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THERMODYNAMICS ANALYSIS OF OXIDIZING BURNING LIMED CAKE AT PRODUCTION PENTAOXIDE OF VANADIUM

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Results of thermodynamic calculations for burning of the limed cake which is form at neutralization of an alumina-vanadium cake by lime are presented. Taking into account the calculate Gibbs energy the possible reactions proceed which are defined at burning, and the compounds pass finished products are fixed. In result of calculation for an equilibrium state it is defined that in claimed products compound of $Ca_2V_2O_6$ who promote decrease of degree for extraction of a vanadium pent oxide to end production is formed.

Keywords: limed cake, oxidizing, thermodynamic analysis, vanadium pent oxide, degree of extraction

At a government plant the «Zaporozhe titan-magnesium combine» the technical tetrachloride of titan is purged from admixtures by a chemical-rectificative method. The mixed salt as pulp of more subzero chlorides of titan is entered in the technical tetrachloride of titan on the stage of preliminary distillation [1]. As a result of the chemical-rectificative cleaning admixture oxytrichloride vanadium restored to oxytrichloride vanadium ($VOCl_2$) which passes to pulp of deep blue bits and pieces. Further deep blue bits and pieces utilize by evaporation pulpe with extraction of tetrachloride of titan and conclusion of hard constituents as a friable alumiun-vanadic cake which does not find useful application [2].

For the decision of this problem by an enterprise the «State scientific-research and project Institute of titan» next methods were offered: cleaning of technical tetrachloride of titan by hydrocarbon repairers [1,3] and liming of alumiun-vanadic cake [2]. At the first method as a repairer instead of $nTiCl_4 \cdot mAlCl_3$ it is suggested to use hydrocarbon repairer, providing the set degree of cleaning from vanadium. Thus it is appeared scrap-material – carbon-vanadic cake which must be utilized. According to the second method, an appearing alumiun-vanadic cake is neutralized by a lime at the stoves of boil-off of pulp with education on the output of the limed cake, that allows to decide the problem of conclusion of hard wastes of tetrachloride of titan.

On the first stage there are carry out preparation of cake to the oxidizing burning – execute washing from the ions of chlorine and basic part of calcium, which pass to solution. The got dechlorinated cake is material, cheaply-breakable at the oxidizing burning. At burning vanadium from difficult soluble connection of tetraoxide vanadium (V_2O_4) passes to easily soluble connection – pentaoxide vanadium (V_2O_5). The burnt cake is exposed to lixiviating by a soda with the purpose of translation of pentaoxide vanadium in soluble connection of $NaVO_3$ and separations of him from admixtures. Further there are carry out besieging of connection of $V_2O_5 \cdot nH_2O$ by sulfur acid. The got sediment there are calcine with the purpose of

moving away by water and on an output get pentaoxide vanadium of technical cleanness [4,5].

At the thermodynamics analysis of the oxidizing burning basic reactions and equilibrium content of appearing foods determined, possible reasons of losses of pentaoxide vanadium set.

Analysis of co-operation of tetraoxide vanadium with oxygen of air and other connections of cake at the reactions given below:

$$2V_2O_4 + O_{2(g)} \xrightarrow{t^\circ} 2V_2O_5 \ ; \quad (1)$$

$$2V_2O_4 \xrightarrow{t^\circ} 2V_2O_3 + O_{2(g)} \ ; \quad (2)$$

$$V_2O_4 \xrightarrow{t^\circ} 2VO_{2(g)} \ ; \quad (3)$$

$$V_2O_4 \xrightarrow{t^\circ} 2VO_2 \ ; \quad (4)$$

$$4V_2O_4 + 2Fe_2O_3 + O_{2(g)} \xrightarrow{t^\circ} 4Fe\left(VO_3\right)_2 \ ; \quad (5)$$

$$2V_2O_4 + Fe_2O_3 \xrightarrow{t^\circ} 2FeV_2O_4 + 1{,}5O_{2(g)} \ ; \quad (6)$$

$$2V_2O_4 + 2CaO + O_{2(g)} \xrightarrow{t^\circ} 2CaV_2O_6 \ , \quad (7)$$

shows that from the thermodynamics position flowing of reactions (1), (4), (5) and (7) is possible for which energy of Gibbs ($G < 0$).

As results of thermodynamics calculations showed, oxides of aluminium, titan, iron and calcium in the considered range of temperatures does not co-operate with oxygen of air and does not dissociate oxygen with a selection, but between these oxides co-operation is possible.

$$8TiO_2 + 2Fe_2O_3 \xrightarrow{t^\circ} 4FeTi_2O_5 + O_{2(g)} \ ; \quad (8)$$

$$2TiO_2 + 2Fe_2O_3 \xrightarrow{t^\circ} 2Fe_2TiO_4 + 5O_{2(g)} \ ; \quad (9)$$

$$TiO_2 + Fe_2O_3 \xrightarrow{t^\circ} Fe_2TiO_4 \ ; \quad (10)$$

$$2TiO_2 + 3CaO \xrightarrow{t^\circ} Ca_3Ti_2O_7 \ ; \quad (11)$$

$$Al_2O_3 + CaO \xrightarrow{t^\circ} CaAl_2O_4 \ ; \quad (12)$$

$$Al_2O_3 + 2CaO \xrightarrow{t^\circ} Ca_2Al_2O_5 \ . \quad (13)$$

For description of the equilibrium state of connections in foods of the oxidizing burning in the interval of temperature 500…1500 °C the applied package of *HSC* «*Chemistry* 5.11» are used. The thermodynamics analysis of the equilibrium state of foods of burning showed that content of connections of Al_2O_3 and TiO_2 did not change up to a temperature 1200 °C, and then there is their insignificant diminishing. It is explained by their co-operating with CaO, Fe_2O_3 and formation of connections of Fe_2TiO_5, $Ca_3Ti_2O_7$, $CaAl_2O_4$, $Ca_2Al_2O_5$, molar content of which with the increase of temperature from 1200 to 1500 °C increases. Pentaoxide of vanadium V_2O_5 is in an

equilibrium with $Ca_2V_2O_6$. Connection of $Ca_2V_2O_6$ appears already at a temperature 500 °C and his concentration does not change to the temperature 1100 °C, which like the conduct of connection of V_2O_5. However at more high temperature content of $Ca_2V_2O_6$ goes down, and content of V_2O_5 is increases.

Evidently, that than anymore molar content of CaO, the anymore content of $Ca_2V_2O_6$ and less than content of V_2O_5, id est connection between contents of $Ca_2V_2O_6$ and V_2O_5 is inversely proportional. The contents of $Ca_2V_2O_6$ in foods of burning can attain 10 %, if in initial raw material will be far of CaO. The increase of stake of $Ca_2V_2O_6$ is accompanied by diminishing of content of V_2O_5, that is the negative phenomenon for the process of the oxidizing burning of the limed cake.

Conclusions. It is set as a result of thermodynamics analysis of the oxidizing burning of the limed cake, that at presence of in initial raw material of oxide of calcium takes place formation of $Ca_2V_2O_6$, which assists diminishing of content of pentaoxide vanadium in the burnt limed cake, and, as a result, reduces the degree of his extraction in commodity products. In order to avoid losses at the oxidizing burning it is necessary to optimize the technological operations of liming of aluminum-vanadic cake and washing of the limed cake from chlorides with the purpose of decline of content of oxide of calcium in the limed cake.

LIST OF LITERATURE

1. Промышленные испытания нового реагента для химической очистки технического тетрахлорида титана от ванадия с оценкой качества титана губчатого [Текст] / И. Ю. Дорда, И. Е. Оверченко, Б. Н. Шкурин [и др.] // Междунар. конф. «Ti – 2011 в СНГ» : сб. трудов, 25-28 апреля 2011 г., Львов. – Киев : ИМФ НАНУ, 2011. – С. 104-109.
2. Обезвреживание отходов химико-ректификационной очистки тетрахлорида титана [Текст] / Л К. Кузина, И. Г. Семенова, С. А. Сидоренко [и др.] // Вісник Запорізького державного університету. Біологічні науки. – 2001. – № 1. – С. 48-53.
3. Альтернативная технология очистки технического тетрахлорида титана от оксотрихлорида ванадия углеводородными восстановителями [Текст] / В. В. Тэлин, С. М. Матвеев, С. А. Сидоренко [и др.] // Междунар. конф. «Ti – 2007 в СНГ» : сб. трудов, 15-18 апреля 2007 г., Ялта. – Киев : ИМФ НАНУ, 2007. – С. 120-125.
4. Сидоренко, С. А. Извлечение ванадия из хлоридных отходов титанового производства (Сообщение 1) [Текст] / С. А. Сидоренко, Т. Н. Нестеренко, Е. Н. Литвинова // Металургія : Наукові праці Запорізької державної інженерної академії. – Запоріжжя : РВВ ЗДІА, 2009. – Вип. 19. – С. 38-42.
5. Условия извлечения пентаоксида ванадия из отходов хлорирования титановых шлаков [Текст] / И М. Гунько, Т. Н. Нестеренко, С. Г. Егоров [и др.] // Теория и практика металлургии. – 2010. – № 5-6 (78-79). – С. 67-69.