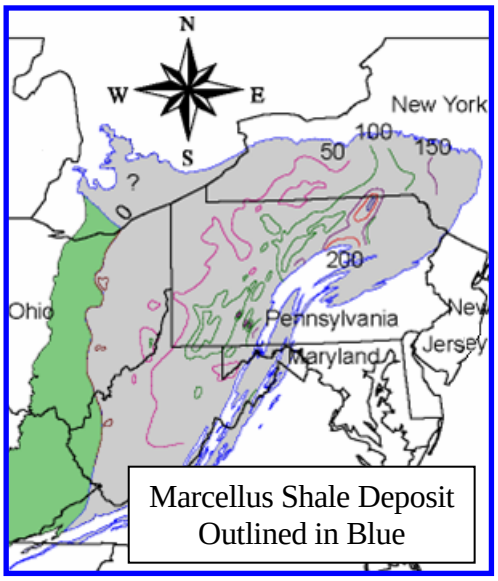
Marcellus Gas Well Water Supply and Wastewater Disposal, Treatment, and Recycle Technology

TAB 1208



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 fracture 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 fracture, "frac", 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 and is commonly referred to as "flowback" water. Obtaining the needed water to makeup frac water, with subsequent disposal of the flowback water, presents significant problems for gas production firms. In many areas, the amount of clean water needed for formulation of frac water is just not available, while disposal of the contaminated flowback water is a very a significant problem.

The best solution to this combined water supply and wastewater disposal problem is to simply treat and recycle the flowback water, over and over again, as frac water. Treatment of the flowback water to remove suspended solids and scale forming impurities renders it suitable for recycle.

Once a gas well is in production, additional water is generated entrained in the gas flow, this is commonly referred to as "production" water and also presents a substantial disposal problem to the gas production firm. Production water can be treated much as flowback water and reused as frac water, or pretreated for removal of specific hazardous constituents, such as barium, and discharged to a publicly owned treatment works (POTW) for additional treatment and subsequent discharge.

Frac Water Chemistry: Frac water is formulated by dosing a clean, low scale forming potential water with the following chemical products.

Friction Reducer: generally a water soluble anionic polyacrylamide polymer with a molecular weight between 2 and 10 million. This material is used at a rate of 3 to 5 lb/1000 gallons and serves to both reduce pumping friction and hold the frac sand or ceramic particles in suspension.

Wetting Agent: generally a nonionic surfactant which reduces the surface tension of the water to enable better formation wetting and recovery of the frac water during the flowback portion of a frac procedure. This material is used at a rate of 5 to 9 lb/1000 gallons.

Biocides: several materials are used as biocides in frac water formulations to control growth of microorganisms which would degrade the other components as well as actually plug the gas producing formation. Typically dibromo nitrilopropionamide, glutaraldehyde, or n,n,dibromosulfamate is used as a biocide at dosages from 1 to 5 lbs/1000 gallons. All biocide products used must carry a USEPA registration number for use in frac water formulation.

Scale Inhibitor: scale inhibitors are generally either a polyacrylate in the 2000 to 5000 molecular weight range or a phosphonate, such as the commonly used aminotri methylenephosphonate or phosphonobutane tricarboxylate. Scale inhibitors are generally dosed at a rate of 1 to 2 lb/1000 gallons.

Note: All dosages given as product, not actives, which vary from almost 100% to as low as 10%. The various actives are diluted for use in the field with solvents such as methyl alcohol, ethylene glycol, and polyoxyethylene glycol.

Flowback Water Chemistry: Chemical analysis[1] of several flowback waters shows the following variations in major chemical constituents.

Parameter	Frac 1	Frac 2	Frac 3	Frac 4
barium mg/l	3,310	2,300	7.75	4,300
calcium mg/l	14,100	5,140	683	31,300
iron mg/l	52.5	11.2	211	134.1
magnesium mg/l	938	438	31.2	1,630
manganese mg/l	5.17	1.9	16.2	7.0
strontium mg/l	6,830	1,390	4.96	2,000
dissolved solids mg/l	175,268	69,640	6,220	248,428
suspended solids mg/l	416	48	490	330
chemical oxygen demand mg/l	600	567	1,814	2,272

In addition to these major constituents, flowback water can also contain lower levels of many other elements and compounds such as hydrocarbons, aluminum, lead, copper, chromium, zinc, nitrogen compounds, fluoride, acidity, bromide, uranium, and surfactants.

Production Water Chemistry: Chemical analysis of a well mixed large storage tank of production water shows the following major constituents present:

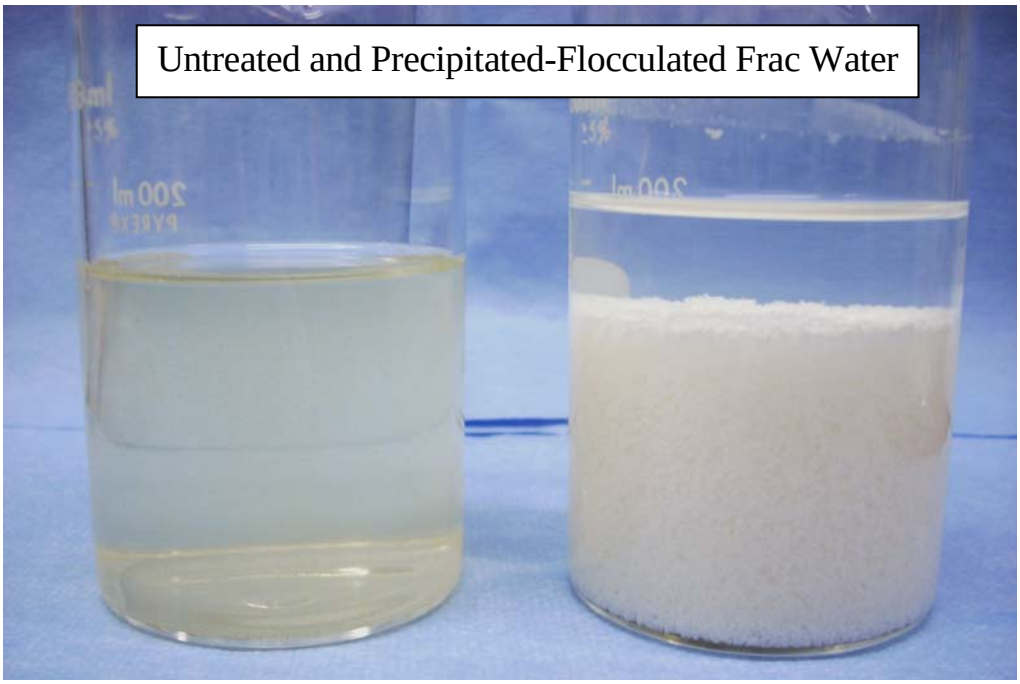
Parameter	Result	Parameter	Result
pH	4.79	conductivity mmhos	366,600
total oil/grease mg/l	9	chemical oxygen demand mg/l	2,332
surfactants mg/l	105.7	barium mg/l	690
calcium mg/l	23,200	iron mg/l	160
magnesium mg/l	2,240	manganese mg/l	10.1
strontium mg/l	732	dissolved solids mg/l	224,300
suspended solids mg/l	33		

As can be seen, production water generally resembles flowback water and has much the same major constituents at levels within the range found for flowback waters. As with flowback waters, production water can also contain lower levels of many other elements and compounds such as hydrocarbons, aluminum, lead, copper, chromium, zinc, nitrogen compounds, fluoride, acidity, bromide, uranium, and surfactants.

Environmental Problems: On review, the major problems with disposal of flowback and production waters are the high dissolved solids, chemical oxygen demand, acidity, and barium levels. Barium is a particular problem as it is a toxic metal, being one of the ones utilized in the USEPA toxic characteristic leaching procedure (TCLP) for hazardous waste determination and is also regulated in drinking water[2] at a maximum contaminant level of 2 mg/l.

Flowback Treatment and Recycle: The major problem with use of flowback, or production, water for makeup of frac 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 frac water.

Recycle Process: ProChemTech has developed a unique sequential precipitation treatment process[3] that removes the majority of these problem constituents to levels suitable for recycle via chemical precipitation which results in the removed constituents being disposed of as a solid cake.



The solid cake from our process is easily disposed of as all toxic materials are chemically bound. Shown below is a sample of the resulting solids as they are produced prior to disposal.

Our sequential process effluent is usable for formulation of frac water as shown by the following typical test results on a flowback water:

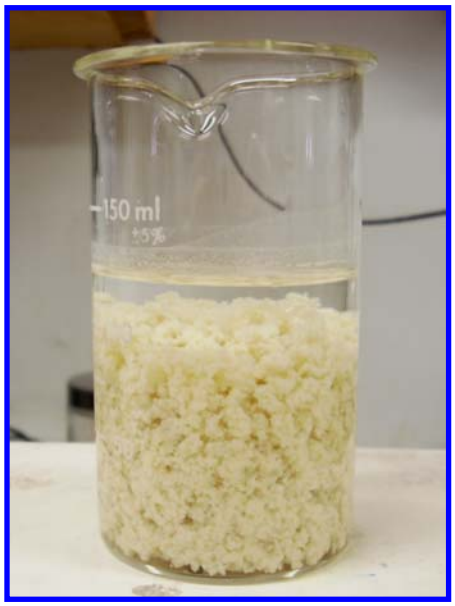
Constituent	Untreated Flowback	Treated Flowback
barium mg/l	3310	22.3
calcium mg/l	14,100	37.8
iron mg/l	52.5	0.20
magnesium mg/l	938	3.77
manganese mg/l	5.17	<0.01
strontium mg/l	6830	75.8
dissolved solids mg/l	175,268	51,900

Chemical cost for our sequential precipitation process has been calculated to be from $0.02 to $0.07 per gallon on the samples tested to date. Chemical cost varies in direct proportion to the amount of material present that must be removed.

Disposal Process: In some cases frac and/or production water will be present in excess of frac water needs and will have to be treated for ultimate disposal. Two methods are available for this at present.

Pretreatment and Discharge to a POTW: can be readily accomplished by a variation of our recycle treatment process where the barium is selectively precipitated and removed from the wastewater. Barium has been identified as the critical component in the wastewater as it can build up in the sludge generated by a POTW to the point where the sludge could be deemed a “hazardous waste” via the USEPA TCLP test.

The remaining constituents of concern, such as chemical oxygen demand and suspended solids, are readily addressed by typical POTW process operations. Removal of the barium via our pretreatment process avoids this costly problem.



Shown at the left is a precipitated – flocculated barium **pretreatment sample** while on the right is a sequential precipitation **recycle sample** as a graphic demonstration of the difference in the amount of solids produced by the two processes. These photos clearly show how important it is to minimize removal of the other constituents present so as to reduce the amount of sludge produced by the POTW pretreatment process.

The following table notes results obtained using our selective pretreatment process for barium.

Constituent	Untreated	Treated
barium mg/l	690	8.7
calcium mg/l	23,200	21,400
iron mg/l	160	0.44
magnesium mg/l	2,240	2,360
strontium mg/l	732	650

For the production water mix tested, chemical treatment cost was calculated as $0.04/gal.

Evaporation: the second disposal method, involves evaporation of the wastewater, producing effectively distilled water, which can be used in various applications or discharged to either surface waters (with an NPDES permit) or a POTW.

Due to the problems presented by scale formation on heat transfer surfaces during evaporation and the positive economics of selling recovered salt for use as a deicing product, removal of the toxic barium, as well as all other scale formers, from the wastewater prior to evaporation is required.

Accordingly, all wastewater to be disposed of by evaporation will first have to be treated by our recycle process for removal of the toxic and scale forming constituents prior to evaporation to avoid heat exchanger scaling. Note that if the barium is not removed, the solids produced by evaporation would be considered a TCLP hazardous waste due to just the barium content alone. Once the toxic constituents are removed, the produced salt, mainly sodium chloride, would be usable as road deicing salt and would contribute on a positive basis to the economics of the process.

Using a steam boiler supplied with natural gas at $10.00/ 1000 cu ft with a vacuum assisted evaporation system, we have estimated the cost to dispose of a gallon of wastewater at $0.17 to $0.22, without any credit for sale of deicing salt.

Technology Leader:

ProChemTech has designed and built many wastewater recycle and reuse systems in the past twenty years in a number of different industries utilizing various treatment chemistries and our unique inclined plate clarifiers.

This well developed technology permits economical treatment of both gas well flowback and production waters for recycle, reuse, or disposal. Our process equipment can be manufactured as either mobile trailer mounted systems, or as stationary units, in flow ratings from 10 to 1000 gpm.

250 gpm clarifier used to treat acid mine drainage used as the water supply for a trout raising facility

ProChemTech International, Inc.

"The Water Management Company"

Apache Junction, AZ, and Brockway, PA

814-265-0959 **www.prochemtech.com**

Prepared by: Timothy Keister, CWT FAIC, Chief Chemist

[1] Chemical analysis by Analytical Services, Inc, PADEP certified laboratory 33-00411.

[2] USEPA Consumer Factsheet on: BARIUM, www.epa.gov/OGWDW/contaminants

[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