"Enhanced Wellbore Stabilization and Reservoir Productivity with Aphron Drilling Fluid Technology"

Topical Report: Task 1.3 "Aphron Air Diffusivity"

by

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Objectives

Determine the effects of pressure and chemical composition of aphron drilling fluids on the rate of loss of air from aphrons and, hence, the importance of air loss on the survivability of aphrons.

Project Description

A method is developed to monitor the rate of loss of air from aphrons at elevated pressures. This technique is used to study the effects of pressure, fluid composition and rates of pressurization and depressurization on the kinetics of air loss from aphrons in APHRON ICS^{TM} drilling fluids.

Conclusions

Initial attempts to measure the diffusion rate of air out of aphrons relied on monitoring the concentration of dissolved oxygen (DO) in the surrounding fluid. Lack of a DO probe resistant to elevated pressure and temperature was considered a temporary setback, until it was learned that DO reacts relatively quickly with some organic components in the drilling fluid. Because of the very low concentration of oxygen, there is little effect on the components or bulk properties of the fluid. However, for the measurement of the loss of air from the aphrons, a different approach was required. Direct optical imaging was determined to be suitable for this purpose. This became possible with the development of an ultra-thin high-pressure transparent viewing cell.

Direct optical imaging not only reveals the dimensions of a population of bubbles, but also the dimensions of single bubbles, so that the technique can be used to characterize the effects of environmental variables on bubble size. The development of an ultra-thin high-pressure viewing cell enables imaging of opaque fluids, too, thus obviating the need for the ABS. This viewing cell was used to carry out the Aphron Air Diffusivity task.

In the course of fulfilling the deliverables of the Air Diffusivity task, it was found that aphrons can survive compression to at least 4000 psi (this result is not discussed in this report, but a video of the test can be found on the website www.masitech.com). The number of visible aphrons at that pressure is small, and the survivors have a limited life. Nevertheless, this finding is of enormous significance, in that it provides the first clear evidence that aphron technology may be useful at pressures higher than previously thought (3000 psi).

Compression of large aphrons initially results in volume reduction that is inversely proportional to the absolute pressure, as is the case for conventional bubbles. However, the latter do not survive pressures of a few hundred psi for more than a few seconds, whereas aphrons can survive pressures of a few thousand psi for at least a few minutes. After initial compression to a fixed pressure, bubbles (including aphrons) continue to shrink at a rate that depends on a number of factors, including fluid composition, bubble size, and rate of pressurization. Continuous shrinkage of bubbles at elevated pressure is caused primarily by diffusion of air out of the bubble and dissolution of the expelled air in the aqueous medium. For aphrons, the rate of diffusion of air is orders of magnitude lower than for conventional bubbles. However, when the aphrons reach a critical minimum size, on the order of 50 μm diameter, they undergo a structural change that leads to fairly rapid collapse, and the aphrons disappear.

When an aphron system at elevated pressure is depressurized, surviving aphrons increase in size as per the modified Ideal Gas Law. Air that was lost from aphrons at elevated pressure and is in solution can be released if the pressure is reduced to a level low enough that the aqueous medium becomes supersaturated with air. The released air preferentially enters existing aphrons, though new aphrons can be formed, too.

Future Work

Optimize the performance of the polymer-based aphron drilling fluid, focusing on how composition and method of aphron generation affect the fluid's microstructure.

Experimental Approach

The kinetics of air loss from aphrons was initially planned to be investigated by monitoring the increase in concentration of dissolved oxygen. Technical difficulties with the dissolved oxygen probes and depletion of oxygen by some components of the drilling fluid created too many difficulties for this approach to be viable. Instead, direct optical imaging was adopted to monitor bubble size as a means of measuring the rate of loss of air from aphrons.

Monitoring Dissolved Oxygen

The first approach taken in measuring the rate of loss of air from aphrons was carried out by directly monitoring the amount of dissolved oxygen in the bulk drilling fluid. The proposed method was to use a conventional dissolved oxygen (DO) probe in which a probe could provide in parts per million (ppm) the actual concentration of DO in our drilling fluid systems. From the rate of increase in the concentration of DO, a diffusion coefficient for oxygen could be determined, and the rate of loss of air could be calculated.

First it was important to establish the expected concentration of DO under ambient conditions. This is a function of the water activity of the fluid. Measurement of water activity of a typical Aphron ICSTM drilling fluid prepared with fresh water showed that the water activity of the mud is essentially that of fresh water, i.e. 1.0. Tables of oxygen level for water under ambient air pressure at room temperature indicate that the concentration of DO should be about 9 ppm.

Several DO probes were tested. Some proved to be more reliable than others, but each had its own advantages and disadvantages. These are summarized in Table 1.

Table 1. Summary of Properties of Various Dissolved Oxygen Probes

Probe Type	*Pressure*	*Temperature*	*Principle Operation*	*Interference*	*Response Time*	*DO measurements*
Conventional	Ambient	Ambient	Anode – Cathode Reaction	Viscosity	Slow	< 4ppm to 0ppm
FOXY T-1000	Up to 3000psi	Up to 150ºF	Fluorescence	pH, Viscosity	Slow	< 2ppm to 0ppm
HACH SC100	Ambient	Ambient	Luminescence	None	Fast	Excellent Results

The first probe tested was a Conventional DO probe. This probe is only to be used at ambient temperature and pressure. Results indicated a gradual decline in DO concentration from a value of about 9 ppm. This effect was thought to be related to the viscosity of the fluid For this probe to work, it is necessary that DO diffuse through the bulk fluid through the membrane cap. Due to the very high low-shear-rate viscosity of the fluid, diffusion of oxygen across the membrane cap is hindered to such an extent that the probe tip cannot distinguish between gaseous O_2 from the aphrons and dissolved O_2 from the bulk drilling fluid. In addition, the probe is not suitable for a closed system, because the polymer in the cap reacts with oxygen and depletes its concentration in solution.

The second probe tested was the FOXY-T1000.. The FOXY probe uses a new technology of flourescence quenching to measure DO, and depletion of oxygen is not an issue. In addition, the FOXY probe can be subjected to high temperatures and pressures. Figures 1 and 2 demonstrate the suitability of the FOXY probe. When the probe was subjected to water at room temperature, the DO reading gave the correct value of ~9ppm. When the probe was immersed in the APHRON ICS^{TM} fluid, however, then exposed to air and back into the fluid, the DO values were 2 ppm, 8 ppm and 2 ppm, respectively. It was not known at the time why such a low ppm was being measured in the APHRON ICS^{TM} fluid. We felt that there was a local phenomenon that was delaying the probe's response at the sensor tip, since the probe gave the correct reading when exposed to water. At this point in our research, the probe was shown to be unacceptably delicate (Silicon coating on probe tip pealed off), and after prolonged exposure the FOXY probe gave incorrect values. See Figure 3.

Figure 1. DO Reading of FOXY Probe in Water at Room Temperature

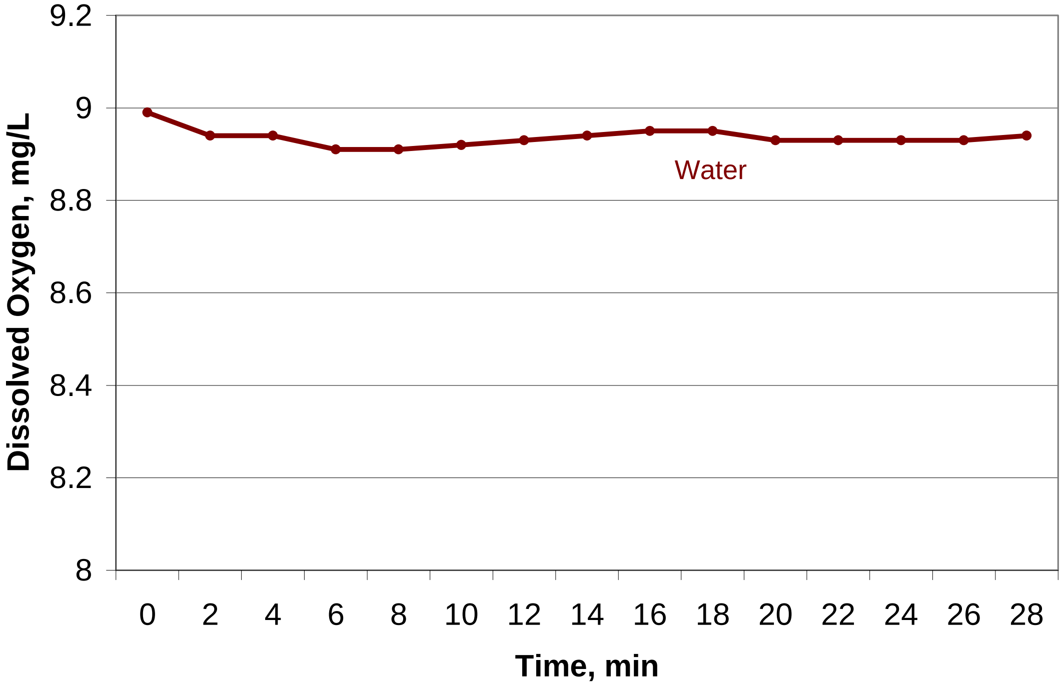


Figure 2.   Effect of Aphron ICS Mud on DO Reading of FOXY Probe

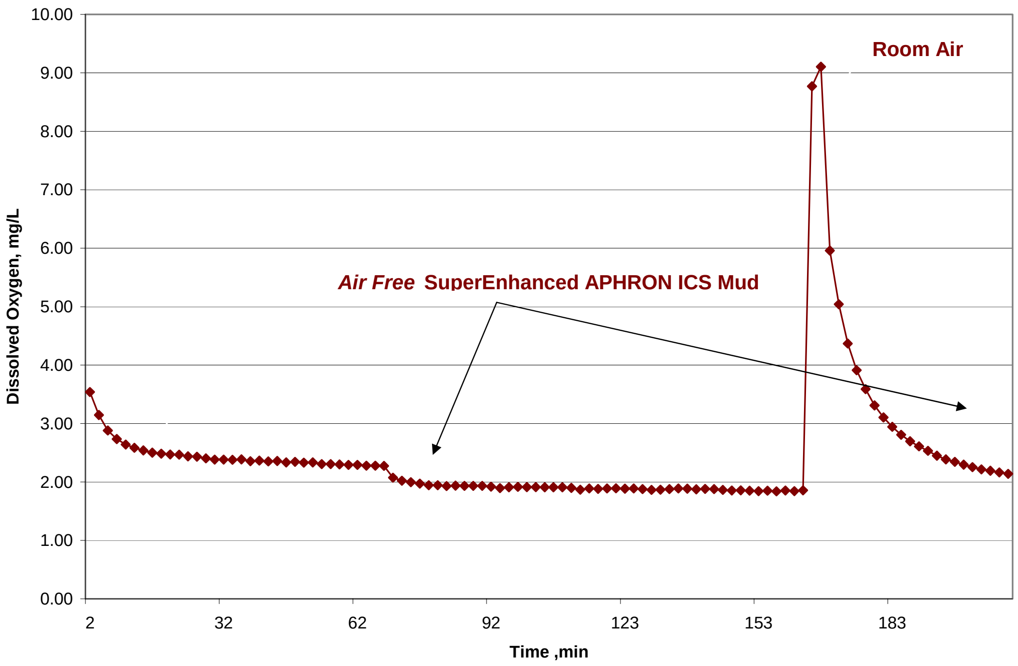


Figure 3. FOXY probe

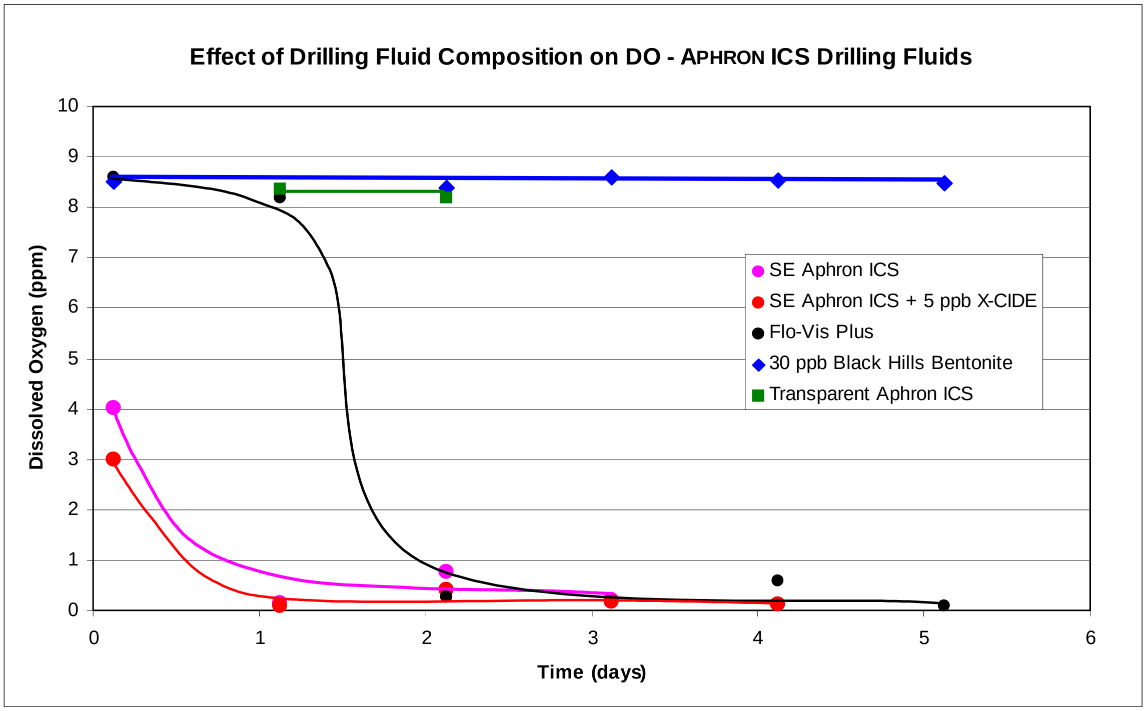
Sol-gel (No overcoat)

Silicon adhesive covering Sol-gel

Our last attempt to a direct approach in measuring dissolved oxygen was using a probe that used a new luminescence technology, the HACH SC100. An advantage of this probe was that the sensor tip was not so delicate which showed to be most reliable. The HACH SC100 showed very encouraging results. The following is what was concluded:

Response time was rapid, generally giving a steady-state value of DO within 15 to 30 min, depending on viscosity and how the probe was introduced into the sample. As shown in Figure 4, the steady-state DO values recorded for the SuperEnhanced (SE) APHRON ICS^{TM} mud dropped very quickly. Indeed over the initial 3-hr period between mixing the mud and getting a steady-state DO reading, the concentration of DO had already dropped by more than 50%. Initial readings were approximately 8.5 ppm (parts per million). As shown in Figure 4, a 30-ppb slurry of Black Hills bentonite retained that value indefinitely. Apparently the “Transparent APHRON ICS” (transparent Enhanced APHRON ICS^{TM}) mud, which lacks the hemicellulose, starch, MgO and EMI-802 of the regular SE APHRON ICS^{TM} mud, also remained high, at least for the first couple of days. But the regular SE APHRON ICS^{TM} mud depleted DO very rapidly, so that within a day the concentration of DO was negligible. This system contains a low level of X-CIDE^{TM}, a powerful biocide. Xanthan gum, one of the main components of the APHRON ICS^{TM} mud system, can undergo aerobic biodegradation, but the process is thought to be relatively slow. Tests here indicate that when long-term DO monitoring tests were conducted of a pH-adjusted solution of xanthan gum, here in the form of a premium grade called FloVis Plus^{TM}, DO did indeed fall, though not as rapidly as it did in the SE APHRON ICS^{TM} mud system. The FloVis Plus^{TM} solution did not contain any biocide. Thinking that aerobic biodegradation might be involved in the depletion of DO in the SE APHRON ICS^{TM} mud, the level of X-CIDE^{TM} was increased from 0.1 to 5 ppb. As is apparent in Figure 4, even with 5 ppb X-CIDE^{TM}, the depletion rate of DO was not affected significantly. It appears, therefore, that some of the other components in the SE APHRON ICS^{TM} system cited above, namely the hemicellulose and starch, are very likely reacting directly with dissolved O_2. This process is so rapid -- and in all likelihood is even more rapid at elevated pressures and temperatures -- that it is not possible to use DO as an indicator of the rate of transport of air from aphrons into solution.

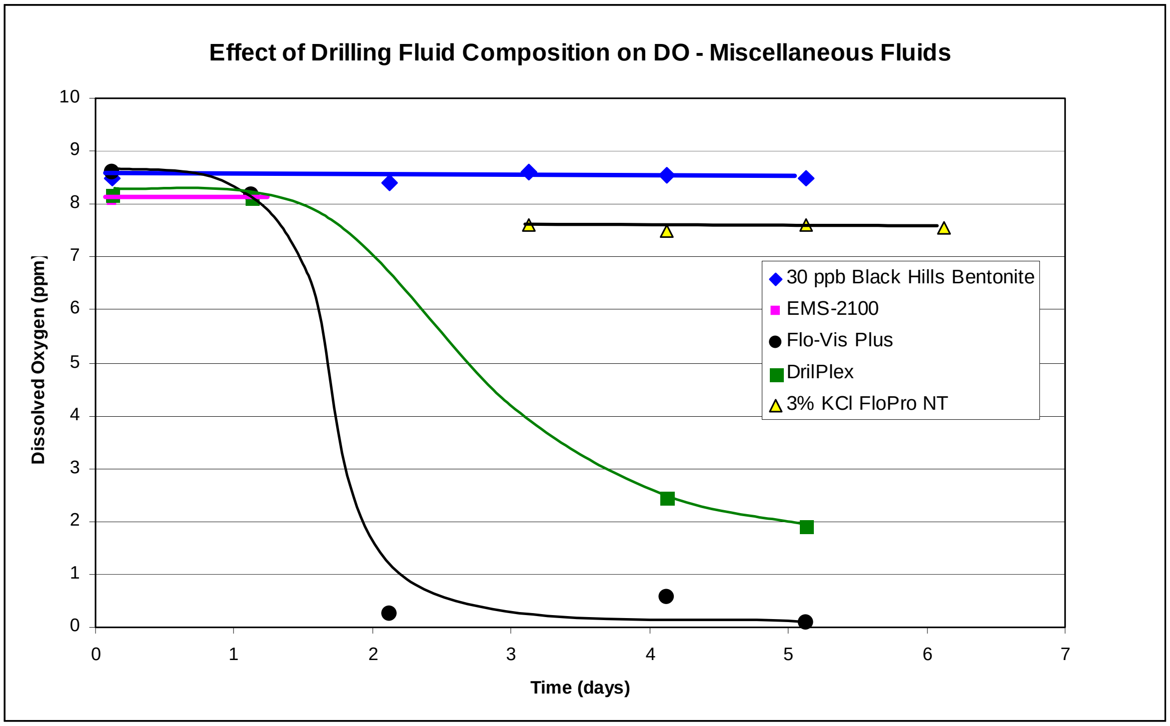
Figure 4. Effect of Time on DO Concentration in Aphron ICS Drilling Fluids



Similar long-term exposure tests were run with other fluids, as shown in Figure 5. While the HYSSTER^{TM} (nee EMS-2100, a clay-based aphron drilling fluid) and 3% KCl FLOPRO NT^{TM} systems (with biocide) did not show any indication of a drop in DO over time, DRILPLEX^{TM} did exhibit a steady drop in DO, though not as rapid as FloVis Plus^{TM} without biocide. The DRILPLEX^{TM} system contains an <u>organic</u> fluid loss control agent which is thought to react easily with oxygen.

Thus, although viscosity is not a problem and aerobic biodegradation can be controlled, some components of the SuperEnhanced APHRON ICS^{TM} mud appear to serve as substrates for direct oxidation. This leads to the inescapable conclusion that, even at ambient pressure and temperature, DO reacts with these components so rapidly that monitoring of DO is <u>not</u> an acceptable method of measuring the rate of loss of air from aphrons.

Figure 5. Effect of Drilling Fluid Composition on DO – Miscellaneous Fluids



Monitoring Bubble Size

Quantitative inspection of bubble size was possible with the National Instruments - Vision Assistant Optical Imaging Software. The primary areas of interest included:

- *Effects of Fluid Composition on Aphron Stability*
- *Effects on Aphron Survivability with Starting Bubble Size*
- *Effects of Rate of Pressurization on Bubble Size*

A viewing cell was designed and constructed specifically for this work. Initially the cell had a deep fluid reservoir that restricted our earlier research to using only transparent fluids. To enable observation of bubbles in opaque fluids like the APHRON ICS^{TM} drilling fluid, a viewing cell was designed that possesses a variable fluid reservoir depth as shallow as 1mm. This is shown in Figure 6.

Figure 6. Variable-Reservoir-Depth Polycarbonate Viewing Cell

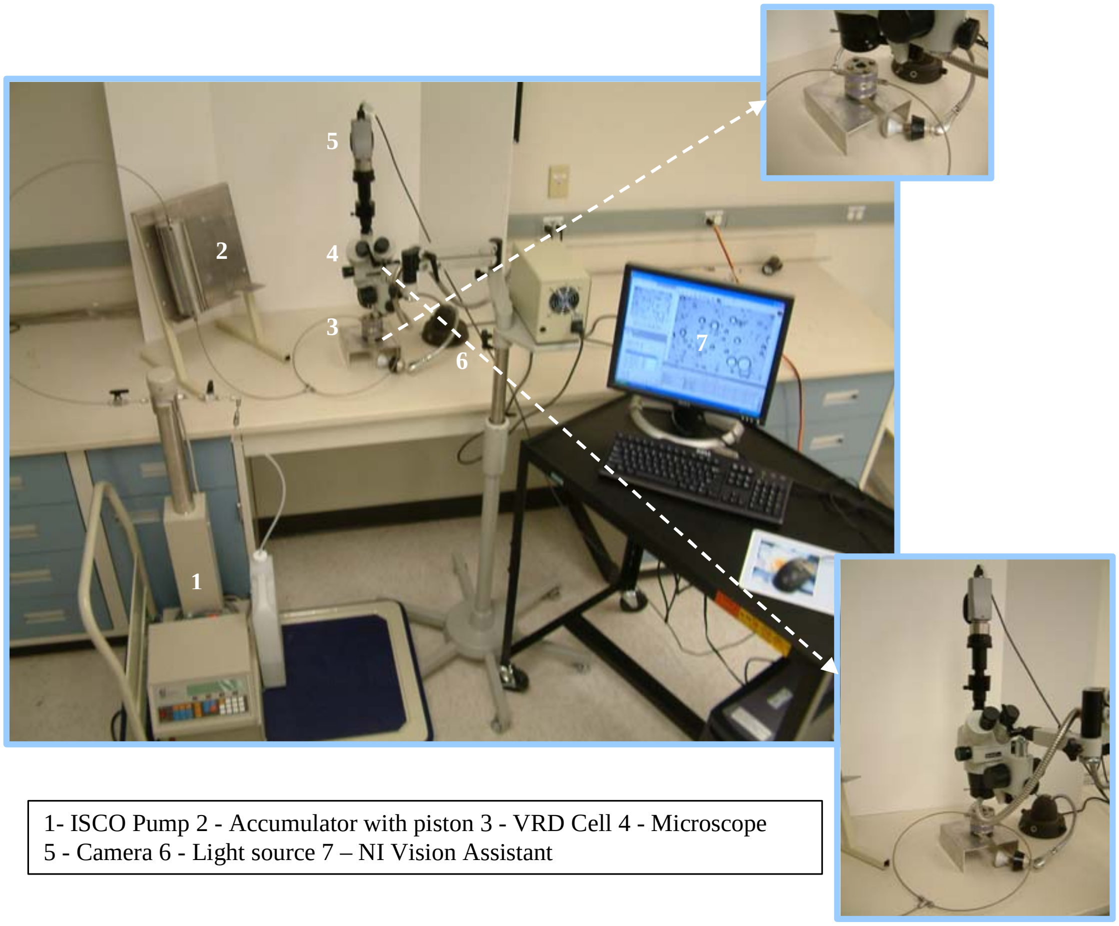
Front View of Cell

Side View of Cell

Disassembled Cell

A photomicrography system employing a stereomicroscope was used to obtain images of the bubbles for subsequent image analysis with the Vision Assistant software. The photomicrography system is shown in Figure 7. With this set-up, the effect of chemical composition on bubble stability was examined. Four Aphron ICS systems were studied: Enhanced, SuperEnhanced and their transparent counterparts. The composition of these four systems is given in Table 2.

Figure 7. VRD Optical System



1- ISCO Pump 2 - Accumulator with piston 3 - VRD Cell 4 - Microscope
5 - Camera 6 - Light source 7 – NI Vision Assistant

Table 2. Composition of Drilling Fluids

Whole Mud			*Transparent*		
Component	**Enhanced**	**Super Enhanced**	**Component**	**Enhanced**	**Super Enhanced**
Soda Ash	X	X	**FLO-VIS PLUS**	X	X
ACTIVATOR II	X	X	**Caustic Soda**	X	X
GO-DEVIL II	X	X	**BLUE STREAK**	X	X
ACTIVATOR I	X	X	**APHRONIZER A**	X	X
BLUE STREAK	X	X	**APHRONIZER B**	X	X
APHRONIZER A	X	X	**PLASTISIZER**		X
APHRONIZER B	X	X	**X-CIDE**	X	X
PLASTISIZER		X			
X-CIDE	X	X			

The effect of fluid composition on the rate of shrinkage of bubbles of similar size is shown in Figures 8 and 9. Here the pressure is maintained at a constant 500 psig and the bubble size is monitored as a function of time. The initial bubble sizes are given in Table 3. It is clear that even immediately after compression from 0 psig to 500 psig, the bubbles were somewhat smaller (by 10 to 24%) than expected from the Ideal Gas Law (Boyle's Law), which stipulated that gas volume should be inversely proportional to absolute pressure.

Figure 8. Effect of Fluid Composition on Aphron Stability – Whole Muds

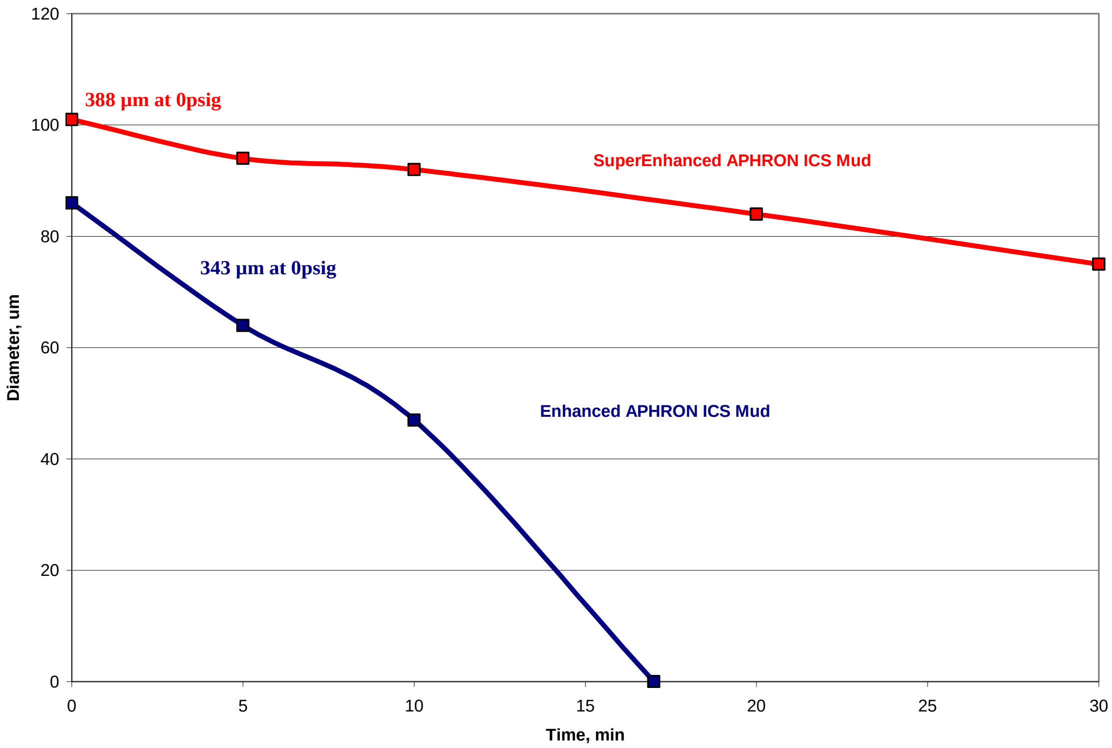


Figure 9. Effect of Fluid Composition on Aphron Stability – Transparent Muds

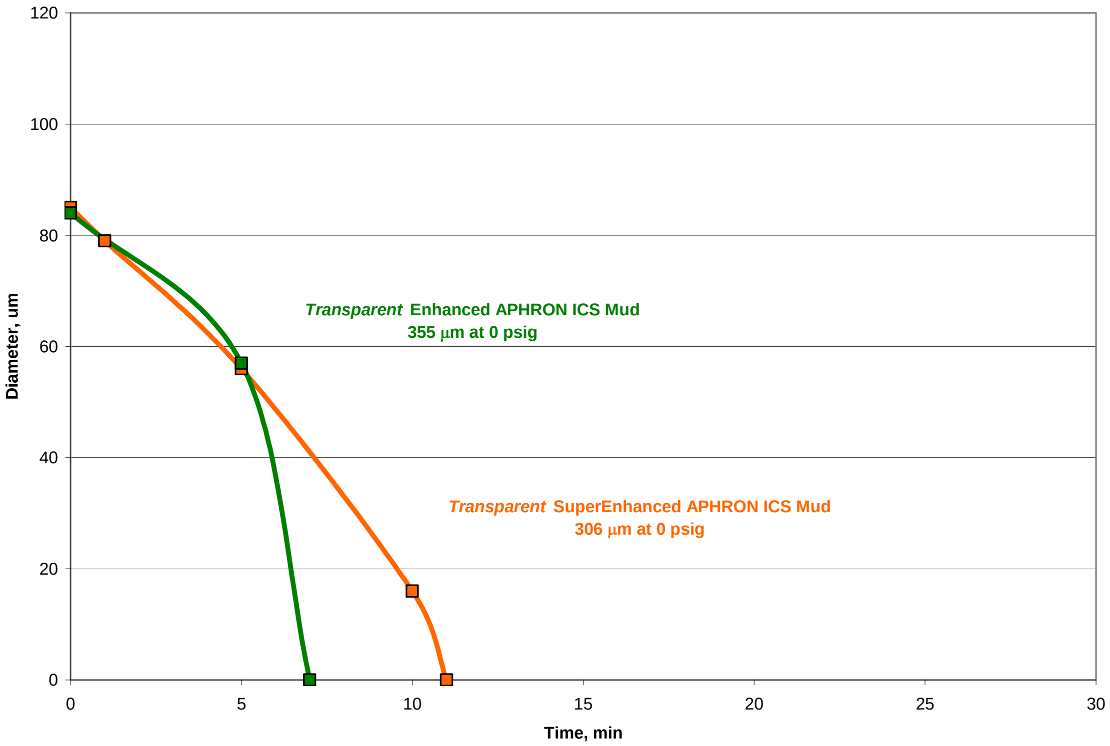


Table 3. Whole Mud vs. Transparent Mud

Fluid Type	Initial Starting Size at 0 psig	Size at 500 psig	Ideal Gas Law	% Deviation
SE APHRON ICS	388µm	101µm	119µm	15
E APHRON ICS	343µm	86µm	105µm	18
Transparent SE APHRON ICS	306µm	85µm	94µm	10
Transparent E APHRON ICS	355µm	83µm	109µm	24

As indicated in Figures 8 and 9, all of the bubbles shrank over time, but the bubbles in the E Aphron ICS muds shrank faster than those in the SE muds. Also, the Transparent versions of both muds shrank faster than the whole mud versions.

Treatment of diffusion of air from a bubble can be approximated as a problem of diffusion from a hollow sphere of dimension $r = S_0$ surrounded by a shell through which the air must diffuse to get to the liquid phase.[1] The initial concentration of air throughout the shell ($r > S_0$) is presumed to be 0 and the air concentration at surface $r = S_0$ is maintained at C_0. This leads to the following expression for the concentration of air within the shell:

$$C/C_0 = S_0/r \, erfc \, [(r-S_0)/2((Dt)^{1/2})]$$

Where *erfc* is the error function complement, D is the diffusion coefficient of air through the shell and t is the time. A simpler way of expressing the rate of loss of air is to treat the shrinking aphron as a spherical dissolving crystal. The rate of "dissolution of the crystal" can be approximated by a first order equation:

$$dS/dt = SD$$

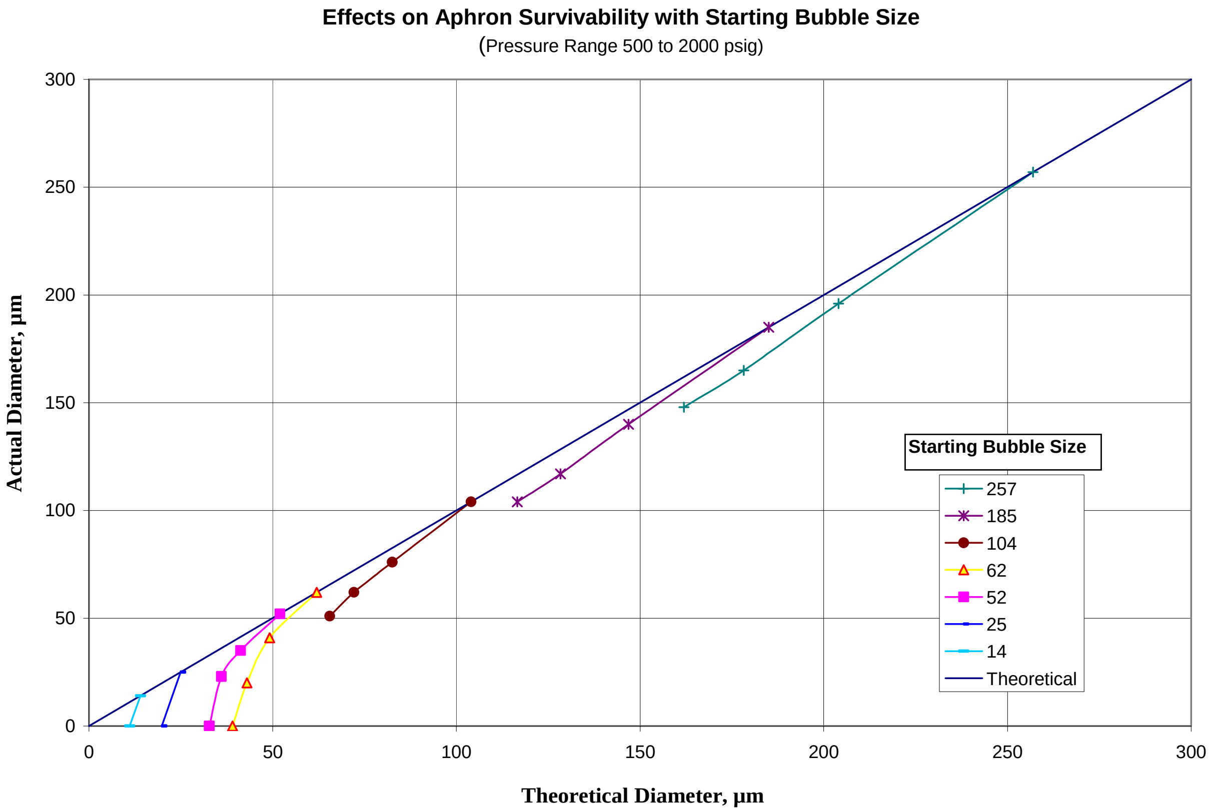
where S is the size or volume of the aphron ($1/6 \, \pi d^3$) and D is the rate (diffusion) coefficient. Here d is the diameter of the aphron. Combining terms and integrating between $t = 0, S = S_0$ and $t = t, S = S$ yields the following:

$$S/S_0 = exp \, (-Dt)$$

For the SE mud, $d_0 = 101$ µm, and $d = 75$ µm at 39 min (see Figure 8). This gives $D = 0.023$ min^{-1}. For the TE mud, the only measurement we have besides $d_0 = 78$ µm is $d = 52$ µm at 5 min, which gives $D = 0.24$ min^{-1} (see Figure 9). Thus, the rate of loss of air is an order of magnitude greater in aphrons from the TE mud than from the SE mud. This conclusion is probably conservative, as it appears from Figure 9 that the rate of air loss accelerates after the aphron shrinks to about 50 µm diameter.

It has been hypothesized that bubble stability increases with decreasing bubble size. While that may be the case for non-interacting bubbles in an isobaric (constant pressure) environment, it does not appear to be the case when aphrons are pressurized. Figure 10 shows the results of pressurization tests carried out on several bubbles. Here initial size measurements of seven well-defined bubbles were determined, as before, at 500 psig. When these are plotted on the graph in the form of Actual (measured) Diameter vs. Theoretical (modified Ideal Gas Law) Diameter, they fall on a line with a slope of 1. Pressurizing the system to 1000, 1500 and 2000 psig generated bubbles with the sizes given by the other three points for each bubble. The Theoretical Diameter is given by the expected size obtained using the modified Ideal Gas Law, $P_1V_1/z_1 = P_2V_2/z_2$, where P is the Pressure (1 is for the 500 psig case, 2 is for the other cases), V the volume, and z the compressibility factor for air (obtained from a standard table in the Chemical Engineering Handbook). Figure 10 shows that, under these conditions, the bubbles follow the modified Ideal Gas Law rather closely when their initial size (at 500 psig) is above 100 µm diameter, but they deviate markedly when the initial size is about 50 µm or less.

Figure 10. Effects of Aphron Survivability with Starting Bubble Size



Sebba[2] hypothesized that aphrons smaller than 25 µm diameter may not be able to survive. This agrees very well with our own observation, as shown in Figure 10, that when an aphron is squeezed to a size of 50 µm or less, at the next pressurization it will shrink to half its size or less. Very likely an aphron in this size range (< 50 µm) will even disappear, though the rate of disappearance is expected to be a function of variables such as composition, pressure and rate of pressurization. On the other hand, Sebba declared that maybe aphrons smaller than 25 µm do survive; perhaps they simply cannot be seen. However, the evidence obtained here at elevated pressure discards that notion. If they seem to disappear at high pressure but in fact have survived, then reducing the pressure should make them visible again. When the pressure on the fluid described in Figure 10 was reduced from 2000 psig to 500 psig, the aphrons that had shrunk to less than 50 µm during the pressure ramp did not re-appear.

In addition to pressure itself, the rate at which pressure is applied appears to have a significant impact on the survivability of aphrons. For example, when an aphron is in an environment where it is being subjected to a slow pressure ramp, such as steps of 500 psi on the way to 2000 psig (instead of 2000 psig immediately), the percentage of original aphrons that are recovered when the system is returned to ambient pressure is greatly reduced. This is contrary to what had been expected, namely that an aphron would be more stable the slower the pressure ramp. The effect of rate of pressurization on the shrinkage rate of aphrons was examined using two protocols in tests with the transparent Enhanced APHRON ICS™ drilling fluid:

- Slow Pressurization – 0, 500, 1000, 1500 and 2000 psig, waiting 15 seconds after each new pressure was reached. The system was then depressurized rapidly to 0 psig and pictures were taken at 0, 5, 10, 20 and 30 minutes.
- Fast Pressurization – 0 and 2000 psig, waiting 15 seconds after reaching 2000 psig. The system was then depressurized rapidly to 0 psig, and pictures were taken at 0, 5, 10, 20 and 30 minutes.

Figure 11. Effect of Rate of Pressurization Rate on Bubble Size

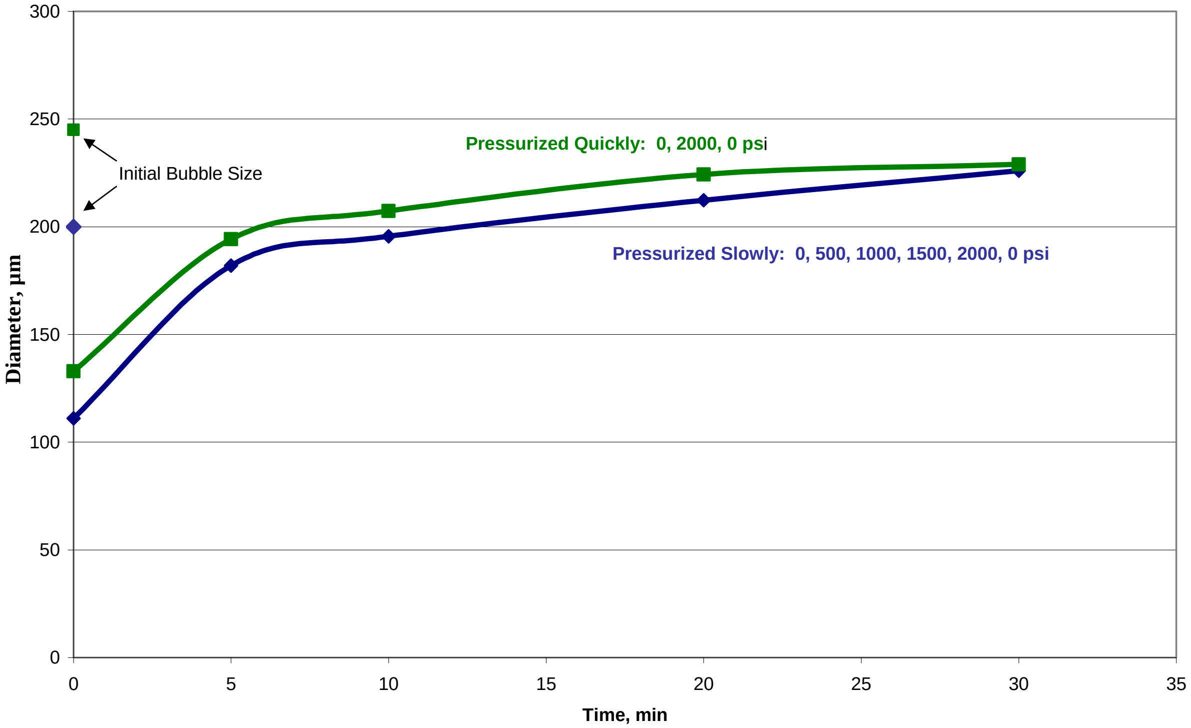


Figure 11 shows first that aphrons do not recover their initial size very quickly; indeed, it appears that 30 minutes is a minimum amount of time necessary for full recovery. Secondly, aphrons recover at a rate and to a steady state size that depends on the rate of pressurization. In Figure 11, two bubbles of similar size were exposed to the two pressurization protocols described above. The aphron that was pressurized slowly began with an initial diameter of 245 μm but only reached 226 μm 30 min after depressurization, a deficiency of 8%. However, the aphron that was pressurized quickly surpassed its initial size of 200 μm to reach 229 μm, a surplus of 13%. With more time, the aphron that was pressurized slowly might have reached its initial size. The aphron that was pressurized quickly, however, appears to have gained some air. The 13% increase in diameter of that bubble translates to a 44% increase in volume. Indeed, the photographs show that there are fewer small aphrons in the vicinity of this aphron after depressurization than were evident at the beginning of the test. This is consistent with the view that small aphrons are destroyed during pressurization, and the lost air goes into solution, only to emerge later when the system is at 0 psig and the system is supersaturated. Some of that air might go to form new aphrons, but it appears that a preferred fate is for the expelled air to be incorporated into existing aphrons. Thus, the aphron shell not only is permeable and susceptible to loss of air, it also appears equally capable of absorbing air from solution.

References

1. Crank, J., The Mathematics of Diffusion, 2nd Edition, Oxford Univ. Press, 1975, pp. 89-103.
2. Sebba, F.: *Foams and Biliquid Foams - Aphrons*, John Wiley and Sons, Toronto, 1987.