# SCA2003-01: EFFECT OF CRUDE OIL COMPOSITION ON WETTABILITY OF MICA

Lei Yang, Jianxin Wang, Tianguang Fan, and Jill S. Buckley
Petroleum Recovery Research Center, New Mexico Tech

## ABSTRACT

While many factors are recognized as influencing reservoir wetting, they do so primarily by controlling the fate of components of the crude oil. Surface mineralogy, brine composition, temperature, pressure, and history of fluid occupation all are important variables, but if the oil does not contain species capable of adsorbing or depositing, reservoir rocks, the majority of which are initially water-wet, would remain in their original water-wet condition, while minerals that are naturally oil-wet would also be unchanged. In this study we focus on specific features of the composition of produced oil samples and relate them to the extent to which these oils alter the wetting of mica surfaces under controlled conditions.

Wetting alteration tests were designed to control water film stability. The extent of wetting alteration was quantified by measurements of probe fluid contact angles. Oil properties were selected on the basis of previous studies that indicated the importance of ionizable species and asphaltene stability in the produced oil samples. Statistical tests between single variables and contact angles show little evidence of correlation, but more significant relationships were found using linear multivariate analyses and non-linear artificial neural networks.

## INTRODUCTION

Historically, much effort has been devoted to identifying either the oil components or bulk crude oil properties that are related to an oil's propensity to alter wetting [1]. Beyond identifying the polar oil fractions—primarily resins and asphaltenes—as containing the wettability altering agents, however, these efforts were generally frustrated by the complexity of crude oils and by an incomplete understanding of the effects of other system variables. It seems reasonable, for example, since resins and asphaltenes are the main source of polar species, that the extent of wetting alteration should be related to the amounts of these fractions. The extreme counter-example of the water-wet Athabasca tar sands [2] is just one illustration of the problems inherent in relating the amount of resins and asphaltenes directly to wetting.

The effect of a crude oil on the wetting of solid surfaces with which it comes in contact depends not only on its composition, but on other factors that include the surface chemistry of the solid,

the presence or absence of an aqueous phase, composition of the aqueous phase if present, temperature and pressure, and contact time. In order to evaluate crude oil wetting propensities it is necessary to select an experimental design that includes all of the essential factors that influence wetting alteration, but is simple enough to allow a clear interpretation of the results.

Insight into the mechanisms of interactions between crude oils, brines, and mineral surfaces can help to define both the crude oil variables of interest and appropriate conditions for tests of wetting alteration. These include ionic interactions that occur between oil components and mineral surfaces that are influenced by brine strength and composition and surface precipitation that can dominate when asphaltenes are close to the onset of flocculation [3]. Ionic interactions can be further subdivided into simple acid-base interactions that can be tested using brines with monovalent ions at controlled values of pH and more complex interactions that can occur when brines contain ions of higher valence.

Wetting changes are minimized if there is a stable water film between oil and solid. This situation occurs, for example, when there is sufficient electrostatic repulsion between a negatively charged oil/water interface and a negatively charged mica surface. For some high-base number oils a stable water film has been observed when the aqueous phase is buffered at a pH of 8 with an ionic strength equivalent to $1M$ NaCl. An unstable water film often results from the use of an aqueous phase buffered at pH 4 with a low salt concentration ($0.01M$ NaCl in this study) because the basic oil/brine interface is positively charged and the mica is negatively charged [4]. In this situation oil components can adsorb, altering the wetting of the mica surface. It is not possible to select a single set of two aqueous solutions that produce one stable and one unstable situation with all oils since water-film stability also depends on the charge at the oil/water interface. For screening purposes, however, these two conditions should tend to bracket the extremes of wettability alteration for many crude oils.

Crude oil properties of particular interest with respect to the mechanisms of wetting alteration relate to the acidic and basic components of the oil and to measures of asphaltene stability. A database with information on more than 200 crude oil samples has been assembled. Details of the measured properties and methods have been published previously [5] and here are only briefly reviewed.

## EXPERIMENTAL MATERIALS AND METHODS
### Mineral Surfaces
Muscovite mica is a convenient model surface because it is molecularly smooth, is well characterized, has a structurally-based surface charge, and is easily cleaved to produce clean surfaces [4]. Since it is negatively charged above pH 2, mica is representative of many silicate and aluminosilicate minerals—including quartz and illite—that are the main constituents of a sandstone reservoir.

**Crude Oil Properties**

Crude oil properties were selected based on their relevance to asphaltene stability and to the acidic and basic properties of the oil. Standard physical measurements of density (and API gravity), average molecular weight, and viscosity completed the crude oil characterizations. Density was measured as a function of temperature using a digital Mettler/Paar DMA40 densitometer. API gravity was calculated from the density measurements, corrected to a temperature of 60ºF. Average molecular weight was determined by freezing point depression using a Cryoscope 5009 (Precision Systems). Kinetic viscosity was measured at 20°C with Cannon-Fenske viscometers and converted to absolute viscosity using the measured values of density. The suite of measurements on a given oil depends primarily on the total amount of sample received.

SARA analysis measures the amount of asphaltene as well as the amounts of asphaltene solvents (aromatics and resins) and asphaltene precipitants (saturates), which relate to asphaltene stability. The HPLC SARA analysis technique has been described previously [6]. Another measure of asphaltene stability is the difference in refractive index (RI) between the dead oil and the onset mixture of oil and n-heptane [7]. Asphaltenes and resins contain the most polar oil components, thus the amounts of these fractions is related to oil polarity. Refractive index (RI) was measured at the sodium D line as a function of temperature using either an Abbe refractometer or an automated Index Instruments GPR 11-37 refractometer. The onset of asphaltene flocculation was observed microscopically one day after mixing oil and flocculants [8]. RI was measured for the onset mixture, using the techniques described above. RI at the onset is denoted as $P_{RI}$.

Acid number [9] and base number [10, 11] measure the total amounts of acidic and basic species in the oil, some fraction of which is interfacially active. Trace metals, especially Ni and V, are associated with naturally occurring porphyrins, another interfacially active group of compounds. The trace metal analyses were carried out according to the ASTM recommended procedure [12]. The isoelectric point of each oil sample was measured by preparing an emulsion of oil in buffered 0.01M NaCl brine. Zeta potential was measured with a Delsa 440 SX zeta potential and particle size analyzer.

**Wetting Tests**

A two-step procedure was used to alter wetting [13]. Clean mica was first equilibrated with one of two buffer solutions (pH4 or pH8). The lower pH buffer has been shown to produce unstable water films with A-93 crude oil as long as the ionic strength is low, whereas the water film produced by the pH8 buffer and a high ionic strength is stable with that oil. Although these conditions are not expected to be general, they were chosen as standards in an attempt to

probe the extremes of wetting alteration by each crude oil. The pH4 buffer had a molar concentration of chloride ions of 0.01M; the concentration of Cl in the pH8 buffer was 1M. After 24 hours the mica samples were removed from the buffer and drained by contacting an edge to absorbent paper. The pre-wetted mica plates were then immersed in crude oil where they remained for 21 days at ambient conditions of temperature and pressure. Previous studies have established this time period as sufficient equilibration time, even when initial water is present [4,13]. Plates were removed from the crude oil, rinsed with toluene (a good asphaltene solvent that avoids precipitation of asphaltenes during the rinsing step), then immersed in decane (a poor asphaltene solvent in which the oil-treated surfaces remain unchanged over the duration of contact angle measurements). Contact angles between water and decane, measured by the captive drop technique [14] quantify the extent of wetting change. Static values were measured after water has been either advanced or receded.

## RESULTS

Details of the CO-Wet dataset are available in a report to the US DOE [15], which includes all of the crude oil properties and wetting alteration data assembled as of August, 2002.

**Interdependence of Crude Oil Properties**

Asphaltenes and resins include the highest molecular weight, most polar components of a crude oil. It is likely, therefore, that measures of molecular weight, density, and polarity should reflect the amount of asphaltenes in the oil. Yang et al. [16] reported relationships among crude oil properties for a group of 25 oils. RI, API gravity, and acid number were weakly correlated to the amount of asphaltenes; base number correlated more significantly to the amount of asphaltenes. These published results are compared in Table 1 with correlation coefficients ($R^2$) calculated for the oil samples in the CO-Wet database. The sign indicates whether each property increases (+) or decreases (-) with increasing amount of asphaltene; n is the number of samples included in each correlation.

Table 1. Correlations between amount of n-$C_7$ asphaltene and other oil properties.

| measured oil properties | CO-Wet data | | | Yang et al. [16] | | |
|---|---|---|---|---|---|---|
| | n | $R^2$ | sign | n | $R^2$ | sign |
| °API | 109 | 0.32 | - | 21 | 0.10 | - |
| avg MW | 109 | 0.28 | + | | | |
| RI (at 20°C) | 107 | 0.38 | + | 21 | 0.17 | + |
| $P_{RI}$ (at 20°C) | 79 | 0.43 | + | | | |
| density (g/ml at 20°C) | 107 | 0.32 | + | | | |
| viscosity (cP at 20°C) | 69 | 0.07 | + | | | |
| saturates (%) | 85 | 0.45 | - | | | |
| aromatics (%) | 85 | 0.00 | | | | |
| n-$C_6$ resins (%) | 85 | 0.21 | + | | | |
| n-$C_6$ asphaltenes (%) | 85 | 0.95 | + | | | |
| acid # (mg KOH/g oil) | 101 | 0.00 | | 24 | 0.13 | + |
| base # (mg KOH/g oil) | 110 | 0.14 | + | 23 | 0.54 | + |
| IEP (pH units) | 70 | 0.01 | - | | | |
| Fe (ppm) | 64 | 0.05 | - | | | |
| Ni (ppm) | 64 | 0.25 | + | | | |
| V (ppm) | 63 | 0.14 | + | | | |
| Zn (ppm) | 65 | 0.05 | - | | | |

Higher correlation coefficients confirm the expected relationships between the amount of n-$C_7$ asphaltenes and API gravity (or density), average molecular weight, and RI. The correlations between asphaltenes and acid and base numbers, however are weaker (base number) or non-existent (acid number) in the CO-Wet database. Both acid and base numbers are better correlated to the amount of the resin fraction ($R^2 = 0.34$ and 0.57, respectively) in the CO-Wet dataset. Acid and base numbers are weakly correlated to one another ($R^2 = 0.25$).

Positive correlations between the amounts of Ni and V and the amount of asphaltenes agree with many previous reports in the literature [1]. The amount of saturates is negatively correlated with amounts of asphaltenes since asphaltenes are defined by their limited solubility in saturated hydrocarbons. Both n-hexane and n-heptane asphaltenes were quantified and the results correlated strongly, as expected; only one of these is used in the statistical tests that follow. There is a weaker correlation between the amounts of asphaltenes and resins.

**Linear Relationships**
Single Parameter
In Table 2, regression of each measured oil property is shown with decane/water contact angles for mica surfaces pretreated with either pH4 ($\theta_{A4}$) or pH8 ($\theta_{A8}$) buffer, followed by aging in crude oil for about three weeks. The angles reported are for water advancing over decane-covered surfaces, hence the subscript A to distinguish from water-receding angles that are

usually lower.  The number of crude oils for which data were available is indicated by n; the sign indicates whether contact angles increased (+) or decreased (-) with increases of each variable.

Table 2. Single-parameter linear relationships between oil properties and wetting alteration.

| measured oil properties | $\theta_{A4}$ | | | $\theta_{A8}$ | | |
|---|---|---|---|---|---|---|
| | n | $R^2$ | sign | n | $R^2$ | sign |
| °API | 78 | 0.02 | + | 76 | 0.01 | + |
| avg MW | 78 | 0.03 | - | 76 | 0.02 | - |
| RI (at 20°C) | 78 | 0.01 | - | 76 | 0.03 | - |
| $P_{RI}$ (at 20°C) | 72 | 0.07 | + | 69 | 0.09 | - |
| density (g/ml at 20°C) | 77 | 0.02 | - | 74 | 0.01 | - |
| viscosity (cP at 20°C) | 65 | 0.06 | - | 65 | 0.00 | |
| saturates (%) | 77 | 0.01 | + | 75 | 0.06 | + |
| aromatics (%) | 77 | 0.01 | + | 75 | 0.00 | |
| n-$C_6$ resins (%) | 77 | 0.10 | - | 75 | 0.00 | |
| n-$C_6$ asphaltenes (%) | 77 | 0.02 | + | 75 | 0.24 | - |
| n-$C_7$ asphaltenes (%) | 76 | 0.03 | + | 73 | 0.25 | - |
| acid # (mg KOH/g oil) | 70 | 0.09 | - | 69 | 0.00 | |
| base # (mg KOH/g oil) | 78 | 0.06 | - | 76 | 0.00 | |
| IEP (pH units) | 64 | 0.00 | | 61 | 0.00 | |
| Fe (ppm) | 61 | 0.10 | - | 60 | 0.03 | + |
| Ni  (ppm) | 61 | 0.00 | | 60 | 0.07 | - |
| V  (ppm) | 60 | 0.11 | + | 59 | 0.12 | - |
| Zn (ppm) | 62 | 0.08 | + | 61 | 0.19 | + |
| **derived oil characteristics** | | | | | | |
| $\Delta RI = RI - P_{RI}$ | 72 | 0.12 | | 69 | 0.02 | |
| base # / acid # | 70 | 0.00 | | 69 | 0.08 | |

None of the variables showed strong correlation with wetting alteration, as defined in our tests. Slightly better correlations were obtained by relaxing the requirement that the relationship be linear [17].

Multiple Parameters
A survey of variables began with those that had the highest correlations in single parameter fits, but even variables that showed no correlation were included in the multiple regression tests. Two correlations were derived, one for water-advancing angles on surfaces pretreated with pH4 buffer and another for water-advancing angles for mica pretreated with pH8 buffer.  The resulting coefficients for the best correlations are summarized in Table 3.  (Blanks in the table indicate that a parameter correlated with changes in wetting under one condition, but not the other.  Values of p represent the level of significance or probability that no correlation exists between a variable and the resulting contact angle.)  In Fig. 1 the measured values of $\theta_{A4}$ (Fig.

1a) and $\theta_{A8}$ (Fig. 1b) are compared to the corresponding values calculated from these relationships.

Table 3. Coefficients from multiple linear regression analyses of contact angle data.

| Term | $q_{A4}$ Coefficient | $q_{A4}$ p | $q_{A8}$ Coefficient | $q_{A8}$ p |
|---|---|---|---|---|
| Intercept | 102.5 | <0.0001 | 44.7 | <0.0001 |
| nC7 asph (%) | 6.16 | <0.0001 | -2.52 | 0.0002 |
| Resins (%) | -3.41 | 0.0002 | | |
| B/A | | | -0.421 | 0.0582 |
| Zn | 1.13 | 0.0086 | 0.497 | 0.0188 |



(a) less stable water films (pH=4, I=0.01M)    (b) more stable water films (pH=8, I=1M)
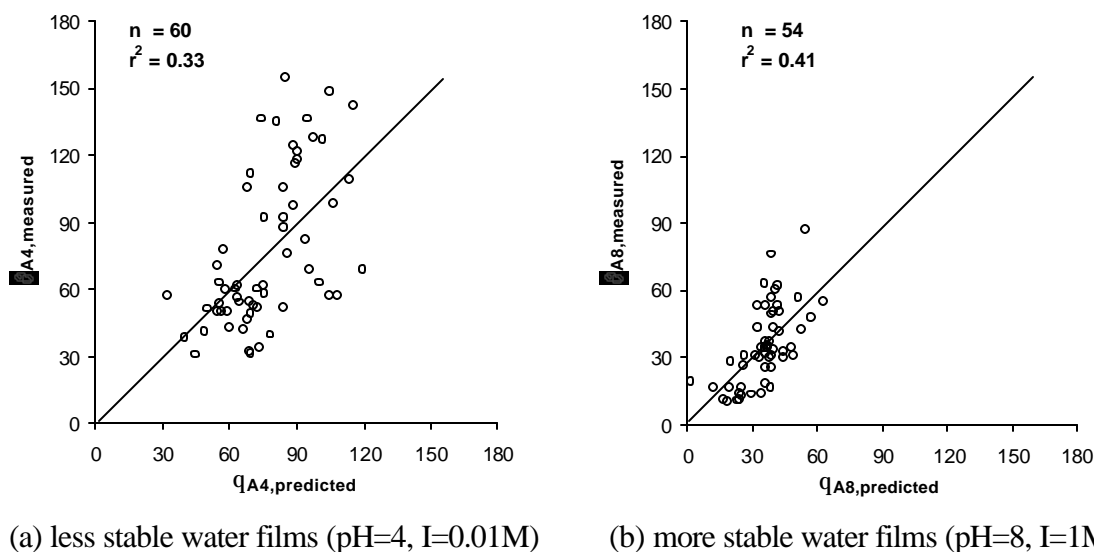
**Figure 1.  Comparisons of measured water-advancing contact angles with those calculated from equations with the coefficients given in Table 3.  The $q_{A4}$ case respresents conditions selected to minimize water film stability (pH=4,I=0.01M); $q_{A8}$ values are measured for the case where stable water films are more likely (pH=8, I=1M).**

The signs of the coefficients in Table 3 show whether a variable tends to increase or decrease contact angles.  It is interesting to note that the amount of n-$C_7$ asphaltenes is the most significant variable in both cases, but its influence on $\theta_{A8}$ is opposite to its effect on $\theta_{A4}$.  The level of significance can be judged from the p-values in column 3, which represent the probability of observing this set of outcomes if the null hypothesis is true, i.e., of finding an apparent correlation when there is no real correlation.  Thus, lower values of p represent greater significance.  Resins as well as asphaltenes contribute to the contact angles measured on mica pretreated with pH4 buffer, but increased resins decrease the contact angle, whereas increased

amounts of asphaltenes increase it. A higher correlation coefficient could be obtained if two additional variables were included: the quantity $RI - P_{RI}$ (a measure of asphaltene stability) and IEP (the pH at which drops of crude oil have no net charge), but the p values exceeded the usual cut-off value of 0.05, perhaps because we impose linearity on the relationships. IEP is measured in logarithmic pH units, which may explain why a strictly linear correlation is not appropriate. Asphaltene stability has been shown to have a very non-linear effect on wetting [18].

The ratio of base number to acid number (B/A) appears in the $\theta_{A8}$ correlation; oils with higher base numbers have lower values of $\theta_{A8}$. This is consistent with the hypothesis that water films are stabilized by the high pH buffer, especially for oils with a high value of B/A. Contact angles well above zero were measured on some mica surfaces because the assumption that a stable water film existed was not correct. Contact angles that are finite, but small, appear to occur when the water film was stable while the mica was aged in oil. Evidence for stable water films is provided not only by the contact angles, but also by AFM images that show little or no adsorbed material on mica pretreated with pH8 or 9 buffers, despite aging for prolonged periods of time in crude oil [19, 20].

Contamination
A noteworthy aspect of both correlations is the significance of the amount of zinc, which is not expected in crude oils above the level of 1ppm [21]. Zinc is used in some drilling fluids; its presence at elevated concentrations (up to 40 ppm) might indicate that surface-active drilling fluid contaminants are also present and are affecting wettability alteration tests. Some of the samples with elevated zinc concentrations were provided in galvanized steel containers, another possible source of zinc. Whether zinc is an indicator of the presence of other contaminants or an active participant in interactions that bind crude oil components to the surface is not known. Removal of samples with more than 3 ppm Zn from the dataset eliminates the significance of Zn as a variable, but does not change the significance of other variables identified in Table 3.

**Non-Linear Relationships**
Linear multivariate regression may overlook physically significant non-linear correlations between contact angle and oil properties. An alternative approach is the use of an artificial neural network (ANN) to investigate non-linear relationships. Back-propagation (BP) neural networks are the most accurate and widely used architecture [22]. Figure 2 illustrates the architecture of a BP neural network with one input layer (2 nodes), one hidden layer (4 nodes), and one output layer (1 node). Biases are used at input layer and hidden layer (empty circles). The hidden and output layers have bipolar sigmoid activation functions [22].

Input layer

Hidden layer

Output layer

1

z1

x1    z2    y1

x2    z3

z4

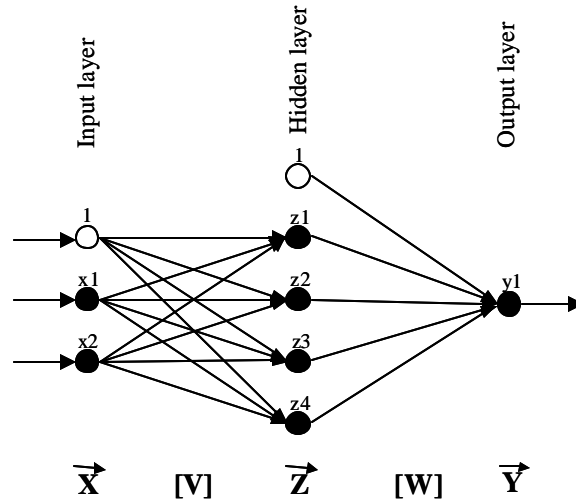$\vec{X}$   [V]   $\vec{Z}$   [W]   $\vec{Y}$

**Figure 2.  Example of a BP neural network with one input layer (two nodes), one hidden layer (four nodes), and one output layer (one node).  Filled circles are nodes; empty circles are biases.**

Training a BP network to obtain a mapping from input variables $\dot{X}$ to the target variables $\vec{T}$ consists of the following steps:

a) From the whole dataset ($\dot{X}$, $\vec{T}$), randomly select a subset to serve as training data ($\dot{X}_1$, $\dot{T}_1$) and reserve the remaining data for testing ($\dot{X}_2$, $\vec{T_2}$).

b) Initialize weights [V] and [W] using the Nguyen-Widrow algorithm [23].

c) Compute the output vectors $\vec{Y_1}$ using input training vectors $\vec{X_1}$ and weights [V] and [W], adjusted by biases at the input and hidden layers and activation functions at the hidden and output layers.

d) Compare the calculated output $\vec{Y_1}$ with known target vector $\vec{T_1}$. The error $\left\|\dot{T_1} - \dot{Y_1}\right\|$ is then propagated back to adjust weights [W] and [V] and biases, following the gradient along which the error $\left\|\dot{T_1} - \dot{Y_1}\right\|$ decreases most rapidly.

e) Use the updated weights [V] and [W] to compute the output $\dot{Y_2}$ and the corresponding residual error $\left\|\vec{T_2} - \vec{Y_2}\right\|$ for the testing data $\dot{X_2}$.

f) If $\left\|\vec{T_2} - \vec{Y_2}\right\|$ is decreasing, repeat steps c to e. If $\left\|\vec{T_2} - \vec{Y_2}\right\|$ begins to increase, stop the training process.

An ANN with one hidden layer of five nodes was trained using a randomly selected subset of 90% of the whole dataset. The remaining 10% of the data were used for testing. The input vector included eight variables (nodes). The variables are acid number, the ratio of base to acid number, and IEP (all of which provide information about the oil's polar components), three of

the four SARA fractions (asphaltenes, resins, and saturates), and RI and $P_{RI}$ (providing information about asphaltenes stability). The decision about what fraction of the dataset to use in training versus the amount of data reserved for testing was based on the size of the dataset and the number of variables in the input vector. Although the dataset represents a significant amount of effort, it is nevertheless a small sample size in statistical terms.

The results of a typical training run are shown in Fig. 3. It is difficult to assign physical significance to the ANN training results, but it is clear that measures of oil polarity, SARA fractions, and asphaltenes stability are able to account for the wetting alteration observed in both the unstable and stable water film cases.
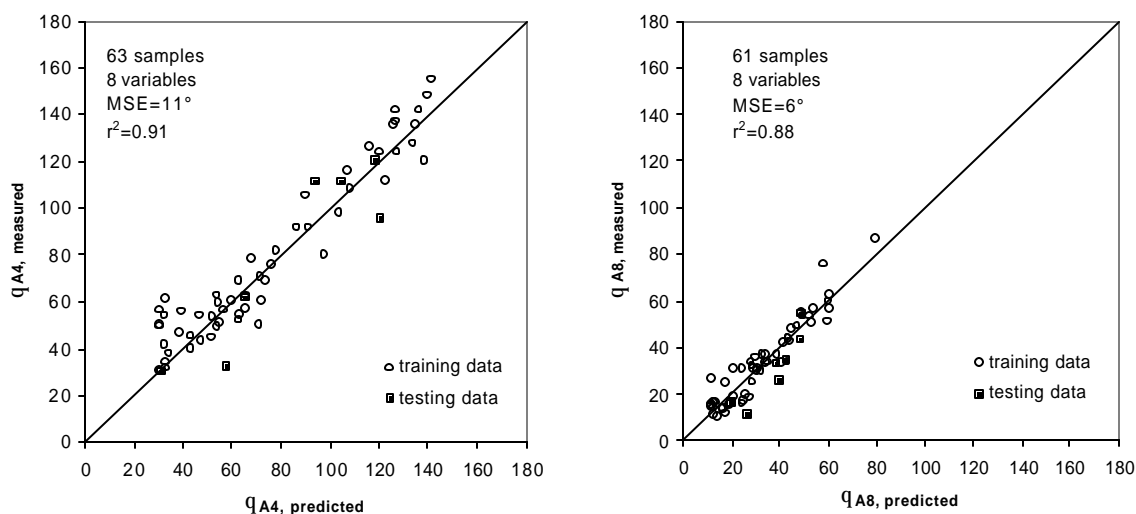


(a) less stable water films (pH4, 0.01M)          (b) more stable water films (pH8, 1M)

**Figure 3. Eight variables, RI, $P_{RI}$, acid#, B/A, IEP, amounts of saturates, resins, and n-C$_6$ asphaltenes, were used as input to the ANN. 90% of dataset was used for training while the remaining 10% was used for testing. (a) Measured vs predicted values of $q_{A4}$. (b) Measured vs predicted values of $q_{A8}$. MSE is mean-square-error.**

## SUMMARY AND CONCLUSIONS

Relationships between specific oil properties and wetting alteration at standard conditions have been demonstrated by linear and non-linear multivariate analyses of a large set of wetting and oil property data.

Statistical analyses that consider only one oil property are insufficient to find relationships because many properties influence wetting alteration either in cooperation or competition with one another.

Relationships can be seen in multiple regression analyses, even when linearity is imposed. Although the trends exhibit considerable scatter, the tendency to alter wetting at standard conditions can be related to measurable oil properties. The amount of asphaltene is found to be a key parameter in all cases, although higher concentrations of asphaltenes can produce either higher or lower contact angles, depending on other factors such as water film stability. Some samples in the dataset appear to be contaminated. High levels of Zn, well above the 0.5–1 ppm expected to occur naturally, have been measured in 13 oil samples.

The effect of asphaltene concentration can be partially masked by elevated levels of resins, which have the opposite effect on contact angles to that of the asphaltenes when water films are unstable. At lower levels of significance, asphaltene stability and oil polarity are also shown to be important parameters. Water film stability is positively correlated to the amount of asphaltenes and to the ratio of base number to acid number.

Artificial neural networks are ideal for handling the complex, nonlinear relationships between oil properties and wetting changes. A preliminary study has shown that oil properties can be used to predict contact angles with reasonable certainty for both the stable and unstable water film conditions. Optimization of the input parameters and expansion of the dataset are in progress.

## REFERENCES

1. Anderson, W.G.: "Wettability Literature Survey—Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *JPT* (Oct. 1986) **38**, No. 11, 1125-1144.
2. Hall, A.C., Collins, S.H., and Melrose, J.C.: "Stability of Aqueous Wetting Films in Athabasca Tar Sands," *SPEJ* (April 1983) 249-258.
3. Buckley, J.S., Liu, Y., and Monsterleet, S.: "Mechanisms of Wetting Alteration by Crude Oils," *SPEJ* (Mar. 1998a) **3**, 54-61.
4. Liu, L. and Buckley, J.S.: "Alteration of Wetting of Mica Surfaces," *J. Pet. Sci. Eng.* (1999) **24**, 75-83.
5. Buckley, J.S. and Wang, J.X.: "Crude Oil and Asphaltene Characterization for Prediction of Wetting Alteration," *J. Pet. Sci. Eng*, (2002) **33**, 195-202.
6. Fan, T., Wang, J.X., and Buckley, J.S.: "Evaluating Crude Oils by SARA Analysis," paper SPE 75228 presented at the 2002 SPE/DOE IOR Symposium, Tulsa, 15-17 Apr.
7. Buckley, J.S., Hirasaki, G.J., Liu, Y., Von Drasek, S., Wang, J.X., and Gill, B.S.: "Asphaltene Precipitation and Solvent Properties of Crude Oils," *Petroleum Science and Technology* (1998) **16**, No. 3&4, 251-285.
8. Wang, J.X. and Buckley, J.S.: "Procedure for Measuring the Onset of Asphaltene Flocculation," PRRC Report 01-18 on Contract No. DE-AC26-99BC15204, US DOE (2001).
9. ASTM D664-89, *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.* ASTM (1989).

10. ASTM D2896-88, *Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration*. ASTM.( 1988).

11. Dubey, S.T. and Doe, P.H.: "Base Number and Wetting Properties of Crude Oils," *SPERE* (Aug.1993) **8**,195–200.

12. ASTM D 5863-95, *Standard Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry*. ASTM (1995).

13. Liu, Y. and Buckley, J.S.: "Evolution of Wetting Alteration by Adsorption from Crude Oil,"*SPEFE* (Mar. 1997) **12**, 5-11.

14. Gaudin, A.M., Witt, A.F., and Decker, T.G.: "Contact angle Hysteresis - Principles and Application of Measurement Methods," *Trans*.,AIME (March 1963) 107-112.

15. Yang, L., Wang, J.X., Fan, T., and Buckley, J.S.: "Effect of Crude Oil Composition on Wettability of Mica," PRRC Report 02-16 on Contract No. DE-AC26-99BC15204, US DOE (August 2002).

16. Yang, S.Y., Hirasaki , G.J., Basu, S., and Vaidya, R.N.: "Statistical Analysis on Parameters That Affect Wetting for the Crude Oil/Brine/Mica System," *J. Petrol. Sci. Eng.* (2002) **33**, 203-215.

17. Yang, L.: "Statistical Analysis of Wetting Alteration and Oil Properties," MS Thesis, New Mexico Tech, Socorro, NM, 2002.

18. Al-Maamari, R.S.H. and Buckley, J.S.: "Asphaltene Precipitation and Alteration of Wetting: The Potential for Wettability Changes during Oil Production," *SPEREE* (Aug, 2003) in press.

19. Yang, S.-Y., Hirasaki, G.J., Basu, S., and Vaidya, R.: "Mechanisms for Contact Angle Hysteresis and Advancing Contact Angles," *J. Pet. Sci. Eng.* (1999) **24**, 63-73.

20. Lord, D.L. and Buckley, J.S.: "An AFM Study of Morphological Features that Affect Wetting at Crude Oil-Water-Mica Interfaces," *Colloids and Surfaces A* (2002) **206**, 531-546.

21. Speight, J.G.: *The Chemistry and Technology of Petroleum*, 2nd ed., M. Dekker, New York (1991), 760 pp.

22. Fausett, L.: *Fundamentals of Neural Networks: Architectures, Algorithms, and Applications*. Prentice Hall, 1994.

23. Nguyen, D., and Widrow, B.: "Improving the Learning Speed of Two-Layer Neural Networks by Choosing Initial Values of the Adaptive Weights." International Joint Conference on Neural Networks, 1990, San Diego, CA, III: 21-26.