THE INFLUENCE OF CRUDE OILS ON WELL TUBING CORROSION RATES

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ABSTRACT

An empirical formula derived from two sets of field data on tubing corrosion gives a satisfactory description for two different oil fields of the influence on corrosion of the API gravity of the oil and its watercut. A remarkably good level of agreement was found between predicted corrosion rates using this formula and field corrosion measurements. It reproduces the general concept that heavier oils are more protective than light ones, and that very light oils give hardly any protection at all. It also reflects the likelihood of various modes of corrosion associated with competitive wetting of the steel by water and oil arising from different modes of water entrainment. The link between API gravity, emulsion stability and water wetting of steel by an oil-water mixture is provided by considering the changes in interfacial tensions in the oil-water-steel system.

KEYWORDS

Field corrosion data, Water cut, API gravity, Wettability, Corrosion Prediction,

INTRODUCTION

It is commonly recognised that the presence of crude oil can reduce corrosion caused by CO_2 or H_2S dissolved in co-produced formation water. Corrosion of steel tubing in water containing dissolved acid gases has been studied extensively[1] leading to established corrosion models, but the prediction of the influence of the presence of crude oil on these corrosion rates has been elusive. It has been reported qualitatively that light oils give less protection than heavy ones, and that gas condensate gives hardly any protection at all, even at very low watercuts[2]. Higher molecular weight oil reduces the corrosivity of water-in-crude oil emulsions[3], but, in general, the influence of the oil on corrosion rates has not been quantified.

The actual hydrocarbon chemistry has been claimed to influence the corrosivity[4] but these effects are not quantified. The presence of light organic acids can increase corrosivity but in oil wells the alkaline constituents in the produced water counteract this effect. For the purposes of this paper the actual oil chemistry is not considered to be a variable.

The solubility of water in oil is low. Water can be entrained in the oil, however, in the form of a water-in-crude oil emulsion. The corrosion rate in these

emulsions is lower than that in water or brine only. The corrosion of steel by CO_2 in these environments is controlled by the wettability of the steel's surface by water, in competition to wetting by oil which prevents corrosion.

Another effect which can play a role is the separation of oil/water emulsions into two separate phases[5], where the corrosion in the waterphase can occur under a separated oil phase without any protective influence of the oil. This effect is found with stratified flowpatterns occurring in pipelines, but water separation can also take place in tubing at certain depths, depending upon the crude oil gravity, as this paper illustrates.

This paper considers how to quantify the influence of crude oil on the corrosion rate of oil - water mixtures by considering the different ways in which water is entrained in the oil as an emulsion or separated phase. Field corrosion data from two oil fields is used as the basis of the model.

Water-Wettability of Steel

Corrosion takes place when there is wetting of the steel surface by water and it can be shown that there is a relationship between the water wettability of steel and the stability of a water-in-oil emulsion.

The wettability of steel by a liquid can be expressed in terms of the interfacial tension $\gamma_{liquid-steel}$: a lower value indicates better wetting. For different crude oils, $\gamma_{oil-steel}$ will be different, but $\gamma_{water-steel}$ can be expected to be virtually independent of the type of crude. In analogue to Antonoff's rule[6], for oil and water saturated with each other, the following equation should hold when the two liquids are in equilibrium:

$$\gamma_{water-oil} = \gamma_{oil-steel} - \gamma_{water-steel} \qquad (1)$$

This formulation implies the assumption that $\gamma_{oil-steel}$ is larger than $\gamma_{water-steel}$ (water wets better than oil), which is a reasonable assumption, especially considering the improved water wetting characteristics of iron carbonate films on the steel's surface[7].

The interfacial tension $\gamma_{water-oil}$ is the energy released when a water-in-oil emulsion breaks: a lower $\gamma_{water-oil}$ corresponds to a more stable (tighter) emulsion, which can accommodate more water before it breaks. In other words, the maximum amount of water which can be emulsified in an oil, varies inversely with $\gamma_{water-oil}$.

When $\gamma_{water-oil}$ is decreased by changing to a different (heavier) crude oil (water-in-oil emulsion more stable), it follows from Eq. 1 that since $\gamma_{water-steel}$ is a constant, then $\gamma_{oil-steel}$ will also decrease. This leads to increased wetting of steel by the oil phase, giving more protection against corrosion.

The amount of water which can be entrained in a crude oil before separation of the emulsion into two phases - water and water-in-crude oil emulsion is termed W_{break}.

W_{break} increases with increasing oil density (heavier oils with low API gravity can entrain more water, forming a more stable emulsion). An increase in W_{break} therefore indicates a decrease in $\gamma_{water-oil}$, a corresponding decrease in $\gamma_{oil-steel}$ and thus more wetting of the steel by the oil. It follows that since the tendency to have oil wetting of the surface is $\propto W_{break}$, the tendency to have water wetting of the surface is $\propto 1/W_{break}$.

The type of crude oil is linked to the type or amount of emulsifiers and it is speculated that lower molecular weight crudes have fewer emulsifying agents that are soluble in the long chain hydrocarbons associated with heavy crudes. Thus the lighter oils are less effective at forming emulsions.

By providing a link between the oil density (API gravity) and the tendency for water wetting of the steel this establishes a basis for the corrosivity of oil-water mixtures which can be quantified as outlined mathematically in the discussion.

FIELD DATA ON TUBING CORROSION

Although there is no lack of laboratory test data, hardly any quantitative field data has been reported for crude oil production tubing. Very often, in-situ mechanical calliper surveys are used to monitor corrosion progress[8], but they are seldom used to quantitatively correlate corrosion rates with different production conditions.

In 1999 and 2000, calliper survey and production data became available[9] from an oilfield producing a very light crude, with an API gravity of about 49. More recently, a similar review yielded data for a field with a heavier crude with an API gravity of 38. In the latter case some wells were sour with about 1% H_2S in the produced gas.

Both fields produced only negligible amounts of gas, and varying amounts of water. Large amounts of production and inspection data were screened, and gathered in various computerised databases. The field with the heavier crude yielded fairly detailed production data with production rates and watercuts as a function of time, while the first field yielded mainly averaged data for each well.

The production data and calliper surveys for the first field covered a time period often in excess of 20 years. The calliper reports always contained the maximum loss of tubing wall thickness, together with the joint number (=depth) where this was measured. The angle of deviation of that part of the tubing could then also be deduced from the database.

ANALYSIS OF THE DATA

Ambiguous or incomplete data were filtered out, as well as data for wells after they had been treated with corrosion inhibitor. Squeeze inhibition was used for some wells. Some idea about the efficiency of these treatments was obtained from corrosion monitoring data -on the basis of resistance or electrochemical measurements - but these data are outside the scope of the present paper.

Watercuts were taken to be equal to the reported average "basic sediment and water" percentage (BS&W %), rather than produced free water. The BS&W values were measured on a regular basis, but are not continuous readings. Thus, for some wells the reported values were very low, even zero, but it was suspected that "slugs" of water may have been produced between measurements.

For each point of maximum wall thickness loss, pressure and temperature were estimated by linear interpolation for the tubing joint in question, using reported values for bottomhole and wellhead. These were used, together with data on flowrate (calculated from production rate), diameter, CO_2 percentage in produced gas, and bicarbonate concentration in produced water samples, to calculate a CO_2 corrosion rate for steel (all L80 tubing).

In the field with the API gravity of 38 a number of flowrates and watercuts for different time durations were available. In this case the calculated corrosion rates in each time period were converted to penetration depths of the tubing wall, and these were then summed for direct comparison with the survey data.

CORROSION MODEL

For the corrosion rate calculations, use was made of a semi-empirical model for typical quenched and tempered tubing steels[10] with the following formula for the corrosion rate V_{cor}:

$$\frac{1}{V_{cor}} = \frac{1}{V_r} + \frac{1}{V_m} \tag{2}$$

with V_r and V_m representing the maximum kinetic reaction rates of protons and mass transfer rates of the dissolved CO_2, respectively. The equation for each term is:

$$\log(V_r) = 5.07 - \frac{1119}{t + 273} + 0.58 \log(pCO_2) - 0.34(pH_{actual} - pH_{CO_2}) \tag{3}$$

$$V_m = 2.7 \frac{U_{liq}^{0.8}}{D^{0.2}} pCO_2 \tag{4}$$

Here pCO_2 is the partial pressure (bar) of the CO_2 multiplied with the fugacity coefficient, t is the temperature in °C, and U_{liq} is the flow velocity in m/s. D is the internal tubing diameter in metres.

pH calculations were based on measured bicarbonate concentrations, CO_2 solubilities and carbonic acid dissociation constants[11] [12], and on best fit equations for their temperature dependence. In general, the calculated pH values were used for the interpretation of the data rather then making use of some of the few reported pH values, since the latter are highly dependent on sampling and analysis protocol.

The bottomhole temperatures were approximately 110ºC and so the formation of a protective iron carbonate scale had to be considered. At temperatures in the order of 80 °C and higher the corrosion rate will be lowered with a factor $F_{scale} < 1$:

$$\log(F_{scale}) = \frac{2400}{t + 273} - 0.6\log(pCO_2) - 6.7 \tag{5}$$

which results in a base corrosion rate V_{base}:

$$V_{base} = V_{cor} \times F_{scale} \tag{6}$$

The resulting corrosion rates V_{base} or penetration depths were then fitted to the observed values by multiplying the predicted values for water with a factor:

$$F_{oil} = c_1 WU_{liq} + c_2 \frac{\alpha}{90} + c_3 WU_{liq} \frac{\alpha}{90} \tag{7}$$

where W is the average water fraction of the liquid measured at the wellhead, and α is the angle of deviation (in degrees) of the tubing from the vertical. The form of this equation with three terms is developed from an analysis of three different modes of oil wetting of the steel, corresponding to the modes I-III described in reference 13.

The constants c_1, c_2 and c_3 were adjusted to obtain a best fit between prediction and field observation of corrosion for each of the two fields.

RESULTS

F_{oil} was derived for the two fields independently such that each gave the best fit of field data with predicted corrosion damage. It appeared that c_1, c_2 and c_3 were different for the two fields i.e. these constants are dependent on the gravity of the produced oil.

For the wells in the oilfield with the API gravity of 49, Equation 7 was found to take the form:

$$F_{oil} = 4.4\,WU_{liq} + 0.54\frac{\alpha}{90} + 4.4\,WU_{liq}\frac{\alpha}{90} \tag{8}$$

while with °API = 38, this became:

$$F_{oil} = 0.27\,WU_{liq} + 0.0093\frac{\alpha}{90} + 0.27\,WU_{liq}\frac{\alpha}{90} \tag{9}$$

The fit between observations and prediction using the above equations is shown in Figure 1 and Figure 2. The figures show two ways to present the data, one comparing predicted corrosion rates with field estimates, and the second showing the comparison of predicted penetration versus actual measured pit depths. Not surprisingly for field data, the standard deviation is high, 0.3 in both cases, but the correlation coefficient is high indicating a good reliability of the prediction using the F_{oil} adjustment factors in each case. It is notable in Figure 2 that the penetration rates in three sour wells fit the correlation for the other sweet wells, indicating that the long

term pitting rate in sour systems is quite comparable to the CO_2 corrosion rate in these cases.

DISCUSSION

Unifying the Results

It was remarkable that the corrosion measured in the two fields, which were analysed quite independently, could be predicted using oil factors which were of such similar structure. Because of this, further work was undertaken to unify the information from the two fields and to try to establish a more universal approach.

The three terms in Eq. 8 and Eq. 9 correspond to the likelihood of 3 modes of water wetting. Mode I relates to completely emulsified liquid wetting, Mode II to wetting by accumulated water volumes at locations of high deviation, and Mode III to wetting by coalesced water droplets (Figure 3). Furthermore,

- Mode I wetting by emulsion is not angle dependent.
- Mode II accumulation of water droplets is strongly angle dependent, but independent of the bulk water content (even occurring with very low water-cuts).
- Mode III wetting by coalesced water droplets is dependent on water cut, flow rate and angle of deviation of the tubing[13].

In a previous paper[13] the concept of water wettability being related to the emulsion stability was used to postulate that c_1 and c_3 (Eq. 7) are dependent on crude oil gravity. The relationship was given via a parameter, W_{break}, which signifies how much water can be entrained in a crude oil[3], before separation of the emulsion into two phases –water and water-in-crude oil emulsion- occurs (Figure 4). It was found that:

$$W_{break} = -0.0166 * API + 0.83 \qquad \text{For } 50 > °API > 20 \qquad (10)$$

It follows that, since the tendency to have oil wetting of the surface is $\propto W_{break}$, the tendency to have water wetting of the surface is $\propto 1/W_{break}$.
Multiplying the general equation 7 by the factor $1/W_{break}$ was used to generalise the constants c_1 and c_3 for different oil types.

From the more recent work, it now appears that constant c_2 is more strongly dependent on the type of oil than c_1 and c_3, and that the middle term in Eq.7 quickly disappears for heavier oils. This term may be interpreted as representing the tendency to accumulate water at deviated parts of the tubing from nominally dry light oils or condensate. (Mode II water entrainment). The strong dependence of c_2 on W_{break} can be accounted for by dividing by W_{break}^2.

All results, for both oil fields, can be reproduced by a general formula for the "oil factor":

$$F_{oil} = 0.059 \frac{W}{W_{break}} U_{liq} + \frac{1.1 \ 10^{-4}}{W_{break}^2} \frac{\alpha}{90} + 0.059 \frac{W}{W_{break}} U_{liq} \frac{\alpha}{90} \qquad (11)$$

For an oil of 49 °API gravity (W_{break}=0.0145 or 1.45%), this equation converts to the form of Eq.8 with c_1 =c_3 = 4.1 and c_2=0.52. For an oil of 38 °API gravity (W_{break}=19.7%), equation 11 converts to the form of Eq.9 with c_1 =c_3 = 0.30 and c_2= 0.0028. These coefficients are close to the values obtained from the field data given in Eq. 8 and 9, although the c_2 value is small for Eq 9. This is not felt to be a significant error, taking into account that the mode II contribution to water wetting is very small for an oil of this gravity.

The above generalised formula, Eq.11, is therefore considered suitable for application to a wider range of crude oils, but is limited for now to the range covered by Figure 4.

General Understanding and Wider Application

Eq. 11 reflects the notion that wetting of steel by water will decrease, and wetting by oil will increase, when the interfacial tension between water and oil is lowered.

W_{break} is an inverse measure for the wettability of steel by water as expressed by this equation.

This reflects why heavier oils are less corrosive: they can contain more emulsified water before separation between oil and water occurs, which means that the interfacial tension between oil and steel is lower, resulting in a better wetting contact of the oil.

The formula in Eq. 11 should never yield values above 1, or below zero. Apart from these constraints, Eq. 11 should also be =1 when the watercut reaches 100%. It is unlikely, however, that in a high watercut regime we are still dealing with water-in-oil emulsions: reversal to an oil-in-water emulsion should be expected, and Eq. 11 is no longer applicable. Theoretically, more than 74 % dispersed phase (= watercut in the emulsion) is not possible (Ostwald[14]). The corrosion protection resulting from very small amounts of oil in a waterphase is minimal and has to be estimated conservatively to be zero. Thus we assume that F_{oil}=1 at W>80%.

The behaviour of F_{oil} as a function of watercut is shown in Figure 5. This shows how the lighter oils are less able to entrain the water at low water-cut levels and so the F_{oil} value more rapidly approaches 1 with low values of water fraction.

The influence of the angle of deviation is much larger for low density (high API gravity) oils, than for high density (low API gravity) ones (Figure 6). The tendency to form a separate water phase (indicated by increasing value of F_{oil}) is further increased when the direction of flow is less vertical (increasing angle of tubing deviation).

The first term in Eq. 11 describes the contributions to overall corrosion caused by the occurrence of a one-phase water-in-oil emulsion (mode I), and by a two-phase system consisting of water and water-in-oil emulsion (mode III). The occurrence of the latter is promoted by an increase in deviation angle α of the tubing.

The second term in Eq. 11 reflects the separation into two phases, as before, but here the waterphase is considered to be semi-stationary ("water pockets"), with the water-in-oil emulsion flowing around or over it (mode II). This has been observed for a light oil, particularly at, or immediately below, the location of maximum deviation of wells. The occurrence of this mode of corrosion appears to diminish quickly for oils which can accommodate some water in the form of an emulsion (Figure 7). This figure illustrates that there are a range of light oils for which low watercut measurements in the field may be deceptive. Water may be accumulating downhole, particularly in highly deviated sections of wells.

The influence of liquid velocity on the oil factor is shown for a range of oils of varying gravities in Figure 8. This example shows an almost vertical well (10° angle of deviation).

Liquid velocity exerts an influence both via the CO_2 corrosion rate in Eq. 4, as well as via F_{oil} (Eq.11). An example of the total result of all factors on the overall corrosion rate is shown in Figure 9 for an oil of API gravity = 49. As expected from the very light condensate there is very little tendency to emulsify water, so the corrosion rate rises quickly from the earliest introduction of water into the produced condensate stream and this is further exacerbated with increasing flow rates. By comparison, Figure 10 shows lower corrosion rates over a greater range of water content and flow rate for a 38 °API oil, which is able to entrain more water.

CONCLUSIONS

An empirical formula derived from two sets of field data on tubing corrosion gives a satisfactory description for two different oil fields of the influence on corrosion of the API gravity of the oil and its watercut A remarkably good level of agreement was found between predicted corrosion rates using this formula and field corrosion measurements. The formula reproduces the general concept that heavier oils are more protective than light ones, and that very light oils give hardly any protection at all. It also reflects the likelihood of various modes of corrosion associated with competitive wetting of the steel by water and oil arising from different modes of water entrainment. The link between API gravity, emulsion stability and water wetting of steel by an oil-water mixture is provided by considering the changes in interfacial tensions in the oil-water-steel system.

The result should be regarded as typical of a "normal" oilfield operation, without the co-production of large quantities of gas. It may be applied generally for oils over a range of API gravities but remains speculative until more statistically significant sets of field data becomes available for crude oils with other gravities than the ones which have been studied up to now.

GLOSSARY OF TERMS

API – Gravity of oil in °API

α - angle of deviation (in degrees) of the tubing from the vertical.

BS&W % - basic sediment and water

D - internal tubing diameter in m.

F_{scale} - scaling factor

F_{oil} - oil factor

$\gamma_{water-oil}$ – interfacial tension between water and oil, mN/m

$\gamma_{oil-steel}$ – interfacial tension between oil and steel, mN/m

$\gamma_{water-steel}$ – interfacial tension between water and steel, mN/m

pCO_2 - the partial pressure (bar) of the CO_2 multiplied by the fugacity coefficient,

pH_{CO2} – pH arising only from dissolved CO_2

pH_{actual} – Actual pH including effect of dissolved bicarbonate

t - temperature in °C

U_{liq} - flow velocity in m/s.

V_{cor} – corrosion rate due to CO_2, mm/y

V_r – contribution to the corrosion rate due to the maximum kinetic reaction rates of protons, mm/y

V_m - contribution to the corrosion rate due to the mass transfer rates of the dissolved CO_2, mm/y

V_{base} - base corrosion rate including scale effect, mm/y

W - average water fraction of the liquid measured at the wellhead

ACKNOWLEDGEMENTS

REFERENCES

1. C. de Waard and U. Lotz, "Prediction of CO_2 corrosion of carbon steel", European Federation of Corrosion Publications number 13, a Working Party Report on Predicting CO2 Corrosion in the Oil and Gas Industry, Institute of Materials 1994.
2. U. Lotz, L. van Bodegom, C. Ouwehand, "The effect of type of oil or gas condensate on carbonic acid corrosion", NACE CORROSION/90, Las Vegas, Paper 41.
3. B. Craig, "Predicting the Conductivity of Water-Oil Solutions as a means to Estimate Corrosiveness", Corrosion Vol. 54, No. 8, p. 657, 1998
4. C. Mendez, S. Duplat, S. Hernandez, J. Vera, "On the Mechanism of Corrosion Inhibition by Crude Oils", NACE 2001 paper 1030
5. M. Wicks and J. P. Frazer, "Entrainment of water by flowing oil", Materials Performance 1975, 14, 9
6. Samuel Glasstone, "Textbook of Physical Chemistry", 2nd ed., MacMillan, London 1955, p.485.
7. John S. Smart, "Wettability-A Major Factor in Oil and Gas Systems Corrosion", NACE CORROSION93, paper 70.

8. Y. Gunaltun, "Carbon Dioxide Corrosion in Oil Wells", SPE Middle East Oil Show, Bahrain, November 1991, SPE 21330

9. C. de Waard, L.M. Smith, P. Bartlett and H. Cunningham, "Modelling Corrosion Rates in Oil Production Tubing" Eurcorr 2001, Lake Garda, Italy September 2001

10. C. de Waard, U. Lotz and A.Dugstad, "Influence of liquid flow velocity on CO_2 corrosion: a semi-empirical model", NACE CORROSION/95, Paper 128.

11. J.N.Butler, "Carbon Dioxide Equilibria and their applications", Addison-Wesley, 1982, p.17, table 2.2.

12. A.Miyasaka, "Thermodynamic estimation of pH", CORROSION/92, Nashville, paper 5.

13. C. de Waard, L. Smith and B. D. Craig, "The influence of crude oil on well tubing corrosion rates", EUROCORR 2001, The European Corrosion Congress, European Federation of Corrosion, Riva del Garda, Italy, October 30, 2001.

14. Samuel Glasstone, "Textbook of Physical Chemistry", 2nd ed., MacMillan, London 1955, p.1275.
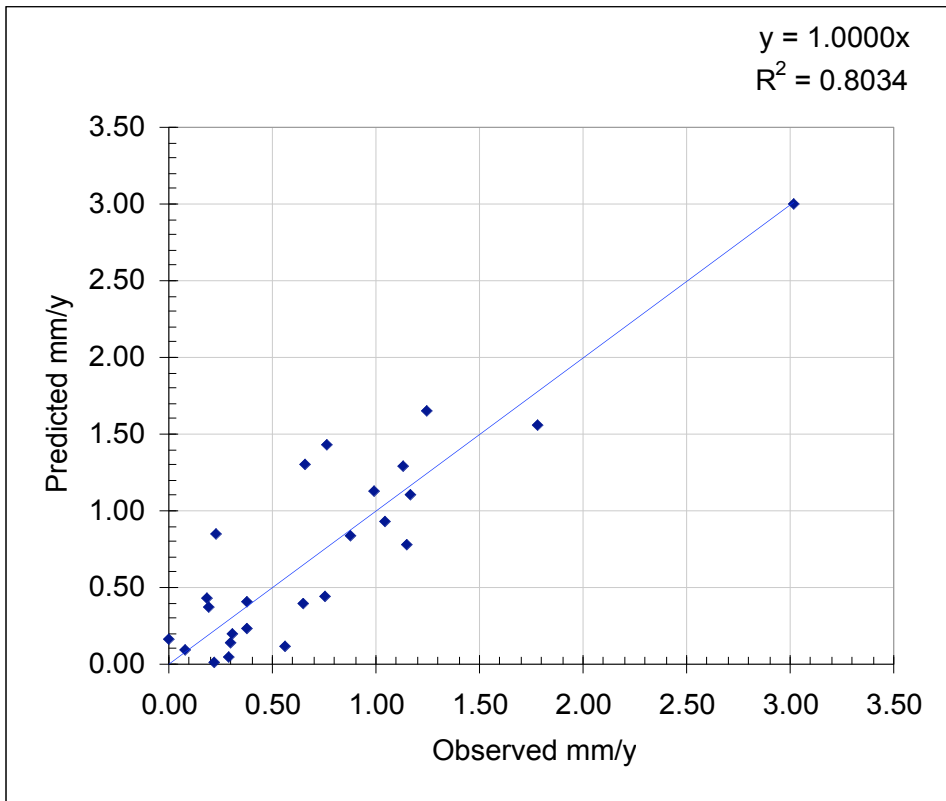
FIGURE 1. Fit between predicted and observed corrosion rates derived from calliper surveys for a field producing a light oil, 49 °API.
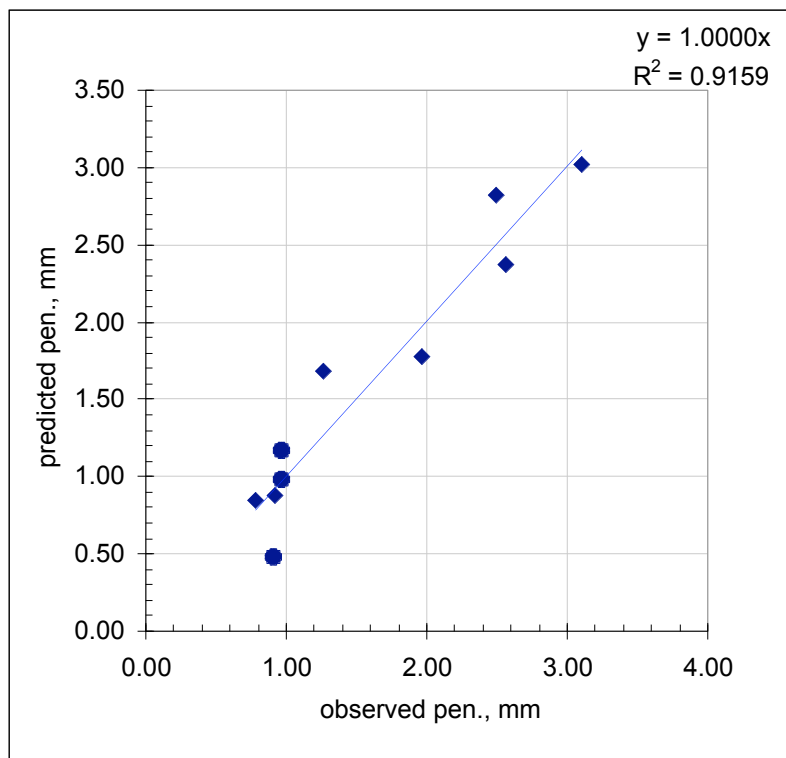
FIGURE 2. Fit between predicted and observed tubing wall penetration from calliper surveys for a field producing an oil with API of 38. Three points indicated by circles are sour wells, the rest are sweet.
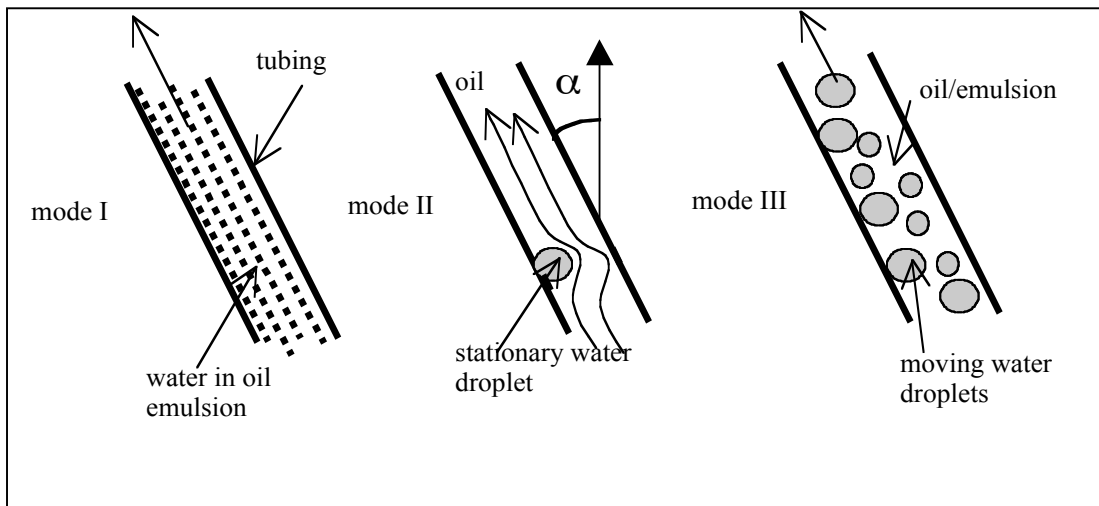
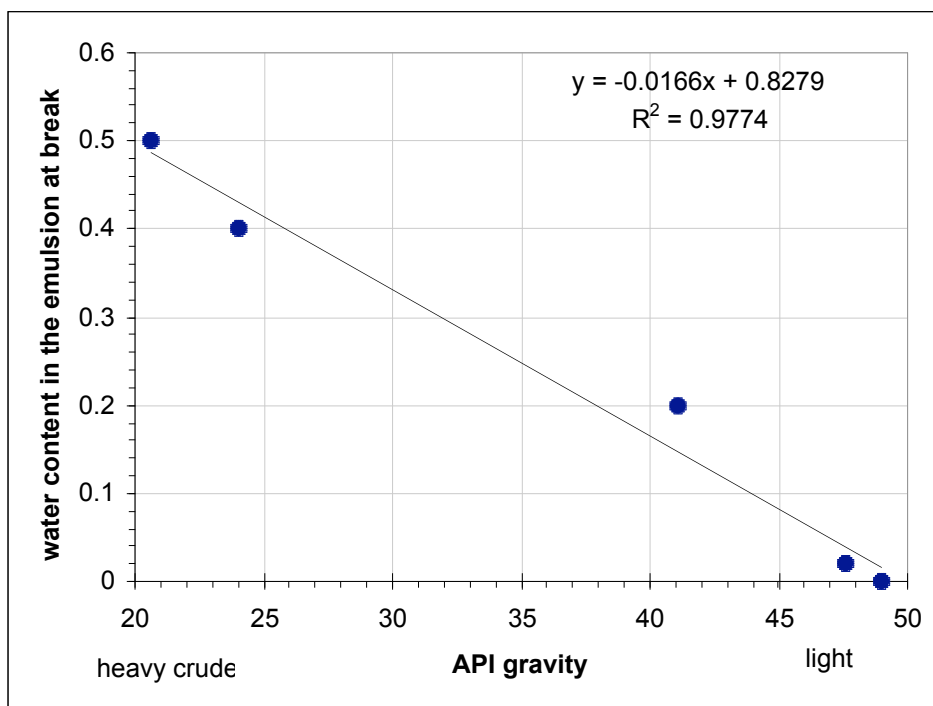FIGURE 3. Modes of water entrainment in wet oil in production tubing at an angle of deviation, α.

FIGURE 4. Watercut readings in the emulsion at the point where at least 10% of the total water has separated from oil-water emulsions.
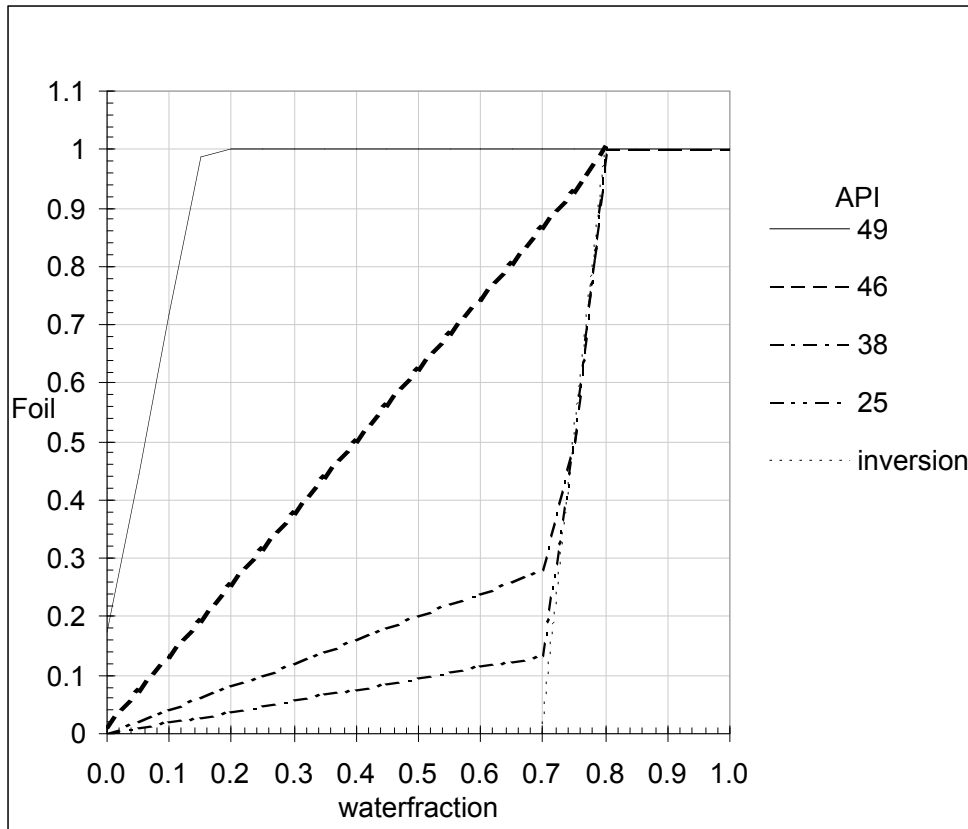
FIGURE 5. Oil factor as a function of watercut for a number of oil gravities for a liquid flow rate of 1m/s and angle of deviation of 30deg.
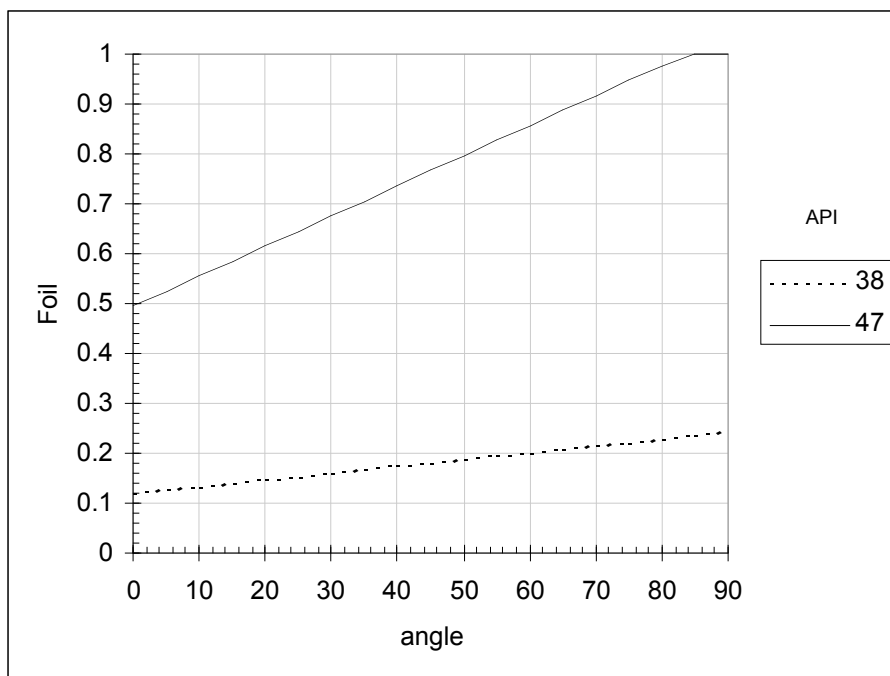

FIGURE 6. Effect of angle of tubing deviation from vertical on oil factor for two oil gravities at 20% water cut and 2m/s flow rate.
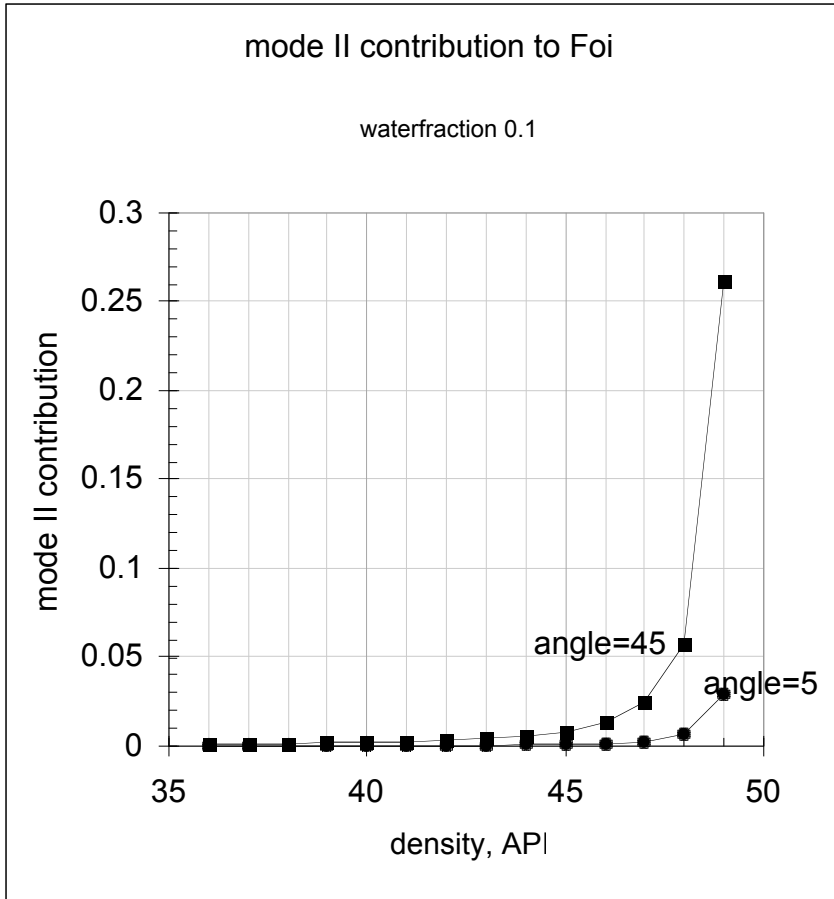
FIGURE 7. Effect of API gravity on oil factor and on the contribution of mode II wetting, liquid velocity 0.5 m/s.
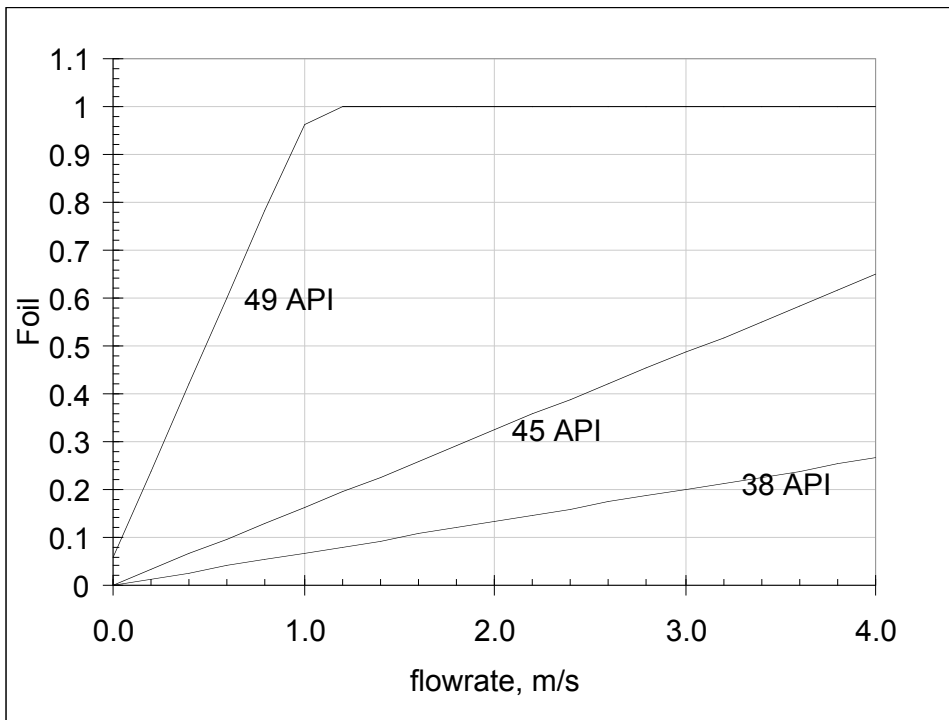
FIGURE 8. Influence of flowrate on oil factor, at 20% watercut and 10 degrees angle of deviation.
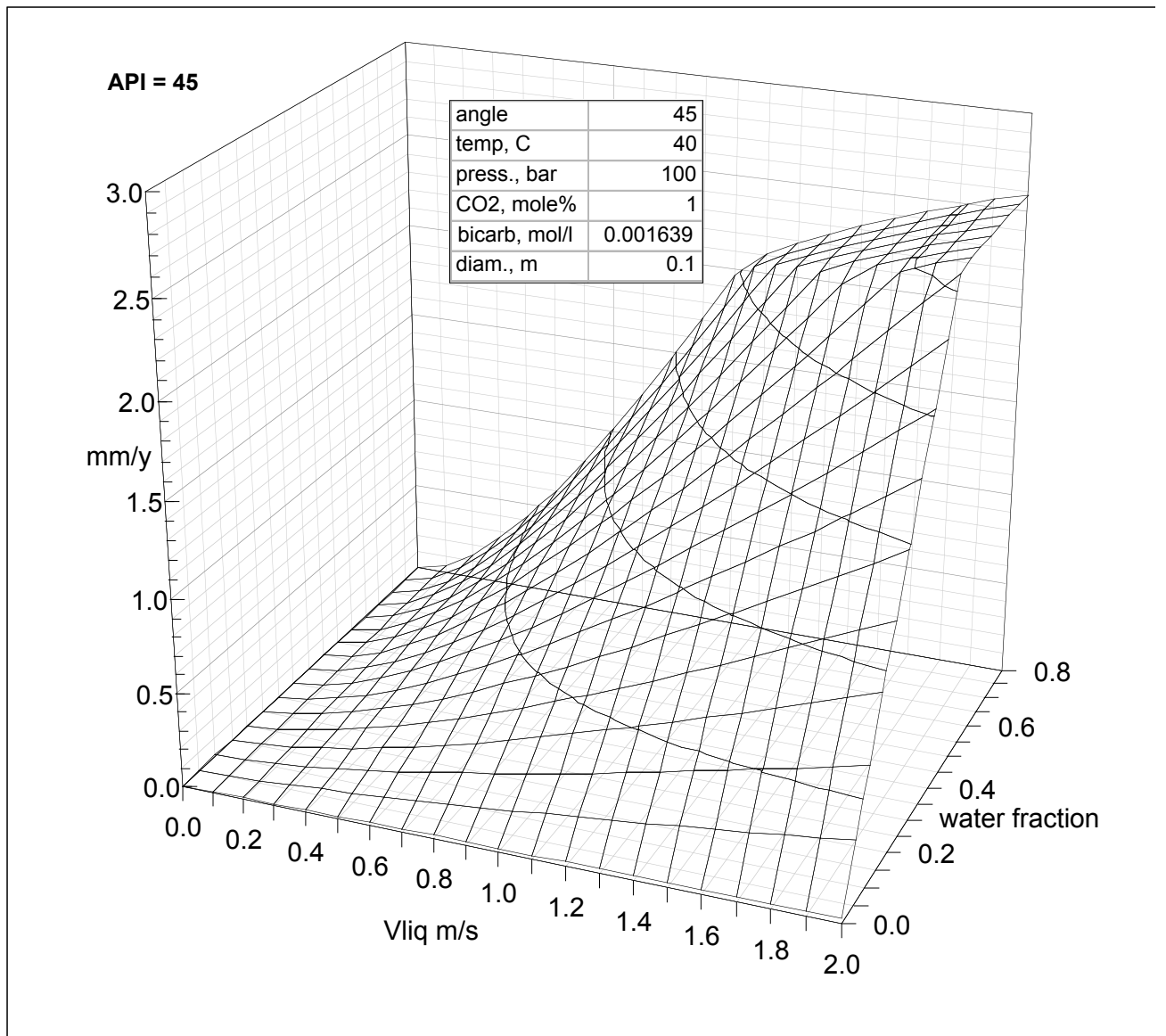
FIGURE 9. CO_2 corrosion rates in the presence of an oil with API gravity of 45, as a function of watercut and flowrate.
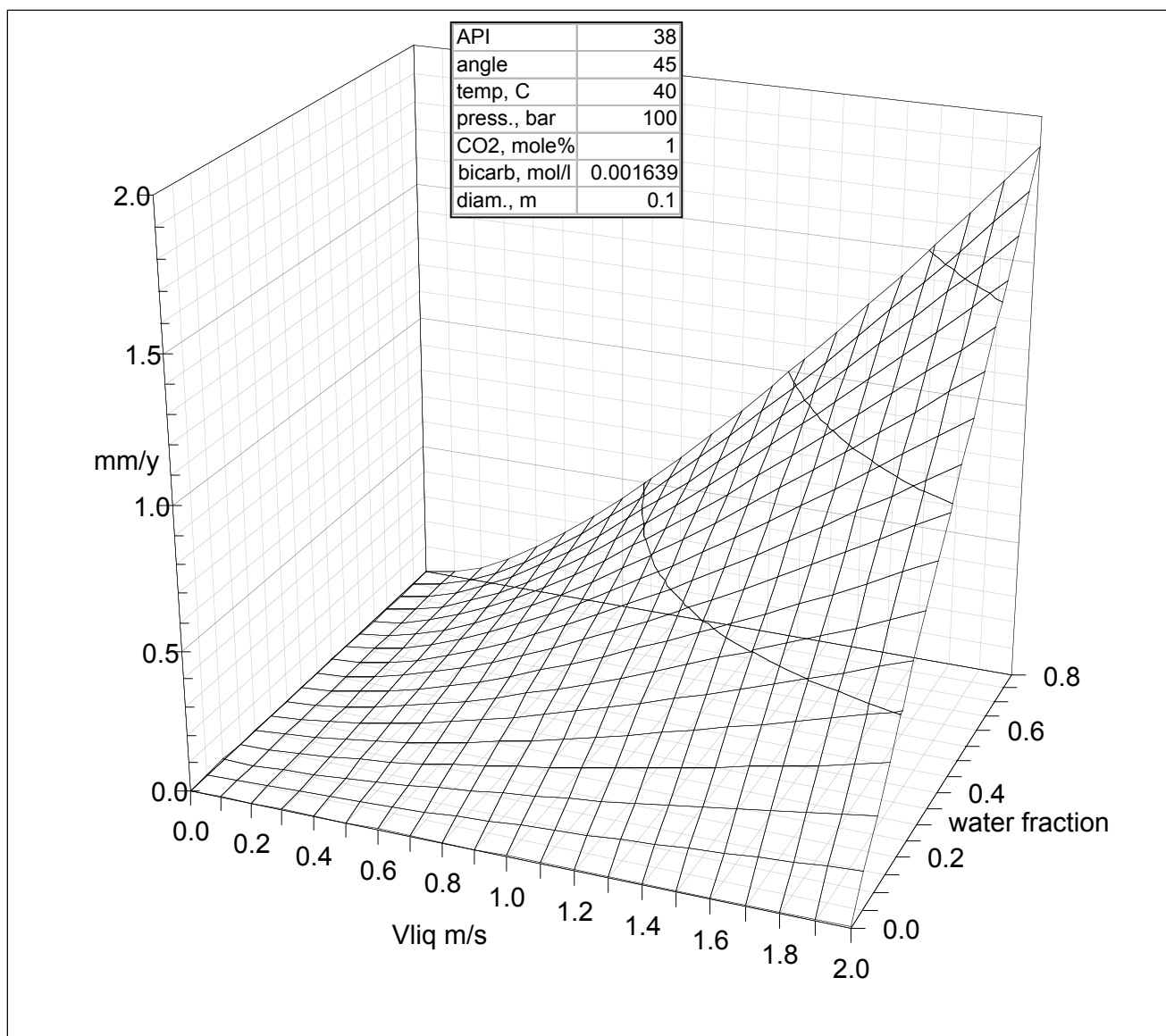
API	38
angle	45
temp, C	40
press., bar	100
CO2, mole%	1
bicarb, mol/l	0.001639
diam., m	0.1

FIGURE 10. CO_2 corrosion rates in the presence of an oil with API gravity of 38, as a function of watercut and flowrate.