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Improved Competence in Water Activity Measurement

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Abstract

While drilling oil and gas wells through shale formations, control of water transport into the formation with proper drilling fluid design is important for wellbore stability. Two critical mechanisms for water transport in shales are the chemical potential difference (i.e., water activity component) between the drilling fluid and the shale, and the hydraulic pressure difference between the wellbore pressure and the shale pore pressure.

The relative rate at which drilling fluids chemically transport water to the formation can be quantified by measurement of water activity. Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in the drilling fluid.

This paper discusses the application of an instrument that facilitates the ease of measuring water activity, replacing cumbersome and time-consuming hygrometer approaches. This particular meter uses chilled mirror technology which determines the dew point temperature of air equilibrated with a sample. Infrared thermometry pinpoints the sample temperature. An internal, data acquisition system converts these measurements to vapor pressures. The ratio of these values indicates the water activity level of the sample.

This novel instrumentation provides convenient, rapid and accurate water activity measurements for water- and oil-based fluids. It has been used to design new types of inhibitive drilling fluids. These experimental fluids were then evaluated with other laboratory tests to provide more definitive fluid performance characterization.

Introduction

Water activity is one tool used to evaluate the effectiveness of drilling fluids, particularly those that are oil- or synthetic-based, for inducing the pressure differential that must be applied to the low-salinity (formation) side of an osmotic system to allow water movement into the high-salinity side (drilling fluid) by osmosis.

Beyond the oilfield, water activity is a criterion used in many other industries. Water activity is more significant for qualitative considerations such as product stability shelf life (e.g. microbiological and enzymatic stability, aroma retention), handling characteristics (e.g. agglomeration of powders), physical properties (e.g. dimensions of paper) and chemical stability (e.g. pharmaceuticals).

Accurate water activity measurement is often critical for meeting health and safety regulations required by many of these industries. In light of the product volumes demanded on a commercial scale, quality assurance personnel need instrumentation to provide quick and accurate measurements.

Defining water activity

Water activity thermodynamic criteria are: pure water (a_w = 1.0) is the standard state, the system is in equilibrium, and the temperature is defined. In the equilibrium state:

$$\mathbf{m = m_o + RT \ln (f/f_o)}$$

where: m (J mol^{-1}) is the chemical potential of the system i.e. thermodynamic activity or energy per mole of substance; m_o is the chemical potential of the pure material at the temperature T (°K); R is the gas constant (8.314 J mol^{-1} K^{-1}); f is the escaping tendency of a substance; and f_o is escaping tendency of pure material (Mathlouthi) (Sereno) (Cazier).

The activity of a species is defined as a = f/f_o. When dealing with water, a subscript is designated for the substance,

$$\mathbf{a_w = f/f_o}$$

a_w is the activity of water, or the escaping tendency of water in the system divided by the escaping tendency of pure water with no radius of curvature. For practical purposes, this is closely approximated by the vapor pressure (f $\simeq$ p), therefore:

$$\mathbf{a_w = f/f_o \simeq p/p_o}$$

Thus, water activity can be expressed as the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water (p_o) at the same temperature. Relative humidity of air is defined as the ratio of the vapor pressure of air to its saturation vapor pressure. When vapor and temperature equilibrium are obtained, the water activity of the sample is equal to the relative humidity of air surrounding the sample in a sealed measurement chamber. Multiplication of water activity by 100 gives the equilibrium relative humidity (ERH) in percent.

$$\mathbf{a_w = p/p_o = ERH\ (\%) / 100}$$

Factors affecting water activity

There are several factors that control water activity in a system:

- Colligative effects of dissolved species (e.g. salt or sugar) in which solutes interact with water through dipole-dipole, ionic, and hydrogen bonds.
- Surface interactions in which water reacts directly with chemical groups on undissolved ingredients (e.g. starches and proteins) through dipole-dipole forces, ionic bonds (H_3O^+ or OH^-), van der Waals forces (hydrophobic bonds), and hydrogen bonds.
- Capillary effects where the vapor pressure of water above a curved liquid meniscus is less than that of pure water because of changes in the hydrogen bonding between water molecules.

It is a combination of these three factors that reduces the energy of the water, and thus reduces the relative humidity compared to pure water. These factors can be grouped under two broad categories as osmotic effects and matrix effects. When applied to an invert emulsion drilling fluid with a brine internal phase, increasing the salt (or other solute) concentration of the internal phase causes a_w to decrease as the vapor pressure of the solution decreases. However, a_w never reaches zero.

Temperature effects

Water activity is temperature dependent. Temperature alters water activity due to changes in water binding, dissociation of water, solubility of solutes in water, or the state of the matrix. Note that the water activity of any aqueous solution in equilibrium with ice (a_w) is equal to the water vapor pressure over ice to the water pressure over pure liquid water and does not depend on the solute's nature or concentration. Solutions with the same ice melting point therefore have the same water activity (Malusis) (Koop).

Free water versus bound water

Water activity describes the continuum of energy states of the water in a system. The water in a sample appears to be "bound" by forces to varying degrees. This is a continuum of energy states, rather than a static "boundness." Water activity is sometimes defined as "free", "unbound", or "available water" in a system. These terms are easier to conceptualize although they fail to adequately define all aspects of the concept of water activity.

Water activity instruments measure the amount of free water present in the sample. A portion of the total water content present in a substrate is strongly bound to specific sites on the chemicals that comprise the substrate. Such group sites may include hydroxyls, carbonyls, aminos, and other polar sites. Such groups are prevalent in typical drilling fluid additives (such as polysaccharides, synthetic polymers and surfactants). Water is bound by hydrogen bonds, ion-dipole bonds, and other strong chemical bonds. Some water is bound less tightly, but is still not available.

Shale/fluid systems consist of solid matrices that contain two kinds of connected voids with different size scales: a) pore spaces that are filled with freely diffusing fluids, and b) interlayer spaces between individual clay platelets occupied by bound water. Capillary pressures can be very high for low-permability water-wet shale where the average pore throat radii are 10 nm or 0.01 m (van Oort). The bound water is the result of the influence of intermolecular surface forces on the water. Such forces include van der Waals, hydration and electric double layers (Ghassemi).

Importance of water activity

Water activity measurement is an important issue in many industries. For the food industry, water activity is one of the most critical factors in determining quality and safety of consumable goods. Water activity affects the shelf life, safety, texture, flavor, and smell of foods. It is also important to the stability of pharmaceuticals and cosmetics.

Because water is present in varying degrees of free and bound states, analytical methods that attempt to measure total moisture in a sample do not always agree. Therefore, water activity tells the real story.

Water activity applications for borehole construction

During the drilling of oil wells, the physical-chemical interaction of drilling fluids upon formations involves ionic species and water moving to and from the rock. The mechanisms of transport in shales, such as osmosis, reverse osmosis, diffusion of ions and hydraulic pressure, can cause chemical changes in the shales and fluids. These chemical changes include variations in mud filtrate composition as well as shale matrix and pore fluid composition. The interaction of these changes becomes evident as shale hydration and swelling pressure. (Chenevert) (Santos) (Yu).

These mechanisms change the physical properties of the fluids, such as the weight and viscosity which are important for well stability and control of fluid invasion into shales (van Oort). Osmotic flows from the shale into the drilling fluid can cause a reduction of the pore pressure immediately adjacent to the borehole wall. Conversely, if the drilling fluid water activity is greater than the shale water activity, then osmotic flows from the drilling fluid into the shale are induced. This can be a destabilizing factor, especially in combination with high overbalance pressure that pushes fluid into the formation.

Stimulating the water flow out of the shale and into the wellbore can strengthen the shale. Water flow out of the shale and into the wellbore requires the existence of an effective osmotic gradient to offset the hydraulic overbalance. In order to build an effective osmotic pressure gradient, shale and the drilling fluid system must produce a high osmotic pressure gradient at the borehole wall and exhibit high membrane efficiency. The influence of water activity factors on the osmotic pressure gradient and shale membrane efficiency has spurred much interest and research (Keijzer) (Chen) (Barbour).

Instrumentation

There is no device that can directly measure water activity of a sample. However, water activity can be determined from the relative humidity of the air surrounding the sample when the air and the sample are at equilibrium. Therefore, the sample must be in an enclosed space where equilibrium occurs. Then the water activity of the sample and the relative humidity of the air are equal. The ERH (equilibrium relative humidity) can then be measured accurately.

Choosing a measurement tool

Two different types of water activity instruments are commercially available. One uses chilled-mirror dewpoint technology while the other measures relative humidity with sensors that change electrical resistance or capacitance. Each has advantages and disadvantages. The methods vary in accuracy, repeatability, speed of measurement, stability in calibration, linearity, and convenience of use.

Chilled-mirror theory

In chilled mirror dewpoint instruments, a sample is equilibrated within the headspace of a sealed chamber containing a mirror, an optical sensor, an internal fan, and an infrared temperature sensor. A thermoelectric cooler precisely controls the mirror temperature. An optical reflectance sensor detects the exact point at which condensation first appears. A beam of infrared light is directed onto the mirror and reflected back to a photodetector, which detects the change in reflectance when condensation occurs on the mirror. A thermocouple attached to the mirror accurately measures the dew-point temperature.

The internal fan provides air circulation which reduces vapor equilibrium time and controls the boundary layer conductance of the mirror surface. Additionally, a thermopile sensor (infrared thermometer) measures the sample surface temperature. Both the dew point and sample temperatures are then used to determine the water activity.

The instrument repeatedly determines the dew-point temperature until vapor equilibrium is reached. Since the measurement is based on temperature determination, calibration is not necessary, but measuring a standard salt solution ensures proper functioning of the instrument. If there is a problem, the mirror is easily accessible and can be cleaned in a few minutes.

Advantages of the chilled-mirror dew point method are accuracy, speed, ease of use and precision. The instrument can measure activities from 0.030 to $1.000a_w$, with a resolution of $\pm 0.001a_w$ and accuracy of $\pm 0.003a_w$. Measurement time is typically less than five minutes.

One drawback of chilled mirror instruments is that they cannot be used when samples contain propylene glycol because this chemical will condense on the mirror and interfere with water condensation measurements.

Another limitation of chilled mirror instruments is that extremely dry substances (i.e., those with water activities less than 0.03) absorb or desorb environmental moisture so slowly that the accurate measurement takes longer than the normal 5-minute time period.

The instrument shown in Figure 1 is a chilled mirror instrument type that the Baker Hughes INTEQ drilling fluids laboratory is currently using, supplied by Decagon Aqualab, Pullman, Washington.

Capacitive sensor theory

Some a_w instruments use capacitance sensors to measure water activity. Such instruments use a sensor made from a hygroscopic polymer and associated circuitry that transmits a signal relative to the ERH. The sensor measures the ERH of the air immediately around it. This ERH is equal to sample water activity only when the temperatures of the sample and the sensor are the same. Since these instruments relate an electrical signal to relative humidity, the sensor must be calibrated with known salt standards.

The standard salt solutions must be kept firmly capped to prevent spillage, evaporation or contamination. Free crystals should be visible in these solutions at all times. Each time before checking the test samples of mud and shale, the hygrometer must be calibrated. Calibration is done by measuring the relative humidity of each known salt standard. Each reading can take up to ten minutes to reach equilibrium. Relative humidity readings are then plotted on a graph against the known activities of the solutions. Some commercial hygrometers are equipped with chart recorders. The resultant line is the calibration curve for the probe and meter in use. Calibration must be done each time before measuring an unknown sample.

Capacitive instruments measure over the entire water activity range—0 to 1.00 aw, with a resolution of ±0.005a_w and accuracy of ±0.015. Some capacitive sensors need between 30 and 90 minutes to come to temperature and vapor equilibrium. Accurate measurements with this type of system require good temperature control.

The instruments shown in Figures 2 and 3 are different types of hygrometers supplied by Tech Instrumentation, Parker, Colorado.

Evaluating instrumentation

When evaluating water activity instruments, precision and accuracy are, of course, important considerations. But equally important to consider is susceptibility of the sensor to contamination and frequency of calibration. Also, when comparing water activity instruments, precision and accuracy over the entire range of water activities measured is important.

Based on extensive literature review of commercially available equipment, an Aqua-Lab Series 3 Model TE water activity meter was evaluated on a trial basis and then purchased. This device uses the chilled mirror technology design.

The following are water activities measured with the instrument, as compared to the accepted calculated water activity values for various solutions:

Salt Solution	Measured aw @ °C	ASTM value @ °C
3% Sea Salt	0.983 @ 20	0.983 @ 20
10% KCl	0.951 @ 20	0.953 @ 20
5% NaCl	0.973 @ 20	0.970 @ 20
10% NaCl	0.938 @ 20	0.935 @ 20
15% NaCl	0.890 @ 20	0.892 @ 20
20% NaCl	0.841 @ 20	0.839 @ 20
25% $CaCl_2$	0.751 @ 20	0.750 @ 20
80/20 Invert Emulsion w/25% $CaCl_2$	0.75 @ 20	

Vendor-supplied standards:

Salt Solution	Measured aw @ °C	ASTM value @ °C
6 M NaCl	0.757 @ 19.9	0.760 @ 20
0.5 M KCl	0.984 @ 20.9	0.983 @ 20
8.57 M LiCl	0.494 @ 20.1	0.496 @ 20
13.41 M LiCl	0.243 @ 20.1	0.245 @ 20

(Pytkowicz and CRC Handbook of Chemistry and Physics as references for ASTM)

This particular water activity meter was deemed viable, providing accurate and reproducible measurements. It has become a standard instrument when needed for INTEQ laboratory investigations.

Water activity and pore pressure transmission studies

Pore pressure transmission tests are conducted to determine the ability of the prototype fluid to control rate of pore pressure transmission into a formation exposed to a fluid. Shales, due to their low permeabilities combined with properties of clay structures, can act as inefficient semi-permeable membranes. Although a shale wellbore is not a perfect model of a semi-permeable membrane, general membrane behavior is as follows:

- With a concentration difference across an interface with no membrane, diffusion, governed by Fick's law, will drive water and solute from high concentration to low concentration until equilibrium is established.

- If a semipermeable membrane is present the water and solute invasion rates are reduced, and most importantly their relative invasion rate is changed. Hence the term membrane transfer rate selectivity.

- If the membrane is perfect, or 100% efficient with respect to a given solute, it will filter out, or reflect all of that solute. If it is imperfect, and allows some solute to flow, it is termed a "leaky" membrane. The efficiency of a leaky membrane is characterized by the reflection coefficient. This coefficient varies between 0 and 1 depending on what percentage of the solute is filtered out.

A 100% percent efficient semi-permeable membrane gives rise to the definition of osmotic pressure. A concentration difference across a semi-permeable membrane results in a chemical potential energy difference. The chemical potential driving the water from the low concentration to the high concentration can be balanced by an opposing hydraulic pressure difference. The pressure difference required to prevent any net water transfer across the membrane is called the osmotic pressure. (Stowe)

A critical component of a fluid's ability to control pore pressure transmission rate in shales is water activity due to the osmotic pressure effect. Pore pressure transmission tests were conducted on unweighted invert emulsion fluids, utilizing preserved Pierre II shale core. Emulsions were prepared with aqueous phases of different water activities to determine what impact this would have on pore pressure transmission reduction. These fluids were compared with a standard calcium chloride invert emulsion fluid to see if performance was similar for reducing pore pressure transmission.

Pore pressure transmission results indicated that a semi-permeable membrane was formed at the shale/fluid interface and connate fluid was actually drawn out of the shale into the emulsion. (It should be noted that the activity of the Pierre shale test core was 0.983.) Note that resultant pore pressure transmission trends correspond with the respective measured water activities of the emulsion fluids (see Figure 4).

The same type of test format was applied for water-based fluids, each composed of equivalent amounts of additives (polymeric encapsulants, viscosifiers and filtrate reducers) but using different salt brines of varying water activities. Again the resultant pore pressure transmission trends correspond with the water activities of the water-based fluids (see Figure 5).

Other laboratory applications for measuring water activity

The duties of a drilling fluid laboratory are multi-faceted, which often include technical support in:

- extensive API protocol testing on submitted field mud samples.
- formulating and testing fluids to meet tender specifications for cost and performance.
- analyzing geological specimens such as shale cores and cuttings, with resultant data used for well program designs.

Water activity measurements may be requested as one parameter for evaluating fluid samples to determine if optimum inhibitive properties are being met while drilling operations are in progress. The following demonstrates comparability of measured a_w by meter to titrated chloride content (as determined by standard API procedures) with corresponding ASTM water activity value for submitted drilling fluid samples from field operations:

Chlorides, ppm (titrated)	% NaCl content	ASTM aw (20°C)	aw, measured by meter (20°C)
115000	16.8	0.87	0.86
135000	19.5	0.84	0.83

Water activity of preserved shale core samples can also be determined. Knowing beforehand such information in addition to x-ray diffraction analysis can aid in designing an appropriate well program. For example, if a submitted shale sample was to have an a_w of 0.90, then a drilling fluid having the same or lower a_w would be chosen for providing optimum borehole stabilization. Water activity measurements of completion fluids can also be used as a quick assessment of salt concentration.

Conclusions

The application of a meter which uses chilled mirror technology has been found to facilitate ease of measuring water activity, replacing cumbersome and time-consuming hygrometer approaches. The instrumentation provides convenient, rapid and accurate water activity measurements for water- and oil-based fluids.

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Figure 1

Figure 2

Figure 3

Figure 4: Pore pressure transmission tests results for water-into-oil emulsions of varying a_w

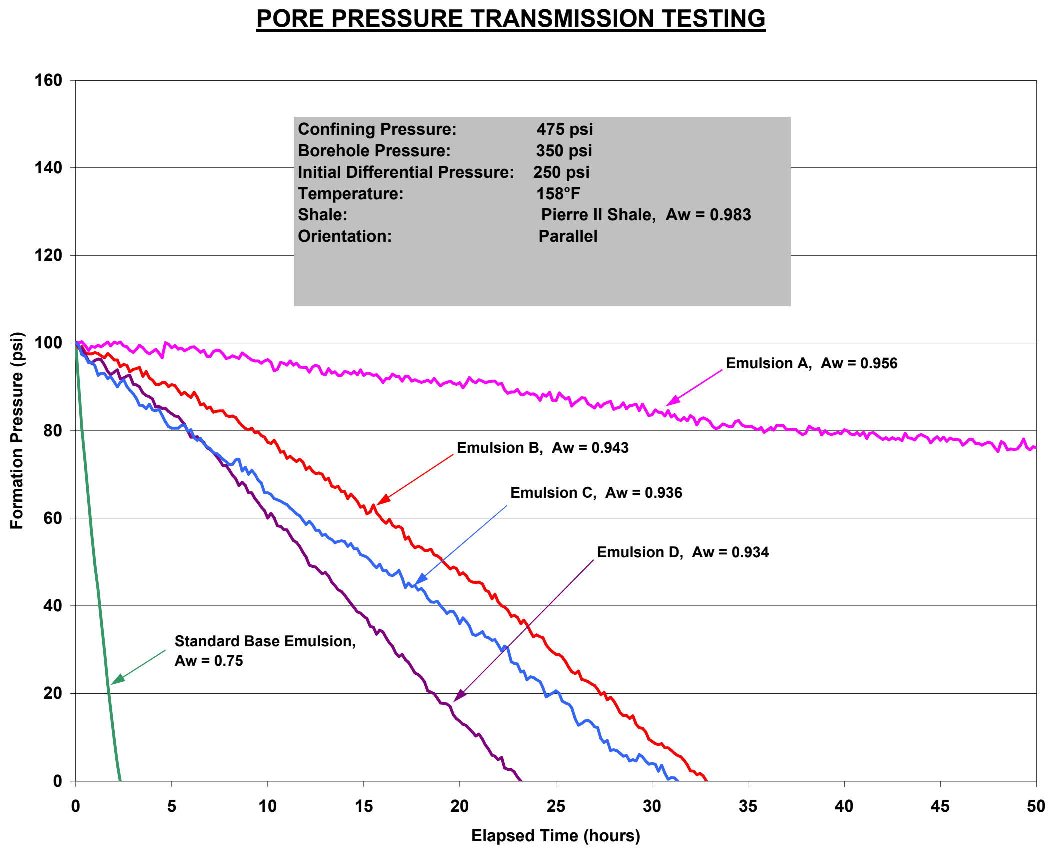

Figure 5: Pore pressure transmission tests results for water fluids of varying a_w