Production of metallic titanium and pigment titanium dioxide has a strict requirement to raw material, in relation to content of TiO₂ and destructive admixtures (Fe₂O₃, Cr₂O₃, V₂O₃, etc.). Therefore the basic titanium raw materials are natural rutile concentrates, containing up to 90-96% of TiO₂. In the event of non-availability of natural rutile, there are used slags with high content of titanium (>85% TiO₂) from electric melting of the good-quality ilmenit concentrates, resources of which are limited. At the same time enormous resources of titanium magnetites are out of the balance of raw materials for titanium production, because for their concentrates (50-60% Fe and 5-15% TiO₂) there is no effective and economical industrial methods of processing with titanium production. In several countries organized production of "artificial rutile", which by its content is close to rutile concentrates and contains >90% of TiO₂ and admixtures, which further has to be removed.

From the other side, great perspectives are discovered by possibility of extraction of minerals resources from offshore, shelf and coastal deposits. Several countries already for a long time developing from offshore deposits such a valuable materials as rutile, titanium magnetite, ilmenit, zircon, etc, which are big sources of raw for production of titanium and its fusions.

Placer-like titanium magnetites, except iron, contain isomorphously replacing Fe³⁺ in the crystal grating of magnetite, such a valuable components as Ti, Cr, V, Mn, etc., which at the magnetic enrichments are concentrated in the magnetite concentrate, and that, considering the easiness and cheapness of their production and enrichment, makes them important source of these elements obtainment. For example, concentrate from titanium magnetites deposits of the south-west coast of Caspian Sea in Azerbaijan contains: Fe- 58%, TiO₂ - 12%, Cr₂O₃ - 1.5%, V₂O₅ - 1%. Therefore we had a task of development of technology for their integrated and effective usage.

Known technological schemes of titanium magnetites processing are distinguished by their complication and expensiveness, they require a big
consumption of fuel-energetic resources, consist of a lot of stages and followed by losses of valuable components.

Technology of integrated processing of placer-like titanium magnetite concentrations has been developed in the institute and was tested, using samples from the coastal and shelf deposits of titanium magnetite of Southwest Caspian coast in Azerbaijan, Black Sea coast of Georgia, Tatar Strait and Kuril range of the Pacific coast of Russia. The process includes the following stages: solid-phase reduction of titanium magnetite by natural gas at 850-900°C, soda being added; leaching of reduced product and magnetic separation of pulp to obtain naturally-alloyed iron powders of high make; treatment of the carbonate-vanadate solutions to make carbonized extraction of \( \gamma \)-aluminum oxide, extraction recovery of vanadium pentaoxide and soda regeneration; hydrochemical processing of titanium-chromium fraction to obtain sodium chromate and titanium dioxide.

Differing from the known methods of titanium magnetites processing, in which product, obtained after iron reduction, melts with production of vanadic cast iron and titanium slag \( /V/ \), in our method iron, reduced at solid phase, separates through wet magnet separation from titanium and chromium, which concentrate in non-magnetic titanium-chromium fraction.

Multifunctional adding of salt in the main process of reduction furthers destruction of grating of stable titanium magnetites, improvement of iron metallization conditions, formation of titanates, aluminates, silicates, chromites, oxidation of \( V^{2+} \) to \( V^{3+} \) and formation of vanadates, and this facilitates separation of \( Fe_{\text{met}} \) from titanium and other components and creates good conditions for further processing.

There have been established the major regularities and factors influencing the iron oxides reduction, the destruction and extraction of titanium, chromium and vanadium (3) oxidation in the reduction medium, when soda participated; thermodynamics and mechanism of the processes have been studied \( /7-9/ \). By means of high-temperature X-ray phase analysis of the mixture being reduced in combination with thermographic studies, the intermediate and final compounds have been identified and the temperature intervals of the processing reactions have been determined \( /7/ \).
According to developed technological scheme of the main process (fig.1), concentrate from coastal deposits, containing 54-60% of Fe, 7-12% of TiO₂, up to 1% of V₂O₅ and up to 1.5% of Cr₂O₃, after milling is mixed with estimated amount of soda and granulating by water in revolving roller. Obtained pellets are reduced at 875-900°C by natural gas in reactor of mexican retort type. Degree of metallization is 98-100%. In purpose of separation of Fe met from Ti, Cr and other components of oxide phase, the reduced pellets after cooling to 60-70°C are placed into water (H:L = 1:4) and milled in ball mill. Alkali environment preserves reduced iron from oxidation. Pulp undergoes wet magnet separation, which separates magnetic and non-magnetic fractions and carbonate-vanadate solution. From magnetic fraction it is extracted a naturally alloyed iron powder of high-make (98% of Fe met). Degree of ion extraction is 98%.

Carbonate-vanadate solution, containing 1.5 g/l of V₂O₅, as sodium vanadate, part of aluminum and silicon, as aluminate and silicate, and soda, undergoes processing with carbonization and extraction γ Al₂O₃, extraction of vanadium from carbonate solution and obtainment of V₂O₅ of high content (99.7%) and regeneration of soda, which follows back to the process of pellets granulation. Degree of V₂O₅ extraction from titanium magnetites reaches 99.5%.

Content of TiO₂ in non-magnetic titanium-chromium fraction reaches 35-45%, Cr₂O₃ - 5%. Titanium-chromium fraction goes to the hydro-chemical processing (fig.2). Waste waters come together with vanadate solution. Degree of titanium extraction - 98.6%, chromium - 100%.

In titanium-chromium fraction, except titanium and chromium, there are calcium, magnesium, manganese, remains of iron, and also part of silicon and aluminum as aluminum silicate. Therefore, after mixing with estimated amount of soda, the fraction frits at 800-850°C and lixiviates at hot water (H:L = 1:4) at 85-95°C and through mixing.

In these optimal conditions Cr³⁺ oxidizes to Cr⁵⁺ and after filtration and ablation of solid phase completely separates from titanium and goes to chromate solution together with part of aluminum and up to 40% of silicon from decomposed aluminum-silicates. Mn²⁺ does not turn to Mn⁶⁺ and completely masses in titanium fraction together with other admixtures. Even significant surplus of soda at the fritting does not increase separation of silicon, because of the difficult aluminum-silicates
Titanium magnetites from coastal and shelf deposits
Fe - 54-60%; TiO₂ - 7-12%; Cr₂O₃ up to 1.5%; V₂O₅ up to 1%

Milling and mixing

Pelletting (granulation) with water

Reduction
T - 875-900°C

Cooling to 60-70°C and placing of reduced product into water (H : L = 1 : 4)

Milling in water

Wet magnetic separation and filtration

Magnetic fraction
Ablution and drying at 60°C
Naturally-alloyed iron powder Fe₉₆ - 98%; Extr.degr.-98%

Non-magnetic fraction
Ablution and drying at 110-115°C
Titanium-chromium fraction TiO₂ - 35-45%; Extr.degr.-98.6%
Cr₂O₃ - up to 5%; Extr.degr.-100%

Carbonate-vanadate solution V₂O₅ - up to 1.5g/l; Extr.degr-100%

Carbonization and extraction of γ-Al₂O₃, extraction of V₂O₅ and regeneration of Na₂CO₃

γ-Al₂O₃, V₂O₅-99.7% E.d.-99.5%

Fig. 1 - Technological scheme of processing of titanium magnetite concentrations from coastal and shelf deposits
Titanium-chromium fraction TiO₂ - 35-45%; Cr₂O₃ - up to 5%

1. Mixing
2. Na₂CO₃
3. Fritting at 800-850°C; t - 30 min
4. Lixiviation by water
   H:L = 1:4; t - 85-95°C; t - 5 min
5. Filtration and ablution
6. Titanium fraction
   TiO₂ - 40-50%; and admixtures:
7. Treatment by HCl
   H:L = 1:8, t - 85-95°C
8. Spinning and ablution by acidified water
9. Enriched titanium product
10. Exsilication of 3-5% NaOH
    H:L = 1:4-6; t - 95-100°C; t - 20-30 min
11. Filtration and ablution by alkaliescent water
12. Drying and calcination at 850-900°C
13. Chromatic solution
14. Staged carbonization
15. CO₂
16. Regeneration of HCl
17. Acid solution
18. Evaporation
19. Surplus for Mn extraction
20. Na₃SiO₃ solution

Titanium dioxide - "artificial" rutile (TiO₂ - 98%; Extraction degree - 97%)

Fig. 2 - Technological scheme of titanium-chromium fraction processing
Titanates are enriched by Na₂O, and content of TiO₂ in titanium fraction increases to 40-50%.

Chromate solution is utilized by method of staged carbonization by CO₂. At the initial carbonization to pH - 8.15 at 60°C, precipitate of sodium aluminum-silicate isolates and solution is refined to silicon and aluminum. After solution evaporation till saturation with soda and cooling to 40°C, secondary carbonization occurs to pH - 7 with separation of basic mass of NaHCO₃. The last carbonization at pH - 7 allows reminders of NaHCO₃ isolation. From cleaned chromiwn solution, technical Na₂CrO₄ (>90%) is produced. NaHCO₃, washed by cool water, is calcinated at 300°C and regenerated soda returns to the fritting process. Degree of chromium extraction is 96%, regeneration of initial soda - 82%, at degree of soda extraction from chromiwn solution - 98%.

To refine from admixtures titanium fraction is treated by HCl. The treatment is carried using 15% HCl, at proportion H:L = 1:8-10, scilicet at 2 times excess of acid at stehiometrics at temperature close to boiling, when coagulant is present. These conditions allows to turn all admixture components, except silicon, to liquid phase, and that ensures deep refining of TiO₂ and prevents its losses. The product of acid decomposition of silicates and aluminum-silicates is an insoluble SiO₂*H₂O, which stays with titanium. Obtained pulp is spunned with separation of waste solution and metatitanium acid, which is washed by hot acidified water.

From waste HCl solution, there are HCl regenerated and manganese extracted.

Enriched titanium product, containing about 90% TiO₂, exsilicated by 3-5% NaOH solution at H:L = 1:4-6, t - 95-100°C during 20-30 minutes. Good dissolubility of the free silicon acid in alkali solutions allows to clean TiO₂ from silicon fully enough. Herewith there are no losses of titanium in alkalescent solutions. Then solid phase is separated from silicate solution by filtering, washed by alkalescent water and dried. TiO₂*H₂O with X-ray amorphous structure is obtained. To turn it to the rutile form it is fritted at 850-900°C. Herewith TiO₂*H₂O firstly (before 400°C) wastes hydrated water, and then turns to anatase form and at temperature over 800°C takes stable rutile form. Simultaneously the product is refined from volatile admixtures.

Features of developed technology are frugality, integration and unwastableness and high extraction of TiO₂ - 96-97% and obtainment of high quality artificial rutile.
(98% TiO₂) valuable raw for production of metallic titanium and obtainment of pigment titanium dioxide.

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