Personality and Environmental Issues, 2023. Issue 1, Vol. 3.

UDC 547.539.2:622.349.4 **DOI: 10.31652/2786-6033-2023-1(3)-39-43**

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Method of uilizaion of the forbidden chlorinated pesticides through the recycling of the raw materials that include titanium

Abstract. *The article is dedicated to the actual problem of the recycling of the forbidden Chlorinated pesticides. The capacity of the usage of the forbidden Chlorinated pesticides as the chlorinating agents in the process of ilmenite concentrate recycling on the example of hexachlorobenzene is described. The thermodynamic parameters and equilibrium concentrations of obtaining carbon tetrachloride from hexachlorobenzene are defined. The process of chlorinating of the ilmenite concentrate is researched, the change of equilibrium to the concentration starting reagents and the reactions' products with the carbon tetrachloride from Mining and Metallurgical Complex of Vilnogirsk with the carbon tetrachloride is calculated. It is also showed that with the help of metabolic reactions of carbon tetrachloride and ilmenite it is possible to avoid the difficult redox transformations, which take place in the traditional technology of titanium obtaining.*

Keywords: *forbidden pesticides, hexachlorobenzene, chlorinating, carbon tetrachloride, ilmenite concentrate*

Introduction. The intensification of the environmental objects' pollution with pesticides is caused by the processes of their long-term usage and accumulation. The ecological situation in Ukraine is becoming more difficult due to the almost absolute ignorance of the long-term problem of the obsolete pesticides recycling even though the annual formation of amount of those was high and the level of secondary use was incredibly low. Also, as the result of disruption of economic activity, the huge masses of obsolete and forbidden to use pesticides were accumulated. Today, the world is trying to solve the problem of recycling, utilization or the secondary use of the synthetic chemical pesticides. Hexachlorobenzene, or perchlorobenzene is a chemical compound with the formula C_6Cl_6, which is used for fighting the ustilaginales; and also used as insecticide and fungicide. Moreover, it was used in a mixture with other products to poison the seeds of the grain crops. It is the Stockholm Convention on Persistent Organic Pollutants that was applied regarding hexachlorobenzene, due to which this substance is forbidden all over the world [1].

Currently, more than a half of the amount of Titanium (IV) oxide is obtained by the chlorine technology. Elemental chlorine is widely used in the industry of rare and non-ferrous metals [2]. It is due to its high reactivity. In the interaction of Chlorine with the mineral raw materials that include titanium it's relatively easy to obtain not only Titanium chloride, but also the chlorides of the other present metals. Variety of the properties of chlorides, the easy way of their interaction with the other chemical compounds lets us to exclude them out of the reaction products, emitting valuable components effectively. The main advantage of the chlorine technology of producing $TiCl_4$ is the opportunity of obtaining some specific metals, the production of which is possible only due to the chlorides [3, 4]. Furthermore, this technology can be realized in the continuous mode. Due to the high reactivity of Chlorine, degree of the starting material conversion to the chlorides can reach 99% [5]. Also, the little amount of waste, a very few stages of production, almost full absence of the wastewater, and the possibility to create the closed Chlorine cycle (Chlorine may be rotating) might be important to mention.

The purpose of this work is to research the possibility of the use of the forbidden Chlorinated pesticides as the chlorinating agents in the process of ilmenite concentrate recycling on the example of hexachlorobenzene.

The results of the discussion. During the first stage, we calculated the value of enthalpy, entropy, Gibbs energy, and the equilibrium constant of interaction of hexachlorobenzene with the elemental Chlorine (table 1) for the cumulative equation of the reaction:

$$C_6Cl_6 + 9Cl_2 = 6CCl_4 \quad (1)$$

Table 1. Dependence of the enthalpy, entropy, Gibbs energy, and the equilibrium constant change on the temperature of the interaction reaction of hexachlorobenzene and Chlorine

T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	log(K)
0	-540,231	-589,531	-379,200	3,317E+072	72,521
100	-538,173	-583,161	-320,567	7,544E+044	44,878
200	-535,133	-575,978	-262,609	9,859E+028	28,994
300	-531,598	-569,209	-205,356	5,211E+018	18,717
400	-527,933	-563,315	-148,738	3,488E+011	11,543
500	-524,360	-558,363	-92,661	1,823E+006	6,261
600	-521,016	-554,293	-37,035	1,643E+002	2,216
700	-517,932	-550,946	18,221	1,052E-001	-0,978
800	-515,091	-548,165	73,173	2,742E-004	-3,562
900	-512,435	-545,798	127,868	2,024E-006	-5,694
1000	-509,878	-543,706	182,341	3,298E-008	-7,482

Out of conducted thermodynamic calculations, it is obvious that as the result of the process of hexachlorobenzene chlorinating the formation of CCl_4 is possible, so there emerged a problem of defining the optimal conditions that would lead to the maximum degree of conversion. To study the impact of temperature on the hexachlorobenzene chlorinating, the change of equilibrium concentrations of the starting and chlorinating reaction products was calculated (figure 1).

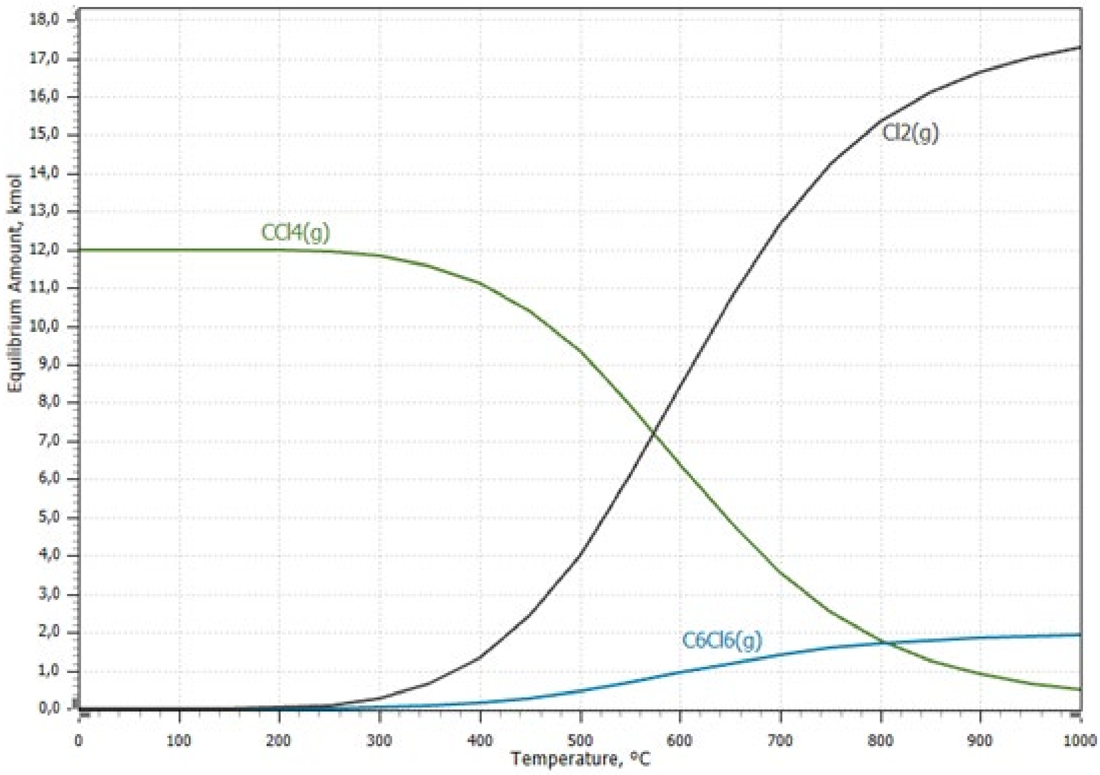

Fig.1. Impact of the temperature on the equilibrium composition in the system C_6Cl_6 - Cl_2

Out of the results of calculating equilibrium concentrations of the system C_6Cl_6 - Cl_2 that is depicted on the illustration 2, it may be stated that relatively full degree of conversion of hexachlorobenzene in the temperature range of 180 to 200 ^{0}C is reached. The lower temperature bound is due to the condensation of carbon tetrachloride, and the upper – to the low degree of hexachlorobenzene conversion.

The ilmenite ores are the solid solutions of variable composition in the systems $FeTiO_3$ – $MgTiO_3$ – Fe_2O_3 and $FeTiO_3$ – $MgTiO_3$ – $MnTiO_3$ – Fe_2O_3, moreover, the impurities such as Al, Si, Nb, Cr, Ca, V, Co, Ni are also used. Ilmenite concentrates are obtained via gravitational enrichment and magnetic separation.

The chemical composition of the ilmenite concentrate of the Mining and Metallurgical Complex of Vilnogirsk is shown in the table 2.

Table 2. The chemical composition of the ilmenite concentrates of the Mining and Metallurgical Complex of Vilnogirsk

Компоненти:	TiO_2	Fe_2O_3	FeO	$Fe_{(заг.)}$	Al_2O_3	SiO_2	MnO	CaO	MgO	P_2O_5	Інші	Разом
Quantity, %	0,65	24,2	0,97	17,7	1,9	1,0	0,75	1,4	0,23	0,13	4,42	100

As we can see in the table 2, basic, acidic, and amphoteric oxides are the part of ilmenite concentrate. They are almost never excluded during the enrichment process and can negatively affect the excluding of titanium. In the process of using CC_4 for ilmenite concentrate decomposition, it is avoided the complex redox transformations that take place in the traditional technology of titanium obtaining.

Carbon tetrachloride was used for the ilmenite concentrate decomposition. We studied the cumulative schemes of the ilmenite concentrate decomposition processes according to the schemes of the following reactions:

$TiO_2 + CCl_4 = TiCl_4 + CO_2$ (2)

$2Fe_2O_3 + 3CCl_4 = 4FeCl_3 + 3CO_2$ (3)

$2FeO + CCl_4 = 2FeCl_2 + CO_2$ (4)

$SiO_2 + CCl_4 = SiCl_4 + CO_2$ (5)

$2Al_2O_3 + 3CCl_4 = 4AlCl_3 + 3CO_2$ (6)

$2MnO + CCl_4 = 2MnCl_2 + CO_2$ (7)

$2MgO + CCl_4 = 2MgCl_2 + CO_2$ (8)

$2CaO + CCl_4 = 2CaCl_2 + CO_2$ (9)

$2P_2O_5 + 3CCl_4 = 4POCl_3 + 3CO_2$ (10)

After analyzing the obtained results, we can state that the examined ilmenite concentrate decompositions with Carbon(IV) chloride are thermodynamically possible in the considered temperature interval and happening with the high exothermic effect.

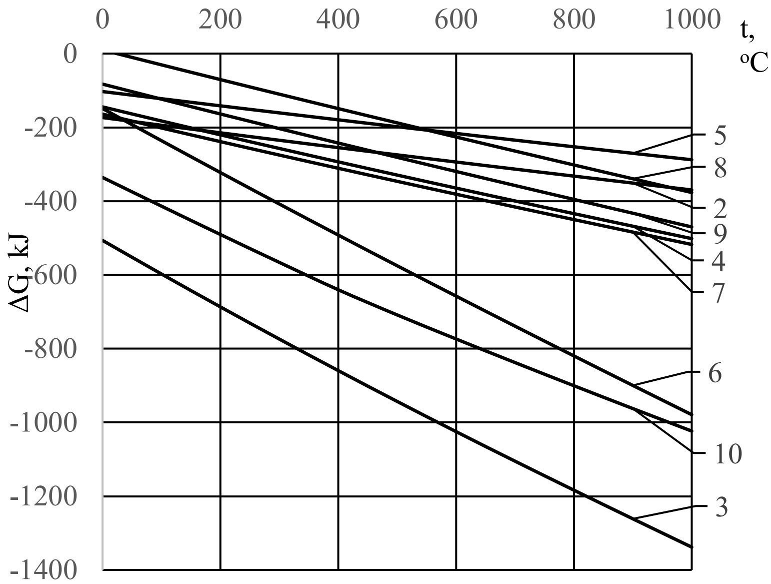

Fig. 2. Dependance of the conversion of Gibbs energy on the temperature of the ilmenite concentrate reactions of interaction with carbon tetrachloride (numbers of dependents are appropriate to the reactions numbers in the text).

Conducted analysis of the literary sources and thermodynamic researches claim that as the result of ilmenite concentrate decomposition processes it is possible to obtain such gas-phased products as Aluminum, Iron (III) and Silicium chlorides, and on the base of the temperatures' adjustment difference it is possible to selectively obtain Titanium tetrachloride.

To study temperature impact on the process of obtaining Titanium (IV) chloride, the change of equilibrium to concentration starting reagents and products of interaction reactions of ilmenite concentrate with carbon tetrachloride was calculated according to the schemes of reactions 2 – 10 (Figure 3).

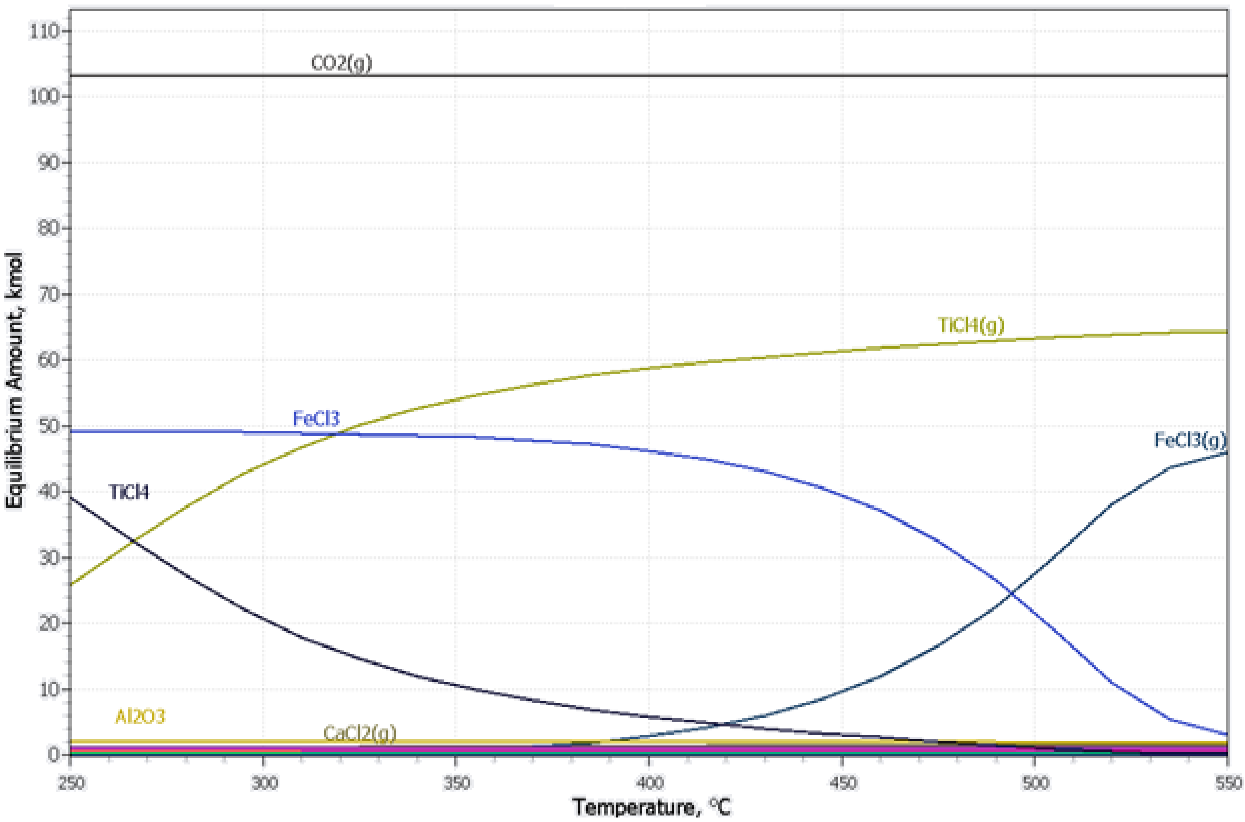

Fig. 3. Temperature impact on the equilibrium composition of products of ilmenite concentrate interaction with carbon tetrachloride

According to the calculating of equilibrium component concentrations results (illustration 3), it is statable that all of the ilmenite concentrates components almost fully react as it may be seen due to quite high degree of the concentrate components conversion into the final reaction products – Titanium, Aluminum, Iron, Calcium, Manganese, and Cranium chlorides.

Thus, such gas products thermodynamically most probably may be expected in the multicomponent reactionary system ilmenite – carbon tetrachloride: $TiCl_4$, $FeCl_3$, $FeCl_2$, $MnCl_2$, $MgCl_2$, $CaCl_2$. The split of such multicomponent compound is possible due to the rectification – split on the base of chlorides boiling temperatures of the appropriate salts.

Conclusions. In the system C_6Cl_6 - Cl_2 a relatively full degree of conversion of hexachlorobenzene in the temperature range of 180 to 200 ^{0}C is reached. The lower temperature bound is due to the condensation of carbon tetrachloride, and the upper – to the low degree of hexachlorobenzene conversion.

1. The process of the ilmenite concentrate of the Mining and Metallurgical Complex of Vilnogirsk chlorinating was studied. It was also showed that with the help of metabolic reactions of carbon tetrachloride and ilmenite it is possible to avoid the difficult redox transformations, which take place in the traditional technology of titanium obtaining.
2. Such process conducting rational conditions were defined: temperature regime of interaction process of CCl_4 with the ilmenite concentrate 390…400^{0}C and the stochiometric carbon tetrachloride expense.

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Review received 26.02.2023