Water management in hydraulic fracturing technology

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Abstract. Shale gas is a clean and efficient unconventional natural gas energy, which has gradually become a new hotspot in global oil and gas exploration and development. Hydraulic fracturing technology is one of the core technologies in shale gas production, which consumes a lot of water resources and produces a lot of polluted flowback fluid. How to effectively deal with the treatment of flowback fluid is a crucial issue. By analyzing the characteristics of fracturing flowback fluid, this paper lists the treatment technologies of fracturing flowback fluid, which can relieve the worries of shale gas exploitation and wide application.

1. Introduction

With the rapid development of world economy, shale gas, as an important unconventional natural gas resource, is becoming a new hot-spot in the field of exploration and development of oil and gas resources. In recent years, China's shale gas industry has developed rapidly. Hydraulic fracturing is a kind of hydraulic pressure drilling technology widely used in shale gas exploitation, which has a large demand for water [1]. In order to prevent shale layer damage and mitigate water lock effect, many chemical additives will be added to the fracturing fluid. Fracturing flowback fluid is a mixture of flowback fluid from wells in the early stage of hydraulic fracturing completion. It has the characteristics of large water volume, high organic content, high salinity and high viscosity, so the water treatment is complicated [2]. Therefore, in order to protect the environment and save water, it is necessary to recycle and reuse the fracturing flowback fluid after treatment. Summarizing the advantages and disadvantages of fracturing flowback fluid treatment technology can better guide the "green" exploitation of shale gas in China.

In this paper, the composition of the fracturing flowback fluid and the treatment technology of fracturing flowback fluid are studied in detail. Among them, microbial control technology, sedimentation technology, adsorption technology, electrocoagulation technology and membrane technology are the main technologies used in fracturing flowback fluid treatment. The summary of these technologies is of great significance for further research and guiding engineering application of fracturing flowback fluid.

2. The composition of hydraulic fracturing flowback fluid

2.1. The definition of hydraulic fracturing flowback fluid

In hydraulic fracturing, there are three types of water: injected water, flowback water and produced water. Injected water contains many chemical additives as well as a large volume of water. This fluid
is pumped down into the well at very high pressures in order to cause fractures in the shale layers of the formation. Once this process is completed, the pressure is released [3]. As a result, much of the injected water flows back up to the surface within a matter of days or weeks. This is considered to be the flowback water and it will contain all the components of the original injected water along with some of the chemicals present in the formation, possibly including salt ions, natural gas, and naturally occurring radionuclides (NORM)[4]. Produced water differs from flowback water in that it is the natural formation water which is being pumped back to the surface along with the natural gas [5]. The characteristics of produced water also differ from flowback water. Since produced water has had longer to equilibrate with the formation, it contains more compounds found in the formation and less chemical additives from the injected water. These compounds may include higher levels of salt ions, oil and grease, and naturally occurring radionuclides[6].

In this paper, the fracturing flowback fluid indicates flowback water.

2.2. The composition of fracturing fluid
The fracturing fluid used in drilling is the main component of fracturing flowback fluid, which can be divided into three parts: water, proppant and additives, accounting for about 90%, 8% and 2% respectively [7]. Among them, proppants are generally sand, zirconia or ceramic particles. Additives including lubricants, crosslinking agents, demulsifiers, pH controllers, fungicides, scale inhibitors, acids, iron ion controllers, surfactants, etc.[8]. These are the main pollutant components in fracturing flowback fluid. Also, the component of fracturing fluid will change slightly depending on the geologic characteristics of the formation and the circumstances of the operation.

2.3. The composition of fracturing flowback fluid
The composition of fracturing flowback fluid is mainly chemical reagent, sand, clear water and groundwater in shale formation. The environmental pollution caused by the fracturing flowback liquid mainly includes dissolved solid (TDS), suspended solid particles (TSS), metal content, microbial content, naturally occurring radioactive material (NORM), oil and grease and so on[9]. Oil and grease in produced water occurs in three forms: free oils, which are large droplets that can be readily removable by gravity separation methods, dispersed/emulsified oils, which are small droplets (< 20 μm), and dissolved organics [10]. The composition of the fracturing flowback liquid is quite complex. It not only has the characteristics of high chemical oxygen demand (COD), high chroma, high dissolved solid (TDS) and high suspended solid particle (TSS), but also has a large fluctuation range with the production of shale gas[11].

3. Treatment technologies of fracturing flowback fluid
Management of wastewater produced during shale gas production is an important aspect of mitigating the human health and environmental risk of shale gas development. The treatment of hydraulic fracturing fluid discussed in this paper mainly includes microbial control, removal of suspended solids, removal of heavy metal content and desalination. The main treatment technologies include microbial control technology, sedimentation technology, adsorption technology, electrocoagulation technology and membrane technology.

3.1. Microbial Control technology
Bacteria will cause souring of the reservoir and microbial induced corrosion, which are major concerns in shale gas production. The source water used for hydraulic fracturing contains various microorganisms, and the fracturing fluids often contain polysaccharides that can serve as energy sources for bacteria growth [12]. Therefore, the surface equipment and down hole pipelines are prone to microbial induced corrosion.

A recent study found bacteria that most often associated with microbial induced corrosion are the sulfate reducing bacteria (SRB) and acid producing bacteria (APB)[13]. SRB are a group of anaerobic bacteria and are best known for reducing available sulfate to hydrogen sulfide (H₂S) or ferrous sulfide,
which can directly initiate corrosion [13]. The presence of SRB activity can result in pitting, stress corrosion cracking, and blistering of carbon steel [14]. APB strains are another major player in the microbial induced corrosion process. They produce organic or inorganic acids as by-products of their metabolism, lowering the local pH. Low pH enhances SRB induced corrosion, during which the APB produce fatty acids as nutrients for the growth of SRB [15].

Disinfection can be achieved by ozonation and chlorine compounds or chemical biocides. Ozonation and chlorine dioxide are commonly used for disinfection of hydraulic fracturing flowback fluid as they can be generated onsite. Ozonators use corona discharge to convert oxygen in the air flow into ozone. Ozone dose can be as low as 0.5% ~ 3% to meet the treatment goal of 1000 CFU/mL bacteria [16]. Ozonation also can help reduce the concentration of iron, manganese and sulfide. A very specific ozonation system, the Ozonix, is patented by the Ecosphere Technologies Inc. The treatment train combines several advanced oxidation processes including ozonation, hydrodynamic and acoustic cavitation, and electrochemical oxidation [16]. The microbial control technology has been widely used in China fracturing flowback fluid treatment. The advantages of this technology are high efficiency and low cost.

3.2. Sedimentation technology
Basic separation processes aim to remove suspended particulates and oils from the wastewater stream. Several conventional separation technologies have been used in the oil and gas industry for a long time with great success and have been applied in the treatment of fracturing flowback liquid in shale gas production. In many occasions, shale gas produced water can be recycled after basic separation processes and blended with freshwater and chemicals to form the fracturing fluid for the next fracturing job [17].

On many fracturing sites in China, especially in Sichuan and Xinjiang, the fracturing flowback liquid is usually impounded in holding ponds/tanks as temporary storage to buffer the varying water quality and flow rate before subsequent treatment, reuse, or disposal. Meanwhile, it is also the simplest way to separate large particulates and free oils from the aqueous phase. Long term settling also leads to water evaporation that reduces the volume of the stored wastewater. The different phases are separated by gravity. As a result, it performs best when the densities of the particles/oils are significantly different from water, and requires long retention time and hence large footprint [18]. Settling holding ponds are often constructed and lined to hold the fracturing flowback liquid. Mobile storage tanks are sometimes used as part of the on-site treatment system. The use of holding/settling ponds was the common case in early development of shale gas. However, its use has declined due to environmental concerns. They need to be carefully inspected and maintained to avoid overflow and leaks, which could lead to contamination of surface water and groundwater [19]. The advantages of this technology are low cost and easy to realize. However, the disadvantages are long retention time and large footprint, as well as the risk of leakage.

3.3. Adsorption technology
Adsorption is a well-established treatment technique in China. Adsorption refers to the adsorption of gases or liquids on solid surfaces. Solids are called adsorbents, and adsorbed substances are called adsorbates. According to the nature of the binding force between adsorbate and adsorbent surface molecules, it can be divided into physical adsorption and chemical adsorption. Physical adsorption is caused by the intermolecular attraction between adsorbate and adsorbent. Chemical adsorption is caused by chemical bonds between adsorbate and adsorbent [20]. Common sorbents include activated carbon, organoclays, and zeolites. Activated carbon can be used to remove dissolved organic compounds, heavy metals, and radionuclides in produced water [21]. The adsorption capacity of activated carbon relies on its extremely large surface area and abundant surface functionalities. After being saturated with absorbates, the media can be either regenerated or disposed of. Regeneration process can be carried out onsite if the plant is large enough. However, it is often performed offsite. The media are backwashed periodically to remove particulates trapped in the sorbent bed [22].
The advantages of adsorption treatment technology are minimal chemical addition and low energy use. It’s very efficient in removing oils and dissolved organic chemicals, as well as heavy metals, and the total organic carbon (TOC) of effluent water can be very low [23]. The disadvantages of adsorption process are the high operation and maintain costs due to high media usage and solid waste management.

3.4. Electrocoagulation technology
In electrocoagulation (EC), sacrificial anodes corrode to release cations (usually aluminum or iron cations) and cathode releases gases such as hydrogen bubbles. It is a technology that utilizes electrochemistry, floatation and coagulation [24]. EC targets a wide range of contaminants including suspended particles, oils, bacteria, etc. It requires simple equipment, it is easy to operate and maintain, and produce small amount of sludge. No chemical additions needed in the EC process. Its modular and flexible design is highly desirable for shale gas wastewater treatment. The whole system can be powered by solar panel if necessary [24]. Because the sacrificial electrodes gradually dissolve into the wastewater to produce cations, they need to be replaced regularly. Electrode passivation, during which an impermeable oxide film forms on the cathode, is a commonly observed phenomenon that leads to lower reactor performance [25]. The energy cost is also a concern. The gas generated by the system is hydrogen and oxygen, which is flammable and potentially explosive.

Several vendors provide commercial electrocoagulation systems for produced water treatment. Halliburton’s mobile Clean Wave system can be powered by a diesel generator and housed in two convex containers with a throughput of 57 m³/hr. It can be used to treat water with TDS ranging from 10-300,000 mg/L. The system is claimed to achieve 95-99% removal of total petroleum hydrocarbon, total suspended solids, and total iron and heavy metal, and coagulate particles larger than 1 μm. It also can reduce the turbidity of the produced water to less than 10 NTU and break emulsions. The average sludge generation is expected to be less than 5% [26].

A recent study reported a field test of electrocoagulation system in Brushy Canyon formation, New Mexico. The flowback water with TDS of 267,588 ppm was treated with electrocoagulation to remove > 99% of TSS and iron, 18.28% boron, 27.58% magnesium, and 8.39% strontium. However, the TDS didn’t change after treatment. The treated water was mixed with a gum, zirconium-based cross linker, sodium chloric breaker, breaker catalyst, and a non-emulsified surfactant to form the gel fracturing fluid for fracturing seven wells with a total of 97 fracturing stages [27]. Electrocoagulation (EC) technology is a "green" treatment technology since no chemical addition is needed, and it is easy to operate and maintain. However, the disadvantage of this technology is its high energy cost and the safety issue.

3.5. Membrane technology
The membrane technology is widely used in China's hydraulic fracturing flowback fluid treatment. Due to the complex composition of fracturing flowback fluid, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis have been widely used for different treatment purposes.

The main functions of microfiltration membrane technology are mechanical interception, adsorption interception, bridging interception and network interception. Because of the large pore size of the microfiltration membrane, it can only effectively remove colloids and suspended solids with larger particle size in fracturing flowback fluid, while the removal rate of pollutants with smaller particle size is low [28]. Compared with microfiltration, ultrafiltration has smaller pore size and better removal effect for particles with relative molecular weight of 1000-300000. It can effectively remove macromolecular substances, colloids and particles in fracturing fluid. Because of the small pore size of the membrane, UF is generally not directly used for the treatment of the backflow fluid, and is generally used in combination with other processes. The nanofiltration membrane has smaller pore size and better removal effect for small molecules with relative molecular weight of more than 200. Because of the Donnan effect of ions with different valence states and charges on the surface of
nanofiltration films, the separation of ions with different valence states can be achieved, and the removal of salt can reach 93%. Nanofiltration technology has a high removal rate of high concentration TDS, organic matter and Fe$^{2+}$ ions in fracturing flowback fluid. However, due to the small pore size of the membrane, the membrane fouling problem is serious [29].

Reverse Osmosis (RO) and Forward Osmosis (FO) are the main desalination technologies used in fracturing flowback fluid treatment at present. They have high removal effect on small molecular substances smaller than 1 nm in water. Reverse osmosis (RO) treatment technology uses the selective permeability of reverse osmosis membrane. High pressure is generated on one side of the membrane to push solvents (usually water) from high concentration to low concentration, and the salt ions and other contaminants will stay on the membrane surface of high concentration side [30]. Forward osmosis (FO) technology uses the osmotic pressure difference caused by the concentration difference of solution on both sides of the membrane to make water molecules permeate from the high chemical potential side to the low chemical potential side [31].

RO treatment needs to provide external pressure, so it requires the equipment with higher pressure resistance ability, and it causes higher energy consumption and more serious membrane fouling. Under the scouring effect of mechanical impurities, some damage problems will occur on the membrane surface, and soluble hydrocarbons can also make the membrane lose the function of separation. For this reason, when reverse osmosis technology is applied to the treatment of the fracturing flowback fluid, the influent can be pretreated by filtering and softening methods. RO can treat wastewater with TDS less than 35 000 mg/L [32]. FO uses osmotic pressure instead of external pressure to desalinate high salinity water (TDS > 70000 mg/L) through low pressure device. The operation time of using membrane under low pressure increases, and the cost of water treatment decreases [33]. In some foreign areas, Reverse Osmosis (RO) technology and Forward Osmosis (FO) technology have been directly applied in shale gas fields, and have shown good results [34]. The advantages of the membrane technology are high removal rate and high desalination efficiency. Nevertheless, the serious membrane fouling issue limits the application of this technology.

4. The problems existing in hydraulic fracturing fluid treatment in China
(1) At present, there is no environmental standard for the reuse of fracturing flowback fluid in China, so other control requirements that may affect groundwater quality need to be considered from the perspective of environmental protection.

(2) There are many potential environmental risks in the process of injection and transportation of fracturing flowback fluid. Especially for the fracturing flowback fluid that cannot be reused, it is mostly disposed by deep well injection, so it is necessary to formulate relevant injection control standards.

(3) There is a lack of reliable technical specifications and standards for treated fracturing flowbackfluid. The treated fracturing flowback fluid has the characteristics of high salinity, high concentration of organic matter and environmental risk substances. The existing discharge standards cannot fully cover the characteristic pollutants in the fracturing flowback fluid. Hence, relevant technical specifications and standards need to be formulated.

5. Conclusions
Energy and water resources issues have always been the focus of global attention. On the one hand, shale gas exploitation will produce lots of energy resources, on the other hand, it will also produce a lot of fracturing flowback fluid [35]. If the fracturing flowback fluid cannot be effectively treated, it will certainly pollute the environment and restrict shale gas development. The microbial control technology, sedimentation technology, adsorption technology, electrocoagulation technology and membrane technology are the main technologies for hydraulic fracturing flowback fluid treatment nowadays. These treatment technologies can treat the fracturing flowback fluid with high efficiency and is friendly to the environment, which are feasable to spread. At present, there are some limitations in the application of fracturing flowback fluid treatment technologies in China. Based on this, it is
necessary for us to study the application of various kinds of fracturing flowback fluid treatment technology, and constantly explore ways to improve the technology level, so as to effectively carry out the development of shale gas in China and provide sufficient production energy for industrial production.

References

[1] Vengosh A, Jackson RB, Warner N, et al. 2014A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States [J]Environmental science & technology 48(15) 8334-8348

[2] Theodori GL, Luloff AE, Willits FK, et al. 2014Hydraulic fracturing and the management, disposal, and reuse of frac flowbackwaters: Views from the public in the Marcellus Shale [J]Energy Research & Social Science 266-74

[3] Hellmann JR, Scheetz BE, Luscher WG2014Proppants for shale gas and oil recovery[J] Am. Ceram. Soc. Bull. 93 (1) 28-35

[4] Anderson T, Hooker C, Uttech U, et al. Dust collection system for personnel health during fracturing operations[J]. SPE 163528, 2013.

[5] Seth K, Shipman S, Mc Connell D, et al. 2013Maximizing flowback reuse and reducing freshwater demand: case studies from the challenging Marcellus shale[J] SPE 165693

[6] Pérez G, Fernández - Alba A R, Urtiaga A M, et al. 2010Electrooxidation of reverse osmosis concentrates generated in tertiary water treatment [J] Water research 44 (9) 2763-2772

[7] Alkhudhiri A, Darwish N, Hilal N2012Membrane distillation: A comprehensive review [J] Desalination 2872-18

[8] Rahm BG, Riha SJ2012Toward strategic management of shale gas development: Regional, collective impacts on water resources[J] Environmental Science & Policy 1712-23

[9] Lutz BD, Lewis AN, Doyle MW2013Generation transport and disposal of wastewater associated with Marcellus shale gas development [J] Water Resources Research 49(2) 647-656

[10] Li J, Wang C, Tian HY2012Environmental concerns in the development of shale gas [J] Environmental Protection of Oil & Gas Fields 22 (6) 42-43

[11] Rivard C, Lavoie D, Lefebvre R, et al. 2014An overview of Canadian shale gas production and environmental concerns [J] International Journal of Coal Geology 126(5) 64-76

[12] Struchtemeyer CG, Elshahed MS2012Bacterial communities associated with hydraulic fracturing fluids in thermogenic natural gas wells in north central Texas, USA[J] Fems Microbiology Ecology 81(1) 13-25

[13] Moore S, C Cripps2012Bacterial Survival in Fractured Shale-Gas Wells of the Horn River Basin[J] Journal of Canadian Petroleum Technology 51(4) 283-289

[14] Little B, RRay, et al. 2000 Relationship between corrosion and the biological sulfur cycle: a review [J] Corrosion 56(4) 433-443

[15] Hubert C, GVoordouw2007Oil field souring control by nitrate-reducing Sulphurospirillum spp. that outcompete sulfate-reducing bacteria for organic electron donors[J] Applied and environmental microbiology 73(8) 2644-2652

[16] Kidder M, T Palmgren, et al. 2011 Treatment options for reuse of frac flowback and produced water from shale. World Oil

[17] Rahm D2011Regulating the hydraulic fracturing in shale gas plays: The case of Texas [J] Energy Policy 39 (5) 2974-2981

[18] Trevor Smith2013Water Management for Shale Gas Development [M] Chicago: American Gas Technology Institute 1-102

[19] Howarth RW, Ingraffea 2011Anatural gas: Should fracking stop [J] Nature 477(1) 271-275

[20] Ekstrom V2011The future of natural gas [M] Massachusetts, USA: Massachusetts Institute of Technology 1-200

[21] Shields D, Verga FM, Blengini G2013Sustainability Versus Sustainable Development-The Case of Shale Gas[C] Society of Petroleum Engineers 16(4) 82-84
[22] Rozell DJ, Reaven SJ 2012 Water pollution risk associated with natural gas extraction from the Marcellus shale [J] Risk Analysis 32(8) 1382-1393

[23] Gregory KB, Vidic RD, Dzombak DA 2011 Water management challenges associated with the product of shale gas by hydraulic fracturing [J] Elements 7(3) 181-186

[24] Samuel JMB and Andrew RB 2014 Organic compounds in produced waters from shales gas wells. Environ Sci.: Processes Impacts 16 2237-2248

[25] Council GWP, Consulting A 2009 Modern shale gas development in the United states [J] Oklahoma City: Ground Water Protection Council 96

[26] Lebas R, TShahan, et al. 2013 Development and Use of High-TDS Recycled Produced Water for Crosslinked-Gel-Based Hydraulic Fracturing., Paper SPE 163824 presented at the SPE Hydraulic Fracturing Technology Conference, The Woodlands, Texas, USA, 4-6 February

[27] Ziemkiewicz P, JHause, et al. 2012 Zero Discharge Water Management for Horizontal Shale Gas Well Development

[28] Kargbo DM, Wilhelm RG, Campbell DJ 2010 Natural gas plays in the Marcellus shale: Challenges and potential opportunities [J] Environmental Science & Technology 44(15) 5679-5684

[29] Wilson JM, Van Briesen JM 2012 Oil and gas produced water management and surfacedrinking water sources in Pennsylvania [J] Environmental Practice 14 288-300

[30] Cath TY, Childress AE, Elimelech M 2006 Forward osmosis: Principles, applications, and recent developments [J] Journal of Membrane Science 281(1/2) 70-87

[31] Kondash A, Vengosh A 2015 Water Footprint of Hydraulic Fracturing [J] Environmental Science and Technology Letters 2(10) 276-280

[32] Nicot JP, Scanlon BR, Reedy RC, et al. 2014 Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective [J] Environmental Science and Technology 48(4) 2464-2471

[33] Hoover LA, Phillip WA, Tiraferri A, et al. 2011 Forward osmosis: Emerging applications for greater sustainability [J] Environmental Science & Technology 45(23) 9824-9830

[34] Pirzadeh P, Lesage KL, Marriott RA 2014 Hydraulic fracturing additives and the delayed onset of hydrogen sulfide in shale gas [J] Energy & Fuels 28(8) 4993-5001

[35] Theodori GL, Luloff AE, Willits FK, et al. 2014 Hydraulic fracturing and the management, disposal, and reuse of frac flowback waters: Views from the public in the Marcellus Shale [J] Energy Research & Social Science 266-74