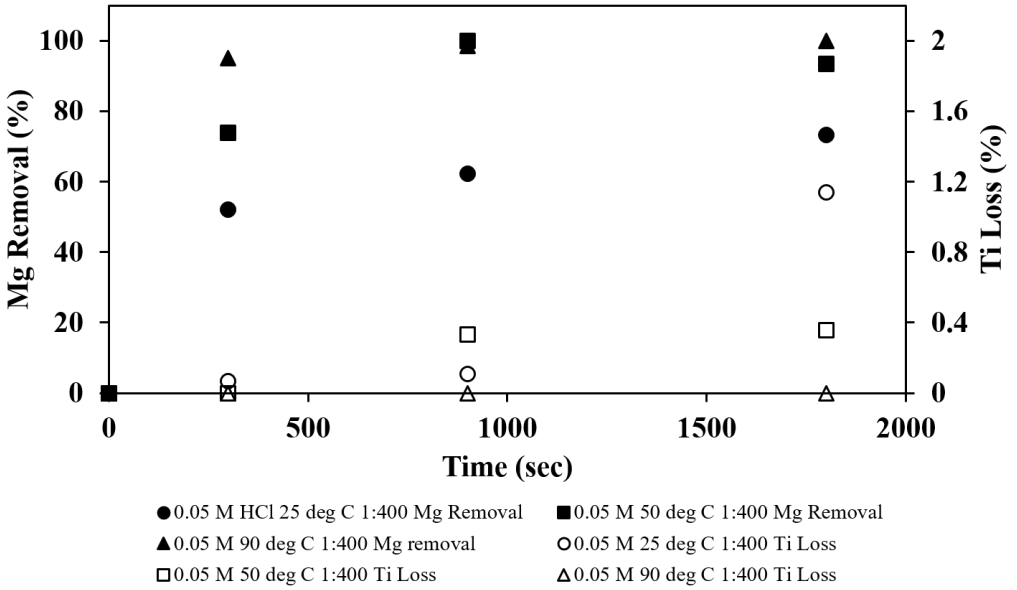


Figure 6.10. Effect of leaching temperature when lixiviant initially contained 0.05 M hydrochloric acid and a solid-liquid ratio of 1 g to 400 ml was used.

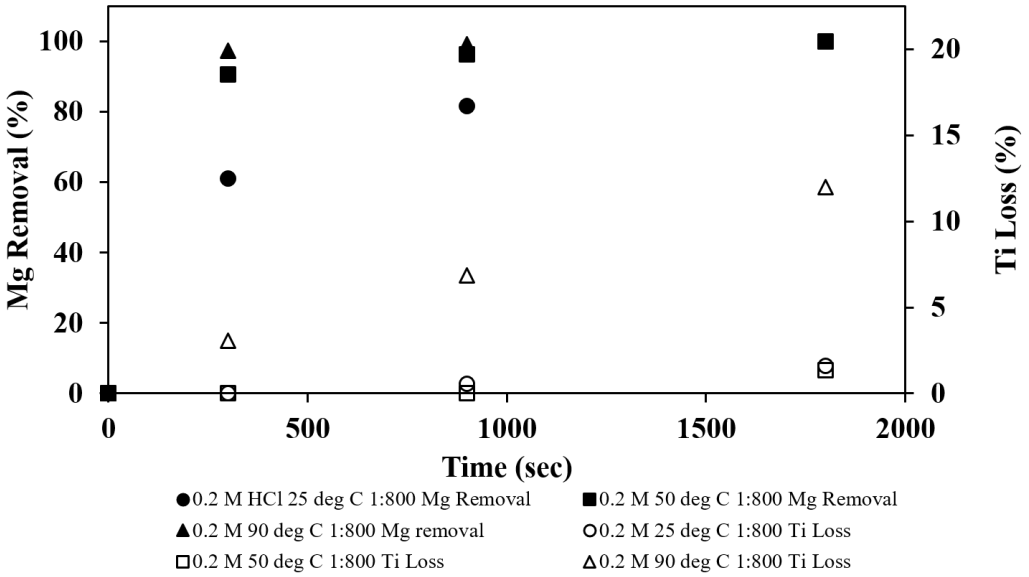


Figure 6.11. Effect of leaching temperature when lixiviant initially contained 0.2 M hydrochloric acid and a solid-liquid ratio of 1 g to 800 ml was used.

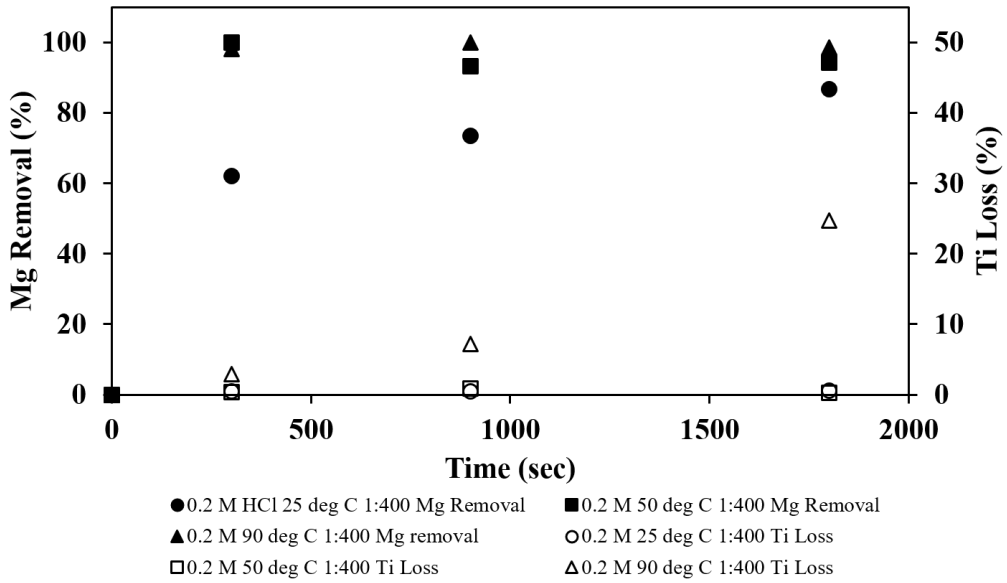


Figure 6.12. Effect of leaching temperature when lixiviant initially contained 0.2M hydrochloric acid and a solid-liquid ratio of 1 g to 400 ml was used.

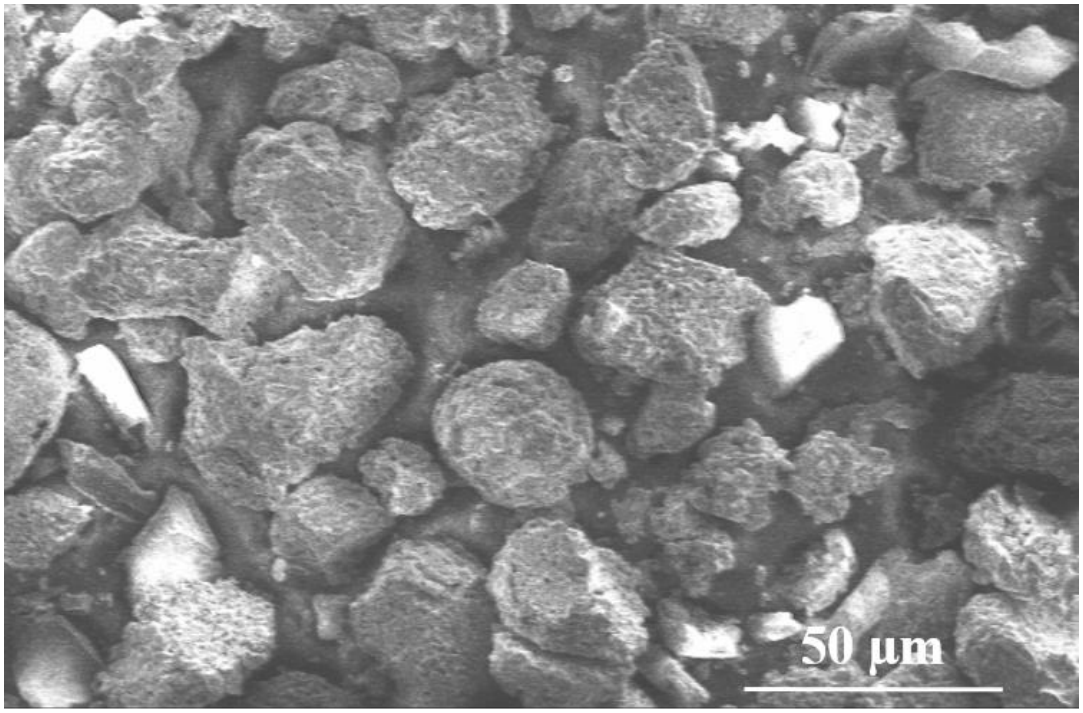


Figure 6.13. SEM image of reduced titanium dioxide after leaching with 0.05 M hydrochloric acid at a solid to liquid ratio of 1g to 400 ml for 15 min.

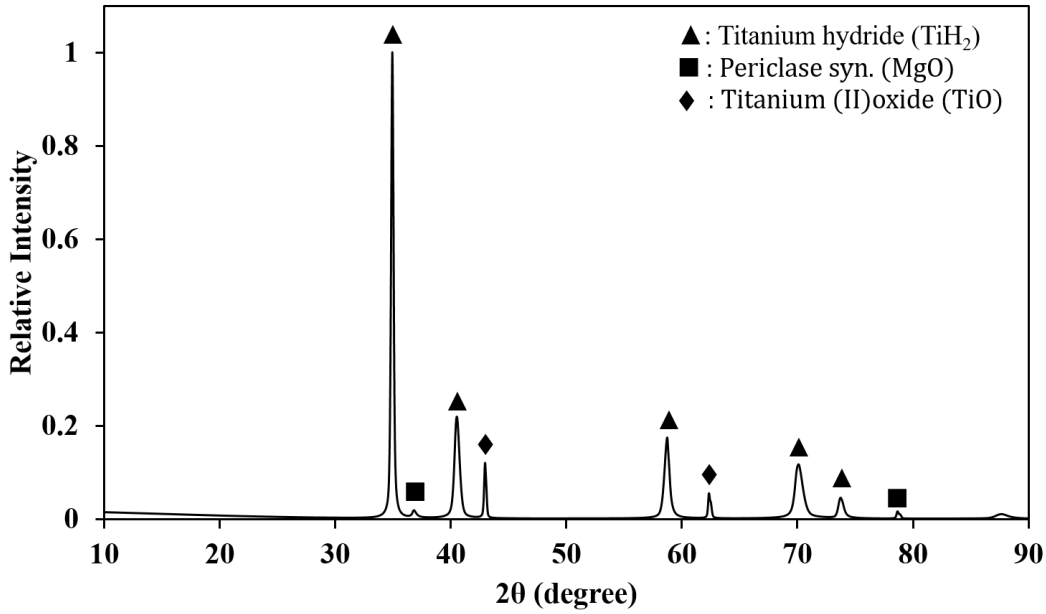


Figure 6.14. X-ray diffraction pattern of reduced titanium dioxide after leaching with 0.05 M hydrochloric acid at a solid to liquid ratio of 1g to 400 ml for 15 min.

CHAPTER 7

SELECTIVE EXTRACTION OF TITANIUM FROM ILMENITE VIA CHEMICAL SOLUTION ROUTE USING DIHYDROXYBENZENES

7.1 Materials and Methods

7.1.1 Preparation of Feed Material

For the experimental results presented hereafter in this chapter the initial feed material was ilmenite ore. The ilmenite ore was obtained from a commercial supplier which had a particle size of a few millimeters on average. The ore was milled to a few hundreds of microns to make the feed more suitable for handling on a laboratory scale.

7.1.2 Experimental Procedure

7.1.2.1 Dissolution of ilmenite

Although the proposed method is expected to have a high degree of flexibility with regard to the type and grade of titanium resource used as feed for this particular study, the titanium bearing source was chosen to be ilmenite. Ilmenite is an abundant and fairly low grade ore of titanium. Demonstration of feasibility of the technique starting with ilmenite would imply the possibility of extension of the technique to higher grade titanium bearing sources, with system specific modifications of parameters.

Ground ilmenite powder was reacted into a mixture of concentrated sulfuric acid (16M) and ammonium sulfate at 300°C for 8 h. This produced a titanium bearing solution according to the reaction:

$$FeTiO_3 + H_2SO_4 + (NH_4)_2SO_4 \xrightarrow{300^oC,8\ hours} Ti\ bearing\ solution \qquad (7.1)$$

The experiment was carried out in a round bottom flask, fitted with a condenser and the solution was continuously stirred with a magnetic stir-bar at 500 rpm. The ammonium sulfate was added into the sulfuric acid solution to provide some of the ammonium ions for the metal-organic complex during the subsequent complexation step. This also helped elevate the boiling point of the sulfuric acid, and therefore minimized the evaporation of the solution.

7.1.2.2 Selective complexation of titanium

In this step, titanium bearing solution obtained from the previous ilmenite dissolution step was titrated with catechol dissolved in ammonium hydroxide. Careful control over the acidity was maintained to selectively precipitate titanium as ammonium-titanium-catecholate complex as described by the chemical reaction given by equation 7.2.[21] The molecular structure of the complexing agent and the titanium-organic complex are schematically shown in Figure 7.1 panels (a) and 7.1 (b), respectively. This precipitate is filtered out using a vacuum filtration setup; the filter cake was thoroughly washed with 0.1 M hydrochloric acid solution to remove traces of trapped acid soluble impurities, followed by washing with cold isopropyl alcohol to remove unreacted catechol, if any. Then it was dried at room temperature and on complete drying the cakes were pulverized into powder.

This powder was subsequently used as feed for reduction in a hydrogen environment at an elevated temperature, the details of which are not included in this study.

$$Ti\ (IV) + 3\ 1{,}2 - C_6H_4(OH)_2 + 2\ NH_4OH \xrightarrow{pH=5.5} [NH_4]_2[Ti(1{,}2 - C_6H_4O_2)_3].3H_2O \quad (7.2)$$

7.1.2.3 Simulation

The density functional theory (DFT) simulation was carried out to investigate the equilibrium geometry and stability of titanium catecholate. Structural optimization was employed using B3LYP method with 3-21G basis using a computational chemistry software, General Atomic and Molecular Electronic Structure System (GAMESS).[50]

7.1.3 Analysis of Result

The results were analyzed using variety of techniques which included inductively coupled plasma optical emission spectroscopy (ICP-OES), energy dispersive spectroscopy (EDS) and laser induced breakdown spectroscopy (LIBS) for elemental analysis, scanning electron microscopy (SEM) for the study of microstructure and X-ray diffraction (XRD) for obtaining diffraction pattern. The simulation results were visualized using ChemCraft.

7.2 Results and Discussion

7.2.1 Dissolution of Ilmenite

The titanium bearing solution is a multielement solution, containing all the elements from the parent ilmenite as ions, in an acidic medium. As ilmenite has iron as one of the other principal components along with titanium, a large fraction of impurities in the titanium bearing solution are iron-based compounds. The titanium bearing solution on drying produces a residue which was analyzed to be predominantly titanium oxide sulfate along with impurities such as aluminum, chromium, iron, magnesium, and vanadium from the X-ray diffraction (XRD) pattern presented in Figure 7.2. This analysis was supported by the observations from laser induced breakdown spectroscopy (LIBS) carried out on the dried residue as shown in Figure 7.3 (a).

7.2.2 Selective Complexation of Titanium

Titanium from the multielement solution was selectively complexed using catechol dissolved in ammonium hydroxide. The selective extraction of Ti (IV) was demonstrated by comparing the elemental analysis of the starting multi-element solution and that of the filtrate obtained after the complexation process as tabulated in Table 7.1.

It should be noted that there is a very good agreement among the predicted and observed values of elemental distribution in the filtrate after titanium-organic complex has been precipitated. The slight deviations in the values observed might be due to change in solubility of different elements due to changed solution conditions or even due to presence of other elements in solution which are not accounted for. The selectivity of this catechol complexation step is also illustrated by comparing the LIBS results of the dried multi-

element solution, Figure 7.3(a), compared to washed and dried titanium catecholate precipitate in Figure 7.3(b).

It is clearly seen that the impurity peaks present in the spectroscopic data in the multi-element solution are not seen in the spectrum for the titanium catechol precipitate. The selectivity of the complexation is further demonstrated by the very high titanium content (98.7%) observed from the energy dispersive spectroscopy (EDS) elemental mapping of ammonium titanium catecholate precipitate. From the scanning electron microscopy (SEM) image in Figure 7.4, it is observed that the complex is present as irregular shaped aggregates with a fibrous morphology.

The IR spectrum of the complexing reagent catechol (Figure 7.5 (a)) shows aromatic -OH bond stretching at 3316 cm^{-1} and at 1368 cm^{-1}, which are expected in accordance to the molecular structure as drawn in Figure 7.1 (a).[51] In the spectrum for the ammonium-titanium-catechol complex (Figure 7.5 (b)) there is a shift in the phenolic stretching at 3316 cm^{-1} to 3372 cm^{-1}. The peak at 1368 cm^{-1} is absent and also the peak at around 3300 cm^{-1} is much broader than that of pure catechol in Figure 7.5 (a). This is a strong indication of bulky groups formed due to complexation as drawn. In Figure 7.5 (b), the absence of a peak at 1368cm^{-1} may indicate the conversion of free –OH group into –O(NH_4). In both the spectra characteristic peaks for aromatic stretching are also observed, at 1516 cm^{-1} and 1604 cm^{-1} for catechol and at 3042 cm^{-1} for ammonium-titanium-catechol complex.[51]

7.2.3 Simulation

Structural optimization was determined using the B3LYP method with the 3-21G basis. B3LYP exchange-correlation functional is well known as the most effective method for

the simulation of organic complexes.[52] The visualization of the simulation result was conducted by ChemCraft.[53] Figure 7.6 shows the schematic diagram of the complex based on equation 7.1 and the optimized geometry of titanium catecholate. The complex was stabilized based on energy minimization calculations.

The degree of stability of the complex can be determined by the energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). In more generic terms, a higher HOMO-LUMO gap contributes to higher stability of the complex. Figure 7.7 shows HOMO-LUMO gap of the complexes, which is found to be 2.914 eV. The HOMO-LUMO gap of 2.914 eV of titanium catecholate is large enough to indicate the energetic feasibility for the formation of the complex.

Table 7.1. Elemental analysis of the multielement solution with expected and observed elemental composition of filtrate according to the scheme for precipitation of titanium bearing complex.

Sample	Composition (wt %)		
	Fe	**Ti**	**others**
Multi-element solution	49.22	44.21	5.1
Filtrate after precipitation (theoretical amount based on complete precipitation)	90.61	0.0	9.39
Filtrate after precipitation (observed)	92.64	1.15	6.19

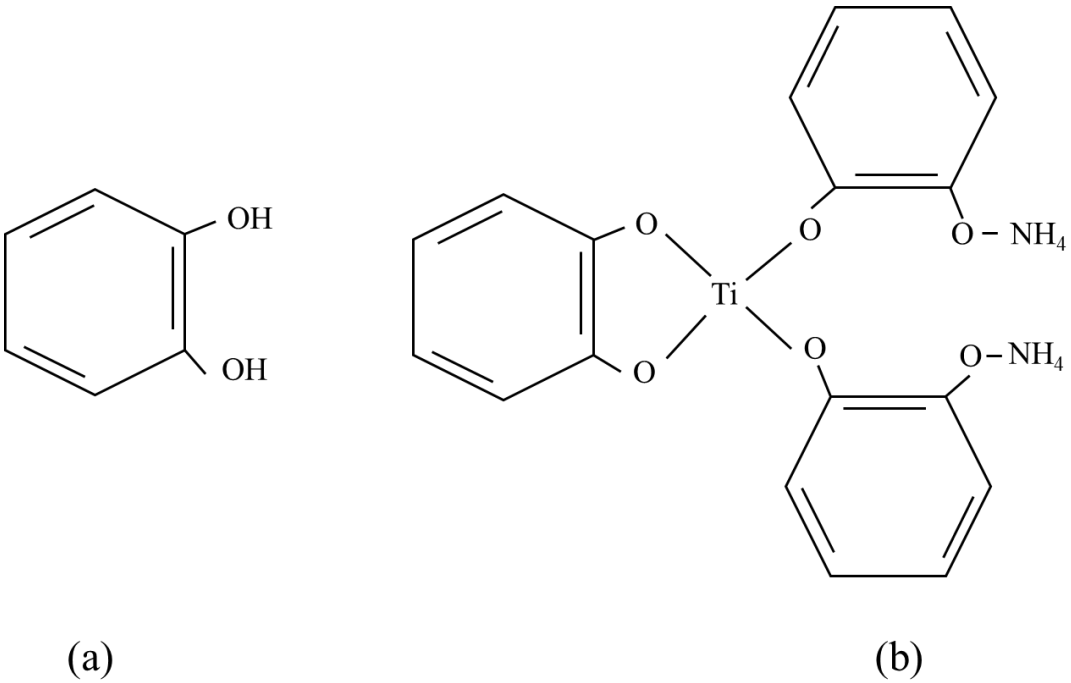


Figure 7.1. Molecular structures of (a) catechol and (b) ammonium-titanium-catecholate.

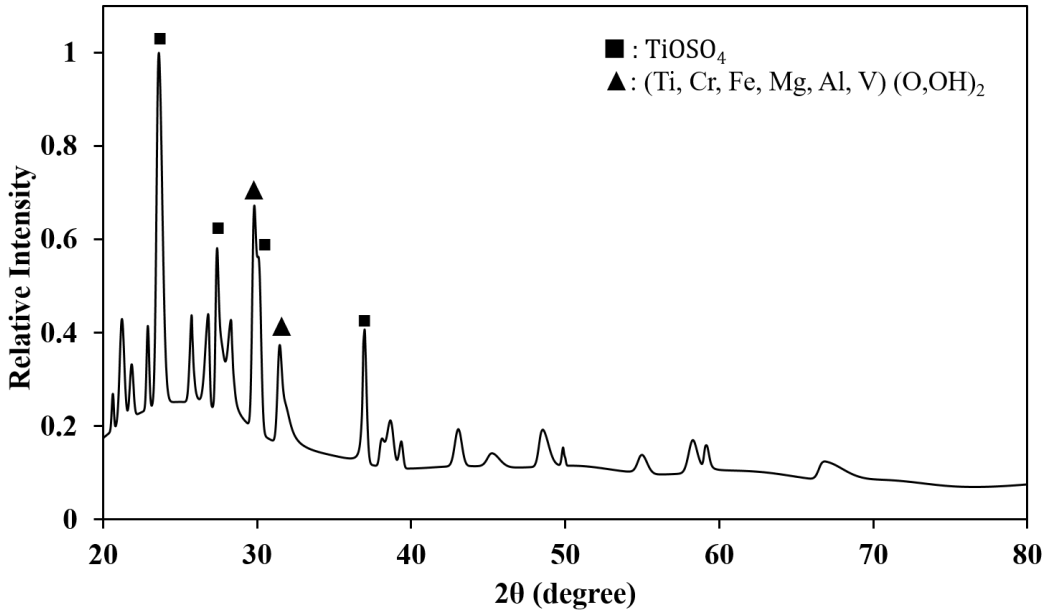


Figure 7.2. XRD of the residue obtained by drying the titanium bearing solution prepared from ilmenite.

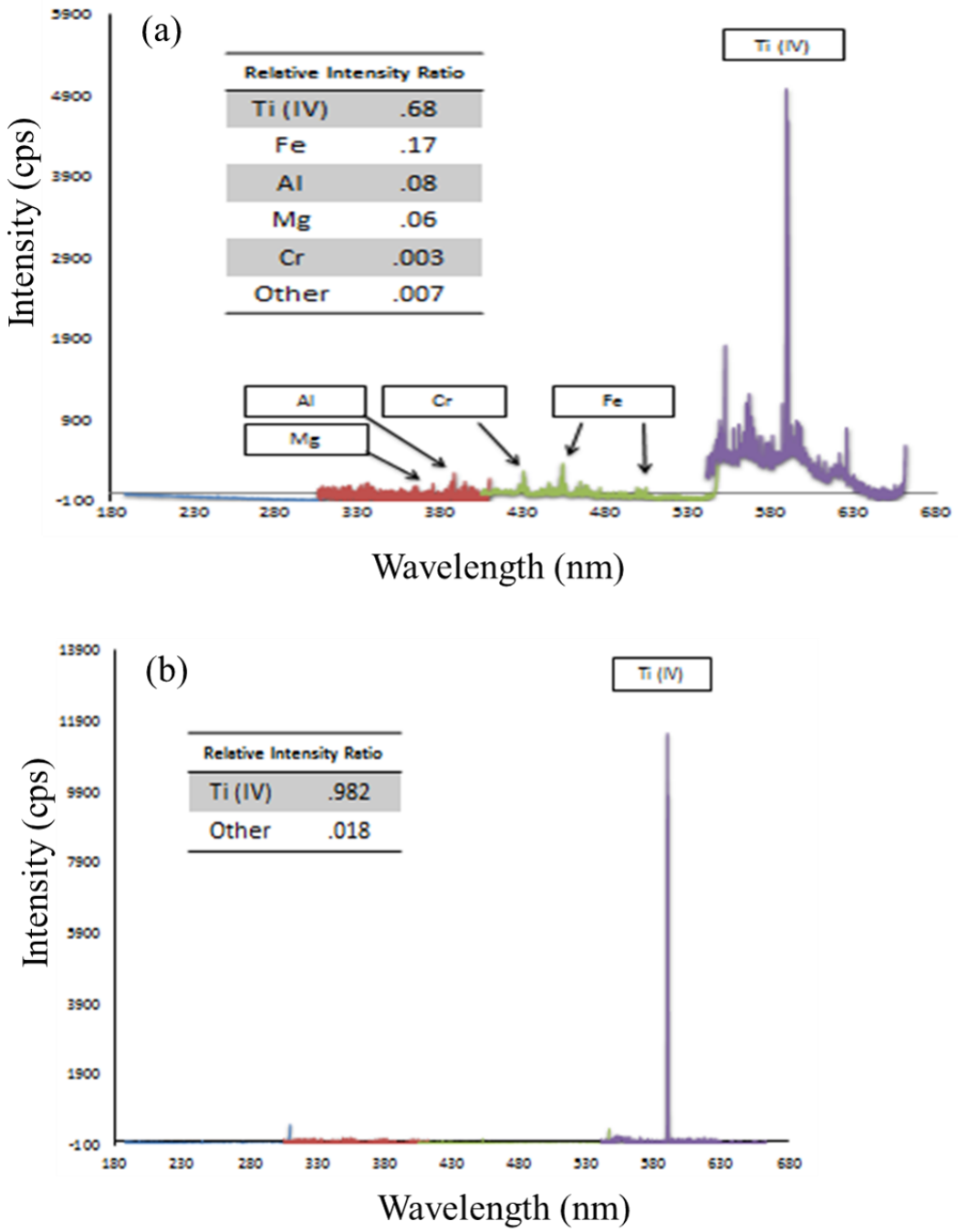


Figure 7.3. LIBS on (a) dried multielement solution, (b) washed and dried titanium catecholate precipitate.

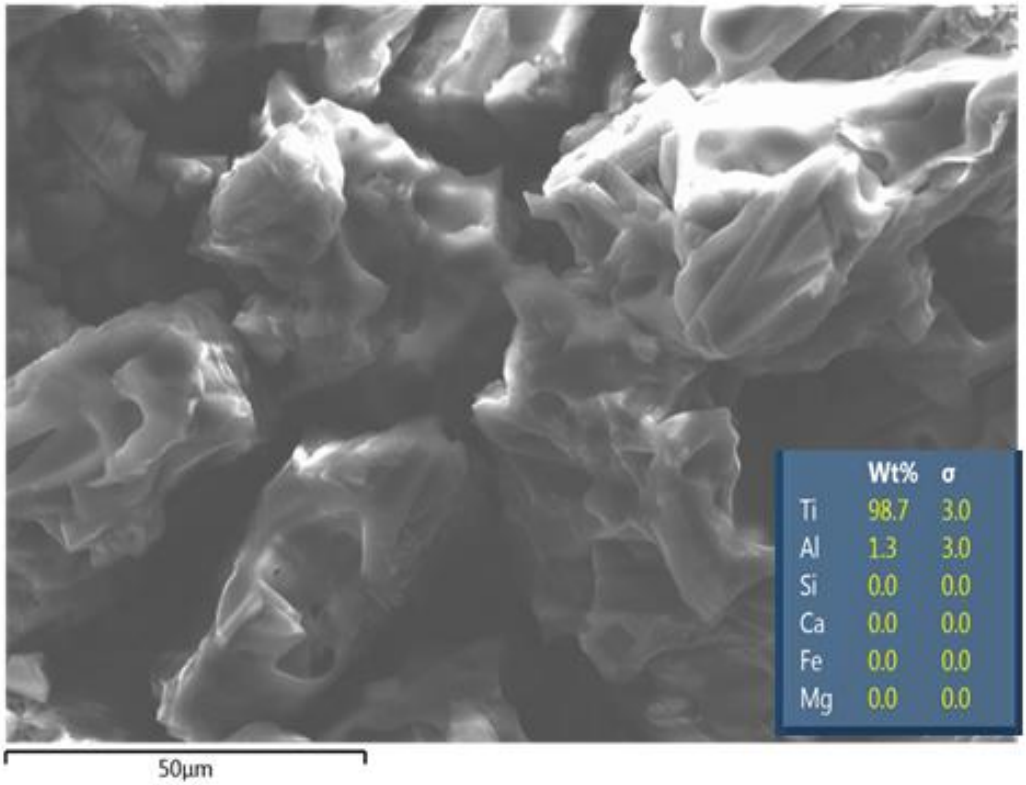


Figure 7.4. SEM micrograph and EDS elemental mapping for titanium catecholate precipitate.

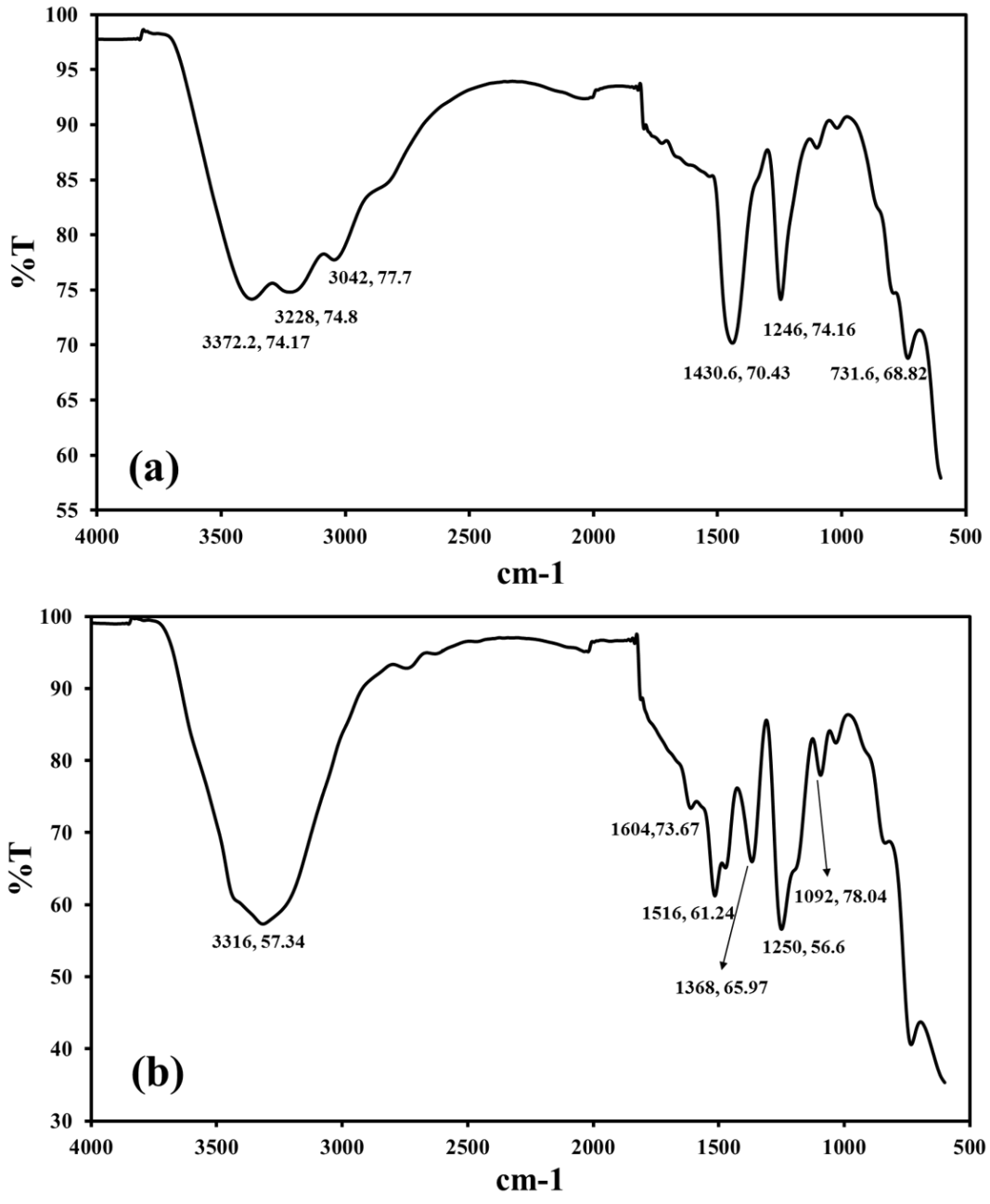


Figure 7.5. FTIR spectrums for (a) catechol and (b) ammonium-titanium-catechol complex.

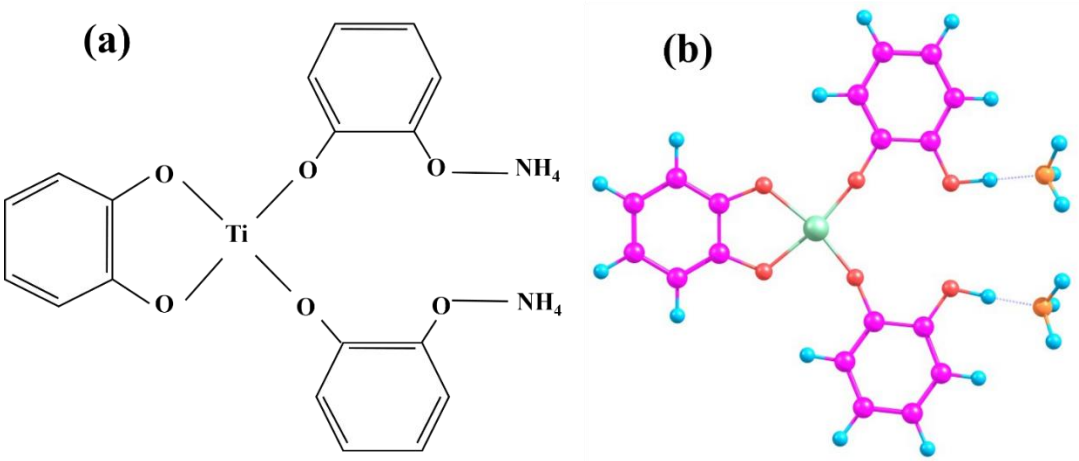


Figure 7.6. (a) The schematic and (b) optimized structure of titanium catecholate by DFT, Color schematic: Carbon (pink), nitrogen (orange), oxygen (red) and hydrogen (blue), titanium (white).

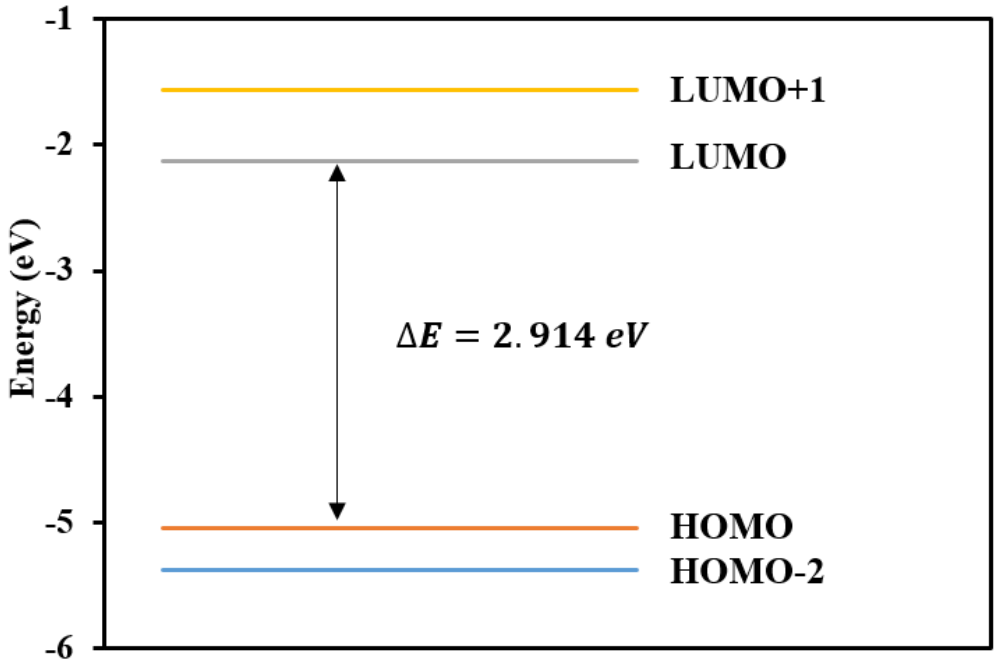


Figure 7.7. The molecular orbitals' energy levels at LUMO + 1, LUMO, HOMO and HOMO - 2 of titanium catecholate.

CHAPTER 8

CONCLUSIONS

Based on the studies on leaching of pure minerals and surrogate reduced upgraded slag the following conclusions can be made.

(1) Removal of aluminum and silicon impurities seem to be more effective in alkaline solutions than in acidic solutions.

(2) Selective removal of iron impurities seemed to be difficult from the pure minerals and surrogate reduced upgraded slag experiments. There was always some degree of titanium loss associated with removal of iron impurities.

(3) Magnesium bearing impurities could be removed with relative ease.

(4) There was a difference in leaching charcteristics of pure minerals and surrogate reduced upgraded slag. This was probably because selectivity of a lixiviant towards a particular impurity element may depend on the chemistry and form in which the impurity element exists as well as its crystal structure and other properties.

The effective lixiviants found from pure mineral and surrogate reduced UGS tests would just serve as references for selection of lixiviants chemistry for leaching the actual reduced UGS.

In conclusion, from the experimental observations made on removal of impurities

containing aluminum from reduce upgraded titanium slag the following conclusion can be made within the context of this study:

(1) Removal of aluminum from reduced upgraded titanium slag seemed to be more effective in an alkaline medium than in an acidic medium.

(2) The ASTM recommended aluminum specification in titanium products can be met by leaching reduced upgraded titanium slag with a 2 M sodium hydroxide solution at 140^{o}C for 3 h.

(3) The operating temperature seemed to be the most important parameter, followed by alkalinity of lixiviant for aluminum leaching from reduced upgraded titanium slag.

(4) There exists a maximum temperature of leaching under alkaline condition to maximize the fraction of aluminum removal while preventing the loss of product.

(5) Addition of boric acid to acidic medium led to improved aluminum removal from reduced upgraded titanium slag. The increase in fraction of aluminum removed was unaffected by temperature in the range of 90^{o}C to 190^{o}C.

Addition of sodium gluconate in alkaline medium increases aluminum removal but is associated with increased titanium loss. When added in concentrations so that the titanium loss is acceptable, aluminum removal is decreased. The suppression of aluminum removal seemed to be dependent on the alkalinity of base solution, amount of sodium gluconate added as well as the temperature of operation. This phenomenon can be utilized to selectively suppress aluminum removal over selected temperature, alkalinity ranges by adjustment of the additive.

In conclusion, from the experimental observations made on removal of impurities containing silicon from reduce upgraded titanium slag the following conclusions can be made within the context of this study:

(1) Removal of silicon from reduced upgraded titanium slag seemed to be more effective in an alkaline medium than in an acidic medium.

(2) The ASTM recommended silicon specification in titanium products can be met by leaching reduced upgraded titanium slag with a solution containing 2 M sodium hydroxide and 2.5 g/l of sodium gluconate at 140^{o}C for 3h.

(3) The operating temperature seemed to be the most important parameter, followed by alkalinity of lixiviant and concentration of additives for silicon leaching from reduced upgraded titanium slag.

(4) There exists a maximum temperature of leaching under alkaline conditions to maximize the fraction of silicon removal while preventing the loss of product by oxidation.

(5) For leaching of silicon containing impurities with acidic lixiviant higher acid concentration led to improved silicon removal from reduced upgraded titanium slag. The increase in fraction of silicon removed on increasing temperature was not observed beyond 140^{o}C.

In conclusion, from the experiments on removal of magnesium bearing compounds from reduced titanium dioxide, the following conclusions can be made within the context of this study:

(1) Magnesium bearing compounds can be effectively separated from reduced titanium dioxide on using a mild hydrochloric acid solution.

(2) The following operating conditions were found to be effective:

(i) 0.2 M hydrochloric acid, 25^{o}C, 1 g in 800 ml, 30 min.

(ii) 0.05 M hydrochloric acid, 50^{o}C, 1 g in 400ml, 15 min.

(iii) 0.05 M hydrochloric acid, 90^{o} C, 1 g in 400 ml, 5 min.

In terms of fraction of magnesium removal with low titanium losses, all of the parameters listed above were found to be similar. Therefore, any one of the above operating conditions can be chosen depending on requirements and economic justification in a particular application.

(3) The combination of temperature and acid concentration seem to be the most important factors for the kinetics of removal of magnesium bearing compounds.

(4) The analysis of the solid residue obtained after the reduced titanium dioxide was leached with 0.05 M hydrochloric acid, at a solid to liquid ratio of 1g to 400 ml and 50^{o}C for 15 min produced satisfactory results.

In conclusion from the studied on selective precipitation of titanium from ilmenite the following conclusions can be made within the context of this study:

We have proposed a new cost effective energy efficient route for the making titanium from ilmenite. The process for selective extraction of titanium as a complex was successfully demonstrated.

(1) A variety of characterization techniques, all of which verify the formation of high purity titanium complex according to the proposed scheme.

(2) The stability of the complexation was also assessed by density functional theory which indicates stability of the predicted complex.

(3) Elimination of formation of corrosive and hazardous intermediates such as

chlorine gas or titanium tetrachloride vapor present in conventional titanium production processes makes this process very environmentally friendly.

This process eliminates additional reagent cost of Mg for reduction into titanium hydride according to the method proposed by Fang et al. therefore would bring down the cost of titanium hydride assuming the catechol can be recycled during the reduction process.

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