

COGAC

(Chemically Oxygenated Granular Activated Carbon)

Combining In-Situ Chemical Oxidation, Bio-Stimulation and Carbon Adsorption for Maximum Effect in the Subsurface

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EXECUTIVE SUMMARY

COGAC™ is the culmination of 12 years of research on remedial injection technology. After extensive chemical analyses, micro-biological testing, post-graduate studies and field applications, Remington Technologies, LLC (Remington) developed and patented COGAC™ in July 2013. The result is a combination of Sodium Persulfate, Calcium Peroxide and Activated Carbon. This patented combination of oxidizers and activated carbon material was developed with a goal of creating a smooth transition from chemical oxidation to aerobic bacterial growth combined with carbon adsorption. COGAC™ allows for extended remediation after the application by promoting a favorable subsurface environment for a population bloom of native petroleum hydrocarbon/BTEX degrading aerobic bacteria.

The uniquely combined characteristics of COGAC™ (**Oxidation, Bio-stimulation and Carbon Adsorption**) drive remediation to the highest level for project closure in the shortest amount of time, usually at a cost less than traditional remedial approaches.

With 14 years of injection experience, combined with extensive bench scale, pilot scale and full scale data, Remington is able to provide an incomparable depth of expertise in this field. Over 750,000 pounds of COGAC™ has been injected at over 300 sites with an unprecedented success rate making Remington the leading resource for environmental consultants when it comes to developing an effective remedial approach utilizing injection technology.

HOW DOES COGAC™ WORK

COGAC™, in one application, utilizes three of the most commonly known mechanisms for in-situ injection remediation of subsurface hydrocarbons and chlorinated compounds. These are [In-Situ Chemical Oxidation \(ISCO\)](#), [Bio-stimulation and Carbon Adsorption](#). The use of activated carbon also provides a microscopic bio-habitat for degrading bacteria.

In-Situ Chemical Oxidation - ISCO

Chemical oxidation of contaminants uses the strong attraction of electrons in the oxidizer to remove an electron from the carbon-carbon bonds found in hydrocarbons. The result is the rapid separation of the methyl and ethyl groups from the benzene ring(s) and the subsequent breakdown of the ring itself. The daughter products are carbon dioxide, water and hydrogen.

The oxidation of contaminants in-situ using oxidizers first utilized primarily Fenton's Reagent, which is a process involving the creation of hydroxyl radicals from catalyzing hydrogen peroxide with either heat, metal (ferrous iron most commonly) or high pH. Beginning in 2001, Remington injected over one-million gallons of catalyzed hydrogen peroxide at hundreds of sites across the country. During this time, Remington became aware of the many challenges associated with this process. In particular, the rapid exothermic reaction of the hydrogen peroxide in contact with subsurface organic matter (including naturally occurring material) proved to be problematic (surfacing) and created potential safety concerns (explosive surfacing, rapid expansion into utilities and potential for chemical burns).

Through funding research at the Colorado School of Mines, the hydroxyl radical from Fenton's Reagent was compared to the persulfate radical from catalyzed sodium persulfate. Results of the research showed the extended reaction times associated with the sodium persulfate combinations lasted days to weeks, as compared to the hydrogen peroxide which lasted only minutes. Based on these research results, Remington transitioned rapidly to the use of sodium persulfate combinations.

Extensive bench scale testing of the various commercially available oxidizers indicated that the most cost effective combination was hydrogen peroxide activated sodium persulfate. However, to avoid the short reaction times associated with hydrogen peroxide, Remington began bench scale testing calcium peroxide as the catalyst. Bench test results with sodium persulfate catalyzed by hydrogen peroxide ([Sample T-1](#)) and calcium peroxide ([Sample T-](#)

4, Table 1) showed similar reductions in benzene concentrations, however the reaction time was slowed dramatically with calcium peroxide. This extended reaction time allowed the remedial material to come into contact with additional impacted subsurface materials, therefore increasing the potential for remediation. As demonstrated in Table 1 (a representative sample test), bench scale test results comparing COGAC™ and other oxidizers, indicate that COGAC™ is the most effective remedial material at reducing benzene concentrations.

Table 1

Groundwater - Benzene					
	BEFORE (ug/L)	AFTER (ug/L)	REDUCTION (ug/L)	% REDUCTION	CORRECTED % REDUCTION
T-1 (SP/HP 4:1)	640	210	430	67.2%	74.8%
T-2 (CP/HP 4:1)	624	436	188	30.1%	37.7%
T-3 (CP/FeEDTA 4:1)	624	151	473	75.8%	83.4%
T-4 (SP/CP 1:1)	614	231	383	62.4%	70.0%
T-5 (RegenOx®)	592	201	391	66.0%	73.6%
T-6 (CP)	549	418	131	23.9%	31.5%
T-7 (COGAC-N™)	597	0.76	596	99.9%	107.5%
T-8 (COGAC™)	541	0.63	540	99.9%	107.5%
T-9 (PersulfOx®)	639	457	182	28.5%	36.1%
T-10 (Standard)	554	596	-42	-7.6%	0.0%

Table Key: SP=Sodium persulfate, HP=Hydrogen Peroxide, CP=Calcium Peroxide, FeEDTA=Chelated Iron

Economic “Final Cost Factor”

In addition to the data collected for each test, Remington designed an economic model that combines laboratory data with the known costs for 2,000 pounds of material used in these tests. The model takes this dollar figure and assumes a linear decline to 0.0 ug/L benzene based on the observed decline.

The end result is the “Final Cost Factor”. This figure does not reflect absolute cost, but it does provide a useful tool for economic comparisons of the different materials. As shown on Table 2, COGAC™ had the lowest “Final Cost Factor”. As is often observed in these calculations, the relatively low cost of hydrogen peroxide and sodium persulfate makes this combination competitive in the “Final Cost Factor”. However, one factor that is not well represented by the testing process is the rapid reaction time of the hydrogen peroxide, which may result in

a lesser effective radius of influence (ROI) and therefore increase the "Final Cost Factor" beyond that of COGAC™.

Table 2

Groundwater - Benzene					
	COST FACTOR	COST/ % REDUCTION	EVENTS/ 100% REDUCTION	L & E COST	FINAL COST FACTOR
T-1 (SP/HP 4:1)	\$4,200	\$56	1.34	\$5,000	\$12,328
T-2 (CP/HP 4:1)	\$6,160	\$163	2.65	\$5,000	\$29,574
T-3 (CP/FeEDTA 4:1)	\$8,000	\$74	0.93	\$4,000	\$11,160
T-4 (SP/CP 1:1)	\$5,800	\$83	1.43	\$4,000	\$14,014
T-5 (RegenOx®)	\$6,000	\$82	1.36	\$5,000	\$14,960
T-6 (CP)	\$7,200	\$229	3.17	\$4,000	\$35,504
T-7 (COGAC-N™)	\$8,000	\$74	0.93	\$4,000	\$11,160
T-8 (COGAC™)	\$7,500	\$69	0.93	\$4,000	\$10,695
T-9 (PersulfOx®)	\$6,500	\$180	2.77	\$4,000	\$29,085

Table Key: L&E= Labor and Equipment, SP=Sodium Persulfate, HP=Hydrogen Peroxide, CP=Calcium Peroxide, FeEDTA=Chelated Iron

Field parameters were also collected from each test vessel. As shown on Table 3, the dissolved oxygen (DO) and oxygen/reduction potential (ORP) in COGAC™ was comparable to the oxidizers tested indicating that the carbon did not adsorb the oxygen generated by the oxidizers. This was one of the first indications that oxidizers could be combined with carbon such that the remedial properties of both materials can be utilized. The table below is typical of the bench scale data collected with an YSI 556 multi-meter groundwater monitoring device.

Table 3

Groundwater - Field Parameters					
	Conductivity (µS/cm)	TDS (g/L)	DO (mg/L)	pH	ORP (mV)
T-1 (SP/HP 4:1)	6931	3.643	35.54	6.39	345.3
T-2 (CP/HP 4:1)	2315	1.117	46.97	11.68	-27.0
T-3 (CP/FeEDTA 4:1)	2581	0.893	39.92	11.74	-20.8
T-4 (SP/CP 1:1)	4874	2.350	31.16	10.46	104.8
T-5 (RegenOx®)	3620	1.279	19.03	9.25	59.7
T-6 (CP)	2558	1.518	42.21	11.93	-61.5
T-7 (COGAC-N™)	3911	4.294	36.22	7.54	196.4
T-8 (COGAC™)	3770	1.968	44.27	7.58	180.1
T-9 (PersulfOx®)	7314	3.692	7.21	6.66	311.6
T-10 (Standard)	2618	0.834	0.70	7.54	-154.3

Bio-Habitat, Bio-Stimulation and Carbon Adsorption,

The goal of COGAC™ is to create a smooth transition from oxidation to bacterial degradation, while effectively remediating contaminated material to reach BTEX closure criteria for industry, state or federal funded projects. The activated carbon used in COGAC™ includes granular size particles for excavation backfill to micron size for injection into the subsurface. The process of activating carbon material facilitates the capability for adsorption of organic material to the surface and the micro-pores.

Through this activation process, adsorption sites are created for organics as well as bio-habitat for petroleum hydrocarbon/BTEX degrading bacteria. Bio-stimulation is promoted by oxidizers leaving the groundwater with highly elevated DO enhancing aerobic bio-activity. The sodium persulfate provides sulfate as an electron acceptor and nutrient while other nutrients are added on an as needed basis. Below is a picture of powdered COGAC™.



Fact: 1 Pound of Activated Carbon has as much as 3 million square feet of surface area for adsorption.

The COGAC™ oxidizer ratios have been developed and tested to provide a post-treatment neutral pH. In addition, the COGAC™ oxidizer mass was based on providing maximum oxidation without disrupting the native bacterial population in the injection area. Since the oxidation reaction will last for a few days or weeks, the bacterial degradation can continue as long as the environment is compatible.

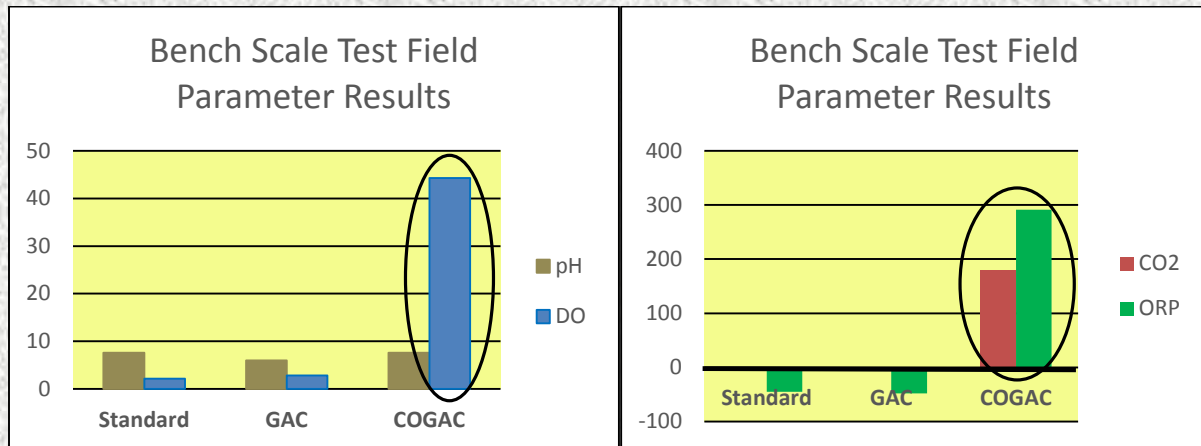
Remington conducted several bench scale tests comparing field parameters and microbial counts of COGAC™ and an activated carbon amendment with engineered microbes.

In Tables 4 and 5 and Graphs below, note that:

- COGAC™ showed increased levels of DO, CO2 and ORP
- COGAC™ remained at a neutral pH

Table 4

Amendment	DO mg/L	CO2 mg/L	ORP (mV)	pH
Standard	2.1	<100	-45	7.56
GAC	2.83	97.5J	-48	5.95
COGAC	44.27	180	291	7.58



- Microbial population increased with COGAC™

Table 5

Amendment	Initial Microbe Count cells/ml	Post Test Microbe Count cells/ml
COGAC	79,000	120,000
GAC	79,000	<2,000
Standard	79,000	79,000

SELECTING COGAC™ Bench Scale to Injection Application

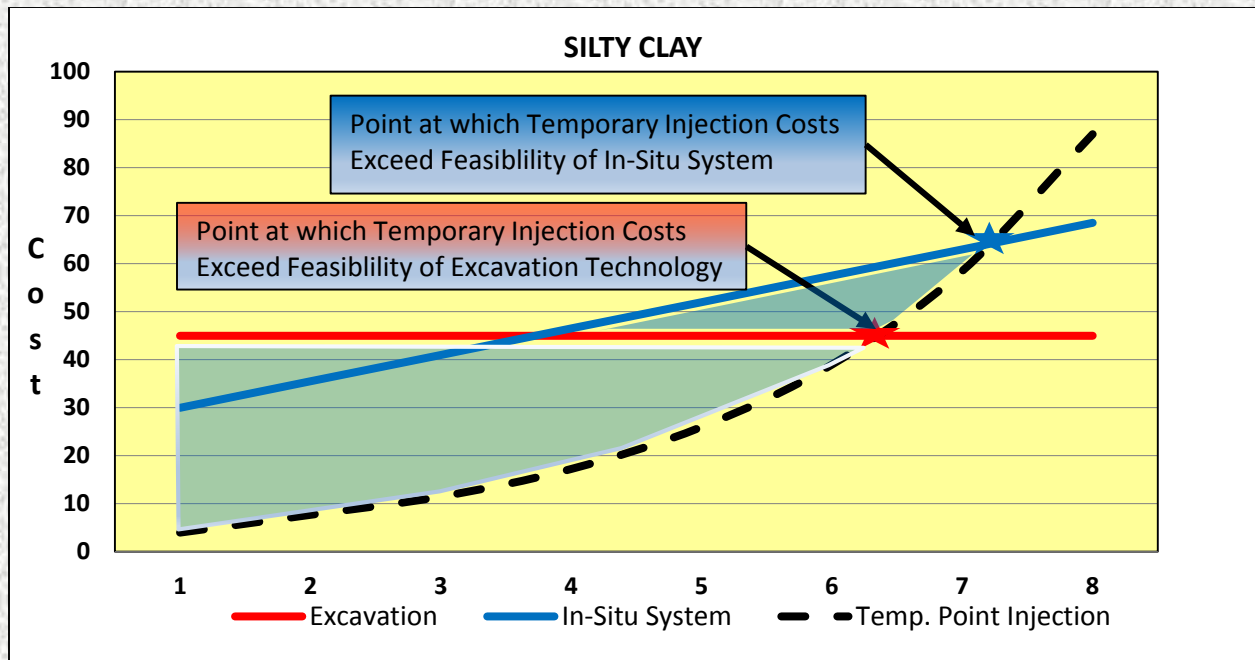
Remington's extensive experience with injection technology can be a key resource in reaching project remedial goals for site closure. With the unique combination of laboratory bench scale testing and field experience, Remington can apply this database to develop a technically and economically effective remedial approach utilizing injection technology.

Remington provides investigation and bench scale testing services to design and implement an effective remedial approach using COGAC™. In the absence of bench scale test data, site specific data are compared with our extensive library of data for every type of subsurface condition and contaminant suite. The data are then entered into our proprietary contaminant mass calculation software and the contaminant/remedial material ratio is determined. This ratio is then adjusted according to potential difficulties associated with the subsurface conditions to estimate the injection efficiency, or the assumed percent of injected material that will actually come into contact with the contaminant.

When possible, Remington's site evaluation and design is confirmed with a variety of pilot test options to confirm our assumptions, calibrate the contaminant/remedial material ratio and assess the injection efficiency factor.

Design of a full-scale injection event is always compared to the economic feasibility of the project. Occasionally, the injection of COGAC™ may not be cost effective until other remedial approaches are implemented. Remington's values and stewardship of a project's design helps ensure the highest probability of reaching the remedial goals through one or multiple technological approaches.

The graph on the next page is a representative comparison of the different technologies with contaminant mass increasing to the right on the x-axis. As shown, excavation if possible or a remedial system installation may be the most cost effective approach for highly impacted media. However, the range of contaminant mass at most sites or specifically the plume portion of a highly impacted source area indicates the economic feasibility of temporary point injection technology.



CASE STUDY

Chemically Oxygenated Granular Activated Carbon (COGAC™) Injection

This case study presents site information, contaminant mass calculation, injection design summary and results at a petroleum hydrocarbon underground storage tank release site.

Site Information

- Former Leaking Underground Storage Tank Project (Colorado)
- Chemicals of concern (COCs) BTEX, MTBE and TVPH
- Predominant lithology in the unsaturated zone is Silty Clay
- Predominant lithology in the saturated zone is Claystone
- Depth to groundwater ranges 5 to 21 feet
- Hydraulic Conductivity is 1.55×10^{-6} cm/sec
- Hydraulic gradient is 0.138 ft./ft.

Contaminant Mass Calculation

A contaminant mass calculation was prepared to determine the required remedial mixture and solution quantities for the treatment area. Remington utilized average soil and groundwater concentrations and a 1,800 square feet treatment area to calculate contaminant mass. Based on these assumptions, the calculated mass was estimated to be 107.6 pounds. Table 6 summarizes the

contaminant mass calculation and COGAC™ quantity summary for the treatment area.

It was also estimated that injection efficiency in this type of material was 20% and that 5 pounds of remedial material was needed for each pound of contaminant. Therefore, the estimated dose, based on the contaminant mass calculation for the site was approximately 2,691 pounds.

Table 6

Mass Calculation and COGAC™ Quantity Summary			
Site Data (Adsorbed Phase)	Units	Quantity	Comments
Benzene	mg/Kg	0.964	Average Soil Conc. Near MW-2, 9, 13
Toluene	mg/Kg	3.531	Average Soil Conc. Near MW-2, 9, 13
Ethylbenzene	mg/Kg	1.520	Average Soil Conc. Near MW-2, 9, 13
Xylenes	mg/Kg	7.531	Average Soil Conc. Near MW-2, 9, 13
TVPH	mg/Kg	69.6	Average Soil Conc. Near MW-2, 9, 13
Sum of Constituents	mg/Kg	83.1	Average Soil Conc. Near MW-2, 9, 13
Water Table High	ft.	12.76	Avg. of MW-2,9 and MW-13
Water Table Low	ft.	15.10	Avg. of MW-2,9 and MW-13
Vertical Water Table Fluctuation	ft.	2.34	
Adsorbed Mass Calculation	Units	Quantity	
Top Interval	ft.	10.00	
Bottom Interval	ft.	18.00	
Vertical Thickness	ft.	8.00	
Treatment Area (Extent)	Sq. ft.	1,800	
Treatment Area Volume	cu ft.	14,400	
Conversion of Treatment Area Volume	cu yds.	533	
Conversion to Kilograms	Kgs	586,667	
Concentration	mg/Kg	83.1	Average Soil Conc. BH3
Milligrams	mg	48,778,596	
Sorbed Phase Contaminant Mass	lbs.	107.3	
Site Data (Dissolved Phase)	Units	Quantity	
Water Table High	ft.	12.76	
Water Table Low	ft.	15.10	
Vertical Water Table Fluctuation	ft.	2.34	
Benzene	mg/L	0.129	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
Toluene	mg/L	0.097	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
Ethylbenzene	mg/L	0.069	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
Xylenes	mg/L	0.060	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
TVPH	mg/L	3.50	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
Dissolved Mass Calculation	Units	Quantity	
Top Interval	ft.	12.14	Min WL: MW-1 and MW-2
Bottom Interval	ft.	14.69	Max WL: MW-1 and MW-2
Vertical Thickness	ft.	2.55	
Treatment Area (Extent)	Sq. ft.	1,700	
Treatment Area Volume	cu ft.	4,335	
Sum of Constituents	mg/L	3.9	Avg. GW Conc. @ MW-2, MW-9, MW-13 (9/25/12)
Treatment Area Volume	cu ft.	4,335	
Porosity	%	30%	Assumed
Dissolved Phase Contaminant Mass	lbs.	0.31	
Summary of Mass			
Adsorbed	lbs.	107.3	
Dissolved	lbs.	0.3	
Subtotal Calculated Mass	lbs.	107.6	
Assume Prior Remediated Mass	lbs.	0.0	0%
Total Calculated Mass	lbs.	107.6	
COGAC™ Quantity Estimates			
Number of Injection Point	points	23	
Injectate gallons per point	gal.	90	
Total Gallons per Treatment Event	gal.	2,070	
% Solution	% Injectate	15.5%	
Total Pounds of COGAC per event	lbs.	2,673	
Total Calculated Mass	lbs.	107.6	
Injection Efficiency 20% of Contaminated Mass	lbs.	538	See Note
Ratio of 5 pounds COGAC to 1 pound contaminant	lbs.	2,691	See Note
Number of Events	events	1	
Total Pounds of COGAC per project	lbs.	2,673	

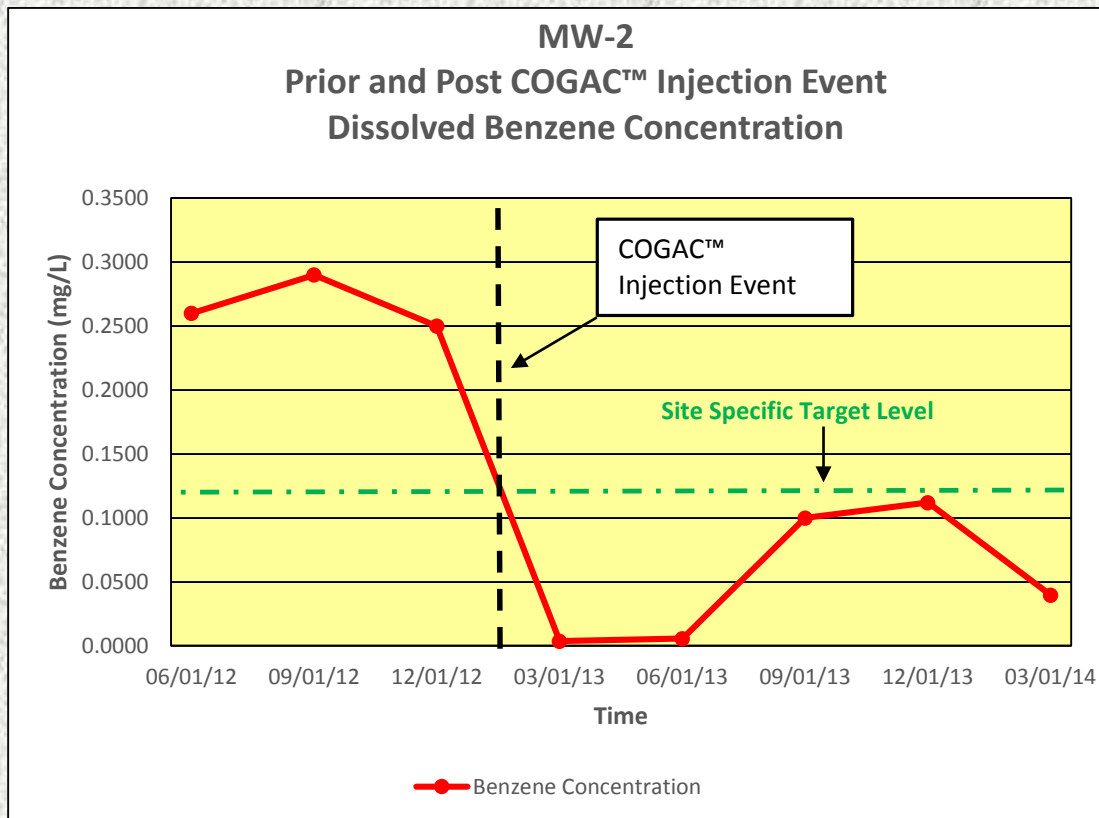
Note: It is estimated that the injection efficiency in this type of material is 20% and that 5 pounds of remedial material will be needed for each pound of contaminant. This assumption is currently being evaluated using ongoing studies.

Injection Design Summary

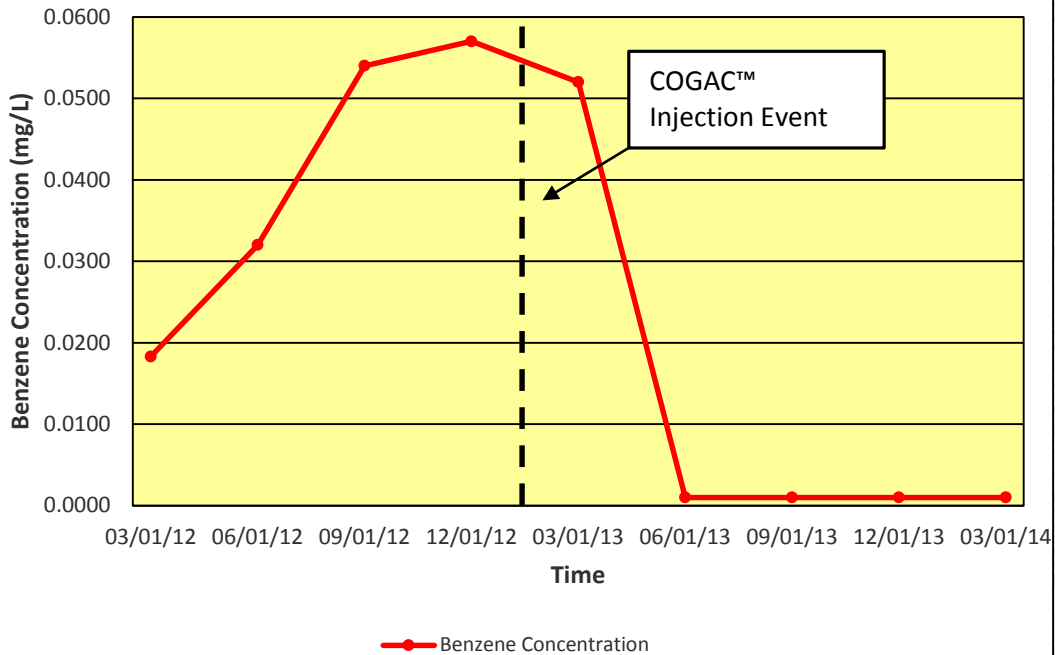
- 1,800 square foot treatment area
- Average BTEX, MTBE and TVPH 5,800 ppb
- Site specific target levels to obtain project no further action
- Varied treatment intervals 8 to 23 feet
- 23 injection points
- 15.5% COGAC™ Solution
- Direct push technology for injection points
- Average 90 gallons per injection point
- 2,673 pounds of COGAC™ remedial material
- Injections completed in 2 days

COGAC™ Remedial Injection Results

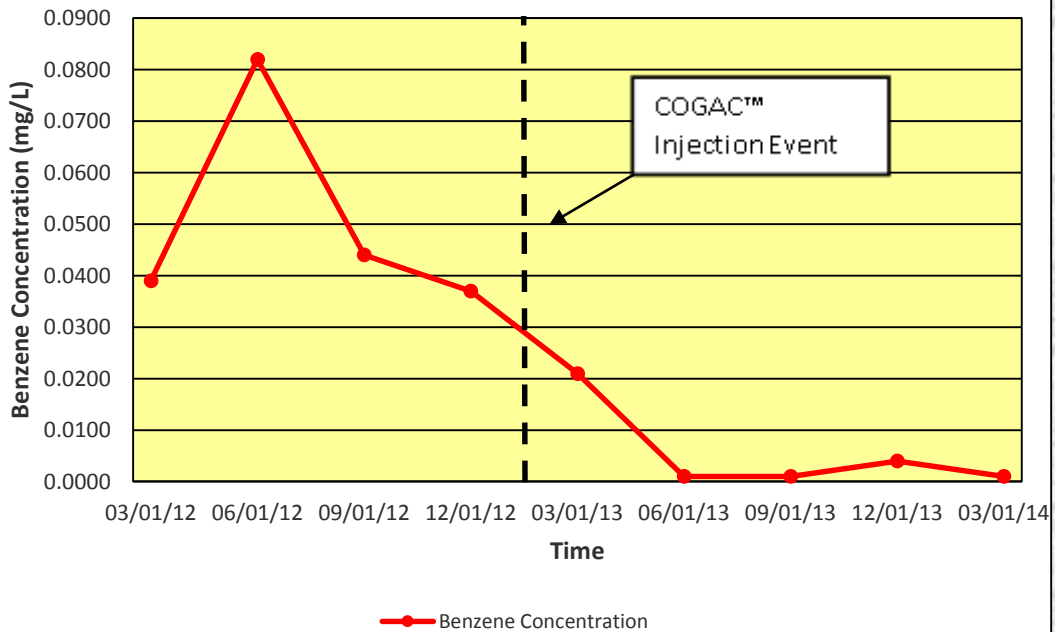
As shown on the following graphs, dissolved benzene concentrations decreased after the COGAC™ injection event. To obtain site closure, site specific target levels were utilized for MW-2 and the state dissolved benzene MCL of 5 ug/L was required for MW-9 and MW-13. Based on these results, the COGAC™ injection was successful in degrading the calculated contaminant mass remaining at the site. Regulatory remedial goals were achieved for no further action at this project.



MW-9
Prior and Post COGAC™ Injection Event
Dissolved Benzene Concentration



MW-13
Prior and Post COGAC™ Injection Event
Dissolved Benzene Concentration



This example is one of multiple case studies in which COGAC™ post-injection groundwater monitoring results indicate reduction of BTEX and TVPH constituents to below state remedial goals. It is the goal of Remington to provide a resource for consultants and their industry partners that will facilitate efficient and cost effective site closures.



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