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EXERGY BALANCES AND ENTROPY GENERATION RATES AS THE MATHEMATICAL MODELS FALSIFICATION METHOD APPLIED FOR ALUMINIUM ELECTROLYSIS PROCESSES

FALSYFIKACJA MODELI MATEMATYCZNYCH NA PODSTAWIE INTENSYWNOŚCI ŹRÓDEŁ ENTROPII NA PRZYKŁADZIE PROCESU ELEKTROLIZY ALUMINIUM

A new method of falsification of the mathematical model of the processes taking place inside the aluminium electrolysis cell has been proposed. The method is based on the comparison of the calculation results of the entropy generation rates obtained in theoretical way with the exergy losses estimated from global exergy balance equation. Following irreversible processes have been analyzed – electric current flow, diffusion at the cathode, heat and electric current flow through the anode and cathode, irreversible carbon combustion, heat transfer from electrolyser to the surroundings and convection inside the electrolyte. Exergy balance calculations have been based on the experimental results from industry. The proposed procedure shows good accuracy between mathematical model and experimental data.

Keywords: energy, entropy generation rate, mathematical modeling

W artykule zaproponowano metodę falsyfikacji modelu matematycznego procesów jednostkowych zachodzących w elektrolizerze aluminium poprzez porównanie wartości sumarycznego źródła entropii z wartością strat egzergii wynikającą z zamknięcia globalnego bilansu egzergii. Wiarygodność porównania uściślono poprzez uzgodnienie bilansów substancji i energii. Wyniki obliczeń oparto na bezpośrednich pomiarach przemysłowych. Stwierdzono dobrą zgodność modelu matematycznego z wynikami pomiarów.

1. Introduction

Falsification of the mathematical models of physical and chemical processes play important rule in model acceptation procedure. Falsification methods can be different but their mathematical independence to the experimental data is necessary. In this paper statistical agreement between entropy generation rates calculated on the basis of thermodynamics of irreversible processes and independently calculated rates from global exergy balance equation has been proposed as the general comparison criterion. To improve accuracy of measurement results, the method of adjustment of chemical elements mass balances has been adopted. Such a procedure allowed to estimate a posteriori errors of the measurement data.

2. Description of the process

General scheme of the aluminium electrolysis cell is shown in Fig. 1.
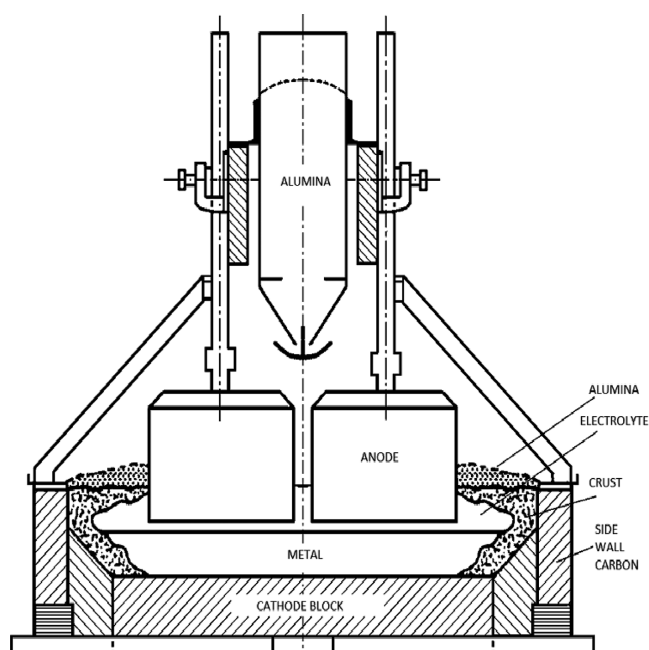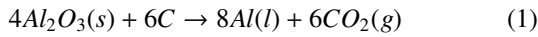

Fig. 1. Aluminium electrolysis cell [1] (with permission from the authors)

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Most important driving chemical reaction taking place inside liquid criolite $Na_3AlF_6(l)$ is

$$4Al_2O_3(s) + 6C \rightarrow 8Al(l) + 6CO_2(g) \qquad (1)$$

Carbon dioxide escapes from the melt and is collected at the top of the cell. Additionally because the carbon anode is in contact with atmospheric air, carbon monoxide CO is formed according to reaction

$$2C(s) + O_2(g) \rightarrow 2CO(g) \qquad (2)$$

and CO(g) is also collected at the top of the cell. Pure aluminium is formed in the bottom of the cell. The cathode is the metal layer on the top of the carbon blocks. The liquid product is collected at regular intervals. The electrolyte is contained on the top of the liquid aluminium. The anode and cathode consist of several carbon blocks and conduct electric current from the liquid aluminium. Electrolyser is insulated in the bottom and on the sides. The electrolyte and liquid aluminium temperature is about 960°C. The cell electric potential is about 4.2 V and anode-catode distance is 4.50 cm. Cathodic current density is about $4.6 \cdot 10^3$ A/m^2 to secure average aluminium production of 75 kg_{Al} per hour. Usually, aluminium electrolysis cell operates between 100 to 300 kA. Joule heat is transferred through cell external refractories to the surroundings. The heat losses are almost 6.5 kWh/kg_{Al} at current efficiency of 0.95. In our case electric potential of the cell was 4.1 V, current density 4.5 A/m2, aluminium production 73.3 kgAl/h and estimated heat losses

$$\dot{Q}_o = 6.5 kWh/kg_{Al} \qquad (3)$$

Electric energy was continuously measured and equal

$$\dot{W}_{el} = I\Delta\Phi = 12.9 \text{ kWh/kg}_{Al} \qquad (4)$$

From theory of electrolysis process

$$\dot{W}_{el,min} = I\Delta\Phi_{min} = 5.4 \text{ kWh/kg}_{Al} \qquad (5)$$

Thus, thermodynamic efficiency is

$$\eta_{th} = \frac{\dot{W}_{el.min}}{\dot{W}_{el}} = \frac{5.4}{12.9} = 0.42 \qquad (6)$$

The difference $\delta B = W_{el} - W_{el,min}$ is unavoidable exergy (available energy) losses due to the irreversibilities of the processes taking place in the electrolyzer. Entropy generation rate can be calculated from expression

$$\dot{S}_{gen} = \frac{\delta\dot{B}}{T_o} = \frac{\dot{W}_{el} - \dot{W}_{el,min}}{T_o} \qquad (7)$$

and is equal

$$\dot{S}_{gen} = \frac{7.5}{300} = 0.025 kWh/kg_{Al} \cdot K \qquad (8)$$

where $\delta\dot{B}$ represents exergy losses of the process.

3. Theoretical estimation of exergy losses

The result of any real irreversible process occurs in the form of exergy (available energy) losses. They are usually calculated on the basis of entropy generation rate from expression [4]

$$W_{lost} = \delta\dot{B} = T_o\dot{S}_{gen} \qquad (9)$$

where $\dot{W}_{lost}, \delta\dot{B}$ are lost work and energy losses respectively, T_o is surroundings temperature and $\dot{S}_{gen}$ represent entropy generation rate.

All estimations of the lost work of elementary processes have been taken directly from the book of Kjelstrup and Bedeaux [1] (with permission from the authors). The following numerical data have been used in calculation:

$I = 230$ kA – electric current,

$\Delta\Phi_I = -1.7$ V – potential drop across the electrolyte,

$T_o = 300$ K – surroundings temperature,

$T_c = 960$ ^oC – molten electrolyte temperature,

$\Delta x = 1$ mm – thickness of diffusion layer at the cathode surface,

$\kappa = 19.0$ $k\Omega m^{-1}$ – electric conductivity of the cathode diffusion layer,

A = 50 m^2 – surface area of the cathode.

The work losses are:

– **Lost work due to charge transfer**

  – **The bulk electrolyte**

$$W_{lost,1} = \frac{T_o}{T_c}(-I\Delta\Phi_l) = 1.3 \text{ kWh/kg}_{Al} \qquad (10)$$

$$\dot{S}_{gen,1} = 4.33 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (11)$$

It mainly describes ohmic losses through the electrolyte layer

  – **The diffusion layer at the cathode**

$$W_{lost,2} = \frac{T_o}{T_c}\frac{I^2}{\kappa A}\Delta x = 0.05 \text{ kWh/kg}_{Al} \qquad (12)$$

$$\dot{S}_{gen,2} = 0.17 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (13)$$

It represent entropy generation due to the chemical potential gradient of the ions Na^+ and Al^{3+} at the layer close to the cathode surface and electric potential drop.

  – **The electrode surfaces**

$$W_{lost,3} = 0.48 kWh/kg_{Al} \qquad (14)$$

$$S_{gen,3} = 1.60 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (15)$$

It describes entropy generation rates of several elementary processes occurring at the electrode surfaces estimated by the electrode overpotential (~0.50 V). The above value represents processes at the anode surface as at the cathode surface value of $\dot{S}_{gen}$ is negligible.

  – **The carbon electrodes**

It results from the simultaneous heat and electric current flows through the carbon parts of the anode and cathode, According to the thermodynamics of irreversible processes

$$\dot{S}_{gen} = \dot{q}_j \cdot \nabla\left(\frac{1}{T_j}\right) + \frac{I}{T}\left(-\Delta\Phi_j\right) \qquad (16)$$

($j = 1,2$ and denotes anode and cathode blocks, respectively.) where

– heat flow

$$\dot{q}_j = -k_j A_j \frac{\Delta T}{\Delta x} + \pi_j \frac{I}{F} \qquad (17)$$

$$\Delta \Phi_j = -\frac{\pi_j}{T} \frac{\Delta T}{\Delta x} - \frac{\Delta x}{\kappa_j} I \qquad (18)$$

where π_j is Peltier heat.

Introducing Eq. (17) and (18) into Eq. (16)

$$\dot{S}_{gen,j} = k_j A_j \frac{\Delta T}{\Delta x} \nabla \left(\frac{1}{T_j} \right) + \frac{I^2}{A} \frac{\Delta x}{\kappa_j T} \qquad (19)$$

Data for calculation are given in Table 1.

TABLE 1

Lost work In the bulk anode and cathode

	units	Anode	Kathode
Thermal conductivity k_j	W/mK	10	13
Temperature interval ΔT	K	960-785	960-860
Diffusion layer thickness Δx	m	0.35	0.44
Surface area A	m^2	30	50
Electric conductivity κ	$\Omega^{-1} m^{-1}$	19 000	40 000
Peltier heat π	$J \cdot kmol^{-1}$	1520	2446
Work losses W_{lost}	kWh/kg$_{Al}$	0.33	0.33

– Lost work by excess carbon consumption

$$W_{lost,r} = 0.1 kWh/kg_{Al} \qquad (20)$$

This value is usually estimated from the carbon consumption which average value is 0.35 to 0.4 kgC/kgAl. From entropy change calculation of the reaction $(2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)})$ and Gibbs free enthalpy change equal to -219.5 kJ/mol$_{CO}$.

$$\dot{S}_{gen} = 0.33 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (21)$$

– Lost work due to heat transfer through the walls of container

$$W_{lost} = T_o \dot{Q}_o \left(\frac{1}{T_o} - \frac{1}{T_c} \right) = 4.8 kWh/kg_{Al} \qquad (22)$$

It is equal to the Carnot-cycle efficiency where $\dot{Q}_o = 6.50$ kWh/kg$_{Al}$. is total heat transferred to the surroundings.

– Conduction across the wall material

$$W_{lost,j} = -k_j T_o \frac{\Delta T_j}{\Delta x_j} A_j \Delta \left(\frac{1}{T_j} \right) \qquad (23)$$

Where j denotes different walls of the electrolyser (top, sides and bottom), ΔT_j is temperature difference between boundary surfaces, Δx_j is thickness of the wall and $\nabla(1/T)$ describes temperature gradient along wall thickness. Details and results of calculation can be found in [1]. Finally, the lost work is

$$W_{lost} = 1.6 kWh/kg_{Al} \qquad (24)$$

and

$$\dot{S}_{gen} = 5.33 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (25)$$

– Radiation and convection

Simplified calculations of the radiative and convective fluxes lead to the final value

$$W_{los,rad} = 0.90 kWh/kg_{Al} \qquad (26)$$

$$\dot{S}_{gen,rad} = 3.0 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (27)$$

$$W_{lost,con} = 2.30 kWh/kg_{Al} \qquad (28)$$

$$\dot{S}_{gen,con} = 7.67 \cdot 10^{-3} kWh/K \cdot kg_{Al} \qquad (29)$$

– Result of calculation

All contributions are summarize in Table 2.

TABLE 2

The lost work of the cell

Loss type	Loss location	Amount lost (kWh/kg$_{Al}$)
Charge transfer	Electrolyte resistant	1.30
	Diffusion layer	0.10
	Electrode surfaces	0.50
	Bulk cathode	0.30
	Bulk anode	0.30
Hot reactants	Al and CO_2	0.30
Chemical reaction	Anode	0.10
Thermal	Wall, surroundings	4.80
	Σ	7.70

Entropy generation rate for the cell is equal

$$\dot{S}_{gen} = \frac{\sum W_{lost}}{T_o} = \frac{7.70}{300} = 2.57 \cdot 10^{-2} kWh/K \cdot kg_{Al} \qquad (30)$$

4. Entropy generation rate calculation from exergy balance equation

General scheme of the system for exergy analysis purposes is shown in Fig. 2.
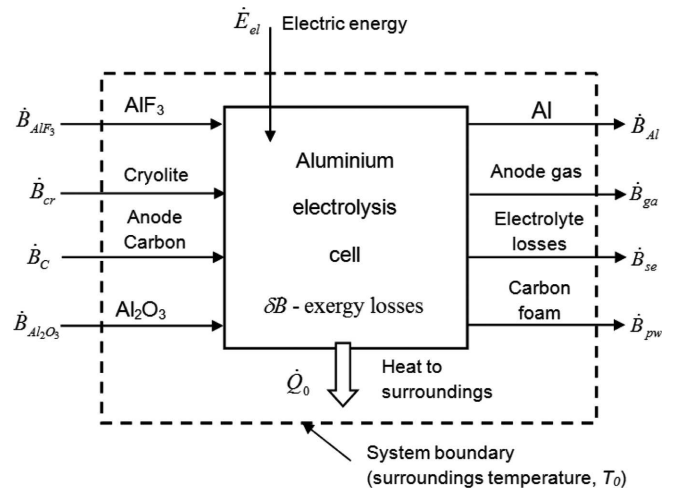

Fig. 2. System under consideration

Assuming steady-state conditions, the exergy balance equation takes the following form

$$\dot{B}_{Al_2O_3} + \dot{B}_{cr} + \dot{B}_{AlF_3} + \dot{E}_{el} = \dot{B}_{Al} + \dot{B}_A + \dot{B}_l + \dot{B}_{cf} + \delta \dot{B} \qquad (31)$$

Where $\delta\dot{B}$ denotes global exergy losses as the result of the irreversibilities inside the system including exergy losses due to heat transfer to surroundings.
Thus

$$\delta B = \dot{B}_{Al_2O_3} + \dot{B}_{cr} + \dot{B}_{AlF_3} + \dot{E}_{el} - \dot{B}_{Al} - \dot{B}_A - \dot{B}_l - \dot{B}_{cf} - \dot{B}_{Q_0} \quad (32)$$

Calculation procedure is presented below.

Exergy fluxes

$$\dot{B}_i = \dot{m}_i b_{th,i} \quad (33)$$

where $\dot{m}_i$ is mass flow rate of the i−th substrate or product of the process and $b_{th,i}$ their thermal exergy [2]

$$b_{th,i} = b_{ph,i} + b_{ch,i} \quad (34)$$

where $b_{ph,i}$ and $b_{ch,i}$ denotes specific physical and chemical exergy, respectively.

Values of $b_{ch,i}$ are tabulated in engineering thermodynamic monographs (for example [2]) and $b_{ph,i}$ are calculated from equation

$$b_{ph} = c_p \left[(T - T_o) - T_o \ln \frac{T}{T_o} + RT \ln \frac{p}{p_o} \right] \quad (35)$$

where c_p is specific heat, T – is temperature of the substance, P – pressure of the system and T_o, P_o are temperature and pressure of surroundings.

Before exergy balance calculation to increase its accuracy the method of adjustment of mass balances of principal chemical elements of the process has been adopted and applied. General theory the adjustment of the directly measured variables is describes on Appendix1. [3].

In the case of aluminium electrolysis process the following chemical elements have been assumed to be involved in adjustment procedure – Al, F, C, O_2, Na. Mass balance equations take the form:

○ – balance Al.

$$2\frac{\dot{m}_{Al_2O_3}}{M_{Al_2O_3}} + \frac{\dot{m}_{cr}}{M_{Na_3AlF_6}} + \frac{\dot{m}_{AlF_3}}{M_{AlF_3}} - \frac{\dot{m}_{Al}}{M_{Al}} - \dot{m}_{se}\left(\frac{x_{se}^{AlF_3}}{M_{AlF_3}} + \frac{x_{se}^{Na_3AlF_6}}{M_{Na_3AlF_6}} \right) = 0 \quad (36)$$

○ – balance F

$$6\frac{\dot{m}_{kr}}{M_{Na_3AlF_6}} + 3\frac{\dot{m}_{AlF_3}}{M_{AlF_3}} - \dot{m}_{se}\left(\frac{3x_{se}^{AlF_3}}{M_{AlF_3}} + \frac{6x_{se}^{Na_3AlF_6}}{M_{Na_3AlF_6}} \right) = 0 \quad (37)$$

○ – balance C

$$\frac{\dot{m}_C}{M_C} - \frac{\dot{m}_{pw}}{M_C} - \dot{n}_{ga}\left(y_{ga}^{CO} + y_{ga}^{CO_2} \right) = 0 \quad (38)$$

○ – balance O_2

$$\frac{3}{2}\frac{\dot{m}_{Al_2O_3}}{M_{Al2O_3}} + 0.21\dot{n}_p - \dot{n}_{ga}\left(\frac{1}{2}y_{ga}^{CO} + y_{ga}^{CO_2} \right) = 0 \quad (39)$$

○ – balance Na

$$3\frac{\dot{m}_{cr}}{M_{Na_3AlF_6}} - 3\dot{m}_{se}\frac{x_{se}^{Na_3AlF_6}}{M_{Na_3AlF_6}} = 0 \quad (40)$$

Where $\dot{m}_i$ are mass flow rate, M_i – molecular weight of i-th element or compounds, x – mass fraction, $\dot{n}$ – mole flow rate of gasous substances, y – mole fraction.

Measurement results with a priori errors are shown in Table 3.

TABLE 3

Measurement results with priori errors

Substance	Mass flow rate	Mass fraction	Temperature
	kg/kg$_{Al}$	–	K
Substrates			
Al_2O_3	1.889 ± 0.05	1.0	298 ± 5%
Anode carbon	0.534 ± 0.02	1.0	298 ± 5%
Criolite (Na_3AlF_6)	0.01 ± 0.005	1.0	298 ± 5%
AlF_3	0.039 ± 0.015	1.0	298 ± 5%
Products		1.0	
Liquid Al		1.0	
Electrolyte losses		0.7939	
AlF_3	1.0	0.2061	1223 ± 10%
Na_3AlF_6	0.049 ± 0.015	1.0	1223 ± 10%
Carbon foam	0.088 ± 0.030	1.0	1223 ± 10%
Anode gasses	0.088 ± 0.030	0.324	1223 ± 10%
CO	(kmol/kg$_{Al}$)	0.362	
CO_2		0.311	
N_2			
Electric consumption	54180 kJ/kg$_{Al}$ (15.05 ± 1.0 kWh/kg$_{Al}$)		
Heat losses to surroundings (calculated)	34514 kJ/kg$_{Al}$ (9.31 ± 1.0 kWh/kg$_{Al}$)		

Calculation results of exergy balance elements are shown in Table 4.

TABLE 4

Exergy balance a priori and a posteriori (after adjustment of mass balances)

Substance	Exergy kWh/kg$_{Al}$	
	(a priori)	(a posteriori)
Substrates		
Al_2O_3	1.05 ± 0.03	1.05 ± 0.03
Anode carbon	5.08 ± 0.76	4.43 ± 0.68
Criolite (Na_3AlF_6), AlF_3	0.03± 0.01	0.03 ± 0.007
Electric energy	15.05± 1.0	14.91 ± 0.81
Σ	21.21 ± 1.58	20.72 ± 1.12
Products		
Liquid Al.	9.27 ± 0.37	9.35 ± 0.36
Electrolyte losses	0.15 ± 0.05	0.15 ± 0.02
Carbon foam	0.15 ± 0.05	0.15 ± 0.02
Anode gases	2.50 ± 0.50	2.64 ± 0.48
Σ	12.07 ± 0.62	12.29 ± 0.60

Thus, from a posteriori exergy balance, exergy losses are

$$\delta\dot{B} = 20.72 - 12.29 = 8.43 kWh/kg_{Al} \quad (41)$$

and

$$\left(\dot{S}_{gen}\right)_1 = \frac{8.43}{300} = 0.0281 \pm 0.0025 kWh/K \cdot kg_{Al} \qquad (42)$$

$$\left(\dot{S}_{gen}\right)_2 = \frac{7.70}{300} = 0.0257 kWh/K \cdot kg_{Al} \qquad (43)$$

Relative difference is

$$Diff\% = \frac{\left(\dot{S}_{gen}\right)_1 - \left(\dot{S}_{gen}\right)_2}{\left(\dot{S}_{gen}\right)_m} \qquad (44)$$

where

$$\left(\dot{S}_{gen}\right)_m = \tfrac{1}{2}\left[\left(\dot{S}_{gen}\right)_1 + \left(\dot{S}_{gen}\right)_2\right] =$$
$$\frac{1}{2}\,(0.281 + 0.0257) = 0.0269 kWh/K \cdot kg_{Al} \qquad (45)$$

Thus

$$Diff\% = \frac{0.0281 - 0.0257}{0.0269} = 0.089 \quad (8.9\%) \qquad (46)$$

Taking under consideration problem of the accuracy and necessary simplifications of mathematical model of elementary processes occurring inside the electrolysis cell system, the difference of the estimation of entropy generation rates can be accepted.

5. Conclusions

New approach to the falsification of mathematical models of the electrolysis cell elementary processes Has been proposed, The method is based on the exergy balance equation which allows estimation of exergy losses and entropy generation rates. Additionally, to improve accuracy of the falsification procedure the adjustment method of the chemical elements mass balances has been used.

Acknowledgements

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APPENDIX 1

Because of inevitable measurement error mass balance equation for the principal chemical elements of the process are not exactly satisfied. From mathematical point of view, the system of algebraic balance equation is internally contradicted. To obtain most probable values the orthogonal least square method is proposed. General consideration are discussed bellow.

Lest n_o denotes a minimum number of independent variable necessary for unique solution of the mass balance equation and n be a number of given functionally independent observation. Where n is greater than n_o, the redundancy of number of statistical degrees of freedom defines as $r = n - n_o$ is said to exist, and adjustment becomes necessary on order to obtain a unique solution. Les l denote a vector of all experimental results and $\tilde{l}$ be a vector of estimates that satisfies the balance equation. In general the values of $\tilde{l}$ are different from l and a difference vector

$$\mathbf{V} = \tilde{\mathbf{l}} - \mathbf{l} \qquad (A1)$$

which has been termed as either a correction or a residual, plays an important role in calculation. Due to the redundancy the number of estimates for $\tilde{l}$ and V is infinite. To calculate te most probable solution, the least squares principle is commonly used as an additional criterion. The least square principle requires the condition

$$f(\mathbf{V}) = \mathbf{V}^T \mathbf{M}^{-2} \mathbf{V} = \sum_{i=1}^{n} \left(\frac{v_i}{\mu_i}\right)^2 \to minimum \qquad (A2)$$

To be satisfied simultaneously with the mass balance equations where $\mathbf{M}^{-2}$ is the weight matrix of the observations (experimental result). The weight $\mathbf{M}^{-2}$ matrix is square and diagonal and of order equal to the number of observations.

Les us assume that mass balance equations can be performed by the following system of the algebraic non-linear equations

$$f_i(\tilde{\mathbf{l}}, \tilde{\mathbf{x}}) = 0 \quad (i = 1, ..., J), \qquad (A4)$$

were vector matrices $\tilde{l}$ and $\tilde{x}$ represent a set of variables the values of which are estimated a priori by direct measurement l and a set of unknowns x non-measurement variables.

Introducing experimental results l and approximations of unknown x the system of equations is replaced by

$$f_i(\mathbf{l}, \mathbf{x}) = \tilde{w}_i \qquad (A5)$$

where $\mathbf{l} = (l_1, ..., l_k)$, $\mathbf{x} = (x_1, ..., x_m)$ and $\tilde{w}_i$ represents the residua of origin system of non-linear equations.

To solve the problem numerically, a linearization procedure is applied using the zero and first order terms of the Taylor expansion. Defining the estimates (most probable values) as

$$\tilde{\mathbf{l}} = \mathbf{l} + \mathbf{V} \text{ and } \tilde{\mathbf{x}} = \mathbf{x} + \mathbf{Y} \qquad (A6)$$

where V represents unknown corrections to the experimental result l, and Y corrections to the approximations of non-measured variables x, the system can be written in the form

$$f_i = (\mathbf{V}, \mathbf{Y}) = w_i \qquad (A7)$$

And after linearization, in the matrix form

$$\mathbf{AV} + \mathbf{BY} = \mathbf{W} \qquad (A8)$$

where

$$\mathbf{A} = \frac{\partial \mathbf{f}}{\partial \mathbf{l}} \qquad (A9)$$

is a $J \times k$ Jacobi matrix of rank equal to J,

$$\mathbf{B} = \frac{\partial \mathbf{f}}{\partial \mathbf{x}} \qquad (A10)$$

is a $J \times m$ Jacobi matrix of rank equal to m, and $f = \{f_1, ..., f_J\}^T$

The least squares procedure can now be formulated as follows:

minimize

$$\phi(v) = \mathbf{V}^T \mathbf{M}^{-2} \mathbf{V} \qquad (A11)$$

subject to mass balance equations

$$\mathbf{AV} + \mathbf{BY} = \mathbf{W} \qquad (A12)$$

The variables $(\mathbf{V}, \tilde{\mathbf{l}}, \mathbf{l}, \mathbf{Y}, \tilde{\mathbf{x}}, \mathbf{x}) \in E^n$, where E^n denotes an n-dimensional Euclidean space ($n = m + k$).

To solve the problem effectively, the Lagrange multipliers method can be used, which leads to the system of additional linear equations

$$\mathbf{A}^T \mathbf{K} = \mathbf{M}^{-2} \mathbf{V} \qquad (A13)$$

and

$$\mathbf{B}^T \mathbf{K} = 0 \qquad (A14)$$

where K is the column matrix of Lagrange multipliers. A routine calculations gives finally

$$\mathbf{Y} = \mathbf{G}^{-1} \mathbf{B}^T \mathbf{F}^{-1} \mathbf{W} \qquad (A15)$$

$$\mathbf{V} = \mathbf{M}^2 \mathbf{A}^T \mathbf{F}^{-1} (\mathbf{W} - \mathbf{BY}) \qquad (A16)$$

where

$$\mathbf{F} = \mathbf{AM}^2 \mathbf{A}^T \qquad (A17)$$

and

$$\mathbf{G} = \mathbf{B}^T \mathbf{F}^{-1} \mathbf{B} \qquad (A18)$$

If the accuracy of solution of linearized problem is not sufficient the iterative procedure must be applied. In such case, to get the solution of an original non-linear problem the values of elements of Jacobi matrices A and B are continuously corrected at each iteration step. The solution a now be used to calculate , a posteriori errors of directly measurement variables, unknowns and any function containing model variables. Using the law of error propagation, the expressions for the covariance matrices can be derived in the form

$$\mathbf{M}_l^2 = \mathbf{M}^2 - \mathbf{CAM}^2 \qquad (A19)$$

and

$$\mathbf{M}_x^2 = \left[\mathbf{B}^T \mathbf{F}^{-1} \mathbf{B} \right]^{-1} \qquad (A20)$$

where

$$\mathbf{C} = \mathbf{M} - 2\mathbf{A}^T \mathbf{F}^{-1} \left[\mathbf{E} - \mathbf{BG}^{-1} \mathbf{B}^T \mathbf{F}^{-1} \right] \qquad (A21)$$

and E is the unit diagonal matrix.