

# **THE USE OF PARAMAGNETIC DOPANTS IN OPTIMISING THE ACCURACY OF CRITICAL AND RESIDUAL OIL SATURATION DETERMINATION**

Phil Mitchell, Lukasz Gromala and Mahmood Siddiqui

Engineering and Technology Services, Saudi Arabia

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## **ABSTRACT**

The use of paramagnetic dopants to alter the relaxation characteristics of reservoir fluids is well established in downhole procedures such as the log-inject-log method for determining remaining oil saturation with NMR (Nuclear magnetic resonance) logging tools.

However, in the laboratory under controlled conditions much of the effort expended in recent decades has been research to reduce uncertainty in surface relaxivity with the goal of determining fluid saturations in oil zones as well as estimates of permeability from logging tools.

Benchtop spectrometers are now affordable and are rapidly becoming a standard tool in most SCAL (Special core analysis) laboratories for numerous purposes including basic characterisation as well as rapid capillary pressure determination (in conjunction with centrifuge) among others. There is however, relatively little published work on the use of paramagnetic dopants to improve the practical determination of water and oil saturation – whose NMR  $T_2$  profiles in reservoir rocks typically overlap – as a tool to optimise end-point saturations for advanced studies by centrifuge or relative permeability waterflood studies.

This paper offers some practical insights into how NMR  $T_2$  (spin-spin relaxation time) profiles determined using paramagnetic dopants with judicious care to separate oil and water signal can not only provide important quality assurance but even become the definitive measure of saturation at crucial points in the saturation range during displacement studies. This is particularly true if detecting small changes in saturation is an experimental objective. Comparisons with established methods such as Dean-Stark and retort extraction are also presented to demonstrate the underused potential of NMR spectrometers as a practical laboratory tool for fluid saturation determination.

## INTRODUCTION

The accurate determination of residual oil saturation after some displacement experiment is a continuous challenge in the SCAL laboratory. Increasingly in recent times redundancy in the form of an independent cross-check of this parameter is mandated by clients as part of a rigorous quality control procedure. A non-destructive method to confirm final oil saturation is clearly preferable in this regard. The use of laboratory NMR spectrometers has yet to acquire a routine status in SCAL laboratories despite decades of research aimed at distinguishing between oil and water during NMR relaxation experiments both in the laboratory [1] and in operational environments [2].

In the case studies discussed in this paper, we chose to use Manganese as a paramagnetic dopant to separate the oil and water in the measure  $T_2$  distributions, which was added to the aqueous phase in the form of  $MnCl_2$ .

This paper focuses on two case studies, both carbonate core samples originating from Middle-East hydrocarbon producing formations, with somewhat differing objectives but in each case accurate final oil saturation being required to achieve the ultimate goal.

### **Case 1 – Residual Oil Zone (Between current and original gas-oil contact)**

Samples were cut and preserved at rigsite from core drilled with low-invasion technology from a depth zone believed to capture the original and current gas-oil contact in a field which has been under production for around a decade. The objective was to preserve samples and transfer them to the laboratory to enable determination of residual oil saturation in this zone to aid in recovery estimates from a gas cap expansion mechanism.

### **Case 2 – Critical Oil Saturation (In oil-water transition zone)**

A set of samples were taken and preserved at original oil saturation at rigsite in similar fashion to Case 1 with the objective of establishing critical oil saturation in the well – the threshold point in the oil-water transition zone where the oil first becomes mobile when moving from the water zone to the hydrocarbon zone. The final oil saturation was compared with the value determined by direct extraction (by retort) for quality assurance purposes.

## EXPERIMENTAL PROCEDURES

NMR  $T_2$  (transverse relaxation) decay measurements were made using an Oxford Instruments Maran Ultra spectrometer with 75mm probe operating at 35 °C and 2.2 MHz frequency. The typical CPMG (Carr-Purcell-Meiboom-Gill) sequence was used with an inter-echo spacing 0.4ms, 1024 echos and sufficient scans to attain a SNR (Signal to noise ratio) of at least 50. All samples were either soaked or flushed in brine solutions containing  $MnCl_2$ . The system response with increasing dopant levels was investigated in order to achieve an optimal level of dopant to attain the study objectives. A typical carbonate sample showing the transformation of the  $T_2$  distribution as a function of increasing dopant levels in the 100% water saturated state is given in Figure 1. The same sample was then flushed to high initial oil saturation prior to being flooded to residual oil. The sample was then flushed with increasing strength of dopant (without mobilising oil) to show the resulting transformation of the brine  $T_2$  distribution in the presence of a constant remaining oil saturation. The result is displayed in Figure 2.

### **Case 1 – Residual Oil Zone (Between current and original gas-oil contact)**

A total of eight samples were selected for study originating from the depth range in the well covering the interval between the original and current gas-oil contact and a short distance into the oil zone. The current gas-oil contact in the well was independently qualitatively determined from log data. The selected samples were pressure-saturated with undoped brine to remove any air. This provided a base  $T_2$  distribution to measure total porosity. The samples were then submerged in a concentrated solution of manganese chloride and the  $T_2$  distribution measured again after several hours of soaking and then after a period of two days to observe the transient effect of the dopant. The samples were then subjected to Dean-Stark extraction [3] to compare residual oil determination by the two methods.

### **Case 2 – Critical Oil Saturation (In oil-water transition zone)**

The transition zone samples had  $T_2$  distributions measured in the “as-received” state. They were then immersed in concentrated manganese chloride solution and the  $T_2$  distribution re-measured. Finally, they were flushed to produce any recoverable oil with a weaker solution (2g/l) of manganese chloride in order to retain signal in the aqueous phase and therefore derive total porosity as well as the saturations of the two aqueous and oleic phases present. The samples were then extracted by the retort method [3] as an independent quality assurance procedure to confirm final residual oil saturation.

## **RESULTS AND DISCUSSION**

### **Case 1 – Residual Oil Zone (Between current and original gas-oil contact)**

Table 1 shows residual oil saturation calculated from both the NMR data and by Dean-Stark extraction. Figure 3 shows a typical NMR response (Sample 3) before and after soaking in 1M Manganese-doped brine solution. The NMR-derived residual oil saturation was calculated by taking the ratio of the area under the peak associated with residual oil (above 10 ms relaxation time). The agreement between Dean-Stark-derived saturation and NMR is generally good and the position of the current gas-oil contact is unequivocal and independently qualitatively confirmed by wireline data.

### **Case 2 – Critical Oil Saturation (In oil-water transition zone)**

A summary of the results for this zone is given in Table 2. The objective in this zone was to determine oil saturation before and after flushing. The initial oil saturations were derived from the 100g/l doped case and the final oil saturations from the 2g/l doped experiment. The latter also yielded total porosity. The native-state experiment was not used quantitatively in the calculations but serves to illustrate that prior to doping, the two phases cannot be distinguished in the measured  $T_2$  distribution. The distributions after flushing yield bimodal distributions, with the shorter relaxation time mode (water) invariably larger than the peak at higher relaxation times (oil) since after flushing the samples are at residual oil saturation. Examples plots are given in Figures 4 & 5 showing the shallowest and deepest samples tested.

A plot of initial versus final oil saturation for the whole population in this zone is given in Figure 6. All samples exhibited some mobilisation of oil except the deepest sample whose initial oil saturation was low and evidently below the critical value. The linear extrapolation (black dotted line) on the plot gives a pessimistic indication of critical oil saturation since the true relation is essentially asymptotic to the equivalence (solid) line. The extrapolated value of 0.057 is only a little higher than the sole sub-critical example in the population (0.044) so the critical saturation clearly lies in a very narrow range somewhere in the region of 0.05. The NMR determinations were intended to be as accurate as possible in order to

detect small changes in saturation before and after flushing. Quality assurance of these data is similarly demanding so consideration was given as to whether retort or Dean-Stark final extraction would be the more accurate for this purpose. Accordingly, we subjected a significant population of samples spanning water volumes between around 0.5 ml to 4ml. The volume of water within the samples was known very accurately because they were artificially prepared with gravimetric determination of the added water to an accuracy of 0.01g. A comparison plot is given in Figure 7 with an equivalence line demonstrating the considerably better performance of the retort method, at least in our laboratory. Systematic water loss resulting in underestimation of water saturation is a perennial cause for concern in the Dean-Stark extraction method, especially for low water volumes as is demonstrated in the comparison plot.

## CONCLUSIONS

1. The method described in this paper provides an important quality assurance procedure for final saturation confirmation for a variety of SCAL procedures.
2. The procedure is non-destructive and therefore minimises or eliminates potential conflicts with other testing objectives.
3. The method can be tuned to very high accuracy if required to detect small changes in fluid saturation or when small or low porosity samples are being tested.

## REFERENCES

1. Horkowitz J., Hartman D.E, Clerke E.A, Coates G.R. “Residual oil saturation measurements in carbonates with pulsed NMR logs”, (1998).
2. Dunn K.-J, Bergman D.J, LaTorraca G.A.: “Nuclear Magnetic Resonance: Petrophysical and Logging Applications”, Handbook of Geophysical Exploration, Seismic Exploration, Volume 32, (2002).
3. API Recommended Practice 40, “Recommended Practices for Core Analysis, Second Edition”, *American Petroleum Institute*, 1220 L Street, N.W., Washington, D.C.20005, (1998).

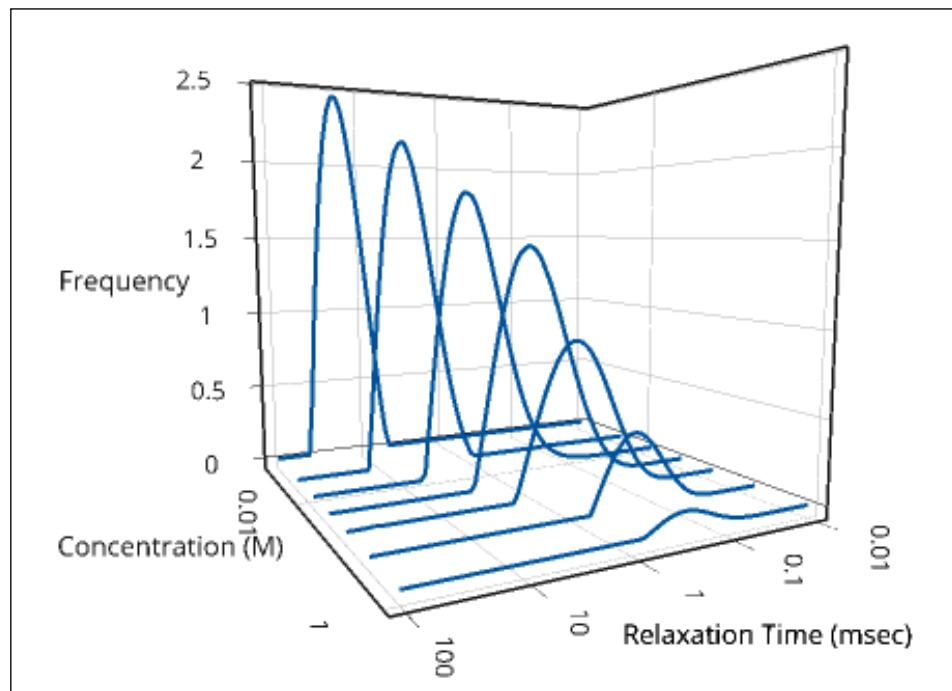


Figure 1 - Effect of increasing  $Mn^{2+}$  dopant concentration on NMR  $T_2$  distribution

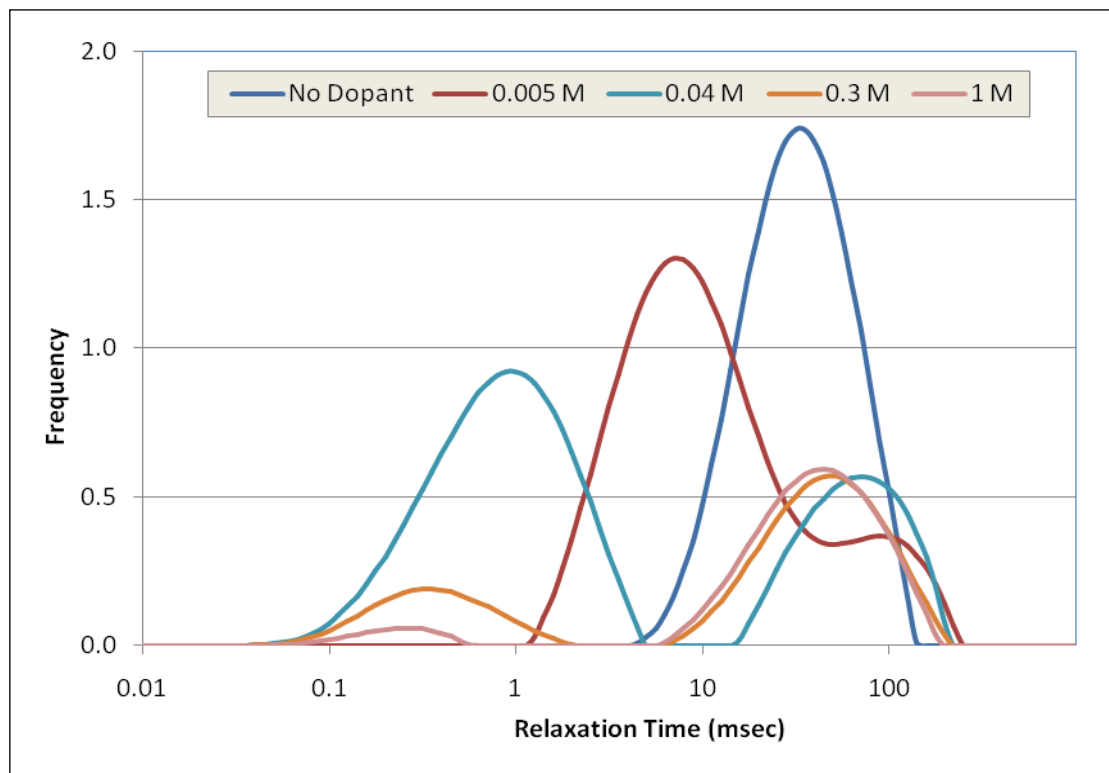


Figure 2 – Separation of brine and oil peaks (oil peak around 30 msec) with increasing  $Mn^{2+}$  dopant concentration

Table 1 - Residual Oil Saturation Comparison between NMR and Dean-Stark

| Sample | NMR Porosity frac | NMR Sor frac | D&S Sor frac | Zone         |
|--------|-------------------|--------------|--------------|--------------|
| 1      | 0.223             | 0.105        | 0.118        | Residual Oil |
| 2      | 0.195             | 0.215        | 0.256        | Residual Oil |
| 3      | 0.235             | 0.326        | 0.377        | Residual Oil |
| 4      | 0.173             | 0.310        | 0.328        | Residual Oil |
| 5      | 0.217             | 0.412        | 0.446        | Oil Zone     |
| 6      | 0.172             | 0.551        | 0.546        | Oil Zone     |
| 7      | 0.229             | 0.512        | 0.573        | Oil Zone     |
| 8      | 0.214             | 0.637        | 0.580        | Oil Zone     |

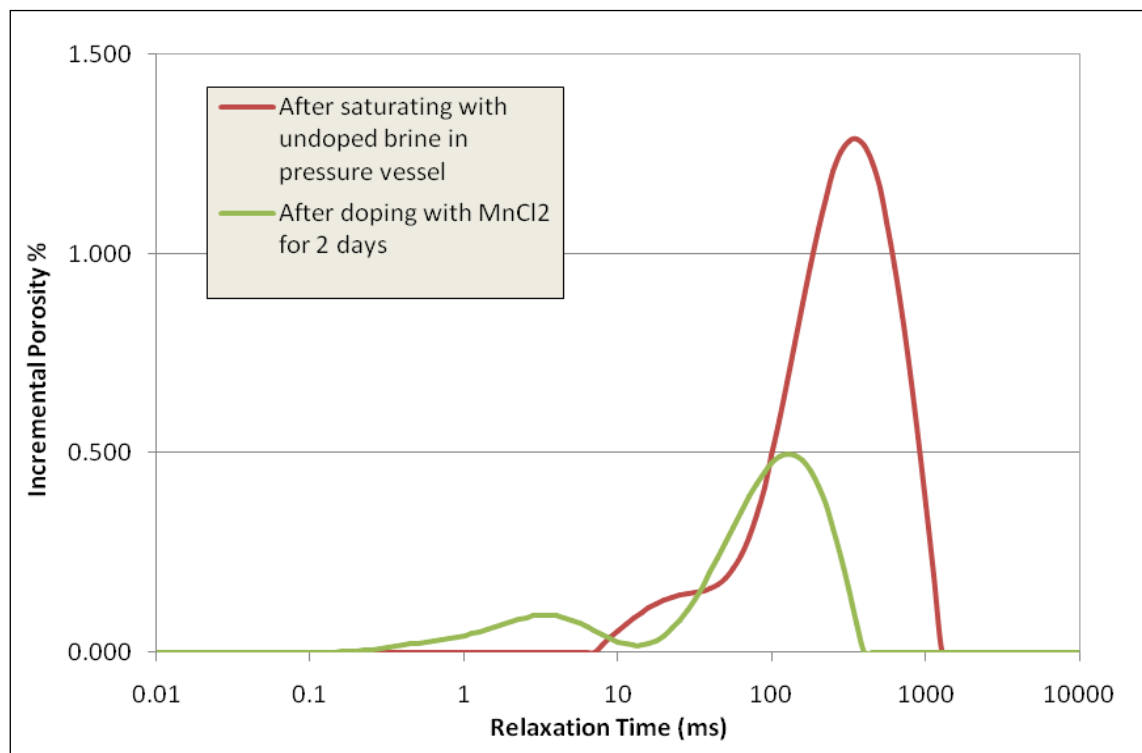


Figure 3 - NMR  $T_2$  distribution in sample 3 before and after  $Mn^{2+}$  doping

Table 2 – NMR T2 Data Summary (Transition Zone)

| <b>Sample</b> | <b>Depth</b> | <b>NMR<br/>Porosity</b> | <b>NMR<br/>Soi</b> | <b>NMR<br/>Sor</b> | <b>D&amp;S<br/>Sor</b> |
|---------------|--------------|-------------------------|--------------------|--------------------|------------------------|
|               | <b>D. ft</b> | <b>frac</b>             | <b>frac</b>        | <b>frac</b>        | <b>frac</b>            |
| 128           | 4992.45      | 0.237                   | 0.542              | 0.246              | 0.238                  |
| 134           | 4995.55      | 0.223                   | 0.450              | 0.256              | 0.244                  |
| 140           | 4998.55      | 0.256                   | 0.407              | 0.203              | 0.176                  |
| 146           | 5001.45      | 0.225                   | 0.477              | 0.175              | 0.177                  |
| 152           | 5004.25      | 0.228                   | 0.471              | 0.239              | 0.249                  |
| 158           | 5007.55      | 0.212                   | 0.430              | 0.237              | 0.225                  |
| 164           | 5010.65      | 0.212                   | 0.480              | 0.255              | 0.261                  |
| 170           | 5013.65      | 0.229                   | 0.436              | 0.216              | 0.218                  |
| 176           | 5016.55      | 0.215                   | 0.355              | 0.220              | 0.226                  |
| 182           | 5019.55      | 0.220                   | 0.520              | 0.213              | frac                   |
| 188           | 5022.55      | 0.189                   | 0.296              | 0.234              | 0.228                  |
| 194           | 5025.65      | 0.231                   | 0.375              | 0.255              | 0.263                  |
| 200           | 5028.55      | 0.233                   | 0.344              | 0.214              | frac                   |
| 212           | 5034.55      | 0.232                   | 0.366              | 0.214              | 0.223                  |
| 218           | 5037.45      | 0.239                   | 0.320              | 0.222              | 0.222                  |
| 224           | 5040.45      | 0.236                   | 0.397              | 0.212              | 0.217                  |
| 230           | 5043.55      | 0.258                   | 0.415              | 0.216              | 0.218                  |
| 236           | 5046.45      | 0.210                   | 0.173              | 0.138              | 0.137                  |
| 248           | 5052.65      | 0.218                   | 0.297              | 0.222              | frac                   |
| 254           | 5055.65      | 0.217                   | 0.250              | 0.188              | 0.194                  |
| 260           | 5058.55      | 0.250                   | 0.225              | 0.187              | frac                   |
| 272           | 5064.55      | 0.215                   | 0.210              | 0.152              | 0.150                  |
| 278           | 5067.55      | 0.209                   | 0.044              | 0.041              | 0.049                  |

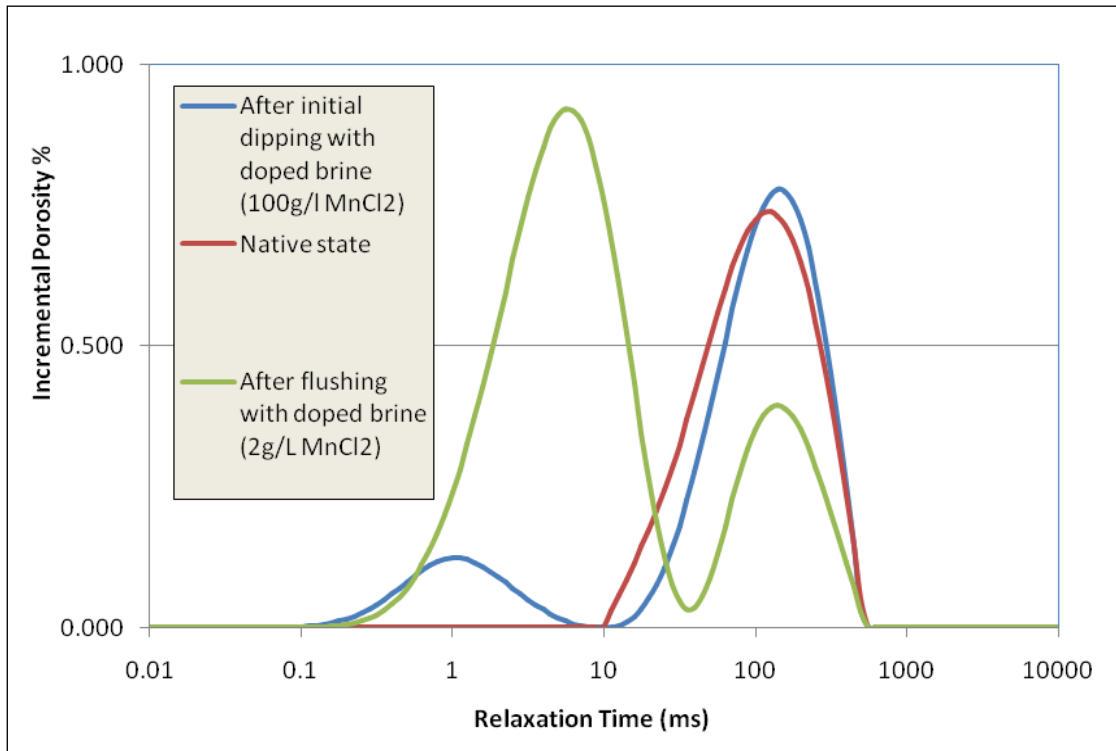


Figure 4 - Top of the oil zone before and after flushing with  $Mn^{2+}$  doped brine

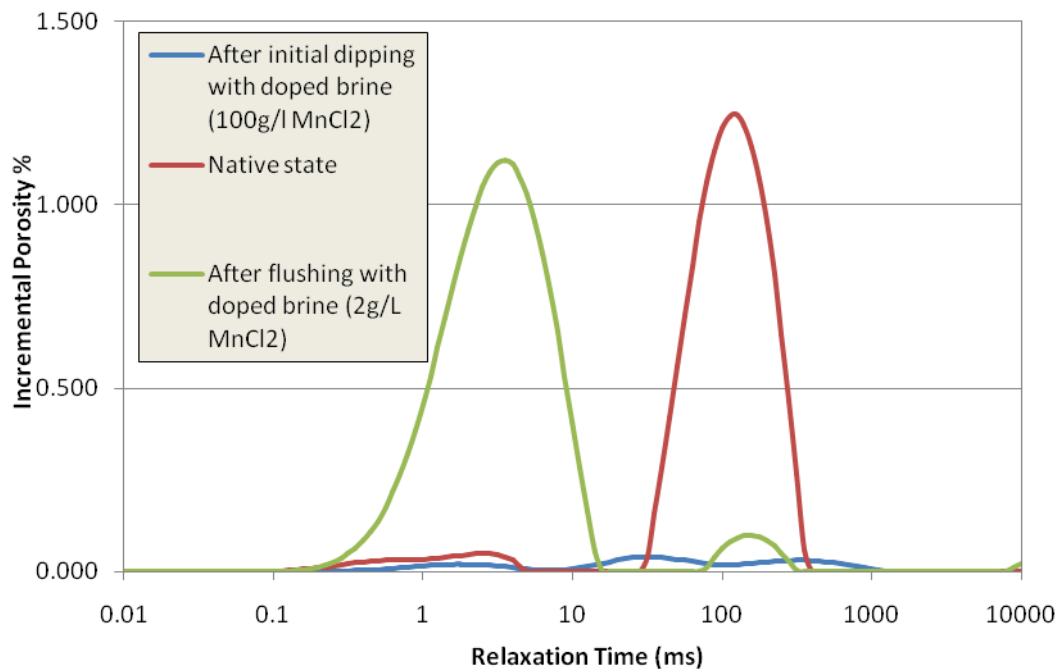


Figure 5 - Base of the transition zone before and after flushing with  $Mn^{2+}$  doped brine



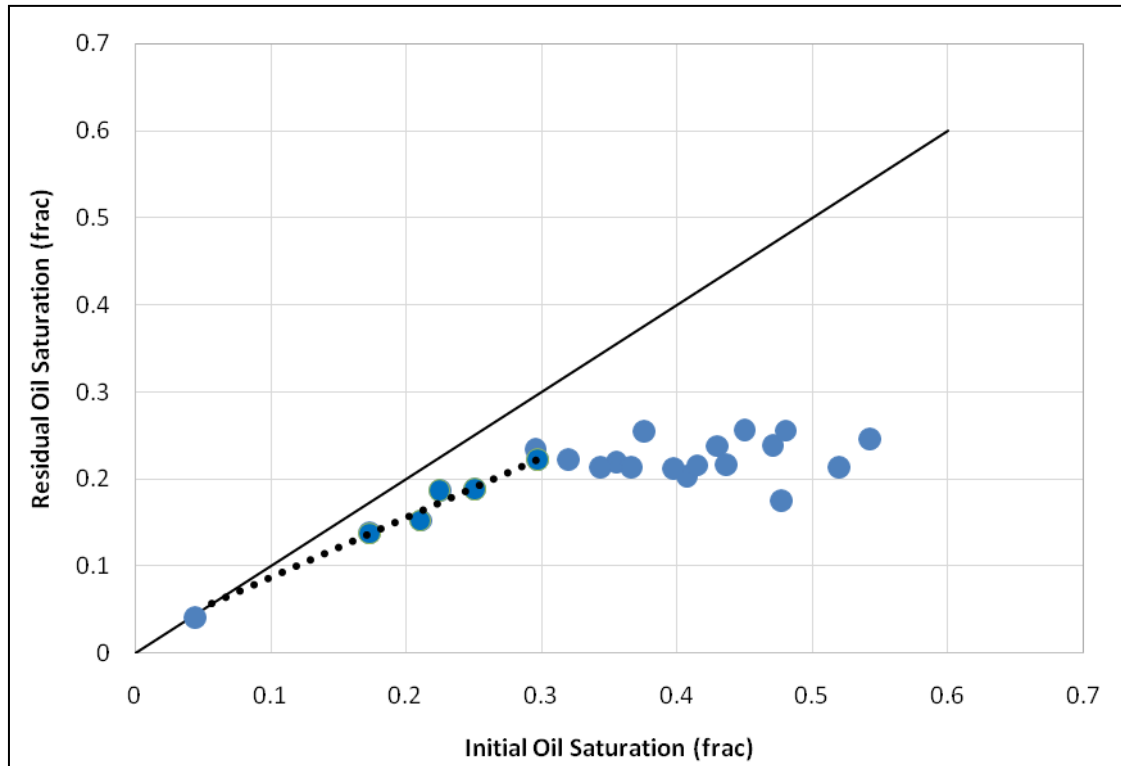


Figure 6 - Initial versus Residual Oil Saturation in Transition Zone

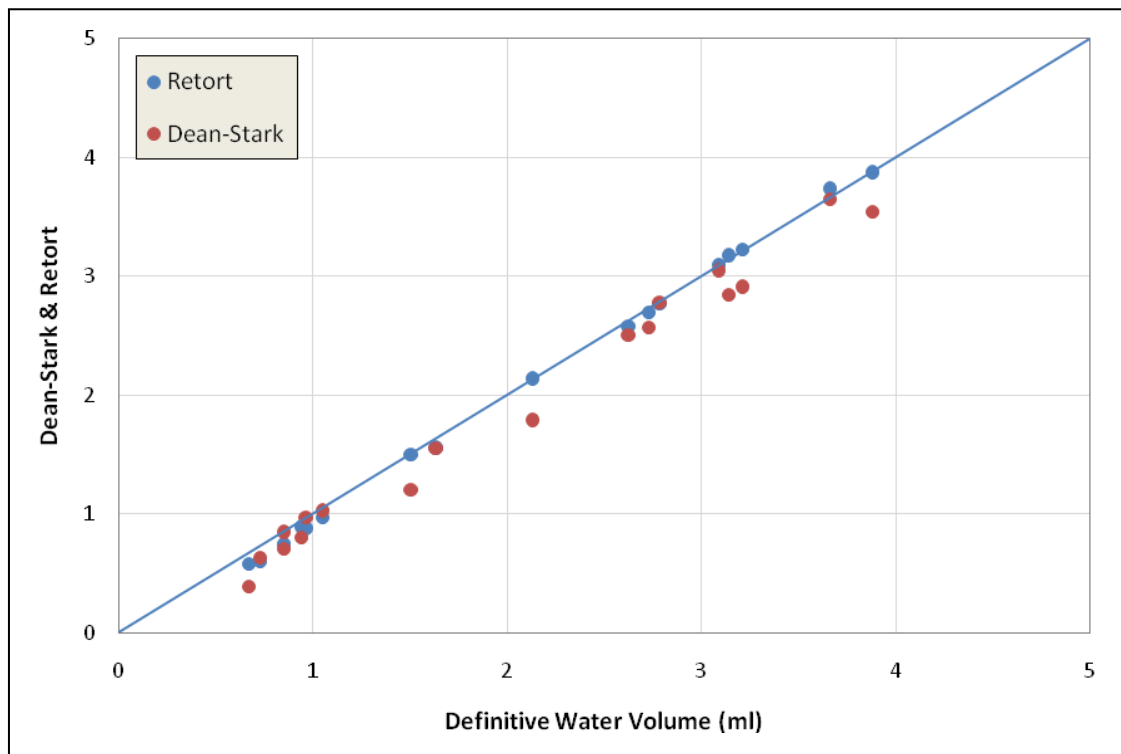


Figure 7 - Comparison between Dean-Stark and Retort water extractions