

Title:

## Property-Performance Relationships of Commercial Diluents in Sub-Sahara Africa Copper Solvent Extraction Conditions

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#### Summary

The purpose of this study was to evaluate correlations between physical properties of commercial diluents and copper extraction performance specifically for high extraction loadings utilized in the Sub-Sahara Africa copper belt. A study of five commercially available solvent extraction diluents in combination with three commercially available extractant reagents for copper extraction under sub-Sahara Africa solvent extraction conditions yielded intriguing results. A variety of physical and chemical property analyses of the neat diluents showed that the diluents have some property differences, but overall the properties are similar and provide comparable solvent extraction performance. Although each physical chemical property technique provides useful information, no individual test result suffices for prediction of diluent performance, and multiple methods should be used concertedly to obtain a good understanding of any diluent's characteristics. Furthermore, a diluent should be evaluated within the conditions for which it is targeted to determine a true measure of performance. Overall, the diluents studied possess appropriate physicochemical properties for sub-Sahara Africa copper solvent extraction conditions and can be utilized to achieve efficient, safe, and reliable operations.

#### Introduction

#### **Background**

The term "diluent" is used to refer to hydrocarbon mixtures that are relatively constant in composition developed specifically for use in solvent extraction processes. This term stands in contrast to "kerosene" or "metallurgical kerosene" used in times past to refer to hydrocarbons used in solvent extraction processes. Although kerosenes were utilized for solvent extraction operations, their performance and flammability properties were not optimal, thus leading to development and production of solvent extraction diluents.<sup>1</sup> Modern diluents receive extensive manufacturing controls to ensure safe handling properties and consistent performance.

Today, commercial solvent extraction (SX) diluents are available globally from a limited number of manufacturers. Production quality and consistency of these diluents have improved tremendously over the past 20 years. For example, diluent flash points have been increased incrementally to improve transport and handling while reducing fire hazards. In addition, properties have been successfully modified to minimize evaporative losses, ultimately reducing SX plant raw material costs. Diluent manufacturers have also focused on meeting performance requirements of SX plants, including eliminating components detrimental to SX operations such as olefinic groups that can react with various species resulting in changing phase disengagement properties over time, as well as insuring that proper



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hydrocarbon components are present within diluent mixtures to maintain good reagent-metal complex solubility. These challenges have been met in the midst of ever increasing stringent environmental regulations.

Sub-Sahara Africa copper SX operations pose a unique set of conditions for diluents due to inherent ore compositions and the associated high reagent concentrations required for complete copper extraction. Chevron Phillips Chemical Company, LP has been manufacturing hydrocarbons and hydrocarbon -based diluents since the mid-80s, applying this experience to identify the physical properties considered crucial for proper performance in SX operations. This paper documents the findings of a study utilizing commercially available diluents in combination with extraction reagents commonly utilized in Africa SX operations to evaluate the relative performance of the diluents under sub-Sahara Africa copper SX conditions.

### <u>Scope</u>

This study evaluated physical/chemical properties of a several commercial diluents, including flash point, aromatics content, boiling range, viscosity and evaporative loss (among others) as a function of diluent source. Physical properties of 80% of maximum copper-loaded organic solution were also studied as a function of diluent source and extraction reagent. Finally, solvent extraction performance, including phase disengagement time, copper extraction kinetics and extraction reagent-copper complex solubility was evaluated as a function of diluent source, reagent type and temperature.

For all solvent extraction experiments the reagent concentration was made up to be 38% (v/v) in the desired diluent. This reagent concentration was selected to represent about the highest concentration in use in sub-Sahara Africa, and that if the diluent/reagent blend performed well at this concentration it should do so at lower reagent concentrations.

### Experimental

### **Materials**

- 1. Reagents
  - a) Orfom<sup>®</sup> SX80 obtained from Chevron Phillips Chemical Company, LP Mining Chemicals and utilized as received
  - b) Orfom® SX12 obtained from Chevron Phillips Chemical Company, LP Mining Chemicals and utilized as received
  - c) Orfom<sup>®</sup> SX11 obtained from Chevron Phillips Chemical Company, LP Mining Chemicals and utilized as received
  - d) BP Mining Solvent utilized as received
  - e) Shellsol<sup>®</sup> 2325 utilized as received
  - f) Acorga® OPT 5510 obtained from Cytec Industries Inc., Mining Chemicals and utilized as received
  - g) Acorga® OPT 5540 obtained from Cytec Industries Inc., Mining Chemicals and utilized as received
  - h) LIX<sup>®</sup> 984N obtained from BASF Mining Solutions and utilized as received



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- i) Cupric sulfate pentahydrate reagent grade obtained from Fisher Scientific and utilized as received
- j) Ferric sulfate pentahydrate reagent grade obtained from Fisher Scientific and used as received
- k) Ammonium sulfate reagent grade obtained from Fisher Scientific and utilized as received
- I) Concentrated ammonia (30 %) obtained from Fisher Scientific and used as received
- m) Concentrated Sulfuric Acid (95-98%) obtained from Fisher Scientific and utilized as received
- n) Nitrogen (N<sub>2</sub>, high purity, cylinder) obtained from Airgas, Inc. and used as received

### 2. Equipment

- a) Phase disengagement and copper extraction kinetics
  - i. Square glass mixing vessel: I.D. = 3.5 in x 3.5 in x 7.5 in (height). Glass wall ~3/16 in thick with relatively sharp corners to ensure good mixing.
  - ii. Impellor is a polyethylene 5/16 inch thick flat disc 2 inches in diameter. It has 6 equally spaced hard plastic blades 1/8 inch thick and 3/8 inch in height on the bottom radiating from the center of the impellor. It also has 2 equally spaced hard plastic blades 1/8 inch thick and 5/16 inch in height on the top of the impellor radiating from the center of the impellor.
  - iii. The impellor is firmly attached to a stainless steel shaft ¼ inch in diameter about 9 inches in length with which to attach impellor
  - iv. Stirring motor capable of maintaining a constant stirring speed of 1650 RPM
  - v. RPM meter
  - vi. Stop watch (or similar) timer
  - vii. pH meter
  - viii. 100 mL separatory funnel
  - ix. 1000 mL separatory funnel
  - x. Glass cup capable of holding ~10 mL that can be dipped into the SX stirring dispersion and easily withdrawn
  - xi. Assorted normal laboratory glass ware

### Procedures

*Physical properties of neat diluent* samples – all neat diluent physical property measurements, including evaporative loss, were performed by SGS Laboratories (Deer Park, Texas USA) according to the specifications set for the corresponding ASTM procedure and analyses. The analyses were performed in triplicate and the results reported are the average of the three measurement results. Analyses performed on all diluent samples are listed as follows (in no particular order):

- Flash point (Pensky-Martens Closed Cup, PMCC) ASTM D93
- API Gravity 60/60 ASTM D1298
- Specific Gravity 60/60 ASTM D1298
- Density (lb/gal) Calculation from ASTM D1298
- KB Value ASTM D1133
- Pour Point ASTM D97



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- Total Sulfur ASTM D2622
- Bromine Number ASTM D1159
- Fluorescent Indicator Analysis (FIA) ASTM D1319
- Hydrocarbon Types ASTM D2425
- Kinematic Viscosity ASTM D445
- Atmospheric Distillation ASTM D86
- Evaporative Loss ASTM D972

*Evaporative losses* – Evaporative loss measurements were conducted utilizing ASTM D972. This method, which is specific for lubricating greases and oils, was modified slightly to be relevant for diluent hydrocarbon mixtures. Approximately 10 g (12 mL) of the desired diluent sample was measured into the ASTM D972 apparatus "cup". The sample was placed into the temperature control chamber and equilibrated to 35 °C (95 °F). A flow of nitrogen (N<sub>2</sub>) gas was started through the apparatus and over the diluent sample, maintained at a constant flow rate of 5 mL/min. At desired time intervals, the sample cup was removed and quickly weighed on a nearby, 4-place analytical balance to measure weight loss. At each weight measurement the room temperature and barometric pressure were also recorded for reference purposes (in °F and mmHg, respectively). This procedure was followed for a total of 9 days. The target conditions were to subject the diluents to 35 °C at standard (room) atmospheric pressure utilizing a slight inert gas (N<sub>2</sub>) sweep across the surface of the liquid to facilitate evaporation of any light components while minimizing any "chemical reactions" occurring due to the presence of oxygen.

*Phase disengagement performance* – all phase disengagement tests were performed at room temperature (25 °C) in triplicate. All of the results of the phase disengagement tests, including phase disengagement time, metals analyses, and resulting loaded organic phase viscosity are reported as the average of the three measurements.

Synthetic pregnant leach solution (PLS) for the phase separation and copper extraction kinetics set of tests was prepared using reagent grade copper sulfate pentahydrate, reagent grade ferric sulfate pentahydrate, distilled water and sulfuric acid. It contained 16.0 g/L Cu, 2.0 g/L Fe iron and had a pH of 2.0. One lot of PLS solution was prepared and used for all phase disengagement tests to eliminate batch-to-batch variability. Analysis for this sample was by SGS in Tucson, AZ.

Procedure – exactly 350 mL of the respective organic extraction solution was placed in the mixing vessel. The stirrer/impellor assembly was placed in the mixing vessel such that the top of the impellor was 1 cm below the surface of the organic extraction solution (This process resulted in an organic-continuous mode of testing). The stirrer was then started and the impellor speed adjusted to  $1650 \pm 10$  RPM. Then exactly 350 ml of the synthetic PLS was added smoothly over 5 seconds to the mixing vessel and the timer was started. Without stopping the stirrer, 10 mL samples were taken using the glass cup sampler at 30, 60 and 90 seconds (for Cu extraction kinetics measurements). These samples were immediately placed into individual separatory funnels where the layers quickly separated completely. The lower (aqueous) layer was drained away and the organic layer was collected. After stirring the mixture for a total of 5 minutes, the stirrer was stopped, a new timer was started and the impellor was quickly raised out of the mixing vessel. The phase disengagement time was then measured by recording the time from the cessation of the stirrer until the formation of a definitive interface between the aqueous and organic phases with only a single layer of small bubbles between the two phases (no movement of bubbles breaking at the interface).



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A 20 mL aliquot of the organic phase was taken from this final mixture as a 5 min (300 sec) sample to include with the 30, 60 and 90 sec kinetic samples in atomic absorption analysis. A sample of the aqueous phase after 5 min of mixing was also analyzed by atomic absorption (AA). All organic samples were filtered through filter paper that will not pass the aqueous phase before further AA analysis. A sample of this organic phase was also removed and viscosity measurements were completed by CP Chem personnel according to ASTM D445 at 22, 30, 38, and 45 °C and reported in SUS.

Then the impellor was reinserted into the stirring vessel this time such that the impellor was well into the aqueous phase and the impellor was turned on and run for 5 minutes. This provided for an aqueous-continuous dispersion. After stirring the mixture for a total of 5 minutes, the stirrer was stopped, a new timer started and the impellor was quickly raised out of the mixing vessel. The phase disengagement time was then measured by recording the time from the cessation of the stirrer until the formation of a definitive interface between the aqueous and organic phases with only a single layer of small bubbles between the two phases (no movement of bubbles breaking at the interface). This time was recorded as the aqueous continuous phase disengagement time.

*Copper complex solubility performance* – a solution containing about 20 g/L Cu, 27 g/L free ammonia and 100 g/L ammonium sulfate was made up from reagent grade copper sulfate pentahydrate, concentrated ammonia and ammonium sulfate. Then 40 mL of the respective reagent diluent pair was vigorously contacted for about 2 minutes with the ammonia copper solution at an O/A ratio needed to achieve 80% of copper maximum loading. Under these conditions, copper within the PLS is quantitatively transferred from the ammonia solution to the respective organic phase. After phase separation the respective organic phase was split with about 10 mL added to one small glass vial and a second 10 mL sample added to a second small glass vial. The glass vials were sealed with caps and labeled. One vial was then place in a refrigerator (7 °C) and the second vial was kept at room temperature (25 °C). These samples were inspected visually one time per day for a total of seven days to determine any precipitation (crystallization) of the extraction reagent-copper complex from the solution, indicating insufficient solubility of the copper complex in the respective diluent/extractant solution.

### <u>Analyses</u>

All organic phase samples (30, 60, 90 and 300 sec) from the organic-continuous mode phase disengagement tests were analyzed at SGS Laboratories (Tucson, AZ) for Cu content by atomic absorption (AA) spectroscopy. In addition, the 300 sec (5 min) organic phase was analyzed for Fe content and the final (5 min) aqueous phase was analyzed for Cu content.

Viscosity measurements and the daily solubility/stability inspections at the 80% of maximum loaded organic solutions from the organic-continuous mode phase disengagement tests were completed at the CPChem Laboratory (Tucson, Arizona USA). Viscosity measurements were completed according to specifications listed in ASTM D445 and the solubility evaluations were accomplished visually by ranking the solutions as having none, slight, moderate or severe precipitation/crystallization.



### Results

The study results are divided into two major sections below: physical and performance properties of "neat" diluent and physical and performance properties of 38 volume % reagent/diluent blends. The property section discusses the physical/chemical property measurements of each diluent as well as evaporative loss measurements on select diluents (for comparison). The "properties of diluent/reagent blends" section discusses phase disengagement time (and behavior) as well as resulting loaded organic physical properties, including viscosity and extractant reagent-copper complex solubility.

### Diluent "Neat" Physical and Chemical Properties

The diluent properties measured in this study are summarized in Tables 1-5. All of the results reported are the average of three measurements and all measured values were within the acceptable variance as reported for each ASTM procedure. Table 1 summarizes typical physical/chemical properties including flash point, density, pour point and viscosity at varying temperature. Table 2 lists the atmospheric distillation data from ASTM D86 analysis (percent removed at a varying temperature range) and Table 3 records details on hydrocarbon types present within each diluent, such as aromatics, paraffins and naphthenes (FIA, ASTM D1319). Furthermore, the hydrocarbon types are classified by aromatic hydrocarbon type (as per ASTM D2425) in Table 3. Tables 4 and 5 summarize the evaporative loss data (per ASTM D972) for Orfom<sup>®</sup> SX80 Diluent and BP Mining Solvent, respectively.

The diluent typical properties were measured independently by a single lab to provide a good comparison; the resulting data compares adequately with the published data for the products from various sources. This consistency with known values provided confidence in the measured data and a reasonable comparison of the diluent properties.

Several interesting observations can be made when comparing the typical property data. First, all of the measured flash points of the diluents are quite similar (near 82 °C), except for Orfom<sup>®</sup> SX11 (114 °C) – see Table 1. This difference in flash point for Orfom<sup>®</sup> SX11 is expected since this product is manufactured by tailored processing to achieve specific, desired physical properties including flash point. Its properties make it suitable for higher temperature operations. The range for all other diluents evaluated in this study is 81 °C (Orfom<sup>®</sup> SX 12) to 85 °C (Shellsol<sup>®</sup> 2325).

### Table 1 – SX Diluent Typical Physical Properties

Analysis	Test Method	Orfom <sup>®</sup> SX12	Orfom <sup>®</sup> SX80	Orfom <sup>®</sup> SX11	<b>BP Mining Solvent</b>	Shellsol <sup>®</sup> 2325
Flash Point (°C)	ASTM D93	81	82	114	83	85
API Gravity (15.5 °C)	ASTM D1298	40.3	39.4	43.0	40.6	39.2
Specific Gravity (15.5 °C)	ASTM D1298	0.8236	0.8280	0.8109	0.8222	0.8289
Density (lb/gal)		6.87	6.91	6.77	6.86	6.92
KB Value	ASTM D1133	33.5	30	24.5	35	36.5
Pour Point (°C)	ASTM D97	-40	-34	-57	-50	-47
Total Sulfur (ppm)	ASTM D2622	<3.0	<3.0	<3.0	154	144
Bromine Number (g Br/100 g)	ASTM D1159	<0.5	<0.5	<0.5	0.5	0.5
Viscosity (SUS at °C)	ASTM D445					
0		40.8	44.9	112.0	38.3	38.7
10		37.3	40.1	73.6	35.6	35.9
25		34.1	35.9	50.9	33.0	33.2
45		32.0	32.7	40.0	32.0	32.0





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Another similarity arises in the specific gravity of these diluents. The range is also relatively small from 0.8236 (Orfom<sup>®</sup> SX12) to 0.8289 (Shellsol<sup>®</sup> 2325), resulting in an overall difference of up to approximately 0.6%.

Bromine numbers measured for all of the diluents were relatively low as well (Table 1). BP Mining Solvent and Shellsol<sup>®</sup> 2325 samples were measured to have a bromine number of 0.5 g Br/100 g sample compared to a bromine number of <0.5 g Br/100 g sample for the Orfom<sup>®</sup> SX diluents (<0.5 value is reported as being below the detection limits of the method). Although 0.5 g Br/100 g sample is slightly higher than a <0.5 g Br/100 g sample measurement, all of the bromine number values were very low. This data suggests that all of the diluents evaluated in this study have a very low concentration of reactive olefinic groups, especially primary olefins. Therefore, the diluents should all exhibit a low susceptibility to chemical reactions that produce species detrimental to phase disengagement properties (such as sulfonation).

The range of pour point values measured for the diluents (Table 1) is somewhat broader than that for some of the other basic physical properties. The pour points measured ranged from the highest at -34 °C (Orfom<sup>®</sup> SX80) to the lowest at -57 °C (Orfom<sup>®</sup> SX11). Again, Orfom<sup>®</sup> SX11 has a tailored structure due to the manufacturing process, producing a primarily branched aliphatic hydrocarbon character (isoparaffins) compared to the other diluents, which results in a lower pour point. Comparing the pour point of the other diluents (excluding Orfom<sup>®</sup> SX11) shows a range of -34 °C (Orfom<sup>®</sup> SX80) to -50 °C (BP Mining Solvent). While this is a significant difference as far as the measurement is concerned, the pour points reported would have little impact on practical plant operation. All of the pour points were significantly lower than temperatures SX plant operations would encounter.

Viscosity of the diluents was also measured as a function of temperature ranging from 0 °C to 45 °C – Table 1. These values examine possible handling differences for the diluents, both from simply moving the material (pumping) to mixing with an aqueous PLS. These results are also illustrated graphically in Figure 1.

The viscosity of Orfom<sup>®</sup> SX11 can be noted as being significantly higher than the other diluents, which is due to the highly branched aliphatic character of the hydrocarbon components. This re-emphasizes the application of Orfom<sup>®</sup> SX11 for higher temperature operations. The viscosities of the remaining diluents show a reasonable range within the diluents and by temperature. BP Mining solvent and Shellsol<sup>®</sup> 2325 demonstrated a similar viscosity profile over the temperature range studied, with BP Mining Solvent having the lowest viscosities measured. Orfom<sup>®</sup> SX12 was slightly higher than BP Mining Solvent and Shellsol<sup>®</sup> 2325 and Orfom<sup>®</sup> SX80 was measured as having the highest viscosity across the entire temperature range. At 0 °C the viscosities measured ranged from 44.9 SUS (Orfom<sup>®</sup> SX80) down to 38.3 SUS (BP Mining Solvent).

Although there is a measurable difference in the viscosities of the diluents within this study, this difference did not appear to significantly influence the extraction and phase disengagement performance, as discussed in the following section (phase disengagement times and copper extraction kinetics were not vastly different for the various diluents). Furthermore, a systematic study of phase disengagement and/or extraction performance as a function of diluent viscosity has not been found in a



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search of public literature. Although there may be effects that arise from diluent viscosity at some point, the viscosities measured for the products within this study are within SX operational capabilities (pumping, etc.) and provide desirable performance.





One easily noted difference in physical property measurements for these diluents was total sulfur (Table 1). The Orfom<sup>®</sup> SX diluents were all measured to have very low total sulfur content, listed as <3.0 ppm, which is essentially below the detection limit of the method. The BP Mining Solvent and Shellsol<sup>®</sup> 2325 were measured as having 154 ppm and 144 ppm, respectively. The total sulfur analysis (ASTM D2622 – X-Ray Fluorescence, XRF) measures every form of sulfur which can include elemental sulfur and organosulfur compounds (such as thioethers, thiols and sulfates). This difference in total sulfur is likely due to regional production regulations that refineries must adhere to for fuels sulfur content. While SX diluents are not classified as "fuels", they are produced by similar conditions as diesel or jet fuels within refinery equipment. Therefore, these products contain the amount of sulfur as stipulated by regional regulations. Orfom<sup>®</sup> SX diluents are all produced in U.S. refineries, and current regulations for U.S. refineries state that diesel/jet fuels produced by these refineries must have <15.0 ppm total sulfur.<sup>2</sup> These limits were imposed for environmental protection to yield cleaner air emissions. However, not all global regions, where the other diluents used in this study may be produced, are currently held to the same total sulfur specification for fuels. For example, fuel-based products produced in South Africa do not currently have the same total sulfur limit for diesel/jet fuels produced in the U.S. Therefore the total sulfur contained in diluents produced within South Africa may be (by way of processing) slightly higher. However, sulfur content does not appear to correlate to diluent performance.



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The Kauri-Butanol (KB) tests were developed as a measurement of product solubility. The test is not directly applicable to diluent solubility, but can provide an interesting comparison of the physical/chemical properties of the diluents analyzed within this study. The measured "KB" values ranged from 24.50 (Orfom<sup>®</sup> SX11) to 36.50 (Shellsol<sup>®</sup> 2325) – Table 1. Orfom<sup>®</sup> SX11 is somewhat different in nature than the other diluents within this study as it is manufactured to have no aromatic content and composed almost entirely of branched (saturated) hydrocarbons. Since aromatic content can increase the KB value in the test and Orfom<sup>®</sup> SX11 has no aromatics content, this may help explain this observed difference. The remaining diluents evaluated have KB values that range from 30.00 to 36.50, which is not a significant difference in terms of SX operation performance. While KB values provide some insight into relative solubility of different diluents, KB values are only a small part of the subject of solubility, and there are many different solubility scales.<sup>3</sup>

KB values are measured by determining the amount of a given hydrocarbon that can be added to a solution of Kauri resin in nbutanol. Kauri resin is a fossilized resin derived from the sap of the Kauri pine tree, which grows primarily in New Zealand. This resin dissolves easily in n-butanol but does not dissolve readily in hydrocarbon solvents. The Kauri–Butanol value definition is, according to the ASTM (method D1133), the volume given in milliliters of any solvent with which, at 25 °C (77 °F), a standard Kauri–Butanol solution is titrated and a certain amount of turbidity is detected. KB values are often misinterpreted and directly related with "universal solvent power". However, there is no such a thing as "universal solvent power". Each solvent (diluent) has its own capacity to dissolve a certain type of substance more or less effectively than others depending on its own physicalchemical properties as well as those of the substance that has to be dissolved. The optimum scenario is to test the desired diluents within the conditions for which they are targeted to determine solubility effectiveness for specific reagent-metal complexes. Therefore, the listed diluents were examined within the operational conditions of sub-Sahara Africa copper SX conditions to compare solubility of the resulting reagent-copper complex (discussed in the following section on phase disengagement behavior and loaded organic physical properties).

Another physical property measured within this study for the various diluents was the distillations range (by ASTM D86). The distillation data for all for all the diluents evaluated is summarized in Table 2 and plotted graphically in Figure 2.

	Atmos	pheric Di	stillation	(ASTM D8	6, °C at %	6 removal)
Diluent	IBP	1 <b>0</b> %	20%	30%	40%	Range (°C)
Orfom <sup>®</sup> SX12	202	213	219	223	227	24
Orfom <sup>®</sup> SX80	203	216	220	223	228	25
Orfom <sup>®</sup> SX11	236	257	259	261	264	28
<b>BP Mining Solvent</b>	207	216	217	218	219	12
Shellsol <sup>®</sup> 2325	208	217	217	218	219	11

### Table 2 – SX Diluent Distillation Data

The data shown is from the initial boiling point (IBP) to the 40% removal temperature (the temperature at which 40 volume % of the diluent is removed by distillation). This data provides an indication of the range of hydrocarbon molecular weights present within a given diluent (especially the possible lighter



molecular weight hydrocarbons that could evaporate) which may result in a change in diluent viscosity with time, and therefore possibly cause SX performance changes. Excluding Orfom<sup>®</sup> SX11, the other diluents have very similar distillation profiles. Although there is a slightly broader distillation temperature range for the Orfom SX diluents relative to BP Mining Solvent or Shellsol<sup>®</sup> 2325, these differences are minor and the data suggests that all the diluents studied should provide a consistent viscosity profile with time and sufficient SX performance.

One common misconception is that the presence of relatively higher molecular weight hydrocarbons within a given mixture always explains a higher relative viscosity. Indeed higher molecular weight hydrocarbon content can result in increasing viscosity to some extent. However, molecular weight is not the only factor that affects viscosity. This can be noted by reviewing the data for Orfom<sup>®</sup> SX11. Orfom<sup>®</sup> SX11 has a much higher viscosity than any of the other diluents evaluated. Through various internal analyses and production processes with Chevron Phillips Chemical, Co. it is known that Orfom<sup>®</sup> SX11 has a hydrocarbon content in this range of  $C_{13}$ - $C_{16}$  chains. Orfom<sup>®</sup> SX80 also has a hydrocarbon predominant chain length content in this range of  $C_{13}$ - $C_{16}$  but also does contain some hydrocarbon chains slightly higher than  $C_{16}$ . If viscosity were strictly a function of hydrocarbon molecular weight then Orfom<sup>®</sup> SX11 should have a lower viscosity than Orfom<sup>®</sup> SX80 due to the relative difference in hydrocarbon chain lengths (molecular weights) within the two products, but it does not. The significantly higher viscosity measured for Orfom<sup>®</sup> SX11 is most probably a function of the higher branched hydrocarbon content relative to the other diluents. Although there are some differences in physical properties of the various diluents studied, all appeared to perform similarly and adequately throughout the tests.

## Figure 2 – SX Diluent Distillation Data Plot







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Evaluation of the hydrocarbon types present within each of the targeted diluents was also an objective for this study. Two methods were selected for this comparison – FIA (ASTM D1319) and hydrocarbon types (ASTM D2425). Data from these analyses is summarized in Table 3. FIA data recorded included the amount (volume %) of aromatics, olefins, and paraffins. ASTM D2425 was employed as a second measurement of hydrocarbon types and recorded the weight content of aromatics, naphthenes and paraffins. Furthermore, ASTM D2425 provided a breakdown of the aromatic types within each diluent, including mono-, di-, tri-, tetra-, penta-, thiophenes and "unidentified". Two methods were used to obtain a reasonable understanding of the hydrocarbon types and content. Both methods provide some detail about hydrocarbon mixture compositions with physical properties in the range of the SX diluents within this study, but neither provides all of the information desired. There are a variety of techniques beyond the two employed in this study that are known for analyzing mixtures for hydrocarbon types and all have advantages and disadvantages. These two were selected due to their familiarity for analysis of these types of products, their practicality and the reasonable reliability of the data produced from them.

### Table 3 – SX Diluent Hydrocarbon Types

Analysis	Test Method	Orfom <sup>®</sup> SX12	Orfom <sup>®</sup> SX80	Orfom <sup>®</sup> SX11	<b>BP Mining Solvent</b>	Shellsol <sup>®</sup> 2325
FIA (volume %)	ASTM D1319					
Aromatins		20.5	5.0	<5	18.3	18.4
Olefins		1.9	2.9	3.3	0.8	0.8
Paraffins		77.6	92.1	94.4	80.9	80.8
Hydrocarbon Types (weight %)	ASTM D2425					
Aromatics		23.42	5.53	1.43	21.69	18.84
Naphthenes		45.12	66.57	51.76	46.46	53.02
Paraffins		31.46	27.9	46.81	31.85	28.14
Aromatic Types (weight %)	ASTM D2425					
Mono		21.76	5.06	0.00	20.43	17.87
Di		1.62	0.41	0.46	1.24	0.94
Tri		0.00	0.00	0.96	0.00	0.00
Tetra		0.02	0.02	0.01	0.00	0.01
Penta		0.00	0.00	0.00	0.00	0.00
Thiophenes		0.00	0.01	0.00	0.01	0.02
Unidentified		0.02	0.02	0.00	0.00	0.00

By comparing the FIA aromatics content (Table 3) it can be seen that Orfom<sup>®</sup> SX12, BP Mining Solvent and Shellsol<sup>®</sup> 2325 have similar concentrations of alkyl-aromatic hydrocarbons – approximately 20%. These values agree well with reported data for these products. One difference to be noted in aromatics content is in comparing Orfom<sup>®</sup> SX80 with Orfom<sup>®</sup> SX12 and BP Mining Solvent and Shellsol<sup>®</sup> 2325. Orfom<sup>®</sup> SX80 was measured to have 5% aromatics (by both FIA and ASTM D2425). Although Orfom<sup>®</sup> SX80 does have significantly less aromatic content than these other three diluents mentioned, the data measured also agrees well with known/reported data for Orfom<sup>®</sup> SX80 diluent.

The aromatics values measured by both FIA (ASTM D1319) and hydrocarbon types (ASTM D2425) agree reasonably well also for all of the diluents analyzed (all of the aromatics values from the two methods measured within approximately 3%). In addition, the paraffins content measured by FIA compares reasonably with the total of naphthenes and paraffins obtained by hydrocarbon types (Table 3). For example, FIA analysis for Orfom<sup>®</sup> SX12 resulted in a total of 77.6 volume % and hydrocarbon types



analysis measured a total of 76.6 weight % of naphthenes plus paraffins (45.12 + 31.46). The slight difference is likely due to the difference in techniques and units of measure. In addition, FIA analysis provides a "total" paraffin content while ASTM D2425 (hydrocarbon types) provides further detail of the paraffin hydrocarbon types – saturated cyclic rings (naphthenes) and paraffins. This trend of FIA paraffin content being consistent with the total of naphthenes and paraffins measured by ASTM D2425 appeared to be consistent throughout the series of diluents. All of the results comparing paraffin content by FIA to naphthenes plus paraffin content by ASTM D2425 are within approximately 4% units of each other. These results provide more confidence in the data measured and suggest these two analyses are complimentary to one another.

Another noteworthy observation can be made by evaluating the aromatic hydrocarbon types (Table 3). ASTM D2425 provides this additional level of detail to understand a little more about the aromatic hydrocarbon character within a given sample. Of all the aromatics measured within all of the diluents analyzed (excluding Orfom<sup>®</sup> SX11), the composition is predominantly due to mono-aromatic structures. The remaining aromatic content for all the diluents is then composed of di-aromatic compounds (illustrated graphically in Figure 3). This suggests that most of the aromatic content of all of the diluents analyzed is alkylated benzene structures (mono-aromatic ring) followed by a small content (<2%) of alkylated naphthalene (di-aromatic ring) compounds. However, this does not mean that these mono-aromatic or di-aromatic structures have various carbon length chain substitutions on a single or di-aromatic ring. A more sophisticated analysis technique must be utilized to arrive at concentrations of specific compounds.

### Figure 3 – SX Diluent Aromatics Types Plot







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Limitations in both methods can be noted when evaluating Table 3 data for Orfom<sup>®</sup> SX11. Orfom<sup>®</sup> SX11 is specially manufactured to have no aromatic content, no olefin content and a high concentration (>99%) of saturated, branched paraffins. The FIA data for Orfom<sup>®</sup> SX11 does not agree. For example, the olefin content measured by FIA for Orfom<sup>®</sup> SX11 was 3.3% (Table 3). Although FIA has been utilized for many years to perform hydrocarbon type analysis, the results are not necessarily accurate and lab-to-lab reproducibility is poor. Lubeck and Cook state regarding FIA ASTM D1319 that it "is questionable for a number of reasons, including poor inter-laboratory reproducibility, erroneous results (particularly at low olefin levels), and inappropriate units of measurement".<sup>4</sup>

FIA analysis is performed by introducing a hydrocarbon sample onto an activated silica gel column packed in a small glass column with uniform bore size. Before sample introduction the top of the column is treated with fluorescent dyes. Once the sample is introduced, isopropyl alcohol is added as an eluent to desorb the hydrocarbons and move them down the column at different rates according to their affinity for the silica gel – saturates have the least affinity and move first/faster and then progressively slower rates (higher affinity) are observed with olefins and finally aromatics. The hydrocarbon types carry the fluorescent dyes into separate "zones" and the dyes are detected under UV light, each type of hydrocarbon showing up as a different color. These colors mark the zone "boundaries" of the hydrocarbons, saturates, olefins and aromatics. The volume % of each hydrocarbon type is then calculated from the length of each zone on the column. One source of error in this technique is due to the difficulty in determining the position of the zone "boundaries" of the hydrocarbon layers, which is performed visually. Because of the nature of the method it cannot be automated and thus is subject to some "human" error. In addition, the isopropyl eluent is applied under pressure, which can vary somewhat depending on the operator and thus influence the speed at which hydrocarbon components travel down the silica gel column and the efficiency of separation. Furthermore, individual hydrocarbon compounds can be somewhat complex, having for example aromatic character and paraffin character (having a long carbon chain substituted aromatic ring). Such compounds may lie in a "boundary layer" within the analysis, obscuring the results slightly sand making the distinction between zones more difficult.

In the case of Orfom<sup>®</sup> SX11 and the FIA measured olefin content, the FIA ASTM D1319 method states that for low olefin content materials the reproducibility is 1.7% units at best, meaning the reported number could range from 1.6% to 5.0%. With this information and knowledge of the production method this number is likely not accurate for Orfom<sup>®</sup> SX11.

Another limitation to mention for ASTM D1319 is the aromatics concentration range. The method states that measurement is designed for aromatics content ranging from 5% to 99%.<sup>5</sup> Therefore, samples having aromatics levels below 6% may not be good candidates for this method to achieve a reasonable aromatics concentration. This restriction makes the aromatics results for Orfom<sup>®</sup> SX80 suspect as well. However, the hydrocarbon types analysis also measured 5% which suggests this value is trustworthy.

Aromatics types analysis (from ASTM D2425) for Orfom<sup>®</sup> SX11 suggests that the product contains di- and tri-aromatic ring structures. Based on knowledge of the product and production methods these cannot be present. This data points to some limitations in the ASTM D2425 analysis also. First, the



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method is a GC-mass spectrometry technique for identifying compounds. As such, it also requires separation of hydrocarbon components by a silica gel column before introduction into a mass spectrometer to measure component masses. Because these products can contain complex hydrocarbon structures, the individual components are not always completely resolved and separated which can lead to misleading data. Once the separated hydrocarbon components enter the mass spectrometer a mass spectrum is obtained for each. The parent molecular ion (mass) is referenced to known compounds to identify type and calculate mass fractions. Again, because diluent products can contain complex hydrocarbon compounds, some may be misidentified as being an aromatic compound when it may be an aliphatic compound, or vice versa. Because Orfom<sup>®</sup> SX11 is composed of entirely branched, isoparaffin-type compounds, many of the components are not in the reference compounds used for the method, and thus some components were misidentified.

FIA (ASTM D1319) and hydrocarbon types (ASTM D2425) analyses provide useful information for interpreting the nature of SX diluents, but it should be understood there are limitations associated with these methods. All of this information underscores the need to utilize multiple analysis techniques to determine structural information about complex hydrocarbon mixtures. Because every analysis technique has limitations, no individual analysis should be used to determine application performance of SX diluents.

A final analysis comparison made for neat diluent physical properties was evaporative loss. This was performed by modifying ASTM D972. This method is designed to measure evaporative losses of lubricating greases and oils that have much higher molecular weight (and boiling ranges) than the SX diluents of interest in this study. Therefore, the temperature and gas sweep over the liquid surface utilized for this study were modified to be more appropriate for SX diluents (see procedure section for details). Only the evaporative losses for Orfom<sup>®</sup> SX80 and BP Mining Solvent are discussed here as all were similar and these provide a reasonable representation of the diluents analyzed in this study. Evaporative data for Orfom<sup>®</sup> SX80 and BP Mining Solvent are summarized in Tables 4 and 5, respectively. The results are the average of two measurements. The range of measured incremental losses averaged approximately 8%, which is reasonable considering the nature of the measurement technique. Cumulative evaporative loss rate data (in L/m<sup>2</sup>/hr) for Orfom<sup>®</sup> SX80 and BP Mining Solvent are plotted in Figure 4 for comparison purposes.

The tables list data including weight loss percentages as well as volume losses per unit area and volume losses per unit area per hour. As can be noted from Figure 4, both evaporation curves follow closely to a logarithmic declining curve as would be expected. This suggests that there are likely small amounts of "lighter" components within the diluents that evaporate initially out of the mixture and then the evaporative rate quickly declines as these are removed. The evaporative rate for BP Mining solvent was measured to be slightly higher than that for Orfom<sup>®</sup> SX80 over the first 8 hours, but after 24 hours both diluents demonstrated virtually identical evaporative rate loss curves, which were very low.

By averaging the evaporative loss rates for the first 24 hours for Orfom<sup>®</sup> SX80 and BP Mining solvent the results are 0.02661  $L/m^2/hr$  and 0.04829  $L/m^2/hr$ , respectively. Using these averages for a mixer settler sized at 21.3 m x 14.4 m Orfom<sup>®</sup> SX80 would yield a maximum loss of 196 L in the first 24 hours while the BP Mining solvent would lose a maximum of 355 L. The evaporative losses would then quickly slow down to near zero. Furthermore, the experimental setup utilized a gas (N<sub>2</sub>) flow rate of 5 mL/min which



may be slightly high when normalizing to practical operations. Thus the evaporative losses are probably artificially large relative to what would be noted in practical use. Given the very low evaporative loss rates measured in this study for both diluents after 24 hours and mixer settler enclosures utilized in most SX operations today, either of these two diluents would demonstrate very minimal losses due to evaporation.

## Table 4 – Orfom<sup>®</sup> SX80 Diluent Evaporative Loss Data

		Increment	Cumulative	Weight	Cumulative Vol	Vol Loss/hr
Time (hr)	Weight (g)	Loss (%)	Loss (%)	Loss (g)	Loss (L/m <sup>2</sup> )	(L/m²/hr)
0	139.5894	0.000	0.000	0.0000	0.0000	0.0000
1	139.4860	0.074	0.074	0.1034	0.0537	0.0537
2	139.4680	0.013	0.087	0.1214	0.0631	0.0315
3	139.4260	0.030	0.117	0.1634	0.0849	0.0283
4	139.4130	0.009	0.126	0.1764	0.0917	0.0229
8	139.3570	0.040	0.166	0.2324	0.1208	0.0151
24	139.2170	0.100	0.267	0.3724	0.1935	0.0081
30	139.1500	0.048	0.315	0.4394	0.2283	0.0076
72	138.8940	0.184	0.498	0.6954	0.3614	0.0050
96	138.8120	0.059	0.557	0.7774	0.4040	0.0042
120	138.6710	0.102	0.658	0.9184	0.4772	0.0040
144	138.5300	0.102	0.759	1.0594	0.5505	0.0038
168	138.4250	0.076	0.834	1.1644	0.6051	0.0036
192	138.3060	0.086	0.919	1.2834	0.6669	0.0035
216	138.2100	0.069	0.988	1.3794	0.7168	0.0033

### Table 5 – BP Mining Solvent Evaporative Loss Data

		Increment	Cumulative	Weight	Cumulative Vol	Vol Loss/hr
Time (hr)	Weight (g)	Loss (%)	Loss (%)	Loss (g)	Loss (L/m <sup>2</sup> )	(L/m²/hr)
0	139.6960	0.000	0.000	0.0000	0.0000	0.0000
1	139.4680	0.163	0.163	0.2280	0.1185	0.1185
2	139.4550	0.009	0.173	0.2410	0.1252	0.0626
3	139.4260	0.021	0.193	0.2700	0.1403	0.0468
4	139.4250	0.001	0.194	0.2710	0.1408	0.0352
8	139.4160	0.006	0.200	0.2800	0.1455	0.0182
24	139.3040	0.080	0.281	0.3920	0.2037	0.0085
30	139.2440	0.043	0.324	0.4520	0.2349	0.0078
72	139.0610	0.131	0.455	0.6350	0.3300	0.0046
96	138.8900	0.123	0.577	0.8060	0.4188	0.0044
120	138.7540	0.098	0.674	0.9420	0.4895	0.0041
144	138.6470	0.077	0.751	1.0490	0.5451	0.0038
168	138.5190	0.092	0.843	1.1770	0.6116	0.0036
192	138.4140	0.076	0.918	1.2820	0.6662	0.0035
216	138.3380	0.055	0.972	1.3580	0.7057	0.0033





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### Figure 4 – Orfom<sup>®</sup> SX80 and BP Mining Solvent Evaporative Loss Rate Plot



### Performance Properties of 38 volume % Reagent/Diluent Blends

The performance properties of 38 volume % reagent/diluent blends evaluated in this study are summarized in Table 6 as an appendix at the end of this report. Table 6 was included separately to allow for different formatting and easier viewing. Note from Table 6 that both neat diluents and also 80/20 and 60/40 blends of BP Mining Solvent with Orfom<sup>®</sup> SX80 and 80/20 and 60/40 blends of Shellsol<sup>®</sup> 2325 with Orfom<sup>®</sup> SX80 were tested. Table 6 lists phase disengagement and copper extraction kinetics data for each of the topic diluents when combined with 3 different extractant reagents (Cytec Acorga<sup>®</sup> OPT 5540, and BASF LIX<sup>®</sup> 984N). Phase disengagement times utilizing both organic continuous and aqueous continuous modes are recorded along with observation comments for both. Table 6 also records the kinematic viscosity measured for each of the respective organic phases from the kinetics/phase separation tests at the 5 minute point of the organic continuous mixing mode over temperatures ranging from 22 °C up to 45 °C. All of the data reported is the average of three tests for each combination/condition. Phase disengagement times within a test series varied generally <3%, viscosity measurements varied <5%, and copper extraction kinetics ranged <2%.

Reviewing the phase disengagement times for the various diluent/extractant reagent combinations yields interesting comparisons. The phase disengagement times for organic-continuous mode and aqueous-continuous mode are plotted separately as Figures 5 and 6, respectively. First, it can be seen that Orfom® SX11 diluent resulted in the highest phase disengagement times both by organic-continuous and aqueous-continuous modes. This observation was true regardless of the extractant reagent utilized. All of the extractant reagents in combination with Orfom® SX11 provided very similar phase disengagement times by the mode of operation. Orfom® SX11 phase disengagement times by organic-continuous mode ranged from 188 to 182 seconds and from 179 to 176 seconds by aqueous



continuous mode. These higher phase disengagement times may have been due, in part, to the higher viscosities of the neat diluent as well as the loaded organic relative to the other diluents (see Tables 1 and 6). However, the Cu extraction kinetics observed for Orfom<sup>®</sup> SX 11 were quite good (all  $\geq$ 91%) regardless of the reagent used (see Table 6). Furthermore the quality of all phase disengagement tests with Orfom<sup>®</sup> SX11 was observed as being "clean with a clear break". Because all of the phase disengagement tests with Orfom SX11 were observed as being "clean with a clear break", it could be that the tests intended to be aqueous continuous actually "flipped" to organic continuous mode while stirring. It is not clear why this would occur with Orfom SX11, but it is an interesting observation and one worthy of note.

### Figure 5 – Phase Disengagement Time with Varying Diluent/Extract Reagent (organic-continuous)



Comparing the phase disengagement times of the other diluent-reagent combinations (excluding Orfom<sup>®</sup> SX11) reveals additional trends. All of the diluent combinations with Acorga<sup>®</sup> reagents resulted in lower phase disengagement times relative to those using LIX<sup>®</sup> 984N (this was observed by both organic-continuous and aqueous-continuous tests). Use of the Acorga<sup>®</sup> reagents in organic-continuous mode resulted in phase disengagement times that ranged from approximately 101 to 114 seconds, with Acorga<sup>®</sup> OPT 5510 producing the higher of these of the Acorga reagents (see Figure 5). An exception to this trend was with the use of Orfom<sup>®</sup> SX12. Orfom<sup>®</sup> SX12 in combination with the Acorga<sup>®</sup> reagents resulted in phase disengagement times of 86 and 84 seconds, which is measurably lower than the other diluent-reagent combinations. Acorga<sup>®</sup> OPT 5510 did result in the higher phase disengagement time of these two at 86 seconds (as with the other diluents), but it is unclear why Orfom<sup>®</sup> SX12 yielded these lower phase disengagement times.





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#### Figure 6 – Phase Disengagement Time with Varying Diluent/Extract Reagent (aqueous-continuous)



While the aqueous-continuous tests and organic-continuous tests showed a similar trend of LIX<sup>®</sup> 984N producing higher phase disengagement times relative to the Acorga<sup>®</sup> reagents, most all of the phase disengagement times via aqueous-continuous mode were lower compared to the organic-continuous mode tests (compare Figures 5 and 6). An exception to this was Orfom<sup>®</sup> SX12 used with the Acorga<sup>®</sup> reagents. The combination of the Acorga<sup>®</sup> reagents with Orfom<sup>®</sup> SX12 via aqueous-continuous conditions were the only two phase disengagement tests that resulted in higher phase disengagement times relative to the organic-continuous conditions. Although they were not large changes in phase disengagement times (approximately 5 seconds) it was an interesting observation nonetheless, as these were the only tests to not lower in phase disengagement time when moving from organic-continuous to aqueous-continuous mode. Again, it is unclear as to why this difference of performance is observed when using Orfom<sup>®</sup> SX12.

The use of LIX<sup>®</sup> 984N resulted in higher phase disengagement times with all diluents relative to the Acorga<sup>®</sup> reagents evaluated within this study. Generally the phase disengagement times were 20 – 30 seconds higher when using LIX<sup>®</sup> 984 N relative to the Acorga<sup>®</sup> reagents, except when in combination with Orfom<sup>®</sup> SX12 or Orfom<sup>®</sup> SX80 (see Figures 5 and 6). For example, the use of LIX<sup>®</sup> 984N with Orfom<sup>®</sup> SX80 under organic-continuous conditions resulted in a phase disengagement time of 153 seconds compared to 102 seconds observed using Orfom<sup>®</sup> SX80/Acorga<sup>®</sup> OPT 5540 (a difference of more than 50 seconds). An initial consideration to explain this difference might be viscosity. For example, if the viscosity of the loaded organic of Orfom<sup>®</sup> SX80/Acorga<sup>®</sup> OPT 5540 is significantly lower than that of Orfom<sup>®</sup> SX80/LIX<sup>®</sup> 984N then one may expect such a large phase disengagement time difference, with the Orfom<sup>®</sup> SX80/Acorga<sup>®</sup> OPT 5540 having a lower phase disengagement time.



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However, upon examination of the viscosities of the 80% of maximum loaded organic samples (Table 6) it can be seen that the viscosity of the Orfom<sup>®</sup> SX80/Acorga<sup>®</sup> OPT 5540 sample is actually higher than that of the Orfom<sup>®</sup> SX80/LIX<sup>®</sup> 984N (a viscosity difference of approximately 6.1 SUS at 22 °C). A measurably higher viscosity loaded organic sample resulted in a significantly lower phase disengagement time. This characteristic is also observed when comparing the phase disengagement times of Orfom<sup>®</sup> SX12 with the Acorga<sup>®</sup> reagents in organic-continuous mode. The viscosities of the two loaded organic samples was were higher than that of any of the other single diluents in combination with the Acorga<sup>®</sup> reagents (Table 6), but the resulting phase disengagement times were lower by comparison.

The 80% of maximum loaded organic phase resulting viscosities from Table 6 are illustrated graphically in Figure 7 as a function of temperature. The measured Orfom<sup>®</sup> SX11 loaded organic phase viscosities were notably higher than the other diluent-reagent combinations at all temperatures. Excluding Orfom<sup>®</sup> SX11, the various diluent-reagent loaded organic phases ranged in viscosities of approximately 41 – 52 SUS at 22 °C down to 35 – 40 SUS at 45 °C.

It seems reasonable that viscosity of the loaded organic phase would have an effect on phase disengagement time at some point as viscosity increases. As materials become more viscous it is more difficult to mix them, and once mixed, more viscous materials should require a longer time to phase separate. Perhaps this is the reason Orfom<sup>®</sup> SX11 demonstrated higher phase disengagement times. The loaded organic phase when using Orfom<sup>®</sup> SX11 may have achieved a "critical point" in viscosity, above which the phase disengagement time starts to increase rapidly. As mentioned in the previous section discussing neat diluent physical properties, a systematic study of extraction performance and phase disengagement characteristics as a function of diluent viscosity has not been found in a search of public literature. Such a study as a function of loaded organic phase viscosity has not been identified either, although it would be very interesting.

From the data gathered within this study it appears that the diluent-reagent combinations evaluated would have acceptable performance within sub-Sahara Africa copper solvent extraction conditions, most certainly those not utilizing Orfom<sup>®</sup> SX11. The Cu extraction kinetics data (Table 6) was also consistent throughout the various combinations studied. However, from review of the data here it is quite clear that there was not a direct correlation between phase disengagement characteristics and diluent viscosity or loaded organic phase viscosity. Viscosity is only one of many variable properties within SX operations that should be evaluated for desired performance.

Mixtures of Orfom<sup>®</sup> SX80 and BP Mining Solvent or Shellsol<sup>®</sup> 2325 were also evaluated for phase disengagement performance and the resulting data is summarized along with the individual diluent data in Tables 6 and 7 and Figures 5 – 7. Mixtures of 20% and 40% by volume Orfom<sup>®</sup> SX80 were prepared with BP Mining Solvent and Shellsol<sup>®</sup> 2325 independently. The resulting mixtures would contain either 20% Orfom<sup>®</sup> SX80 and 80% of the other diluent or 40% Orfom<sup>®</sup> SX80 and 60% of the other diluent. These mixtures were evaluated through the same set of phase disengagement and solubility tests as the neat diluentreagent combinations. The tests were performed to determine any detrimental effects on copper SX performance within the sub-Sahara Africa conditions. As can be noted from reviewing Table 6 and the plots in Figures 5 – 7 these diluent mixtures performed very similarly to the stand alone diluents. All of the phase disengagement properties (time and quality) as well as resulting loaded



organic viscosity were quite comparable to those of the other diluent-reagent combinations within the study.

Another performance property that was of interest for this study was the final loaded organic phase stability. Specifically, the solubility of the reagent-copper complex within the given diluents of interest was examined to observe any performance differences. This comparison was accomplished by placing aliquots of the final 80% of maximum loaded organic phase from the organic-continuous mode tests in glass test tubes and subjecting them to room (25 °C) and cooled (7 °C) temperatures for one week. The test tubes were inspected visually one time per day to check for crystallization or precipitation, which would indicate insufficient solubility of the reagent-copper complex within the given diluent.









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None of the diluent-reagent combinations demonstrated any precipitation after one week of storage at room temperature or under refrigeration, including the diluent mixtures of Orfom<sup>®</sup> SX80 with BP Mining Solvent or Shellsol<sup>®</sup> 2325. Therefore this data is not provided in table form within this report. Although these results are not dramatic, they do suggest a couple of interesting considerations.

Solubility is a complex phenomenon involving a variety of factors and therefore there is no single analytical technique that may be used to predict diluent solubility performance. A technique such as the Kauri-Butanol method (ASTM D1133) provides some useful information but is not sufficient by itself to determine diluent solubility performance. This data suggests that the KB values measured for the diluents within this study (Table 1) are not significantly different as to predict solubility performance within sub-Sahara Africa copper SX conditions. While KB values may provide a comparison of solubility at very large KB value differences, the solubility performance is for a specified resin and set conditions.

The data also suggests that aromatics content does not provide an individual measure for diluent solubility performance. Aromatics content does provide some contribution to solubility properties, but it is apparent from the data that the diluents evaluated within this study contain the appropriate molecular structures to successfully maintain solubility of the reagent-copper complex under sub-Sahara Africa copper SX conditions. These observations serve to re-emphasize the thought that any diluent (or solvent for that matter) should be evaluated by multiple techniques including subjection to the conditions for which it is targeted to obtain a true measure of performance.

### Conclusion

Various techniques exist for analyzing solvent extraction diluents and all provide useful insight into the properties and composition of such complex hydrocarbon mixtures. However, no individual analytical method provides sufficient data to predict diluent performance in practical operation. While some analyses provide a quick and consistent measurement for reference such as specific gravity (ASTM D1298), other methods yield data that must be utilized cautiously or complimented by another analyses, such as KB value (ASTM D1133) or aromatics content by FIA (ASTM D1319) or hydrocarbon type (ASTM D2425).

The data compiled within this study suggests that all of the diluents evaluated in this study possess sufficient properties to perform similarly and successfully for sub-Sahara Africa copper SX conditions (except perhaps Orfom<sup>®</sup> SX11). Although the diluents differ slightly in physical properties and composition, diluent suppliers provide diluents with needed physicochemical properties for successful SX plant operation. SX plants should be able to utilize these diluents to achieve efficient, safe, and reliable operation.



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Thanks are also extended to Cytec and BASF for providing samples of reagents for use in this study.

### Appendix: Table 6a – SX Diluent Phase Disengagement Performance

			Phase Disengagemen	t Time (sec)
Product and Extractant <sup>1</sup>	Organic Continuous	Aquous Continuous	Comments Organic Continuous	Comments Aquous Continuous
SX12-OPT 5510	86	91	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX12-OPT 5540	84	89	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX12-LIX 984N	153	137	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX80-OPT 5510	109	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX80-OPT 5540	102	91	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX80-LIX 984N	153	149	Clean, Clear	Cloudy, small droplet of org. within aq. phase
SX11-OPT 5510	184	177	Clean, Clear	Clean & clear break
SX11-OPT 5540	188	179	Clean, Clear	Clean & clear break
SX11-LIX 984N	182	176	Clean, Clear	Clean & clear break
Shellsol 2325-OPT 5510	114	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325-OPT 5540	106	92	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325-LIX 984N	136	125	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent-OPT 5510	112	101	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent-OPT 5540	105	97	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent-LIX 984N	132	124	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent/SX80 (80/20)-OPT 5510	111	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent/SX80 (80/20)-OPT 5540	104	101	Clean, Clear	Cloudy
BP Mining Solvent/SX80 (80/20)-LIX 984N	132	124	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent/SX80 (60/40)-OPT 5510	114	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent/SX80 (60/40)-OPT 5540	101	98	Clean, Clear	Cloudy, small droplet of org. within aq. phase
BP Mining Solvent/SX80 (60/40)-LIX 984N	139	122	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325/SX80 (80/20)-OPT 5510	113	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325/SX80 (80/20)-38% OPT 5540	105	101	Clean, Clear	Cloudy
Shellsol 2325/SX80 (80/20)-38% LIX 984N	142	129	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325/SX80 (60/40)-38% OPT 5510	110	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase
Shellsol 2325/SX80 (60/40)-38% OPT 5540	102	97	Clean, Clear	Cloudy
Shellsol 2325/SX80 (60/40)-38% LIX 984N	149	136	Clean, Clear	Cloudy, small droplet of org. within aq. phase

<sup>1</sup> All extractants were added to diluents and diluent blends at 38 volume percent



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### Appendix: Table 6b – SX Diluent Phase Disengagement Performance

			sity (mPas) emp (°C)		Cu Extraction Kinetics (%) at Time (sec		
Product and Extractant <sup>1</sup>	22	30	38	45	30	60	90
SX12-OPT 5510	6.6	5.1	4.0	3.5	94	96	97
SX12-OPT 5540	6.5	5.1	3.9	3.5	93	94	98
SX12-LIX 984N	5.2	4.0	3.2	2.8	97	97	99
SX80-OPT 5510	7.7	5.9	4.7	4.0	95	96	97
SX80-OPT 5540	8.2	6.3	4.6	4.2	91	93	94
SX80-LIX 984N	6.3	4.8	3.8	3.3	90	91	93
SX11-OPT 5510	17.1	12.4	9.5	7.3	96	98	98
SX11-OPT 5540	18.4	13.3	10.1	7.8	96	96	98
SX11-LIX 984N	13.2	9.6	7.4	4.8	91	99	100
Shellsol 2325-OPT 5510	5.0	4.0	3.3	2.9	94	94	99
Shellsol 2325-OPT 5540	5.8	4.7	3.9	3.4	93	96	98
Shellsol 2325-LIX 984N	4.9	3.9	3.3	2.9	91	96	98
BP Mining Solvent-OPT 5510	5.5	4.6	3.7	3.2	94	98	99
BP Mining Solvent-OPT 5540	5.5	4.6	3.7	3.2	95	96	97
BP Mining Solvent-LIX 984N	4.7	3.9	3.2	2.8	84	90	92
BP Mining Solvent/SX80 (80/20)-OPT 5510	6.0	5.3	4.3	3.6	91	94	94
BP Mining Solvent/SX80 (80/20)-OPT 5540	6.1	4.9	3.9	3.3	98	98	100
BP Mining Solvent/SX80 (80/20)-LIX 984N	4.6	4.1	3.4	2.9	92	96	98
BP Mining Solvent/SX80 (60/40)-OPT 5510	5.5	4.8	3.9	3.3	94	96	98
BP Mining Solvent/SX80 (60/40)-OPT 5540	6.2	5.3	4.2	3.6	98	98	98
BP Mining Solvent/SX80 (60/40)-LIX 984N	4.9	4.3	3.5	3.0	93	95	96
Shellsol 2325/SX80 (80/20)-OPT 5510	6.1	5.3	4.3	3.6	98	99	99
Shellsol 2325/SX80 (80/20)-38% OPT 5540	6.4	5.1	4.1	3.5	97	99	100
Shellsol 2325/SX80 (80/20)-38% LIX 984N	5.0	4.2	3.3	2.9	95	99	99
Shellsol 2325/SX80 (60/40)-38% OPT 5510	6.8	6.0	4.5	4.0	93	94	97
Shellsol 2325/SX80 (60/40)-38% OPT 5540	7.0	5.6	4.4	3.7	97	97	98
Shellsol 2325/SX80 (60/40)-38% LIX 984N	5.4	4.5	3.5	3.1	92	94	98

<sup>1</sup> All extractants were added to diluents and diluent blends at 38 volume percent

#### References

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- 4. Lubeck A. J., Cook R.D. Bromine Number Should Replace FIA in Gasoline Olefins Testing. *Oil & Gas Journal*, December 28, 1992.
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Before using this product, the user is advised and cautioned to make its own determination and assessment of the safety and suitability of the product for the product for the specific use in question and is further advised against relying on the information contained herein as it may relate to any specific use or application. It is the ultimate responsibility of the user to ensure that the product is suited and the information is applicable to the user's specific application. Chevron Phillips Chemical Company LP does not make, and expressly disclaims, all warranties, including warranties of merchantability of fitness for a particular purpose, regardless of whether or oral or written, express or implied, or allegedly arising from any usage of any trade or from any course of dealing in connection with the use of the information contained herein or the product itself. The user expressly assumes all risk and liability, whether based in contract, tort or otherwise, in connection with the use of the information contained herein or the product itself. Further, information contained herein is given without reference to any intellectual property issues, as well as federal, state or local laws which may be encountered in the use thereof. Stuch questions should be investigated by the user.