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METHODOLOGY FOR DETERMINATION OF MATERIAL AND  
ENERGY BALANCES IN CHEMICAL PROCESSING INDUSTRIES<sup>1/</sup>

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Summary

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<sup>1/</sup> The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO.

The author discusses the various steps leading to the determination of material and energy balances of operating chemical processing plants. First the technology has to be described, the conceptual flow-sheet has to be determined, the process has to be divided into unit operations. Then the material and energy balances of the unit operations are determined. This requires the determination of the variability of the unit operations, the selection of the data to be measured, the preparation of a measuring program, the organization of the measurements, the processing of the measured data and the setting up of the balances in an appropriate form. Finally some expedient forms are described for the compiling of the material and energy balances of the whole chemical processing plant: gross and detailed balances, technological flow-sheets and Shankey diagrams.

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## INTRODUCTION

The material balance is the quantitative accounting of the material flows (inputs and outputs, in some cases accumulating materials) of some chemical process or unit operation. The energy balance is the contrasting of the amounts of energy introduced into the studied system with the input materials, transferred to it during the operation and set free during the chemical process with those leaving the same with the output materials, absorbed in the process, removed during the operation and dissipated as heat losses (1,2).

The material and energy balance of a chemical processing plant is the sum of the material and energy balances of the individual processes and of the equipment realizing them.

Material and energy balances of chemical processing plants may be calculated with two different aims:

- (a) In the cases of designing new plants or expanding or reconstructing old ones it is necessary for the designers to know the materials and their quantity passing through, originating in or absorbed in various equipment, the amounts of heat to be transferred or removed, the pressure and temperature of the system, i.e. all those data which have to be given on a proper technological flow-sheet. It is characteristic for such material and energy balances that they are prepared before the start-up (even before the detailed designing) of the plant and that they are the result of theoretical calculations (based naturally on laboratory tests or on measurements carried out in similar plants).

- (b) Material and energy balances of plants already in operation can also be prepared. Such balances are always based on measurements carried out in the given plant, and their aim is to check the process, to throw light on losses and, in some cases, to collect data for the designing of new plants.

The technical literature (1,3,4,5,6) contains a number of references and even methods elaborated in details for the determination of material and energy balances of the first type, but only a few of the authors deals with those of the second one. It will be tried to give a brief summary of the methods for the determination of material and energy balances of operating chemical processing plants without laying claim to completeness.

#### I. DESCRIPTION OF THE TECHNOLOGY, DETERMINATION OF THE CONCEPTUAL FLOW-SHEET, DIVISION INTO UNIT OPER- ATIONS

To be able to determine the material and energy balance of a chemical processing plant first of all one has to get thoroughly acquainted with the technology of the same. (In the context of this paper technology means the totality, connections and sequence of the operations of the process from raw materials to products, including operations carried out on eventual recycled materials, too.) After getting acquainted with the technology it is useful to put it down in the form of a conceptual flow-sheet. The various operations are marked with their standard or conventional symbols in this flow-sheet, without showing the number, type or size of the equipment used but indicating the chemical formula, composition and estimated flow rate of the materials participating in the operations. The technology of a chemical processing plant can be read off a proper conceptual flow-sheet without further explanation.

The process is usually shown in the conceptual flow-sheet from left to right, the main process is emphasized by connecting the equipment taking part in it with thick lines representing the main material flows while the equipment of auxiliary processes are connected with thin lines. The directions of the material flows are marked with arrows put on the connecting lines. The chemical formulae and compositions are usually written above the lines, the flow rates below them. The conceptual flow-sheet shows:

- (a) the chemical composition of the raw materials, intermediate and final products,
- (b) the sequence of the operations,
- (c) the nature of the equipment.

Usually there is no possibility to determine the material and energy balance of the whole plant at the same time since in the case of a complicated technology hundreds of data would have to be measured simultaneously. Therefore, the process has to be divided into part-processes, operations or suitably chosen groups of operations, the material and energy balances of which are determined one by one and the summary of which gives the balance of the whole plant. This dividing is carried out on the conceptual flow-sheet. The group of equipment in which such a part-process takes place is termed unit operation.

## II. MATERIAL AND ENERGY BALANCES OF THE UNIT OPERATIONS

### A. Variability (degree of freedom) of material and energy balances of unit operations

The variability of a unit operation is equivalent to the number of data necessary and sufficient to describe it unequivocally (2). In the chemical processing industry complete, unequivocal description means the determination of the quantity of every material, of every thermodynamical data and of every heat flow. Only in the rarest cases is it necessary to take into consideration electrical, magnetical, etc. phenomena.

$m + 2$  data are required for the unequivocal description of a homogenous phase ( $m$  is the number of components) since the intrinsic energy and the volume of the phase have to be determined over and above the quantities of all the components, in accordance with the principle of the conservation of mass, intrinsic energy and momentum declared by the first major premise of thermodynamics. In practice the phases are described by two intensive thermodynamical data, pressure and temperature instead of the above two extensive parameters since these unequivocally determine the intrinsic energy and momentum with the full knowledge of the material quantities.

Just these data describing the various phases are compiled in the form of balances when material and heat balances are prepared. The quantity of materials participating in chemical processes is usually given with their mass since this remains practically constant during the transformations in question whereas other characteristics like number of moles, volume, etc. may considerably change. Therefore, material balance in practice means mass balance.

It is very advantageous to use the concept of enthalpy for describing the energy balance of the chemical processes since that includes the generally unavoidable volumetric work, so it simplifies significantly the calculations, and the various thermodynamical tables in circulation usually show enthalpies as a function of temperature and pressure.

From the point of view of chemical engineering it is unusual to set up intrinsic momentum balances. These could be used to determine the work required for pumping, etc.

The composition and thermodynamical characteristics of every input and output material have to be determined for the complete description of a unit operation, as shown above, but a certain number of equations can be set up for these characteristics. If the number of characteristics is  $C$  and that of the equations  $E$ , the variability of the unit operation will be:

$$F = C - E \quad (1)$$

In order to determine the material and energy balance of a unit operation a number of independent data corresponding exactly to the variability  $F$  have to be measured. Some examples are given below to show how this variability can be calculated for various types of unit operations.

It is characteristic for stationary operations of the chemical industry that the material and energy stock of the unit operation is constant in time, i.e. the sum of the material and energy quantities entering and leaving the system is equal:

$$\sum_{i=1}^n L_i = 0 \quad (2)$$

and

$$\sum_{i=1}^n L_i \cdot h_i = Q + \sum H \quad (3)$$

where  $L_i$  is the mass of the phases entering or leaving the unit operation,  $n$  is the total number of phases,  $h_i$  the specific enthalpy of the various phases,  $Q$  is the heat transfer between the system and its surrounding, and  $\sum H$  is the total of eventual reaction, solution, blending, etc. heats. (Inputs have a + sign, outputs a - one.)

The mass balances of the individual components are as follows:

$$\sum_{i=1}^n L_{ij} = 0 \quad (j = 1, 2, \dots, m) \quad (4)$$

where  $L_{ij}$  is the mass of component No. "j" in phase No. "i" and  $m$  is the total number of components. A component does not necessarily mean an element, it may be a compound, root or ion remaining chemically unchanged during the process.

Figure I. shows the principal scheme of a unit operation.

The total number of characteristics is:

(a)	the mass of $m$ components of $n$ phases	$n \cdot m$
(b)	2 extensive thermodynamical characteristics of $n$ phases	$2n$
(c)	heat transfer between the system and its surrounding	1
	total:	$\frac{1}{n(m+2) + 1}$

The number of equations is:

(a)	specific mass balances for m components	m
(b)	enthalpy balance of the system	<u>1</u>
	total:	m + 1

The variability of the system is:

$$F = n(m + 2) - m \quad (5)$$

In some cases it is not possible to set up the mass balance of every component. In such cases the undefined rest can be treated as a single component. E.g. for most practical purposes the evaporation of the sugar industry can be described by using only three components: sugar, water and "rest". On the other hand, instead of the undefined rest the total mass of the phases can be used as a component, too. Naturally, the total mass is an independent variable only if the sum of the defined components is less than the total.

More complicated formulae can be set up for such cases, if

- (a) the unit operation is divided into sub-units,
- (b) some physical and/or chemical equilibria exist between some phases,
- (c) not only the unchanged components, but the various compounds in which they enter and leave the system have also to be taken into consideration.

Such formulae for various possible cases are described in the author's PhD thesis (7). They can be summarized in the following complex formula:

$$F = (n+a+p-k) \cdot (m+r+2) - p \cdot m - e \cdot f \quad (6)$$

where a is the number of phases crossing from one sub-unit to another one,

e is the number of chemical reactions leading to equilibrium,

f is the number of those phases in which these chemical equilibria are achieved,

k is the number of those phases which are in physical equilibrium with any other phase (if there is no equilibrium at some of the sub-units, one phase per such sub-unit has to be considered when calculating the value of k),

m is the number of components (elements, unchanged compounds, roots or ions), as above,

n is the number of phases entering and leaving the unit, as above,

p is the number of sub-units the unit operation is divided into,

r is the difference of the number of (changing) compounds and components (called sometimes the number of free reactions, too).

If the unit operation is not divided into sub-units,  $p=1$  and  $a=0$ , and if there is no chemical equilibrium,  $e=0$ .

Should only mass and enthalpy balances be set up but no balance of intrinsic momentum, a simplification can be made. Since the enthalpy of solid or liquid phases is independent of the pressure (at least within the accuracy margins of the usual measurements) except if the pressure is extraordinarily high, such phases can be adequately described thermodynamically with only one parameter, the temperature. For gas phases the determination of both intensive parameters is necessary. So the number of data necessary in practice for setting up the mass and enthalpy balances is:

$$F' = (n+a+p-k) \cdot (m+r+1) - p.m. - e.f + g \quad (7)$$

where  $g$  is the number of gas phases within the unit operation.

For batch chemical processes it is characteristics that the material and energy stock of the unit operation is the same at the beginning and the end of the operational cycle. So equations (2), (3) and (4) can be used for batch processes, too. The main difference is that whereas the various quantities given in the balances may be valid for any time period, material and energy balances of batch processes can be set up only for a complete cycle or an integer multiple of the same. The equations (5), (6) and (7) deduced for the variability of stationary operations can also be used for batch processes, naturally only for complete cycles, too. The most important difference between the two types of operations lies in the fact that batch processes can be divided into sub-units not only in space but in time, too. They are usually divided into the following part-processes:

- (a) introducing the inputs into the unit,
- (b) carrying out the operation,
- (c) removing the products from the unit.

Naturally this threefold division can not be used schematically for every batch operation. There can be materials introduced into and/or removed from the unit during the operational phase (e.g. seed is fed into and water is removed from the crystallizers during sugar crystallization). Sometimes some of these part-processes can be further subdivided (e.g. the operational phase of the above crystallization into evaporation, seeding and crystallization). When using equations (6) or (7) for batch processes,

p means the number of periods the whole operation is divided into and a the total number of phases present in the equipment at the moments dividing the part-processes.

There is a special problem in the case of batch processes: that of the stagnating material. Since its amount, composition and thermodynamical state is the same at the beginning and the end of a cycle, it does not influence either the material and energy balance or the variability of the operation. But if the latter is divided into part-processes, the stagnating material already exerts some influence. It can be taken into consideration by adding the number of its phases to those of the inputs and outputs, and should it form separate phases during the operation, also to those phases crossing over from one part-process to the next.

There is a great variety of transitional cases between purely stationary and purely batch processes. As a matter of fact, there is no purely stationary operation, since every equipment has to be shut down and restarted periodically for maintenance, etc. A very common phenomenon is the periodical accumulation of materials in the equipment (e.g. scaling). In practice those processes are considered to be stationary at which these periodicities are negligible. E.g. the start-up and shut-down of an evaporator working more or less stationarily for the best part of a year can be neglected, but if the same evaporator has to be washed every day for 2 hours, it is better to calculate it as a batch operation with a cycle time of 24 hours.

#### B. Selection of the data to be measured

Having determined the variability of a unit operation the number of data to be known for the calculation of the material and energy balances is clarified. If possible, every data registered continuously in the plant should be used provided that their

accuracy is satisfactory. Should the plant register continuously as much (or more) data as the variability of the unit operation, there is no need to make extra measurements, and there is no point in making them either, since the results of a single measurement (even if it is repeated or prolonged) can not reach the accuracy of the data continuously registered.

A number of data can usually be determined from the balances of the adjoining unit operations. A repeated measurement of the same can be spared in most cases.

Some measurements can be spared by some logical conclusions drawn from the knowledge of the way of operation of the unit. E.g. if a three-component liquor is preheated in a tubular preheater with steam, equation (7) gives a variability of 14. But since both the steam and its condensate have only 1 component and their masses have to be equal as the impermeable wall of the tubes separates them from the liquor being preheated, the number of data to be measured can be reduced by 5.

The real number of parameters to be measured can be determined by subtracting the number of registered and logically excluded data and those determined by the balances of adjoining operations from the number calculated from equations (6) or (7).

The next task is to decide, which parameters should be measured. No general prescription can be given for that but some basic principles may be laid down. If there is a possibility to measure more parameters than necessary, those should be preferred, which can be determined with the slightest relative error margin. If possible, a small quantity should not be calculated as a difference of two large ones, even if they can be measured more accurately. In some cases it may be advantageous to determine more

parameters than absolutely necessary since this provides an internal control for the measurements. Material quantities should be measured by weight (for solid materials) or by volume in tanks (for liquids) rather than by flow measurements since the latter have usually a larger error margin than admissible for the calculation of the material and energy balances. Chemical analyses usually also give more accurate results than flow-meters do. In the case of vapour-liquid equilibria pressure data are usually more reliable than temperature ones, since pressure gauges respond faster to changes than thermometers.

C. Preparation of the measuring program, organization  
of the measurements

First of all the necessary connections for thermometers, pressure gauges, etc. have to be installed at the selected measuring points. Instruments with the appropriate measuring range have to be selected. Though the instruments to be used are usually rather simple, their accuracy has to be checked and, if necessary, correction tables have to be prepared.

When all instruments are in place their fluctuation has to be observed and the frequency of their reading has to be determined on the basis of the observed fluctuation. E.g. a fairly constant temperature of a more or less stationary process has to be read only 5 to 10 times during the whole measuring period, but a flow meter showing considerably varying flow rates has to be read every minute or even more frequently. As a rule of thumb, if the standard deviation of the measurements is  $s$  and their accuracy is  $d$ , at least  $s/d$  readings have to be made. Since  $s$  is not known in advance, its value has to be estimated during the preliminary observation of the instruments.

The time period of the measurement has to be fixed in advance. For batch processes this is given: the time of a complete cycle. For stationary processes it should be determined so that the material quantities could be measured with an error of about 1 per cent.

The measuring group has to be organized in the knowledge of the required number of readings and the measuring period. At least as many people are required as sufficient to make the necessary readings without undue physical strain. Experience suggests that a thermometer can be read and the reading can be noted within 15 to 20 seconds if it is located at a bright place, in the height of one's eye and within 30 seconds if otherwise. A pressure gauge can be read in 10 seconds, a differential manometer in 30. No person can be expected to walk more than 2,000 metres horizontally and 100 metres vertically (on stairs, ladders, etc.) during a 2-hour measuring period. For longer periods the burden should be even less, otherwise the accuracy of the measurements will suffer.

In the case of larger measuring campaigns it is expedient to organize the measuring group so that it should include one person without actual reading duties to coordinate the measurements, to make arrangements in unforeseen cases and to take care that the process parameters should not be changed by the interference of an outsider.

Every member of the measuring group has to be briefed in details on his duties, on the starting and closing time of the measuring, on the frequency of the readings, his attention has to be drawn to eventual irregularities and he has to be instructed, how to behave in such cases, etc. This is especially important if the group consists of relatively uneducated people but a detailed briefing can not be neglected even if the group consists of well trained members.

It is expedient to check the correctness of the detailed measuring program by a trial measurement to enable any unforeseen defect to be corrected in time.

#### D. Processing of the measured data

The processing of the data obtained during the measurements is usually a simple routine work. The arithmetical means of the data can be used in most cases (especially in the case of stationary processes) for the calculations. Only if both the extensive and the intensive parameters to be multiplied with each other show a large standard deviation will lead the use of the arithmetic means to incorrect results. (7) contains - among others - some methods for estimating the maximum possible errors committed and for their elimination.

The detailed processing of the data is usually done after the conclusion of the measuring campaign. But it is expedient to check the measurements immediately by calculating some of the characteristic data since some errors committed during the measurements are discovered only at the calculations.

The fact that the plant systematically records some parameters and so their mean values are available for an extended period, but that during the measurements the values of the same parameters differ significantly from the recorded averages may cause quite often some problems. In such cases the recorded and the measured data are not in harmony. This disharmony can be eliminated by measuring the actual values of the recorded data during the campaign and correcting the balances for the difference between the actual values and the recorded averages of these parameters.

### E. Setting up of the balances

The material and energy balances can be set up from the data processed without further problems. The last job to be done is their clear presentation. The most expedient form for this is a table which shows every input phase on the left side and the output phases on the right one (3,4). The units are shown in the heading of the table. Should the material balance be set up for more than one component, the quantities of the various components have to be put in separate columns. One or two columns may be set aside for intensive parameters like temperature, pressure, concentrations, etc. Table 1 shows such a balance for the wet grinding and classifying of bauxite.

The material and energy balance of a more complicated unit operation can be set up in this form, too, but sometimes this form is not clear enough since it does not show from which phases the various components originate and into which phases they cross over. The same applies for the various amounts of heat. In such cases a method similar to accounting may be used: all the inputs and outputs are separately listed and it is shown at all of them, which phases can be credited or debited with the amounts of material or energy crossing from one phase to another. Table 2 shows the material and energy balances of bauxite digestion set up with the "accounting" method.

The balances of unit operations divided into sub-units can be set up using either of the above methods. The tables have to be filled in for the whole unit and for all sub-units separately if the tabular method is used. When using the accounting method, the phases crossing from one sub-unit into another have to be described in three columns: the middle one shows the data of the crossing phase itself, the left one the phases from which its components, mass and energy content originate in the first sub-

unit and the right one the phases into which the same are transformed in the second one.

### III. COMPILING OF THE MATERIAL AND ENERGY BALANCES OF THE WHOLE PROCESSING PLANT

When the material and energy balances of every unit operation of the chemical processing plant are set up, they can be compiled in various forms. Gross and detailed balances can be prepared. The detailed balance is a simple assembly of the balances of the unit operations. This can be made so that the tables containing the material and energy figures are ordered along the conceptual flow-sheet, the unit operations and the material flows being schematically indicated on the same (3,8,9). But this method is difficult, sometimes unrealizable in the case of complicated processes.

Gross balances do not contain the material and energy flows between the various unit operations, only the plant inputs and outputs are contrasted. While the mass of data of the detailed balances is difficult to study, the gross balances give very little information. But there are two other more expedient forms to compile plant balances: the technological flow-sheet and the Shankey diagram.

A standard technological flow-sheet shows the equipment, their connections, all the material flows entering and leaving them, together with the necessary physical, chemical and quantitative data. Only one of the parallelly operating equipment has to be shown but the number and type of the same has to be indicated. It has to show not only the data of the main technological processes but those of the auxiliary ones, too. As this description shows, the technological flow-sheet has to contain

all the data of the material and energy balances, therefore, it is very suitable to represent vividly these balances.

The other vivid representation is the so-called Shankey diagram (10,11). In this the various equipment or unit operations are represented with quadrangles and the material and energy flows between them with stripes connecting these, the width of which is proportional to the flows. The material and energy flows are represented in separate diagrams. The amount of the various components can be shown in the diagram representing the material flows, especially if their amount is not very small. For minor components it is suitable to prepare separate diagrams with a different scale. For better clarity the stripes representing various components may either be colored or it may be written into them, what component they represent.

Even though the Shankey diagrams are very descriptive, their accuracy is usually not sufficient, therefore, it is advisable to indicate the various amounts with numbers in them, too. Temperatures and pressures may be indicated in the energy flow diagrams. Both the technological flow-sheets and the Shankey diagrams may refer to time units (t/h, MJ/h) or product units (t/t, MJ/t).

After compiling the material and energy balances the most important job follows: the discussion of the conclusions which can be drawn from them. If the balances have been set up to study the energy house-hold of the plant, they have to be analyzed to find out the heat losses of which operations can be reduced or what technological changes may lead to a reduced energy consumption. (7) contains a number of examples for both possibilities.

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Table 1. Material and energy balances of wet grinding and classifying of bauxite  
(Tabular form)

Unit operation: wet grinding and classifying											
Inputs						Outputs					
Phases	t °C p bar	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t	Phases	t °C p bar	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t
Bauxite dry phase	20 -	2.46	-	1.242	42	Classified slurry solid phase	62.5 -	2.24	-	1.090	117
Bauxite adh.moisture	20 -	0.54	-	-	46	Classified slurry liquid phase	62.5 -	7.10	1.194	0.655	1566
Grinding liquor	73.5 -	6.34	1.194	0.503	1641	Heat losses	-	-	-	-	46
Total		9.34	1.194	1.745	1729	Total		9.34	1.194	1.745	1729

Table 2. Material and energy balances of bauxite digestion  
("Accounting" form)

Inputs									
Input Phases	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t	Credited to Output Phases	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t
Bauxite slurry					Blow-off slurry				
solid phase	1.70	-	0.713	113	solid phase	1.04	-	0.196	71
					liquid phase	0.66	-	0.517	42
Bauxite slurry					Blow-off slurry				
liquid phase	13.04	2.211	1.460	3538	solid phase	0.08	0.081	-	4
					liquid phase	12.96	2.130	1.460	3534
Steam	2.72	-	-	8181	Condensate	1.96	-	-	1294
					Steam with cond.	0.36	-	-	1013
					Blow-off slurry				
					liquid phase	0.40	-	-	5192
					solid phase	-	-	-	100
					Heat losses	-	-	-	582
Total:	17.46	2.211	2.173	11832	Total:	17.46	2.211	2.173	11832

Table 2. Material and energy balances of bauxite digestion  
("Accounting" form)

(continued)

Inputs					Outputs				
Debited to Input Phases	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t	Output Phases	Mass t/t	Na <sub>2</sub> O t/t	Al <sub>2</sub> O <sub>3</sub> t/t	H MJ/t
Bauxite slurry					Blow-off slurry				
solid phase	1.04	-	0.196	71	solid phase	1.12	0.081	0.196	175
liquid phase	0.08	0.081	-	4					
Steam	-	-	-	100					
Bauxite slurry					Blow-off slurry				
solid phase	0.66	-	0.517	42	liquid phase	14.02	2.130	1.977	8768
liquid phase	12.96	2.130	1.460	3534					
Steam	0.40	-	-	5192					
Steam	1.96	-	-	1294	Condensate	1.96	-	-	1294
Steam	0.36	-	-	1013	Steam with cond.	0.36	-	-	1013
Steam	-	-	-	582	Heat losses	-	-	-	582
Total:	17.46	2.211	2.173	11832	Total:	17.46	2.211	2.173	11832

Figure I.

Principal scheme of a unit operation

