

# The Science of Marcellus Shale

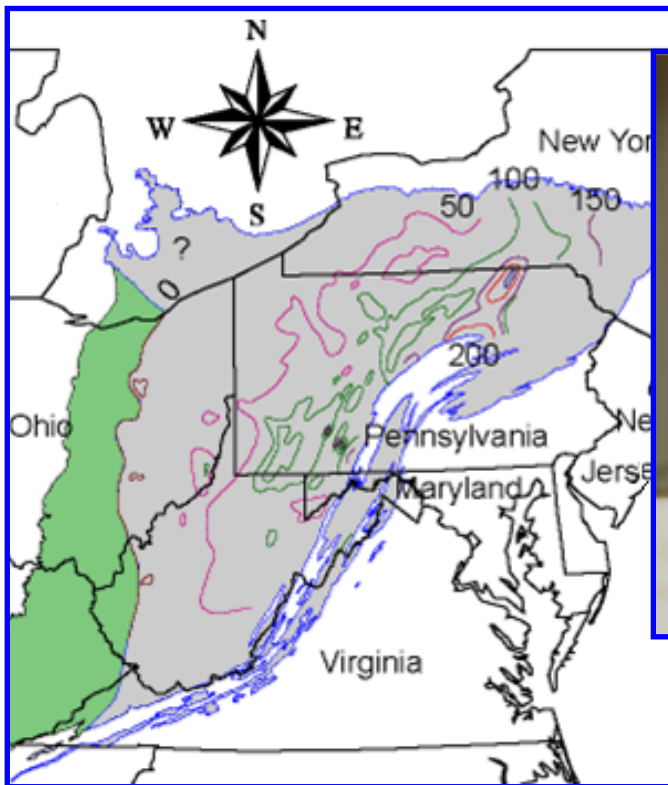
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## Marcellus Hydrofracture Flowback and Production Wastewater Treatment, Recycle, and Disposal Technologies

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**Introduction:** Development of the Marcellus gas play in the Northeast; primarily Pennsylvania, New York, and West Virginia, will generate an estimated 7,000 million gallons per year (mgy) of hydrofracture flowback and production wastewater that will have to be managed. This wastewater, as shown by the following “typical” analysis, contains substantial amounts of toxic barium as well as large amounts of many other elements and compounds.

Parameter	“Typical” Analysis – NE PA
pH	6.0
aluminum, mg/l	3.0
barium, mg/l	6,500
calcium, mg/l	18,000
chloride, mg/l	116,900
iron, mg/l	60
lithium, mg/l	150
magnesium, mg/l	1,300
manganese, mg/l	5.0
sodium, mg/l	48,000
strontium, mg/l	4,000
sulfate, mg/l SO <sub>4</sub>	130
dissolved solids, mg/l	195,000
total hardness, mg/l CaCO <sub>3</sub>	54,500
total suspended solids, mg/l	1,200

Three methods for management of this wastewater are considered viable today, pretreatment prior to additional treatment and discharge to stream via publicly owned treatment works (POTW), evaporation<sup>i</sup> (with and without subsequent water recovery), and various chemical precipitation processes<sup>ii</sup> with either recycle of the treated water or subsequent evaporation.

### **Pretreat and Discharge Via POTW**

The Brockway Area Sewer Authority (BASA) operates a new extended aeration, oxidation ditch activated sludge POTW treating a mix of industrial and domestic wastewater from Brockway and two nearby townships. BASA was approached by a gas well service company in 2006 as to accepting brine wastewaters for treatment and discharge. A treatment contract was agreed upon; following which BASA obtained an NPDES permit amendment from the PADEP on April 17, 2007, for treatment of up to 14,000 gpd (9.7 gpm) through the BASA plant. The service company then constructed a pretreatment system consisting of an oil/solids separator and aerated equalization tank at the BASA plant, with the first wastewater accepted in early November, 2008.

Several effects have been noted on treatment plant operation due to introduction of the brine water.

Development of a floating sludge layer on the final clarifiers has limited the brine flow rate to no more than 8 gpm of brine water at an average POTW flow of 0.5 mgd. This floating material is believed to result from combination of calcium in the brine water with soaps and fats in the plant influent.

A substantial increase in sludge generation has also been noted. On analysis, the sludge was found to have a barium content of 1,490 mg/kg, which was of some concern as barium is a USEPA toxic (hazardous) metal. Fortunately, a subsequent hazardous waste determination (TCLIP) on the sludge gave a barium extract value of just 1.56 mg/l, well below the 100 mg/l level for classification as a hazardous waste. It has been calculated that at our average brine treatment rate, an extra 780 lb/day of barium sludge is being produced.

Mass balance calculations on the plant effluent and input from the brine water also demonstrated that a substantial amount of calcium was being removed by the plant processes. Typically, about 240 lb/day of additional calcium sludge is being produced by treatment of the brine water.

The dissolved solids in the plant effluent, less than 400 mg/l prior to acceptance of brine, typically are in the area of 2500 to 3000 mg/l when brine water is being treated. The following table compares some typical brine and BASA effluent results.

Parameter – mg/l	Composite Brine	BASA Effluent
barium	690	8.0
calcium	23,200	240
iron	160	0.06
magnesium	2,240	27.6
manganese	10.1	0.41
strontium	732	8.1
dissolved solids	224,300	3,005

From these results, it is evident that the plant process also removes significant amounts of iron, magnesium, manganese, and strontium from the brine water. The amount of brine water that can be treated via a POTW is restricted by plant operational problems caused by various brine constituents and water quality criteria limits for the receiving stream.

### **Evaporation**

While evaporation is a viable method to dispose of this wastewater, its use presents several problems that have not been addressed by the various process promoters.

Evaporation of untreated wastewater will produce a substantial amount of residual soluble salt solids that will be considered a hazardous waste on testing with the required USEPA TCLP method. For example, using our typical wastewater above, evaporation would produce a mixture of soluble chloride salts containing 3.33% barium by weight. Running the TCLP test on this mixture would result in a leachate containing 1,665 mg/l of barium, the USEPA limit for being considered a hazardous waste is 100 mg/l barium.

Accordingly, the residual salt mixture produced by evaporation of the untreated wastewater would be considered to be a hazardous waste and have to be disposed of as such, a costly proposition.

This problem has been recognized and is addressed by treating the wastewater prior to evaporation by chemical precipitation of the barium. Removal of the toxic barium as an insoluble, non-hazardous sludge results in a treated wastewater that can be evaporated without producing a hazardous waste.

Another, generally unrecognized, problem with evaporation is the amount and chemical composition of the residual salts produced and how they can be managed. Using our typical wastewater, treated for barium removal, evaporation of 250,000 gpd will produce 397,823 lb/day (approximately 200 tons/day) of a mixture of residual salts. Some of these salts, such as calcium chloride, are deliquescent (absorbing moisture from the air); all are very soluble in water as shown in the following table<sup>iii</sup>:

Chemical	Solubility	Chemical	Solubility
barium chloride	37.5 g/100 ml	calcium chloride	74.5 g/100 ml
lithium chloride	63.7 g/100 ml	magnesium chloride	54.25 g/100 ml
sodium chloride	35.7 g/100 ml	strontium chloride	53.8 g/100 ml

Based on the solubility of these salts, disposal of the residual salt mixture from treated wastewater evaporation in a landfill of any kind would appear to be impractical due to their ready formation of liquid salt solutions on contact with any water or moisture.

Use of the residual salts, in either solid form or as a brine solution, for roadway deicing has been proposed. This would appear to be ruled out by the recent PADEP proposal<sup>iv</sup> to regulate strontium in aqueous effluent at 10 mg/l.

Due to the deliquescent properties of calcium chloride, and its presence in large amounts (26% in our typical treated wastewater residual salt), use of the residual salt in any solid form would in practice be impossible due to its tendency to rapidly form a liquid solution in higher humidity conditions and cake the rest of the time.

To address these concerns with disposal of the solids produced by evaporation, the process will have to be preceded by chemical precipitation to remove the calcium, magnesium, and strontium from the brine water, effectively converting the brine to sodium chloride brine. Sodium chloride brine can then be concentrated for use as a deicing solution or evaporated to make salt for industrial use.

### **Chemical Precipitation Processes**

Current practice for treatment of brine waters is to adjust the pH using calcium hydroxide, clarify the water to remove any heavy metal precipitates, and then discharge the treated water to stream. This process is used to treat and discharge an estimated 550 mg/y by the several brine water treatment plants currently operating in the state.

New facilities will not be able to use this treat and discharge process due to the new dissolved solids, barium, and strontium effluent requirements in pending state regulations.

Treatment of high barium and strontium content brine waters, most Marcellus wastewaters, will not be possible due to the high solubilities, 31,165 mg/l as barium, and 6,123 mg/l as strontium, of the barium and strontium hydroxides produced by calcium hydroxide pH adjustment given the 10 mg/l effluent limits for barium and strontium in the pending state regulations.

Considering recycle of the brine water following treatment, the calcium hydroxide precipitation process can be modified to remove both barium and strontium as insoluble precipitates by adding sulfate ion prior to the calcium hydroxide addition. A number of sources<sup>v</sup> have been utilized to determine the following parameters for successful recycle of treated brine water as hydrofracture makeup water.

**Recycle Water Specifications**

maximum scale formers – 2,500 mg/l as calcium carbonate	
maximum dissolved solids – 50,000 mg/l	maximum iron – 3.5 mg/l
maximum calcium – 250 mg/l	pH range – 6.5 to 7.5

Unfortunately, use of calcium hydroxide as the treatment reagent, even with addition of sulfate ion to remove barium and strontium, will result in finished water that far exceeds the calcium and total hardness values for successful recycle. Even with addition of sufficient sulfate ion to react with all the calcium present in our typical brine water to produce a calcium sulfate precipitate, the calcium level in the finished water would be in the area of 2,100 mg/l with the scale former level exceeding 5,000 mg/l. We note that one proposed treatment and recycle facility<sup>vi</sup> does not give a specification for calcium in their finished water, likely due to the use of a sulfate/calcium hydroxide treatment process.

**Sequential Precipitation Process (SPP)**

The SPP was developed to address the problems presented by treatment of Marcellus wastewater for recycle or final disposal by evaporation. The process first removes barium from the wastewater as barium sulfate sludge via precipitation under controlled pH and ORP conditions.

Following barium removal, the remaining scale formers; calcium, iron, magnesium, manganese, and strontium are precipitated as carbonates and hydroxides in two separate precipitation steps using sodium carbonate and sodium hydroxide additions. After clarification, the pH of the finished water is adjusted to meet recycle specifications by addition of carbon dioxide. As the chemical composition of Marcellus flowback and production wastewaters 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 wastewaters to determine the widespread applicability of the SPP. The following test results are typical:

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>	90,633	14.9
total dissolved solids mg/l	248,428	150,520

The amounts of sludge produced by any precipitation process used to treat a Marcellus wastewater will be large. Using our typical brine water concentration of 6,500 mg/l barium, treatment of 100,000 gallons/day of this water would produce about 9,200 lb/day of dry barium sulfate sludge. We believe that this material can be further processed and reused as a weighting agent for drilling mud. The amounts estimated to be produced by treatment of Marcellus wastewaters when the play is fully developed, 250,000 tons/yr, would approximate 10% of the annual use of barium sulfate used in drilling mud in the United States. Of interest, the majority of the barium sulfate used is imported and acid mine drainage, common in some areas of the Marcellus gas play, can be used as a low cost sulfate ion source in the SPP.

The second mixed sludge produced by the SPP is almost insoluble as shown in the following table<sup>vii</sup>:

Chemical compound	solubility as compound, mg/l	solubility as element, mg/l
calcium carbonate	140	56
iron hydroxide	7.2	3.75
magnesium hydroxide	11.7	4.9
manganese hydroxide	0.35	0.22
strontium carbonate	10.9	6.3

Using our typical brine water concentrations of 18,000 mg/l calcium, 1,300 mg/l magnesium, and 4,000 mg/l strontium; treatment of 100,000 gallons of this water would produce about 45,700 lb/day of dry mixed carbonate/hydroxide sludge.

Reuse of this sludge as a raw material for production of cement has been proposed. Other potential uses would be as an acid soil neutralization reagent, a phosphate removal reagent in POTW, or as a replacement for limestone in fluidized bed boilers.

In the event that reuse of either, or both, of the sludges produced by the SPP cannot be accomplished, they can be disposed of in an approved landfill as they have been TCLIP tested and found to be non-hazardous.

For recycle, the SPP treated wastewater will normally have to be blended with a low dissolved solids water, treated acid mine drainage is ideal, to reduce the dissolved solids value to below the maximum value. Recycle will be a viable option for management of hydrofracture flowback and production wastewaters as long as the need for hydrofracture makeup water is substantially greater, a factor of four, than the amounts of wastewater produced. This will likely hold true in the Marcellus gas play for a period of 5 to 10 years from 2010.

At that point in time when wastewater production exceeds demand for hydrofracture makedown water, evaporation of SPP treated wastewater will be required. Unlike the current proposed evaporation methods, evaporation of SPP treated wastewater will produce an almost pure sodium chloride residual salt, which has several potential uses such as softener regeneration, road deicing, and raw material for chemical manufacture.

In addition to the high temperature thermal evaporation processes currently marketed, the SPP patent application discloses a low temperature method which utilizes low grade heat, such as condenser water at a power plant, for evaporation of SPP treated wastewater. As an example, a low temperature evaporator designed to evaporate 3,750 gpd of treated wastewater would require a condenser water flow of 150 gpm at 105 F, returning to the power plant cooling system at 85 F and using 7 hp of electrical power for unit operation.

With reuse of produced barium sulfate, insoluble mixed sludge, short term recycle of the treated wastewater, and reuse of the residual salt produced by evaporation, the SPP appears to be the best method for management of Marcellus gas play wastewaters.

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<sup>i</sup> STW Resources, Inc., “GE Thermal Evaporation Technology”; Heartland Technology Partners LLC, LM\_HT Wastewater Concentrator”, and several others.

<sup>ii</sup> USPTO Application 61/199,588, “Treatment of Gas Well Hydrofracture Wastewaters”, filed 11/19/2008, ProChemTech International, Inc.

<sup>iii</sup> CRC Handbook of Chemistry and Physics, 57 th Edition, Physical Constants of Inorganic Compounds

<sup>iv</sup> PAEQB, proposed rulemaking, 25 PA code, Chapter 95, PA Bulletin, Volume 39.

<sup>v</sup> personnel communications, L. Case, Halliburton to T. Keister, ProChemTech and Proceedings and Minutes of the Hydraulic Fracturing Expert Panel, XTO Facilities, Fort Worth, TX, 09/26/07

<sup>vi</sup> TerraAqua Resource Management, WEB page memo dated 01/11/10

<sup>vii</sup> American Chemical Society “Solubilities of Inorganic and Metal Organic compounds”, Fourth edition, 1958

### Speaker Biography

Timothy Keister, CWT, holds a B.Sc. in Ceramic Science from Penn State and is the Chief Chemist/President at ProChemTech International, Inc. He is an Association of Water Technologists Certified Water Technologist, Fellow of the American Institute of Chemists, Senior Member of the American Institute of Chemical Engineers, and member of the American Society of Heating, Refrigeration, and Air Conditioning Engineers, American Chemical Society, and the Water Environment Federation. His career in the environmental/technical water field began at Brockway Glass Company in 1973, where he was responsible for management of water and wastewater activities at 38 manufacturing plants across the country. In 1987 he founded ProChemTech, which specializes in innovative water and wastewater management technology with emphasis on treatment/recycle and zero discharge projects. Some spare time is also devoted to activities as Chairman of the Brockway Area Sewerage Authority and Technical Director of the Toby Creek Watershed Association.

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