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ACHIEVEMENTS IN THE TITANIUM PRODUCTION DEVELOPMENT

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Titanium sponge process flowchart includes the following main operations: concentrates reduction melting (example for concentrate from the Obukhovskoe field, the Republic of Kazakhstan), chlorination of obtained titanium slug, refining of industrial tetrachloride and magnesium-thermic reduction of titanium tetrachloride purified from any impurities. This paper presents the results of material flows balance studies and quality analysis of the technological products. It is shown that stillage bottoms pulp feed on the melt mirror of potassium chloride electrolyte with a speed less than 2,5 t/h excludes the temperature overshoot within 570 - 620 °C of titanium tetrachloride vapors sublimation. Chlorinator melt bubbling in the process initial period with dried air (nitrogen) can significantly improve the quality of titanium products.

Keywords: titanium production, stillage bottoms pulp, titanium chlorides, vanadium oxychloride/pentoxide, Kazakhstan

INTRODUCTION

The main way to produce titanium is titanium tetrachloride reduction with magnesium under the Krol method [1]. Modern alternative technologies are still at the stage of laboratory and experimental research and mainly based on the titanium dioxide reduction [2].

The Ust-Kamenogorsk Titanium Magnesium Plant (UK TMP JSC) is one of the largest vertically integrated global manufacturers of titanium sponge, ingots and alloys, provides production of titanium products in Kazakhstan. Products of UK TMP JSC are certified by all leading aerospace companies.

At nowadays UK TMP processes domestic concentrate of the Satbaev field with imported from Ukraine concentrate of the Volnogorsk field.

Titanium-zircon ilmenite concentrate of the Obukhovskoe field is enough attractive Kazakhstani raw material for sponge titanium production [3]. Despite all its attractiveness, this concentrate is not suitable for processing by industrial methods due to mismatch of the main component mass fraction to the regulated requirements and high iron trioxide, silicon dioxide, chromium trioxide and other undesirable impurities. Therefore, the Institute of Metallurgy and Ore Beneficiation (IMOB) JSC (Kazakhstan) conducts research to find the ways for ilmenite concentrates preliminary processing to be involved in processing including the Obukhov field to refine the main components content to the standards regulated by technical conditions for the titanium product production [4-6].

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Titanium tetrachloride purification from related impurities is a key operation in the titanium sponge production, because titanium sponge chemical composition, physicochemical, technological and mechanical properties are largely determined by the quality of production and refined titanium tetrachloride. Therefore, extremely great attention is given to titanium tetrachloride purification.

Purification of technical titanium tetrachloride from impurities, the majority of which differs significantly from $TiCl_4$ by melting and boiling points, can be carried out by usual physical (settling, filtration, centrifugation, and adsorption), mass transfer (rectification, distillation) and chemical methods [7-9].

The hydrogen sulfide purification method has become widespread in industrial practice. [10]. The main disadvantage of this method is using toxic chemical agent and huge pollution of $TiCl_4$ with sulfur compounds.

Mineral oils and other organic substances effectively bind $VOCl_3$ and allow obtaining $TiCl_4$ with vanadium low concentration [11]. However, titanium tetrachloride is contaminated with organic compounds difficult to separate.

More advanced and widespread purification method of $TiCl_4$ is to remove $VOCl_3$ by low titanium chlorides pulp [12]. Advantages of this method before copper powder cleaning are in use of the less deficit and cheaper reagent; increasing completeness of titanium extraction due to conversion of insoluble $TiOCl_2$ contained in the technical titanium tetrachloride into volatile $TiCl_4$; using the raw materials complexity due to the ease of extraction from the aluminum-vanadium pulp of $TiCl_4$ and $VOCl_3$.

Results of the balance studies of the separation efficiency are presented in this paper. $TiCl_4$ and $VOCl_3$ was received by processing of the distillation residue pulp from rectification unit by continuous feed of anode chlorine gas during the whole process and series supply of dried air (nitrogen) at first and then anode chlorine gas through the layer of waste electrolyte from the magnesium production.

MATERIALS AND METHODS

Initial materials: industrial $TiCl_{4,}$ pulp of low titanium chlorides, anode chlorine gas, dried air (nitrogen).

Chemical purification of industrial $TiCl_4$ from $VOCl_3$ is realized by reduction and conversion of vanadium into an oxychloride form by pulp of low titanium chlorides prepared by chlorination of mixture of aluminum powder and titanium tetrachloride.

Distillation residue pulp (DRP) of the rectification unit is evaporated in a rectifying still during 2 hours for volume contraction and obtaining of 30 - 45 % emission of titanium tetrachloride flying vapors. Condensable distillate product in shell and tube heat exchanger is pumped into a collection tank and purified as required, conditioned $TiCl_4$ is accumulated in tanks.

Evaporated DRP is pumped into a vanadium chlorinator by dosed supply of processed potassium chloride electrolyte (DRP) of magnesium production on the melt mirror and bubbled by anode chlorine gas, or by dried air (nitrogen) at first and then by anode chlorine gas. White flying vapors of $TiCl_4$ are removed until availability of orange-red vapors of vanadium oxychloride at the chlorinator output. Completion of the $VOCl_3$ distillation process is determined by lowering the temperature and vapor-gas color decolouration.

Parameters of process conditions and levels of raw materials and derived products in the equipment tanks are regulated by an automated monitoring system.

DRP weighted mass, wasted PCE, industrial $TiCl_4$ and $VOCl_3$, vanadium chlorinator dump dusts (VCDD) are determined by recalculation of parameters at its volume according to the rated tables.

Chemical composition of products was established by spectral atomic absorption and photocolorimetric analysis.

RESULTS AND DISCUSSION

Vanadium composition in ilmenite concentrates is ranged from 0,2 - 0,35 % in equivalent to pentoxide V_2O_5. So in the processed Volnogorsk concentrate the V_2O_5 content is 0,353 %, in Satbaev concentrate – 0,21 %, while in the resulting titanium slag it contains 0,38 %, and the recovery in the discharge titanium slag is 84,89 %.

The vanadium main mass during ilmenite concentrates reduction melting passes into titanium slag. During chlorination of titanium slag mixed with petroleum coke in a molten mass of used potassium chloride electrolyte from magnesium production and common salt containing 95,0 - 99,4 % of NaCl. About 75 % of vanadium is concentrated in sublimates of vapour gas mixture (VGM) of industrial $TiCl_4$ mainly as oxychloride $VOCl_3$ and partially as VCl_4 tetrachloride. Metal oxides chlorination in the melt of potassium and sodium chlorides that bind the resulting iron and aluminum chlorides provides the most intensive catalytic acceleration of the process and industrial $TiCl_4$ quality improvement.

As long as non-volatile chlorides are accumulated the spent melt, i.e. titanium chlorinator dump waste slime (Table 1), changing own physical and chemical properties, especially viscosity, impairing its saturation with chlorine, is periodically drained and updated by continuous loading salt wastes of magnesium electrolysers into the titanium chlorinator.

Main bulk of mechanically entrained by steam gas flow solid highly- and low boiling chlorides, and thin suspensions of charge materials of titanium slags are mechanically entrained by steam gas flow, captured in dust chambers as dry solid sublimates. VGM goes from the dust chambers into water-drip condensers with closed cycle irrigation, where $TiCl_4$ condenses together with $VOCl_3$, low boiling liquid chlorides and remaining suspensions of solid chlorides, oxides and carbon.

Purification from vanadium by aluminum powder is combined with a two-stage continuous rectification process of industrial $TiCl_4$.

$SiCl_4$ and other volatile impurities are separated out from the condenser dephlegmator to the gas purification system at the first rectification stage.

Distillation residue pulp, i.e. industrial $TiCl_4$ with an admixture of high-boiling chlorides and oxychlorides enters the second stage of purification. High-purity branded product of $TiCl_4$ is received after continuous output of II rectification distillate.

Continuously took out distillation residue pulp of II rectification containing ~ 90 % of $TiCl_4$, high boiling chlorides and oxychlorides after evaporating and pulp low titanium chlorides processing are pumped into a vanadium chlorinator on the mirror of used magnesium industrial electrolyte at speed of not more than 2,5 t/h to avoid exceeding the melt temperature above 570 - 620 °C, at which volatile $TiCl_4$ vapors are sublime primarily.

Now distillation of industrial $TiCl_4$ and $VOCl_3$ vapors is made by barbotage of chlorinator melt firstly by dried air (nitrogen) with a flow rate 10 - 15 nm^3/h, and then with anode chlorine gas in the same above specified normalized mode.

Below are the assessment results of technical and economic efficiency of cyclic processing of distillation residue pulp in quantity of 64,33 tons with anode chlorine gas (Table 2); 65,0 tons with dried air (nitrogen) and anode chlorine gas (Table 3).

Table 1 **Chemical composition of dump slime from a titanium chlorator / wt.%**

TiO_2	V_2O_5	KCl	NaCl	$FeCl_2$	$FeCl_3$	MgCl	$AlCl_3$	C	SiO_2
2,41	0,06	24,24	10,70	22,40	1,12	11,4	2,51	3,53	3,32

Table 2 **Results of distillation residue pulp barbotage by anode chlorine gas**

DRP			$TiCl_{4\ ind.}$				$VOCl_{3\ ind.}$				Vanadium recovery/ %	
mass	vanadium content		mass	output	vanadium content		mass	output	vanadium content			
kg	%	kg	kg	%	%	kg	kg	%	%	kg	$TiCl_4$	$VOCl_3$
31 040	1,0	310,4	27 388	88,2	0,2	54,8	1 124,9	3,6	16,6	186,7	17,7	60,2
33 288	1,2	392,8	28 209	84,7	0,3	78,9	1 374,8	4,1	17,2	236,5	20,1	60,2
total			total				total				at the average	
64 328		703,2	55 597			133,8	2 499,7			423,2	18,9	60,2

Table 3 **Results of distillation residue pulp barbotage by with dried air (nitrogen) and anode chlorine gas**

DRP			$TiCl_4$ (brand IRTT-1)				$VOCl_3$ (brand VOCl-1)				Vanadium recovery, %	
mass	vanadium content		mass	output	vanadium content		mass	output	vanadium content			
kg	%	kg	kg	%	%	kg	kg	%	%	kg	$TiCl_4$	$VOCl_3$
25 000	1,1	277,5	19 240	76,9	0,022	4,2	986,75	3,95	21,8	215,1	1,53	77,52
20 000	1,1	220,0	15 860	79,3	0,021	3,3	779,80	3,89	21,4	166,9	1,51	75,85
20 000	1,0	208,0	14 000	70,0	0,023	3,2	738,00	3,69	21,8	160,9	1,55	77,35
total			total				total				at the average	
65 000		705,5	49 100			10,7	2 504,5			542,9	1,53	76,91

Table 4 **Chlorine and solid suspensioned matter content in industrial titanic of IRTT-1 grade and off-grade**

№	DRP	$TiCl_4$ (brand IRTT-1)		№	DRP	$TiCl_{4\ ind.}$ (off-grade)	
	content				content		
	solid suspensioned matter	chlorine	solid suspensioned matter		solid suspensioned matter	chlorine	solid suspensioned matter
	g/dm³	%	g/dm³		g/dm³	%	g/dm³
1	151,0	0,011	< 1,0	1	153,0	0,05	1,8
2	135,0	0,010	< 1,0	2	155,0	0,09	1,4
3	156,0	0,090	< 1,0				

It was found by removing the balance of material flows and analyzing product samples that the quality of entire batch of industrial $TiCl_4$ (49,1 t) and $VOCl_3$ (over 2,5 t) after processing of 65 tones of SBP initially with dried air (nitrogen), then with anode chlorine gas is complied with grade IRTT-1 and VOCI-1 as per the standard industrial requirements of ST AO 00202028-112 and CT AO 00202028-134.

Vanadium content in industrial recycled titanium tetrachloride (IRTT) is decreased by 11 times (Table 3), free chlorine – by 7 times, suspended solids – by more than 1,6 times (Table 4), because of selective distillation of dried air (nitrogen) greatly facilitating its further purification by distillation.

Titan remaining content in vanadium chlorinator dump waste slime is less than 0,5-0,8 % in equivalent to TiO_2, vanadium – 0,013 - 0,019 % in equivalent to V_2O_5.

Titan and vanadium completeness and selectivity extraction come from the fact that the titanium trichloride with very strong reducing properties and aluminum trichloride catalyzing the interacting process of $TiCl_4$ with Al are formed during production of low titanium chlorides pulp using aluminum powder (consumption is 0,8 - 1,2 kg/$TiCl_4$).

After processing of distillation residue pulp the low titanium chloride ($TiCl_3$), interacting with $VOCl_3$ and oxytitanium chloride ($TlOCl_2$) with $AlCl_3$ goes to higher tetrachloride form easily removed by dried air (nitrogen).

Reduced vanadium under the strong oxidizing agent chlorine changes from lowest oxychloride ($VOCl_2$) from to higher easily removed oxychloride form.

The extraction of vanadium to industrial $VOCl_3$ (industrial vanadium oxychloride) increases by almost 17 % as a result of the full separation from titanium.

UK TMP previously used a very complex, multi-operational, labor-intensive and unprofitable technology [13] for processing of industrial $VOCl_3$ purified from suspended solids by evaporation in a reboiler.

By replacing the used technology on the technology developed in IMOB [14], vanadium through output into commercial products was increased from 65 - 67 to 94 - 96 % with significantly lower material and energy costs. High-speed vanadium countercurrent extraction from hydrochloric acid solutions of industrial $VOCl_3$ in a continuous operation box-type apparatus with an automated flow control system made it possible to significantly facilitate and increase labor productivity. Applied technology ensures production of high-purity pentoxide and vanadium in VnO-0 (99,4 - 99,7 % V_2O_5), VnO-1 (99,4 - 99,5 % V_2O_5) and VnO-2 (98,8 - 99,5 % V_2O_5) qualifications with quality excessing the quality of similar products of Russian manufacturers producing only industrial V_2O_5.

Effectiveness of the extracting technology for branded vanadium pentoxide production applied in UK TMP throughout the entire service life is supported by the modernization of its individual key components.

Besides branded pentoxide vanadium UK TMP produces high-purity $VOCl_3$, which is of the great value in production of solid lasers, phosphors and alloy steels.

CONCLUSIONS

Refining of industrial titanium tetrachloride by continuous two-stage rectification combined with distillation, processing of evaporated distillation residue pulp of the II rectification stage during 2 hours by low titanium chlorides pulp, prepared using aluminum powder at flow rate 0,8 - 1,2 kg Al/t $TiCl_4$, pumping in of distillation residue pulp in the chlorinator with feed rate not more than 2 5 t/h on the mirror of used electrolyte magnesium production, feed of dried air (nitrogen) at a temperature within 570 - 620 °C and then anode chlorine gas under 60 - 100 nm^3/h and temperature 600 - 680 °C under the melt layer of chlorinator with the speed 10 - 15 nm^3/h, results in:

– raw materials deep processing with minimization of valuable elements losses;
– high separation selectivity with obtaining quality certified titanium tetrachloride products for production of aerospace sponge titanium and vanadium oxychloride to produce branded vanadium pentoxide.

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