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## **SIMULATION OF PROCESSES WITH HIGHLY CONCENTRATED SOLUTIONS: AN EcosimPro LIBRARY FOR ENVIRONMENTAL APPLICATIONS**

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### **Abstract**

*This presentation gives a summary of the work carried out by the Research and Development Division of Técnicas Reunidas in collaboration with Empresarios Agrupados and Bristol Water during the period 1999 – 2000 for the European Union SIMTECO project. A study was carried out of the possible applications of EcosimPro in the research and development division, and the improvements that the use of a versatile simulator like EcosimPro could offer in the development of industrial processes. To this effect, the basic process selected for simulation was the recovery of zinc with a high level of purity by a combined extraction cycle with solvents and electrolysis, using raw materials or zinc compounds either in liquid or solid form. This process was selected because it contains the majority of the stages normally employed in the recovery of heavy metals from industrial and mining wastes.*

**Key words:** Treatment of industrial waste, zinc extraction, lixiviation, neutralisation, electrolysis, sedimentation, filtration.

### **1 INTRODUCTION**

The research activities of the research and development division of Técnicas Reunidas (TR) basically focus on the recovery of spent chemical reagents, the recovery of heavy metals from liquid and solid wastes, the benefit of secondary materials, etc.

The main objective of our research is to develop a process for industrial application. Before the leap can be taken from the stage of laboratory research on a process to its introduction on the commercial market as industrial plant, the new process is tested in a pilot plant to verify its technical and economic validity.

Such tests involve numerous costs for installation, operation and labour, reagent and electricity consumption, etc, which can be minimised with the use of a dynamic simulator like EcosimPro.

Another fundamental advantage in using simulators in these cases is the reduction in time needed to obtain optimum operating conditions, since the speed of simulation is far higher. This combined with the possibility of using it as a vehicle for training operators makes simulation tools essential for the development of new processes.

Owing to a general lack of knowledge of these new processes, the tool to be used must be easy to program (so that it would not take more time to program the tool than it would to build the pilot plant), flexible and versatile (so that it can be easily reprogrammed as research progresses), intuitive and user friendly (so that the operators being trained with it can handle it as they handle the industrial plant, without knowing its internal program).

EcosimPro fulfils these requirements and therefore serves not only as a good support tool for research into new technologies, but also as a marketing tool for such processes.

## 2 APPLICATION OF ECOSIMPRO TO THE TREATMENT OF WASTES

In order to assess the real benefit of using EcosimPro in the processes developed in the Research and Development Division of Técnicas Reunidas, it was proposed that this simulator be applied to an electrolytic zinc extraction process.

It is a process of purification of a solid or a liquid by extraction with solvents and its subsequent subjection to electrolysis to obtain metal zinc with a high level of purity.

The solid or liquid that feeds this process may have different origins, such as:

- Dust from spent domestic batteries
- Raw materials and natural zinc secondaries
- Treatment of mining wastes
- Treatment of zinc oxides from different industries like the manufacture of beer cans
- Any matter with an acceptable zinc content

The library has been built up without taking into account either energy or thermal balances; consideration has been given only to the chemical reactions produced and their evolution in time.

The library is comprised of four ports and seven basic components.

### PORTS:

- Liquid
- Solid
- Pulp
- Organic

### COMPONENTS:

- Lixiviation
- Neutralisation
- Extraction
- Stripping
- Thickener
- Filter
- Electrolysis

To conclude the study, a comparison was made between the improvements that the use of EcosimPro can offer and other calculation and/or simulation tools, and this new tool made a favourable impression.

## 2.1 ADVANTAGES OF ECOSIMPRO OVER SPREADSHEETS

The advantages that this tool has over spreadsheets like EXCEL, Lotus 123, etc, are fairly clear:

- EcosimPro can carry out a large number of experiments without having to change the formulation; that is, the boundary conditions which define the system can be changed without having to reformulate all the equations (there is no need to solve for any variables based on the new boundary conditions).
- It offers the possibility of introducing kinetic equations, if known, in the study so the user can then see how the species evolve at different points of equilibrium.
- It allows the study of the transition points of the system when any change is introduced, for example: change in equilibrium due to a change in the temperature, accumulation of volume, emptying of tanks, etc.

## 2.2 IMPROVEMENTS OFFERED BY ECOSIMPRO COMPARED TO OTHER SIMULATORS

Significant differences are also evident when EcosimPro is compared with other specialised dynamic simulators in the chemical industry, such as ASPEN or METSIM, especially with regard to its simplicity and versatility.

- Elements created previously can be adapted with ease; for example, an equation can be replaced by a data table, or a kinetic equation can be changed for another which is more suited to the new system.
- State-of-the-art elements not included in the prefabricated databases of ASPEN or METSIM can be easily created, such as reverse osmosis units, ozonisation, organic material reducing agent, ionic-exchange resins. In addition, these components can be created as complex as the user's mathematical and chemical knowledge of the process permits (ranging from a simple mass balance study of a single steady-state ion, to a kinetic study including mass balance of infinite compounds and ions, energy and heat balance, hydraulic studies, etc.)

### **2.3 IMPROVEMENTS OBTAINED WITH THE USE OF SMARTSKETCH**

The SmartSketch program associated with EcosimPro allows the user to assign colours to each port, assign icons to each component, and create new, more complex components based on the basic components by graphic connection of their ports.

The use of this combined tool makes the use of EcosimPro far more intuitive, because it can be handled without having to know how the mathematical formulation is obtained.

This tool allows EcosimPro to be easily employed as a training vehicle for new operators or for operators of new processes.

## **3 PORTS CREATED FOR THE WASTE TREATMENT PROCESS**

The ports are points of connection between one component and another. In chemistry they are similar to fluid flows.

They are used to transmit the properties of the fluid from one port to another

Which variables have to be input to a port? All those that are transmitted from a reaction chamber or a tank to another port (outlet of one tank – inlet of another) without changes, even if they change inside a reaction chamber. They are variables of the following types: concentrations, mass flows, temperature of the current, densities, viscosities, etc. In summary, everything which characterises a solid, or a fluid, or an electric current.

For this project, four different ports have been defined.

### **3.1 LIQUID PORT**

This port reproduces any aqueous solution of metal sulphates and sulphuric acid characterised by its mass flow, pH, density, concentration of different metal ions, temperature, etc.

The port is limited to solutions in a sulphate medium by introducing an equation which adjusts the density in this medium based on the metal concentrations. But it can adapt to an aqueous solution of metal ions, eliminating that equation and introducing the value in each case as a boundary condition, or adjusting the corresponding equation in each case.

### **3.2 SOLID PORT**

This port defines a solid flow of metal oxides of variable concentration.

As with the previous port, limitation to these types of elements is imposed by the density calculation. However, by limiting that calculation initially and defining that parameter from outside, the same port can be used for any type of solid.

The remaining variables defining the port are the mass flow and the metal composition of the element.

This port can be improved with the introduction of parameters such as the resting angle, particle size, etc, which may help to define the solid.

### **3.3 PULP PORT**

This component is a suspension without dissolving a solid in an aqueous solution.

It transmits the same properties as the two previous ports as well as some that are specific to pulps, such as pulp density, etc.

This port was created because of the need to work with solid-liquid suspensions during the first stages of the process in this project.

### **3.4 ORGANIC PORT**

This port represents a very specific organic liquid solution used as a selective zinc extractant which is immiscible in water, as is phosphoric hexyl di-ethyl acid (D<sub>2</sub>EPHA) dissolved, if necessary, in kerosene.

The properties transmitted by this port are the same as those of any liquid port, with the exception of pH which is only defined in the liquid solutions.

In addition, a new parameter which defines the D<sub>2</sub>EPHA / kerosene ratio used in each experiment should be included. The molecular weight of the aforementioned organic compound (D<sub>2</sub>EPHA) is also defined as a constant.

## **4 BASIC COMPONENTS OF THE LIBRARY**

We can liken the word “Component” used in EcosimPro with something much more intuitive in chemistry, such as: reactor chambers, storage tanks, agitator tanks and other physical parts which comprise a chemical process.

To define a component, expressions must be used showing how the port variables change in the interior of such a component (variations that take place between the In and Out ports). Therefore, equations of the following kind have to be included:

$$T_{in} = T_{out} \quad (1)$$

$$C_{out} = 10 C_{in} \quad (2)$$

If necessary, these components include variables pertaining to the tank, reagents or reactions, such as: efficiency of the reaction, tank volume, temperature of the reaction (different to the input flow temperature).

It should be noted that the connections between components must be made between ports of the same characteristics.

The following are the basic components in this library:

- Lixiviation
- Neutralisation
- Extraction with solvents
- Stripping
- Thickener
- Filtration
- Electrolysis

Once the components had been built, numerous experiments were carried out to validate them.

In addition, numerous tests were carried out on the connections between different components that had been created, in order to validate the basic components and to be able to simulate the complete process of zinc extraction —electrodeposition.

#### 4.1 LIXIVIATION

This component represents a lixiviation reaction chamber. The chemical reaction studied in the component is the dissolving of metal oxides using sulphuric acid as the lixiviating agent. This reaction produces the corresponding metal sulphate and water:



(The solids are underscored)

This component therefore receives two inflows: a solid current (represented by a solid port) with the metal oxides, and a liquid current (represented by a liquid port), which produces a pulp (pulp port) composed of the aqueous solution and the residual solid which has not reacted with the acid.

Figure 1 shows the icon assigned to this reaction chamber with SmartSketch. Also shown are the In and Out currents:

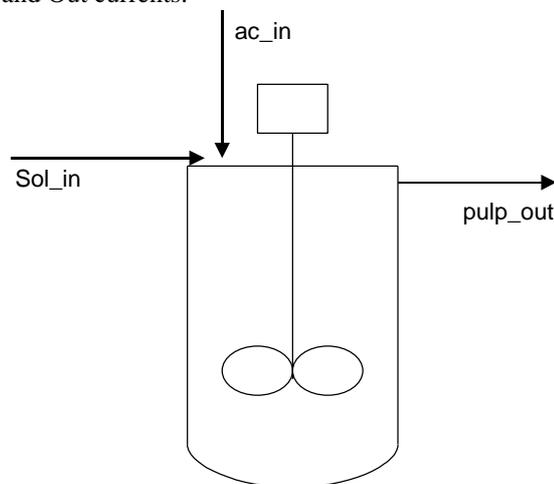


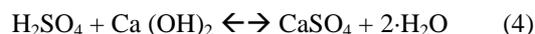
Figure 1: Representation in SmartSketch of the Lixiviation Component

For the time being, the kinetic simulation of this reaction has been made to depend on the pH of the final pulp and the size of the particle of the initial solid. In any event, we have assumed a reaction in excess of acid.

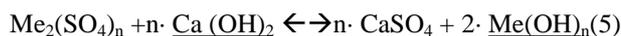
#### 4.2 NEUTRALISATION

This component represents a neutralisation reaction chamber of sulphuric acid with calcium hydroxide. Two types of different reactions take place in these chambers:

- The neutralisation of sulphuric acid with calcium hydroxide. In this process there is a loss of pH between the In pulp and the Out pulp ports.



- A precipitation during which a solid appears. This precipitation takes place when a particular compound concentration becomes larger than its solubility product. In this event, the precipitation reaction of the metal sulphates are studied as metal hydroxides with calcium hydroxide:



(The solids are underscored)

This component therefore receives two inflows: a solid current (represented by a solid port) which represents the lime, and a pulp current (represented by a pulp port) which may stem from the previous stage, which produces a pulp (pulp port) composed of the aqueous solution and the solid formed in the precipitation reaction.

Figure 2 shows the icon assigned to this reaction chamber with SmartSketch. Also shown are the In and Out currents:

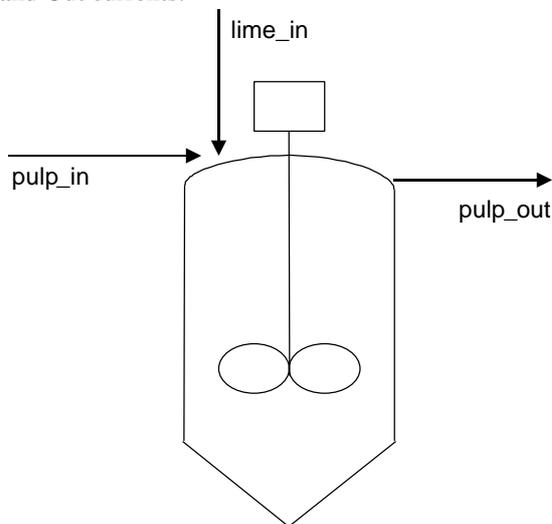


Figure 2: Representation in SmartSketch of the Neutralisation Component

This component is formulated assuming that the precipitating agent is lime, that the lime neutralises the sulphuric acid, that the reduction in pH which takes place is responsible for the precipitation of hydroxides. It is also assumed that the lime is added as a solid and not as a pulp and, in addition, that this solid does not contain moisture.

Another important assumption is that neutralisation take place at 100%, which means that there will be no  $\text{Ca}(\text{OH})_2$  left without reacting on the Out port pulp.

### 4.3 EXTRACTION WITH SOLVENTS

This component represents an extraction unit with solvents. It is a chemical process by which a component of a liquid solution is distributed between two immiscible liquids (aqueous and organic).

It is quite a complex physical-chemical process which takes place in several stages:

- - Ionic exchange between the aqueous stage and the organic stage
- Separation by gravity of the two immiscible stages, owing to the difference in density between the organic stage and the aqueous stage

The process of extraction with solvents is one in which a metal that is initially dissolved in the aqueous stage (solute) changes with the protons which are present in the molecules of the organic stage.



It is very important that the two stages mixed for this reaction be immiscible. What this means is that the two phases must separate to give way to a net interface.

With these reaction chambers the separation of liquids takes place due to the difference in density between them, so that the more dense liquid falls to the bottom of the settler, while the lighter liquid remains suspended above the other one.

This component receives two liquid inflows (In ports), one of them organic (organic port) with the distribution in the corresponding metal already carried out. It also has two associated Out ports.

Figure 3 shows the icon assigned to this reaction chamber with SmartSketch. Also shown are the In and Out currents:

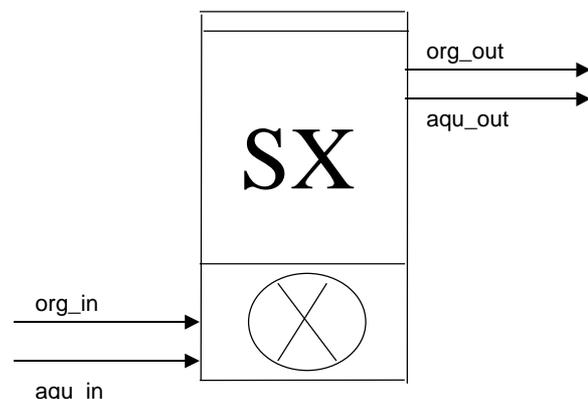


Figure 3: Representation in SmartSketch of the Extraction Component

This component is programmed with a series of approximations between which we can emphasise that the extraction agent is  $\text{D}_2\text{EPHA}$ . It is adjusted to experimental curves, the proton concentration in the aqueous stage is infinite and the liquid-liquid separation stage is complete; in other words, the in and out volumes are the same.

### 4.4 STRIPPING

This component is used to simulate the opposite reaction to that produced in the extraction unit with solvents.

As with the previous component, it simulates a complicated process which takes place in two stages:

- Ionic exchange between the aqueous stage and the organic stage
- Separation by gravity of the two immiscible stages, owing to the difference in density

One process of stripping is that in which a metal dissolved in an organic stage is changed for protons in the aqueous solution. In the case being simulated, the protons come from the sulphuric acid, although they may also come from the chloric acid. The reaction is completely the opposite to that addressed in point 4.3, that is:



This component receives two liquid currents (ports), one of them is organic (organic port), with the distribution in the corresponding metal already carried out. It also has two associated Out ports.

Figure 4 shows the icon assigned to this reaction chamber with SmartSketch. Also shown are the In and Out currents:

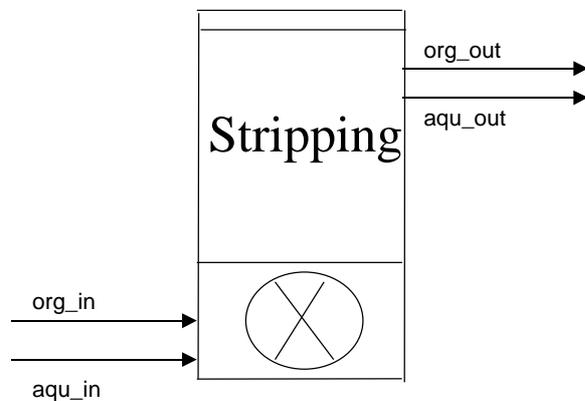


Figure 4: Representation in SmartSketch of the Stripping Component

This component is programmed with a series of approximations between which we can emphasise that the extraction agent is D<sub>2</sub>EPHA. It is adjusted to experimental curves, the proton concentration in the aqueous stage is infinite and the liquid-liquid separation stage is complete; in other words, the in and out volumes are the same.

#### 4.5 THICKENER

This component studies the physical process of sedimentation. Through this process a pulp is separated in two stages; one is the clarifying stage and the other is the pulp stage which has a much greater content of solids.

The equipment being simulated in this section is a thickener-clarifier. The objective of the thickening process is to increase the concentration of solids in the initial current, while the objective of the clarification process is to eliminate the solids in suspension from the initial solution to obtain a clear, aqueous stage. These two processes take place simultaneously.

It is a physical process, or chemical if we use an agglomerating agent, by which the solid particles are deposited on the bottom, while the liquid collects with much less concentration of solids in the upper part of the tank.

This component therefore has a single In current (one pulp port), but two Out currents (two pulp ports), one with very little pulp density and the other with a far greater pulp density.

Figure 5 shows the icon assigned to this reaction chamber with SmartSketch. Also shown are the In and Out currents:

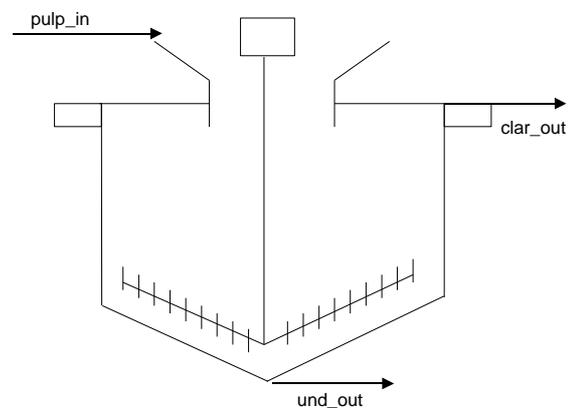


Figure 5: Representation of the Thickener Component chosen for SmartSketch

This component is based on the calculation of a unit area depending on the concentration of metals in the initial pulp solid, on the density of the pulp, and on the sedimentation temperature. The tabulation of this unit area is based on experimental data obtained by adding an N-100 flocculant in different quantities.

#### 4.6 FILTER

This component represents an ideal filter. The main objective of a filter is to achieve the complete separation of a liquid-solid mix by making the initial pulp pass through a porous barrier which lets most of the liquid through and completely prevents the solid particles from passing.

An ideal filter is one that manages to completely separate the solid, getting two currents in the Out port: one liquid current (represented by a liquid port) completely free from solids, and one solids port (one pulp port) which exclusively retains water owing to the moisture of the mass.

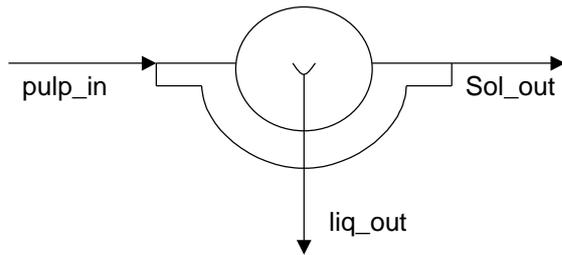


Figure 6: Representation in SmartSketch of the Filter Component

As mentioned previously, it is the representation of an ideal filter; in other words, the filter is infinite and completely impedes the passage of the solid, and the behaviour is more like that of continuous filters than that of the Buchner-type discontinuous filters.

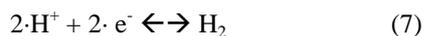
Variables which are important for filtration, such as mass thickness, filter pressure, etc, have not been taken into account during the programming of this filter.

#### 4.7 ELECTROLYSIS

This component represents the electrolytic reaction of zinc to electrolysis to produce metal zinc, including a recirculation current with which a lot more electrolyte is dissolved. It is a very complex system in which it is possible to obtain metal zinc plates with a purity greater than 99.999%.

In these kinds of reaction chambers, several reactions take place simultaneously:

*Cathodic Reactions:*



Where  $\text{Me} = \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Cu}^{2+} \dots$

*Anodic Reactions:*

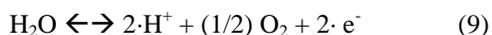


Figure 7 shows the representation of this component in SmartSketch.

It is a component with a single liquid In port (liquid port) and two Out ports, one liquid port and one solid port comprising the metal zinc plate. In addition it has two other liquid interconnected ports, one In port and one Out port, which represent the electrolyte recirculation current.

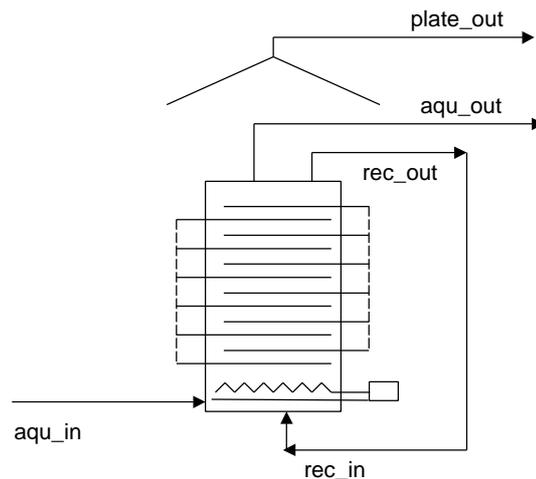


Figure 7: Representation of the In and Out Currents of the Electrolysis Reagent

This component manages more than 110 variables pertaining to the system, in addition to those of the ports, which makes it a very complex component to program.

The limitations of this component stem from the fact that it only studies the reaction of zinc deposits; the other reactions that occur are considered as parasites. It has also been considered that the extraction of zinc is continuous, and that the current applied is continuous and does not oscillate.

## 5 COMPONENTS RESULTING FROM THE COMBINATION OF BASIC LIBRARY COMPONENTS

The library created by Técnicas Reunidas contains three components which have been built with SmartSketch by combining different basic components.

These new components have been created with a view to obtaining a final (very complex) component which is capable of simulating the complete chemical process of purification-extraction of extremely pure zinc from different raw materials.

### 5.1 PRELIMINARY TREATMENT

This component was created by joining the lixiviation, neutralisation, thickener and filter components in series.

This component represents the conditioning stage of the raw material used in each case. The fact that the process begins with lixiviation indicates that in this case the matter that feeds the system is solid.

In the Out port of this system we obtain (in the filter) a solid free of zinc, and a liquid with characteristics

which make it suitable for treatment with solvents during extraction.

## 5.2 SX CIRCUIT

To create this component, three extraction reagents and two stripping reagents are connected, with cross-current in the organic and liquid ports.

This stage permits purification of the zinc solution, preparing it in order to obtain suitable electrolyte to extract the zinc (see Figure 8).

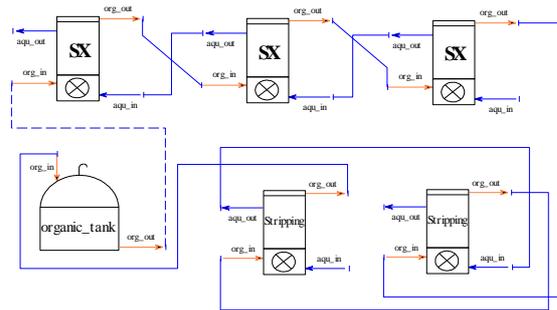


Figure 8: Connections between the Extraction Mixers-Settlers obtained with SmartSketch

This component not only serves to validate the components which are created, but also to perform some engineering calculations; for example, to verify, in an easy way, the number of stages necessary to obtain good zinc extraction and stripping.

## 5.3 ZINC PROCESS

This is the main objective of this library. It represents each one of the reagents and currents which appear in the zinc production plant. Thanks to this component, important data can be obtained on the behaviour of the plant when all the currents are connected.

It can also be used to verify how certain reactions are going to be affected due to the evolution of the previous stage, thus being able to see how much time is needed for the plant to stabilise, which parameters are affected and to what extent, and above all to check how changing one parameter in a reagent affects the rest of the process.

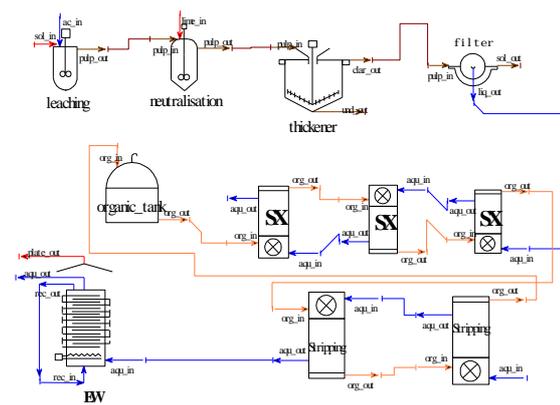


Figure 9: Sketch of the Complete Zinc Production Plant

In reality, it is a system in which we have connected a lixiviation stage, a neutralisation stage, a thickener, a filter, three stages of extraction with solvents, two stripping stages and one electrolysis reagent.

This process is very similar to the one installed in PROCES, S.A. in Barcelona for the treatment of domestic batteries.

## Acknowledgements

The European Economic Community, since the acceptance of SIMTECO as an ESPRIT project has made the creation of the library possible.

Empresarios Agrupados, for their technical support throughout the project.

Bristol Water, for their collaboration in the project.

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