

SHALY SAND ANALYSIS WITH THERMAL MEMBRANE POTENTIALS

R.K.J. Sandor, J.P. Hofman, A. de Kuijper, J.A. de Waal and H.H. Yuan

Royal Dutch/Shell

ABSTRACT

A new method is described to investigate the contribution of clay conductivity, as characterised by the parameter Q_v , to the conductivity of rock. This method, which makes use of Thermally induced Membrane Potentials (TMP), allows the measurement of Q_v at reservoir conditions. A new experimental set-up, devised and constructed at KSEPL, has been shown to accurately measure Q_v of a core sample saturated with brine at laboratory conditions. First measurements confirm that TMP can also be measured on oil-saturated samples, although a new core-holder and better experimental procedures are necessary for quantitative evaluation. It is speculated, that the liquid permeability of a sample can be measured as a by-product.

INTRODUCTION

Throughout the history of well logging, the interpretation of resistivity logs in formations consisting of a mixture of shale and sand has posed a challenging problem. The presence of shale, due to its low resistivity, can lead to an underestimation of reserves. The correction for excess shale conductivity can be determined by measurement. In the past, several methods have been developed to measure the excess shale conductivity, characterised by the parameter Q_v , on core samples. The most common methods are discussed below, together with their main (dis)advantages.

The most widely used method is chemical titration. A sample is crushed and the amount of clay is determined by conductimetric titration. The main advantage is that the method is cheap. However, by crushing the sample, the geometrical contribution of the clay distribution to the clay conductivity is lost. In addition, the procedure itself is sensitive to the degree of crushing. Errors in excess conductivity due to clays have been shown to amount to 50% standard deviation for the Waxman-Smits data set [1]. Moreover, no subsequent measurements on the same sample can be performed after crushing.

A second method is the measurement of the Co-Cw curve. Here, the sample is saturated with a brine of known salinity (conductivity Cw) and the bulk conductivity (Co) is then measured. This is repeated for a wide range of salinities. The formation factor F^* can be estimated from the slope of the line connecting the two highest salinity points. The

excess conductivity at a certain salinity is then defined as the increase in C_o with respect to the line with slope $1/F^*$ passing through the origin. With this method, the excess conductivity can be measured very accurately, depending on the experimental set-up (for comparison: the typical accuracy of the Waxman-Smits data set is 1%). In principle, it is possible to perform measurements at elevated temperatures and pressures, at different oil saturations and with different cation types. Main drawback of the method is, that it is very time-consuming and therefore expensive. Moreover, the analysis with the F^* line is not model independent.

A third method is the technique of measuring the Concentration Membrane Potential (CMP) [2]. Here, a core sample is flushed on both sides with two brines of different salinity. The concentration difference leads to a difference in ion-activity of the ions, which will then diffuse through the core sample (the membrane), from the high salinity side to the low salinity side. Since the speed of the diffusion is different for cations and anions, an electrical potential will build up until an equilibrium is reached. Clay has the property of increasing the diffusion speed of the cations. This induces a larger potential difference, the magnitude of which can be directly translated to the Q_v of the sample. Although CMP's have been shown to be reliable and to give accurate results, there are some technical limitations to this method. Essential for the technique is a continuous concentration gradient over the sample. This can be difficult to realise for very high and very low permeable samples or for samples partly saturated with oil. For similar reasons, measurements under reservoir conditions are virtually impossible.

TMP: THEORY AND EXPERIMENTAL PROCEDURES

With TMP, the activity difference is induced by a thermal gradient over the core sample. Again, diffusion will occur from the high-temperature to the low-temperature side, giving rise to a thermally induced membrane potential. TMP has various advantages over CMP: first, it is much easier to achieve and maintain a continuous temperature gradient than a concentration gradient. Second, TMP experiments do not require flushing. This makes it a static experiment, which in principle allows the experiment to be performed under reservoir conditions (elevated pressure and temperature) and at partial oil saturations.

The price to pay is that the process of TMP is much more complicated: apart from ion and solvent fluxes, also the heat flux has to be taken into account. Therefore, one has to resort to the theory of irreversible thermodynamics for describing TMP. The few publications in the open literature about the subject all deal with thin membranes [3] and the interpretation is not well-established. Extending the theory in [3] to thick membranes (core samples), the following relation between the measured potential $\Delta\psi$ as a function of the applied temperature gradient ΔT and the activity of the ions in the solution a may be derived:

$$\frac{\Delta\psi}{\Delta T} = At + \ln a + B \quad (1)$$

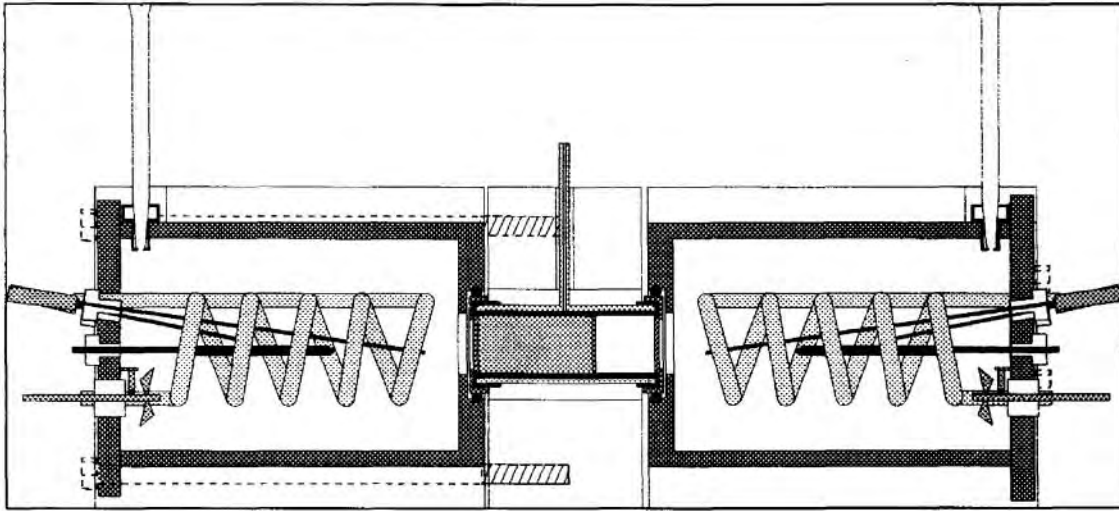


Fig. 1 Schematic drawing of the experimental set-up

Shown are two vessels with the pressurised core-holder in between. Each vessel is filled with brine and contains a heating tube, an electrode, two temperature probes, a burette to allow expansion of the brine and two mechanical stirrers to ensure temperature homogeneity within the cell. The whole set-up is thermally isolated from its surroundings and hooked up to a computer for data taking.

Here, A is a constant of known value and B is a constant containing the transport properties of the membrane. The activity a as a function of the NaCl concentration is well known from literature [4]. t^+ is the transport number of the cation which in the present study is Na^+ . It expresses the fraction of the current carried by cations and is the quantity related to Q_V , the shalyness of a sample; it has a value between 0.38 for a clay-free sample, and 1 for a pure shale. Hence, t^+ may be determined by measuring $\frac{\Delta\psi}{\Delta T}$ at minimally 2 different salt concentrations.

The experimental setup, shown in fig. 1, consists of 2 vessels, both thermally isolated, which are connected by a sample holder. Each vessel contains a heat exchange spiral for heating or cooling, two PT-100 temperature probes with an accuracy of 0.05 °C, an electric stirrer to ensure a homogeneous temperature distribution throughout the vessel and at the face of the sample, and an Ag/AgCl electrode to measure the potential. To allow the brine in the vessel to expand with temperature, the vessels are equipped with a burette. The spirals are each connected to a temperature bath to adjust the temperature. The whole experiment is automated, both in measurement and in control. In principle, the set-up is suitable to perform measurements at elevated temperatures up to 60 °C.

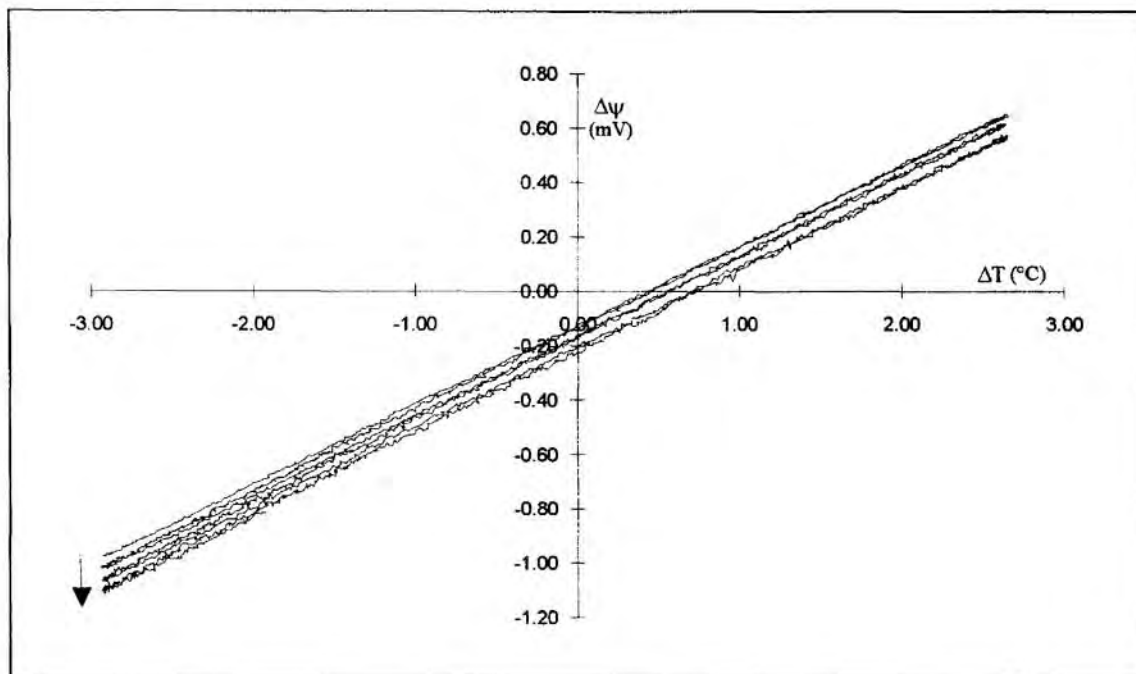


Fig. 2 Example of the measurement of the potential difference over the sample as a function of the temperature difference between the cells
Notice the electrode drift.

A set of 11 brine-saturated core samples, with varying clay content (Q_v : 0.03-1.5 meq/ml), porosity (ϕ : 12%-33%) and permeability (k : 1-1700 mD) was selected to serve as a benchmark. The samples were cleaned and saturated with brine, after which they were mounted in a pressurised sleeve to prevent bypass of brine along the surface of the sample. For experiments with partially oil-saturated samples, the brine was replaced with oil by a centrifuge. The salinity of the brine ranged from 8.4 up to 50 g NaCl/litre. The temperature gradient over the sample was generated by fixing one side at a constant temperature of 25 °C and cycling the other side around that temperature several times.

In fig. 2, the measured potential as a function of the temperature difference over the sample is displayed. As can be observed the relation is linear, which is in accordance with the theoretical prediction. Also observed is a drift of the measured potential during the experiment. This is due to deterioration of the electrodes and limits the total length of the experiment. On the other hand, cycling the temperature too fast causes incomplete diffusion of the ions through the sample, which leads to hysteresis effects. As a trade-off a cycling speed of 4 °C/hr was used for the water saturated samples and 1.5 °C/hr for the partly oil saturated samples, resulting in a total duration of one day/sample for the

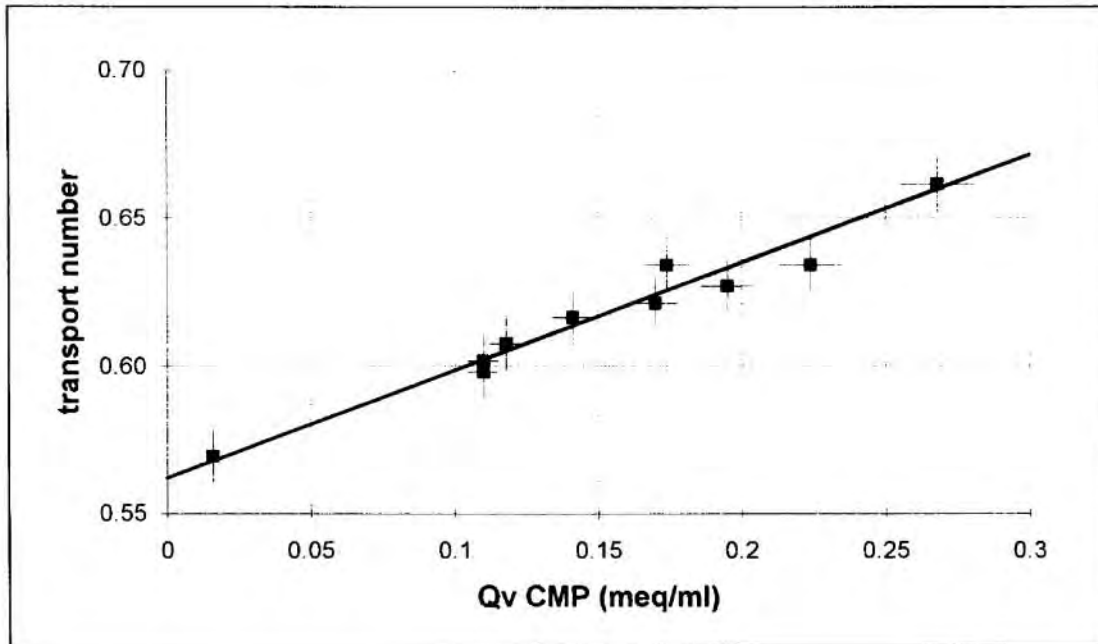


Fig. 3 The transport number t^+ as measured with TMP compared to the CMP derived Q_v for the samples with $Q_v < 0.3$ meq/ml

experiment at each salinity. The slope $\frac{\Delta\psi}{\Delta T}$ could thus be determined with an uncertainty of 4.2 - 7 $\mu\text{V}/^\circ\text{C}$, depending on the salinity.

RESULTS

In fig. 3 t^+ and its uncertainty, determined by measuring the above-mentioned slopes at 4 different salinities, is displayed as a function of the Q_v of the 11 samples, measured with the CMP method. As can be observed there is an excellent correlation between TMP and CMP and also the uncertainties of the two methods are similar. A surprising result was, that the value of B (see eq. (1)) is the same for all core samples: 0.204 ± 0.002 $\text{mV}/^\circ\text{C}$. This is unexpected, since the transport properties of the samples (e.g. the permeability) are vastly different. A possible explanation is, that the cycling speed during the experiments was low enough for all transport processes in the membrane to take place in an unhindered manner. If this observation holds generally for any sample, the determination of the clay content of a sample would be greatly facilitated, since only a measurement at a single salinity would be required. Future measurements on a larger sample set will help to clarify this point. A speculative application of increasing the cycling rate could be, that the liquid permeability of the sample might be measured directly from the lag in ion diffusion.

Note, that the transport number t^+ for the sample with the lowest clay content ($Q_v = 0.01$ meq/ml) has a value of 0.57 ± 0.01 . This is significantly larger than the theoretical value of 0.38, which is determined from CMP measurements. This discrepancy is not yet fully understood and will be further investigated by measurements on completely clay-free samples and a salt bridge. The latter experiment will serve as a means to determine how the temperature affects the electrodes, which generate a potential themselves during the measurement.

First experiments have confirmed, that TMP can also be measured on the partly oil-saturated samples. However, the scatter in the measured potentials was much too large for quantitative evaluation. This has been attributed to seepage of the oil out of the sample. A new core-holder and better experimental procedures should resolve this problem.

CONCLUSIONS

Thermal Membrane Potentials (TMP) is a new technique with which the clay content of a sample can be measured accurately. There is an excellent correlation with Concentration Membrane Potentials (CMP). The static nature of the experiment circumvents problems with CMP, such as measurements on very high or very low permeable samples and samples with a partial oil saturation. Moreover, the technique can, in principle, be applied at reservoir conditions.

An interesting observation is, that at the reported experimental conditions the permeability of the sample does not affect the TMP. This permits measurements at a single salinity and therefore facilitates the determination of Q_v .

Pilot experiments demonstrate, that the principle also works for oil-saturated samples, although some experimental problems need to be resolved.

It should be investigated, whether changing the experimental procedures allows the measurement of the liquid permeability of the sample.

Further theoretical work is required for a better understanding of the fundamentals underlying the transport processes through core samples due to temperature gradients.

REFERENCES

- [1] de Waal, J.A.: "The influence of clay distribution on shaly sand conductivity", Ann. Fall Tech. Conf. and Exhibition, SPE, A.I.M.E., SPE paper 16786 (1987)
- [2] Smits, L.J.M.: "SP log interpretation in shaly sands", *Transactions A.I.M.E.*, **243** (1968) 123
- [3] Tasaka, M.: "Thermal membrane potentials and thermoosmosis across charged membranes", *Pure and appl. Chem.* **58,12** (1968) 1637
- [4] "Properties of aqueous solutions of electrolytes", *CRC* (1992), pages 1428-1433.