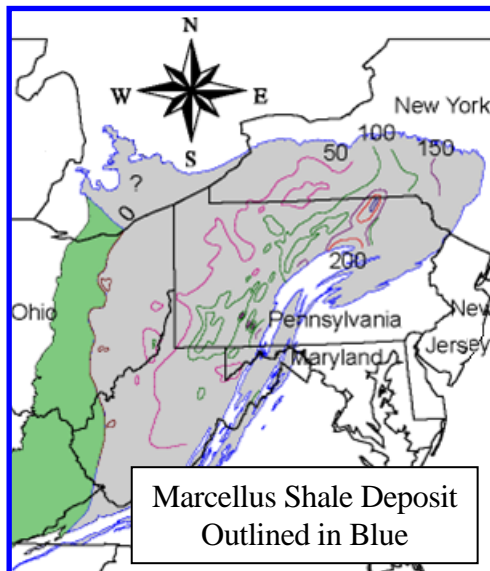


Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle Treatment Process

TAB 1009



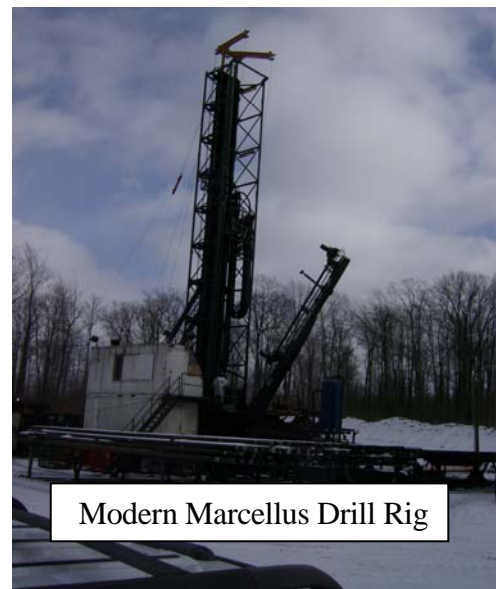
Background: The huge Marcellus black shale deposit, which underlies most of northern Appalachia, is estimated to contain 168+ trillion cubic feet of natural gas. Due to the depth and compact nature of this formation, horizontal drilling with follow-up hydrofracture of the formation using a mixture of high pressure water and sand is required to obtain economic gas production.

From 2 to 5 million gallons of hydrofracture water, mixed with various additives, is required to completion fracture each horizontal deep well. Once used, this now contaminated water must be removed from the well, generally 10 to 20% is recovered, and is commonly referred to as “flowback” water. Typically, flowback water contains high dissolved solids with varying levels of various constituents such as barium and strontium.

Due to the high dissolved solids content, disposal of flowback water is very difficult and costly. The PADEP has stated that their goal is prohibition of new high dissolved solids wastewater discharges by January 1, 2011¹. In addition to the disposal problem, in many areas suitable water needed for formulation of hydrofracture water is just not available when desired in the amounts needed.

The best solution to this combined wastewater disposal and water supply problem is to **simply treat and recycle the flowback water**, over and over again, as hydrofracture water. For hydrofracture use, the flowback water must be treated to remove anything that would cause plugging of the fractures in the shale; constituents such as suspended solids, aluminum, barium, calcium, iron, magnesium, manganese, and strontium must be removed to a maximum total hardness of 2,500 mg/l² measured as CaCO₃.

A recent development by a major gas well service provider has removed the previous maximum limit of 50,000 mg/l for dissolved solids in hydrofracture makeup water, thus the treated flowback water may be used without any further treatment for dissolved solids or mixing with lower dissolved solids concentration makeup water.



Flowback Treatment and Recycle: The major problem with use of flowback water for makeup of hydrofracture water is the very high content of scale forming constituents present. The high levels of barium, calcium, iron, magnesium, manganese, and strontium common in flowback water will readily form precipitates, scale, which would rapidly block the fractures in gas bearing formations required for economic gas production. Removal of these constituents to much lower levels is thus required for recycle of flowback water, or use of production water, as hydrofracture water.



Using our 35+ years experience in treating wastewater for recycle and reuse, ProChemTech has invented a sequential precipitation process (SPP)³ for treatment of flowback water. The first precipitation removes suspended solids, iron, and barium from the flowback water as a solid, non-hazardous, sludge cake. Barium is removed prior to the second precipitation as it is a toxic heavy metal and would not be rendered insoluble, and thus non-hazardous, by the following processes. If the barium is not removed prior to the second step, the resultant sludge would be considered a “hazardous waste”, which is a very costly item for proper disposal.

The remaining scale formers, calcium, magnesium, manganese, and strontium; are precipitated in the following two steps where the precipitate formed is combined to make one solid sludge cake product.

Due to the amounts of sludge cake produced, beneficial reuse of both produced sludges is an important design consideration in the treatment process design. Currently, it is believed that the barium sludge can be reused as a component of “drilling mud”, while several options for the second sludge, such as phosphate removal in sewage treatment plants, soil amendment, use in fluidized bed boilers, or treatment of acid mine spoils; are being investigated.

As the chemical composition of Marcellus flowback water varies dependent upon the well location and elapsed time since the fracture was completed, we have undertaken an extensive series of treatability tests on a wide range of flowback waters to prove the widespread applicability of the SPP. The following test results are typical of the results obtained.

Marcellus flowback water sample – low dissolved solids, Hydrofracture 2

Parameter	untreated	treated
barium mg/l	2,300	<0.1
calcium mg/l	5,140	6.0
iron mg/l	11.2	0.04
magnesium mg/l	438	1.09
manganese mg/l	1.9	<0.04
strontium mg/l	1,390	45.8
total hardness mg/l as CaCO ₃	17,941	71.8
total dissolved solids mg/l	69,640	57,660

Marcellus flowback water sample – moderate dissolved solids, Hydrofracture 1

Parameter	untreated	treated
barium mg/l	3,310	<0.1
calcium mg/l	14,100	7.25
iron mg/l	52.5	1.7
magnesium mg/l	938	1.6
manganese mg/l	5.17	<0.04
strontium mg/l	6,830	10.4
total hardness mg/l as CaCO ₃	49,416	39.6
total dissolved solids mg/l	175,268	59,850

Marcellus flowback water sample – high dissolved solids, Hydrofracture 4

Parameter	untreated	treated
barium mg/l	4,300	< 0.1
calcium mg/l	31,300	2.15
iron mg/l	134.1	1.60
magnesium mg/l	1,630	1.10
manganese mg/l	7.0	0.14
strontium mg/l	2,000	1.60
total hardness mg/l as CaCO ₃	90,633	14.9
total dissolved solids mg/l	248,428	150,520

Engineering Considerations: Any process for treating hydrofracture flowback must consider disposal of the large amount of sludge solids produced by the process. The SPP process, operating on a hydrofracture flowback water to treat 300,000 gpd with an “average” chemical composition of 3,300 mg/l barium, 16,850 mg/l calcium, 1,000 mg/l, magnesium, and 3,400 mg/l strontium, would produce, at 40% solids sludge cake, 67,000 lb of barium sludge and 281,815 lb of calcium/strontium/magnesium sludge per day. PADEP residual waste permitting requirements and the cost of moving large quantities of flowback water, hydrofracture makeup water, and produced sludge solids shows the need for a number of dedicated SPP flowback treatment systems sited across the area under laid by Marcellus shale formation.

Exclusive of the incoming hydrofracture flowback and treated water storage tanks, we have estimated that a 300,000 gpd SPP process system would require approximately a 25,000 sq ft area for the installation. The process train would consist of transfer pumps, two sequential chemical reaction tanks, an equalization tank, filter presses, a second equalization tank followed by two more chemical reaction tanks, a third equalization tank followed by filter presses, and a final chemical reaction tank discharging to treated water storage. In the event that excess treated water is produced, due to mismatch of hydrofracture operations with flowback generation, treated water can be concentrated by low temperature, waste heat evaporation to produce either road deicing brine or solid sodium chloride salt.

As the hydrofracture flowback water has a high dissolved salt concentration, most potential uses for the produced sludges will require that the sludges be “washed” to reduce the retained salt to fairly low levels. We have incorporated this process step into our filter press operation.

Economics: We have calculated the chemical operating cost for the above 300,000 gpd SPP system at \$0.055 per gallon. For proper operation, we believe that a five (5) man crew will be required for 24 hour operations.

Capital equipment cost for this system has been estimated at \$3,500,000; less building, site, or incoming and outgoing water tank costs.

Technology Leader: ProChemTech has designed and built many wastewater recycle and reuse systems in the past twenty + years for many different industries utilizing various treatment chemistries and treatment equipment. Specific projects have included three systems for removal of barium from wastewater.

Our approach to design of a wastewater treatment system starts with determination of the best process chemistry via laboratory testing of actual wastewater samples for removal of the target constituents. Once an appropriate chemical process has been devised, we then custom design the system equipment to work with the chemical process. This unique approach, where the treatment chemistry controls the equipment design, results in the most economical process possible. We have applied this time proven method to treatment of hydrofracture flowback waters for recycle, resulting in the current SPP treatment process.



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¹ Permitting Strategy for High Total Dissolved Solids (TDS) wastewater Discharges, PADEP, 04/11/09

² Personal communication, L. Case, Halliburton to T. Keister, PCT 02/09

³ USPTO Patent Application 61/199,588, "Process for Treatment of Gas Well Completion, Fracture, and Production Wastewaters for Recycle, Discharge, and Resource Recovery", filed 11/19/08