Improvement of the process and apparatus in production of titanium tetrachloride

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ANNOTATION

The results of theoretical and experimental studies of the institute employees on improvement of technology and equipment for titanium slag chlorination in a melt of chloride salts and purification of crude titanium tetrachloride are summarized.

Key words: titanium slag, chlorination, melt of chloride salts, titanium tetrachloride, purification.

The titanium tetrachloride - a major intermediate product in a chlorine metallurgy of titanium - in Russia is produced by method of titanium slag chlorination in the chlorides melt. The application of this technology began in 1961 at the Titanium and Magnesium Works in the town of Berezniki. Necessity for designing of high capacity equipment had required performance of physico-chemical investigations of such processes as chlorination of titaniferous raw materials, suspended in the melt of chloride salts, condensation of chlorination products and titanium tetrachloride purification.

The employees of the institute A.B.Bezukladnikov, V.A.Bezvoritny, D.P.Bajbakov and A.M. Stupina have executed in melts of alkaline and earth metals chlorides investigations of kinetics and mechanism of titanium dioxide chlorination, have studied diffusion coefficients of chlorine and ferric ions, have investigated equilibrium concentrations of iron chlorides, have determined velocity of absorption and solubility of chlorine [1-8].

The results of performed investigations are applied for making a calculation procedure for gas-lift type chlorinator as an absorbing device [9]. In the procedure, proposed by the authors, the gasodynamic characteristics determined at testings of an experimental chlorinator are applied. By results of experiments the nomogram interlinking duration of gas contact with the melt, velocity of a bubble, gas content in a melt and gas reduced velocity in chlorinator is obtained.

Design feature of a gas-lift type chlorinator is the division of the device salt bath by vertical partitions on the bubble and circulation chambers communicating through flow channels located at a lower part of the partitions [1]. The separating partitions ensure an optimum hydrodynamical mode of circulation flows in a salt bath of a chlorinator.

The improved computational method of gas-lift type chlorinator with use of conjugate physical and mathematical model was worked out [10]. The physical model allows to determine an aggregate coefficient of local resistances along a circulation loop, mathematical model allows to determine characteristics of chlorinator gas-liquid flows (gas content, reduced velocities, etc.). It is shown, that velocities of melt in bubble and circulation chambers, amount of circulating gas flow and the degree of chlorine absorption depends to great extent on the sizes of flow channels located at a bottom of chlorinator. The chlorine consumption has much smaller effect on these magnitudes. During chlorinator testings, which design was carried out with taking into account numerical experiment results, an expected chlorine absorption was achieved. The chlorinator steadily worked under gaseous loadings ranged in value to 40 %; there had been no charge depositions on a bottom within 3 months.

Gastightness and thermal properties of stamped mixes on a base of powdered graphite and mineral oil were determined, the dependences of these properties on composition and thermochemical treatment by components of vapor-gaseous mixture were investigated. It is shown, that the gastightness of the proposed compositions makes up approximately one tenth part of that of the known compositions. At filling-up of the...
expansion gap between lining and chlorinator steel shell by the stamped mix containing wastes of treatment of graphitized blocks and mineral oil, shell protection against corrosion by vagabonding gases and reduction of gas emission from tuyeres by 40-50 % are ensured and also chlorinator service life is doubled.

At titanium dioxide concentration in the chlorinator melt less than 1 mass % "melttable" sublimates are precipitated in condensation system [11]. By laboratory investigations [12] it is shown, that the base of "melttable" sublimates make up NaCl, AlCl₃ and FeCl₃, which contents was in a range 22 -27; 39,8 - 48,9 and 26 - 36 mass. % respectively, the crystallisation temperature of "melttable" sublimates makes up 144 – 150 °C. It is found, that under acidification of melttable sublimates by air in a temperature range 250-350 °C the specific velocity of chlorine emission is changed from 0,82 up to 5,23 g / (h * m³). The results of investigations became the basis for construction of the precooling chamber of vapor-gaseous mixture with the melt receiver. The optimum geometrical sizes of the melt receiver and bubble channels, quantity and arrangement of latter were determined by model testings of the device on system " water - air ". For observance of similarity requirements the full-scale model was made [14]. At sketching equipment a two-stage device had been proposed, its stages were integrated by the warmed melt receiver. Gas-lift type devices for melt agitation and for spraying of vapor-gaseous mixture by the melt to catch charge particles were located in a plane that separated two stages. The process conducting with the permissible chlorine contents in off-gases is possible either by inert gas feed into the melt or by air feed (in this case the melt temperature should not exceed 350 °C).

The major part of heat transferred by vapor-gaseous mixture in system of condensation (55 - 65 %) is taken away in scrubber. The device should ensure prompt cooling of vapor-gaseous mixture down to the temperature which is lower than a dew-point of titanium tetrachloride and maximal catching of impurity chlorides. The two-stage spray scrubber with tangential feed of vapor-gaseous mixture in the second stage that corresponds to the indicated requirements and ensures practically a complete catching of drops from a flow is designed.

The experimental and theoretical studies became the basis for designing high capacity chlorinating installation including a gas-lift type chlorinator, chamber for precooling of vapor-gaseous mixture with a melt receiver of sublimates, spray scrubber, condensers, pumps and tanks [14]. The base technical solutions and computational method of dimensions of the chlorinator salt bath allow to design chlorinating installations with productivity of 150 - 300 tons of titanium tetrachloride per 24 hours.

Major stage of titanium tetrachloride production which determines technological and mechanical properties of materials is the purification of the crude product from impurities. The existing flow sheet includes two-stage chemical purification from vanadium (by copper powder - down to the residual vanadium content less than 0,01 mass. % and lowest titanium chlorides - down to vanadium content no more than 0,0002 mass. %), rectification and distillation. During the chemical purification vanadium oxychloride forms slightly soluble in titanium tetrachloride chloride vanadium compositions [1]. An obtained copper-vanadium pulp is treated in accordance with chloride - rectifying technology, founded on chlorination of the pulp in the melt of chlorine salts at 450 – 550 °C and separation of an obtained mixture of TiCl₄ – VOCl₃ on components by rectification. In this case vanadium extraction does not exceed 70 %. The distillation residue including an aluminium – vanadium pulp and surplus of the lowest titanium chlorides is processed in a chlorinator with titanium slag. Flow chart for production of titanium tetrachloride (chlorination; fractional condensation, purification and Cu-V pulp utilization) is shown in Figure.

The low-waste rectification - chemical technology was tested and the high capacity equipment for crude titanium tetrachloride purification from vanadium oxychloride was proposed. The technology includes vanadium separation down to content of 0,01 mass % by method of rectification and final purification down to vanadium content of no more than 0,0002 mass. % by the lowest titanium chlorides (LTC). A low-boiling fraction containing 10 - 15 mass. % of VOCl₃, is directed for separation by rectification method for commercial vanadium oxychloride production. The distillation residues are processed in chlorinator [15]. The proposed technology will allow to exclude an application of copper powder, to disassemble reactors for copper purification and for copper-vanadium pulp processing , to free the industrial areas, to reduce the personnel, to increase vanadium extraction by 30% , to exclude ecological damage. Standard rectifying towers (diameter should be 1.2 m ) with perforated plates are applied in the process.

Production of vanadium pentoxide from a vanadium - containing raw material by a hydrometallurgical method is characterized by low vanadium extraction and great amount of toxic drains. So, at processing of converter slags vanadium extraction makes up 70 % and 70 - 100 m³ of drains per 1 ton of vanadium pentoxide are obtained. The amount of drains is considerably reduced under synthesis of \( V_2O_5 \) from \( \text{VOCl}_3 \). An obtaining of latter is proper for production of titanium sponge now. The magnification of \( \text{VOCl}_3 \) production is achieved either by involving of additional vanadium - containing raw material at titanium slag chlorination or by obtaining of \( \text{VOCl}_3 \) on separate chlorinating installation.
Opportunity of pure VOCl₃ obtaining with cascade of rectifying towers had been demonstrated (content of Ti, Si and Fe impurities makes up $1 \times 10^{-3}$, $3 \times 10^{-3}$, $5 \times 10^{-4}$ mass percent respectively). Such vanadium oxychloride can be applied to produce high-quality products containing vanadium - luminophors, catalytic agents for processes of fine organic synthesis, ductile vanadium and others. Joint production of pure titanium and vanadium chlorides creates the background for production of spongy titanium – vanadium alloys by magnesium reduction process.

REFERENCES

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