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TECHNICAL DEVELOPMENTS LEADING TO MODERN SOLVENT EXTRACTION DILUENTS

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INTRODUCTION

Early solvent extraction circuits in the uranium industry utilized bona fide kerosenes as diluents for extractant chemicals. These kerosenes were used successfully in the uranium industry; however, at least one plant was destroyed by fire resulting from the use of a low flash point kerosene. Although the term "kerosene" is used throughout the solvent extraction industry, the authors have been unable to find any use of kerosene in copper solvent extraction circuits. A term that is occasionally used with reference to diluents, is "metallurgical kerosene." Such a term is unrecognizable in the petroleum industry.

Kerosene [or kerosine] is a flammable hydrocarbon mixture that is less volatile than gasoline. It is produced for combustion purposes and may have variable compositions of organic compounds including alkanes, alkenes, alkines, and aromatics.

Diluents are constant composition hydrocarbon mixtures developed specifically for use in solvent extraction processes. These products usually have much lower vapor pressures and higher flash points than kerosene. In solvent extraction systems, they typically comprise 70 to 95 v/o percent of the circuit organic. The primary purpose of the diluent is to adjust the extractant concentration to the working range of the operation. The diluent and extractant must be completely soluble or miscible with each other. Secondary diluent effects are to promote transfer kinetics, optimize phase disengagement, and minimize both organic in aqueous and aqueous in organic entrainment.

The authors are indebted to Mr. Jim Lake of Tucson, Arizona, for providing extensive information on the early Ranchers Blue Bird pilot plant operation and actual plant operation. According to early reports in Mr. Lake's possession, [1966] the first diluent utilized in the copper industry was the old Napoleon 470B solvent produced by the Kerr McGee Corporation. Jones [1977] also reported that Cyprus Bagdad's SX circuit started up with Napoleon 470B. This year, the Kerr McGee Corporation [1995] sold off all of its refining units to three separate companies, and it no longer produces any refined products. The first paper that the authors found using the term "diluent" for the organic carrier, and the first paper to recognize the costs of solvent extraction entrainment and evaporation losses was presented in 1975 by P.M. Paige.

A number of other diluents and solvents have been tried in the copper industry such as the Chevron IES diluent, which is also no longer manufactured. In the international market there are three major diluent producers; Shell, Exxon, and Phillips.

Concern about plant safety is reflected in high flash point requirements and in the requirement that a diluent be free from benzene and other carcinogens. Modern diluents must meet stringent quality control requirements. Plant operations demand that the performance of diluents be consistent over time. As processes evolved, additional requirements of rapid phase breaks, minimal organic entrainment, and low volatility have been instituted.

Modern diluents receive extensive quality control to ensure high performance. This quality control must start in the refinery and continue until delivery. In several instances carriers not controlled by the diluent manufacturer hauled diluents in tank wagons that were not thoroughly cleaned, which either resulted in rejections of loads or, in the worst cases, severe plant problems due to consequential contamination. The criteria discussed in the next section relate to the proper selection of a diluent. However, the perfect diluent for plant operation can be rendered harmful if delivered in an improperly cleaned tank wagon. The use of dedicated equipment for the transportation of diluents is highly recommended.

DILUENT SELECTION CRITERIA

During the early, less sophisticated days of solvent extraction, many papers were published that not only did not recognize the effects of diluent on solvent extraction circuits but failed to identify the diluent in use. Since the diluent makes up over 90% of the circuit organic in many plants, this material logically should be expected to exert a strong influence on the behavior of the circuit.

There are many factors to consider in selecting a modern diluent-extractant combination for a given SX circuit. These include in approximate order of importance:

- Phase Break
- Pour Point
- Transfer Kinetics
- Metal Extractant - Diluent Compatibility
- Diluent Chemistry
- Separation Efficiency from Contaminants
- Entrainment of Organic in Aqueous Phase
- Flash Point
- Evaporation Loss
- Supplier's Support
- Price

Some of these factors are immediately obvious, while others are much more subtle and require detailed evaluation. Each of these factors is discussed in the following sections.

Phase Break

Each plant evaluating a new diluent should measure *break times*, using the standard break time tests in use in its laboratories. Every plant has a unique set of factors that will affect the break time. These include extractant chemistry, extractant concentration, aqueous phase

content, operating temperature, and plant design. Several plants have reported that the use of a high performance diluent in their circuit allowed them to increase flow rates. One plant reported a 30% increase in plant flow rate with the use of a high performance diluent.

Diluent Viscosity plays a major role in rapid, clean phase breaks. The viscosity value should be supplied by any vendor attempting to sell a new diluent. High viscosity generally results in poor mixing, poor copper transfer due to slow copper kinetics, and slow phase break. A high viscosity diluent may make it difficult to retain phase continuity; i.e., organic continuous or aqueous continuous. High viscosity may also greatly increase a dispersion band when the material is placed in actual plant operation.

While lower break times are generally preferable, the break time can become too low. If the break time becomes extremely short, the organic and aqueous phases can begin to separate in the mixer section. This causes poor metal transfer and slow kinetics.

Pour Point

The pour point of a diluent is an extremely important value that is frequently overlooked. The generally accepted value for pour point should be around -26.1 °C (-15 °F). Jobbers, or re-sellers, frequently neglect this feature and at times have offered diluent material with pour points as high as 4.4 °C (40 °F). A material with this pour point would, of course, not be pumpable in the winter. When testing a new diluent it is recommended that the phase break of the diluent be measured at the lowest temperature the plant expects to experience throughout the year as changes in viscosity, density, and pour point will become readily apparent.

Transfer Kinetics

Metal of value *transfer kinetics* should be evaluated with any new diluent. Unless rapid transfer of metal is achieved in the mixer section, which has a finite retention time, extraction efficiency in the solvent extraction unit will decline.

Metal Extractant - Diluent Compatibility

Solubility of organic compounds in diluents may be changed by the composition of the diluent. Thus, a diluent should be checked at the highest concentration of extractant ever expected in plant operations. For example, certain plants may wish to try a new diluent at 30% extractant; whereas, another copper facility may want to try a new diluent at only 10% extractant. The solubility of an extractant loaded with copper may be less than that of an unloaded extractant. Also, *phase breaks* should be determined with the maximum amount of extractant as increasing the amount of extractant typically increases phase break time.

Diluent Chemistry

Diluents supplied should be free of *reactive multiple bonds*. Such bonds may react with the extractants and reduce their capability to transfer metal.

Diluent should be guaranteed to contain extremely low amounts of carcinogens, such as benzene and polynuclear aromatics. For example, Phillips' diluents contain less than 100 ppm of benzene, 400 ppm toluene, and 2,000 ppm xylenes.

Separation Efficiency From Contaminants

If a diluent increases the amount of contaminant species into the stripping circuit, product quality and recovery can be adversely affected. Increased contamination in the stripping may result in increased bleed stream volume necessary to maintain contaminants within acceptable limits. This increased volume can increase costs due to additional losses of modifiers such as cobalt.

Entrainment Of Organic In Aqueous Phase

Organic entrainment has been recently recognized as one of the largest hidden costs of a diluent. The costs associated with entrainment losses are very large due to the fact that a very expensive component, the extractant, is lost with organic entrainment. The formula shown below is illustrative of the type of calculation needed to assess this hidden cost.

Equation 1

Cost of Entrainment $/Day =

[{Loss in ppm * PLS flowrate (m^3/min) * 1440 min/day}*1L/1000mL] * Cost of Barren Organic ($/1)

Using the assumptions about the organic shown in Table 1, the hypothetical plant shown in Table 2, and a low entrainment value of 5 ppm(mL/m^3); the cost per day in entrainment loss is $246 or nearly $90 thousand per year.

Table Assumptions about Organic Phase

Extractant			
$/lb	$/kg	$/L	sp gr
$6.50	$14.33	$13.11	0.915

Diluent		
$/gal	$/L	sp gr
$1.05	$0.28	0.81

Table 2. Hypothetical Plant Characteristics

Mixer settler area	57.4	m2	6,000	ft2
PLS Flowrate	12.0	m3/min	3,170	gpm
Extractant Strength	20 V/o			
Barren Organic sp gr	0.831			
Barren Organic Cost	$ 2.84/L			

Evaluation of entrainment costs is probably only practicable under pilot plant operating conditions. Laboratory scale equipment will only produce the most general indications of entrainment.

Solubility data for a diluent can provide its minimum entrainment value. However, this number will not reflect the true diluent-extractant entrainment losses. The solubilities at 25°C for the two most widely used diluents, SX-7 and SX-12, are respectively 4.5 and 3.8 ppm.

Flash Point

Flash Point is related to the most volatile fraction of a diluent, but does not measure the amount of the fraction. For example, a diluent that has a Flash Point of 150 degrees Fahrenheit may have only a small percentage of a component having 150 degree Flash Point or it may have a very large percentage of that low flash component. The Flash Point is measured by three different methods; The Pensky Martin Closed Cup [PMCC] and the Tag Closed Cup [TCC] give the lowest Flash Point readings. The Cleveland Open Cup [COC] will give the highest reading. All three methods are ASTM approved procedures. The values reported are corrected to sea level. A diluent having a PMCC of about 165 degrees Fahrenheit will have a COC of about 190 degrees Fahrenheit. The Closed Cup values are usually reported as this is the value used in Department of Transportation shipping regulations and is applicable to closed trailers, tank cars, and tanks. The Cleveland Open Cup may be more applicable to non-hooded plant operations which usually take place in open areas. The Flash Point of actual circuit organic is usually slightly higher than that of the as received diluent. Although the term kerosene is frequently erroneously used to describe the organic diluents that are added to SX circuits, most diluents have Flash Points and distillation ranges much higher than commercial kerosenes.

Evaporative Loss

Modern diluents have *vapor pressures* that are too low to have meaningful Reed Vapor Pressures. However, Phillips has adapted an ASTM approved apparatus to measure the very low evaporation rates associated with these diluents. The errors introduced in beaker evaporation tests are usually so great due to fluctuating air drafts, differential heating of beakers due to sunlight, etc., that the data can be considered only indicative of relative evaporation rates. Evaporation losses can be minimized by reducing the air flow across the organic phase.

The cost associated with this loss is minimal as compared to entrainment. This is because only the lower cost diluent is lost to evaporation. The formula shown below is illustrative of the type of calculation needed to assess this cost.

Using the assumptions shown in Tables 1 and 2 above and an evaporative loss rate of 100 (g/m^2)/day, the formula yields a cost of $19 per day or $7,000 per year.

Equation 2.

Cost of Evaporation $/Day =

[{(((Area of Mixer-Settler (m^2) * Loss (g/m^2)/day)) / Diluent Density (g/L)) * 1L/mL1000} * Cost of Diluent $/L]

Changing a diluent to avoid evaporation loss may be counterproductive. For example, a diluent with a low vapor pressure but a high viscosity may produce low vapor pressure losses but higher entrainment losses. If assumptions used are the same as before, including a 100 g/m^2/day reduction of evaporation loss but a 5 ppm increase in entrainment loss, then the results are shown in Table 3.

Table 3. Net Change in Operating Cost

	$/day	$/year
Additional Cost of Entrainment	($ 245.77)	($89,704)
Cost of Evaporation:	$ 19.09	$ 6,968
Net Change in Operating Cost:	($226.67)	($82,736)

Supplier's Support

It normally has been considered a necessity to have the diluent *supplied* by a producing company rather than a jobber or a re-sale company since the producing company can respond to heavy demands by increasing its production whereas, a company reselling a diluent may have limited quantities available and may substitute in cases of emergency without notifying the customer. A basic producer of diluent should be able to respond very rapidly and during off hours. An SX plant should be able to contact a supplier 24 hours a day, 7 days a week, 365 days a year to place orders and expect these orders to be filled within 24 hours.

A major supplier of diluent should have *multiple locations* to draw product from. Thus, a customer runs no risk of supply interruption even if one or two of the locations should experience problems.

Familiarity of the vendor with solvent extraction is a necessity as jobbers or distributors in particular may make changes in a solvent without realizing the significance that such changes can have on solvent extraction. For example, a few parts per million of certain organic soluble corrosion inhibitors may create disastrous results by interacting with the extractant, or the addition of a biocide to a diluent could result in the partial sterilization of heaps under leach resulting in lower copper extractions.

Use of *dedicated equipment* for the transportation of solvent extraction diluents is extremely critical. As little as 20 ppm of certain organic compounds can completely alter a solvent extraction plant's performance. Some surfactants used in steam cleaning of trailers may leave residues that can have significant effects on plant operations. Tank trailers used to haul scale inhibitors may contain residual

products that could detrimentally affect copper transfer in an SX Plant.

Price

Price, although important, by itself may not be a direct evaluation of true product cost as the factors listed above contribute to the overall cost effectiveness of a diluent.

The price of diluents is dependent upon the price of raw materials. In addition to the price of crude, prices are influenced by the point of yield in refinery processing, and whether or not further refining of the yielded stream is necessary. For example, some crudes are unsuited to diluent production because of the presence of compounds containing double and triple bonds. Fluctuating crude sources can also render a refinery incapable of producing consistent high quality diluents. When the price of crude oil fluctuates, diluent prices can be expected to fluctuate. Prices are usually higher if long term price commitments are required. In SX plant operations, diluent costs are usually the third or fourth highest cost experienced by a plant. This cost ranking depends upon such things as the power required for pumping, electrowinning, etc., and the consumption and cost of sulfuric acid. The extractant normally is the highest single cost of SXEW circuits. The combination of extractant and diluent costs represents a very large portion of the total costs of producing copper from an SXEW circuit.

In an effort to continuously develop new solvent extractant diluents for an increasingly sophisticated market, Phillips conducts ongoing product development research. This has led to the current commercialization of five diluents; SX-1, SX-7, SX-11, SX-12, and SX-18. Three topics related to diluents that currently appear to be of interest to the solvent extraction industry are the effect of aromaticity on diluent performance, the influence of flash point on diluent properties, and diluent loss by volatilization.

EXPERIMENTAL GOALS

As a result of Phillips' ongoing research efforts to establish the basic foundations of diluent understanding, the tests described in the following sections of this paper were conducted to better understand the effects of aromatic contents and higher flash point diluents on copper and iron extractions with a selected extractant. The extractant was chosen to give fairly rapid phase breaks. Also, one experiment with a different extractant to show the interaction of another extractant with the test diluents was conducted. Experiments also were performed to show the evaporation losses of samples from actual plant organic phases.

LABORATORY PROCEDURE

Solutions of test diluents were prepared volumetrically. The samples prepared are shown in Table 4. The diluents used as the aliphatic components are Phillips Mining Chemical's commercial products. The diluents used for the aromatic portion are pure aromatic products. Each test series used a different aromatic product. Series A used an aromatic product with a flash point of 65.6°C (150°F). Series B used a product with a flash point of 93.3°C (200°F). The flash points of the test diluents were determined by ASTM procedure D-93, Pensky-Martens Closed Cup.

Table 4. Composition of Test Diluents

Diluent Series	Aliphatic	Aromatic
A-1	100% SX-10	------
A-2	90%	10%
A-3	80%	20%
A-4	70%	30%
A-5	50%	50%
A-6	25%	75%
A-7		100%
B-1	100% SX-11	
B-2	90%	10%
B-3	80%	20%
B-4	70%	30%
B-5	50%	50%
B-6	25%	75%
B-7	------	100%

The organic extraction solution was prepared by diluting 35 mL of a commercially available mixture of tridecanol and 5-dodecylsalicylaldoxime with 315 mL of test diluent. The viscosity of the diluent-extractant mixture was determined by ASTM procedure D-445.

In addition, experiments were conducted with several A series diluents, and 10% of a commercial extractant that consists of a 50:50 mixture of 5-nonylacetophenone oxime and 5-dodecylsalicylaldoxime in a diluent.

Synthetic pregnant leach solutions were composed of 6 g/l Cu^{2+} and 3 g/l Fe^{3+}, with pH adjusted to 2.0 ± 0.05.

The laboratory mixer cell was a 1.7 liter square glass cell. The impeller-stirrer was 4.5 cm in diameter, 7 mm high with 6 slots of 3 mm each on the bottom radiating from center to edge. The stirrer motor head was regulated to 1650 rpm ± 10 rpm. A thief sampler capable of quickly withdrawing 10 mL of sample was also used.

The stirrer and impeller assembly was placed in the cell so that the bottom of the impeller was 2.5 to 3 cm above the bottom of the cell. The cell received 350 mL of the organic. The stirrer was started, and the impeller speed adjusted. While the organic was stirring, 350 mL of synthetic pregnant leach solution was quickly added (<5 seconds) to the cell, and the timer was started.

Without stopping the mixer, 10 mL samples were withdrawn after 30, 60, 90, 120, and 300 seconds. The samples were immediately put into individual small separatory funnels. The aqueous phase was drained away and discarded and the organic phase submitted for atomic absorption analysis.

After the final sample was withdrawn, the mixer was turned off. The break time is the time from the cessation of the turning of the impeller until the formation of a definitive interface between the aqueous and organic phase with only a single layer of small bubbles between the two phases.

Evaporative loss experiments were conducted on samples obtained from an operating circuit. The procedure used was ASTM D-972.

Two different wind speeds over the liquid were tested. The wind speed was varied by changing the volume of liquid in the cell. The low speed had 10 mL in the cell, while the high speed used 20 mL in the cell. The higher sample value decreased the air volume space in the cell, thus increasing the wind speed. The procedure cell is shown in Figure 1. As can be seen the wind speed will be lowest at the entry and highest at the exit.

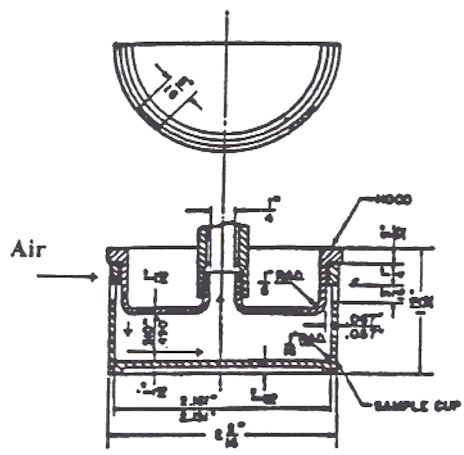

Figure Experimental Cup for Evaporation Test

EXPERIMENTAL RESULTS

The results of the physical tests on the diluent mixtures are shown in Table 5. The flash point was determined on the test diluent while the viscosity was determined on the diluent-extractant mixture and is reported in centistokes.

Table 5. Physical Characteristics of Test Diluents

Diluent	Arom.	sp gr	Flash Pt, °C	Visc., cSt	Phase Break, Sec
A-1	0%	0.80	84.4	4.57	81
A-2	10%	0.81	80.0	3.84	60
A-3	20%	0.82	75.0	3.29	57
A-4	30%	0.83	70.0	3.16	45
A-5	50%	0.85	67.8	2.35	43
A-6	75%	0.87	67.2	1.90	61
A-7	100%	0.90	66.1	1.61	81
B-1	0%	0.81	>110	5.88	115
B-2	10%	0.83	>110	5.20	91
B-3	20%	0.85	>110	4.66	84
B-4	30%	0.87	>110	4.21	70
B-5	50%	0.90	>110	3.83	115
B-6	75%	0.95	99.4	3.39	147
B-7	100%	1.00	97.8	3.27	362

The isotemporal (identical times plotted on same line) extraction curves for the SX-10, aromatic, and extractant are shown in Figure 2. The data shows that for moderate flash point diluents of around 75° C (167° F) an aromaticity of between 10 to 30 percent gives the best extraction. Because of the lower flash point of the aromatic used, increased aromaticity results in a lower flash point. With the diluents tested in these series, higher aromaticity increases the phase break time and lowers the extraction kinetics.

The phase break curve clearly indicates that phase breaks are reduced by 10 to 50 percent aromatic content. However, the maximum loading at 300 seconds is highest between 10 and 30 percent aromaticity. Also, the kinetics illustrated by the curves representing specific times indicate that the kinetics of copper transfer decrease as the aromaticity increases above 30%. A review of Figure 2 clearly demonstrates that the 10 to 30 percent aromatic content gives the best overall performance.

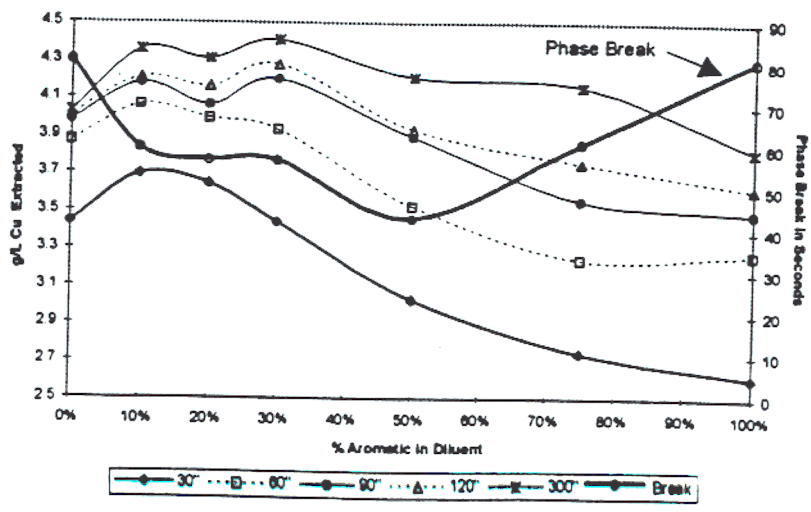

Figure 2. Isotemporal Graph of Copper Extraction for "A" Series Test Diluents with Phase Break

The effects of aromaticity on iron co-extraction are shown in Table 6 and Figure 3. Increased aromaticity appears to help suppress iron co-extraction up to 50% aromaticity. Note, however, that these curves indicate that iron extraction decreases with increased mixing time showing that copper is preferentially extracted. Also note that a 1.0 ppm analytical variation in an iron value can make a large difference in the Cu:Fe extraction ratio shown in Figure 3 because all Fe levels are very low.

Table 6. Series "A" Diluents ppm Iron Extracted At Time

Aromatic	30"	60"	90"	120"	300"
0%	13	10	8	8	6
10%	11	12	8	7	5
20%	9	7	6	6	7
30%	8	8	7	7	6
50%	7	5	5	3	3
75%	13	8	7	7	6
100%	5	4	4	2	1

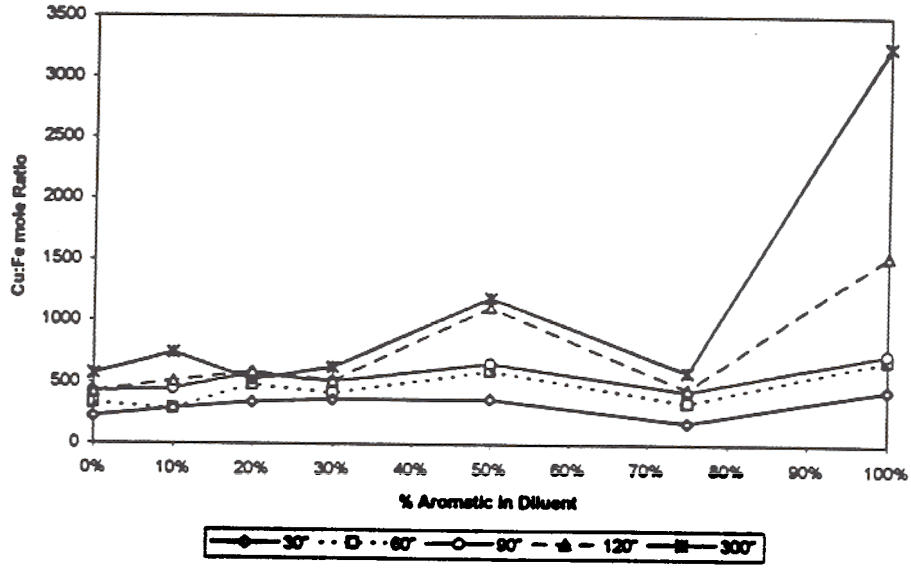

Figure 3. Isotemporal Graph of Iron Co-Extraction for Series "A" Test Diluents

The effect of aromaticity on copper extraction for the higher boiling diluent is shown in Figure 4. Here again the 10 to 20 percent aromatic range gives the highest copper extraction, and the 10-30 percent range gives the fastest break times.

The effects of aromaticity on iron co-extraction are shown in Table 7 and Figure 5. Increased aromaticity appears to help suppress iron co-extraction. Note, however, that these curves show that iron extraction decreases with increased mixing time showing that copper is preferentially extracted.

Table 7. Series "B" Diluents ppm Iron Extracted At Time

Aromatic	30"	60"	90"	120"	300"
0%	12	9	9	8	10
10%	15	21	13	12	9
20%	11	10	10	10	13
30%	12	10	9	8	8
50%	13	9	8	9	12
75%	13	12	10	9	11
100%	18	16	10	9	7

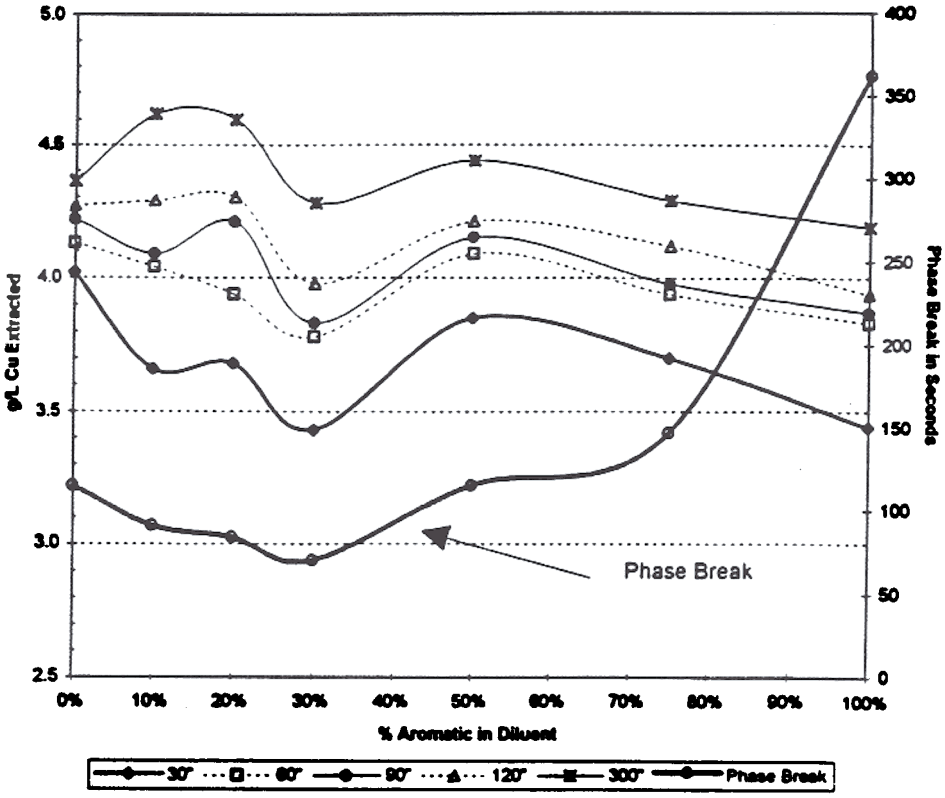

Figure 4. Isotemporal Graph of Copper Extraction for "B" Series Test Diluents Showing Phase Break

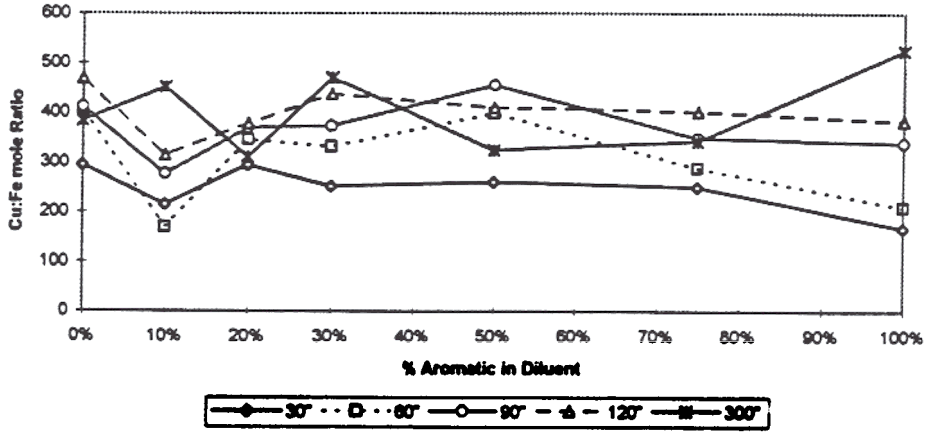

Figure 5. Isotemporal Graph of Iron Co-Extraction for Series "B" Test Diluents

Modern diluents are refined from production streams. Three products obtained from the same production stream were tested. The difference between the products is that each comes off in a different boiling range. This is because each product has an increased average molecular weight over the previous product. Figure 6 shows the effect of increasing average molecular weight on the physical properties of the diluent. Although there are relatively large changes in flash point, phase break, and viscosity, the change in density is quite small. It appears that viscosity has a much greater impact on phase break than density.

Figure 7 shows the effect of increasing flash point on the amount of copper extracted after a given mixing time.

The molar copper-iron extraction ratios versus molecular weights are presented in Figure 8. Increased mixing time increases the ratio as does lower molecular weight [lower flash point].

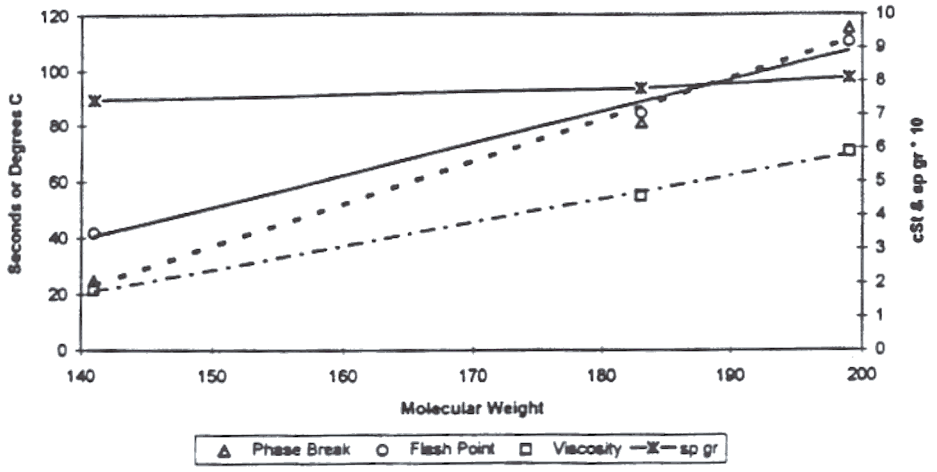

Figure 6. Physical Properties versus Molecular Weight

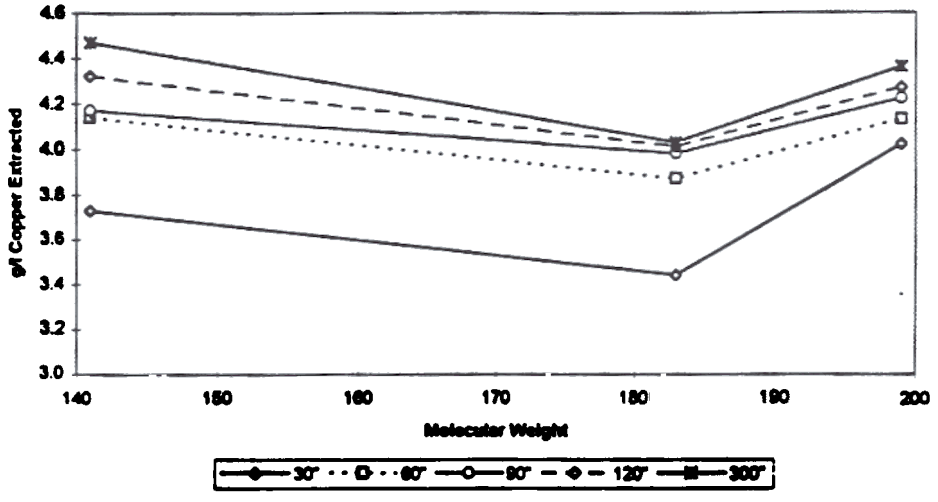

Figure 7. Isotemporal Extraction Curves versus Product Flash Point

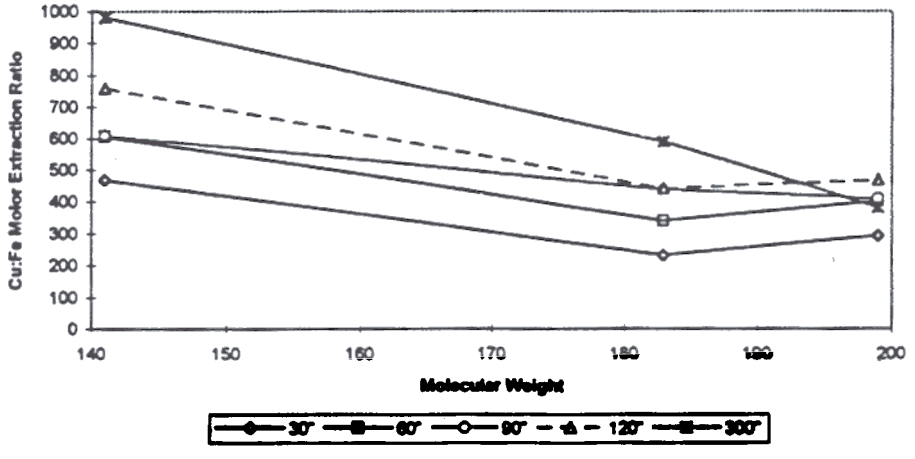

Figure 8. Isotemporal Cu:Fe molar Extraction Ratios versus Diluent Flash Point

Commercial diluents are refined from production streams. It is more expensive to custom blend a diluent than to refine and clay treat a production stream. A comparison of Phillips' commercial diluent composition is shown in Table 8. SX-12 is clay treated SX-7. SX-1 is sourced from a different refinery than the other products, and it is also clay treated. It is considered to have a performance that is intermediate between SX-7 and SX-12.

Table 8. Characteristics of Commercial Diluents

Diluent	% Aromatic	°C (°F) Flash Point	Average Molecular Wt.
SX-1	13	80.0 (176)	191
SX-1HF	13	86.7 (188)	204
SX-7	22	70.0 (158)	169
SX-10	0	84.4 (184)	183
SX-11	0	>110 (>230)	199
SX-12	22	70.6 (159)	169
SX-18	0	41.7 (107)	141

The physical properties of the above diluents are shown in Figure 9.

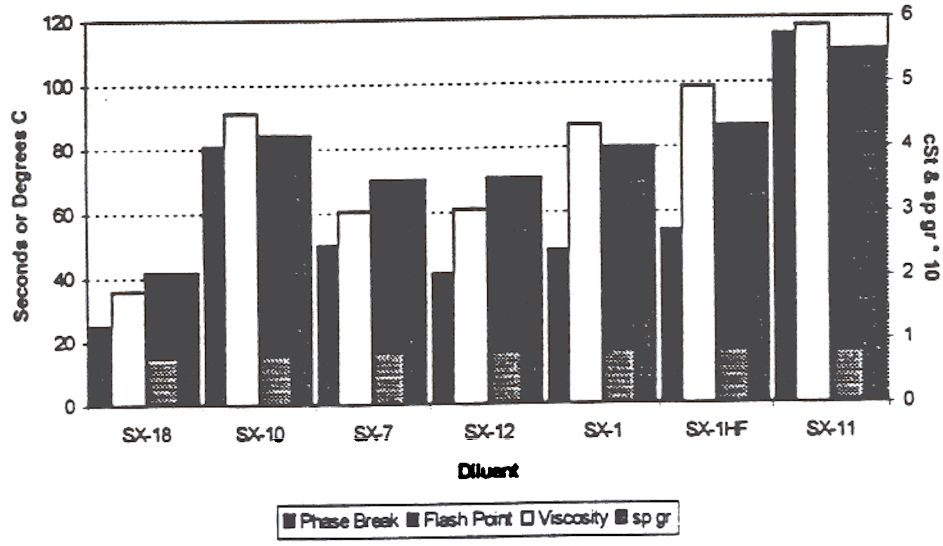

Figure 9. Physical Properties of Selected Commercial Diluents

The isotemporal copper extraction curves of the selected commercial diluents with the mixture of 5-dodecylsalicylaldoxime and tridecanol that was used in these tests are shown in Figure 10.

The molar copper-iron extraction ratios for the different commercial diluents are shown in Figure 11. This Figure indicates that SX-12 has the highest selectivity against iron of the six diluents. Clay treatment of diluents and extractants may appreciably decrease break time and also may render the diluent more selective against iron. Clay treatment was discussed by Mattison, Kordosky and Champion in 1983. Clay treatment involves contacting the organic with specially prepared clay to remove trace quantities of polar organic compounds from the hydrocarbon stream. The clay functions as an ion exchange material and absorbs the polar compounds. Phillips uses acid activated calcium montmorillonite and low volatile matter (LVM) attapulgite clays. The selection depends on which is more efficient on the specific diluent. This, in turn, is dependent upon the crude feed stocks.

The original application was to treat the plant organic if a load of contaminated diluent was used in the plant circuit It has also been used to treat contaminated product in the diluent storage tank. *The use of high quality diluents has eliminated the requirement to treat the entire circuit due to contamination*. Clay treatment is now primarily used for treating organic reclaimed from raffinate ponds and "crud" in an effort to improve the quality of the reclaimed product before it is reintroduced to the circuit. It is also used by some operations as a method to maintain the quality of the plant organic during normal operation. By periodically clay treating a portion of the plant organic, the operation can remove any polar organic degradation products of the extractants and contaminants that may be present in the pregnant leach solution. This allows the operation to optimize plant conditions.

The most obvious change that occurs when a product is clay treated is the change in phase disengagement time of the organic aqueous emulsion. Removal of the polar compounds from diluents or extractants normally results in a reduced phase break time under a given set of conditions.

Clay treating can have a significant influence on break times, even when sophisticated, highly refined diluents are treated. For example, clay treating of the SX-11 reduced its break time to about the same break time as the minimum break time shown in Figure 4 for SX-11 combined with 30% aromatic diluent. The clay treated pure SX-11 gave a break time of 58 seconds for the same conditions. Clay treatment can also influence copper transfer kinetics and iron selectivity.

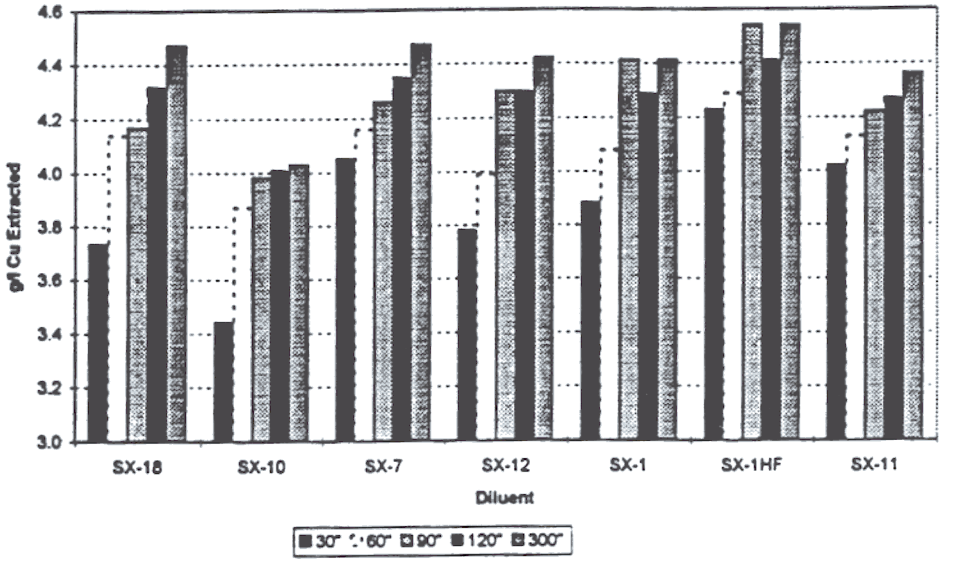

Figure 10. Copper Extraction at Time for Selected Commercial Diluents with Given Extractant

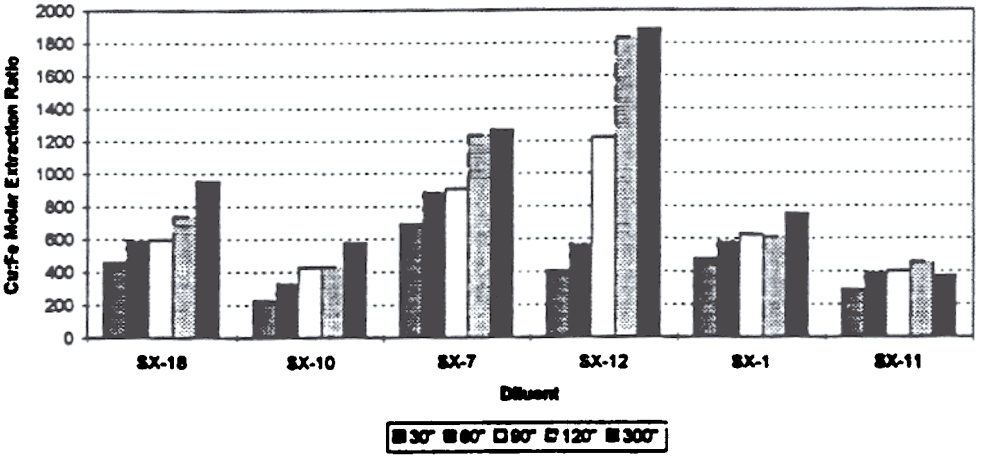

Figure 11. Cu:Fe Molar Extraction Ratios for Selected Commercial Diluents

The effects of the interaction of the extractant and diluent on the properties of the organic phase are shown in Table 9 and Figures 12 and 13. The standard extractant mixture of 5-dodecylsalicylaldoxime and tridecanol was used in all the previous experiments at ten volume percent. The alternative extractant was a 50:50 mixture of 5-nonylacetophenone oxime and 5-dodecylsalicyl-aldoxime; it was used at eight volume percent. The diluents used with this alternate extractant were 10, 20, or 30% aromatic in SX-10.

Table 9. Effect of Extractant-Diluent Interaction

Extractant	% Aromatic	(sec) Phase Break	(cst) Viscosity	(°C) Flash Point
Standard	10	60	3.84	80.0
	20	57	3.29	75.0
	30	57	3.16	70.0
Alternate	10	170	3.39	82.8
	20	156	2.99	78.9
	30	102	2.68	76.7

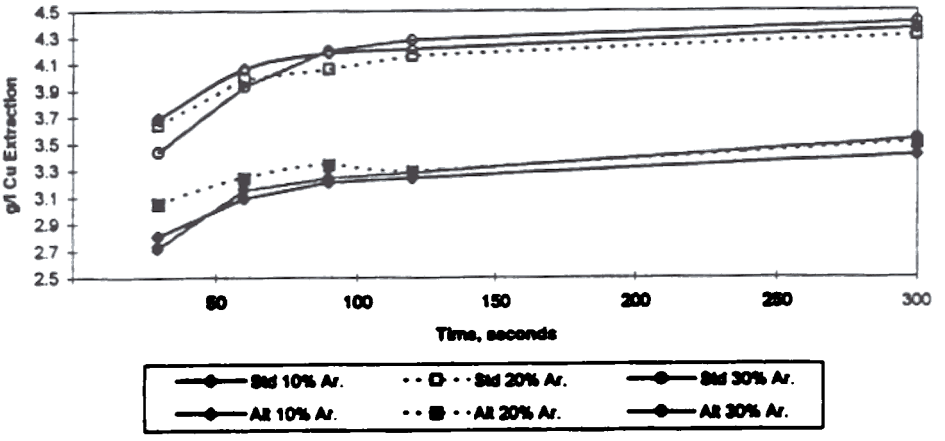

Figure 12. Cu Extracted by 8% or 10% Extractant in 10% to 30% Aromatic and SX-10 Diluent

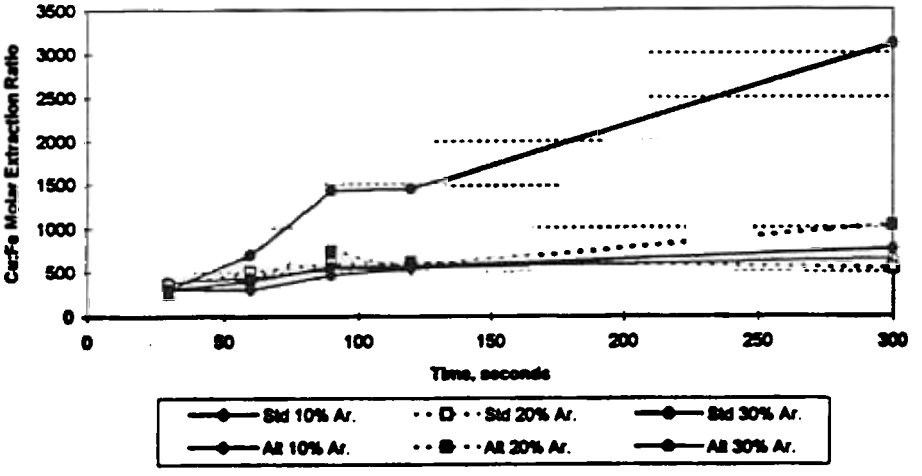

Figure 13. Cu:Fe Extraction Ratio for 8% or 10% Extractant in 10 % to 30% Aromatic and SX-10 Diluent

Although the amount of copper extracted with the alternative extractant is less, the general shapes of the curves in Figure 12 remain the same. However, when the Cu:Fe extraction ratio in Figure 13 is viewed, the 30% aromatic diluent has a very strong effect on the suppression of iron extraction.

A plot of the copper extraction kinetics for test diluents: A-2,A-3, A-4, B-2, B-3, and B-4 is shown in Figure 14. This figure shows that the kinetics are independent of the base aliphatic component of the diluent when the diluent contains 10% to 30% aromatic. Yet as can be seen from Figure 10, the two base diluents SX-10 and SX-11, have significantly different kinetics.

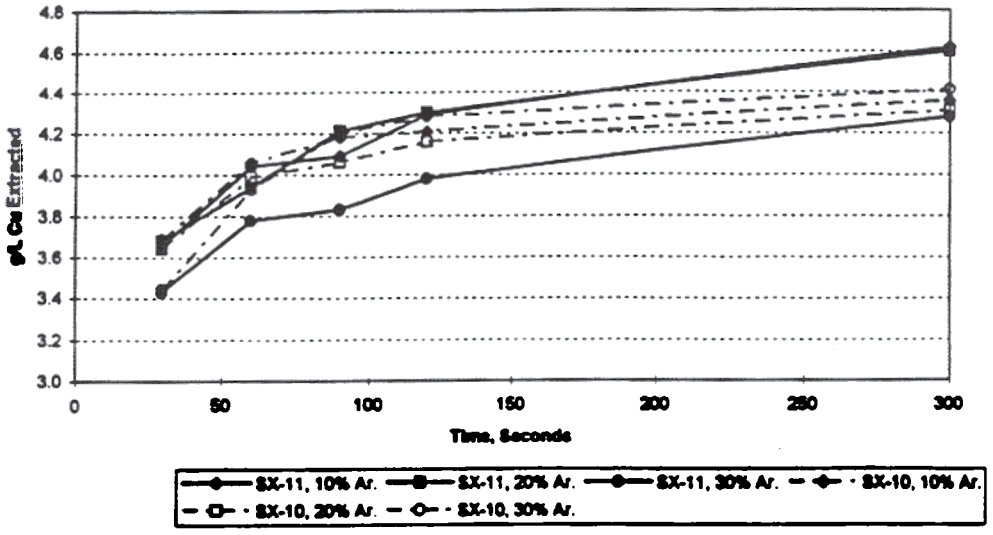

Figure 14. Copper Extraction Kinetics for Selected Test Diluents

The authors have started an extensive study on evaporative loss from operating circuit organic phases. Results from two of the experiments conducted to-date are shown in Tables 10 and 11 below.

The experiments were conducted at two different wind speeds at 38.9°C. The maximum loss per 24 hours is 0.521 L/m^2 (0.0128 gal/ft^2) at the lower wind speed and 0.641 L/m^2 (0.0157 gal/ft^2) at the higher wind speed. This last number corresponds to a maximum loss of 354.5 liters (93.7 gallons) of diluent per day for a 21.3 by 25.9 meter (70 by 85 foot) mixer settler.

So far in the cell used, greater wind speeds appear to promote the formation of an aerosol from the surface of the liquid. The authors hope to gather enough data for a future article on this subject.

Figures 15 and 16 show the rate of evaporation loss per square meter from the two tests. As one would expect the loss rate follows a logarithmic declining curve. This is due to the preferential evaporation of the lower boiling constituents of the diluent.

Table 10. Evaporative Loss at 38.9°C (102F) with 0.02 to 0.18 KPH (0.01 to 0.11 MPH) Wind Speed

(hours) Time	(g) Weight Loss	(L/m^2) Volume Loss Cumulative	(L/m^2)/hr) Volume Loss Per Hour	(gal/ft^2) Volume Loss Cumulative	(gal/ft^2/hour) Volume Loss Per Hour
1	0.041	0.0212	0.0212	0.0005	5.20E-04
2	0.083	0.0429	0.0217	0.0011	5.32E-04
4	0.145	0.0749	0.0160	0.0018	3.93E-04
8	0.261	0.1348	0.0150	0.0033	3.67E-04
24	0.674	0.3480	0.0133	0.0085	3.27E-04
30	0.810	0.4182	0.0117	0.0103	2.87E-04
72	1.532	0.7910	0.0089	0.0194	2.18E-04
96	1.862	0.9614	0.0071	0.0236	1.74E-04
120	2.132	1.1008	0.0058	0.0270	1.43E-04
144	2.402	1.2402	0.0058	0.0304	1.43E-04
168	2.670	1.3786	0.0058	0.0338	1.42E-04
192	2.895	1.4948	0.0048	0.0367	1.19E-04
216	3.092	1.5965	0.0042	0.0392	1.04E-04

Table 11. Evaporative Loss at 38.9°C (102F) with 0.04 to 0.36 KPH (0.03 to 0.22 MPH) Wind Speed

(g) Time	(g) Weight Loss	(L/m^2) Volume Loss Cumulative	($L/m^2/hr$) Volume Loss Per Hour	(gal/ft^2) Volume Loss Cumulative	($gal/ft^2/hour$) Volume Loss Per Hour
1	0.043	0.0223	0.0223	0.0005	5.48E-04
2	0.093	0.0483	0.0259	0.0012	6.37E-04
4	0.196	0.1017	0.0267	0.0025	6.56E-04
8	0.354	0.1837	0.0205	0.0045	5.03E-04
24	0.962	0.4991	0.0197	0.0123	4.84E-04
48	1.740	0.9028	0.0168	0.0222	4.13E-04
72	2.395	1.2427	0.0142	0.0305	3.48E-04
96	2.959	1.5353	0.0122	0.0377	2.99E-04
103	3.128	1.6230	0.0125	0.0398	3.07E-04

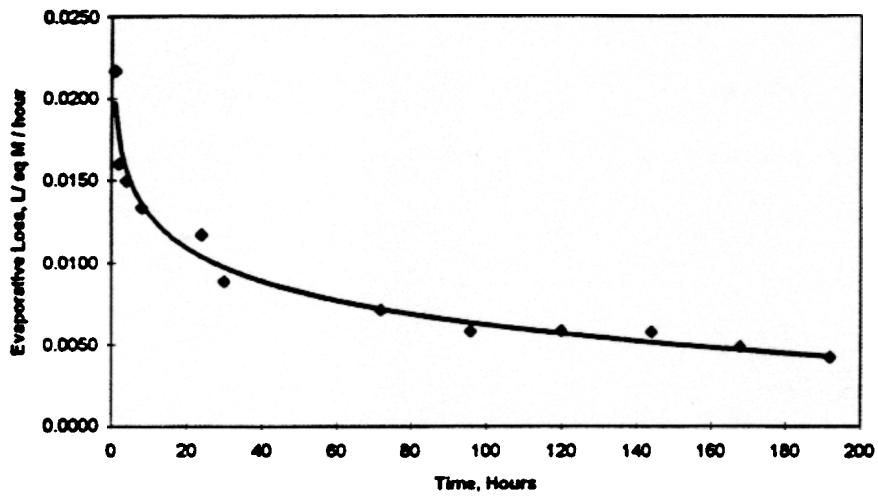

Figure 15. Evaporative Loss per Hour at 38.9°C (102F) with 0.04 to 0.36 KPH (0.03 to 0.22 MPH) Wind Speed

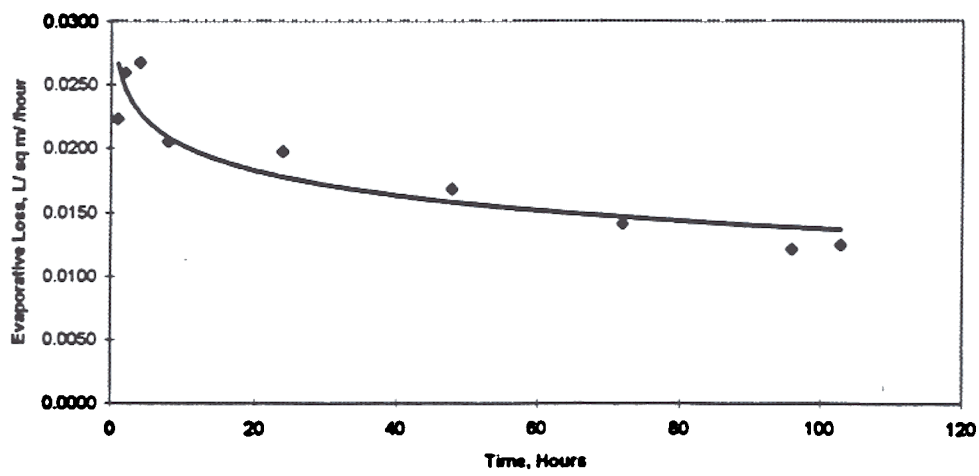

Figure 16. Evaporative Loss per Hour at 38.9°C (102F) with 0.02 to 0.18 KPH (0.01 to 0.11 MPH) Wind Speed

DISCUSSION

Data presented graphically in this paper indicate that an ideal range for the aromatic content of a diluent for the given extractant mixture of 5-dodecylsalicylaldoxime and tridecanol would be between 10% and 30%. Above this range, phase break times appear to increase as the aromaticity increases.

The data presented for SX-18, SX-10, and SX-11, represent data for purely aliphatic hydrocarbons. These three diluents are produced from the same base stock. It appears that an ideal diluent could be constructed from the information presented in the graphs; however, the additional parameters necessary to make a good diluent are not available.

Conventional wisdom is that as aromaticity of the diluent increases the copper-iron extraction mole ratio decreases. For the extractant tested this does not appear to be the case. There is a distinct trend towards higher extraction ratio for the A series diluents (see Figure 3). The data for the B series diluents are a little more ambiguous but appear to be similar to that of the A series. (see Figure 5).

The eleven criteria addressed earlier in this report indicate the general factors that must be considered as new diluents are prepared. In addition to these criteria, consideration of stability of crude sources and potential availability of material from specific yield points within the refining process must be considered. The relationships of flash point, density, viscosity and other effects on phase breaks all must be considered. For example, as the graph in Figure 6 indicates, the flash point, of course, increases with increasing molecular weight as does the phase break which is also related to density and viscosity.

FUTURE WORK

Although not covered in this paper, Phillips diluents are used extensively in circuits that use di 2-ethyl hexyl phosphoric acid and other such extractants. Thus, discussions of diluents' effects in these circuits need to be reviewed. In addition, work will continue on entrainment and evaporation losses, in copper and other solvent extraction circuits as well as work on the solvation characteristics related to the dissolving of both the non-loaded and loaded chelating extractants. Screening of products from potential refinery yield points that led to the development of SX-1HF also will continue. Additional papers are planned when sufficient data are generated from these projects.

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