Wastewater from production of oxide-ruthenium titanium anodes as a raw material for TiO₂, NaOH and HCl production

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Abstract. The article presents the results of studies of the waste acid pickling solution processing (WAPS) formed during the etching of titanium products with hydrochloric acid. The processing includes the neutralization of WAPS with alkali, filtering, drying and calcining a precipitate of titanium hydroxide and electrochemical processing of the filtrate containing sodium chloride in an electrolytic cell with ion-exchange membranes. In the electrolysis process, sodium hydroxide and hydrochloric acid are obtained. The proposed WAPS processing scheme makes it possible to obtain titanium dioxide, sodium hydroxide, and hydrochloric acid. Titanium dioxide can be used in the paint industry. Alkali can be used in the process of neutralizing WAPS. After adjustment, hydrochloric acid is suitable for use in the etching process of titanium products.

1. Introduction
Interest in titanium and alloys based on it is caused by their good structural properties, high strength-to-density ratio, high corrosion resistance, high melting point. Titanium is used in various fields: aviation, rocket engineering, mechanical engineering, shipbuilding, medicine, petrochemical chemical engineering, etc.

The manufacture of titanium products, especially the application of modifying coatings to its surface, is hindered by a strong oxide film. Removal of this film is carried out by various methods [1-3]. Processing of the titanium surface with acids has become widespread [4]. In particular, at Bashkir Soda Company, the preparation of the titanium surface consists of degreasing, etching and washing operations. Etching of titanium occurs in 25-27% hydrochloric acid at a temperature of 80-850 °C. In this case, a waste acid etching solution (WAPS) is formed containing TiCl₄ and residual HCl. This solution is toxic enough and must be either diluted or recycled before discharge. Existing WAPS processing methods result in precipitation of titanium hydroxide and substances containing chlorides. As a result, the problem arises of their disposal [5-10].

The article presents the results of studies of the WAPS processing formed during the etching of titanium products with hydrochloric acid.

2. Materials and methods
We studied the processing of WAPS obtained by etching titanium with hydrochloric acid containing 242 g/l of titanium chloride and 110 g/l of hydrochloric acid.

The processing consisted of a number of operations. Initially, the WAPS was neutralized by NaOH and, after precipitation, Ti(OH)₄ was filtered. The precipitate Ti(OH)₄ was calcined for 1 hour at a...
temperature of 900 °C. The filtrate with wash water containing about 50 g/l NaCl was subjected to electrochemical processing in a membrane electrolyzer, schematically shown in Figure 1.

![Diagram of Electrolyzer](image)

**Figure 1.** The scheme of the experimental installation: 1,2,3,4 – chambers of the electrolyser; 5 – tank with the filtrate; 6,8 – pumps; 7 – tank with the sulfuric acid; 9 – direct current source; 10 – tank with the alkali; 11 – tank with the hydrochloric acids.

The electrolyser consisted of four chambers - cathode 1, anode 4 and two middle 2,3. To separate the chambers, cation exchange K and anion exchange A membranes of the MK-40 and MA-40 brands were used. The electrode chambers are made in the form of recesses in plexiglass plates. The middle chambers are made in the form of frames from a PVC plate 2 mm thick. Plates of titanium coated with ruthenium oxide are used as electrodes. The whole structure of the studs pulled together in a single package. To prevent contact between the ion-exchange membranes, a mesh expanded from calendered vinyl plastic was placed in the chambers. The working surface of each ion-exchange membrane was 30 cm².

The test solution containing sodium chloride was pumped through the middle chamber 2 of the electrolyzer. Under the influence of an electric current, sodium ions were transferred to the cathode chamber 1 of the apparatus. In this chamber at the cathode, water decomposed with the evolution of hydrogen and formation of hydroxyl ions. As a result, an alkali solution was concentrated in the
cathode chamber. The cathode chamber has an outflow and the alkali accumulating in it left the chamber by gravity and collected in a container 10.

Chlorine ions migrated through the anion-exchange membrane into chamber 3 of the apparatus. Their further advance to the anode was hindered by a cation exchange membrane. A 0.1 N solution of sulfuric acid was pumped through the anode chamber 4. In this case, water decomposed on the anode with evolution of oxygen and the formation of hydrogen ions, which were transferred to the cell 3 of the electrolyzer. In this chamber, hydrochloric acid was concentrated by gravity flowing out of the apparatus as it accumulated and collected in tank 5. To provide the necessary electrical conductivity of the electrolyzer, at the initial times, a 0.1 N sodium hydroxide solution was poured into cathode 1, and a 0.1 N solution was poured into the hydrochloric acid electrolysis chamber 3. An adjustable rectifier was used to power the electrolyzer, which made it possible to provide the required current load.

Every 30 min, the solutions collected in containers 10 and 11 were analyzed for alkali and hydrochloric acid.

3. Results and Discussion

To study the process of extracting titanium from WAPS with alkali treatment, various amounts of sodium hydroxide were added to a number of samples containing 50 ml of WAPS. After the formation of a precipitate of titanium hydroxide, it was filtered off, dried and calcined at a temperature of 900 °C for 1 hour. In this case, titanium hydroxide was converted into dioxide. The maximum amount of titanium dioxide, which can be obtained in this case, is 0.835 g. The pH value was determined in the filtrate. The dependence of the degree of extraction of titanium from WAPS by its treatment with alkali on the pH of the filtrate is presented in table 1.

| pH   | Mass of the TiO₂ (grams) | Recovery degree (%) |
|------|--------------------------|---------------------|
| 3.75 | 0.724                    | 86.7                |
| 5.5  | 0.765                    | 91.6                |
| 6.45 | 0.799                    | 95.7                |
| 7.2  | 0.815                    | 97.6                |
| 7.6  | 0.830                    | 99.4                |
| 7.8  | 0.835                    | 100.0               |
| 9.4  | 0.836                    | 100.1               |
| 9.85 | 0.835                    | 100.0               |
| 10.6 | 0.834                    | 99.9                |

An increase in the pH of the filtrate after isolation of titanium hydroxide to a value of 7.6 leads to an increase in the degree of extraction of titanium from WAPS. At a pH of the filtrate of more than 7.6, the degree of titanium extraction from the WAPS reaches 100%. The optimal pH of the filtrate after treatment with WAPS with sodium hydroxide is in the range of 7.6 - 7.8.

The process of electrochemical processing of the filtrate obtained from WAPS after its treatment with alkali was studied at membrane current densities of 10 mA / m², 20 mA / m², 30 mA / m² and 40 mA / m², which corresponded to a current load on the cell of 0.3 A, 0.6 A, 0.9 A and 1.2 A. The electrochemical treatment of the filtrate was carried out until the concentration of solutions of sodium hydroxide and hydrochloric acid at the outlet of the apparatus stopped growing. Thus, the maximum concentration of products of electrochemical processing of the filtrate was obtained.

Figure 2 shows the relationship between the concentration of sodium hydroxide and the time of the electrochemical treatment of the filtrate at various current loads.
The increase in the concentration of sodium hydroxide in the cathode chamber of the electrolyzer continues for 90 minutes. Moreover, its formation rate and final concentration are determined by the current density. So, at a current density of 10 mA/cm², the rate of sodium hydroxide formation is 1.1 g/l·min, and at a current density of 40 mA/cm², the rate of sodium hydroxide formation is 2.4 g/l·min. The maximum concentration of sodium hydroxide flowing from the apparatus varies from 100 g/l with a current density of 10 mA/cm² to 216 g/l with a current density of 40 mA/cm².

**Figure 2.** The dependence between the concentration of NaOH and time:

Current density, mA/cm²: 1 - 10; 2 - 20; 3 - 30; 4 - 40.

**Figure 3.** The dependence between the concentration of HCl and time:

Current density, mA/cm²: 1 - 10; 2 - 20; 3 - 30; 4 - 40.
Figure 3 shows the relationship between the concentration of hydrochloric acid and the time of electrochemical treatment of the filtrate at various current loads.

In contrast to the dependence of the sodium hydroxide concentration on the time of the filtrate electrochemical treatment (Figure 2), the time to reach the maximum concentration of hydrochloric acid in the chamber 3 of the electrolyser decreases with increasing current density. So, at a current density of 10 mA / cm$^2$, the maximum concentration of hydrochloric acid is reached after 120 minutes, and at a current density of 40 mA / cm$^2$, the maximum concentration of hydrochloric acid is reached after 80 minutes. In this case, the rate of formation and the maximum concentration of hydrochloric acid behave similarly to the behavior of sodium hydroxide. The rate of hydrochloric acid formation varies from 0.3 g / l·min at a current density of 10 mA / cm$^2$ to 1.1 g / l·min at a current density of 40 mA / cm$^2$. The maximum concentration of hydrochloric acid flowing from the apparatus is 36.5 g / l at a current density of 10 mA / cm$^2$ and 89.4 g / l at a current density of 40 mA / cm$^2$.

4. Conclusion
Based on the results obtained in the study of the processing of WAPS for production of titanium products, a technological scheme is proposed, as shown in Figure 4. The WAPS is treated with sodium hydroxide to a pH of 7.6 - 7.8. The precipitate of titanium hydroxide is filtered off, dried and calcined. The resulting titanium dioxide can be used in various industries. The filtrate containing sodium chloride is processed in a four-chamber electrolyser with cation exchange and anion exchange membranes. The result is sodium hydroxide with a concentration of up to 216 g / l and hydrochloric acid with a concentration of about 89.4 g / l, respectively. Sodium hydroxide can be used in the process of neutralizing WAPS, and hydrochloric acid after adjusting its concentration during etching of the titanium surface.

![Figure 4. Technological scheme of WAPS processing](image)

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