



**LUT**  
Lappeenranta  
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LUT School of Engineering Science

Degree Program of Chemical & Process Engineering

**MASTER'S THESIS**

**NUMERICAL STUDY ON FORCED PERIODIC OSCILLATIONS IN  
SOLVENT EXTRACTION OF METALS USING THE OBJECT-ORIENTED  
SIMULATION METHODOLOGY**

**EXAMINERS:**

TUOMO SAINIO

SAMI VIROLAINEN

JUAN CALIXTO SOTO AFONSO

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*The universe is nothing more than a set of systems that communicate through their inputs and outputs.*

*The complex behavior of the universe results from the interaction of a large number of simple non-linear systems.*

*The oscillation of the inputs is one of the ways in which nonlinear chemical systems can exhibit complex behavior, change in the pattern (magnitude and form) of the outputs*

# ABSTRACT

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Juan Soto

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**Theoretical-experimental study of the effect of forced periodic oscillations in the solvent extraction of metals through the modern object-oriented simulation methodology.**

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Examiners:

**Keywords:** Nonlinear chemical dynamics, Complexity, Forced periodic oscillations, Solvent extraction, Object-oriented simulation, DAE system, Simscape-Simulink, Design Space Exploration, Global Sensitivity Analysis.

The computational advances of the modelling and simulation tools in Chemical Engineering open up the possibility of studying in a general, robust and efficient way (avoiding the peculiarities and restrictions of analytical methods) the possible improvement of certain non-linear chemical systems switching from the steady state mode of operation to a dynamic one with forced oscillations that enable the emergence of complex behavior in these systems.

In this work, we propose to apply this idea to a case of interest in the industry, the single and multicomponent solvent extraction of metals in mixer-settlers, one of the main hydrometallurgical processes. To do so, following the latest trends, the process is modelled mathematically applying the modern object-oriented modelling and simulation paradigm, using the Simscape equation based language within the Simulink environment, which allows solving the complex DAE systems that arise from dynamic models. The fundamental and complex problem of determining the optimal value of the parameters of the inputs to oscillate (amplitude and frequency of the sine wave oscillations of the flowrates of the aqueous and organic streams) is addressed by a Global Sensitivity Analysis (GSA), through statistical sampling with Monte Carlo simulations that explore the design space of the problem.

For the discussion of the results, obtained by means of simulation, a comparison between the steady state and the dynamic oscillatory modes of operation is carried out. In the case of the single component study, the variable to be optimized is shrinkage of metal, while in the multicomponent case, it is necessary to study together the productivity and purity of the process in the whole range of operation.

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To the 1<sup>st</sup> examiner of this thesis, Tuomo Sainio, for selecting and proposing a research problem according to my vocation and professional interests, tutoring and giving me a great margin of personal initiative and flexibility in the development of the work. In addition, to 2<sup>nd</sup> examiner Sami Virolainen and supervisor Fedor Vasilyev for their availability and support both when it comes to answering questions and giving the appropriate guidelines for the preparation of this work.

# TABLE OF CONTENTS

1	INTRODUCTION .....	11
1.1	Problem statement and justification .....	11
1.2	Scope and limitations.....	11
1.3	Objectives.....	12
1.3.1	General objectives .....	12
1.3.2	Specific objectives.....	12
1.3.3	Academic objectives .....	13
1.4	Methodology.....	13
2	THEORETICAL FRAMEWORK AND STATE OF THE ART .....	14
2.1	Oscillations in Chemical Engineering: fundamentals and applications .....	14
2.1.1	Nonlinear chemical dynamics .....	14
2.1.2	Evaluation of Forced Periodic Oscillations.....	20
2.1.2.1	Early approaches.....	20
2.1.2.2	Design Space Exploration through Global Sensitivity Analysis .....	22
2.2	Solvent extraction process for metal recovery and its modelling .....	29
2.2.1	Process and equipment.....	30
2.2.2	Modelling of metal solvent extraction.....	33
2.3	Modelling and simulation paradigms in engineering .....	36
2.3.1	Introduction: concepts of system, model, simulation and modularization.....	36
2.3.2	Block - oriented approach.....	42
2.3.3	Object - oriented approach.....	46
3	SOLUTION ADOPTED .....	52
3.1	Mathematical models of the systems equipment-process .....	52
3.1.1	Single component model of the mixer tank .....	52
3.1.2	Multicomponent case .....	56
3.1.3	Linearity of the models .....	59
3.2	Computational implementation .....	59
3.2.1	Single component model .....	59
3.2.2	Multicomponent model .....	63
4	MATERIALS AND RESOURCES.....	65
4.1	Hardware .....	65
4.2	Matlab-Simulink software.....	65
5	EXPERIMENTAL DESIGN, SIMULATION AND RESULTS .....	66

5.1	Single component case with countercurrent cascade.....	66
5.1.1	Experimental design.....	66
5.1.2	Simulation, sensitivity analysis optimization and results .....	67
5.1.3	Results analysis .....	76
5.2	Multicomponent case with single mixer tank.....	77
5.2.1	Experimental design.....	77
5.2.2	Simulation, sensitivity analysis and results.....	78
5.2.3	Results analysis .....	84
6	SUMMARY OF CONCLUSIONS AND FUTURE WORK.....	85
7	REFERENCES.....	89

# LIST OF FIGURES

Figure 2.1 Lorenz mathematical model and its attractor (2-D perspective) .....	15
Figure 2.2 Controlled cycle operation.....	16
Figure 2.3 Heat production curve and heat removal line showing steady-state multiplicity in CSTR for a the first-order reaction (Favache & Dochain, 2009) .....	17
Figure 2.4 Process modification for forced periodic oscillations operation .....	18
Figure 2.5 Results of forced oscillations on a nonlinear system (solvent extraction).....	19
Figure 2.6 Global Sensitivity Analysis methodology for Design Space Exploration.....	24
Figure 2.7 MATLAB implementation of a Monte Carlo simulation.....	26
Figure 2.8 Comparison of random and Sobol sampling methods .....	27
Figure 2.9 Scheme of a copper hydrometallurgical plant (Metallurgist, n.d.).....	29
Figure 2.10 Solvent extraction principle (a) Extraction (b) Stripping (Kathryn, 2008). .....	30
Figure 2.11 Flow diagram of a typical SX process.....	31
Figure 2.12 Conventional mixer-settler unit (Kathryn, 2008).....	33
Figure 2.13 McCabe-Thiele diagram for solvent extraction process (Xie, et al., 2014) .....	34
Figure 2.14 Generic unit operation .....	37
Figure 2.15 Model of a generic unit operation .....	39
Figure 2.16 Classical analog computers.....	43
Figure 2.17 Control system of a helicopter implemented in the Simulink environment.....	44
Figure 2.18 Screenshot of a chess game for PC .....	47
Figure 2.19 Mass-spring-damper expressed as a block diagram and a schematic. ....	49
Figure 2.20 Modelica and gPROMS code of the dynamic tank problem.....	49
Figure 2.21 Scheme of Simscape execution sequence .....	50
Figure 3.1 Mixer tank diagram.....	53
Figure 3.2 Simulink design of the single component mixer tank .....	59
Figure 3.3 Simulink block diagram of the single component model .....	60
Figure 3.4 Simscape design of the mixer tank.....	61

Figure 3.5 Counter-current cascade in Simscape.....	63
Figure 3.6 Simscape design of the multicomponent mixer tank.....	64
Figure 5.1 Single component steady state simulation result.....	67
Figure 5.2 Initial single component parameter sample .....	69
Figure 5.3 Single component MATLAB cost function code.....	69
Figure 5.4 Single component Global sensitivity Analysis for the first parameter sample.....	70
Figure 5.5 Amplitudes contour plot for the first parameter sample.....	70
Figure 5.6 Frequency contour plot for the first parameter sample .....	71
Figure 5.7 Tornado plot for the first single component parameter sample .....	71
Figure 5.8 Triangular distributions for sampling of amplitude parameters.....	72
Figure 5.9 Restricted single component parameter sample.....	72
Figure 5.10 Single component Global Sensitivity Analysis scatter plots for the second parameter sample .....	73
Figure 5.11 Amplitudes contour plot for the second parameter sample .....	73
Figure 5.12 Frequencies contour plot for the second parameter sample .....	74
Figure 5.13 Optimal flowrate modulation for the single component case.....	75
Figure 5.14 Performance comparison between both modes of operation in the single component case.....	76
Figure 5.15 Steady state performance curve.....	78
Figure 5.16 Multicomponent case 1 parameter sample .....	79
Figure 5.17 Multicomponent case 2 parameter sample .....	79
Figure 5.18 Multicomponent case 3 parameter sample .....	80
Figure 5.19 Multicomponent case 4 parameter sample .....	80
Figure 5.20 Multicomponent productivity MATLAB objective function code .....	81
Figure 5.21 Multicomponent purity MATLAB objective function code .....	81
Figure 5.22 Multicomponent case 1 Global Sensitivity Analysis scatter plots .....	82
Figure 5.23 Multicomponent case 2 Global Sensitivity Analysis scatter plots .....	82
Figure 5.24 Multicomponent case 3 Global Sensitivity Analysis scatter plots .....	83

Figure 5.25 Multicomponent case 3 Global Sensitivity Analysis scatter plots .....	83
Figure 5.26 Performance comparison of steady state and dynamic oscillatory modes for the multicomponent case .....	84

## LIST OF TABLES

Table 2.1 Necessary processes in Chemical Engineering.....	37
Table 5.1 Input values for the single component case.....	66
Table 5.2 Range of oscillation parameters for the single component case .....	67
Table 5.3 Optimal parameter space for the single component case .....	74
Table 5.4 Optimal parameter values for the single component case .....	75
Table 5.5 Steady state single component parametric study.....	76
Table 5.6 Input values for the multicomponent case .....	77
Table 5.7 Range of oscillation parameters for the multicomponent case .....	78
Table 5.8 Multicomponent steady state simulations results.....	78

# LIST OF SYMBOLS

$A_{in}$	inlet aqueous volumetric flow
$A_{out}$	outlet aqueous volumetric flow
$H_{in}$	inlet $H^+$ concentration
$H_{out}$	Outlet aqueous $H^+$ concentration
$HR_{in}$	inlet extractant concentration
$HR_{out}$	Outlet organic extractant concentration
$K$	equilibrium reaction constant
$k_{LA}$	volumetric mass transfer coefficient
$O_{in}$	inlet organic volumetric flow
$O_{out}$	outlet organic volumetric flow
$P$	purity
$p$	productivity
$Q$	mol transfer flow
$V$	total volume in the mixer tank
$V_A$	aqueous volume in the mixer tank
$V_o$	organic volume in the mixer tank
$X_{in}$	inlet aqueous concentration
$X_{out}$	outlet solute aqueous concentration
$Y_{in}$	inlet organic concentration
$Y_{out}$	outlet solute organic concentration

# 1 INTRODUCTION

## 1.1 Problem statement and justification

This work is realized, assuming the question suggested by the tutor within the research line of the department that is formulated as:

Numerical study of the effect of forced periodic oscillations in the solvent extraction of metals (single and multicomponent) through the modern object-oriented modelling and simulation methodology.

It is considered that the aforementioned research problem is relevant given the growing interest in the application of oscillations in Chemical Engineering, since this process disturbance is one of the ways in which nonlinear chemical systems can exhibit complex behavior that can be utilized to outperform traditional steady state operation. In fact, this is the case of the solvent extraction process, in which the study of oscillations is a novelty, compared to the classical works of this field in chemical reactors. This process has an intrinsic interest given the current full validity of metallurgy for the obtaining, purification and recovery of metals, which are considered strategic resources. In particular, the high environmental requirements and quality standards, as well as technological advances, have made the hydrometallurgical industry a viable alternative of great development, being the solvent extraction one of its fundamental processes.

In addition, the resolution of the research problem poses the use of modern computational tools, which open new possibilities in the study of forced oscillations method.

## 1.2 Scope and limitations

The scope of this work, as is natural, is determined by the academic level (master thesis) to which correspond and by the specifications or requirements stipulated for it. Specifically, it is assumed a grey-box macroscopic modelling level (multistage for the single component case) with perfect mixing consideration in the mixer tank for the metal solvent extraction process. Given the approach of this work, we opt for a thermodynamic model (limiting factor) based on the classical theory of chemical equilibrium (Law of mass action) corresponding to a competitive ion-exchange (complexation) reaction and not the alternative that consists of using experimental equilibrium isotherms.

Also, in order to not mask the effect of the oscillations in the process, high values of mass transfer coefficients are considered, so that this mechanism does not act as a limiting factor.

Regarding the type of modulation of the variables, the sinusoidal oscillations standard is followed, although extending its application to multiple inputs (organic and aqueous flowrates) in order to increase the possibilities of finding an optimal configuration that improves the performance of the steady state mode of operation.

In relation to the limits of the work, obviously they are fixed or determined by the above. Since an direct industrial-scale application of the work is not considered, the process's fluid mechanics (ideal mixer tank and settler not considered) is not modeled given the minor relevance of the effect on the oscillations effect. In addition, although the degree of generality of the study is significant, it is restricted since it does not contemplate the indiscriminate modulation of all the inputs nor the extraction of metals of different valences.

## 1.3 Objectives

### 1.3.1 General objectives

- Demonstrate the suitability and efficiency of object-oriented modelling and simulation to solve general models (DAE), overcoming the difficulties and restrictions presented by conventional simulation tools.
- Determine the principles, characteristics and operation of mixer-settlers, as well as the its different modelling alternatives of the solvent extraction process.
- Find a general and robust alternative to analytical methods for studying the effects of forced oscillations applied to non-linear systems.

### 1.3.2 Specific objectives

#### Primary

- Of final character, evaluate the degree of improvement that can be obtained by forced oscillations in the solvent extraction of equal valence metals.

#### Secondary

- Of instrumental character, dynamic modelling and simulation using Simscape of the single and multicomponent cases of the process to be studied.

### 1.3.3 Academic objectives

- Get introduced in the object-oriented programming paradigm for the implementation of unit operations through high-level mathematical modelling languages, expanding the knowledge acquired with traditional simulators such as Aspen Plus or Hysis.
- Acquire the competences and skills necessary for the resolution of DAE systems that arise in the dynamic simulation of complex processes.
- Become familiar with the application of statistical methods and data analysis for the design and optimization of processes.

## 1.4 Methodology

Taking into account the objectives to be achieved, as well as the scope and limits of the proposed problem, a theoretical-experimental methodology is used, with contrast of the results through the application of computational methods. Specifically, the methodology consists of the following:

### **Theoretical phase** (obtain a solution)

- Literature-documentary review: to determine the state of the art of the question and the conceptual framework of the research.
- Exposition of the theoretical and practical foundations required to solve the problem.
- Deductive method applied in two steps: analytical and numerical.
  1. Analytical: To infer, from the assumptions of the problem, the mathematical correlations of the model.
  2. Numerical: To obtain by computational means (acausal object-oriented methodology) a solution to the research problem from the correlations of the model.

### **Experimental phase** (test the solution adopted)

- Determination of the materials and resources necessary for experimentation
- Selection of case studies and experimental design
- Execution of the developed implementation
- Data processing
- Validation and discussion of results

## 2 THEORETICAL FRAMEWORK AND STATE OF THE ART

### 2.1 Oscillations in Chemical Engineering: fundamentals and applications

From the works developed since the 70s, the possibility of improving the non-linear chemical processes through the transition from static to continuous dynamic modes of operation has been considered and studied. Of the techniques applicable to achieve these improvements, the most promising and widespread consist in introducing oscillations in the process variables.

#### 2.1.1 Nonlinear chemical dynamics

This field studies how chemical systems with a nonlinear behaviour in their key variables evolve in time (Sagués & Epstein, 2003). Nearly all systems of interest in nature are nonlinear, in systems with chemical reactions, nonlinearities typically arise from the rate equations of mass action.

Traditionally they are studied under conditions (steady state) where they can be considered to behave linearly. This is done because nonlinear systems are very hard to analyse and most of them impossible to solve analytically. On the other hand, linear systems, thanks to the principle of superposition, have the great advantage that the response (output) to a complex input can be obtained as a superposition of the outputs corresponding to the simple inputs that are the result of the decomposition of the complex input (Strogatz, 1994, pp. 4-9). Well established and efficient mathematical methods have been developed to exploit these characteristics, such as Fourier analysis or Laplace transforms. However, as it has been said, most of the interactions in the real world are nonlinear, producing the principle of superposition to fail, in some cases stunningly.

Besides, linear mathematics doesn't allow to replicate-simulate the complex behaviour that even simple nonlinear systems shows: chaotic, oscillatory or quasi-periodic behaviours, bifurcations, instabilities or pattern formation. In fact, the complicated behaviour of the world is nothing more than a superficial complexity that arises from the interaction of many simple non-linear systems. However, this type of chaotic behaviour does not imply that guidelines or regularities do not exist in it. In fact, although these systems do not evolve towards a state of equilibrium, they do so towards a set of states that follow a pattern called an attractor. According to thermodynamics, these states tend to maximize the entropy of the system.

For example, the meteorologist Edward Lorenz discovered the first attractor (in butterfly wings), that he denominated strange to be surprised that it arose from the simulation of a tremendously simplified but non-linear mathematical model (Strogatz, 1994, pp. 301-330).

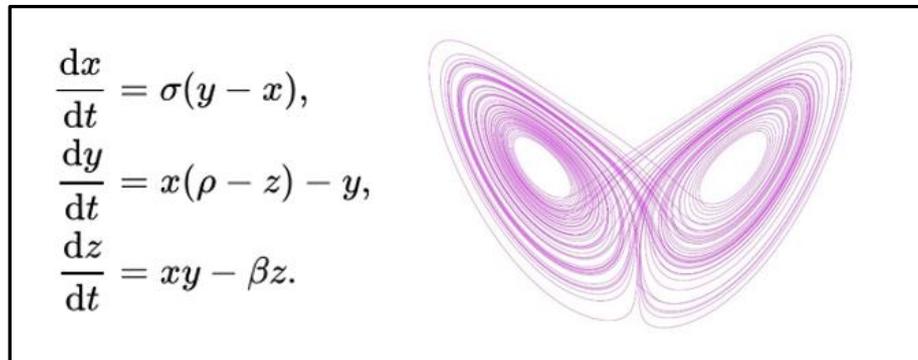


Figure 2.1 Lorenz mathematical model and its attractor (2-D perspective)

In conclusion, nonlinear dynamics show how scientific knowledge based on simple laws can replicate the seemingly inexplicable behaviour of weather systems, stock markets, earthquakes, and even the origin of life. The main idea is that chaos and complexity can arise from simple laws, but with sensitivity to initial conditions and feedback.

The field of nonlinear dynamics, as many new areas in science, has become highly interdisciplinary (Field & Schneider, 1989), covering all fields of chemistry as well as in engineering, physics, biology, geology, astronomy, or economics. Focusing on the chemical engineering field, the area of application where nonlinear dynamics can be beneficial is unsteady state continuous processing (Suman, 2004). Process engineering has traditionally been committed to steady state processes, where there is not accumulation of material or energy and the inputs and outputs do not vary with time. They are easier and safer to design operate and control, and more economical due to higher capacities, so to date there has been no true incentives to intentionally disturb this stationary state approach.

However since the pioneering work of (Douglas & Rippin, 1966) and (Horn & Bailey, 1971) a considerable number of papers both theoretical and experimental have been published studying the possible enhancement of chemical processes by intentionally moving to a dynamic operation. Practically all of the literature refers to chemical reactors, since most of reactions have nonlinear behaviour and CSTR weaknesses such as lower product yield or selectivity can be improved. Specially much larger improvements can be achieved on non-isothermal reactors, since the inclusion of heat effects introduces an exponential nonlinearity into the process.

There are three general categories of unsteady state continuous operation: Controlled cycling, Natural Oscillations and Forced Periodic oscillations (FPO).

### Controlled cycling

Developed in the 1950s, is one of the most industrially relevant techniques applied to staged separation processes, and based on the existence of intervals of time where only some of the streams flows.

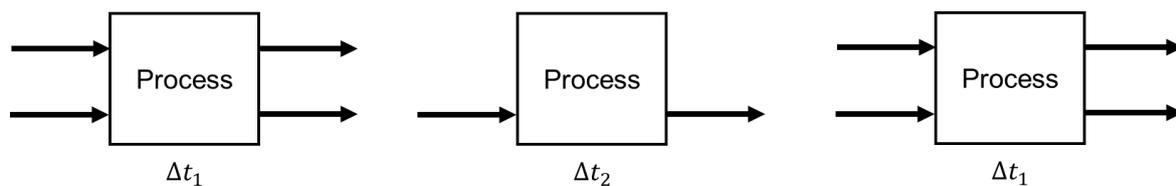


Figure 2.2 Controlled cycle operation

It must be noted that the improvements of this technique are not based on nonlinear behaviour, but rather in combining the advantages of batch and continuous operation at the same time. One of the firsts applications of this method was cycled distillation, consisting of switching liquid and gaseous input flows to obtain a batch behavior in each of the trays of the column achieving increases in efficiency of around 100% (Pour, 1976, pp. 21-22).

### Natural oscillations

For chemists, the main phenomenon of nonlinear dynamics is chemical oscillation, the natural and periodic, or nearly periodic, variation of the concentrations of the species in a reaction. This phenomena was discovered accidentally in the 1950s in the Belousov–Zhabotinsky (BZ) reaction (Sagués & Epstein, 2003), that consists of bromate, citric acid and cerium.

Belousov was astonished when he discovered that the reaction, instead of monotonically changing from yellow  $\text{Ce}^{4+}$  to colourless  $\text{Ce}^{3+}$ , changed between these two colours in intervals close to one minute. This discovery created lot of confusion in the chemical community, since chemical oscillations were considered impossible due to a violation of the Second Law of Thermodynamics.

Today it is understood that most of the reaction processes commonly considered to be 'stationary' are composed of partial steps of a periodic nature. For a chemical engineer it is well known that an exothermic CSTR fitted with a cooling jacket may have more than one steady state and that the reactor can move between these states.

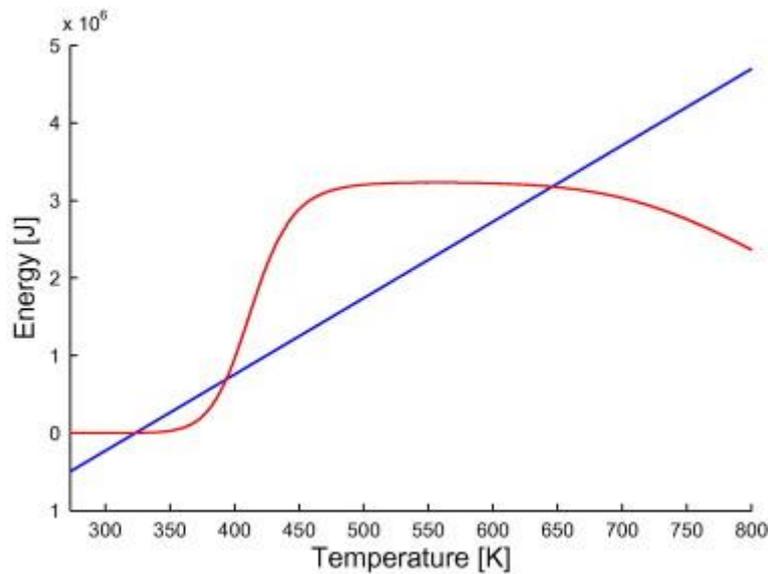


Figure 2.3 Heat production curve and heat removal line showing steady-state multiplicity in CSTR for a the first-order reaction (Favache & Dochain, 2009)

The objective of this mode of operation is to, introducing steady state inputs, find the range of parameters that make the system to naturally move from its stable points of operation producing an oscillation of its outputs that improves performance (Schuker, 1974, pp. 4-5). Although this technique has a promising future and has received attention from engineers concerned with the stability and control of nonlinear systems, still today this is a field more typical of chemists and biologists without industrial applications yet.

### Forced periodic oscillations

In practice, the range of parameter values that produce a system to naturally oscillate is rather narrow, and these oscillations doesn't necessarily improve the process. Furthermore, many processes (like the one studied in this thesis) cannot produce oscillations by themselves, so they have to be introduced into the system by a periodic variation in its inputs (flowrates, concentrations, temperatures, pressures...). They introduce a whole new class of adjustable process parameters or degrees of freedom, giving more flexibility to the plant engineer to operate the process.

For these reasons, without taking into consideration controlled cycling, this is the most popular technique of unsteady state continuous processing in chemical engineering, since it allows every system to oscillate and there is a wider range of parameters that increases the possibilities to find a periodic configuration that outperforms the steady state mode, for example enhancing mass transfer, increasing productivity or selectivity, or bypassing thermodynamic limitations without the use of recycling streams (Stankiewicz & Kuczynski, 1995).

The key consists of finding an optimal steady state operation that acts as an upper limit in performance, once it is found, some or all the inputs are oscillated around their steady state values, meaning that the time average values are the same and therefore the amount of consumed input materials is the same. After an initial settling out interval, output oscillations will be deformed periodic function of time with different time average values, existing the possibility that they are better than the optimal steady state.

To ensure that oscillations of the unit operation does not upset the performance of other processes within the plant, sufficient downstream and upstream surge capacity must be available to damp the oscillations, meaning that generally surge capacity needs to be installed with the additional cost this involve.

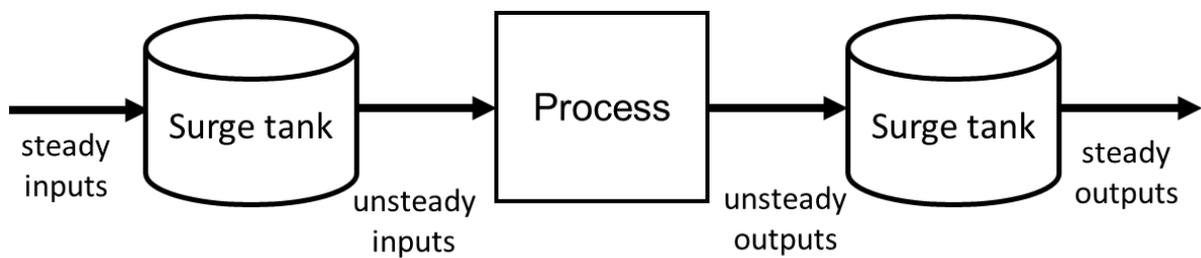


Figure 2.4 Process modification for forced periodic oscillations operation

Moreover, some practical concerns arise such as: difficulties in the control of the process, worse predictability respect to stability and safety, more complicated heat integration or possible catalyst degradation (Stankiewicz & Kuczynski, 1995).

The consequence of this is to justify the introduction of forced oscillations into a process it is not sufficient to improve the optimal steady state, the enhancement must be large enough to overcome the possible appearance of the disadvantages mentioned.

As an example, it is shown in the following page the results of an exploratory simulation, where sinusoidally varying the inlet flowrates, purity (output of the system) is modified producing a different time average value.

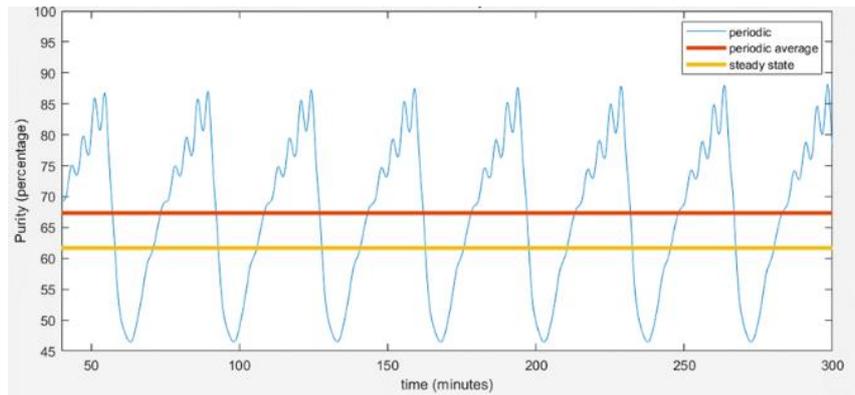


Figure 2.5 Results of forced oscillations on a nonlinear system (solvent extraction)

The reason for this modification and therefore the source of improvement is the nonlinearity of the process (Nikolic, et al., 2014). Still today there is not sufficient knowledge to understand the phenomena in the molecular level (Renken, 1972), therefore the explanations has been based on the mathematical implications that are derived from the nonlinear correlations of the model.

Douglas work, the pioneer in this field, is based on the application of perturbation theory to the analytical resolution of nonlinear systems. The theory was developed in the early 1900s by Poincaré and others to solve problems in celestial mechanics (three-body problem), and today it is heavily used in many fields, specially in quantum mechanics.

It comprises a series of mathematical methods for finding an approximate solution to a complex problem, by starting from the exact solution of a related, simpler problem (Szebehely, 1987). Douglas used it to analyse dynamically stable chemical problems, where the complex problem is the behaviour of the nonlinear plant, and the simplified one is the linearized model obtained by Taylor series expansions.

Perturbation analysis leads to an expression for the functional solution of the complex problem  $Y$  in terms of a formal power series (in this case called perturbation series) in some "small" parameter ( $\mu$ ) that quantifies the deviation from the exactly solvable problem. The leading term in this power series is the solution of simplified problem, while secondary terms describe the deviation in the solution:

$$Y = Y_0 + \mu^1 Y_1 + \mu^2 Y_2 + \mu^3 Y_3 + \dots$$

In this example  $Y_0$  is the linearized model, while  $Y_1, Y_2, Y_3 \dots$  are higher-harmonics terms. It should be highlighted that the set of differential equations that represent  $Y_1, Y_2, Y_3 \dots$  are linear equations, therefore the tremendous advantage of this method consists in replacing a nonlinear ordinary differential equation which might have variable coefficients by a larger set

of nonhomogeneous linear differential equations with constant coefficients, but that can be solved with classical linear methods.

Applying the method to solve nonlinear problems, Douglas realized that although for mild nonlinearities the difference from the steady state produced by these higher harmonics is small, for highly nonlinear systems or those which exhibit resonance, the deviations might be very significant.

## 2.1.2 Evaluation of Forced Periodic Oscillations

As it has been said Forced Periodic Oscillations can improve classical steady state processes, but they also have drawbacks, and testing whether a periodic operation leads to better performance generally demands a tedious experimental and/or numerical effort. Therefore, since the work of Douglas, researches have been working on methods that can answer three main questions (Petkovska & Seidel-Morgenstern, 2013, p. 388): how to identify candidate systems for enhancement through this mode of operation, which is the magnitude of such enhancements, and what system properties result in improvements. In this section, these methods are explored, and Global Sensitivity Analysis is introduced as a general, fast, and efficient alternative.

### 2.1.2.1 *Early approaches*

Experimental studies have proven to be very expensive and time-consuming, so to reduce this effort, analytical mathematical methods have been used to answer the previous questions. However, accurate models are frequently complex, usually in the form of coupled nonlinear partial differential equations that can be solved, generally, only numerically, meaning that analytical methods have a limited application.

As it was mentioned, Douglas applied the standard methods of nonlinear mechanics to the determination of the frequency response of a nonlinear stirred tank reactor and presented approximate analytical procedures with sinusoidal inputs. Although the detailed mathematics of these methods is not excessively complicated, it is exceptionally lengthy and tedious, especially when more complex processes than a single CSTR want to be studied.

Other alternative, more general for functional maximization-minimization is represented by the calculus of variations, specifically the Pontryagin Maximum Principle, used in optimal control theory to find the best possible control for taking a dynamical system from one state to another, especially if there are constraints in the inputs or the states (Pour, 1976, pp. 82-85).

Another similar technique that also applies the Maximum Principle is the Hamilton–Jacobi equation based on relaxed steady state analysis, which involves the study and determination of optimal high frequency periodic operations. (Horn & Lin, 1967) showed that fast temperature constant shifts in CSTR results in increased catalytic performance over the optimal steady state. The results prove that whenever the optimal steady-state violates the maximum principle, the optimal steady state operation can be enhanced by a periodic *bang-bang* (on-off) strategy with a sufficiently large frequency with respect to the dynamics of the system.

A third option is the pi-criteria (Guardabassi, et al., 1974) which could cover broader frequency ranges than the other two methods, however, as the forcing amplitude increases, the deviation from the linearization of the nonlinear equations is amplified (Zhai, et al., 2016), forcing to apply small amplitudes to obtain reliable results.

In the last few years, new methods based on Fourier analysis have also appeared, (Hernandez-Martinez, et al., 2011) uses a first-harmonic balance approach based on approximating nonlinearities by means of the first-harmonic Fourier series to study the performance of nonlinear bioreactors under periodic operation.

In a series of articles, (Petkovska & Seidel-Morgenstern, 2013) develop a nonlinear frequency response (NFR) method, based on the Volterra series and the concept of higher order frequency response functions. In the method the periodic quasi-steady output of the system is calculated directly without the need of numerical integration, since both the inputs (as Fourier series) and the outputs (as Volterra series) are approximated by finite length sums.

A series of analytical and optimization methods to evaluate forced periodic oscillations have been reviewed, despite the interest they have aroused among researchers, even the newer approaches have not been used for a series of reasons:

- The complexity of their application makes that till the moment they have been only used to study relatively simple cases.
- They are not general, their application is usually limited to certain frequency or amplitude ranges and mild nonlinearities.
- The results obtained are not completely reliable, and they have to be contrasted with numerical simulations or empirical experiments.

The mentioned limitations of traditional methods for evaluation of Forced Periodic Oscillations create the need of new more general, efficient and reliable approaches. That is, a quick and relatively easy evaluation characterization of candidates for process performance improvements.

### 2.1.2.2 Design Space Exploration through Global Sensitivity Analysis

An alternative method to solve this typical problem that arises in engineering is Design Space Exploration, that consists in evaluate the outputs of a process assigning different combinations of the value of free parameters in order to understand their impact on the model and determine their optimal values. The main challenge however is that as the number of design parameters increase (for example if multiple inputs are oscillated) the system can have thousands or millions of possible combinations, and so evaluating every point in a high dimension design space (formed by the set of points corresponding to all possible combinations) is not viable even with modern computers.

Global Sensitivity Analysis (GSA), implemented through Monte Carlo techniques, allows to systematically explore the design space in an efficient manner. The key idea is that with a proper random sampling, only a small subset of the space needs to be evaluated. SA can also help reduce the dimensions the design space by identifying the influence of the parameters in the output of the system and dismissing non-relevant parameters, in other words, to establish the grade of sensibility of the system to its parameters. This is important since it is usual to have only a few influential parameters, even when the number of parameters in large.

The classical definition in terms of uncertainty is given by (Saltelli, et al., 2004):

*The study of how uncertainty in the output of a model (numerical or otherwise) can be apportioned to different sources of uncertainty in the model input, using qualitative or quantitative approaches under a given set of assumptions and objectives (cost functions).*

Sensitivity analysis methods can be applied for multiple purposes (Song, et al., 2015), including: uncertainty assessment, prioritise efforts for uncertainty reduction, model calibration and diagnostic evaluation, to support robust decision-making, to determine the influence of the parameters of a model, and of course to efficiently explore and understand high dimensional design spaces of models.

However, in spite of it possibilities in many fields of science and engineering, its application has been limited mainly to econometrics, propagation of error theory, risk analysis, and more recently in environmental modelling (Sarrazin, et al., 2016).

The main reason is that advanced statistical data analysis knowledge that were not part of the academic training of engineers and researches. This drawback was recently attenuated when user friendly specific software that allowed non-specialist users to take advantage of this techniques: (Pianosi, et al., 2015) developed a MATLAB toolbox for this purpose in 2015,

Simulink Design Optimization toolbox implemented the sensitivity analysis tool in version 2016a, and PSE introduced GSA in gProms 5.0, launched in 2017.

### **Local Sensitivity Analysis vs Global Sensitivity Analysis**

One option is local sensitivity analysis, it calculates the local partial derivatives or finite differences of the output functions with respect to the input variables around a specific value  $x$ , used for example to show how model performance changes when moving away from an optimal point. The main limitation of the local approach is that the local partial derivatives only give information of the base point where the calculations are and do not explore the entire space of the input parameters. In addition, when the model contains discontinuous functions, the derivatives do not exist.

Local sensitivity analysis is a One-At-a-Time (OAT) technique (Pianosi, et al., 2016), meaning that only the effect of one parameter on the cost function is analysed at a time, keeping all others fixed. OAT methods explore only a small fraction of the design space, this problem is accentuated as the number of parameters increases. Also, they do not reflect the interactions between parameters influence the cost function.

On the other hand, global sensitivity analysis, often implemented through Monte Carlo methods uses a representative (global) set of samples to explore the design space.

GSA typically use an All-At-a-Time (AAT) technique, so output variations are induced by varying all the input parameters simultaneously, and therefore it considers the parameters interactions (Sarrazin, et al., 2016). The disadvantage of GSA is that it requires a higher number of iterations since a wider sampling is needed. This could be a problem for computationally expensive simulations, but it has the advantage that since each simulation is independent, the method is well suited for parallel computing, which significantly speed up evaluation on multicore processors or multiprocessor networks.

### **Methodology of Global Sensitivity Analysis by Monte Carlo simulations**

When the GSA approach is used for Design Space Exploration four basic steps are needed, they are shown in the diagram of the following page:

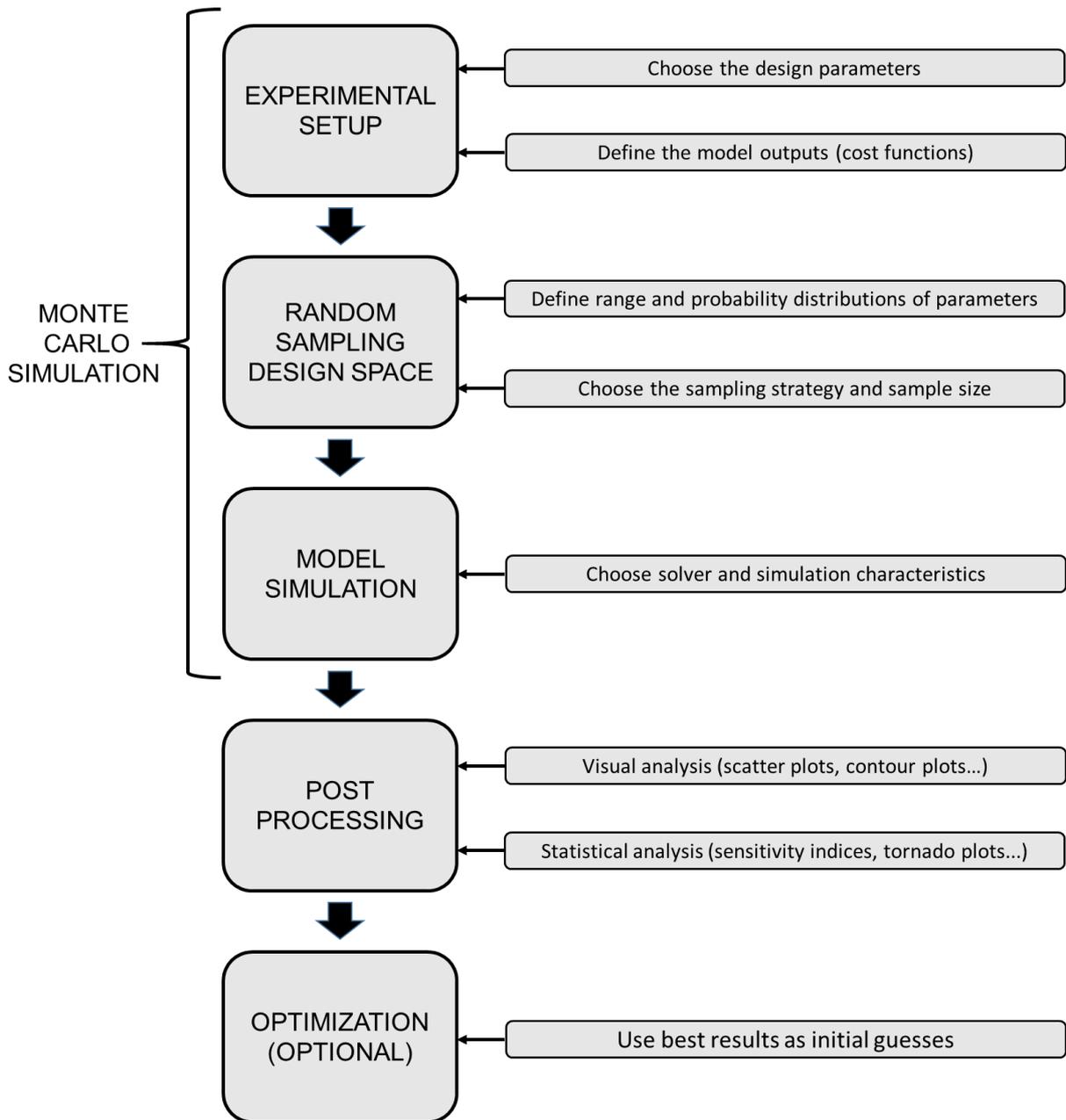


Figure 2.6 Global Sensitivity Analysis methodology for Design Space Exploration

The first three steps are what is known as a Monte Carlo simulation, a technique used to study how a model responds to a randomly generated sample of inputs. Jon Von Neumann and Stanislaw Ulam, who made it popular in the 1950s, named it this way because of the Principality of Monaco, famous for its casino, since the roulette is one of the simplest mechanical devices that allow to obtain values to simulate random variables. However, the idea of the Monte Carlo method is much older than the appearance of computers and was previously known by the name of "statistical sampling".

The current importance of the Monte Carlo method is based on the existence of problems that are difficult to solve by analytical or numerical methods, but that depend on random factors or can be associated with an artificial probabilistic model and can therefore be solved by means of a relatively simple algorithm (Sobol, 1994). In fact, initially, it was not a method to solve probabilistic problems in physics, but to evaluate integrals that could not be evaluated in another way: the calculation of integrals of complicated functions and integrals in multidimensional spaces were the two initial areas in which the Monte Carlo simulation proved to be very useful, two eminently deterministic problems.

Its recent popularity is due to Monte Carlo simulations that once would have been inconceivable, nowadays they are presented as affordable for the resolution of certain problems thanks to the advance in computing capacity of computers.

(Sobol, 1998) presents the concept mathematically as follows:

To obtain an unknown value of a variable  $a$ , it is associated to an arbitrary random variable  $\xi$  with a statistical expectation that coincides with  $a$

$$\frac{1}{N} \sum_{i=1}^N \xi_i \xrightarrow{P} a$$

Where  $\xi_1, \xi_2, \xi_3, \dots$  are independent values of  $\xi$  and  $\xrightarrow{P}$  is the stochastic convergence as  $N \rightarrow \infty$

But the method is not determined until the random variable is modelled:

$$\xi = g(\gamma_1, \gamma_2, \dots)$$

Where  $\gamma_1, \gamma_2, \dots$  are random numbers. Both of these relations define a Monte Carlo method for the determination of  $a$ .

A simple example that is usually used to illustrate the method is the calculation of areas, in this case a circle inscribed with the "Hit-or-Miss" method. Known the area of the square, that of the circle can be approximated as:

$$\frac{\text{Circle area}}{\text{Square area}} \approx \frac{\text{Points inside the circle}}{\text{Total points}} \Rightarrow \text{Circle area} \approx \frac{\text{Points inside the circle}}{\text{Total points}} * \text{square area}$$

Once the problem is defined, a number of random points  $N$  are generated, and how many have fallen within the circle are counted. Obviously the result will be more accurate as  $N$

increases. The example is very easily implemented in Matlab. The real area is 0.7853, and by means of a simulation with 1000 points an area of 0.8080 is obtained.

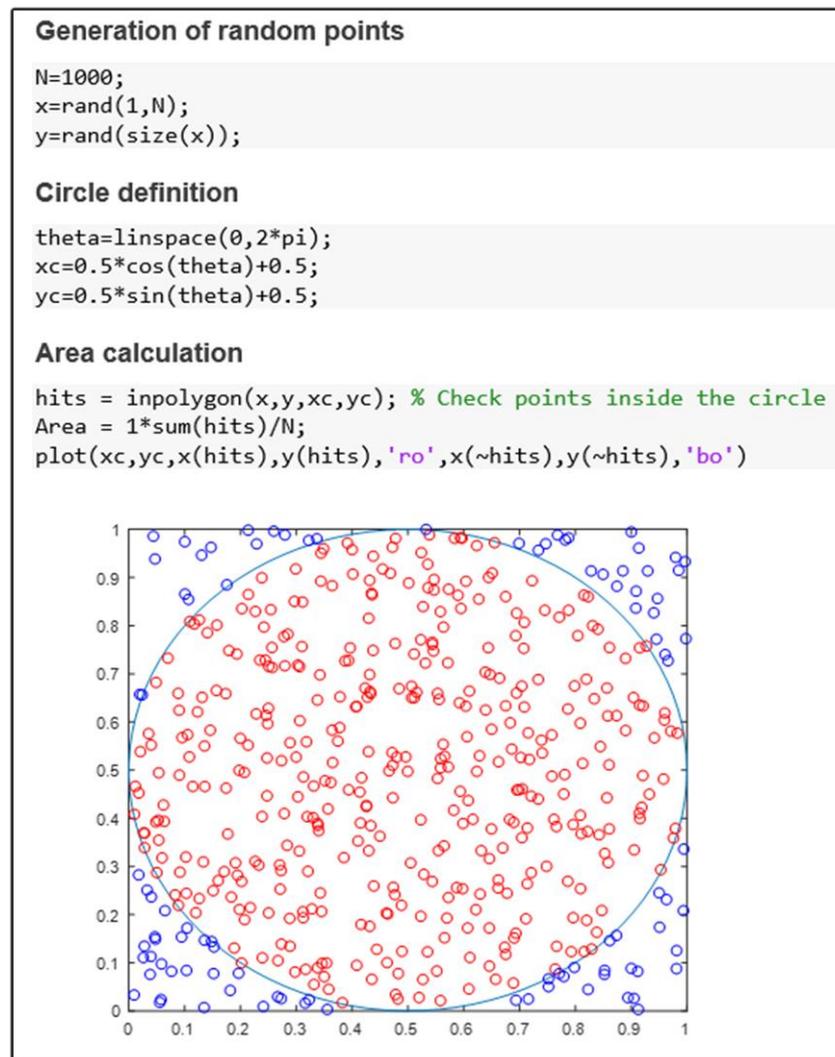


Figure 2.7 MATLAB implementation of a Monte Carlo simulation

### Random variables: statistical sampling

A variable  $X$  that can take a set of values  $\{x_0, x_1, x_2, \dots, x_{n-1}\}$  with probabilities  $\{p_0, p_1, p_2, \dots, p_{n-1}\}$  is defined as a random variable. There are two types:

- Discrete: can take a value from a set of values, each of which is assigned a certain probability.
- Continuous: a random variable represented by a continuous probability distribution that can take any value within a certain range.

Once the probabilistic model is known, the crucial problem of the application of the Monte Carlo method is to find the values of a random variable when its probability distribution is known. This is equivalent to the statistical design space sampling in GSA, usually through Design of Experiments (DOE) (also referred to as experimental design) techniques.

In DSE we must first choose the range of design parameters and their probability distributions, which serve to increase the definition (the number of points) of a subset of interest in space design. Once this is done, a probabilistic sampling technique is applied, some of the main ones are (Mathworks, n.d.):

**Random:** random samples are drawn from the probability distributions.

**Latin hypercube:** is a lattice technique where the sampling region is spatially subdivided into different strata, and random sampling is applied to each strata. This option is more systematic space-filling than random sampling.

**Sobol:** it employs Sobol quasirandom sequences to allow a highly systematic space-filling, more than Latin hypercube. A comparison between Sobol and random techniques is shown to demonstrate its benefits:

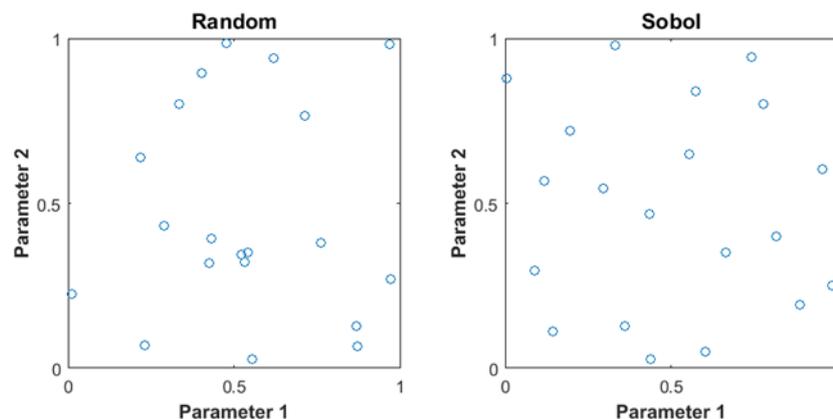


Figure 2.8 Comparison of random and Sobol sampling methods

Comparison of Random and Sobol techniques of 20 samples for two design parameters from a uniform distribution.

**Systematic:** a random selection is made of the first element for the sample, and then the subsequent elements are selected using fixed or systematic intervals until reaching the desired sample size.

## Formulation of Global Sensitivity Analysis method

Once the design parameters and their range have been defined, a random sampling technique is used. A GSA problem with parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ ... produces N combinations of parameters that are represented by a matrix in which the number columns equals the number of parameters and the number of rows equals the size of the sample:

$$\begin{pmatrix} \alpha^{(1)} & \beta^{(1)} & \gamma^{(1)} & \dots \\ \alpha^{(2)} & \beta^{(2)} & \gamma^{(2)} & \dots \\ \dots & \dots & \dots & \dots \\ \alpha^{(N-1)} & \beta^{(N-1)} & \gamma^{(N)} & \dots \\ \alpha^{(N)} & \beta^{(N)} & \gamma^{(N-1)} & \dots \end{pmatrix}$$

Then the input matrix is fed to the model and the Monte Carlo simulation is performed producing a matrix output of the outputs Y, Z, ...

$$\begin{pmatrix} Y^{(1)} & Z^{(1)} & \dots \\ Y^{(1)} & Z^{(2)} & \dots \\ \dots & \dots & \dots \\ Y^{(N-1)} & Z^{(N-1)} & \dots \\ Y^{(N)} & Z^{(N)} & \dots \end{pmatrix}$$

Once the results are obtained, the last step is visual and statistical post-processing.

With the matrix of model inputs and outputs, scatter plots can be obtained by projecting in turn the N values of the selected output against each of the input factors to investigate the behaviour of the model and identify trends. Contour plots are another option to observe the impact of two parameters on one output in one graphic.

In the statistical analysis the goal is to determine how much each parameter affects the outputs (Saltelli, et al., 2008). Different correlations are computed to quantify the sensibility of each parameters, and those with higher values are the most influent. Usually results are shown in a *tornado plot*.

One optional last step is to employ the results (exporting best results as initial guesses) and the knowledge of the behaviour to an optimization procedure.

## 2.2 Solvent extraction process for metal recovery and its modelling

In nature, there are very few metals that are in pure state, these being precious metals. Normally metals are chemically combined with other elements, forming compounds of various kinds, such as, for example, oxides, carbonates, sulphides, silicates and halides. Therefore, a series of metallurgical processes are necessary for their separation and purification. The extraction of metals can be done by pyrometallurgy or hydrometallurgy. The difference between both processes is the pyrometallurgy is carried out by dry route at high temperatures, while hydrometallurgy is carried out by aqueous chemistry at low temperatures (Habashi, 1999).

### **Hydrometallurgy as a technique for metal production**

Hydrometallurgy is the branch of metallurgy that covers the extraction and recovery of metals that uses aqueous and organic solutions. In contrast to the pyrometallurgy, which is a millenary technique, hydrometallurgical consolidation took place in the 20th century, and today it is used to produce more than 70 metallic elements with fewer emissions than classical methods, some of them as important as gold, silver, copper, nickel, or uranium (Britannica, n.d.).

The process comprises three essential stages: leaching, which converts metals into soluble salts in aqueous media, solution concentration and purification, and recovery from the leach solution by chemical or electrolytic means (Habashi, 1999). One of the most illustrative examples is the copper leaching - solvent extraction - electrowinning process:

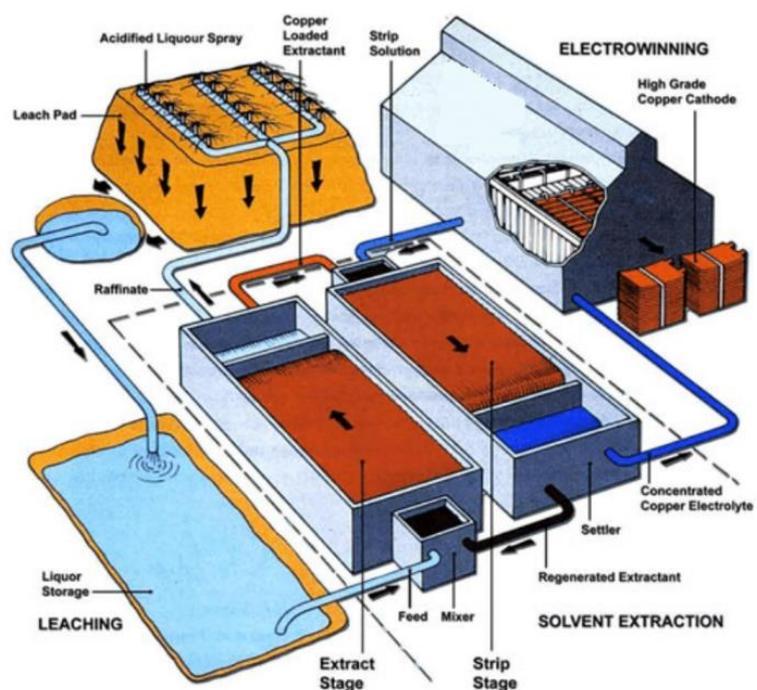


Figure 2.9 Scheme of a copper hydrometallurgical plant (Metallurgist, n.d.).

## 2.2.1 Process and equipment

After leaching, the leach liquor must be concentrated in the metal ions that are to be recovered, and undesirable metal ions and impurities must be removed. This is done through liquid-liquid extraction also known as solvent extraction, which will be the stage considered in this work since it is an area of specialization of the department and shares many similarities with continuous stirred tank reactors (CSTR), which are the most studied nonlinear systems in the literature for the application of FPO.

It is a mass transfer process that involves putting a liquid mixture, called pregnant leach solution (PLS), in contact with a second liquid called solvent that contains the extractant, and that must be partially or totally immiscible in the feed. This is usually done repeatedly through a cascade of equilibrium stages, to improve performance upon reaching a more favourable final equilibrium. Once in contact, the transfer mechanism is based on a diffusion process whose driving force towards the chemical equilibrium of a reversible cation exchange reaction, and which causes the metal ions in the feed to transfer to the organic phase (Lo, et al., 1991).

Subsequently the organic solution loaded with metal is separated from the feed in a settler by density difference between the phases. To return the metal to an aqueous phase with proper characteristics for the last recovery stage, the solvent is contacted with an electrolyte which has a high acidity in a step called stripping. This high acidity causes a displacement in the opposite direction of the reaction between the extractant and the metal ions causing them to be transferred to the electrolytic solution (Kathryn, 2008). The extraction and stripping stages described above are illustrated in the following figure.

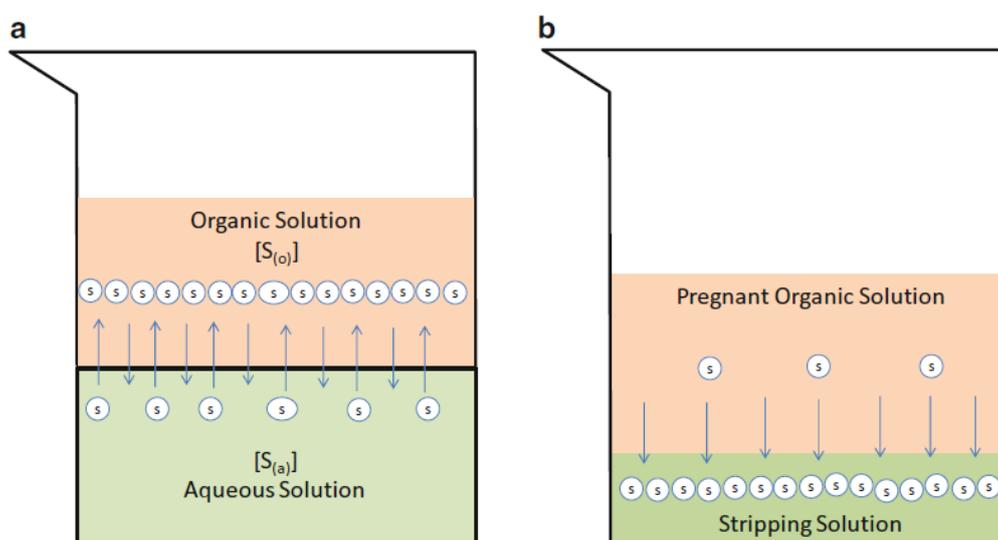


Figure 2.10 Solvent extraction principle (a) Extraction (b) Stripping (Kathryn, 2008).

Most of the SX plants have incorporated a washing or scrubbing stage in their operation. Its function is to wash the organic loaded with clean water, and in this way reduce the impurities of physical nature that contain this organic, preventing them from passing to the stripping stage. If, in addition, acid is added to the wash water, for example by mixing it with weak electrolyte, a chemical cleaning can be additionally achieved in which the washing water can extract part of the unwanted metals carried by the organic. There can also be a step for the regeneration of the extractant before it is recycled, because it may suffer for degradation (Metallurgist, n.d.).

The typical flowsheet of a hydrometallurgical SX process is as follows:

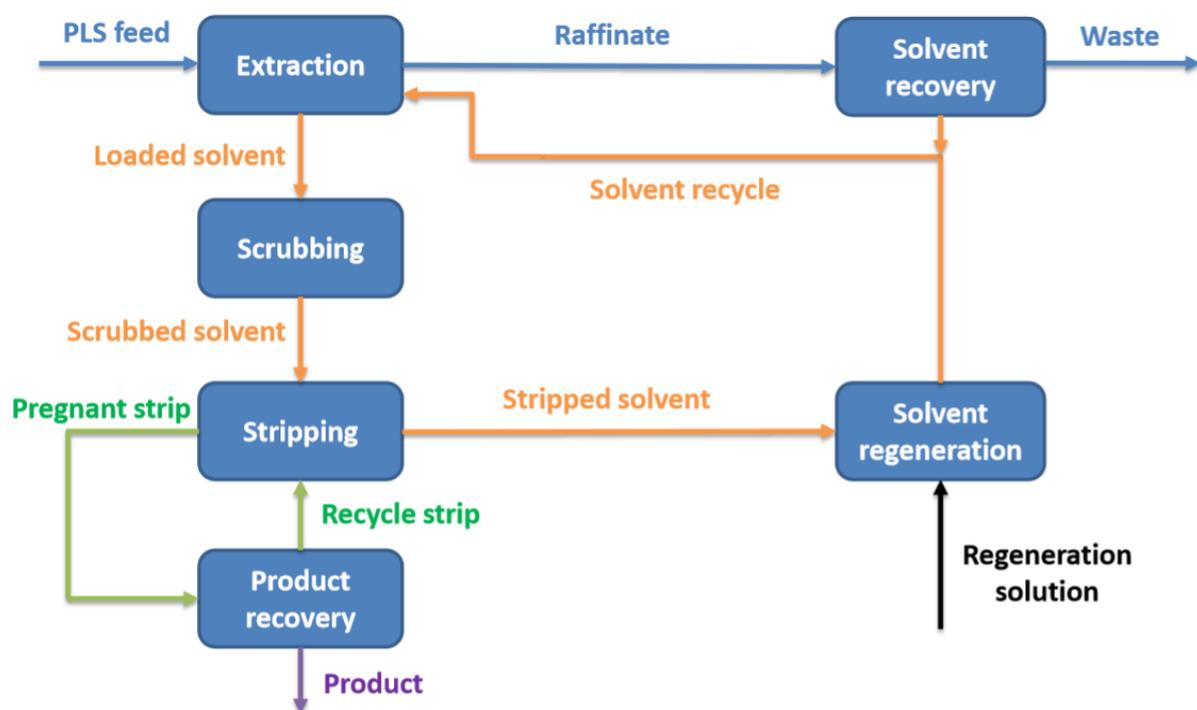


Figure 2.11 Flow diagram of a typical SX process

### Components of extraction

Extraction is the critical stage, because it determines principally the performance of the whole SX process, and consequently is the subject of attention in this work. As is seen in previous diagram, it has two inputs, the organic phase and the pregnant leach solution, and two outputs, the extract and the raffinate (Hernandez & Marcelo, 2007).

**Organic phase:** apart from a diluent and a phase modifier to improve performance, it contains a reagent called extractant, which is responsible for extracting the dissolved element. Extractants chemical structure have a hydrophobic hydrocarbon chain with good solubility in

diluent and low solubility water, whose purpose is to keep the extractant in the organic phase. Then there is a more hydrophilic functional group, that captures the metals from the aqueous phase. Examples of extractants are hydroxyoximes, that are used in copper extraction.

The function of the diluent is to act as a vehicle for the extractant, which is why it is required to reduce the high viscosity, the specific gravity and the volumetric cost of the organic phase. The most commonly used diluents are hydrocarbon solvents, such as kerosene. Since it does not intervene in chemical reactions, its choice is mainly made by its physical properties, being of special importance its flash point, solubility, viscosity and toxicity.

**Pregnant Leach solution (PLS):** The aqueous solution corresponds to a leaching solution, which comes from the previous stage of leaching. Its most characteristic parameters that need to be controlled are:

- Concentration of metal and impurities
- pH
- Oxidation potential of the solution (to avoid the extraction of impurities)
- Total suspended solids
- Temperature
- Anions concentration (because of the formation of complexes in solution that could affect the efficiency of the process)

**Extract:** It is the current rich in solvent and contains the desired solute, it is usually constituted by the liquid phase of lower density so it leaves the top of the settler. It is washed to remove possible impurities and sent to the stripping stage.

**Raffinate:** it is the aqueous stream that leaves the system after having been contacted several times in a cascade with the organic phase, to which much of the metal it contained gave way. It is usually recycled to an upstream leaching process, although care should be taken that it does not contain organic traces, since it does not only represent a loss of material, but it can also cause problems during leaching.

### **Solvent extraction equipment**

In liquid-liquid extraction, as in other similar mass transfer processes such as absorption and distillation, it is necessary to contact two phases to allow the transfer of matter and then separate them. In the absorption and the distillation, the separation of the phases is easy and fast, because they are gas-liquid systems. In extraction, however, the two phases have comparable densities, so they are difficult to mix and even more difficult to separate. In addition, the viscosities of both phases are also relatively high and the speeds through most

of the extraction equipment are low, so the energy of mixing and sometimes the one needed for separation is usually provided mechanically (Marcilla Gomis, 1999, pp. 59-64).

The above comparison, allow to explain why instead of the compact and simple columns that are used in the distillation and absorption, in hydrometallurgical industry, mixer-settler units have traditionally dominated the market for commercial-scale solvent extraction (Metallurgist, n.d.) over other alternatives.

When operating in continuous flow, which is the usual mode of operation in hydrometallurgical processes due to the high levels of production, the mixer and the settler are different parts of the equipment. The mixer is a small tank with agitator, which causes the mixing of the phases (with residence times of between 1 and 3 minutes) equipped with entry and exit lines, as well as with baffles to avoid the formation of dead zones. The settler is often a simple continuous passive decanter that works by gravity. For more difficult separations, tubular or disk type centrifuges are used (McCabe, et al., 2007, pp. 810-811). They are usually arranged in countercurrent cascades in which each mixer-settler is equivalent to one stage. The number of stages required depends mainly of the thermodynamic performance of the reagent and of the leach solution characteristics.

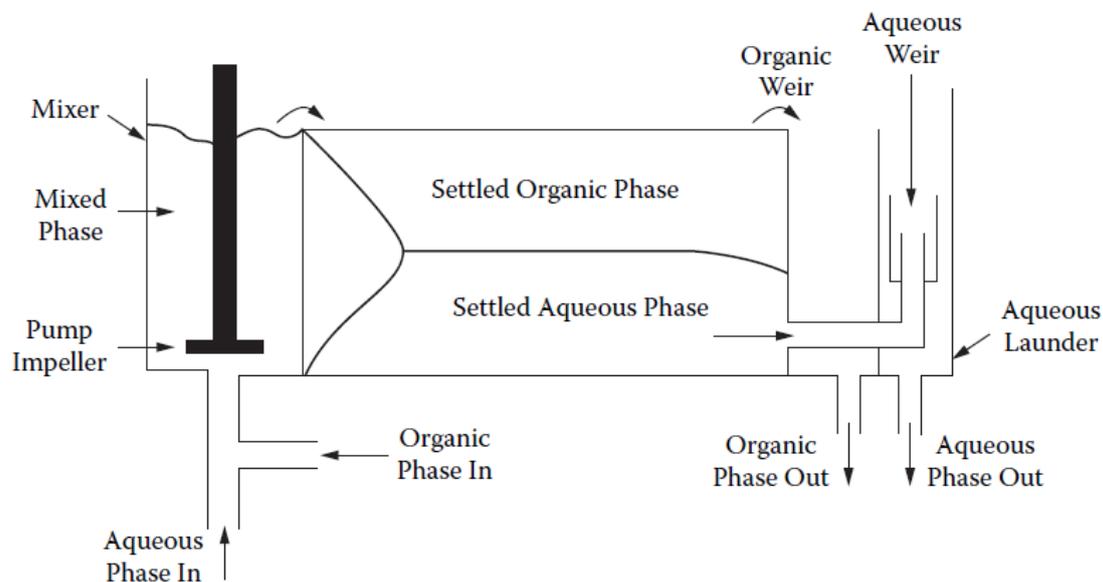


Figure 2.12 Conventional mixer-settler unit (Kathryn, 2008)

## 2.2.2 Modelling of metal solvent extraction

### McCabe-Thiele method

As already mentioned, the fundamentals of absorption and distillation apply to liquid-liquid extraction. In addition, when it comes to immiscible and diluted extractions (which is the case of hydrometallurgical extractions), the quick and simple McCabe-Thiele method, shown below,

can be used. This enables the metallurgist or engineer to graphically calculate the number of stages required, or alternatively, to predict the performance of a given set of conditions.

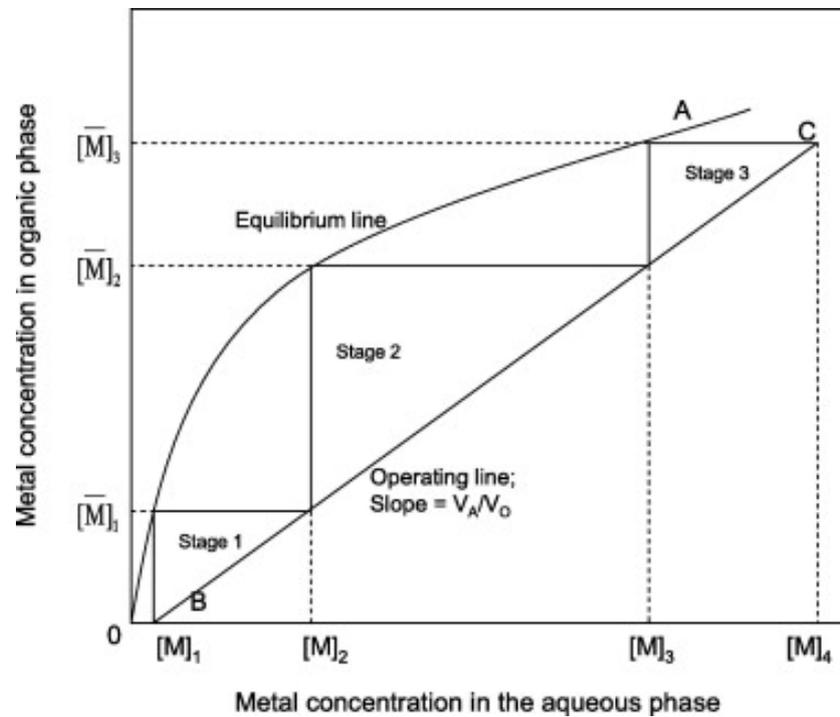


Figure 2.13 McCabe-Thiele diagram for solvent extraction process (Xie, et al., 2014)

Although as it can be seen the implementation is practically identical to that used in distillation, there are three differences:

- In extraction, two independent diagrams are needed, one for the extraction stage and another for the stripping stage, so that each diagram has a single operating line, product of the material balances.
- The equilibrium curve is called extraction isotherm, and defines the maximum amounts of metal which may be removed from the PLS for each organic to aqueous volumetric ratio (O/A) ratio). In the distillation the equilibrium curve is usually obtained by thermodynamic models, while in the extraction of metals, although there are also some models (Liddell, 2005), these are very complex and need a large amount of experimental information difficult to obtain in an industrial plant. Therefore, the usual technique is to assume a non-linear relationship for the extraction isotherm and to adjust its parameters with experimental data (Aminian, et al., 2000).

- The equilibrium curve is called the equilibrium isotherm because it is assumed that the process is operated at a constant temperature, while in the distillation the temperature varies along the column. It is also considered that the heat of mixing is negligible and therefore the energy balances are automatically satisfied.

Although the method is widely used in the industry for plant design and production optimization, it only considers steady-state operation, and therefore is not valid for dynamical modelling.

### **Dynamical models**

They arise several decades after the stationary models because of the computing requirements of dynamic simulation. (Wilkinson and Ingham, 1983) is considered the reference for dynamic modelling of mixer-settlers. The mixer is modelled as an ideal continuous stirred tank reactor (CSTR) through mass balances and empirical isotherms, the settler as separated plug flows (time delays) for aqueous and organic phases, and the mass transfer through the interphase theory.

(Komulainen, et al., 2006) achieved to develop a model that predicts process dynamics of an industrial SX copper plant requiring only industrially measured variables and utilize plant-specific McCabe-Thiele diagrams calibrated with plant data. However, the simplicity of the model makes difficult to use it in more complex plants.

(Wichterlova & Rod, 1999) created a model for a rare-earth solvent extraction cascade, where each extraction stage is considered as an CSTR of two phases with mass transfer representing the mixer, and two CSTR of aqueous and organic phase, respectively representing hydrodynamics of the settler.

Following Komulainen work, (Moreno, et al., 2009) developed a more flexible model able to reproduce the complex dynamics of any industrial copper plant including McCabe–Thiele specific diagrams and complex settler hydrodynamics. The mixer is also considered as a CSTR, and the settler is modelled with total and copper balances for each phase assuming that the output of the mixer is split into two streams, one that moves fast and the other that moves slowly.

(Shahcheraghi, et al., 2016) extended previous models that consider the mixer as a CSTR, because in the most modern units there are two mixing chambers (a pump–mixer and a mixer). Better fitting was obtained compared to existing models, since both mixing chambers are considered, the pump-mixer is modelled as a plug flow in series with two CSTRs with their volumes estimated (RTD equation) by CFD simulation, and the mixer is another CSTR.

However these models are based on experimental equilibrium isotherms and therefore they are not suitable for this work given its theoretical nature.

## 2.3 Modelling and simulation paradigms in engineering

This work is inserted in the systems paradigm (von Bertalanffy, 2015), that has been so successful in providing a unifying conceptual framework for many fields including chemical engineering, developing within it a highly productive specialty area called Process Systems Engineering (PSE).

The systems methodology (Bunge, 1979) is based on a generalist approach, which tries to capture and focus on: wholes instead of parts, interrelations instead of elements, patterns and regularities instead of events, processes instead of states.

### 2.3.1 Introduction: concepts of system, model, simulation and modularization

Obviously, the central concept of the aforementioned paradigm is that of system. An object whose parts or components interact with each other is called a **system**. A system is not a mere aggregation or collection of elements, it must necessarily possess properties that its components lack. These systemic properties are called emergent (the dissociation energy of a molecule, the life of a cell, the music of an orchestra ...). In short, a system is more than the sum of its parts. This abstract notion, in the epistemology of the General Systems Theory, is characterized by (Bunge, 2002, p. 11) as:

***An entity S is a system if and only if S is representable by the quatern***

$$\mathbf{S} = \langle \mathbf{composition, environment, structure, mechanism} \rangle$$

#### **Composition**

Set of all the elements of S.

#### **Environment**

Elements not belonging to S that may or may not interact with the components of S.

#### **Structure**

Set of relationships between its components, and between them and their environment.

#### **Mechanism**

Set of S processes that makes the system behave as such. Only the material systems have mechanism, in chemical engineering the mechanisms correspond to the so-called driving forces: gradients of concentration, temperature, speed, chemical potential ...

This systematic conceptualization covers both Artur D. Little unitary operation (UO) and transport phenomena paradigms. In effect, UOs are nothing more than process-device technosystems that transform the inputs into outputs (products) with emergent properties inside a device with the intervention of heat work and entropy flows. Precisely, this is the foundation on which the whole chemical industry is based by combining a series of UO.

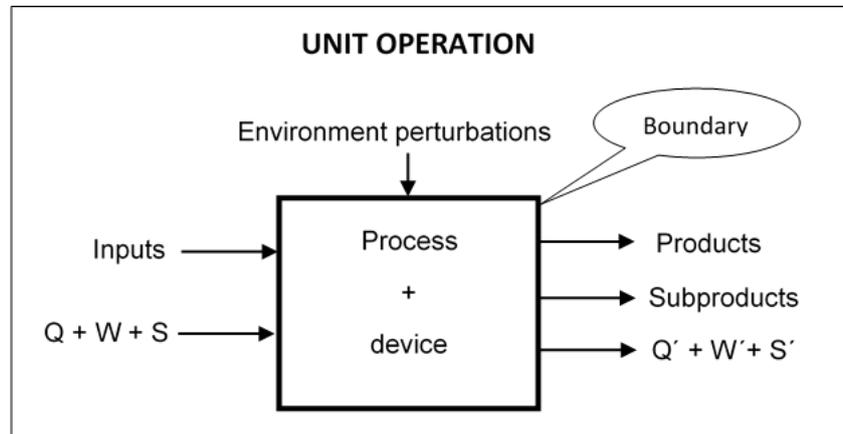


Figure 2.14 Generic unit operation

The UO technosystem corresponds to:

**Composition:** parts or components of equipment and streams of the system.

**Environment:** everything that is outside the boundary of the device.

**Structure:** set of interactions between the different elements of the composition.

**Mechanism:** the driving forces that make the process evolve.

It is worth mentioning that, although a large variety of equipment is used in chemical engineering, fortunately, only four kinds of processes and their corresponding mechanisms are necessary (the first three base the transport phenomena paradigm).

PROCESS	TYPES OF PROCESS	MECHANISM
Mass transfer	Diffusion	Concentration gradient
Heat transfer	Conduction, Convection, Radiation	Temperature gradient
Momentum transfer	Impulsion, mixing	Velocity gradient
Chemical reaction	Conversion of reactivities to products	Chemical potential gradient

Table 2.1 Necessary processes in Chemical Engineering

In the research problem, for simplicity, it is assumed that only processes of mass transport and chemical reaction intervene.

A **model** aims to replace the real system (process + device), with all its complexity, by a simplified representation, of any type, that allows to replicate the behaviour of the system through its simulation. According to Bunge:

***Any entity M is a model of the system S for the experimenter E ↔ E can use M to correctly answer questions about S.***

The model entities can be:

### **Physical**

- Static: miniatures
- Dynamic: prototypes, pilot plant and in general devices with hydraulic, electric, mechanical ... components such as flight simulators.

### **Symbolic**

- Linguistic: qualitative, descriptive
- Iconic: maps, drawings, plans, schemes
- Mathematical: quantitative, functional, stochastic

In engineering, physical, iconic and mathematical models are of greater interest. The former are expensive, difficult to perform and even dangerous for the experimenter. Hereby, thanks to advances in computational resources, mathematical symbolics have become the main ones for both industry and research.

### **Mathematical model of a unit operation**

As previously mentioned, in chemical engineering mathematical models are predominant. They are conceptual symbolic systems, whose components are their variables and parameters, their structure is the set of their correlations and their environment is composed of the variables and parameters of the system to be modelled, which for simplicity are not considered. Because they are symbolic systems, they lack a mechanism, which would consist in the execution of the resolution algorithm (simulation). Its schematic structure is:

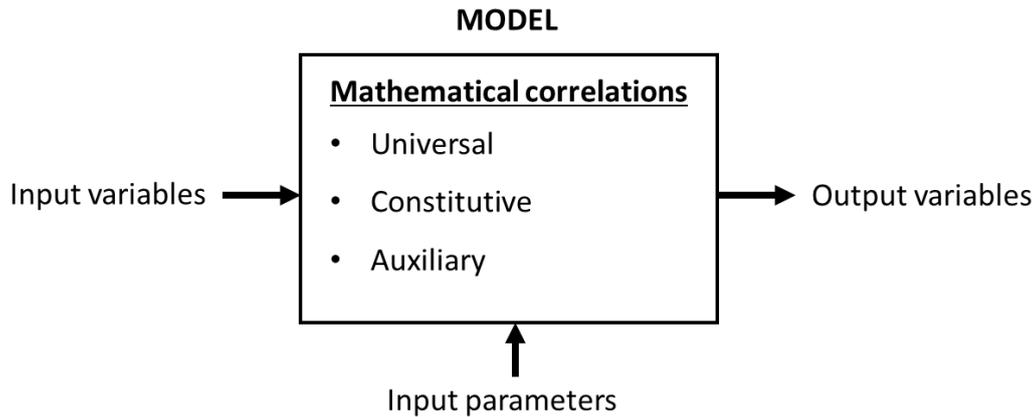


Figure 2.15 Model of a generic unit operation

**Universal:** as the laws of mechanics, electricity, thermodynamics or conservation principles.

**Constitutive:** any relationship between tensor magnitudes, which is not derivable from universal laws and that are specific to the type of problem studied.

**Auxiliary:** correlations for the calculation of intermediate variables and internal parameters.

The characteristic correlations in the mathematical models in chemical engineering are:

- Fundamental physical and chemical laws
- Principles of mass, energy and moment conservation
- Transport phenomena
- Thermodynamics (equations of state, equilibrium)
- Kinetics (rate of reactions)
- Configuration, which depend on the geometry and the dependence or not of the variables with respect to the position

By **simulation**, in a broad sense, Bunge understands:

***Any activity carried out on the model  $M$  by the experimenter  $E$ , which allows the latter to extract information or replicate the behaviour of the system  $S$ .***

In mathematical models this activity corresponds to the resolution of their equations. However, since the vast majority of engineering models do not have analytical solutions, in the field of process engineering, the numerical resolution of the characteristic correlations of the model by means of digital computation is known as simulation.

## **Modularization: the application of the divide and conquer principle**

The analysis by reduction (modularization) consists of dividing non-elementary systems into parts, assuming that they will be simpler than the whole and that, understanding the behaviour of each part and how they interact with each other, we can predict and understand the operation of the system as a whole. Since chemical plants are not simple systems, it is convenient to model them in a modular way, decomposing them into subprocesses.

The method of modularization consists of the following steps:

1. Determination of the structure of the system. Identification of its different parts.
2. Determination of the interaction between parts.
3. Determination of the internal behaviour of each part independently of the others.

This methodology is valid for complicated systems, which are the most frequent in engineering, but not for complex ones.

### **Complicated vs complex systems**

This relevant dichotomy is fully recognized within the framework of General Systems Theory (**GST**), for example see (Bunge, 2004).

A complicated system is composed of many different elements that interact in different but fixed and predetermined ways, so its emergence is predictable and does not vary. If a component is modified or replaced, it can be determined how this affects the systemic properties of the whole. Any chemical plant, such as nickel refinery, is a classic example of a complicated system in which this technique is essential, since the plant is made up of thousands of different parts and to address its design and operation it is broken down into subsystems in which groups of specialized engineers work in a coordinated but independent way.

On the other hand, complex systems are also composed of many elements (which are usually the same or similar) interconnected, but their interactions are dynamic and self-organized by the system, even modifying its components and structure. Therefore, the behaviours and phenomena that appear are not predictable or understandable from the individual ones. In this case, if the system is modularized, the components and their interactions are fixed, so this methodology is not capable of representing the dynamics of a system. For example, in chemical engineering complexity arises when considering unit operations with turbulent flow or through membrane, chemical reactions with multiple equilibrium state as the aforementioned Belousov-Zhabotinsky (BZ), biochemical reactions and even with simple non-

linear perturbed chemical systems in a specific way, such as forced oscillations. To analyse these systems, techniques of a new field called The Science of Complexity are necessary.

In summary, the emergence of complicated systems arises fundamentally from the combination of the different properties of their elements, while in complex systems this is due to the enormous diversity and dynamics of the interactions between similar or equal elements.

### **Requirements for modelling modularization**

When the structure of the system studied allows modularization, its design and implementation is facilitated, which speeds up its development by allowing different specialists to work independently without having to know all the details of the rest of the system. The above also improves the capacities of reuse and update of the modules, thus reducing development times and costs.

Modular modelling also requires that the simulation tool enables abstraction, which is the ability to implement each part of the model (modules) without knowing its internal details (black box) (Urquía, 2000). One way to facilitate abstraction is to differentiate, in each module, between the interface and the internal description. The interface is the part that describes the interaction of the module with its environment, while isolating it from its internal description, so that they can be considered separately. The internal description of the module contains information about the structure and behaviour.

Abstraction and modularity are closely related to the encapsulation of information, consisting of only the variables belonging to the interface being accessible from the outside of the module by other modules that communicate through compatible interfaces. This criterion of encapsulation of information as a design method for modular systems facilitates modifications, testing and maintenance of the models.

On the other hand, the hierarchy of the modules consists in implementing the model progressing from a lower level of detail to higher ones: the model is divided into submodels and so on. For the SX process, it can be divided into extraction and stripping, the extraction section can be considered as a cascade of mixer-settlers, and these units can be subdivided into a mixer and a settler that are modelled independently and then connected.

### **The computational implementation of modular simulation and modelling**

Traditional technical computing languages with scripting characteristics such as Fortran, C or MATLAB are not suitable for this kind of problems, since to simulate a typical flowsheet of a chemical process, thousands of lines of code would be necessary, a very time consuming process also prone to mistakes. Assuming that the necessary code has been obtained, it

would be very difficult for other engineers to understand it, and if they wanted to modify the process by adding or removing other unit operations, significant changes in the code would have to be made, making this option practically unfeasible.

Due to these problems, specific modelling environments were developed in order to model and simulate large systems. These tools are based on modularization and also use higher level modelling languages, the user only has to develop a code that contains the equations of the model, being the same resolved automatically by the solvers integrated in the program. Once all the components are implemented, whether they are developed by the user or obtained from libraries, it is only necessary to connect them and manipulate them using a graphical interface.

These tools can be divided in two major categories: the more traditional block oriented ones inspired in analog simulation, and the more advanced object oriented tools that started to appear in the 1990s (Sanz, 2010).

The main difference between these two paradigms consists in their causality. In fact, both categories are also known as causal and acausal modelling. The computational causality corresponds to an explicit and univocal functional correlation between the causes (input variables) and the effects (output variables). In acausality, the correlation is implicit, so it is not determined what are the causes and the effects. Therefore the causality determines a priori a direction of the flow of the algorithm, something that does not happen in the acausality where the flow of the algorithm is established by the simulator during the execution of the same.

### 2.3.2 Block - oriented approach

#### **Background**

Modelling using block diagrams can be considered as an evolution of the paradigm of analog modelling used during the first half of the 20th century before the advent of digital computers. This is based on the fact that a sequence of operations on the components of a physical system can replicate mathematical operations (abacus, slide rule ...).

In analog computing, the dynamic system is modelled in terms of ordinary differential equations (**ODE**), in which computational causality is explicitly defined. These equations were represented in block diagrams in terms of the fundamental operations: integration, addition, multiplication, and function generation. Then an electronic device that implements the block diagram was built, where variables were represented as voltages, interconnections were made by patching cables in a board and parameters were set with potentiometers. Although the execution was fast, the whole procedure of setting up a problem was tedious and precision

was limited, so as soon as the digital computers appeared, the analogical ones disappeared (Astrom, et al., 1998).



Figure 2.16 Classical analog computers

Due to the lack of graphical capabilities of the early digital computers, simulators were initially reverted to textual (alphanumeric) descriptions of the models. However, graphical description reappeared strongly with the availability of graphical displays for workstations and computers, and the consequent development of graphical user interfaces (GUIs).

### **Digital implementation**

The block-oriented paradigm allows to describe models in a hierarchical and modular way without the need to know any programming language, only the management of the user interface (UI): the model is designed graphically and the resolution of the model is done by the simulator automatically. Each model is composed of a combination of blocks, input and output ports, and interconnections between ports and blocks. In the diagram, connections are represented by lines between ports. Block libraries contain commonly used blocks to facilitate the development of new models, by simple drag and drop of the required blocks (Martin, 2007, p. 13). Simulink (originally called SIMULAB) which is integrated with MATLAB, appeared in 1991 and since then it has been the most widely used block-oriented simulator between engineers. An open-source alternative is Scicos, developed by the French Institute for Research in Computer Science and Automation (INRIA).

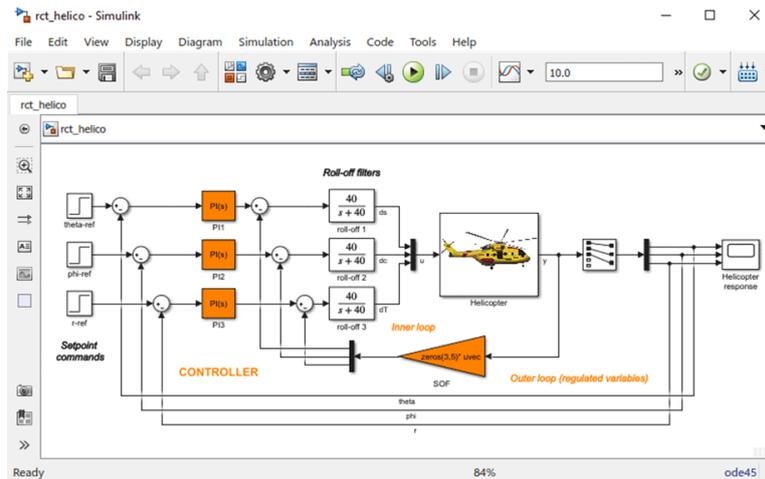


Figure 2.17 Control system of a helicopter implemented in the Simulink environment

Any block in a diagram has the following general structure in the state space representation:

$$\begin{aligned} \dot{x} &= f(t, x, u) \\ y &= g(t, x, u) \end{aligned}$$

Where  $u$  represents the input signals vector,  $x$  represents the internal states vector and  $y$  represents the output signals vector. The whole systems of blocks are used to represent complete simulation models, showing all the significant interactions involved in the response of the system model to input disturbances.

Thus, in addition to specific output variables, all the other system variables are shown as well, making block diagrams a natural way of expressing a control system.

Unlike a typical schematic diagram of object-oriented simulators (Simscape), which shows the physical connections, the block diagram (Simulink) shows the cause and effect of relations between the components (see Figure 2.15), and thus it helps to understand the system's dynamics. The Jacobians of the  $f$  and  $g$  functions can be used to determine the poles, zeros and overall transfer function for a linear system. All this together with the great variety of control algorithms included have made Simulink the most used environment for designing control systems (Tiller, 2001). However, for describing plant model or physical system behaviour, block diagrams take more work to create, are more difficult to understand and are less reusable than acausal models.

In addition to this, an important formal-mathematical difficulty arises since the dynamic physical systems are usually described by DAEs (Differential-Algebraic Equations) instead of by ODEs. In Chemical Engineering, DAE systems typically arise from differential equations that describe the dynamic balances of mass and energy, and from algebraic equations that

describe thermodynamic equilibrium relationships, hydraulic relationships, and certain heuristic correlations. The differential equations are responsible for the dynamical evolution of the system, while the algebraic equations serve to constrain the values of the solution to certain manifolds. A simple example of a DAE is:

$$\begin{aligned}x &= 3y \\ \dot{x} &= -2x\end{aligned}$$

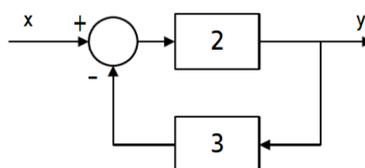
DAEs are characterized by their differential index, which is a measure of their singularity. By differentiating equations, algebraic variables can be eliminated, and if this is done enough times then the equations take the form of a system of explicit ODEs. The differential index of a system of DAEs is the number of derivatives needed to express the system as an equivalent system of explicit ODEs. Thus, ODEs have a differential index of 0. The user must be aware that if algebraic equations are replaced with their derivatives, then some constraints might have removed. If the equations no longer include the original constraints, then the numerical solution can drift (Mathworks, n.d.).

Therefore, when trying to simulate a DAE system, such as block-oriented simulators that do not have implemented DAE solvers, these must be manipulated by the user to replace them with an explicit ODE system. These manipulations are easy to do in simple cases but they are quite difficult and error prone for more complex systems. Also, when the system is implicit, algebraic loops that cannot be eliminated appear.

An algebraic loop occurs when a block output depends on the value of an input port; the value of the input directly controls the value of the output (Mathworks, n.d.). A simple example in which an algebraic loop appears is the following implicit correlation:

$$y = 2(x - 3y)$$

Whose block diagram is:



The loop is easily eliminated by introducing the causality in the correlation by clearing y:

$$y = \frac{2}{7}x$$

Finally, a significant limitation of this methodology consists in its impossibility to model distributed parameter systems in which geometry is relevant, since Partial Derivative Equations (PDE) in partial derivatives cannot be solved in these simulators.

In conclusion, although block-oriented simulators are ideal for designing control systems, it became necessary to develop other tools to be able to handle DAE systems that arise from real physical models.

### 2.3.3 Object - oriented approach

The limitations of the block-oriented tools were solved in the 90s when the first simulators emerged based on Equation-based object-oriented (**EEO**) methodology. The object-oriented design is a method of software engineering, consisting of analysing the system as a set of interacting objects. This method is based, among others, on the three conceptual elements already explained: modularity, abstraction and the encapsulation of information (Booch, 1993). While a submodel encapsulates data and structure (behaviour), similarly, in object-oriented programming (**OOP**) attributes and methods are encapsulated.

#### Characteristic components of the OOP paradigm

By contrast to the classic paradigm of algorithms, the OOP, that supposes a qualitative leap towards the emulation of *intelligent* behaviour through computation (Peña, 2006). This, is based on the work done in the 1960s at the Norwegian Computing Center in Oslo, by Ole-Johan Dahl and Kristen Nygaard to perform simulations of military ships, giving place to the first object-oriented language denominated Simula 67.

OPP try to obtain a replica-simulation within the framework of the GST of a given universe (set of systems that interact by signals) as a set of *objects* that interact through of *messages*. Therefore the execution flow of the program is not predetermined, but depends on the interactions that the user makes on the objects (events).

The fundamental notion is that of **object**, that in the conceptualization of (Bunge, 2002) is characterized as a symbolic system that has a composition (its elements are attributes), structure (its interrelations correspond to the so called methods, or set of actions that the object can perform) and environment (set of different objects that may or may not relate to it). Objects (individuals) belong to entities called classes (gender or type), the specification of an individual within a class is called **instantiation**.

A good example of this would be a chess simulator, in which the types of pieces are represented by classes (the horse class has 2 instantiations), the representative icon, its position on the board, mobility (free or blocked), availability (playable or captured) would be attributes, and the rules of the game would be the methods of the classes. In the simulator, the course or development of the game (flow of the program) and its result (output) is not predetermined and depends on the actions of the player (events).



Figure 2.18 Screenshot of a chess game for PC

Mathematical models are implemented as classes rather than as instances, since a model is usually a description of a system type rather than a representation of a particular system. The simulation is performed on an instantiation of the model (assignment of values to the attributes-parameters of the same). A parameter can be, in a broad sense, from a simple variable (diameter of a mixer) to a complete structure of submodels (number of mixer settler in a cascade).

The two main modes of class reuse are **composition** and **specialization**. Composition is the ability to define new models formed by submodels, previously defined, interconnecting them (such as cascade as a combination of mixer-settlers). On the other hand, specialization is the ability to define new models by modifying existing ones.

**Parameterization** is key to the reuse (generality) of the model, it consists of the assignment of variables to the parameters.

**Inheritance** is a procedure of transmitting information (attributes and methods) between classes through specialization. After composition, it is the most used component reuse mode. A class A can be defined as a subclass of class B, then it is said that B is the superclass of A. When the class has only a single superclass, there is simple inheritance, and if it inherits characteristics of different superclasses, it is said that there is multiple inheritance.

The subclass inherits all the attributes and methods defined in its superclass, with which it can be considered as a refinement or specialization of the general concept defined in its superclass (inverse relationship between the intention and extension of a concept), to which

new components of the subclass are added. If the methods of a class are in contradiction with those inherited from its superclass, their own prevail in the actions performed by the objects of the class (Urquía, 2000, p. 18). Parameterization can be considered a kind of reverse inheritance, that is, from class to superclass.

When different classes must share a certain action-method, this is implemented through a common interface (which is usually inherited from a superclass) and a specific content for each class (internal composition). It is said that in this case there is polymorphism, allowing components with different internal compositions to communicate with each other through a common interface that is developed only once and reused in each component.

### **Object oriented simulator languages and its characteristics**

Initially, at the end of the 80s, different languages were developed for its application in specific fields, such as ASCEND, SPEEDUP, EcosimPro, gPROMS, ACM. The Modelica language (Fritzson & Bunas, 2002), unlike the previous ones, does not have its own simulation environment, but can be used in several simulators such as Dymola, OpenModelica, Jmodelica.org, System Modeler... This is because it emerged with the intention of being a standard that unify all previous languages and that was used to model any type of system, thus facilitating the exchange of models between different disciplines.

In this thesis Simscape (Mathworks, n.d.) is used, very similar and with the same objective as Modelica, because it allows to create models of diverse physical systems within the Matlab-Simulink environment in a more intuitive and efficient way. It lets you define custom components as textual files with equations as acausal implicit differential algebraic equations (DAEs) and complete with parameterization. Simscape components represent physical elements, such as pumps, motors, or valves. Lines in the model that connect these components correspond to actual physical connections instead of signals (Simulink). This approach allows to describe the structure of the physical systems of a system rather than its equations.

As an example of this advantage, the Simulink representation of a mass-spring-damper system as a block diagram and a Simscape physical network is illustrated in the following page.

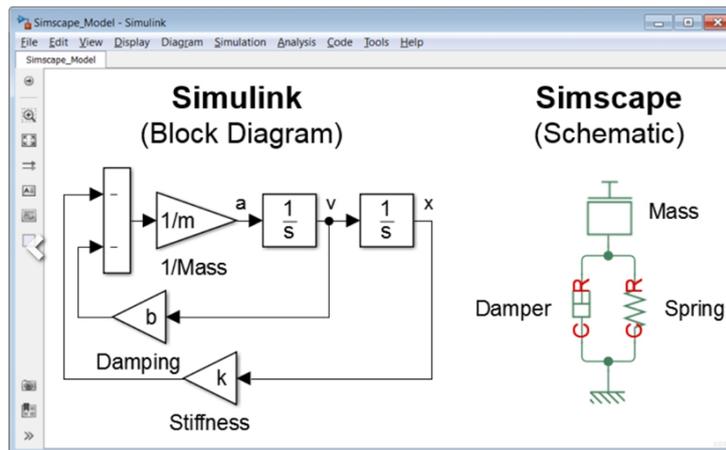


Figure 2.19 Mass-spring-damper expressed as a block diagram and a schematic.

Although, as has been seen, there is a great alternative of options, all these languages are based on a series of common principles: the object-oriented methodology, the acausal description of the model and the need for the simulation environment to symbolically manipulate the equations of the model (Urquia & Dormido, 2003). These characteristics allow that the code of the models is practically equal to the mathematical formulation of the same, composed of parameters, variables and equations.

As an example of the power of these languages, the Modelica and gProms code of the typical dynamic problem of a discharge tank is shown (a tank with a liquid inside, an inlet and an outlet where the outlet flowrate depends on the liquid level in the tank).

<pre> 1 model BufferTank 2   /* Import libs */ 3   import Modelica.Math.*; 4 5   parameter Real Density; 6   parameter Real CrossSectionalArea; 7   parameter Real Alpha; 8 9   Real HoldUp(start = 0.0); 10  Real FlowIn; 11  Real FlowOut; 12  Real Height; 13 14  equation 15  // Mass balance 16  der(HoldUp) = FlowIn - FlowOut; 17 18  // Relation between liquid level and holdup 19  HoldUp = CrossSectionalArea * Height * Density; 20 21  // Relation between pressure drop and flow 22  FlowOut = Alpha * sqrt(Height); 23 24 end BufferTank; </pre>	<pre> 1 PARAMETER 2   Density as Real 3   CrossSectionalArea as Real 4   Alpha as Real 5 6 VARIABLE 7   HoldUp as Mass 8   FlowIn as Flowrate 9   FlowOut as Flowrate 10  Height as Length 11 12 EQUATION 13 # Mass balance 14 \$HoldUp = FlowIn - FlowOut; 15 16 # Relation between liquid level and holdup 17 HoldUp = CrossSectionalArea * Height * Density; 18 19 # Relation between pressure drop and flow 20 FlowOut = Alpha * sqrt(Height); </pre>
---	---

**a) Modelica**

**b) gPROMS**

Figure 2.20 Modelica and gPROMS code of the dynamic tank problem

These languages support a declarative description of the models based on equations (equation-oriented approach) instead of based on assignments (explicit correlations). The information on which variable must be solved in each equation is not included in the model (acausal modelling). This allows a better reuse of the models, since the equations do not

specify a specific direction in the information flow (signals) as it happened in the block diagrams.

The symbolic manipulations carried out by these programs on the models can be classified into two types according to their purpose (Fritzson, 2004). First, the manipulations whose purpose is to translate the object-oriented description into a flat model, consisting of the set of equations and functions of the model, eliminating all object orientation.

Secondly, the manipulations whose purpose is to transform the flat model in such a way that it can be solved efficiently by the simulator solver (elimination of redundant variables, reduction of the DAE system index ...).

As an illustration of the necessary steps for the execution to perform by the simulator, the following flow chart presents the Simscape simulation sequence.

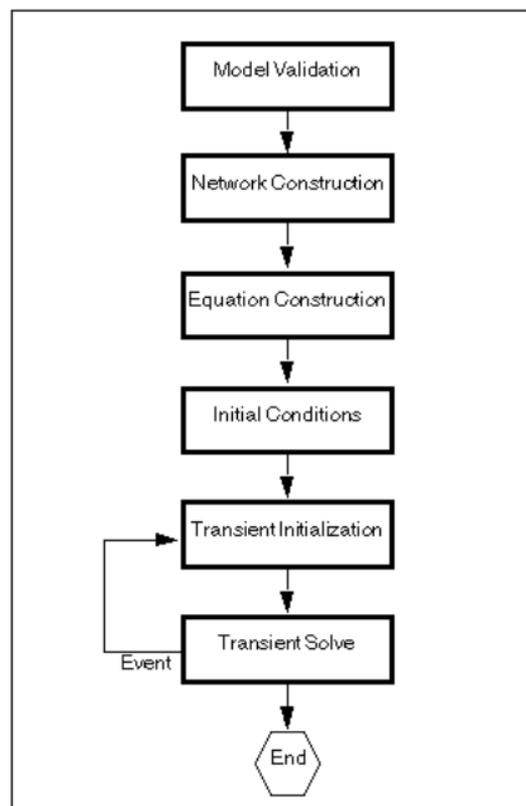


Figure 2.21 Scheme of Simscape execution sequence

### The initial conditions problem

The step where major complications usually arise is that of the formulation of initial conditions for DAE systems. They must not contradict any of the equations in the model, they should make physical sense and represent an appropriate state for the system.

Given the vectorial representation of the DAE system:

$$F(x, \dot{x}, y, t) = 0$$

Where

F is a vector whose components are the left terms of each equation

x is a vector whose components correspond to the variables for which derivatives are present (differential variables)

y is a vector whose components correspond to the algebraic variables

t is a scalar that represents time

For the set of initial conditions  $(x_0, \dot{x}_0, y_0, t_0)$  to be consistent, it is a necessary condition that they satisfy the original DAE system at the initial instant. That is to say that is satisfied:

$$F(x_0, \dot{x}_0, y_0, t_0) = 0$$

However, sometimes this condition is not enough to ensure the consistency of the system. This happens when making the necessary derivations to know the initial state of the system, we obtain equations that impose new restrictions that must be satisfied by the initial conditions. These equations that impose additional restrictions on the initial conditions are called hidden restrictions (Urquía, 2000, pp. 61-69).

Sometimes these difficulties cause the simulators are not able to find consistent initial conditions, hereby tools like Aspen Dynamics or Simulink have added the option to initialize the simulation with known stationary operating points, importing plant data or previous stationary simulations.

## 3 SOLUTION ADOPTED

### 3.1 Mathematical models of the systems equipment-process

According to the prescriptions established in the research problem; two models are required, corresponding to the single and multicomponent cases, which are designed following the guidelines set in section 2.2.2 for the mixer tank, with the difference that a theoretical thermodynamic model is used instead of the classical empirical approach. Models are based on conservation equations, the mass action laws applied to ion exchange reactions and Fick law of diffusion. As argued when discussing the scope and limitations of the work, the solution adopted does not include the settler and high mass transfer coefficient values are taken to don't mask oscillations effect.

#### 3.1.1 Single component model of the mixer tank

##### Notation

$O_{in}$	inlet organic volumetric flow ( $m^3/min$ )	<b>input variable</b>
$A_{in}$	inlet aqueous volumetric flow ( $m^3/min$ )	<b>input variable</b>
$Y_{in}$	inlet organic concentration ( $mol/m^3$ )	<b>input variable</b>
$X_{in}$	inlet aqueous concentration ( $mol/m^3$ )	<b>input variable</b>
$H_{in}$	inlet $H^+$ concentration ( $mol/m^3$ )	<b>input variable</b>
$HR_{in}$	inlet extractant concentration ( $mol/m^3$ )	<b>input variable</b>
$K$	equilibrium reaction constant	<b>parameter</b>
$k_{LA}$	volumetric mass transfer coefficient ( $1/min$ )	<b>parameter</b>
$V$	total volume in the mixer tank ( $m^3$ )	<b>parameter</b>
$Q$	mol transfer flow ( $mol/min$ )	<b>internal variable</b>
$V_o$	organic volume in the mixer tank ( $m^3$ )	<b>internal variable</b>
$V_A$	aqueous volume in the mixer tank ( $m^3$ )	<b>internal variable</b>
$Y_{out}$	outlet solute organic concentration ( $mol/m^3$ )	<b>output variable</b>
$X_{out}$	outlet solute aqueous concentration ( $mol/m^3$ )	<b>output variable</b>
$O_{out}$	outlet organic volumetric flow ( $m^3/min$ )	<b>output variable</b>
$A_{out}$	outlet aqueous volumetric flow ( $m^3/min$ )	<b>output variable</b>
$H_{out}$	Outlet aqueous $H^+$ concentration ( $mol/m^3$ )	<b>output variable</b>
$HR_{out}$	Outlet organic extractant concentration ( $mol/m^3$ )	<b>output variable</b>

## Schematic design of the tank with overflow

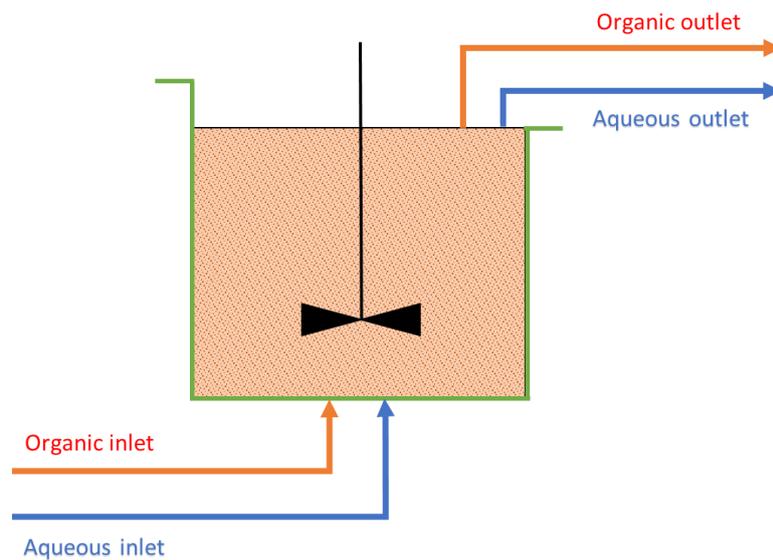


Figure 3.1 Mixer tank diagram

### Assumptions

- Perfect mixer.
- Sufficiently fast ion-exchange reaction kinetics and mass transfer so ideal thermodynamic equilibrium is almost achieved.
- Constant density, composition does not affect phase densities.
- $k_{LA}$  is constant.
- Initial organic and aqueous volumes exist in the mixer tank (to avoid infinite terms in the equations).
- Temperature is constant.
- Volumetric additivity, liquid volume in the tank is equal to the sum of organic and aqueous volumes

### General correlations: principles of conservation

Total outlet flowrate is:

$$Q_{out} = O_{in} + A_{in} \quad (3.1)$$

When perfect mixing is assumed, outlet flowrates are proportional to phase volumes in the mixer tank, which gives rise to the following auxiliary correlations:

$$O_{out} = Q_{out} * \frac{V_O}{V_O + V_A} \quad (3.2)$$

$$A_{out} = Q_{out} * \frac{V_A}{V_O + V_A} \quad (3.3)$$

### Organic and aqueous phases volume balances

$$\frac{dV_o}{dt} = O_{in} - O_{out} = O_{in} - Q_{out} * \frac{V_o}{V_o + V_A} \quad (3.4)$$

$$\frac{dV_A}{dt} = A_{in} - A_{out} = A_i - Q_{out} * \frac{V_A}{V_o + V_A} \quad (3.5)$$

### Metal mol balances in each phase

*Rate of accumulation = flow in - flow out ± mass transfer flow*

Considering X and Y volumetric concentrations

$$\frac{d(V_o * Y)}{dt} = V_o * \frac{dY}{dt} + Y * \frac{d(V_o)}{dt} = O_{in} * Y_{in} - O_{out} * Y + Q \quad (3.6)$$

$$\frac{d(V_A * X)}{dt} = V_A * \frac{dX}{dt} + X * \frac{d(V_A)}{dt} = A_{in} * X_{in} - A_{out} * X - Q \quad (3.7)$$

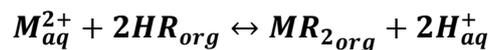
Substituting volume derivatives (3.4 and 3.5) in 3.6 and 3.7

$$V_o * \frac{dY}{dt} = O_{in} * Y_{in} - O_{out} * Y + Q - Y * (O_{in} - O_{out}) \quad (3.8)$$

$$V_A * \frac{dX}{dt} = A_{in} * X_{in} - A_{out} * X - Q - X * (A_{in} - A_{out}) \quad (3.9)$$

### **Constitutive equations**

The equilibrium model is based on the competitive ion exchange reaction:



### Mass action law of the reaction

$$K = \frac{[MR_{2eq}] * [H_{eq}^+]^2}{[M_{eq}^{2+}] * [HR_{eq}]^2} \quad (3.10)$$

To solve the four unknowns, three additional correlations are necessary

Equilibrium extractant (R) balance in organic phase

$$[\text{HR}]_{\text{in}} = 2 [\text{MR}_{2\text{eq}}] + [\text{HR}_{\text{eq}}] = \text{const}_1 \quad (3.11)$$

Equilibrium charge balance in aqueous phase

$$2[\text{M}^{2+}]_{\text{in}} + [\text{H}^+]_{\text{in}} = 2[\text{M}_{\text{eq}}^{2+}] + [\text{H}_{\text{eq}}^+] = \text{const}_2 \quad (3.12)$$

Total equilibrium solute mol balance

$$\text{O}_{\text{in}} * \text{Y}_{\text{eq}} + \text{A}_{\text{in}} * \text{X}_{\text{eq}} = \text{O}_{\text{in}} * \text{Y}_{\text{in}} + \text{A}_{\text{in}} * \text{X}_{\text{in}} \quad (3.13)$$

It is assumed that:

$$\text{Y}_{\text{eq}} = [\text{MR}_{2\text{eq}}]$$

$$\text{X}_{\text{eq}} = [\text{M}_{\text{eq}}]$$

Output extractant and hydrogen ion concentrations are obtained from:

Output extractant mol balance (2Y is the extractant used)

$$[\text{HR}_{\text{out}}] = [\text{HR}]_{\text{in}} - 2\text{Y} \quad (3.14)$$

Output charge balance in aqueous phase

$$[\text{H}_{\text{out}}] = 2\text{X}_{\text{in}} + [\text{H}]_{\text{in}} - 2\text{X} \quad (3.15)$$

Transport correlation based on Fick's law

$$\text{Q} = \text{k}_{\text{LA}} * \text{V}_{\text{A}} * (\text{X} - \text{X}_{\text{eq}}) \quad (3.16)$$

Mol transfer flow is proportional to volume and concentrations gradient.

### 3.1.2 Multicomponent case

#### Notation

$O_{in}$	inlet organic volumetric flow ( $m^3/min$ )	<b>input variable</b>
$A_{in}$	inlet aqueous volumetric flow ( $m^3/min$ )	<b>input variable</b>
$Y_{in1}$	inlet organic concentration ( $mol/m^3$ )	<b>input variable</b>
$X_{in1}$	inlet aqueous concentration ( $mol/m^3$ )	<b>input variable</b>
$Y_{in2}$	inlet organic concentration ( $mol/m^3$ )	<b>input variable</b>
$X_{in2}$	inlet aqueous concentration ( $mol/m^3$ )	<b>input variable</b>
$H_{in}$	Inlet aqueous $H^+$ concentration ( $mol/m^3$ )	<b>input variable</b>
$HR_{in}$	inlet organic extractant concentration ( $mol/m^3$ )	<b>input variable</b>
$K_1$	equilibrium reaction constant	<b>parameter</b>
$K_2$	equilibrium reaction constant	<b>parameter</b>
$k_{LA1}$	volumetric mass transfer coefficient ( $1/min$ )	<b>parameter</b>
$k_{LA2}$	volumetric mass transfer coefficient ( $1/min$ )	<b>parameter</b>
$V$	total volume in the mixer tank ( $m^3$ )	<b>parameter</b>
$Q_1$	mol transfer flow ( $mol/min$ )	<b>internal variable</b>
$Q_2$	mol transfer flow ( $mol/min$ )	<b>internal variable</b>
$V_o$	organic volume in the mixer tank ( $m^3$ )	<b>internal variable</b>
$V_A$	aqueous volume in the mixer tank ( $m^3$ )	<b>internal variable</b>
$Y_{out1}$	outlet solute organic concentration ( $mol/m^3$ )	<b>output variable</b>
$X_{out1}$	outlet solute aqueous concentration ( $mol/m^3$ )	<b>output variable</b>
$Y_{out2}$	outlet solute organic concentration ( $mol/m^3$ )	<b>output variable</b>
$X_{out2}$	outlet solute aqueous concentration ( $mol/m^3$ )	<b>output variable</b>
$P$	purity	<b>output variable</b>
$p$	productivity	<b>output variable</b>
$O_{out}$	outlet organic volumetric flow ( $m^3/min$ )	<b>output variable</b>
$A_{out}$	outlet aqueous volumetric flow ( $m^3/min$ )	<b>output variable</b>
$H_{out}$	outlet aqueous $H^+$ concentration ( $mol/m^3$ )	<b>output variable</b>
$HR_{out}$	outlet organic extractant concentration ( $mol/m^3$ )	<b>output variable</b>

## General correlations: principles of conservation

Same auxiliary correlations for outlet flowrates are applied

### Solute 1 mol balances in each phase

*Rate of accumulation = flow in - flow out ± mass transfer flow*

$$\frac{d(V_o * Y_1)}{dt} = V_o * \frac{dY_1}{dt} + Y_1 * \frac{d(V_o)}{dt} = O_{in} * Y_{in1} - O_{out} * Y_1 + Q_1 \quad (3.17)$$

$$\frac{d(V_A * X_1)}{dt} = V_A * \frac{dX_1}{dt} + X_1 * \frac{d(V_A)}{dt} = A_{in} * X_{in1} - A_{out} * X_1 - Q_1 \quad (3.18)$$

Substituting volume derivatives as in the single component case

$$V_o * \frac{dY_1}{dt} = O_{in} * Y_{in1} - O_{out} * Y_1 + Q_1 - Y_1 * (O_{in} - O_{out}) \quad (3.19)$$

$$V_A * \frac{dX_1}{dt} = A_{in} * X_{in1} - A_{out} * X_1 - Q_1 - X_1 * (A_{in} - A_{out}) \quad (3.20)$$

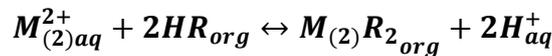
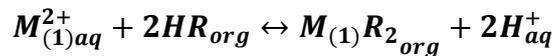
Equally for solute 2:

$$V_o * \frac{dY_2}{dt} = O_{in} * Y_{in2} - O_{out} * Y_2 + Q_2 - Y_2 * (O_{in} - O_{out}) \quad (3.21)$$

$$V_A * \frac{dX_2}{dt} = A_{in} * X_{in2} - A_{out} * X_2 - Q_2 - X_2 * (A_{in} - A_{out}) \quad (3.22)$$

## Constitutive equations

In this case there are two competitive ion exchange reactions:



### Mass action law of the reactions

$$K_1 = \frac{[M_{(1)}R_{2eq}] * [H_{eq}]^2}{[M_{(1)eq}] * [HR_{eq}]^2} \quad (3.23)$$

$$K_2 = \frac{[M_{(2)}R_{2eq}] * [H_{eq}]^2}{[M_{(2)eq}] * [HR_{eq}]^2} \quad (3.24)$$

To solve the six unknowns, four additional correlations are necessary

Equilibrium extractant (R) balance in organic phase

$$[\mathbf{HR}]_{\text{in}} = 2 \left[ \mathbf{M}_{(1)} \mathbf{R}_{2_{eq}} \right] + 2 \left[ \mathbf{M}_{(2)} \mathbf{R}_{2_{eq}} \right] + [\mathbf{HR}_{eq}] \quad (3.25)$$

Equilibrium charge balance in aqueous phase

$$2[\mathbf{M}_{(1)}]_{\text{in}} + 2[\mathbf{M}_{(2)}]_{\text{in}} + [\mathbf{H}]_{\text{in}} = 2 \left[ \mathbf{M}_{(1)_{eq}} \right] + 2 \left[ \mathbf{M}_{(2)_{eq}} \right] + [\mathbf{H}_{eq}] \quad (3.26)$$

Total equilibrium solute 1 mol balance

$$\mathbf{O}_{\text{in}} * \mathbf{Y}_{eq1} + \mathbf{A}_{\text{in}} * \mathbf{X}_{eq1} = \mathbf{O}_{\text{in}} * \mathbf{Y}_{\text{in1}} + \mathbf{A}_{\text{in}} * \mathbf{X}_{\text{in1}} \quad (3.27)$$

Total equilibrium solute 2 mol balance

$$\mathbf{O}_{\text{in}} * \mathbf{Y}_{eq2} + \mathbf{A}_{\text{in}} * \mathbf{X}_{eq2} = \mathbf{O}_{\text{in}} * \mathbf{Y}_{\text{in2}} + \mathbf{A}_{\text{in}} * \mathbf{X}_{\text{in2}} \quad (3.28)$$

Output extractant and hydrogen ion concentrations are obtained from:

Output extractant mol balance

$$[\mathbf{HR}_{\text{out}}] = [\mathbf{HR}]_{\text{in}} - 2\mathbf{Y}_1 - 2\mathbf{Y}_2 \quad (3.29)$$

Output charge balance in aqueous phase

$$[\mathbf{H}_{\text{out}}] = 2\mathbf{X}_{\text{in1}} + 2\mathbf{X}_{\text{in2}} + [\mathbf{H}]_{\text{in}} - 2\mathbf{X}_1 - 2\mathbf{X}_2 \quad (3.30)$$

Transport correlations based on Fick's law

$$\mathbf{Q}_1 = \mathbf{k}_{LA1} * \mathbf{V}_A * (\mathbf{X}_1 - \mathbf{X}_{eq1}) \quad (3.31)$$

$$\mathbf{Q}_2 = \mathbf{k}_{LA2} * \mathbf{V}_A * (\mathbf{X}_2 - \mathbf{X}_{eq2}) \quad (3.32)$$

Purity of the organic outlet

$$\mathbf{P} = \frac{\mathbf{Y}_1}{\mathbf{Y}_1 + \mathbf{Y}_2} * 100 \quad (3.33)$$

Productivity of the organic outlet

$$\mathbf{p} = \mathbf{O}_{\text{in}} * \mathbf{Y}_1 \quad (3.34)$$

### 3.1.3 Linearity of the models

Because the models contain non-linear algebraic correlations together with differential equations, the condition of linearity for them is not fulfilled. That is to say:

$$\forall c_1, c_2 \in R \quad f(c_1 * Input_1 + c_2 * Input_2) \neq c_1 * f(Input_1) + c_2 * f(Input_2)$$

What implies that the outputs do not have to be proportional to the inputs neither the output of the superposition of several inputs is equal to the superposition of the outputs of these inputs, and therefore the system can exhibit complex behavior through the use of oscillations.

## 3.2 Computational implementation

### 3.2.1 Single component model

Since in this case the model features allow it, initially a native implementation is made in the computational environment of the master thesis (Simulink), which is also used as a contrast for the validation of the resolution in Simscape. In the block diagram (Figure 3.3) that resolves the corresponding Simulink design (Figure 2.2), it is found that, as required by the block-oriented approach, the system that represents the thermodynamic submodel has had to be transformed by means of tedious algebraic manipulations to introduce the causality in it. Even so, an algebraic loop arises, which can be solved in certain cases with the Algebraic Constraint block of the Math Operations library, which has limitations and restrictions. The above, together with the modular and explicit implementation of each and every of the mathematical operations (adder, multiplier, integrator...) by individual blocks causes the semantics (content of the correlations of the model) and the overall vision to be lost. In addition, the solution is particular since you have to specify which are the input and output variables, which predetermines the execution flow of the algorithm.

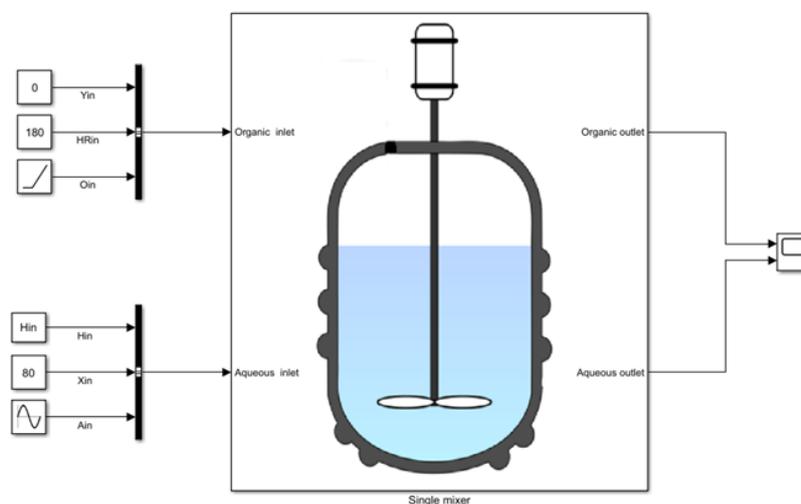


Figure 3.2 Simulink design of the single component mixer tank

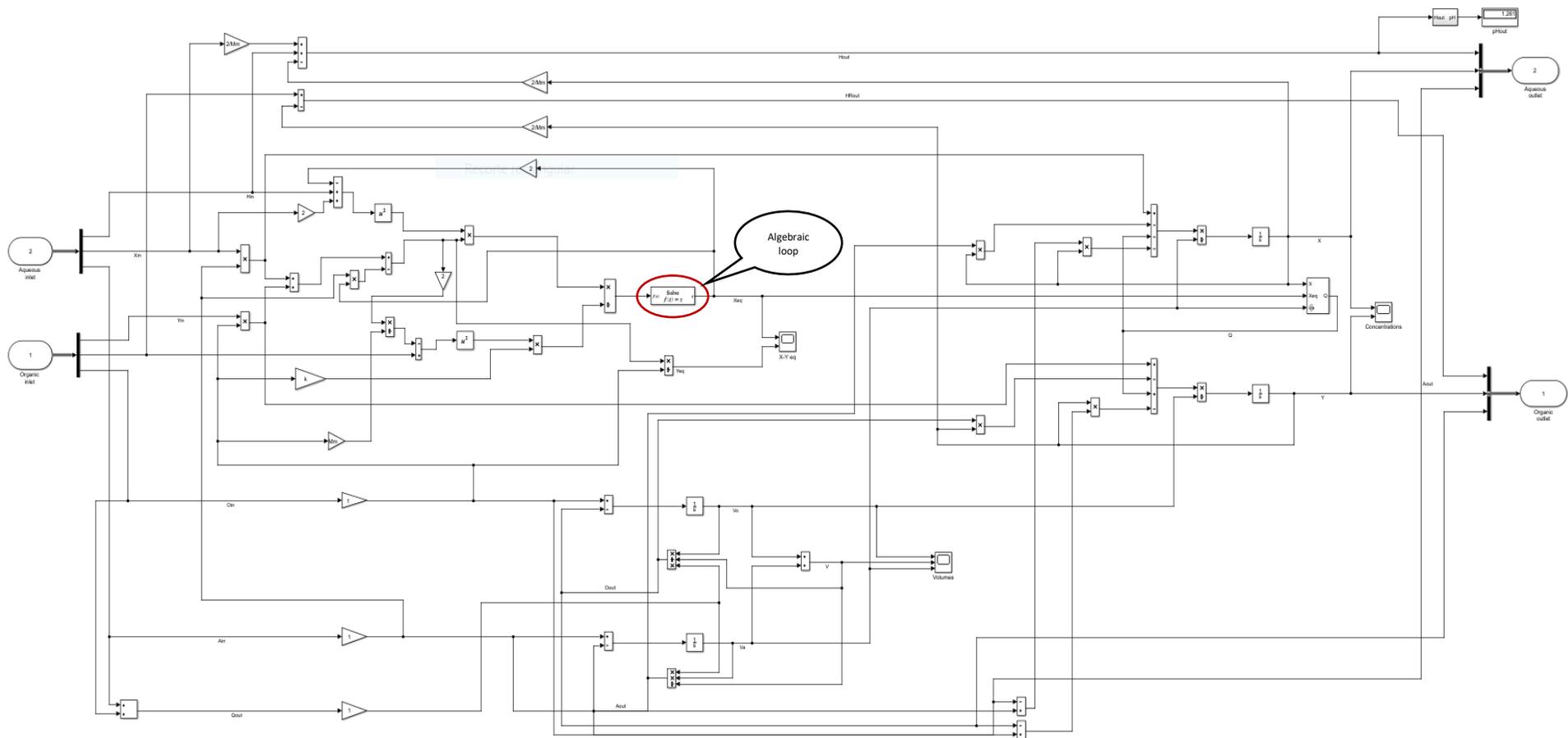


Figure 3.3 Simulink block diagram of the single component model

## Simscape

As in Simulink, the Simscape component that simulates the mixer tank has the following structure that responds to the classic black-box input-output scheme:

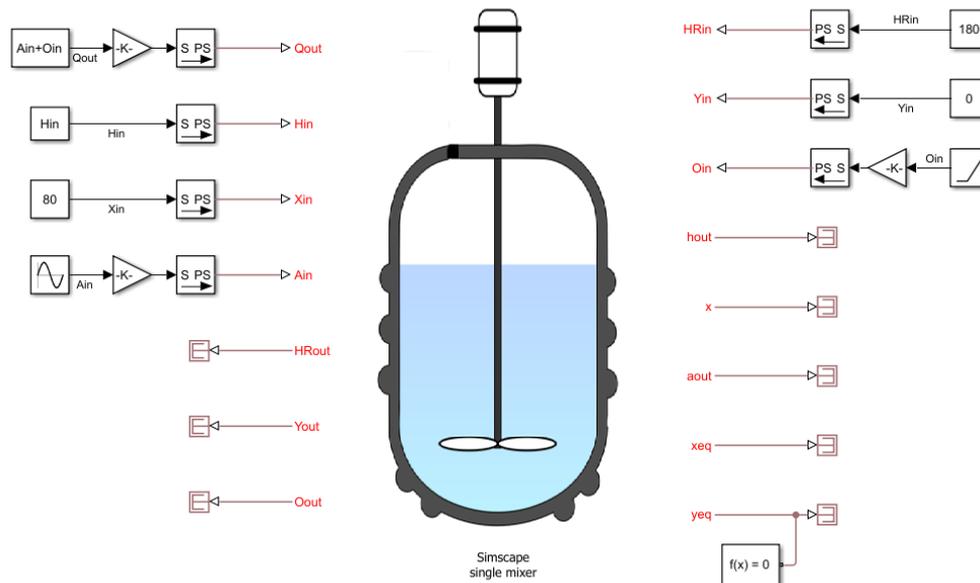


Figure 3.4 Simscape design of the mixer tank

However, in Simscape the user enters a script in MATLAB (formatted with extension .ssc) in which it is only necessary to specify the fields: inputs, variables, outputs, parameters and equations (as they appear in the model, which is usually implicit form). To execute the simulation, the program itself determines the flow of the model's resolution algorithm. The content of the aforementioned fields is shown in the script corresponding to this case:

```

component mixer tank
inputs
HRin=0; % HRin:right
Yin=0; % Yin:right
Oin=0; % Oin:right
Qout1=0; % Qout:left
Hin=0; % Hin:left
Xin=0; % Xin:left
Ain=0; % Ain:left
end

variables
Heq=0;
HReq=0;
Xe=0;
Ye=0;
Va=0;
Vo=0;
Oout=0;
Aout=0;
Qout=0;

```

```

Vtotal=0;
X=0;
Y=0;
Q=0;
HRout=0;
Hout=0;
OAratio=0;
end

outputs
hrout=0; % HRout:left
y=0; % Yout:left
oout= 0; % Oout:left
hout=0;
x=0;
aout=0;
xeq=0;
yeq=0;
end

parameters
k = 0;
kla=0;
end

equations
% Equilibrium model
k == (Yeq*Heq^2)/(Xeq*HReq^2);
HRin == 2*Yeq+HReq;
2*Xin+Hin == 2*Xeq + Heq;
Oin*Yeq + Ain*Xeq == Oin*Yin + Ain*Xin;
HRout == HRin -2*Y;
Hout == 2*Xin +Hin -2*X

% Organic and aqueous phase volume balances
Vo.der == (Oin - Oout)*{ 1, '1/s' };
Va.der == (Ain - Aout)*{ 1, '1/s' };
Oout == Qout*Vo/(Vo+Va);
Aout == Qout*Va/(Vo+Va);
Qout == Ain+Oin;

% Component mol balances
Vo*Y.der == (Oin*Yin - Oout*Y + Q - Y*(Oin-Oout))*{ 1, '1/s' };
Va*X.der == (Ain*Xin - Aout*X - Q - X*(Ain-Aout))*{ 1, '1/s' };
Vtotal == Vo+Va;
OAratio == Vo/Va;

% Transport correlation
Q == kla*Va*(X-Xeq);

% Auxiliiar output assignments
hout == Hout;
x == X;
aout == Aout;
hrout == HRout;
y == Y;
oout == Oout ;
xeq == Xeq;
yeq == Yeq;
end
end

```

This example illustrates in practice the advantages already exposed of the methodology of object-oriented simulation, by separating the modeling of the specific technicalities of the resolution algorithms. In addition, the solution has a general character, independent of the simulation mode (analysis, design and control).

### Case implementation with countercurrent cascade

Once the Simscape mixer tank component has been designed, it is only necessary to duplicate it and make the corresponding connections to the countercurrent mode using the graphical interface as shown below, without the need for any additional code and therefore equalizing the ease of use of simulators like Aspen Plus.

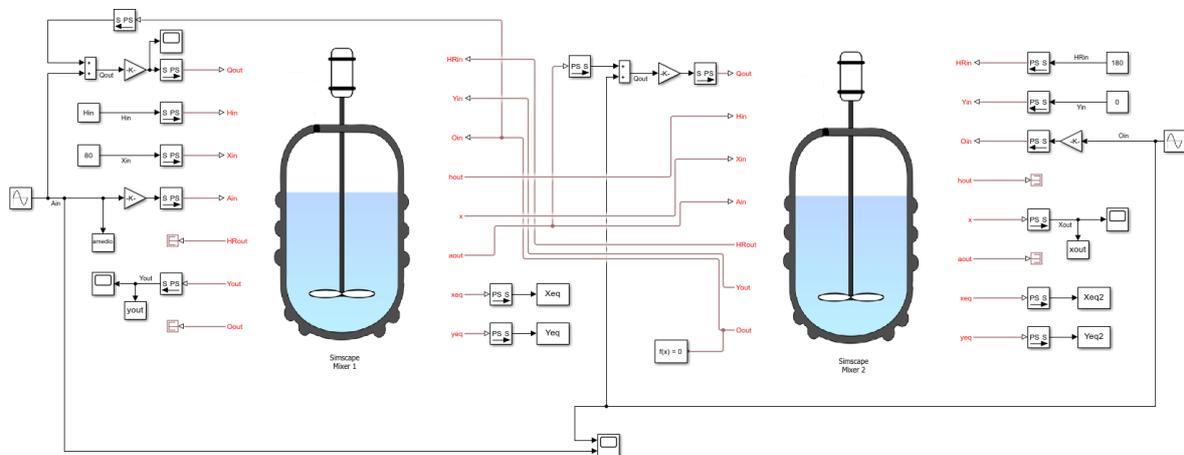


Figure 3.5 Counter-current cascade in Simscape

### 3.2.2 Multicomponent model

Given the insufficiencies and limitations of the Simulink solution, and once the results obtained for the previous case have been validated by both methods, we opted to directly implement the multicomponent model in Simscape, whose design is shown in the next page (Figure 3.6).

Its code is incorporated into a new ssc file. For the implementation of the multicomponent model it is not necessary to create a new script from scratch, but it is created from the single component file, making the necessary modifications easily thanks once again to the characteristics of the object-oriented approach.

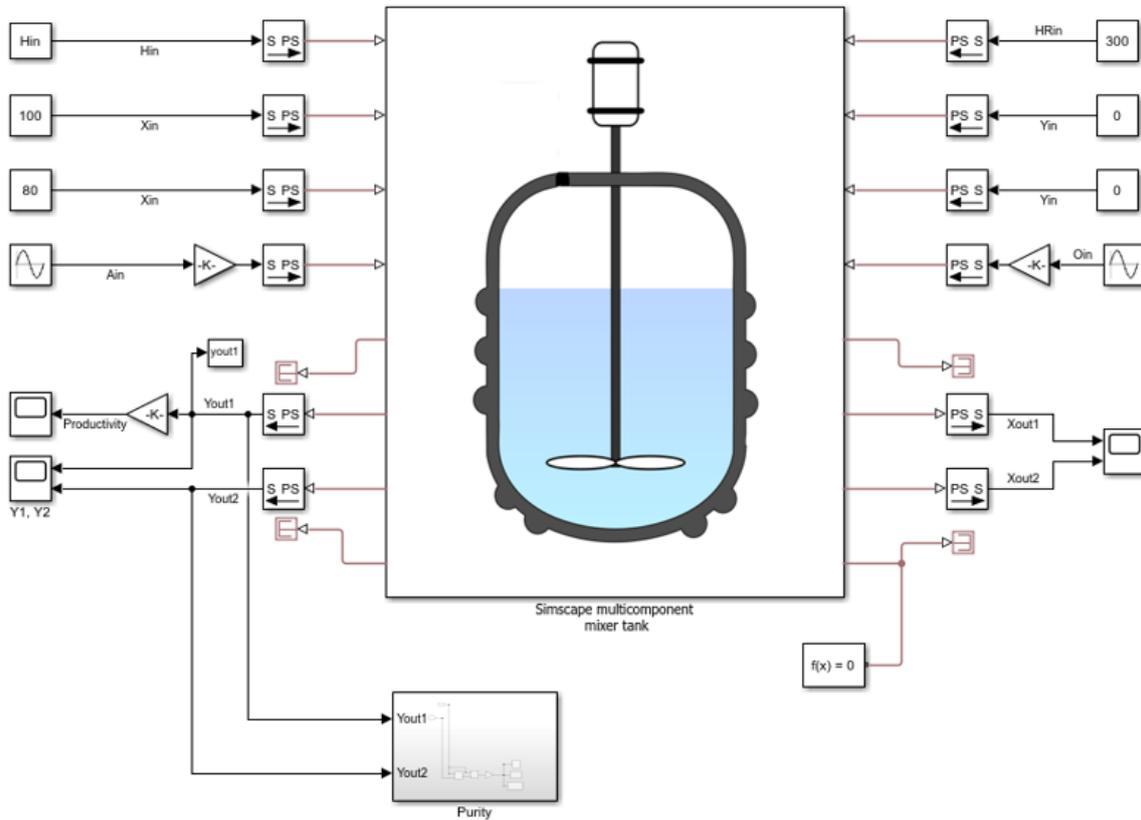


Figure 3.6 Simscape design of the multicomponent mixer tank

In the scheme is worth mentioning that the module that calculates the purity of the product stream is implemented directly in Simulink for the purpose of later carrying out the analysis of the effect of the FPO with the Simulink Design Optimization toolbox. For the same reason productivity is also calculated directly on Simulink.

Also, as explained in the scope and limitations of the thesis, in this case only one mixer tank is considered.

## 4 MATERIALS AND RESOURCES

For the realization of this work the following resources have been used

### 4.1 Hardware

Microsoft Surface Pro 4 computer: Intel i5 processor, 8 GB RAM, 256 GB SSD under Windows 10 platform.

### 4.2 Matlab-Simulink software

#### **MATLAB (R2018A)**

Proprietary software (mathematical character) of the company The Mathworks that offers a development environment with the programming language m, widely used in engineering. Available through the university through a student's license.

#### **SIMULINK 9.1**

Integrated with MATLAB and Simscape language, is a block-oriented simulator for modelling, simulating and analysing multidomain dynamical systems.

#### **SIMULINK DESIGN OPTIMIZATION (R2018A)**

It is a Simulink toolbox that provides functions, interactive tools, and blocks for parameter estimation and tuning, design exploration and sensitivity analysis, and robust optimization of Simulink-Simscape models.

## 5 EXPERIMENTAL DESIGN, SIMULATION AND RESULTS

According to the objectives of this thesis, the effect of periodic sinusoidal oscillations in the liquid-liquid extraction process will be studied for the corresponding cases of the experimental design, comparing the results obtained through simulation and Global Sensitivity Analysis between the steady state and the dynamic periodic modes of operation.

### 5.1 Single component case with countercurrent cascade

#### 5.1.1 Experimental design

First, a steady state pattern case must be established to conduct a comparison. Once this is done, the dynamic periodic case is defined based on the steady state one. The cost function used to compare both modes is the metal concentration in the aqueous outlet stream, that obviously must be minimised.

##### Steady state mode

Periodic oscillations effect must be compared with the optimised steady state case to guarantee that the possible improvements of FPO cannot be achieved by a different steady state configuration. Given the theoretical nature of this thesis, bivalent generic metals are considered and, therefore, input values for the parameters and variables referenced in the revised literature have been assigned:

Input	Value	Units
$O_{in}$	0.48	$m^3/min$
$A_{in}$	0.33	$m^3/min$
$Y_{in}$	0	$mol/m^3$
$X_{in}$	80	$mol/m^3$
$H_{in}$	15.85	$mol/m^3$
$HR_{in}$	180	$mol/m^3$
$k$	5	-
$k_{LA}$	30	$1/min$
$V$	1.35	$m^3$

Table 5.1 Input values for the single component case

It should be mentioned that the value assigned to the mass transfer coefficient is high enough to guarantee that the extraction is carried out close to the thermodynamic equilibrium and therefore the mass transfer (linear process) does not reduce the effect of the oscillations.

## Dynamic oscillatory mode

The dynamic case corresponds to a stationary case extension since forced periodic oscillations (FPO) tries to improve performance with the same time-average input values, therefore it is only necessary to choose which inputs will oscillate and how.

According to (Pour, 1976, p. 37) , there are two configurations that show better results when two inputs are oscillated simultaneously: the first is to establish the same amplitude and frequency in the inputs and introduce a phase difference between them and the second to assign different amplitudes and frequencies. Because the first option would involve starting from different stationary points (because of the phase difference) with the initialization problems that this would produce in the simulation, and given the lower number of available degrees of freedom (3 vs 4) and therefore less possibilities of improvement, the second option is chosen.

Obviously, the amplitudes cannot be less than zero or greater than the stationary values, while the minimum value of the frequencies is zero and the maximum reasonable value that can be reached is set at a value corresponding to an angular velocity of 30 rad/min.

	Organic inlet	Aqueous inlet
Amplitude	0 – 0.48	0 – 0.33
Frequency	0 – 30	0 – 30

Table 5.2 Range of oscillation parameters for the single component case

### 5.1.2 Simulation, sensitivity analysis optimization and results

#### Steady state mode

The simulation of the steady state mode is performed using Simscape option “Start simulation for steady state”. The result for the cost function is 12.94 mol/m<sup>3</sup>.

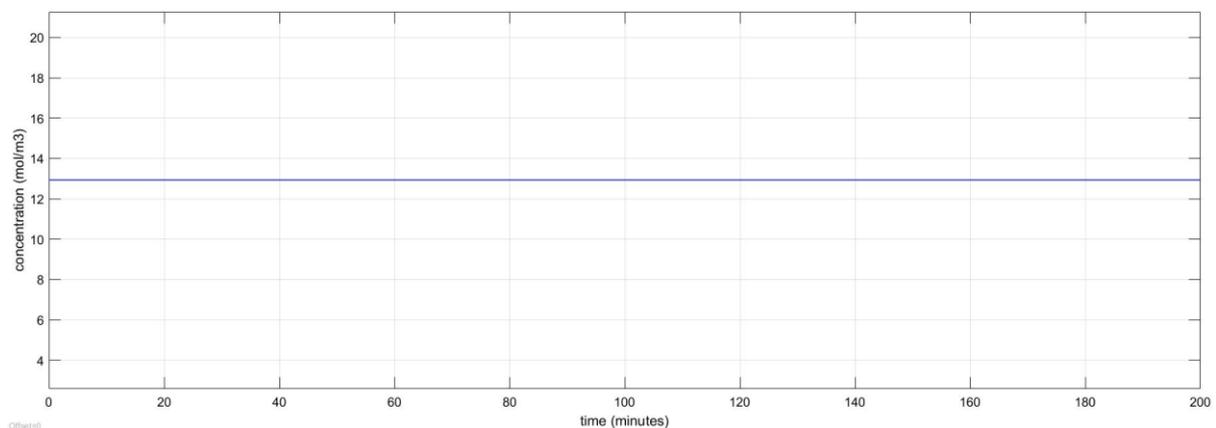


Figure 5.1 Single component steady state simulation result

## Dynamic oscillatory mode

Once the experimental design has been established, the design space is fixed: there is one performance indicator or cost function (steady state time-average metal concentration in the aqueous outlet), and four parameters, leading to a 5-D space. This space is explored using Global Sensibility Analysis and optimization through Simulink Design Optimization toolbox. Volumetric flowrate units are changed from  $\text{m}^3/\text{min}$  to  $\text{l}/\text{min}$  for a better visualization of the results.

The workflow of the analysis will be the following:

- 1) Sample the parameter sample space specifying probability distributions for each parameter.
- 2) Define a cost function by creating the design requirement (minimise metal concentration in aqueous outlet) on its corresponding Simulink signal.
- 3) Evaluate the requirement (objective function) at each combination of parameter values using Monte Carlo simulations.
- 4) Exploration and analysis of the design space.
- 5) Export results from Global Sensitivity Analysis as initial guesses for Response Optimization.

**Step 1.** Samples are generated through random values, for which the following characteristics must be specified:

- **Sample size:** there must be a balance between detail and computational expense, 80 points are found suitable.
- **Sampling Method:** Sobol method is chosen because of its higher systematic space filling compared to other alternatives.
- **Probability Distributions:** initially all the design space wants to be explored without bias, so uniform distributions are chosen. This distribution need to define the limit values of the parameters, that as stated before, for amplitudes these limits go from zero to steady state values (330 and 480  $\text{l}/\text{min}$ ) and for frequencies from 0 to 30  $\text{rad}/\text{min}$ .
- **Parameter Correlations:** there are not correlations between the parameters.

Once this has been done, the parameter sample space (4 dimensions), whose two-dimensional graphical representation includes the following six projections, is obtained. The histograms represent the distribution of the coordinates of the points of the sample along the four axes of the parameter space, in this case the distributions are uniform.

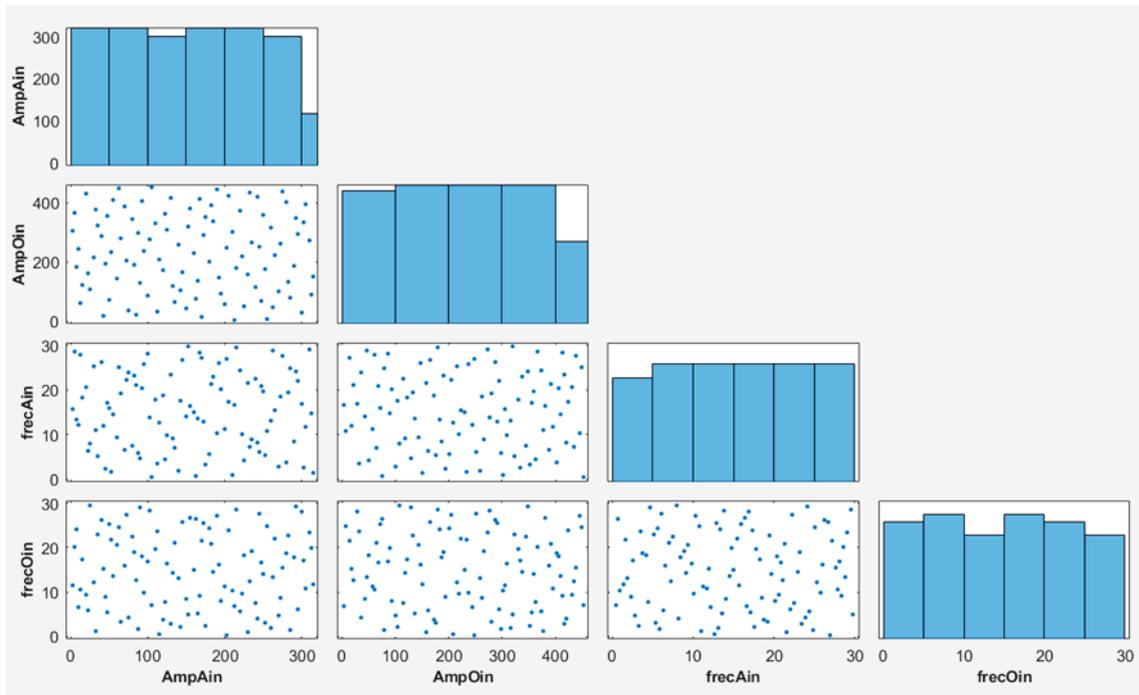


Figure 5.2 Initial single component parameter sample

**Step 2.** The cost function for the problem is defined as the time average value of the metal concentration in the aqueous outlet flowrate. Because we are interested in comparing steady-states, the time average value is computed after 40 minutes, when stationary state is achieved, to neglect the initial transient effects. This custom requirement is implemented coding a MATLAB function:

```

1  function vals=myCustomRequirement(data)
2
3  Xsignal=data.Nominal.Sig.Data;
4  Tsignal=data.Nominal.Sig.Time;
5  idx = find(abs(Tsignal-40.01) < 0.05);
6  time=Tsignal(idx:length(Tsignal));
7  xsteadyoscillation = Xsignal(idx:length(Tsignal));
8  xmean=mean(xsteadyoscillation);
9  vals = xmean;
10
11 end

```

Figure 5.3 Single component MATLAB cost function code

**Step 3.** With the parameter sample and the cost function determined, Global Sensitivity Analysis can now be computed employing Monte Carlo simulations. Results are shown through four scatter plots, one for each parameter. The histogram shows the probability distribution for the different values of the cost function of the sample, being more likely the values close to the steady state (12.94).

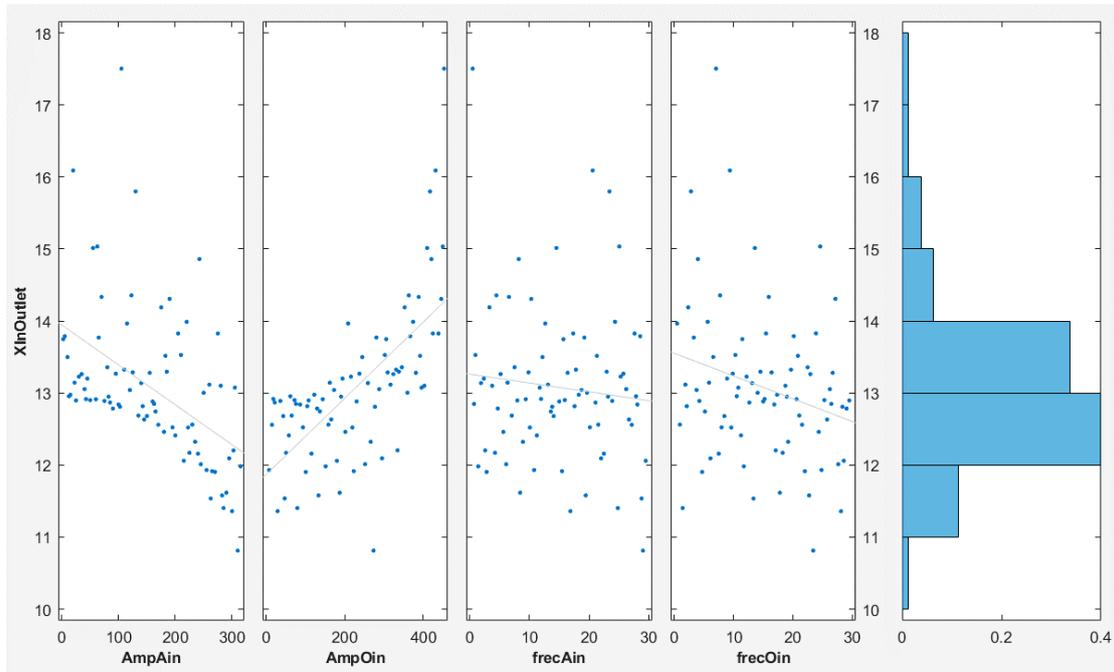


Figure 5.4 Single component Global sensitivity Analysis for the first parameter sample

To improve visualisation, results are also shown using contour plots:

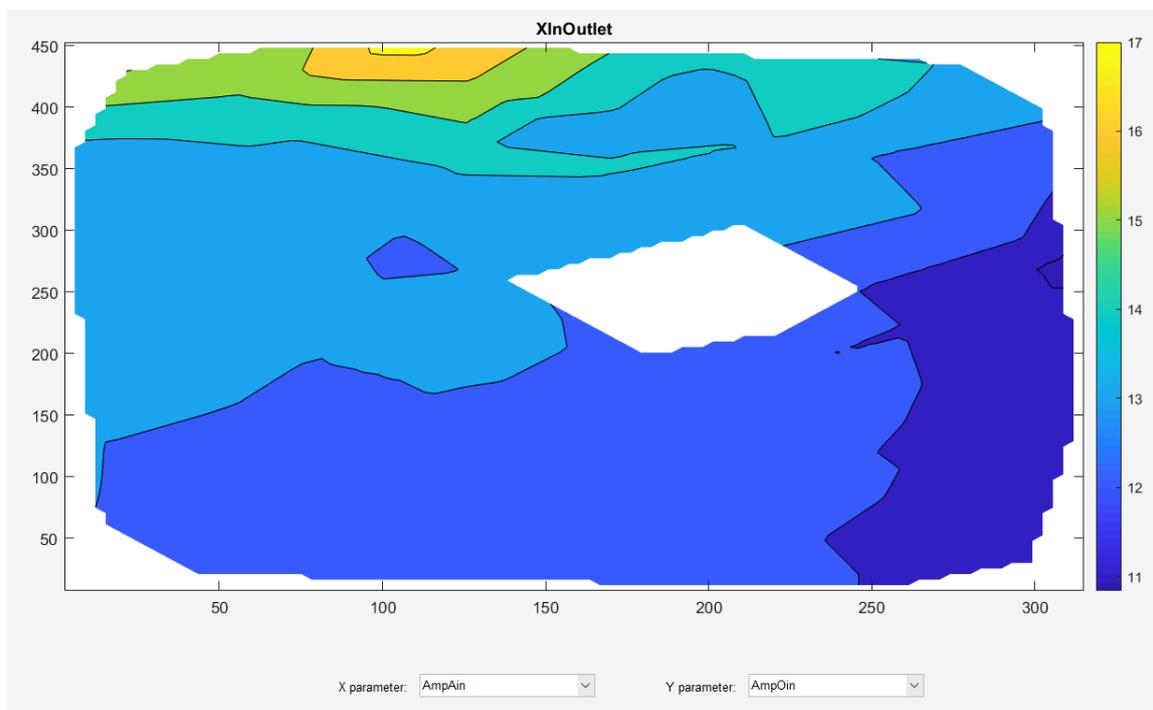


Figure 5.5 Amplitudes contour plot for the first parameter sample

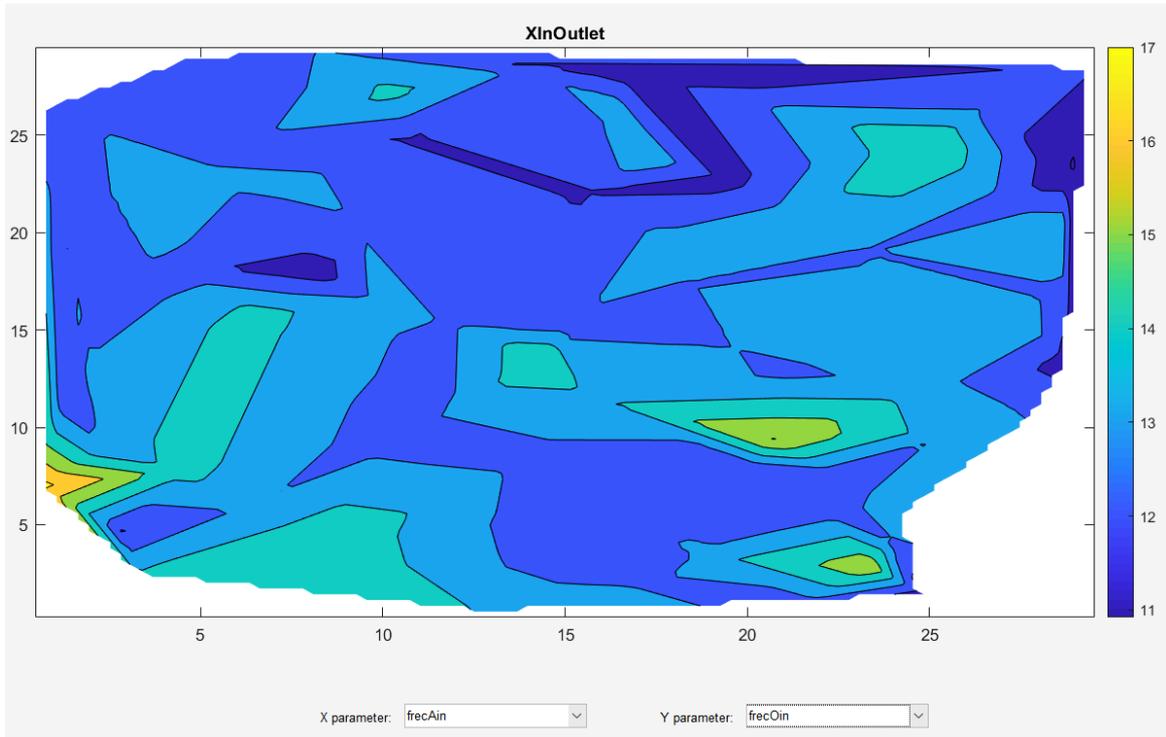


Figure 5.6 Frequency contour plot for the first parameter sample

**Step 4.** The analysis of the plots clearly shows that high aqueous amplitudes and low organic amplitudes minimise the cost function. However no clear relations can be obtained for the frequencies.

Additionally, the results of the influence analysis on the cost function using three different statistical correlations available in the toolbox are illustrated using a tornado plot.

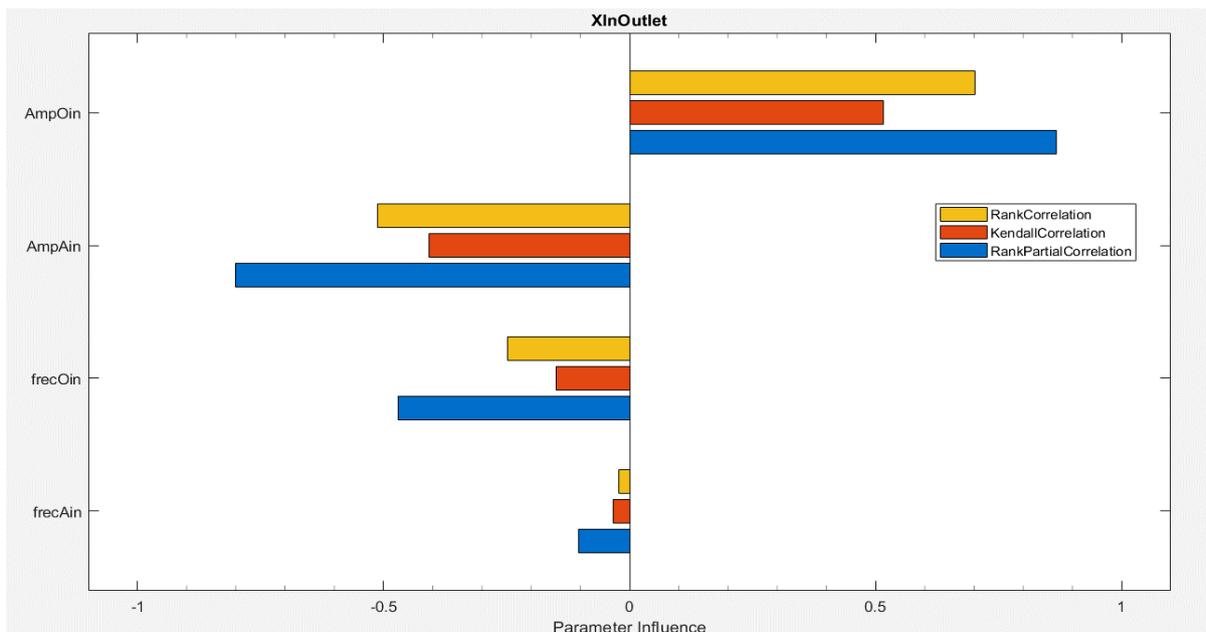


Figure 5.7 Tornado plot for the first single component parameter sample

The parameter with the greatest magnitude of influence on the cost function, in this case the organic amplitude, is displayed on the top, giving the plot a tornado shape. On the contrary, changes on the aqueous frequency will have very little impact on the performance.

### Restricted exploration

The initial exploration has detected correlations between the cost function and two of the parameters, which allows to reduce the design space. Thus, a new restricted exploration is performed on the corresponding subspace to high aqueous (280-330) and low organic amplitudes (0-100) to try to obtain relations for the other two parameters. To achieve this, triangular parameter distributions for the amplitudes are used (in which the value of the probability density is proportional to the value of the parameters):

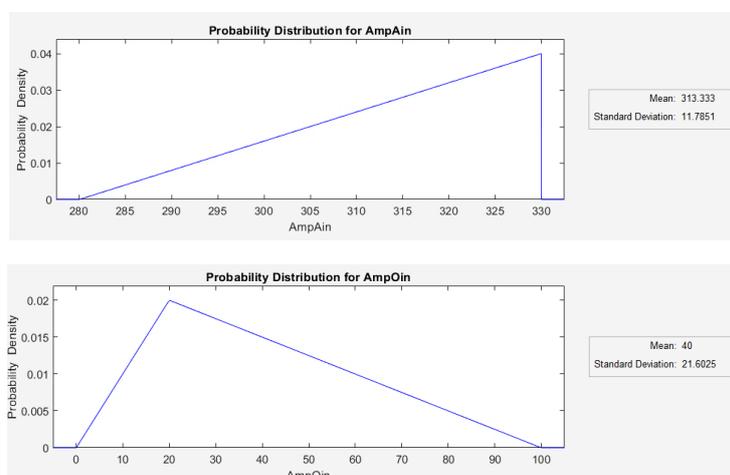


Figure 5.8 Triangular distributions for sampling of amplitude parameters

The graphical representation of the new parameter sample space is:

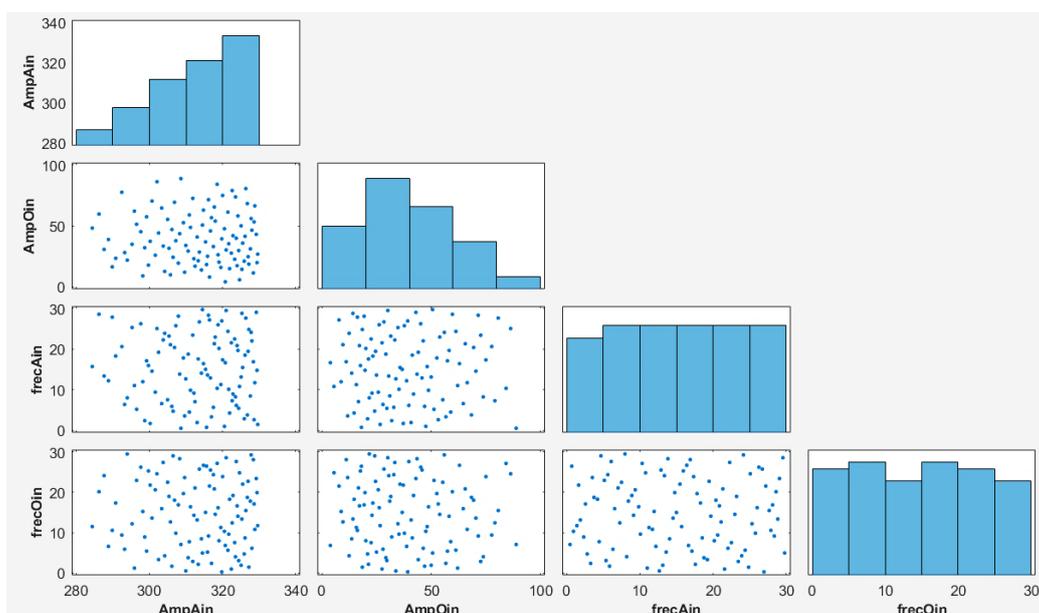


Figure 5.9 Restricted single component parameter sample

In this case it is observed that the sample is not uniform, there being a greater number of points in the subspace of interest.

The scatter plots of the Monte Carlo simulations results for the sample are:

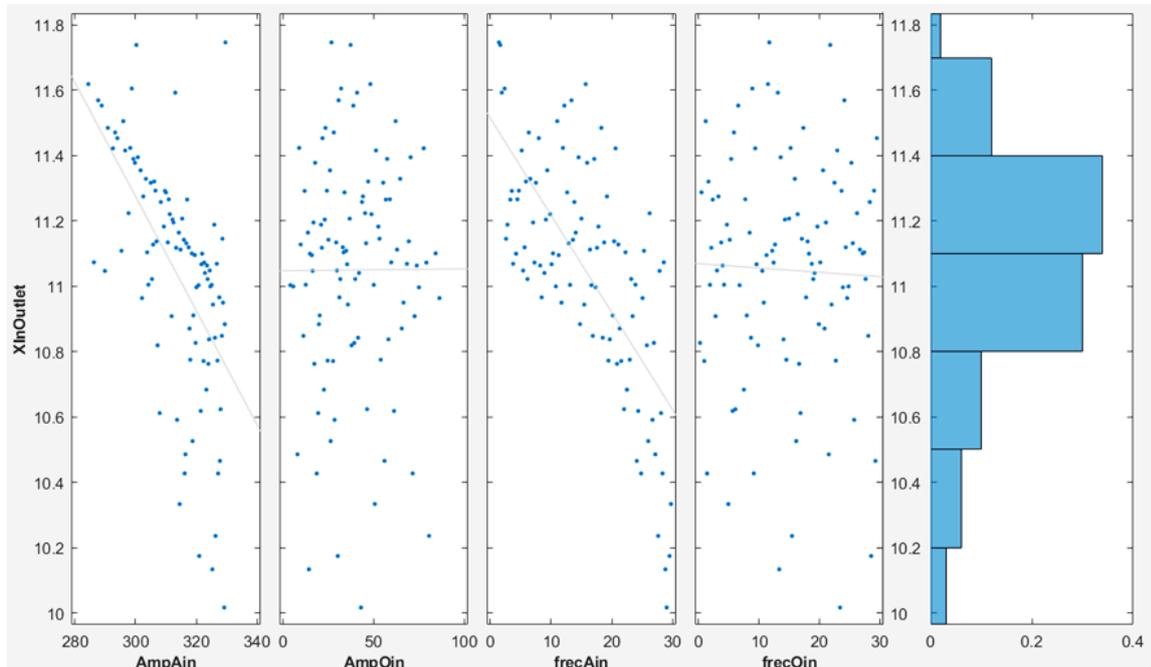


Figure 5.10 Single component Global Sensitivity Analysis scatter plots for the second parameter sample

And the corresponding contour plots are:

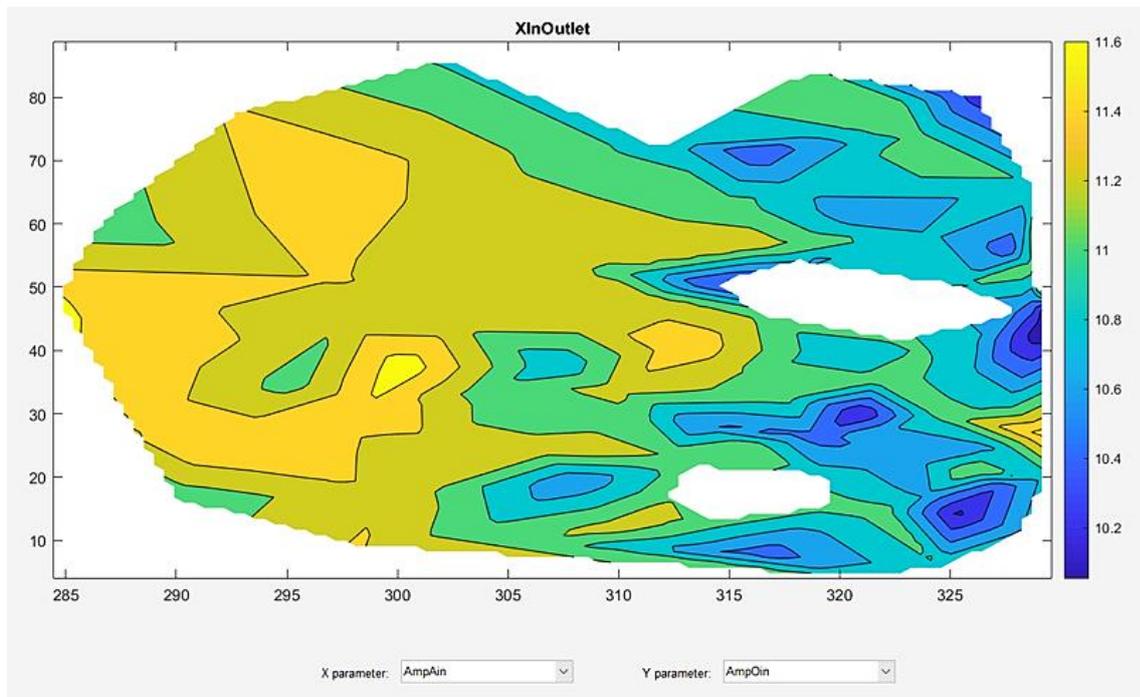


Figure 5.11 Amplitudes contour plot for the second parameter sample

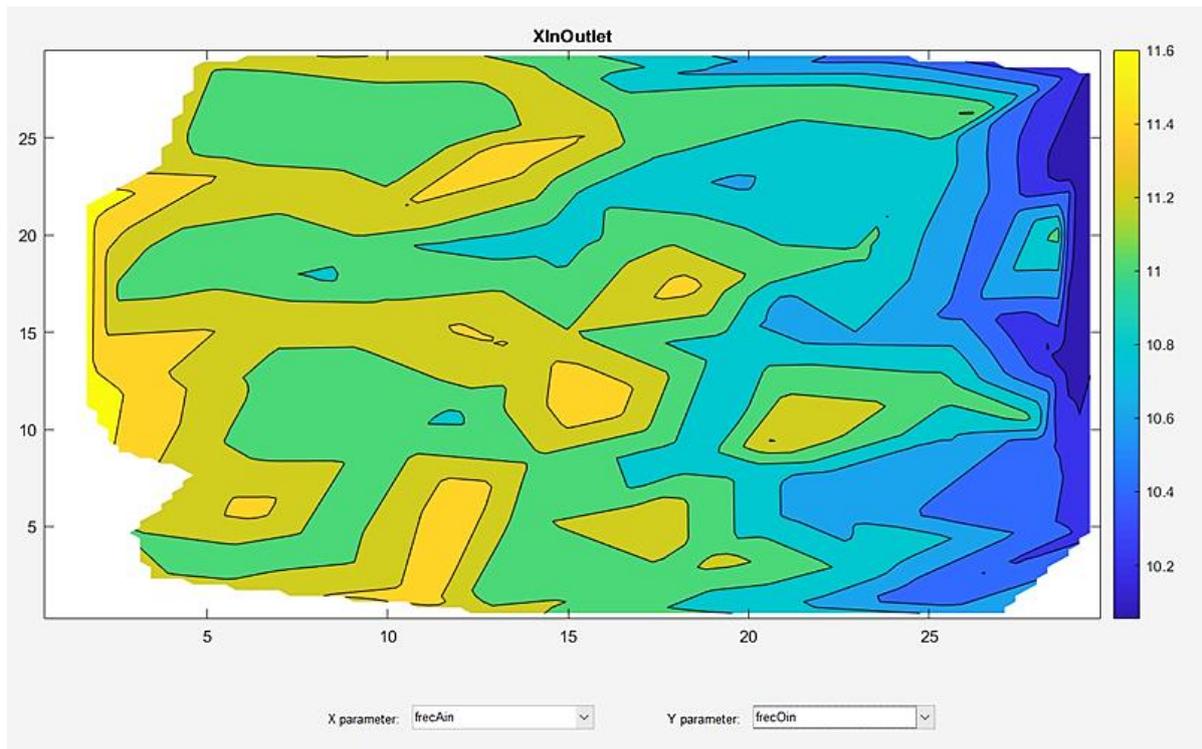


Figure 5.12 Frequencies contour plot for the second parameter sample

The scatter plot clearly shows that the cost function will be minimised when the values of amplitude and frequency for the aqueous stream are close to its maximum possible values. In the first contour plot the optimal values (dark blue) for the organic amplitude are in a range between 40 and 45, and from the second contour plot it is observed an optimal range from 12 to 30 rad/min for the frequency of the organic flowrate. With this information, the optimal subspace is determined by the following intervals:

Parameter	Optimal range
Aqueous amplitude	328-330
Organic amplitude	40-45
Aqueous frequency	29-30
Organic frequency	12-30

Table 5.3 Optimal parameter space for the single component case

## Optimization

Simulink Design Optimization toolbox give the option to export the defined cost function and the best point of the parameter sample space as initial guess from sensitivity analysis to a Response Optimization session. This allow to easily perform a dynamic optimization to find the optimal point of the subspace, that does not have to belong to the sample.

Following MATLAB guidelines, the method used is Gradient Descent and the algorithm is Sequential Quadratic Programming, designed to find minimum of constrained nonlinear multivariable function, and implemented in the GUI through the popular fmincon function from the optimization toolbox. Optimization successfully converges, and values of the optimal point are:

Parameter	Optimal value
Aqueous amplitude	329.26
Organic amplitude	42.99
Aqueous frequency	30
Organic frequency	23.45

Table 5.4 Optimal parameter values for the single component case

With these parameter values, the flowrate optimal modulation is obtained:

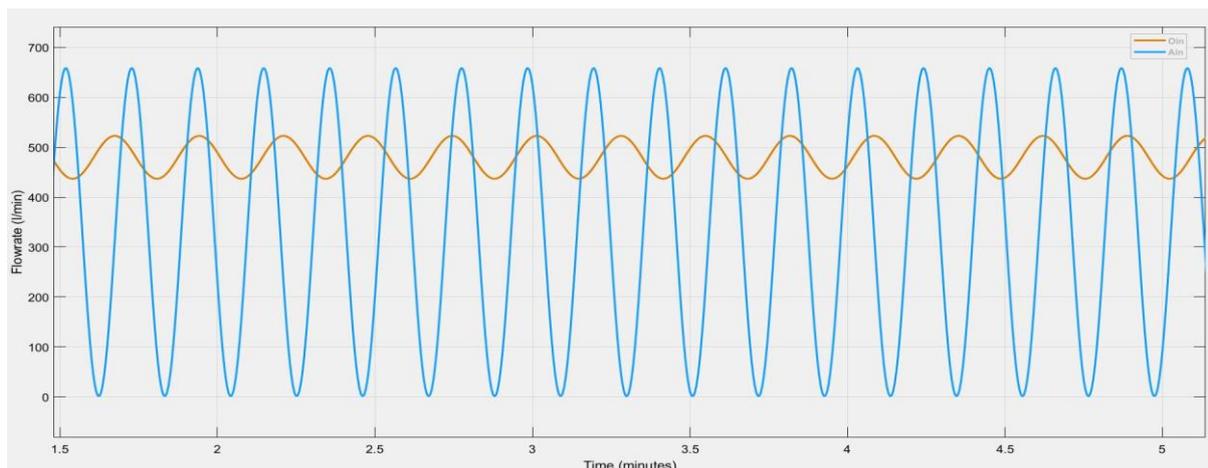


Figure 5.13 Optimal flowrate modulation for the single component case

As it corresponds to the results, the graph shows that the organic flow oscillates slightly on its stationary point, while the oscillation of the aqueous flow is of such magnitude that in the valleys of the same its value is practically null.

With this optimal modulation of the selected inputs, the cost function, time average value of the metal concentration in the aqueous outlet, for the dynamic periodic mode of operation is  $9.93 \text{ mol/m}^3$ .

### 5.1.3 Results analysis

For the comparison of the results between the stationary and dynamic periodic cases, the joint plot of time average values of the metal concentration in the aqueous outlet for both cases is used:

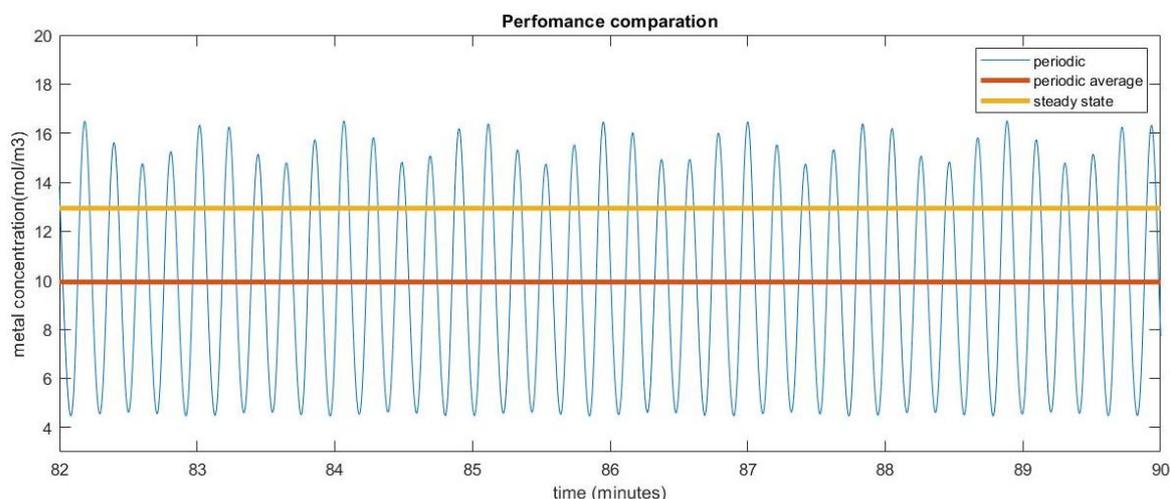


Figure 5.14 Performance comparison between both modes of operation in the single component case

The plot shows that there is a minimisation of the cost function from 12.94 mol/m<sup>3</sup> in the steady state mode to a value of 9.93 mol/m<sup>3</sup> in the dynamic periodic mode. This means a reduction of 23,26% in the amount of metal lost.

#### Assessment of the improvement obtained

Alternatively, in this case in which purity does not intervene, this same improvement could be obtained by operating in steady state mode but increasing the organic input flowrate. This is shown in the following table that collects the results of the parametric study of the stationary simulation, that allows to determine the magnitude of the flowrate increase needed.

Organic flowrate (l/min)	Cost function (mol/m <sup>3</sup> )
480	12,94
485	12,06
490	11,25
495	10,52
499,5	9,92

Table 5.5 Steady state single component parametric study

To equalize the performance of the periodic dynamic mode, it is necessary to increase the flowrate of organic 20 l / min, from 480 to 500. Which of the two options is better depends on the cost of the additional inconveniences generated by the periodic dynamic operation mode on the one hand, and the cost of the solvent and the extractant by another.

## 5.2 Multicomponent case with single mixer tank

### 5.2.1 Experimental design

As in the single component case, a steady state pattern is used to perform a comparison between both modes of operation. The difference is that in the extraction of multiple metals two non-independent performance indicators (productivity and purity) are required. Increasing the O/A ratio increase productivity, but in exchange for a decrease in purity. The optimal relation between both indicators is not pre-established since in some situations it will be more beneficial higher purity and in others higher productivity, so to determine the performance of the process the values of the points on the Productivity vs Purity plot will be compared. To obtain the global performance curve from the graph, four different O/A ratios (2, 0.8, 0.4 and 0.1) will be studied keeping the rest of inputs and parameters constant.

#### Steady state mode

The input values, following same criteria used in the single component case ,for the parameters and variables of the steady state cases for two bivalent generic metals (metal one being the desired product and metal two an undesired impurity) are:

Input	Value	Units
$O_{in}$	0.6 - 0.24 - 0.12 - 0.03	$m^3/min$
$A_{in}$	0.33	$m^3/min$
$Y_{in1}$	0	$mol/m^3$
$Y_{in2}$	0	$mol/m^3$
$X_{in1}$	100	$mol/m^3$
$X_{in2}$	100	$mol/m^3$
$H_{in}$	15.85	$mol/m^3$
$HR_{in}$	300	$mol/m^3$
$k_1$	6	-
$K_2$	1	-
$k_{LA1}$	30	$1/min$
$k_{LA2}$	30	$1/min$
$V$	1.35	$m^3$

Table 5.6 Input values for the multicomponent case

Again, the same values are assigned to the mass transfer coefficients to guarantee that the extraction is carried out close to the thermodynamic equilibrium. Metal two that is considered

an impurity has a lower equilibrium constant since the extractant is designed to extract metal one.

### Dynamic oscillatory mode

Since the process principles and equipment is exactly the same as in the single component case, the same inputs (organic and aqueous flowrates) will be modulated in the same way. The ranges of the oscillation parameters for each case are:

	Case 1 (O/A = 2)		Case 2 (O/A = 0.8)		Case 3 (O/A = 0.4)		Case 4 (O/A = 0.1)	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
Amplitude	0 - 600	0 - 300	0 - 240	0 - 240	0 - 120	0 - 120	0 - 30	0 - 30
Frequency	0 - 30	0 - 30	0 - 30	0 - 30	0 - 30	0 - 30	0 - 30	0 - 30

Table 5.7 Range of oscillation parameters for the multicomponent case

## 5.2.2 Simulation, sensitivity analysis and results

### Steady state mode

Again, the Simscape option “Start simulation for steady state” is used to perform the simulations. The results for the performance indicators are:

Case 1 (O/A = 2)		Case 2 (O/A = 0.8)		Case 3 (O/A = 0.4)		Case 4 (O/A = 0.1)	
Productivity (mol/min)	Purity (%)						
24.39	64.97	17.71	74.93	11.42	80.23	4.05	84.17

Table 5.8 Multicomponent steady state simulations results

And the performance curve is:

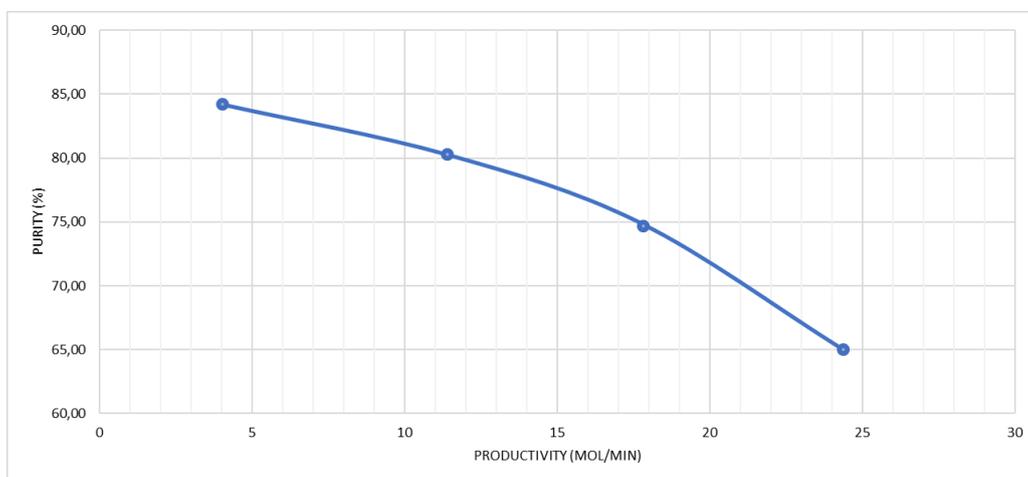


Figure 5.15 Steady state performance curve

## Dynamic oscillatory mode

In this case the design space has 6 dimensions: 2 performance indicators (purity and productivity) and four parameters. The same workflow will be followed as in the one-component case with the exception of optimization, since it is intended to perform a global study instead of determining optimal values of the parameters.

**Step 1.** The parameter space samples of the 4 cases shown below have a population of  $N = 100$ , uniform distributions are chosen for all the parameters and Sobol method is used.

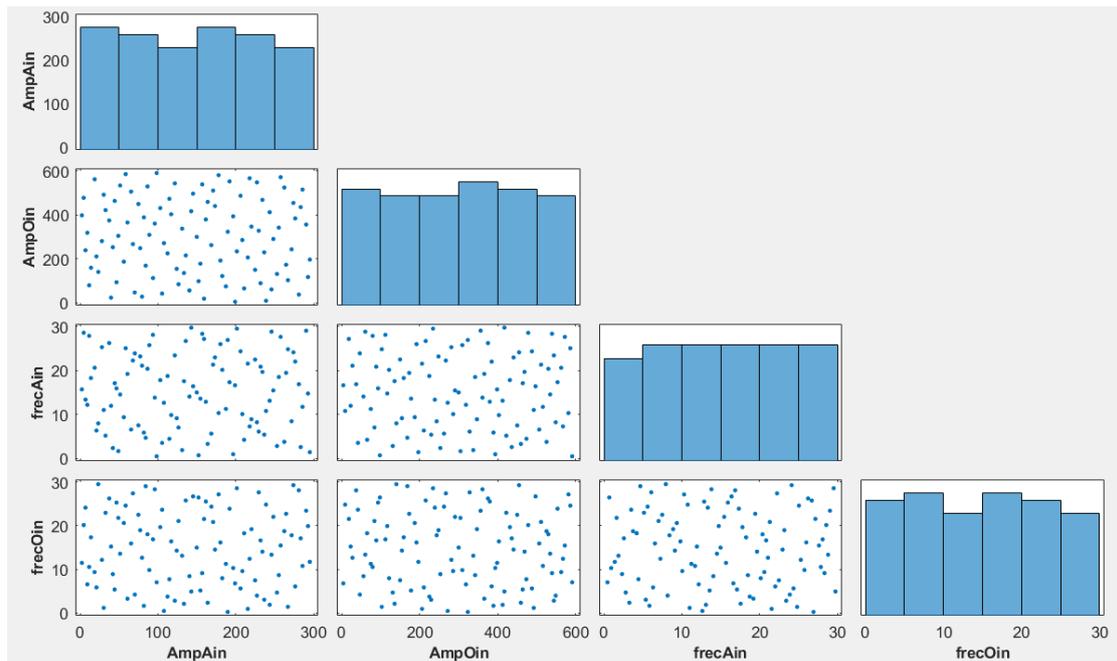


Figure 5.16 Multicomponent case 1 parameter sample

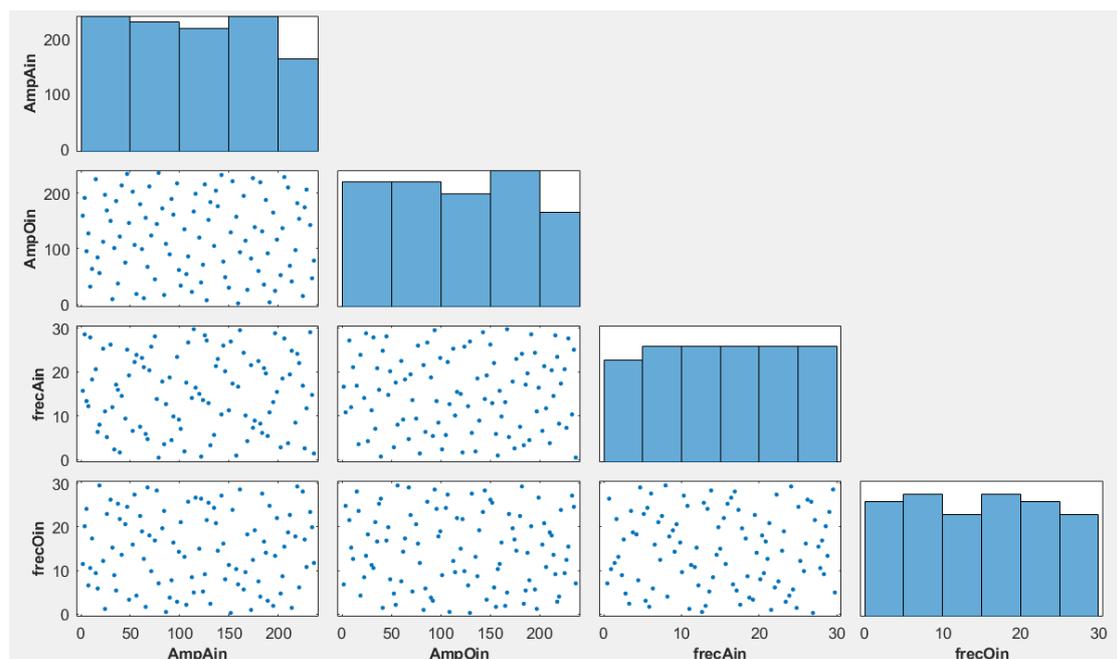


Figure 5.17 Multicomponent case 2 parameter sample

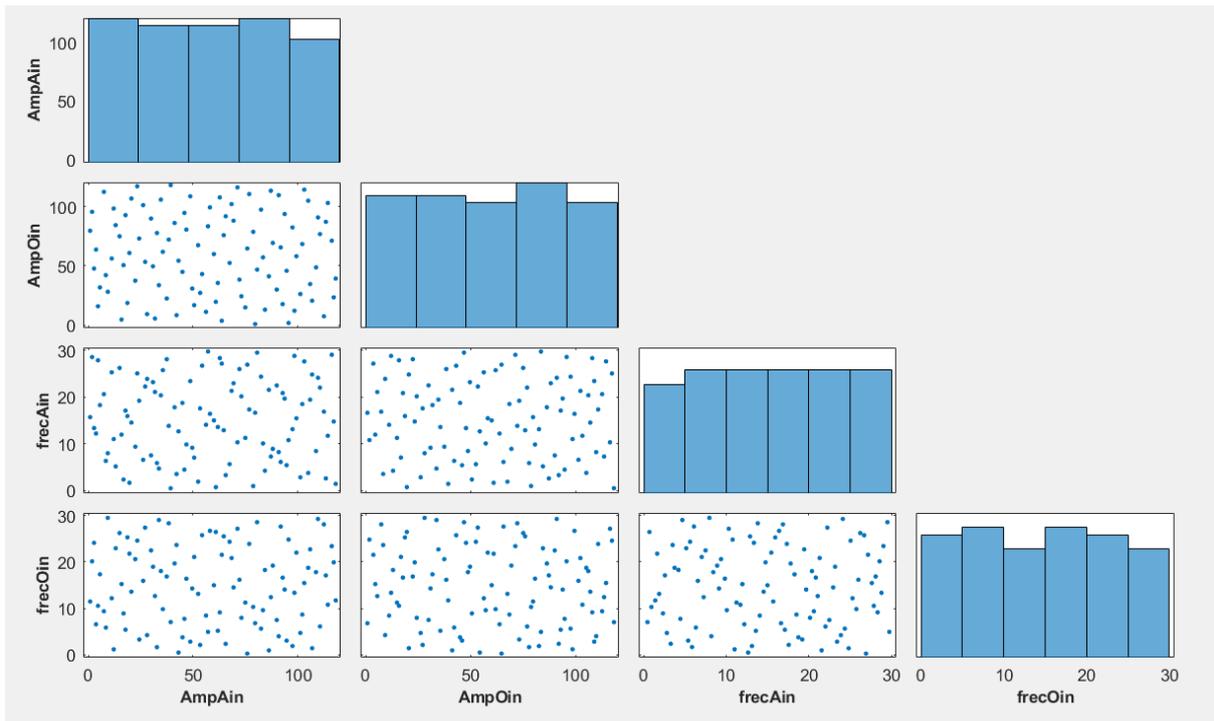


Figure 5.18 Multicomponent case 3 parameter sample

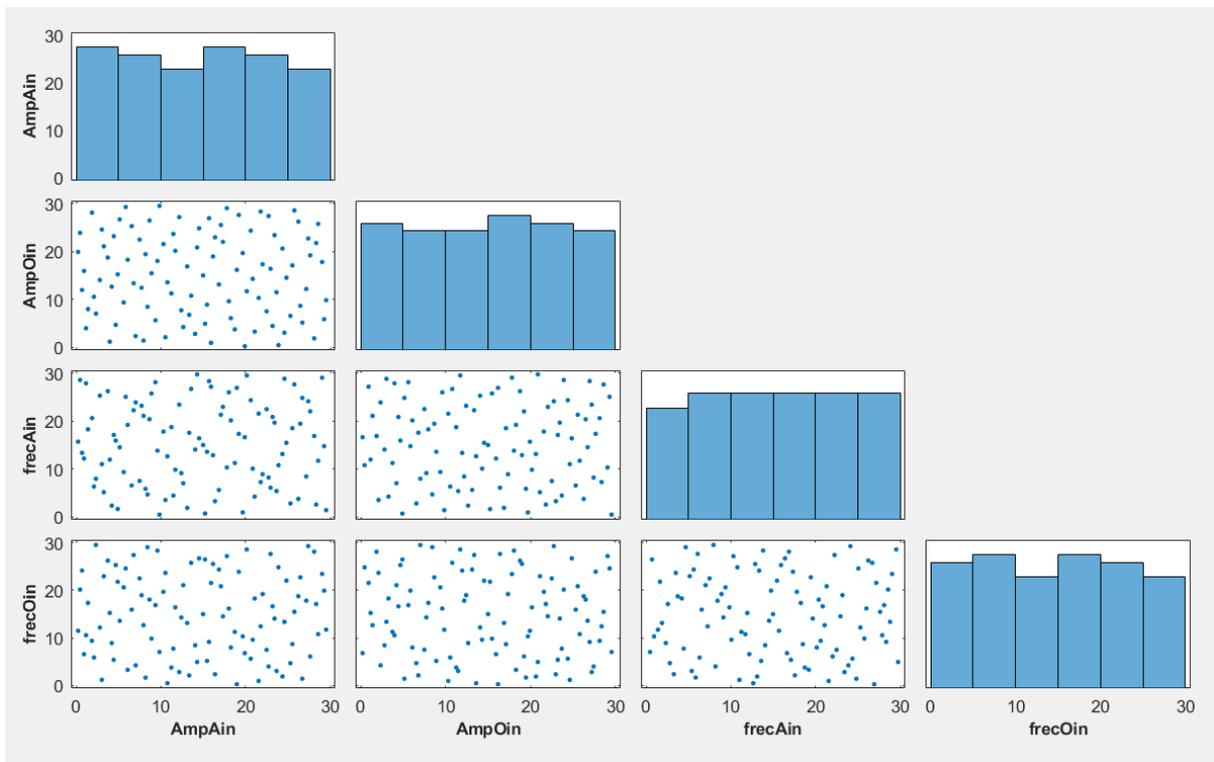


Figure 5.19 Multicomponent case 4 parameter sample

**Step 2.** In this case there are two objective functions: steady state productivity and purity. The two MATLAB functions used to specify the requirements again compute the average value between 40 and 200 minutes:

```
1  function vals=productivity(data)
2
3  -   Xsignal=data.Nominal.Sig1.Data;
4  -   Tsignal=data.Nominal.Sig1.Time;
5  -   idx = find(abs(Tsignal-20.01) < 0.05);
6  -   time=Tsignal(idx:length(Tsignal));
7  -   ssteadyoscillation = Xsignal(idx:length(Tsignal));
8  -   smean=mean(ssteadyoscillation);
9  -   vals = smean;
10
11 - end
```

Figure 5.20 Multicomponent productivity MATLAB objective function code

```
1  function vals=purity(data)
2
3  -   Xsignal=data.Nominal.Sig.Data;
4  -   Tsignal=data.Nominal.Sig.Time;
5  -   idx = find(abs(Tsignal-20.01) < 0.05);
6  -   time =Tsignal(idx:length(Tsignal));
7  -   ssteadyoscillation = Xsignal(idx:length(Tsignal));
8  -   smean=mean(ssteadyoscillation);
9  -   vals = smean;
10
11 - end
```

Figure 5.21 Multicomponent purity MATLAB objective function code

**Step 3.** Global Sensitivity Analysis is computed for each of the four cases with its respective parameter sample. Since there are two objectives functions and four parameters, now 8 scatter plots are needed in each case:

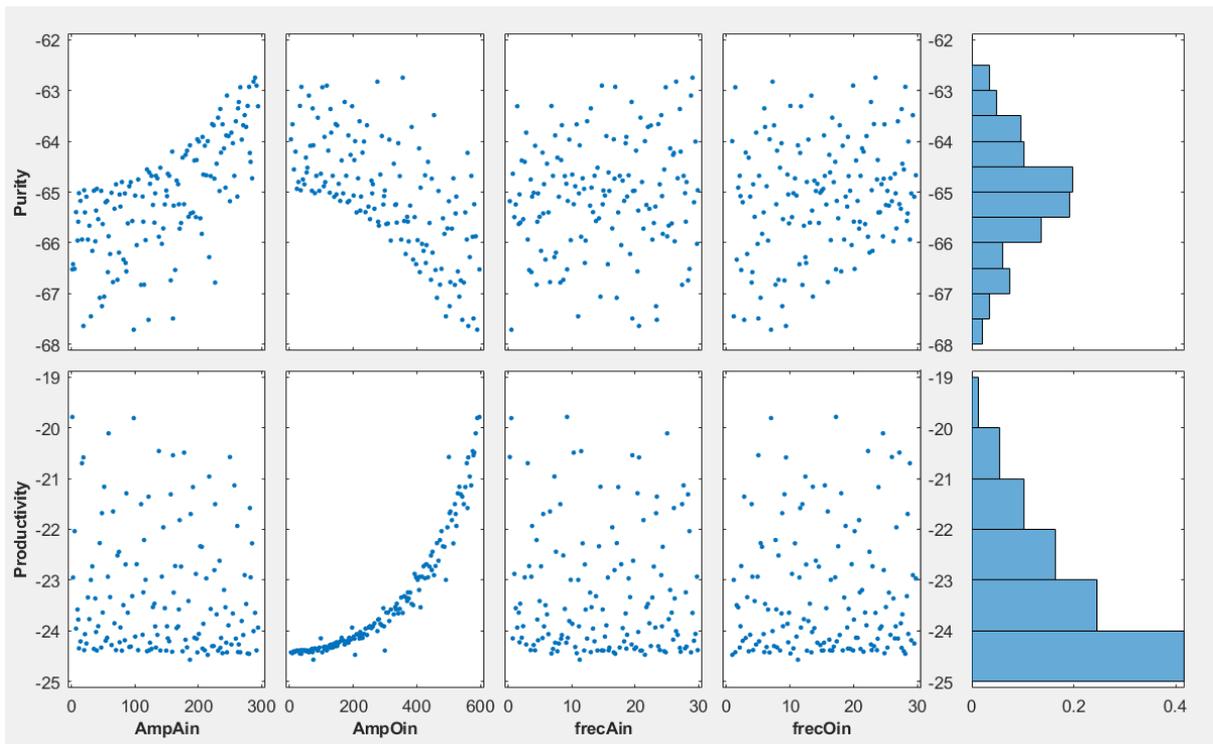


Figure 5.22 Multicomponent case 1 Global Sensitivity Analysis scatter plots

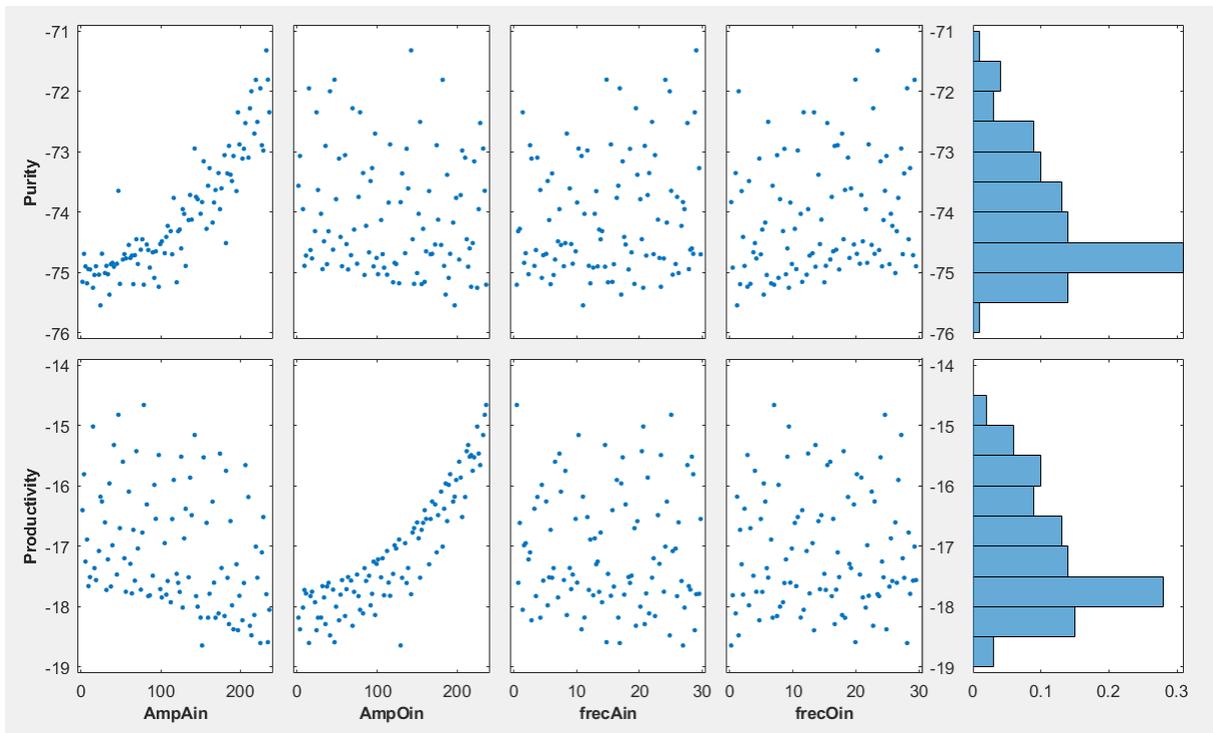


Figure 5.23 Multicomponent case 2 Global Sensitivity Analysis scatter plots

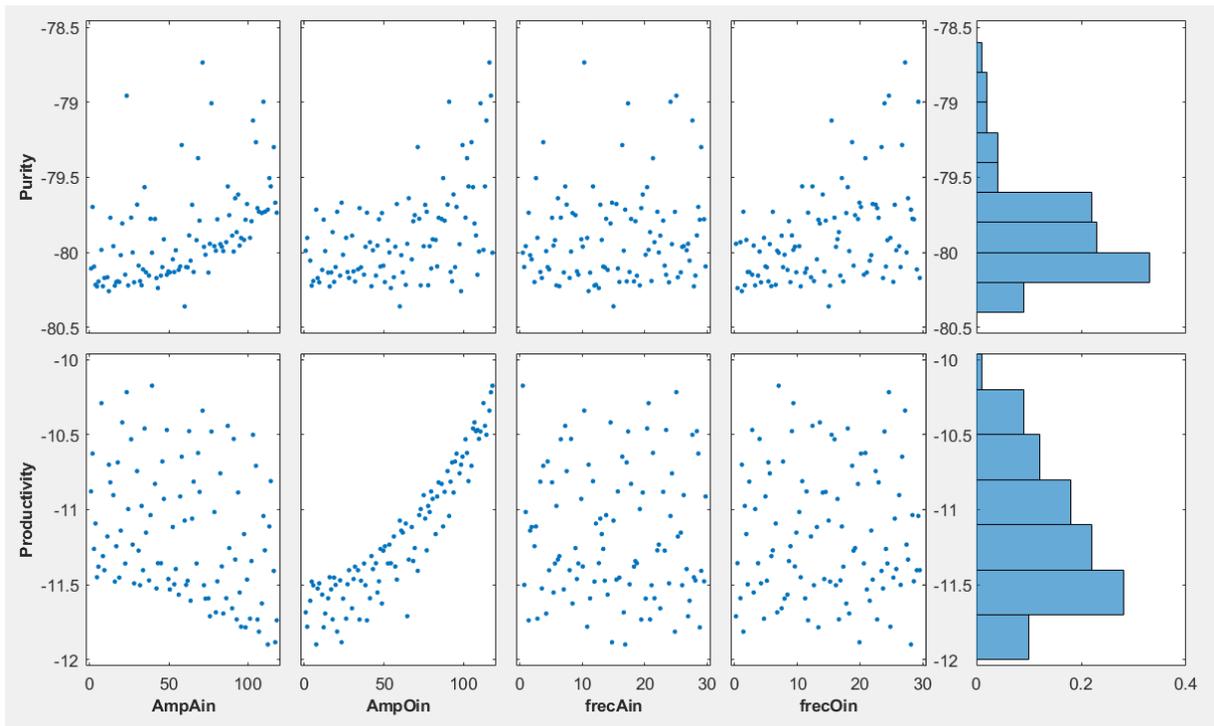


Figure 5.24 Multicomponent case 3 Global Sensitivity Analysis scatter plots

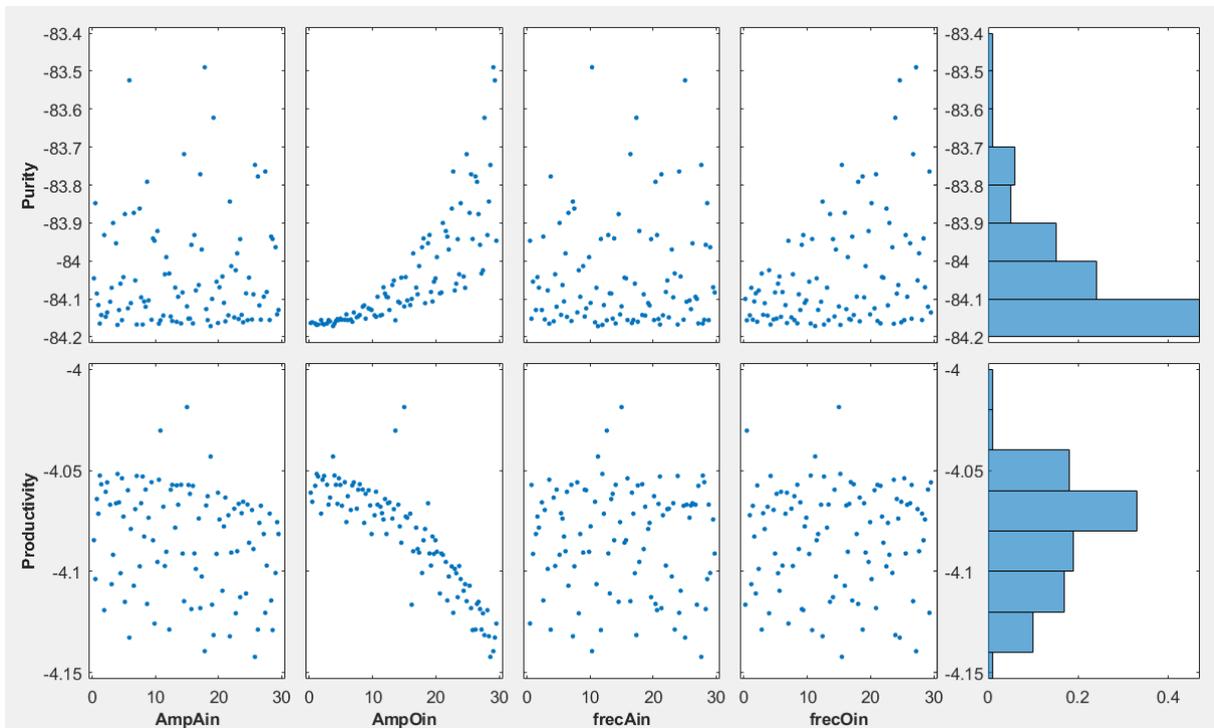


Figure 5.25 Multicomponent case 3 Global Sensitivity Analysis scatter plots

**Step 4.** These results show that although there are ranges of parameters that maximize one of the objective functions (Case 1 AmpOin vs. Purity scatter plot), there are no parameter ranges that simultaneously satisfy the two objective functions, therefore a second biased or restricted sample for certain ranges of the parameters is not necessary.

### 5.2.3 Results analysis

As already explained, in this case the comparison between the steady state and the dynamic oscillatory modes is made through the analysis of the Productivity vs Purity plot (Figure 5.15), for which the results of the four cases of the objective functions obtained in the simulation (Step 4) are exported:

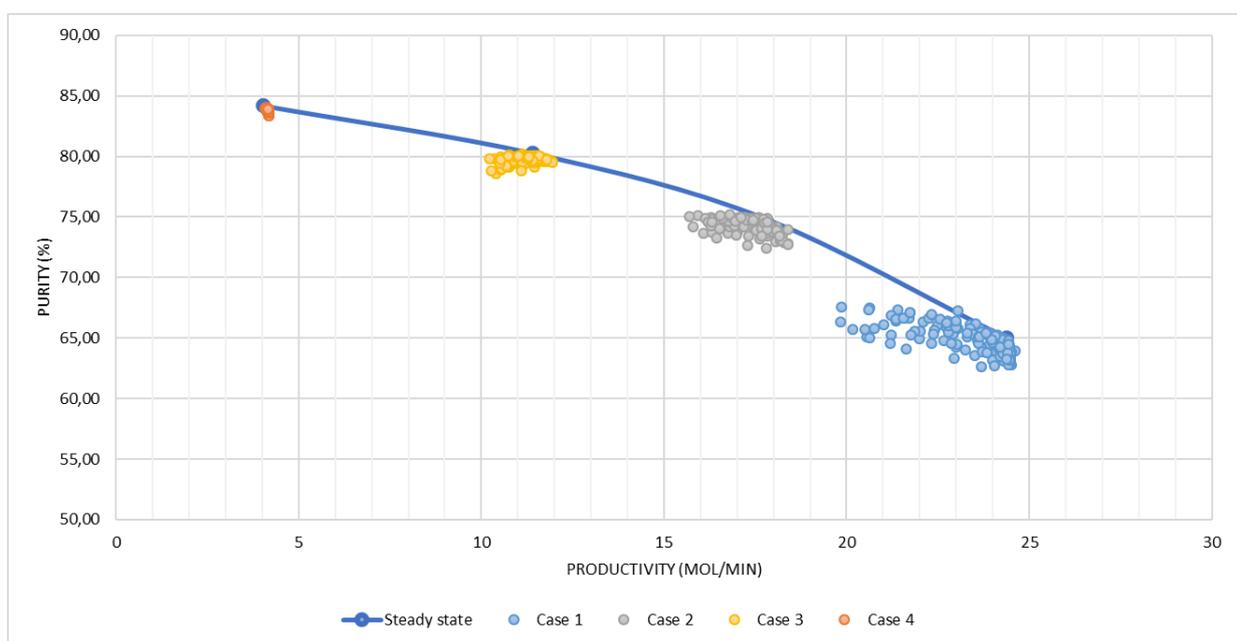


Figure 5.26 Performance comparison of steady state and dynamic oscillatory modes for the multicomponent case

In the graph it is observed that the points corresponding to the periodic dynamic mode are on the curve of the stationary mode or below it, meaning that there is no combination of oscillatory parameters that improve the stationary operation. In addition, an inverse functional dependence between productivity and purity is generally appreciated, if one variable increases the other decreases and vice versa.

On the other hand, it is verified that the dispersion of the points corresponding to the four samples of the periodic dynamic mode increases in cases of higher O/A ratios. This is because as shown in Table 5.8, case one has the widest range of available amplitudes (0 - 600) and therefore of dispersion due to high organic flowrate, gradually decreasing in the following cases.

## 6 SUMMARY OF CONCLUSIONS AND FUTURE WORK

Once the adopted solution has been executed and its results analysed, the following conclusions are presented according to the scope and limits of the work as well as the nature of the proposed objectives:

### **Regarding the general objectives**

As can be seen in the results of the solution adopted, the feasibility and suitability of the object-oriented simulation methodology (in this case Simscape) to fully address the modelling and simulation of real chemical engineering problems is fully demonstrated. These problems require the simultaneous solution of Partial Differential Algebraic equations (PDAE systems) such as the case of the dynamic study of solvent extraction of metals treated in this work. This methodology, as it has been shown, allows to overcome the limitations of traditional non object-oriented languages. MATLAB was developed as a classical scripting language for the typical small to medium engineering programmes, not being efficient for complex simulation applications that require languages with higher code economy, transparency and flexibility capabilities. On the other hand, block-oriented dynamic simulation tools such as Simulink, has a very specialised character, suitable only for causal systems modelled by ODEs that evolve with time, and not for an evolution also by user events as required in OO simulators.

The work shows that Global Sensibility Analysis through Monte Carlo Simulations implemented in the toolbox Simulink Design Optimization is a general (numerical) method that allows to study in a practical and global way (unlike optimization) the effect of forced oscillations on non-linear chemical processes. This method, unlike the analytical ones, is applicable regardless of the number of inputs to oscillate and the complexity of the input-output correlations of the system, being only the computational cost affected. Additionally, this method also achieves greater reliability of results throughout the operating range.

### **Regarding the primary specific objective**

As it corresponds, the valuation of the degree of improvement of the oscillations on the solvent extraction of metals is carried out separately for each one of the cases of study:

#### **Single component case**

In the single component extraction, with the application of forced oscillations to the inlet flowrates of the organic and aqueous streams, a significant reduction of about 25% in the amount of metal not recovered with respect to the steady state mode of operation is achieved.

However, this improvement is only possible with amplitudes of the aqueous stream close to its maximum admissible value, which would imply cost increases due to oversizing of the equipment. On the other hand, as can be deduced from the parametric study of the stationary mode performed in the analysis of the results, in general, it is more convenient to achieve the same improvement by slightly increasing the flow of organic (from 480 to 500 l / min), given also that it is usually recirculated in this type of processes.

### **Multicomponent case**

The analysis of results for the bicomponent extraction made by the global study of the Productivity vs Purity plot shows that it is not possible to achieve a better performance of the process through the application of oscillations, as dynamic operating points cannot be obtained above the curve of the stationary mode. Hypothetically it is considered that this could be explained by the similar non-linearity of the corresponding correlations (bivalent metals), which cause coincidental effects of the oscillations on both metals and no opposed (more product and less impurities) as required. On the other hand, since there is an inverse functional dependence between productivity and purity (if one variable increases the other decreases and vice versa) in this case it is not possible to consider improving the performance by modifying the inputs of the stationary mode.

### **Regarding the secondary specific objective**

The review and analysis of the characteristics and operating principles of solvent extraction, shows the enormous complexity of the internal mechanisms (molecular level) of the transformations and phenomena that occur in them. This requires in practice to have to assume large simplifications that make the models are black or grey boxes, and in which factors or ad hoc coefficients appear that arise from experimental correlations, and not from the application of theories, principles or fundamental laws, which is nothing but a sample of our degree of ignorance.

In this case we have opted for a macroscopic grey box model taking as constitutive equations phenomenological laws as the mass action law and Fick law of diffusion. In the same has been considered perfect mixing for the mixer tank and an ideal settler (complete separation), not taking into account the complex internal fluid dynamics of the process, since to study the effect of oscillations on it would be necessary to apply tedious CFD models.

The implementation of the model in Simscape, in addition to overcoming the limitations of traditional tools, provides relevant values such as: transparency and concision, since the code of the model is practically equal to the mathematical formulation of the same, generality, since the acausal implementation does not depend on the particular assignment of the inputs and

outputs of the model, and the native integration with the powerful MATLAB-Simulink environment. However, at the moment Simscape does not allow access to thermodynamic servers, which obviously supposes a serious limitation for its use in chemical engineering.

### **Regarding the academic objectives**

On this issue it is necessary to mention the high degree of difficulty that supposes the command of all the concepts methods and procedures proper techniques such as computer programming, the resolution of complex mathematical models and data science, that in fact overflow the academic curriculum of the chemical engineer. Nevertheless, the experience obtained with the realization of this thesis shows that new *user friendly* software such as the toolbox Simulink Design Optimization, enable the engineer, in a reasonable amount of time, expand its knowledge to correctly and efficiently use these techniques.

### **A reflection about the state of the art of the oscillations**

From the study I have made of the work done in this field to date, it follows that as in many problems of chemical engineering, the state of the art is at an empirical level in which at most the effects of oscillations are attributed to the mathematical implications of the non-linearity of the model correlations. This assumes de facto that we find the complex situation of the so-called *inverse problems* (Bunge, 2004), in which the causes must be inferred from the effects. In fact, what we are certain about is that oscillations perturbate equilibrium producing an alternating series of equilibrium states (with minimum energy and maximum entropy) causing the mean value of the concentrations to be modified.

This is reflected in engineering in the use of black-box models with their corresponding correlations between inputs and outputs, such as the one obtained in this thesis for the effect of oscillations.

Logically, I consider that the foundation of this field would suppose the identification and especially quantification of the interaction mechanisms at the intra and intermolecular level (mixture, Van der Waals forces, dipole-dipole, ...) responsible for the effects of the oscillations, which is nowadays an open, highly complex issue that is in an initial stage and corresponds to a level of basic or fundamental research.

## **Possible future work**

This kind of work arises logically from the possibility of exceeding the limits corresponding to this thesis, which have already been analysed in section 1.2. Consequently, it would be necessary to consider those aspects that have not been taken into account but keeping the approach and methodology of the thesis.

With regard to the modeling of the process, we can advance towards a more complete and realistic model that would incorporate the complex internal fluid dynamics through CFD, non-ideal thermodynamics and rigorous mass transfer (Maxwell-Stefan diffusion) modelling. Also metals of different valences could be contemplated, which would suppose a greater degree of non-linearity.

Regarding the effect of the oscillations, it would be possible to extend its study exploring the modulation of the rest of the inputs, in case they are industrially viable, including non-sinusoidal oscillations.

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