Case Study on the Recovery of Salt from Produced Water Coming from Shale Gas Facilities

Salt, Safety and Environment

Key words: Shale Gas Recovery, Produced Water Disposal, Salt Processing, Evaporated Salt, Pennsylvania

Abstract

The production of unconventional gas has undergone a fast and impressive development in recent years. Especially in the Marcellus Shale and Utica Shale formations in the north east of the USA, where new sources have been opened up and changed the gas market significantly.

The technology of hydraulic fracturing (fracking), which is utilized for the production of shale gas results in environmental side effects, which are causing a lot of attention not only in the USA, but also worldwide. In particular, the waste water that is generated, which is pumped into the drilling hole and comes partially back to the surface as back flow or produced water. This back flow increases the challenges to the operators of drilling sites and the cost of disposal influences the economic evaluation of such projects.

Although produced water can be disposed of by well injection, this results in high transportation and disposal costs, so that the treatment of produced water has now become a standard procedure.

Recently, an important step was achieved in the field of the waste water treatment by not only minimizing the volume by evaporation but also recovering a valuable product from the waste water.

In Pennsylvania, USA, a crystallization plant has been successfully put into operation which takes the produced water after chemical pre-treatment and not only concentrates it. but also selectively crystallizes the dissolved salt. The recovery of clean condensate fulfils the specifications for municipal water discharge and the production of salt for de-icing and other applications are the outgoing products, while the volume of purge for disposal is reduced to a fraction of the material feed.

While the first plant has proven the economic and environmental feasibility of thermal waste water treatment in the field of shale gas applications, SEP has now developed further steps to recover more valuable products from the remaining mother liquor.

Introduction

The unconventional recovery of natural gas, which the shale gas recovery belongs to, has developed over a long period, and great progress in the technology of hydraulic fracturing has led to a fast improvement and expansion of drilling sites and natural gas recovery in many locations throughout the US.

Shale gas has been recovered for over 100 years in the Appalchian and the Illinois shale basins and, since the 1970s, a steady increase has been observed[1]. The initial economic obstacle of higher drilling cost than gas value to be recovered has meanwhile changed, thanks to technology improvement, into a boom on the natural gas market[2].

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[1] Sunshine, W.L., About.com Energy: Rise of U.S. Shale Gas Production – An Introduction, http://energy.about.com/od/drilling/a/Waste-Water-Byproducts-Of-Shale-Gas-Drilling.htm

[2] EIA - U.S. Energy Inforamtion Administration: Shale Gas Production, 4th April 2014, http://www.eia.gov/dnav/ng/ng_prod_shalegas_s1_a.htm

Driving forces such as elevated natural gas prices and the improvement of technology resulted in a spread of hydraulic fracturing (or hydrofracking or fracking) to other locations such as basins in Texas, Wyoming and Pennsylvania over the last decade.

For the recovery of the shale gas, water is utilized as a medium for the fracturing process. After the drilling process, the fracturing fluid is prepared by using water and adding various chemicals and sand to it. This mixture is pumped into the well under high pressure and the rock formation is broken apart so that the captured natural gas in the rock is released. The gas is brought back to the surface and collected together with some of the water that also returns in the course of the gas recovery to the surface.

The water that comes back to the surface is considered a hazardous waste water. It can occur in the form of so called flowback or produced water. Flowback is considered as the reverse flowing liquid after the fracking is completed and the pressure on the well is released. It contains the process fluid used for fracking with excess proppant[3]. Produced water is considered the sum of reverse flowing fracking fluid together with water that occurs naturally in the rock formation and is released to the well.[4]

A typical composition of such waste water is depicted in table 1 (Hammer R., VanBriesen J, 2012).

It is known that the waste water from fracking has a **high salinity**, because salts are added to the fracturing liquid during the preparation for addition to the well and also because salt is dissolved from the geologic formation.

Besides its salinity, the waste water contains **industrial chemicals** that have also been added before the fracking process in order to support the drilling.

Hydrocarbons, which are sometimes summarized under the expression "oil and grease" are also found in the waste water. These components are mainly from the drilling process.

The waste water brings along in some formations radioactive materials, which are naturally occurring and are called NORM.

This composition of various hazardous chemicals leads to the requirement of good waste water management, because the risks to health and the environment should be kept to a minimum.

Table 1: Chemical Constituents in Produced Water from Marcellus Shale Development[5][6]

[3] Proppant is a substance which is granular, such as sand, that is added to the fracturing liquid and has the purpose of keeping the cracks in the formation open when the fracturing process is finished.

[4] EPA United States Environmental Protection Agency: The Hydraulic Fracturing water Cycle, 16th March 2014, http://www2.epa.gov/hfstudy/hydrolic-fracturing-water-cycle

[5] T. Hayes, Gas Technology Institute, *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, report prepared for Marcellus Shale Coalition, December 2009, http://www.bucknell.edu/script/environmentalcenter/marcellus/default.aspx?articleid=14; E.L. Rowan et al., *Radium Content of Oil and Gas-Field Produced Waters in the North Appalachian Basin (USA): Summary and Discussion of Data*, 2011, 31, http://pubs.usgs.gov/sir/2011/5135/pdf/sir2011-5135.pdf

[6] Hammer A., vanBriesen J., NRDC Document May 2012 D:12-05-A: *In Fracking's Wake: New Results are Needed to Protect Our Health and Environment from Contaminated Wastewater*, May 2012, http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Chemical constituent or surrogate parameter	Unit of measure	Range reported in produced water from wells drilled in Marcellus Shale 5 days post hydraulic fracturing	Range reported in produced water from wells drilled in Marcellus Shale 14 days post hydraulic fracturing
Total Suspended Solids (TSS)	mg/L	10.8-3'220	17-1'150
Turbidity	NTU	2.3-1'540	10.5-1'090
Total Dissolved Solids (TDS)	mg/L	38'500-238'000	3'010-261'000
Specific Conductance	umhos/cm	79'500-470'000	6'800-710'000
Total Organic Carbon (TOC)	mg/L	3.7-388	1.2-509
Dissolved Organic Carbon (DOC)	mg/L	30.7-501	5-695
Chemical Oxygen Demand (COD)	mg/L	195-17'700	228-21'900
Biochemical Oxygen Demand	mg/L	37.1-1'950	2.8-2'070
BOD/COD Ratio (% biodegradable)			0.1 (10%)
Alkalinity	mg/L	48.8-327	26.1-121
Acidity	mg/L	<5-447	<5-473
Hardness (as CaCO3)	mg/L	5'100-55'000	630-95'000
Total Kjeldahl Nitrogen (TKN)	mg/L as N	38-204	5.6-261
Ammonia Nitrogen	mg/L as N	29.4-199	3.7-359
Nitrate – N	mg/L as N	<0.1-1.2	0.1-0.92
Chloride	mg/L	26'400-148'000	1'670-181'000
Bromide	mg/L	185-1'190	15.8-1'600
Sodium	mg/L	10'700-65'100	26'900-95'500
Sulfate	mg/L	2.4-106	<10-89.3
Oil and Grease	mg/L	4.6-655	<4.6-103
BTEX (benzene,toluene, ethylbenzene, xylene)	ug/L		Non-detect-5'460
VOC (volatile organic compounds)			Non-detect-7'260
Naturally occuring radioactive compounds (NORM)		Non-detect-18'000 pCi/L; median 20460 pCi/L	
Barium	mg/L	21.4-13'900	43.9-13'600
Strontium	mg/L	345-4'830	163-3'580 J
Lead	mg/L	Non-detect-0.606	Non-detect-0.349
Iron	mg/L	21.4-180	13.8-242
Manganese	mg/L	0.881-7.04	1.76-18.6

Contemporary Possibilities of Waste Water Management

There are nowadays five different ways that are commonly used to manage the waste water – flowback or produced water – that is generated in the process of fracking and recovery of natural gas:

- Reduction of waste water being generated
- Recycling of waste water in the fracking process
- Disposal of the waste water
- Beneficial reuse of the waste water
- Treatment of waste water for further processing or disposal

The reduction of the generated waste water takes mostly place during the development of a well. Which means it is related to the early flowback period. Most of the improvements are being gained on-site through the development of techniques that require less water to be applied in the well bore.

The reuse of the waste water for fracking operations is in many cases related to a pretreatment and chemical adjustment of the recycled fluid, because constituents such as salt, suspended solids or scale forming chemicals may cause problems with the well performance. The related logistical effort, as mentioned below, is one of the drivers for an investment in waste water reuse development.

Disposal in ponds for solar evaporation is only possible in southern areas and, due to weather conditions in the north and north east of the US, not carried out, although on-site solutions with no transportation cost and effort would be preferable. The most common disposal of waste water from shale gas operations is conducted off-site through underground injection into disposal wells. Prior to the injection, the waste water has to be pretreated in order to avoid well plugging or formation clogging due to scale-forming chemicals in the waste water. A favorable condition for deep well injection is an area with porous sedimentary rock, such as found in the mid-continent and the Great Plaines. Concerning the disposal of waste water through injection, there are concerns about seismic occurrences in the nearby areas of such wells. A major factor that impacts the economics of this disposal option is the related transportation cost and effort.

The beneficial reuse of the waste water is only permitted in a very strict and limited way. Some waste waters that are low in total dissolved solids may be utilized for dust control on unpaved roads and for de-icing applications for winter maintenance. Most of the waste water is not subject to any direct beneficial reuse.

Treatment of the waste water is generally required for most of the waste water management options that have been described above. The type of treatment that is scheduled depends upon the further usage of the waste water and on the constituents that have to be removed, which are the suspended solids, the hydrocarbons and the dissolved solids.

Suspended solids are usually removed by settling or filtration processes. For hydrocarbon removal, filtration, centrifuging and hdrocyclones are utilized or in some cases extraction and adsorption processes are possible.

The above mentioned methods for waste water treatment do not affect the salinity of the treated fluids, which is one major constituent that makes it difficult to discharge to municipal waste water plants. During the treatment, ions such as calcium, magnesium, iron or sulphates, are often removed by means of precipitation, monovalent ions such as sodium, potassium, chloride or bromide have to pass through so-called desalination processes to be removed.

Desalination can be carried out by means of thermal or non-thermal processes. Thermal processes can be distillation, which is stopped when the concentration reaches the point where scaling occurs in the processing equipment. It can be evaporation with or without crystallization, whereas the crystallized solids can be a mixture of salts for no further usage and disposal or it can be a clean and marketable salt.

Non-thermal processes for desalination can, for example, be reverse osmosis, ion exchange, forward osmosis and electrodialysis.

Publicly owned treatment works (POTW) can and do accept some of the produced water for treatment, but they are normally not able to remove the salinity from the waste water. Also, some of the chemicals in the waste water have the potential to hinder biological processes. The capacity to treat such waste water is limited and so there are centralized waste treatment facilities that cover most of the need for treatment of shale gas produced waters.

These facilities have additional treatment possibilities such as the removal of iron, barium, radium or other ions through pH adjustment and subsequent precipitation through the addition of other chemicals.

Recovery of Road Salt from Treated Shale Gas Produced Water

The desalination through thermal methods has been applied many times in the field of produced water treatment. Many of them have been implemented as distillation processes and are able to concentrate the waste water up to a level of approx. 100,000 mg/l of TDS.

Besides this, evaporation and crystallization plants have been under discussion for a long time. A typical approach is a zero-liquid-discharge concept, which allows the pre-treated feed to boil most of the water off and leads to a complete separation of condensate as water together with the remaining organic compounds that would evaporate with it, and a mixture of all inorganic compounds that crystallize out as salts and remain as solid waste material to be disposed of. In case the mixed salt is completely dewatered, it can be considered as solid waste disposal and can be disposed of in landfills, as long as the radioactivity is below a given value. The salt mixture cannot be utilized for further applications.

The latest approach for evaporation and crystallization has been the recovery of a valuable product from the waste water in combination with reduction of the total volume of the liquid waste material.

Such a project has been put into operation in 2014 and is located in Standing Stone, Pennsylvania. The plant is owned by Eureka Resources LLC. The evaporation and crystallization unit was developed, designed and supplied by SEP Salt & Evaporation Plants Ltd.

The waste water treatment facility has a pre-treatment section in place, which utilizes common pre-treatment technologies in operation. Details regarding this process are not the subject of this paper.

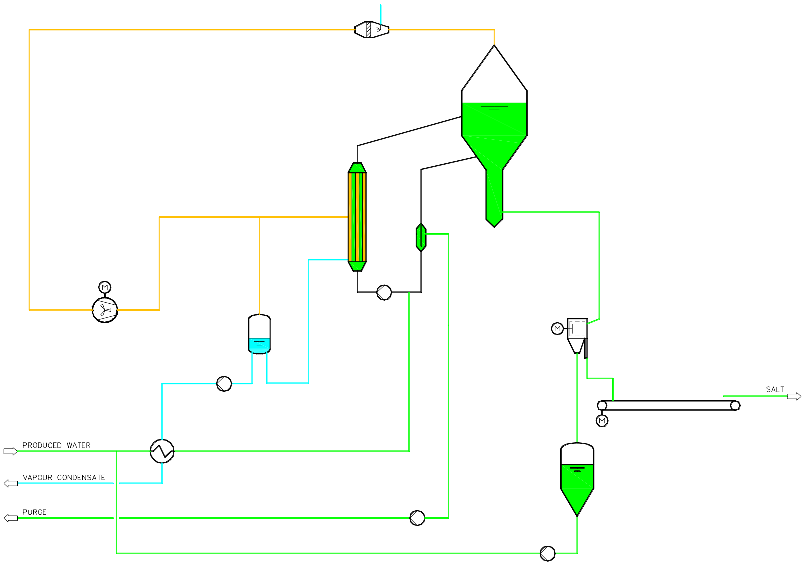
The Crystallization Plant Concept

The principle of the process is depicted in picture 1 and explained in the following section.

The concept of the evaporation and crystallization plant, which will now be called crystallizer, is to evaporate the waste water significantly above the solubilities of the salts that are present in solution. In order to avoid scaling, the plant is designed as a crystallizer, which can facilitate a controlled crystallization with very little scaling and incrustation. The maintenance schedule foresees cleaning cycles similar to the ones of regular salt production facilities.

The plant feed is pre-treated waste water. The energy concept preheats the feed, so most of the heat generated in the process can be recovered. The waste water, which is herein now called brine, is fed into the evaporator which is a forced circulation type evaporator. This type is very often used for crystallization in the salt industry and ensures a good control of crystal size and is simple in operation. In the evaporator, the liquid is recirculated by a circulation pump through the external circulation pipe and heat exchanger, where it is heated up above the boiling point. Once the liquid re-enters the evaporator body, boiling occurs and due to the evaporation of water, the concentration of the brine increases in the evaporator. Through oversaturation of the salt concentration, crystals are formed and the crystals grow. The crystals fall by gravity into the lower section of the evaporator. There they are collected in the salt leg and withdrawn. The withdrawn salt is dewatered and washed again in a centrifuge and transported to a storage facility for sale. The salt may be processed optionally through a dryer if required.

Picture 1: Typical Flow Scheme of a Mechanical Vapor Recompression Plant for Recovery of NaCl from Shale Gas Produced Water



The entrained brine droplets in the water vapor that is generated in the evaporator through boiling is cleaned in a demister. From there, it enters into the vapor recompression system of the plant. The vapor is recompressed to higher pressure and temperature and reused on the shell side of the heat exchanger to heat the brine for concentration and crystallization. The energy for this process is electrical energy, which drives the compressors. Steam is only needed for start-up of the plant, afterwards that process is independent of any heating source, besides electrical energy.

The condensate that leaves the plant is clean and mainly free of any salts. It may contain some volatile organics that were present in the feed, which evaporate and condense together with the water. The presence of such organics in the feed and later in the condensate determines whether it may directly be discharged to surface water or POTWs with a permit or if it requires a biological treatment ahead of such a step.

The process is designed with a liquid purge which is discharged from the plant. This ensures that the concentration of all components in the boiling waste water are controlled and only the sodium chloride precipitates selectively in the evaporator. The pureness of the solid product can be determined by the purge ratio. The amount of purge depends strongly on the concentration of the components in the waste water. However, the process reaches the volume of liquid to a fraction of the initial waste water volume after pre-treatment.

Picture 2 depicts the evaporation and crystallization plant during its construction period, before the steel structure has been shielded.

Picture 2: View of the Evaporation and Crystallization Plant during its construction period in 2013

Technical Frame Data

The plant is driven by electrical energy during steady operation. Table 1 in this article shows how wide the range of produced water compositions can be. Of course there are local limitations to this and not the entire range must be expected for the design of such a plant. However, this plant is designed to handle waste water with a fluctuating composition in a certain range that had to be agreed upon ahead of the realization of the project. In case fluctuations occur, more intense operator attention is required.

The technical frame values that can be fixed in any case of waste water composition are the following:

- Evaporation capacity
- Specific electrical consumption
- NaCl purity

Picture 3 shows the first salt that has been produced during commission in the guaranteed quality for road salt application.

The purge that leaves the plant contains everything else that has not been recovered beforehand in the crystallizer. It is a concentrated brine, rich in Ca, Ba, Sr and other components. It might still be disposed of in an injection well, whereas the volume is significantly reduced as is the transportation and disposal costs. In this specific case, there is even an application for reuse of the brine in the fracking process at the wells, so that it is not being considered a waste material to be disposed of. The only waste material that is being produced is the sludge generated during the pre-treatment.

For future applications, the development has gone further and it is possible to process the purge in such way that there will be no more liquid left that has to be transported to a well and several inorganic compounds can be recovered in industrial grade for sale. Some of the components are rare and have a good market value, which makes the feasibility of such plants attractive.

Picture 3: Salt Pile generated during the Commission of the Evaporation and Crystallization Plant in 2014

Conclusion

The centralized treatment of produced water has proven to be an economically and environmentally attractive concept with the possibility of multiple benefits. The elimination of liquid volume to be disposed of in injection wells is one of them. Another benefit is the production of marketable products. Solids that are crystallized in the evaporation plant can be recovered selective and in a market equivalent quality. The vapor condensate recovered from evaporation reaches a quality for further water treatment in order to be fed into POTWs.

Depending on the pretreatment of the waste water, the liquid purge of the crystallizer may contain valuable components, such as Calcium, Strontium or Lithium, which can be recovered separately at suitable qualities for industrial applications.

The recovery of calcium chloride is a well proven concept and has been refined and adapted for this new and more complex application. Research work for recovery of further components has been completed and may be applied to the upscale of this technology.

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