

This article documents the first known in situ electrochemical production of perchlorate within a public water distribution system. In this detailed incident, perchlorate (ClO_4^-) was detected in the distribution system of Levelland, Texas, and was eventually isolated to one elevated storage tank. Theoretical considerations supported the production of ClO_4^- by an electrochemical process within the tank. ClO_4^- was produced (64–113 $\mu\text{g/L}$ in 338 h) in laboratory experiments that simulated the cathodic protection system in place in the storage tank. Because cathodic protection systems are widely used, this research confirms a potentially troubling mechanism of ClO_4^- generation.

TECHNICAL NOTE:

electrochemical generation of perchlorate IN MUNICIPAL DRINKING WATER SYSTEMS

BY ANDREW JACKSON,
SANGEETHA ARUNAGIRI,
RICHARD TOCK,
TODD ANDERSON,
AND KEN RAINWATER

Continued advances in sensitivity and reliability of analytical procedures now make detection of perchlorate (ClO_4^-) concentrations possible in the microgram-per-litre range in water. Less than a decade ago these low-level ClO_4^- concentrations would have gone undetected. Today increased instrumental sensitivity has led to more frequent detections of ClO_4^- in water resources. In most instances the ClO_4^- source can be traced to military, industrial, or agricultural operations (Urbansky, 1998). In other instances it has been suggested that ClO_4^- salts are generated by natural “oxidative weathering” phenomena, which involve pathways attributable to microbial activity, ultraviolet radiation, or atmospheric generation of activated oxygen moieties, such as ozone and peroxide complexes (Becking et al, 1958).

Even at the low microgram-per-litre levels, however, ClO_4^- contamination causes concern for potential chronic ecological and human health effects (Greer et al, 2002). ClO_4^- is known to affect thyroid gland function, and numerous studies are under way on the associated risk from ingestion of ClO_4^- . The current US Environmental Protection Agency–recommended Interim Action Level is listed as 4–18 $\mu\text{g/L}$, whereas some state regulatory agencies have established a range of 1–18 $\mu\text{g/L}$.

In the spring of 2002, as part of its Uncontrolled Chemical Monitoring Program, the Texas Commission on Environmental Quality (TCEQ) conducted sampling

TABLE 1 Levelland incident summary

Date	Incident
April 17, 2002	ClO ₄ ⁻ * (32 µg/L) was detected in sample from Lee Street Pump Station.
April 18, 2002	Lee Street Complex (five active wells, two inactive wells, one ground storage tank, and one EST†) isolated from the remainder of the city's distribution system.
April 19, 2002	ClO ₄ ⁻ was not detected in sample collected at Lee Street point of entry, which at the time was not receiving water from the Lee Street system.
April 23, 2002	ClO ₄ ⁻ was not detected in any of the seven wells that make up the Lee Street Complex.
April 26, 2002	Several other points in the Lee Street Complex were sampled, including the EST. All samples were nondetections for ClO ₄ ⁻ , with the exception of the EST sample and a duplicate from the EST (122 and 123 µg/L, respectively).
May 1, 2002	ClO ₄ ⁻ was not detected in any of the samples collected from 18 private wells in the vicinity of the Lee Street well field.
May 2, 2002	Lee Street EST was resampled. ClO ₄ ⁻ was detected (82 µg/L).
May 13–16, 2002	Lee Street EST was emptied at a rate of 100,000 gpd (378,500 L/d). Duplicate, 1-L samples were collected from every 25,000 gal (94,600 L) of water discharged. The concentration of ClO ₄ ⁻ in the 32 samples ranged from 71 to 77 µg/L.

*Perchlorate
†Elevated storage tank

at points of entry to potable water distribution systems across a wide area of West Texas. As a result, ClO₄⁻ contamination was found in the potable water distribution system of Levelland. The chronology of the detection events is summarized in Table 1. Subsequent testing eliminated any possibility of contamination from either the groundwater or surface water sources used by the city. The presence of the ClO₄⁻ was eventually isolated to one specific elevated storage tank (EST) in the distribution system. The Lee Street EST was found to contain approximately 400,000 gal (1.5 × 10⁶ L) of water with ClO₄⁻ concentration ranging from 71 to 77 µg/L. This finding represented the first documented incident of in situ generation of ClO₄⁻ in a municipal drinking water distribution system.

The TCEQ contacted the Texas Tech University Water Resources Center (TTUWRC) to investigate this issue.

Even at the low microgram-per-litre levels, however, perchlorate contamination causes concern for potential chronic ecological and human health effects.

The objectives of its research were to determine the most probable cause of the ClO₄⁻ discovered in the Levelland system and to estimate the potential for future occurrences. Task assignments for this research included the development of a summary of the known facts pertaining to the Levelland incident, presentation of a the-

oretical framework for potential ClO₄⁻ generation mechanisms, and performance of laboratory experiments to recreate the mechanism most likely responsible. Results from this research were expected have significant national implications for many similar municipal drinking water sources.

THEORETICAL FRAMEWORK

Possible mechanisms for ClO₄⁻ generation. Industrial technology for commercial production of perchloric acid and ClO₄⁻ salts was established during the early 1900s (Schilt, 2003). Today, electrochemical processes are used widely for large-scale commercial production of both chlorate and ClO₄⁻ salts. Electrolytic generation of ClO₄⁻ begins with aqueous solutions of either chloride or chlorate salt as raw material. In general, the overall operating conditions for these electrolytic units are well-established, and a core of patent literature is available for electrolytic cell design,

particularly with respect to materials selection for electrodes and for electrode arrangement. In the following discussions of possible sources for ClO₄⁻ contamination of drinking water in an EST, the same principles and theoretical concepts developed for commercial ClO₄⁻ production are used. Thus, even though ESTs are not designed as electrolytic cells, it is possible that the use of internal cathodic corrosion protection systems and/or external lightning strikes could promote electrochemical reactions within the tanks and generate ClO₄⁻ contamination.

Seven possible methods for the production of aqueous ClO₄⁻ are found in the literature (Schilt, 2003; Becking et al, 1958):

- (1) neutralization of perchloric acid with an appropriate base or metal;
- (2) reaction of a strong mineral acid with a chlorate to produce ClO₄⁻, chloride, and chlorine dioxide;
- (3) natural oxidative weathering or microbial oxidation of chlorides;
- (4) electrolytic conversion of an aqueous chlorate to ClO₄⁻ by anodic oxidation;

(5) electrolytic anodic oxidation of aqueous chloride to ClO_4^- ;

(6) thermal decomposition of a chlorate to ClO_4^- , chloride, and oxygen; and

(7) direct chemical oxidation of chlorates to ClO_4^- by strong oxidants, such as ozone, persulfates, lead oxide, and permanganate.

These seven methods are not equally well-understood, nor are all equally possible within the constraints known to exist for the conditions in the Lee Street EST. These constraints are discussed in this article, along with evidence collected as part of the EST investigation.

The construction and operating conditions of the Lee Street EST preclude the possibility of mechanisms 1, 2, and 3 being responsible for the ClO_4^- contamination. No strong acids or oxidants, other than the combination of chlorine at the upstream water treatment plant, were used in the treatment of the water before storage. The EST completely enclosed the stored water in a carbon-steel tank. Therefore, only the last four mechanisms were given further consideration in this investigation. Each process requires that chlorate ions, as either the acid or salt, must be present or generated in situ before ClO_4^- is formed. With no evidence of an external source for the Lee Street EST contamination, only in situ chemical reactions involving chloride or hypochlorous ions were possible. The investigation turned to the examination of possible sources for electrochemical generation of ClO_4^- contamination.

Electrochemical generation of ClO_4^- . Table 2 shows the typical concentrations of anions and related param-

TABLE 2 Composition of Lubbock and Levelland tap water*

Constituent	Levelland Tap Water—mg/L (except pH)
Chloride	385
Fluoride	0.5
Nitrate	0.07
Sulfate	357
Total hardness	312
Total alkalinity (as calcium carbonate)	183
Total dissolved solids	1,308
pH	7.5

*Provided by the cities of Lubbock and Levelland, Texas.

TABLE 3 Experimental details

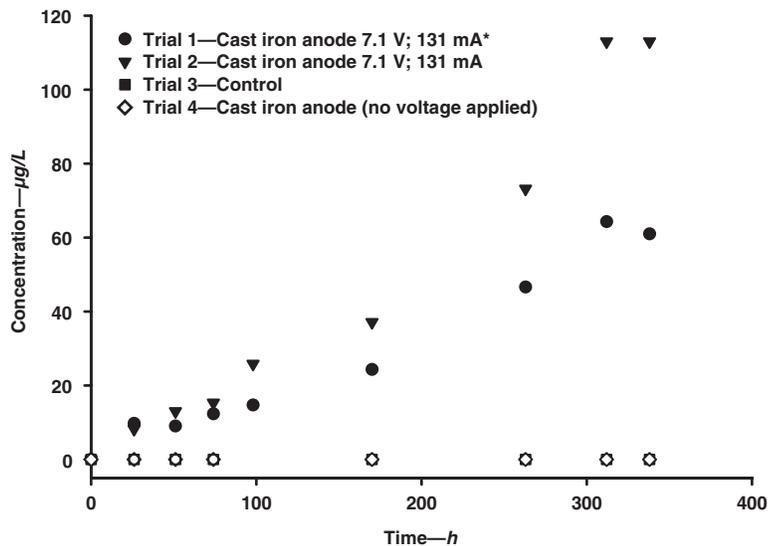
Treatment	Area— cm^2 (sq in.)		Voltage V	Current mA
	Anode	Cathode		
Trial 1—Cast-iron anode with power	419 (65)	3.5 (0.54)	7.1	131
Trial 2—Cast-iron anode with power	400 (62)	4.4 (0.68)	7.1	131
Trial 3—Control with water only	0	0	0	0
Trial 4—Control with water and anode	397 (61)	0	0	0

eters as measured by the city of Levelland that could affect the electrochemical processes. The city of Levelland is one of the 11 member cities that make up the Canadian River Municipal Water Authority, and as such receives its primary drinking water supply from the city of Lubbock, whose water treatment plant handles water from Lake Meredith on the Canadian River. Lubbock's treatment plant employs conventional coagulation, flocculation, sedimentation, filtration, and disinfection by chloramination. Table 2 is based on the treated effluent quality. Levelland supplements that surface water supply with local groundwater, which receives only disinfection by chlorination, occasionally during peak demand periods. Because gaseous chlorine is used for disinfection in the upstream water treatment processes, both chloride and hypochlorite ion (OCl^-)/hypochlor-

Even though elevated storage tanks are not designed as electrolytic cells, it is possible that the use of internal cathodic corrosion protection systems and/or external lightning strikes could promote electrochemical reactions within the tanks and generate perchlorate contamination.

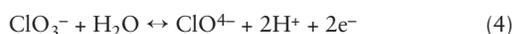
ous acid (HOCl) were present in the water being stored in the Lee Street EST. Initially both lightning strikes and internal cathodic protection were considered as possible energy sources to drive the electrochemical processes. Lightning was suspected to have struck the Lee Street EST sometime during the period in question. The lightning strike could have

FIGURE 1 Production of perchlorate by a simulated cathodic protection system



sent a surge of high voltage potential across the EST and its cathodic protection circuit, damaging its rectifier. The tank was examined for external evidence of a recent lightning strike. Weather data sources from government meteorological agencies now compile records of the timing and locations of lightning strikes. It was documented that the Lee Street EST had an active cathodic protection system mounted inside the EST beneath the water line. Active cathodic protection systems use an impressed current to force an anode to corrode and thus protect the steel tank shell. Details of these systems can be found in National Association of Corrosion Engineers (NACE) Standard RP0388-2001 (NACE, 2001).

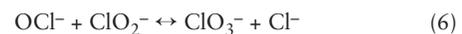
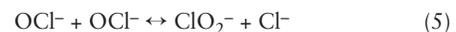
Electrochemical production of chlorine, hypochlorous acid, chlorate, and ClO_4^- has been understood and exploited for more than a century. There are numerous possible reactions that produce or consume the presence of the various oxidized states of chlorine. The primary electrochemically induced reactions that could occur in drinking water with pH, temperature, and total dissolved solids similar to the Lovelland water supply as exposed to metal anodes are



Equation 1 relates the dissolved chloride and chlorine concentrations. Equation 2 represents the reaction of

gaseous chlorine with water to form hypochlorous acid and chloride ions. The reaction in Eq 2 demonstrates how formation of OCl^- or HOCl depends on the pH of the water. The pK for disassociation of hypochlorous acid is 7.6, at which the species would exist in equal amounts. Equation 3 represents electrochemical generation of chlorate ions in water along with liberation of gaseous hydrogen and free electrons to the anode. Equation 4 represents the final oxidation step in which chlorate is electrochemically transformed into ClO_4^- with additional release of protons to solution and electrons to the anode (Janssen & Vanderheyden, 1995; Grotheer & Cook, 1968).

The other most likely possible reaction mechanisms for the production of chlorate and ClO_4^- would be the following:



Equation 5 represents the decomposition of hypochlorite to chlorite, and Eq 6 represents the further decomposition of chlorite to chlorate, which is known to proceed at a faster rate (Weinberg et al, 2003; Kraft et al, 1999). However, these reactions would be exceedingly slow at neutral pH and temperatures less than 30°C (86°F). Equation 7 is the chemical decomposition of chlorate to ClO_4^- , which is only significant left to right at elevated temperatures and under acidic conditions.

Equations 5–7 are important reactions for the manufacture of oxidized chlorine species and for storage of high-strength solutions of hypochlorite. However, in the absence of a lightning strike, which could produce localized high temperatures, these reactions most likely would not have contributed significantly to the production of ClO_4^- in the EST (Jonassen, 2002). This limitation leaves the impressed-current corrosion protection system as the more probable cause for the ClO_4^- contamination detected in the Lee Street EST. Therefore, to determine whether it was possible that the cathodic protection system was responsible for the ClO_4^- presence in the EST, the following experiments were conducted.

EXPERIMENTAL APPROACH

Apparatus. The laboratory apparatus included completely mixed water baths in which a cathode and anode

pair could be exposed to the local tap water and the electrical potential and current typical of the EST's cathodic protection system. The water baths were made of high-density polyethylene plastic and held 1 gal (4 L) of Levelland tap water. Cathodes were square plates of 2.5-cm- (1-in.-) thick galvanized steel. Anodes were taken from a small piece of the high-silicon cast-iron anode from the Lee Street EST. The initial chloride concentration in the water used for this experiment was 227 ± 24 mg/L, and the pH was approximately 7.9. Both anode and cathode were connected by brass banana clips to wire leads from the power sources. Four tanks were run simultaneously, and referred to as trials 1–4 in Table 3. Trials 1 and 2 were intended as duplicates of the EST cathodic protection circuit. Trial 3 was a simple water-only control, with no cathode or anode. Trial 4 was a second control with a

the period of March 2–May 1, 2002, surrounding the time when the ClO_4^- contamination was detected. It remains an open question, however, as to whether ClO_4^- contamination of chlorinated drinking water could be produced from a lightning discharge.

The data supplied for the ClO_4^- incident in Levelland strongly suggests that it was produced by the cathodic corrosion protection system. The anodes in the Lee Street EST were found to be high-silicon cast-iron and heavily coated with manganese oxide. Manganese oxide is a well-known catalyst for production of chloro-oxygen compounds. By comparison, all other ESTs in the Levelland system used titanium-based mixed metal anodes. Although it is unclear as to the role anode composition and surface conditions play in the generation of ClO_4^- , it is well-established that both can influence the generation rate

The data supplied for the perchlorate incident in Levelland strongly suggests that it was produced by the cathodic corrosion protection system.

cathode and no anode in the water bath. The circuits in Trials 1 and 2 were connected to a current/voltage power source¹ for a total of 338 h. Samples of water were taken from all four trials at periodic intervals over this time and analyzed for ClO_4^- . All samples were taken by glass pipette and stored in 50 mL vials at 4°C until analysis.

Analytical instrumentation. A chromatograph² equipped with an oven³ maintained at 35°C and an autosampler⁴ were used. A guard column⁵ (4 × 50 mm [0.16 × 2 in.]) was used in conjunction with an analytical column⁶ (4 × 250 mm [0.16 × 10 in.]) for separation. The 100-mM sodium hydroxide eluent was applied isocratically at a flow rate of 1.0 mL/min. A suppressor,⁷ operated at 300 mA in the external water mode, was also used. A conductivity meter⁸ was used to measure the conductivity of samples before analysis.

RESULTS AND DISCUSSION

ClO_4^- was generated in both replicates that received electrical power (trials 1 and 2, Figure 1). ClO_4^- generation was generally similar between replicates, although the absolute amount of ClO_4^- differed between each replicate, with maximum concentrations of 64 and 113 µg/L in trials 1 and 2, respectively. These experiments demonstrated it is feasible for impressed-current corrosion protection systems to produce ClO_4^- in batch systems. ClO_4^- was not detected in either the control (trial 3) or in the treatment with electrodes but no power (trial 4).

The investigation of a possible lightning strike as the cause of the April 2002 ClO_4^- concentrations found no evidence of a recent strike at or near the EST. Atmospheric generated flash data, which can be obtained from the US Lightning Detection Network, showed no lightning strikes within a 2 mi (3 km) radius of the storage tank for

of ClO_4^- in electrochemical systems. The chloride concentration in the Lee Street EST (near 400 mg/L), although high for drinking water, was much lower than that for typical industrial generation of ClO_4^- . Higher concentrations of chloride increase the potential for ClO_4^- production, and either chloride or OCl^-/HOCl could have served as the feed material for the ClO_4^- production in the Lee Street EST. The voltage potential reported for the Lee Street EST cathodic protection system was approximately 6 V, which was about 1 V higher than those used in the cathodic protection systems in the other tanks. Cell voltages higher than 6.3 were reported in the literature to be advantageous for the production of ClO_4^- . The recorded pH levels (7.2 to 7.75) and temperatures (<30°C) within the water storage tanks in the Levelland system appear to be immaterial to the observed ClO_4^- contamination, because neither is in the range known to promote nonelectrochemical mechanisms for the generation of ClO_4^- .

CONCLUSIONS

Primarily on the basis of documentation assembled from the Levelland incident, experimental verification, and published literature, the cathodic protection system used in the Lee Street EST was the probable cause of in situ ClO_4^- contamination of the chlorinated drinking water in the tank. Although it was originally speculated that lightning adversely affected the cathodic corrosion system and that a malfunction of a rectifier in the impressed-current system may have led to the generation of the ClO_4^- contamination, no evidence for that cause was uncovered.

Fortunately it is unlikely that ClO_4^- production in cathodically protected storage tanks is a common occur-

rence at relevant chlorine concentrations because of a combination of factors. Most storage tanks are operated for fairly fast turnover rates of the stored water, which would not allow buildup of ClO_4^- . There may be concern for older tanks that are treated as static storage for fire protection or other peaking concerns. In addition, most current cathodic protection systems are run at operating voltages well below 6 V, which is less likely to generate ClO_4^- . However, older systems that use high-silicon cast-iron anodes appear to be more likely to be affected, and the overall relation of anode material to ClO_4^- generation should be investigated further. In addition, because chlorate is a required intermediate for ClO_4^- formation, potential generation of chlorate within chlorinated drinking water systems should also be evaluated.

The TTUWRC is pursuing other studies of cathodic protection systems that are in use on pipelines, buried tanks, and water and oil wells to see if these anticorrosion systems could also generate ClO_4^- from natural chlorides present in the surrounding soils and groundwater. If operational cathodic corrosion protection systems represent active sources of ClO_4^- , then operators of municipal drinking water systems will need to be cognizant of this fact and exercise remedial action.

ACKNOWLEDGMENT

This work was funded by the Texas Commission for Environmental Quality (TCEQ). The authors appreciate the cooperation of Pat Riley and the city of Levelland as well as TCEQ personnel who facilitated this research.

ABOUT THE AUTHORS:

Since 1998 Andrew Jackson⁹ has been an assistant professor of civil engineering at Texas Tech University, 10th and Akron St., Lubbock, TX, 79409; e-mail andrew.jackson@coe.ttu.edu. For the past four years he has researched the fate and remediation of perchlorate in the environment. His work includes the use of electrokinetics to stimulate bioremediation of perchlorate in subsurface soils, the role of plants in the fate of per-

chlorate in natural systems, the fate of perchlorate in wetlands and their use as treatment systems, and the natural production and distribution of perchlorate in the environment. Jackson was awarded the Civil Engineering Researcher of the Year Award for 2002 and 2004, and the Lockheed Martin Excellence in Teaching



Award for 2002. He is a member of the American Chemical Society, the Association of Environmental Engineering and Science Professors, and the Water Environment Federation.

Jackson has had articles previously published in Environmental Science & Technology, Water, Air, & Soil Pollution, Journal of Environmental

Quality, Bioremediation Journal, Environmental Toxicology and Chemistry, Water Research, and others.

Richard Tock is a professor in the department of chemical engineering at Texas Tech University. Sangeetha

Arunagiri is a graduate assistant in the department of Civil Engineering at Texas Tech University. Todd

Anderson is an associate professor in the department of Environmental Toxicology at Texas Tech University.

Ken Rainwater is a professor in the department of civil engineering and director of the Water Resources Center at Texas Tech University.

FOOTNOTES

¹Hewlett Packard 6212C, Hewlett-Packard Corp., Avondale, Pa.

²Dionex IC25, Dionex Corp., Sunnyvale, Calif.

³LC25, Dionex Corp., Sunnyvale, Calif.

⁴AS40, Dionex Corp., Sunnyvale, Calif.

⁵AG11, Dionex Corp., Sunnyvale, Calif.

⁶AS16, Dionex Corp., Sunnyvale, Calif.

⁷ASRS-ULTRA, Dionex Corp., Sunnyvale, Calif.

⁸Accumet AB30, Fisher Accumet, Springfield, NJ

⁹To whom correspondence should be addressed

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