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# Flexibility analysis of nondispersive solvent extraction plant

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# FLEXIBILITY ANALYSIS OF NONDISPERSIVE SOLVENT EXTRACTION PLANT

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## ABSTRACT

The objective of this work is to analyze the behavior of a nondispersive solvent extraction plant in the uncertain space of concentration and flow rate of the feed stream. To carry out this task, a superstructure with a maximum number of 64 modules distributed in 8 parallel lines of 8 modules in series for both extraction and stripping subprocesses is developed. A flexibility analysis on the optimal design obtained with this superstructure is implemented using the equation-oriented flowsheeting package SPEEDUP (Aspen Technology, Inc). Further studies of the flexibility index for different overdesigns are done in order to obtain a deeper insight of the operability characteristics of the system. The results show that the optimal nondispersive solvent extraction processes for the case of removal and concentration of Cr(VI) with Aliquat 336 present low flexibility indices.

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## INTRODUCTION

The application of nondispersive solvent extraction process, NDSX, as a replacement to the conventional liquid–liquid extraction set-ups has been studied extensively during the past two decades. Several works and reviews that point out its advantages, possible applications and modeling can be found in literature (1–3). In order to promote the industrial applications of the nondispersive solvent extraction processes, a better understanding of their behavior is required. A deeper insight of the process through its simulation and optimization improves the knowledge of the operability characteristics of the system.

The case of study selected in this work is the extraction and concentration of Cr(VI) from waste waters of some surface treatment industries using Aliquat 336 as a selective carrier. Aliquat 336 is a quaternary ammonium salt commercialized as a mixture of tri-*n*-alkylammonium chlorides. The process provides not only a valuable technology for removal of the toxic metal from waste waters, but also allows recovery of the heavy metal decreasing the necessities of the raw material.

A semicontinuous NDSX process (Fig. 1) comprises at least two hollow fiber modules, one for extraction and the other for stripping. In addition, a storage tank for the concentration of the stripping stream is required. The dotted lines represent the replacement of the stripping solution by a fresh one at the end of each batch. In hollow fiber modules, the aqueous and the organic solutions flow continuously, one through the lumen of the fibers and the other through by the shell side. Both phases make contact through the pores of the fiber wall. The feed solution enters the extraction module and the carrier in the organic phase extracts the solute at the aqueous–organic interface. The new species formed at this

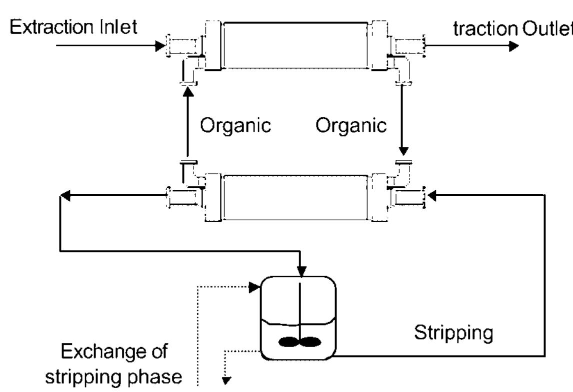


*Figure 1.* Schematic diagram of a semicontinuous NDSX process.

interface diffuses across the microporous wall filled with organic solution (hydrophobic fibers) to the outer side of the fibers. The decontaminated aqueous stream exits the extraction module. The organic stream containing the solute–carrier complex is sent to the stripping module. The solute–carrier complex diffuses across the microporous wall filled with organic solution (hydrophobic fibers) to the stripping–organic interface. At the interface, the carrier is regenerated releasing the solute into the aqueous stripping solution. After that, the organic phase is recycled to the extraction module. The solution coming out of the stripping module is stored in the stripping tank. A semicontinuous process means that after a certain period of time the stripping solution is replaced by a fresh one while the organic solution remains the same and the extraction solution flows in a continuous mode. It is always good to work with a constant batch time and with a recurrent behavior of the batches. This facilitates the system control and the working mode. To have a recurrent behavior, the concentration of solute in the organic solution at the end of a batch must be the same as the concentration at the beginning of the batch. In an optimal situation, the concentration of solute in the organic solution should remain constant during the batch allowing a real continuous run of the extraction process. A more detailed description of the process and its semicontinuous behavior can be found in Alonso et al. (4).

The selected system has been analyzed experimentally by Ortiz et al. (5) and Alonso et al. (4) working in a laboratory scale and pilot plant scale. Simulation studies of the system and the optimal selection of operating variables for a pilot plant have been reported by Alonso and Pantelides (6) and Eliceche et al. (7). Recently, the optimal design of a nondispersive solvent extraction process for the removal and recovery of chromium(VI) from waste waters of surface treatment industries have been presented by Alonso et al. (8). In this work, nominal conditions for the values of the input waste-water stream (solute concentration and flow rate) are given as specifications of the design. However, these conditions can change during the operation of the process. It is important in that sense to quantify the capacity of the optimal design plant to tolerate different feed flow rates and concentrations. This capacity of a design to tolerate and adjust to variations in conditions that may be encountered during operation is called flexibility of the process. The quantitative measure that will indicate how much flexibility can be achieved by a given design is the flexibility index (9,10). The index is defined as the maximum scaled deviation of uncertain parameters (conditions that can change during operation) from their nominal values for which operation can be guaranteed by proper manipulation of the control variables.

Therefore, the main objective of this work is to find the deviations from the nominal conditions that can be tolerated by different designs remaining in the feasible region of operation. This study will provide a deeper insight of the process and therefore a better understanding of its behavior. The consideration of only two dimensions in the uncertain space (inlet concentration and flow rate of the feed stream) facilitates calculation of the flexibility index and the analysis of the behavior of the plant.

## OPTIMAL DESIGN PROBLEM

The objective of the optimal design of an NDSX process is to synthesize a process that can separate a waste feed stream into an environmentally acceptable stream and a stream in which the pollutant is concentrated for further processing and exploitation with the minimum cost. The design problems are normally solved for a set of nominal conditions and a number of requirements must be fulfilled. In this case, the variables, inlet concentration, $C_{e,in}$ and flow rate, $F_e$, of the feed stream are given. An upper bound on the concentration of the solute at the outlet of the extraction stream is given by environmental regulations, $C_{e,out} \leq 9.61 \times 10^{-3}\,\mathrm{mol/m^3}$, and the concentration of the solute in the stripping stream required for reuse is used as lower bound on the stripping concentration, $C_{s,final} \geq 76\,\mathrm{mol/m^3}$. The optimal design requires the identification of the optimal configuration, number and connectivity of the various hollow fiber modules and the optimal operation conditions such as flowrates, volumes and concentrations.

The previous work (8) on the optimal design of an NDSX process for the removal and concentration of Cr(VI) from a $2\,\mathrm{m^3/hr}$ feed solution with a concentration of $1.234\,\mathrm{mol/m^3}$ of Cr(VI) shows as optimal structure a design of two extraction modules in a series and four stripping modules arranged in two parallel lines of two modules in a series each. The organic and aqueous phases flow in countercurrent flow between the modules in both subprocesses. The outlet extraction concentration is $8.316 \times 10^{-3}\,\mathrm{mol/m^3}$ and the stripping concentration is $76.080\,\mathrm{mol/m^3}$. The inlet organic concentration into the extraction subprocess is $70.514\,\mathrm{mol/m^3}$ and the organic flow rate is the minimum allowed flow rate, $0.1\,\mathrm{m^3/hr}$. These results were obtained solving a Mixed Integer Nonlinear Programming, MINLP, problem using an extension of the Outer Approximation algorithm (PSANO) (11,12) combined with a bound tightening strategy. A superstructure with a maximum amount of four modules for the extraction and four modules for the stripping distributed in two parallel lines of two modules each was considered in that work. The modules considered were commercially available modules with $130\,\mathrm{m^2}$ effective surface area (Liqui-Cel Extra Flow) from the company Celgard LLC (Charlotte, NC).

Since the optimum stripping subprocess makes use of the maximum number of modules in the superstructure, a new superstructure, which includes a larger number of modules, was used in this work to allow a deeper study of the flexibility of the process. The superstructure, Fig. 2, consists in a maximum amount of 64 modules for the extraction ($E1$, $E2$,…) and stripping ($S1$, $S2$,…)

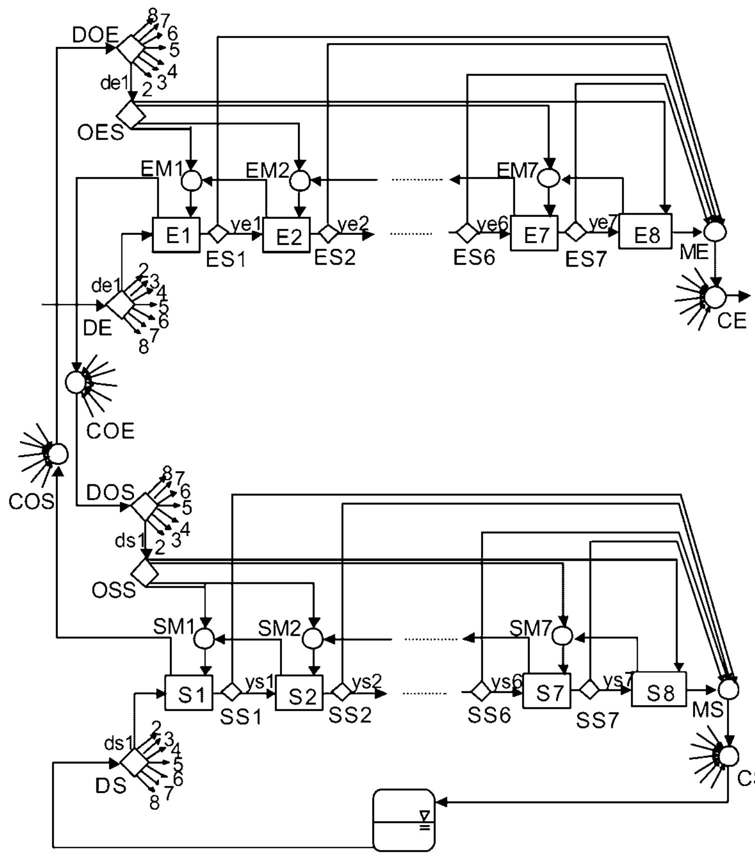


*Figure 2.* Superstructure for an NDSX process with 64 extraction modules and 64 stripping modules.

distributed in eight parallel lines of eight modules in series each. The modules are the same commercial modules used in the previous work.

Splitters (◇) and mixers (○) are introduced to enable the choice of the optimum structure configuration. This choice is implemented through the use of integer variables, *yei* ($i = 1$–7), *ysi* ($i = 1$–7), *dei* ($i = 1$–8), *dsi* ($i = 1$–8). The integer variables are used to enable or disable certain units or lines within the flowsheet. The integer variables, *yei* and *ysi* ($i = 1$–7), determine the number of modules in a line and the integer variables, *dei* and *dsi* ($i = 1$–8), determine the number of lines. All the lines are considered to have the same number of modules and therefore its performance is exactly the same. So only one line needs to be simulated. The aqueous and organic flow rate to each line will depend on the number of lines but all lines will show an identical performance. For example, the extraction stream enters the superstructure through the splitter, DE. In this splitter, the number of lines is chosen ($dei$, $i = 1-8$). If only one line is chosen the splitter will not be in the final structure while if two or more lines are chosen this will be a real splitter dividing the extraction stream into a number of identical streams equal to the number of lines chosen. The aqueous outlet solution for each line goes into the first module of the line, $E1$. The aqueous outlet of this first module can be fed to a second module, $E2$, or can be considered as the end of the line and be sent to the mixer, ME. The value of $ye1$ in the splitter ES1 will determine this choice. The splitter ES1 is a logical splitter. It allows the problem to make a choice but it will not appear in the final structure. The exit of each line is mixed in the mixer CE. As the splitter DE, this mixer will be in the final structure only when more than one line is chosen as optimal structure.

The organic stream enters the extraction subprocess through the splitter DOE. This splitter is similar to the aqueous splitter DE. It will divide the organic stream into a number of identical streams equal to the number of lines chosen for the aqueous stream. The number of lines is determined by the value of the integer variables, $dei$ ($i = 1$–$8$) as in the splitter DE. The organic outlet solution for each line goes into the splitter OES. The function of this splitter is to send the organic solution of each line to the last module of the line. As the number of modules in each line is not fixed, the superstructure has to allow the entrance of the organic stream to each of the eight possible modules in a line. Only one of these eight possible organic inlets will be real in the final structure and it will be determined by the values of the integer variables $yei$ ($i = 1$–$7$). The organic outlets of the first module of each line are mixed in the mixer COE composing the organic inlet solution to the stripping subprocess. The superstructure for the stripping subprocess is defined in a similar way. Therefore, the splitters ES-$i$, SS-$i$ ($i = 1-7$), OES, OSS and the mixers EM-$i$, SM-$i$ ($i = 1-7$), ME, MS are logical. They will not appear as real splitters and mixers in the final structure. The splitters DOE, DOS, DE, DS, and the mixers, COE, COS, CE, and CS are real splitters and mixers which will be present in the final structure when more than one line is chosen as optimal structure.

The results of the previous optimization work always show as better structures, the ones in which the organic solution of one parallel line flows in countercurrent flow with the aqueous solution without been mixed or been connected with the organic solution from the other line. Therefore, only this possibility is considered in this new superstructure in order to simplify the optimization problem. Otherwise, a very high number of integer variables would be required to take into account all the possible connections between the 64 modules of each subprocess. Thus the aqueous stream always flows from the first module to the last one in each line while the organic flows from the last module in the line to the first one.

The optimal design problem is formulated as an MINLP problem (8).

$$Z = \min_{x,y} f(x, y) \tag{1}$$

subject to

$$h(x, y) = 0 \quad g(x, y) \leq 0 \qquad y \in \{0, 1\}^m \quad x \in R^n$$

$Z$ constitutes the objective function defined as the minimization of the total cost of the network considering as cost the number of modules, the flow rate of the organic phase and the amount of solute that remains in the feed stream. A complete definition and explanation of this objective function can be found in the work from Alonso et al. (8). Vector $x$ represents continuous variables and $y$ corresponds to binary variables. The binary variables, $y$ ($yei$, $ysi$, $dei$, $dsi$), are used as switches to enable or disable certain units or connections within the superstructure. The constraints of this problem correspond to the modeling equations of the modules, tank, mixers and splitters, $h(x, y)$, as well as design specifications and logical conditions, $g(x, y)$ (Appendix I).

A solution strategy based on an extension of the Outer Approximation algorithm through the program system PSANO has been used (11). PSANO is based on common computer aided tools which are normally used in the total process of design and engineering (12). In the Outer Approximation approach, the MINLP problem is divided into Non Linear Programming (NLP) and Mixed Integer Linear Programming (MILP) subproblems. These subproblems are alternately solved until the final solution is attained. In PSANO, the NLP subproblem is solved by using a SRQP method (13) within the equation-oriented flowsheeting package SPEEDUP (Aspen Technology, Inc., Cambridge, MA). With this, the active structure is evaluated and optimized. The software CPLEX (ILOG, Inc., Mountain View, CA) has been used for solving the MILP subproblem. By the solution of the MILP subproblem a new structure is proposed, which is defined by a specific combination of the binary variables $yi$, $di$ ($yei$, $ysi$, $dei$, $dsi$). Since the MILP subproblem can only consist of a set of linear equations, an intermediate step is required. In this step, the nonlinear equations of the NLP subproblem are linearized. The first NLP subproblem is solved by relaxing the binary variables in order to enable an adequate approximation of the whole superstructure. The software SPEEDUP and CPLEX were used on a workstation, IBM 3AT RS6000 and on a personal computer, Pentium II, 233 MHz, respectively.

The optimum solution is found in the third iteration (Table 1) and another three iterations are necessary to check that no other distribution of modules give a

*Table 1.* Resolution of the MINLP Problem for the Optimal Design

| Iter. | $Z_{NLP}$ | $Z_{MILP}$ | *yi*, *di* Combination | Design[a] |
|---|---|---|---|---|
| 1 | 4.22159 | 0.758 | 1000000 10000000<br>1100000 10000000 | 2s3s |
| 2 | 2061.77161 | 0.886 | 1000000 10000000<br>1110000 10000000 | **2s4s** |
| 3 | **0.88826** | 0.887 | 1000000 10000000<br>1000000 11000000 | 2s2d |
| 4 | 0.88831 | 0.888 | 1000000 10000000<br>0000000 11110000 | 2s1c |
| 5 | 0.88842 | 0.888 | 1100000 10000000<br>1100000 10000000 | 3s3s |
| 6 | 993.75713 | 0.889 | 0000000 11000000<br>1110000 10000000 | 1d4s |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.



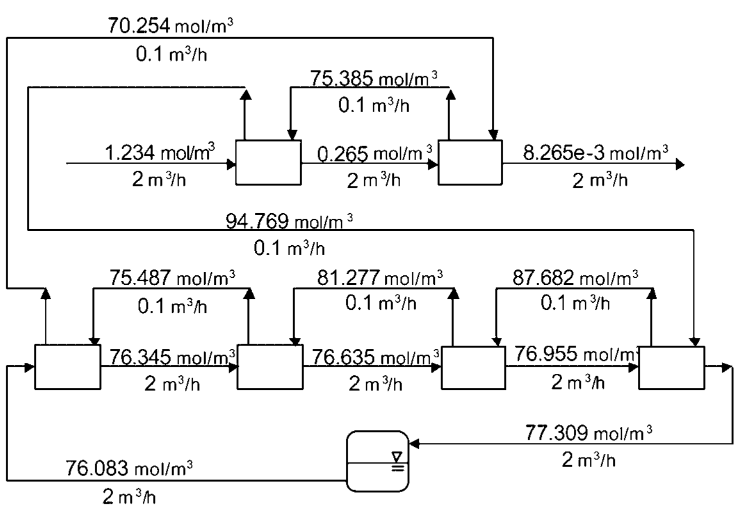


***Figure 3.*** Optimal structure for the nominal values, $C_{e,in} = 1.234\,\text{mol/m}^3$ and $F_e = 2\,\text{m}^3/\text{hr}$ working with the superstructure in Fig. 2.



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better value of the objective function. The optimal design, referred to as 2s4s as defined in Table 1, for the nominal input values ($C_{e,in} = 1.234\,\mathrm{mol/m^3}$ and $F_e = 2\,\mathrm{m^3/hr}$) is shown in Fig. 3. Two modules in series for the extraction and four modules in series for the stripping are selected. This optimal structure is not the same as the one obtained in the previous optimal design work (8), which shows an optimal structure of two extraction modules in series and two stripping modules distributed in two parallel lines of two modules in series each. The reason is that the superstructure in that work did not allow a structure of more than two modules in series and therefore the result obtained here was not considered as a possible design. Apart form this, both results have the same number of modules and very similar outlet aqueous and organic concentrations and the same organic flow rate which is the operation variable to be optimized.

The optimal designs for different values of the feed variables shown in Table 2 show always a structure of modules in series, with the exception of case 7 ($C_{e,in} = 1.851\,\mathrm{mol/m^3}$, $F_e = 2.0\,\mathrm{m^3/hr}$) where three extraction modules in series and three parallel lines of three stripping modules in series, referred to as 3s3t as defined in Table 1, constitute the optimal structure. The maximum number of modules in a series allowed by the superstructure is 8 and as in case 7, 9 stripping modules are required, these modules have to be distributed in parallel lines. Superstructures with more modules in series will result in an optimum design, referred to as 3s9s with 9 modules in a single line for the stripping. So the optimum structure is as far as it is possible a distribution in series of the necessary modules.



***Table 2.*** Optimal Designs for Different Values of the Feed Variables

| Case | $C_{e,in}$ (mol/m$^3$) | $F_e$ (m$^3$/hr) | Design[a] | $C_{e,out}$ (mol/m$^3$) | $C_{s,tank}$ (mol/m$^3$) | $Z$ |
|---|---|---|---|---|---|---|
| 1 | 1.234 | 2.0 | 2s4s | $8.265\times10^{-3}$ | 76.083 | 0.888 |
| 2 | 1.234 | 2.1 | 2s4s | $8.973\times10^{-3}$ | 76.040 | 0.889 |
| 3 | 1.234 | 2.2 | 2s5s | $7.169\times10^{-3}$ | 76.151 | 1.017 |
| 4 | 1.234 | 3.0 | 3s5s | $8.962\times10^{-3}$ | 76.040 | 1.149 |
| 5 | 1.295 | 2.0 | 2s5s | $7.326\times10^{-3}$ | 76.135 | 1.017 |
| 6 | 1.357 | 2.0 | 2s5s | $8.679\times10^{-3}$ | 76.053 | 1.018 |
| 7 | 1.851 | 2.0 | 3s3t | $9.192\times10^{-3}$ | 76.017 | 1.669 |
| 8 | 1.295 | 2.1 | 2s5s | $8.129\times10^{-3}$ | 79.892 | 1.018 |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.

A larger number of stripping modules than extraction modules are necessary in all cases. The extraction process is described by a chemical equilibrium that makes the organic interface concentration, $C_{oi}$ (extraction), to vary between high values ($\approx 300\,\mathrm{mol/m^3}$) at the entrance of the waste water to low values ($C_{oi}$ (extraction) in equilibrium with the $C_{e,out}$) at the final exit. The stripping process is modeled by a distribution coefficient, which makes the organic interface concentration, $C_{oi}$ (stripping) to vary very little around a value of $22\,\mathrm{mol/m^3}$ for aqueous stripping solutions with concentrations around $76\,\mathrm{mol/m^3}$. The total variation of the organic concentration in the bulk of both processes is required to be the same to keep the system working always under the same conditions. Therefore, the differences between the organic concentrations in the bulk of the module and the interface organic concentrations are much higher for the extraction process in the first module than for any module of the stripping process (Table 3). The total sum of the difference of organic concentration has to be the same for both subprocesses to keep the total mass balance concentration. As the sum of the first extraction module is higher than the sum of any of the stripping modules, it will be necessary to have more stripping modules than extraction modules.



## FLEXIBILITY INDEX: PROBLEM DEFINITION

The objective of this work is to analyze the behavior of an NDSX plant in the uncertain space of values of concentration and flow rate of the feed stream. This task can be achieved by carrying out a flexibility analysis of the optimal designs. Flexibility of a design represents the ability of the design to adjust to variations of a set of uncertain parameters. Since the degree of flexibility is determined by the range of parameter variations that the design can tolerate remaining in the feasible region, a scalar index of flexibility can be defined to measure the size of the feasible region in the space of uncertain parameters (9).

$$F = \max \delta \tag{2}$$

$$\mathrm{st.}\forall \theta \in T(\delta)\{\exists z | f(d, z, \theta) \leq 0\}$$

$$T(\delta) = \{\theta | \theta^N - \delta\Delta\theta^- \leq \theta \leq \theta^N + \delta\Delta\theta^+\}$$

The flexibility index, $F$, corresponds therefore to the maximum deviation, $\delta$, of the uncertain parameters, $\theta$, from the nominal values, $\theta^N$, for which a feasible operation, $f(d, z, \theta) \leq 0$, can be guaranteed by proper manipulation of the control variables, $z$. The vector $d$ is the vector of design variables that defines

***Table 3.*** Difference of Organic Concentrations Between the Interface and the Bulk, $C_{oi} - C_o$, Along the Modules for the Design of Fig. 3

| *E*-1 $C_{oi} - C_o$ | *E*-2 $C_{oi} - C_o$ | *S*-1 $-(C_{oi} - C_o)$ | *S*-2 $-(C_{oi} - C_o)$ | *S*-3 $-(C_{oi} - C_o)$ | *S*-4 $-(C_{oi} - C_o)$ |
|---|---|---|---|---|---|
| 219.808 | 159.971 | 53.285 | 58.951 | 63.219 | 72.154 |
| 214.892 | 142.843 | 52.826 | 58.443 | 64.656 | 71.531 |
| 209.842 | 119.824 | 52.370 | 57.939 | 64.099 | 70.914 |
| 204.618 | 88.692 | 51.918 | 57.439 | 63.546 | 70.302 |
| 199.213 | 52.244 | 51.470 | 56.943 | 62.997 | 69.695 |
| 193.550 | 22.904 | 51.027 | 56.452 | 62.453 | 69.094 |
| 187.587 | 7.993 | 50.586 | 55.965 | 61.915 | 68.499 |
| 181.213 | 2.501 | 50.149 | 55.482 | 61.381 | 67.907 |
| 174.346 | 0.753 | 49.717 | 55.003 | 60.851 | 67.321 |
| 166.823 | 0.224 | 49.288 | 54.529 | 60.326 | 66.741 |
| 158.426 | 0.066 | 48.863 | 54.058 | 59.806 | 66.165 |
| 148.841 | 0.020 | 48.441 | 53.591 | 59.29 | 65.594 |
| $\Sigma = 2259.150$ | $\Sigma = 598.035$ | $\Sigma = 609.94$ | $\Sigma = 674.795$ | $\Sigma = 744.539$ | $\Sigma = 825.917$ |
| Total $\Sigma$ | 2857.185 EXT(1+2) | Total $\Sigma$ | 1284.735 STR(1+2) | 2029.274 STR(1+2+3) | 2855.191 STR(1+2+3+4) |

the equipment. Equations $f$ are the inequalities that determine the feasibility of the process. They are obtained by elimination of the state variables from the inequalities, $g$, using the equalities, $h$ (Eq. (1)).

The solution of the above optimization problem is not an easy task. Swaney and Grossmann (9) have shown that if the constraint functions, $f$, are jointly quasi-convex in $z$ and one dimensional quasi-convex in $\theta$, the solution lies at a vertex of the hyper rectangle $T(\delta)$. Then, the computation of the index of flexibility can be simplified considerably, as only the finite number of directions from the nominal point to vertices would have to be analyzed to determine the maximum rectangle. The simplest approach to calculate $F$ is to compute the maximum $\delta$ along each vertex direction and then the solution will be given by the minimum value of those maximums. The procedure is direct and for cases where the number of uncertain parameters, $\theta$, is small ($\leq 4$) it is probably the best way to calculate the flexibility index (9). For more complicated cases, the flexibility analysis problem can be formulated as a mixed-integer optimization problem. These formulations do not rely on the assumption that critical parameter values are vertices, nor do they require exhaustive enumeration of vertices (14).

The constraint functions, in the model used for the description of the NDSX process (Appendix I), are nonlinear functions. The state variables cannot be easily eliminated form the inequalities, $g$, using the equalities, $h$, and therefore the equalities, $h$, will be handled explicitly. Two parameters, inlet concentration, $C_{e,in}$ and flow rate, $F_e$ of the feed stream, can vary during the operation and therefore the uncertain space of interest has two dimensions. One variable, $\delta$, defines the uncertainty of both parameters (Eq. (3)–(6)) and therefore the problem has only one degree of freedom. Considering that the critical point lies at a vertex, the calculation of the flexibility index requires the resolution of 4 NLP subproblems for 4 vertices with a nonlinear programming code. The flexibility index will be the minimum of the four solutions. In this work, the SRQP solver (13) integrated in the equation-oriented flowsheeting package SPEEDUP (Aspen Technology, Inc.) is used. SPEEDUP was used as optimization software in the determination of the optimal design of the plant and can be used in the calculation of the flexibility index for a given design with little changes in the description of the optimization problem.

Four NLP optimization problems have to be resolved, one for each vertex. The objective of all of them is to find the maximum deviation, $\delta$, of the uncertain parameters, $C_{e,in}$ and $F_e$, that a given design can tolerate along that vertex having as control variable the organic flowrate, $F_o$.

Objective function to be maximized: $\delta$;
Control variable: $F_o$ with the following interval of possible values: 0.1–4 $m^3$/hr;

***Table 4.*** Nominal Values and Maximum Expected Deviations of the Uncertain Parameters

| | Nominal Values $\theta^N$ | Range of Possible Deviations $T$ | $\Delta\theta^+$ | $\Delta\theta^-$ |
|---|---|---|---|---|
| $F_e$ ($m^3$/hr) | 2 | 0.1–4 | 2 | 1.9 |
| $C_{e,in}$ (mol/$m^3$) | 1.234 | 0.01–2.5 | 1.266 | 1.224 |

Operation constraints, $g$: $CE \times C_{out} \leq 9.61 \times 10^{-3}\,\mathrm{mol/m^3}$ and $DS \times C_{in} \geq 76\,\mathrm{mol/m^3}$; and
Equality constraints, $h$: modeling of the NDSX plant (Appendix I).

The nominal values and range of possible deviations of the uncertain parameters are shown in Table 4. The value of uncertain parameters stays within the range of concentrations necessary for the validity of the model (15,16).

The equations that define the uncertain parameters with positive and negative deviations are the following:

$$F_e = 2 + 2\,\delta \tag{3}$$

$$F_e = 2 - 1.9\,\delta \tag{4}$$

$$C_{e,in} = 1.234 + 1.266\,\delta \tag{5}$$

$$C_{e,in} = 1.234 - 1.224\,\delta \tag{6}$$

Each vertex direction is specified by a combination of two from these four equations (Fig. 4):

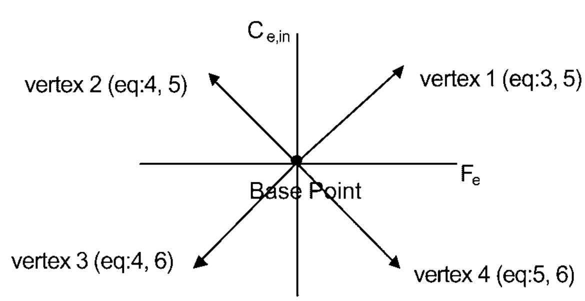


***Figure 4.*** Vertex directions.

***Table 5.*** Maximum Values of $\delta$ for Each Vertex and Flexibility Index

| | Vertex 1 | Vertex 2 | Vertex 3 | Vertex 4 | $F$ |
|---|---|---|---|---|---|
| $\delta$ | 0.0278 (1) | 0.0764 (2) | 1 (3) | 1 (4) | 2.78 % |

vertex 1: positive deviations of both parameters, $C_{e,in}$ and $F_e$: Eqs. (3) and (5);
vertex 2: positive deviation of $C_{e,in}$ and negative deviation of $F_e$: Eqs. (4) and (5);
vertex 3: negative deviations of both parameters, $C_{e,in}$ and $F_e$: Eqs. (4) and (6); and
vertex 4: negative deviation of $C_{e,in}$ and positive deviation of $F_e$: Eqs. (5) and (6).



## RESULTS AND DISCUSSION

The maximum deviations of the uncertain parameters that the optimal design (Fig. 3) can handle along each of the four different directions are shown in

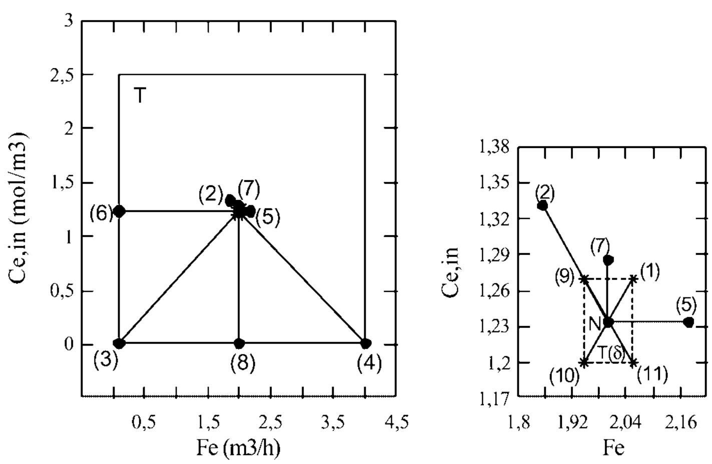


***Figure 5.*** Maximum deviations in eight different directions of the uncertain space. $T$: rectangle defined by the uncertain space. $T(\delta)$: feasible rectangle defined by the flexibility index. $N$: nominal conditions.

***Table 6.*** Maximum Values of $\delta$ Along the Axes Directions from the Nominal Point

| | | |
|---|---|---|
| $C_{e,in}$ fixed = 1.234 mol/m$^3$ | $\delta_{Fe}^{+} = 0.0896$ (5) | $F_e$ max = 2.179 m$^3$/hr |
| | $\delta_{Fe}^{-} = 1$ (6) | $F_e$ min = 0.1 m$^3$/hr |
| $F_e$ fixed = 2000 L/hr | $\delta_{Ce}^{+} = 0.0408$ (7) | $C_e$ max = 1.2857 mol/m$^3$ |
| | $\delta_{Ce}^{-} = 1$ (8) | $C_e$ min = 0.01 mol/m$^3$ |

Table 5. Vertices 3 and 4 where the variable, $C_{e,in}$ has a negative deviation, show a value for $\delta$ equal to 1, and therefore the design can handle the maximum expected deviations along these two directions. However, the direction of vertex 1 where both uncertain parameters have positive perturbations shows a maximum deviation of only 0.0278, which gives a flexibility index equal to 2.78%. Therefore, the plant can tolerate only 2.78% of the expected perturbations from the nominal capacities and therefore the feasible rectangle, $T(\delta)$ (1-9-10-11 in Fig. 5) is defined by 1.947 m$^3$/hr$<F_e<$2.056 m$^3$/hr and 1.1999 mol/m$^3<C_e<$1.2693 mol/m$^3$.

To analyze further the behavior of the optimal design and its capacity to adjust to variations of the uncertain parameters, the maximum deviations in the direction of the axes from the nominal point are determined (Table 6). They are plotted together with the maximum deviations for the vertices in Fig. 5.

The results show that for negative deviation of only one of the uncertain parameters, the maximum deviation is equal to 1 (points 6 and 8 lie on the border of the uncertain space, $T$). On the other hand, only 8.96% of positive deviation of $F_e$ (point 5) and 4.08% of positive deviation of $C_e$ (point 7) are tolerated by the plant. Both deviations are higher than the index of flexibility given by vertex 1 (point 1) when both uncertain parameters have positive deviations. Although the feed stream of point 5 presents a higher flow of chromium into the process (2.688 mol/hr) than the one of point 7 (2.5714 mol/hr) or the one of vertex 1 (2.609 mol/hr), point 5 is among the three, the one with the maximum positive deviation, showing that the total chromium flow of the feed stream, is not enough information to assure if a plant can operate with this feed stream. Flow rate and concentration of the feed stream must be known and evaluated to assure the operability of the plant. Table 7 shows that the design referred to as 3s4s as defined in Table 1 is feasible for the first case but not for the second although the flux that needs to be extracted is the same in both cases. For higher feed inlet concentrations, $C_{e,in}$, the maximum organic interface concentrations at the exit of the extraction subprocess, max. $C_{oi}$ (extraction), that allows to fulfill the constraint of the outlet feed concentration are smaller. The organic concentration

*Table 7.* Operability of a 3s × 4s Design for Two Different Inlet Conditions

| $C_{e,in}$ (mol/m$^3$) | $F_e$ (m$^3$/hr) | Flux to be Extracted (mol/hr) | Design[a] | $C_{e,out}$ (mol/m$^3$) | $C_{s,out}$ (mol/m$^3$) | $C_{o,in}$ Extraction (mol/m$^3$) | max. $C_{oi}$ Extraction (mol/m$^3$) |
|---|---|---|---|---|---|---|---|
| 1.3138 | 2.1262 | 2.773 | 3s4s | $9.616 \times 10^{-3}$ | 77.386 | 76.593 | 76.6124 |
| 1.6607 | 1.6698 | 2.773 | 3s4s | $15.149 \times 10^{-3}$ | 77.374 | 76.094 | 56.7019 |
| | | | | infeasible | | | |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.

at the interface in the extraction modules is always higher than the organic concentrations in the bulk, $C_{o,in}$ (extraction), at the same axial position. In the first case, the bulk organic concentration at the entrance of the last extraction module (exit of the extraction subprocess), $C_{o,in}$ (extraction) is less than the maximum organic concentration at the interface, max. $C_{oi}$ (extraction) that allows a feasible operation of the plant (76.593 mol/m$^3$ > 76,614 mol/m$^3$). In the second case, this value is larger than the maximum value (76.094 mol/m$^3$ > 56.701 mol/m$^3$) and therefore the plant shows an infeasible operation.

In order to analyze more deeply the response of the plant when positive deviations of the uncertain parameters occur, the shape of the feasible region, *R*, within the uncertain space, *T*, is determined. The limits of the feasible region, *R* are calculated through the solution of NLP optimization problems at fixed values of $F_e$ or $C_{e,in}$. In each problem, the maximum deviation of the no-fixed uncertain parameter is determined. Figure 6 shows the shape of the feasible region inside the uncertain space, *T*. The region is one-dimensional convex with which vertex solutions are guaranteed for the flexibility index (9). It can be seen that the constraints, *h* and *g* (Eq. (1)), define a feasible region which is very much reduced when positive deviations of both uncertain parameters are considered (zone 1). As it could be expected, a higher concentration or higher flow rate of the feed stream will require more modules in order to fulfill the outlet concentration requirements. An increase in the flow rate is better tolerated (zone 4) than an increase of the concentration (zone 2) while an increase in both uncertain

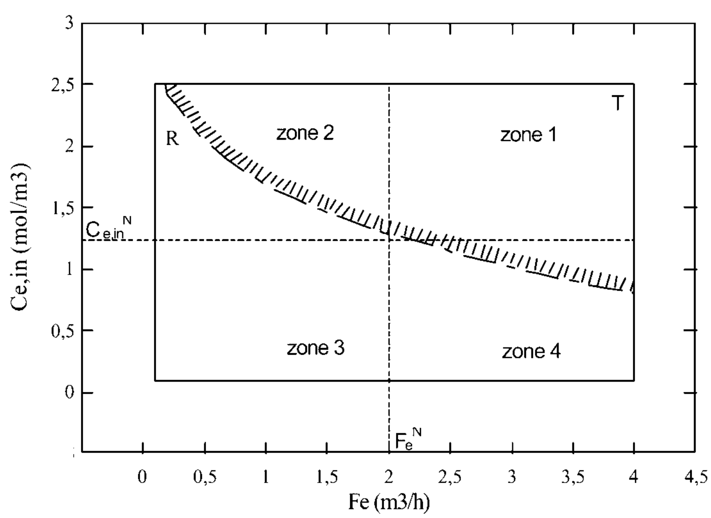


***Figure 6.*** Intersection of the feasible region, *R*, with the uncertain space, *T*.

*Table 8.* Flexibility Index for Designs with Different Arrangement of Stripping Modules

| Extraction Modules | Stripping Modules | Flexibility Index (vertex 1) |
|---|---|---|
| 2: one line | 4: one line | 0.02787 |
| 2: one line | 2: two parallel lines | 0.02672 |
| 2: one line | 1: four parallel lines | 0.02432 |

parameters concentration and flow rate (zone 1) is very badly tolerated by the plant. In zone 1 the feasible region is much smaller than the feasible region when any of the uncertain parameters have negative deviations (zones 2, 3, and 4). Due to this fact, the flexibility index of the plant is very small although the plant present good operability characteristics to input values with negative deviations of one of the uncertain parameters or with negative deviations of both uncertain parameters.

Table 8 shows the flexibility index for design with different distributions of the number of stripping modules. It can be seen that the arrangement of modules in different configurations with one, two or four parallel lines does not have a big influence on the flexibility index. Nevertheless, the distribution in series of the stripping modules shows a slightly better value of the flexibility index than distributions with parallel lines.



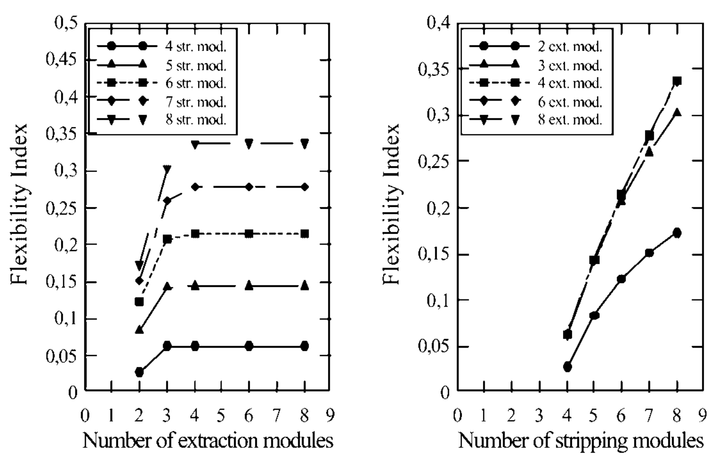


***Figure 7.*** Variation of the flexibility index for the different overdesigns with modules in series.

To increase the flexibility index, designs with a larger number of modules for the same nominal conditions (overdesigns) should be considered. Figure 7 shows the flexibility index for overdesigns with different number of extraction and stripping modules in series. The nominal values and range of possible deviations of the uncertain parameters, $C_{e,in}$ and $F_e$ are the ones shown in Table 4. Only the maximum deviation along the vertex direction with positive deviations for both uncertain parameters (vertex 1) is calculated. According to what can be deduced from the system and corroborated by the results of the flexibility index for the optimal design, this is the direction that tolerates the minimum deviation. The flexibility index increases when the number of stripping modules increases. This increase is smaller when the overdesign presents a larger number of stripping modules. The difference in the flexibility index between having 4 or 5 modules stripping modules (0.0561 for two extraction modules or 0.08026 for eight extraction modules) is higher than the difference between having 7 or 8 (0.0214 for two extraction modules or 0.0589 for eight extraction modules). There is a nonlinear relation between the flexibility index and the number of stripping modules. The designs with more stripping modules operate with smaller levels of organic concentration (Table 9) to treat the same feed solution. This allows a higher capacity of extraction for the same extraction subprocess and this higher capacity means a higher flexibility index of the design. An increase in the number of extraction modules produces an increase of the flexibility index only



***Table 9.*** Level of Concentration of the Organic Phase at the Inlet of Both Subprocesses for a Feed Solution with $C_{e,in} = 1.314\ mol/m^3$, $F_e = 2.126\ m^3/hr$

| Design[a] | $C_{o,in}$ extraction | $C_{o,in}$ stripping |
|---|---|---|
| 4s4s | 76.592 | 104.321 |
| 4s5s | 63.374 | 91.156 |
| 4s6s | 54.602 | 82.414 |
| 4s7s | 48.387 | 76.218 |
| 4s8s | 43.773 | 71.617 |
| 4s20s | 25.914 | 53.801 |
| 4s50s | 21.891 | 49.787 |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.

***Table 10.*** Behavior of the Extraction Subprocess for Designs with Different Number of Extraction Modules; Input Conditions: $C_{e,in} = 1.617\,mol/m^3$, $F_e = 2.605\,m^3/hr$

| Design[a] | $C_{e,out}$ ($mol/m^3$) | $C_{oi}$ ($mol/m^3$) in Equilibrium with $C_{e,out}$ | $C_{o,in}$ Extraction ($mol/m^3$) |
|---|---|---|---|
| 2s8s | 0.126 | 189.16 | 52.483 |
| 3s8s | $9.607 \times 10^{-3}$ | 58.78 | 54.889 |
| 4s8s | $8.707 \times 10^{-3}$ | 54.93 | 54.908 |
| 5s8s | $8.702 \times 10^{-3}$ | 54.91 | 54.907 |
| 6s8s | $8.702 \times 10^{-3}$ | 54.91 | 54.907 |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.



when few extraction modules constitute the structure of the design. In any case with a maximum number of eight stripping modules, the use of more than four extraction modules does not improve the flexibility index (Fig. 7a). The addition of more extraction modules increase the extraction capacity and therefore the flexibility index as long as the outlet of the feed and the inlet of the organic bulk solution are not in chemical equilibrium. For the input conditions presented in

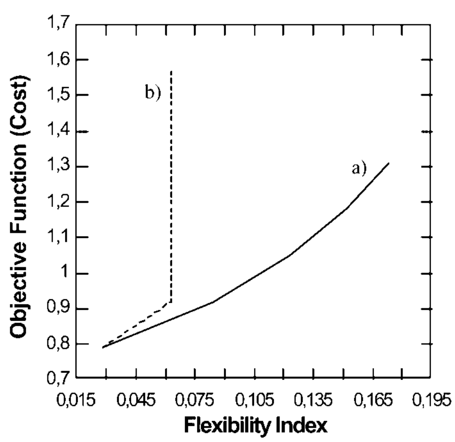


***Figure 8.*** Objective function (cost) vs. flexibility index: (a) structures with two extraction modules and four to eight stripping modules; (b) structures with four stripping modules and two to eight extraction modules.

Table 10 (1.617 mol/m$^3$−2.605 m$^3$/hr) and eight stripping modules, the chemical equilibrium is reached between the outlet extraction concentration and the organic inlet concentration in the extraction bulk when four extraction modules are used ($C_{o,in}$ into the extraction $\cong C_{oi}$ in equilibrium with $C_{e,out}$). More extraction modules will not improve the flexibility because the aqueous and organic concentrations are in chemical equilibrium. Only a decrease in the inlet organic concentration to the extraction subprocess will allow a higher level of extraction. This decrease can be obtained increasing the number of stripping modules. Therefore, for a fixed number of stripping modules, the capacity of the design to extract the solute and therefore its flexibility index can be improved by adding extraction modules only when the inlet organic concentration into the extraction subprocess is not in chemical equilibrium with the aqueous extraction outlet concentration. Otherwise, the flexibility index can only be increased by adding stripping modules. As the number of modules increases the flexibility index increases but accordingly the process cost represented by the objective function increases also. Figure 8 shows the relation between the values of the objective function and the flexibility for the system with two different types of structures: (a) structures with two extraction modules; and (b) structures with four stripping modules. The curve was generated by calculating the flexibility index for structures with 4–8 stripping modules for case (a) and for 2–8 extraction modules for case (b). It can be seen from curve (a) that for values of flexibility that lie within 0 and 0.08, the increase of the objective function is 2.3 times the increase of the flexibility index. However, for flexibility values greater than 0.15, the value of this ratio increases to 6. So, the addition of more stripping modules to improve the flexibility index is economically better when the structure is formed with a small number of modules. Curve (b) shows that for flexibility values greater than 0.06, a sharp increase in the objective function is experienced since the addition of more extraction modules does not improve the flexibility of the system.

Within the studied superstructure, the maximum flexibility index is 0.337 (Fig. 7). This flexibility index corresponds to a structure with eight stripping modules in series and at least four extraction modules in series. This structure allows treating a flow rate of 2.674 m$^3$/hr with a concentration equal to 1.660 mol/m$^3$, so the maximum extraction rate for this superstructure is 4.44 mol/hr.

Designs with more than eight modules in a series (maximum number allowed by the superstructure) show that more stripping area (Table 11: designs 1–3) provide a higher reextraction. Therefore, the values of the inlet organic concentration to the extraction subprocess ($C_{o,in}$ extraction) are smaller, which provides a higher extraction capacity and therefore higher flexibility index. More extraction area (Table 11: designs 1, 4, 5) does not provide more extraction capacity always because if the extraction equilibrium concentrations are reached ($C_{oi} \cong C_{o,in}$), the outlet concentrations will not be changed with more extraction modules.

*Table 11.* Flexibility Index for Designs Which are Not Included in the Superstructure

| | Design[a] | Flexibility | $F_o$ ($m^3$/hr) | $C_{e,in}$ (mol/$m^3$) | $F_e$ ($m^3$/hr) | $C_{e,out}$ (mol/$m^3$) | $C_{oi}$ (mol/$m^3$) in Equilibrium with $C_{e,out}$ | $C_{o,in}$ Extraction (mol/$m^3$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 4s20s | 0.641 | 0.112 | 2.046 | 3.282 | $9.611\times10^{-3}$ | 41.940 | 33.379 |
| 2 | 4s50s | 0.749 | 0.299 | 2.182 | 3.498 | $9.612\times10^{-3}$ | 37.989 | 27.538 |
| 3 | 4s75s | 0.776 | 0.470 | 2.215 | 3.549 | $9.610\times10^{-3}$ | 37.109 | 26.002 |
| 4 | 10s20s | 0.854 | 0.1 | 2.315 | 3.708 | $9.610\times10^{-3}$ | 34.951 | 34.589 |
| 5 | 20s20s | 0.854 | 0.1 | 2.315 | 3.708 | $9.610\times10^{-3}$ | 34.951 | 34.589 |

[a] Design: first number: number of extraction modules in series; first letter: number of extraction lines; second number: number of stripping modules in series; second letter: number of stripping lines first number; letters: s:1 line, d:2 parallel lines, t:3 parallel lines c: 4 parallel lines.

## CONCLUSIONS

The optimal design of a nondispersive solvent extraction process for the removal and concentration of Cr(VI) working with a superstructure that includes a big number of extraction and stripping modules ($64 \times 64$) shows that the optimal design is always a structure of modules in series. Nevertheless, the value of objective functions of designs with the same number of modules but different distributions do not differ much (Table 1: iter. 3–5).

All designs show that a larger number of stripping modules than extraction modules are required to have feasible operations. This is due to the different mechanisms that describe the extraction and stripping process. The extraction process is described by a chemical equilibrium equation and the stripping process by a distribution coefficient. The first one makes the organic interface concentration vary from high values to low values along the modules while the second one makes the organic interface concentration have a low value with little variations. This difference causes the necessity of having more number of stripping modules in the design in order to have a feasible operation.

The flexibility analysis of the nondispersive solvent extraction process provides a deeper insight of the process and a better understanding of its operability characteristics.

The optimal design can tolerate 2.78% of the expected perturbation (100% maximum possible perturbation for flow rate and concentration of the inlet feed stream). The critical point corresponds to positive deviations of both uncertain parameters. The plant can operate with higher deviations when these deviations are negative for both parameters or at least negative for the flow rate. So although the plant present good operability characteristics to input values with negative deviations of one of the uncertain parameters or with negative deviations of both uncertain parameters, the flexibility index is low due to the very restrictive constraints when both uncertain parameters show positive perturbations.

The flexibility analysis shows as well that the total chromium flow that needs to be extracted is not enough information to assure whether a plant presents a feasible operation for that inlet feed stream. Flow rate and concentration of the feed stream must be known and evaluate to guarantee the feasibility of the design.

The flexibility indices of overdesigns show that the capacity of the design to extract the solute and therefore its flexibility index can be increased by adding extraction modules only when the input organic concentration into the extraction subprocess is not in chemical equilibrium with the aqueous extraction outlet concentration. Otherwise, the flexibility index can be increased by adding stripping modules.

## APPENDIX I: CONSTRAINTS OF THE OPTIMISATION PROBLEM

### Modeling Equations, $h(x, y)$

The algebraic model for NDSX processes has been developed in a previous work (8). The initial partial differential equations (time and axial position) model (4) is reduced to an algebraic equations model through the discretization of the spatial variation of concentrations and simplifications on the time dependency. The algebraic model has been shown to be valid for simulations in which the extraction and the stripping rate are constant. As this is the optimal behavior of the process, the algebraic model is valid for optimization and flexibility analysis purposes (8). The final algebraic model is the following.

Extraction Module

- Aqueous solution

$$-(C_{\mathrm{e}}^{\mathrm{E}}(i) - C_{\mathrm{e}}^{\mathrm{E}}(i-1))F_{\mathrm{e}}N = AK_{\mathrm{m}}(C_{\mathrm{oi}}^{\mathrm{E}}(i) - C_{\mathrm{o}}^{\mathrm{E}}(i)) \quad i = 1, \ldots, N \tag{A1}$$

- Organic solution

$$(C_{\mathrm{o}}^{\mathrm{E}}(i) - C_{\mathrm{o}}^{\mathrm{E}}(i-1))F_{\mathrm{o}}N = AK_{\mathrm{m}}(C_{\mathrm{oi}}^{\mathrm{E}}(i) - C_{o}^{E}(i)) \quad i = 1, \ldots, N \tag{A2}$$

- Equilibrium (15)

$$K = \frac{C_{\mathrm{Cl}}^{2} C_{\mathrm{AlCr}}}{C_{\mathrm{Cr}} C_{\mathrm{AlCl}}^{2}} \mathrm{CT}^{0.6} = \frac{4(C_{\mathrm{e,in}}^{\mathrm{E}} - C_{\mathrm{e}}^{\mathrm{E}}(i))^{2} C_{\mathrm{oi}}^{\mathrm{E}}(i)}{C_{\mathrm{e}}^{\mathrm{E}}(i)(CT - 2C_{\mathrm{oi}}^{\mathrm{E}}(i))^{2}} (\mathrm{CT} \times 10^{-3})^{0.6} \quad i = 1, \ldots, N \tag{A3}$$

Stripping Module

- Aqueous solution

$$-(C_{\mathrm{s}}^{\mathrm{S}}(i) - C_{\mathrm{s}}^{\mathrm{S}}(i-1))F_{\mathrm{s}}N = AK_{\mathrm{m}}(C_{\mathrm{oi}}^{\mathrm{S}}(i) - C_{\mathrm{o}}^{\mathrm{S}}(i)) \quad i = 1, \ldots, N \tag{A4}$$

- Organic solution

$$(C_{\mathrm{o}}^{\mathrm{S}}(i) - C_{\mathrm{o}}^{\mathrm{S}}(i-1))F_{\mathrm{o}}N = AK_{\mathrm{m}}(C_{\mathrm{oi}}^{\mathrm{S}}(i) - C_{\mathrm{o}}^{\mathrm{S}}(i)) \quad i = 1, \ldots, N \tag{A5}$$

- Equilibrium (16)

$$H = \frac{C_{\mathrm{Cr}}}{C_{\mathrm{AlCr}}} = \frac{C_{\mathrm{s}}^{\mathrm{S}}(i)}{C_{\mathrm{oi}}^{\mathrm{S}}(i)} \quad i = 1, \ldots, N \tag{A6}$$

Stripping Tank

$$C^{\mathrm{T}}_{\mathrm{s,tf}} - C^{\mathrm{T}}_{\mathrm{s,t=0}} = \frac{tf}{V_{\mathrm{s}}} F_{\mathrm{s}}(C^{\mathrm{T}}_{\mathrm{s,in}} - C^{\mathrm{T}}_{\mathrm{s,tf}}) \tag{A7}$$

Mixers

$$F_{\mathrm{out}} = \sum_i F_{in,i} \quad i = 1, \ldots, \text{number of input streams} \tag{A8}$$

$$F_{\mathrm{out}} C_{\mathrm{out}} = \sum_i F_{\mathrm{in},i} C_{\mathrm{in},i} \quad i = 1, \ldots, \text{number of input streams} \tag{A9}$$

Splitters

$$C_{\mathrm{out},i} = C_{\mathrm{in}} \quad i = 1, \ldots, \text{number of output streams} \tag{A10}$$

$$F_{\mathrm{in}} = \sum_i F_{\mathrm{out}\,i} \quad i = 1, \ldots, \text{number of output streams} \tag{A11}$$

$$F_{\mathrm{out},i} = \zeta_i F_{\mathrm{in}} \quad i = 1, \ldots, \text{number of output streams} - 1 \tag{A12}$$

The superscripts indicate the module or the tank and the subscripts indicate the phase within the module. Therefore $C_e^E$ and $C_s^S$ represent the concentration of chromium in the extraction and stripping phase. $C_o^E$ and $C_o^S$ represent the concentration of chromium in the organic phase in the extraction and stripping module and $C_s^T$ represent the concentration of chromium in the stripping tank. $F$ are the flowrates, $V_{\mathrm{s}}$ the volume of the stripping phase in the tank and $A$, the interfacial area. In the equilibrium expressions, $C_{\mathrm{Cl}}$ is the chloride concentration, $C_{\mathrm{AlCl}}$ is the free carrier concentration, $C_{\mathrm{Cr}}$ the concentration of chromium, $C_{\mathrm{AlCr}}$ the complex carrier—chromium concentration and CT is the total carrier concentration. A value for the mass transfer coefficient of $K_{\mathrm{m}} = 2.2 \times 10^{-8}$ m/sec was obtained in a previous work from the comparison of the simulated results and the experimental data (16). The extraction chemical equilibrium can be described through Eq. (A3) with a value of 0.2 for the equilibrium constant (15). The stripping chemical equilibrium can be described by a distribution coefficient equal to 3.5 when NaCl, 1 mol/L, is used as stripping agent (16). A value of $N = 12$ leads to accurate results without requiring excessive computations (8).

## Design Specifications, $g(x, y)$

The objective is to design the process in such a way that the concentration of the outlet extraction stream is always less than $9.61 \times 10^{-3}$ mol/m$^3$ (Spanish

Law: BOE de 30 de abril de 1986) and the concentration at the end of the batch of the stripping solution in the tank is higher than 76 mol/m$^3$. These two constraints are the design specifications.

$$C_{e,out} \leq 9.61 \times 10^{-3}\ \mathrm{mol/m^3} \quad C_{s,final} \geq 76\ \mathrm{mol/m^3} \tag{A13}$$

Logical Conditions, g(x, y)

The logical constraints used in this work are:

$$\begin{array}{lllll} de1 = 1 & ye2 \leq ye1 & ys2 \leq ys1 & de2 \leq de1 & ds2 \leq ds1 \\ ds1 = 1 & ye3 \leq ye2 & ys3 \leq ys2 & de3 \leq de2 & ds3 \leq ds2 \\ & ye4 \leq ye3 & ys4 \leq ys3 & de4 \leq de3 & ds4 \leq ds3 \\ & ye5 \leq ye4 & ys5 \leq ys4 & de5 \leq de4 & ds5 \leq ds4 \\ & ye6 \leq ye5 & ys6 \leq ys5 & de6 \leq de5 & ds6 \leq ds5 \\ & ye7 \leq ye6 & ys7 \leq ys6 & de7 \leq de6 & ds7 \leq ds6 \\ & & & de8 \leq de7 & ds8 \leq ds7 \end{array} \tag{A14}$$

The two first equalities mean that at least one extraction line and one stripping line must exist in the optimal structure. The rest of inequalities assure that a new line or a new module can only be selected from the superstructure if the previous line or module has been selected.

## Reformulations of Bilinear Terms

The number of total modules is described for this superstructure by nonlinear equations in the integer variables:

$$\mathrm{NME} = \left(1 + \sum_{i=1}^{7} yei\right)\left(\sum_{i=1}^{8} dei\right) \tag{A15}$$

$$\mathrm{NMS} = \left(1 + \sum_{i=1}^{7} ysi\right)\left(\sum_{i=1}^{8} dsi\right) \tag{A16}$$

To apply an Outer Approximation algorithm to the solution of the MINLP problem, the problem has to be linear in the integer variables and therefore

Eqs. (A15) and (A16) need to be reformulated using 256 linear inequalities (big M formulations). Four of these inequalities are the following equations, the others are written in a similar way:

$$\begin{aligned}\mathrm{NME} \leq 64 &+ 100(7 - ye1 - ye2 - ye3 - ye4 - ye5 - ye6 - ye7)\\ &+ 100(8 - de1 - de2 - de3 - de4 - de5 - de6\\ &- de7 - de8)\end{aligned} \tag{A17}$$

$$\begin{aligned}\mathrm{NME} \geq 64 &- 100(7 - ye1 - ye2 - ye3 - ye4 - ye5 - ye6 - ye7)\\ &- 100(8 - de1 - de2 - de3 - de4 - de5 - de6 - de7 - de8)\end{aligned}$$

$$\begin{aligned}\mathrm{NME} \leq 40 &+ 100(4 - ye1 - ye2 - ye3 - ye4 + ye5 + ye6 + ye7)\\ &+ 100(8 - de1 - de2 - de3 - de4 - de5 - de6 - de7 - de8)\end{aligned}$$

$$\begin{aligned}\mathrm{NME} \geq 40 &- 100(4 - ye1 - ye2 - ye3 - ye4 + ye5 + ye6 + ye7)\\ &- 100(8 - de1 - de2 - de3 - de4 - de5 - de6 - de7 - de8)\end{aligned}$$

The first two inequalities assure that NME will be 64 when all the integer extraction variables are 1 and the second two that it will be 40 when there are 8 parallel lines and 5 modules in each line.

The bilinear model Eq. of splitter (A12) and mixers (A9) are reformulated in a similar way as in the previous optimization work (8) using big M formulations. The bilinear aqueous equations in the model for the modules (A1 and A4) are replaced as well by big M formulations (8) taking into account in this work that the aqueous flow rate depends on eight integer variables. These variables determine the number of parallel lines (*dei* and *dsi*).

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