Thermodynamic Simulation of Simultaneous Extraction of Metals During Waste Processing Industry

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Article info

Abstract

The depletion of ores, a rise in the cost of their extraction, enrichment and processing led in the last 10–15 years to a sharp rise in prices for tungsten products. Therefore, the processing began to involve technogenic waste – dumps of enrichment factories and metallurgical industries, which previously did not represent the commercial interest on this case, we present the information on the results of the thermodynamic modeling of tungsten and bismuth chloride distillation in the processing of industrial waste using NaCl as a chlorinating agent. To calculate thermodynamic models for the associated extraction of tungsten and bismuth from industrial wastes, the ASTRA-4 software complex was used which created on basis of the maximum entropy of all possible reactions occurring during the retrieval of refractory metals from waste. Thus, the calculations carried out and experimental studies of the main provisions of thermodynamic calculation have shown the possibility of using NaCl salts for bismuth chlorination. At the same time, the maximum degree of sublimation of bismuth not be lower than 98% and can be achieved even at a temperature of 1200 K and a pressure of 0.01–0.1 MPa. At the same time, NaCl is not an effective chlorinating agent for retrieving of tungsten during high-temperature processing of industrial wastes.

1. Introduction

At present time, Kazakhstan has more than 20 billion tons of waste, of which over 9 billion tons is accounted for the metal-containing waste of the mining and metallurgical industries. It is should be noted that in industry waste, especially in the electronics industry waste, silver, tin and copper are often found. Due to the fact, that these wastes found in small sizes (less than 1–2 mm), magnetic, electrostatic, electrolytic and the other selective methods are used for their processing [1–5]. The content of metals in industrial waste often exceeds their content in natural raw materials. For the processing of such wastes and the intermediate products, pyrometallurgical, hydrometallurgical, electrometallurgical, agglomeration, etc. are also used to extract the valuable components contained therein methods [6–15].

Thermodynamic models are used for determine the equilibrium phase of metals in metallurgical slags using CEQCSI (Chemical Equilibrium Calculations for the Steel Industry) [16]. After the creation of universal computer programs, the determination of the equilibrium parameters of multicomponent heterogeneous chemical reactions, the degree of cognition of the studying processes had significantly expanded to produce the large number of output parameters.

In this paper, we present the information on the results of thermodynamic modeling of tungsten and bismuth chloride distillation during the recycling of industrial waste using as chlorinating agents NaCl. Thermodynamics makes it possible to determine the possibility of carrying out chemical reactions without penetrating the mechanism of processes and determining the speed of the process.

Intensive studies to determine the equilibrium parameters of multicomponent heterogeneous reactions carried out recently with using of the many types of software and tool complexes [17–20].

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2. Experimental

The "ASTRA" complex created on basis of the maximum of entropy. The entropy value related to the degree of ordering of the energy state of the microparticles, of which the working bodies are composed. Since every thermodynamic system contains a large number of microparticles (molecules, atoms, ions, etc.), its thermodynamic parameters (including component concentrations) can be taken with a high degree of accuracy equal to the average static values determined from the distribution of microparticles by its energy levels.

The equilibrium state of the system corresponds to the least ordered, most chaotic of all possible particle distributions over energy levels. Such a distribution for a large number of particles is the most probable and can calculated on basis of the laws of probability theory applied to possible energy states of microparticles. Any isolated microsystem that is not in a state of static equilibrium as result of the interaction of microparticles between itself, will be transformed into an equilibrium state with a higher probability, within the limits - to the most probable energy state. Statistical physics allows us to find the number of discrete states by which this macrostate realized.

Comparison of this value with entropy, as represented in the phenomenological thermodynamics, reveals that the latter is a measure of the probability of the system state. Therefore, accordingly, the maximum of entropy corresponds to the equilibrium conditions of the considered set of particles.

Thus, equilibrium calculation essence consists in determining the most probable state to which the system moves because of a spontaneous change in the energy level of the microparticles during their interaction with each other. In this case, the thermodynamic systems considered in isolation from the environment and quantitatively expressed in the form of the law of conservation of mass (M) of energy (U). For each of the chemical elements that make up the systems (when the vehicle is switched on, the possibility of the occurrence of nuclear reactions) is valid: M = const. The constancy of the total internal energy U_n = const expresses the law of conservation of energy for equilibrium systems do not perform mechanical work in relation to the environment: V = const.

When equilibrium is established, all the thermodynamic parameters of the system (temperature, pressure, enthalpy, etc.) are equalized over the occupied pressure and such a composition change is made in which the population of the energy levels of the microparticles corresponds to the most probable one. The connection between the probability of the state of the system and its entropy allows us to formulate an extremely condition that determines the equilibrium state of the system in the form (1):

$$S = S_{max} \text{ at } Mi = const \ (1), \ U_n = const, \ V = const.$$

Thus, the maximum entropy method represents a unique opportunity to generalize the description of any high-temperature state with the help of only the fundamental laws of thermodynamics, regardless of the conditions and methods for achieving equilibrium. The method requires minimal information about the system itself and its environment.

Thermodynamic modeling by the ASTRA software complex requires solving two equilibrium conditions of the system under study with the environment (either numerical values of thermodynamic equilibrium characteristics or functional relationships between the parameters of this state). In order to describe the system itself as a material object, it is necessary to know only the content of the chemical elements that form it. Internal and interphase interactions are described by model thermodynamic states, for the closure of which the properties of only individual substances - equilibrium components are used.

The scope of the software complex "ASTRA" is limited only by the assumptions of the mathematical model, which is the basis of the computational algorithm. Outgoing assumptions in the program are as follows:

- systems are considered in a state of external and internal thermodynamic equilibrium (complete or local);
- closed systems are considered;
- presence of a gas phase is necessary, the gas phase being described by the equation of state of an ideal gas;
- surface effects at the phase boundary are not taken into account, the solubility of gases in the liquid and solid phases is absent;
- Condensed substances form single-component mixing phases or are included in the composition of ideal condensed solutions.

The database of the ASTRA-4 software complex consists of thermodynamic, thermophysical and thermochemical properties of 5559 substances, 81 elements of the system of the D.I. Mendeleyev's table systematized in the Institute of High Energies

of the Russian Academy of Sciences, National Bureau of Standards USA [5].

The output parameters of the "ASTRA" software package are the parameters given in Table 1. In addition, the program calculates the distribution of components (ions, elements, compounds), the composition of the gas condensed phases. After some calculations (provided by the software system), it is possible to determine the equilibrium distribution of the elements between all participants in the reaction, i.e. it is possible to determine the equilibrium degree of transition of elements in reaction products expressed in mass.

The long experience of using the ASTRA software package in chloride-air processes and the good agreement between the results of thermodynamic modeling and the experimental data were the basis for carrying out equilibrium studies in systems containing non-ferrous metals for raw materials undergoing agglomeration, in particular for processing W – containing raw material containing Bi_2S_3, Bi_2O_3 or WO_3 [21].

Table 1
Output parameters of the "Astra-4" software package

Parameter	Parameter name	SI	Engineer`s system of units
P	Pressure	MPa	kgs/cm^2
T	Temperature	K	K
V	Specific volume	m^3/kg	m^3/kg
S	Entropy	kJ/(kg × K)	kcal/(kg × K)
H	Enthalpy	kJ/kg	kcal/kg
U	Internal energy	kJ/kg	kcal/kg
M	Total number of moles of components	mol/kg	mol/kg
$C_{p'}$	Specific heat at the constant pressure (frozen)	kJ/(kg × K	kcal/(kg × K)
k	$k = C_p/C_v$	1	1
$C_{p''}$	Specific heat at the constant pressure (equilibrium)	1	1
k'	$k = C_{p'}/C_{v'}$	1	1
A	Equilibrium velocity of sound	m/s	m/s
η	Coefficient of dynamic viscosity	Pa × c	kg × c/m^2
λ	Coefficient of thermal conductivity	W/(m × K)	kcal/(h × m × K)
$λ'$	Total thermal conductivity	W/(m × K)	kcal/(h × m × K
M_a	Average molar mass	g/mol	g/mol
C_p, g	Specific heat capacity of the gas phase at constant pressure (frozen)	kJ/(kg × K)	kcal/(kg × K)
k, g	$k_g = C_{pg}/C_{vg}$	1	1
R, g	Gas constant	kJ/(kg × K)	kcal/(kg × K)
ω	Mass fraction of all condensed phases	1	1
$ω_1$	Mass proportion of solution 1	1	1
$ω_2$	Mass proportion of solution 2	1	1
P	Initial mixture density	kg/sm^3	kg/sm^3
E	Ox-Red potential	B	B
N	Indicator of process of expansion	1	1
V	Velocity of flow	m/s	m/s
M	Mach number	1	1
S_r	Relative flow area	1	1
$S_{s'}$	Specific flow area	kg/(m^2 × s)	kg/(m^2 × s)
I_s	Specific thrust (impulse) in vacuum	C	C
B	Expendable complex	C	C

3. Results and Discussion

The distribution of components in the system $Bi_2S_3 - WO_3 - NaCl - O_2$ given by the (predicted) response $Bi_2S_3 + WO_3 + 8NaCl + 6O_2 = WO_2Cl_2 + 2BiCl_3 + 4Na_2SO_4 + 2SO_2$. The primary information obtained on the computer of the SYSTEM under consideration, which makes it possible to calculate the distribution of elements and the composition of the gas phase at various pressures and temperatures.

As can be seen from Table 2, with P = 0.1 MPa, in the system bismuth initially chlorinated $BiCl_3$ to 98.81%, with a maximum at T = 200 K.

Table 2
Effect of temperature on the distribution of the degree of Bi, W at P = 0.1 MPa

Distributed element	Compounds	Degree of distribution (%) at temperature, K					
		1200	1300	1400	1500	1600	1700
O	Bi_2O_3k	0.186	0.78	2.70	7.18	8.23	2.75
	BiO	-	<0.001	<0.001	0.014	0.073	0.53
	Bi_4O_6	<0.001	0.001	0.001	0.025	0.094	0.16
	WO_3 (k)	19.86	19.51	18.58	16.96	16.87	17.03
	WO_2Cl_2	0.091	0.32	0.94	2.02	1.97	0.595
	W_3O_9	-	-	<0.001	0.005	0.43	1.25
	SO_2	0.328	0.37	5.39	16.06	27.36	28.64
	W_4O_{12}	-	-	-	0.002	0.051	0.701
	Na_2SO_4	79.30	76.96	68.96	47.33	24.64	22.20
	O_2	0.22	0.88	3.24	10.0	24.2	25.53
	SO_3	0.011	0.047	0.16	0.387	0.42	0.267
Bi	Bi_2O_3	0.47	3.92	13.52	35.92	41.2	13.76
	BiO	-	-	-	0.054	0.55	3.94
	Bi	-	-	-	0.01	0.27	3.10
	$BiCl_3$	98.81	94.98	82.33	48.82	9.64	0.42
	BiCl	0.25	1.1	4.1	15.06	47.86	77.43
	Bi_4O_6	-	-	-	0.128	0.47	1.21
W	WO_3 (k)	99.31	97.56	92.91	84.79	84.35	85.17
	WO_2Cl_2	0.68	2.43	7.08	15.16	14.80	4.47
	W_3O_9	-	-	-	0.05	0.52	6.24
	W_4O_{12}	-	-	-	-	0.02	3.50
S	Na_2SO_4	-	-	-	-	-	0.31
	Na_2SO_4k	99.16	96.24	86.23	59.18	30.86	27.72
	SO_2	0.84	3.68	13.50	40.16	68.43	71.63
	SO_3	-	0.08	0.27	0.77	0.71	0.44
Na	NaCl	0.08	0.34	1.34	5.59	24.47	57.84
	NaClk	25.57	27.3	33.14	46.59	38.65	-
	Na_2SO_4k	74.27	72.1	64.6	44.34	23.4	20.79
	Na_2Cl_2	0.03	0.26	0.88	3.31	13.02	20.34
	Na_3Cl_3	-	<0.01	0.04	0.17	0.734	0.908
CI	$BiCl_3$	73.98	71.11	61.77	19.52	7.21	0.311
	BiCl	0.062	0.27	1.023	6.94	11.94	19.33
	WO_2Cl_2	0.170	0.606	1.77	4.27	3.69	1.11
	NaClk	25.56	27.28	33.12	50.29	38.63	-
	Na_2Cl_2	0.066	0.606	0.883	659	13.02	20.34
	Na_3Cl_3	<0.01	0.01	0.042	0.35	0.73	0.908
	Cl_2	0.023	0.050	0.091	0.11	0.056	0.008
	CI	0.002	0.010	0.033	0.10	0.177	0.145

At T > 1200 K, the degree of transition of Bi in $BiCl_3$ – decreases to 0.42%, reaching its minimum value at T = 1700 K, and in BiCl – increases, which is 77.43% at T = 1700 K.

The total degree of transition of Bi in gaseous chloride ($BiCl_3$ and BiCI) also depends on the temperature (Table 4). From Table 4 it follows that an increase in temperature negatively affects the transition of Bi to gaseous chlorides.

With an increase in temperature an extreme degree of the Bi transition to Bi_2O_3 is observed with a maximum (41.2%) at T = 1600 K. At T = 1500 K, the transition of Bi to BiO, Bi, Bi_4O_6 becomes noticeable. The degree of transition of W to the target product – WO_2Cl_2 with an increase in temperature is extreme, with a maximum of 15.16% at

T = 1500 K. At T >1600 K, the transition of W into gaseous W_3O_9 and W_4O_{12} becomes noticeable at 1700 K is 5.24 and 3.50%, respectively.

In system $Bi_2S_3 - WO_3 - NaCl - O_2$ large part of sodium (Fig. 1) at a temperature of 1200 K stored in the form of sodium sulfate (74.27%), and 25.57% in the form of condensed NaCl. Moreover, as the temperature increases the degree of transition in NaCl increases and reaches to a maximum – 46.59% at T = 1500 K, Na and the transition in Na_2SO_4 smoothly decreases to 20.79% when T = 1700 K. Furthermore, since the process proceeds 1400 K sodium volatilization in the form of NaCl and Na_2Cl_2, with a maximum degree of sublimation at 1700 K Na_2Cl_2 at 1700 K (20.34%) and NaCl (57.84%).

Table 3
The effect of temperature on the composition of the gas phase (vol. %)
of the Bi_2S_3–WO_3–NaCl–O_2 at P = 0.1 MPa

Compounds	Temperature, K										
	1700	1650	1600	1550	1500	1450	1400	1350	1300	1250	1200
1	2	3	4	5	6	7	8	9	10	11	12
BiCl	13.64	14.22	12.89	10.32	7.52	5.04	3.14	1.84	1.00	0.51	0.24
$BiCl_3$	0.07	0.44	2.59	9.67	24.38	44.15	63.18	77.87	87.68	93.60	96.9
BiO	0.69	0.33	0.149	0.06	0.027	0.011	0.004	0.001	$0.56·10^{-3}$	$0.17·10^{-3}$	-
Bi_3	$0.24·10^{-3}$	-	-	-	-	-	-	-	-	-	-
Bi	0.54	0.21	0.07	0.02	0.008	0.003	0.001	$0.41·10^{-3}$	$0.1·10^{-3}$	-	-
W_2O_5	0.02	0.01	0.003	0.001	$0.4·10^{-3}$	$0.13·10^{-3}$	-	-	-	-	-
W_5O_{10}	$0.2·10^{-3}$	$0.56·10^{-3}$	-	-	-	-	-	-	-	-	-
W_3O_9	0.18	0.07	0.02	0.007	0.002	$0.6·10^{3}$	$0.14·10^{-3}$	-	-	-	-
WO_2Cl_2	0.39	0.904	1.99	3.17	3.79	3.52	2.72	1.83	1.12	0.63	0.33
W_4O_{12}	0.07	0.026	0.008	0.002	$0.7·10^{-3}$	$0.17·10^{-3}$	-	-	-	-	-
NaCl	40.82	37.74	26.41	17.45	11.18	6.91	4.11	2.34	1.27	0.65	0.31
Na_2Cl_2	7.17	9.26	7.02	4.89	3.31	2.16	1.35	0.81	0.469	0.25	0.13
Na_3Cl_3	0.21	0.35	0.26	0.17	0.11	0.069	0.041	0.022	0.012	0.006	0.002
Na_2SO_{4k}	0.04	0.02	0.01	0.007	0.003	0.001	$0.86·10^{-3}$	$0.37·10^{-3}$	$0.15·10^{-3}$	-	-
SO_2	18.93	19.12	27.66	32.20	30.08	23.26	15.54	9.30	5.10	2.58	1.21
SO_3	0.11	0.14	0.28	0.43	0.48	0.42	0.304	0.19	0.108	0.056	0.027
SO	$0.29·10^{-3}$	$0.15·10^{-3}$	$0.1·10^{-3}$	-	-	-	-	-	-	-	-
Cl_2	0.002	0.009	0.03	0.07	0.11	0.14	0.14	0.12	0.09	0.067	0.05
Cl	0.102	0.139	0.19	0.21	0.20	0.16	0.107	0.066	0.037	0.02	0.01
O_2	16.87	16.90	20.33	21.24	18.75	14.10	9.32	5.57	3.08	1.60	0.79
O	0.001	0.001	$0.65·10^{-2}$	$0.36·10^{-3}$	$0.2·10^{-3}$	$0.75·10^{-4}$	-	-	-	-	-

Table 4
Effect of temperature on the degree of Bi transition to gaseous chlorides

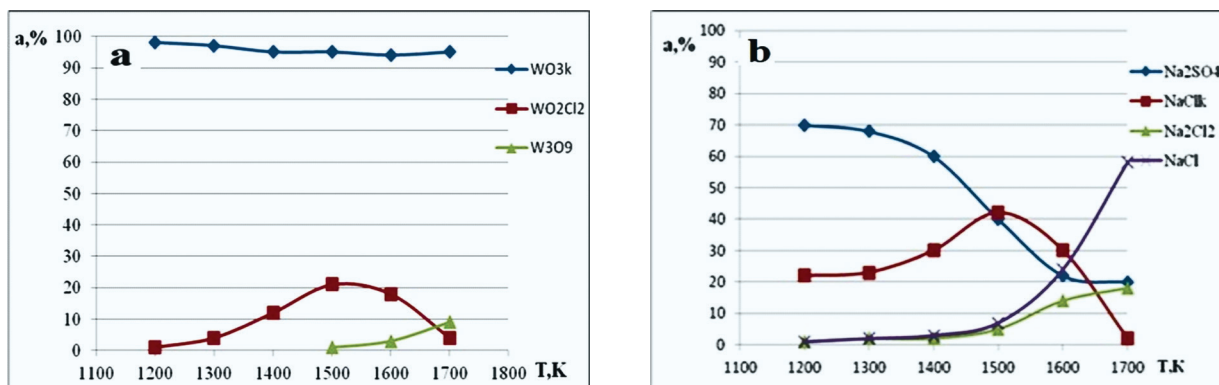| T, K	1200	1300	1400	1500	1600	1700
The degree of transition of Bi Σ BiCl + $BiCl_3$, %	99.06	96.08	86.43	63.88	57.50	77.86

Fig. 1. Influence of temperature for degree of distribution of elements (a) in system $Bi_2S_3 - WO - NaCl - O_2$ at P = 0.1 MPa: a – indicator of extraction of tungsten by sodium chloride; b – distribution of sodium compounds

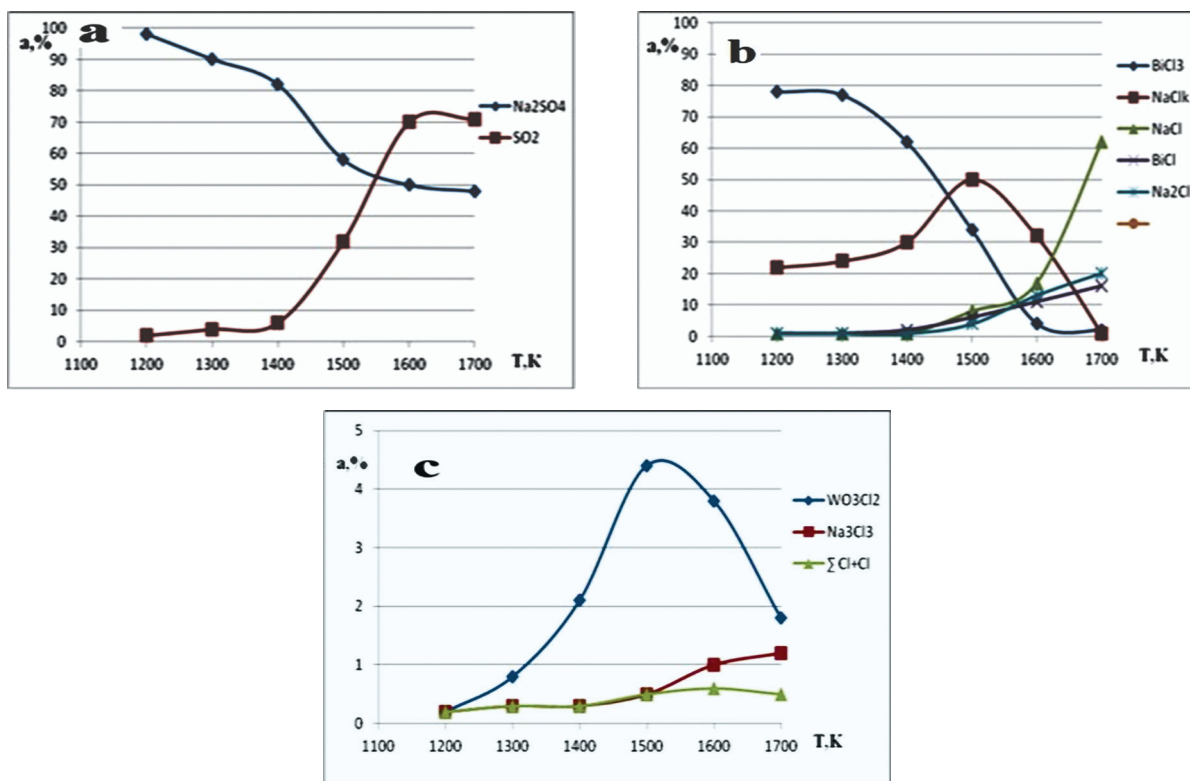Fig. 2. Influence of temperature for degree of distribution S, Cl (α) in system $Bi_2S_3 - WO_3 - NaCl - O_2$ at P = 0.1 MPa: a – dependence of presence in reaction zone of sodium sulfate and oxygen from temperature change; b – index of distribution of bismuth chloride on condition of presence of sodium chloride; c – dependence of tungsten oxychloride formation in presence of sodium chloride.

The absence of sulfide compounds of Bi in the observed system indicates about the complete oxidation of Bi_2S_3 at T = 1200 K. Moreover, in the temperature range of 1200–1525 K sulfur advantageously proceeds in SO_2 (Figs. 2 and 3).

Gas phase composition of the system $Bi_2S_3 - WO_3 - NaCl - O_2$ strongly depends from temperature (Table 3, Fig. 4). If T = 1200 K it mainly (96.88%) consists of $BiCl_3$, at T = 1550 K main components thereof are SO_2 – 32.20%, O_2 – 21.24%, NaCl – 17.45%, BiCl – 10.32% and

$BiCl_3$ – 9.67%. At T = 1700 K main components are NaCl – 40.82%, SO_2 – 18.93%, O_2 – 16.88%, BiCl – 13.6%, Na_2Cl_2 – 7.17%.

Concentration of WO_2Cl_2 does not exceed 4% and amounts to only 3.7% when T = 1500 K. Thus, in the system $Bi_2S_3 - WO_3 - NaCl - O_2$ at P = 0.1 MPa the maximum distillation of Bi (in system $BiCl_3$) to be expected at T = 1200 K. Under these conditions (at P = 0.1 MPa) NaCl is not an effective chlorinating agent for W in that chloride distillation is only 15.16% at 1500 K.
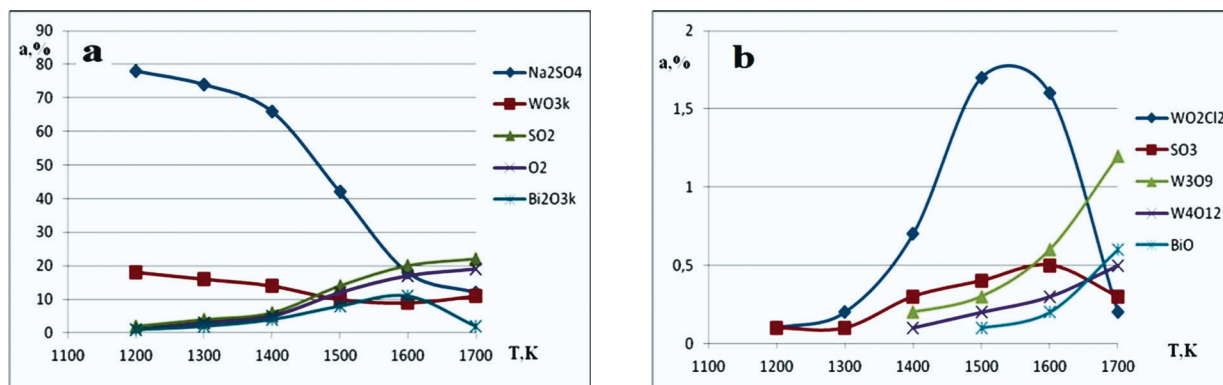
Fig. 3. Influence of temperature for degree of distribution of oxygen (α) in system $Bi_2S_3 – WO_3 – NaCl – O_2$ at P = 0.1 MPa: a – dependence of oxygen distribution in presence of sodium chloride; b – indicators of extraction of the trivalent bismuth, trioxide and oxychloride of tungsten in dependence of temperature change.
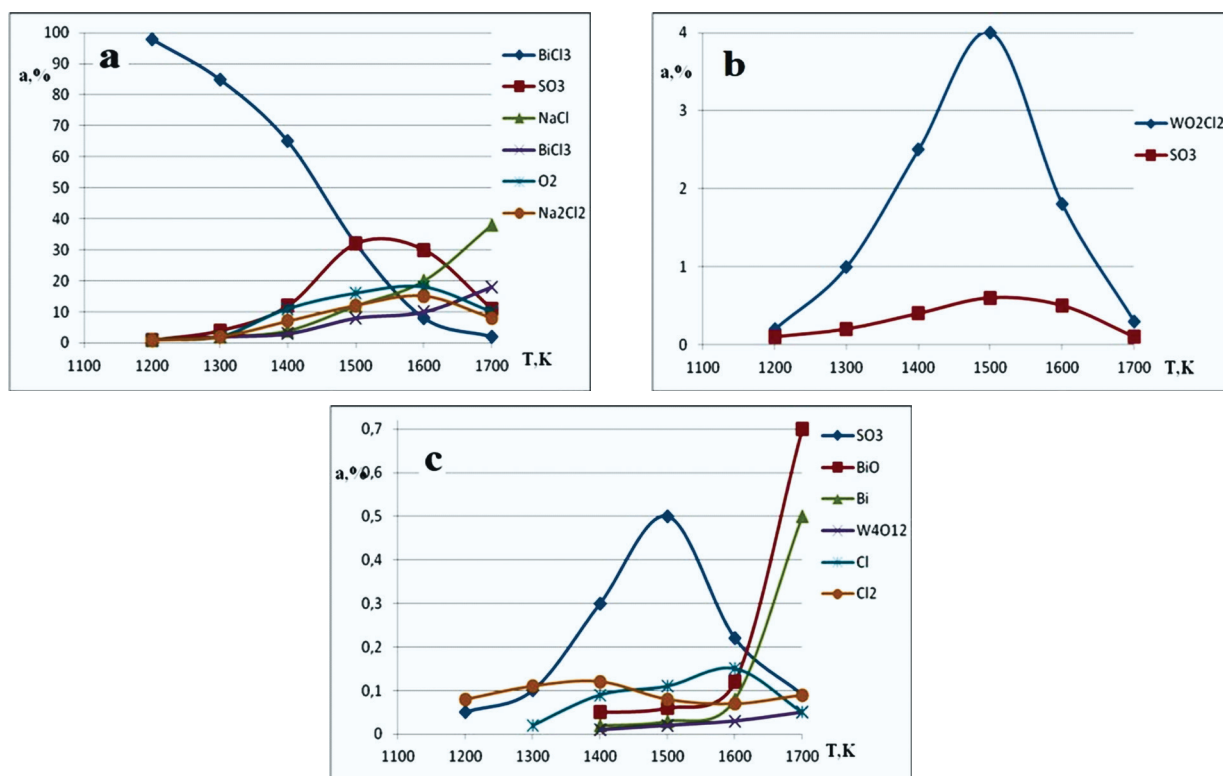

Fig. 4. Influence of temperature on the content of components in gas phase(V) in the system $Bi_2S_3 – WO_3 – NaCl – O_2$ at P = 0.1 MPa: a, b, c – the indicators of distribution of tungsten compounds and trichloride of bismuth incase of presence of sodium chloride and temperature change.

Pressure changes in Bi_2S_3 system WO_3–NaCl–CO_2 to P = 0.01 MPa leads to a substantial change quantities tungsten bismuth distribution between the original components and reaction products. The change in the equilibrium distribution of components in this system, as a function of temperature, is given in Table 6 and in Figs. 5 and 6.

From Fig. 5 it follows that at a temperature of 1200 K in the degree of transition of Bi is $BiCl_3$ – 96.88%, and BiCl – 2.0%. The degree of the Bi transition to BiCl increases up to 82% with increasing the temperature up to 1550 K. When the temperature reached to 1700 K, the value of BiCl decreased to 16.6%. Simultaneously, with an increase in the degree of the Bi transition to BiCl, an increase in the transition of Bi to Bi_2O_3 (13.96% at T = 1450 K) is observed, which ends at a temperature of 1550 K. But since 1400 K bismuth volatilization already resumed in elemental form and reaches 56.93% at T = 1700 K remaining from Bi_2S_3 with a portion of bismuth is redistributed between maxima – 22.96% (1700 K) and Bi_6O_4 – 5.68% (1550 K). The total transition in Bi gaseous BiCl and $BiCl_3$ decreases with increasing temperature, and most sharply at T>1500 K (Table 5).

Table 5
Effect of temperature on the transition of Bi to gaseous chlorides

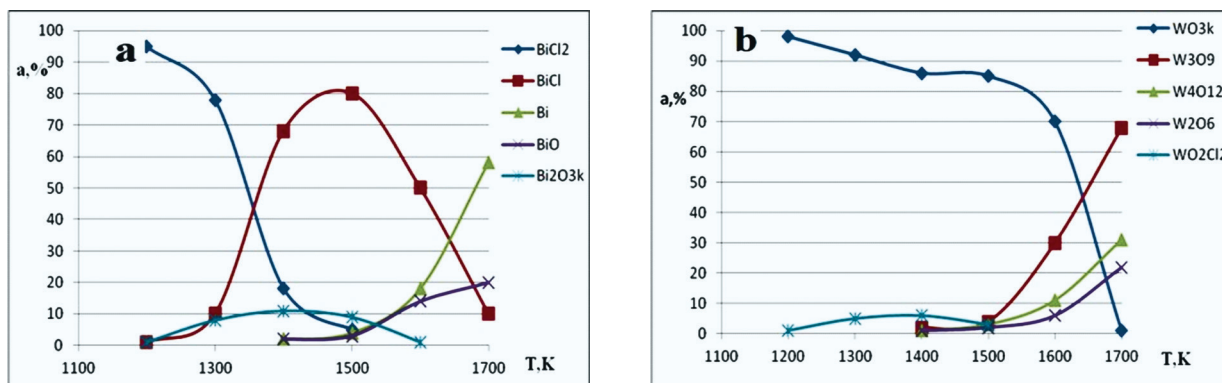| T, K	1200	1300	1400	1500	1600	1700
The degree of transition in Bi Σ $BiCl_3$ + BiC1,%	96.88	91.04	86.11	79.30	57.16	16.6

Fig. 5. Influence of temperature on distribution of Bi, W (a) in the system $Bi_2S_3 - WO_3 - NaCl$ at P = 0.01 MPa: a, b – impact of temperature on distribution in gas phase the bismuth and tungsten compounds.
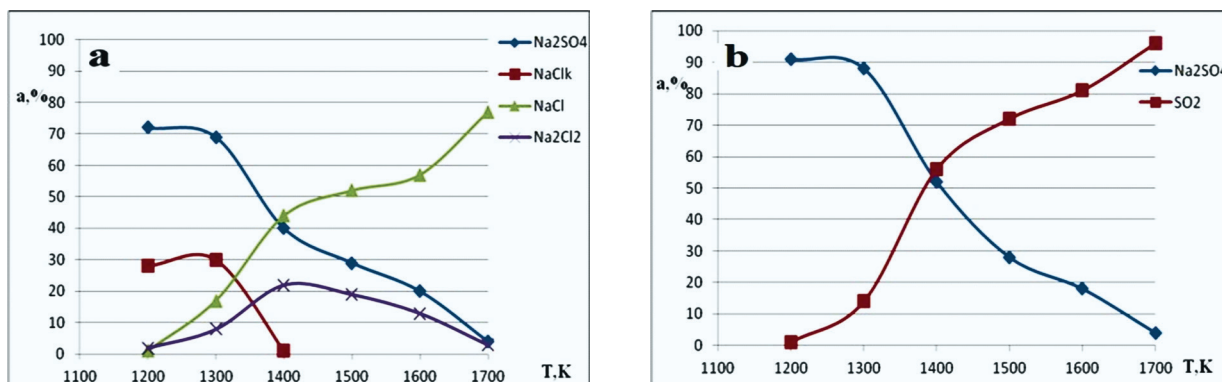

Fig. 6. Influence of temperature on the degree of distribution Na and S: a – in the sodium compounds; b – in the sulfur dioxide and sodium sulfate.

As follows from Fig. 5, at P = 0.01 MPa in a temperature range of 1200–1500 K up to 1700 K W proceeds mainly in WO_{3k} of 98.52% (1200 K) ~ 97.51% (1200 K) with a small maximum (up to 96%) at T – 1400 K. The maximum shift of W into WO_2Cl_2 is observed at T = 1400 K (8.97%). At T = 1600 K W begins to pass into the gaseous W_9O_3, W_4O_{12}, W_2O_6. For example, when T = 1700 K in the transition W in W_3O_9 is 61.89 %, W_4O_{12} – 31%, W_2O_6 – 6.66%.

Sodium in the system $Bi_2S_3 - WO_3 - NaCl - O_2$, with P = 0.01 MPa presented with several compounds which are distributed as follows: temperature rising transition in Na gaseous NaCl increases from 0 (1200 K) to 1700 K 92% (Fig. 6). Na sublimation is carried chloride dimer and trimer Na_2Cl_2 and Na_3Cl_3. Where in the maximum sublimation Na_2Cl_2 – 23.82%, and Na_3Cl_3 – 0.93% from T = 1400 K. A further increase in temperature

to 1700 K results in lower degree of sublimation Na_2Cl_2 to 3.8% Na_3Cl_3 to 0.02%. It should be noted that the distribution S in SO_2 increases at reaches 94.47% at T = 1700 K.

Table 7 and Fig. 7 include information about the composition of the gas phase of the system at P = 0.01 MPa, which reflects the degree of chlorination processes and the formation of Bi and gaseous chlorides W. Thus, at T = 1200 K, the gas phase contains 85.99% $BiCl_3$ and 1.79% BiCl.

At 1500 K, the main components of the gas phase are NaCl (44.24%), SO_2 (18.69%), O_2 (16.62%), BiCl (13.58%) and at 1700 K – NaCl (48.06%), SO_2 (18.48%), O_2 (17.00%), BiO (2.99%), Bi (7.42%). Due to a small extent in the form of chloride W WO_2Cl_2, this oxochloride content exceeds 2%, accounting for only 0.97% in the temperature range of 1300–1400 K.

Table 6

Effect of temperature on the extent of distribution of the Bi, W, Na, S in
the system $Bi_2S_3 - WO_3 - NaCl - O_2$ at a pressure of 0.01 MPa

Distributed element	Compounds	The degree of distribution (%) at the temperatures, K					
		200	1300	1400	500	600	1700
Bi	Bi_2O_3k	1.09	8.8	12.12	10.92	-	-
	$BiCl_3$	96.88	80.16	19.64	0.22	0,001	-
	$BiCl$	2.0	10.88	66.47	79.08	57.16	16.6
	BiO	<0.001	0.012	0.32	2.92	14.37	22.96
	Bi_4O_6	0.022	0.14	1.4	3.72	3.12	-
	Bi	<0.001	0.005	0.2	3.04	23.67	56.93
	Bi_2	-	-	0.001	0.085	1.67	3.44
W	WO_3k	98.52	94.68	90.96	97.51	84.92	-
	WO_2Cl_2	1.48	5.32	8.97	1.28	0.16	-
	W_3O_9	-	-	0.014	0.78	9.3	61.89
	W_4O_{12}	-	-	-	0.33	4.6	31.32
	W_2O_6	-	-	-	0.051	0.52	6.66
Na	$NaCl$	0.08	5.08	41.49	64.31	78.12	92.0
	Na	-	-	<0.001	0.001	0.041	0.665
	$NaClk$	25.69	26.84	-	-	-	-
	Na_2SO_4k	72.0	64.2	33.74	20.2	13.9	2.44
	Na_2SO_4	<0.001	0.004	0.020	0.11	0.45	1.57
	Na_2Cl_2	-	3.74	23.82	15.06	7.44	8
	Na_3Cl_3	-	0.14	0.93	0.305	0.075	0.02
S	SO_2	2.94	14.13	54.49	72.53	80.6	94.42
	Na_2SO_4k	97.02	85.69	45.03	26.97	18.54	3.248
	SO_3	0.04	0.17	0.44	0.28	0.24	0.186
	Na_2SO_4	<0.001	0.001	0	0.14	0.62	2.009

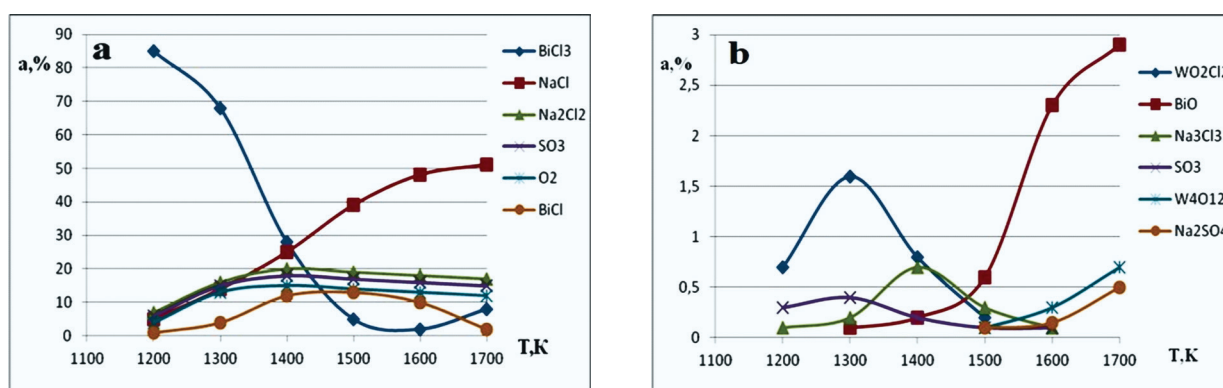
Fig. 7. Influence of temperature for composition of gas phase of system $Bi_2S_3 - WO_3 - NaCl - O_2$ at P = 0.01 MPa: a, b – the gas composition at low pressure.

Total degree of transition in Bi, BiCl and $BiCl_3$ decreases from 99.96% to 4.21% as the temperature increases from 1200 K to 1700 K as follows (Table 8).

The formation of oxochloride W in the system is noted only in the temperature range 1200–1500 K

with a maximum at 1200 K (3.99%). For T>1500 K chlorination W occurs and proceeds in WO_3, $W_3O_9, W_4O_9, W_2O_6, W_5O_{15}, W_3O_8, W_4O_{12}$.

Moreover, if T>1600 K for W basic compounds are $W_3O_9, O_{12}, W_4, W_2O_6$.

Table 7
Composition of the gas phase, vol.% of the system $Bi_2S_3 - WO_3 - NaCl - O_2$ at P = 0.01 MPa

Content of components, vol.%	Temperature, K					
	1200	1300	1400	1500	1600	1700
$BiCl_3$	85.99	50.23	4.23	0.038	0.001	-
$BiCl$	1.79	6.82	14.32	13.58	8.64	2.16
BiO	<0.001	0.007	0.069	0.50	2.17	2.99
Bi_4O_6	0.005	0.021	0.067	0.16	0.12	0.002
Bi	0.001	0.003	0.043	0.52	3.58	7.42
Bi_2	-	-	<0.001	0.007	0.126	0.22
WO_2Cl_2	0.665	1.667	0.967	0.11	0.012	0.001
W_3O_9	-	<0.001	0.002	0.022	0.23	1.39
W_4O_{12}	-	-	0.001	0.007	0.087	0.51
W_2O_6	-	-	0.001	0.004	0.039	0.21
$NaCl$	3.174	12.75	35.82	44.24	47.31	48.06
Na_2SO_4	<0.001	0,002	0.008	0.038	0.13	0.41
Na_2Cl_2	1.303	4.69	10.27	5.18	2.22	0.993
O_2	2.92	10.04	15.99	16.62	16.89	17.00
SO_2	3.958	13.28	17.61	18.69	18.28	18.48
CI	0.035	0.11	0.13	0.059	0.025	0.012
SO_3	0.054	0.16	0.14	0.09	0.054	0.036
Na_3Cl_3	0.028	0.121	0.27	0.069	0.015	0.004
Cl_2	0.056	0.07	0.021	0.001	0.001	-

Table 8
Effect of temperature on the transition of Bi to gaseous chlorides

T, K	1200	1250	1300	1350	1400	1500	1600	1700
The degree of transitionin Bi Σ $BiCl_3$ + $BiCl$, %	99.69	88.67	80.72	76.18	65.71	17.94	5.15	4.21

The received results of thermodynamic modeling of a chlorination of tungsten and bismuth in the environment of ionic fusions are very important for creation of scientific bases and development of new technologies of receiving non-ferrous metals from industrial wastes and secondary raw materials. It will allow to solve a number of the major technological, economic and ecological tasks: to return valuable and scarce metals to the sphere of production activity; to lower power costs of production of non-ferrous metals; to prevent or to significantly reduce hit of toxic products to the environment.

4. Conclusions

According to the work done we can conclude that the use of NaCl as chlorinating agent at a chlorinating roasting joint Bi_2S_3 and WO_3 is not effective in the form of chloride W WO_2C_{12}. The degree of tungsten chlorination deteriorates with a decrease in pressure from 0.1 to 0.01 MPa, respectively, 15.16% to 3.99%. Therefore, NaCl as a chlorinating agent in the system: $Bi_2S_2–WO_3–NaCl–O_2$ can only be used to chlorination Bi, which at T = 1200 K and pressures of 0.01–0.1 MPa can reach 98.0–99.69%. Besides the problem of complex processing of mineral raw materials and the associated problems of creating Non-waste technologies is the most important strategy for sustainable social and economic development of the world community. The intensity of this development largely determined by the rationality and ideality technology of processing of difficult-to-digest raw materials and man-caused waste, including waste from mining and metallurgical enterprises. Accumulated world experience processing of natural and technogenic raw materials indicates that

one of the promising methods of extracting metals from difficult enrich raw materials is the method by use of chloride refining. Opportunity of combining in one furnace aggregate the processes of chlorination of metals and the formation of various building materials can be attributed to technologies with large potentially production, economic and environmental opportunities. In this regard, the development of this method is directly depends on the degree of study of complex simultaneous-flowing processes of chlorination, formation of a building composition, combustion of fuel in a layer of material.

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