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ADJUSTMENT OF CHEMICAL ELEMENTS MASS BALANCES IN METALLURGICAL PROCESSES

UZGADNIANIE BILANSÓW MASOWYCH PIERWIASTKÓW CHEMICZNYCH W PROCESACH METALURGICZNYCH

Mass balances of the principal chemical elements are usually based on non-adjusted measurement results. Such an approach may lead to serious errors in energy and exergy analysis of the processes when chemical reactions are taking place in the system.

Orthogonal least squares method with constraints is proposed to be applied to improve accuracy of the measurement results. Theoretical considerations are illustrated with adjustment mass balances for chemical elements of the shaft furnace and flash smelting processes of copper production.

Bilanse masowe głównych pierwiastków chemicznych procesu są wykonywane przy użyciu nieuzgodnionych danych pomiarowych. Takie podejście może prowadzić do istotnych błędów w bilansach energii i egzergii procesów chemicznych. W artykule zaproponowano zastosowanie ortogonalnej metody najmniejszych kwadratów z warunkami ograniczającymi w celu zmniejszenia wartości błędów pomiarowych. Rozważania teoretyczne zobrazowano uzgadnianiem bilansów pierwiastków w procesach szybowym i zawiesinowym otrzymywania miedzi katodowej.

Nomenclature

$\dot{m}$ – mass flow rates (kg/s, kg/year)
g_i – mass fraction of $i-th$ chemical element (kgi/kg),
$\tilde{x}$ – most probable value of the measurement result or unknown variable,
l – measurement result (observation) ($\dot{m}$ or g_i)
k – Lagrange multipliers,
$\mathbf{A}$ – Jacobi matrix of observation (measurement results),
$\mathbf{B}$ – Jacobi matrix of unknown variables,
$\mathbf{W}$ – residuum matrix of unknown variables,
$\mathbf{M}$ – error diagonal matrix, (*a priori*),
$\mathbf{M}_u$, $\mathbf{M}_n$ – error diagonal matrices for observations and unknown variables respectively (*a posteriori*),
v, y – unknown corrections to the measured results and unknowns.

Subscripts

blister c. – blister copper,
briq – briquettes,
conv.slag – converter slag,
flue d. – flue dust.

1. Introductions

Method usually used in the mathematical formulation of the mass balances are based on unique (in mathematical sense) description without the possibility of checking the correctness of the balance equations. With such methods it is also impossible to evaluate the accuracy of the mass balances. By introducing the supplementary data concerning the process, the accuracy of the mass balances can easily be evaluated. From mathematical point of view such an approach means the system of mass balances consist of more equations than the number of unknowns which in consequence leads to a finite set of probable solutions.

The mass balances are based on the laws of conservation of mass. This law – when applied to the principal chemical elements – leads to a system of algebraic equations. These equations contain directly measured variables such a mass flow rates and chemical composition

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of substrates and products of the process. If some of the variables can not be directly measured, the system of balance equations contains unknown variables (non measured variables). The solution of the system of mass balances is possible when the number of unknown variables is equal or less than the number of independent equations. When the number of independent equations is equal to the number of unknowns the system can be solved without possibilities to control the correctness of measurement results. However, such a control is possible when the number of non-measured variables is less than that of equations, basing on expression containing the variables directly measured. Because of inevitable errors of measurements the mass balance equations are not exactly satisfied (it is the result of imperfection of the method of measurement and fluctuations of the process variables). The problem which arises is: how to correct the values of directly measured variables to obtain a most probable solution? Such a corrections are called *adjustment of mass balances*. Such a procedure is necessary and its neglecting may lead to the following consequences:

- a result obtained by evaluating the non-measured variables depend on way of calculation (theoretically correct in all cases),
- the values of unknowns calculated from some equations do not satisfy the other equation (not used in calculation),
- the value of heat losses to surroundings calculated from energy balance equations depends on the method used in evaluating the chemical enthalpy.

A problem no less important is: how to control that the errors of measurements do not exceed the assumed limits. The problem described above, known as the theory of the adjustment of mass and energy balances, was for the first time formulated by Szargut and Ryszka [1]. More rigorous mathematical analysis of the problem of the adjustment of mass and energy balances has been done by Szargut and Kolenda [2,4].

2. Theoretical development

Mass balances are formulated for the boundary system. They are adjusted on basis of the system of constraint equations which consists of the following expressions:

- mass balances of principal chemical elements (principal elements are the elements predominating in the process)
- mole fraction balances for substrates and products of the process.

Let us write the system of constraint equations in a general form

$$\varphi_s(\tilde{x}_1,\ldots,\tilde{x}_u,\tilde{x}_{u+1},\ldots,\tilde{x}_{u+n}) = 0 \quad (\mathrm{s} = 1,\ldots,\mathrm{r}) \qquad (1)$$

The first group $(\tilde{x}_1,\ldots,\tilde{x}_u)$ represents most probable values of the directly measured variables and the second $(\tilde{x}_{u+1},\ldots,\tilde{x}_{u+n})$ is the set of most probable values of unknown parameters or constraints. The problem can be uniquely solved, in the mathematical sense, if the number of unknowns is equal to the number of equations (1) i.e. when $n = r$. The problem could also be uniquely solved under the condition $n < r$ when values of all variables $(\tilde{x}_1,...,\tilde{x}_u)$ were exactly known i.e. the error values equal to zero. Such an assumption can only be considered theoretically and has no practical meaning. Assuming that the values of the directly measured variables are known with some errors $(\mu_1,...,\mu_u)$ the system of Eqs. (1) can be solved under the condition $n < r$ if and only if an additional criterion is imposed. Such a criterion allows choosing one of the possible solutions that we believe to be the most probable solution. One of the possibilities is the well known least square principle which requires the function

$$f(\tilde{x}) = \sum_{i=1}^{u} \frac{(x_i - l_i)^2}{\mu_i^2}, \qquad (2)$$

where l_i represents the observations (measurement results) of $\tilde{\mathbf{X}} = (\tilde{x}_1,\ldots,\tilde{x}_u)$, to reach a minimum with simultaneous fullfilment of the system of Eqs.(1).

If error values are small enough to compare to $\mathbf{L} = (l_1,...,l_u)$ a linearization procedure for Eqs.(1) can be applied using the zero and first-order terms of the Taylor expansion. This convert the system of Eqs.(2) into the linear form

$$\underset{(r,u+n)}{\mathbf{C}}\ \underset{(u+n,1)}{\mathbf{X}} + \underset{(r,1)}{\mathbf{W}} = \underset{(r,1)}{\mathbf{0}}, \qquad (3)$$

where $\mathbf{C}$ is the Jacobi matrix evaluated at $\mathbf{L} = (l_1,\ldots,l_u) = \mathbf{X_u} = (x_1,\ldots,x_u)$ and approximations $\mathbf{X_n} = (x_{u+1},\ldots,x_{u+n})$. Vector $\mathbf{X} = [\mathbf{X}_u,\mathbf{X}_n]^{\mathbf{T}}$.

Free terms vector $\mathbf{W} = -\mathbf{W}_o - \mathbf{C}[\mathbf{L},\mathbf{X}_n]^{\mathbf{T}}$ where $\mathbf{W}_O$ represents the residues of the original system of non-linear Eqs.(1) evaluated of $\mathbf{L} = (l_1,\ldots,l_u)$ and $\mathbf{X} = (x_{u+1},\ldots,x_{u+n})$.

Using Lagrange method the function which is minimized takes the form

$$\Phi(x_1,\ldots,x_{u+n}) = f(\tilde{x}) - 2\mathbf{K}^T(\mathbf{CX} + \mathbf{W}), \qquad (4)$$

where $\mathbf{K_T} = [k_1,...,k_r]$ is the Lagrange multipliers vector. Dividing matrix $\mathbf{C}$ into two submatrices $\mathbf{A}$ and $\mathbf{B}$, the system of Eqs.(3) can be rewritten in the form

$$\mathbf{AX}_u + \mathbf{BX}_n + \mathbf{W} = 0 \qquad (5)$$

Introducing from definition

$$\tilde{\mathbf{X}}_u = \mathbf{L} + \mathbf{V} \qquad (6)$$

$$\tilde{\mathbf{X}}_n = \mathbf{X}_n + \mathbf{Y} \qquad (7)$$

where $\mathbf{V} = [v_1, \ldots, v_u]^T$ and $\mathbf{Y} = [y_{u+1}, \ldots, y_{u+n}]^T$ are unknown corrections to **L** and **X** respectively, the system of Eqs.(5) takes the form

$$\mathbf{AV} + \mathbf{BY} = \mathbf{W}_o \qquad (8)$$

where $\mathbf{W}_o = -(\mathbf{AL} - \mathbf{BX} + \mathbf{W})$

Thus, the function (4) becomes

$$\Phi(\mathbf{V},\mathbf{Y}) = \mathbf{V}^T\mathbf{M}^{-2}\mathbf{V} - 2\mathbf{K}^T(\mathbf{AV} + \mathbf{BY} - \mathbf{W}_o) \qquad (9)$$

where $\mathbf{M} = [\mu_1, \mu_2, \ldots, \mu_u]_{diagonal}$.
Routine calculation to find minimum of (9) leads to the equations

$$\mathbf{A}^T\mathbf{K} - \mathbf{M}^{-2}\mathbf{V} = 0 \qquad (10)$$

$$\mathbf{B}^T\mathbf{K} = 0 \qquad (11)$$

Solving (8), (10) and (11) we finally obtain [2,4]

$$\mathbf{V} = \mathbf{M}^2\mathbf{A}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\left(\mathbf{E} - \mathbf{B}\left(\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\mathbf{B}\right)^{-1}\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\right)\mathbf{W}_o \qquad (12)$$

$$\mathbf{Y} = \left(\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\mathbf{B}\right)^{-1}\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\mathbf{W}_o \qquad (13)$$

The most important advantages of the least squares method is the fact that so called *a posteriori* errors are always smaller that the measurement errors $\mu = (\mu_1, \ldots, \mu_u)$. Using the law of error propagation the *a posteriori* errors can easily be calculated. The final result is [2]

$$\mathbf{M}_u^2 = \left(\mathbf{M}^2 - \mathbf{g}_{12}\mathbf{AM}^2\right)_{diagonal} \qquad (14)$$

$$\mathbf{M}_n^2 = \left(\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\mathbf{B}\right)^{-1}_{diagonal} \qquad (15)$$

where

$$\mathbf{g}_{12} = \mathbf{M}^2\mathbf{A}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\left(\mathbf{E} - \mathbf{B}\left(\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\mathbf{B}\right)^{-1}\mathbf{B}^T\left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}\right)$$

E – identity matrix.

2.1. Condition for model adequacy

The condition for mass balances can be formulated in a more or less sophisticated way. Every proposed condition has its own advantages or disadvantages. The use of the least squares principle allows the formulation of one of the simplest condition in the form [5]

$$|x_i - l_i| < k\mu_i \quad \text{for all } i = 1, \ldots, u \qquad (16)$$

where k is the arbitrarily chosen constant and can be interpreted as Lipschitz constant. The term $k\mu_i$ in condition (16) represents he maximum acceptable deviation of every single datum used in calculation. The choice of the value of k is open for discussion but on the basis of the assumption relating to normality of errors its value depends on the assumed reliability level. However, the strongest form of the condition (16) is for $k = 1$. The choice of this value is proposed in the present analysis.

Finally, under condition (16) the accuracy of the mass balances can be acceptable if the inequality

$$|x_i - l_i| < \mu_i \qquad (17)$$

is satisfied for all measurement results.

2.2. Unified approach

In many practical problems the necessary, from a mathematical point of view, condition that the rank of the Jacobi matrix **A** must be equal to the number of balance equation r is not satisfied. Such a situation is observed when the number of directly measured variables is less than the number of equations. Solutions (12) and (13) cannot be used in such a case as an inverse matrix $\mathbf{F}^{-1} = \left(\mathbf{AM}^2\mathbf{A}^T\right)^{-1}$ does not exist ($\det\left(\mathbf{AM}^2\mathbf{A}^T\right) = 0$) and another method of solution must be sought. One of the possibilities is a unified least squares method proposed by Mikhail and Ackermann [6] for surveying problems. This method will be adapted here for the adjustment of mass balance equations.

The basic principle and the most important assumption in the unified approach is that all variables are observations (result of direct measurement). It means that unknown variables are treated numerically in the some manner as directly measurement variables, but with sufficiently large error values in comparison with a priori errors μ_i

Eqs.(3) can now be written in a simplified form:

$$\bar{A}\bar{V} = W \tag{18}$$

where

$$\bar{A} = [A, B] \tag{19}$$

and

$$\bar{V} = \left[V^T, Y^T\right] \tag{20}$$

and corresponding a priori weight matrix is

$$\bar{M}^{-2} = \begin{bmatrix} M^{-2} & 0 \\ 0 & M_y^{-2} \end{bmatrix}, \tag{21}$$

where no correlation is assumed between two vectors **L** and **X**.

A new weight matrix M_y^{-2} is the inverse of an a priori covariance (diagonal) matrix for unknowns (zero matrix in classical approach). Using, as previously, the Lagrange multipliers method the final solution is in the form

$$\bar{V} = \bar{M}^2\bar{A}^T\bar{F}^{-1}W, \tag{22}$$

where

$$\bar{F} = \bar{A}\bar{M}^2\bar{A}^T \tag{23}$$

with the covariance matrix for all variables

$$\tilde{\bar{M}}^2 = \bar{M}^2 - \bar{M}^2\bar{A}^T\bar{F}^{-1}\bar{A}^T\bar{M}^2. \tag{24}$$

The partition of the calculated variables into measured and unknowns is not necessary in the calculation.

3. Adjustment of mass balances of shaft furnace and flash smelting technologies

Adjustment of principal chemical elements has been carried out for each elementary units of the shaft furnace and flush smelting process chains from copper ore mine to cathode copper. On the basis of preliminary evaluations the set of principal chemical elements contains mass balances of Cu, Pb, Fe, S, As, SiO_2, CaO, Al_2O_3, Ag, C, O_2, H_2, MgO and N_2. Schematic flow-sheets for shaft furnace and flash smelter are shown in Fig.1 and Fig.2 (measurement data from[6]).

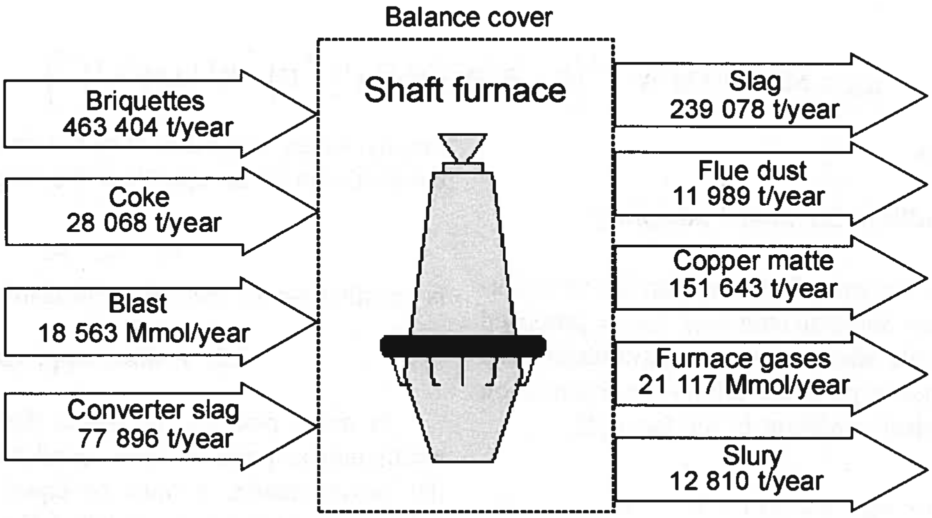

Fig. 1. Shaft furnace material flows

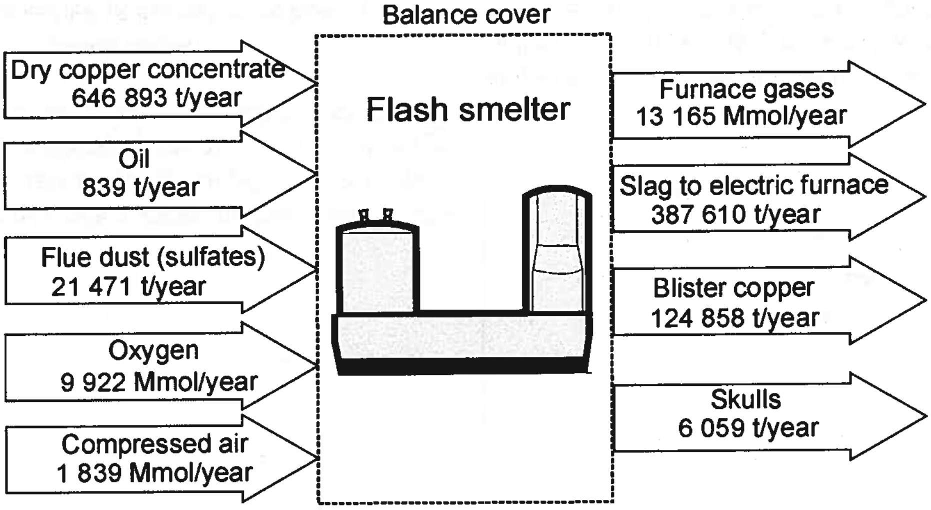

Fig. 2. Flash smelting material flows

As the example, copper balance equation for shaft furnace process takes the form:

$$\tilde{\dot{m}}_{briq}\tilde{g}_{Cu,briq} + \tilde{\dot{m}}_{conv.slag} + \tilde{g}_{Cu,conv.slag} = \tilde{\dot{m}}_{flued.}\tilde{g}_{Cu,flued.} + \tilde{\dot{m}}_{blisterc.}\tilde{g}_{Cu,blisterc.} \tag{25}$$

where $\tilde{\dot{m}}_i$ is the most probable value of mass flow rate (in kg/s) and $\tilde{g}_{Cu}$ is the most probable value of copper concentration (in kg_{Cu}/kg).

According to the theory of the adjustment of measurement results presented in chapter 2, the most probable evaluations of the directly measured variables $\tilde{\dot{m}}_i$ are:

$$\tilde{\dot{m}}_i = \dot{m}_i + v_i \tag{26}$$

where – measurement result of i-th flow rate known with measurement a priori error mu_i, v_i – unknown correction. Introducing Eqs(25)

$$\tilde{\dot{m}}_{brig} = \dot{m}_{brig} + v_{brig}$$
$$\tilde{g}_{Cu,briq} = g_{Cu,briq} + v_{Cu,briq}$$
$$\tilde{\dot{m}}_{conv.slag} = \tilde{m}_{conv.slag} + v_{conv.slag}$$
$$\tilde{g}_{Cu,conv.slag} = g_{Cu,conv.slag} + v_{Cu,conv.slag}$$
$$\tilde{\dot{m}}_{flued.} = \dot{m}_{flued.} + v_{flued.}$$
$$\tilde{g}_{Cu,flued.} = g_{Cu,flued.} + v_{Cu,flued.}$$
$$\tilde{\dot{m}}_{blisterc.} = \dot{m}_{blisterc.} + v_{blisaterc.}$$
$$\tilde{g}_{Cu,blisterc.} = g_{Cu,blisterc.} + v_{Cu,blisterc.}$$

into Eqs.(24) we obtain

$$\begin{aligned}&\left(\dot{m}_{briq} + v_{brig}\right)\left(g_{Cu,brig} + v_{Cu,briq}\right) + \\ &+ \left(\dot{m}_{conv.slag} + v_{conv.slag}\right)\left(g_{Cu,conv.slag} + v_{Cu,conv.slag}\right) = \\ &= \left(\dot{m}_{flued.} + v_{flued}\right)\left(g_{Cu,flued.} + v_{Cu,flued.}\right) + \\ &+ (m_{blisterc.} + v_{blisterc.})\,(g_{Cu,blisterc.} + v_{Cu,blisterc.})\end{aligned} \tag{27}$$

and after linearization

$$\begin{aligned}&\dot{m}_{briq}v_{Cu,briq} + g_{Cu,briq}v_{briq} + \dot{m}_{conv.slag}v_{Cu,conv.slag} + \\ &+ g_{Cu,con.slag}v_{conv.slag} - \dot{m}_{flued}v_{Cu,flued.} - g_{Cu,flued.}v_{flued.} - \\ &- \dot{m}_{blisterc}v_{Cu,blisterc.} - g_{Cu,blisterc.}v_{blisterc.} = \\ &- \dot{m}_{briq}g_{Cu,briq} - \dot{m}_{conv.slag}g_{Cu,conv.slag} + \\ &+ \dot{m}_{flued.}g_{Cu,flued.} + \dot{m}_{blisterc.}g_{Cu,blisterc.}\end{aligned}$$

Elements of the matrices **A** and **W** are:

$$A = \left[\dot{m}_{briq}, g_{Cu,briq}, \dot{m}_{con.slag}, g_{Cu,conv.slag}, -\dot{m}_{flued.}, -g_{Cu,flued.}, \dot{m}_{blisterc.}, g_{Cu,blisterc.}\right]$$
$$W = \left[-\dot{m}_{briq}g_{Cu,briq} - \dot{m}_{conv.slag}g_{Cu,conv.slag} + \dot{m}_{flued.}g_{Cu,flued.} + \dot{m}_{blisterc.}g_{Cu,blisterc.}\right]$$

Equations of the same form are written for each chemical element to form matrices **A** and **W** (in the case when unified method is used). The elements of the a priori error matrix are

$$\mathbf{M}^2 = \begin{bmatrix} \mu^2_{briq} & 0 & 0 & 0 & \cdots & \cdots \\ 0 & \mu^2_{Cu,briq} & 0 & 0 & \cdots & \cdots \\ 0 & 0 & \mu^2_{conv.slag} & 0 & \cdots & \cdots \\ 0 & 0 & 0 & \mu^2_{Cu,conv.slag} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

3.1. Example of chemical elements mass balance adjustment

As an example of calculation, measurement results of the mass flow rates and chemical composition of the substrates and products for shaft furnace and flash smelting are presented in Table 1 and Table 2.

TABLE 1

Shaft furnace measurement results (mass flow rates of solids in t/year, mass flow rates of gases in Mmol/year, chemical composition kg$_i$/kg) or kmoli/kmol

No	Notation	Measurement result	Measurement error a priori	Most probable value	Measurement error a posteriori
1.	Briquettes	482 836	4 828	463 404	4 582
	Cu	0.1526	0.01523	0.15540	0.00753
	Pb	0.0309	0.00309	0.03191	0.00117
	Fe	0.0661	0.00331	0.06599	0.00297
	S	0.1132	0.02264	0.07960	0.0040
	As	0.0029	0.00029	0.00209	0.00008
	SiO_2	0.1804	0.00902	0.19099	0.00771
	CaO	0.0486	0.00486	0.03219	0.00064
	Al_2O_3	0.0631	0.00316	0.06383	0.00245
	Ag	0.0007	0.00004	0.00078	0.0003
	C	0.0820	0.00410	0.05897	0.00830
	CO_2	0.0403	0.00403	0.04131	0.00348
	O_2	0.0208	0.00104	0.02176	0.00104
	H_2O	0.0200	0.00200	0.02179	0.00098
	C_7H_8	0.0300	0.00150	0.02899	0.00145
	MgO	0.0317	0.00159	0.00611	0.00040
2.	Coke	28 042	1 402	28 068	1 323
	Fe	0.0123	0.00615	0.01230	0.0062
	S	0.0082	0.00041	0.00819	0.00041
	SiO_2	0.0350	0.00175	0.03502	0.00175
	CaO	0.0055	0.00028	0.00549	0.00028
	MgO	0.0034	0.00017	0.00338	0.00017
	Al_2O_3	0.0016	0.00008	0.00158	0.00008
	C	0.8800	0.00440	0.87322	0.00413
3.	Blast	23 358	2 367	18 563	629
	O_2	0.2100	0.00021	0.2100	0.00021
	N_2	0.7900	0.00079	0.7900	0.00079
4.	Slag 1	65 554	3 278	65 448	3 027
	Cu	0.0405	0.00203	0.0405	0.00203
	Pb	0.0262	0.00131	0.0262	0.00130
	Fe	0.4348	0.02174	0.4341	0.01998
	S	0.0126	0.00063	0.0126	0.00063
	As	0.0010	0.00005	0.0010	0.00010
	SiO_2	0.1925	0.01930	0.1990	0.01903
	CaO	0.0027	0.00014	0.0027	0.00014
	MgO	0.0020	0.00010	0.0021	0.00021

TABLE 1 (continue)

No	Notation	Measurement result	Measurement error a priori	Most probable value	Measurement error a posteriori
	Al_2O_3	0.0020	0.00020	0.0020	0.00020
	Ag	0.0001	0.00001	0.0001	0.00001
5.	Slag 2	12 449	622	12 448	621
	Cu	0.2690	0.001346	0.2691	0.01344
	Pb	0.0610	0.00305	0.0610	0.00305
	Fe	0.3436	0.01718	0.3435	0.01715
	S	0.0043	0.00022	0.0043	0.00022
	As	0.0011	0.00006	0.0011	0.00006
	SiO_2	0.1175	0.00588	0.1178	0.00588
	CaO	0.0038	0.00019	0.0038	0.00019
	MgO	0.0019	0.00009	0.0019	0.00009
	Al_2O_3	0.0019	0.00009	0.0019	0.00009
	Ag	0.0002	0.00001	0.0002	0.00001
6.	Flue dust	11 590	579	11 989	578
	Cu	0.1100	0.00505	0.1099	0.00505
	Pb	0.1302	0.00651	0.1302	0.00651
	Fe	0.0578	0.00289	0.0578	0.00289
	S	0.1074	0.00537	0.1074	0.00537
	As	0.0087	0.00044	0.0087	0.00044
	SiO_2	0.1520	0.01520	0.1513	0.01520
	CaO	0.0335	0.00168	0.0336	0.00167
	MgO	0.0246	0.00123	0.0250	0.00123
	Al_2O_3	0.0500	0.00250	0.0499	0.00250
	Ag	0.0006	0.00003	0.0006	0.00003
	C	0.2200	0.01100	0.2240	0.01099
	CO_2	0.0602	0.00301	0.0601	0.00301
7.	Copper matte	154 191	3 084	151 643	2 863
	Cu	0.5012	0.02506	0.4988	0.00223
	Pb	0.0440	0.00220	0.0438	0.00215
	Fe	0.2154	0.01077	0.2158	0.00957
	S	0.2314	0.01157	0.2234	0.01142
	As	0.0030	0.00015	0.0031	0.00015
	Ag	0.0024	0.00012	0.0021	0.00009
8.	Slag	245 281	12 264	239 078	8 145
	Cu	0.0038	0.00019	0.0038	0.00019
	Pb	0.0116	0.00058	0.0116	0.00058
	Fe	0.1254	0.00627	0.1256	0.00568
	S	0.0017	0.00009	0.0017	0.0009
	As	0.0001	0.00001	0.0001	0.00001
	SiO2	0.4600	0.02300	0.4251	0.01701
	CaO	0.0160	0.00080	0.0166	0.00079
	MgO	0.0100	0.00050	0.0113	0.00049
	Al_2O_3	0.1230	0.00615	0.1216	0.00678
	Ag	0.0002	0.00002	0.0002	0.00002
	O_2	0.0800	0.00400	0.0730	0.00396
9.	Skulls	12 543	627	12 810	609
	Cu	0.0115	0.00058	0.0115	0.00058
	Pb	0.4928	0.02464	0.4911	0.02418
	Fe	0.0078	0.00039	0.0078	0.00039
	S	0.0578	0.00289	0.0579	0.00289
	As	0.0347	0.00174	0.0355	0.00172
	SiO_2	0.0285	0.00143	0.0285	0.00143
	CaO	0.0066	0.00033	0.0066	0.00033

TABLE 1 (continue)

No	Notation	Measurement result	Measurement error a priori	Most probable value	Measurement error a posteriori
	MgO	0.0049	0.00030	0.0049	0.00030
	Al_2O_3	0.0074	0.00037	0.0074	0.00037
	Ag	0.0002	0.00001	0.0002	0.00001
10.	Furnace gases	26 855	2 686	21 117	823
	CO	0.1510	0.00755	0.1370	0.00658
	CO_2	0.1460	0.00730	0.0947	0.00433
	O_2	0.0220	0.00110	0.0198	0.00108
	H_2	0.0080	0.00080	0.0074	0.00080
	H_2O	0.0800	0.00800	0.0464	0.00256
	N_2	0.4000	0.40000	0.6944	0.00672

TABLE 2

Flash smelter measurement results (mass flow rates of solids in t/year, mass flow rates of gases in Mmol/year, chemical composition kg_i/kg) or kmoli/kmol

No	Notation	Measurement result	Measurement error a priori	Most probable value	Measurement error a posteriori
1.0	Dry concentrate	654 440	32722	646 893	18 452
	Cu	0.2824	0.0141	0.2792	0.0076
	Pb	0.0152	0.0008	0.0153	0.0006
	Fe	0.0277	0.0014	0.0278	0.0010
	S	0.0984	0.0049	0.0843	0.0038
	As	0.0009	0.0001	0.0008	0.0001
	SiO_2	0.1876	0.0094	0.1884	0.0070
	CaO	0.0753	0.0038	0.0754	0.0031
	MgO	0.0414	0.0021	0.0416	0.0016
	Al_2O_3	0.0584	0.0029	0.0586	0.0022
	Ag	0.0005	0.0001	0.0007	0.0001
	C	0.0800	0.0040	0.0854	0.0035
	CO_2	0.1300	0.0065	0.1320	0.0065
	H_2O	0.0040	0.0002	0.0040	0.0002
2.	IOS dust	21597	1080	21471	1070
	Pb	0.0002	0.0001	0.0002	0.0001
	Fe	0.0025	0.0001	0.0025	0.0001
	S	0.1157	0.0058	0.1151	0.0058
	As	0.0004	0.0001	0.0004	0.0001
	SiO_2	0.0105	0.0005	0.0105	0.0005
	CaO	0.5327	0.0266	0.5332	0.0264
	MgO	0.0095	0.0005	0.0095	0.0005
	Al_2O_3	0.0059	0.0003	0.0059	0.0003
	O_2	0.1965	0.0098	0.1963	0.0098
	H_2O	0.0500	0.0025	0.0500	0.0025
2.	Oil	838	42	839	41
	C	0.9200	0.0460	0.9200	0.045
	H_2	0.0800	0.0040	0.0800	0.0004
3.	Oxygen	10 193	509	9 922	365
	N_2	0.3000	0.0150	0.3126	0.0131
	O_2	0.7000	0.0350	0.6874	0.0131
4.	Compress. air	1 822	91	1 840	91
	O_2	0.2100	0.0021	0.2100	0.0203
	N_2	0.7900	0.0079	0.7900	0.0790
5.	Blister copper	128 460	3 212	124 858	2 996
	Cu	0.9878	0.04939	0.9881	0.0030
	Pb	0.0024	0.0001	0.0024	0.0001

TABLE 2 (continue)

No	Notation	Measurement result	Measurement error a priori	Most probable value	Measurement error a posteriori
	Fe	0.0001	0.0001	0.0001	0.0001
	S	0.0004	0.0001	0.0004	0.0003
	As	0.0011	0.0001	0.0011	0.0001
	Ag	0.0034	0.0002	0.0030	0.0001
6.	Skulls	6 053	303	6 060	303
	Cu	0.9878	0.0494	0.9881	0.0494
	Pb	0.0024	0.0001	0.0024	0.0001
	Fe	0.0001	0.0001	0.0001	0.0001
	S	0.0004	0.0001	0.0004	0.0001
	As	0.0011	0.0001	0.0011	0.0001
7.	Slag	386 508	19 325	387 610	12 761
	Cu	0.1322	0.0066	0.1336	0.0039
	Pb	0.0248	0.0012	0.0331	0.0014
	Fe	0.0468	0.0023	0.0502	0.0026
	S	0.0004	0.0001	0.0004	0.0001
	As	0.0010	0.0001	0.0011	0.0001
	SiO_2	0.3163	0.0158	0.3149	0.0118
	CaO	0.1564	0.0078	0.1557	0.0055
	MgO	0.0703	0.0035	0.0700	0.0026
	Al_2O_3	0.0986	0.0049	0.0982	0.0037
	Ag	0.0002	0.0001	0.0002	0.0001
	O_2	0.0700	0.0070	0.0716	0.0057
8.	Furnace gases	10 200	10 200	13 166	414
	H_2O	0.0200	0.0110	0.0180	0.0011
	CO_2	0.3500	0.2500	0.5015	0.0155
	SO_2	0.1000	0.0100	0.1345	0.0069
	N_2	0.5000	0.5000	0.3460	0.0152

Fig. 3 presents the Sankey diagrams of mess balance of copper (es chemical element) for shaft furnace and blast smelter.

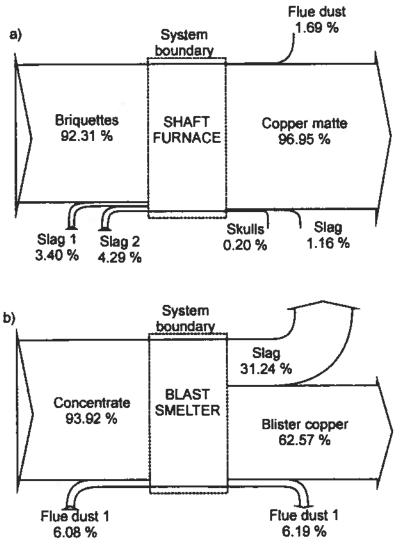

Fig. 3. Sankey diagram of mass balance for copper (a) shaft furnace, (b) blast smelter

4. Conclusions

The method of the adjustment of chemical element mass balances has been presented and applied for material balances of shaft furnace and blast smelting technologies of cathode copper. The advantage of method proposed is that the values of directly measured variables and unknowns can be treated as the most probable one in the sense of least squares method. Additionally, mass balance equations are exactly satisfied and the errors of all variables (measured and unknowns) can be determined. Energy and exergy balances calculated on the basis of adjusted mass balances of chemical elements are more accurate and no systematic error occurs in balance equations.

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