Chemical Precipitation and Ballasted Flocculation

**Rationale to Recycle Fracing Flowback and Produced Water**

As the unconventional oil/gas industry faces an evolving regulatory environment, increasing public scrutiny of oil/gas operations, and long term drought conditions in many states; operator implementation of recycling programs for fracing flowback fluids and produced water is becoming imperative and cost effective. Operators have long recognized the potential for significant operational cost savings derived from recycling and reuse through minimization of fresh water make-up water, reduction of trucking activity and minimization of disposal costs. However, treatment and reuse has been avoided in the past for several reasons:

1) It was perceived that fresh or drinking water quality standards were required to reuse flowback without impacting well production
2) It was commonly believed that frac fluids could not be successfully formulated using water with high Total Dissolved Solids (TDS) content.
3) Because of the perceived need to desalinate treated fluid, it was thought that recycling was not cost effective since expensive desalination technologies were required.
4) Some state regulations prohibited recycling because all produced water was labeled as waste requiring disposal.
5) Regulations often prohibited the mingling of waters from several leases, hampering efforts to collect sufficient recycled water at new frac sites.

As unconventional extraction technology has developed, regulations have changed and competition for water sources has escalated. Operators conducting research into recycling have discovered that previous fears were unfounded. First, drinking quality water is not required for reuse and very high TDS waters (in excess of 200,000 ppm) can successfully frac wells without negatively impacting well production. Second, use of clean brine reduces or eliminates the amount of KCL added to some frac fluids for clay stabilization. Third, regulatory bodies recognize the need to promote recycling and are revamping regulations to remove hurdles to reuse and at the same time tightening regulations on disposal. For example, due to the rise in seismic events associated with deep well injection for the disposal of frac flowback and produced water, some states are shutting down disposal wells located within a specified radius of seismic events. Hence, recycling frac flowback and produced water is becoming more acceptable, cost effective and achievable.

**Contaminants Targeted for Treatment**

For unconventional oil and gas production, flowback and produced water need only be treated to a level that allows the successful creation of the desired fracture stimulation fluid and not impact well production. Solids which could clog the proppant pack, compounds leading to scale formation and
bacteria which can sour the well are the main contaminants which directly affect well production. Removal of residual polymers, organics, crosslinking and emulsion breaking compounds allows proper hydration of gelling materials, and achievement of the target fluid viscosity. If the fracing fluid requirements are not met, fractures may not sufficiently extend into the formation, or the required amount of proppant will not be delivered to the fractures detrimentally effecting the permeability of the fractured formation. Hence the chosen treatment solution must focus on removal of:

- Total Suspended Solids (TSS)
- Oil/Grease (O&G)
- Biological or Chemical Oxygen Demand (BOD or COD)
- Bacteria
- Some heavy metals depending on fracing fluid

**Treatment Technologies**

As the industry has evolved to recognize that recycled water need not be treated to drinking water quality for reuse in fracing operations, the need to employ high cost technologies like Reverse Osmosis (RO) and Thermal Distillation (TD) has been alleviated. RO and TD both require considerable energy input as well as extensive pre-treatment of the influent waste stream to avoid fouling of membranes and evaporative surfaces. Further, only a portion of the RO process stream is reclaimed as fresh water, the balance is an even saltier brine which requires disposal.

Anguil performed a survey to determine the available cost effective solutions with the ability to remove the previously mentioned target contaminants. Metrics for candidate technologies were:

- Performance – Ability to remove desired contaminants at the desired through-put
- Cost – Provide a cost effective treatment solution
- Size – Smaller equipment footprint to minimize capital costs

The results of the survey returned the following three viable candidates to treat flowback and produced water for reuse.

1. Chemical Coagulation and Precipitation (CC)
2. Electro Coagulation (EC)
3. Advanced Oxidation (AO)

1. **Chemical Coagulation and Precipitation (CC)**

Widely used in municipal treatment of drinking and waste water, Chemical Coagulation and Precipitation (CC) systems effects the removal of contaminants by the addition of inorganic salts and polymers to the treatment stream. Large particles are typically removed by sedimentation, however, TSS remains dispersed and will not settle since the small, and negatively charged particles continually repel each other. The addition of the salts helps to neutralize the particle charges, allowing the TSS to agglomerate into larger particles for removal. Further, other contaminants, such as metals, can be precipitated out and emulsions broken. Coagulant chemicals are added in a flash or rapid mixer. The neutralized particles are
allowed to coalesce and mature, sometimes with the addition of a polymeric flocculation aid. Finally, the floc is clarified from the water by filtration, floatation or sedimentation techniques.

2. **Electro Coagulation (EC)**

Electro coagulation (EC) systems are a relatively new technology being offered as an alternative to CC methods. EC systems inject charged ions from a sacrificial metallic anode into the water to neutralize suspended particles and produce a floc similar to CC. In addition to charge neutralization, metals are oxidized, emulsions are broken and bacteria disinfected via oxidation reactions from the electric current passed through the water and reduction reactions at the anode. Typically, EC systems consist of the electrolytic cell followed by a clarifier to remove the flocculated species.

3. **Advanced Oxidization (AO)**

Advanced Oxidization (AO) systems generally rely on the introduction of hydroxyl radicals (-OH) directly into the treatment stream. The highly reactive hydroxyl radicals oxidize and convert contaminants into small, stable inorganic molecules, i.e. mineralized salts. Hydroxyl radicals are produced with the help of one or more precursor oxidants (e.g. ozone, hydrogen peroxide, oxygen) in conjunction with an energy source (e.g. ultraviolet light) and sometimes a catalyst such as titanium dioxide. Often AO systems are combined with filtering and membrane systems to remove the oxidized species.

**Technological Tradeoffs**

CC, EC and AO are all promising treatment technologies to bring flowback and produced water to standards acceptable with reuse, the choice of a particular technology lies in the application details.

Comparing first EC and CC, the primary function of both systems is to remove contaminants by introducing charged ions into the waste stream. For example, aluminum ions are added via Alum (aluminum sulfate) in CC and through the reduction of aluminum electrodes in EC. Both systems produce a floculated species requiring a clarification system for removal. EC may also provide some additional oxidation by the generation of hydroxyl radicals near the electrode. Both systems effect the pH of the water, CC tends to acidify (lowers the pH) of the treatment stream, whereas EC tends to raise the alkalinity (raises the pH) of the treatment stream. Both systems may require post treatment pH balancing depending on the requirements of the site.

Differences between the two systems lie in system robustness, the amount and character of sludge production and the character of the floc. CC systems are more robust as the equipment itself is simpler. For example the electrodes of EC systems are susceptible to fouling from large concentrations of organics and scaling of the electrodes, both of which reduce the ion dose and increase power consumption. Further, EC systems have more design variables, such as electrode shape, electrode gap and detailed flow patterns around the electrodes, possibly leading to application specific designs. In terms of operating expense, CC requires chemical input, whereas EC requires frequent electrode replacement requiring system downtime. In regards to sludge production, it has been reported that CC flocs contain higher bound water than flocs generated by EC. This implies increased sludge production and less water recovery for CC systems.

While potentially possessing very high oxidation potentials and the ability to address a wide range of contaminants, AO systems tend to require significant power inputs, and very costly chemical costs when
hydroxyl radicals are generated via precursor chemicals. AO also often requires pretreatment of the influent, for example, high turbidity can interfere with ultraviolet light penetration hindering hydroxyl production, or dissolved bicarbonates may scavenge most of the produced hydroxyl radicals. Further, some AO systems are not tolerant of high TDS waters.

**Anguil Aqua Systems’ Solution**

Considering the trade-offs of the discussed technologies, Anguil Aqua Systems has elected to provide an enhanced version of a conventional Chemical Coagulation and Precipitation (CC) treatment process since CC is a mature and proven technology with the ability to handle the treatment requirements for fracing flowback and produced water in a cost effective manner. CC equipment is robust, relatively simple and does not require specialized operator knowledge and oversight. An extensive list of coagulant and flocculation chemicals are available to meet the treatment needs of specific applications and allow treatment process optimization for both cost and performance without redesigning the equipment. In summary, CC technology can handle the rugged and variable treatment needs of well site operations.

![Diagram of Ballasted vs Conventional CC](image)

**Ballasted vs Conventional CC**

Anguil Aqua Systems is offering an enhanced version of conventional CC techniques referred to as Ballasted Flocculation (BF). For BF, conventional CC techniques are augmented with the addition of a dense ballast material to the coagulated water. Ballast can consist of any dense particulate including sand, magnetite and even the sludge normally produced from the CC treatment process. The primary effect of
adding the ballast material is to dramatically increase the sedimentation rate by weighing down the floc. Ballast also strengthens the floc against shearing, allowing faster stirring rates. Typically, the ballast can be recovered and recycled back into the waste stream reducing the need to add replacement ballast and lowering operation expenses. Further, recycled ballast can reduce the required coagulation and flocculation chemical doses as recycled ballast acts as nucleation sites for floc formation. Because of the rapid mixing and settling rates, BF units can handle significantly higher throughputs for a given footprint, reducing capital and operational costs over a conventional CC unit.

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