

Stage Efficiency in Copper Solvent Extraction Plants

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Introduction

In a solvent extraction (SX) plant, stage efficiency calculations are used to determine mixer efficiency. With modern extractants and mixing equipment, it is generally taken for granted that stage efficiencies will be above 95%, but this is not always the case. Dependant on mixer/solution conditions, stage efficiencies can occasionally be low, therefore leading to higher reagent usage. Proper methods to identify when stage efficiency performance is below expectations, and ways to identify if it is an equipment or chemical issue are valuable tools for a plant metallurgist. With these tools and skills an on-site metallurgist can more quickly return their SX plant to proper operation. This paper will discuss methods for analyzing stage efficiency, evaluating factors that may affect stage efficiency, and evaluating the impact of stage efficiency on the overall operation.

Methods for Determining Stage Efficiency

Stage efficiency is a critical parameter to monitor in solvent extraction plants in order to ensure cost efficient operation. Stage efficiency calculations may be completed in a number of different ways however they are most commonly determined via McCabe-Thiele construction. Stage efficiency

calculations give an indication of how well the solutions are being mixed and their approach to equilibrium.

Graphical Method

Typically stage efficiencies are calculated by graphical methods comparing the circuit performance to that which could be achieved based on the equilibrium isotherms.

The isotherms are generated by mixing the aqueous feed solution (Pregnant Leach Solution, or PLS) and plant organic to equilibrium at various O/A ratios. PLS is mixed with the barren organic for an extract isotherm. Lean electrolyte is mixed with the loaded organic for a strip isotherm. The aqueous and organic solutions are then separated, filtered, and the copper concentrations in both the aqueous and organic phases are measured. This data is then graphed to show the equilibrium conditions achievable, as shown in Figure 1 and 2.

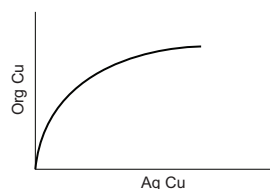


Figure 1 - Extract Isotherm

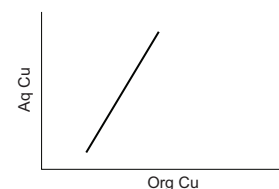


Figure 2 - Strip Isotherm

A full metallurgical profile of the plant (i.e. analyzing the copper concentration of all inlets, outlets and intermediate stages of the plant) is obtained and plotted against the equilibrium isotherms generated under the plant conditions at the time. Figure 3 shows an example process flow diagram.

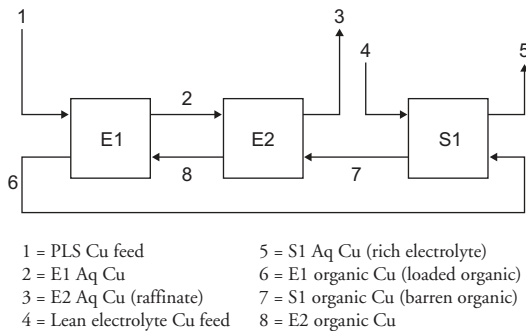


Figure 3 - Process Flow Diagram

Samples 1-8 would then be analyzed and plotted against the extract and strip isotherm graphs previously created, as shown in Figures 4 and 5 for extract and strip stages respectively.

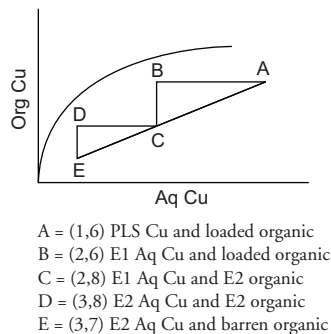
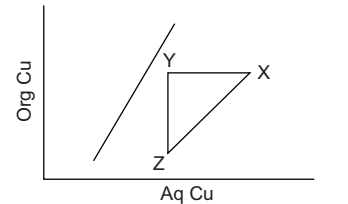


Figure 4 - Extract McCabe-Thiele Diagram

After completion of the McCabe-Thiele construction, stage efficiency for any stage can be determined graphically. The distance between the isotherm and the McCabe-Thiele diagrams indicates the efficiency at which each stage is running.



X = (6,5) Loaded organic and rich electrolyte
Y = (7,5) Barren organic and rich electrolyte
Z = (7,4) Barren organic and lean electrolyte

Figure 5 - Strip McCabe-Thiele Diagram

Figure 6 shows a graphical example of calculating stage efficiencies with the McCabe-Thiele diagrams.

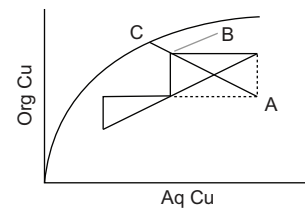


Figure 6 - Stage Efficiency, Graphical Method

The distance AB divided by the distance AC (multiplied by 100%) is the stage efficiency for that stage. Note: This method takes into account the approach to equilibrium of both the aqueous and organic phases, as opposed to a Muphree method which only examines one phase's approach.

At 100% stage efficiency (or 100% mixer efficiency), the point representing the aqueous and organic copper concentrations exiting each stage should lie on the isotherm, as shown in Figure 7.

Grab-Sample Method

An alternative method for determining stage efficiency is to sample and analyze the inlet and outlet streams of a given mixer and compare those

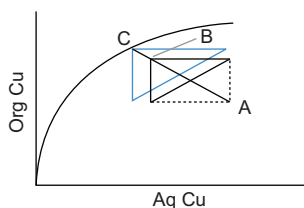
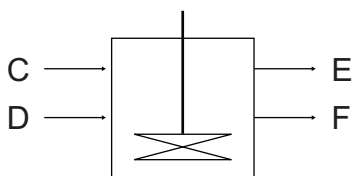


Figure 7 - Stage Efficiency, Graphical Method

results to what could be obtained by mixing the inlet streams to equilibrium separately using the flow O/A ratio. The stage efficiency can then be calculated as shown by Figure 8 and Equation 1:

$$\text{Equation 1} \quad \text{Stage Efficiency} = \sqrt{\frac{(C - E)^2 + (D - F)^2}{(C - B)^2 + (D - A)^2}} * 100\%$$



A = Aqueous from equilibrated mixer sample
 B = Organic from equilibrated mixer sample
 C = Organic entering the mixer
 D = Aqueous entering the mixer
 E = Organic exiting the Mixer
 F = Aqueous exiting the Mixer

Figure 8 - Stage Efficiency, Batch Method

If a circuit profile indicates a low stage efficiency, it should be rechecked through additional McCabe-Thiele evaluations or using the grab-sample method for determining stage efficiency. There can be a number of reasons for poor stage efficiency (i.e. poor mixing due to short circuiting, non-homogeneity, organic quality, impurities within the feed, insufficient retention time, low temperatures, etc.). Whatever the cause, improving stage efficiency will result in lower operating costs and overall better operation.

Impact of Poor Stage Efficiency

Poor stage efficiency has a direct impact on reagent utilization and net transfer properties – therefore operating costs. Low stage efficiency will lead to low copper recovery for the given operational conditions.

Table 1 shows the impact of stage efficiency on copper recovery and the net transfer achieved for fixed circuit conditions.^[3]

Operational conditions:

Circuit: 2 extract stages, 1 strip
 Feed: 3 gpl Cu pH 2.0
 Lean electrolyte: 30 gpl Cu; 180 gpl acid
 Rich electrolyte: 45 gpl Cu
 Extract O/A ratio 1:1
 Reagent 10 vol% ACORGA® M5774
 Strip Stage Efficiency: 95%
 Extract Stage Efficiency: Variable

Extract Stage Efficiency	Recovery	Net Transfer (gpl Cu per v/o extractant)
85%	87.7%	0.263
90%	90.6%	0.272
95%	93.3%	0.280
97%	94.3%	0.283

Table 1 - Recovery and Net Transfer with Varying Extract Stage Efficiencies

To compensate for poor stage efficiency an operation would need to add additional extractant to achieve the same Cu recovery. Note, there is a limit to the recovery gain by reagent addition alone. Using the above circuit conditions, the additional reagent required to achieve 94.3% recovery (i.e., recovery corresponding to 97% stage efficiency) was calculated, as shown in Figure 9.

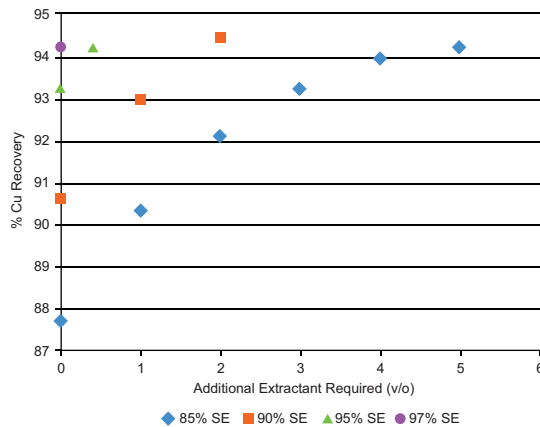


Figure 9 - % Cu Recovery vs. Additional Extractant Requirement

For the extreme case (comparing 85% Stage Efficiency to 97%) an additional 5 vol% reagent would be required to achieve the same recovery. Under these conditions, the circuit would be far from optimized and the net transfer would suffer. The additional extractant required to achieve the Cu recovery target would result in more uncomplexed oxime, which would then be available for potential Fe transfer. The cost implications of low stage efficiency can be estimated. The impact on reagent consumption is shown in Table 2. (Basis: 8000 gpm flow, 40 ppm entrainment, Equivalent SX Cu transfer, \$10 USD/kg reagent cost)

Extract Stage Efficiency	Reagent Cost /yr	Cost Difference /year
97%	\$611,142	\$0
95%	\$635,588	\$24,446
90%	\$733,371	\$122,228
85%	\$916,714	\$305,571

Table 2 - Reagent Consumption as a Function of Extract Stage Efficiency

The other cost implications of low stage efficiency and the approach selected to overcome it (more extractant; more mixer energy; etc.) also need to be considered. Higher mixer agitation can lead to

higher entrainments. Higher extractant concentration can potentially lead to higher Fe transfer, adding other costs (Co loss, current efficiency, Cu re-circulated, mist suppressants, leveling agents, etc.)^[2]

Graphical Method for Determining Mixer Efficiency from Kinetics Data²

Although difficult to scale, batch kinetic data gives a real and accurate method to evaluate different variables for their potential impact on stage efficiency under the given mixing conditions. Some variables are listed below.

- Temperature
- Residence time
- Tip speed/energy input
- Reagent quality
- Surfactants / impurities
- Solution viscosity
- Mix box O/A ratio
- Reagent Formulation

Note: Dependant on plant mixing conditions, the kinetic or mixing differences brought about by a change may or may not result in lower plant stage efficiency. Example: a plant with efficient multi-stage mixing and/or longer retention times may be able to tolerate a greater variation in conditions – without a noticeable variation in stage efficiency. However plants with limited mixing, limited retention times, or operating significantly beyond design may be more limited in their tolerance to changing operational conditions.

Using standardized mixing equipment, as shown in Figure 10, generate a kinetics curve under pre-determined conditions (O/A, continuity, mixer speed, temperature, etc.).

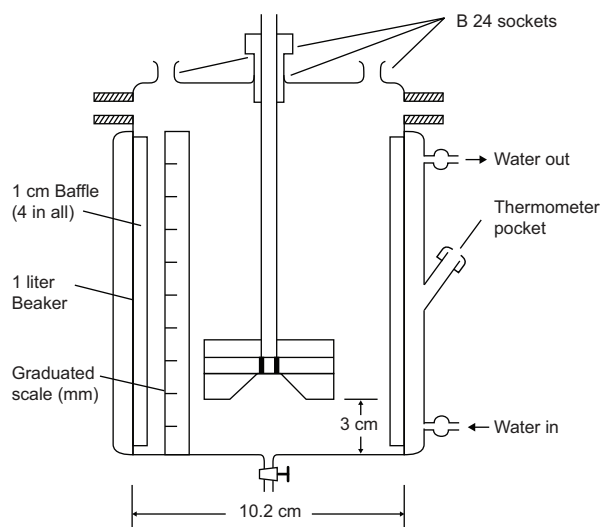


Figure 10 - Standard Mixing Vessel

- 1) Mix the aqueous and organic samples together and sample the mixture at various time intervals (for example 0, 15, 30, 60, 90, 120, 900 seconds).
- 2) Allow the phases to separate and analyze the metal concentration in one phase (both to confirm accuracy).
- 3) Plot the results as metal concentration (g/l) in one phase against time (sec).
- 4) Draw a smooth curve through the points and draw tangent lines to the curve at several metal concentration points along the curve (shown in Figure 11).

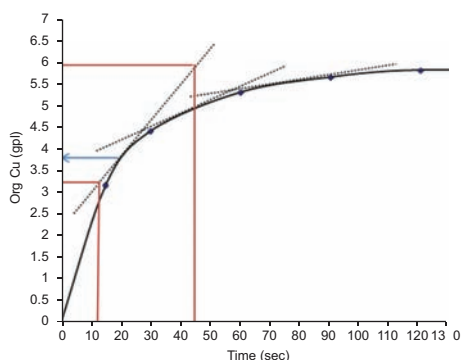


Figure 11 - Organic Cu Concentration vs Time

The slope of the tangent lines for each metal concentration will give a rate of change (gpl metal per unit time) vs the specified metal concentrations as shown in Table 3.

Org Cu (gpl)	1.57	3.74	4.80	5.41	5.66
Rate (gpl/sec)	0.209	0.082	0.029	0.011	0.005

Table 3 - Transfer Rate as a Function of Metal Concentration

Once the rate/concentration data has been collected, plot the rate of change against concentration. Draw a line with a slope equivalent to the reciprocal of the target residence time – begin at the inlet/starting concentration and a rate of zero (0). Stage efficiency can then be estimated for different residence times by drawing lines of different slopes as shown in Figure 12.

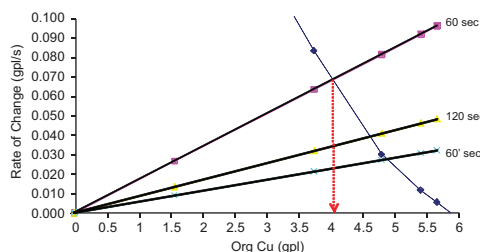


Figure 12 - Stage Efficiency for a Single Mixer Stage

The point of intersection of the retention time line and rate curve is the expected exit concentration of the phase under consideration at the given residence time. The intersection of the rate curve with the X axis provides the expected equilibrium value.

Once the exit concentration is known, the stage efficiency can be calculated from the equilibrium value (900 second value). The stage efficiency is calculated as the exit concentration minus the starting concentration divided by the equilibrium concentration minus the starting concentration. Table 4 shows the results for Figure 12.

Time (sec)	Starting Conc (gpl)	Outlet Conc (gpl)	Equilibrium Conc (gpl)	SE%
60	0	4.05	5.877	68.9
120	0	4.60	5.877	78.3
180	0	4.85	5.877	82.5

Table 4 - Stage Efficiency vs. Retention Time

Multiple Mixers

For multiple mixers the same technique may be used. Draw a straight line representing the residence time of the first mixer. Use the exit concentration as the starting concentration for the line representing the residence time in the second mixer.

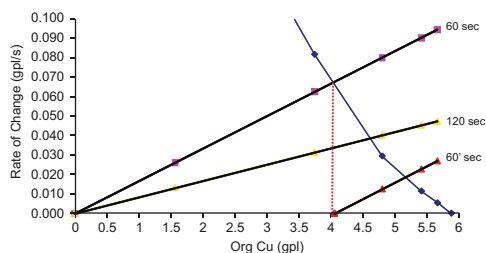


Figure 13 - Stage Efficiency for a Multi-Stage vs Single Mixer Stage

Figure 13 shows an example of a single mixer with a residence time of two minutes in comparison to two-stage mixing with a primary and secondary mixer each with a residence time of one minute. The two stage mixer has a first outlet concentration of 4.05 gpl which is used as the starting concentration in the second mixer. The resulting exit concentration of the second stage mixer is 5.20 gpl corresponding to a stage efficiency of 88.5%. The exit concentration of the single stage mixer after an equivalent residence time of two minutes is 4.60 gpl corresponding to a stage efficiency of 78.3%.

Stage Efficiency Based on Batch Kinetic Data

Oxime comparison

Three commercial oximes samples were compared under identical extract mixing conditions in the laboratory. The reagents were made up to 20 vol% solutions in standard diluent, and mixed with a synthetic feed solution containing 6 gpl Cu at pH 2.0. The mixing vessel was a one liter jacketed flask, fitted with baffles. The mixer was a six bladed flat turbine mixer located three cm from the vessel bottom. The agitation rate was set at 600 rpm. (Note: 600 rpm was selected as a low agitation setting for this test equipment to increase sensitivity for kinetic differences.)

The organic solutions were added to the mixer, the agitator was started and the aqueous solution was then added (maintaining organic continuity). Ten ml samples of the solution were then taken from the mixer at set time intervals (15, 30, 45, 60, 90, 500 seconds). The plot of organic metal concentration vs. time was generated and from it a transfer rate vs. organic metal concentration curve was generated. The expected results for a single stage mixer using a three minute mixer retention

Formulation	Stage Efficiency
20 vol% C9 aldoxime	90%
20 vol% C12 aldoxime	7%
20 vol% ketoxime	72%

Table 5 - Stage Efficiency

time was then calculated as shown in Table 5. As shown the C9 aldoxime formulation is expected to obtain the highest stage efficiency, followed by the C12 aldoxime and then the ketoxime.

Formulation comparison

Numerous commercial reagent formulations were then compared under identical conditions. The

expected stage efficiency for a single mixer (3 minute mixer retention time) is shown in Table 6.

Formulation	Stage Efficiency
ACORGA® M5774 (C9 modified aldoxime)	86.5%
ACORGA® OPT® 5510 (modified C9 aldoxime/ketoxime blend)	81.1%
LIX* 984N (C9 aldoxime /ketoxime blend)	80.0%
LIX 984 (C12 aldoxime/ketoxime blend)	77.3

*LIX is a registered trademark of Cognis Corp.

Table 6 - Formulation Comparison

As shown the C9 aldoxime formulations tend to have the faster kinetics and therefore expected to provide higher stage efficiencies for given mixing conditions. Note: All the calculated stage efficiencies are lower than what would typically be seen in practice – but demonstrates the relative kinetic differences.

Impact of Aqueous viscosity

20 v/o ACORGA M5640 kinetic behavior was evaluated with numerous aqueous solutions containing varying amounts of impurity ions. Each aqueous solution was prepared by diluting a real leach liquor sample (one with a high content of impurities) with water and then adjusting Cu and pH to the same original value. Solutions were mixed at a mixer speed of 600 rpm, under organic continuity at room temperature. The analysis was completed assuming three stage mixing, each stage with one minute retention time (3-minutes total). The results are shown in Table 7.

Water Dilution, %	Aqueous Viscosities, cP	Stage Efficiency, %
0	7.8	91.6
25	4.2	94.1
50	2.8	95.6
75	1.7	98.3

Table 7 - Impact of Aqueous Viscosity

The leach liquor sample for this evaluation had extremely high aqueous viscosity due to the buildup of Al and Mg sulfate over time. The higher the aqueous viscosity, the lower the stage efficiency under the test conditions.

Plant Organic Quality Comparison

Although the quality of the supplied reagent is critical to its performance in the SX circuit, with any formulation, the overall organic quality will tend to decrease with time if the organic remains untreated. Build up of surfactants/impurities from leaching, presence of oxidative degradation products, or other impurities may have a significant impact on the stage efficiencies obtainable for given mixing conditions. A 10 v/o ACORGA M5640 formulation was intentionally degraded within the laboratory through contact with an electrolyte containing permanganate ions (resulting in oxidative degradation). The kinetics and impact on stage efficiency for the fresh organic and the degraded organic is shown in Table 8. Conditions: 600 rpm; 3-minute retention time; organic continuity; one mixer; 25°C.

	Stage Efficiency	Phase Disengagement Time(s)	IFT
Fresh	91%	15	35.8
Degraded	88%	105	35.0

Table 8 - Organic Quality Comparison

Oxidative degradation (or the presence of any other impurities) within the organic phase can have a significant effect on stage efficiency. The presence of impurities within the organic phase can often (but not always) be seen in the phase disengagement or interfacial characteristics of the organic. Low interfacial tension or prolonged phase disengagement is often the sign of poor organic quality and should be considered for its potential impact on stage efficiency. Standard practice to remove the impurities is treatment with activated clay.

Organic/Aqueous Mixer Ratio

A sample of plant organic was tested utilizing two O/A ratios under strip conditions. Conditions: 600 rpm; organic continuity; 25°C; single mixer; 1.8 minute mixer retention time. Results are shown in Table 9.

O/A Mix Ratio	Stage Efficiency
5.2/1	75%
2.0/1	84%

Table 9 - Impact of Strip O/A Ratio

Under these mixing conditions, the mix was non-homogenous at the high O/A ratio resulting in low stage efficiency.

Typical Plant Operating Stage Efficiency

Table 10 shows typical stage efficiencies (determined via McCabe-Thiele analysis) for a number of North and South American Cu SX operations. As shown, stage efficiency tends to be high, especially in stripping. Nearly 50% of the stages have stage efficiencies averaging above 95%; and over 80% have stage efficiencies greater than 90%.

Stage efficiency is shown as-measured from commercial plant profiles using McCabe-Thiele techniques. Some variability is expected. When evaluating a plant via McCabe-Thiele techniques there are a number of factors to be considered: bleed addition location; acid make-up location; impact of entrainments; temperature variation between isotherm generation and plant operation; and plant conditions when sampling (i.e., is the plant at steady state).

Practical Example

McCabe-Thiele analysis showed low stage efficiency in a strip mixer. Based on these results, grab-sample stage efficiency analysis

was completed on-site confirming the low stage efficiency. Samples were then taken to the laboratory for further analysis. The kinetics of

Plant/Train	E1	E2	E3	S1	S2
1	89	94		98	
2	90	93		94	
3	90	96		99	
4	93	91	97	72	
5	92	84	97	79	
6	99	98	97	97	
7	100	98		98	
8	93	95		101	
9	93	96		101	
10	87	91	93	91	
11	86	89	98	89	
12	98	98		105	
13	93	86		102	
14	87	95		102	
15	98	100		90	
16	92	94		102	
17	88	92		101	
18	88	98		92	
19	95	100		93	
20	95	97	93	100	
21	96	96		100	100
22	92	95		100	100
23	98	87		91	
24	96	90		93	
25	96	90		99	
26	99	98		98	
27	94	97	98	93	
28	92	100	95	96	
29	88	87		97	
30	85	93		91	
31	97	96		97	87
32	92	92		94	66
33	92	92		90	
34	92	98		92	75
35	87	98		94	77
36	93	90		78	75
37	98	98		96	
38	92	92		98	
39	89	85		90	

Table 10 - Plant Stage Efficiency

plant organic was compared to the kinetics of fresh organic under controlled conditions. The results indicated equivalent stage efficiency would be expected for the two organics, therefore not organic-quality related. Testing with synthetic and plant electrolyte also showed equivalent performance between plant and fresh reagent, therefore not likely due to impurities in the electrolyte. The investigation was then focused on plant mixing conditions. Numerous options for improving stage efficiency were identified. Through plant testing, improvement of stage efficiency was obtained through optimization of aqueous recycle flow, creating a more uniform mix (flow had been diminished by scaling issues).

Conclusions

Stage efficiency is an important metallurgical parameter for Cu SX plants. The McCabe-Thiele and Grab-Sample techniques are valid methods for monitoring stage efficiency of the plant. Batch kinetic data may be generated within the lab under controlled conditions to allow a relative comparison of the impact of operational changes or solution characteristics. The methodology can assist greatly in troubleshooting an operation. The kinetic performance of the extractant formulation is one key criteria which should be considered when comparing reagents. Do not assume all reagents will achieve the same stage efficiency, especially when non-ideal mixing conditions (low temperatures, higher-than-design flows, etc.) exist.

References

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