

International Water Conference
IWC 12-72

**Sequential Precipitation - Fractional
Crystallization Treatment of Marcellus Shale
Flowback and Production Wastewaters**

Timothy Keister, James Sleigh, and Megan Briody

ProChemTech International, Inc.
Brockway, PA

Keywords: Marcellus, shale, flowback, production wastewater, treatment, resource recovery, sequential, precipitation, fractional, crystallization

ABSTRACT

By 2016 development of the Marcellus shale gas play in the Northeast will generate an estimated 60 million gallons per day of hydrofracture flowback and production wastewater. This wastewater is close to saturation with sodium, calcium, magnesium, strontium, and barium chlorides as major constituents. Discharge of such wastewater has been outlawed in Pennsylvania, leaving deep well injection and treatment for recycle/reuse as current disposal options. Resource recovery by sequential precipitation and fractional crystallization, which produces salable products from the wastewater, has been developed as an economic disposal method for Marcellus wastewaters.

BACKGROUND

The Marcellus gas 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 8 million gallons of water, mixed with sand and various additives, is required to completion fracture each horizontal deep well. Following hydrofracture, free water must be removed from the well, generally 10 to 20% is recovered, and is commonly referred to as “flowback” wastewater. Recent developments permit recycle of flowback, with minimal treatment, as hydrofracture makeup water.

Once a Marcellus gas well has been drilled and hydrofractured, “production” wastewater is produced for the 15 to 20 year life of the well at rates from 400 to 4,000 gpd. By 2016, with 30,000 wells expected to be in production, it is estimated that 60 million gallons per day of production wastewater will be generated and require proper management. Production wastewater is “dispersed”; the wells producing it are geographically spread over wide areas with low daily flows. Management of this wastewater will require well site tankage and tank truck based collection to convey it to either transshipping locations for transport to injection wells, out of state treatment; or to central resource recovery facilities.

In contrast to production wastewaters from other gas shale plays, Marcellus production wastewater has a very high level of dissolved solids with large amounts of barium, calcium, magnesium, sodium, and strontium chlorides; with many other constituents, such as bromine and lithium, present in lesser

quantities. Table 1 is a typical analysis of a Marcellus Production Wastewater.

Table 1, Marcellus Production Wastewater

Parameter as mg/l	Result
aluminum	3.0
barium	6,500
bromide	800
calcium	18,000
chemical oxygen demand	8,000
chloride	116,900
iron	60
lithium	150
magnesium	1,300
sodium	48,00
strontium	4,000

Note that chemical analysis of Marcellus production wastewaters presents a challenge to analytical laboratories due to the high dissolved solids content.

PAST AND CURRENT TECHNOLOGY

Past and current practice for disposal of flowback and production wastewaters has included use as a roadway deicer in winter and dust control agent in the summer, discharge to surface waters via publicly owned treatment works (POTW), treatment with direct discharge to stream, and treatment with recycle as hydrofracture makeup water.

ROADWAY DEICER/ DUST CONTROL- Gas well production wastewaters have been generated and disposed of in Pennsylvania for over 100 years. In the past, the majority of these wastewaters were either dumped around the producing well or used for roadway deicing and dust control. The advent of environmental regulation has correctly eliminated these disposal practices. **DISCHARGE VIA POTW (Publicly Owned Treatment Plants) -** Prior to the Marcellus shale development, a substantial amount of gas well production wastewater was

disposed of via POTW with subsequent discharge to surface waters. This did not result in any major problems as non-Marcellus gas well production wastewaters are low volume and contain much lower amounts of barium and strontium than Marcellus wastewaters. In 2008, the rapid increase in Marcellus wastewater production and disposal via POTW that the Monongahela River was severely impacted, dissolved solids levels increasing by a factor of more than two. This prompted the PA Department of Environmental Protection (PADEP) to ban disposal of Marcellus wastewaters by almost all POTW. Currently less than ten (10) POTW are permitted for gas well wastewater disposal and continue to accept limited amounts of gas well wastewaters. Some specific problems noted by POTW accepting Marcellus gas well wastewaters include increased sludge generation, increased barium content in produced sludge leading to concerns as to a potential hazardous waste designation, and flotation of sludge in final clarifiers.

TREATMENT WITH DISCHARGE- Prior to development of the Marcellus shale, several facilities existed for chemical treatment of gas well wastewaters with direct discharge to stream. These facilities use chemical precipitation with calcium hydroxide to remove suspended solids and some dissolved metals. The PADEP has prohibited discharge of additional, or new, high dissolved solids (over 500 mg/l) wastewaters into waters of the Commonwealth. This prohibition has restricted these facilities to treat no more than historical flows, estimated at 1.5 mgd, and dissolved solids loading, which existed prior to the regulation change. These facilities face an additional challenge if Marcellus wastewaters are to be treated in that as their discharge permits are renewed, or modified, they must comply with an effluent limitation of 10 mg/l maximum for both

barium and strontium.

TREATMENT WITH RECYCLE AS HYDROFRACTURE MAKEUP WATER- Since start of Marcellus development, several facilities have been constructed which treat gas well wastewaters by precipitation using sulfate to lock up barium and strontium followed by calcium hydroxide for general metals removal.

The resulting clear brine is then returned to gas well drillers for use as hydrofracture makeup water. There is a substantial debate as to what standards are needed for reuse of treated water as hydrofracture makeup water. The following Table 2, Recycle Criteria, summaries some generally accepted recycle criteria.

Table 2, Recycle Criteria

Parameter	Criteria
pH	6.0 to 8.0
maximum total hardness	2,5000 mg/l as CaCO ₃
maximum calcium hardness	350 mg/l as CaCO ₃
maximum total iron	2 to 20 mg/l
maximum sulfate	100 mg/l
maximum dissolved solids	40,000 to 150,000 mg/l

Note that these criteria are usually achieved by precipitation treatment of the Marcellus wastewater followed by a high rate of dilution with fresh water.

Major problems with this approach include a large volume of mixed sludge to be landfilled and the potential to become water logged as Marcellus hydrofracture activity is replaced by production operations.

TOTAL EVAPORATION- Various promoters have advanced use of total evaporation with production of a condensate as a viable means to dispose of Marcellus wastewater. Evaporation has two major problems.

Evaporation of Marcellus wastewaters produces a solid material for disposal which, if the barium content is not removed or

chemically rendered insoluble, will often test out as a USEPA Toxic Characteristic Leach Procedure (TCLP) test hazardous waste due to soluble barium content. This specific problem has been demonstrated by operation of a total evaporation pilot facility where the produced solids were determined to be a TCLP hazardous waste due to soluble barium content.

The other problem with total evaporation is the amount and chemical composition of the solid material produced and how to manage it. Based on the typical Marcellus wastewater, pretreated for barium removal, evaporation of 250,000 gallons would produce 397,823 pounds (approximately 200 tons) of a mixture of residual salts. Some of these salts, such as calcium chloride, are deliquescent; all are very soluble in water as shown in the following Table 3, Residual Salts Solubility.

Table 3, Residual Salts Solubility

Residual Salt	Solubility
barium chloride	37.5 g/100 ml
calcium chloride	74.5 g/100 ml
lithium chloride	63.7 g/100 ml
magnesium chloride	54.3 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 total evaporation treatment in a landfill of any kind would appear to be impractical due to their ready formation of liquid salt solutions on contact with water or moisture. While use of the residual salts for roadway deicing has been proposed, this appears to be ruled out by the regulation of strontium in aqueous effluent at a maximum of 10 mg/l and would also present substantial logistics problems.

CHEMICAL PRECIPITATION TO SALT BRINE- Chemical precipitation of barium, calcium, magnesium, and strontium from Marcellus wastewater results in production of a sodium chloride brine, which could be utilized for roadway deicing if other toxic

constituents were at suitable levels. This brine could also be evaporated to produce a solid sodium chloride that may be suitable for other uses. Drawbacks include generation of very large amounts of mixed sludge requiring landfill disposal and a substantial logistics problem.

DEEP WELL INJECTION- Currently, a substantial amount of Marcellus wastewater is disposed of by deep well injection, most of the injection wells being located in Ohio. This disposal method has two problems, the first being simply that the wastewater has to be transported considerable distances by tank truck or rail tank car to the injection well site. Transportation costs on the order of \$0.05 to \$0.25/gallon have been reported.

A second problem has been recently noted around Youngstown, OH, with several deep well injection sites being linked to earthquakes. The Ohio EPA has responded by shutting several injection wells down and restricting both the amount of wastewater that can be injected and development of additional wells.

SEQUENTIAL PRECIPITATION FRACTIONAL CRYSTALLIZATION

We have developed the Sequential Precipitation Fractional Crystallization Process (SPFCP) to address economic disposal of Marcellus wastewater by resource recovery. This patent pending technology disposes of the wastewater by processing it into salable commodity chemical products with no landfill disposal of residual material or discharge of liquids. Cost of process operation is generally less than the revenue produced by product sales.

The SPFCP must first address the high content of barium found in Marcellus wastewater. As barium is a USEPA hazardous heavy metal, it is desired to remove it to low levels from the wastewater as a salable product.

BARIUM RECOVERY- The first precipitation step in the SPFCP is to chemically remove the barium as insoluble barium sulfate under closely defined conditions where precipitation of calcium, magnesium, and strontium are minimized. The concentration of barium and strontium in the wastewater is first determined, then sulfate ion (as sulfuric acid) is added in an amount of 40% over the calculated stoichiometric amount to remove the barium as the sulfate to low levels. In this first mix tank, potassium permanganate is also added in an amount to obtain a faint pink color, indicating excess permanganate, which oxidizes the majority of the organics present in the wastewater and to oxidize any ferrous iron present. Sodium hydroxide is also added to this mix tank to maintain the pH in the range of 2.5 to 3.5.

In a second mix tank, the wastewater pH is adjusted to 3.5 to 4.0 by addition of sodium hydroxide to complete the barium sulfate precipitation. Under these process conditions, a fine barium sulfate precipitate is formed which is then flocculated in a third mix tank, equipped with a VFD slow speed mixer, by addition of a low anionic charge, high molecular weight polyacrylamide polymer. The flocculated barium sulfate is removed from the wastewater using an inclined plate clarifier, dewatered and washed with distilled water for retained soluble salt removal in a plate and frame filter press, discharged, and dried. The recovered barium sulfate at this point is a commercial product, "barite" with barium stripped brine remaining.

STRONTIUM RECOVERY- Dependent upon its concentration and economics involved, strontium can be removed from the barium stripped wastewater as the sulfate in a process similar to that for barium and recovered for sale.

SODIUM CHLORIDE RECOVERY- We have discovered that sodium chloride can be removed from the barium stripped wastewater

by fractional crystallization to produce a very high purity sodium chloride crystal and a commercial grade solution of calcium chloride.

Evaporation of the stripped wastewater results in concentration of the various salts present. As shown in the following Table 4, Three Phase Solubility, as the concentration of calcium and magnesium salts increase, the solubility of sodium chloride decreases, resulting in fractional crystallization of sodium chloride from the concentrating wastewater.

Table 4, Three Phase Solubility

Calcium Chloride	Magnesium chloride	Sodium chloride
33.8	8.4	2.3
52.9	8.2	0.9
60.1	0	0
60.2	0	0

as grams/100 ml @ 95 C

We have also discovered that sodium chloride crystal size and potential scaling of the evaporator are controlled by equipping the evaporator with a high energy mechanical mixer.

Sodium chloride crystals are removed by sidestream filtration of the condensed wastewater from the evaporator on a continuous basis using a linear vacuum belt filter. Filtered crystals are washed with saturated sodium chloride brine, to remove the more soluble salts, and dried. The sodium chloride crystal at this point is a commercial product.

CALCIUM CHLORIDE RECOVERY- By controlling the concentration of calcium chloride in the evaporator to remove sodium chloride to below 2.5%, the resulting calcium chloride solution is a salable commercial product.

After removal of the sodium chloride crystals by sidestream filtration, the filtered calcium chloride solution passes through a specific gravity measurement device and if the specific gravity is above 1.44, routed to the

calcium chloride solution storage tank. Calcium chloride solution below this specific gravity is returned to the evaporator for further concentration.

Calcium chloride solution at a specific gravity of 1.44 will have to be diluted with distilled water to a specific gravity between 1.275 and 1.310 to make a commercial grade product at 28 to 31% calcium chloride content.

DISTILLED WATER- Evaporator water vapor will be condensed to recover energy by preheating incoming barium stripped wastewater in a heat exchanger. This distilled water will provide the facility with barite rinse water, water for sodium chloride brine preparation, calcium chloride solution concentration adjustment, and cooling tower and boiler makeup.

Any excess water could be sold for use as hydrofracture makeup water or even discharged to stream with an appropriate permit.

LABORATORY RESULTS

The SPFCP has been tested in laboratory scale experiments to ascertain process operating parameters on a variety of actual Marcellus flowback and production wastewaters.

The following Table 5, FRAC 15 Test Results, shows typical results obtained on one test of a Marcellus production wastewater from Tioga County, PA, where first the barium is precipitated (Ba ↓) followed by fractional crystallization removal of sodium (Na ↓).

Table 5, FRAC 15 Test Results - as mg/l

Parameter	untreated	Ba ↓	Na ↓
barium	6,000	43	50
bromide	812	1,020	9,632
calcium	17,500	19,300	182,000
lithium	189	220	2,050
magnesium	1,800	1,540	14,750
sodium	80,000	55,500	2,600
strontium	3,600	1,280	10,100

The sodium chloride crystal recovered from this test run was analyzed with the following results obtained, Table 6, Sodium Chloride Results.

Table 6, Sodium Chloride Results

Parameter	Result - mg/kg
sodium	410,000
calcium	1,535
magnesium	107
barium	60

A sample of produced barite was tested using the USEPA TCLP to determine if the product could be classified as USEPA hazardous waste. As shown in the following Table 7, Barite TCLP Results, the product is not a hazardous waste.

Table 7, Barite TCLP Results

Parameter	Result - mg/l
arsenic	0.016
barium	0.465
cadmium	<0.005
chromium	0.0236
lead	<0.02
mercury	<0.0002
selenium	0.402
silver	<0.01

To date, a total of fourteen (14) Marcellus flowback and thirteen (13) production wastewaters from across Pennsylvania have been tested to determine if the SPFCP was applicable to that specific wastewater. This testing has confirmed that the SPFCP can be used to treat all of the tested Marcellus wastewaters.

ECONOMICS

BARITE- An average value for barium in production water is 5,000 mg/l, so a 500,000 gpd SPFCP facility would produce 17.7 dry tons of barite per day or 6,469 tons per year. Annual world use of barite was estimated at 7,000,000 tons in 2010 with the product found in drilling mud, glass, brake linings,

paints, and mold release compounds. Annual US use of barite is estimated at 2,700,000 tons with about 80% imported. Good quality barite sells for up to \$1.00/lb, with wholesale prices in the \$0.15 to \$0.25/lb range. From this information it is evident that the barite product by resource recovery of Marcellus gas shale wastewaters can be easily absorbed into the existing market and that significant revenue can be generated by barite sales.

SODIUM CHLORIDE- An operating SPFCP facility will produce large amounts of sodium chloride. With a typical production water sodium level of 58,500 mg/l, a 500,000 gpd SPP facility will produce about 122 tons/day, annual output of 44,530 tons, of sodium chloride crystal.

Annual production of sodium chloride in the US is estimated at 45,000,000 tons with a bulk wholesale price of \$30/ton. Bagged, good quality material can be sold at up to \$160/ton.

As with the barite, the sodium chloride output of several SPFCP facilities can be readily absorbed into the existing market with significant revenue generated by salt sales.

CALCIUM CHLORIDE- Assuming typical production water content of 15,000 mg/l calcium, a 500,000 gpd SPFCP facility will produce 96.5 dry tons per day, 241 tons of 40% liquid calcium chloride product. This product is used in de-icing fluids and freeze proofing coal, coke, stone, and ore; production paper, fungicides, starch paste, concrete additive, fabric sizing, and electrolytic cells. Current wholesale price for 40% calcium chloride solution is \$160/ton.

When the annual output of one SPFCP facility of 35,223 dry tons is compared to 2002 annual worldwide use of 1,687,000 tons, it is evident that the output from several SPFCP facilities can be readily absorbed in the market. As with the barite and sodium chloride, significant revenue can be generated by sale of calcium chloride solution.

OPERATING ECONOMICS- Based on the chemical and energy use of a 250,000 gpd capacity SPFCP facility, market pricing of the various inputs, and labor costs; a daily operating cost of \$22,000 has been calculated. Sale of produced commodities, at wholesale prices as noted, will return approximately \$35,500/day, resulting in \$13,500/day income to pay for construction of the facility.

FACILITY COST- Our Engineered Services Division recently estimated the cost to build a 250,000 gpd capacity SPFCP facility at \$11,316,000, exclusive of site acquisition and development costs. With this cost and the \$13,500/day operating cost credit, there is a simple payback of 2.3 years on a SPFCP facility of this capacity.

FUTURE RESEARCH

Both bromine and lithium are concentrated in the calcium chloride solution to levels which may be economical to consider recovery of one, or both, materials. Future research will be directed towards examination of methods for recovery of both materials.

CONCLUSION

Based on extensive laboratory research, the SPFCP has been determined to be an economical method for disposal of Marcellus wastewaters. Production of salable commodities from the wastewater provides a positive cash flow which will pay for construction of a facility in a reasonable amount of time.

References

- Case, L., Halliburton Inc., personal communications
- CRC Handbook of Chemistry and Physics, 57th Edition, Physical Constants of Inorganic Compounds
- Keister, T. 2010. Marcellus Hydrofracture Flowback and Production Wastewater Treatment, Recycle, and Disposal Technologies”, The Science of Marcellus Shale Conference, Lycoming College, Williamsport, PA.
- Proceedings and Minutes of the Hydraulic Fracturing Expert Panel, XTO Facilities, Fort Worth, TX, 09/26/07
- USPTO application #13,222,481, “Treatment of Gas Well Production Wastewaters”, filed 08/31/2011
- USPTO application #61,199,588, “Process for treatment of gas well completion, fracture, and production wastewaters for recycle, discharge, and resource recovery” filed 11/19/2008