ALTERNATIVE METHODS FOR DETERMINING WATER SATURATIONS IN CORE PLUGS

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Abstract This paper presents some alternative methods for determining water saturation in plugs during and after water/oil floods. Detailed procedures, comparison tests with other methods and a discussion on complications and possible systematic errors are presented. Tests have been performed on plugs during oil and water floods and on plugs to which were added a known volume of water.

INTRODUCTION

In order to obtain valid SCAL data during series of water/oil displacement tests, it is essential to have a good control of water saturations, S_w. This can be a problem, especially in long programs and /or in use of fresh plugs. The common methods to complement material balance are weighing and Dean & Stark extraction.

Whereas an error in a pressure reading usually only affects that specific measurement, an erroneous volume reading may influence all saturation values in a series of tests on a plug. Errors in material balance can have many causes; separator reading or calibration, porevolume, leaks, hold up volumes, emulsions etc.

The purpose of this paper is to describe alternative methods for determining water saturation in core plugs. The methods have not been described in the oil industry literature, except the CT-technique. All methods have limitations as to where they can be applied. But with several available methods it is usually possible to find one to verify material balance data.

PROCEDURES

Volume of Brine by Titration of Solvent with Karl Fischer Reagent

This method can be used at all saturation levels. The plugs are flooded with solvents and the water content is determined by titration of the solvents with Karl Fischer reagent. This technique is used in conjunction with cleaning the plug and it is an alternative method to the Dean & Stark method. This technique to determine volume of water in a core plug is new, but the titration with Karl Fischer reagent is a well known technique (Vogel, 1962).

Detailed procedure

1. Flood the plug with toluene, 8-10 porevolumes or 200 ml, at rate 3 ml/min. Collect the effluent in a 1000 ml volumetric flask.
2. Make a solution of methanol/toluene (50/50), 600 ml. Recycle this solution through the plug, for about 16 hours, at rate 3 ml/min. Collect the recycled solution in the 1000 ml volumetric flask. Since methanol easily absorbs water from the air, special precautions must be made to avoid that.
3. Flood the plug with about 200 ml pure methanol, at rate 3 ml/min. Collect the effluent in the 1000 ml volumetric flask, and dilute to 1000 ml with methanol.
4. The water content in the effluent, the pure methanol and the pure toluene are measured by titration with Karl Fischer reagent.
5. Make a correction for water in the solvents and calculate the total volume of water from the plug. The salt content is corrected for using equation (1).

The salt content = A g salt/g brine
Density of the brine = ρ_b (g/ml)
Density of water = ρ_w (g/ml)

$$ml\ brine = \frac{\rho_w}{(1 - A) \bullet \rho_b} \bullet ml\ water \qquad (1)$$

Advantages (+) and disadvantages (-):

+ All levels of saturations can be measured
+ Used in conjunction with cleaning
+ Leaves no salt crystals in the pores in contrast to the Dean & Stark method
+ Heterogeneities have no effect
+ Can also be used on poorly consolidated materials
+ Simple technique and low equipment cost

- Affects the wettability in most cases
- Methanol easily absorbs water from the air
- Rough plug ends can increase the brine volume
- Accurately measured hold up volumes are important
- Solvents cause potensial health risks

Volume of Brine by Titration of Chloride.

This method is preferred for plugs at residual oil saturation S_{or}. The procedure is a miscible displacement of chloride by nitrate brine. The ionic strength of chloride in the chloride brine and in the effluent are measured by titration with standard 0.1 N $AgNO_3$. This technique is applied at different laboratories, but is not described in the literature. The titration methods with 0.1 N $AgNO_3$ are standard techniques and are not discussed here (Vogel, 1961).

Detailed procedure

1. Collect a reference sample of brine containing chloride that has been flooded through the plug. Dilute 50.0 ml (SDref ml) of the reference sample to 500 ml (Sref ml) in a volumetric flask.
2. Displace (approx rate = 2 ml/min) the chloride brine by a nitrate brine of similar ionic strength. (One monovalent cation, Na^+, and one divalent cation, Ca^{2+}, are recommended.) Initial injection of nitrate brine is 6-10 porevolumes. Collect the displaced brine into a 250 ml volumetric flask. This sample will be diluted to 250 ml (S1 ml) prior to the analysis.
3. It is recommended to recycle about 100 ml nitrate brine for more than 10 hours. Displace out and collect the recycled volume in a volumetric flask, and dilute to a known volume (S2 ml).
4. Two or more additional samples are recommended to verify that all cloride brine is displaced (S3 ml, S4 ml, etc.)
5. Analyse each sample, including reference samples of chloride brine and nitrate brine, by titration with a standard 0.1 N $AgNO_3$. It is recommended to use nitrate brine absolutely free of chloride. Use potassium chromate as the indicator (Mohrs procedure) or potentiometric titration:
(i) Aref = ml $AgNO_3$/ml Sref
(ii) A1 = ml $AgNO_3$/ml S1
(iii) A2 = ml $AgNO_3$/ml S2
etc.
6. Calculate the volume of chloride brine by equation (2).

$$ml\ brine = \frac{A1 \bullet S1 + A2 \bullet S2 + A3 \bullet S3 + etc}{\frac{Aref \bullet Sref}{SDref}} \quad hold\ up\ vol. \qquad (2)$$

Note that it is not required that the silver nitrate is accurately calibrated as long as the same standard is used for all titrations in the analysis.

Advantages and disadvantages:

+ Measurement on poorly consolidated materials is possible
+ Low equipment cost and simple technique
+ Less influence on the wettability or other core characteristics than for the Dean & Stark or the Karl Fischer methods
- Heterogeneities may influence the displacement efficiency.
- Rough plug ends can increase the brine volume
- Accurate measured hold up volumes are important
- Can be difficult to displace chloride in the smallest pores and the disconnected water in weakly wetting plugs

Volume of Oil by Tracer in the Oil.

The plug should contain a low initial water saturation (S_{wi}) and refined, light oil with a tracer of nonane added. Miscible displacement of the tracer oil by pure refined, light oil is performed. The tracer in the effluent is analysed using gas chromatography. This is a new method to determine volume of oil in core plugs, and has not been described elsewhere. Gas chromatography is a well known technique and not described here.

Detailed procedure

1. The main components in the refined, light oil (base oil) used in this study are unbranched alkanes from decane to tridecane. Prepare 1000 ml of the same base oil added about 2 % nonane exactly.
2. Collect a reference sample of the oil added 2 % nonane. The oil is flooded through the plug before sampling.
3. Displace (approx rate = 2 ml/min) the 2 % nonane oil with the base oil. An initial injection of 5-6 porevolume base oil is preferred. Collect the displaced oil in a 250 ml volumetric flask.
4. Recycle about 100 ml base oil. Displace out with fresh base oil and collect the recycled oil in the 250 ml volumetric flask after 15-20 hours. Dilute to 250 ml prior to analysis.
5. One or two additional samples are recommended to verify that all the tracer has been displaced.

6. Analyse each sample, in duplicate, including the reference sample and the pure oil, using gas chromatography.
7. Calculate the total volume of oil.

Advantages and disadvantages:

+ Less influence on the wettability or other core characteristics than for the Dean & Stark or the Karl Fischer methods
+ Measurement on poorly consolidated materials is possible
+ Simple technique
+ Other refined oils and tracers can be selected
- Heterogeneities may influence the displacement efficiency.
- Rough plug ends can increase the oil volume
- Accurately measured hold up volumes are important
- Equipment cost (gas chromatograph)

Volume of Oil by Density or Viscosity Difference.

The plug should contain a low initial water saturation (S_{wi}) and a high density, refined oil. Miscible displacement of the high density oil by a low density, refined oil is performed. The density of the effluent and the base oils are determined. This is a new method to determine volume of oil in core plugs, and has not been described elsewhere.

In the description of the procedure it is assumed that density differences are measured. The same procedure is used if viscosities are measured. Density difference is recommended due to the present accuracy of measurement.

The method could also be performed by starting with a low density oil in the plug and displace the oil with high density oil. However, this could lead to additional production of water and is not recommended.

Detailed procedure

1. Collect a reference sample of the high density oil. The oil is flooded through the plug before sampling.
2. Displace the high density oil in the plug with low density oil (approx. rate = 2 ml/min). An initial injection of 2-3 porevolumes is preferred. Collect the effluent in a 100 ml volumetric flask.
3. Recycle by pumping about 50 ml low density oil. Displace out and collect the recycled oil in the 100 ml volumetric flask after 15-20 hours. Dilute to 100 ml prior to analysis.
3. One or two additional samples are recommended to verify that all high density oil has been displaced.

4. Measure the density of each sample, including the reference samples of the pure oils.
5. Make a calibration curve with 0.0, 10.0, 30.0, 50.0, 70.0, 90.0, 100.0 % high density oil.
6. Measure the total volume of oil with use of the calibration curve.

Advantages and disadvantages:

+ Less influence on the wettability or other core characteristics than for the Dean & Stark or the Karl Fischer methods
+ Measurement on poorly consolidated materials is possible
+ Performed in conjunction with establishing S_{wi}
+ Low equipment cost and simple technique
- Heterogeneities may influence the displacement efficiency.
- Rough plug ends can increase the oil volume
- Accurately measured hold up volumes are important
- Pollution, gas or fines in the oil, can affect the results

Saturation Determination by use of CT-Technique

This method can be used during or after a displacement test and at all levels of saturations. An X-ray Computer Tomograph (CT) is used for scanning and visualizing a chosen slice of the plug. The technique and different applications are described elsewhere (Hove et.al., 1987, Wellington and Vinegar, 1987).

Detailed procedure

1. Choose a representative slice of the plug to be studied. In the experiments reported an 8 mm thick axial slice is used. Alternatively radial slices can be used.
2. CT-scan of an actual fluid distribution.
3. CT-scan of the plug fully saturated with fluid 1 or fluid 2 respectively.
4. The fluid saturation can be calculated by normalizing between the fluid 1 and fluid 2 CT-levels.

Advantages and disadvantages:

+ All levels of saturations can be measured
+ Saturation determinations are independent of previous estimations in contrast to material balance
+ Saturation distribution in addition to the average value is determined
+ Fast test
- Only a fraction of the pore volume is used in the

estimation of saturation (about 25% with one axial slice).
- The quality of the estimate depends on a representative slice regarding heterogeneities
- High equipment cost

The Gas-Oil Ratio Procedure

This method is used to determine the volume of oil at S_{wi} in a plug at reservoir conditions. The variation in gas/oil-ratio (GOR) during a miscible displacement is analysed and the oil volume in the plug estimated.

Detailed procedure

1. A plug saturated with a refined oil and initial water saturation is flooded at low rate $\leq$ 2 ml/h for about 2 porevolumes. Produced oil and gas are measured and the flooding is stopped when produced GOR is equal to the R_s of the injected recombined oil.
2. The ratio GOR/R_s is plotted versus volume of oil injected. Volume of oil in the plug is found when the ratio is 0.5.

Advantages and disadvantages:

+ Measurements during the preparation of the plug before a reservoir condition study (at high pressure).
- The viscosity ratio between the two different oils has to be close to 1 to give exact volume of oil in the plug
- Heterogeneities may influence the displacement efficiency.

RESULTS AND DISCUSSION

Calibration tests versus known standards have been performed for all methods. Comparisons were carried out for most of the methods. In many of these tests, three methods were compared simultaneously; for example material balance, CT and a chemical method. All plugs used had a diameter of 3.8 cm and a length of 5-7 cm.

Tests on Outcrop and Artificial Porous Media

Bentheim and Berea sandstones and sintered $Al_2 O_3$ -plugs were used. Results from different methods are shown in figure 1.

Fluids used were refined oil, gas, brine and brine added NaI. All tests were carried out at room conditions. Saturations were estab-

lished by spontaneous imbibition, flooding or centrifuging. The plugs were strongly water wet. Porosity ranged from 15 to 40 % and permeability ranged from 50 to 4000 mD.

There is a good agreement between the Karl Fischer- (K.F.), chloride titration-(Cl-titr), CT-method and the material balance, (see figure 1).

Only two tests using the density method have been carried out. The results indicate too high oil saturation. Pollution by gas or fines in the oils can be the explanation. The method can not be recommended before additional tests and improvements are made.

Only five tests have been carried out using the tracer method. The results were not satisfactory and the method can not be recommended before additional tests and improvements are made. This method can be "tailored" to fit different oils and other tracers should be tested.

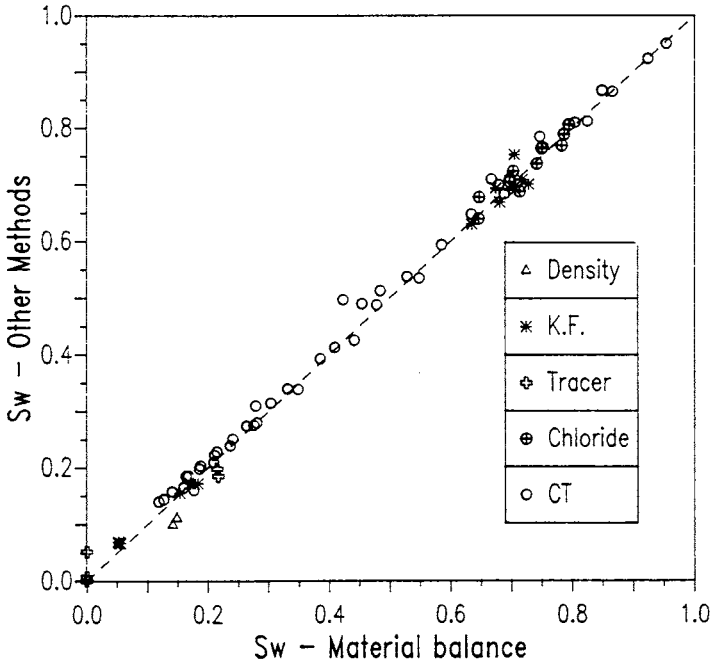

FIGURE 1 Outcrop and artificial porous media

Tests on Reservoir Sandstone Samples

Reservoir sandstone from three different reservoirs were used. Results from the different methods tested are shown in figures 2 to 6. Fluids used were refined oil, brine and brine added NaI. Saturations were established by flooding and centrifuging. Wettability tested according to the Amott procedure (Amott, 1958) ranged from near neutral to strongly water wet. Porosity ranged from 20 to 35 % and permeability ranged from 30 to 8000 mD. Neither of these variables influenced the accuracy of the saturation determination methods.

Figure 2 shows the results from repeated tests on 10 reservoir plugs. CT- and/or weight- method were used to verify material balance. All tests were carried out at room conditions on plugs cleaned with solvents to strongly water wet.

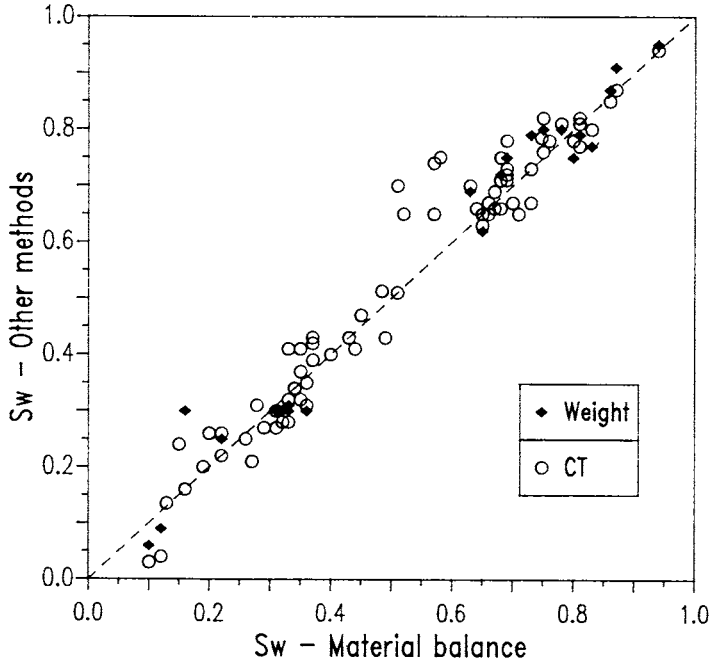

FIGURE 2 Tests on reservoir sandstone samples

The 4-5 CT-estimates, $S_w \simeq 0.70$, that differ most from material balance, represent the most heterogeneous plugs in the set. The differences can therefore be explained by difficulties in obtaining a representative CT-slice for such material.

In 10-15 of the tests there is a disagreement between material balance and the two other methods. In these tests the weight and CT-estimations agree well. The material balance is inaccurate, due to uncertainties in hold up volumes and/or emulsions in these tests. An error in volume reading will also influence all *succeeding* saturation values in a series of tests on a plug in the material balance method.

If the CT-estimates from the most heterogeneous plugs and the inaccurate material balance values are excluded from figure 2, a good agreement between all three methods is obtained as shown in figure 3.

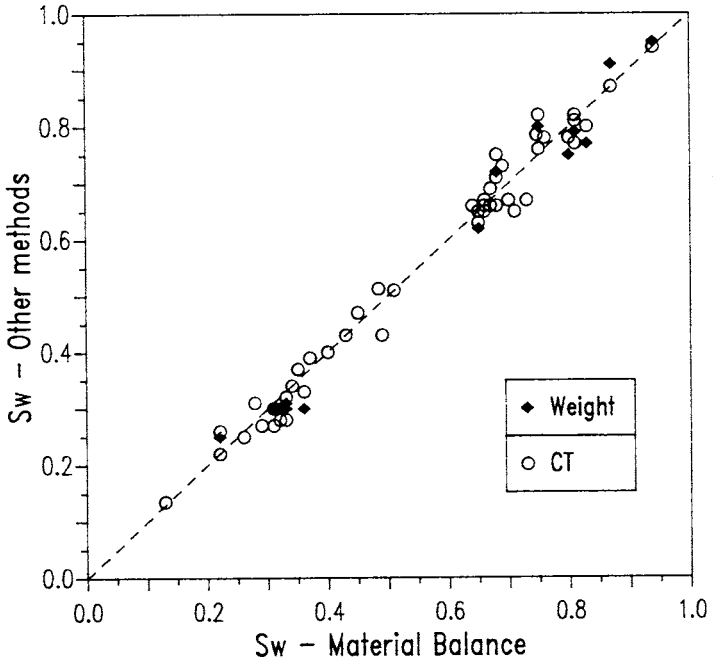

FIGURE 3 Reservoir sandstone samples, erroneous values excluded

Volume of Brine by Titration of Solvent with Karl Fischer Reagent

The method was tested on outcrop plugs versus material balance by adding known volumes of brine to the plugs. As shown in figure 1, there is a good agreement.

Figure 4 shows the results of 17 water saturation determinations on fresh reservoir sandstone samples, by both the Karl Fischer- and chloride titration method. Fluids used were refined oil, brine and brine added NaI. All tests were carried out at room conditions. The saturations are established by high rate waterfloods. Wettability ranged from near neutral to weakly water wet.

Six of these results indicate a higher S_w by the Karl Fischer-method. This is probably due to water being absorbed in the methanol from the air. In the other tests, special precautions were made to avoid such absorption, hence the agreement is much better.

In three of the tests, CT-estimates were used to verify the S_w-values. There is a good agreement in two of the tests.

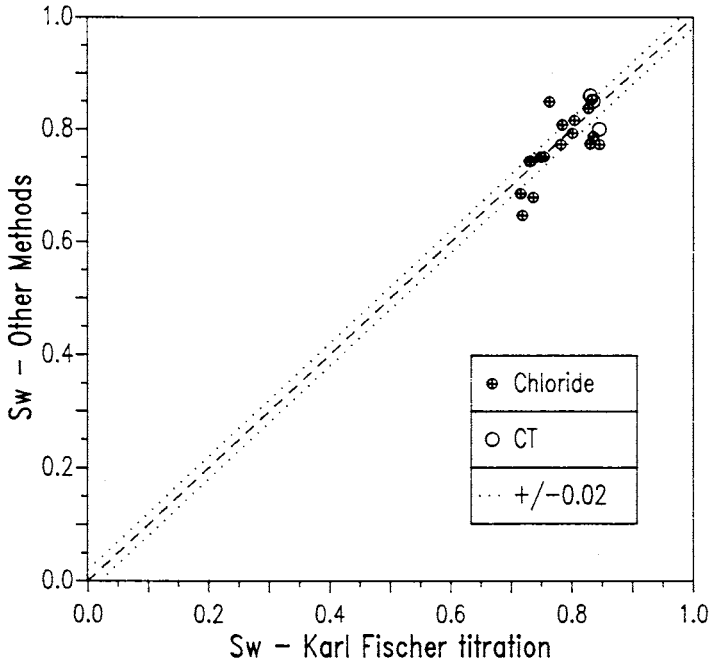

FIGURE 4 Karl Fischer-method used on fresh reservoir sandstone samples

If the Karl Fischer-method is performed as described in the given procedure, the data indicates that an accuracy of $\pm$ 0.02 S_w-units (see figure 4) can be expected. Less accuracy might be expected for low porosity rocks.

Volume of Brine by Titration of Chloride

Figure 1 shows a good agreement between data obtained from the chloride titration method (Cl-method) and the material balance on outcrop plugs.

In figure 5 the Cl-method is compared to Karl Fischer and CT-data on fresh reservoir sandstone samples.

Fluids used were refined oil, brine and brine added NaI. All tests were carried out at room conditions. The saturations were established by waterflooding. Wettability ranged from near neutral to weakly water wet.

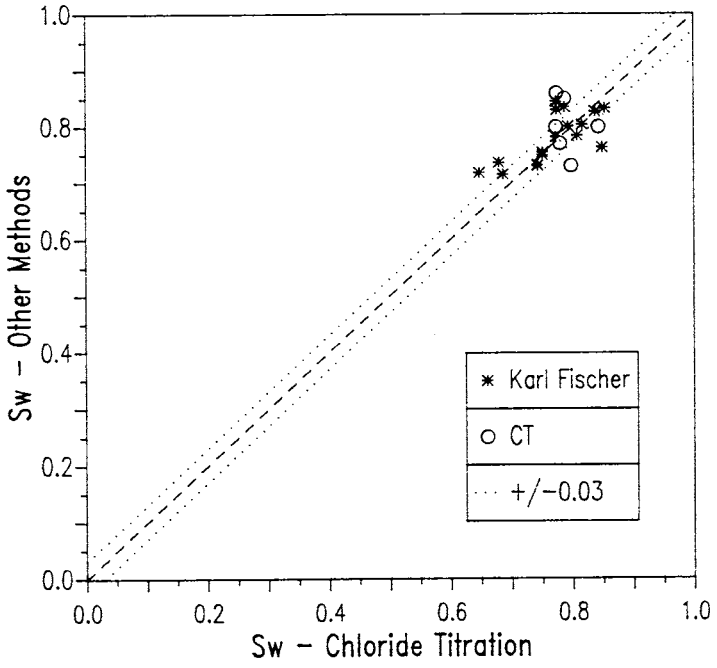

FIGURE 5 Cl-methods on used fresh reservoir sandstone samples

Most of the tests of the Cl-method are comparisons with the Karl Fischer method. This is discussed above. The result of the two methods agree well if correct procedures are used for the Karl Fischer method.

Only three of the six CT-estimates are within $\pm$ 0.03 S_w -units of the Cl-titration method. We have no explanations for the discrepancies.

Figure 6 shows the good agreement between data from the Cl-, the GOR- and material balance methods. All tests were carried out at reservoir conditions on near neutral and water wet reservoir sandstone samples.

The accuracy of the Cl-titration method is generally estimated to $\pm$0.03 S_w-units according to figure 6.

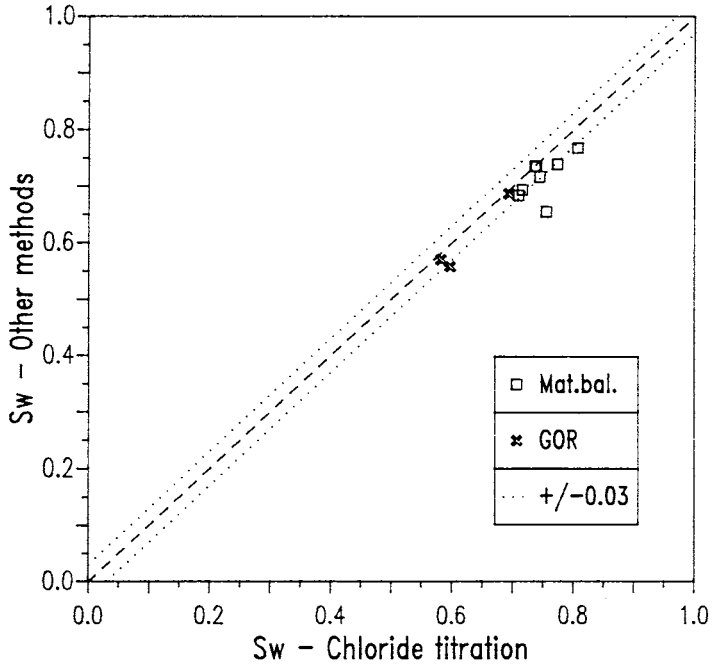

FIGURE 6 Cl-method tested at reservoir conditions

CONCLUSIONS

Based on the results from this study and general experience, the following conclusions can be made:

1. The Karl Fischer titration method is recommended as a fast and accurate alternative to the Dean & Stark method. The use of solvents might change the wettability, and rough plug ends should be avoided.
2. The cloride titration method is recommended as a good method of determining S_w at S_{or} during a series of displacement tests. Rough plug ends and heterogeneities can influence the data.
3. The tracer and the density methods can not be recommended until additional tests and improvements are made.
4. The CT-technique is recommended as a fast and accurate method of determining saturations at all levels. Heterogeneities require special precautions.
5. The material balance is in principle an accurate method. However, an error in a volume reading will influence all succeeding saturation values in a series of tests on a plug. Rough plug ends may influence the data.
6. Variables in the comparison tests, such as fluids, core materials, test conditions and wettability did not seem to influence the accuracy of the saturation determinations. The methods used to establish the saturations; centrifuging, flooding and spontaneous imbibition, did not affect the results.
7. For a fresh plug we recommend using the chloride titration method in the beginning and the Karl Fischer titration method at the end of a series of displacement tests.
8. For a cleaned plug we recommend performing chloride titration during and/or Karl Fischer titration at the end of a series of displacement tests, to verify the material balance.

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