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Comprehensive Resource Treatment of Titanium White Waste Acid by Chlorination Method Based on Mechanical Separation Method

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Abstract: Using the chlorination method to produce titanium dioxide, approximately 6~8t of waste acid with a mass fraction of about 20% is generated per 1t of titanium dioxide produced.In order to address the issue of acid waste pollution and resource recycling, domestic and international scientists and researchers have developed and studied various governance processes and methods, such as rare metal extraction, concentration neutralization, membrane separation technology, and so on.This article analyzes the advantages and disadvantages of various processes and proposes the mechanical separation method to treat waste acid of titanium dioxide, which has certain reference significance for carrying out new research on acid waste treatment processes.

Keywords: Chlorination method; Waste acid; Mechanical separation; Process.

1. Introduction

Titanium dioxide, also known as TiO_2, is a non-toxic substance with stable chemical properties, a high melting point, and excellent whiteness. It possesses good optical activity and is regarded as the best white powder solid pigment in the world today, exhibiting exceptional comprehensive performance. It finds a wide range of applications, with approximately 55%~60% used in the coating and rubber industries, and 23%~25% utilized in the plastic industry. Apart from these sectors, titanium dioxide is also utilized in areas such as coating, chemical fiber, cosmetics, photosensitive catalyst, and other industrial applications[1-3]. Currently, the mainstream production methods of titanium dioxide include the sulfuric acid method and the chloride method. The sulfurization method is the process of obtaining hydrated titanium dioxide ($TiO(OH)_2$) through sulfuric acid oxidation and a series of intricate procedures, After undergoing dehydration treatment, surface treatment, and so on, the final product is obtained. The process of craftsmanship is intricate, and the quality of the final product often falls short of expectations. As a novel green production technique, chloride method primarily obtains high-quality finished products through chlorination oxidation and surface treatment. Compared to the sulfurization method, the chloride method has the advantages of shorter process flow, less waste emission, the emitted gas can participate in atmospheric circulation, high sustainability, and high degree of automation. But high technical difficulty, many operational difficulties, complex and dangerous production equipment, not easy to master. Acidic waste liquid will be generated during the production process, and the acidic waste liquid generated during the chloride process can be reused for secondary circulation or sold as an industrial by-product hydrochloric acid to downstream customers. However, most of the acid liquid that has gone through recycling contains a large amount of milky white flocculent colloid particles.

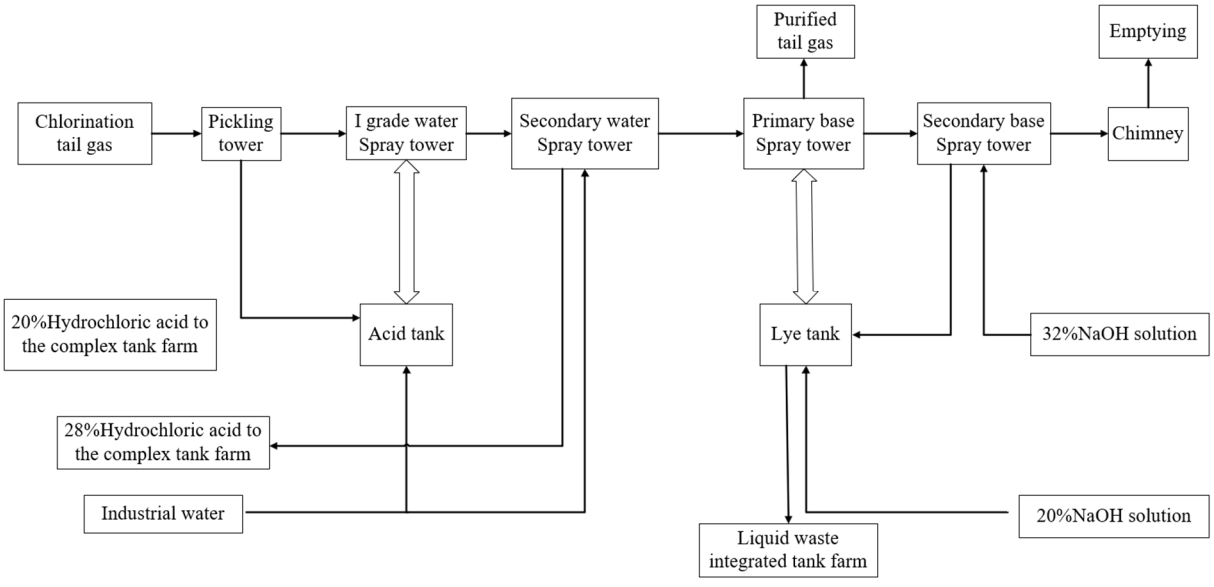

Figure 1. A Schematic diagram of the waste acid production

The acidic wastewater generated during the chlorination process collects all the drainage from key processes including pickling, precipitation, hydrolysis, rinsing, and salt treatment in the titanium dioxide production workshop. If a large amount of acidic wastewater is discharged directly, it will pollute natural water bodies and acidify the soil, causing significant harm to the ecological environment, agricultural and fishery production, and drinking water for residential areas. Therefore, solving the problem of chlorination of titanium dioxide acid wastewater is the foremost technical challenge faced by titanium dioxide production enterprises and scientific research institutions in China.

2. Titanium White Waste Acid Treatment Technology

2.1. Resource utilization of titanium dioxide waste acid

Titanium waste acid contains a large number of titanium, zirconium and other metal elements, has a high resource utilization value.Hongbin Qiu et al.[4] have developed a method for recovering trace amounts of scandium ions from titanium waste acid. This process involves using dual (2-ethylhexyl) phosphoextracextraction and combines pre-enrichment and purification through solvent extraction.In the pre-enrichment step, the researchers optimized the volume fraction of the dual (2-ethylhexyl) phosphate extractant, synergist tributyl phosphate, and water-organic extractant (A/O) to achieve high extraction efficiency with minimal amounts of extractant.The extraction process was repeated for a total of four cycles. By the third cycle, the extraction efficiency of scandium remained stable. This method proves effective in recovering trace scandium elements from pure titanium waste acid. Guoquan Z[5] et al. investigated the process of acid pressure leaching of vanadium from LD converter slag using titanium white, and simultaneously extracted Fe^{2+}, Fe^{3+}, Mn2+, Cr^{2+}, and Cr^{3+} from the titanium white acid solution. The optimal conditions for vanadium extraction from LD converter slag were found to be as follows: a temperature of 140°C, a liquid-solid ratio of 10:1, an acid concentration of 200 g · L-1, a speed of 500 r/min, and a leaching time of 90 min. Under these conditions, the vanadium extraction rate reached 96.85%. Zhou J[6]People et al. proposed a process for the synergistic recovery of scandium, using waste acid from titanium white to leach alkaline red mud. Initially, the acidity of the titanium waste acid was adjusted to 5 mol/L H_2SO_4. It was observed that the waste acid hindered the formation of silica gel in the leachate, resulting in a scandium recovery rate of 70%. Subsequently, scandium was extracted from the leachate using P204 (diethyl phosphate) - TBP (tributyl phosphate) - sulfonated kerosene under optimized conditions. The purity of Sc enrichment product in the process was 17.4%, and the total recovery rate was 68.6%. The resource utilization of titanium oleic acid mainly involves the extraction and concentration of trace elements. However, the resource utilization is mostly limited to the extraction of a single metal element. The extraction steps are complex, leading to high costs and inadequate large-scale treatment of titanium oleic acid.

2.2. Concentrate neutralization

The research on the treatment process for titanium dioxide acid wastewater mainly focuses on physical separation methods, concentration methods, neutralization methods, etc. Among these, the concentration method is considered the mainstream process used by most titanium dioxide enterprises for treating titanium dioxide waste acid.

Most enterprises use concentration devices to treat titanium waste acid to achieve comprehensive utilization. Waste acid pretreatment involves the introduction of 20% of the waste acid generated in the washing section of the titanium dioxide production line into a curing tank. Additionally, auxiliary materials and crystal crystals are added to the tank.After stirring and curing for a certain period of time, 80% of the iron and titanium in the acid precipitate out. They are then separated by membrane filter press through filtration, and the filtrate is directed into the filtrate tank to achieve comprehensive utilization. The filtered liquid in the tank is pumped to the pre-concentration tower after pre-treatment. Directly contact the high-temperature flue gas from the calcination process of the titanium dioxide production line for heat exchange pre-concentration, raising the concentration to about 25%~26%, then clarifying and separating the recovered TiO_2 through plate and frame filtration, and sending it to the steam concentration system. Acid concentration after pre-treatment of waste acid has been increased, while a certain degree of purification has also been achieved.Enter the steam-heated multi-effect vacuum concentration device, and elevate the waste acid concentration to 70%. From the three-effect evaporator, the overflow flows into the intermediate tank, and then it is pumped to the clarification tank for clarification. The clarified acid in the upper part of the clarification tank is sent to the 70% finished acid storage tank to be used in the titanium dioxide acid decomposition section. The clarification bottom slurry pump is returned to the pre-treatment maturation tank for processing[7]. The process flow chart of the waste acid enrichment unit is as follows:

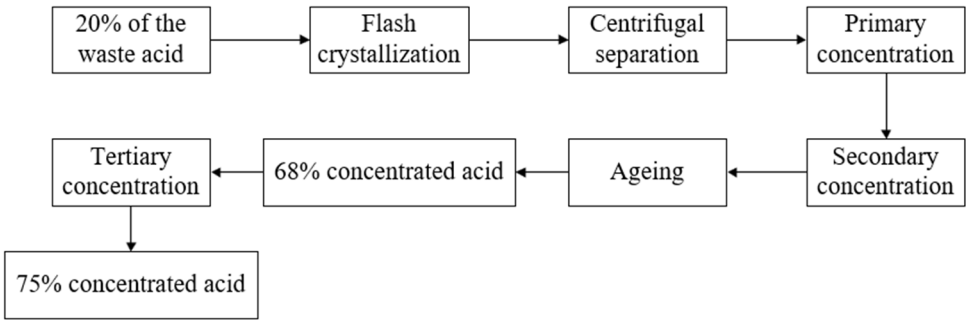

Figure 2. Process flow chart of the waste acid concentrating unit

After years of operation, the operational efficiency of the waste acid concentration device in certain titanium dioxide enterprises is unsatisfactory. Mainly reflected in several aspects including complex crafts, high operating costs, high equipment maintenance costs, and large amount of "three waste" emissions. In terms of capital investment, the waste acid concentration device has a high initial investment. The one-time investment in the equipment of a waste acid concentration device for a 10,000 t/a titanium dioxide production line is typically over 4 million yuan. For each ton of waste acid processed, the total cost, including steam consumption, water consumption, electricity consumption, labor costs, equipment depreciation costs, and operating costs for environmental facilities, is approximately 220 yuan. The high investment in equipment and operating costs have brought a lot of pressure to the company. In terms of technology, the acid concentration device has a complex process, with difficulties in equipment selection, severe equipment corrosion during operation, and high equipment maintenance costs. Most titanium dioxide enterprises' waste acid concentration equipment in the process of operation all have impurities blockage problems, making it difficult to maintain stable continuous operation. Normally, when a single unit operates continuously for 7 to 11 days, the heater will scale and block, requiring shutdown and maintenance, which affects the normal production of the enterprise. In addition, during the waste acid concentration process, there are also secondary pollutants emissions including acid mist, waste gas spray waste water, and filter residue. If mishandled, it may cause secondary pollution to the environment. Based on the above reasons, some titanium dioxide enterprises in the actual production process, choose a "passive" method of acid waste disposal, namely, the lime neutralization method. The titanium dioxide waste acid and the acidic production wastewater are pumped to the sewage treatment station together, and after being neutralized with lime milk and filtered under pressure, the wastewater is discharged, while the generated gypsum residue is piled up at the slag yard. Use lime neutralization method to treat waste acid, each ton of waste acid requires a consumption of 0.3~0.5 tons of lime, and produces 2~3 tons of gypsum residue (wet residue). Not only does it consume a large amount of lime resources, but it also produces a large amount of gypsum residue. At present, these gypsum residues cannot be effectively utilized and can only be piled up in landfill sites, occupying land resources and causing the loss of sulfur resources. Therefore, the use of lime neutralization method in treating titanium dioxide waste acid does not comply with the current environmental protection management requirements.

2.3. Treatment of titanium white waste acid by membrane separation method

Due to the high content of suspended solids and iron ions in the titanium white acid waste, it is difficult to achieve effectiveness using a single membrane treatment. Therefore, membrane integrated technology is adopted for processing. Zhao Yijiang et al.[8] proposed a new process using ceramic membrane microfiltration and diffusion dialysis in combination to treat titanium dioxide waste acid. Using ceramic membrane to filter suspended water-soluble titanium dioxide particles in the acid waste, resulting in clarified acid waste and a permeate turbidity lower than 0.5 NTU. Use ion exchange membrane diffusion dialysis technique to separate salts such as sulfuric acid and ferrous sulfate, thus obtaining purer sulfuric acid for recycling through concentration. Wang Zhigao and others[9] adopted the integrated process of ceramic membrane and nanofiltration membrane to treat titanium dioxide waste acid. The ceramic film achieves a recovery rate of 100% for titanium dioxide, while the nanofiltration membrane retains an average of over 99.9% of iron ions. The mass concentration of iron ions in waste acid can be reduced to below 15 mg/L, which can be used as wash water for washing titanium dioxide. But the operation time of this experimental study is short, and the membrane flux of the nanofiltration is greatly affected by pressure and concentration factors. When the operating pressure is 2 MPa ~ 3.1 MPa, the flux can reach 27 L/h or above. As the concentration factor increases, the flux decreases. Peng Wenbo et al.[10] adopted a ceramic membrane + reverse osmosis + nanofiltration integrated process to treat chlorination waste acid of titanium white production. The ceramic membrane recycles titanium dioxide from the waste acid, and the titanium dioxide mass concentration in the ceramic membrane effluent is below 1 mg/L, with an average flux of over 650 L/(m^2·h). The mass concentration of titanium dioxide in the concentrate is above 90 g/L. Under the conditions of operating pressure at 3.0 MPa and water recovery rate at 50%, the flux can reach above 24 L/(m^2·h) in an anti-infiltration system. Nano filtration membrane system, under the conditions of operating pressure at 8 MPa and water recovery rate at 75%, the average flux reaches 20 L/(m^2·h), and the flux recovery rate after membrane cleaning is above 96%. However, in this method, the operation of the ultrafiltration membrane causes a decrease in flux as pollutants accumulate on the membrane layer, which cannot meet normal production requirements. The cleaning method is rather cumbersome and complex, requiring acid-base chemical cleaning and continuous adjustment of pH values for washing.

Membrane treatment technology has the characteristics of simple process and no secondary pollution for waste acid treatment. However, the acidic waste containing titanic acid belongs to a particle wastewater system with strong adsorption. In the membrane treatment process, it is easy to cause membrane surface adsorption. In the course of operation, if the process control is improper, it is easy to cause a dramatic increase in membrane surface adsorption pollution, thereby resulting in membrane channel blockage. And the titanium white waste acid has high ion content and large emissions, and the membrane process treatment has high investment and high cost. Therefore, membrane fouling and high cost are huge obstacles in the large-scale promotion and application of titanium white waste acid.

2.4. Mechanical separation method

Mechanical separation method is to use mechanical structure and porous media filtration components to purify and treat chlorination titanium white waste acid. Remove the suspended particles and sediments in the turbid liquid. Sell or use it as industrial hydrochloric acid on the condition of meeting the secondary salt index requirements. This article, by designing a mechanical separation process and conducting experimental verification of the feasibility of this method.

During the experiment, the device handles hydrochloric acid flow rate of 50~80 L/h and maintains the feed pressure at approximately 0.3 MPa. The consumption of compressed

gas is approximately 0.3m^3/min. The power consumption of the device running for 72 hours is approximately 3.6 kWh. With the increase of running time, the feeding pressure rises gradually. 8 hours later, the feeding pressure will increase by 0.05MPa, and the feeding pressure will exceed 0.38MPa. And the handling of hydrochloric acid flow will also gradually decrease. After the flow decreases by 50%, it is necessary to use 10L of clean water for backwashing.

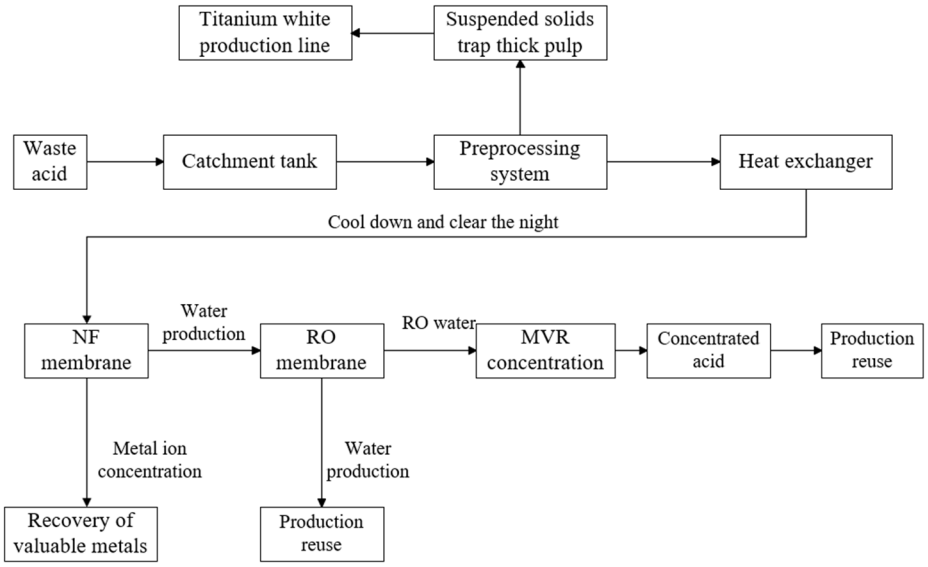

Figure 3. Treatment process of titanium waste white acid membrane treatment method

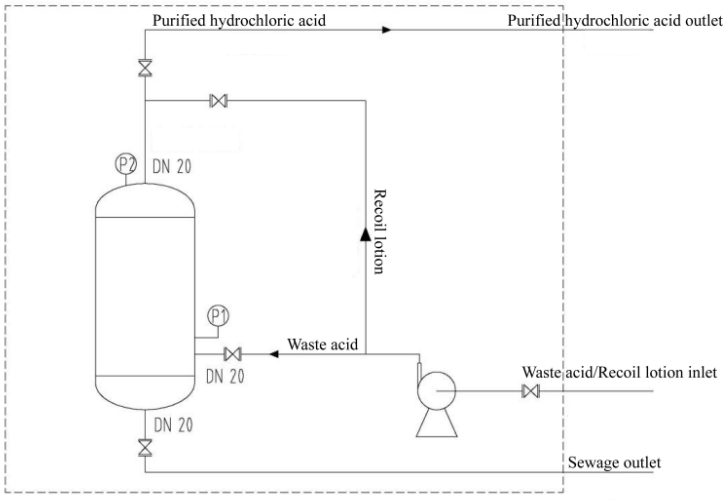

Figure 4. Flow chart of mechanical separation processing

Figure 5 presents the original liquid of a device's waste acid storage tank with a solid concentration of 292 mg/L. After continuous operation of the filter for 8 hours, the trend curve of the change in the content of purified acid outlet is observed. By the graph, it can be seen that under the condition of an inlet concentration of 292mg/L for the filter, after going through the tank filling process, the purified acid outlet quickly obtains a low solids content concentration of 79mg/L. Although during the 8-hour operation, until 4 hours of motion, the exit flow rate of the tank showed a gradual decrease, the solid content at the exit remained stable at around 76mg/L, and the solid-removal efficiency reached 75%.

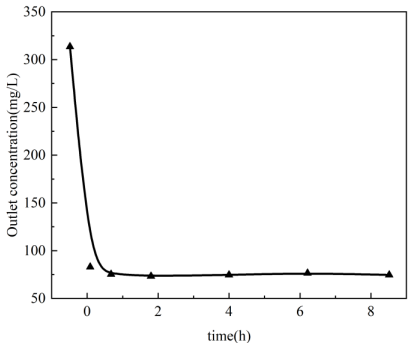

Figure 5. Change of solid concentration at the outlet of filter purification liquid (I)

Table 1 presents a comparison of hydrochloric acid components in the same apparatus tank before and after the secondary treatment. From the table, it can be seen, The composition of the pre-filtered liquid is similar to the

hydrochloric acid produced at the production site. The acid storage tank cleaning is relatively clean. Comparing the pre-filtered and post-filtered liquids, it was found that the solid content decreased from 263mg/L to 75mg/L. The solid content has decreased by 71.5%. There is a notable separation effect. The concentration of hydrochloric acid before and after filtration and the content of TiO_2 are similar, while the content of SiO_2 decreases by 74%, indicating that the biased titanium acid in the acid solution is relatively stable. If the impurities such as original silica are more likely to form, they will be intercepted by the filter plate, making the intercepting effect on SiO_2 more pronounced than that on TiO_2. And from the concentrated liquid discharged from the backwashing outlet of the filter tank, it can be seen that the filtered impurities deposit in the filter tank, further indicating that the filter has a significant interception effect on solid impurities in the waste hydrochloric acid.

Table 1. Analysis of HCl components

sample	HCl (%)	TiO_2 (mg/L)	SiO_2 (mg/L)	Fe (mg/L)	Solid content (mg/L)
Before filtration liquid 1	24.7	5578	213	3.2	263
After filtering liquid 2	25.1	5579	45.2	3.3	75
Reverse wash liquid 3	25.7	5618	525	3.4	995

As shown in Figure 6, the process of running continuously for 12 hours during this stage of the experiment is further demonstrated. The trend curve shows the variation of the outlet concentration of the filter purifying liquid over time. According to the graph, the solid concentration in the raw material liquid is 263mg/L. When the solid content in the outlet of the purifier is rapidly reduced to 75mg/L after the feed is introduced. Reflects that the filter has a rapid and significant intercepting filtering effect on particulate matter in waste acid. Afterward, the solid content of the purification liquid exported is maintained at around 75mg/L. Even after experiencing a 12-hour running time to complete the entire backwash process, the solid content of the purifying liquid remains relatively stable, and achieves a solid removal efficiency of 71.5%, with noticeable separation effects.

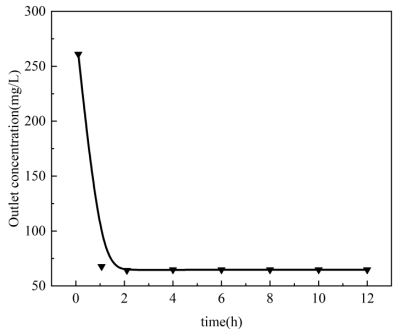

Figure 6. Change of solid concentration at the outlet of filter purification liquid (II)

Figure 7 shows the curve of pressure variation during the operation of the filter.As can be seen from the graph, when the material is pumped into the filter and adjusted to a stable operating state, the inlet pressure of the equipment is approximately 0.2MPa. As the particulate matter in the material continues to be intercepted by the filtering element, the solid concentration of the accumulated material in the tank gradually increases. And due to the colloidal nature of particulate matter, more and more particles adhere to the surface of the filtering elements. Causing the reduction of the surface area for flow through the filtering element, the decrease in flux leads to a gradual increase in pressure inside the tank, until after 8 hours of operation, the inlet pressure increases by 0.05MPa. Soon afterwards, the pressure rapidly increases, and at this time, the influence of the particles intercepted by the filtering element on the filtering flux becomes even more significant. When the operation reaches 12 hours, the inlet pressure of the tank increases to 0.38 MPa. At this time, the solid content of the purified liquid outlet remains unchanged, but the flow rate has significantly decreased by 50%, reaching the backwashing condition of the equipment. Subsequently, utilize 10L of clean water to flush the equipment, and the concentration of materials flushed out from the outlet can reach up to 1500mg/L.

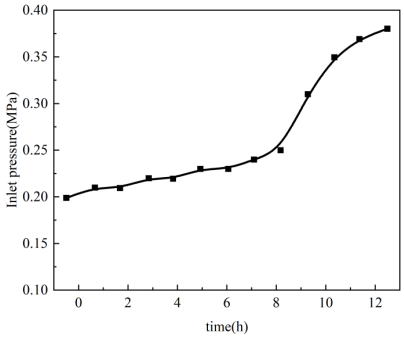

Figure 7. Material inlet pressure change of the filter

Figure 8 shows HCl, Fe, and SiO_2 over time The change trend of the same impurity content. The SiO_2 is clearly seen in Fig.The content was intercepted at the beginning of the filtration stage and was reduced from 213mg/L to 45.2mg/L, indicating that the filter element pairs SiO_2 .The impurities formed have an extremely significant filtration effect. The HCl content remained essentially constant before and after filtration, indicating that the concentration of byproduct hydrochloric acid was not affected after the filter treatment. The Fe content was detected in the filtrate, and it is speculated that the hydrochloric acid reacts with the metal at the outlet of the large acid storage tank to form the Fe^{3+}, So that the Fe content in the form of Fe elements left in the acid solution is not intercepted by the filter plate, and then discharged with the filtrate.

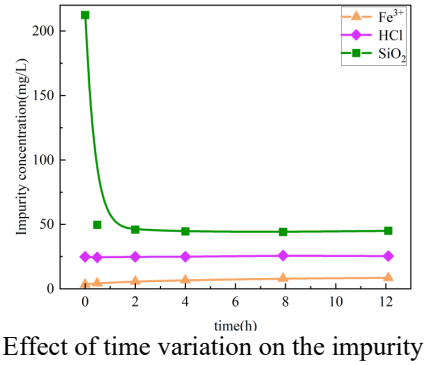

Figure 8. Effect of time variation on the impurity content of HCL, Fe and SiO_2

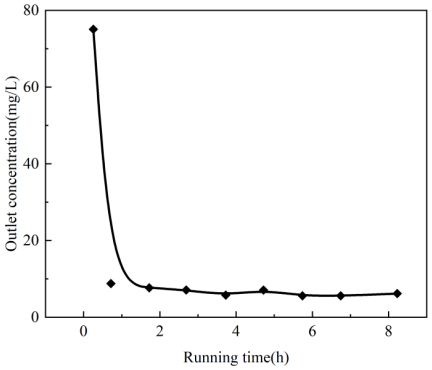

Figure 9. Solid concentration change of secondary filtration HCl outlet

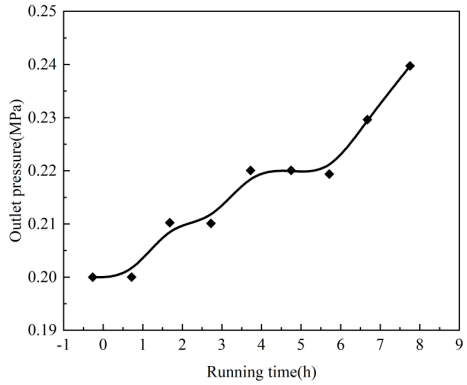

Figure 10. Pressure change at the secondary filtration inlet

The two-stage experimental results presented by Figure 5 and Figure 6 indicate. The material with an initial concentration of 263~292mg/L. The material with an initial concentration of 263~292mg/L. Furthermore, the filtrate with a solid content of 75mg/L should be filtered again, by adjusting the filtration components, to reduce the solid content in the byproduct hydrochloric acid. The change of solid content in purified hydrochloric acid during the continuous operation of the device for 8 hours is shown in Figure 9. From the graph, it can be seen that after the secondary filtration of the filter, the solid content in the waste acid is further reduced from 75mg/L to about 6mg/L. The secondary separation efficiency is 92%, while the overall separation efficiency reaches 98%. The trend in the change of inlet pressure of the filter shown in Figure 10 suggests. Due to the low solid content in the material during this process, the relatively small amount of solid impurities intercepted by the filter ensures minimal impact on the filter's flux, guaranteeing smooth operation of the filter. Through this experiment, the effect shows that the mechanical separation method can achieve the deep purification of by-product hydrochloric acid and achieve the expected result.

3. Conclusion

The waste acid generated during the production process of titanium dioxide by the chloride method is used as the raw material. Adoption of physical methods for the resource utilization of waste acid has become the mainstream method at present. However, rare metal extraction methods, concentration neutralization methods, and membrane separation techniques all have drawbacks such as complex operations and high economic costs. While the mechanical separation method is utilized to treat waste acid, it exhibits characteristics such as simple and easy operation, low equipment investment, short construction period, and stable quality of the purified by-product hydrochloric acid. All indicators meet the secondary production hydrochloric acid index and can be sold as by-products externally. All indicators meet the secondary production hydrochloric acid index and externally can be sold as by-products. Realized the resource utilization of waste chloride-process titanium dioxide, significant economic and environmental benefits. The mechanical separation method provides another new way for reusing waste acid from the chloride method of titanium dioxide.

Acknowledgment

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