MATERIAL BALANCE APPROACH FOR PARAMETER DETERMINATION IN BIOLEACHING PROCESS

Durance M.V. [a]**, Brochot S.** [a]**, Mugabi M.** [b]

[a]*BRGM, 3 Av. Claude Guillemin, BP 6009*
45060 Orléans Cedex 2, France
[b]*KCCL, Kasese road, PO Box 524, Kasese, Uganda*

Abstract: The Kasese Cobalt Company – Limited (KCCL) plant reprocesses a pyrite concentrate produced and stockpiled during the operation of the Kilembe copper mine (Uganda). This concentrate, prior to the KCCL operations, was causing an environmental damage to the Queen Elisabeth National Park since the 70s. The KCCL bioleaching process aims at extracting the valuable cobalt trapped in sulfide minerals by destroying the mineral matrix, thus avoiding further pollution from these sulfides. Both for economic and environmental reasons the process has to oxidize a maximum of sulfides.
Embedded in a relatively complex flowsheet, the evaluation of performances of the bioleaching stage represents a real challenge, considering the poor level of instrumentation in this section and the sampling difficulties.
In this case, the use of a material balance algorithm represented the only efficient tool for estimating performances of the different process stages and identifying the possible optimization points. Using the BILCO™ software package, developed by BRGM, a specific tool has been created in the Microsoft Excel environment for the automation of the mass balance computation and of the main operating parameter determinations.
After a short recall of the material balance theory, the paper presents the KCCL plant process and the application developed for the material balance of this specific circuit. It shows how the non-measurable parameters can be obtained by the aid of the application.

Keywords: biotechnology – material balance – circuit recovery – accuracy – parameter estimation

1. CONTEXT AND OBJECTIVE

Since June 1999, the Kasese Cobalt Company Ltd. plant (Uganda) has been processing a sulfide concentrate (pyrite) deposited during the operation of the Kilembe Copper Mine, between 1956 and 1977. This pyrite concentrate contains cobalt at an economic concentration of around 1.4%, which is recovered by a bioleaching process, followed by a purification process which includes precipitation, solvent extraction and electrowinning. The process used by the KCCL treatment plant addresses environmental and economic objectives. Firstly, it aims at extracting the valuable cobalt, trapped in sulfide minerals, from the mine tailings. The end result is an industrial activity that became a significant economic resource for Uganda. Secondly, by processing these tailings, the process significantly reduced the ongoing pollution of the Queen Elisabeth National Park caused by natural leaching.

In 2000, a significant amount of cobalt was observed to be lost in the solids residues. It was suspected that bioleaching was not efficient enough, meaning that the dissolution of sulfides was not sufficient for the cobalt liberation. The objective was to confirm or invalidate this hypothesis by a full material balance.

Several elements make it difficult to establish a material balance of such a circuit, thus to estimate the performances of the different parts of the circuit, which would allow their optimization: i) recycling of several streams, ii) a long residence time in the circuit (around a week), iii) difficulties for sampling and measurements and iv) during the starting period, a poor stability of the circuit due to numerous power-cuts and capacity increases. The objective for implementing a mass balance computation system is to define the performances of each section and then to locate the stage(s) where cobalt is lost in the solids residues.

The paper briefly presents the theory of mass balance and the BILCO tool with its COM module. Then a description of the Material Balance Implementation at the KCCL plant is described and its contribution in the determination of non-measurable parameters.

2. MATERIAL BALANCE

2.1 What is data reconciliation by material balance?

Wherever there are relationships (theoretical or empirical) between measured parameters, there is a data reconciliation problem. Due to measurement errors the experimental data are inconsistent, as they do not verify the theoretical relationships: they are, therefore incoherent (Hodouin, and Everell., 1980, Herbst, *et al.*, 1988, Fourniguet, *et al.*, 1997).

The objective of the data reconciliation is to find a set of estimates of the measured values which are as close as possible to the measurements and verify the theoretical relationships. When the relationships are material conservation laws the problem can be solved using data reconciliation by material balance.

Material balancing is a general approach and is used in a vast number of domains. Everywhere there are networks with flows and transformations, data are to be evaluated. Material balance is largely used in process engineering. It allows describing the material flowing in the process. Knowledge of the process performances is then improved. Sometimes, balancing behavior reveals non-stationary process or bad accuracy estimation. The information redundancy allows delivering coherent estimators more accurate than the initial measurements (Ragot, *et al*, 1990). This approach allows to detect aberrant values and to reduce error due to the sampling and the measurement.

2.2 Theory

The objective of a material balance computation is to find a set of estimates, which is i) complete (all streams are perfectly described), ii) as close as possible of the experimental values and iii) in agreement with the material conservation laws.

For each stream, the decomposition of the circulating material is as follows:

- Q_{pi}: flowrate of phase p in stream i
- X_{pig}: fraction by weight of particle class g
- T_{pigk}: fraction of component k in the particle class g
- P_{pik}: fraction of component k

The measured values $\overline{Q}_{pi}$, $\overline{X}_{pig}$, $\overline{T}_{pigk}$ and $\overline{P}_{pik}$ never satisfy constraints of material conservation because of deviation from the balance position and because of uncertainties in the measurements. Material balance calculates the estimates Q_{pi}, X_{pig}, T_{pigk} and P_{pik} which first, satisfy constraints and second, have the greatest probability to be reality. This last point is taken into account by seeking the estimates Q_{pi}, X_{pig}, T_{pigk} and P_{pik} which are as close as possible to the measured values $\overline{Q}_{pi}$, $\overline{X}_{pig}$, $\overline{T}_{pigk}$ and $\overline{P}_{pik}$, taking into account the accuracy attached to each measurement (BILCO User's guide, 2002).

Mathematically, this is equivalent to minimize the objective function:

$$J(Y) = \sum_i \sum_p J_{pi}(Y)$$

by means of the materials conservation constraint equations (see below), where Y is the estimate vector $(Q_{pi}, X_{pig}, T_{pigk}, P_{pik})$ and where $J_{pi}(Y)$ is the objective function of the phase p in the stream i (Le Guirriec, *et al.*, 1995, Le Guirriec, 1996). *J* can be expressed as:

$$J_{pi}(Y) = \left(\frac{Q_{pi} - \overline{Q}_{pi}}{\sigma_{pi}\overline{Q}_{pi}}\right)^2 + \sum_g \left(\frac{X_{pig} - \overline{X}_{pig}}{\sigma_{pig}\overline{Q}_{pig}}\right)^2 + \sum_k \left(\frac{P_{pik} - \overline{P}_{pik}}{\sigma_{pik}\overline{P}_{pik}}\right)^2 + \sum_g \sum_k \left(\frac{T_{pigk} - \overline{T}_{pigk}}{\sigma_{pigk}\overline{T}_{pigk}}\right)^2$$

The constraints can be divided into:i) material conservation constraints, ii) user-defined constraints and iii) data integrity constraints. The material conservation constraints are attached to each unit of equipment. The basic conservation laws are:
i) the global quantity conservation for phase *p* around node *j*

$$\sum_i M_{ij} Q_{pi} = 0$$

ii) the partial quantity conservation for class *k* of phase *p* around node *j*

$$\sum_i M_{ij} Q_{pi} X_{pik} = 0$$

iii) the partial quantity conservation for component l of phase p around node j

$$\sum_i M_{ij} Q_{pi} P_{pil} = 0$$

iv) the partial quantity conservation for component l into class k of phase p around node j

$$\sum_i M_{ij} Q_{pi} X_{pik} T_{pikl} = 0$$

It is possible to sum some conservation constraints around node j to obtain a new conservation constraint which can be used to take into account, for example, the phase transfer in a leaching or precipitation model.

The data integrity constraints are:
i) the closure constraint, such as the 100% fitting

$$1 - \sum_k X_{pik} = 0$$

$$1 - \sum_l P_{pil} = 0$$

$$1 - \sum_l T_{pikl} = 0$$

ii) the mean ratio constraint

$$P_{pil} - \sum_k X_{pik} T_{pikl} = 0$$

The set of constraints attached to a unit is relative to the material conservation laws of each phase. Not all of the above constraints are used for a given node. For example, a grinding mill conserves only the mineralogical or chemical composition of the material but not the size distribution.

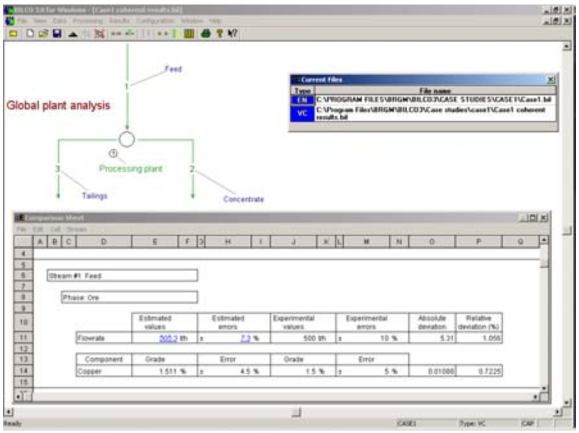
The resolution of the system is based upon a Lagrange formalism and the iterative algorithms Newton-Raphson and Ito-Kunish (Le Guirriec, 1996).

The originality of the BILCO algorithm concerns its capability to solve all the equations presented above simultaneously, with no need of hierarchy. This leads to a better accuracy of the results.

2.3 The BILCO™ tool

BILCO offers an interactive, quick and accurate way of solving material balance problems in a vast number of applications. In just minutes, BILCO provides solutions for complex flowsheet problems in mineral or food processing plants, chemical or petrochemical plants. It also provides solutions for urban or industrial waste management, distribution network and pollution balances.

The BILCO software was developed by BRGM to solve material balance problems in the field of the mineral processing, which is characterized by its great complexity in the material description. In fact, the modeling tools (such as the material description and the graph drawing), the solving algorithms and the methodology used form a powerful help for complex data analysis. Figure 1 presents the main windows of the application with a result presentation sheet.



Type	File name
EN	C:\PROGRAM FILES\BRGM\BILCO3\CASE STUDIES\CASE1\Case1.bil
VC	C:\Program Files\BRGM\BILCO3\Case studies\case1\Case1 coherent results.bil

Stream #1 Feed

Phase: Ore

	Estimated values		Estimated errors	Experimental values		Experimental errors	Absolute deviation	Relative deviation (%)
Flowrate	505.3 t/h	±	7.3 %	500 t/h	±	10 %	5.31	1.058
Component	Grade		Error	Grade		Error		
Copper	1.511 %	±	4.5 %	1.5 %	±	5 %	0.01088	0.7225

Fig. 1. The BILCO 3.0 main Window

BILCO 3.0 can communicate with other applications using a COM (Component Object Modeling) interface. The main tool that can be used to communicate with BILCO is Visual Basic. Then Microsoft® Office applications (Excel™, Access…) can communicate with BILCO 3.0 via macros written with VBA (Visual Basic for Application).

The COM interface can be used to:

- automate some data import and export, such as transfer some experimental values from an Excel sheet to BILCO, then calculate the material balance and then transfer results from BILCO to another Excel sheet,
- link many material balance calculation to evaluate results sensibility versus some experimental values and errors,
- improve online process data by automatic material balance calculation.

COM interface allows data exchange with BILCO and material balance calculation using a predefined problem (dependence graph, data description and constraints definition) configured in BILCO 3.0 and saved in an experimental data file (BILCO COM User's guide, 2002).

3. THE KCCL APPLICATION

3.1 The process

The KCCL process plant is made of two main areas (Figure 2). The upper plant prepares a pregnant liquor. This involves bioleaching in BIOCO reactors, slurry neutralization, filtration and iron removal. The bottom plant produces the cobalt cathodes and hydroxides from the pregnant liquor produce in the upper plant. This area mostly includes solvent extraction loops end cobalt electrowinning.

A limestone crushing and grinding section prepares a pulp of limestone for pH control in bioleaching (also providing CO_2 for bacteria), neutralization and iron removal sections.

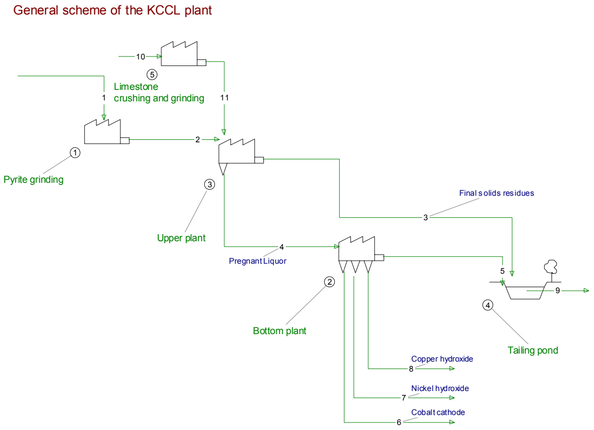


Fig. 2. The Kasese Cobalt Company Ltd. general flowsheet

The bottom plant circulates mostly rather homogenous liquids and this limits number of problems related to sampling and stability. Furthermore, performances of the bottom plant are generally good. On the contrary, the upper plant that mostly circulates pulps, is rather unstable and seems to present a bad recovery of cobalt in the liquor. A detailed flowsheet of the upper plant is presented on Figure 3. The ground pyrite is bioleached by a consortium of bacteria in a cascade of bioreactors (BIOCO^{TM}, 3 primaries, and one secondary, 1380m^3 each). Then the final bioleached product is sent to neutralization for precipitating most of the iron. The pulp is filtered and washed on a belt filter.

The wash filtrate from the belt filter is recycled to the BIOCO feed. The primary filtrate is eventually sent to a cascade of three reactors where limestone is added for a final iron removal. After the iron removal a thickener recycles the underflow either to the bioleaching feed or to neutralization, whereas the overflow is sent to the bottom plant.

The average residence time in the three primary BIOCOs is between 3 and 5 days depending on the feed rate and between 1 and 2 days in the secondary. Mixing and aeration in the tanks are provided for by a rotating shaft system equipped with two upper impellers and one bottom turbine. Air, provided by five blowers, is injected under the turbine.

The other data available on this plant are of several types: pulp flowrates measured with online flowmeters, pulp density measured on line and a series of chemical and physical (%solids, solids specific gravity, liquid densities, etc.) analyses carried out at the laboratory on samples collected at different locations. Flowmeters on every air feed pipe provide airflow rates in Nm3/h.

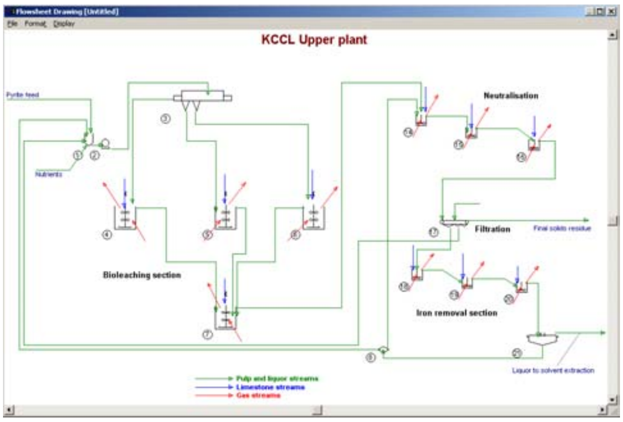


Fig. 3. The KCCL upper plant flowsheet

Off-gas from the tank is sampled by means of a vertical pipe with open slots at different levels. The pipe is fixed in the tank, near the tank wall, and its length goes down to about half a meter from the bottom. Assuming that the tank is perfectly mixed, the gas taken by this way was supposed to be representative of all the off-gas. (Morin, *et al*, 2003). The oxygen and carbon dioxide volumetric concentrations in the inlet and outlet gas of each reactor are thus measured.

Rather little data of flowrates are available. Thus, calculation of recoveries is difficult and inaccurate. The example presented in Table 1 shows the balance of cobalt for the global upper circuit for September 22nd, 2000.

Table 1 – Example of a mass balance for September 22nd 2000

	Co (t/d)
Pyrite feed	1.88
Wash water on filter	9.1 10^{-5}
Total input	1.88
Liquor to solvent extraction	1.14
Final residues	0.42
Total output	1.57

The total output of the upper plant for this day is measured as 1.57t of cobalt while we have input for the same day 1.88t. This difference makes it difficult to determine the exact yield of the upper section and proves the interest to balance the circuit, and determine intermediate performances.

3.2 The graph, data and constraint model

Because no slurry or liquor flow rate were measured between the BIOCOs, nor between the neutralization tanks and the iron removal tanks, it was decided to study these sections globally.

The global upper plant flowsheet has then been modeled as in the diagram of Figure 4. As the residence time in BIOCOs and in neutralization tank is rather long and the circuit is not really in steady-state conditions, it has been compulsory to take into account the inventory variations of each section.

Thus incoming streams to each of the tanks have been added. When the inventory is increasing, corresponding to "storage", the flowrate of these streams is negative, when the inventory is decreasing, corresponding to "restoration" into the circuit, the flowrate is positive.

The critical chemical elements that have been used to monitor the upper plant performances are cobalt and sulfur, plus calcium and magnesium to allow the determination of limestone additions. For each stream, we considered the data description presented in Table 2. Mass flowrates for liquid are determined using liquor densities. For gas, we consider normal conditions of pressure and temperature.

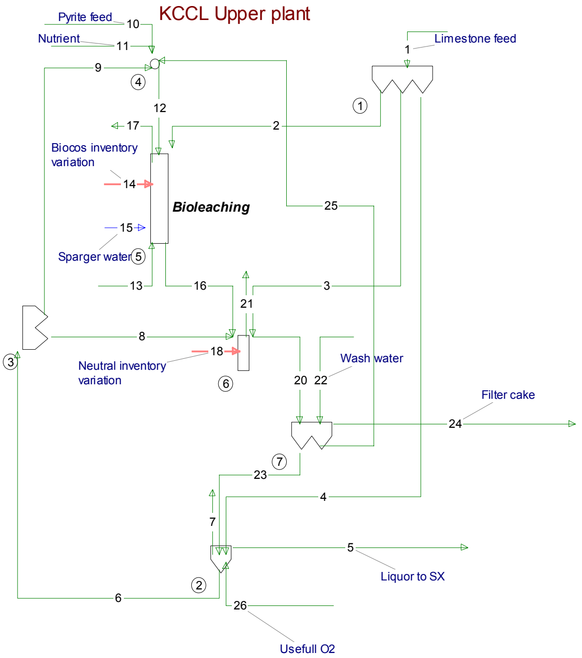


Fig. 4. Graph used for the upper plant description

Table 2 – Data description

Liquid and solids					Gas		
Co	S	Ca	Mg	Other	O2	CO2	N2

Different types of conservation laws (constraints) exist in the circuit. Splitters 1 and 3 conserve all partial flowrates. For the other nodes the conservation constraints are presented in Table 3.

Table 3 – Constraint definitions

Node	Constraint laws
Feed sump	Pulp/Flowrate [(1)] Pulp/Solids Pulp/Liquid Pulp Co[(2)] Pulp Ca, Mg, S, Other
Bioleaching	Gas/N2 Pulp/Flowrate + Gas/O2 + Gas/CO2 Pulp Co, Ca, Mg, S
Neutralization	Pulp/Flowrate + Gas/CO2 Pulp Co, Ca, Mg, S
Belt filter	Pulp/Flowrate Pulp Co, Ca, Mg, S, Other
Iron removal	Gas/N2 Pulp/Flowrate + Gas/Flowrate Pulp Co, Ca, Mg, S

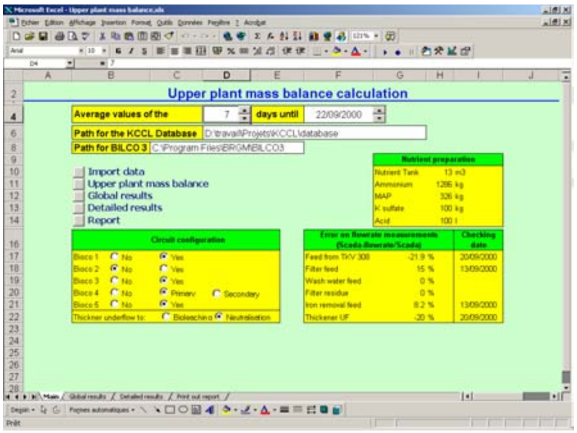
(1) "Flowrate" for global mass flowrate. The other constraints concern partial mass flowrates of solids, liquids or components of solids or liquids

(2) This indicates that the component is globally conserved in the pulp but moves from solid phase to liquid phase during leaching or conversely during precipitation

3.3 A Microsoft Excel interface

Microsoft Excel with Visual Basic for Application has been chosen to constitute the platform of the Material Balance Application. Because of the long residence time in the upper plant, the application allows computation of material balance for long periods (several days), using average values of these periods.

The application realizes the importation of data from the database and runs BILCO just pressing the corresponding buttons on the main page (Figure 5).



Upper plant mass balance calculation

Average values of the 7 days until 22/09/2000

Path for the KCCL Database D:\travail\Projets\KCCL\database

Path for BILCO 3 C:\Program Files\BRGM\BILCO3

Nutrient preparation	
Nutrient Tank	13 m3
Ammonium	1286 kg
MAP	326 kg
K sulfate	100 kg
Acid	100 l

Circuit configuration			
Bioco 1	○ No	● Yes	
Bioco 2	● No	○ Yes	
Bioco 3	○ No	● Yes	
Bioco 4	○ No	● Primary	○ Secondary
Bioco 5	○ No	● Yes	
Thickner underflow to:	○ Bioleaching	● Neutralisation	

Error on flowrate measurements (Scada flowrate/Scada)		Checking date
Feed from TKV 308	-21.9 %	20/09/2000
Filter feed	15 %	13/09/2000
Wash water feed	0 %	
Filter residue	0 %	
Iron removal feed	8.2 %	13/09/2000
Thickener UF	-20 %	20/09/2000

Fig. 5. Main sheet of the Material Balance Application

The Material Balance Application carries out in hidden sheets all the unit conversions, the initialization calculations and the initial error estimations.

3.4 Results and operating parameter determination

Once the "Upper Plant Mass Balance" is computed, the user obtains a set of flowrates and compositions for each stream. A set of pages has been developed for the presentation of results. The application also computes different operating parameters presented in a printout report.

Among the interesting parameters, only available owing to material balance, we can list: limestone feedrate per section, inventory variations in BIOCOs and neutralization tanks, allowing estimation of the circuit stability and also a real-time yield, residence time in bioleaching tanks, sulfides oxidation rates and cobalt dissolution in BIOCOs, precipitation of cobalt during neutralization and filtration, washing efficiency, global recovery of cobalt for the upper plant taking into account the inventory variations and recycling.

4. CONCLUSIONS AND PERSPECTIVES…

4.1 … For the KCCL process

In such a process, where steady state is difficult to reach and sampling and measurements are not easy, a material balance system is essential for the follow-up of the plant performances. The capability of BILCO 3.0 to be integrated in a spreadsheet system allows a very interactive and simple computation of the main parameters of the process.

Since the end of the implementation of the material balance application a gravity section has been added to the circuit after the bioleaching section with the aim of recovering unleached sulfides and recycling them to the BIOCO feed. If the current material balance application is still operational (the Bioleaching node groups the bioleaching and gravity sections), it would be interesting to integrate the new section as an independent node so that its performances could be evaluated.

Besides the implementation of such a system on the bottom plant would improve the quality of data and comfort the performance estimation.

4.2 … For other processes

This type of application can be developed for any type of processes. The interest of such an approach is the possibility of using all the available data simultaneously; even visual characteristics determined by well-trained operator can be integrated in the set of data.

A second interest, and not the least, is the preliminary analysis of the existing process required before the implementation of such a tool. Eventually, a material balance application helps production engineers to follow the important parameters and to focus on the right objectives.

This analysis facilitates the link between the local (unit operation, workshop) performances and the plant objectives, allowing a better involvement of the operation teams in the production management system.

ACKNOWLEDGEMENTS

The authors wish to thank the Kasese Cobalt Company Ltd., which allows them the publication of this paper (BRGM contribution n°2777).

REFERENCES

BILCO 3.0: User's guide (2002). BRGM, Orléans.

BILCO 3.0 COM: User's guide (2002). BRGM, Orléans.

Brochot, S., M.-V. Durance, S. Foucher, J.-C. Guillaneau, D. Morin, J. Villeneuve (2000). Process simulation to enhance complex flowsheet development: examples in biotechnology. SME-Control 2000 Conference, Salt Lake City, Utah, USA – Feb 28-Mar 1.

Fourniguet, G., J. Villeneuve, L. Rocchia., H. Védrine, S. Brochot, J.-C. Guillaneau (1997). Analyse par bilans matière d'un procédé hydrométallurgique de recyclage de déchets d'aciéries électriques. 6e French congress of Process Engineering. Paris. September 24-26.

Herbst, J.A., R.K. Mehta, W.T. Pate (1988). A Hierarchical Procedure for Mass Balance Closure and Parameter Estimation: Application to Ball Mill Grinding. *Proceedings of the XVI International Mineral Processing Congress*, K.S.E. Forssberg Editor, Elsevier, p. 1719-1732.

Hodouin, D. and M.D. Everell (1980). A Hierarchical Procedure for Adjustment and Material Balancing of Mineral Process Data. *International Journal of Mineral Processing*, **Vol. 7**, pp. 91-116.

Le Guirriec, E., S. Brochot, M. Bergounioux (1995). An Augmented Lagrangian Method for Problems Arising in Mineral Processing. *Proceedings of the 17th IFIP TC7 Conference on System modelling and Optimization*, July, Prague, Czech Republic. **Vol. 1**, pp. 65-68,

Le Guirriec, E. Modélisation et résolution mathématique de problèmes de bilans matière statistiquement cohérents (1996). PhD thesis, Orléans University, France.

Morin, D., P. d'Hugues, M. Mugabi (2003). Bioleaching of metallic sulphide concentrate in continuous stirred reactors at industrial scale experience and lessons. To be presented at the International Symposium of Biohydrometallurgy, September, Athens, Greece.

Ragot, J., M. Darouach, D. Maquin, G. Bloch (1990). Validation de données et diagnostique, Ed. Hermes.