URS

March 5, 2001

Mr. Randall Whitmore
El Dorado Chemical Company
P.O. Box 231
El Dorado, Arkansas 71731

Re: Results of Pilot Test
Enhanced In-Situ Bioremediation
El Dorado Chemical Company
El Dorado, Arkansas Facility
URS File No. 35-00009153.00 00003

Dear Mr. Whitmore:

URS has prepared this letter report to summarize the results of the pilot tests of enhanced in-situ denitrification of shallow groundwater at the El Dorado Chemical Company, El Dorado, Arkansas facility.

1.0 INTRODUCTION

El Dorado Chemical Corporation (EDCC) entered into Consent Administrative Order (CAO) LIS 98-119 with the Arkansas Department of Environmental Quality (ADEQ) which became effective in October, 1998. The CAO requires EDCC to implement several actions. One of the provisions of the CAO requires EDCC to submit to the ADEQ a work plan for in-situ bioremediation. The work plan was submitted in December 1998.

The Work Plan delineated a step-wise approach to the in-situ bioremediation, as follows:

- **Initial sampling and testing.** Data were collected from 10 monitor wells to provide baseline data necessary to design the in-situ bioremediation pilot test. The 10 monitor wells that had nitrate concentrations of 10 mg/L or greater were sampled and the groundwater samples were analyzed for parameters that identify geochemical conditions, parameters that are degradation products of microbiological mediated oxidation/reduction reactions, microbiological parameters, and parameters that are alternate electron acceptors in microbiological mediated oxidation/reduction reactions. In addition, slug tests to determine hydraulic conductivity were completed in each of the 10 monitor wells. These tests were used to design the quantity and type of organic supplement added to enhance in-situ bioremediation in the pilot test and to provide baseline information which can be used to assess effectiveness of the bioremediation.

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- **Preliminary field testing (pilot tests).** Based on the results from the initial sampling and testing, two monitor wells (MW-1 and MW-17) were selected to represent the range of conditions present in the 10 wells. These selected monitor wells were then used in field tests of the addition of organic supplement. These field tests were used to evaluate the feasibility of implementation of in-situ bioremediation at all 10 monitor well locations. This letter report documents the findings from the field tests and presents conclusions with respect to feasibility of the in-situ bioremediation. The field testing was initiated in May 1999 and was completed in December 2000.

2.0 SUMMARY OF RESULTS

2.1 Initial Sampling and Testing

The initial sampling and analysis was documented in a report dated April 14, 1999 which was submitted to ADEQ.

Table 1 summarizes the results of the hydraulic conductivity tests which were completed in March 1999. The results range from 1.04×10^{-5} ft/min (5.28×10^{-6} cm/sec) to 2.08×10^{-3} ft/min (1.06×10^{-3} cm/sec).

Table 2 summarizes the results of the sampling and analysis of the monitor wells. The wells were sampled March 9-10, 1999. Important results were the following:

- pH values among the 10 wells ranged from 3.39 to 5.27 and averaged 4.03. This pH is inhibitory to the growth of many microorganisms. The optimum pH range for denitrification is 7.0 to 8.0. pH would need to be raised for enhanced bioremediation of nitrate.

- Dissolved oxygen (DO) concentration among the 10 wells ranged from 0.24 mg/L to 1.3 mg/L and averaged 0.6 mg/L. The DO concentrations suggest denitrification is limited in part due to the presence of DO. Adding organic substrate to the water would use up the DO in microbiological mediated oxidation/reduction reactions, and it should not limit enhanced bioremediation of nitrate.

- Total organic carbon (TOC) among the 10 wells ranged from 2.8 – 51 mg/L. These values indicate that some areas may have significant natural organic matter to support denitrification, if pH is raised.

- Phosphorous was <0.05 mg/L in all but one well and is likely to be a limiting nutrient for denitrification. Consequently, phosphorus would probably need to be added for enhanced bioremediation.

Based on these results, an approach was developed for the preliminary field tests. Since pH appeared to be the primary inhibitor of natural denitrification, groundwater pH adjustment by addition of sodium carbonate to the groundwater was planned. Phosphate was also to be added, in the form of trisodium phosphate. Sodium citrate was chosen as the organic supplement since it is readily utilized by microorganisms and also provides some pH buffering.

Monitor wells MW-11 and MW-17 were chosen for the preliminary field test. Test protocol was as follows:

- Groundwater from the test wells is extracted from the wells and collected into containers (e.g., 55 gallon drums) located next to the well. The groundwater from the drums is amended with nutrients and well mixed. The pH and dissolved carbon dioxide is tested and sodium carbonate is added, if necessary, until the pH is between 6 and 6.5. Groundwater in the containers is then returned to the wells by siphoning the water though flexible tubing. The test wells are sampled weekly and analyzed for selected parameters. During each sampling event, approximately one casing volume is removed from the well before samples are collected for analysis. After samples have been collected, an additional two casing volumes of water are removed from the well. Purge water withdrawn from the well is returned to the well after the addition of additional nutrients and/or sodium carbonate. Nutrient additions are adjusted based on the most recently available groundwater data. After each sampling event, the available data are evaluated to determine if field changes are required to the preliminary field test.

2.2 Preliminary Field Testing

The preliminary field tests in MW-11 and MW-17 were conducted during May 27-August 6, 1999 and were documented in a report dated October 13, 1999 which was submitted to ADEQ.

The initial amendments to the groundwater were as follows:

- Groundwater volume withdrawn-initially 20 and 50 gallons at MW-11 and MW-17, respectively, and 7 and 17 gallons, respectively, after May 27, 1999.
- Carbon/electron donor source-trisodium citrate at approximately 31 and 27 mg/l at MW-11 and MW-17, respectively.
- Phosphate-trisodium phosphate at 3.8 and 10 mg/L at MW-11 and MW-17, respectively.
- pH buffering-soda ash to bring pH to between 6 and 6.5.

Nitrate, pH and other parameters were monitored in the withdrawn groundwater. Withdrawal and amendment of groundwater was on a weekly basis from May 27 through July 8, 1999 and was completed every other week from July 8 through August 6, 1999.

Based on monitoring results, additional pH buffering and nutrients were added in the amendments during the course of the test. The pH was adjusted to 7.5 – 8.5. Trisodium citrate concentration was increased starting July 1, 1999 to approximately 190 and 624 mg/L at MW-11 and MW-17, respectively. Trisodium phosphate was increased to approximately 19 and 24 mg/L at MW-11 and MW-17, respectively, starting July 1, 1999. The volume of groundwater withdrawn and amended at MW-11 was also increased to 55 gallons starting July 1, 1999. Beginning July 23, 1999, the withdrawn groundwater was also amended with glucose to an approximate concentration of 100 mg/L to provide additional carbon/electron donor source.

To evaluate the capability for denitrification under controlled pH conditions, a laboratory test was conducted as follows:

- On July 23, 1999, four samples were collected of withdrawn groundwater from MW-17 after addition of nutrient and pH buffering amendments. The samples were collected in BOD bottles, sealed and transported to the laboratory. The pH of the amended water was 8.5.
- One bottle was analyzed for nitrate and Total Organic Carbon (TOC) approximately each week for four weeks.

Tables 3 and 4 present summaries of the analytical results for the withdrawn groundwater (pre-addition of amendments) from MW-11 and MW-17, respectively. Note, the field test kit analytical results for nitrate were found to be unreliable, probably due to a negative interference, and are consistently much lower than the concentrations from the laboratory analyses. Consequently, the laboratory results for nitrate were used for interpretation of results rather than the field analyses.

Two analytes (pH and nitrate) are key in interpreting the results. The pH data indicate that the addition of soda ash as a buffering agent during the preliminary field test did not result in raising the in-situ groundwater pH to near neutral during the duration of the test. The pH at MW-11 was essentially unchanged by the addition of the amended groundwater and ranged from only 4.2 to 4.6 during the test. The pH at MW-17 increased from a low of 4.24 to a maximum of 6.2 during the test, but appeared to stabilize at approximately 5.9. Nitrate concentration at MW-11 and MW-17 was essentially unchanged. Nitrate concentration at MW-11 fluctuated within a range of 7.8 to 13 mg/L and at MW-17 fluctuated within a range of 66.9 to 102 mg/L.

By contrast, the samples of amended groundwater withdrawn from MW-17 on July 23, 1999 and analyzed in the laboratory at one-week intervals demonstrated rapid and near complete denitrification. The analytical results were as follows:

- Nitrate concentration at time of sample collection – 98 mg/L.
- Nitrate concentration at approximately one week after sample collection – 0.01 mg/L.
- Nitrate concentration at approximately two weeks after sample collection – 0.04 mg/L.
- Nitrate concentration at approximately three weeks after sample collection – 0.03 mg/L.
- Nitrate concentration at approximately four weeks after sample collection – 0.31 mg/L.

These results indicate that the amended groundwater that had been kept in the laboratory in anaerobic conditions similar to that in the subsurface but with pH above 7 exhibited essentially complete denitrification within one week. Conditions toxic to denitrifying bacteria were not indicated, rather, the results indicate that the conditions in the amended groundwater are very

favorable for denitrification. Percent removals of nitrate ranged from 99.68 to 99.99 percent. The resulting nitrate concentrations were far below the MCL of 10 mg/L.

The preliminary field tests and laboratory test demonstrated that denitrification is potentially applicable to the site if sufficient additional base can be added to the groundwater to raise the in-situ pH to a range conducive to denitrification.

Consequently, additional field testing was conducted to determine whether it would be practical to raise the pH to near or above neutrality. The additional field tests focused on raising the in-situ pH to neutral or above at MW-17. MW-17 was selected since the nitrate concentration is much higher than at MW-11. Note that nitrate concentrations at MW-11 were frequently (five of seven laboratory analyses) slightly below 10 mg/L during the preliminary field tests. In the additional field testing, pH was the only parameter monitored

The additional field tests involved installing four small diameter piezometers around MW-17 to be used for adding water pumped from MW-17 and amended prior to recharge through the piezometers.

2.3 Additional Field Tests

Four small diameter (1-inch) piezometers were installed with Geoprobe® type techniques in a semicircle upgradient of MW-17. The piezometers were located approximately 6 feet from MW-17 and were screened from approximately 19 to 29 feet below ground surface (bgs). Periodically, water was pumped from MW-17 and amended with sodium hydroxide or sodium carbonate to a pH of between 8.5 and 10. The amended water was recharged into each of the small diameter wells. pH of the water withdrawn from MW-17 was then measured.

These piezometers were installed during January 2000. The program of pumping water from MW-17, raising the pH of the water to 8.5 – 10 and recharging the water back into the piezometer was implemented by EDCC personnel beginning January 13, 2000.

Typically, only 100 to 200 gallons of water per week could be recharged. This was not sufficient to raise the pH of the groundwater. Consequently, on May 22, 2000, EDCC notified ADEQ that installation of four 2-inch diameter piezometers was planned in an attempt to increase the amount of amended water recharged. These piezometers were installed during June 2000 and were then utilized for recharging the amended water. These piezometers were screened from approximately 23 to 33 feet bgs. Table 5 shows the amount of recharged water and the pH of

water from MW-17 for each recharge event. The pH remained at 5 and the amount of water that could be recharged remained in the 100 to 200 gallon range.

A groundwater sample was collected by EDCC from MW-17 on January 15, 2001. The sample was analyzed for nitrate by Gulf Coast Analytical Laboratories, Inc. The nitrate concentration was 93.5 mg/L.

The results indicate that the procedures used were not able to raise the pH of the groundwater to the ranges at which denitrification would be effective.

3.0 CONCLUSIONS

The tests conducted at the EDCC site for enhanced bioremediation of nitrate confirmed that low pH conditions in the water are preventing denitrification. Laboratory tests determined that when the pH of the groundwater is raised and an organic substrate is added, denitrification can proceed rapidly. However, attempts to raise the pH of the groundwater in-situ to pH values favorable for denitrification were unsuccessful due to buffering of the low pH and the limited rate at which amended water can be recharged to the shallow groundwater. Raising the pH of the groundwater is expected to be prohibitively expensive and not practical. Consequently, EDCC is terminating the field tests of enhanced in-situ bioremediation.

If you have questions or comments please contact me at (225) 756-1431.

Very truly yours,

Dennis E. Reece

DER:wv

Attachments

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TABLES

TABLE 1

SUMMARY OF HYDRAULIC CONDUCTIVITY VALUES
EL DORADO CHEMICAL COMPANY
EL DORADO, ARKANSAS

Monitor Well Number	Hydraulic Conductivity (ft/min)		
	Slug In	Slug Out	Mean
MW-EDC-6	3.72×10^{-4}	4.92×10^{-4}	4.32×10^{-4}
MW-EDC-7	6.00×10^{-4}	5.98×10^{-4}	5.99×10^{-4}
MW-EDC-8	1.52×10^{-3}	2.08×10^{-3}	1.80×10^{-3}
MW-EDC-9	1.50×10^{-4}	1.56×10^{-4}	1.53×10^{-4}
MW-EDC-10	7.30×10^{-5}	1.04×10^{-5}	4.17×10^{-5}
MW-EDC-11	1.33×10^{-4}	3.12×10^{-4}	2.23×10^{-4}
MW-EDC-14	1.49×10^{-4}	1.77×10^{-4}	1.63×10^{-4}
MW-EDC-15	1.88×10^{-4}	1.58×10^{-4}	1.73×10^{-4}
MW-EDC-16	4.41×10^{-4}	5.70×10^{-4}	5.06×10^{-4}
MW-EDC-17	3.84×10^{-4}	3.84×10^{-4}	3.84×10^{-4}

NOTE: Slug tests were conducted in March 1999.

TABLE 2

ANALYTICAL RESULTS
SAMPLING AND ANALYSIS OF MONITOR WELLS
SAMPLES COLLECTED MARCH 9 AND 10, 1999
EL DORADO CHEMICAL COMPANY
EL DORADO, ARKANSAS

Analyte	Units	MW-EDC-6	MW-EDC-7	MW-EDC-8	MW-EDC-9	MW-EDC-10	MW-EDC-11	MW-EDC-14	MW-EDC-15	MW-EDC-16	MW-EDC-17
pH	S.U.	4.39	3.39	3.49	5.27	3.75	4.02	4.33	4.09	3.9	3.69
Specific Conductance	umhos/cm	1448	2852	8808	1948	1830	1020	853	260	1012	1008
Temperature	Degrees C	18.5	19.4	19.3	18.9	20.9	18.1	17.6	14.6	16.1	19.8
Turbidity	NTU	8.72	3.08	0.95	29.02	1020.68	26.72	56.9	5	3.01	5.93
Dissolved Oxygen	mg/L	0.4	0.25	0.29	1.1	0.43	0.24	1.3	0.34	0.33	1.11
Oxidation Reduction Potential	mv	102	384	188	94	180	155	133	142	161	144
Ferrous Iron	mg/L	ND	1.09	0.16	ND	0.07	0.03	ND	0.04	0.01	0.03
Carbon Dioxide	mg/L	83	980	990	80	155	275	155	118	100	115
Denitrifying Bacteria	CFU/ml	1000	Negative	Negative	Negative	1000	1000	Negative	1000	Negative	Negative
Total Iron	mg/L	0.071	0.9	<0.03	0.166	5.4	0.456	0.31	0.29	<0.03	0.055
Total Manganese	mg/L	0.516	0.789	0.764	0.354	0.594	0.097	0.092	0.135	0.508	0.581
Ammonia	mg/L as N	0.2	460	700	0.1	0.1	38.5	0.1	0.5	5.2	1.3
Chloride	mg/L	47.9	32.1	39.6	332	24.3	7.13	76.8	1	5.5	12.8
Methane	mg/L	0.0008	0.006	0.015	0.017	0.0006	0.18	0.003	0.003	0.002	0.014
Nitrate	mg/L as N	162	312	1060	26.5	187	10.2	27.4	28.4	120	86.5
Nitrite	mg/L as N	<0.01	0.2	0.05	0.06	0.31	0.03	0.02	0.02	<0.01	0.03
Sulfate	mg/L as SO4	12.6	373	80.8	438	143	368	20.6	10.2	<10	159
Total Alkalinity	mg/L as CACO3	<1	<1	<1	24	<1	<1	5	<1	<1	<1
Total Kjeldahl Nitrogen	mg/L as N	<1	154	510	1.5	<1	11.2	1.7	<1	<1	<1
Total Organic Carbon	mg/L as C	2.8	6.5	10.3	51	9.8	25.8	20.2	3.2	3.2	5.8
Total Phosphorous	mg/L as P	<0.05	<0.05	0.05	0.37	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

NOTES:

pH, Specific Conductance, Temperature, Turbidity, Dissolved Oxygen, and Oxidation Reduction Potential values are means of four replicate measurements.
Total Iron, Total Manganese, and Carbon Dioxide values are means of duplicate measurements.
Denitrifying Bacteria results are reported as either Positive -Aggressive(1000 CFU/mL) or Negative-NonAggressive (<1000).
ND indicates the analyte was not detected by the field measurement.

TABLE 3

ANALYTICAL RESULTS
PRELIMINARY FIELD TESTS
IN-SITU ENHANCED BIODEGRADATION MONITORING RESULTS FOR MW-11
EL DORADO CHEMICAL COMPANY
EL DORADO, ARKANSAS

Parameter	5/27/1999	6/3/1999	6/10/1999	6/17/1999	6/24/1999	7/1/1999	7/8/1999	7/23/1999	8/6/1999
pH (S.U.)	4.21	4.21	4.2	4.25	4.3	4.3	4.6	4.5	4.3
Dissolved Oxygen (mg/L)	0.42	0.41	0.41	0.34	0.32	0.25	0.35	0.36	0.4
Carbon Dioxide (mg/L)	250	325	400	NA	350	400	350	NA	350
Nitrite (mg/L as N)	0.02	0.08	0.05	NA	0.7	0.07	0.05	NA	0.05
Phosphate (mg/L as P)	ND	ND	ND	ND	ND	ND	NA	0.1	ND
Denitrifying Bacteria (CFU/ml)	Negative	Negative	Negative	NA	Negative	NA	Negative	NA	Negative
Ferrous Iron (mg/L)	0.03	0.08	NA	NA	0.12	NA	NA	NA	ND
Oxidation Reduction Potential (mv)	350	NA	NA	303	322	327	272	192	NA
Field Nitrate (mg/L as N)	7	1	9	5	7	7	4	7	8
Laboratory Nitrate (mg/L as N)	NA	10.9	13	9.6	9	NA*	9.1	7.8	8
Ammonia (mg/L as N)	>3	7	>3	NA	>3	NA	>3	NA	>3
Total Kjeldahl Nitrogen (mg/L as N)	6.2	14	NA	NA	6.7	NA	NA	NA	5.9
Total Organic Carbon (mg/L)	24.2	22.9	21.8	NA	27.8	NA	24.5	NA	40.8
Alkalinity (mg/L as $CaCO_3$)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Temperature (degrees C)	18.5	21.3	20.4	20.7	19.4	20.2	19.4	20.8	20.5

NOTES:
ND = Not Detected
NA = Not Analyzed
* Indicates sample bottle broke during transport to the laboratory.

TABLE 4

ANALYTICAL RESULTS
PRELIMINARY FIELD TESTS
IN-SITU ENHANCED BIODEGRADATION MONITORING RESULTS FOR MW-17
EL DORADO CHEMICAL COMPANY
EL DORADO, ARKANSAS

Parameter	5/27/1999	6/3/1999	6/10/1999	6/17/1999	6/24/1999	7/1/1999	7/8/1999	7/23/1999	8/6/1999
pH (S.U.)	3.93	4.24	4.8	4.71	5	5.6	6.2	5.9	5.9
Dissolved Oxygen (mg/L)	0.49	0.51	0.5	0.9	0.43	1.4	3.65	0.43	1.2
Carbon Dioxide (mg/L)	120	130	120	NA	110	110	60	NA	70
Nitrite (mg/L as N)	ND	0.2	0.45	NA	0.4	0.5	0.5	NA	0.3
Phosphate (mg/L as P)	ND	ND	ND	ND	ND	0.15	0.45	0.4	0.8
Denitrifying Bacteria (CFU/ml)	Negative	Negative	Negative	NA	Negative	NA	Negative	NA	Negative
Ferrous Iron (mg/L)	0.02	0.07	NA	NA	0.05	NA	NA	NA	ND
Oxidation Reduction Potential (mv)	352	NA	NA	225	285	264	204	139	169
Field Nitrate (mg/L as N)	20	15	25	22	23	20	13	15	20
Laboratory Nitrate (mg/L as N)	NA	102	75	96	88	NA*	66.9	98	73
Ammonia (mg/L as N)	2.3	1.3	2	NA	2.5	NA	2.8	NA	3
Total Kjeldahl Nitrogen (mg/L as N)	ND	ND	NA	NA	ND	NA	NA	NA	ND
Total Organic Carbon (mg/L)	ND	3.9	ND	NA	4.3	NA	4.2	NA	4
Alkalinity (mg/L as $CaCO_3$)	ND	3	ND	ND	ND	NA	70	35	37
Temperature (degrees C)	19.2	21.3	19.4	20.1	20.3	18.8	18.9	19.2	19.5

NOTES:
ND = Not Detected
NA = Not Analyzed
* Indicates sample bottle broke during transport to the laboratory.

TABLE 5

SUMMARY OF VOLUMES OF AMENDED WATER RECHARGED THROUGH PIEZOMETERS AND PH OF GROUNDWATER IN MW-17 ADDITIONAL FIELD TESTS EL DORADO CHEMICAL COMPANY EL DORADO, ARKANSAS

Date	Volume Recharged (gallons)	pH of Groundwater at MW-17 (S.U.)	Adjusted pH of Recharge Water (S.U.)
13-Jan-00	150	5	9.5
18-Feb-00	120	5	9
07-Mar-00	100	5	9.5
17-Mar-00	100	5	9.5
28-Mar-00	200	5	10
07-Apr-00	140	5	9.5
13-Apr-00	200	5	10
19-Apr-00	200	5	10
01-Aug-00	150	5	10
02-Aug-00	100	5	10
28-Aug-00	150	5	10
29-Aug-00	150	5	10
30-Aug-00	150	5	10
31-Aug-00	150	5	10
05-Sep-00	150	5	10
06-Sep-00	150	5	10
07-Sep-00	150	5	10
09-Sep-00	150	5	10
11-Sep-00	150	5	10
13-Sep-00	150	5	10
15-Sep-00	150	5	10
18-Sep-00	150	5	10
19-Sep-00	150	5	10
20-Sep-00	150	5	10
14-Nov-00	150	5	10
28-Nov-00	150	5	10
29-Nov-00	150	5	10
30-Nov-00	150	5	10
01-Dec-00	150	5	10
04-Dec-00	150	5	10
05-Dec-00	150	5	10
06-Dec-00	150	5	10
07-Dec-00	150	5	10
08-Dec-00	200	5	10
Total	**5,110**		