Application Note
Hydraulic Fracturing - pH and Conductivity

Oil & Gas: Enhanced Recovery

Hydraulic fracturing is perhaps the most debated form of energy production in recent years. What is well known is that over the last decade this type of unconventional oil and gas recovery has completely changed America's energy supply from net import to net export. In this paper we will explore the water treatment aspect of this process and how Barben liquid analysis products can provide reliable measurements for these processes.

Introduction

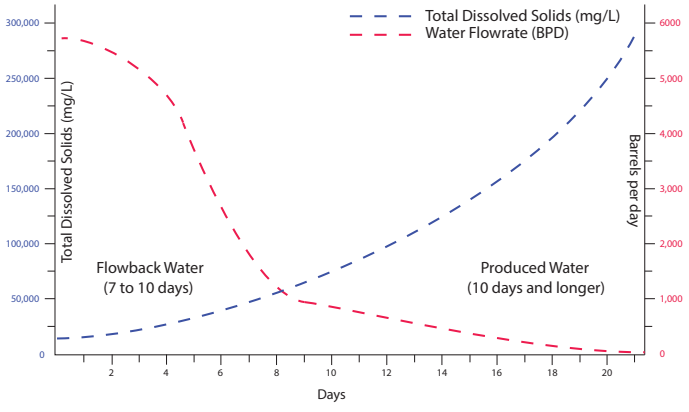
Hydraulic fracturing of underground shale uses high pressure water injection into horizontal wells to free trapped natural gas and oil. The water (90%) is mixed with silica sand (9%) and specialized "frac" chemicals (1%) prior to downhole injection. The sand lodges within small cracks in the shale to help release the trapped hydrocarbons. In shale containing natural gas the frac chemicals are normally comprised of a blend of surfactants, friction reducers, biocides, scale inhibitors, and acid. This liquid mixture is often referred to as "slickwater". In shale containing crude oil a the composition of the water includes a gel polymer such as guar gum (up to 7%) to increase the viscosity of the water aiding in hydrocarbon removal.

Flowback & Produced Water

After injection the pressure is let off releasing the hydrocarbons and causing some of the water to flow out of the well. This commonly referred to as "flowback". Flowback water will contain drilling mud, residual hydrocarbons, dissolved salts, suspended solids and frac chemicals. Over the course of 7-10 days the composition of the flowback water will change (figure 1). Generally the hydrocarbons and fracking related additives will diminish while the Total Dissolved Solids (TDS) will increase. This increase in TDS is a common occurrence since shale deposits are typically situated close to saline water aquifers. The saline water coming from the well is now referred to as "produced water". The dissolved salt level in produced water are 2-3 times higher than found in sea water thus the produced water must be treated. The water flowrate will slowly diminish over the life of the well.

From Flowback to Produced water Figure 1

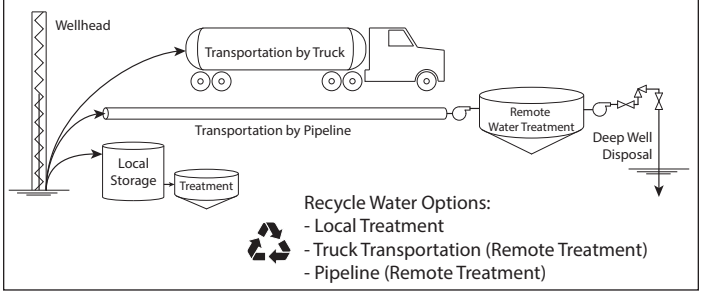
After the first 7-10 days the water flowrate drops sharply as the injected water is replaced by saline groundwater. This change in water supply increases the dissolved salts (TDS). Water treatment strategies may also need to adapt.



Water Treatment Issues

A hydraulically fractured well will require approximately 4 to 8 million gallons of water during its lifespan. 20 to 40% of this water will come back to the surface in the form of flowback / produced water. A retention tank is used to store this reclaimed water on-site. The driller must have a strategy to deal with this water. There are multiple options as illustrated below:

Water Treatment Strategies Figure 2



Water usage has become a defining issue for hydraulic fracturing for multiple reasons. Environmental concerns about contamination of groundwater aquifers has led many drillers to move away from disposal wells and recycle water through treatment and reinjection strategies. Many wellheads are in remote areas, thus strategies such as trucking water to-and-from the site creates damage to rural road networks. Municipal water treatment facilities are not designed to deal with contaminated frac water so specialized treatment plants must be built to deal with the changing nature of flowback and produced water. In the Western United States shale deposits are underneath arid land where water is scarce. Often these areas also have agricultural development that competes with drillers for water usage. This further increases the pressure to recycle the water.

Whether water treatment is performed on-site or off-site, there are common concerns with frac water treatment.

Hydrocarbons - If crude oil is present is must be removed. A separator or skimmer is used.

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BTEX **-** An acronym for Benzene, Toluene, Ethyl-benzene, and Xylene. All are naturally occurring volatile organic compounds that can evaporate when the frac water comes to the surface.

H_2S Removal - H_2S is a poisonous gas. A scrubber may be required for removal. Residual H_2S will increase corrosion in metal piping.

Turbidity - Turbidity is a measure of suspended solids. Excess turbidity can plug fractures reducing the effectiveness of the well.

Iron - Fe+ can affect the frac chemical reactions as well as plug the downhole well.

Biological - Microbes can create sulfides and acids within the well leading to corrosion.

Hardness & Alkalinity - Salts such as Ca^+, Mn^+, Sr^+, and BA^+ can create scale on piping.

Treatment Strategies
Due to the changing nature of the flowback water over time, treatment strategies can vary. Minimally treated water with high suspended solids may actually plug cracks in the shale reducing the effectiveness of the fracturing. In another example, the fluctuating TDS levels of the water can create problems. Typically, low TDS levels in recycled water would seem desirable for reinjection since the water is considered “cleaner”. In reality the low TDS water may hinder drilling efforts when shale deposits are located by saline aquifers. Underground clay which has grown accustom to the high dissolved salt levels of the aquifer can swell when exposed to “clean” frac water. The swelling hinders movement of the gas thus reducing the effectiveness of the well.

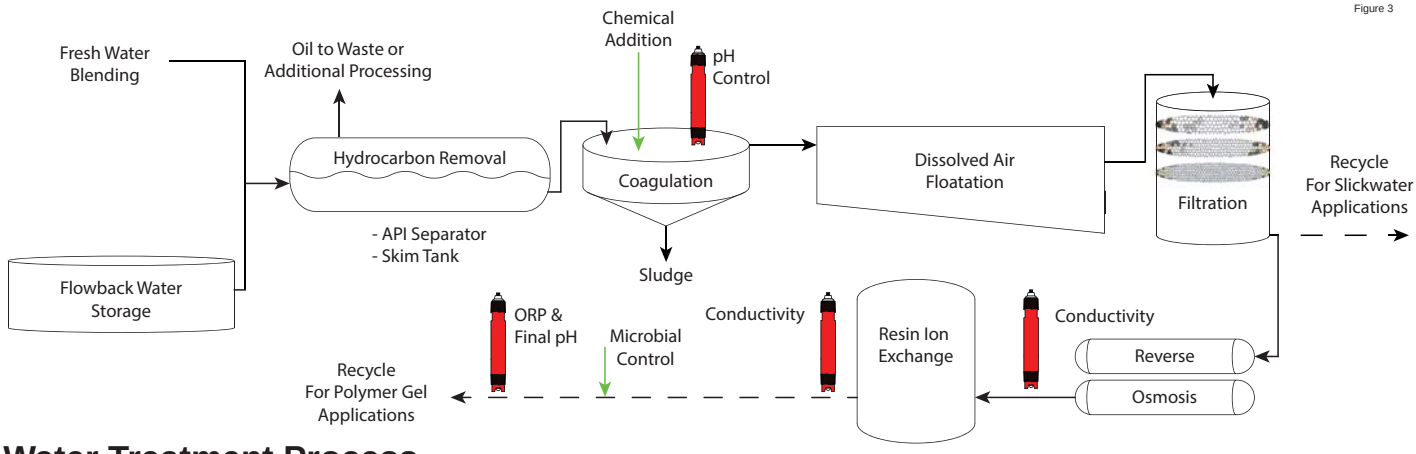
Water treatment will also vary depending on the type of frac chemicals that need to be added for reinjection. Gel polymers used for crude oil extraction are a great example. These polymers typically need additional treatment such as reverse osmosis and ion exchange to deal with hardness and boron. If the hardness and boron are not reduced then cross-linking of the polymers cannot be controlled.

A typical water treatment strategy can be seen in Figure 3. This system will vary depending on the components in the water. For example, depending on the level of hydrocarbons, an API separator or a skim tank might be employed as a first stage treatment. Also note that slickwater applications may not require the advanced filtration that gel polymers require.

pH Measurement Solutions
Barben Analytical Performance Series pH / ORP sensors offer an ideal design for frac water measurement. Most issues with pH measurement in these applications are due to reference failure. Hydrocarbons and high particulates tend to plug the porous reference junction creating increased impedance and a noisy pH measurement. Naturally occurring sulfidesandheavymetalscanattack the Ag/AgCl element in the reference leading to drift and shortened sensor lifespan.

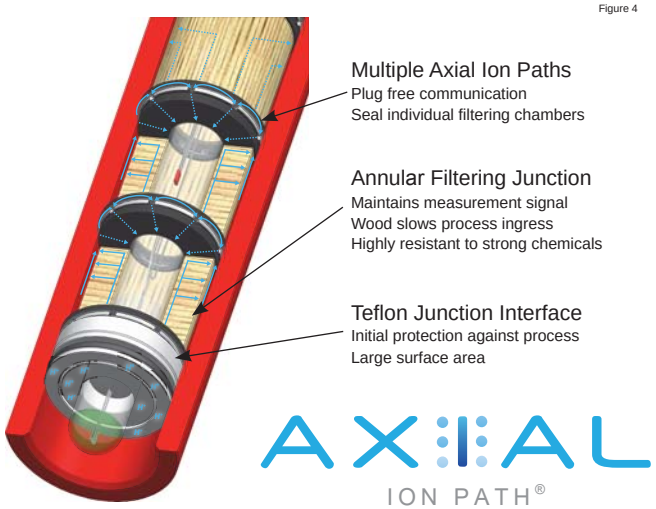
The Barben Axial Ion Path® reference technology (Figure 4) works extremely well to solve these issues. The filtering design of the reference keeps outside chemicals and particulates away from the internal Ag/AgCl element while still maintaining a strong signal path. The superior reference design allows Barben sensors to maintain higher accuracy with less frequent calibration intervals. The end result is less operator time dealing with pH sensors and higher quality effluent recycled water.

Figure 3



Water Treatment Process

Figure 4

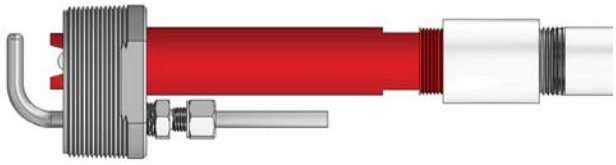


Barben sensors should be specified with “CR” coating resistant glass electrodes. The coat resistant layer on the glass provides additional protection against buildup in submersible applications such as clarifiers. Kynar (PVDF) should be specified as the sensor body material due to it’s chemical compatibility.

If the pH measurement is taken directly in the clarifier than the Barben 546 threaded submersible pH sensor used with a jet spray cleaner accessory (figure 5) can aid in keeping coating from forming on the sensor tip. Either air or water can be used to blast away build-up.

546 Submersible pH Sensor with Jet Cleaner

Figure 5



The pH sensor with jet cleaner (shown sideways above) is a good way to prevent coating and buildup in coagulation and settling ponds. The Jet cleaner mounts vertically on a 2 inch NPT pipe. Pressurized air or water is connected to the tubing fitting on the jet cleaner. The cleaning can be either manually or automatically actuated from a timer. Consult Barben Analytical for more information.

Many drilling sites are using portable trailer mounted water treatment systems. For these applications proper grounding of the pH sensor should be considered. If plastic piping is used then the liquid flow can generate static voltages. The voltage can cause noise in the pH sensor reading. Upsteam / downstream grounding with grounding rings may be required to prevent this problem. Since a trailer mounted installation is isolated by the tires, proper grounding of the pH transmitter and all other instrumentation to a common earth ground can also aid in reducing noise due to static voltage and ground loops.

Conductivity Measurement Solutions

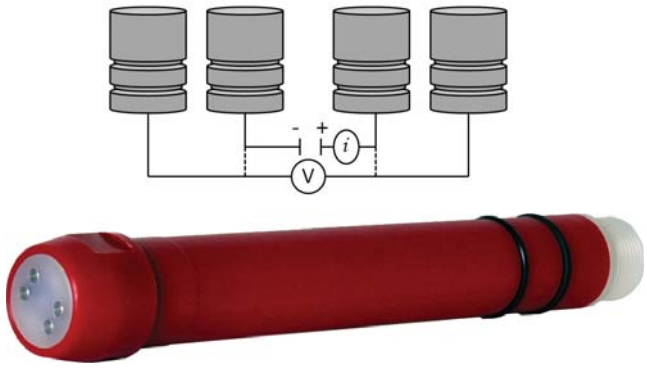
Total Dissolved Solids (TDS) levels in frac water can be monitored throughout the water treatment process with the use of conductivity sensors. As the mineral and salt impurities increase the electrical conductivity of the water will increase as well.

Barben four electrode sensors are well suited for measurements in the treatment plant. The four electrode design provides two circuits - Measurement & Reference. If particulates in the process begin to coat the tip of the sensor the reference circuit voltage can be increased to compensate the measurement and maintain the accuracy of the reading (figure 6). A secondary benefit of this design is advanced sensor diagnostics to know when the sensor fouling has gotten to the level where cleaning might be required. This is a significant advantage over two electrode conductivity sensors which can be “blinded” by coatings with no notification to the operator.

A common application for Barben four electrode sensors is the upstream / downstream conductivity around filters and ion exchange resin beds. Not only does conductivity indicate the effectiveness of the filter or resin but it can also signal when breakthrough has occurred. Barben four electrode conductivity sensors can be specified with 316 stainless, Titanium, or Hastelloy C-276 electrodes. Two ranges are available - 0 to 2 Siemens & 0 to 1,400 MicroSiemens depending on the application.

Four Electrode Conductivity Technology

Figure 6



Four electrode sensor designs keep a constant current through two of the electrodes and let the drive voltage change. If fouling occurs then the drive voltage can be increased to compensate the measurement. The electrodes can be seen on the tip of the 547 conductivity sensor shown above. Barben conductivity sensors and pH sensors use the same installation fittings which allows interchangeability between the two product lines.

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Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of Ametek.

Ametek has nearly 14,000 colleagues at over 120 manufacturing locations around the world. Supporting those operations are more than 80 sales and service locations across the United States and in more than 30 other countries around the world.

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