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Processing of spent pickling liquor formed during treatment of titanium products

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Abstract. The article presents the research findings on processing of spent acid pickling liquor (SAPL) formed during etching of titanium products. The processing includes neutralizing the SAPL with alkali, filtering, drying and calcining the titanium hydroxide precipitate as well as electrochemical processing of the filtrate in an ion-exchange membrane cell. The proposed SAPL processing procedure allows obtaining titanium dioxide, sodium hydroxide and a mixture of acids. Titanium dioxide can be used in paint-and-varnish industry. The alkali can be used in neutralizing the SAPL. A mixture of acids is suitable for use in etching process of titanium products.

1. Introduction

The interest in titanium and titanium-based alloys is explained by their good mechanical properties, high strength-to-density ratio, high corrosion resistance and high melting point. Titanium therefore is used across various fields: aviation, rocket engineering, mechanical engineering, shipbuilding, chemical engineering, medicine, etc.

The manufacture of titanium products especially the application of modifying surface coatings is prevented by a strong oxide film. This film is removed by various methods. Treatment of titanium surface by acids is widely used. One of the promising liquors for etching of titanium is a mixture of hydrofluoric and hydrochloric acids. As a result of titanium etching by this liquor a spent acid pickling solution (SAPL) containing in its composition titanium fluoride, hydrofluoric acid and hydrochloric acid is formed. This liquor is quite toxic and must be subjected to either repeated dilution or processing. The existing methods of SAPL processing lead to formation of titanium hydroxide precipitates and substances containing fluorides. As a result, there is a problem of disposal of these precipitates [1-10].

The article presents the research findings on processing of SAPL to obtain titanium hydroxide and a mixture of acids suitable for preparation of etching liquor used in manufacture of titanium products.

2. Materials and methods

The processing of SAPL obtained during etching of titanium with a mixture of hydrofluoric and hydrochloric acids has been analyzed. The SAPL contained 21.9 g/l of titanium fluoride, 1.7 g/l of hydrofluoric acid and 6.2 g/l of hydrochloric acid.

The processing procedure contained a number of operations. Initially, the SAPL was neutralized with NaOH and after precipitation of Ti(OH)₄ was filtered. Ti(OH)₄ precipitate was dried and
calcined. Filtrate containing NaF and NaCl was electrochemically processed in a membrane cell shown in Fig. 1.

The cell consisted of four chambers – cathode chamber 1, anode chamber 4 and two medium chambers 2 and 3. To separate chambers cation-exchange K and anion-exchange A membrane of MK-40 and MA-40, respectively were used. Electrode chambers are made in form hollows in plexiglass plates sized 5 mm. The middle chambers are made in form of frames made of a polyvinylchloride plate 2 mm thick. Titanium plates coated with ruthenium oxide were used as electrodes. The entire structure tightened with studs into a single package. To prevent contact between ion-exchange membranes, an expanded mesh of calendered vinyl plastic was placed into chambers. The working surface of each ion-exchange membrane was 30 cm$^2$.

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 hydrofluoric and hydrochloric acids.

The test liquor containing fluoride and sodium chloride was pumped through the cell’s middle chamber 2. Under electric current sodium ions were transferred to the cathode chamber 1 of the apparatus. In this chamber at the cathode water decomposed with release of hydrogen and formation of hydroxyl ions. As a result an alkali solution was concentrated in the cathode chamber. The cathode chamber was non-flowing and the alkali accumulating in it left the chamber by gravity and was
collected in a container 10. The fluorine and chlorine ions migrated through the anion-exchange membrane to the chamber 3 of the apparatus. Their further advancement to the anode was prevented by the cation-exchange membrane. A 0.1 N sulfuric acid solution was pumped through the anode chamber 4. At the same time, on the anode water decomposed with release of oxygen and formation of hydrogen ions which were transferred to the cell’s chamber 3. In this chamber hydrofluoric acid and hydrochloric acid were concentrated and gravity flowed out of the apparatus as they accumulated in a container 5. To ensure the necessary electrical conductivity of the cell at the initial time 0.1 N sodium hydroxide solution was poured into cathode chamber 1 and 0.1 N hydrochloric acid solution was poured into cell’s chamber 3. To supply the cell an adjustable rectifier was used to provide the necessary current load.

Every 30 minutes the solutions collected in containers 10 and 11 were analyzed for the content of alkali, hydrochloric acid and hydrofluoric acid.

3. Results and Discussion

To study the extraction of titanium from SAPL by its alkali treatment a different amount of sodium hydroxide was added to a series of samples containing 50 ml of SAPL. After formation of titanium hydroxide precipitate it was filtered, dried and calcined at 900°C for 1 hour. At the same time titanium hydroxide has gone over to dioxide. The maximum amount of titanium dioxide which in this case can be obtained is 0.835 g. The pH in the filtrate was determined. Degree of titanium recovery from SAPL by its alkali treatment versus pH of the filtrate is presented in Table 1.

Table 1. Dependency of the recovery degree of titanium from SAPL on the pH of the filtrate

| 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                |
| 12.8| 0.837                    | 100.2               |

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

The electrochemical processing of the filtrate obtained from SAPL after its treatment with alkali was investigated at membrane current densities of 200 A/m², 400 A/m², 600 A/m² and 800 A/m² which corresponds to a current load of 0.6 A, 1.2 A, 1.8 A and 2.4 A. The electrochemical processing was carried out until the concentration of sodium hydroxide solutions and a mixture of hydrochloric and hydrofluoric acids ceased to grow. Thus, the maximum concentration of products of the filtrate electrochemical processing was obtained.

Figure 2 shows the dependence of sodium hydroxide concentration on duration of electrochemical treatment of the filtrate at different current loads on the cell. The rate of the sodium hydroxide formation increases by increasing the current density. Thus, at a current density of 200 A/m² the rate of alkali concentration is 26.1 g/l·h, and at a current density of 800 A/m² it is 179.2 g/l·h. The maximum concentration of sodium hydroxide in the cathode chamber was at a current density of 800 A/m² after 5 hours and amounted to 374 g/l.
Figure 3 shows the dependence of hydrofluoric acid concentration in the acid concentration chamber on duration of electrochemical treatment of the filtrate at different current loads on the cell. The concentration rate of hydrofluoric acid increases by increasing current load on the cell. At a current density of 200 A/m² the rate of hydrofluoric acid formation is 16.8 g/l·h, and at a current density of 800 A/m² is 33.1 g/l·h. The maximum concentration of hydrofluoric acid is observed at a current density of 800 A/m² and amounts to 65.2 g/l.

Figure 2. Dependence of concentration NaOH on time: Current density 1 - 200 A / m²; 2 - 400 A / m²; 3 - 600 A / m²; 4 - 800 A / m².

Figure 4 shows the dependence of hydrochloric acid concentration in acid concentration chamber on duration of electrochemical treatment of the filtrate at different current loads on the cell. The behavior of hydrochloric acid concentration versus the processing time is similar to that considered earlier. The rate of hydrochloric acid concentration is higher than that of hydrofluoric acid. At a current density of 200 A/m² it is 24.5 g/l·h, and at a current density of 800 A/m² it is 40.9 g/l·h. The maximum concentration of hydrochloric acid is observed at a current density of 800 A/m² and is 51.1 g/dm³.

4. Conclusion
Based on the results obtained during processing of the SAPL, a process flow diagram is proposed, shown in Figure 5. The SAPL is treated with sodium hydroxide to pH of 7.6 - 7.8. The titanium hydroxide precipitate is filtered, dried and calcined. The resulting titanium dioxide can be used in paint-and-varnish industry. The filtrate containing sodium fluorides and chlorides is processed in a membrane cell. The result is sodium hydroxide with a concentration of up to 374 g/l and a mixture of hydrochloric and hydrofluoric acids with a concentration of about 51.1 g/l and 65.2 g/l, respectively. Sodium hydroxide can be used in neutralizing of SAPL and a mixture of hydrofluoric and hydrochloric acids can be used in surface etching of titanium.
Figure 3. Dependence of concentration HF on time: Current Density. 1 - 200 A / m$^2$; 2 - 400 A / m$^2$; 3 - 600 A / m$^2$; 4 - 800 A / m$^2$.

Figure 4. Dependence of concentration HCl on time: Current Density. 1 - 200 A / m$^2$; 2 - 400 A / m$^2$; 3 - 600 A / m$^2$; 4 - 800 A / m$^2$. 
Figure 5. Technological scheme of processing SAPL

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