SOME PARTICULARITIES OF HIGH-PURITY TITANIUM TETRACHLORIDE PRODUCTION FROM SYNTHETIC TITANATES

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To produce titanium tetrachloride natural synthetic rutile is generally used. To these ends, the Soviet Union uses titani-ferrous slags - synthetic titanates - having a general formula $m[(Ti, Fe, Mg, Mn)_{2}TiO_{2}]n[(Ti, Fe, Al, Cr)_{2}O_{3}TiO_{2}]$ obtained from ilmenite and arizonite concentrates.

Synthetic titanates ("slags") may be considered from the thermodynamical point of view as oxide impurities solutions in anosovite and tagircvite. Non-equilibrium crystal structure, the presence of titanium forms having a valency of two and three, titanium lower oxides oxidation with the reformation of crystal lattice - these particularities substantially take on the chlorination process technology.

Thus, titanium monoxide $TiO$ and sesquioxide $Ti_{2}O_{3}$ are comparatively easily chlorinated by chlorine gas with no reducing agent forming titanium tetrachloride and titanium dioxide ($1,2$), while the dioxide can be chlorinated only in the presence of carbon. On the other hand, non-equilibrium structure of synthetic titanates substantially facilitates the conditions of their chlorination.

The question of phase state of chlorination products, which in turn is associated with a maximum process temperature is of a very theoretical and practical importance. The latter can be comparatively easily determined using an adiabatic process model ($3$). In industrial conditions, the chlorination process approximates the adiabatic one in the centre of reaction zone.

It follows from the table data that in the presence of lower titanium oxides in synthetic titanates the process exothermicity increases and the adiabatic chlorination temperature of synthetic titanates in comparison with rutile becomes significantly higher.

The estimated adiabatic temperature for the chlorination of synthetic titanates of a various composition in shaft chlorinators is in a range of 1220-1550 K. The temperatures measured in the reaction zone practically coincide with the theoretical calculation ($3$).

In reality, at some areas of a briquette in a local zone of the reaction, the temperature can be still higher (1300-1600 K). In this conditions, all the products of chlorina-
tion are in vapour state due to which there is an abrupt decrease in diffusional retardation of the process.

### Chlorination reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^{298}_{\text{KJ}}$</th>
<th>$\Delta S_{\text{J/K}}$</th>
<th>$T_{ad, K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $[\text{TiO}_2]^p + 2[\text{C}] + 2(\text{Cl}_2) = (\text{TiCl}_4) + 2(\text{CO})$</td>
<td>-40.6</td>
<td>153.5</td>
<td>260</td>
</tr>
<tr>
<td>2. $[\text{Ti}_2\text{O}_3] + 3[\text{C}] + 4(\text{Cl}_2) = 2(\text{TiCl}_4) + 3(\text{CO})$</td>
<td>-362.3</td>
<td>278.2</td>
<td>1300</td>
</tr>
<tr>
<td>3. $[\text{TiO}_2]^p + [\text{C}] + 2(\text{Cl}_2) = (\text{TiCl}_4) + (\text{CO}_2)$</td>
<td>-213.0</td>
<td>132.6</td>
<td>1610</td>
</tr>
<tr>
<td>4. $[\text{Ti}_3\text{O}_5] + 5(\text{C}) + 6(\text{Cl}_2) = 3(\text{TiCl}_4) + 5(\text{CO})$</td>
<td>-731.3</td>
<td>431.8</td>
<td>1690</td>
</tr>
<tr>
<td>5. $[\text{Ti}_2\text{O}_3] + 3/2[\text{C}] + 4(\text{Cl}_2) = 2(\text{TiCl}_4) + 3/2(\text{CO}_2)$</td>
<td>-596.7</td>
<td>246.4</td>
<td>2420</td>
</tr>
<tr>
<td>6. $[\text{TiO}] + [\text{C}] + 2(\text{Cl}_2) = (\text{TiCl}_4) + (\text{CO})$</td>
<td>-355.2</td>
<td>123.0</td>
<td>2890</td>
</tr>
<tr>
<td>7. $[\text{Ti}_3\text{O}_5] + 5/2[\text{C}] + 6(\text{Cl}_2) = 3(\text{TiCl}_4) + 5/2(\text{CO}_2)$</td>
<td>-1153.1</td>
<td>379.1</td>
<td>3040</td>
</tr>
<tr>
<td>8. $[\text{TiO}] + 1/2[\text{C}] + 2(\text{Cl}_2) = +1/2(\text{CO}_2)$</td>
<td>-441.4</td>
<td>110.9</td>
<td>3980</td>
</tr>
</tbody>
</table>

Since the chlorination follows the radical mechanism (4-8) it is of especial importance the degree of contact between carbon and titanium oxides. The routes for the preparation of a pelletized charge to be chlorinated may be divided into two quite different methods, when a carbon reducing agent is dosed with double-triple excess, and when charge components are dosed with a strict stoichiometric ratio. With a great excess of carbon, the chlorination of a pelletized charge goes on with keeping the shapes of starting briquettes. The process rate lowers due to diffusion resistance of the reacted layer.

During the chlorination of a charge with a stoichiometric component ratio there is a continuous renewal of reaction surface which allows to substantially intensify the chlorination process. Because of the decrease in sizes and mass of briquettes, theretofore, as well as high gas-dynamic parameters of the process the stratification of a charge occurs. Large briquettes sink to the bottom of a reactor forming a distribution grating, and fine briquette residues and unchlorinated residue particles are carried out of charge layer forming a fluidized bed over the layer of briquettes (9-11). Such a procedure of the process allows a several-fold increase in specific chlorinator capacity because a continu-
ous renewal of specific surface removes diffusion resistance created by a layer of unchlorinated residue. In these conditions, the macrokinetics of the process is governed by the two main parameters: linear velocity of chlorine gas in a layer of charge $- \omega_{cl2}$ and specific surface of reacting solid phases. The specific volumetric capacity of the chlorinator per a unit of reaction space of the chlorinator $- q_v$ can be finally found by the equation (1):

$$q_v = \omega_{ct2} \cdot \rho_{ct2} \cdot C_{ct2} \cdot \frac{f}{h_c}$$

where $K$ - coefficient of chlorine discharge per titanium tetrachloride $(kg/m^3)$;

$\rho_{ct2}$ - chlorine density $(kg/m^3)$;

$C_{ct2}$ - volumetric chlorine concentration (%);

$h_c$ - charge layer height providing for complete chlorine absorption.

For granules having diameter $- d$, with thickness of reacting layer $- \delta$ and $TiO_2$ concentration $- C_{TIO2}$, charge layer height $h_c$ providing for complete chlorine absorption with its linear velocity calculated for a complete cross-section - can be determined by the equation (2):

$$h_c = \omega_{ct2} \cdot d \cdot C_{ct2} \cdot \rho_{ct2} \cdot M_{TIO2} \cdot \eta_{TIO2}$$

or

$$h_c = \omega_{ct2} \cdot d \cdot C_{ct2} \cdot \frac{K'}{\rho_{TIO2} \cdot C_{TIO2}}$$

where

$$K' = \frac{\rho_{TIO2} \cdot M_{TIO2} \cdot \eta_{TIO2}}{4 \rho_{TIO2} \cdot M_{TCl_4}}$$

$M_{TIO2}$, $M_{TCl_4}$ - molecular mass of titanium dioxide and tetrachloride respectively $\rho_{TIO2}$ - TiO$_2$ density; $\eta$ - degree of TiO$_2$ chlorination.

The redistribution of granules in a charge layer occurs at chlorine linear velocity of higher than $0.5$ m/s. The minimum height of complete chlorine absorption by the charge, thereat, amounts to 20-25 diameters of granules (12-13). The practical height of charge layer is twice-thrice as much as the minimum one.

Owing to a significant difference in thermodynamic characteristics of starting synthetic titanates components in the zone of a charge, where free chlorine is already absent, there is a great development in the reactions of exchange interactions of oxide components with chlorides and oxychlorides of vapour-gas mixture (14).

The reactions of exchange interaction between chlorides and oxides are, on one hand, of a positive significance because allow to get rid of such undesirable impurities as silicon chloride and oxychloride; on the other hand, they play a negative role because the exchange reactions involve titanium tetrachloride forming highly dispersed secondary titanium dioxide.
With the chlorination in the melted chlorides of alkali and alkali-earth metals the process goes on in the conditions approximate to the isothermic ones because the melt is the main mass participating in the process, and the process temperature is controlled by the removal of heat from the melt by various methods (13, 14). Titaniferrous slag and a carbon reducing agent are present in the melt as suspension. Chlorine gas is fed under the melt layer where its intensive agitation and chlorine gas dispersion occur. Floating up, chlorine bubbles meet finely dispersed slag and coke particles. The surface of the melt and solid particles of reacting substances are constantly under renewal.

Thus, a chlorine bubble represents an individual heterogeneous microsystem consisting of several solid phases, one liquid and one gas phase. With the chlorination in the melt the process goes on predominantly at the inner surface of a chloride bubble where the particles of starting materials and unchlorinated oxides are inlaid. The melted chlorides actively participate in the process transporting the interaction reaction into the melt volume due to the formation of complex chlorides of transition elements, dissolution of chlorine and metal oxides in the melt. The major transport of chlorine from the gas phase into the melt volume is done by the chlorides having a variable valency (13).

As in the case of chlorinating a pelletized charge, with the chlorination in the melt the course of the process and the composition of vapour-gas mixture are substantially effected by the secondary reactions between chlorination products and charge oxides.

In contrast to rutile, synthetic titanates contain more impurities the chlorides of which during the condensation precipitate on the inner heat exchange surfaces of condensing systems, thus, deteriorating heat pick-up. The condensing system with heat exchange within the volume of vapour-gas mixture, therefore, proved the most effective.

The composition of starting raw material, and the flow sheet and engineering for chlorination and condensation govern the content and the molecular composition of impurities in technical-grade titanium tetrachloride. Technical-grade titanium tetrachloride is a compound non-equilibrium heterogeneous system containing about fifty impurities in macro- and microquantities. The compounds present in titanium tetrachloride have a wide spectrum of physicochemical properties. When solving the problem of purification one should ground on the postulate that titanium tetrachloride contains a continuous series of various microimpurities with continuously increasing coefficients of distribution ($\alpha$), both toward lower and higher boiling temperatures. With the degree of microimpurities removal of one order and more a minimum reflux ratio ($Q_{\text{min}}$) can be approximately estimated by the equation (5), (16).
from which it follows that the rectifying purification is economically expedient to remove the impurities having the coefficient of distribution more than two. To remove the impurities having low coefficients of distribution it is more advantageous to apply reducing purification, transforming the impurities into the compounds which are easy to separate from titanium tetrachloride by rectification.

The technology of producing titanium tetrachloride developed in the Soviet Union taking into account the particularities of using synthetic titanates, its reducing and rectifying purification provide for the obtaining of purified high-quality titanium tetrachloride to produce therefrom titanium sponge and titanium dioxide pigment.

Vanadium, niobium, and other compounds accompanying synthetic titanates are, by the way, concentrated from the tenth and the hundredth fraction to tens percent and can be recovered in the form of various compounds.

References

(9) Patent 970 328 (Japan).