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An ASABE Meeting Presentation

Paper Number: 096156

# Hydrogen Peroxide Treatment of Manganese Clogged SDI Emitters

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Written for presentation at the 2009 ASABE Annual International Meeting Sponsored by ASABE Grand Sierra Resort and Casino Reno, Nevada June 21 – June 24, 2009

**Abstract.** Dissolved manganese in irrigation water has contributed to emitter clogging of subsurface drip irrigation (SDI) systems in the Texas High Plains. During the 2002 growing season, areas of clogged emitters occurred in a 6-ha research field at the Texas AgriLife Research and Extension Center at Halfway, Texas. Water samples from the irrigation source were analyzed and SDI emitters in the affected areas were uncovered and examined in a laboratory setting. Evaluations indicated clogging was caused primarily by manganese oxides deposited inside SDI laterals and emitters. Observations of reactions of manganese compounds with combinations of acids and hydrogen peroxide ( $H_2O_2$ ) resulted in a protocol that dissolved these oxides in open laboratory containers. Further tests examined pressurized sections of excavated, clogged SDI laterals with  $H_2O_2$  / acid solutions for periods of up to 96 hours. This exercise led to the successful field treatment that cleared clogged emitters at the research site. Continued maintenance of the research system involved the injection of 2.5 ppm  $H_2O_2$  in slightly acidic irrigation water during normal irrigation. Issues with the use of these procedures include human safety, due to the caustic nature of the required materials, and high chemical cost.

Keywords. Subsurface drip irrigation, emitter clogging, manganese, Mn, hydrogen peroxide.

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### Introduction

Subsurface drip irrigation (SDI) can be the most efficient in-season irrigation application method in the Southern High Plains of Texas (Bordovsky and Porter, 2003, Colaizzi, et al., 2004) and its use is expected to expand as water supplies in the Ogallala aquifer decrease. However, associated with reduced pumping levels is the problem of decreased water quality.

More for SDI than any other delivery system, irrigation water quality is critical for long term performance due to the potential for emitter clogging. Drip emitter clogging results from physical, biological, and/or chemical factors. The physical threats to emitter clogging include suspended solids such as sand or plastic particles; biological threats from microbial slimes, algae, or root intrusion; and chemical threats associated with pH, iron, manganese, hydrogen sulfide, or dissolved solids. Critical levels of these constituents are reported in several publications (Rogers, et al., 2003, Burt and Styles, 2007, and Nakayama and Bucks, 1986).

In the summer of 2002, SDI emitter clogging caused severe drought stress to cotton plants in areas within a 6-ha research field at the Texas AgriLife Research Center, Helms Research Farm at Halfway, Texas. Irrigation zone flow rates were near the design rates in September 2001 and during initial pre-plant irrigation in 2002, however they soon declined. Further investigation and analysis of residue and water samples by the Soil, Water, and Forage Testing Laboratory (Texas A&M University, College Station, TX) led to the conclusion that the primary constituents causing the emitter clogging problem were manganese oxides. Figure 1 shows drip laterals and clogged emitters removed from the problem SDI field.

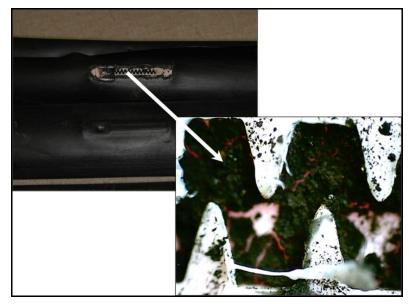


Figure 1. Clogged SDI emitters removed from research test plots at the Texas AgriLife Research Center, Halfway, 2002.

The critical dissolved manganese (Mn) levels in irrigation water that result in "minor", "moderate", and "severe" emitter clogging concerns are <0.1 ppm, 0.1-1.5 ppm, and > 1.5 ppm, respectively (Nakayama and Bucks, 1986). A 2002 water sample taken from the well supplying the emitter-clogged drip field had Mn levels of 0.15 ppm, which was just within the moderate level of risk for Mn clogging.

This water well had been treated for algae by chlorination in the recent past (Cotey Chemical Corp., Lubbock, Texas). The assumption was made that the problem was aggravated by the

use of drip oil required to lubricate the line shaft of the turbine pump. Due to the history of algae growth and the presence of carbonates in the irrigation water supply, the SDI system was flushed every 2-3 weeks during the growing season, and acidized and chlorinated prior to and following pre-plant irrigation and at the end of each growing season. Chlorinated water was left in the SDI system from the fall of 2001 to spring of 2002 as has been done with several drip systems at the research center since 1996. It is hypothesized that over time, and particularly over this winter, the chlorine used to treat biological residues also oxidized the available Mn in the water resulting in beginning of significant emitter clogging problems.

Information is available on methods to prevent Mn precipitation in water. These include the use of phosphate compounds (sequestering agents), ion exchange water softeners, oxidizing filters, aeration followed by filtration, and chemical oxidation followed by filtration. There are, however, few known sources of information on methods to recover a SDI system clogged with Mn and Mn compounds. The objective of this paper is to describe the laboratory and field process used to remove Mn compounds from a SDI system at the Helms Research Farm.

# Laboratory Evaluations

Field installation of the problem SDI system was in 2000 with 2001 being the first full year of crop irrigation. Drip laterals had emitter spacings of 0.51 m and emitter flow rates of 0.60 L h<sup>-1</sup> at 69 kPa (Typhoon 0.16 gph emitter, Netafim Irrigation, Inc, Fresno, CA). Lateral wall thickness was 0.3 mm. Seven zones were individually metered with flow rates and pressures recorded on a daily basis during the 2001 growing season. No variation from the design pressures and flows were noticed until June 2002. At that time drip laterals were uncovered and flow measurements from individual emitters were obtained with flows ranging from zero to the design rate. By July, areas of cotton plants were visibly water stressed. The locations of clogged emitters were primarily at the lower elevations of the 6-ha site. Sections of drip laterals were uncovered and removed from the field for laboratory evaluation.

#### Dissolving manganese oxides

A black powdery material was obtained from drip lateral walls, flush water (following water evaporation), and emitters of the affected zones. The material was a combination of manganese oxides and very fine mineral or sand particles. In an attempt to dissolve the Mn compound, it was mixed in open containers with various levels of different acids and then different concentrations of hydrogen peroxide ( $H_2O_2$ ). With the exception of prohibitively high acid concentrations the Mn was not dissolved.

Based on a method to extract manganese oxides from soil nodules using  $H_2O_2$  in a 3 pH solution (Taylor, et al.,1964), combinations of  $H_2O_2$  and acid solutions were mixed with the Mn material. Hydrogen peroxide rates ranged from 3%, as used by Taylor, et al. (1964), down to 0.0312%. These  $H_2O_2$  quantities were mixed with acid solutions ranging from 0 to 8 pH. A qualitative evaluation of the %Mn dissolved was periodically recorded for up to 48 hours.

The results were promising. Figure 2 shows two jars containing 0.02 g of the Mn compound in 0.5 L of irrigation water with  $H_2O_2$  at 0.125%. The pH of the container on the left was 7.6 while that of the container on the right was 6.5. Only residual sand particles were visible in the right container as the Mn had been dissolved. The time required to dissolve the material at room temperature was within seconds.



Figure 2. Two jars containing Mn at 0.04 g material/L of irrigation water, both at 0.125% H<sub>2</sub>O<sub>2</sub> concentration. The pH of the container on the left was 7.6; the pH of the container on the right was 6.5. The right jar had no visible Mn compound.

The quantity of Mn material dissolved in solutions having  $H_2O_2$  concentrations of 0 to 3% using muriatic acid or N-pHuric<sup>TM</sup> to change pH is shown in Figure 3. At pH 3, 90% of the Mn compound was dissolved at 0.0312%  $H_2O_2$  in six hours. The acid source did not change the outcome. Due to its relative safety, N-pHuric<sup>TM</sup> (Agrium, Calgary, Canada) which contain 49% equivalent sulfuric acid and 15% of water soluble organic nitrogen was used for the remaining evaluations.

Figure 4 displays the relative quantity of Mn material dissolved in solutions having acidity ranging from 0 to 7 pH, with and without  $H_2O_2$ . This, as well as previous figures, show relatively small levels of  $H_2O_2$  dissolved the troublesome compound, but only if the pH of the solution was below 7. Acid alone was not a reasonable means for opening clogged emitters with this type Mn materials.

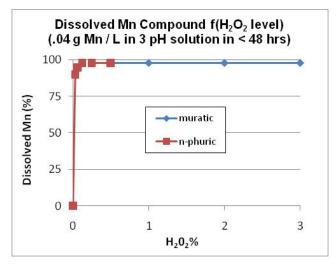


Figure 3. Percent of Mn material dissolved in solutions having H<sub>2</sub>O<sub>2</sub> concentrations of 0 to 3% using muriatic acid or N-pHuric to lower solution pH.

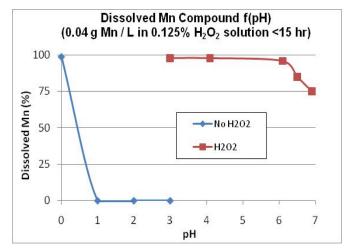


Figure 4. Percent of Mn material dissolved in solutions having pH that ranged from 0 to 7, both, with and without  $H_2O_2$  in the solution.

#### **Opening clogged emitters**

After successfully dissolving Mn with  $H_2O_2$  / acid solutions in open containers, these same solutions were used in attempts to open sections of SDI drip laterals with clogged emitters in the lab. Drip laterals having at least one clogged emitter were placed in pressure controlled test stands to determine the effect that combinations of  $H_2O_2$  levels, pH levels, and operating pressures had on opening emitters. All emitters were from the problem field, completely clogged (zero flow), and had undergone all field treatments (discussed below) through mid August. The tests involved closing one end of the lateral, filling the lateral with a solution, attaching a constant pressure source to the other lateral end, and monitoring pressure and emitter flow over time.

Under identical but separate treatments, two of three emitters returned to 100% design flow after 3.5 and 6 hours, respectively, when treated with 3% H<sub>2</sub>O<sub>2</sub> solution at pH 3 and pressured to 200 kPa (Figure 5). Sand particles as well as additional black Mn compounds were found in the third emitter after dissection following the test. Pressure effect on unclogging emitters is shown in Figure 6. Clogged emitters were treated with a 0.5% H<sub>2</sub>O<sub>2</sub> solution at pH 3 and pressurized to 83 then 200 kPa versus continuous 200 kPa. Immediately elevating the lateral pressure to 200 kPa (emitter P3) versus starting with 83 kPa then changing to 200 kPa (emitters P1 and P2) resulted in full emitter flow in 4.75 h instead of 23.5 and 33 h, respectively. Although SDI installations are typically designed for 140 kPa or less, pressure greater than standard operating pressures had major impact on the time required to open clogged emitters. The time required to open emitters was also affected by the pH and  $H_2O_2$  level of water forced through the emitters (Figure 7). Relative time for emitters to clear were 3.5, 20, and 78 h from solution treatments with 0.25% H<sub>2</sub>O<sub>2</sub> at pH 3, 0.25% H<sub>2</sub>O<sub>2</sub> at pH 4.7, and 0.5% H<sub>2</sub>O<sub>2</sub> at pH 4.7, respectively with pressure at 200 kPa. For these three emitters, elevated pH and reduced H<sub>2</sub>O<sub>2</sub> levels increased time for full flow. In all evaluations, once initial flow started, emitters typically cleared within a few hours.

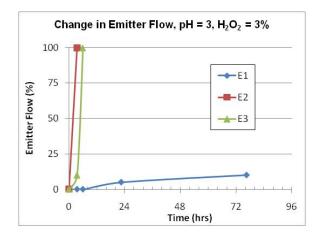


Figure 5. Relative emitter flow over time of three random clogged emitters treated with 3% H<sub>2</sub>O<sub>2</sub> solution at pH 3 and pressurized at 200 kPa. Following the test, sand particles were found in emitter 3.

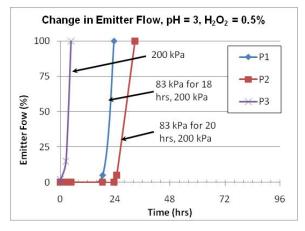


Figure 6. Relative emitter flow over time of three clogged emitters treated with a 0.5% H<sub>2</sub>O<sub>2</sub> solution at pH 3 and pressurized to 83 then 200 kPa versus continuous 200 kPa.

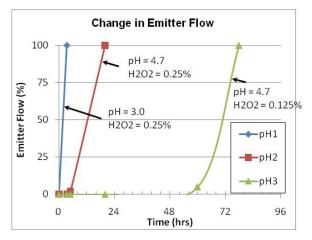


Figure 7. Relative emitter flow over time of clogged emitters treated with 0.25% H<sub>2</sub>O<sub>2</sub> at pH 3, 0.25% H<sub>2</sub>O<sub>2</sub> at pH 4.7, and 0.5% H<sub>2</sub>O<sub>2</sub> at pH 4.7 solutions with pressure at 200 kPa.

### **Field Treatments**

As noted earlier, flow rates of certain SDI zones in the 6-ha research field had begun to decrease by June 2002. Several field treatments were conducted in an attempt to reestablish zone flow rates and pressures prior to the laboratory tests just described. These procedures included chlorinating the irrigation well supplying water to the SDI system (3 times), flushing SDI laterals (5 times), the treatment of clogged zones with 3% H<sub>2</sub>O<sub>2</sub> without reducing the water pH (1 time), and the continuous chlorination of irrigation water as seasonal irrigations progressed. A list of significant treatment events and the resulting zone flow of one severely clogged zone (Zone 3) and a less severely clogged zone (Zone 6) from May until flow was reestablished in September, 2002 is given in Table 1 and Figure 8, respectively. Attempts to alleviate the problem by initial field treatments with H<sub>2</sub>O<sub>2</sub> and chlorination may have further increased emitter clogging.

Date	Chlorinate W ell	Start Seasonal Irrigation	Obtain Water Sample From Well	Acid & Chlorine Treatment of SDI Lines	Flush SDI Lines	Continuous Chlorine Injection @ Well	$H_2O_2$ Treatment	Filter Mesh Size	Continuous $H_2O_2 @ 6.8$ pH @ Well	Start Emitter Cleaning Process	Lab Evaluation of $H_2O_2$ at low pH
28-May	х							120			
10-Jun		х						120			
12-Jun			х	х				120			
8-Jul	х				х			120			
10-Jul							Zone 2 & 3	120			
12-Jul						х		120			
15-Jul					х	х		120			
25-Jul					х	х		120			
31-Jul	х					х		120			
2-Aug					х	х		120			
7-Aug						х	Zone 1,4, & 7	120			
8-Aug					х	х		120			
14-Aug						х		120			х
15-Aug						х		200			х
16-Aug					х	stop chlorine		200			х
23-Aug					х			200			х
23-Aug								200	х		х
27-Aug					х			200	х		
30-Aug			х					200	х		
2-Sep					х			120	х	Zone 1,4,5,6	
4-Sep					х			120	х	Zone 2, 3, 7	

Table 1. Chronology of events leading to the opening of SDI emitters clogged with manganese compounds at the Texas AgriLife Research Center, Halfway, TX, 2002.

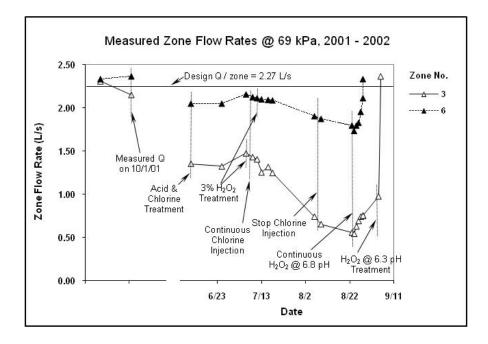


Figure 8. Flow rates and treatment events of a severely clogged zone (Zone 3) and a less severely clogged zone (Zone 6) from May until full emitter flow was reestablished in September, 2002.

#### Initial hydrogen peroxide and continuous chlorination treatments

One procedure recommended by a local SDI service company for treating Mn in SDI systems was to backfill a 3%  $H_2O_2$  solution into the flush valves of the drip system using sufficient volume to fill all drip tapes that might have clogged emitters. This procedure was completed in early July. The volume of the SDI drip laterals and manifold system were determined to be slightly less than 2000 L per zone. A solution of 3600 L of well water and 200 L of 50%  $H_2O_2$  were mixed in a 4000 L tank trailer and two zones were treated. This solution was pumped into flush valves at a rate of 120 L / m until reaching the filter station. The solution was left in the drip lines and flush and header lines for 18 h with the header line open to the atmosphere.

The 3% H<sub>2</sub>O<sub>2</sub> solution reacted with the Mn compound on the inside walls of the drip tubing and drip emitters. Violent bubbling appeared to suspend the black Mn particles, however the solution did not dissolve them.

Both zones were then flushed with filtered well water as pressure at the zone inlet was restricted to less than 7 kPa. The initial flush water was black from the Mn compounds released from the walls of the drip laterals. Flush water started to clear after 45 m, or after 3 to 4 exchanges in plumbing volume. The low pressure flushing continued for an additional 2 h until the water cleared. The flush valves were closed and the zones were pressured to 20 kPa for 16 h. The zones were again flushed with the water clearing after several minutes. The zone was then placed back into the scheduled irrigation cycle.

Several emitters from the affected area were uncovered and observed during and for several days following the treatment. Based on these observations as well as zone flow rates and pressures, the  $H_2O_2$  treatment had no immediate beneficial effect on the clogged emitters. The treatment, however, removed significant amounts of the Mn compound that would have continued to cause emitter clogging.

Chlorination (oxidation) and filtration is one method of removing manganese from water. Following the initial  $H_2O_2$  treatment (early July) until August 10, chlorine in the form of 12% sodium hypochlorite was continually injected during irrigations at the irrigation well. The well was 500 m from the filter station and was thought to provide sufficient time for chemical mixing and Mn precipitation prior to filtration. The filter was a Netafim USA, Disc Kleen Filter (PN 26ASK2A3-120, Fresno, CA) with 130 micron discs and then later, 200 micron discs. This procedure failed to improve the situation as zone flows continued to decline as more emitters were clogged (Figure 8). The apparent problem with this procedure was insufficient time for Mn precipitation and / or the inability to filter the fine Mn particles.

#### Unclogging emitters with hydrogen peroxide and acid

Cost of materials to clean emitters on a field scale was a major concern, therefore the initial  $H_2O_2/acid$  field treatment used very low levels of  $H_2O_2$  in 6.8 pH irrigation water. Hydrogen peroxide was injected at the well at 2.5 ppm downstream from acid introduction. This process continued for 7 days in the normal irrigation cycle with notable increases in flow of all zones. However numerous emitters in the highly clogged zones did not recover. Based on the lab experiments, a field emitter reclamation process was outlined and executed.

The general procedure used at the Texas AgriLife Research and Extension Center, Helms Research Site, Halfway, Texas to open SDI emitters clogged with manganese oxide compounds was:

- Several drip lateral sections with adjacent clogged emitters were uncovered in the zone to be treated. Water from the zone was drained and sections of drip lateral containing single clogged emitters were replaced with lateral sections having new emitters with the design flow rate. During the cleaning process, differences in flow rates of the adjacent new and clogged emitters were monitored to determine the effect of the process.
- 2) The pH of irrigation water was lowered at the well to 6.3 using N-pHuric<sup>™</sup>.
- 3) Drip laterals in the target zone were flushed with filtered water until clear.
- 4) With the flush valve open,  $H_2O_2$  was injected prior to filters at a rate resulting in a 0.1%  $H_2O_2$  solution with this rate maintained until it reached the flush valve. The flush valve was closed; the  $H_2O_2$  injection stopped; and the solution left in the drip laterals overnight (16 h).
- 5) Simultaneously, zone and flush valves were opened and chemical injection started resuming the 0.1% H<sub>2</sub>O<sub>2</sub> concentration in 6.5 pH irrigation water.
- 6) Flush water was allowed to clear before closing the flush valve and pressurizing the target zone to normal operating pressure (70 kPa). The zone flow rate was recorded.
- 7) Injection rates were readjusted to maintain pH and H<sub>2</sub>O<sub>2</sub> concentrations as zone pressures were increased to 138 kPa. As emitters began to open, zone flow increased and chemical concentrations adjusted to maintain desired levels. This process continued for 6 h in Zone 3, the zone most severely clogged. Terminating this part of the process was based on evidence of low levels of continuous emitter flow from uncovered emitters. Hydrogen peroxide bubbles "erupted" on the soil surface above emitters that were not fully clogged early in this process.
- 8) After this injection period, the H<sub>2</sub>O<sub>2</sub> concentration was reduced to 2.5 ppm at 6.8 pH with 138 kPa pressure for an additional 6 h. Pressure was then readjusted to normal levels and zone flow rates recorded. Throughout this process, uncovered emitters, zone flow rates and pressures were monitored to determine the effectiveness of the cleaning procedure.
- 9) After all zones were treated, the normal operational cycle for irrigation was resumed. In all zones, flow rates recovered to the original design level.

Figure 9 shows the effects of emitter clogging on cotton growth in 2002 and the result of the reclamation process at the same locations in 2003.



Figure 9. Effects of SDI emitter clogging on cotton production in 2002 (left) and cotton in 2003 at the same location following SDI system reclamation (right).

# Long Term Considerations

#### System maintenance and costs

Over 40 hectares are currently irrigated at the Texas AgriLife, Helms Research Site and are irrigated from two wells each having Mn levels greater than 0.1 ppm. To prevent emitter clogging maintenance treatments have been continually used during irrigation from 2003 to 2008. The treatment consisted of injecting N-pHuric<sup>TM</sup> using a pH controlled injection pump to 6.8 pH, then adding dilute  $H_2O_2$  (4.54 % solution) to achieve a final concentration 2.5 ppm. Manganese oxide buildup on system components has been monitored with site glasses at the filter stations, by observing zone flow rates, and by noting color variations in flush water.

The maintenance procedure was changed in 2005 in an attempt to reduce the cost of materials. Injections of chemical were modified from continual injection to injection every other 2-week period. At the end of a period without injection, brown and black deposits can be seen on the site glasses at filter stations. At this point, zone flows have not been affected. Reestablishing  $H_2O_2$  / acid injections at the maintenance rates have removed these deposits within 2 weeks. There has been no evidence of emitter clogging since 2002.

The cost of maintenance treatments from 2003 to 2006 is given in Figure 10.

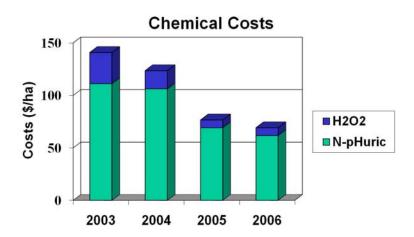


Figure 10. Hydrogen peroxide and acid costs for maintenance of SDI systems at the Texas AgriLife Research Center, Helms Research Farm, 2003-2006.

#### Mn build up in the soil

Dissolved Mn was kept in solution using  $H_2O_2$  in 6.8 pH irrigation water. In September of 2003, an array of soil samples were taken around drip laterals at four locations within the problem research field to quantify any increase of Mn in the soil. High Mn concentrations can be toxic to cotton plants.

Manganese found in these soil samples ranged from <1 ppm to slightly greater than 5 ppm. Figure 11 shows soil sample locations and average residual Mn concentrations around drip laterals in treatments irrigated at approximately 80% crop evapotranspiration. Although Mn concentrations have appeared to follow SDI wetting patterns, the quantities of this element are well below toxic levels for cotton plants. Mn concentrations in the root zone have continued to be monitored with no significant increases since 2003.

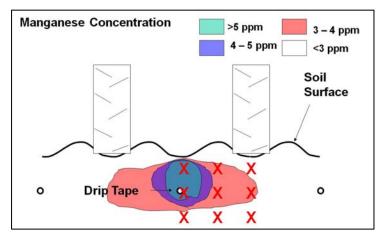


Figure 11. Soil sample locations and average residual manganese concentrations around SDI laterals, Helms Farm, Halfway, TX, 2003.

# **Summary and Conclusions**

Dissolved manganese in irrigation water has contributed to emitter clogging of subsurface drip irrigation (SDI) systems in the Texas High Plains. Laboratory observations of reactions of manganese compounds from clogged SDI zones with acids and  $H_2O_2$  resulted in a protocol that dissolved these oxides in open containers. Further tests involved pressurizing sections of clogged SDI laterals with  $H_2O_2$  / acid solutions for periods of up to 96 hours. This led to successful field treatments that cleared clogged emitters at the research site. Maintenance of the SDI system included the continuous injection of 2.5 ppm  $H_2O_2$  in slightly acidic irrigation water during normal irrigations.

Issues with the use of these procedures include human safety, due to the caustic nature of the chemicals, and high chemical cost. Also elevating drip lateral pressures above manufacturer's recommendations can void warranties and possibly damage the drip system.

Alternative maintenance methods are being considered due to safety and cost issues.

#### Acknowledgements

The authors would like to acknowledge project funding by the Texas State Support Committee of Cotton Incorporated and the USDA-ARS Ogallala Aquifer Initiative.

This paper is also part of a year-long SDI technology transfer effort in 2009 involving Kansas State University, Texas A&M University and the USDA-ARS and is funded by the Ogallala Aquifer Project. To follow other activities of this educational effort, point your web browser to http://www.ksre.ksu.edu/sdi/. Watch for this logo.



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