

**ISEC '96 - INTERNATIONAL SOLVENT EXTRACTION
CONFERENCE**

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R.E.S.EX A COMPUTER SIMULATION PROGRAM
FOR RARE EARTH SEPARATION PROCESSES

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ABSTRACT

Lanthanides are most commonly separated using complex solvent extraction circuits.

By ENEA, a simulation code has been developed called R.E.S.EX. (Rare Earth Solvent Extraction) which algorithm is able to simulate a solvent extraction battery up to 200 stages, using different configurations.

The contemporary utilisation of an equilibrium data bank and of a simulation code allows the theoretical study of new rare earth separative processes or the optimisation of existing ones. As an example of this strategy are reported the results of the Pr/Nd separation in TBP 50 % in aromatic solvent.

INTRODUCTION

The separation of the lanthanides is usually accomplished using a complex solvent extraction circuits⁽¹⁾.

Optimisation of the circuits is becoming increasingly important.

Numerous reasons exist for the lack in the development of solvent extraction simulation programs. Probably the main reason is that solvent extraction circuits are inherently more complicated than, for example, distillation circuits.

A further reason is that the equilibria of solvent extraction is complicated. The equilibrium frequently can only be empirically understood and correlated. Extrapolation beyond experimental conditions can result in gross errors.

As the number of industrial processes and plant based on metallurgical separative techniques is growing up, larger attention is focused on simulation codes, as a tool to optimize the process and the plant design.

Several methods for analyzing liquid-liquid circuits have been developed. Graphical methods such as the McCabe-Thiele diagram have been used for decades. The graphical method becomes unmanageable when several species are present, large numbers of stages are required, and scrubbing and stripping are involved.

DESCRIPTION OF THE SYSTEM MODE

By ENEA, a simulation code has been developed called R.E.S.EX. (Rare Earth Solvent Extraction)⁽²⁾ which algorithm, shortly described in the next section, is able to simulate a separation battery up to 200 stages, using different configurations.

In particular it is possible to simulate, see Fig.1, both a battery utilized as a normal countercurrent equipment and with partial or total reflux of aqueous and/or organic phases.

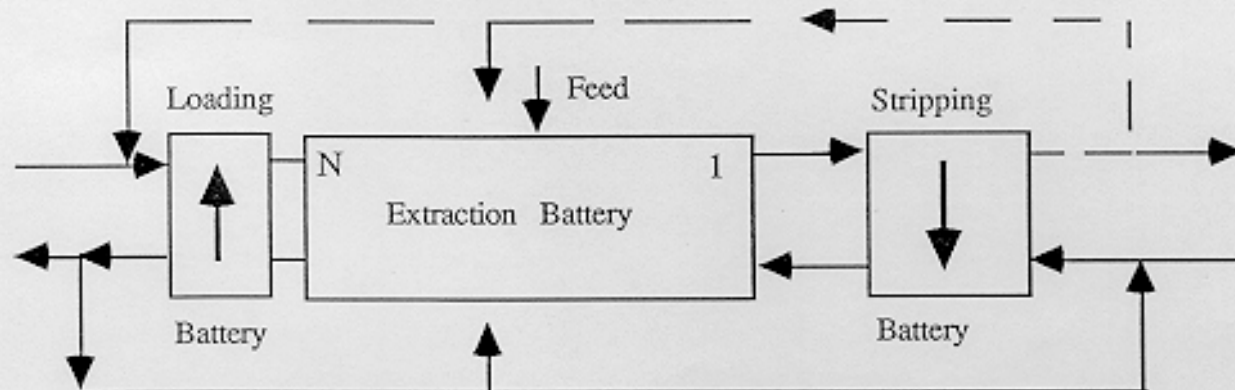


Figure.1 General configuration of an extraction battery with partial or total reflux for aqueous and/or organic phase.

The total reflux method was employed in the past years⁽¹⁾ in the preparation of Lanthanum, Praseodymium and Neodymium using TBP as extractant.

Also Yttrium was obtained utilizing a partial reflux battery as well as Samarium and Gadolinium with DEHPA extractant.

CALCULATION PROCEDURE

For both dynamic and steady state options, the calculation proceeds from stage 1 through the last stage specified by the user for successive time intervals, beginning at time zero with pure aqueous media and pure solvent in the bank⁽³⁾.

For steady state calculations, an arbitrary time interval of unity is used which has no relation to real time.

In that case, "time" merely corresponds to the number of iterations to that point in the calculation.

The calculation is based on the concept of "well mixed tanks", see Fig. 2.

The rate of change in the inventory of a given component in either the mixer or a settler zone is proportional to the flow of that component into the tank less the component flow out, assuming that the concentration leaving corresponds to the uniform concentration in the well mixed tanks.

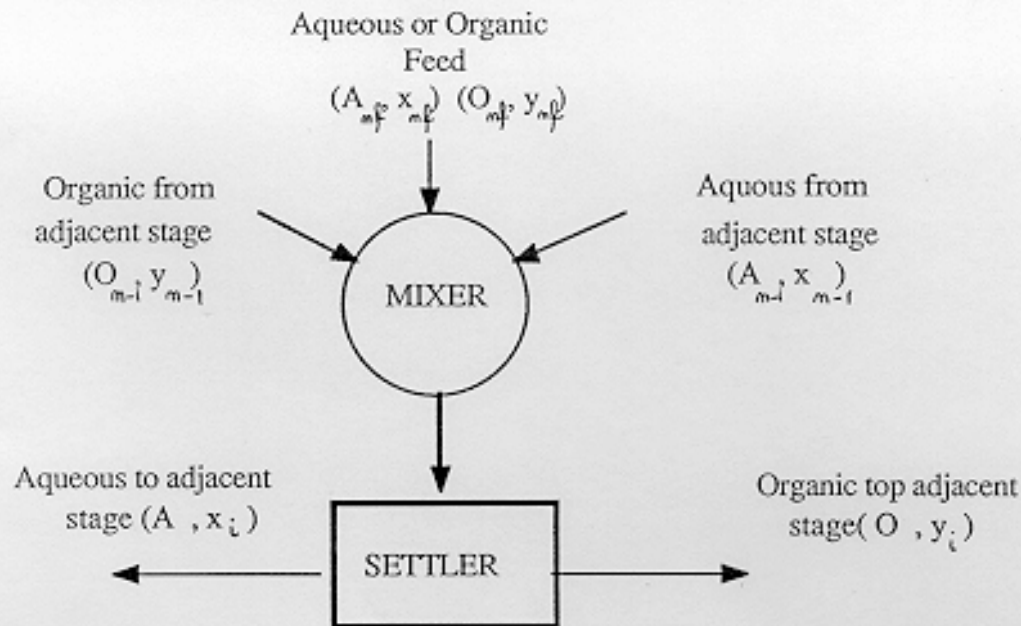


Figure.2 General material balance for a "well mixed" mixer-settler stage.

The differential equation describing that material balance

$$V_{ma} \frac{dx}{dt} + V_{mo} \frac{dy}{dt} = A X_i + O y_i - A x' - O y'$$

is translated into finite difference form:

$$V_{ma} \frac{\Delta x}{\Delta t} + V_{mo} \frac{\Delta y}{\Delta t} = A x_i + O y_i - A x' - O y'$$

with the general assumption coming from the material balance, and introducing the stage efficiency and the distribution equilibrium between phases, we can solving for x:

$$x = \frac{A(x_i - \frac{x'}{2}) + O \left\{ y_i - \frac{1}{2} [y_i (1-E) + y'] \right\} D t + V_{ma} x' - V_{mo} [y_i (1-E) - y']}{V_{ma} + V_{mo} E D + \frac{A+O E D}{2} D t}$$

If D is dependent upon x, the program iterates until the specified closing tolerance is satisfied on both D and x.

The same procedure is repeated for each component and if distribution coefficient are mutually dependent, the entire cycle is iterated until all x and y values close to the specific tolerance.

INPUT PROCESS PARAMETER

General Parameter

The most convenient way to input the process variables is to directly define them into the program. A convenient method of directly entering the data in the program is to list the program, then scroll through until the line containing the variable's definitions are found. Modify the parameter as required directly on the screen. After completion of the variable entries, run the program.

A large part of the required input specification are relatively easy to specify, i.e. the component's name, the mixer and settler volume, the composition of initial organic and aqueous input streams, the number of stages, the settler zone as well as the number of stage, the flow rate and the concentration of components in the feed and the organic stream.

Moreover, there are a series of information required, peculiar to the choice of extraction strategy.

In particular, the program need information to define in which system we want work, i.e. in force feeding, in partial or in total reflux methods.

On the basis of this information, the input subroutine required different type of input variable such as concentration factor of raffinate or stripping stream, the reflux ratio, the stripping stage's number, the number of reflux stream's stage and so on⁽²⁾.

Distribution Coefficient data Bank

The equilibrium data bank consist of files containing the experimental distribution coefficient of each ion as a multivariable function of ion concentration, acidic concentration, and other co-extracting ions concentration.

With this program is possible to treat till to 5 ions included the acidity.

Since is difficult obtain an analytical function, we utilize distribution coefficient values for fixed x,y,z experimental points.

For the calculation of the whole set of data, the program provide to interpolate the experimental data.

OUTPUT FILES AND RESTART PROCEDURE

One of the main characteristic of R.E.S.EX. is the possibility to make a restart from a previous situation. This can be realize by using the output file like a new input file. So it is possible modify some parameters and see the evolution of concentrations profiles.

As graphical output, RESEX present the battery profile for each component as bar graph with stage number, the numerical percentage of the component in the stage and the concentration in g/l.

Moreover, we can obtain for each stage some informations for the restart procedure, i.e. aqueous and organic flow rate, and aqueous and organic concentration of i-component in mixer and in settler zone for time t-Dt and t.

Nd/Pr SEPARATION : AN EXAMPLE

As an example of this strategy in figure are reported the results of the Pr-Nd separation in TBP 50 % in aromatic solvent⁽⁴⁾.

We had choice this process because was possible to compare the calculated results with the experimental value obtained by tests carried out in an existing Italian pilot plant.

After an initial scheme necessary to load the battery, the mixer-settler assembly was operated under total reflux without further feeding .

By continuously reintroducing rare earth solutes at each end of the multi-stage assembly, appropriately in organic and aqueous phases, the components were segregated into bands.

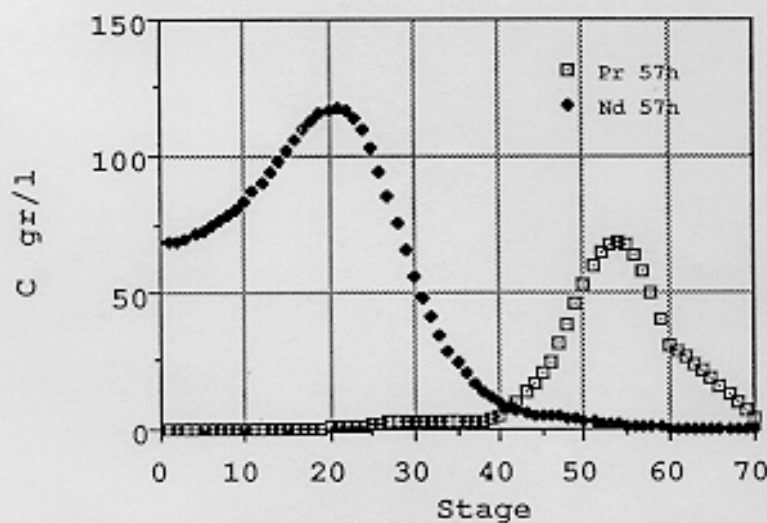


Figure.3 Internal battery profile of Nd and Pr at the end of total reflux step.

When we have reached the required purity, see fig. , the product stream left partially the battery as final product (partial reflux configuration) while the feed was supply again.

The Pr/Nd theoretical separation is very good and became every better for longer time.

These results are comparable with the experimental value obtained by tests carried out⁽⁵⁾ where we were obtained several kilogram of Praseodymium with an 99.9 % of purity degree and Neodymium heavies rare earth in which the Nod had a 98 % of purity.

ON GOING WORK

At the present, March 1995, the RESEX code is under implementation, especially in the graphic subroutine, in order to become more user friendly.

Moreover, we are testing another option of he R.E.S.EX code, that is the possibility to simulate a

whole plant section consisting of an extraction battery in partial or total reflux mode, a stripping battery, two storage tank and two evaporators for the concentration of exit streams before the reflux.

FINAL REMARKS

The contemporary use of equilibrium data bank and simulation code allow the theoretic study of new rare earth separative processes or the optimization of existing one. This is obtained by analyzing the effects that change of some process parameters produce on the purity of the final products

Use of the program frequently results in the same type of tail chasing that operators experience with real circuits. Changing one parameter to meet some criteria causes other restrictions to be violated. While this may seem a weakness in the program, the insight gained in understanding the interactions and sensitivities of the input parameters is a great aid in being able to operate a real circuit. Testing more than three or four process variables in a pilot plant is prohibitive, while with the computer these changes can be evaluated in a matter of hours. A few days spent testing the effects of changed conditions on circuit through the model can replace years of pilot plant testing even if the experimental run remain a fundamental task for the process chemists and engineers.

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