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SOLVENT EXTRACTION DILUENTS WHAT ARE THEY AND HOW DO THEY AFFECT SX PLANT COSTS?

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ABSTRACT

Solvent extraction diluent and extractant are blended in the appropriate ratios as determined by the plant operational requirements. The resultant solution is the plant organic. The diluent is normally the majority fraction of the plant organic and, as such, plays an essential roll in efficient operation of the solvent extraction circuit. This paper discusses some of the terms associated with diluents, their characteristics, and considerations for minimizing operating costs.

Modern solvent extraction diluents are constant composition petroleum distillates that have been developed specifically for use in solvent extraction circuits. They contain a range of hydrocarbons composed of aliphatic, aromatic, and naphthenic compounds. The terms are used in the petroleum industry to denote the structure of the chemical compound. Aliphatic compounds are open chain molecular structures; alkanes, alkenes, and alkynes, including both normal (linear) and iso (branched) species and their cyclic analogs¹. Aromatics are those compounds that contain one or more unsaturated ring structures² somewhere in the molecule. Although this term includes classical aromatics such as benzene and toluene, these compounds are not present in any appreciable concentration in modern diluents. The aromatics in modern diluents are heavier compounds more accurately called alkylaromatics or arenes. The distinguishing feature of these aromatics is an unsaturated ring structure with one or more aliphatic chains attached to the ring. Cycloalkanes are known as naphthenes in the petroleum industry. This term should not be confused with naphthalene (camphor). The original meanings of the term "aliphatic" (fatty) and "aromatic" (fragrant) are no longer significant.¹

All diluents in current commercial use are volatile organic compounds (VOCs) as defined by regulation. US regulations define a VOC as any compound of carbon and hydrogen unless excluded by legislation. For example, methane (CH₄) is composed of only carbon and hydrogen but is not a VOC. It is excluded by legislation.

The regulation was designed to decrease ground level ozone and is based on studies, which have shown that hydrocarbon vapors can contribute to the formation of ground level ozone. The compounds, which are excluded by legislation, have been studied and determined to not contribute to ozone formation. High molecular weight hydrocarbons are generally considered to have minimal impact due to their low volatility.

The California Air Resources Board (CARB) recognizes the low impact of higher molecular weight hydrocarbons. CARB defines hydrocarbons of greater than C₁₂ or with vapor pressures less than 0.1 mm of Hg at 20° C as LVP-VOC (Low Vapor Pressure - VOC) substances. The LVP-VOC designation includes those chemical compounds and the weight percent of a mixture with a boiling point greater than 216° C (421° F).⁴ These compounds are excluded from some regulatory requirements when used in consumer goods. However, there are no exemptions for industrial point sources.

There are two general trends in distillate physical properties that help define the boundaries for practical diluents. Although these trends are well known, it is important to review them in consideration of solvent extraction operations. Consideration of these factors generally limits commercial diluents to those compounds with carbon numbers primarily between C₁₀ and C₂₀.

- The vapor pressure of the hydrocarbon decreases as the molecular weight (carbon number) increases.
- The viscosity of the hydrocarbon increases as the molecular weight increases.

The vapor pressure of a hydrocarbon is related to its volatility. Lower molecular weight hydrocarbons have higher vapor pressure. This leads to increased volatility; i.e. they evaporate more rapidly. The vapor pressure of typical diluents is in the range of 1 to 3 mm Hg at 38° C. Since vapor pressure is related to flash point, lower molecular weight hydrocarbons will have a lower flash point. However flash point is, as discussed later, not definitive.

Table 1.
Temperature – Vapor Pressure Comparison
Aromatic - Aliphatic Compounds

Name	Formula	Type	Temperature ° C	
			10 mm	100 mm
Hexane	C6 H14	Aliphatic	-25.0	15.8
Cyclohexane	C6H12	Naphthenic	-15.9	25.5
Benzene	C6H6	Aromatic	-11.5	26.1
Decane	C10H22	Aliphatic	55.7	108.6
Butyl benzene	C10H14	Aromatic	62.0	116.2
Napthalene	C10H8	Aromatic	85.8	145.5
Dodecane	C12H26	Aliphatic	90.0	146.2
Biphenyl	C12H10	Aromatic	117.0	180.7

Temperature at which the listed compound exhibits the specified Vapor pressure.
v

A common misconception is that aromatic compounds evaporate faster than aliphatic compounds. Evaporation rate is related to the vapor pressure of the product. Table 1 provides the temperatures required for the selected compounds to achieve the specified vapor pressure. The data demonstrates the aromatic compounds shown require a higher temperature than the corresponding aliphatic compounds to achieve a specified vapor pressure. Therefore, for a given carbon number and temperature, an aromatic compound may have a lower vapor pressure than the corresponding aliphatic compound. It would have lower volatility.

High molecular weight compounds are preferred from a volatility standpoint. However, the other characteristic of longer chains, viscosity, comes into play. Increasing the carbon chains tends to increase the viscosity of the diluent. Higher viscosity oils will require increased power and higher shear rates to form the emulsion. This can result in increased phase disengagement times and potential increases in entrainment losses. Commercial diluents will have a viscosity between 2 to 5 cSt at 25° C.

It is important to note that commercial diluents are not "kerosene." Kerosene typically has a significantly lower distillation range than commercial diluents. The distillation range of diluents usually exceeds the maximum limits for kerosene. The flash point for kerosene typically ranges between 125 and 135° F (51 to 57° C). Diluents will typically exhibit a flash point at least 30° F (16.7° C) higher than the flash point of kerosene. These differences can contribute to a better public and regulatory perception for solvent extraction operations.

What do diluents do?

A diluent's primary function is to adjust the extractant concentration to the desired operating range. The desired operating range is determined by the type of extractant, the metal content of the pregnant leach solution (PLS), and other site-specific requirements.

The diluent's secondary effects can significantly affect plant operation. Secondary affects include:

- Promoting rapid transfer kinetics
- Optimizing phase disengagement
- Enhancing selectivity
- Minimizing entrainment => both organic in aqueous and aqueous in organic

Transfer kinetics is the rate at which the metal is loaded on or eluted from the organic phase. The diluent enhances this by contributing to the formation of uniformly sized droplets in the discontinuous phase. The droplets must form rapidly in the mixer without excessive shear and remain distributed throughout the continuous phase during mixing and initial discharge to the settler. Droplet size must be small enough to allow rapid metal exchange but large enough to coalesce rapidly and completely in the settler. A viscous diluent will require additional shear or mixing energy to form and distribute the droplets and will tend to have extended phase disengagement time. Slow transfer kinetics leads to increased residence time in the mixer. Extended shear can lead to smaller droplets which, in turn, can lead to increased entrainment.

Phase disengagement time is the time required for the aqueous and organic phases to separate. Phase break time is easily measured in a laboratory batch cell and correlates to the dispersion band in the plant. Large droplets coalesce faster but require longer times for metal transfer. Small droplets transfer metals rapidly but may not coalesce rapidly or completely. Optimized phase disengagement contributes to maximizing plant flow rates and production.

A slow phase break can lead to reduced production. This would be a result of decreased flow rates due to failure of the phases to disengage in the settler. Slow phase breaks can result in increased entrainment and increase in the associated costs.

Conversely, a rapid phase break can contribute to increased copper production. This is provided additional PLS is available and the tank house has the capacity. Extremely rapid phase disengagement is not always beneficial as metal transfer is occurring as the phases coalesce. This could result in reduced metal transfer. In some cases, extremely fast phase breaks can trend to poor coalescence, potentially leading to higher entrainment.

Studies have demonstrated that the diluent composition will affect copper iron selectivity in oxime based systems. An alkylaromatic content of 10 to 30 volume percent appears to enhance Cu: Fe selectivity. The optimum alkylaromatic content appears to be in the 22 to 25% range.⁶ Reduced iron transfer will result in reduced electrolyte bleed stream volume and reduced cobalt consumption provided iron is the controlling factor in bleed stream volume.

Entrainment is a measure of incomplete coalescing of the discontinuous phase. Organic in aqueous entrainment in the loading stage is one of the major sources of organic loss. Organic exiting the circuit in raffinate is normally recovered from the raffinate pond. Organic in the electrolyte is absorbed in the electrolyte filters. Aqueous entrainment contributes to transfer of undesirable ions such a Cl^- through the circuit.

Each of these elements is also influenced by and interrelated with the other plant variables including extractant type and concentration, pH, mixer design, circuit temperature, and PLS quality.

FLASH POINT

The flash point is defined as "the minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid."

There are three common methods for determining flash point:

- Pensky Martin Closed Cup [PMCC] ASTM D 93
- Tagliabeu Closed Cup [TCC] ASTM D 56
- Cleveland Open Cup [COC] ASTM D 92

All three methods involve placing a sample of the material to be tested in a brass cup, heating the material in a controlled manner and rate, and periodically introducing an ignition source into the vapor space above the liquid. The flash point is the point at which the vapors ignite when the ignition source is introduced.

Both the PMCC and TCC incorporate a cover over the sample to contain the vapors in a fixed headspace. The ignition source is introduced through a port in the cover. The port is opened just before introducing the ignition source and closed

immediately after the ignition source is withdrawn. The primary difference between the methods is that the PMCC USES a stirring mechanism while the TCC does not.

The COC method, as the name implies, does not incorporate a cover over the sample. The vapors are free to the atmosphere. The ignition source is periodically introduced into the vapor at a prescribed distance above the liquid. The sample is not stirred. For diluents, the open cup flash point will typically be 20 - 25° F (11 - 14° C) higher than the closed cup value for the same material.

The Setaflash method (ASTM D 3828) may be used as an alternative to the TCC or PMCC methods. The Setaflash makes use of a smaller sample and utilizes a timed interval in approaching the estimated flash point.

Flash point is not linear with composition and can not be relied on to predict overall volatility. Since the closed cup flash point apparatus contains the vapors in the headspace and the lighter components are volatilized preferentially, the light components will have a disproportionate effect on the flash point. Blending a 1:1 mixture of a low flash material such as hexane (a C_6 hydrocarbon) with a high flash point material such as hexadecane (C_{16}) would not result in a flash point half way between the two products. It would actually be very close to that of pure hexane. A relative small amount of a light component can reduce the flash point by several degrees.

Barometric pressure has a significant effect on flash point. The lower the barometric pressure the lower the measured flash point. ASTM methods specify that the reported flash point be corrected for variations in barometric pressure. All values reported are corrected to standard pressure (sea level), 760 mm Hg. Since barometric pressure decreases by approximately 2.5 mm Hg for each 30.5 meters in increased elevation⁸, we can predict the flash point at various altitudes. The flash point at a given altitude can be estimated by decreasing the reported flash point (corrected to sea level) by 0.228° C per 100 meters elevation above sea level. For example, an operation at 4,000 meters would expect to observe a 9° C decrease in flash point ($4,000 \div 100 \times 0.228$).

The distillation range and carbon number are directly related. The higher the distillation range, the higher the average carbon number. Table 2 provides typical distillation ranges for some common diluents.

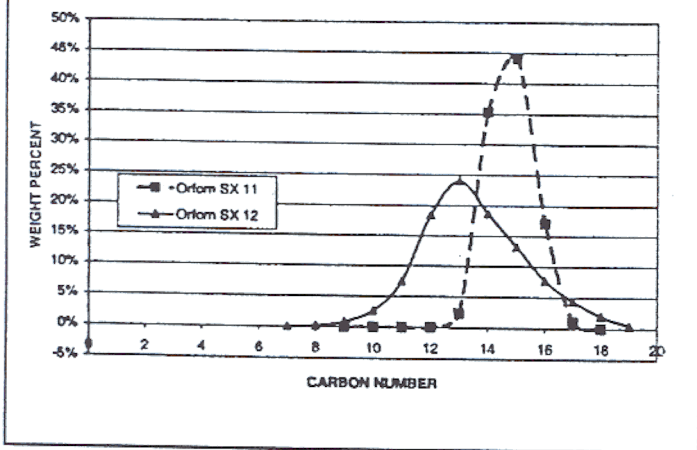
Table 2. Distillation Range

	ORFOM [®] SX 11		ORFOM [®] SX 12		C 1		E 1	
	° F	° C	° F	° C	° F	° C	° F	° C
IBP	451	233	381	194	403	206	392	200
10 %	459	237	410	210	413	212	403	206
50%	472	244	443	228	429	221	421	216
90%	510	266	490	254	466	241	444	229
FBP	536	280	527	275	502	261	462	239

IBP = initial boiling point

FBP = final boiling point (dry point)

Figure 1
Carbon Number Distribution



Carbon number distributions for SX 11 and SX 12 are shown in Figure 1. Comparing Table 2 with Figure 1 shows the correlation between the distillation range and the carbon number. SX 11 has an average carbon number of 14.7 while SX 12 has an average carbon number of 13.3. Although the average carbon number for SX 11 is only 1.4 units more than the average for SX 12, its viscosity is about 1.5 cSt higher at 25° C. Higher distillation ranges are available but will exhibit higher viscosity as discussed earlier.

The primary areas where distillation range and flash point affect operating costs are electrical area classification and safety issues. The National Fire Protection Agency classifies flammable and combustible products based on their closed cup flash point. The classifications are:

- Flash point < 100° F (37.8° C) → Class I Flammable Liquid
- Flash point at or > 100° F (37.8° C) and < 140° F (60.0° C) → Class II Combustible Liquid
- Flash point at or > 140° F (60.0° C) and < 200° F (93.3° C) → Class IIIA Combustible Liquid
- Flash point at or > 200° F (93.3° C) → Class IIIB Combustible Liquid*

The flash point of most commercial diluents is such that they are classified as Class IIIA combustible liquids. NFPA Guideline 497M states that Class IIIA combustible liquids do not form flammable mixtures with air at ambient temperatures unless they are heated above their flash points. The vapors cool rapidly and condense. The Guideline goes on to state that the area requiring electrical classification for Class IIIA liquids is very small or non-existent.¹⁰

Each operation must conduct a site-specific evaluation to identify hazardous areas. However, consideration of these guidelines and proper classification of the area may result in reduced capital costs through reduced requirements for explosion proof electrical equipment.

There are many sources of diluent loss. They include but are not limited to the following.

- Entrainment
- Evaporation
- Filter Loss
- Crud Loss
- Solubility
- Carryover to Electrolyte

Entrainment

Organic entrainment is recognized as one of the largest hidden costs of a diluent. Entrainment is the incomplete coalescence of the dispersed phase prior to discharge from the settler. Plant organic is the extractant - diluent mixture. Although both organic in aqueous and aqueous in organic entrainment occur, only organic entrainment in the aqueous phase results in diluent loss. (Aqueous entrainment in organic contributes its own set of problems.) Since organic entrainment results in the loss of both the low cost diluent as well as the higher cost extractant its costs are significantly greater than the diluent component alone. The cost of the organic can be easily calculated.

Entrainment losses are difficult to reliably evaluate in laboratory and pilot plant trials. This is due to the difficulties encountered in trying to duplicate plant shear rates, temperatures, and residence times. It is difficult to obtain representative samples in any circuit due to the nature of the system. The entrained organic continues to coalesce leading to inhomogeneous samples. In our opinion, entrainment losses should be evaluated during actual plant operations.

Many factors contribute to entrainment losses. PLS quality is extremely important. The presence and amount of polar compounds in the PLS can significantly affect entrainment levels. Sources of polar compounds include vegetation, old mine timbers, oils and greases from mining equipment, etc. High levels of suspended solids are well known to contribute to increased entrainment. We have seen evidence of microorganisms contributing to entrainment.

Organic recovered from the raffinate ponds often exhibits slow phase break, high entrainment, and other signs of degradation. These detrimental effects are diluted when the material is returned to the circuit but may still contribute to a small decrease in performance. The recovered organic should be tested and treated, if necessary, before being returned to the circuit.

Entrainment losses are minimized by standard plant practices such as controlling suspended solids to the extent possible, and keeping the circuit clean. The mixers should be operated at the minimum speed required to provide sufficient mixing to achieve copper transfer. Monitoring the organic condition and treating as necessary to remove contamination is beneficial.

Diluent solubility provides a measure of the minimum entrainment loss. Solubility for Orfom[®] SX 7 and SX 12, two widely used diluents, was determined to be 4.5 and 3.8 ppm respectively.

Figure 2.
Comparative Evaporation Loss as KG/M²

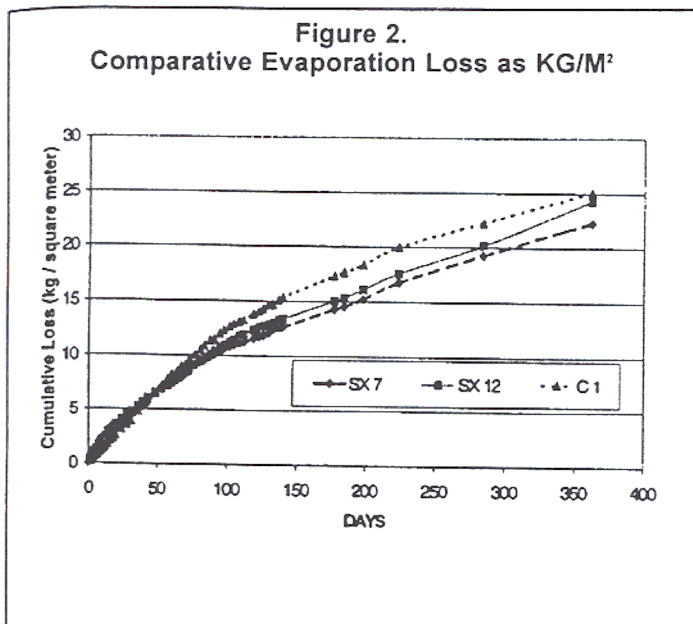
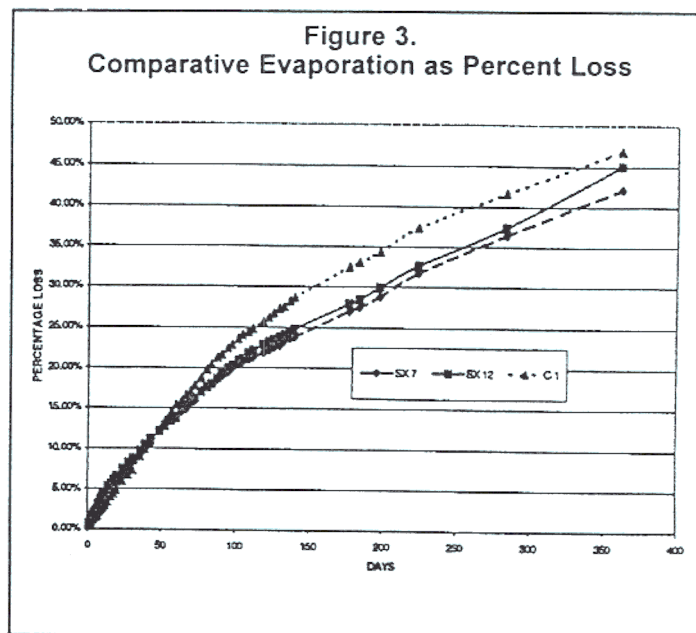


Figure 3.
Comparative Evaporation as Percent Loss



Evaporation

Evaporative losses are a concern to operations for both cost and environmental reasons. Factors affecting evaporative loss include circuit temperature, altitude, and plant design. Higher circuit temperatures will tend to increase evaporative loss. High altitude operations are expected to have higher evaporative losses due to reduced barometric pressure. Plant design also affects evaporative losses as covered mixer-settlers will have less air movement over the organic surface than uncovered circuits.

It is well accepted that diluent is preferentially lost from plant organic. The amount of diluent required to maintain the plant organic's extractant: diluent ratio is greater than the amount of diluent required based on the quantity of extractant added for make-up. "Conventional wisdom" has contributed this differential loss to evaporation. Logic supports this concept. Since diluents are lower molecular weight than extractants the diluent would evaporate while the higher molecular weight extractant would not evaporate.

Phillips Mining Chemicals has investigated evaporative loss in an effort to quantify the contribution of evaporation to diluent loss. We have adapted ASTM method D 972 Standard Test Method for Evaporation Loss of Lubricating Greases and Oils to measured diluent evaporative losses. We have also measured evaporation from beakers.

Figure 2 presents a summary of a long-term comparison of three diluents using data obtained from a simple beaker test. In this test, approximately 300 grams of test diluent was dispensed into a 600 ml beaker. The average internal diameter of the beaker was determined and the exposed surface area calculated. The beaker was periodically weighed and the loss calculated as kg/m² of surface area. Using this method, it was determined that the cumulative loss after 60 days is approximately 7.4 kg/m². The average loss over this period is 0.123 kg/m² • day. Restating the losses based on volume and using a density of 0.82

g/ml yields a cumulative loss of 9.02 l/m² over the 60 day period with an average loss of 0.150 l/m² • day.

Incremental evaporative losses change with time as the lighter components are preferentially lost from the liquid. Overall, evaporative losses are relatively low. The cumulative losses after one year range from 22 to 25 kg/m² for the three diluents. The average loss ranges from 0.062 to 0.069 kg/m² • day.

Again, restating the results as volume results in losses of 0.076 to 0.084 l/m² a day. The difference between SX 7 and SX 12 provides some indication of the variability of the test as well as some variation between lots.

Figure 3 presents the test data as percent loss. Referring back to the distillation ranges shown in Table 2, we can see the correlation between distillation range and evaporation rate. The IBP for SX 12 is lower than C 1 and we observe a higher evaporation rate for SX 12. The temperature differential at the 10% distillation point for the two products is much less and the cumulative evaporative losses for the two products are merging. The 20% distillation point is higher for SX 12 and we observe the cumulative evaporative loss for SX 12 is now lower than for C1. Evaporative losses are highly related to the distillation range of the diluent. The entire distillation range should be considered when evaluating evaporative losses.

It is apparent from the data that the evaporation rate decreases over time. This is probably due to the lower molecular weight components evaporating first. This data would be representative of a circuit at the time of the initial fill. It must also be recognized that this data does not account for the presence of extractant.

SX circuits are dynamic and are operated for extended periods. The circuit organic will reach a quasi steady state composition dependent on the amount of organic lost through all mechanisms and the corresponding make-up volumes. Although it would be difficult to determine the point in time

when a circuit has reached a steady state, the composition at that time will give a more reliable indication of evaporative loss and emissions.

Evaporation is related to the amount of exposed surface. Evaporative losses can be significantly overstated if the sample depth does not accurately reflect the depth of the organic layer in plant operations. A high area: volume ratio leads to an increased evaporation rate. This factor becomes especially significant if the results are calculated as percentage loss. Tests should be designed to approximate the depth of the organic layer in the settler.

Evaporative losses can be minimized by following a few simple steps.

- Locate the plant to minimize wind exposure
- Cover the mixer settler
- Promptly recover organic from the raffinate pond

Think about a closed bottle containing a highly volatile substance. As long as the bottle is closed and the saturated vapors are not removed, there is no evaporative loss. Every time you open the bottle and allow some of the vapor saturated air to escape some material is lost. The same thing happens in SX operations. Minimizing the air exchanges reduces the evaporative loss. Diluent vapors are heavy and tend to condense near the surface of the organic. Obviously, wind will have less impact on covered mixer-settlers. Consideration of site location with an effort to minimize wind around the mixer-settlers will help minimize evaporative loss.

Raffinate ponds are typically uncovered and have a large surface area. Organic on the raffinate pond is subject to solar heating accentuated by the dark color of the organic and to more air exchanges. These factors increase evaporative losses. Organic on the raffinate pond is subject to more biological and chemical degradation. Prompt recovery from the raffinate pond will help minimize this source of loss.

This paper has presented an overview of some of the physical characteristics of solvent extraction diluents including viscosity, flash point, distillation range, and carbon number. The electrical area classification for diluents is considered. The primary functions of diluent are discussed. Information regarding evaporation losses and possible ways to minimize those losses are presented.

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