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**LEAST SQUARES EVALUATION OF THE GLOBAL ENTROPY GENERATION  
IN THE ALUMINIUM ELECTROLYSIS CELL**

**OSZACOWANIE GLOBALNEGO ŹRÓDŁA ENTROPII W PROCESIE ELEKTROLIZY  
ALUMINIUM**

Classical thermodynamic analysis of any thermal and chemical process is usually based on the first law of thermodynamics. Such an approach is not sufficient when deeper understanding of the mechanism and nature of each elementary process is required. The use of the first and second law of thermodynamics together is necessary to solve practical problems more effectively. Especially, application of the entropy generation rate and lost available energy (or exergy) concepts enhance our understanding of thermal process. Such an extended analysis is proposed to detect possible ways to decrease the electric energy consumption. Additionally, least squares adjustment procedure is proposed to make mathematical models of elementary processes taking place inside electrolysis cell more reliable.

Powszechnie prowadzona analiza termodynamiczna przebiegu różnego rodzaju procesów cieplnych i chemicznych opiera się zazwyczaj na I-szej zasadzie termodynamiki. W przypadkach, gdy wymagane jest głębsze zrozumienie mechanizmu i natury procesów elementarnych, takie podjęcie nie jest wystarczające. Bardziej efektywne wyniki otrzymać można łącząc I-szą i II-gą zasadę termodynamiki. Szczególnie wartościowe jest wprowadzenie pojęcia produkcji entropii w celu wykrycia wszystkich źródeł nieodwracalności termodynamicznej i ich wielkości. Takie rozszerzenie analizy zostało zaproponowane w artykule w odniesieniu do procesu elektrolizy aluminium. Jej celem jest wskazanie możliwości obniżenia zużycia energii elektrycznej. Ponadto pokazano jak ortogonalna metoda najmniejszych kwadratów umożliwia uzyskanie bardziej wiarygodnych wyników obliczeń rozkładu źródeł entropii.

Key words: Entropy generation, lost available energy, least squares adjustment, minimization of energy consumption

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## 1. Introduction

Classical thermodynamic analysis of any technological process is usually based on the First Law of Thermodynamics in the form of energy (enthalpy) balances. Such an approach is useful in engineering practice as it makes analysis easier in the global scale neglecting modeling of the elementary processes, allows calculation of the thermal efficiency and makes possible to control quality of the measurement results. Additionally, graphical presentation of the energy balance is simple in the form of Sankey diagram.

In the case of aluminium electrolysis process, design of the new electrolyzer or its modernization is always based on the enthalpy balance.

However, deeper thermodynamic analysis leads to the conclusion that such an approach is not sufficient. The First Law of Thermodynamics guarantees the exact equivalence of the various forms of energy (allowing all forms to be measured in the common unit such as joules ) but it does not guarantee interconvertibility. Thermal energy (heat) is in a peculiar and unique position, for whereas all other forms can be completely converted into thermal energy, the reverse process is impossible, only a portion of the heat can be converted into mechanical energy [7]. This general conclusion comes from the Second Law of Thermodynamics using entropy as the state function describing degree of irreversibility of the process. There are many effects whose presence [2] during a process renders it irreversible. In aluminium electrolysis process most important are:

- heat transfer through a finite temperature difference,
- spontaneous chemical reactions between anode and cathode,
- mixing of matter at different composition and states (alumina and liquid electrolyte),
- friction in the flow of liquid electrolyte and aluminium,
- electric current flow through a resistance.

The term irreversibility is used to identify effects such as these. As stated in [2], engineers should be able to recognize irreversibilities, evaluate their influence and develop cost-effective means for reducing them. However, the need to achieve profitable rates of production, high heat transfer rates, high electric current densities and so on invariably dictates the presence of significant irreversibilities. Irreversibilities are tolerated to some degree in every type of system but their magnitude should be as low as possible and necessary from the engineering point of view.

The measure of the irreversibility of any process is entropy generation called also — entropy source end entropy production. To define it, consider open thermodynamic system and its interaction with the environment (Fig.1)

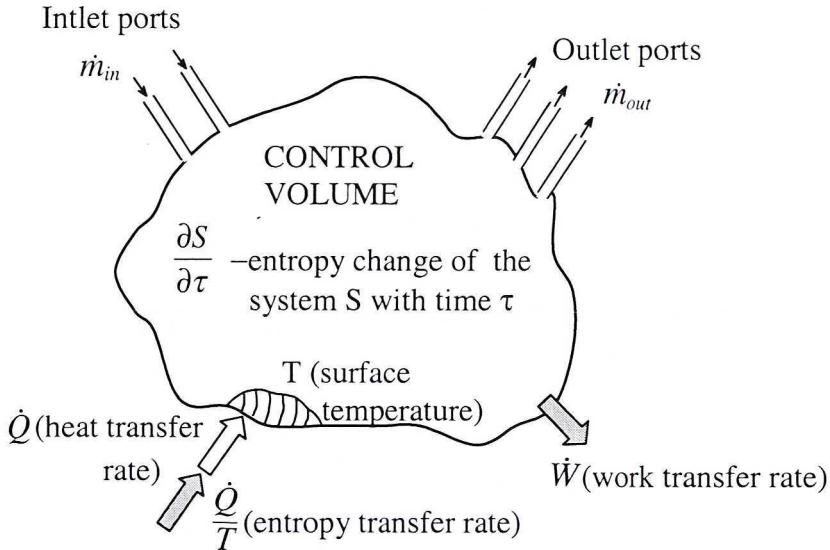


Fig.1. Open thermodynamic system and its interaction with the environment

From the Second Law of Thermodynamics [1]

$$\sum_{in} \dot{m}s - \sum_{out} \dot{m}s + \frac{\dot{Q}}{T} \leq \frac{\partial S}{\partial \tau}. \quad (1)$$

Thus, entropy generation rate is

$$\dot{S}_{gen} = \frac{\partial S}{\partial \tau} - \frac{\dot{Q}}{T} + \sum_{out} \dot{m}s - \sum_{in} \dot{m}s. \quad (2)$$

As Bejan states [1], the essence of the second law of thermodynamics is expressed by the inequality sign in Equation (1). The change from state 1 to state 2 can be effected in a variety of ways, that is along many paths. The special path along which entropy is not generated is the termed reversible. Path for which  $\dot{S}_{gen} > 0$  are considered irreversible. It means that if

$$(\dot{S}_{gen})_A < (\dot{S}_{gen})_B$$

it makes sense to say that path *A* is more reversible than path *B*. The entropy generation  $\dot{S}_{gen}$  is *path dependent*, hence, not a thermodynamic property. *It should never be confused with the thermodynamic property entropy change ( $S_1 - S_2$ ).*

The most important conclusion derived from the above considerations is the relationship between lost available work  $\dot{W}_{lost}$  or exergy [3] and entropy generation  $\dot{S}_{gen}$ . It is known in thermodynamics as the Gouy-Stodola theorem and takes the form [1,3]

$$\dot{W}_{lost} = T_0 \dot{S}_{gen}, \quad (3)$$

where  $T_0$  represents temperature of environment.

This theorem states that the lost available energy is directly proportional to the entropy production which depends solely on the degree of thermodynamic irreversibility of the process. If engineering systems and their components are to operate such that the destruction of available work is minimized, then the design of such systems must begin with the minimization of entropy generation [1]. It means that the most important problem is the identification of the entropy generation rates as the effects of different elementary processes such as momentum, heat and mass transfer, chemical reactions and so on.

## 2. Two ways of calculation of entropy generation rates

In general, two theoretically independent methods can be proposed to evaluate entropy generation rates. It is proposed to term them as direct and indirect ways. The direct method results from the solution of the mathematical models of each elementary process and then using them for calculation of entropy sources. For example, from the solution of the boundary value problem of heat transfer, the map of entropy sources is possible to be done. Considering simultaneous heat and electric current flows, the solution of the system of Poisson equations with appropriate boundary conditions gives possibility to analyse the influence of internal heat sources on the entropy production.

The indirect method is based on the exergy analysis (balance) of the process. In such a way, only the global value of the entropy generation can be obtained. It results from the fact that the exergy is exempt from the law of conservation and the exergy balance equation is closed by the term called exergy losses which are equal to the previously defined lost available energy. Both methods for an aluminium electrolysis cell will be described in the following considerations.

### 2.1. Direct method analysis of elementary processes

The cross section of the aluminium electrolysis cell is presented in Fig. 2.

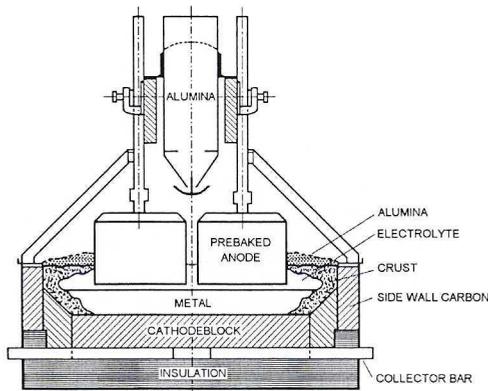
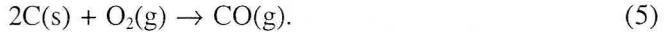


Fig.2. Schematic illustration of the aluminium electrolysis cell [4]

The electrolyte contains  $\text{Al}_2\text{O}_3(s)$  dissolved in molten cryolite,  $\text{Na}_3\text{AlF}_6(l)$ . The overall cell reaction is:



Liquid aluminium is produced in the volume between the carbon anode and carbon cathode. Because of the contact of the carbon anode with air, an excess reaction in which carbon is consumed take place



The feeding of alumina is almost continuous so the steady state thermodynamic conditions can be assumed. The anode consists of carbon blocks and steel connectors. Alumina covers the anode. Electric current is flowing from the liquid aluminium to the steel bars. The bottom and the sides of the electrolyser are insulated with refractories. Average electrolyte temperature is  $960^\circ\text{C}$ . The cell potential is 4.1V. The current density is about  $4.6 \cdot 10^3 \text{ A/m}^2$  and current efficiency is equal to 0.95. Additionally in the case of a 230 kA cell of Hydro Aluminium in Ovre Ardal, Norway [4], the cathode and anode surface areas are  $50 \text{ m}^2$  and  $30 \text{ m}^2$  respectively. Aluminium production is 73.3 kg Al per hour. Heat losses to the surroundings through external surfaces of the electrolyser have been evaluated from energy balance equation and are equal

$$\dot{Q} = 6.5 \text{ kWh/kg}_{\text{Al}}.$$

The measured average input of electric energy was

$$W_{el} = I\Delta\Phi = 12.9 \text{ kWh/kg}_{\text{Al}},$$

where  $I$  is the electric current (230 kA) and  $\Delta\Phi$  is the cell potential (4.1V).

The minimum work necessary for the process obtained from thermodynamic calculation is

$$W_{el, \min} = I\Delta\Phi_{\min} = 5.4 \text{ kWh/kg}_{\text{Al}}.$$

Therefore, thermodynamic efficiency of the process is

$$\eta_{th} = \frac{W_{el, \min}}{W_{el}} = \frac{5.4}{12.9} = 0.42.$$

The difference

$$W_{el} - W_{el, \min} = \delta W_{lost}$$

represents the total lost work in the electrolysis cell and from second law of thermodynamics is directly proportional to the entropy generation according to Equation (3).

Thus,  $\delta W_{lost}$  can be obtained by calculating  $\dot{S}_{gen}$  for all elementary processes occurring in the cell. Below, the results of calculation carried out by Kjelstrup and Bedeaux [4] are presented.

*Lost work due to charge transfer.*

The potential drop across the electrolyte produces losses (mainly ohmic) which can be evaluated from the equation

$$W_{lost,1} = T_0 (\dot{S}_{gen})_1 = T_0 \frac{I}{T_c} (-\Delta\Phi_1) = 1.3 \text{ kWh/kg}_{Al},$$

where  $T_c$  (960°C(1233K)) is bulk electrolyte temperature and electric potential drop is ( $\Delta\Phi_1 = -1.7$  V).

The diffusion layer at cathode surface is the next source of reversibility. Close to the cathode, ions of  $Na^+$  are accumulated creating thin diffusion layer with gradients in chemical potential and in electric potential. Typical thickness of the diffusion layer is  $\Delta x = 1$  mm.

The lost work is

$$W_{lost,2} = \frac{T_0}{T_c \chi} \frac{I^2}{A} \Delta x = 0.05 \text{ kWh/kg}_{Al},$$

where  $A$  is the cathode surface area,  $\chi$  represents conductivity of the boundary layer ( $19 \text{ kS} \cdot \text{m}^{-1}$ )

The anode overpotential of about 0.50 V is the main source of the lost work at the electrode surfaces. The lost work given by the thermal and electric forces is

$$W_{lost,3} = 0.48 \text{ kWh/kg}_{Al}.$$

Because of the low overpotential at the cathode surface, the entropy production can be neglected.

Heat and electric current flow through carbon parts of the anode and cathode. From linear thermodynamics of irreversible processes, the entropy production is

$$(\dot{S}_{gen})_3 = \dot{Q} \Delta \left( \frac{1}{T} \right) + \frac{I}{T} (-\Delta\Phi),$$

where

$$Q = -kA \frac{\Delta T}{\Delta x} + \pi \frac{T}{F}$$

$$\Delta\Phi = -\frac{\pi}{T} \frac{\Delta T}{\Delta x} - \frac{\Delta x}{\chi} I,$$

where  $\Delta x$  represents thicknesses of anode and cathode blocks,  $k$  is thermal conductivity of the carbon and  $\pi$  is Peltier heat.

After calculation

$$\begin{aligned} W_{lost} |_{anode} &= 0.33 \text{ kWh/kg}_{Al} \\ W_{lost} |_{cathode} &= 0.34 \text{ kWh/kg}_{Al}. \end{aligned}$$

*Lost work due to carbon consumption.*

According to the reaction (5) the anode carbon consumption is about 0.4 kg/kg<sub>Al</sub>. The Gibbs free enthalpy of the reaction (4) is -219.5 kJ/mol<sub>CO</sub>, so

$$W_{lost,4} = 0.1 \text{ kWh/kg}_{Al}$$

and is negligible in comparison to other losses (according to [4]).

*Lost work due to heat transfer to surroundings.*

Entropy production results directly from the entropy fluxes exchanged through the wall between heat sources having temperatures  $T_c$  and  $T_0$ . Lost work is

$$W_{lost,5} = T_0 \dot{Q}_0 \left( \frac{1}{T_0} - \frac{1}{T_c} \right) = 4.8 \text{ kWh/kg}_{Al},$$

where  $\dot{Q}_0 = 0.65 \text{ kWh/kg}_{Al}$  is the heat flow to surroundings (from enthalpy balance equation). It is necessary to point out that the above evaluation can be inaccurate as the exact data can only be obtained from the solution of the boundary value problem of heat transfer described by partial differential Kirchhoff equation (conduction and convection in liquid electrolyte and aluminium) with appropriate boundary conditions.

Summing up, the lost work in the total cell is equal to

$$\sum W_{lost} = 7.7 \text{ kWh/kg}_{Al}$$

and differs from the value 7.5 kWh/kg<sub>Al</sub> obtained on the basis of theoretical considerations  $W_{el,min}$  and measurement results in industry as

$$\sum W_{lost} = W_{el} - W_{el,min} = 12.9 - 5.4 = 7.5 \text{ kWh/kg}_{Al}.$$

To obtain the most probable value of the total lost work, exergy approach together with least squares adjustment is proposed.

### 2.2. Indirect method — exergy approach

Let's consider aluminium electrolysis cell as the „black box” with exergy flows as shown in Fig.3.

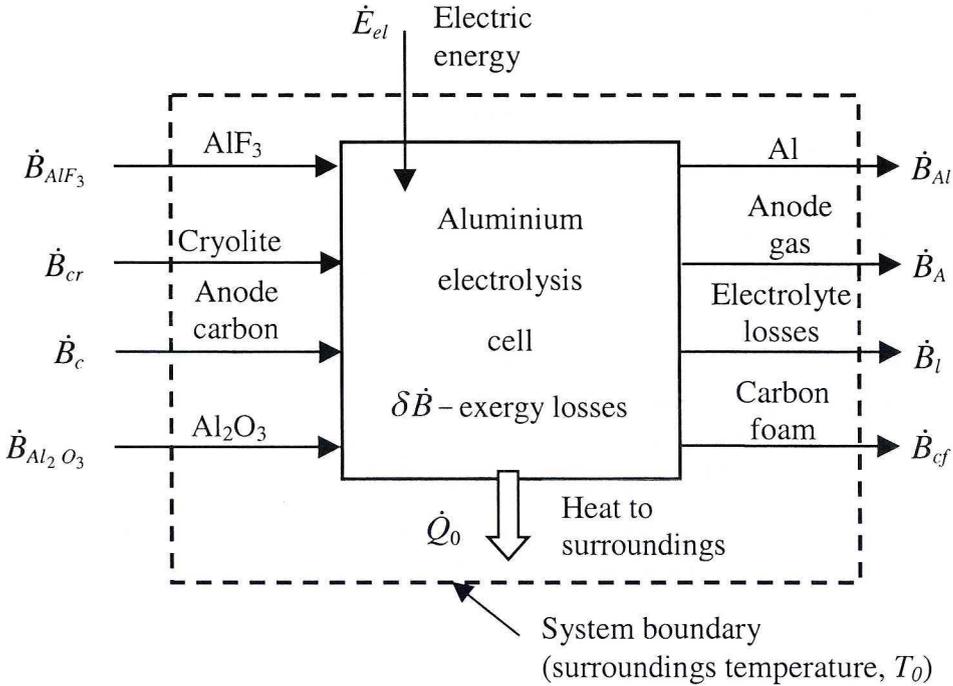


Fig. 3. System under consideration

Assuming steady-state process, the *exergy balance* takes the following form [3]

$$\dot{B}_{Al_2O_3} + \dot{B}_c + \dot{B}_{cr} + \dot{B}_{AlF_3} + \dot{E}_{el} = \dot{B}_{Al} + \dot{B}_A + \dot{B}_l + \dot{B}_{cf} + \delta\dot{B}, \tag{6}$$

where  $\delta\dot{B}$  denotes global exergy losses, due to the irreversibilities inside the system including exergy losses due to the heat flux to surroundings (system boundary temperature equal to the surroundings temperature).

From Eq. (6) we obtain

$$\delta\dot{B} = \dot{B}_{Al_2O_3} + \dot{B}_c + \dot{B}_{cr} + \dot{B}_{AlF_3} + \dot{E}_{el} - \dot{B}_{Al} - \dot{B}_A - \dot{B}_l - \dot{B}_{cf} \tag{7}$$

and using expression that

$$\delta\dot{B} = T_0 \dot{S}_{gen} \tag{8}$$

we have finally

$$\dot{S}_{gen} = \frac{1}{T_0} \delta \dot{B}.$$

*Calculation results.*

Exergy fluxes have been calculated using the equation

$$\dot{B}_i = \dot{m}_i b_{th,i},$$

where  $\dot{m}_i$  is the mass flow rate of the  $i$ -th substrate or product of the process and  $b_{th,i}$  represents thermal specific exergy of the  $i$ -th flux according to relation

$$b_{th,i} = b_{ph,i} + b_{ch,i},$$

where  $b_{ph,i}$  and  $b_{ch,i}$  are physical and chemical specific exergies, respectively. They were calculated from the equation [3]

$$b_{ph} = c_p \left[ (T - T_0) - T_0 \ln \frac{T}{T_0} \right] + RT \ln \frac{P}{P_0}, \quad (9)$$

where  $b_{ch}$  is taken from the table of normal chemical exergies. [3].

The second term in (9) is related to the anode gas and its value is zero as  $P = P_0$ . Our measurement results for one of the Polish aluminium plant is listed in Table 1.

TABLE 1  
Measurement results

Substance	Mass or mol flow rates	Chemical composition	Temperature
	kg/kg <sub>Al</sub> or kmol/kg <sub>Al</sub>	-	K
<b>Substrates</b>			
Al <sub>2</sub> O <sub>3</sub>	1.889 ± 0.05	1.0	298
Anode carbon	0.534 ± 0.02	1.0	298
Cryolite (Na <sub>3</sub> AlF <sub>6</sub> )	0.01 ± 0.005	1.0	298
AlF <sub>3</sub>	0.039 ± 0.015	1.0	298
			} ± 5
<b>Products</b>			
Al (liquid)	1.0	1.0	1223
Electrolyte losses	0.049 ± 0.015	{ AlF <sub>3</sub> = 0.07939 Na <sub>3</sub> AlF <sub>6</sub> = 0.2061 } ± 5%	1223
Carbon foam	0.088 ± 0.030	1.0	1223
Anode gas	0.088 ± 0.030	{ CO = 0.324 CO <sub>2</sub> = 0.362 N <sub>2</sub> = 0.311 } ± 5%	1223
			} ± 10

The electric energy consumption = 54 180 kJ/kg<sub>Al</sub> (15.05 ± 1.0 kWh/kgAl) and the heat flux to surroundings = 34 514 kJ/kg<sub>Al</sub> (9.31 ± 1.0 kWh/kgAl) (from the enthalpy balance equation).

Calculation results for the exergy balance are presented in Table 2.

Exergy balance

TABLE 2

Substance	Exergy flux kWh/kg <sub>Al</sub>		
	Chemical	Physical	Thermal
<b>Substrates</b>			
Al <sub>2</sub> O <sub>3</sub>	1.05	0.	1.05 ± 0.03
Anode carbon	5.08	0.	5.08 ± 0.76
{Cryolite (Na <sub>3</sub> AlF <sub>6</sub> ) AlF <sub>3</sub> }	0.03	0.	0.03 ± 0.007
Electric energy	15.05	0.	15.5 ± 1.0
$\Sigma$	21.21	0.	21.21 ± 1.26
<b>Products</b>			
Al (liquid)	0.13	0.14	9.27 ± 0.37
Electrolyte losses	0.14	0.01	0.15 ± 0.022
Carbon foam	0.14	0.01	0.15 ± 0.022
Anode gas	2.15	0.35	2.50 ± 0.50
$\Sigma$	11.56	0.51	12.07 ± 0.62

From the exergy balance (Eq. 7)

$$\delta \dot{B} = 21.21 - 12.07 = 9.14 \text{ kWh/kg}_{Al}$$

and from Eq. 8

$$(\dot{S}_{gen})_1 = \frac{9.14}{298} = 0.0307 \text{ kWh/kg}_{Al}$$

From [4]

$$(\dot{S}_{gen})_2 = \frac{7.70}{293} = 0.0263 \text{ kWh/kg}_{Al}$$

Percentage difference is

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

where  $(\dot{S}_{gen})_m$  is the mean value  $= \frac{1}{2}[(\dot{S}_{gen})_1 + (\dot{S}_{gen})_2]$ ,

$$Diff\% = \frac{0.0307 - 0.0263}{\frac{1}{2}(0.0307 + 0.0263)} 100 = 15.4\%$$

Using data from Table 2, thermodynamic efficiency ratio (or reversibility ratio)

$$\eta_{th,eff} = \frac{\dot{B}_-}{\dot{B}_+}$$

can be calculated ( $\dot{B}_-$  and  $\dot{B}_+$  are exergy flows entering and leaving the system, respectively).

Also, the exergy dissipation of the process can be expressed as

$$\delta\dot{B} = \delta\dot{B}_{diss} = \dot{B}_+ - \dot{B}_-$$

together with exergetic efficiency

$$\eta_b = \frac{\text{chemical exergy of the useful product}}{\text{exergy entering the system}}$$

After calculations:

$$\begin{aligned} \text{--- } \eta_{th,eff} &= \frac{12.07}{21.21} = 56.9\% \\ \text{--- } \delta\dot{B}_{diss} &= 21.21 - 12.07 = 9.14 \text{ kWh/kg}_{Al} \\ \text{--- } \eta_b &= \frac{9.14}{21.21} = 43.1\% \end{aligned}$$

### 3. Least squares adjustment

Because of the inevitable measurement errors the result of entropy generation rates depends on the method of calculations. The values from direct and indirect methods are different as stated in 2.2. To obtain most probable values the least squares method is proposed. General considerations are discussed bellow.

Let  $n_0$  denote a minimum number of independent variables necessary for unique solution of the mathematical model and  $n$  be a number of given functionally independent observations. When  $n$  is greater than  $n_0$ , the redundancy or number of statistical degrees of freedom defined as  $r = n - n_0$  is said to exist, and an adjustment becomes necessary in order

to obtain a unique solution. Because of the statistical properties of the experimental results, redundant observations are not compatible with the model and any arbitrarily chosen subset of experimental results can be used to satisfy the model equations. In such a case a unique solution when redundant measurements are considered can only be obtained when an additional criterion is imposed.

Let  $\mathbf{l}$  denote a vector of all experimental results and let  $\tilde{\mathbf{l}}$  be a vector of estimates that satisfies the model equations. In general the values of  $\tilde{\mathbf{l}}$  are different from  $\mathbf{l}$  and a difference vector

$$\mathbf{V} = \tilde{\mathbf{l}} - \mathbf{l}$$

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

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

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

#### *Calculation procedure.*

Mathematical model equations, usually in a differential form, describing any physical or chemical process are always divided into two groups: governing equations and conditions for unique solution. Their mathematical form is usually non-linear and an analytical solution can be obtained only for very simple problems. To obtain a solution, numerical methods are widely used. It means that the system of differential model equations is transformed into a system of nonlinear algebraic equations and our further discussion will be focused on such an approach.

Let us assume that the mathematical model can be performed by the following system of algebraic non-linear equations:

$$f_i(\tilde{\mathbf{l}}, \tilde{\mathbf{x}}) = 0 \quad (i = 1, \dots, J), \quad (10)$$

where vector matrices  $\tilde{\mathbf{l}}$  and  $\tilde{\mathbf{x}}$  represent a set of variables the values of which are estimated a priori by experimental results ( $\mathbf{l}$ ) and a set of unknowns ( $\mathbf{x}$ ), calculated from the model Eqs. (10)

Introducing experimental results  $l$  and approximations for unknowns  $x$  the system of model Eqs. (10) is replaced by

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

where  $l = (l_1, \dots, l_k)$ ,  $x = (x_1, \dots, x_m)$  and  $\tilde{w}_i$  represents the residua of the original system of non-linear model Eqs.(10) and their values are evaluated using experimental results and approximations of the unknowns.

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:

$$\tilde{l} = l + V$$

and

$$\tilde{x} = x + Y,$$

where  $V$  represents unknown corrections to the experimental results  $l$ , and  $Y$  corrections to the approximations of non-measured variables  $x$ , the system (10) can be written in the form:

$$f_i(V, Y) = w_i$$

and after linearization, in the matrix form

$$AV + BY = W,$$

where

$$A = \frac{\partial f}{\partial x}$$

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

$$B = \frac{\partial f}{\partial x}$$

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

The least squares procedure can now be formulated as follows: minimize

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

subject to the model equations

$$AV + BY = W.$$

The variables  $(V, \tilde{l}, Y, \tilde{x}, x) \in E^n$ , 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 [5,6]

$$A^T K = M^{-2} V$$

and

$$B^T K = 0,$$

where  $K$  is the column matrix of Lagrange multipliers. A routine calculation gives finally:

$$Y = G^{-1} B^T F^{-1} W \quad (11)$$

$$V = M^2 A^T F^{-1} (W - BY) \quad (12)$$

where

$$F = AM^2 A^T$$

and

$$G = B^T F^{-1} B.$$

If the accuracy of the solution of a linearized problem is not sufficient the iterative procedure must be applied. In such a case, to get the solution of an original non-linear problem the values of elements of the Jacobi matrices  $A$  and  $B$  are continuously corrected at each iteration step. The solutions (11) and (12) are now used to calculate, a posteriori, errors of the directly measured 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 forms [6]

$$M_i^2 = M^2 - CAM^2$$

and

$$M_x^2 = [B^T F^{-1} B]^{-1},$$

where

$$C = M^2 A^T F^{-1} [E - BG^{-1} B^T F^{-1}]$$

and  $E$  is the unit diagonal matrix.

A condition for the model's adequacy can be formulated in different ways, but the Lipschitz condition in the form [6]

$$|\tilde{l} - l| < k\mu_i$$

or

$$|v_i| < k\mu_i$$

(where  $k$  is the Lipschitz constant) seems to be most effective from the numerical point of view. The mathematical model is then accepted if the Lipschitz condition is satisfied for all experimental results. In our calculations  $k = 2$  will be chosen (confidence level = 95%).

*Condition equation.*

The single condition equation is obtained in an easy way comparing total  $W_{\text{lost}}$  from direct method and exergy balance equation and takes the form

$$W_{\text{lost},1} + W_{\text{lost},2} + W_{\text{lost},3} + W_{\text{lost}|anode} + W_{\text{lost}|cathode} + W_{\text{lost},4} + W_{\text{lost},5} = \\ = \dot{B}_{\text{Al}_2\text{O}_3} + \dot{B}_C + \dot{B}_{cr} + \dot{B}_{\text{AlF}_3} + \dot{E}_{el} - \dot{B}_{\text{Al}} - \dot{B}_A - \dot{B}_l - \dot{B}_{cf}$$

or in the direct form

$$T_0 \frac{I}{T_c} (-\Delta\Phi_1) + \frac{T_0 I^2}{T_c \chi A} \Delta x + W_{\text{lost},3} + W_{\text{lost}|anode} + W_{\text{lost}|cathode} + W_{\text{lost},4} + T_0 \dot{Q}_0 \left( \frac{1}{T_0} - \frac{1}{T_c} \right) = \\ \dot{m}_{\text{Al}_2\text{O}_3} b_{ch,\text{Al}_2\text{O}_3} + \dot{m}_C b_{ch,C} + \dot{m}_{cr} b_{ch,cr} + \dot{m}_{\text{AlF}_3} b_{ch,\text{AlF}_3} + E_{el} - \\ - \dot{m}_{\text{Al}} \left\{ b_{ch,\text{Al}} + c_{p,\text{Al}} \left[ (T_c - T_0) - T_0 \ln \frac{T_c}{T_0} \right] \right\} - \\ - \dot{m}_A \left\{ b_{ch,A} + c_{p,A} \left[ (T_A - T_0) - T_0 \ln \frac{T_A}{T_0} \right] \right\} - \\ - \dot{m}_{cf} \left\{ b_{ch,cf} + c_{p,cf} \left[ (T_{cf} - T_0) - T_0 \ln \frac{T_{cf}}{T_0} \right] \right\}.$$

Measurement results together with a priori errors are given in the text. In the case of data from [4], a priori measurement errors were assumed to be 5% (lack of information). Calculation have been carried out using least square procedure described above, and the results of exergy balance equation are presented in the Table 3.

After adjustment, total lost work in the electrolysis cell is

$$\delta \dot{W}_{\text{lost}} = (20.72 \pm 1.12) - (12.20 \pm 0.60) = 8.43 \pm 1.61 \text{ kWh/kg}_{\text{Al}}$$

and entropy generation rate

$$(\dot{S}_{\text{gen}})_{\text{total}} = \frac{8.43}{298} = 0.029 \pm 0.005 \text{ kWh/K} \cdot \text{kg}_{\text{Al}}.$$

Percentage difference to the Kjelstrop and Bedeaux [4] result is

$$\text{Diff}\% = \frac{0.029 - 0.0263}{\frac{1}{2}(0.029 + 0.0263)} 100 = 9.8\%$$

and thermodynamic efficiency

$$\eta_b = \frac{9.34}{21.32} = 0.44.$$

TABLE 3  
Calculation results (exergy balance)

Substance	Thermal exergy flow rates kWh/kg <sub>Al</sub>	
	Before adjustment (a priori)	After adjustment (a posteriori)
<b>Substrates</b>		
Al <sub>2</sub> O <sub>3</sub>	1.05 + 0.03	1.05 ± 0.03
Anode carbon	5.08 ± 0.76	4.73 ± 0.68
{ Cryolite (Na <sub>3</sub> AlF <sub>6</sub> ) AlF <sub>3</sub> }	0.03 ± 0.01	0.03 ± 0.007
Electric energy	15.05 ± 1.00	14.91 ± 0.81
$\Sigma$	21.21 ± 1.58	20.72 ± 1.12
<b>Products</b>		
Al (liquid)	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 gas	2.50 ± 0.50	2.64 ± 0.48
$\Sigma$	12.07 ± 0.62	12.29 ± 0.60

#### 4. Discussion

Total lost work calculated with adjustment procedure  $8.43 \pm 1.61$  kWh/kg<sub>Al</sub> is not very close to the difference between real industrial energy consumption and the minimum work

$$\delta \dot{W}_{lost} = 14.91 - 5.40 = 9.51 \text{ kWh/kg}_{Al}$$

even the difference is within the error band. Comparison with Kjelstrup and Bedeaux model calculation [4] shows that the more rigorous mathematical models of elementary processes taking place in the electrolysis cell are necessary. Simplified assumptions in [4] could lead to the large uncertainties. The largest lost work due to the irreversibilities is observed in the charge conducting pathways and heat transfer to surrounding resulting from electric resistance of the electrode block and electrolyte layer. Both losses, as it is seen from deeper analysis, can be reduced by a better cell design based on the minimization of entropy generation in the cell. Additional research effort especially in the more rigorous mathematical modelling of heat, momentum, mass and charge transfer is necessary.

## 5. Conclusions

The use of the first and second laws of thermodynamics together to analyze thermal and chemical processes is necessary to solve practical problems more effectively. Application of the entropy generation and lost work (or lost available energy or exergy) concepts enhance our understanding of thermal and chemical processes [3]. These functions allow us to examine any process, no matter how complex, in relation to the theoretically more efficient manner. As Szargut stated [3], engineers and scientist have been using enthalpy balances for more than a century to quantify the loss of efficiency in a process due to the loss of energy. Entropy generation assessment allows to quantify the lost of efficiency in a process due to the loss of quality of the energy. The majority of the causes of thermodynamic imperfection of thermal and chemical processes cannot be detected by means of a energy balance. The main purpose of entropy generation analysis is to evaluate quantitatively the causes of the thermodynamic imperfection of thermal processes. Such an analysis gives information about the possibilities of improving thermal processes, but cannot state whether or not the possible improvement is practicable. This question can only be answered by an economic analysis. Adjustment procedure proposed in this paper makes possible the mathematical models of elementary processes and entropy generation calculations to be more reliable.

## REFERENCES

- [1] A. Bejan, Entropy Generation Minimization, CRC Press, Boca Raton, 1996.
- [2] A. Bejan, G. Tsatsaronis, M. Moran, Thermal Design and Optimization, John Wiley and Sons, New York 1996.
- [3] J. Szargut, D.R. Morris, F.R. Steward, Exergy Analysis of Thermal, Chemical and Metallurgical Processes, Hemisphere Publ. Corp., New York 1988.
- [4] S. Kjelstrup, D. Bedeaux, Elements of Irreversible Thermodynamics for Engineers, Int. Centre for Applied Thermodynamics, Istanbul 2001.
- [5] Z. Kolenda, J. Donizak, J.C. Escobedo-Bocardo: *Met. Tran.B*, **303**, 505 (1999).
- [6] Z. Kolenda, J. Szmyd, S. Słupek, L.M. Baez, *Can. J. Chem. Eng* **61**, 627 (1983).
- [7] D. Rose, Learning about Energy, Plenum Press, New York 1986.

REVIEWED BY: STANISŁAW SŁUPEK

*Received: 10 March 2003.*