Clay Treatment Improvements Using ACORGA® CB1000 Clay Binder

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In copper solvent extraction, managing the quality of the organic phase is key to ensuring optimal physical and metallurgical performance in the plant. This is even more so in Africa, where agitation leaching is ubiquitous, and in the Americas, where declining ore grades have resulted in increased throughputs and where advances in plant design and practice have reduced organic losses. Clay treatment at the optimal dosage is critical in maintaining organic quality. However, achieving the optimal dosage using existing equipment is a challenge, the bottleneck often presenting itself in the filtration process after clay treatment. To alleviate the problem, Cytec has developed ACORGA® CB1000 Clay Binder, a process aid that increases the efficiency of filtration equipment and enables higher dosages of clay through existing filtration capacity. This paper discusses common industry practices and related issues in organic clay treatment, and presents the benefits achieved in two commercial operations.

INTRODUCTION

In North and Latin America, decreasing ore grades have prompted copper solvent-extraction (SX) operations to raise pregnant leach solution (PLS) flow rates, increasing plant throughput to maintain production (Robinson *et al.*, 2003). The ability to process higher flow rates through existing mixer–settlers historically came at the expense of increased entrainments (Brueggemann, 2006). However, advances in mixer–settler design, practices and improvements in organic recovery processes have enabled operations to maintain and, in some cases, reduce organic losses while achieving higher flow rates through existing equipment. With increased demand on the SX equipment resulting in a more intense utilization of the organic inventory, and reduced losses meaning the inventory is less frequently renewed with fresh organic, proper maintenance of the circuit organic quality through efficient clay treatment is now more important than ever. This is also the case in the African region, where agitation leaching is common practice. Crud problems are typically more severe here, making it challenging for installed crud treatment capacity to return high quality recovered organic to the SX process. The African agitation-leach plants are pushed hard to maximize throughput and recovery but many of these plants do none, or at best, ineffective clay treatment. Those who do use clay, for the most part, evaluate treatment effectiveness by measurement of phase disengagement time (PDT). This practice is often misleading because the fine particles present in poor quality organic are known to accelerate phase-break time. The resulting apparent PDT improvement is short lived because the solids eventually wash out of the organic.

ORGANIC QUALITY AND CLAY TREATMENT

Mixer–settler technology has greatly improved since the first commercial copper SX operation in the late 1960s, contributing to reductions in entrainments (Giralico *et al.*, 1998). Organic recovery processes have also evolved. Operations often install additional equipment to assist in organic recovery from aqueous streams exiting the plant. These include sparge columns and electrolyte filters to reduce the amount of organic entrained in the electrolyte. Additionally, skimmers, belt mops and other organic-recovery systems can assist in recovering the organic lost to the raffinate ponds. The quantity of organic recovered by these processes can often be 80 to 90 % of the total organic leaving the circuit (Brueggemann, 2006). Reduced losses, improved organic recovery processes, and the on-going desire to push the plant capacities all highlight the importance of maintaining high organic quality.

Over time, the organic inventory accumulates contaminants from the PLS, electrolyte or organic that is recovered and returned to the circuit. These contaminants tend to be interfacially active and can negatively impact the physical and metallurgical performance of the circuit. Organic contaminants result in higher phase-break times, increased dispersion-band depth, lower stage efficiencies, reduced Cu:Fe selectivity and higher entrainments. In extreme cases, the physical performance of the plant deteriorates to the point that the dispersion band over- or underflows the weir, resulting in excessive loss of organic, contamination of the electrolyte and/or excessive electrolyte loss. In these extreme cases, flows must be reduced to maintain operation, resulting in significant impact to production.

In agitated-leach plants, this deterioration in organic quality is not always as evident as it is in other operations due to the high level of solids which tend to enter the plant, altering the phase separation properties of the system.

Current Clay Treatment Practices and Issues

Clay treatment is a critical support process to remove interfacially active contaminants that build up in the circuit. Current practices involve treating circuit and/or recovered organic with acid-activated clay followed by a filtration step. Processed organic should then be tested to ensure that the PDT has been restored prior to introducing it back to the inventory. However, since PDTs can be misleading, a secondary view of the organic quality is recommended by determining the improvement in interfacial tension (IFT) of the plant organic as a result of clay treatment. Such improvement is measured by ΔIFT, the difference between the IFT of the clay-treated organic (at x% mass fraction of clay) and the IFT of the non-treated recovered organic:

$$\Delta IFT(x\%) = IFT(x\%) - IFT(0\%) \quad [1]$$

Unfortunately, current clay treatment (CT) practices and the associated quality control (QC) measures to ensure the effectiveness of the CT are often not practised. Quite often, the current treatment practices produce little benefit and are occasionally detrimental. The most common issues when completing clay treatment and performing the phase break quality control are:

- **Insufficient clay utilization**
  - Plants do not use sufficient quantity of clay to remove interfacially active impurities.
- **Clay deactivation**
  - Insufficient removal of aqueous from the organic results in clay deactivation and inefficient impurity removal.
- **Inefficient Solids Removal**
  - Solids returned to the circuit impact physical performance.
  - Surfactants get re-dispersed into the organic as a result of mechanical breaking of emulsions.
- **Non-standardized equipment and procedures to assess organic quality**
  - Organic of poor quality returned to the circuit detrimentally impacts performance.

Ensuring CT practices are utilized properly is especially important when treating recovered organic because it only takes a relatively small amount of 'bad' organic to compromise the quality of the entire organic inventory. To demonstrate this, organic from a commercial Cu solvent extraction–electrowinning (SX/EW) facility was recovered and added to fresh organic in varying concentrations. These solutions were then evaluated in the laboratory, as shown in Table I. IFT and PDTs (organic and aqueous continuity) were measured for each dose of poor quality organic. IFT measurements were carried out using a Kruss DVT-50 drop volume tensiometer.

Table I. Poor quality recovered organic impact on plant organic inventory (assumed organic inventory of 1 700 m^3).

Dosage of poor quality recovered organic to plant inventory (volume fraction) (%)	Equivalent volume added to plant inventory (m^3)	$\Delta IFT_{5\%}$ [IFT of thoroughly clay treated organic blend at 5% mass fraction of clay minus IFT of non-clay treated organic blend] (dyne/cm)	PDT (s)	
			Org. continuity	Aq. continuity
0	–	0	30	83
1	17	0.46	76	94
2.5	43	1.35	133	133
5	85	3.09	198	173

As shown, a small quantity of poor quality organic can have a drastic negative impact on the phase-separation performance. A 1% addition of poor quality organic is shown to more than double the organic PDT, which would have a direct impact on the dispersion-band depth and its proximity to the weir in the settler. As the addition of poor quality organic increased, the $\Delta IFT_{5\%}$ and PDTs, regardless of continuity, increased. A plant operating with a large dispersion band or pushing the flows to the limits of the equipment could easily run into severe issues if the organic inventory was contaminated by a bad batch of recovered organic.

Clay Dosage Requirements

The dosage of clay is often chosen based on operator experience and beliefs regarding the capacity of the filtration/processing equipment. However, the required dosage to efficiently remove the organic impurities varies with the source of organic and the level of contamination. Nonetheless, the clay dosage employed needs to be of a sufficient level to remove the impurities and restore the interfacial properties. Construction of an IFT clay dosage curve (IFT as a function of the mass fraction of clay), shown in Figure 1, is recommended to show the expected improvement in IFT as a function of clay dosage. The plant should select a clay dosage sufficient to remove the majority of the impurities based on the IFT curve established in the laboratory, meaning that plant organic IFT is restored to close to that of fresh organic. Clay dosages at mass fractions between 0.1 – 1.0% are commonly used (Mattison *et al.*, 1983; Hutzler *et al.*, 2015) but the IFT curve shows this is significantly less than what is required.

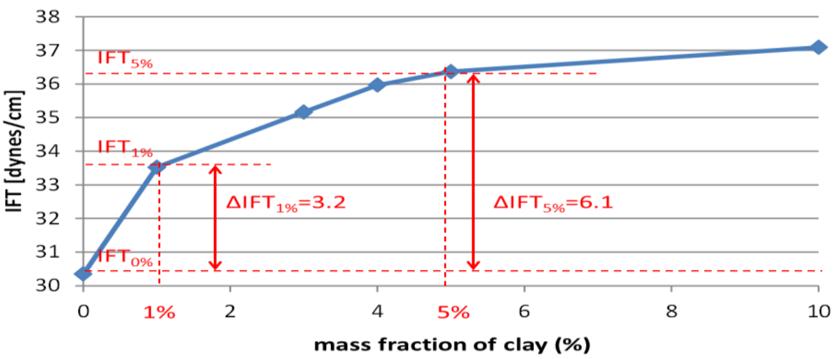

Figure 1. Interfacial tension measurements as a function of clay dosage.

The example depicted in Figure 1 shows that treating at a mass fraction of clay of 1% results in only half of the IFT benefit achievable when using a mass fraction of clay of 5%. Oftentimes, operations are hesitant to increase dosages out of concern to achieve acceptable filtration performance while maintaining a satisfactory rate of batches treated in a given amount of time. As a consequence, operations often use insufficient clay to remove the impurities and therefore have to treat the organic repeatedly to see the full benefit. Many operations, however, return poor quality organic to the plant inventory inadvertently due to lack of attention to QC.

Consumption of Extractant vs. Clay Dosage

There is a conception in the industry that higher clay usages may remove non-degraded oxime and increase reagent consumption. However, this concern tends to be overstated. While there is some organic loss, the data show that it is minimal. For illustration, maximum copper loading was measured at a commercial SX operation in Latin America without clay treatment vs. with "heavy" clay treatment at a mass fraction of clay of 5%. The results appear on Figure 2.

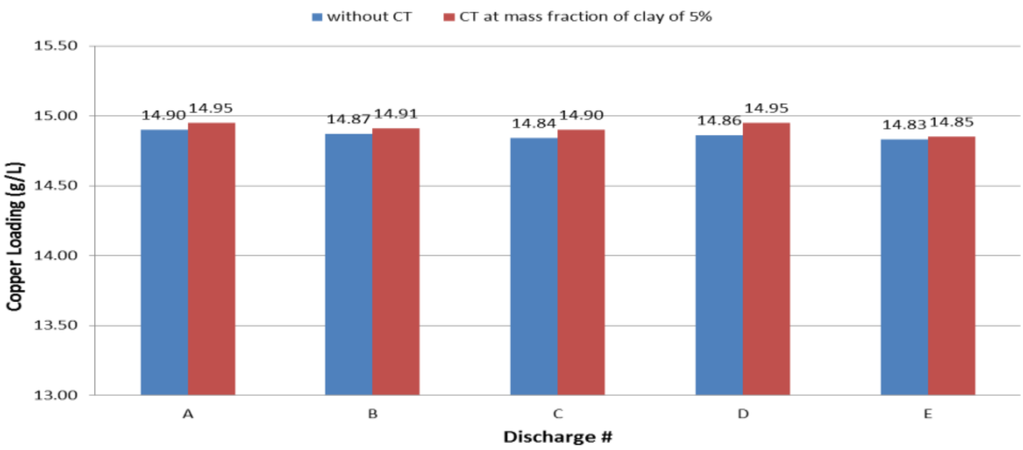

Figure 2. Maximum copper loading without CT vs. with CT at mass fraction of 5%.

The values of maximum copper loading are essentially the same for the two data sets (within experimental variability), with no reduction in maximum load value, which indicates very little actual oxime has been lost through the "heavy" clay treatment.

Clay Deactivation

In addition to operations using insufficient clay to remove the desired contaminants, the clay is often deactivated due to the organic not being sufficiently 'dry'. The presence of aqueous within the CT process deactivates the clay and prohibits the adsorption of the interfacially active compounds. The tank of organic being treated will occasionally contain entrained aqueous (PLS, raffinate or electrolyte) or even water if it is utilized for pre-coating the filtration equipment. In many African operations, organic clay treatment is carried out in the crud collection tank. As a consequence of clay deactivation by aqueous, operations will inadvertently return poor quality organic to the circuit inventory.

Organic Quality Affected by Crud Processing

Table II shows the interfacial tension of plant organic and organic recovered from crud processing activities. The IFT values are from maximum-loaded organic solutions measured against distilled water. These were then compared to the interfacial tension that was achieved after the plant organic (PO) was treated with clay at a mass fraction of 5%.

On average, IFT from crud processing is slightly lower than IFT from PO. Both IFT from crud processing and from plant organic are significantly lower than IFT after CT with mass fraction of 5% clay. Processing crud through a three-phase centrifuge to recover the entrained organic requires mechanical rupturing of the solid-stabilized aqueous and organic emulsion. The surfactant impurities which likely promoted the crud formation are released into the organic phase, lowering the interfacial tension. The organic is returned to the plant, impacting the quality of the plant inventory. The data shown suggest that the crud-processing activities are contributing to the diminished plant organic quality. Table II further shows how the IFT can be restored with efficient clay treatment.

Table II. *IFT of plant organic, organic recovered from crud and $\Delta IFT_{5\%}$ of the plant organic (IFT after CT with mass fraction of 5% clay minus IFT of non-treated plant organic).*

Sample	IFT (dynes/cm)			
	Plant Organic	Organic from Crud Processing	PO after CT with mass fraction of 5% clay	$\Delta IFT_{5\%}$
1	29.3	28.6	35.2	5.9
2	28.9	29.4	33.1	4.2
3	29.9	29.4	33.8	3.9
4	29.6	29.6	34.0	4.4
5	29.1	28.0	33.9	4.8
Average	29.4	29.0	34.0	4.6

Possible Misinterpretation of PDT and Importance for Quality Control Testing
The presence of solids in the organic phase (especially hydrophilic particles) is known to accelerate phase-break time. The presence of solids makes it impossible to determine if phase-break improvement is related to surfactant removal or due to particulates. The improved physical performance as a result of solids' content is superficial and short-lived. As the solids begin to wash out in the aqueous phase, the true organic quality will be reflected in diminished plant performance. Most operations do not filter or thoroughly filter the QC sample prior to conducting PDT testing, resulting in a false indication of organic quality improvement. Not only do operations often not filter the organic to be able to accurately determine if the PDT is the result of solids or surfactant removal, but they also often do not follow a standard procedure. As discussed, poor organic quality can have a drastic impact on operating costs and, at times, plant productivity. Maintenance of the plant organic quality can be easily accomplished with proper clay treatment – however the filtration process and subsequent QC require attention.

Time to Remediate Organic Inventory
Armed with knowledge of the clay dosage data, an estimate of the time required to remediate the quality of a plant's organic inventory is possible. The time required to recover the quality of the organic inventory is shown for CT at various clay dosages for one of the African Cu SX operations in Figure 3. The calculation uses the volume of the organic inventory and assumes a frequency of batch clay treatments within the capacity constraints of the CT equipment. Note that this type of analysis is indicative and does not take into account the possible continued contamination of the organic inventory and assumes complete removal of aqueous from the organic being treated.

At clay dosage mass fraction of 1%, the organic quality will be 90% restored in 210 days, in 130 days for 3% and, for 5% dosage, the time is reduced to 110 days.

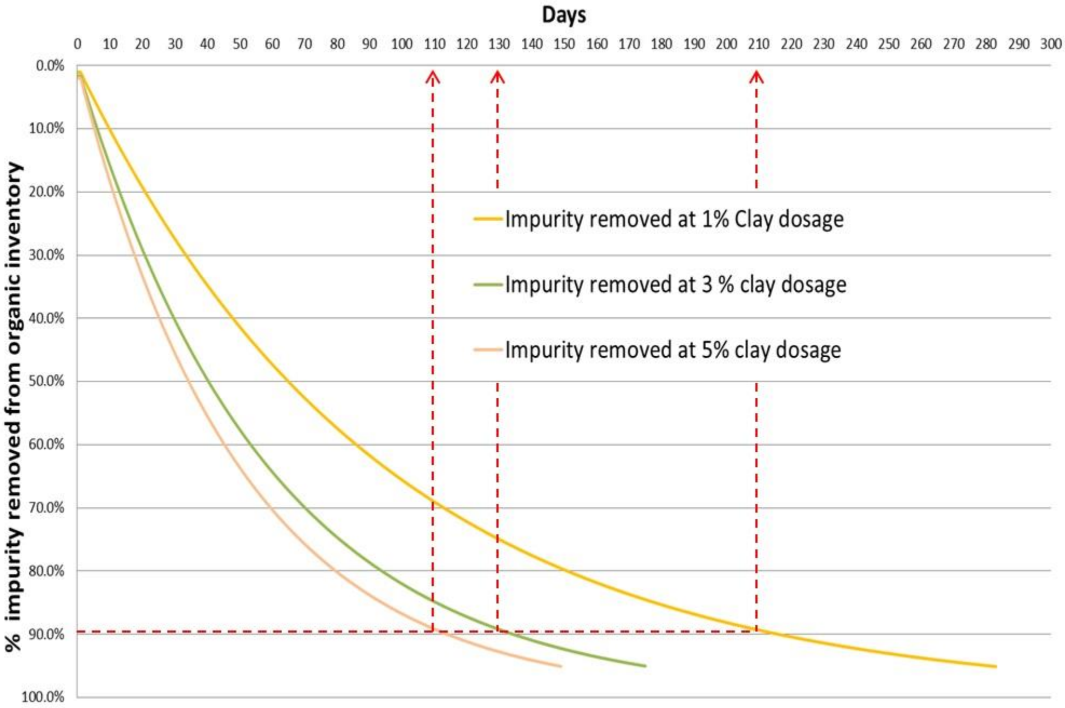

Figure 3. Time for complete organic remediation for an African Cu SX operation for various clay dosages.

ACORGA® CB1000 CLAY BINDER

CYTEC Industries has developed a clay treatment process aid that has been shown to improve filtration performance, allowing operations to achieve higher clay treatment dosages through existing equipment. ACORGA® CB1000 works by collecting the fine particulates, making them easier to remove from the organic. In commercial applications utilizing a filter press, the use of CB1000 was shown to improve the filtration operation without requiring addition of diatomaceous earth (DE) in the body feed. Elimination of DE addition with the clay allows operations to attain the higher clay treatment dosages through existing filtration capacity. The higher clay dosage is more effective in restoring the interfacial tension properties, resulting in improved phase-separation performance, higher Cu:Fe selectivity and has been shown to improve kinetics. In addition, the organic treated in this manner has been shown to be more highly clarified, returning fewer micro-solids to the plant inventory which improves the physical operation of the SX plant, lowers crud formation and reduces entrainments.

The efficiency of ACORGA® CB1000 as a filtration aid is demonstrated in the following laboratory investigation (Hutzler *et al.*, 2014). Two identical organic samples were clay treated at the same clay dosage. The first organic was filtered through 11-µm filter paper employing DE as a body feed to simulate current filtration practices. The second, following clay addition, was treated with 500 mL/m^3 ACORGA® CB1000, eliminating the body feed, then filtered through identical 11-µm filter paper. The resulting filtrates were then passed through a silver membrane filter with a pore size of 1.2 µm and the resulting filter papers were analyzed via scanning electron microscopy (SEM) imaging. Figure 4 is the SEM image of the virgin silver membrane filter paper at 10 000x magnification.

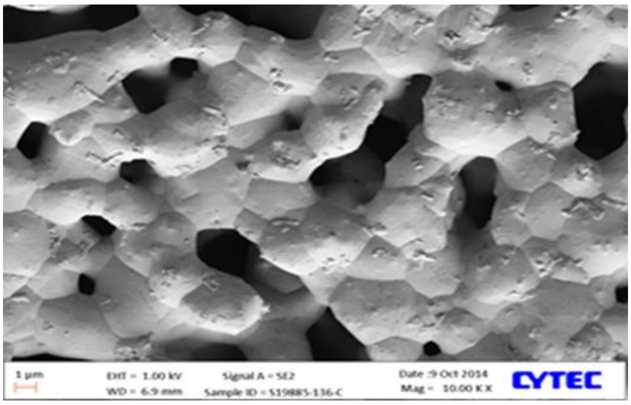

Figure 4. SEM image of fresh silver membrane filter at 10k x magnification.

Figure 5(a) is the SEM image at 10 000x magnification from filtration methods employing a body feed. It shows numerous sub-11 µm particles on the filter paper, demonstrating the inability of current filtration methods in removing fine particulates. Figure 5(b) is an SEM image of the same magnification highlighting the filtration improvement provided by ACORGA® CB1000. Many African Cu SX operations do not filter after clay treatment and rely on the organic/clay slurry being separated in a three-phase centrifuge. The use of ACORGA® CB1000, together with a centrifuge for removing fine particulates, will be investigated further.

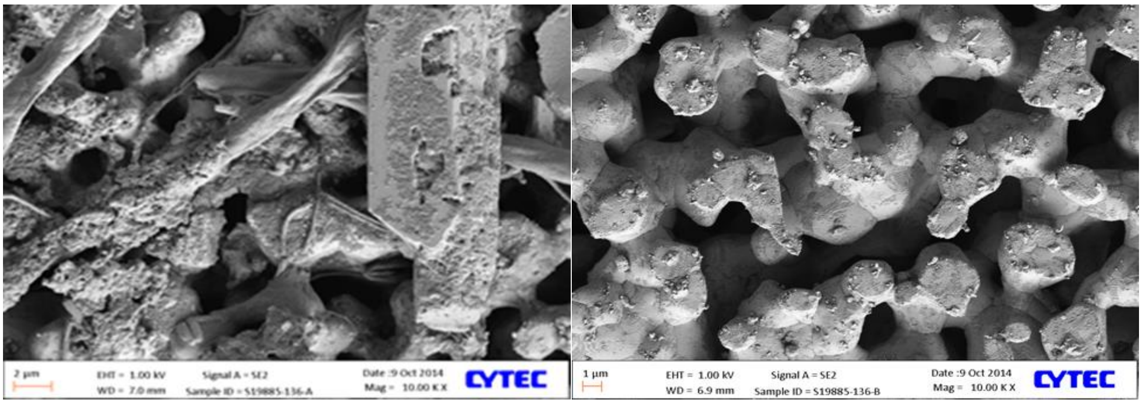

Figure 5. (a) SEM image of silver membrane filter post-filtering of organic processed using DE as body feed at 10k x magnification. (b) SEM image of silver membrane filter 10k x magnification processed using ACORGA® CB1000.

COMMERCIAL DEMONSTRATIONS

Following successful demonstration on a commercial scale, ACORGA® CB1000 is now being used at two North American copper SX facilities and is being trialed at several other properties in North America and Latin America. In North America (Hutzler *et a.l,* 2014) batches of organic were clay treated via conventional methods employing a body feed with low clay dosages. Conversely, batches were treated at double the clay treatment dosage. The higher CT dosages were made possible by eliminating the body feed using 500 mL/m^3 of ACORGA® CB1000 per batch. Feed and discharge samples for each batch were obtained. Measurements and observations were made on clarity, ability to increase clay dosage while maintaining filterability, IFT improvement and Cu:Fe selectivity. While the results require further statistical analysis for quantitative validation, they confirm the beneficial effects of efficient clay treatment on the quality of plant organic, as well as the benefits of using ACORGA® CB1000 along with the higher clay dosage.

Clarification

The effectiveness of ACORGA® CB1000 in improving the organic clarification step was compared to traditional clay treatment practices. Shown in Figure 6 are particle-size distribution data of various clay treatment batches for two plants filtered through conventional practices. Plant 1 data show a larger amount of micro solids (less than 6 µm in size) in the treated organic consistently throughout the batches. Plant 2 shows inconsistencies in the particle-size distribution from batch to batch, suggesting variability in the filtration performance.

Figure 7 shows the particle-size distribution of solids in the filtrate after clay treatment batches using 500 mL/m³ ACORGA® CB1000. These data show a more highly clarified organic filtrate when compared with filtration using a body feed (Figure 6). In addition, the filtration performance is more consistent, as evidenced by the uniform size distributions shown in Figure 7.

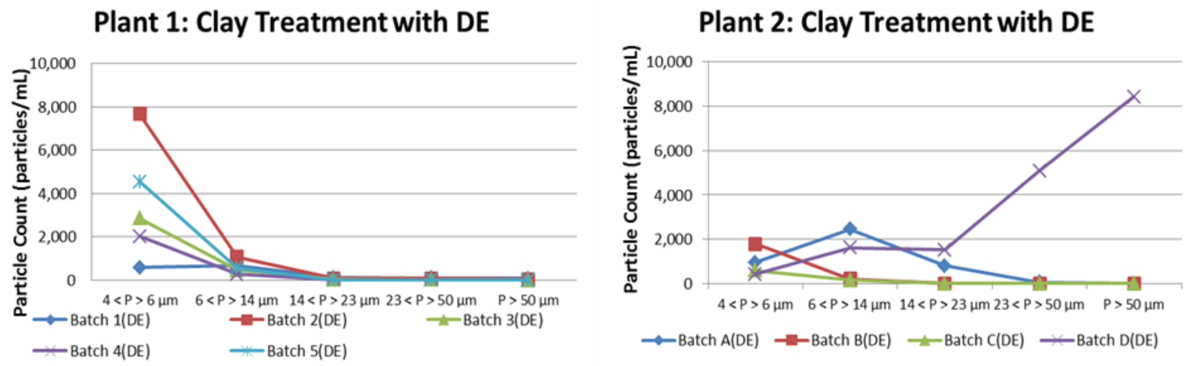

Figure 6. Particle size distribution data of clay treated organic filtered using only DE body fill.

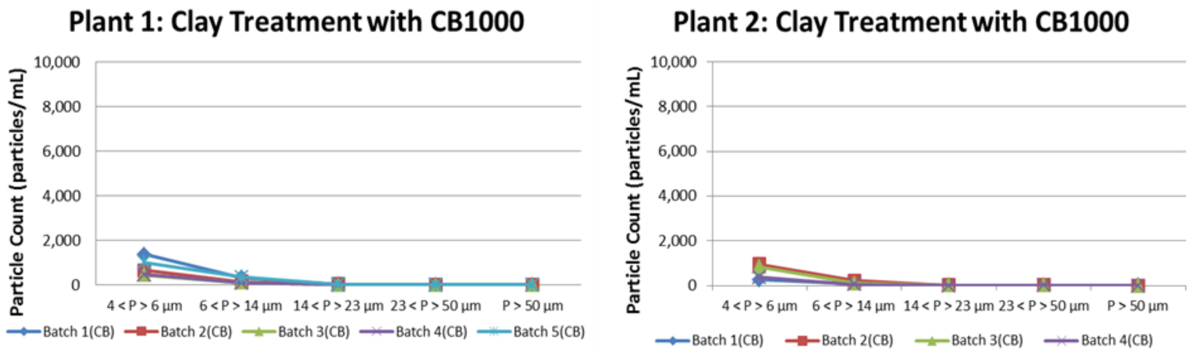

Figure 7. Particle size distribution data of clay treated organic using ACORGA® CB1000.

Organic Quality (assessed through IFT and PDT)

Figure 8 shows IFT measurements with and without the use of ACORGA® CB1000 for the two commercial trials. Samples were collected at the same clay dosage with and without the use of CB1000 to demonstrate equivalent organic quality. Additionally, samples were collected at twice the clay dosage. Doubling the clay dosage was accomplished by eliminating DE in the body feed using ACORGA® CB1000. Eliminating the body feed freed up additional press capacity to allow for a higher clay dosage.

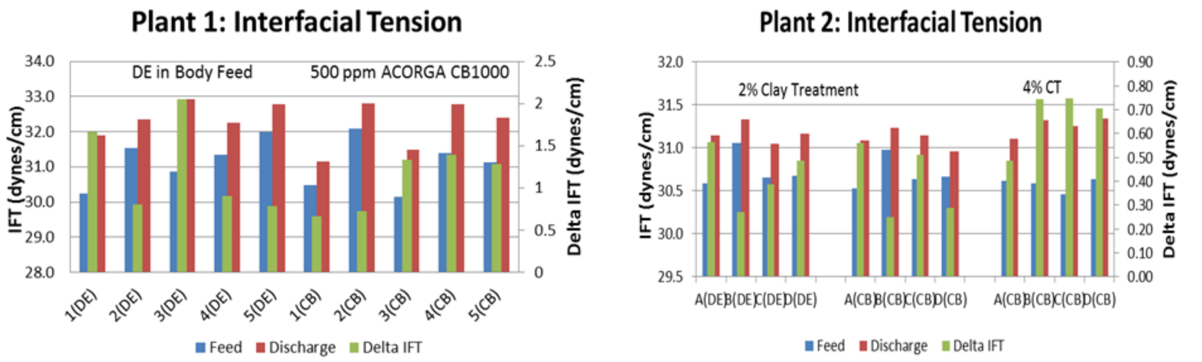

Figure 8. Interfacial tension results from two commercial trials utilizing ACORGA® CB1000.

The IFT improvement was similar between batches filtered using DE in the body feed to those treated with ACORGA® CB1000 with no body feed. The similar IFT results indicate that clay treatment using CB1000 is as effective in removing an equivalent amount of surfactant impurities as the conventional clay treatment process employing a body feed. Additionally, it was shown that doubling the clay dosage was possible through existing filtration capacity. Higher ΔIFT values were achieved at the higher clay treatment dosages. The ΔIFT increased by as much as 75%, resulting in better organic quality being returned to the process.

Organic and aqueous continuous PDTs were determined for all batch samples collected and are compared in Figure 9. PDTs were determined using a standard test method with plant PLS as appropriate. Improved PDTs were always obtained with clay-treated organic, most significantly demonstrated in disengagement times determined in organic-continuous mode.

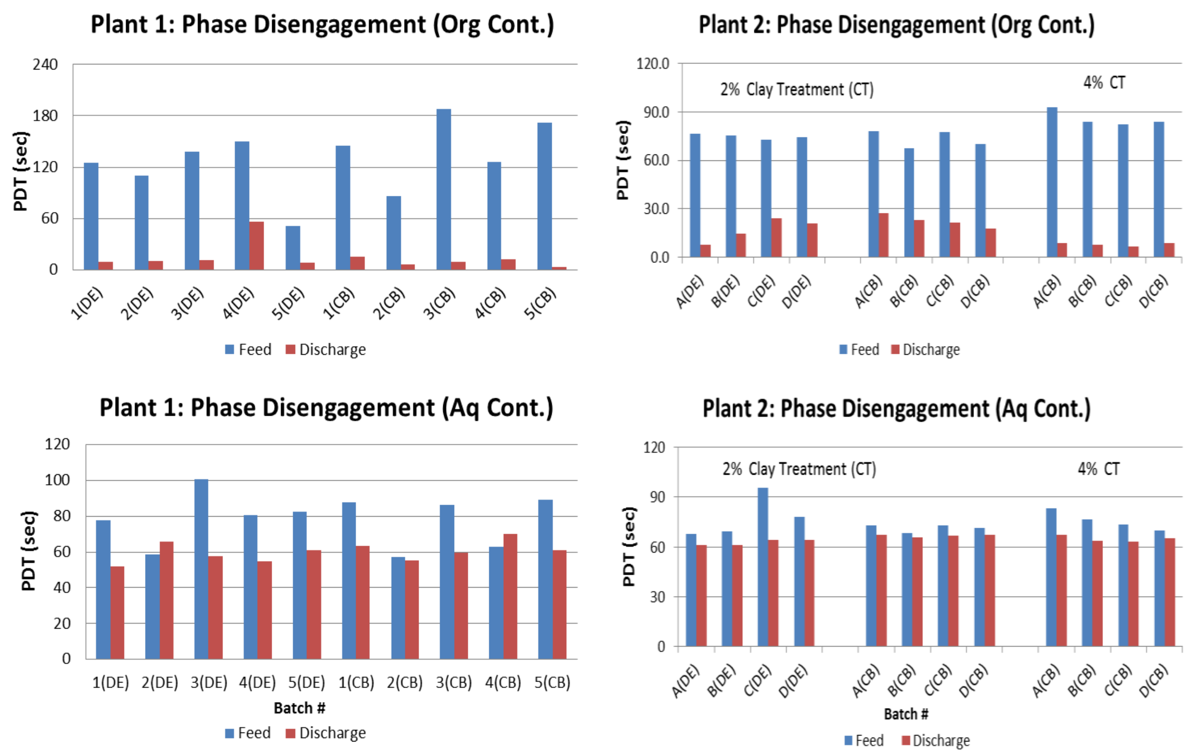

Figure 9. PDTs for batch samples from plant trials with and without ACORGA® CB1000.

Cu:Fe Selectivity

By enabling the use of higher mass fractions of clay in the existing filtration equipment, ACORGA® CB1000 Clay Binder allows the removal of more of the impurities present in the organic as part of the clay-treatment process. As some impurities are known to promote iron transfer, an improvement in Cu:Fe selectivity was anticipated with the use of the product, in some cases. This was confirmed in the laboratory and commercial tests conducted at two SX operations in North America.

Plant A – Laboratory Test Showing Selectivity Improvement Through Clay Treatment

In Plant A, the initial selectivity was calculated by measuring the copper and iron loadings in the plant organic The actual operating copper loading of the plant was 2.2 g/L Cu (82% loading), and the Fe loading was 5 mg/L (cf. Figure 10), leading to an initial Cu:Fe selectivity of 440.

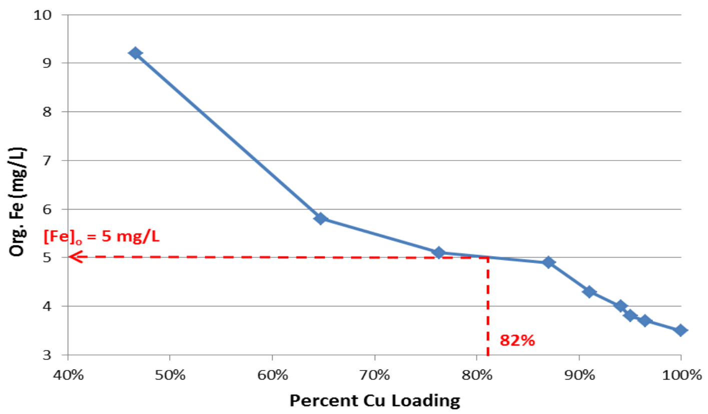

Figure 10. Plant A: Iron loading in the organic phase as a function of percentage copper loading.

The organic, after thorough clay treatment at 5% mass fraction of clay, was then contacted with PLS at an organic-to-aqueous (O/A) volumetric ratio of 0.4 (to achieve an equivalent % loading of copper). The following loadings were measured: $[Fe]_{treated\_org}$ = 2.6 mg/L and $[Cu]_{treated\_org}$ = 2.2 g/L, giving a Cu:Fe selectivity of 846. The 92% increase of selectivity from 440 to 846 is the largest improvement in Cu:Fe selectivity observed so far in the North America region.

Plant B – Commercial Trials Show Selectivity Improvement with ACORGA® CB1000

In Plant B, different feed and discharge samples were collected during the commercial trials corresponding to the following treatment conditions: i) CT at 2 % mass fraction of clay with DE, ii) CT at 2 % mass fraction of clay with ACORGA® CB1000 (instead of DE), iii) CT at 4 % mass fraction of clay with ACORGA® CB1000 (instead of DE). The organic samples were contacted with PLS solution and Cu and Fe loading analyzed to calculate Cu:Fe selectivity. The results presented in Table III show a selectivity improvement of 7 to 8% when ACORGA® CB1000 is used along with the clay.

While the laboratory results at Plant A and the commercial tests at Plant B both point towards a Cu:Fe selectivity benefit of the product, it is important to note that improvement in Cu:Fe selectivity depends on the nature of the impurities present in the organic phase. Not all impurities have an effect on iron transfer. Therefore, some plants will realize a selectivity improvement with clay treatment, while some may not.

Table III. Cu:Fe selectivity data from Plant B commercial trials with and without the use of ACORGA® CB1000.

Batch	2% mass fraction clay + DE			2% mass fraction clay + CB1000			4% mass fraction of clay + CB1000		
	Feed	Discharge	Improvement (%)	Feed	Discharge	Improvement (%)	Feed	Discharge	Improvement (%)
A	356	347	–3	331	374	13	337	358	6
B	353	381	8	354	380	7	358	382	7
C	357	357	0	334	364	9	330	360	9
D	354	371	5	328	334	2	322	345	7
Avg	355	364	3	337	363	8	337	361.3	7

CONCLUSIONS

Over the past decades, improvements in equipment design and plant practices have greatly reduced organic entrainment losses, lowering the natural bleed of organic contaminants which cause plant performance issues. In addition to the lower organic losses, SX plant design capacities are being exceeded in response to maturing ore bodies, declining PLS grades and/or higher production requirements. Reduced organic losses and higher plant throughputs have put new emphasis on maintaining satisfactory plant organic quality through efficient clay treatment. Contamination of the plant inventory by poor quality recovered organic, even in small quantity, can have a dramatic impact on phase separation and interfacial tension, leading to severe plant performance issues.

Although the benefits of clay treatment are well known, the treatment processes utilized in the industry are often inefficient at removing the targeted impurities. A number of deficiencies have been highlighted and suggestions made to improve the efficiency of this process. In addition, ACORGA® CB1000 Clay Binder has been developed and shown to solve many of the challenges faced in the clay treatment operation. Used as a processing aid, it allows for more efficient clay treatment, thereby resulting in improved ΔIFT, phase disengagement, phase stability and clarity of the treated organic returned to the plant inventory. In addition, depending on the impurities present in the organic, it can also improve Cu:Fe selectivity.

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