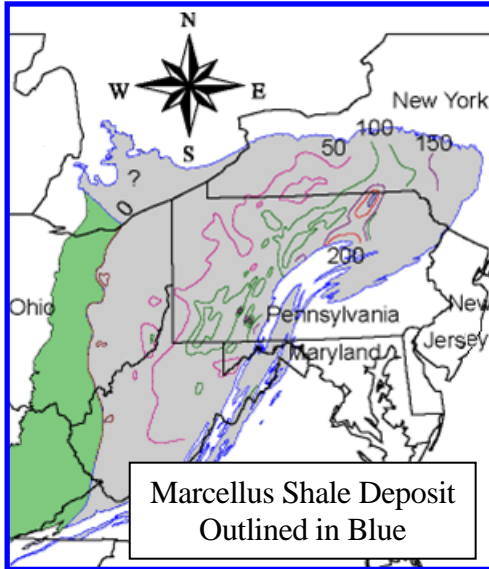


# Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle

TAB 0509



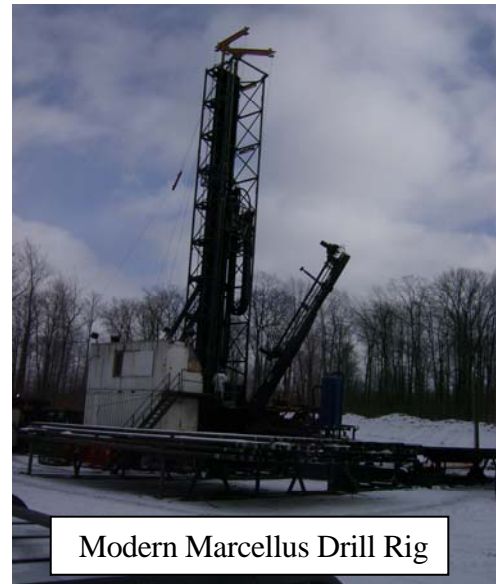
**Background:** The huge Marcellus black shale deposit, which underlies most of northern Appalachia, is estimated to contain 168+ trillion cubic feet of natural gas. Due to the depth and compact nature of this formation, horizontal drilling with follow-up hydrofracture of the formation using a mixture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

From 2 to 10 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 40% is recovered, and is commonly referred to as “flowback” water. Typically, flowback water contains high dissolved solids with varying levels of various other 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, 2011.<sup>1</sup> In addition to the disposal problem, in many areas suitable water needed for formulation of hydrofracture water is just not available when required 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 level measured as a maximum total hardness of 2,500 mg/l<sup>2</sup> as CaCO<sub>3</sub>.

As the maximum dissolved solids level for use as hydrofracture water makeup is 50,000 mg/l<sup>3</sup>, the treated flowback water will often have to be mixed with lower concentration makeup water. This is feasible given that the loss of water in hydrofracture operations always requires a substantial makeup for preparation of new hydrofracture water with use of recycled 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. Halliburton, a major supplier of fracture water chemicals, has noted that fracture makeup water should have a maximum scale former level of 2,500 mg/l measured as CaCO<sub>3</sub>.



Using our 35+ years experience in treating wastewater for recycle and reuse, ProChemTech has invented a sequential precipitation process (SPP)<sup>4</sup> 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.

The remaining scale formers, calcium, iron, magnesium, manganese, and strontium; are precipitated in the following two steps where the precipitate formed is combined to make one solid sludge cake product which could be used as an alkaline soil amendment or for abandoned mine spoil reclamation uses.

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 <sub>3</sub>	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 <sub>3</sub>	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 <sub>3</sub>	906,337	14.9
total dissolved solids mg/l	248,428	150,520

The reduction of dissolved solids in all three of these samples is significant, varying from 17.2% to as high as 65.9% dependent upon the specific constituents present in the flowback water.

**Hydrofracture Makeup Water Supply:** With the substantial amount of makeup water needed, from 60 to as high as 90% for new wells, supply of makeup water has been a limiting factor for many well drillers. In many areas of the state where the Marcellus shale is present, acid mine drainage from past coal mining activities is present in large amounts and is a major water quality problem. In February, 2009, approximately 1.5 million gallons of treated acid mine drainage water was obtained from the Blue Valley Fish Culture Station (BVFCS) for what is believed to be the first use of such water in a Marcellus completion hydrofracture.

Samples of the untreated and treated acid mine drainage were obtained during the course of the supply and analyzed with the following results obtained:

Parameter	untreated	treated
barium mg/l	<0.2	<0.2
calcium mg/l	196	198
iron mg/l	13.0	0.32
magnesium mg/l	56.0	55.5
manganese mg/l	2.6	3.54
strontium mg/l	3.6	3.6
total hardness mg/l as CaCO <sub>3</sub>	752.7	734.5
total dissolved solids mg/l	1,004	1,076



The BVFCS effluent, however, is not typical of treated acid mine drainage as it utilizes a unique chemical process with advanced design inclined plate clarifiers for removal of iron prior to use as makeup to the fish culture tanks and subsequent discharge into an on site lagoon. Since no calcium hydroxide is used in the process, and the acid and iron levels are low in the mine discharge, the treated water is lower in hardness than typical treated acid mine drainage.

While the communication with Halliburton addressed criteria for total hard hardness and dissolved solids, iron levels were not discussed and with the high levels of iron often found in acid mine drainage a maximum limit was needed. Information was subsequently obtained to the effect that a maximum level of 20 mg/l<sup>5</sup> iron could be tolerated in hydrofracture water. This same document also noted that calcium levels over 350 mg/l require increased levels of completion chemicals to be used.

To confirm that any acid mine drainage could be utilized, with specific treatment, as makeup water for Marcellus hydrofracture jobs, a “typical” sample of acid mine drainage was obtained from the extensively studied discharge at Hawk Run, PA. This sample was treated in our laboratory with the following results obtained:

Parameter	untreated	treated
aluminum mg/l	3.4	<0.1
barium mg/l	<0.1	<0.1
calcium mg/l	154	16
iron mg/l	58.5	<0.03
magnesium mg/l	65.5	42.0
manganese mg/l	5.45	<0.04
strontium mg/l	0.12	<0.02
total hardness mg/l as CaCO <sub>3</sub>	788.6	212.9
total dissolved solids mg/l	1,004	1,520

This “typical” acid mine drainage, when treated using a non-calcium process, produced a very acceptable Marcellus hydrofracture makeup water.

**Economics:** The cost of a process is always of concern and should be compared to any known alternatives. Presently, the only known alternative to SPP – recycle for disposal of frac flowback water is the GE Thermal Evaporation (GETE) process as advanced by STW Resources.

We have obtained a budget price of \$40 million for a GETE for a unit that can process 250,000 gpd of flowback water. Using the Hawk Run source as our basis for design, a combined SPP and AMD system designed to recycle 250,000 gpd of flowback water would cost about \$5 million and provide 1,250,000 gpd of hydrofracture water with use of 1,000,000 gpd of acid mine drainage, which eliminates discharge of 488 lb/day of iron to the environment.

To date, no operating cost information has been obtained on the GETE process. Using a steam boiler supplied with natural gas at \$5.00/ 1000 cu ft and a vacuum assisted evaporation system, we have estimated the operating cost to dispose of wastewater at \$85 to \$110/1000 gallons, without any pretreatment costs considered.

Chemical operating cost for the SPP has been calculated to be from \$10 to \$70/1000 gallons on the flowback samples tested to date. The chemical operating cost to treat the Hawk Run acid mine drainage has been calculated at \$2.50/1000 gallons.

**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 our unique inclined plate clarifiers. This well developed technology permits economical treatment of gas well flowback and acid mine drainage waters for recycle and reuse. Our process equipment can be manufactured as either mobile trailer mounted systems, or as stationary units, in flow ratings from 10 to 1000 gpm.



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

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

<sup>3</sup> Personal communication, L. Case, Halliburton to T. Keister, PCT 02/09

<sup>4</sup> 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

<sup>5</sup> Proceedings and Minutes of the Hydraulic Fracturing Expert Panel, XTO Facilities, Fort Worth, TX, 09/26/07