Fracking Wastewater Treatment at Collection Facility

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ABSTRACT

Engineering company operates a wastewater collection and treatment facility for their clients in Myton, Utah. The facility receives fracking and produced wastewater from various pumping stations, and then treats the water for disposal at the injection well located on site. Electrocoagulation followed by two clarifiers and 5 micron filter was used. Since many particles float or just "swim" inside the clarifier we performed a flocculation - flotation pilot study followed by full scale installation of the flocculation flotation -- the GEM Systems. This manuscript summarizes the results of the pilot studies and operational performance and problems of the full scale 600 GPM GEM Systems.

KEYWORDS: flocculation - flotation, electrocoagulation, fracking wastewater

INTRODUCTION

Problem

Engineering company (EC) serves the oil and gas industries, providing water reclamation for produced water, fracking water, flow back water and black water. EC sought the assistance of Clean Water Technology Inc. (CWT) in order to improve their wastewater treatment system. EC was in need of advanced primary treatment, flocculation - flotation technology.

EC currently operates a water treatment facility for their clients in Myton, Utah. The facility receives fracking and produced wastewater from various pumping stations, and then treats the water for disposal at the injection well located on site. Electrocoagulation followed by two clarifiers and 5 micron filter was used. Since many particles float or just "swim" inside the clarifier we performed a flocculation - flotation pilot study followed by full scale installation of the flocculation flotation -- the GEM Systems.

Goals and Objectives

The primary goal of this study was to perform pilot study with advanced flocculation - flotation primary treatment to replace the existing inefficient clarifiers. Upon completion of the pilot study the installation of the full scale treatment system that can handle up to 600 gallons per minute of wastewater was a final objective. The stated goals and objectives were achieved. Some operational problems still exist and will be discussed in this manuscript.
The Existing Process Description

Fracking (hydraulic fracturing) is the fracturing of various rock layers by a pressurized liquid. A liquid mixture with additives is pumped underground at high pressure to crack the rock and release oil or gas. A pumper truck injects such mixture of sand, water and treatment chemicals down a well and past a bend in the pipe. It is pushed into the shale rock under extreme pressure through holes at the end of the well pipe. Pressure from the pumped fluids creates fissures that allow the natural gas or oil to escape from the shale and flow into the well. The gas or oil then rises up the well to the surface, where it is collected. Recovered gas or oil is stored in tanks, where it is then either pumped into a pipeline system or placed in trucks.

In general, fracking process can generate more than 2,000,000 gallons of frac blowback water per well. An efficient treatment process is absolutely necessary.

All water from different clients is collected in a series of equalization tanks (EQ). Water is disinfected with bleach, and then sent through an electrocoagulation unit. Once electrocoagulation flocs are produced, a dose of anionic flocculant is introduced in order to create settable large heavy flocs. The water is then passed to a primary clarifier. Effluent from the primary clarifier is passed to a secondary clarifier for further treatment, followed by 5 micron filters for the removal of carry-over flocs. After the treatment, effluent is delivered to the injection well facility to be used for the injection and oil extraction process.

EC operators were unsatisfied with the operation of the primary clarifier, and were looking for an alternative to replace it. Many oily flocs, loaded with hydrogen and oxygen after electrocoagulation process, float or swim rather than sediment inside the clarifier. This produces effluent with carry-over that completely fouls 5 micron filters. As a result, ECS has trouble meeting the discharge requirements set by their clients.

PILOT STUDY at MYTON SITE

CWT and EC decided to perform on site pilot study with the electrocoagulation followed by flocculation - flotation with the GEM System that will be described later in the manuscript. GEM System is designed so that aeration of 100% of the influent is possible (no need for recycle stream aeration as is in DAF). Therefore, one can vary the amount of air introduced to the water.

The following treatment programs for testing were proposed:

- Minimum aeration flotation with cationic and anionic flocculants
- High aeration, with flotation with cationic and anionic flocculants
- High aeration, no chemicals added

Prior to flotation influent was treated in electrocoagulation unit with iron electrodes at around 20 A for 15 minutes. Average TDS of influent was 12,000 mg/l, maximum up to 30,000 mg/l. Most of the ions were chloride (50%) but some hardness is also present (up to 5% calcium). Such high TDS are beneficial for the EC process.
The following chemicals were tested in the flocculation - flotation GEM System:

C-498 HMW, 55% charge, high molecular weight cationic polyacrylamide flocculant from KEMIRA

A-130 HMW, 30% charge, ultrahigh molecular weight anionic polyacrylamide flocculant from KEMIRA.

Plant staff installed a tap into the effluent line of the electrocoagulation unit. From this tap, the wastewater was delivered to the screen (800 micron) set atop of the GEM EQ tank. The pH was adjusted in the EQ tank. Testing of TSS, COD, FOG and turbidity was performed by CWT.

Minimal Aeration Observations

While running the GEM System with a minimal aeration setup the system produced good flocs, however flocs carry-over was higher than normal in the effluent. Most carry-over flocs that have more buoyant tendencies, would stay suspended within the internal flow patterns of the GEM System, and eventually be carried out, suspended in the effluent.

This is undesirable because suspended flocs which neither float nor settle will be passed downstream. Flocs will be caught in the filters at the end of the process, but the bags in the filters will need to be replaced more often.

Increased Aeration - Treatment Observation

Later, the GEM System was configured to dissolve more oxygen into the wastewater stream. At such setup large amount of small bubbles (up to 15 microns) are available and water looks very turbid (even tap water). Upon start-up, the difference in flotation and floc formation was noticed immediately within the bloom chamber. Flocs appeared somewhat larger, and immediately floated to the top of the sample jar whenever a sample of the stream was taken from the top of the GEM flotation tank. It was clear that with this particular setup, the GEM System would be able to treat all of the wastewater streams at this location.

Increased Aeration with no chemicals added.

After a short period of time, once the chemicals were no longer dosed into the system, the electrocoagulation produced flocs simply passed through the system. All oily floatable solids floated well within the system. However, as expected, hydrophilic solids (clay, metal oxides, solid) did not float at all.
Increased Aeration Increased Chemical Dosing - Treatment Observations

The effects of higher chemical dosing (more than 30 ppm of anionic and some cationic flocculant) were also followed. Floatable solids size and removal efficiency remained the same, however settle-able solids increased in size and volume. It was determined that this was undesirable since GEM unit is a flotation System (some solids can be removed from the bottom), and since it is better to leave such solids for the secondary clarifier.

Resulting Data Overview

TSS Reductions: TSS reductions were 90%, on average. The effluent TSS were usually below 200 ppm when increased aeration and flocculants were used. When both EC unit and the GEM unit were running under optimum conditions, the average TSS in the effluent were 110 ppm at pH 6.5 and 55 ppm at pH 9.5.

COD Reductions Lab tests (Hach - High Range) indicated that with chemical treatment and dosages adjusted according to the jar tests, the GEM System reduced COD by approximately 23% on average. Effluent COD's were 1,312 ppm, on average.

Sludge Results: Lab tests show that the GEM Sludge was 20% of dry solids on average off the flotation tank.

FOG Reductions: FOG/TPH reductions were 92% on average. Effluent FOG/TPH were on average around 15 ppm and as low as 3 ppm at pH 9.5.

Average dosage of anionic flocculant was 30 -40 ppm and cationic flocculant 10 ppm (to save money cationic flocculant can be omitted). GEM System aerates 100% of the stream (no recycle as in the DAF). For this stream such high air to solids ratio was indeed required. System was operated at HRT of 9 GPM/ft². System tank is equipped to collect solids on top and the bottom.

THE DESCRIPTION OF THE GEM SYSTEM

We proposed that a more efficient flotation system (than current DAF's) could be developed by combining high-energy centrifugal mixing of a liquid cyclone system (we termed it the liquid cyclone particle positioner, LCPP) with dissolved air as a source of flotation. Coagulants and flocculants can be delivered in situ directly into the flotation hydrocyclone unit. Pressurized air can be delivered to
LCPP heads at the same time as flocculants. Such a procedure results in flocs, which are very porous and loaded with entrained and entrapped air.

As shown in Figure 1 the LCPP also acts as a liquid-solid-gas mixer (LSGM). Replacing the classical hydrocyclone head with the LCPP provides extremely energetic mixing by sequentially transporting liquid and entrained particles and gas bubbles throughout a centrifugally rotating liquid layer. Microturbulence in such vortices results in all particles and bubbles down to colloidal and molecular size acting as little mixers. Axial and radial forces inside the LCPP help mix coagulants and flocculants with the particles. Uncoiling of polymer and better mixing of ultrahigh-molecular-weight polymers (and more concentrated emulsions) is achieved in the LCPP. Such efficient mixing is important for proper flocculation of suspended particles. Centrifugal mixing also results in less floc breakage than with commonly used impeller or floc tube mixers.

Further modification of LCPP heads, as opposed to hydrocyclone heads, introduced multiple holes with plugs inside the LSGM heads, as shown in Figure 2. By changing the number of plugs, we can modify the mixing energy and head pressure from very low to very high. In this way, we can mix low-molecular-weight coagulant at relatively high energy and high-molecular-weight flocculants at relatively medium and low mixing energy to promote final large floc formation.

Hybrid centrifugal – dissolved air flotation technology (The GEM System developed at CWT [see Figure 3]) provides the best of both centrifugal and dissolved air systems: efficient continuous flow mixing and in line flocculation with the nucleation and entrainment of fine dissolved air bubbles. This development
has resulted in systems with very efficient removal of particulate contaminants, a small footprint, drier sludge, durable long lasting flocs, fast response.

![Diagram of Liquid Solid Gas Mixer Head](image)

**Figure 2 – Schematic Presentation of the LSGM Heads**

and treatment of the total wastewater stream (no recycling characteristic for DAFs). The design of on-line turbidity or fluorescence driven sensors for automatic control of coagulant and flocculant dosage is also underway. Computational fluid dynamics (CFD) has been used to design better flotation tanks with a vortical flow pattern that results in the formation of a dense air bed inside the tank. Such fine bubble layers prevent sedimentation of already floated heavier particulates, which results in significantly higher flotation rates.
SYNERGISM OF CHEMICAL AND MECHANICAL ASPECTS OF THE SOLID/LIQUID SEPARATION SYSTEMS

Solid/liquid separation processes are only as efficient as the weakest “link in a chain”. New generation of high performance flotation units can only deliver if appropriate chemicals are used to coagulate and flocculate particles and emulsions in wastewater.

Figure 3 – Schematic Presentation of the Hybrid Centrifugal – Dissolved Air Flotation System
Coagulation, flocculation and flotation are among the most effective approaches to remove fats oils and grease, suspended solids and colloidal materials (even some proteins and macromolecules) from any industrial wastewater, such as for instance food processing. Solids, colloids and macromolecules present in food processing wastewater are generally charged. Charge stabilization often produces very stable colloidal suspensions. Solids and colloids that are charge stabilized repel each other and produce systems that have a tendency to “swim” within the wastewater bulk, rather than sediment or float. Surface charge has to be neutralized in order to get particles close together so that other attractive forces such as hydrophobic or van der Waals forces result in formation of larger aggregates that either sediment or attach to bubbles and float. Most colloids, macromolecules and solids in food processing wastewater are of organic nature. Ionization of carboxyl and amino groups from fatty acids or proteins produces some charge. Oil and grease particles are often emulsified and charge is present in the surfactants used as emulsifying agents. Many neutral colloids will preferentially adsorb hydroxyl ions and become negatively charged.

Most colloids present in any food processing wastewater are negatively charged, probably due to preferential adsorption of hydroxyl ions and widespread surface availability of carboxyl groups. The surface charge/dissociation of such groups is pH dependent. It is possible to find a pH at which total surface charge is zero (point of zero charge). At such pH colloids are quite unstable. However, coagulants and flocculants are designed so as to promote even faster, more efficient destabilization of colloids with growth of large, stable aggregates. The pH, therefore, should be adjusted close to the point of zero charge, in order to save on dosage of coagulants and flocculants needed to neutralize the surface charge. If surface charge is fully neutralized, the performance of flocculants is low.

Once the pH is adjusted, coagulation and flocculation process follow. Coagulation is addition of oppositely charged ions or molecules in order to neutralize surface charge and destabilize colloidal suspensions. Inorganic coagulants such as sulfate or chloride salts of trivalent iron (Fe[III]) or aluminum (Al[III]) have been quite popular in food processing wastewater treatment. However, such salts hydrolyze as part of coagulation process and produce oxohydroxyde sludge that is bulky and difficult to dewater. Prehydrolyzed –inorganic polymeric aluminum reagents such as polyaluminum chloride (PAC) or aluminum chlorohydrate (ACH) are more efficient in charge neutralization. Such salts also produce less bulky sludge. Cationic polyelectrolytes (organic low molecular weight polymers) such as quaternary polyamines produce less sludge that is easier to dewater. Such reagents are also much more efficient in charge neutralization. Therefore, the dosages needed to neutralize surface charge with polyelectrolytes are often more than order of magnitude lower compared to dosages of aluminum or iron salts. However, ferric salts have to be used if blood clarification is to be achieved. Precipitation of phosphate or sulfide ions also can be achieved only with inorganic ions. Finally some proteins can be removed with proper pH adjustment and use of inorganic coagulants.

Flocculation is a process of formation of large stable flocs that either sediment or float. Flocculants are reagents that achieve flocculation. Flocculants are large polymeric molecules that bind together smaller flocs produced by coagulation. Synthetic high molecular weight polyacrylamides are the most commonly used flocculants. Cationic polyacrylamides can neutralize residual negative surface charge and also bind smaller flocs together. Flocs may also be overcharged with coagulants and cationic flocculants, with subsequent use of anionic polyacrylamide. Such approach, termed dual flocculants approach, will be described in detail later in this manuscript (also see Figure 4).

Several steps are involved in the coagulation and flocculation processes. First, coagulants are added to the wastewater with the precise dosing pumps. Then coagulants are mixed with the particles in the high energy mixing process in order to uniformly distribute adsorbed coagulant molecules or ions. Upon
initial charge neutralization, flocculants are added. Even more precise dosing is needed in order to avoid under or overcharging of particles. Flocculants are mixed with less energy in order to avoid breakup of formed flocs or even polymer molecules, which are large delicate chains. On the other hand, enough mixing intensity is needed to achieve uniform distribution of polymer and adsorption on all particles, rather than over - absorption on nearby particles only. (Mixing is also needed to activate polymeric flocculants. Such giant molecules are coiled into the tight coils. Linearization is needed to achieve polymer configuration that can bind numerous smaller flocs together (see Figure 5).

Wastewater samples tested while developing the system described in the manuscript were coagulated and flocculated at numerous pHs ranging from 3 to 11. For most samples, best flocculation can be achieved at pH between 5 and 6. Removal of fine emulsions and proteins is also most efficient in this pH range. Some wastewater samples had a very small amount of TSS and colloidal materials. For such samples, the pH was adjusted between 7 and 9. Similar approach was used for samples with colloidal materials that are almost neutral. Increasing pH above 8 results in higher surface charge and stronger adsorption of flocculants. At pHs below 5, performance of flocculants was found to be sub optimal with smaller, weaker flocs and more carryover in laboratory flotation tests. At pHs above 9, consumption of coagulants and flocculants was very high.

Numerous inorganic, organic and blend coagulants were tested with food processing wastewater. Ferric (FeIII) and aluminum (III) sulfate require the highest dosages and produce sludge with the lowest % solids that is most difficult to dewater and dry. As wastewater becomes loaded with TSS and FOGs, the necessary dosages to achieve coagulation can be as high as 6,000 mg/l. These two coagulants also interfere with the performance of flocculants, producing “pinpoint” floc with very small particles and high amount of carryover (often over 200 mg/l) in laboratory flotation tests. However, if water is rich in blood proteins, small amount of ferric coagulant (10-60 ppm) is needed to clarify wastewater and reduce foaming problems.

Prepolymerized inorganic coagulants suffer from similar deficiency, namely large dosages needed; carryover after flotation produced, and sludge with low % solids produced. Needless to say, dosages are lower than that of monomeric ferric or aluminum ions based coagulants. The most popular reagents from this group are polyaluminum chlorides, (PAC) with various basicity and aluminum chlorohydrate (ACH). Also, inorganic coagulants produce sludge with tendency to sediment, rather than to float.

Organic polyelectrolyte coagulants are the most advanced new generation of coagulant reagents. Usually, those are small cationic polymers with 100% backbone charge. Polyethyleneimines were the first reagents used for such purpose. Modern quaternary polyamines, epamine, and polydiallyldimethyl chlorides (polyDADMAC’s) are most often used in wastewater treatment applications. Such reagents do not interfere significantly with the performance of flocculants. They also produce sludge with high solid % and dosages needed to coagulate the wastewater can be an order of magnitude lower than that of inorganic reagents. Total cost of wastewater treatment is actually lower when using such reagents rather than inorganic coagulants. Low molecular weight epamines and quaternary polyamines (10,000 – 25,000 D) coagulated food processing wastewater with the lowest dosages and least interference with the performance of flocculants downstream. Higher molecular weight and crosslinked polyamines (weight over 50,000 D) interfered with the performance of flocculants, and surprisingly were less efficient in coagulating wastewater colloidal contaminants. If combination of ferric and polyamine coagulants are needed, it is often better to add them separately then as a blend. Blend coagulants contain fixed ratio of ferric to polyamine coagulants. However, when treating changing wastewater influents, the ratio of
amount of ferric and polyamine ions can vary quite significantly. From economic standpoint, blend coagulants are also very expensive.

Flocculants are the key component of any successful flotation wastewater treatment. We tested granular, emulsion, direct dispersion and brine flocculants. Flocculants with molecular weight between 1,000,000 D and 70,000,000 D were tested. Flocculants with charge (mole%) between 2 and 100% were tested and the effects of ionic strength (salinity, temperature, pH and surfactant present were studied). In all cases studied, granular high molecular weight, high charge polyacrylamides performed best. Such reagents yielded best flocs, sludge with the highest % solids, and least amount of TSS in the effluent. Dual flocculant approach in which addition of cationic flocculant is followed by addition of anionic flocculant always yielded the best performance (Fan et al., 2000). Emulsion flocculants produced smaller flocs, sludge with less solids and more TSS in the effluent. The higher the % active polymer in the emulsion, the better the performance. The same applies for brine and direct dispersion flocculants. Granular high charge (50% or more), high molecular weight (5,000,000 D or higher), cationic polyacrylamides were always the cheapest solution, with the best performance, and lowest dosage needed for efficient flocculation. At high temperature (over 40°Celsius) or high salinity (over 10,000 micromhos/cm) cationic flocculants could not flocculate colloidal components anymore. Cationic polyamine coagulants were then used to overcharge colloids with the subsequent addition of granular or emulsion ultrahigh molecular weight polyacrylamides. Medium charge mole % (20-30%) or very high charge % flocculants (100%) were needed to achieve flocculation at high salinity.

**DUAL POLYMER FLOCCULATION**

1. Negatively Charged Particles + Cationic Flocculant → Mixing → Small Flocs

2. Anionic Flocculant + Large Flocs

3. Mixing → Large Flocs
Figure 4. Dual polymeric flocculant approach.

UNCOILING (ACTIVATION) OF POLYMERIC FLOCCULANTS

Coiled Flocculant  Partially Uncoiled Flocculant

Mixing

Oppositely Charged Flocculant

Figure 5. Uncoiling of high molecular weight polymeric flocculant molecules.

FULL SCALE GEM INSTALLATION at MYTON SITE

Full scale GEM System running at 600 GPM has been installed. The operational data show that it is quite challenging to obtain good effluent with low TSS and FOG at all times. As expected sometimes wastewater coming from the fracking operation can have very high TDS. At TDS above 15,000 ppm no flocculants can be linearized and activated. Such wastewater cannot be treated and EC rejects incoming trucks with it. Occasionally, trucks with standard produced wastewater with highly emulsified oils and low conductivity arrive. Electrocaogulation cannot operate with low conductivity streams, and such streams are also rejected. Finally, some influents have particles with very high surface charge. To flocculate such particles one needs...
very high dosages of coagulants (up to 600 ppm), which is not feasible and such trucks are also rejected.

Figure 6. Full scale GEM Installation at the Myton Site.

CONCLUSIONS

The flocculation - flotation with the GEM System and tank equipped for both flotation and sedimentation is better solution than clarifiers for electrocoagulation treated fracking wastewater treatment.

Due to high TDS of the fracking water cationic flocculants are less efficient. Anionic flocculant A-130 HMW from Kemira at pH around 8.3 was efficient. Electrocoagulation produces ferric that overcharges particles. If additional coagulants are needed, either epiamine or blend coagulants can be used. When TDS are higher than 6,000 ppm a specialized anionic flocculant A-190 K from Kemira can be used for more efficient flocculation.
Most of the time when GEM System is operated properly with right dosage of coagulant and flocculant the resulting effluents TSS can be kept below 150 ppm and TPH as FOG below 15 ppm. Some solids carry -over will always stay in the effluent. Overall, the higher the conductivity of influent, the lower is the efficiency of flocculation.