

RESULTS OF THE TREATMENT OF PRODUCTION, FLOWBACK, AND POND WASTE WATERS IN GAS FIELD PRODUCTION FIELDS

Robert G. Allred
Richard E. Allred
Alpine Technical Services
Midvale, Utah

Feb. 1, 2012

INTRODUCTION:

The need for an economically feasible means of treating the wastewater from well drilling, gas production and hydraulic fracturing is well understood. Increasing pressure is being placed on local and federal regulators to command the release of information about the chemical composition of additives used in the gas and oil fields and of the wastewaters themselves.

Alpine Technical Services has been working to find an effective and affordable method to deal with these issues with the following objectives:

1. Develop a method that will allow applications usable at or near the production site.
2. Develop a method that can treat higher volumes of water in a shorter time with a target of 1,200 bbls/ 8 hour shift to 10,000 bbls/day that is scalable to larger flows, if needed.
3. Design a system that can be transported within the production field from site to site using equipment normally available in a production field.
4. Develop chemistry using additives that are listed, or can be listed with NSF for approval for use in drinking water applications.
5. Develop a treatment protocol to produce treated water that can be reused within the production field, injected in an approved re-injection well, or be discharged within the requirements of a discharge permit.

OBSTACLES

The major obstacle in meeting the above objectives has been the lack of information regarding the target chemical make-up of the treated wastewater from either the production company or the local and federal regulators. This is on-going with the ideal of drinking water quality on the one hand and “reasonable and affordable” on the other hand. **The results reported here may help to reach an acceptable range.**

WORK HISTORY

One of the first projects brought to us in May of 2009 was from the truck wash of a large oil field service provider in Wyoming. This sample was treated with an iron salt, aluminum salt, and a polymer, all of which are listed with NSF.

Parameter	Sample as Received	Treated Water
Barium	26.7 mg/l	2.59 mg/l
Calcium	126 mg/l	90.1 mg/l
Magnesium	16.1 mg/l	14.2 mg/l
Silica	54.3 mg/l	23.8 mg/l

A later project brought to us was from a non-integrated oil and gas company with operations in Wyoming in July 2009. This water was treated with iron and aluminum salts and a high molecular weight polymer. All of the products used are listed with NSF and are used in the treatment of drinking water.

Parameter	Sample as Received	Treated Water
Iron, as Fe	10.9 mg/l	0.94 mg/l
Selenium, as Se	0.04 mg/l	0.02 mg/l
Gasoline Range Organic	7.0 mg/l	4.3 mg/l
Diesel Range Organic	24.6 mg/l	6.7 mg/l

A second sample was sent in October 2009 and treated at a slightly high rate.

Parameter	Sample as Received	Treated Water
Gasoline Range Organic	13.3 mg/l	ND
Diesel Range Organic	72.0	ND

The selection of tests to be run was directed by the client. From these sets we learn that the treatment can accomplish two important goals:

1. The removal of some of the scale forming compounds such as calcium, barium, magnesium and silica. This can help for reuse or for pretreatment for other methods such as distillation or membrane separation.
2. Hydrocarbons can be removed easily.

We were provided with a sample from the gas field near Riverton, Wyoming in the summer of 2009 and were also given the opportunity to perform a limited pilot plant study on water from one of the ponds. There was also a concern about microbiological growth so we added a very effective biocide to the treatment.

Parameter	Sample as Received	Treated Water
Anaerobic Plate Count	6 CFU	<1 CFU
Heterotrophic HPC	4,800,000 CFU	1 CFU
Sulfide	1.4 mg/l	ND
Iron, as Fe	5.0 mg/l	0.91
Selenium, as Se	0.102 mg/l	0.0989
Gasoline Range Organic	32.6 mg/l	32.1 mg/l
Diesel Range Organic	8.5 mg/l	ND

In November 2009 we were able to run another sample from a different pond in the same field and saw the following results:

Parameter	Sample as Received	Treated Water
Pre-Separator		
Gasoline Range Organic	11.1 mg/l	1.2 mg/l
Diesel Range Organic	1,560 mg/l	12.2 mg/l
Pit Outfall		
Gasoline Range Organic	6.6 mg/l	3.4 mg/l
Diesel Range Organic	76.6 mg/l	12.2 mg/l

We received an additional sample in the Fall of 2009 from a different field in Wyoming and found the following results with production water:

Parameter	Sample as Received	Treated Water
Gasoline Range Organic	1.6 mg/l	ND
Diesel Range Organic	36.2 mg/l	6.9 mg/l

From these sets we learned that the treatment is very good for removal of iron that it worked well for the removal of hydrocarbons under a range of conditions. Some of the lighter fractions seem to take a little more treatment. We also found that a registered biocide for use in the gas and oil field was able to provide excellent control and at the same time had a shorter life so would not remain in the water cycle for extended periods.

TREATMENT BY ATS PROTOCOL FROM NOVEMBER 2009

FLOWBACK WATER

Parameter	Sample as Received	Treated Water
Inorganic		
Alkalinity, bicarbonate	3,340 mg/l	2,190 mg/l
Alkalinity, carbonate	62 mg/l	ND
Alkalinity, CO ₂	2,500 mg/l	1,840 mg/l
Alkalinity, Hydroxide	ND	ND
Chloride	2,120 mg/l	2,010 mg/l
pH	8.1	7.0
Sulfate	220 mg/l	2,100 mg/l
Metals		
Boron	27.2 mg/l	27.3 mg/l
Calcium	23.9 mg/l	10.5 mg/l
Iron	32.6 mg/l	1.14 mg/l
Magnesium	4.1 mg/l	3.1 mg/l
Silica, as SiO ₂	68.1 mg/l	2.2 mg/l
Sodium	2,090 mg/l	3,090 mg/l

Treatment with the ATS Protocol provided significant reductions in:

Alkalinity	34.43%
Calcium	56.07 %
Iron	96.50 %
Silica	96.77 %

The reduction in each of these will make the water more suitable for use or for additional treatment.

TREATMENTS FROM ADDITIONAL AREAS

In the Spring of 2011 we received samples from Williamsport, PA for testing. We applied the same type of treatment using iron and aluminum salts with a polymer and we applied a second generation product that does not use the aluminum salts.

SECOND GENERATION TREATMENT

This new treatment did not use the metal salts. We used a naturally occurring coagulant aid that carries NSF approval for use in drinking water treatment applications along with a polymer that also carries the NSF listing. This approach has great potential for use in gas and oil fields where contamination of drinking water is of concern.

For the Williamsport sample, we also used the registered biocide because biological growth was a concern.

Parameter	Sample as Received	Treated with metal salts	Treated with new protocol
Oil & Grease	559 mg/l	23 mg/l	ND
Total Dissolved Solids (TDS)	116,000 mg/l	109,000 mg/l	119,000 mg/l
Total Suspended Solids (TSS)	388 mg/l	108 mg/l	325 mg/l
Barium	5,280 mg/l	4,840 mg/l	4,760 mg/l
Calcium	5,080 mg/l	4,970 mg/l	4,720 mg/l
Iron	204 mg/l	100 mg/l	108 mg/l
Silica	32.9 mg/l	10.3 mg/l	16.1 mg/l
Gasoline Range	0.5 mg/l	ND	ND
Diesel Range	946 mg/l	180 mg/l	14.2 mg/l
Micro Bio HPC	>>5,700 CFU	>5,700 CFU	ND

These results show real promise for a natural product based treatment without adding metal salts. The microbiological results are exceptional.

MINING OPERATIONS

Our next opportunity came from a company in Nevada wanting to treat ponds filled with drilling fluid wastewater. They had a much longer list of parameters they wanted to check and we could see that there would be an overlap to solutions found in the oil and gas fields so we took the samples and worked with the new chemistry.

The second and third samples are from the wells providing the water; the fourth is from the pond and the fifth is the treated water.

Nevada Mines Lab Summary

Discription	Ref. Value	Big Springs	Oasis	LC Project Drill Fluid	Treated Drill Fluid
Chemtech-Ford					
Lab Ref. #		1110409-02	1110409-01	1110130-01	1110130-02
Sample Date		12/9/11	12/9/11	12/1/11	12/1/11
Lab Test Date		12/9/11	12/9/11	12/2/11	12/2/11
Sampled By		R.G. Allred	R.G. Allred	R.G. Allred	R.G. Allred
Alkaline Bicarbonate (HCO ₃)	-	198	264	726	186
Alkaline Carbonate (CO ₃)	-	ND	ND	ND	ND
Alkaline CO ₂	-	144	194	545	160
Alkaline OH	-	ND	ND	ND	ND
Alkaline Total as CaCO ₃	-	163	216	596	153
Aluminum	0.2	ND	ND	0.07	1.8
Antimony	0.006			ND	ND
Arsenic	0.01			ND	ND
Barium	2	0.147	0.052	0.04	0.08
Beryllium	0.004	ND	ND	ND	ND
Bismuth	-				
Boron	-	ND	0.08	0.09	0.09
Cadmium	0.005	ND	ND	ND	ND
Calcium	-	38	72	117	130
Chloride	400	3	26	32	80
Chromium	0.1	ND	ND	ND	0.014
Cobalt	-	ND	ND	0.02	0.01
Copper	1	ND	0.027	0.005	0.011
Fluoride	4	ND	ND	0.2	ND
Gallium	-				
Iron	0.6	ND	0.02	8.32	7.32
Lead	0.015			ND	0.02

Lithium	-	ND	0.005	0.027	0.028
Magnesium	150	13.9	18.6	21.7	23.6
Manganese	0.1	ND	ND	0.251	0.197
Mercury	0.002				
Molybdenum	-	ND	ND	ND	0.01
Nickel	0.1	ND	ND	0.02	0.006
Nitrate+Nitrite					
Total as N	10	0.5	1.3	0.2	ND
Nitrogen					
Total as N	10				
pH Standard Units	6.5-8.5	8.2	7.8	7.6	6.3
Phosphorus	-	ND	0.03	1.6	0.11
Potassium	-	1.4	2.3	9.7	7.5
Scandium	-				
Selenium	0.05	ND	ND	ND	ND
Silver	0.1	ND	ND	ND	ND
Sodium	-	4.8	21.3	148	146
Strontium	-	0.16	0.16	0.3	0.32
Sulfate	500	12	63	25	430
Thallium	0.002			ND	ND
Tin	-	ND	ND	ND	ND
Titanium	-	ND	ND	ND	0.009
Total Dissolved Solids	1000	198	376	966	932
Vanadium	-	ND	ND	ND	ND
WAD Cyanide	0.2	0.002	0.002	0.003	0.003
Zinc	5	ND	0.32	0.01	0.02

Comment: All analysis as received

Total Suspended Solids, mg/l	715	50
Filtered		14

Summary

Progress is being made in the quest to provide chemistry to remove scale forming and harmful components of wastewater flow common to drilling and production activities in gas and oil fields.

This work has also shown that it is possible to provide the needed separation of contaminants from the water using chemicals approved for use in drinking water. This will reduce the potential for contamination of ground water.

The chemistry used in this work lends itself to applications using equipment that can be easily used on site and can be moved from site to site under conditions common in gas and oil fields.

The expected cost of the treatment is within a reasonable range and may be very cost effective by allowing drilling or production to continue in situations where wastewater is a limiting factor.