GW - 4

WORK PLANS

GW004

SECOR

client focused
consulting management

DISTAL ARRAY INJECTION WORK PLAN FOR THE EUNICE NORTH GAS PLANT

Chevron Environmental Management Company

February 9, 2006

COMMERCIAL REAL ESTA
INFORMATION TECHNOLO
TATE PUBLIC ENERGY
NATURAL RESOURCE MANA
COMMERCIAL REAL EST
REGULATORY COMPLIANCE

GW004

District I
1625 N. French Dr., Hobbs, NM 88240
District II
1301 W. Grand Avenue, Artesia, NM 88210
District III
1000 Rio Brazos Road, Aztec, NM 87410
District IV
1220 S. St. Francis Dr., Santa Fe, NM 87505

State of New Mexico
Energy Minerals and Natural Resources

Oil Conservation Division
1220 South St. Francis Dr.
Santa Fe, NM 87505

Revised June 10, 2003

Submit Original
Plus 1 Copy
to Santa Fe
1 Copy to Appropriate
District Office

DISCHARGE PLAN APPLICATION FOR SERVICE COMPANIES,GAS PLANTS, REFINERIES, COMPRESSOR, GEOTHERMAL FACILITES AND CRUDE OIL PUMP STATIONS

(Refer to the OCD Guidelines for assistance in completing the application)

☐ New ☒ Renewal ☐ Modification

1. Type: Eunice North Gas Plant (GW-004)

2. Operator: Chevron U.S.A. Inc.

Address: 11111 South Wilcrest, Houston, TX 77099

Contact Person: Scott Toner Phone: (281) 561-3653

3. Location: NE /4 SE /4 Section 28 Township 21-S Range 37-E
Submit large scale topographic map showing exact location.

4. Attach the name, telephone number and address of the landowner of the facility site.

5. Attach the description of the facility with a diagram indicating location of fences, pits, dikes and tanks on the facility.

6. Attach a description of all materials stored or used at the facility.

7. Attach a description of present sources of effluent and waste solids. Average quality and daily volume of waste water must be included.

8. Attach a description of current liquid and solid waste collection/treatment/disposal procedures.

9. Attach a description of proposed modifications to existing collection/treatment/disposal systems.

10. Attach a routine inspection and maintenance plan to ensure permit compliance.

11. Attach a contingency plan for reporting and clean-up of spills or releases.

12. Attach geological/hydrological information for the facility. Depth to and quality of ground water must be included.

13. Attach a facility closure plan, and other information as is necessary to demonstrate compliance with any other OCD rules, regulations and/or orders.

14. CERTIFICATION I hereby certify that the information submitted with this application is true and correct to the best of my knowledge and belief.

Name: Keith Hall Title: Facilities Engineering Manager

Signature: Keith Hall Date: November 8, 2005

E-mail Address: Keith.Hall@ChevronTexaco.com

GW 004

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FEB 10 2006

Oil Conservation Division
Environmental Bureau

2321 Club Meridian Drive, Suite E
Okemos, MI 48864
517-349-9499 TEL
517-349-6863 FAX

February 9, ~~2005~~ 2006

Mr. Glenn von Gonten
New Mexico Oil Conservation Division
1220 South St. Francis Dr.
Santa Fe, NM 87505

RE: Permit Renewal for the Eunice North Gas Plant (GW-004), Lea County, New Mexico

Dear Mr. von Gonten:

SECOR International Incorporated (SECOR) is pleased to provide the enclosed *Distal Array Injection Work Plan for the Eunice North Gas Plant* to comply with the requirements in the Discharge Plan Application to renew the discharge permit for the Eunice North Gas Plant (GW-004) in Lea County, New Mexico.

A preliminary Discharge Plan Application, topographic map, and $100.00 filing fee were submitted on November 11, 2005. The work plan attachment and Discharge Plan Application are being submitted within 90 days of the original filing date for your review. Specific details of the following application line items are described in the attached work plan and cross-referenced below:

1. *See Permit Application.*
2. *See Permit Application.*
3. *See Permit Application*
4. Attach the name, telephone number and address of the landowner of the facility site.
   Section 1.0 second paragraph
5. Attach the description of the facility with a diagram indicating location of fences, pits, dikes and tanks on the facility.
   Section 1.0 third and fourth paragraphs and Figure 4
6. Attach a description of all materials stored or used at the facility.
   Section 3.1
7. Attach a description of present sources of effluent and waste solids. Average quality and daily volume of waste water must be included.
   Section 1.1-chromium plume present, no further discharge.
8. Attach a description of current liquid and solid waste collection/treatment/disposal procedures.
   Sections 3.2, 3.3, and 3.4

GW004

9. Attach a description of proposed modifications to existing collection/treatment/disposal systems.
   Section 1.1 and Appendix A

10. Attach a routine inspection and maintenance plan to ensure permit compliance.
    Section 2.0 and Section 3.4

11. Attach a contingency plan for reporting and clean-up of spills or releases.
    Section 3.5

12. Attach geological/hydrological information for the facility. Depth to and quality of ground water must be included.
    Section 1.2

13. Attach a facility closure plan, and other information as is necessary to demonstrate compliance with any other OCD rules, regulations and/or orders.
    Section 4.0

Should you have any questions regarding the enclosed application, please contact me at (517) 349-9499 extension 275.

Respectfully,

SECOR International Incorporated

Marisa Patterson

Marisa Patterson, E.I.T.
Associate Engineer

Attachments:

Discharge Plan Application
Distal Array Injection Work Plan for the Eunice North Gas Plant

Cc:
Wayne Price, NMOCD
Scott Toner, CEMC
Russ Weigand, SECOR

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Oil Conservation Division
Environmental Bureau

FINAL

DISTAL ARRAY INJECTION WORK PLAN FOR THE EUNICE NORTH GAS PLANT

Chevron Environmental Management Company

February 9, 2006
89CH.49410.92

Prepared by:

Matt Carlson, P.E.
Associate Engineer

Submitted by:

Jeremy Rasmussen, P.E.
Senior Engineer

Reviewed by:

Craig Skiera, P.E.
Principal Engineer

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1.0 INTRODUCTION

On behalf of Chevron Environmental Management Company (EMC), SECOR International Incorporated (SECOR) has prepared this Distal Array Injection Work Plan for the Eunice North Gas Plant. The site is located approximately 0.25 miles north of the town of Eunice, in the south half (S/2) of the southeast quarter (SE/4) of the northeast quarter (NE/4) of Section 28, Township 21 South (T-21-S), Range 37 East (R-37-E), Lea County, New Mexico. The gas plant is bordered by State Highway 207 along the eastern boundary (Figure 1).

The natural gas processing plant was originally constructed in the 1940s. It was owned and operated by Texaco from the 1940s through the late 1990s. During the late 1990s ownership was transferred to Versado LLP, which is currently a partnership between Chevron (former Texaco) and Dynegy Midstream Services (former Warren Petroleum). Dynegy Midstream Services (Dynegy) operates the Plant for Versado and is listed at State Highway 207 (Eunice-Hobbs Highway), Eunice, New Mexico, 88231. The gas plant operator, Lewis Tarin, can be reached at (505) 394-3452.

The site is no longer operated as a gas plant. It has been partially dismantled with much of the equipment shut-in, and is currently operated by Dynegy as a natural gas compressor station under an agreement with Chevron (Figure 4).

The gas plant was constructed and modified to operate as a turbo expander type natural gas processing plant for extraction of NGLC natural gas liquids. There are several buildings, structures, and tanks across the site, including sumps, the compressor building, and the cooling tower. The gas plant was shut down and is currently partially dismantled and out of operation, with the exception of some compression equipment.

1.1 Background

As a result of historical operations at the site, a chromium groundwater plume is present on and off-site. Since 2004, in-situ treatment of the hexavalent chromium has been on-going at the distal end of the plume and within the study area at the plant (Figure 2). The treatment reagent has been molasses, where reducing conditions resulting from the biological consumption of the molasses result in the reduction of chromium from the hexavalent state to the trivalent state.

A bench-scale treatability study was performed in 2005 by SECOR to optimize the in-situ treatment reagent. The November 2005 study entitled *Reductive Treatment Bench-Scale Testing Evaluation for Chevron Environmental Management Company Eunice North Gas Plant Eunice, New Mexico (Appendix A)* evaluated two biological reducing agents (molasses, sodium acetate) and two chemical reducing agents (sodium metabisulfite, calcium polysulfide). The results of the study indicate that calcium polysulfide treatment provided the optimum reduction of hexavalent chromium to trivalent chromium, and subsequent precipitation of the trivalent chromium from solution.

1.2 Geologic Setting

The regional geology and hydrogeology is referenced from the *Groundwater Investigation and Remediation Activities Report 2004*. Monument Draw is the only major surface drainage feature in southern Lea County, and runs north to south slightly over two miles east of the site. The overall topography in the area of the site slopes gently to Monument Draw at an approximate dip of 35 feet per mile. Small closed basins or playas exist on this sloping surface.

The geologic formations of interest at the site include the Triassic Chinle, Cretaceous undifferentiated, Tertiary Ogallala and Quaternary eolian sedimentation, designated the Blackwater Draw. Of particular interest with regard to the impact of hexavalent chromium released to groundwater are the Tertiary Ogallala and Quaternary Blackwater Draw.

The lower Tertiary Ogallala formation is composed of fluvial sediments of the Miocene-Pliocene epochs. It is a heterogeneous combination of clay, silt, sand, and gravel of braided-stream deposits interbedded with, and overlain by, eolian sediments deposited as sand sheets and loess resting directly upon an erosional surface carved into the Triassic Chinle Formation under the site. The fluvial sediments were deposited on a sloping plain in the form of coalescing alluvial fans, by streams that originated in the Rocky Mountains to the west and northwest. The Ogallala Formation was deposited in laterally restricted lenses of material, predominantly medium to yellowish-gray conglomeratic sandstone and fine to medium-grained well-sorted sandstone. The primary fresh water-bearing formation under and in the vicinity of the site is the Ogallala.

In contrast to the fluvial deposition of the lower Ogallala sediments, the upper part of the Ogallala and all of the Blackwater Draw Formation overlying the Ogallala are composed of windblown (eolian) deposits. The very fine sand facies of the upper Ogallala are thick, ranging up to 125 feet and capped by the Caprock caliche or calcrete, marking the top of the Ogallala.

The Blackwater Draw Formation occurs as a mantle of Quaternary eolian sediment locally as thick as 100 feet, covering an area of the South High Plains of northeastern Texas and eastern New Mexico. Throughout the depositional time of the Blackwater Draw Formation, laterally restricted lenticular layers of eolian and playa or lacustrine facies were formed. The Blackwater Draw Formation occurs near the ground surface at the site and contains reddish sediments composed of up to six well-developed buried soils with similar lithology and morphology. The soil development occurred during periods of landscape stability, separated by intermittent periods of deposition or by deflation that stripped surface horizons from newly developed soils.

The primary source of freshwater at the site is the Ogallala Formation, which is hydraulically unconfined in the area of the site. It is bounded on the base of the aquifer by an eroded surface of a firm red silty clay of the Chinle Formation. The base of the Ogallala is composed of a 5 to 10-foot interval of gravel/sand/clay, which is termed the "deep" water-bearing zone. The gravel unit is overlain by a red to yellow sand that exhibits vertical heterogeneity with alternating layers of loose and well-consolidated sand. This overlying unit constitutes the "shallow" water-bearing zone. Wells screened in the gravel unit have 40 to 50 feet of hydraulic head. Wells screened in the shallow water-bearing zone have screens that intersect the groundwater table and typically have 10 to 45 feet of saturation. Overall depth to groundwater varies with local topography and ranges from 37 to 73 feet below the surface.

Regionally, the groundwater gradient was to the southeast in the area of the site. However, a water table high now exists south of the plant, due to lawn watering within the City of Eunice, creating a hydraulic gradient that has southwest, west, northwest, north, and northeast trends. The elevations of the groundwater in the shallow and deep zones are similar, indicating there is hydraulic continuity between the zones.

1.3 Purpose

This work plan is intended to provide detailed information on the specifications and procedures to be followed to address remediation of chromium-impacted groundwater that has migrated outside the plant boundaries and toward Monument Draw.

An injection array has been installed at the distal end of the chromium-impacted groundwater plume, approximately 2,800 feet east-northeast of the plant (Figure 3). Selected injection and monitoring wells, injection and sampling frequency, analytes and analytical methods, quality control (QC) procedures, groundwater injection and sampling procedures, and reporting requirements are described in the subsequent sections.

In-situ treatment using calcium polysulfide will be initiated at the distal array injection well network. The results of the injection activities described in this work plan will be used to develop a work plan for the study area injection wells and the newly installed medial array injection wells.

2.0 GROUNDWATER SAMPLING PLAN

Prior to the chemical injection event, described in Section 3.0, baseline groundwater elevations will be measured in nine monitoring wells located at each end of the distal array, two monitoring wells downgradient of the array, and the fourteen injection wells. Groundwater samples will also be collected at these 11 monitoring wells and 14 injections wells prior to the chemical injection event.

The well list, along with coordinates and top of casing (TOC) information, is included in Table 1. Well locations are detailed on Figure 3. Site-wide semi-annual groundwater monitoring is conducted separately and independently of the chemical injection activities. Groundwater sampling activities and field data collection will follow the procedures outlined in the low-flow sampling section of the *Sampling and Analysis Plan for the Eunice North Gas Plant* dated January 6, 2006. Sampling will be conducted in the order specified on the Groundwater Field Log (Appendix B), and sampling information will be recorded on Groundwater Sampling Field Data Sheets (Appendix C).

To ensure safe completion of sampling activities, the site-specific Health and Safety Plan (HASP) will be updated and task-specific job safety analyses (JSAs) will be created or updated, as necessary, prior to commencing fieldwork. SECOR will perform dry-runs on each activity (gauging, sampling, etc.) to ensure any gaps in the JSAs are filled. Two SECOR personnel will be on-site during sampling and associated activities. Daily health and safety briefings will be conducted at the start of each day and after lunch, to detail upcoming hazards and lessons learned from the previous day's events. Applicable JSAs will be reviewed daily at the two tailgate meetings, and whenever field personnel change tasks.

3.0 CHEMICAL INJECTION FIELD ACTIVITIES

Fourteen injection wells are situated at the distal end of the chromate plume in a north-south orientation, perpendicular to the groundwater flow direction. In-situ injection of calcium polysulfide to reduce hexavalent chromium to trivalent chromium will be conducted on a monthly basis following procedures outlined below.

3.1 Chemical Storage and Delivery

Containers of 29% (10.6 lbs/gallon) BSP Cascade calcium polysulfide will be delivered and stored on-site in 55-gallon drums. The chemical storage area (shown in Figure 2) will be set up in a secondarily-contained bermed area within a locked fenced enclosure. Figure 5 illustrates the details of the proposed chemical storage area. This secondarily-contained area will be constructed prior to the first chemical injection event.

3.2 Injection Chemical Preparation

Chemical injection activities will be conducted using the mobile chemical injection trailer mounted with the following equipment:

- Mixing Pump (electric)
- Injection Pump (electric)
- Chemical Pump (electric)
- 1000-gallon Solution Tank

Injection chemical solution preparation will be conducted in a batch process. Approximately 900 gallons of make-up water will be obtained from the on-site water supply source and stored in the solution tank. Fifty-five gallons of calcium polysulfide will then be pumped from storage drums into the solution tank to prepare a 2% (20,000 mg/l) solution. Calcium polysulfide transfer will be conducted using the chemical pump mounted on the trailer. Following transfer of the calcium polysulfide, a minimum of 20 gallons of water will be pumped through the chemical transfer pump to flush out any residual chemical. This will protect the pump from deterioration caused by the caustic nature of the calcium polysulfide.

Using the mixing pump, the solution will be agitated for approximately five minutes to ensure a uniform solution is generated. All chemical solution preparation will be conducted within the chemical storage area. Figure 2 shows the locations of the chemical storage area, cargo storage box, and other site characteristics. Electric power for the pumps will be supplied by a generator mounted in the back of the site work vehicle or from power available on-site, as applicable.

Calcium polysulfide is caustic, and care should be taken in transferring the raw chemical to the solution tank. Personnel should wear goggles, chemically resistant gloves, and a chemical apron during this activity. An MSDS for calcium polysulfide is included in Appendix D.

3.3 Chemical Injection

Batch injection of the prepared calcium polysulfide solution will be completed using the injection pump mounted on the mobile chemical injection trailer. Injection will begin at IW014, proceed south, and be completed at IW016.

Approximately 950 gallons of solution will be pumped into each injection well at a maximum of 15 gallons per minute (gpm) or a maximum of 5 to 7 pounds per square inch (psi). This pumping rate and pressure will ensure the well is not short-circuited. Higher pumping rates may cause solution to follow a preferential flow path along the well casing and come to the surface. Minor adjustments to the flow rate may need to be conducted at each injection well to eliminate short-circuiting.

The trailer is equipped with a 2-inch hose that can be connected to each wellhead assembly with a cam-lock type fitting. Wellheads are equipped with pressure gauges to monitor pressure. Tank level gradations are used to measure flow. After complete injection of the calcium polysulfide solution at the injection well, activities will proceed to the next well, following batch solution preparation as described in Section 3.1.

Following solution injection at all 14 injection wells, the solution tank will be filled with 950 gallons of water from the on-site water supply source. Approximately 320 gallons of water will be injected into each injection well to chase the chemical solution and drive it further into the geologic formation. Injection wells will be completed with this chase water in sets of three, before refilling the solution tank with an additional 950 gallons of water.

3.4 Schedule

Initially, sampling of the 11 monitoring and 14 injection wells will be completed prior to commencement of injection activities, as discussed in Section 2.0, during the semi-annual groundwater sampling event. Monthly injection of the chemical solution and chase water at the 14 injection wells will be completed following this semi-annual sampling event being implemented in January and February 2006.

The subsequent months, field parameters from the 11 monitoring wells and 14 injection wells, and laboratory samples from the 11 monitoring wells will be collected prior to monthly injection of chemical solution and chase water.

Negative oxidation-reduction potential (ORP) values and pH values of greater than 9.0 are to be maintained at the 11 adjacent monitoring wells for conditions to be conducive to treatment. Because the in-situ treatment chemical is being switched from molasses to calcium polysulfide, SECOR anticipates monthly injections will be required for a short time period, three to four months, to allow adequate subsurface chemical solution contact and reaction time. After this time period, the monthly injection time-frame will be re-evaluated based on the chemistry at the nearby 11 monitoring wells, and likely adjusted to bi-monthly or quarterly.

3.5 Spill Contingency

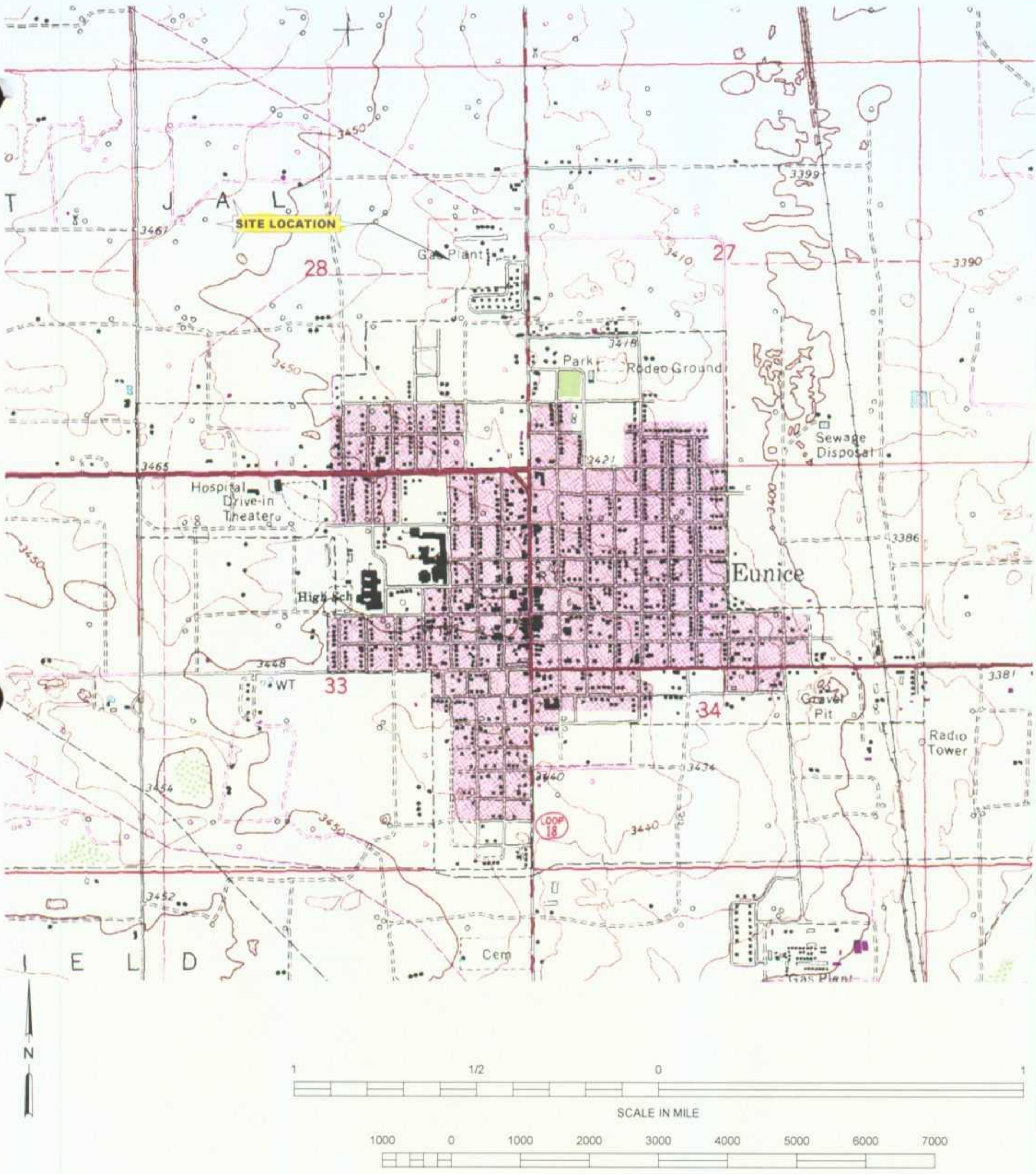
Should a spill or leak occur within the secondarily-contained bermed chemical storage area, it will be pumped out and returned to a new 55-gallon drum for re-use. Any material in leaking drums will be pumped into a new drum and the damaged drum removed from the site.

Transfer from the 55-gallon drums to the trailer-mounted solution tank will be conducted within the secondarily-contained bermed area. Any spill or leak of the non-diluted or diluted calcium polysulfide solution outside of the bermed area will be remediated, per the MSDS and the product label, to protect human health and minimize any effects to the environment. Sand, or other appropriate absorbent material, shall be used to contain a spill. At no time shall acidic substances be used to remedy a spill. Absorbent material that comes in contact with any spilled calcium polysulfide will be containerized for proper disposal. Following removal of the absorbent material, chase water will be applied to the ground surface to further dilute the spilled solution and expedite its infiltration into the geologic formation. Any spill volume that poses immediate danger to human health or the environment or that is greater than or equal to 55 gallons shall be reported, within 24 hours, to the New Mexico Environment Department (emergencies: 505-827-9329, non-emergencies: 866-428-6535).

Further reference should be made to the MSDS and the product label prior to commencing any handling or transport of the calcium polysulfide.

4.0 COMPLIANCE

As stated in Section 3.4, SECOR anticipates after a short time period, three or four months, the monthly injection time-frame will be re-evaluated based on the chemistry at the nearby 11 monitoring wells, and likely adjusted to bi-monthly or quarterly. Injection will continue at the re-evaluated time-frame until the results of the monitoring program demonstrate the chromium New Mexico Water Quality Control Commission (WQCC) Human Health standard of 0.05 mg/l is met in the 11 monitoring wells associated with the distal array injection. At this time, New Mexico Oil Conservation Division (NMOCD) will be petitioned to allow discontinuance of the injection system.



REFERENCE: USGS 7.5 MINUTE QUADRANGLE; EUNICE AND
RATTLESNAKE CANYON, NEW MEXICO

SECOR
2321 Club Meridian Drive, Suite E
Okemos, Michigan
PHONE: (517) 349-9499 FAX: (517) 349-6863

FOR:

CHEVRON
EUNICE NORTH GAS PLANT

EUNICE, NEW MEXICO

SITE LOCATION MAP

FIGURE: 1

JOB NUMBER:	DRAWN BY:	CHECKED BY:	APPROVED BY:	DATE:
89CH.49410.01	ERM	RDT	RDT	10/21/05

Eunice No e Location Map.dwg

LEGEND

● IW001	Injection Well Location
● MW065SA	Monitoring Well Location

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FOR: Chevron
EUNICE NORTH GAS PLANT
EUNICE, NEW MEXICO

INJECTION WELL LOCATIONS

FIGURE: 2

JOB NUMBER: 89CH.49389.01
DRAWN BY:
CHECKED BY:
APPROVED BY:
DATE: 11/11/2005

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FOR: Chevron
EUNICE NORTH GAS PLANT
EUNICE, NEW MEXICO

DISTAL ARRAY
CHEMICAL INJECTION WELL
AND MONITORING WELL LOCATIONS

FIGURE: 3

JOB NUMBER: 89CH.49389.01
DRAWN BY: ERM
CHECKED BY: MC
APPROVED BY: JMR
DATE: 11/11/2005

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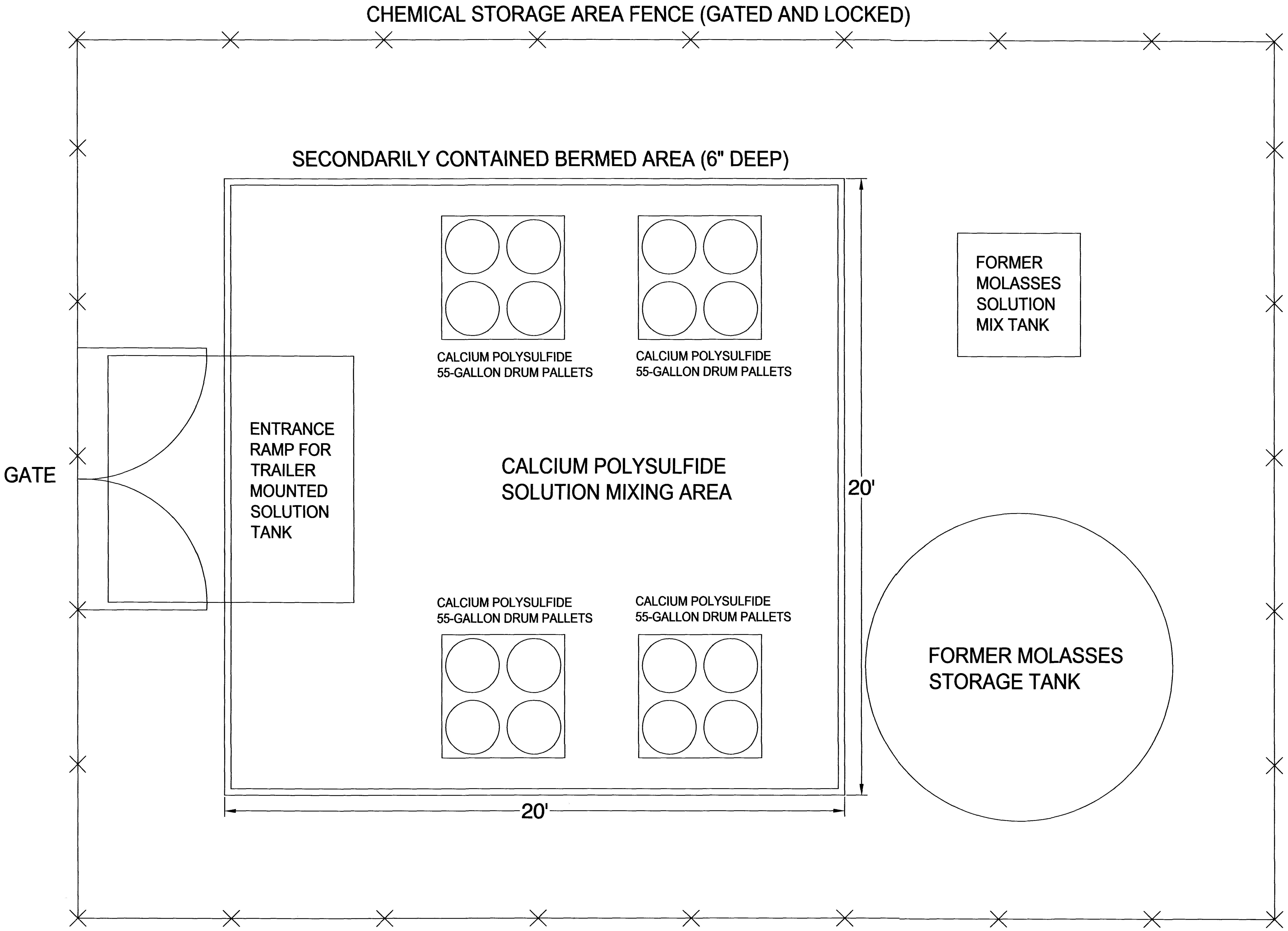
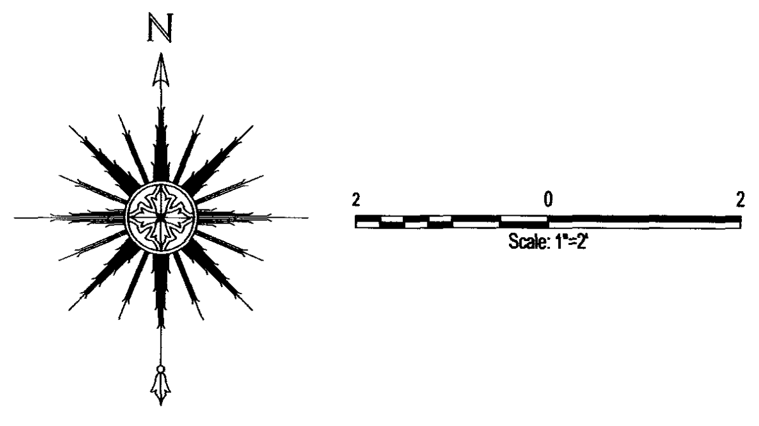
FOR: Chevron
EUNICE NORTH GAS PLANT
EUNICE, NEW MEXICO

NORTH EUNICE GAS PLANT LAYOUT

FIGURE: 4

JOB NUMBER: 89CH.49389.01
DRAWN BY: ERM
CHECKED BY:
APPROVED BY:
DATE: 1/27/2006





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FOR: Chevron
EUNICE NORTH GAS PLANT
EUNICE, NEW MEXICO

PROPOSED CHEMICAL
STORAGE AREA DETAILS

FIGURE: 5

JOB NUMBER: 89CH.49389.01
DRAWN BY: ERM
CHECKED BY:
APPROVED BY:
DATE: 1/27/2006

Table 1: Well Details
Eunice North Gas Plant

Well ID	Surveyed Measuring Point Elevation (ft AMSL)	Surveyed Ground Elevation (ft AMSL)	Screened Interval (ft)	Completed Well Depth (ft)
MW064SA	3405.15	3403.03	35-75	75.50
MW065SA	3402.96	3401.00	40-80	80.46
MW066SA	3404.03	3401.57	41-66	66.39
MW067SA	3409.16	3406.75	43-83	81.90
MW079SA	3408.80	3406.25	37-67	67
MW080SA	3408.92	3406.33	39-69	69
MW081SA	3408.28	3405.71	40-70	70
MW082SA	3406.25	3403.68	45-75	75
MW083SA	3406.11	3403.51	45-75	75
MW084SA	3405.98	3403.36	45-75	75
MW085SA	3406.98	3403.36	45-75	75
IW003	3406.68	3404.68	35-55	55.00
IW004	3406.31	3404.14	35-50	50.00
IW005	3405.36	3403.53	36-46	46.00
IW006	3404.36	3402.39	35-50	50.00
IW007	3405.31	3403.46	36-46	46.00
IW008	3405.37	3403.30	35-50	50.00
IW009	3406.07	3404.04	35-45	45.00
IW010	3405.82	3404.28	33-58	58.00
IW011	3406.83	3404.75	43-63	63.00
IW012	3405.92	3404.11	43-53	53.00
IW013	3406.62	3404.39	45-60	60.00
IW014	3405.48	3403.67	33-73	73.00
IW015	3406.05	3404.05	34-49	49.00
IW016	3408.29	3406.20	29-69	69.00

APPENDIX A
REDUCTIVE TREATMENT BENCH-SCALE TESTING EVALUATION

Distal Array Injection Work Plan
for the Eunice North Gas Plant

Chevron Environmental Management Company
89CH.49410.92
February 9, 2006

FINAL

REDUCTIVE TREATMENT BENCH-SCALE TESTING EVALUATION FOR

CHEVRON ENVIRONMENTAL MANAGEMENT COMPANY

Eunice North Gas Plant -
Eunice, New Mexico

January 23, 2006
89CH.49410.06

Prepared by:

Tony Zapp/Daniel Oberle, P.E.
SECOR Treatability Testing Laboratory
4035 King Road, Suite D
Sylvania, OH 43560

Reviewed by:

Jeremy Rasmussen, P.E.
Senior Engineer

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EXECUTIVE SUMMARY

Three different treatment reagents were tested at the bench-scale level to determine if the reagents could provide similar or better treatment results for hexavalent chromium when compared to the current molasses treatment. The results of the study showed sodium acetate, sodium metabisulfite, and calcium polysulfide were all effective reagents for chromium reduction. Sodium metabisulfite and calcium polysulfide are inorganic reducing reagents that directly treat the hexavalent chromium by chemical reduction. Sodium acetate is an electron donor that stimulates subsurface biological activity which leads to the reduction of chromium.

Although all of the reagents tested showed promise as reducing agents for chromium, the treatment of hexavalent chromium *in-situ* is a two-step process and both steps must be successful for effective treatment. In the first step of treatment, the chromium is reduced from the hexavalent state to the trivalent state. In the second step, the trivalent chromium must precipitate from solution so the amount of chromium remaining in the groundwater is below MCLs.

Each of the reagents was tested to determine how they performed in the second step of the chromium treatment process. The results showed that the calcium polysulfide provided the fastest reduction kinetics and best consistent removal efficiency for chromium from groundwater (> 98% removal). Sodium metabisulfite and sodium acetate also provided good removal efficiencies for chromium (91.4 to > 98%) but higher dosages of treatment chemical were required. The samples treated with molasses were the only samples that did not achieve MCLs during the testing. Although molasses was able to quickly reduce the chromium to its trivalent state, the fermentation of the molasses significantly lowered the pH and prevented the chromium from precipitating out of solution. The total removal efficiency of total dissolved chromium by the molasses treatment was only 20 percent.

The results of this study suggest that molasses treatment will lower the pH of groundwater during treatment and that chelating effects could suspend metals in solution. Site data collected by Arcadis shows groundwater pH values as low as 4.37 and dissolved calcium concentrations in excess of 3,000 mg/L. These are consistent with the results of bench-scale testing. Based on these findings, it is recommended that the treatment chemical for in-situ chromium treatment be changed from molasses to calcium polysulfide.

1.0 INTRODUCTION

The Chevron Eunice #2 North Plant (the site) is a former natural gas processing plant that operated just north of Eunice, New Mexico. Chromate biocides were used in the plant's cooling tower operations when the plant was in operation. Hexavalent chromium impacts have been detected in the groundwater beneath the facility at concentrations exceeding 1,000 ug/L. A plume of hexavalent chromium exceeding 100 ug/L extends approximately 4,000 feet down-gradient of the original source area.

A pilot remedial program was conducted in 2004 and 2005 by Arcadis at the distal end of the chromate plume to evaluate molasses treatment for the reduction and precipitation of chromium. The program included 14 pilot injection wells screened into the deep zone. Once per month, each injection well is injected with between 400 to 800 gallons of 30 percent molasses solution followed by a chase solution of 250 gallons of city water.

In September 2005, Arcadis installed a row of medial array wells within the central portion of the plume along route NM-18, with SECOR providing oversight. Groundwater at this location is approximately 42 feet below grade. Samples of soil were collected from depth intervals of 42 feet, 60 feet and 90 feet below grade during installation of well IW-022. Water samples were collected from the well after it was completed.

The soil and groundwater samples were shipped to SECOR's treatability testing laboratory in Sylvania, Ohio on September 30, 2005 for *in-situ* chemical reduction bench-scale testing. The bench-scale testing compared the effectiveness of molasses treatment with other reduction technologies for hexavalent chromium treatment. The treatment reagents evaluated as part of the study included calcium polysulfide, sodium acetate, and sodium metabisulfite. Bench scale testing with the soil and groundwater samples began on October 3, 2005.

2.0 TREATABILITY STUDY APPROACH

2.1 Test Objectives and Rationale

The objectives of the treatability testing were to:

- Determine if the addition of non-carbohydrate organics to the groundwater would induce *in-situ* reductive treatment of chromium;
- Determine if sodium metabisulfite could be utilized to reduce and precipitate hexavalent chromium *in-situ* and how pH affects the kinetics of the reaction;
- Determine if calcium polysulfide could be utilized for *in-situ* reduction of hexavalent chromium in a soil/water system without interference from reactions with the soil; and
- Compare the effectiveness of each treatment reagent to the current reagent (molasses) and a comparative group to determine which reductive treatment(s) will be most effective for on-going site operations.

2.2 Experimental Design and Procedures

The procedures used for testing are summarized in the sections below.

2.2.1 Testing for Biological Activity

When the site groundwater samples arrived at the laboratory, a sample was immediately tested and found to contain approximately 0.3 mg/L hexavalent chromium. This value is below the value that is typically toxic to bacteria, thus indicating that biologically-driven reducing reactions were a feasible treatment technology for the site. For confirmation, testing was performed on the water sample to identify and quantify baseline populations of indigenous heterotrophic aerobic and anaerobic bacteria.

This testing was performed using a BART^{TM} biological activity reaction test kit manufactured by Droycon Bioconcepts, Inc. Fifteen milliliters of site groundwater were added to the test kit chamber and the chamber was inverted for 30 seconds to dissolve a culture medium into the groundwater. The reaction chamber was then placed upright, out of the sunlight, for a five-day incubation period.

During this period, bacteria present in the groundwater were allowed to multiply within the test chamber. The test chamber included an interceding device to restrict diffusion of oxygen into the groundwater to produce different environments for biological activity. The interceding device created an aerobic zone at the surface of the reaction chamber to support aerobic biological activity and an anaerobic zone at the bottom of the reaction chamber to support anaerobic biological activity. The use of a biodegradable indicator die allowed for a visual determination of whether the predominant bacteria were aerobic or anaerobic based on the location in the chamber in which the indicator die was consumed. The rate in which the die is consumed provides information that is used to determine the initial population of bacteria in the groundwater.

2.2.2 Batch Reaction Tests

Four treatment reagent combinations were evaluated for in-situ chemical reduction testing. The reagents included calcium polysulfide, sodium acetate, sodium metabisulfite (at two pH values), and molasses. The testing was conducted using different concentrations of each reagent. Control samples were also prepared for baseline comparison. Each one-liter glass jar for the batch reaction testing was amended with 200 grams of site soil and 600 milliliters of site groundwater. The treatment reagents were added to each test group at different concentrations and the pH and ORP of the samples were monitored as a function of time after preparation.

Water samples were also tested for hexavalent chromium as a function of time to evaluate reaction kinetics with respect to the chemical reduction of hexavalent chromium. Post treatment samples were then tested for total dissolved chromium to determine the overall effectiveness of each treatment with respect to total removal of chromium from the groundwater. The preparation of each reagent test group is described below.

2.2.2.1 Sodium Acetate

The addition of organics to stimulate chromium reduction is dependant upon biological processes. Bacteria in the soil and groundwater consume organics while using electron acceptors in the groundwater to metabolize them. The loss of electron acceptors causes a decrease in the oxidation-reduction potential (ORP) in the groundwater. This change in geochemistry facilitates the chemical reduction of chromium, especially if ferrous iron dissolves into the groundwater from soil as part of the reduced conditions or biological activity.

The type of organic placed into the subsurface affects the rate at which the chromium will be reduced. For example, simple sugar carbohydrates like molasses degrade quickly which results in rapid reduction of chromium. However, these sugars degrade by fermentation which releases acid into the groundwater and lowers the groundwater pH. The reduced groundwater pH may prevent the necessary second step of chromium treatment which involves precipitating the chromium from solution.

To overcome the problems with carbohydrate fermentation, alkanoic salts such as sodium acetate and sodium lactate may be used as the organic food source for the bacteria. These organics degrade slower than carbohydrates and produce only minor pH effects during degradation, thus allowing the chromium to precipitate out of the groundwater. For this bench-scale test, sodium acetate was selected as the non-carbohydrate, organic food source for stimulation of biological activity. Sodium acetate is the sodium salt of vinegar and is a food grade product. The sodium acetate was evaluated at two different dosages (1,000 mg/L and 2,000 mg/L) in test samples containing 200 grams of site soil and 600 milliliters of site groundwater.

2.2.2.2 Molasses

Molasses is a by-product of the sugar refining process. When sugar cane is harvested, it is mashed and boiled to extract the sugar. After the crystallized sucrose is removed from the boiled-down solution, the remaining by-product is referred to as unsulfured molasses. If the sugar cane is too green, it is often treated with sulfur dioxide to assist in the sugar extraction process. The product of this treatment is referred to as sulfured molasses. Sugar cane is typically extracted in a three-step process. The final by-product from the last extraction is referred to as "blackstrap molasses."

Blackstrap molasses still contains a large amount of sugar, but the economics of extracting the sugar exceeds its market value. The blackstrap molasses is a dark, viscous liquid that typically contains around 20 percent sucrose, 20 percent reducing sugars, 20 percent water, 10 percent organic non-sugars, and 10 percent dissolved solids. The elevated dissolved solids and dissolved organics in the molasses give it a high fluid density of approximately 12.5 pounds per gallon. The dissolved solids in the molasses consist primarily of potassium (3 to 4 percent by weight) and calcium (1 to 2 percent by weight). However, it is also a natural chelating agent and contains many other dissolved metals. These include magnesium at around 3,000 mg/L, iron at around 300 mg/L, sodium at about 800 mg/L, copper at about 30 mg/L, zinc at about 15 mg/L, and selenium at about 0.3 mg/L.

Because of its rich nutrients and carbohydrates, blackstrap molasses is often used in cattle feed. It can usually be purchased inexpensively for less than $0.10 per pound. Because of its low price, molasses is sometimes used as an inexpensive organic food source for biological treatments to produce reducing conditions in groundwater as is currently being performed at the site. The blackstrap molasses for this bench-scale test was evaluated at three different dosages (500 mg/L, 1,000 mg/L and 2,000 mg/L) in test samples containing 200 grams of site soil and 600 milliliters of site groundwater.

2.2.2.3 Calcium Polysulfide

Sulfur atoms have the ability to catenate into linear chains of sulfur atoms to create a polysulfide salt when reacted with a metal. When sulfur is reacted with calcium metal, a calcium polysulfide salt is formed that contains anywhere from two sulfur atoms (CaS_2) to seven sulfur atoms (CaS_7) per calcium atom. The average amount of sulfur is four to five sulfur atoms per calcium atom. This material is called calcium polysulfide.

Calcium polysulfide is a NSF International approved reagent for drinking water treatment. It is a nontoxic reagent that has recently received attention as a reducing reagent for hexavalent chromium due to its ability to quickly reduce chromium without the need for acidification. When the polysulfide anion (S_5^{2-}) reacts with hexavalent chromium in the groundwater, the sulfide converts from the -2 oxidation state to the zero oxidation state, thus releasing two moles of electrons for each mole of polysulfide anion reacted.

Three test samples were prepared to evaluate calcium polysulfide as a reducing agent in a site-specific soil/groundwater system at dosages of 10, 25 and 50 mg/L. The samples were prepared using 200 grams of site soil and 600 milliliters of site groundwater.

2.2.2.4 Sodium Metabisulfite

Sodium metabisulfite is a reducing agent that is commonly used to reduce hexavalent chromium to trivalent chromium in water treatment applications. However, the reactions typically require acidic pH values to achieve reasonable kinetics. Sodium metabisulfite was tested with and without sodium hydroxide amendment at two different concentrations (250 mg/L and 500 mg/L) to determine how the pH of the groundwater would affect reaction kinetics and chromium precipitation. The test samples contained 200 grams of site soil and 600 milliliters of site groundwater.

2.2.3 Testing for Hexavalent Chromium and Total Chromium

Water samples from each of the above groups were tested for hexavalent chromium after 3, 7 and 14 days using a Hach Chromium 6^+ Test Kit. After 14 days, a water sample was removed from each sample at the highest dosage for analysis of total dissolved chromium. The samples were filtered with a 0.45-micron filter to remove any precipitated solids, and the filtered water was placed into four-ounce plastic sample containers preserved with nitric acid. The samples were then placed in a cooler on ice and shipped to Merit Laboratories in East Lansing, Michigan for total dissolved chromium analysis.

After four weeks of reaction time, additional water samples were collected from each reactor. The samples were filtered with a 0.45-micron filter, and shipped to Merit Laboratories for a final analysis of total dissolved chromium. The total dissolved chromium tests were performed to evaluate overall effectiveness of each treatment technology in removing chromium from solution.

2.3 Equipment and Materials

The following equipment/instruments were used during the treatability study:

- Ohaus GT480 Laboratory Balance
- Labconco laboratory fume hood
- 70-mm plastic weigh boats
- Stainless steel spatula
- Oakton pH meter
- Oakton ORP meter
- One-liter glass jars
- BD 10-ml Disposable Syringes
- Cole-Parmer Syringe Filter, pore size 0.45-micron
- 4-oz Nalgene HDPE wide mouth jar preserved with nitric acid
- HACH Chromium 6^+ Test Kit

The following solutions were used in the treatability study:

- Distilled water
- Calcium polysulfide (28% weight: weight)
- Sodium hydroxide (2% weight)

- Sodium metabisulfite (100% pure)
- Sodium acetate (100% pure)
- Unsulfured Blackstrap Molasses
- YSI 3682 Zobell ORP standard
- Oakton pH 7 buffer standards

3.0 RESULTS AND DISCUSSION

3.1 Test Results for Biological Activity

The site groundwater sample tested positive for anaerobic heterotrophs. The biological activity reaction chamber indicated that the initial microbial count in the groundwater was between 7,000 and 50,000 heterotrophic bacteria counts per milliliter. This shows that the groundwater and soil were not sterilized by the presence of hexavalent chromium. Therefore, electron-donor amendments may be used at this site for purposes of stimulating biological processes that result in secondary reduction of chromium.

3.2 Batch Reaction Tests for Chromium Reduction

The pH and ORP of the groundwater in the batch reaction tests were monitored over a one-month testing period. During this time-frame, samples were collected periodically from the batch reaction tests for analyses of hexavalent chromium until the results were below detection limits of 0.05 mg/L. On the 14th day and 28th day of the test, samples were analyzed for total dissolved chromium to evaluate total chromium removal efficiency. The results of the testing are summarized below with respect to each of the test groups.

3.2.1 Sodium Acetate

The sodium acetate solutions slowly degraded as a result of biological activity over the 28-day test period. The most notable drop in ORP occurred during the first 14 days of the test, with the ORP stabilizing in the range of -50 to -100 mV thereafter. The ORP of the sodium acetate solutions are shown as a function of time in Table 1 and are illustrated in Figure 1. The decrease in ORP was noted to occur slightly faster with increased dosage. As the acetate degraded, a sour odor developed in the samples. The pH of the sodium acetate systems decreased only slightly during the testing period, starting at an original pH of approximately 7.0 and ending at a pH value of approximately 6.7. The pH data for the sodium acetate test groups are shown in Table 2 and are illustrated in Figure 2.

Little reduction of hexavalent chromium was initially observed in the sodium acetate samples during biological acclimation. However, the concentrations began to decrease around the 7th day of the study. Hexavalent chromium was reduced to 0.1 mg/L by the 14th day of the study, and the concentrations were below detection limits of 0.05 mg/L by the 28th day of the study. The hexavalent chromium concentrations as a function of time are summarized in Table 3 and are illustrated in Figure 3. Assuming a first-order reaction for reductive kinetics, the data suggests that the hexavalent chromium was being reduced at a pseudo first order reaction rate constant of 0.047 days^{-1} which is equivalent to a half life of approximately 15 days.

The sample containing 1,000 mg/L sodium acetate maintained a clear appearance throughout the study. The 2,000 mg/L sodium acetate turned slightly turbid during the last week of the study. Both samples had a slightly sour odor but did not contain any suspended solids as a result of the treatment.

3.2.2 Molasses

The solutions of molasses degraded very quickly after they were placed into the batch reaction containers. This is not unexpected since molasses is rich in carbohydrates, and carbohydrates are degraded rapidly by many types of bacteria. The ORP of all three test groups dropped to below -100 mV within the first week of the study and remained in this highly negative range throughout the duration of the test. The ORP of the molasses solutions are shown as a function of time in Table 4 and are illustrated in Figure 4. The ORP decrease occurred slightly faster with increased dosage. As the molasses degraded, all three test samples turned dark brown in color and developed a strong sewage odor. White gelatinous solids (presumably biosolids) became suspended within all three test samples with the amount of solids increasing proportionally with dosage.

As the molasses degraded, a notable drop in the pH of the samples was observed. The samples originally started at a pH of approximately 7.0, but ended pH values in the range of 5.42 to 5.92. The pH of the solutions decreased proportional to the dosage of molasses addition. The pH data for the molasses test groups are shown in Table 5 and are illustrated in Figure 5.

Hexavalent chromium reduction occurred quickly in the samples dosed with molasses. The hexavalent chromium concentrations were all below the detection limits of 0.05 mg/L when analyzed on the third day of the test. The fast kinetics are likely partially due to the high concentrations of dissolved iron in the molasses. Assuming a first-order reaction for reductive kinetics, the data suggest that hexavalent chromium was being reduced at a pseudo first order reaction rate constant in excess of 0.4 days^{-1}.

3.2.3 Calcium Polysulfide

The solutions treated with low dosages of calcium polysulfide showed gradual reduction in ORP over time. The gradual reduction in ORP suggested possible under-dosage. However, when samples of the water were tested for hexavalent chromium on the third day of the test, all three samples were below detection limits of 0.05 mg/L. The concentration of hexavalent chromium over time in the calcium polysulfide group is shown in Figure 13. A sample collected on the 14th day of the test from the 50 mg/L dosage sample also showed that the total chromium in the sample had been reduced to 0.006 mg/L. These results are shown as a function of time in Figure 12. This shows that the calcium polysulfide serves as a very effective treatment reagent despite the fact that significant ORP decreases were not observed in the test water at low dosages. The ORP of the calcium polysulfide solutions are shown as a function of time in Table 6 and are illustrated in Figure 6. Assuming a first order reaction for reductive kinetics, the calcium polysulfide reduced hexavalent chromium at a pseudo first order reaction rate constant that exceeded 0.4 days^{-1}. The calcium polysulfide samples remained translucent throughout the study without the formation of odors or solids in the samples. The pH of the samples were monitored over the course of the testing. The pH's of the samples versus time is shown graphically in Figure 14. There was no significant change in pH over the time of testing.

3.2.4 Sodium Metabisulfite

Sodium metabisulfite was tested at two different pH values to determine how both pH and concentration would affect the results. The sodium metabisulfite at pH 7 slowly reduced the ORP of the test systems. The lowest dosage of sodium metabisulfite produced the fastest drop in ORP. The ORP of the metabisulfite samples at pH 7 are shown as a function of time in Table 7 and are illustrated in Figure 7.

The sodium metabisulfite at pH 10 had a more dramatic decrease in ORP which was likely the result of the higher pH values. The ORP of the metabisulfite samples at pH 10 also approached negative values by the end of the study. These data are shown as a function of time in Table 8 and are illustrated in Figure 8. No significant difference was noted as a function of sample dosage.

The reduction of hexavalent chromium in the sodium metabisulfite samples occurred slowly over time. The reaction kinetics were a function of both dosage and pH. Higher concentrations of sodium metabisulfite provided faster kinetics as did lower pH values. Although the kinetics were somewhat slow, each of the sodium metabisulfite test groups were able to reduce the concentrations of hexavalent chromium to below detection limits of 0.05 mg/L by the end of the study. The hexavalent chromium concentrations for the sodium metabisulfite samples at pH 7 and 10 are shown in Tables 9 and 10, respectively. The data are also illustrated graphically in Figures 9 and 10.

Assuming a first order reaction for reductive kinetics, the data suggest that the hexavalent chromium was being reduced at a pseudo first order reaction rate constant of 0.08 days^{-1} at pH 7 with a dosage of 250 mg/L. The reaction rate constant increased to 0.17 days^{-1} when the dosage was increased to 500 mg/L. The test samples at pH 10 had similar kinetics with a pseudo first order reaction rate constant of approximately 0.04 days^{-1}. The samples treated with sodium metabisulfite remained translucent throughout the study without the formation of odors or solids in the samples.

3.3 Total Chromium Removal Evaluation

In-situ treatment of hexavalent chromium requires a two-step process. In the first step, the chromium must be reduced from its hexavalent state to its trivalent state. As the bench-scale testing demonstrates, many different types of chemicals can achieve the first step. However, the second step is equally important. In the second step, the trivalent chromium must precipitate from solution to reduce the concentration of dissolved chromium in the groundwater. If the treatment only reduces chromium but does not remove it from solution, then no real progress has been made with respect to achieving maximum contaminant levels (MCLs).

After 14 days of testing, a water sample was removed from each of the test groups (except the sodium acetate group) from the sample group's highest dosed sample for analyses of total dissolved chromium. These samples were collected to provide a mid-test view of how each treatment reagent was performing with respect to achieving MCLs. The sodium acetate group was not sampled as part of this test because the hexavalent chromium analyses indicated that the hexavalent chromium was still above the MCLs.

The water samples were each filtered with a 0.45-micron filter, and the filtrate was placed into a four-ounce plastic sampling container preserved with nitric acid. The samples were shipped to Merit Laboratories on ice for analyses of total dissolved chromium. The results of the analyses are shown in Table 11.

The results showed that the calcium polysulfide treatment at 50 mg/L had already achieved chromium removal to well below the MCLs. However, none of the other samples had achieved MCLs during the initial 14-day test period. The metabisulfite samples had removed between 42 to 55 percent of the total chromium from the groundwater after 14 days and the molasses treatment had removed only 11 percent of the total dissolved chromium.

After 28 days of testing, samples of water were removed from all of the samples in each test group for analyses. The samples were filtered with a 0.45-micron filter and the filtrates were placed into four-ounce, nitric-preserved, plastic containers. The samples were placed on ice inside a cooler and shipped to Merit Laboratories for analyses of total dissolved chromium. The results of these analyses are shown in Table 12.

Most of the samples tested after 28 days showed good removal for chromium from the groundwater. The three calcium polysulfide samples had reduced the total concentration of chromium in solution to between 0.006 and 0.015, well below the MCL of 0.1 mg/L. The sodium metabisulfite samples and sodium acetate samples also performed well, producing total dissolved chromium numbers ranging from less than detection limits of 0.005 mg/L to 0.062 mg/L. Of the samples tested, only the molasses appeared to perform poorly for removal of total chromium. The total chromium concentrations in the samples treated with molasses ranged from 0.129 to 0.25 mg/L total chromium. All of the values were above the MCLs, and the data showed that the amount of dissolved chromium in the groundwater increased with increased dosages of molasses. This effect is likely the result of acidity released by the fermentation of the molasses.

Table 13 shows a summary of the treatment efficiencies for the highest dosage of each treatment chemical evaluated. The results are also illustrated graphically in Figure 11. The results show that the sodium metabisulfite, calcium polysulfide and sodium acetate treatments were all able to provide greater than 95 percent removal efficiency for total chromium from the groundwater. The molasses, however, was only able to remove 20 percent of the total dissolved chromium. Since hexavalent chromium testing showed that the molasses was very successful in reducing the chromium from its hexavalent state to its trivalent state, the elevated chromium concentrations are likely the result of groundwater acidification and possible chelating effects.

3.4 Cost Analysis

The results of the testing show that calcium polysulfide and sodium metabisulfite are the most effective methods of treatment. The cost of each of these chemicals is between $2.00 and $2.50 per pound depending on the vendor. Because the cost of each chemical is relatively the same, it is important to look at the concentrations of the chemicals needed to for effective treatment. Sodium metabisulfite effective as low as 250 ppm would cost between $4,170 and $5,210 per million gallons of water treated. Calcium polysulfide at its most effective concentration of 50 ppm would cost between $830 and $1045 per million gallons of water treated. The 10 ppm concentration of calcium polysulfide also lowed hexavalent chromium below detection limits of 0.05 mg/L and total chromium to 0.015 mg/L, below the standard of 0.1 mg/L, would cost between $166 and $209 per million gallons of water treated.

4.0 CONCLUSIONS AND RECOMMENDATONS

The following conclusions can be drawn from the treatability testing:

- Non-carbohydrate organics, such as sodium lactate, can be used in place of molasses to achieve effective in-situ reduction of chromium by creating biologically-induced reducing conditions;
- Alkanoic salts like sodium acetate and sodium lactate can also provide pH buffering to prevent the groundwater pH from falling too low during biodegradation processes;
- Metabisulfite can be utilized to reduce and precipitate hexavalent chromium *in-situ*, and reduced kinetics at higher pH values can be overcome by the use of increased dosage concentrations;
- Calcium polysulfide provided the best treatment results at the lowest chemical dosage without significant interference from reactions with the soil;
- Calcium polysulfide and molasses provided the fastest reaction kinetics for chromium reduction, but sodium metabisulfite and sodium acetate were also able to complete reduce the hexavalent chromium with 28 days at dosages of 500 mg/L and 2,000 mg/L, respectively; and
- A low pH developed in the molasses-treated samples from the fermentation of the molasses. The low pH and possible chelating effects of the molasses prevented the chromium from precipitating from solution, thus resulting in a total dissolved chromium removal efficiency of only 20 percent.

The following recommendations can be drawn from the conclusions of this study:

- Molasses treatment should be discontinued since bench-testing indicates that it will reduce the pH of the groundwater and retain dissolved metals in solution. Site data collected by Arcadis showing site groundwater pH values as low 4.37 and dissolved calcium concentrations in excess of 3,000 mg/L corroborate with this observation; and
- Treatment with calcium polysulfide is recommended in place of the molasses treatment since it provides rapid and economic treatment kinetics while increasing the alkalinity of the groundwater to effectively remove dissolved chromium from solution.

Figure 1
Sodium Acetate Test Group - ORP versus Time

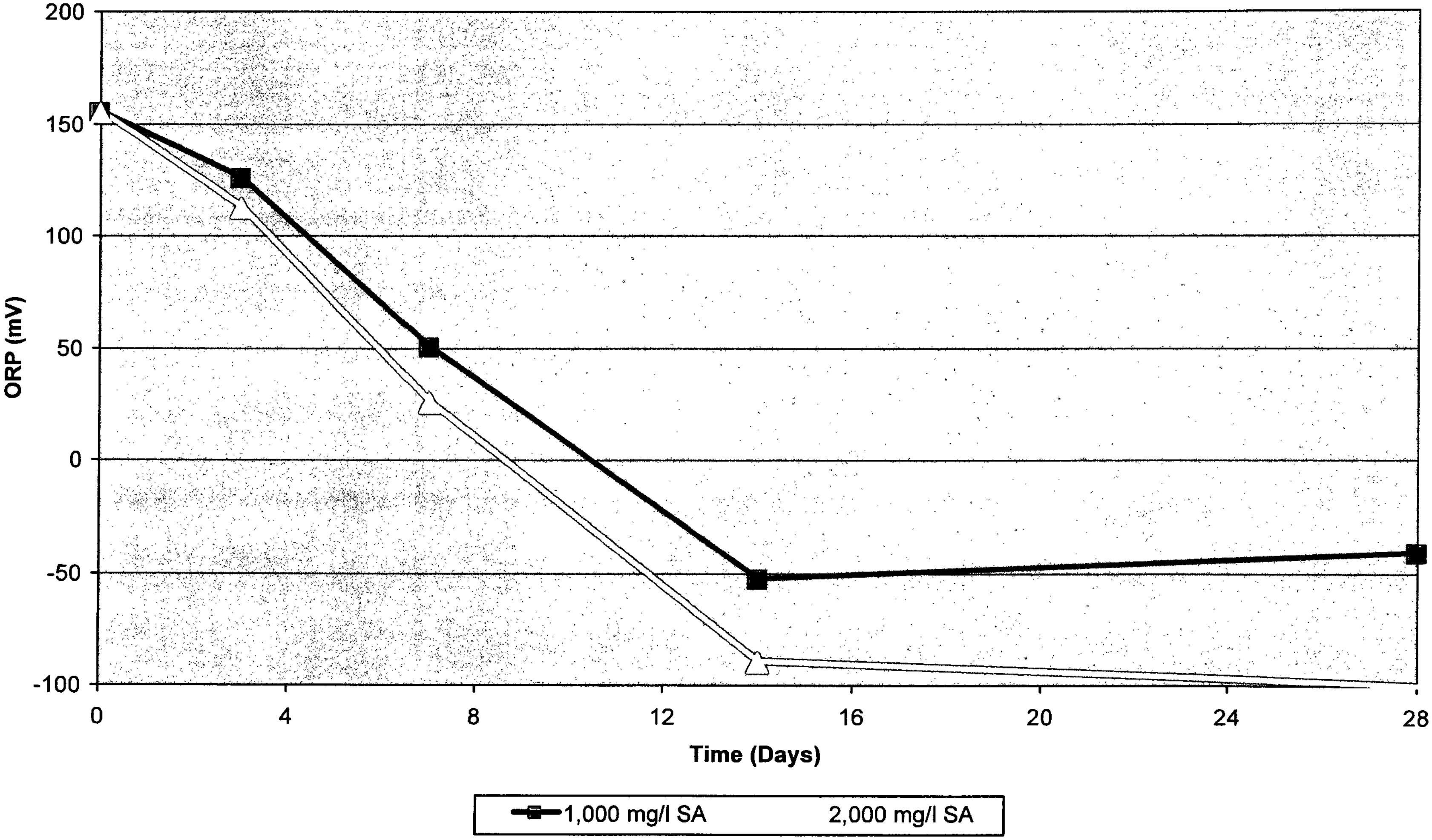

Figure 2

Sodium Acetate Test Group - pH versus Time

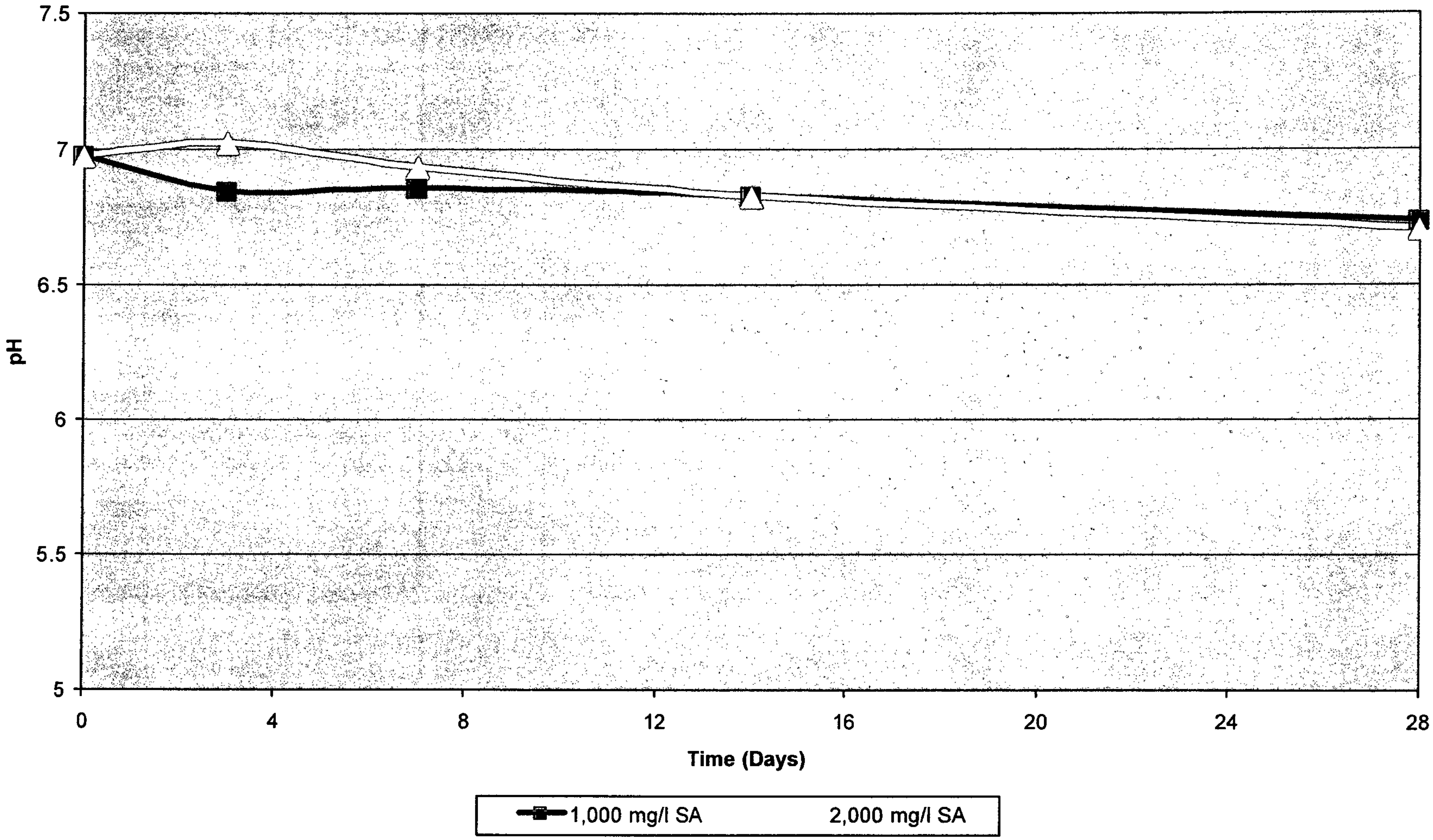

Figure 3
Sodium Acetate Test Group
Hex Chrome Concentration versus Time

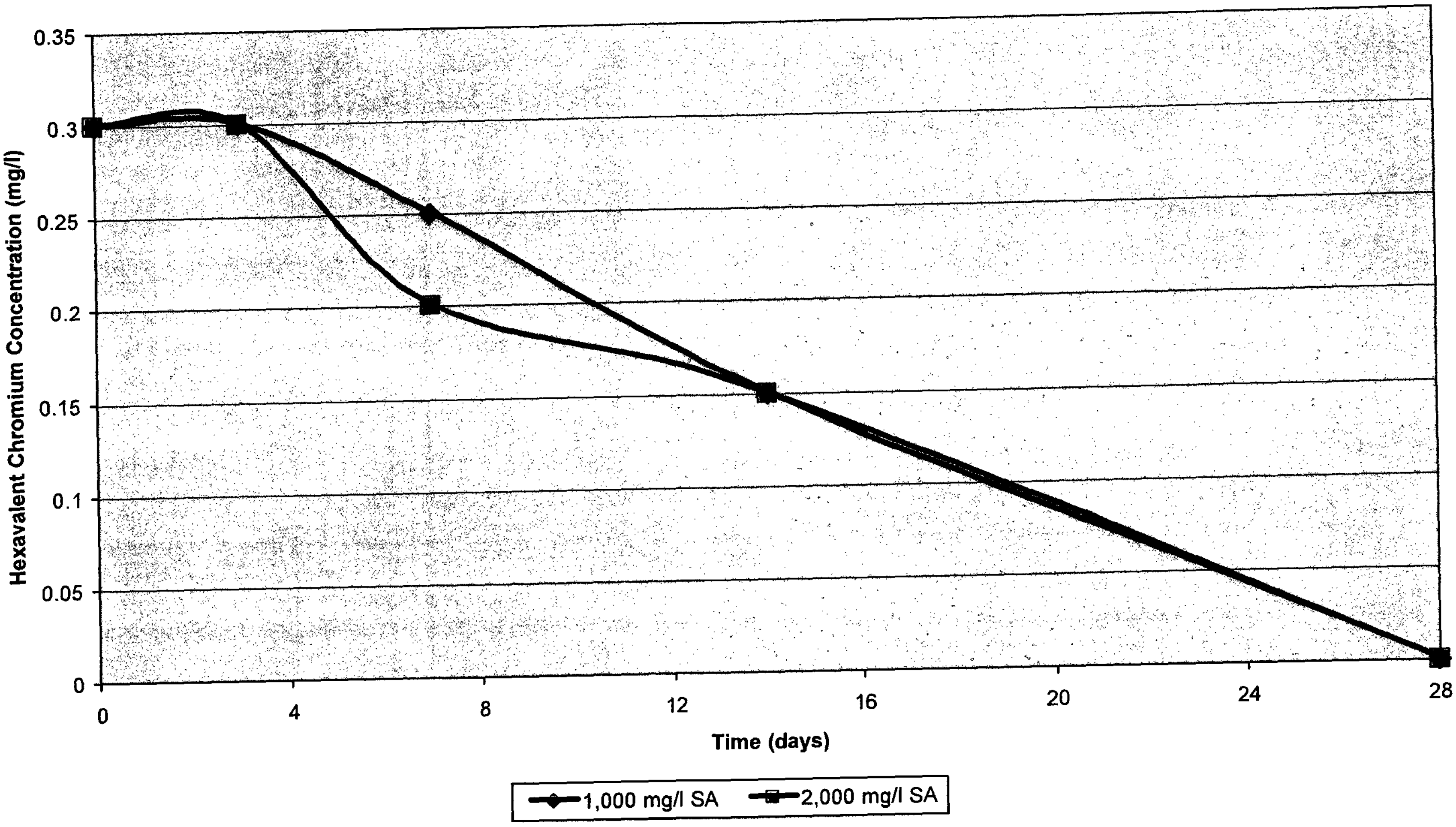

Figure 4

Molasses Test Group - ORP versus Time

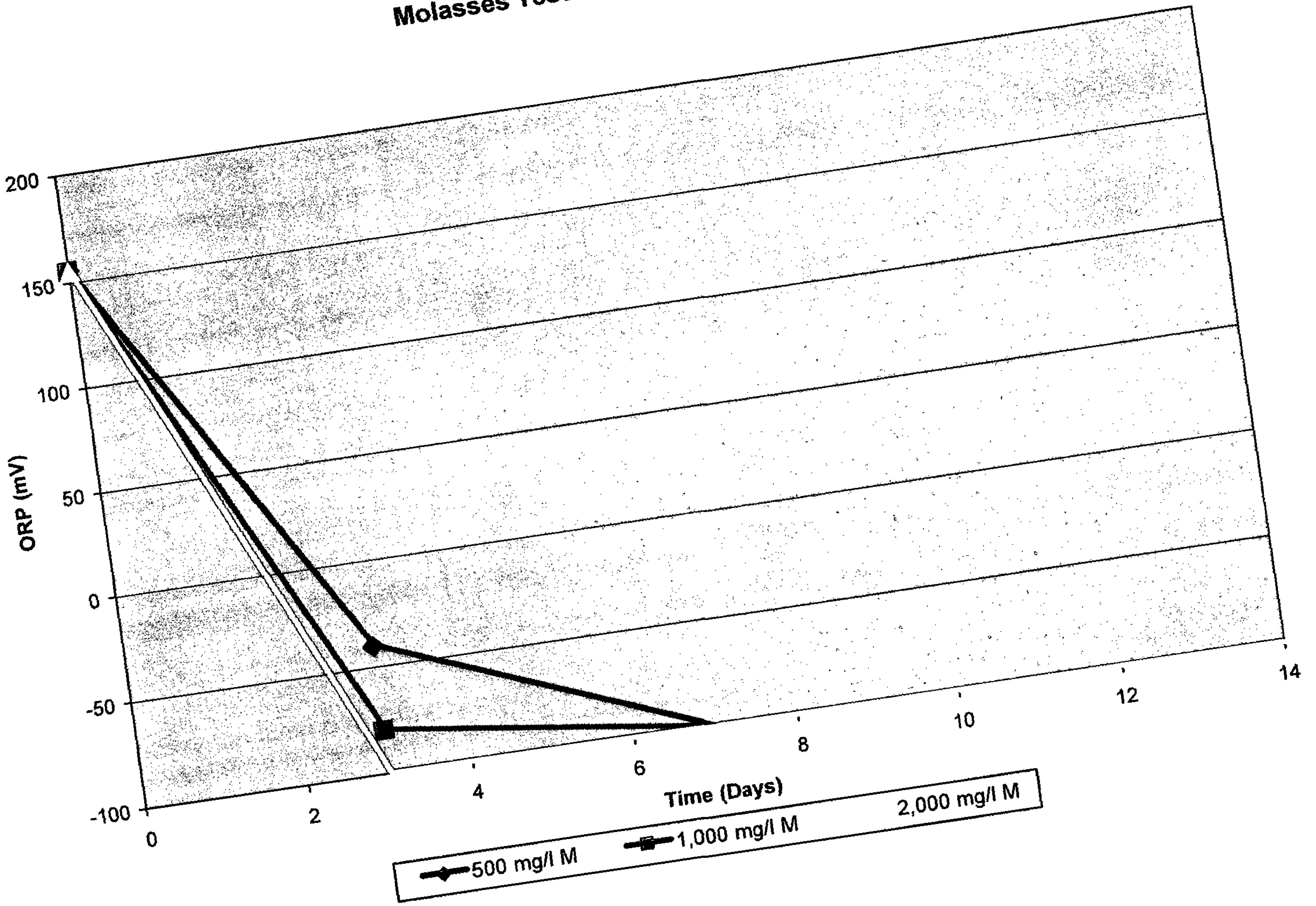

Figure 5

Molasses Test Group - pH versus Time

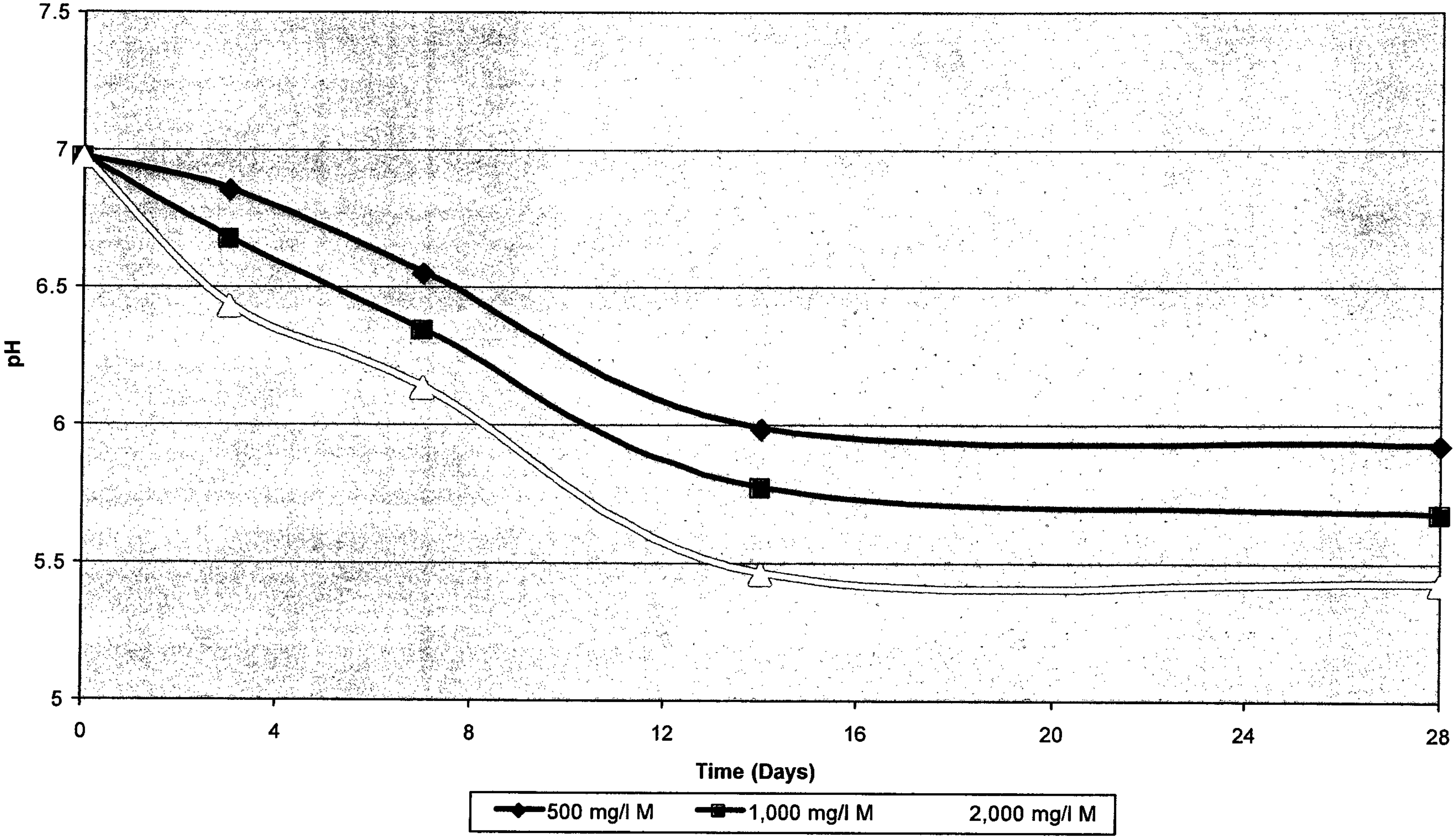

Figure 6
Calcium Polysulfide Test Group - ORP versus Time

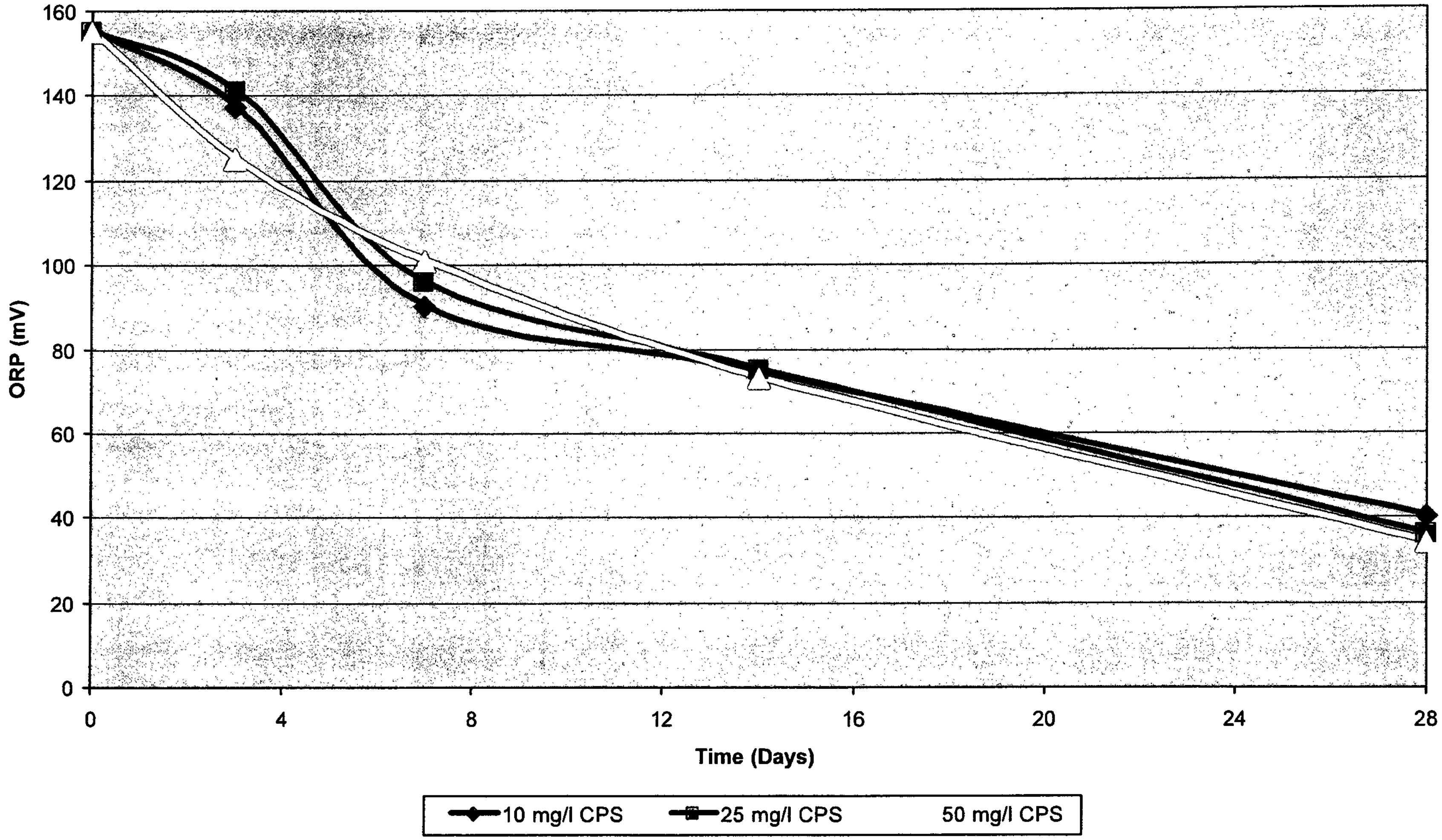

Figure 7

Metabisulfite Test Group @ pH 7 - ORP versus Time

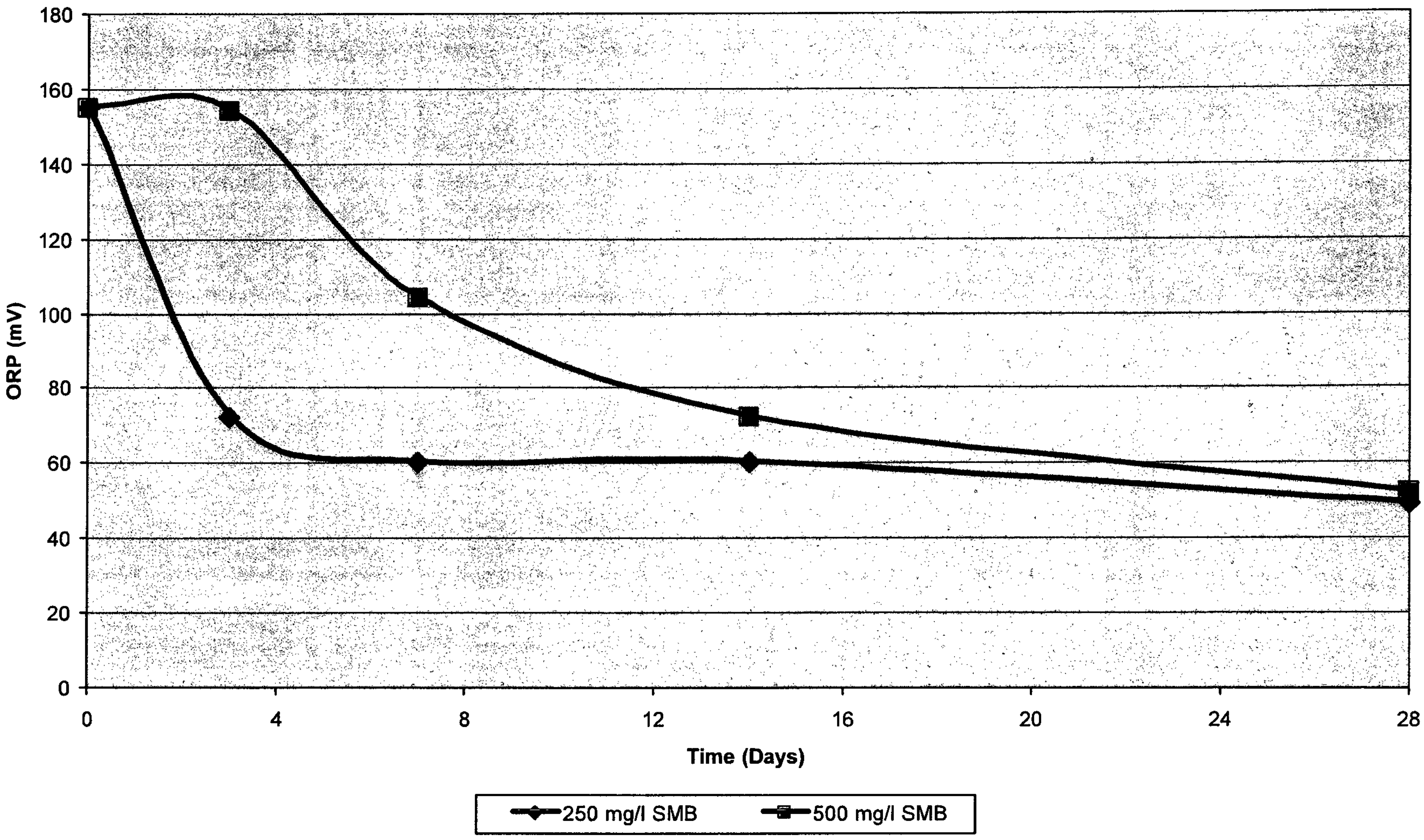

Figure 8

Metabisulfite Test Group @ pH 10 - ORP versus Time

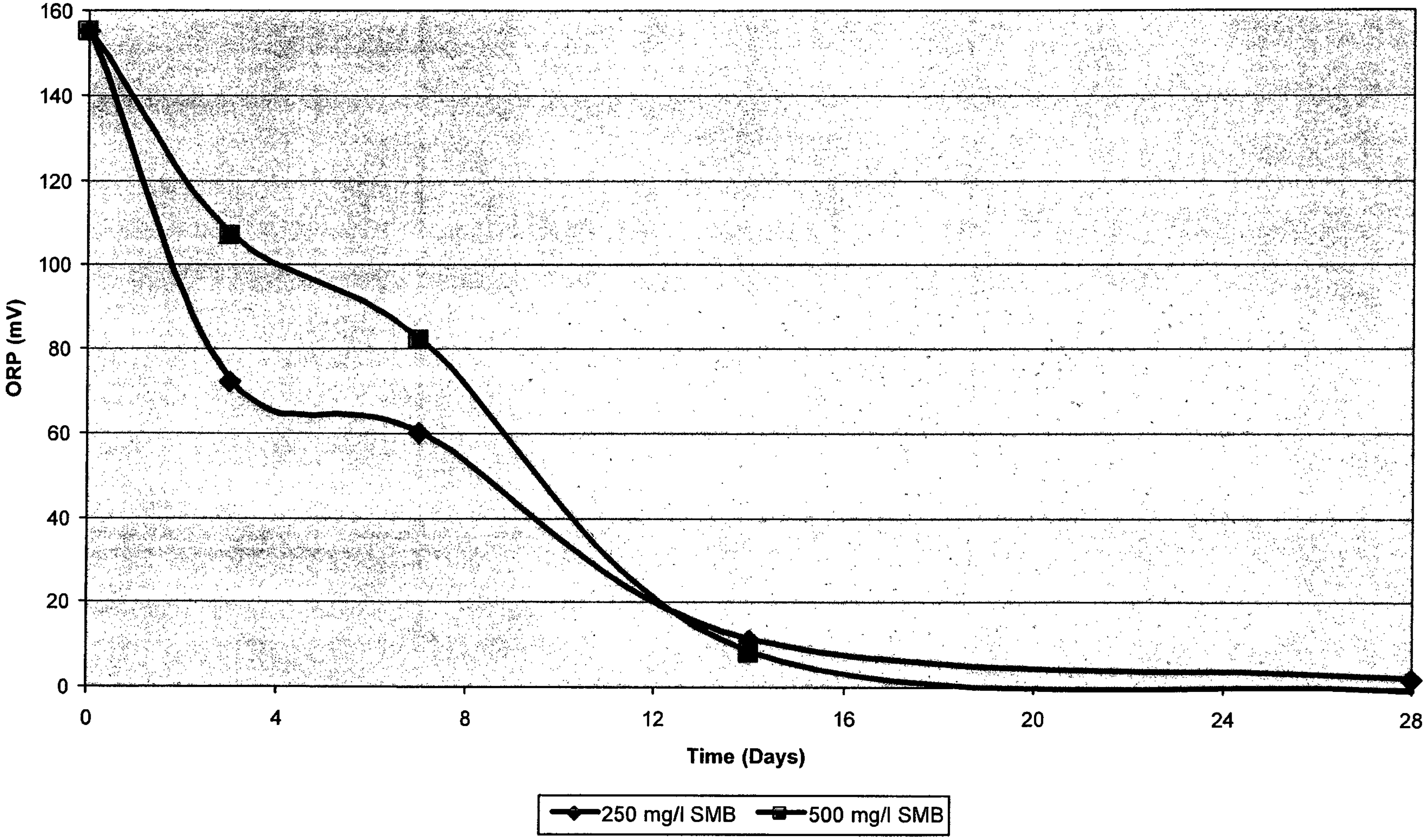

Figure 9

Metabisulfate at pH 7 Test Group
Hex Chrome Concentration verus Time

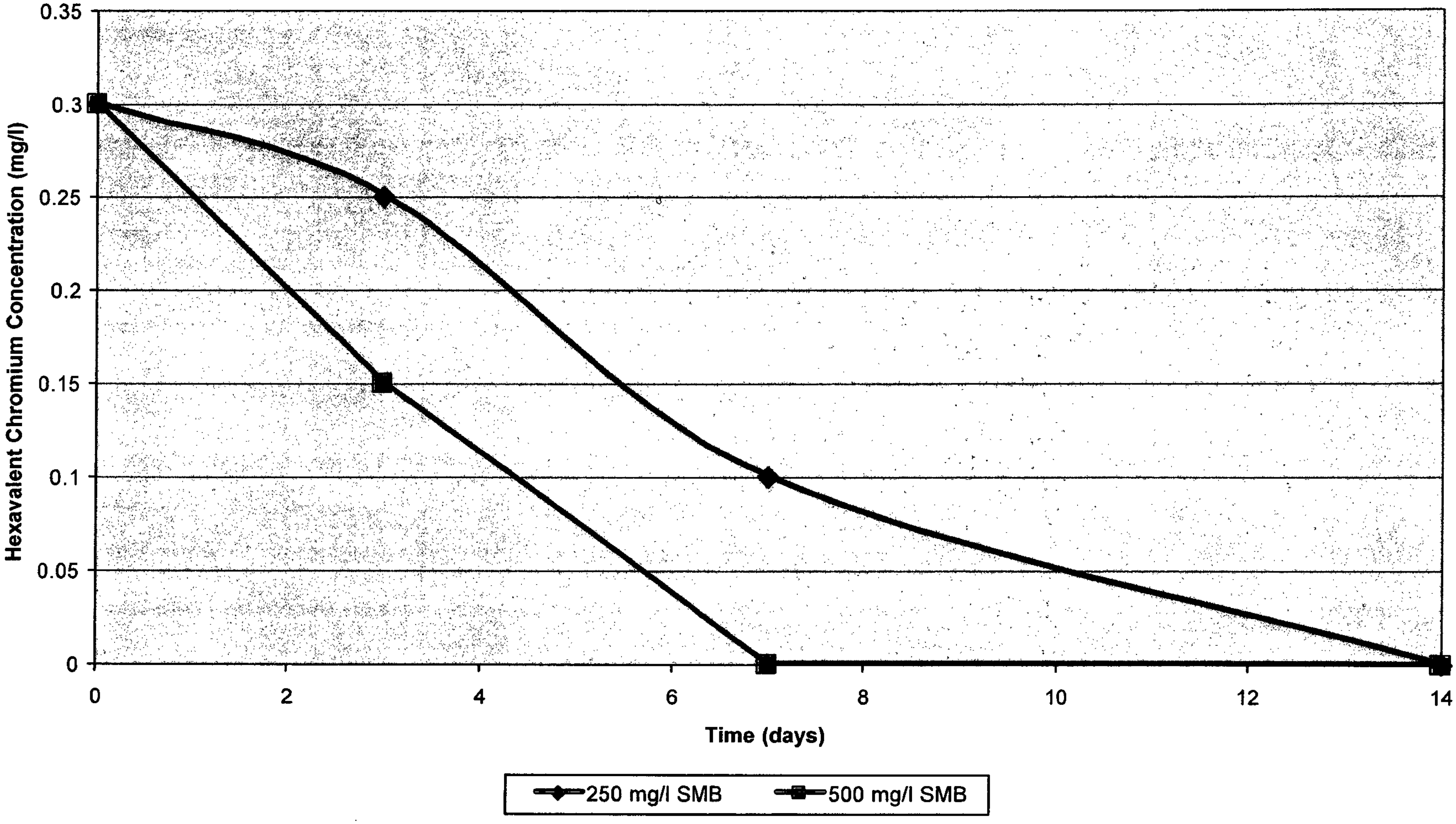

Figure 10

Metabisulfate at pH 10 Test Group
Hex Chrome Concentration verus Time

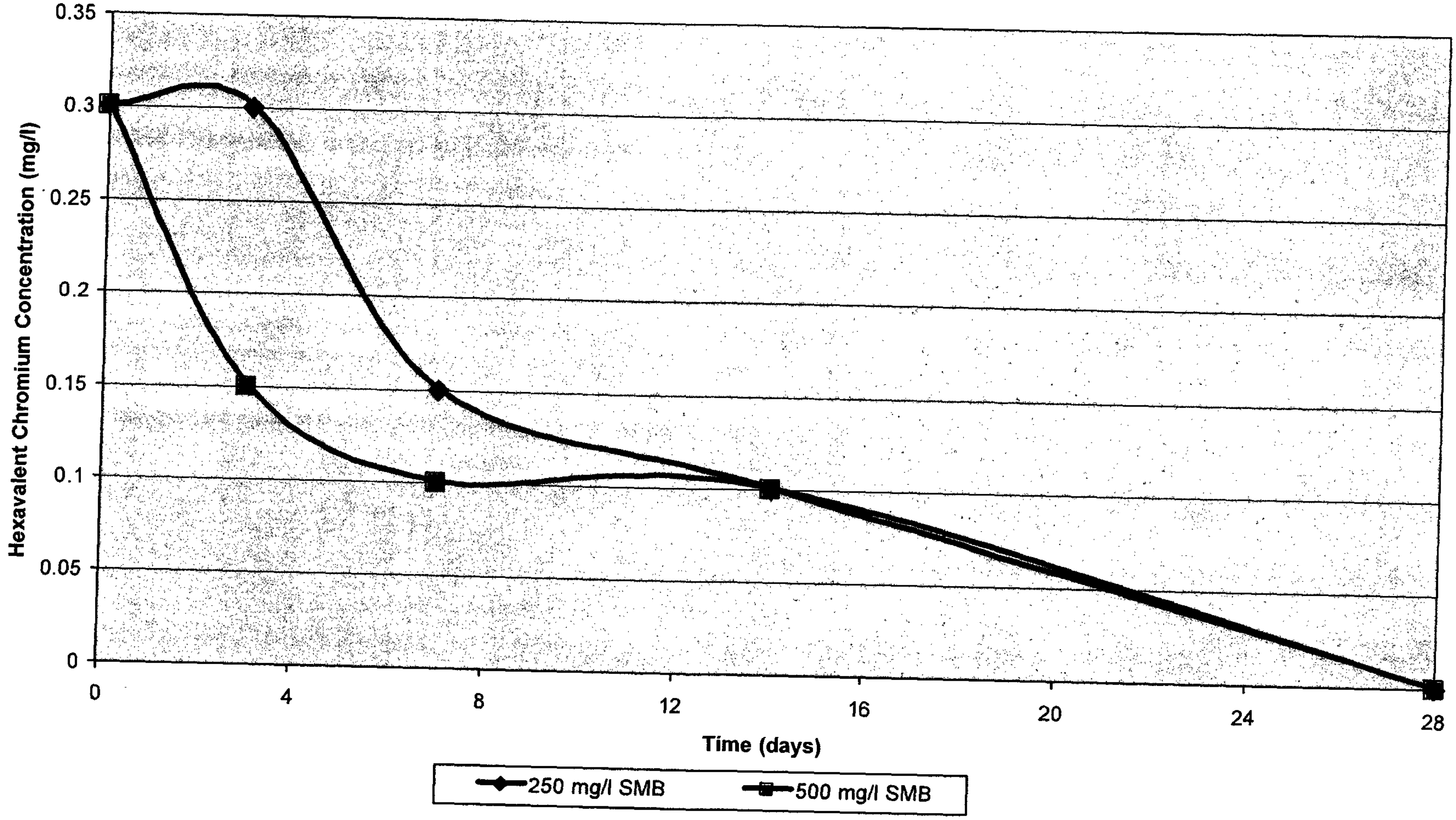

Figure 11

Treatment Efficiency for Total Chromium Removal

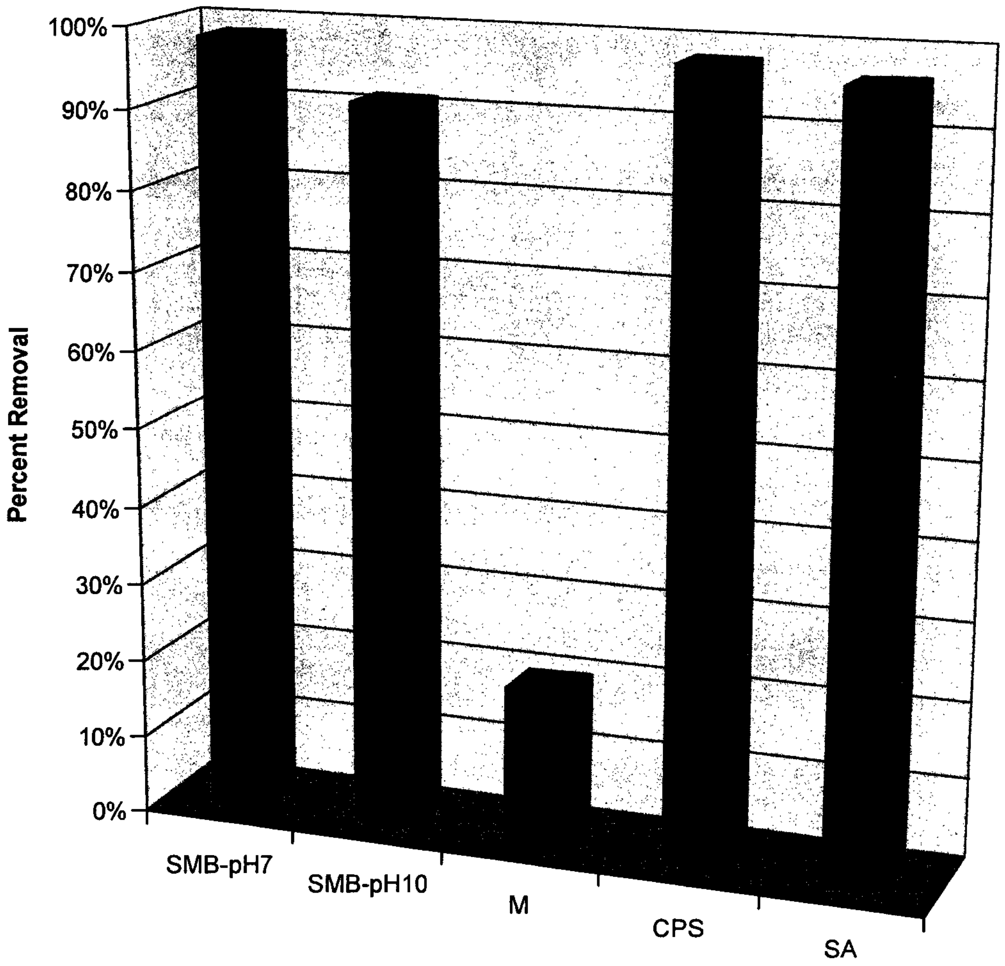

Figure 12
Calcium Polysulfide Test Group
Total Chrome Concentraion versus Time

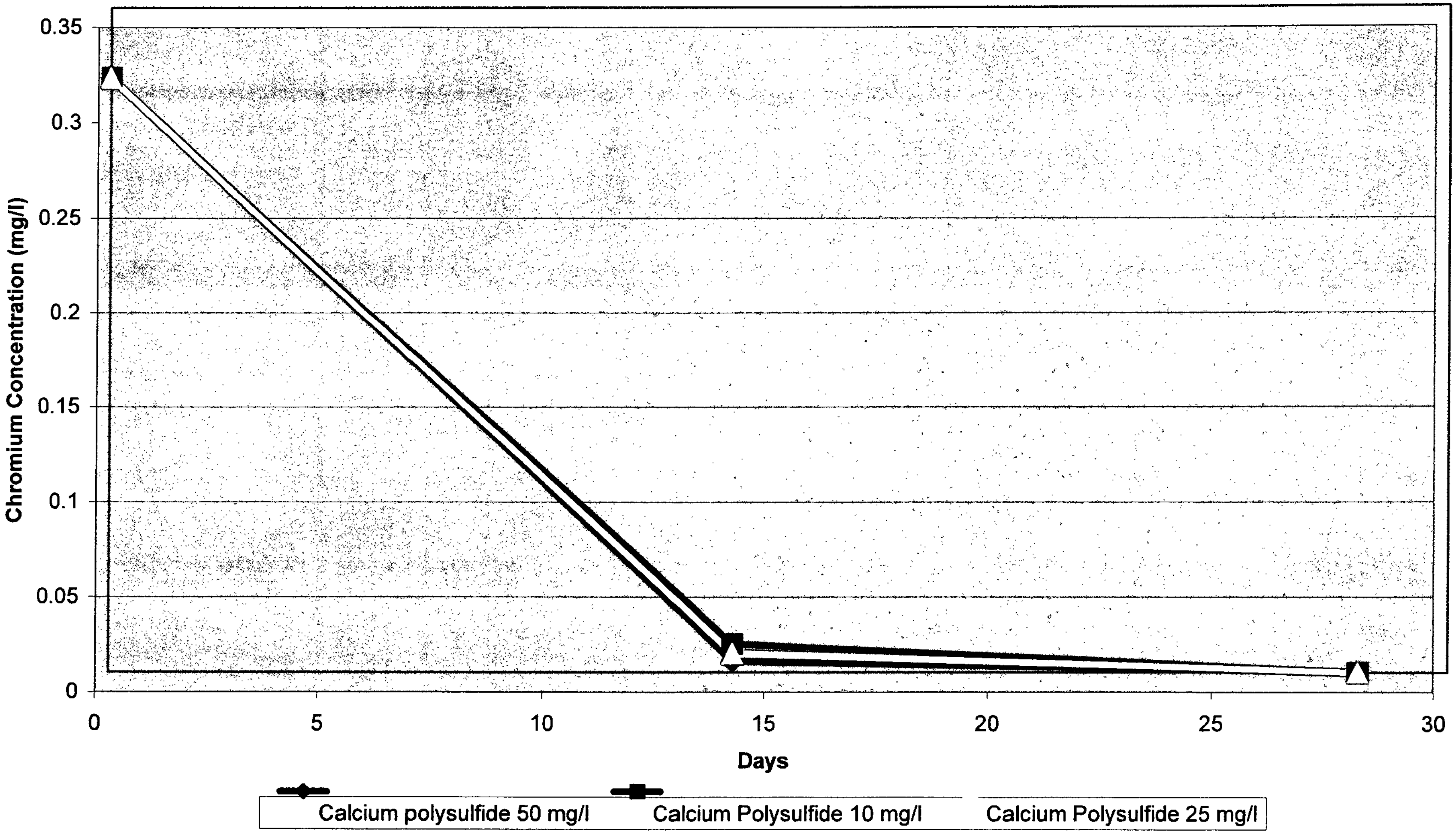

Figure 13
Calcium Polysulfide Test Group
Hex Chrome Concentration versus Time

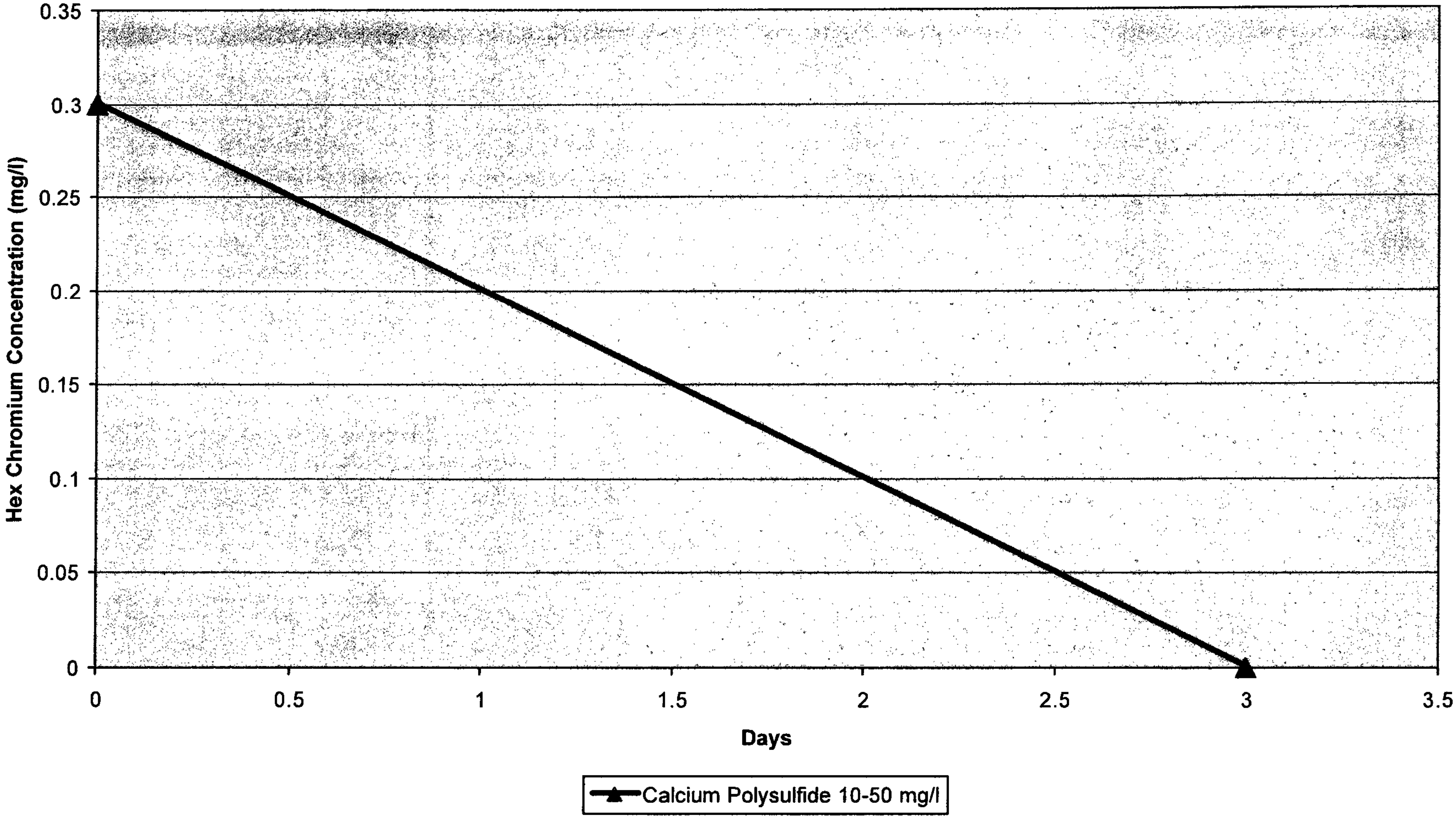

Figure 14
Calcium Polysulfide Test Group
pH versus Time

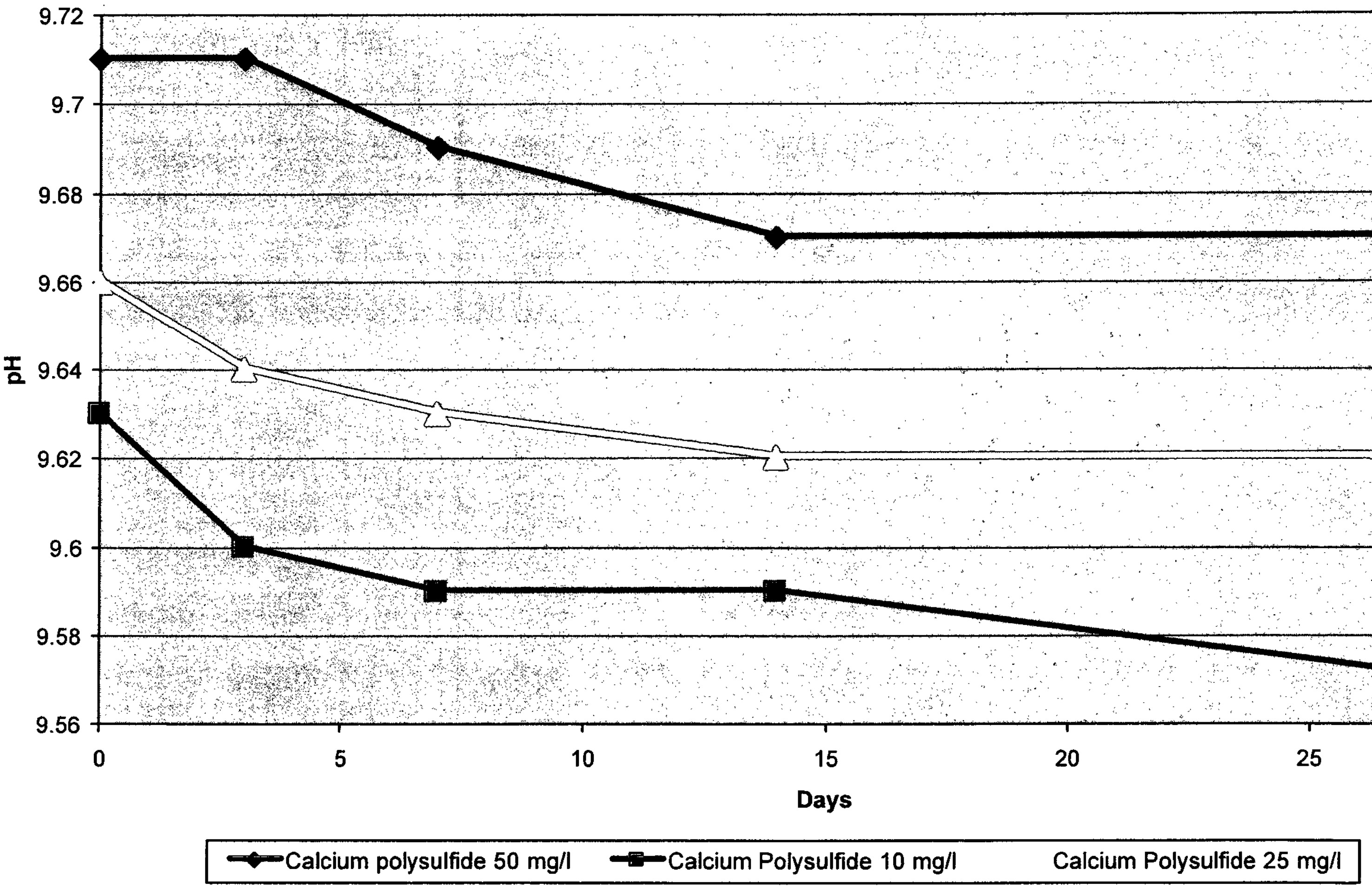

Table 1: Sodium Acetate Test Group - ORP (mV)

Day	1,000 mg/l	2,000 mg/l
0	155	155
3	125	112
7	50	25
14	-53	-90
28	-42	< -100

Table 2: Sodium Acetate Test Group - pH versus Time

Day	1,000 mg/l	2,000 mg/l
0	6.97	6.97
3	6.84	7.02
7	6.85	6.93
14	6.82	6.82
28	6.73	6.7

Table 3: Sodium Acetate Test Group - Hex Chrome (mg/l)

Day	1,000 mg/l	2,000 mg/l
0	0.3	0.3
3	0.3	0.3
7	0.25	0.2
14	0.15	0.15
28	< 0.05	< 0.05

Table 4: Molasses Test Group - ORP (mV)

Day	500 mg/l	1,000 mg/l	2,000 mg/l
0	155	155	155
3	-40	-80	-101
7	< -100	< -100	< -100
14	< -100	< -100	< -100
28	< -100	< -100	< -100

Table 5: Molasses Test Group - pH versus Time

Day	500 mg/l	1,000 mg/l	2,000 mg/l
0	6.97	6.97	6.97
3	6.85	6.67	6.43
7	6.55	6.34	6.13
14	5.98	5.77	5.46
28	5.92	5.67	5.42

Table 6: Calcium Polysulfide Test Group - ORP (mV)

Day	10 mg/l	25 mg/l	50 mg/l
0	155	155	155
3	137	141	125
7	90	96	101
14	74	75	73
28	40	36	34

Table 7: Metabisulfite @ pH 7 Test Group - ORP (mV)

Day	250 mg/l	500 mg/l
0	155	155
3	72	154
7	60	104
14	60	72
28	49	52

Table 8: Metabisulfite @ pH 10 Test Group - ORP (mV)

Day	250 mg/l	500 mg/l
0	155	155
3	72	107
7	60	82
14	11	8
28	2	-1

Table 9: Metabisulfite @ pH 7 Test Group - Hex Chrome (mg/l)

Day	250 mg/l	500 mg/l
0	0.3	0.3
3	0.25	0.15
7	0.1	< 0.05
14	< 0.05	< 0.05

Table 10: Metabisulfite @ pH 10 Test Group - Hex Chrome (mg/l)

Day	250 mg/l	500 mg/l
0	0.3	0.3
3	0.3	0.15
7	0.15	0.1
14	0.1	0.1
28	< 0.05	< 0.05

Table 11: 14-Day Test Results for Total Chromium

Sample I.D.	**Dissolved Cr (mg/l)**
Control	0.313
Calcium Polysulfide	0.006
Molasses	0.278
Sodium Metabisulfite (pH 7)	0.14
Sodium Metabisulfite (pH 10)	0.18

Table 12: 28-Day Test Results for Total Chromium

Sample I.D.	Reagent Dose (mg/l)	Dissolved Cr (mg/l)
Sodium Metabisulfite (pH 7)	250	0.062
Sodium Metabisulfite (pH 7)	500	< 0.005
Sodium Metabisulfite (pH 10)	250	0.048
Sodium Metabisulfite (pH 10)	500	0.027
Molasses	500	0.129
Molasses	1000	0.199
Molasses	2000	0.25
Calcium Polysulfide	10	0.015
Calcium Polysulfide	25	0.01
Calcium Polysulfide	50	0.006
Sodium Acetate	1000	0.033
Sodium Acetate	2000	0.011

Highlighted samples exceed the MCL of 0.1 mg/l Cr

Table 13: Treatment Efficiency for Total Chromium Removal

Sample I.D.	Reagent Dose (mg/l)	Removal Efficiency
Sodium Metabisulfite (pH 7)	500	98.4%
Sodium Metabisulfite (pH 10)	500	91.4%
Molasses	2000	20.1%
Calcium Polysulfide	50	98.1%
Sodium Acetate	2000	96.5%

APPENDIX B
GROUNDWATER FIELD LOG

Distal Array Injection Work Plan
for the Eunice North Gas Plant

Chevron Environmental Management Company
89CH.49410.92
February 9, 2006

Groundwater Field Log
Eunice North Gas Plant

Order	Well ID	Date	Time	Depth to Water (feet)	Total Well Depth (feet)	PSH Thickness (feet)
1	MW065SA					
2	MW067SA					
3	MW066SA					
4	MW064SA					
5	MW079SA					
6	MW080SA					
7	MW081SA					
8	MW082SA					
9	MW083SA					
10	MW084SA					
11	MW085SA					
12	IW003					
13	IW004					
14	IW005					
15	IW006					
16	IW007					
17	IW008					
18	IW009					
19	IW010					
20	IW011					
21	IW012					
22	IW013					
23	IW014					
24	IW015					
25	IW016					

APPENDIX C
GROUNDWATER SAMPLING FIELD DATA SHEET

Distal Array Injection Work Plan
for the Eunice North Gas Plant

Chevron Environmental Management Company
89CH.49410.92
February 9, 2006

SECOR
GROUNDWATER SAMPLING FIELD DATA SHEET

SECOR PN: ______________________ DATE: __________ WELL NO. __________

FACILITY NAME: ______________________ TEMPERATURE: __________ °F or °C

FIELD PERSONNEL: ______________________ WEATHER: ______________________

FIELD MEASUREMENTS:

A. Static Water Level (SWL) below top of casing/piezometer: __________ FT. or IN.

B. Thickness of Free Product, if present: ________ Inches __________ FT. or IN.

C. Total Depth of well (TD) from top of casing/piezometer: __________ FT. or IN.

D. Height of Water Column in casing (h = TD - SWL): __________ FT. or IN.

E. **Useful approximate Purge Volumes (PV) per foot of water column for common casing sizes:**

	3 Well Vols.	5 Well Vols.			
2" Diameter =	0.5 gals/ft	0.82 gals/ft	x feet of water________	=	________PV (Gal)
4" Diameter =	2.0 gals/ft	3.25 gals/ft	x feet of water________	=	________PV (Gal)
6" Diameter =	4.4 gals/ft	7.35 gals/ft	x feet of water________	=	________PV (Gal)

PURGING METHOD: ______________________ DURATION: ______________________

OBSERVATIONS:

Cum. PV (Gal)	Time	Turbidity	DO	ORP	pH	Temp.	Conduct.	SWL

TOTAL VOLUME OF WATER PURGED FROM WELL: ______________________

PURGE WATER STORED/DISPOSED OF WHERE/HOW: ______________________

SAMPLES COLLECTED: Depth to Water at time of sample collection: ______________________

Sample Number(s)	Time	Size/Number of Container(s)	Preservative

COMMENTS:

____

____

Casing Capacities:
2-inch hole.........0.16 gal/lin ft.
4-inch hole.........0.65 gal/lin ft.
6.5-inch hole.......1.70 gal/lin ft.
8-inch hole.........2.60 gal/lin ft.
10-inch hole........4.10 gal/lin ft.

Recharge Calculation at Time of Sample Collection:

Total Depth of Well:
Original Water Column: ________ x 0.80 = -- (________)
Collect sample when Depth to Water measures
Less than or equal to:

Signature: ______________________

Tessenderlo KERLEY

TESSENDERLO GROUP

Material Safety Data Sheet

Calcium polysulfide solution

MSDS Number 6100 (Revised: 1/14/05) 6 Pages

Section 1: CHEMICAL PRODUCT and COMPANY IDENTIFICATION

1.1 **Product Name** .... **Calcium polysulfide solution**
Chemical Family .... Inorganic salt solution
Synonyms .... Calcium polysulfide, CaPS, calcium sulfide, lime sulphur
Formula .... CaS_x

1.2 **Manufacturer** .... Tessenderlo Kerley Inc.
2255 N. 44th Street, Suite 300
Phoenix, Arizona 85008-3279
Information .... (602) 889-8300

1.3 **Emergency Contact** .... (800) 877-1737 (Tessenderlo Kerley)
(800) 424-9300 (CHEMTREC)

Section 2: COMPOSITION, INFORMATION ON INGREDIENTS

2.1 **Chemical Ingredients (% by wt.)**

Calcium polysulfide	CAS #:1344-81-6	24 - 29%
Water	CAS #:7732-18-5	71 - 76%

(See Section 8 for exposure guidelines)

Section 3: HAZARDS IDENTIFICATION

NFPA: Health - 2 Flammability - 0 Reactivity - 1

EMERGENCY OVERVIEW

Warning:
Avoid inhalation of product fumes (hydrogen sulfide) near openings on storage container. Release of the product to the environment may cause the evolution of highly toxic hydrogen sulfide vapors. Product solution is alkaline and may cause irritation to the skin. Eye contact will cause eye irritation and possible corneal damage. Ingestion will result in irritation of tissues and the release of hydrogen sulfide in the gastrointestinal tract.

Section 3: HAZARDS IDENTIFICATION (Cont.)

3.1 POTENTIAL HEALTH EFFECTS

EYE: Contact with the eyes by product mist or solution will cause irritation and a burning sensation. Eye contact may result in severe corneal injury.

SKIN CONTACT: Contact with product mist or solution will cause skin irritation and may result in corrosion of the skin.

SKIN ABSORPTION: Absorption is unlikely to occur.

INGESTION: Ingestion of product solution will cause irritation and corrosion of the gastrointestinal tract to include nausea, vomiting and diarrhea. Contact with stomach acid will cause highly toxic hydrogen sulfide to evolve.

INHALATION: Inhalation of product vapors (hydrogen sulfide) may cause dizziness and unconsciousness possibly resulting in serious falls from elevated positions..

CHRONIC EFFECTS/CARCINOGENICITY: Not listed as a carcinogen by NTP, IARC or OSHA.

Section 4: FIRST AID MEASURES

4.1 EYES: Immediately flush with large quantities of water for 15 minutes. Hold eyelids apart during irrigation to insure thorough flushing of the entire area of the eye and lids. Obtain immediate medical attention.

4.2 SKIN: Immediately flush with large quantities of water. Remove contaminated clothing under a safety shower. Obtain immediate medical attention.

4.3 INGESTION: DO NOT INDUCE VOMITING. If victim is conscious, immediately give large quantities of water. If vomiting does occur, continue to give fluids. Obtain immediate medical attention.

4.4 INHALATION: Remove victim from contaminated atmosphere. If breathing is labored, administer oxygen. If breathing has ceased, clear airway and start mouth to mouth resuscitation. If heart has stopped beating, external heart massage should be applied. Obtain immediate medical attention.

Section 5: FIRE FIGHTING MEASURES

5.1 FLAMMABLE PROPERTIES

FLASH POINT: Not flammable (See Section 5.4) **METHOD USED:** NA

5.2 FLAMMABLE LIMITS H_2S **LFL:** 4% **UFL:** 44%

5.3 EXTINGUISHING MEDIA: Water spray or foam or as appropriate for combustibles involved in fire.

Section 5: FIRE FIGHTING MEASURES (Cont.)

5.4 FIRE & EXPLOSIVE HAZARDS: When heated or diluted, hydrogen sulfide vapors will evolve. This gas may form explosive mixtures with air. (See Section 5.2) Keep containers/storage vessels in fire area cooled with water spray.

5.5 FIRE FIGHTING EQUIPMENT: Because of the possible presence of toxic gases and the irritating nature of the product, wear self-contained breathing apparatus, positive pressure, (MSHA/NIOSH approved or equivalent) and full protective gear.

Section 6: ACCIDENTAL RELEASE MEASURES

6.1 Small releases: Confine and absorb small releases on sand, earth or other inert absorbent. Released material may contain residual sulfides. Spray with weak (~5%) hydrogen peroxide to oxidize sulfides.

6.2 Large releases: Confine area to qualified personnel. Wear proper protective equipment. Shut off release if safe to do so. Dike spill area to prevent runoff into sewers, drains (possible toxic or explosive mixtures) or surface waterways (potential aquatic toxicity). Spray product vapors with fine water spray or mist. Recover as much of the solution as possible. Treat remaining material as a small release (above).

Section 7: HANDLING and STORAGE

7.1 Handling: Handle in enclosed containers to avoid breathing product. Avoid contact with skin and eyes. Dilute only in enclosed containers. Use in a well ventilated area. Wash thoroughly after handling.

7.2 Storage: Store in well ventilated areas in enclosed containers. Do not store combustibles in the area of storage vessels. Keep away from any sources of heat or flame. Store tote, drums and small containers out of direct sunlight at moderate temperatures [<90°F (32°C)]. (See Section 10.4 for materials of construction)

Section 8: EXPOSURE CONTROLS, PERSONAL PROTECTION

8.1 RESPIRATORY PROTECTION: Wear self-contained breathing apparatus, positive pressure, MSHA/NIOSH (approved or equivalent).

8.2 SKIN PROTECTION: Gloves, boots, and chemical suit should be worn to prevent liquid contact. Wash contaminated clothing prior to reuse. Contaminated shoes cannot be cleaned and should be discarded

8.3 EYE PROTECTION: Chemical goggles and a full face shield.

8.4 EXPOSURE GUIDELINES:

	OSHA		ACGIH	
	TWA	STEL	TLV	STEL
Hydrogen sulfide	20 ppm (ceiling)		10 ppm (ceiling)	

8.5 ENGINEERING CONTROLS: Use adequate exhaust ventilation to prevent inhalation of product vapors. Maintain eyewash/safety shower in areas where chemical is handled.

Section 9: PHYSICAL and CHEMICAL PROPERTIES

9.1 APPEARANCE:	Ruby red liquid
9.2 ODOR:	Strong order of rotten eggs
9.3 BOILING POINT:	Not determined
9.4 VAPOR PRESSURE:	Not determined (Believed to be minimal)
9.5 VAPOR DENSITY:	Not determined
9.6 SOLUBILITY IN WATER:	Dissolves with precipitation of elemental sulfur.
9.7 SPECIFIC GRAVITY:	1.20 - 1.27 (10.0 - 10.6 lbs/gal)
9.8 FREEZING POINT:	Not determined
9.9 pH:	10.0 - 11.7
9.10 VOLATILE:	Not applicable

Section 10: STABILITY and REACTIVITY

10.1 STABILITY: This is a stable material

10.2 HAZARDOUS POLYMERIZATION: Will not occur.

10.3 HAZARDOUS DECOMPOSITION PRODUCTS: Heating this product will evolve hydrogen sulfide vapors. Continued heating will also cause oxides of sulfur to be released.

10.4 INCOMPATIBILITY: Strong oxidizers such as nitrates, nitrites or chlorates can cause explosive mixtures if heated to dryness. Acids, acidic materials or dilution with water will cause the release of hydrogen sulfide, a highly toxic gas.

Section 11: TOXICOLOGICAL INFORMATION

11.1 ORAL: Data not available

11.2 DERMAL: Data not available

11.3 INHALATION: INH-Rat LC_{50}: 3.6 mg/L (4 Hr. Exposure)

11.4 CHRONIC/CARCINOGENICITY: No evidence available

11.5 TERATOLOGY: Data not available

11.6 REPRODUCTION: Data not available

11.7 MUTAGENICITY: Data not available

Section 12: ECOLOGICAL INFORMATION

No data available.

Section 13: DISPOSAL CONSIDERATIONS

If released to the environment for other than its intended purpose, this product should be checked to see it meets the criteria of a reactive sulfides D003, Reactive waste.

Section 14: TRANSPORT INFORMATION

14.1 DOT Shipping Name: Calcium Polysulfide solution

14.2 DOT Hazard Class: NA

14.3 UN/NA Number: NA

14.4 Packing Group: NA

14.5 DOT Placard: NA

14.6 DOT Label(s): NA

14.7 IMO Shipping Name: Not Determined

14.8 RQ (Reportable Quantity): NA

14.9 RR STCC Number: Not Determined

Section 15: REGULATORY INFORMATION

15.1 OSHA: This product is listed as a hazardous material under criteria of the Federal OSHA Hazard Communication Standard, 29 CFR 1910.1200.

15.2 SARA TITLE III:

a. **EHS** (Extremely Hazardous Substance) List: No

b. Section 311/312, (Tier I,II) Categories:

Immediate (acute)	Yes
Fire	No
Sudden release	No
Reactivity	Yes
Delayed (chronic)	No

c. Section 313 (Toxic Release Reporting-Form R): No

Chemical Name	CAS Number	Concentration

d. **TPQ** (Threshold Planning Quantity): No

15.3 CERCLA/SUPERFUND: RQ (Reportable Quantity) No

15.4 TSCA (Toxic Substance Control Act) Inventory List: Yes

Section 15: REGULATORY INFORMATION (Cont.)

15.5 RCRA (Resource Conservation and Recovery Act) Status:	Possible D003 (See Section 13)
15.6 WHMIS (Canada) Hazard Classification:	NA
15.7 DOT Hazardous Material: (See Section 14)	No
15.8 CAA Hazardous Air Pollutant (HAP)	No

Section 16: OTHER INFORMATION

REVISIONS: The entire MSDS was reformatted to comply to ANSI Standard Z400.1-1993, by Technical Services-Tessenderlo Kerley, Inc.

Address updated, 4/30/99
Section 8.3, Eye Protection revised and logo revised, 4/29/02
Revised Section 2.1, Ingredients, 3, Hazard Identification, 9,Physical characteristics, 11, Toxicological Information, 14, Transportation, 1/14/05