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Abstract

A small-scale model of the air stripping tanks at TFD was constructed and tested to determine the effect of carbon dioxide additions, to the stripper air, on system water pH. The objective was to determine whether this technique could be used to control and minimize CaCO₃ scale formation. It was found that a concentration of 0.7 vol. % CO₂ is required to maintain the water at its original, influent pH value of 7.4, but lower concentrations may be effective in controlling scale. There is also a possibility of reducing CO₂ consumption by recycling the CO₂-rich air. The use of CO₂ injection at Site 300 water treatment facilities is reviewed.

Introduction

Removal of volatile organics in water is accomplished by sparging the water with air at Treatment Facility D (TFD). Air stripping has the effect of raising the pH of this water from about 7 to 8, presumably as a result of removing the carbon dioxide from the water. Depressurization of the water as it is pumped from the water table, at about 100 feet below surface, to the above ground treatment facility, also results in a loss of CO₂ and an increase in the pH. It is well documented that increases in ground water pH result in shifting the carbonate equilibrium towards calcite scale instability (Cowan and Weintritt, 1976; Patton, 1977; Hem, 1985; Wine and Morrison, 1986; Ruck, 1992). This in turn leads to the deposition of calcium carbonate (CaCO₃) scale if not controlled in some manner. In the TFD facility, scale buildup on equipment has caused downtime and damage. In operation without antiscaling treatment, the influent water pump quit within 48 hr of operation, after pumping 20,000 gallons of ground water (W-351, -907 and -906), due to calcite scale buildup on the pump shaft.

For water in a well in contact with the minerals of the downhole formation, there is a stable equilibrium between the various carbonate species in the water and the CaCO₃ in the minerals. At TFD, the inlet water has a pH of about 7, which indicates that there is a significant concentration of H₂CO₃ in the water. Air stripping shifts the pH to the range of 8-9, which releases

small amounts of free CO_3^{2-} ions, which can react with the dissolved Ca^{2+} ions to form scale. It is obvious that shifting the pH back to the original value would be one approach to retard CaCO_3 scale formation.

Another effect that may contribute to the formation of scale at TFD is that the air used to strip the organics raises the temperature of the water to some extent. Because CaCO_3 has a retrograde solubility characteristic, which is unusual among salts, it becomes less soluble in water as the water temperature is raised. The temperature of the air supplying the diffusers is typically about 55°C , while the temperature of the input water is in the range of $19\text{--}25^\circ\text{C}$.

At present, scale deposition at TFD is controlled by the addition of a proprietary, polyphosphate formulation, JP-7 (Jaeger Products Inc., Houston, TX), but there is interest in examining alternative methods of antiscalant treatment that might be more benign to the environment. The phosphate-based JP-7 supplies the treated water with excess phosphate which stimulates algae growth in discharge ponds. The ideal method of scale control would be one that results in little or no chemical change in the water. Accordingly, we tested a magnetic device designed to reduce scaling in water systems, but found that it was not effective at TFD (Krauter, et al, 1996). We are continuing to evaluate other methods of scale control, with the ultimate objective of comparing scaling rates and production costs of various treatment systems.

This report describes the results of tests to determine (1) whether the pH of the water during the sparging process can be controlled by using CO_2 -air mixtures rather than atmospheric air and; (2) what volume of CO_2 is necessary to maintain the water at its influent pH value. A mixture of CO_2 and air that maintains the influent water pH during the VOC removal process should eliminate the water's scaling tendency. If successful, this method of scale control would be advantageous because no chemicals are used that are not already present in the water.

Equipment and Experimental Procedures

To measure the effect of CO_2 -air mixtures on the TFD water, a small-scale model of the TFD air stripping tanks was constructed and installed in a flow system as shown on Fig. 1. The vessel was constructed from a section of 6-in. acrylic pipe and is approximately 24-in. long. The test vessel was designed so that the air and water ratio was the same ratio as in the large-scale, TFD tanks. The test chamber diffuser contains forty-eight 0.051"-dia. holes. The facility diffusers contain thirty two 0.375" holes on each diffuser.

The test vessel was operated approximately half-full by regulating the headspace air vent and the water outlet valves. The actual residence time of the water in the vessel depended on the vessel's geometry and degree of mixing. Vigorous mixing of the water was achieved with air flow rates above 50 cfh. At a water flow rate of 0.4 gpm and air flow rate of 50 cfh, the residence time was determined by injecting a colored dye in the influent, and found to be 10 min.

The typical characteristics of the TFD facility (which, at the time of this study, operated with two tanks in series) and the small-scale test system are listed below:

	<u>TFD</u>	<u>Test System</u>
Fluid Volume, gal.	200	2
Water Flow Rate, gpm ^a	65	0.1-1.0
Air Flow Rate, cfm ^b	350	0.16-1.6 (10-100 cfh)
Ratio of Air:Water, cfm:gpm	5:1	2:1 to 16:1
Water Residence Time, min	3	2-20
CO ₂ Flow Rate, cfh ^c	----	0.1-0.8 cfh
CO ₂ -Air Mixture Range, vol. %	----	0-1

^agpm = gal. per min.

^bcfm = cubic feet per min.

^ccfh = cubic feet per hour

Figure 1. TFD Scale Treatment Test Chamber Flow Chart

Influent water was obtained from a port (TFD-I004) upstream of the particulate filtration and antiscalant-additive injection systems. At the time of these tests, the water was a mixture from three wells, W- 351, -906, and -1208 which were running at rates of 2.2, 8.2, and 22 gpm, respectively. The carbon dioxide source,

commercial-grade CO₂, was located outside the TFD building. Water from the test vessel was discharged into the headspace of the first main TFD stripper tank (AS2). The pressure in the headspace of AS2 created a back pressure in the vessel of 7.5 in.-H₂O. During the experiments, water and gas flow, and the vent-valve, were adjusted to maintain a constant 10 in.-H₂O (approximately 0.3 psi) headspace pressure within the vessel. This headspace pressure compares with the typical pressure (7-8 in.-H₂O) of the facility air stripping tanks.

General Water Chemistry

A summary of the major parameters of the TFD water is presented in Table 1. Typically, TFD water is a mixture from four wells, W-351, -906, -1208, and -907 which flow at rates of 2.2, 8.2, 22, and 33 gpm, respectively. The following elements were also measured, but were not detected at or above the reporting limits: Al, Cu, Fe, Mg, Ni, and Zn.

Table 1. Major water quality characteristics of the influent water processed in the TFD facility (includes water from W-351, -906, -1208, and -907). The analysis is from the 3rd quarter, 1997.

<u>Analyte</u>	<u>Concentration, mg/L</u>
pH	7.2-7.4 ^a
Specific Conductance	2700 ^b
Total Dissolved Solids	780
Hardness, as CaCO ₃	330
Total Alkalinity, as CaCO ₃	240
Bicarbonate Alkalinity, as CaCO ₃	240
Sodium	160
Potassium	1.7
Calcium	76
Magnesium	33
Chloride	220
Sulfate	88
Fluoride	0.48
Nitrate, as NO ₃ ⁻	24
Nitrite, as NO ₂ ⁻	<2.5
Total Phosphorus, as PO ₄	0.081

^a pH units, measurement at sample port I004

^b μ S

Measurements of system water pH were performed by taking samples at three points: (1) the main upstream influent point (TFD-I004); (2) the vessel influent port and; (3) the vessel effluent port. A Beckman Model 210 pH meter with a Type 39841 electrode was used for the measurements. Ten min. was allowed for the water chemistry within the vessel to stabilize before sampling the waters at a water flow

rate of 0.4 gpm; 20 min. was allowed at 0.2 gpm. Ground water temperatures remained stable at 20 ± 0.5 °C at all of the sample ports.

Results and Discussion

Atmospheric air contains 0.032 vol. % CO₂, therefore, concentrations above 0.032 vol. % must be used to effect measurable changes in the system water pH. The observed degassing of typical well waters when brought to the surface suggests that the inherent partial pressures of CO₂ of these waters is appreciably higher than water in equilibrium with air at sea-level atmospheric pressures. Carbon dioxide concentrations above 1 vol. % were not tested because this volume of CO₂ is impractical from a cost standpoint. Consequently, the test system was designed to introduce CO₂ into the stripper air in the concentration range of 0.1 to 1.0 vol. %.

As shown in Fig. 2, atmospheric air metered into the test chamber substantially increased the pH of the ground water. As air was introduced into the test chamber, the water equilibrium changed, resulting in an increase in the pH of the water from 7.41 to 8.00, at an air flow rate of 80 cfh. The pH of the aerated water is similar to the pH measured at the full-scale TFD effluent, which was between 8.1 and 8.2 during these tests. Consequently, operation of the test chamber is a reasonable simulation of the TFD air stripping process.

When carbon dioxide was added into the air flowing into the diffuser the ground water pH decreased (see Fig. 3). Two tests were conducted to measure how the pH of the water varied with the concentration of CO₂ in the stripper air. The objective was to determine the concentration of CO₂ required to restore the pH of the water to its original value of 7.4. Carbon dioxide delivered as 0.70 vol. % in 80 cfh of air was sufficient to maintain the ground water pH at 7.4, at water flow rates between 0.2 and 0.4 gpm.

The ratios of air:water in these experiments were 6:1 and 3:1 cfm:gpm, respectively, these ratios are similar to the air:water ratios found in the full-scale stripper system (10:1 when treating 35 gpm; and 5:1 when treating 70 gpm). It is interesting to note that the concentration of CO₂ required to reach pH 7.4 in the chamber effluent was virtually independent of the water flow rates, and chamber residence times, within the range examined (0.2 and 0.4 gpm). Thus, equilibrium between the water and the headspace air/CO₂ in the chamber appears to have been achieved.

Site 300 Water Treatment Operations

Because the method of CO₂ introduction into the stripper air to adjust the pH of the waters during treatment was previously used at Site 300, it is of interest to summarize some of this work and compare it to the results of the present study.

Several facilities that involve air stripping to remove VOCs have been in operation at Site 300 during the past few years. One facility was at Eastern

General Service Area (GSA), which now employs a different VOC removal process, and one was at Central GSA. Water processing at Central GSA is

Figure 2. Effect of air flow on W-351, -906 and -1208 water pH in the TFD test chamber.

currently accomplished by means of a Portable Treatment Unit (PTU).

In the operation of these treatment facilities, two situations were encountered that led to the use of CO₂. The first situation that required pH adjustment was the scale formation in the air stripping tanks, air inlets and effluent lines. A 50 lb. CO₂ tank provided 15 cfh of CO₂ to each of the air compressor lines feeding the air stripper tanks. The second situation requiring pH adjustment was due to water produced by the air stripping unit acquiring a pH value that exceeded the environmental discharge limit of 8.5. To lower the pH, CO₂ gas was introduced into the water after it exited the

Figure 3. Effect of carbon dioxide on W-351, -906 and -1208 water pH in the TFD test chamber. Concentration of carbon dioxide does not include that present naturally in the stripper air.

treatment facility, by simple TEE connections on the effluent lines. The required flow rate of CO₂ was determined by monitoring the resulting water pH, while the CO₂ flow rate was manually adjusted. This technique was used successfully at both Eastern and Central GSA facilities.

At Site 300 Central GSA, the discharge water traveled in a black 6" PVC pipe for 100 ft. prior to its release into the arroyo. In the summer months, the temperature of the discharge water climbed to above surface air temperature (>37°C) thus increasing the tendency to form scale. Central GSA employees reported that in the summer the 6"-dia. hose plugged solid with calcite, possibly due to the combined effects of water chemistry, air stripping, and environmental temperatures.

At Eastern GSA severe calcite scaling of the 6"-dia, 1000 ft. long Flex-flume™ hose required 3 to 4 cfh of CO₂ to be constantly injected into the effluent stream during the 24 h/d operation. The water flow rate at Eastern

GSA was 40-43 gpm, 7 d/wk. Operating under continuous flow conditions, one 50 lb. bottle of CO₂ would last for 1.5 d. In the case of Central GSA, the calcium carbonate scaling occurred both in the air stripping manifold unit, which had 1/8" holes and in the effluent discharge line. It was proposed that this scaling might be reduced by introducing CO₂ into the stripper air before it entered the stripper tanks. This approach was implemented at Central GSA during its initial and subsequent operations, and the results were satisfactory. The rate of CO₂ flow typically was 15 cfh at an air flow rate of 560 cfm, so that the concentration of CO₂ in the air was increased from its natural value of about 0.032 to 0.077 vol. %. As can be seen in Fig. 3, this concentration of CO₂ would decrease the pH of TFD water from about 8.1 to 7.9. Apparently, however, there were no detailed measurements of the water pH vs. CO₂ flow rate, nor was there a baseline study of the effects of scaling without CO₂/air introduction. Qualitatively, scaling rates at Central GSA appeared to be much lower than those at Eastern GSA, thus this may not have been a definitive test of the CO₂/air technique. Nevertheless, the very small concentration of CO₂ employed at Central GSA gives some encouragement to the idea that perhaps high concentrations of CO₂ are not required for scale control.

At Central GSA, as mentioned above, the treatment facility that used CO₂ has now been shut down, and the water is now processed using a portable treatment unit (PTU). In two months of operation, no scaling problems have been observed, and it has not been necessary to change the pH of the discharged water by CO₂ introduction. If the use of a PTU decreases the water residence time, thus tending to decrease CaCO₃ scaling rates, it is possible that relatively low concentrations of CO₂ in the air may be sufficient to further minimize scaling.

Scaling Indexes of TFD and Site 300 Central and Eastern GSA water

The Langelier saturation index (LSI) is an index calculated from total dissolved solids, calcium concentration, total alkalinity, pH, and solution temperature (Tchobanoglous and Schroeder, 1987). The index shows the tendency of a water solution to precipitate or dissolve calcium carbonate. A positive LSI indicates the tendency to form calcium carbonate scale.

Table 2 compares the tendencies of several waters toward scale formation based on the Langelier index. Both TFD and Site 300 ground water have the chemical and physical makeup to produce calcium carbonate scale in the treatment facility. TFD influent ground water has a tendency to form calcium carbonate scale, particularly from well W-906. At TFD the influent water has an LSI of 0.52 at a pH of 7.2 -7.4; if the pH increases to 8.0 during the air stripping process, the scaling tendency increases, as indicated by a calculated LSI of 0.81. This is confirmed by the observation that scale does not form in TFD tanks and transfer lines before the air stripping units. The pH at which no scale will form in this water is <7.3.

Table 2. Comparison of the Scaling Indexes of ground water from the main site Treatment Facility-D and site 300 Central GSA.

	Date Sampled	Sample Port or well No.	pH	Langelier Index
Main Site TFD				
	4/09/97	TFD-I004-0800	7.2	0.01
	7/11/96	TFD-STPR2E	8.0	0.81
	8/18/95	MW-351	7.2	0.20
	8/18/95	MW-906	7.0	0.69
	8/30/95	MW-907	7.4	0.34
Site 300 Central GSA				
	2/22/94	W-7I	7.7	0.31
	2/23/94	W-875-08	8.1	0.27
	11/3/93	W-875-07	7.9	0.65
Site 300 Eastern GSA				
	1/30/96	CDF1	7.8	0.14
	1/26/97	CON1	8.4	0.68
	11/11/96	W-25N-20	7.2	0.27

Future Work

Because the measurement of scaling rates in the TFD system requires lengthy experiment times, as long as 9-13 days (Krauter, et al, 1996), a test of the use of CO₂ in the stripper air for scale control appears to be most practical in the full scale, TFD facility. A side-stream test using the model would require the same amount of time, and would still have to be proven at large scale. Further tests should determine whether less CO₂ than required for complete pH restoration might effect adequate scale control.

The quantity and cost of CO₂ that would be required to maintain the water at its influent pH value at TFD can be calculated from the typical air flow used at the facility, which is 350 cfm. At a flow rate set to achieve a concentration of 0.70 vol. % CO₂, 2.45 cu. ft. per min. of CO₂ would be required. Size No. 1A cylinders that are available from the Industrial Gas Group at LLNL hold 50 lb. (22.7 kg) of CO₂ and cost \$6 each. 22.7 kg is 516 moles of CO₂, which would occupy about 400 cu. ft. at a pressure of 1 atm. and temperature of 25°C. At the required flow rate, 9 cylinders would be consumed per 24-h operation, at a cost of \$54. Because of the number of days required for a valid test, this number of cylinders is impractical for the operation, and this cost may be unacceptable. However, larger cylinders or

containers are available commercially, at lower cost. Also, we have calculated this quantity of CO₂ as a worst case; as can be seen in Fig. 3, a factor of 3-5 less CO₂ might be sufficient to lower the pH to a value that would satisfactorily control CaCO₃ scaling. Another approach worth considering is to recycle the CO₂-rich air, after the stripping and VOC removal in the activated charcoal beds. Some CO₂ makeup probably would be required, but this should conserve the use of CO₂ and would be more economical than continuous feed. Monitoring of the CO₂ concentration in the stripper air would be required. Testing of the proposal would also include careful measurements of the VOCs in the air and water.

An alternate antiscaling treatment is the use of chemical antiscalants. Several chemical treatments are commercially available and are widely used in cooling towers, boilers, reverse osmosis and other water treatment systems. Phosphonates or phosphonic acids are one type of chemical agents. They are multifunctional metal ion control agents, containing at least one functional group, PO₃H₂, attached to a carbon atom. About one tenth of the amount of phosphonate compound is needed for antiscaling treatment compared to phosphate-based compounds.

Polymaleic or phosphinocarboxylic acid scale inhibitors are in another chemical group that are general purpose scale inhibitor/dispersants. These compounds enhance solubility which reduces precipitation of low solubility inorganic salts. They also are crystal modifiers, which can deform the growing inorganic salt crystals to give small, irregular, readily fractured crystals that do not adhere well to surfaces. They have dispersing activity, which prevents precipitated crystals or other inorganic particles from agglomerating and depositing on surfaces.

Another chemical scale control type are polymeric additives. These antiscalants use low dose levels compared to the dose levels of phosphate-based scale inhibitors, and they are considered environmentally friendly based on numerous toxicology studies. Also, polymeric additives do not have the hazardous qualities of mineral acid antiscalants. We propose to test suitable chemical antiscalants on the high-flow water treatment system (350 gpm, 24-h/d) at TFA. The only equipment necessary for chemical antiscaling use is a day tank and a feed pump. Chemical antiscalants may be a cost effective means of scale control for the high volume water treatment facilities.

Key Accomplishments

- At TFD a concentration of 0.7 vol. % CO₂ was required to maintain the water at its original, influent pH value of 7.4.
- A useful small-scale model of the air stripping tank at TFD was constructed.
- The use of CO₂ injection at Site 300 water treatment facilities was reviewed.

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References

- Cowan J. C. and D. J. Weintritt, 1976, *Water-Formed Scale Deposits*, Gulf Publishing Co., Houston, TX, Chapt. 3.
- Hem J. D. (1985) *Study and interpretation of the chemical characteristics of natural water* 3rd ed. U. S. Geological Survey Water-supply paper 2254.
- Koch, M. and W. Ruck. 1992. *Injection of CO₂ for the Inhibition of Scaling in ATES Systems*. Proc. Intersoc. Energy Convers. Engineering Conference, 27th, (Vol. 4), pp. 4.89-4.93
- Patton C. C., 1997, *Oilfield Water Systems*, 2nd ed., Campbell Petroleum Series, Norman, OK, p. 54.
- Krauter P. W., J. E. Harrar, S. P. Orloff and S. M. Bahowick, 1996, *Test of a Magnetic Device for the Amelioration of Scale Formation at Treatment Facility D*, Lawrence Livermore National Laboratory Report UCRL-ID-125551.
- Tchobanoglous G. and E. D. Schroeder, 1987, *Water Quality: Characteristics, Modeling, Modification*. Addison-Wesley Publishing Co., Reading, Massachusetts.
- Wine, R. D. and R. D. Morrison. 1986. *Effective Use of Carbon Dioxide For pH Control In Utility Service and Waste Waters*. Proceedings of the American Power Conference 48. pp. 1042-1046.

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