Review article

Processing of titanium-containing ores for the production of titanium products: A comprehensive review

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ABSTRACT

This article discusses the main technologies for processing titanium-containing raw materials, the advantages, and disadvantages of various technological solutions. The analysis of the literature revealed that the traditional methods for the production of titanium products are mainly focused on the use of ilmenite concentrates. In connection with the depletion of ilmenite deposits, in the near future, there will inevitably be a need for a switch to the use of complex ores – titano-magnetite. Obtaining titanium dioxide (TiO_2) from titanomagnetite raw materials with a high content of impurity components requires an individual approach for each specific deposit. The possibility of further improving the development of a technological process for low-temperature (1000–1200 °C) processing of titanomagnetite concentrates via the production of pure TiO_2 is proposed.

1. Introduction

Titanium dioxide (TiO_2) is the most common titanium compound. Commercially, it began to be produced in the early 20th century and is extensively used in paints, as a filler for paper and plastic, in solar batteries [1], in cosmetics, as a food additive [2], in the production of non-toxic tanning materials [3], and as an ingredient in formulations of coatings, adhesives, and sealants [4]. Approximately 12–13 % of TiO_2 is used as a pigment in the production of paper products in the form of rutile (high-grade paper) or anatase (low-grade paper, cardboard). On average, 1.4 kg of TiO_2 is used in the manufacture of 1-ton of paper.

Titanium dioxide (TiO_2) is an opaque, non-toxic amphoteric oxide that exhibits exceptional brightness and whiteness. Powdered and solid TiO_2 is recognized as a necessary ingredient in the production of white pigment. Anatase, rutile, and brookite are the three main crystal forms of TiO_2 [5–7]. The crystal structure of rutile TiO_2 and anatase TiO_2 is more stable than that of brookite type, and these two types of material are widely used in industrial production [7]. The most commonly used resources for rutile preparation are

vanadium titanomagnetite, ilmenite placer, and titanium slag. Titanium slag is a byproduct of ilmenite melting, and it contains enhanced titanium dioxide (approximately 70 %) [5]. In order to maximize the material's effectiveness in the next procedure, pre-drying is necessary for the majority of rutile TiO_2 applications. For example, rutile TiO_2 with an excess of moisture content will have a lower impedance when thin-film material is synthesized. When rutile TiO_2 is employed in the sol-gel method to prepare luminous powder, there is also a pre-drying step involved. Additionally, rutile is a proficient welding material. It must be completely dried before usage because the rutile's moisture content will result in pores during the welding process [7].

There are two main industrial technologies for the production of TiO_2 pigments: sulfuric acid and chloride. In the sulfuric acid process, a titanium-containing product is treated with concentrated sulfuric acid to obtain a sulfate solution, which undergoes hydrolysis and precipitation of TiO_2, and iron passes into the solution in the form of sulfates. According to chloride technology, rutile is first exposed to chlorine gas, and titanium goes into the form of chloride; then, it is converted into a pigment with the removal of chlorine at high temperature in a mixture of air and oxygen. Both technologies result in a high yield of waste or toxic products and require serious environmental protection measures.

Currently, the capacity of the chloride method to produce TiO_2 exceeds the capacity of the sulfate method and continues to increase worldwide. The advantages of the chlorine method or pigment production over the sulfate method include the use of a significantly smaller amount of waste to be neutralized, the use of a slightly higher quality of the product, and the use of lower specific capital investments, which make up 60–75 % of the total investments in the sulfuric acid method.

2. Raw materials for the production of TiO_2

Despite the fact that titanium is the fourth most prevalent structural metal in the earth's crust, at 0.6 %, the expense of producing it has hampered its increase in use relative to other base metals on the market. It follows iron, magnesium, and aluminum, but it remains exotic because of its costly cost, which keeps it from attaining its full potential in maritime and automotive industry uses [4,8]. The mineral sources for the production of TiO_2 are usually titanium-bearing ores, rutile, ilmenite, and lucoxene. Rutile is the richest ore containing 93–96 % TiO_2, ilmenite from 44 to 70 %, and lucoxene concentrates can contain up to 90 % TiO_2. Only 5 % of all the mined titanium ore goes directly to the production of titanium [8]. At present, more than 300 deposits of titanium minerals have been discovered worldwide, including 70 igneous, 10 lateritic, and more than 230 placer deposits. Of these, 90 deposits, mainly placer deposits, have been explored according to industrial categories. Primary (igneous) deposits contain approximately 69 %, carbonatite weathering crusts – 11.5 %, and placer deposits – 19.5 % of the world's titanium reserves. Within this group, more than 82 % are in ilmenite, less than 12 % are in anatase, and 6 % are in rutile [9–11]. As mentioned earlier, there are two main industrial technologies for producing the pigment TiO_2 – sulfate and chloride. The raw materials for these technologies are shown in Fig. 1 [12].

The main raw material for these technologies is high-titanium slag and/or rutile obtained from ilmenite concentrate. The most popular method for producing titanium slag is reduction melting in electric furnaces at a temperature of 1600–1700 °C, during which iron oxide is reduced to metal. The main melting product, titanium slag, contains 75–85 % TiO_2. Pig iron is the second most common product and is utilized as a raw material in steel production. Titanium slag can be utilized to produce rutile with a TiO_2 content of 92–96 %. The industrial production of synthetic rutile consists of two stages: reduction smelting and acid leaching, which generate a large amount of liquid waste – 2 t/1 t TiO_2.

Ilmenite is a major mineral with a titanium dioxide content ranging from 40 % to 65 %. Other components include ferrous oxide or ferric oxide, as well as trace amounts of vanadium, magnesium, and/or manganese. The main sources of ilmenite are heavy mineral sands (alluvial deposits) however, it is also found in hard rock. Ilmenite currently accounts for 92 % of global titanium mineral production. Rutile (TiO_2) contains 93–96 % titanium dioxide but is difficult to locate in natural ilmenite deposits. As a result, the current review focuses on the alluvial deposit, specifically ilmenite, and the extraction of titanium from it [12].
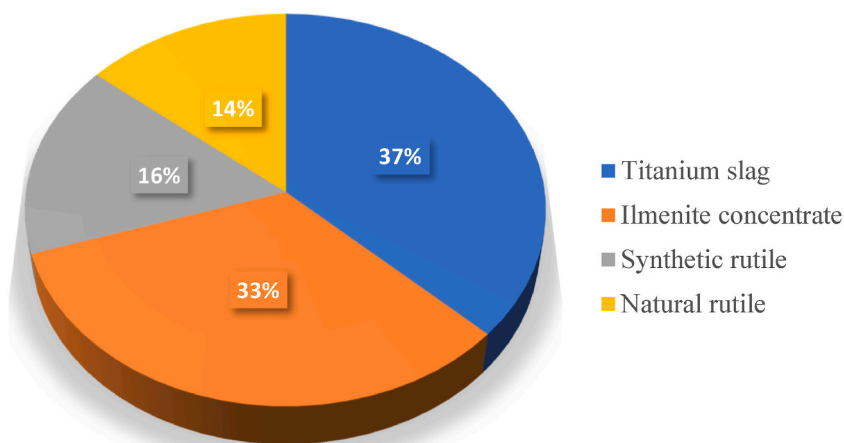

Fig. 1. Raw material sources for the production of TiO_2 pigment.

The ilmenite-magnetite and ilmenite-hematite ores of primary deposits form the basis of mineral resources available form the titanium industry in Canada, China, and Norway. Deposits in the weathering crusts of carbonatites are known and developed only in Brazil. In other countries, the main reserves of titanium minerals are located in alluvial, mainly complex deposits. Modern and ancient coastal-marine and accompanying dune placers are of great industrial importance. The length of each placer is small–from hundreds of meters to several kilometers.

3. Global TiO$_2$ companies

The structure of TiO$_2$ production by the largest companies in the world is shown in Fig. 2. The largest producer of the pigment TiO$_2$ is E.I. du Pont de Nemours & Co. Inc. (Du Pont). Over the past 10 years, its share has risen from 22 to 24 % of the world's production of this product. The company owns plants in the USA (3 plants), Mexico, and Taiwan with a total capacity of 1000 thousand tons/year, that operate using chloride technology [13]. Plants of Millennium Inorganic Chemicals Inc. are located in the USA (2 plants), UK, France (2 plants), and Australia. The production uses Both sulfate (total capacity of 182 thousand tons/year) and chloride (350 thousand tons/year) technologies are used for production. In January 1998, the company commissioned two new sulfate plants in France and then completed the modernization of the chloride plant in Stallingborough (UK), increasing its capacity from 109 thousand tons/year to 150 thousand tons/year. Millennium Chemicals is currently considering a 10–20 % increase in ultrafine TiO$_2$ production capacity at its plant in Tan, France [14]. Tioxide (a subsidiary of Huntsman Corp.) owns 6 plants with sulfate technology (total capacity – 456 thousand tons/year), located in the UK, Spain, Italy, Malaysia, and South Africa, and one plant with chloride technology (100 thousand tons/year) in the UK (Greatham).

Kronos Inc. (a subsidiary of NL Industries, Inc.) owns four plants with sulfate technology in Germany, Canada, and Norway for a total capacity of 24 thousand tons/year. Similarly, Kronos, Inc., owns three plants with chloride technology in Germany, Canada, and Belgium with a total capacity of 230 thousand tons/year [14]. Kemira Pigments OU produces the pigment TiO$_2$ in three plants: the USA, Finland, and the Netherlands. In 1998, the company invested $6 million increasing the capacity of the sulfate plant in Pori (Finland) to 120,000 tons/year. Kerr-McGee operates two of its facilities in Hamilton, USA, which use chloride technology and Bayer's manufacturing facilities in Germany and Belgium. In 1999, the plant was able to expand its capacity in Hamilton, during increased from 150 to 178 thousand tons/year [15]. Sachtleben Chemie, a subsidiary of Metallgesellschaft AG, operates a factory in Duisburg (Germany) and produces mainly anatase TiO$_2$ for synthetic glass fibers, as well as TiO$_2$ for the food and pharmaceutical industries. The Polish company Zaklady Chemiczne operates as the only enterprise for the production of the rutile pigment TiO$_2$ using sulfate technology this company has a capacity of 36 thousand tons/year, and uses Norwegian ilmenite concentrate and Canadian titanium slag [16]. The Czech company Precheza AS owns an enterprise with a capacity of 27 thousand tons per year in Prevov (Czech Republic), producing anatase TiO$_2$. Slovenia is the only enterprise for the production of rutile TiO$_2$ with a capacity of 34,000 tons/year. China is one of the world's largest consumers and producers of TiO$_2$ products. In addition, the demand for TiO$_2$ for paints and coatings is likely to increase in the construction industry. According to China's National Bureau of Statistics, China's construction industry generated approximately 7.3 trillion yuan in added value in the year 2020.

In November 2021, Asian Paints declared plans to invest US$127 million in a plant in Gujarat, India, to increase paint production
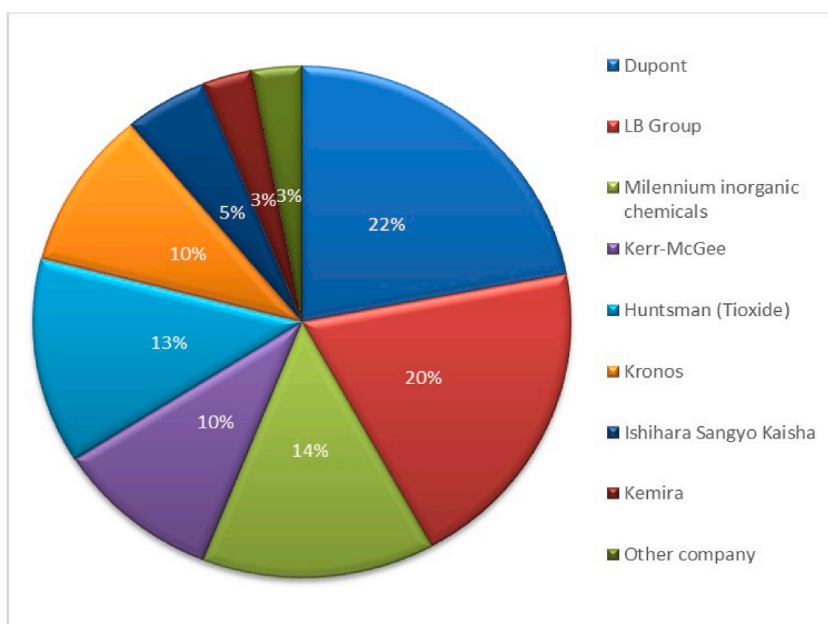

Fig. 2. The structure of TiO$_2$ production by the largest companies in the world.

capacity from 130,000 to 250,000 kL over the next two to three years. In addition, the plastics industry is anticipated to expand in China and India. The Chinese plastics industry is expanding at a fast pace because of the availability of cheaper raw materials and the enormous requirements of developing countries.

According to China's National Bureau of Statistics, approximately 7.95 million metric tons of plastic products were produced in December 2021, whereas 7.32 million metric tons were produced in November 2021. According to the Plastics Export Promotion Council (PLEXCONCIL), plastic exports from India increased by 55 % to $3417 million (cumulative) from April to June 2021, compared to $2211 million from April– to June 2020. The Asia-Pacific region has also experienced a significant increase in the requirement for beauty products, leading to increased use by teenagers and increased awareness of hygiene, which is expanding the researched market. Therefore, such trends are likely to drive TiO_2 demand in the region during the 2022–2027 forecast period [17].

In January 2022, LB Group (China) announced an investment of RMB 1 billion (USD 157.6 million) on capabilities in Xiangyang to build a new titanium dioxide (TiO_2) pigment manufacturing plant with a capacity of 200 thousand tons per year. Two TiO_2 pigment finishing lines will be built, the technology of which will allow the processing of the intermediate pigment product TiO_2 with a capacity of 100 thousand tons per year [18].
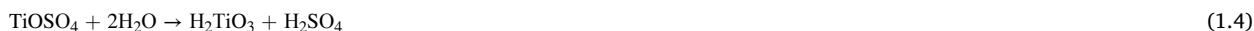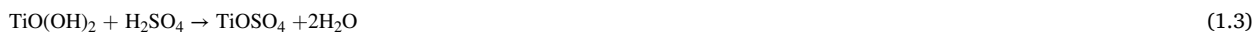
4. Combined technologies for the production of TiO_2

4.1. Processing of ilmenite concentrate by the sulfate method

Ilmenite concentrate serves as a raw material in sulfate technology for the production of TiO_2, it was introduced into the industry in 1931 to produce anatase, and in 1941 to produce rutile [19]. In this method, titanium-containing ore is dissolved in sulfuric acid (H_2SO_4), to form solutions of titanium, iron, and other metal sulfates. Then, as a result of a series of chemical reactions, which include chemical reduction, purification, precipitation, washing, and calcination, basic TiO_2 with the needed particle size is formed. The crystal structure (anatase or rutile form) is controlled during the nucleation and calcination processes [20]. The technology for the production of TiO_2 by this method is established via ilmenite treatment (a natural mixture of various oxides, mainly tetravalent Ti and trivalent Fe) with sulfuric acid. Sulfate treatment requires slightly altered ilmenites, where the content of oxide iron in the mineral is less than or equal to the content of ferrous iron (otherwise, the concentrates will not dissolve in sulfuric acid). These requirements are met by ilmenite concentrates obtained from primary deposits or concentrates from placers of close demolition. According to sulfate technology, the iron contained in ilmenite concentrates is not used, and significant wastes of ferrous sulfate require disposal. At the first stage of the process, ilmenite is crushed, dried, and then decomposed with concentrated sulfuric acid. The degree of decomposition of the concentrate was 96–97 %. The result is a combination of titanium sulfate (reaction 1.1) and sulfates of iron (II) and (III), which are cooled and diluted with water to a certain concentration. At the same time, hydrated titanium dioxide begins to form (reaction 1.2). Then, ferric iron is reduced to ferrous iron in a solution of titanyl sulfate with metallic iron. The resulting solution was settled and fed to a black filter. Ferrous vitriol was crystallized in the filtered solution upon cooling and separated from the mother liquor via centrifugation. The byproduct of production (seven-water iron sulfate) is calcined to obtain monohydrate ($FeSO_4.H_2O$), followed by crushing. The titanyl sulfate solution was evaporated to a standard concentration, adding sulfuric acid to the solution (reaction 1.3), and sent to the next stage of the process-hydrolysis.

Hydrolysis of a solution of titanium sulfate salts was performed by introducing nuclei (prepared by precipitating titanium hydroxide $Ti(OH)_4$ from solutions of titanium sulfate ($TiOSO_4$) with sodium hydroxide (NaOH)). During hydrolysis, amorphous flakes of titanium dioxide hydrate (H_2TiO_3) are released, which have a high adsorption capacity, particularly related to Fe^{3+} salts; consequently, in the preceding stage, Fe^{3+} is reduced to ferrous iron.

The processes described above proceed according to the summary equations (reactions 1.1–1.4):

$$TiO_2 + 2H_2SO_4 \rightarrow Ti(SO_4)_2 + 2H_2O \tag{1.1}$$

$$Ti(SO_4)_2 + 3H_2O \rightarrow TiO(OH)_2 + 2H_2SO_4 \tag{1.2}$$

$$TiO(OH)_2 + H_2SO_4 \rightarrow TiOSO_4 + 2H_2O \tag{1.3}$$

$$TiOSO_4 + 2H_2O \rightarrow H_2TiO_3 + H_2SO_4 \tag{1.4}$$

If concentrated sulfuric acid is taken in excess, complex compounds of the composition $[TiO(SO_4)_2]_{2-}$ or $[Ti(SO_4)_3]_{2-}$ are formed (reactions 1.5 and 1.6):

$$Ti(OH)_4 + 2H_2SO_4 \rightarrow H_2[TiO(SO_4)_2] + 2H_2O \tag{1.5}$$

$$Ti(OH)_4 + 3H_2SO_4 \rightarrow H_2[Ti(SO_4)_3] + 4H_2O \tag{1.6}$$

This process produces a large amount (in terms of monohydrates ~2 tons per 1 ton of TiO_2) of diluted 20–22 % hydrolyzed H_2SO_4 contaminated with iron sulfate ($FeSO_4$), 1–2 % titanyl sulfate ($TiOSO_4$) and several percent of other sulfates. This acid is also a waste product. A possible direction of hydrolytic acid utilization is evaporated to a concentration of 55 % followed by subsequent use for superphosphate production. By varying the hydrolysis conditions (concentration, duration of stages, number of nuclei, acidity, etc.), it is possible to determine the yield of hydrolyzate particles with desirable properties, depending on the promising application. During hydrolysis, up to 95–96 % of the titanium precipitates, and the resulting metatitanic acid sorbs (reaction 1.4) a significant amount of SO_3. During the final stage of the process, metatitanic acid is routed for filtration in two stages, washing from chromophore impurities

and bleaching. After the needed ingredients are added, the titanium dioxide hydrate (H_2TiO_3) paste is calcined in a rotating drum calcining furnace 40–60 m long. As a result, water is first removed from the solution (at 200–300 °C), followed by SO_3 removal (at 500–800 °C), and a neutral (pH = 7) product–TiO_2 is obtained at 850–900 °C. At this stage, by changing the drying temperature, applying additives (such as zinc oxide-ZnO, and titanium chloride-$TiCl_4$), and employing various other methods, it is feasible to achieve rutilization (i.e., the rearrangement of TiO_2 into a rutile phase). The calcined product is crushed in two stages and subjected to surface treatment, which is carried out with certain chemicals to give the TiO_2 pigment certain consumer properties. The processed TiO_2 pigment was dried and subjected to microgrinding, after which it was packaged and sent to the warehouse.

4.1.1. Sulfuric acid method

The approximate consumption of basic materials for the production of 1 ton of TiO_2 from ilmenite concentrates by the sulfuric acid method is as follows: ilmenite concentrate containing 42 % TiO_2 - 3.1 tons; H_2SO_4 (monohydrate) - 4–4.5 tons; iron shavings - 0.24 tons [21,22]. A schematic diagram of obtaining TiO_2 by the sulfate method is shown in Fig. 3. It should be noted that the titanium slag obtained during the ore reduction smelting of ilmenite concentrates can also serve as a source of TiO_2 obtained by the sulfate method. In particular, a plant in Canada (Quebec, near Sorel) operates on slag (70 % TiO_2). When TiO_2 is obtained from slag by the sulfuric acid method, after titanium sulfate leaching, solutions containing 190 g/l TiO_2 and a small amount of hydrolyzed iron are obtained more easily than when processing ilmenite concentrates. The resulting hydrolytic acid contains ~9 g/l iron, which promotes its regeneration (Fig. 3).
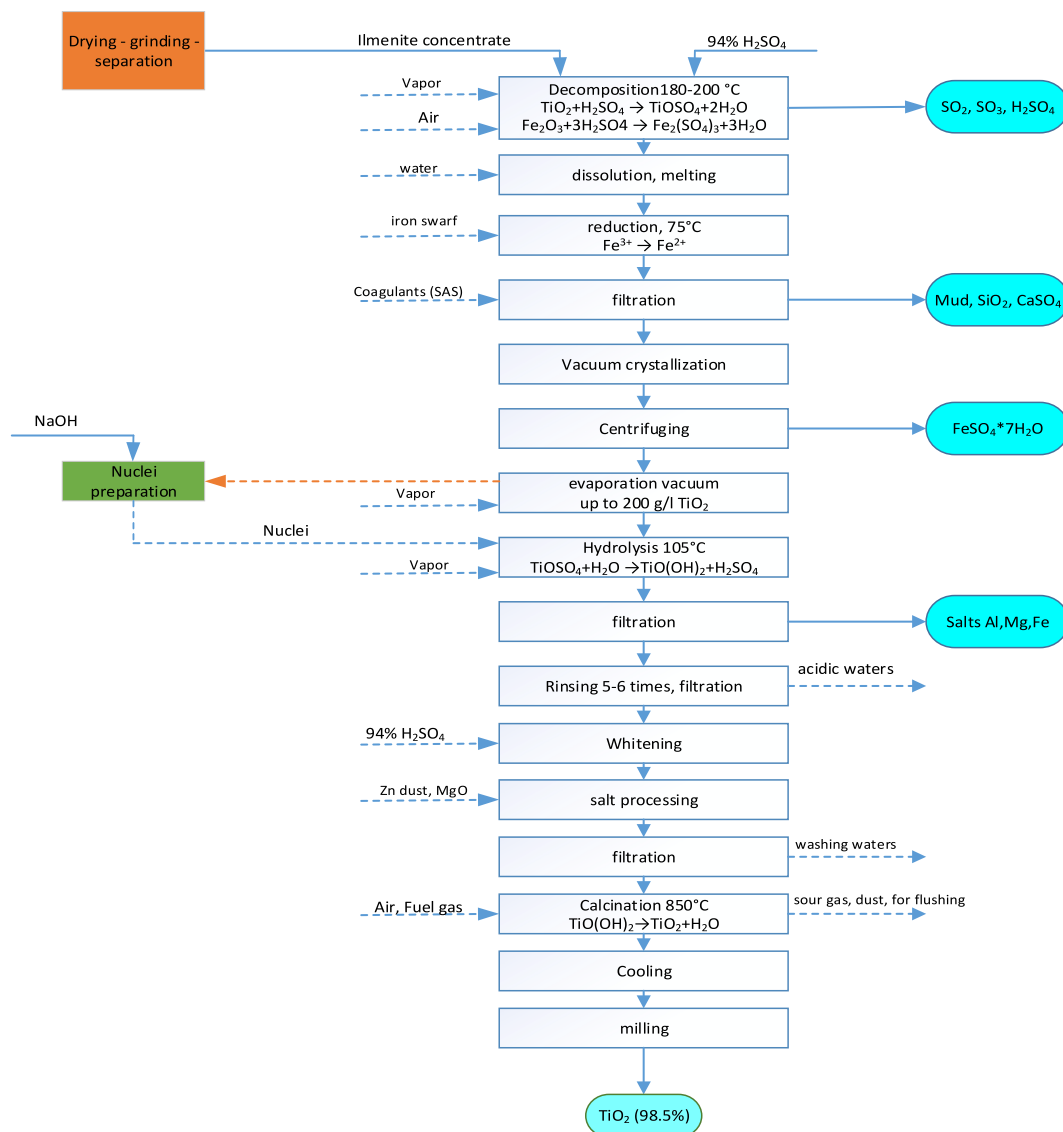

Fig. 3. Schematic diagram of the processing of Ti-concentrates by the sulfate method.

The main advantages of this technology include low capital costs and flexibility in the raw material. The disadvantages are high energy consumption, difference in quality of the obtained pigment, and a large amount of hardly realizable waste. For example, when ilmenite is processed according to a sulfate scheme per ton of TiO_2, large amount of diluted 20–22 % hydrolyzed H_2SO_4 is formed (in terms of monohydrate ~ 2 tons per 1 ton of TiO_2), contaminated with 2–3 tons of iron sulfate, 1–2 % titanyl sulfate, and several percent of other sulfates. Despite these shortcomings, approximately 40 % of all pigments in the world are obtained using sulfate technology.

4.2. Processing of ilmenite concentrates by the chloride method

The chloride method for producing TiO_2 was developed by DuPont; a pilot plant was put into operation in 1948 and in 1958, chloride technology was introduced on an industrial scale.

4.2.1. Chlorine method

The technology consists of reacting natural or synthetic rutile with carbon (coke, petroleum coke, etc.) and chlorine (Cl_2) gas at high temperatures, to form titanium tetrachloride ($TiCl_4$) vapor, which is oxidized by oxygen at 1300–1800 °C to TiO_2 after purification [23]. Since $TiCl_4$ also serves as an intermediate product in the production of metallic titanium, the production of TiO_2 by the chloride method is adjacent to titanium metallurgy (Fig. 4). When TiO_2 is obtained by the chloride method, titanium concentrate reacts with Cl_2 gas under reduced pressure, resulting in the formation of $TiCl_4$ and impurities from metal chlorides, which are subsequently removed (reaction 2).

$$2FeTiO_3 + 7Cl_2 + 3C \rightarrow 2TiCl_4 + 2FeCl_3 + 3CO_2\uparrow \qquad (2)$$

TiO_2 can then be obtained from $TiCl_4$ by one of the following methods.

(a) Hydrolysis of aqueous solutions of $TiCl_4$ (with subsequent heat treatment of the precipitate);
(b) Vapor-phase hydrolysis of $TiCl_4$ (based on the interaction of $TiCl_4$ vapor with water vapor). The process is usually carried out at a temperature of 900–1000 °C;
(c) Heat treatment of tetrachloride (combustion in a stream of oxygen). Industrial methods for the production of titanium pigments by hydrolysis have not yet been established. Their common drawback is an unsatisfactory solution to the problem of using hydrochloric acid (HCl) or hydrogen chloride formed during hydrolysis, which cannot be returned for reuse in the production of TiO_2.

The combustion of $TiCl_4$ with oxygen proceeds according to the following reaction (reaction 3):

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2\uparrow \qquad (3)$$
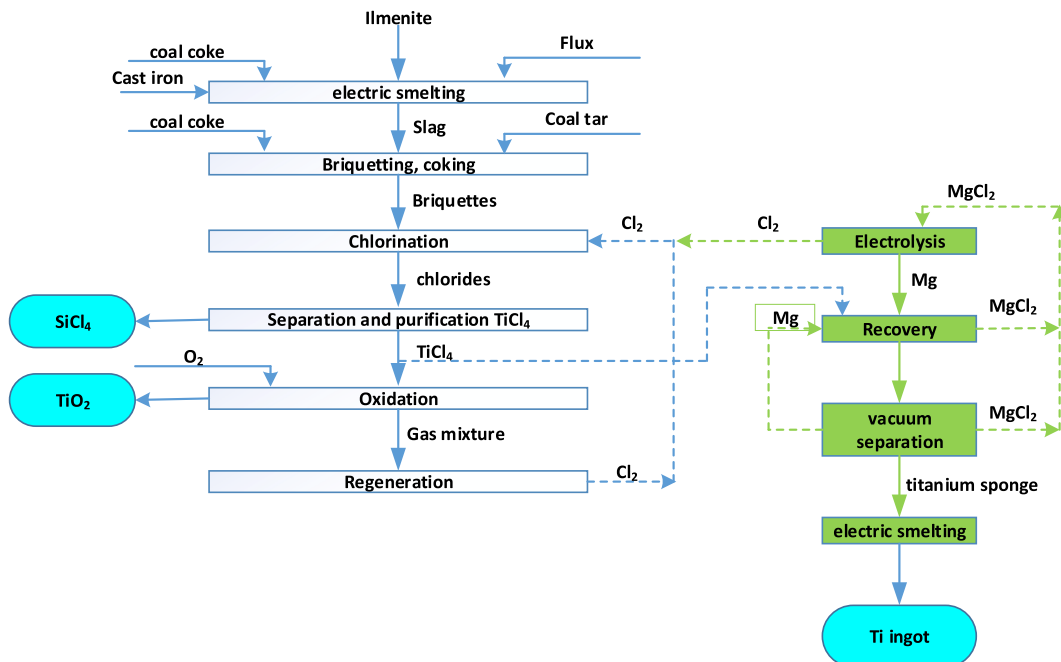

Fig. 4. Schematic diagram of the processing of ilmenite concentrates by the chlorine method.

The released Cl_2 can be returned to production again to produce $TiCl_4$; therefore, the combustion method is used in industry.

The oxidation step in the chloride process allows better control of the particle distribution curve and crystal structure. The result is TiO_2 with high hiding and thinning power. During combustion, it is necessary to maintain the temperature at a constant level to obtain particles of the same size and to regulate the period during which the formed particles are under thermal influence. The combustion conditions determine the structural modification of the resulting TiO_2. Often, this method produces a product unsuitable for the production of paints and varnishes since it contains more than 0.5 % chlorine. Therefore, the process is carried out on burners of a special design, ensuring the maintenance of the reaction temperature within the specified limits, and keeping the combustion products for a certain time. To acquire a monodisperse product, the presence time of TiO_2 in the high-temperature zone should not surpass 0.01–5 s. Depending on the combustion conditions of $TiCl_4$, TiO_2 has an anatase or rutile structure. The mixing of initial reagents at 400 °C leads to the formation of anatase structures with a particle size of 0.5–1 μm. However, preheating them to 1000 °C during combustion results in a product containing up to 60 % rutile.

The combustion of $TiCl_4$ with an admixture of silicon tetrachloride ($SiCl_4$) of 0.5–4 % leads to a decrease in the TiO_2 particle size. $SiCl_4$ also contributes to the reduction of the so-called photoactivity of TiO_2. Furthermore, the addition of 1–5 % aluminum chloride ($AlCl_3$) to the combustion products expedites the transition of anatase to rutile. The proportion of rutile in the finished product depends on the concentration of seed crystals that appear in the first stage of the reaction.

Titanium pigments obtained by burning $TiCl_4$ contain up to 0.6 % adsorbed chlorine. An aqueous suspension of such a product has a $pH > 7$ and is unsuitable for the preparation of paints. Cl_2 is desorbed from the pigment by calcining it at 300–900 °C, after which the Cl_2 impurity content decreases to 0.1 %. Such a product has an aqueous extract pH of 5–6.8 and is appropriate for paint manufacture and enamels but requires surface treatment with Si and Al compounds. Processing with various combinations of components allows optimal properties to be achieved for each specific application of the finished product [24–27]. The chloride method is more environmentally friendly than the sulfate method and advanced, because of the possibility performing the process in a continuous mode, which implies full automation of production. However, these materials are selective for use as raw materials, and because of the high temperature and use of Cl_2; corrosion-resistant equipment is needed. In both methods, the intermediate products are clusters of TiO_2 crystals, which must then be separated to impart optimal optical properties. Several methods exist for modifying TiO_2, including surface treatment with silicon and aluminum oxides.

Environmental problems, such as the unresolved issue of using chlorine and hydrogen compounds in the production of TiO_2 by the chloride method, the large amount of solid waste generated during in the processing of ores with low Ti contents, the contamination of wastewater, and the need for their treatment are important factors that hinder the development of the TiO_2 market. Environmental protection in developed countries is a dominant factor in the development of TiO_2 production via one or another method. According to expert estimates, at the cost of producing TiO_2 from raw materials with high TiO_2 content, the cost of these raw materials is 43 %, for the chloride method, and 28 % for the sulfate method. When using raw materials with low TiO_2 contents, similar values of 20 and 14 % were obtained.

4.3. Processing of titanomagnetites and titanium slags by hydrochloric acid technology

HCl leaching is one of the most frequently used well-proven methods for modernizing titanium-containing raw materials [26,28,29]. One study [24] proposed a method for extracting chromium (Cr), titanium (Ti), iron (Fe), and vanadium (V) from high-chromium vanadium titanomagnetite concentrates. This process includes various stages: partial reduction of the concentrates, magnetic separation, HCl leaching of the Ti-containing tailings, and alkaline treatment of the leach cakes with HCl. With partial reduction, V and Cr are primarily concentrated in Ti tailings. Then magnetic separation was carried out to separate the Fe-containing concentrate with a total Fe content of 94.57 %. During the acid treatment, 90.8 % of the V and 93.4 % of the Cr were extracted into the solution, while the loss of Ti was less than 0.3 %. Then, with alkali treatment, up to 96.3 % silicon (Si) was extracted into the solution, and a Ti-rich slag with a purity of 93.39 % was obtained. The total extraction percentages of Fe, Ti, V, and Cr under the experimental conditions were 88.3 %, 93.7 %, 81.7 %, and 84.4 %, respectively.

In [25], partial reduction experiments were carried out in a temperature-controlled muffle furnace (±5 °C). Approximately 120 g of titanomagnetite concentrate was first mixed with pulverized coal and a small amount of sodium carbonate (Na_2CO_3). The presence of Na_2CO_3 promoted the carbon (C) gasification reaction and promoted the growth of metallic Fe particles. The mixture was placed in a sealed silicon carbide (SiC) crucible and then heated to the desired temperature in a muffle furnace. After the completion of the reduction experiments, the reduced samples were immediately cooled with water to avoid reoxidation and the resulting intermediate was ground for 30 min. Next, the crushed samples were separated by a magnetic separator. The recoveries of Ti, Fe, Cr, and V were determined according to the mass balance.

Leaching experiments were carried out in an autoclave. The Ti concentrate was first diluted with HCl solution at certain S:L ratios. The autoclave was kept at a predetermined temperature for a fixed time and then rapidly cooled. The suspension was filtered, and the cake was washed with distilled water after leaching. Then, the mixture was leached with a dilute solution of NaOH–174.6 g/l, S:L = 1:3 at 80 °C for 1 h. The suspension was filtered, and the residue was washed, dried at 110 °C, Afterwards, the resulting intermediate product was calcined at 750 °C for 2 h, to form a Ti-rich slag. According to previous research [26], when Ti concentrate is leached with HCl, Si is in the form of amorphous hydrated silicon dioxide (SiO_2), which readily dissolves in an alkaline solution of sodium hydroxide (NaOH) [27].

Compared to the existing technologies, the new method has several advantages.

(a) Alternative process with higher recoveries of Ti, Fe, Cr, and V;

(b) The Cr and V are controlled, so that they are concentrated in the Ti concentrate by partial reduction, thus avoiding high-temperature processes such as melting, converting, and calcination.

(c) To some extent, these materials appear to be more environmentally friendly, since Cr and V in the reduced samples exist in the form of V^{3+} and Cr^{3+}, whereas after simple alkaline treatment, these metals are V^{4+} and Cr^{3+} due to the presence of Fe^{2+} and small amount of Fe^{3+} and their respective redox potentials.

The method is proposed [28,29] for the enrichment of Ti slag obtained after electric smelting at 1500–1600 °C or reduction roasting at 900–1000 °C, followed by separation of Fe, with a composition, wt. %: TiO_2 35–40, Fe_{total} 5–15, SiO_2 5–15, Al_2O_3 5–15, MgO 2–12, CaO 2–10, MnO 1–5, and Cr_2O_3 0.5–5. This method consists of treating the slag with HCl at a concentration of 12–18 % at S:L = 1:8 ÷ 10 (with a total twofold excess in stoichiometry), followed by processing the solid product after washing with 3–5 % NaOH solution at S:L = 1:4 ÷ 6. The optimal conditions for leaching time were 2 h and temperature 106–110 °C. The resulting product was hydrated titanium dioxide ($TiO_2 \cdot H_2O$) with an X-ray generated amorphous structure. In order to convert the product to the rutile form, it was calcined at 800–900 °C.

4.4. Carbothermal processing route

The technological route of processing using carbothermal influence on oxide mineral mixtures is a highly effective way of thermochemically processing oxide raw materials and is an alternative to the chloride or sulfate method [30–32]. This allows for the effective separation of Ti and Si components. However, it is possible to regulate the composition and consequently, several technically important properties of the obtained products. Among the most important results of vacuum carbothermal treatment of 50 % leucoxene concentrate is the ability to obtain nanolaminate materials based on the Ti_3SiC_2 carbide-silicide phase [30,33–35].

Carbothermal reduction of the oxide components of leucoxenes by activated carbon was carried out at temperatures up to 1800 K in the range of medium-pressure gas from deep vacuum (10^{-3} Pa) to atmospheric pressure (10^5 Pa). The initial composition of the leucoxene concentrate is wt. %: SiO_2 46–52, TiO_2 45–50, Al_2O_3 2–4, and Fe_2O_3 1–3. The carbothermal process allows the targeted formation of submicron β-SiC and nanolaminate Ti_3SiC_2 phases as a result of two competing reactions (reactions 4 & 5):

$$SiO + 2C \rightarrow SiC + CO \text{ (carbon silicification)}; \tag{4}$$

$$3TiC + SiO \rightarrow Ti_3SiC_2 + CO \text{ (titanium carbide silicification)}. \tag{5}$$

The silicifying agent in both cases is gaseous SiO. At the initial and intermediate stages of the carbothermal process, SiO is generated as a result of the reduction of SiO_2 with C and lower titanium oxides. The possibility of such interactions under the conditions of a carbothermal process was confirmed by thermodynamic calculations and experiments with model systems that were carried out in earlier works [36,37].

The main reactions of Si gasification with the formation of SiO are given below (reactions 6–8):

$$SiO_2 + C \rightarrow SiO + CO; \tag{6}$$

$$SiO_2 + 2TiO \rightarrow SiO + Ti_2O_3; \tag{7}$$

$$SiO_2 + 3Ti_2O_3 \rightarrow SiO + 2Ti_3O_5. \tag{8}$$

At the final stages of the carbothermal process, when the conversion of Si from the oxide to the carbide form is almost complete, the source of SiO is silicon carbide (SiC), which can reduce titanium oxides according to the following reactions (reactions 9–10):

$$SiC + 2Ti_2O_3 = SiO + CO + 4TiO; \tag{9}$$

$$SiC + TiO = SiO + TiC. \tag{10}$$

The presence of free C in the reaction mixture, as well as an increased CO content in the gas phase, suppresses the silicification of titanium carbide (reaction 5), which leads to a shift of the carbothermal process toward the formation of predominantly submicron β-SiC. Thus, the initial C concentration and the mode of removal of gaseous products (SiO and CO) from the reaction zone are the key factors for regulating the final composition of the products.

As a result, it was shown that during the carbothermic processing of leucoxene raw materials at gas pressures below atmospheric pressure and at an activated carbon concentration in the initial charge range from 11 to 17 wt %, a deep separation of Ti- and Si-containing components of leucoxene raw materials is ensured. The composition of the products obtained after carbothermic treatment of leucoxene concentrate was wt. %: SiO_2 0.4–36.0, TiO_2 55.0–95.4, Al_2O_3 0.1–3.6, and Fe_2O_3 1.2–4.6. The disadvantage of this method is that the technology requires high temperatures; therefore, more electricity is consumed. Additional processes are needed for post-treatment of TiO_2 from impurities of Si, Fe, and other elements. With respect to the data obtained, there are large discrepancies in the results of the analysis for TiO_2 and Si.

4.5. Nitric acid opening of Ti slags

According to previous research [38], the slag was crushed to a particle size less than 50 μm, subjected to magnetic separation to

remove metal inclusions, and treated with a 30 % nitric acid (HNO_3) solution at a temperature of 95 °C and T:L = 1:5.5 for 1 h. The resulting pulp was filtered and a cake containing hydrated Ti and SiO_2 was separated. The cake obtained after leaching from TiO_2 and Si was treated three times in 5 % NaOH solution at a temperature of 95 °C, and T:L = 1:5 for 1 h. The cake was additionally treated with a 5 % HNO_3 solution to remove sodium (Na) impurities. In this case, 97 % of the SiO_2 was extracted from the cake and 2 % of the TiO_2 was lost during pulp filtration. The results were as follows: Ti concentrate composition, wt. %: TiO_2 85.4, SiO_2 7.82, Al_2O_3 2.04, MgO 0.40, Fe_2O_3 2.16, and Na_2O 0.24.

4.6. Processing of Ti slag by autoclave alkali leaching (cracking or opening)

In previous study [39], Ti slag, (wt. %: 92.5 TiO_2, Fe_{total} 0.90, MnO 2.82, Al_2O_3 2.17, CaO 0.84, SiO_2 0.64, and MgO 0.41) was treated in an autoclave with a NaOH solution containing10 mol/kg H_2O at a mass ratio of S:L = 1:4, and a temperature of 220 °C for 4 h. The pulp was then cooled, filtered, washed, and dried at 80 °C. The obtained $Na_4Ti_3O_8$ based intermediates were leached in HCl solution at pH 0.2 and S:L = 1:5, sedimented for 5 h and separated from the acidic solution. As a result, TiO_2 containing 98.4–99.4 % TiO_2 was obtained.

4.7. Alkaline leaching process

A technique was proposed for processing slags containing 8–17 % TiO_2 [40] to obtain products that meet the Ti content requirements for the production of pigment TiO_2 and metallic Ti. It includes two directions. To obtain the anosovite concentrate used in the production of pigments by the HCl method, titanium slag was kept at a temperature of 1300 °C with the addition of a modifier during cooling for 4 h. After crushing and grinding, enriched by gravity or anosovite flotation, the sludge is leached with H_2SO_4 and alkali. To obtain Ti metal using chlorine technology, the slag is additionally oxidized in the melt or during annealing with a modifier and then after crushing and grinding, a rutile concentrate is released.

A new process for the production of TiO_2 from Ti slag by decomposition with Na or potassium hydroxide (KOH) has been proposed [40–42]. Ilmenite composes in a concentrated solution of KOH or NaOH at atmospheric pressure and an intermediate product with a high Ti content and a low Fe content is obtained. The decomposition of ilmenite in a concentrated alkaline solution of KOH leads to the formation of potassium titanate ($K_4Ti_3O_8$) and iron oxide (FeO), which proceed according to the following reaction (reaction 11):

$$3FeTiO_3 + 4KOH \rightarrow K_4Ti_3O_8 + 3FeO + 2H_2O \qquad (11)$$

The phase transformation of $K_4Ti_3O_8$ was accomplished by hydrolysis of $K_4Ti_3O_8$ in an acidic solution (pH 2.0) at 25 °C for 60 min. The resulting hydrated TiO_2 was calcined at a temperature of 400°C to form a crystallized anatase structure of TiO_2. Under such conditions, approximately 95–98 % of the Ti is recovered from Ti slag; in addition, the purity of TiO_2 is 99.3 % (Fig. 5). A similar process of caustic leaching for the production of TiO_2 from Ti slag has also been found in other research papers [43,44]. Finely ground Ti slag ($-61 + 51$ μm) was subjected to interaction with 10 M NaOH at a ratio of S:L = 1:4 at a temperature of 220 °C for 4 h. In this
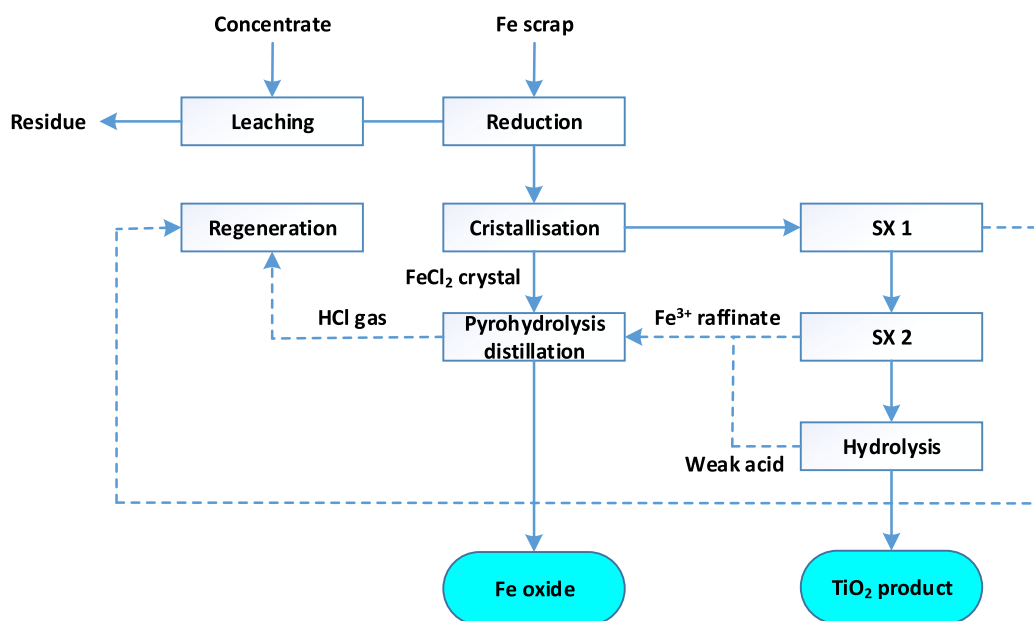

Fig. 5. Schematic diagram of the production of pure TiO_2.

case, almost complete dissolution of TiO_2 in the form of $Na_4Ti_3O_8$ was achieved. TiO_2 with a rutile structure was obtained by acidification with HCl at a temperature of 100 °C and pH of 1.2, and the purity of the obtained TiO_2 was 99 %.

Compared to other Ti slag recycling processes, the alkaline leaching process is relatively mild and high recoveries are obtained at relatively low temperatures and atmospheric pressure. Consequently, the energy consumption of this technology is normally lower than that of existing technologies.

In [45], the researchers proposed a method of enriching Ti slag obtained by electric smelting of titanomagnetite concentrate from the Tymlai deposit (Kazakhstan), with a chemical composition of wt. %: TiO_2 52.0, FeO 2.08, SiO_2 15.32, Al_2O_3 8.4, MgO 11.8, CaO 1.38, MnO 0.97, V_2O_5 0.055, Cr_2O_3 0.032, and C 4.24. The Ti slag was ground to a particle size of 45 μm. The fusion of Ti slag with NaOH was carried out at a TiO_2:NaOH ratio = 1:2 and a temperature of 850 °C. The influence of temperature on the process of aqueous leaching of sinter was evaluated in the temperature range of 25–75°C and at a ratio of S:L = 1:3.8. After the main alkali mixture was separated, the precipitate was washed twice at a ratio of S:L = 1:2.

An increase in the content of TiO_2 in the resulting intermediate product is possibly due to the extraction of impurities into the solution during acid treatment. The influence of the concentration of the solution with HCl on the degree of leaching of the Ti middling product was evaluated at concentrations ranging from 63 to 187 g/dm^3 at S:L = 1:5 at a temperature of 95 °C for 1.5 h, In addition, the following Ti concentrate of composition wt.% was obtained: TiO_2 85.8, FeO 2.26, SiO_2 7.66, Al_2O_3 0.045, Na_2O 0.033, CaO 0.041, MgO 0.052, and humidity 4.

The Si content in Ti slag supplied for Ti sponge production should not exceed 3.5 %. In this regard, the obtained product based on TiO_2 had to be purified from the Si. After that studies on the influence of the duration of the desiliconization process on the rutile concentrate and TiO_2 yield were carried out. The impact of alkali treatment occurred at temperatures above 90 °C, and for the first hour of alkaline treatment, the Si almost completely passed into the solution. As a result of the conducted research, the optimal conditions or desiliconization of the rutile concentrate were determined to be a ratio S:L ratio = 1:6, a NaOH concentration ranging from 14 to 15 g/dm^3, a temperature ranging from 90 to 95°C, and a duration 1.5–2.0 h. Under optimal conditions, a conditioned rutile concentrate was obtained with the following composition wt. %: TiO_2 91–92, FeO 2.3–2.5, SiO_2 1.7–2.0, Al_2O_3 0.008–0.01, CaO 0.06–0.08, MgO 0.07–0.08, Cr_2O_3 0.04–0.06, and humidity 4. According to X-ray phase analysis, TiO_2 is represented by a rutile monophase [45].

4.8. Leeds process

In early 2009, researchers from Leeds University (UK) developed a new, more environmentally friendly, less time-consuming, and less expensive process to produce pigmented TiO_2.

The new process consists of three main stages.

(a) Roasting of complex ore minerals in air at a temperature of 800–900 °C in the presence of alkali, to change their chemical structure.
(b) After processing with a stream of warm water, impurities are leached with acid, and byproducts of industrial use are obtained.
(c) After calcination, the residue is exposed to Cl_2, which is needed to be 20 times less than the volume normally needed under industrial conditions.

The Leeds process provides a pigmented TiO_2 yield of approximately 97 % (the industry average is currently 85 %). An increased yield of the finished product will allow companies to significantly reduce production costs as well as waste disposal costs. The process also utilizes excess heat and carbon dioxide (CO_2). CO_2 is used to regenerate the alkali solution. According to the results of this method, the technology can be improved to increase the TiO_2 yield to 99 %. Additionally, this process can be used to separate TiO_2 from ores with different degrees of enrichment. In this regard, Leeds researchers are working in an industrial partnership with Millennium Inorganic Chemicals to refine the technology for commercial use.

Currently, the capacity of the chloride method to produce TiO_2 exceeds the capacity of the sulfate method and continues to increase worldwide. In the CIS (Commonwealth of Independent States) countries, approximately 97 % of the total volume of TiO_2 is produced by the sulfate method followed by hydrolysis and calcination (JSC Sumykhimprom and CJSC Crimean Titan, Ukraine). The vapor-phase hydrolysis of $TiCl_4$ is used at the OJSC Solikamsk Magnesium Plant (Russia, Solikamsk, Perm Territory) and was used until recently at AVISMA (branch of OJSC VSMPO-AVISMA Corporation, Berezniki, Perm Territory). The JSC "Khimprom" (Volgograd) used the method of processing (combustion) of $TiCl_4$ by the plasma-chemical method [27,28].

The advantages of the chloride method for pigment production over the sulfate method include the use of much smaller amount of waste, for neutralization, the use of a slightly higher quality of the product, and the use of lower specific capital investments, which account for 60–75 % of the total investments in the sulfuric acid method. In spite of the fact that more expensive raw material - rutile is used for the chloride method, the cost of 1 kg of pigmented TiO_2 obtained by the chloride method is ultimately less than that obtained by sulfate technology. Since chloride technology has high requirements for initial Ti raw materials because of the limited content of impurities, in recent years, hydrometallurgical methods have been developed as alternatives for obtaining pigmented TiO_2. Many of these methods involve acid leaching of Ti-rich raw materials.

4.9. Methods for the processing of Ti slag by preliminary roasting and further leaching with various reagents

Other studies are based on the roasting of low Ti slag with various alkaline reagents. Roasting is a common metallurgical process

used to separate metals during the processing of raw ores or intermediate products such as Ti slag. Alkaline firing is widely used. The role of alkali roasting is commonly twofold: first, TiO_2 is chemically separated from Si compounds and other impurities, and second, soluble Na metal salts are formed during alkaline roasting, and can be removed in subsequent aqueous leaching steps. Elemental impurities such as Al and Si readily from soluble compounds that are washed out, while Fe, Mg, and calcium (Ca) form insoluble compounds that are removed by acid leaching.

When Ti slag is sintered with NaOH, Ti, Si, V, and Al form titanates, silicates, vanadates, and aluminates, respectively, which dissolve in water, while Ti remains in the precipitate, and dissolves in H_2SO_4 or HCl with further isolation of titanic acid. The resulting product is converted into a white TiO_2 pigment by calcination [46,47]. A new technology has been developed for the industrial production of the high-quality pigment TiO_2 [48], composition, wt. %: TiO_2 78.5, Fe_{total} 7.73, Al_2O_3 2.36, MgO 5.57, CaO 0.66, MnO 0.30, SiO_2 2.75, and Cr_2O_3 0.21. This technology includes alkaline roasting, leaching with a solution of HCl at a concentration of 2 mol/dm^3, and calcining the titanic acid to produce pigmentary TiO_2. The most interesting technology is the production of pigment TiO_2 from slag obtained from the processing of titanomagnetite concentrate [46,49]. According to the technological scheme (Fig. 6), Ti slag decomposes in an alkaline melt of NaOH with the formation of Na titanate, silicate, and aluminate at a temperature of 500 °C for 60 min and in a ratio of alkali:slag = 1:1. The resulting cake was leached with water at a temperature of 50 °C, and a T:L ratio of = 1:5 for 20 min. V, portion of the Al, Si, and Mn passed into the solution. The resulting solution is returned to slag roasting after purification from impurities and concentration. The washed Ti-containing precipitate was dissolved in a 20 % H_2SO_4 solution to obtain a titanium oxosulfate solution.

After purification, the sulfate solution was thermally hydrolyzed, and H_2TiO_3 was precipitated, afterwards, the mixture was washed until the main impurities were eliminated. This was followed by calcination at 800 °C to obtain pigmentary TiO_2. The disadvantages of this method include the long duration of the process, the low degree of TiO_2 extraction, and the high content of Si and Fe in the final product.

4.10. Processing of high-Ti concentrates of titanomagnetite ores

The complexity and concentration of processed titanomagnetite ores are refractory and difficult to recover. When dealing with such materials, it is imperative to establish conditions for primary solid-phase Fe reduction, ensuring that the rate of iron oxide reduction surpasses the rate of slag formation and charge melting. An important aspect of this problem is also the search for solutions for the hydro-chemical enrichment of slag under conditions (≥80 % TiO_2) suitable for chlorination or the production of the pigment TiO_2.

During reduction-metalizing firing, TiO_2 is partially reduced with the formation of lower oxides. This results in the formation of Ti
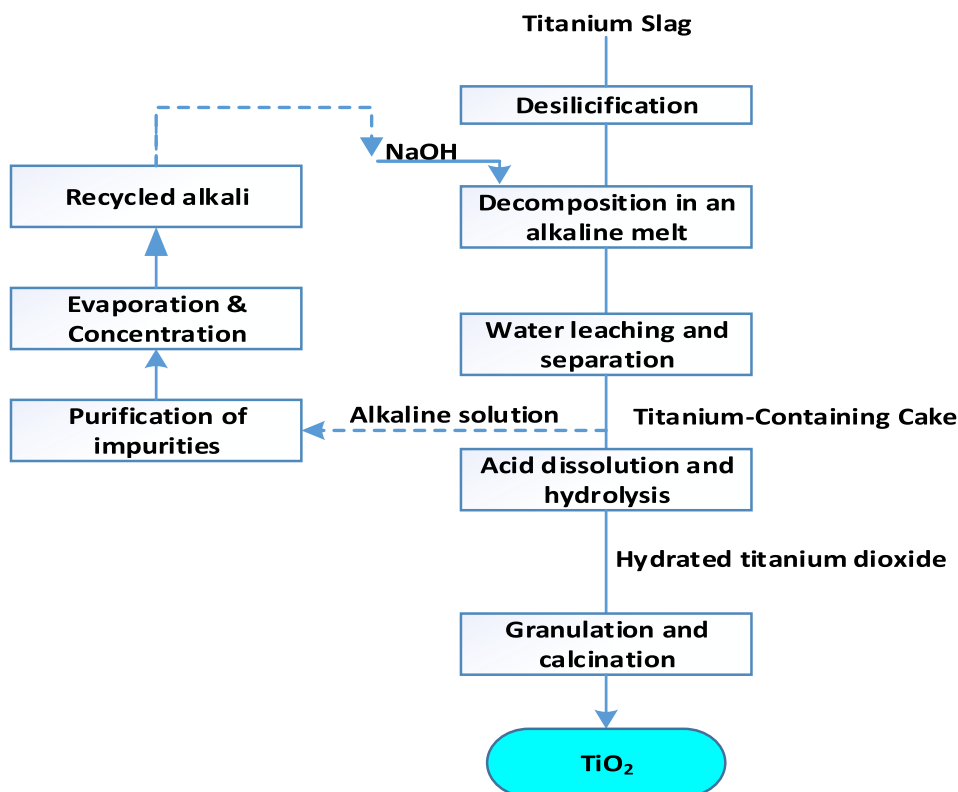

Fig. 6. Schematic diagram of the production of pure TiO_2.

slag. The lower oxides of Ti dissolve ilmenite well, which makes it difficult to restore residual amounts of Fe. In addition, lower Ti oxides are very refractory in nature; slags with a high content of the latter are characterized by an increased melting point. These findings indicate that the reduction of titanomagnetite concentrates should be carried out in such a way as to separate the processes of Fe reduction and the formation of a slag melt.

This problem can be solved by organizing a two-stage method for producing Ti slags. At the first stage of the process, the solid-phase reduction of iron oxides occurs and at the second stage, the process of melting the pre-reduced material with the separation of the slag and alloy. An analog of this technology is the ITmk-3 Fe production process developed by Kobe Steel, Ltd (Japan), in which the agglomerated raw material is reduced in a rotary furnace, after which the metal pellets are separated from the slag on a screen. The disadvantage of the ITmk-3 method is the use of lime (CaO) and silicate fluxes with the formation of refractory slags that impede the coagulation of Fe and impoverish the slag in Ti.

Due to the difficulty of reducing and refractoriness, high-Ti titanomagnetites cannot be melted in a blast furnace, and direct electrothermal reduction melting is associated with process instability, melt boiling, and poor separation of cast iron from slag. Melt instability and effervescence are the result of the intense reduction in FeO in the liquid phase with the release of a large amount of CO gas, which swells viscous Ti-containing slags. The necessary conditions for obtaining stable slags can be created only with a controlled recovery period that occurs at the solid stage before the development of the slag formation process.

In particular, soda is added to the reduction charge [50–52], which is both a reduction catalyst and a flux that reduces the viscosity of the slag. The introduction of sodium oxide (Na_2O) into the mixture leads to the formation of low-melting sodium titanates (Na_2TiO_3 with a melting point of 1030 °C, $Na_2Ti_2O_5$–985 °C, and $Na_2Ti_3O_7$–1128 °C). The influence of soda additives (1.5–2.5 %) on phase transformations during the solid-phase reduction of a poor (3 % TiO_2) titanomagnetite concentrate with hydrogen (H_2) in the temperature range of 700–1200 °C was studied [52]. At the final stage of the process (i.e. at 1200 °C), Na_2O is consumed mainly for the binding of SiO_2 to aluminosilicates with the displacement of FeO, MgO, and CaO from the silicate phase, which leads to the acceleration of the reduction of Fe and an excess of Na_2O forms sodium titanates with TiO_2. To increase the reducibility of titanomagnetite, precalcinating the concentrate to hematite (Fe_2O_3), while mixing alkaline additives into the charge is recommended as a flux and reduction catalyst [53].

In this research [54,55], a two-stage technique for the reductive melting of TMK with soda additives was developed both without oxidation and with preliminary oxidation of TMK to Fe_2O_3. The optimal technological parameters were determined: consumption of 8 % special coke or C/Fe = 0.103, consumption of Na_2O – 3 %, solid-phase reduction temperature 1250 °C, exposure time – 50 min, melting temperature 1650 °C, and exposure time – 35 min. Both options have almost equal and high rates: iron yield from TMK ~55 %, slag yield 23.3–25.8 %, content in C-free slag, wt. %: Fe = 1.0–1.6, TiO_2 = 62.7–61.9, and Na_2O – 5.85. The output of TiO_2 in the slag is 89.6–94.1 % and the degree of sublimation of Na_2O is 56.5 % in the first and 51.9 % in the second. The cast iron contains, wt. %: 5.51C, 0.36 Ti, 0.35 Mn, 0.23 V, and 0.04 Si. The output of V in cast iron is 53 %.

5. Conclusion

The analysis of the scientific, technical, and patent literature showed that due to the significant difference in the chemical composition of ilmenite and titanomagnetite concentrates from various deposits, the content of impurity components in Ti slags varies widely. When developing a method for producing TiO_2, this circumstance determines an individual approach for each specific Ti concentrate or slag. Currently, the production of Ti slag is based on the smelting of ilmenite concentrate in electric ore-thermal furnaces at a temperature of 1600–1700 °C, which is associated with high energy costs (~ 2500 kWh per 1 ton of slag). In the development of a technological process for low-temperature (1000–1200 °C) processing of ilmenite or titanomagnetite concentrates to obtain pure TiO_2 are proposed. The advantage of this process over electric arc smelting in ore-thermal furnaces is the low temperature, which remains within the range of 1000–1200 °C, representing a reduction of 500–600 °C, compared to the temperature needed for ilmenite electric smelting to produce Ti slag and pig iron. This fact undoubtedly results in a reduction in energy costs of at least 2–3 times. Moreover, such a process can be carried out in a continuous mode, which will make it possible to automate it and thereby entail a reduction in labor costs.

Ethics approval

Not Applicable.

Consent

All the authors agreed with the content, gave explicit consent to submit the study, and obtained consent from the responsible authorities at the institute/organization where the work was carried out.

Material and/or code availability

Not applicable.

Availability of data

The data will be made available upon request.

CRediT authorship contribution statement

Galymzhan Maldybayev: Writing – original draft. **Argyn Korabayev:** Formal analysis, Conceptualization. **Rustam Sharipov:** Visualization, Investigation. **Khaldun M. Al Azzam:** Writing – review & editing. **El-Sayed Negim:** Writing – original draft, Conceptualization. **Omirserik Baigenzhenov:** Methodology, Data curation. **Aliya Alimzhanova:** Writing – original draft, Investigation. **Mrutyunjay Panigrahi:** Resources, Project administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Galymzhan Maldybayev reports financial support was provided by Kazakh-British Technical University. Galymzhan Maldybayev reports a relationship with Kazakh-British Technical University that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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