**Practice 3 - Modeling of the liquid extraction process according to the SOLVAY EXTRACTION program**

**2 академических часа**

**Engineering SX Circuits (McCabe-Thiele Diagrams)** - A more detailed discussion of the engineering will be presented in the corresponding lecture course. The theory will be briefly outlined here. Consider an n-stage SX circuit as illustrated in Figure 6, where O is the organic flow rate and A is the aqueous flow rate. Aqueous and organic solutions enter counter-currently. The concentration of metal ion in the aqueous decreases and, concomitantly, that in the organic increases. Given enough time, the mixture attains equilibrium, for example, as per equation [1]. The concentrations exiting each stage are those attained after mixing. The solution concentrations entering the process from the two ends are xo (PLS) and yn+1 (barren organic, which comes from stripping; see Figure 1). Whether or not equilibrium is attained, steady state concentrations develop in each stage. Equilibrium is the limiting case, for which this analysis will be developed. The raffinate concentration is designated xn, as the aqueous phase exits the process at stage n. The loaded organic concentration is symbolized by y1; the loaded organic leaves the process after stage 1.

 Metal ions transfer from the aqueous phase to the organic phase in extraction. Hence a mass balance can be written for each stage and for the overall process. The change in mass of metal ion in the aqueous phase is Axi, where xi is the change in metal ion concentration for stage i. The change in mass of metal ion in the organic phase is, correspondingly, Oyi. For mass balance to pertain,

 Axi = Oyi [4]

This means that metal ion neither accumulates nor depletes in the stage as a whole (organic + aqueous). This is what the term ***steady state*** means in this context. Rearranging the preceding equation gives:

 yi = Axi [5]

 O

That is, the change in metal ion concentration in the organic phase is the ratio of aqueous:organic flow rates multiplied by the change in metal ion concentration in the aqueous phase. One last rearrangement gives,

 yi = A [6]

 xi O

The ratio of changes in *organic-to-aqueous* concentrations is equal to the ratio of *aqueous to organic* flow rates. Equation [6] is obviously the slope of a straight line.



Figure 6. Schematic illustration of an n stage SX circuit.

 Applying the mass balance concept again, at steady state all the metal ion that enters a stage leaves it. For any given stage i this may be expressed as,

 Axi + Oyi = Oyi+1 + A xi-1 [8]

Concentrations xi and yi are the *equilibrium* concentrations of the species in the aqueous and organic phases, respectively. They are the concentrations in the phases exiting the stage. For instance, if A m3/hr of aqueous at concentration xi kg/m3 of metal ion flows out of stage i and O m3/hr of organic with concentration yi kg/m3 of metal ion also flows out, then the total mass of metal ion exiting the stage is Axi + Oyi. The right side of the equation represents what flows in from the organic (stage i+1) and from the aqueous (stage i-1). Over all n stages (the whole process) the mass balance leads to,

 Ax0 + O yn+1 = A xn + O y1 [9]

This can be rearranged,

 yn+1 = A(xn –x0) + y1 [10]

 O

 Equation [10] is essentially the same as equation [5]. Consider the diagram in Figure 7. Organic [Mn+] is plotted versus aqueous [Mn+]. For a stage i the flows with corresponding concentrations are depicted at right. The changes in concentration are indicated at left. Solutions enter with concentrations xi-1 (aqueous) and yi+1 (organic). This is shown as the point xi-1, yi+1 on the diagram. As x decreases upon extraction, y increases, as governed by the phase ratio, A/O (equation [5]), until equilibrium is reached (the point xi, yi). The points xi-1, yi and xi, yi+1 are joined by a straight line with slope given by the equation below (and as per equation [8]).

 y = A = yi - yi+1 [11]

 x O xi-1 - xi

In general then the equation for the straight line is,

 yi+1 = (A/O)xi + b [12]

The intercept b can be calculated given any point on the line. The line is called the ***operating line*** (since it is determined by the A/O ratio and other operational parameters: xo, xn, yn+1).



Figure 7. Changes in metal ion concentrations in organic and aqueous phases as a result of extraction for stage i in an SX circuit.

 The same considerations extended to all stages of a circuit yields a diagram such as that in Figure 8. It is called a ***McCabe-Thiele diagram***. The upper curve is the loading curve. **Note** that the slope of the A/O line is represented on a graph of organic versus aqueous solution concentrations. This seems counter-intuitive, but it merely falls out of the mass balance considerations. **Note** too that the extents of the changes in concentrations in each stage are bounded by the A/O line and the equilibrium curve. Consider stage 1. Aqueous PLS enters at xo, while organic from stage 2 enters at y2. After mixing and separation organic leaves at concentration y1, while aqueous leaves with concentration x1. In stage 2, aqueous enters at x1 and organic enters at y3. After mixing and separation, organic leaves at y2 (goes to stage 1) and aqueous leaves at x2.

Figure 8. Annotated McCabe-Thiele diagram for a 3-stage, counter-current solvent extraction. Extraction stage numbers are indicated in bold.

Factors Affecting the McCabe-Thiele Construction: The precise shape of the equilibrium line (loading curve) depends on the organic extractant concentration and the aqueous phase composition (metal ion concentration, pH and impurities concentrations). The PLS composition is governed by leaching and may not be easily altered. The organic phase composition can be varied to achieve a desirable extent of loading. Often the A/O ratio is quite close to 1 in extraction in order to minimize the volume of costly extractant in the plant. The barren organic concentration is governed by stripping and can be tailored to specific requirements. For a given set of parameters there is a unique A/O line that will yield a unique McCabe-Thiele construction. Parameters such as PLS metal ion concentration, barren organic metal ion concentration, raffinate concentration, loaded organic concentration, A/O value, and equilibrium line are constraints. For a given loading curve, specifying any other three uniquely defines the McCabe-Thiele construction. Given an A/O value, any one point on the line uniquely establishes that line (e.g. raffinate [Mn+], barren organic [Mn+]).

 Figure 9 illustrates some of the effects of varying parameters for copper SX system with a particular hydroxyoxime extractant solution. The PLS [Cu+2] is set at 2.5 g/L. In (a)-(c) the barren organic [Cu+2] is varied at a specified % extraction (95%). This simply means that 95% of the 2.5 g/L [Cu+2] in the PLS is extracted. A given % extraction sets the raffinate concentration:

 % extraction = (xo - xn) x 100 = E % [13]

 xo

 xn = raffinate [Cu+2] = xo - Exo [14]

 100

In the figure below xn = x2. As the barren organic [Cu+2] decreases A/O increases, as does the loaded organic [Cu+2]. Keeping A/O near 1 then puts significant constraints on the system.

 The effects of decreasing % extraction at fixed A/O = 1 (increasing raffinate [Cu+2]) are shown in (d)-(f). Increasing % extraction is good with respect to recovery from the leach solution, but it lowers the loaded organic [Cu+2] and lowers the barren organic [Cu+2]. The latter effect has significant implications for stripping. Low barren organic concentrations are difficult to achieve. In parts (a), (d) and (f) one stage is also being used very inefficiently; the change in concentrations is relatively small compared to the other stage.

 These diagrams are based on equilibrium conditions. In a real SX circuit, steady state conditions may prevail, but the chemical reactions might not necessarily come to equilibrium, particularly when the extraction reactions are not fast.

The same kinds of considerations as described above apply to stripping, although the aqueous phase is now being enriched and the organic depleted. A plot of aqueous strip solution concentration versus organic concentration may be plotted (instead of organic versus aqueous). A McCabe-Thiele diagram for stripping can be similarly drawn. However, the operating line now has a slope of ***O/A***, *not* A/O.

 The loading and stripping operations must be considered together in practice, since the organic is cycled between these two operations. It can be seen that changing the A/O ratio has implications for the inventory of organic reagent required, the number of stages of both loading and stripping and the extent of loading and stripping. In the end an economic minimization must be performed to determine the right balance of tradeoffs between technical possibilities and economics.

**Learning Outcomes:** Solvent extraction can purify a solution by preferentially extracting one chemical species while rejecting others. This is due to the differing equilibrium extents of reaction between the extractant and the metal ions.

 Solvent extraction can concentrate a species (upgrading). This is the result of transfer into an organic phase (loading), then transfer back into a *different* aqueous phase (stripping). The organic phase is just a go-between, a means of transfer between the leach solution and the strip solution. If the strip solution flow rate is less than the feed solution flow rate, the concentration of the extracted species will be higher in the final solution than in the feed; hence upgraded.