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The Treatment of "MGP" Groundwater Contaminated with Complexed Cyanides, Heavy Metals and Various Organics Using a Three Stage Advanced Oxidation Process

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PART IV: Remediation

Chapter 6

THE TREATMENT OF "MGP" GROUNDWATER CONTAMINATED WITH COMPLEXED CYANIDES, HEAVY METALS AND VARIOUS ORGANICS USING A THREE STAGE ADVANCED OXIDATION PROCESS

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1. INTRODUCTION

This paper covers the results of a bench-scale pilot study carried out in order to develop a remediation technology that could be capable of treating contaminated groundwater commonly found at former manufactured gas plants (MGP) sites. These groundwaters are contaminated with complexed cyanide, heavy metals, polynuclear aromatics hydrocarbons (PAHs), and volatile organic compounds (VOCs), and are usually found at MGP sites across the US. The complexed cyanide compounds were commonly produced by the purification process of the gas. The process used for the gas purification involved a treatment with iron oxide impregnated onto solid materials (e.g. wood chips). Thus cyanide complexes of iron were also produced. The data generated by this subject bench-scale pilot test program originates from a pilot study treating groundwater from an MGP site in the Pacific Northwest. The groundwater at the site has elevated levels of contamination with complexed cyanide, iron, PAHs and VOCs and is hydraulically connected to a nearby surface water body. As such, the site is under order to restrict any untreated discharges of contaminated groundwater into the nearby surface water body and require the treatment of any permitted discharges.

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In order to meet these requirements, a groundwater extraction system has been proposed to carefully control any discharges into the surface water body. To meet the stringent discharge limitations proposed by the regulatory agency, a series of bench-scale semi-batch or semi-continuous flow treatment tests were conducted on the groundwater collected from the site. The bench-scale pilo plant testing was performed in order to evaluate and determine the capabilities of a proposed three stage advanced oxidation processes (AOP) to treat the contaminated "MGP" groundwater. The groundwater collected from the site was shipped overnight to the laboratory-pilot plant in Stamford, CT and was treated with a combination of treatment processes including ozone, hydrogen peroxide, and ultra violet (UV) light treatments and filtration for the removal of heavy metal oxides. The bench scale tests were carried out in two sequential treatment process steps; Pre-treatment Process and Main Treatment Process. The Main Treatment Process involved two steps: iron removal by ozone oxidation and filtration followed by final oxidation for the removal of organics.

2. RESULTS AND DISCUSSION

2.1 Pretreatment

In one area of the site the groundwater was found to have extremely high levels of dissolved iron (> 400 mg/L) and complexed cyanide. Based on the assumption that this area of the site would only make up a small portion of the total pumping volume of the contaminated groundwater, an oxidation pretreatment process step was selected and evaluated in order to control and minimize the need for groundwater movement. This area of the site had historically contained the wood chips impregnated with iron oxide. The pre-treatment experiments were carried out to assess and to compare the effects of three oxidant feed gases; air, oxygen, and ozone to be used for the treatment and removal primerely of iron and heavy metals, but also total cyanide, free cyanide, amenable cyanide, VOCs and PAHs from the water treated. The treatment was followed by filtration for the removal of iron oxides. Experiment 1 consisted of oxidation of the pretreatment water with an air feed for a 20 minute reaction periods. The iron oxide produced was removed by filtration. Experiments 2 and 3 were similar to Experiment 1 except oxygen gas or ozone was used for the oxidation. For Experiment 3 a 20 mg/l dosage of ozone was used. Based on the results it was determined that the ozone treatment had the highest level of oxidation and removal of iron and complexed cyanide (Figure 1).

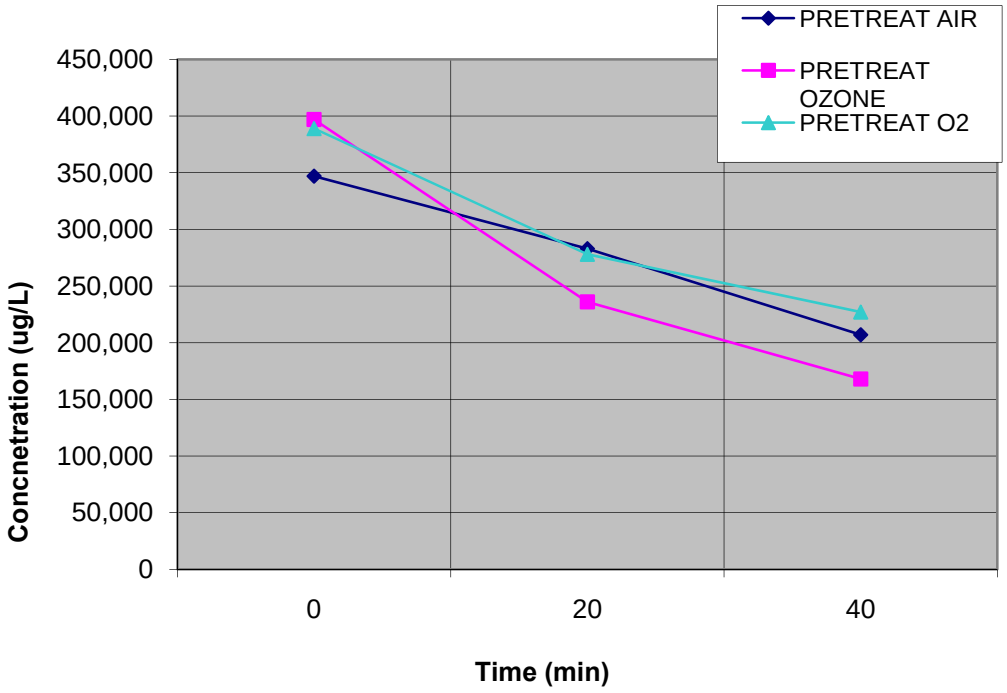


Figure 1. Pretreatment for iron removal

2.2 Main Treatment

Based on the Pretreatment Process test results, ozonation the most effective pre-treatment method was selected for use in the area of extremely high concentrations of iron and complexed cyanide. Next the Main Treatment Process, described below, was used for the complete treatment of a mixture of the a pre-treated water in combination with the remaining yet untreated contaminated groundwater from the site for a complete treatment of the entire groundwater flow. Within this stage of the bench-scale testing, an additional six experiments were carried out. During this Main Treatment Process treatability study the experiments were carried out to evaluate and study further the most promising treatment process parameters that are known to influence the ozone-H_2O_2-UV light reactions. For each experiment the water to be treated was made up from a mixture of a 20% aliquot of pretreated water and an 80% aliquot of untreated groundwater. Thus the total treated flow represented 80% of the flow necessary for groundwater control at the site. Groundwater that represented 80% of the total flow volume treated was collected from existing monitoring wells at the site that contained extremely high concentrations of VOCs and PAHs. These wells also

contained dense non-aqueous phase liquid (DNAPL) and elevated levels of iron and complexed cyanide. The Main Treatment experiments were carried out for a maximum reaction time of 90 minutes. Sampling was conducted at 0, 20, 60, and 90 minutes reaction time to evaluated treatment and dosage effectiveness. The first step of the Main Treatment Process is a treatment with ozone. Approximately 60 mg/L ozone dosage was added during the first 20 minutes of the reaction time to complete the oxidation of iron. Then the iron oxide was removed by filtration. Thereafter the filtered water was treated in a final polishing step with a combination of ozone, UV light, and H_2O_2 in an AOP process for the removal of residual organics. The process parameters were varied throughout each experiment as shown in Figure 2.

2.3 Main Treatment Experiments

2.3.1 Experiment 5

The pretreated aliquot, 20% of the total, was mixed with groundwater representing the 80% of volume flow and subjected to further treatment with approximately 100 mg/L ozone and UV light during a 90 minutes reaction time.

2.3.2 Experiment 6

As with Experiment 5, the pretreatment aliquot was mixed with groundwater representing the 80% volume flow. Then the water was treated with 5.0 mg/L H_2O_2 and with approximately 100 mg/L ozone and UV light simultaneously during 90 minutes.

2.3.3 Experiment 7

This experiment was carried out similarly to Experiment-6 except the H_2O_2 dosage was 10.0 mg/L.

2.3.4 Experiment 8

This experiment was carried out similarly to Experiment-7 except there was no H_2O_2 dosage.

2.3.5 Experiment 9

This experiment was carried out similarly to Experiment-7 except the H_2O_2 dosage was 15.0 mg/L.

2.3.6 Experiment 10

This experiment was carried out similarly to Experiment-7 the H_2O_2 dosage was 10.0 mg/L, but the water sample was treated with lime to a pH of 8.5 for the removal of carbonates and hydro carbonates and possibly other free radical inhibitors.

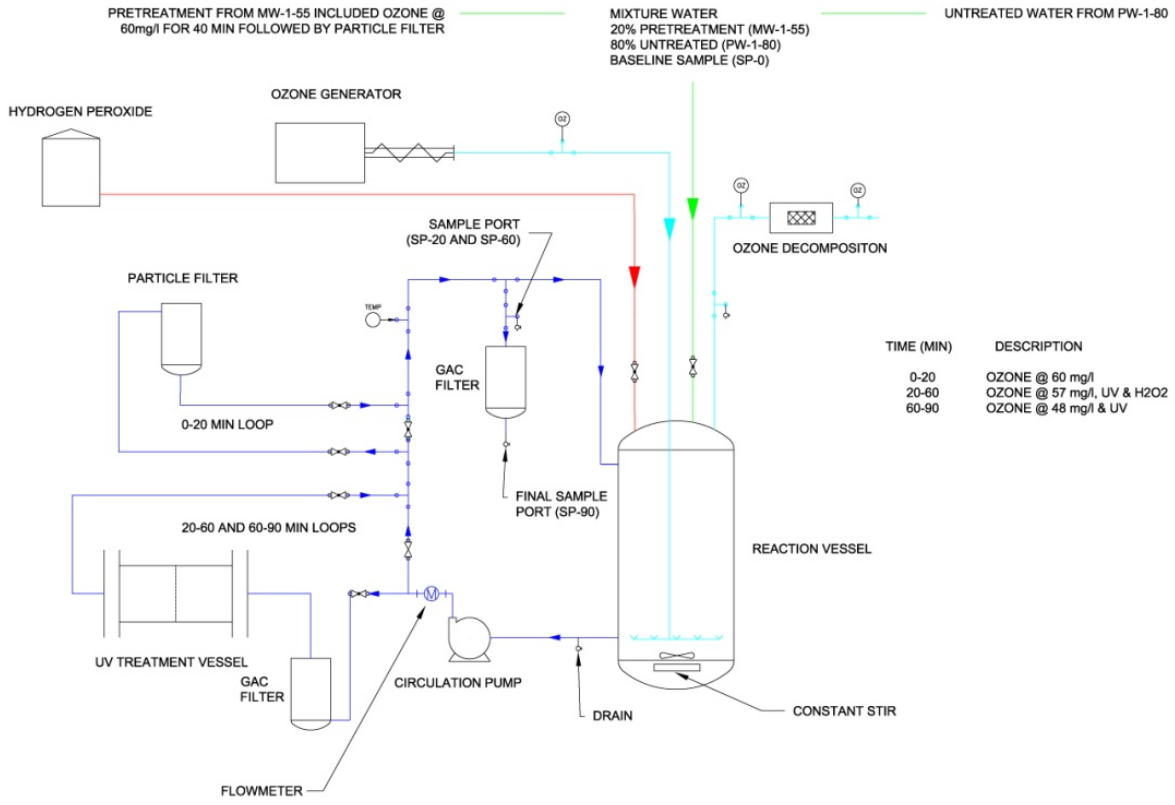
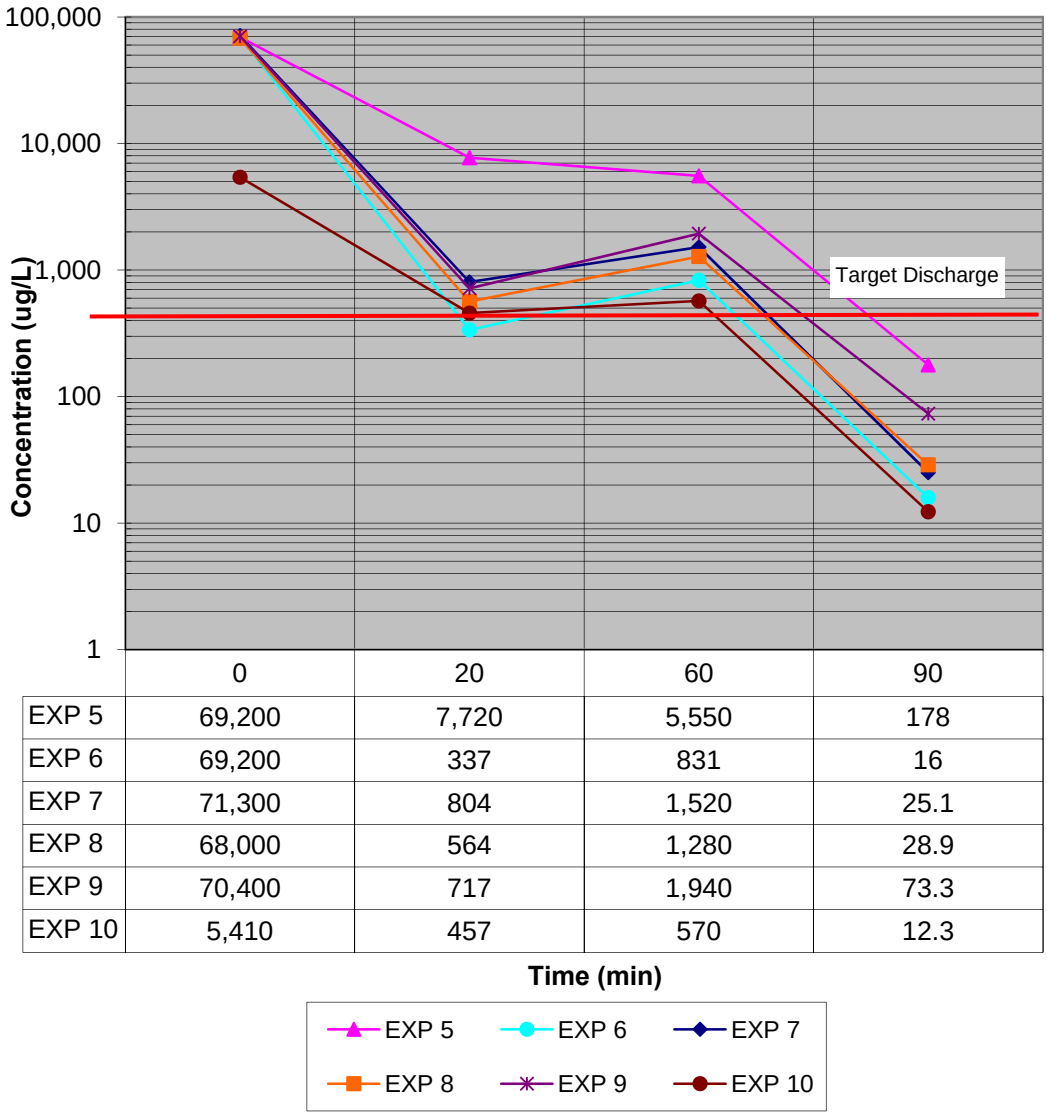


Figure 2. Main Treatment Process

Table 1. DEQ Proposed Discharge Limits

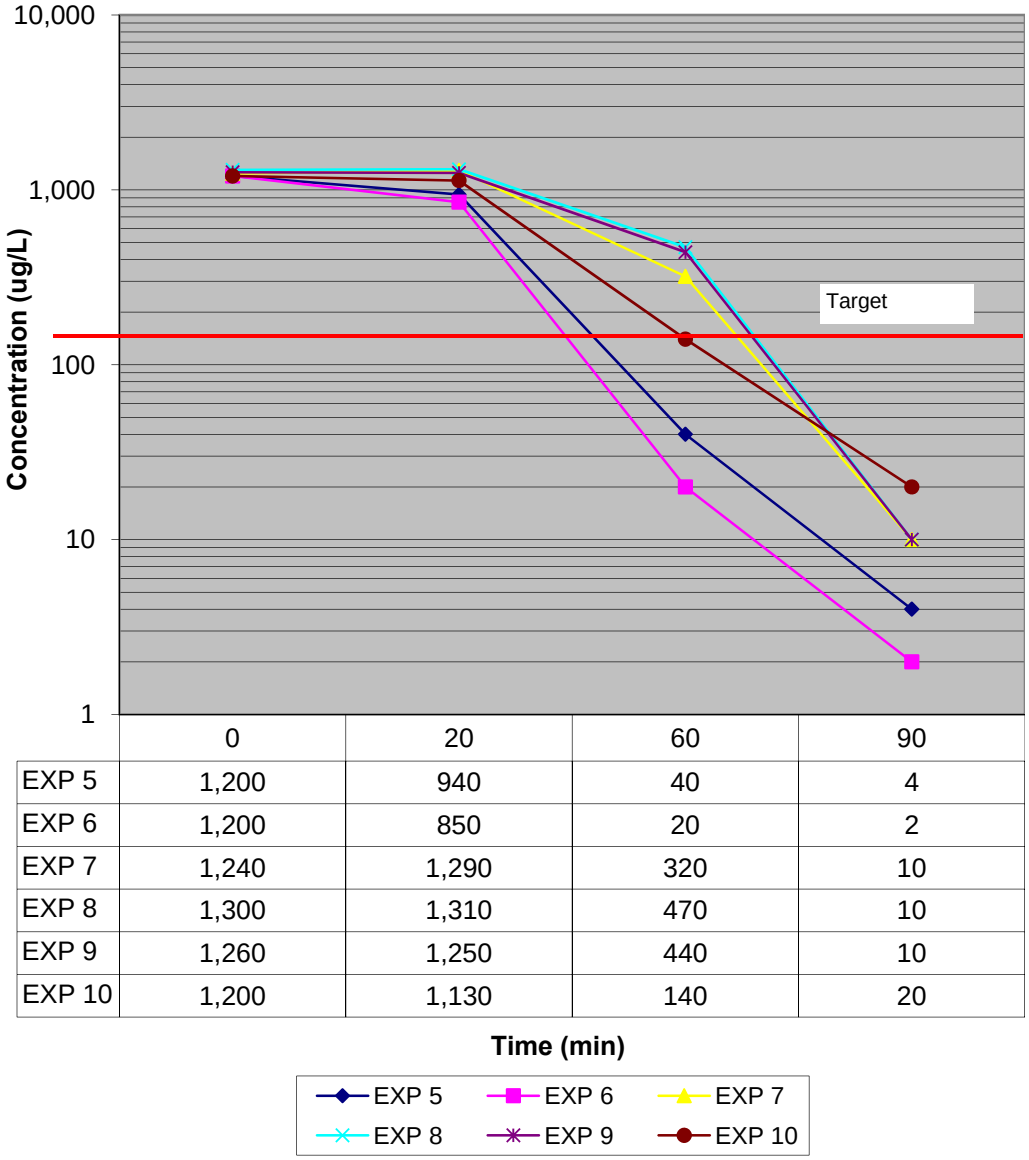
Parameter	**units**	**Limit**
Arsenic	ug/L	0.14
Cadmium	ug/L	0.094
Chromium (VI)	ug/L	11
Chromium (III)	ug/L	67
Copper ug/L	ug/L	2.7
Lead ug/L	ug/L	0.54
Mercury ug/L	ug/L	0.012
Nickel ug/L	ug/L	49
Selenium ug/L	ug/L	35
Silver ug/L	ug/L	0.12
Zinc ug/L	ug/L	33
Iron	ug/L	1,000
Manganese	ug/L	100
Free Cyanide	ug/L	5.2
Total Cyanide	ug/L	140
TPH	mg/L	1
Oil & Grease	mg/L	10 & 15
pH		6.5-8.5
Temperature	F	68
Benzene	ug/L	25
Total BTEX	ug/L	250
Trichloroethene	ug/L	30
Tetrachloroethene	ug/L	3.3
Vinyl Chloride	ug/L	2.4
Benzo(a)anthracene	ug/L	0.032
Benzo(b)Fluoranthene	ug/L	0.032
Benzo(k)Fluoranthene	ug/L	0.032
Benzo(a)pyrene	ug/L	0.032
Chrysene	ug/L	0.032
Dibenzo(a,h)anthracene	ug/L	0.032
Indeno(1,2,3-cd)pyrene	ug/L	0.032
Total PAHs	ug/L	250
Total Phenols	mg/L	0.5/0.7

Results from the experiments (Figures 3 – 6) indicated that all advanced oxidation processes proved effective in reducing the target compounds to below regulatory discharge limits. However, the most effective treatment process involved the treatment with ozone plus hydrogen peroxide and plus UV light. No pH adjustment was necessary.



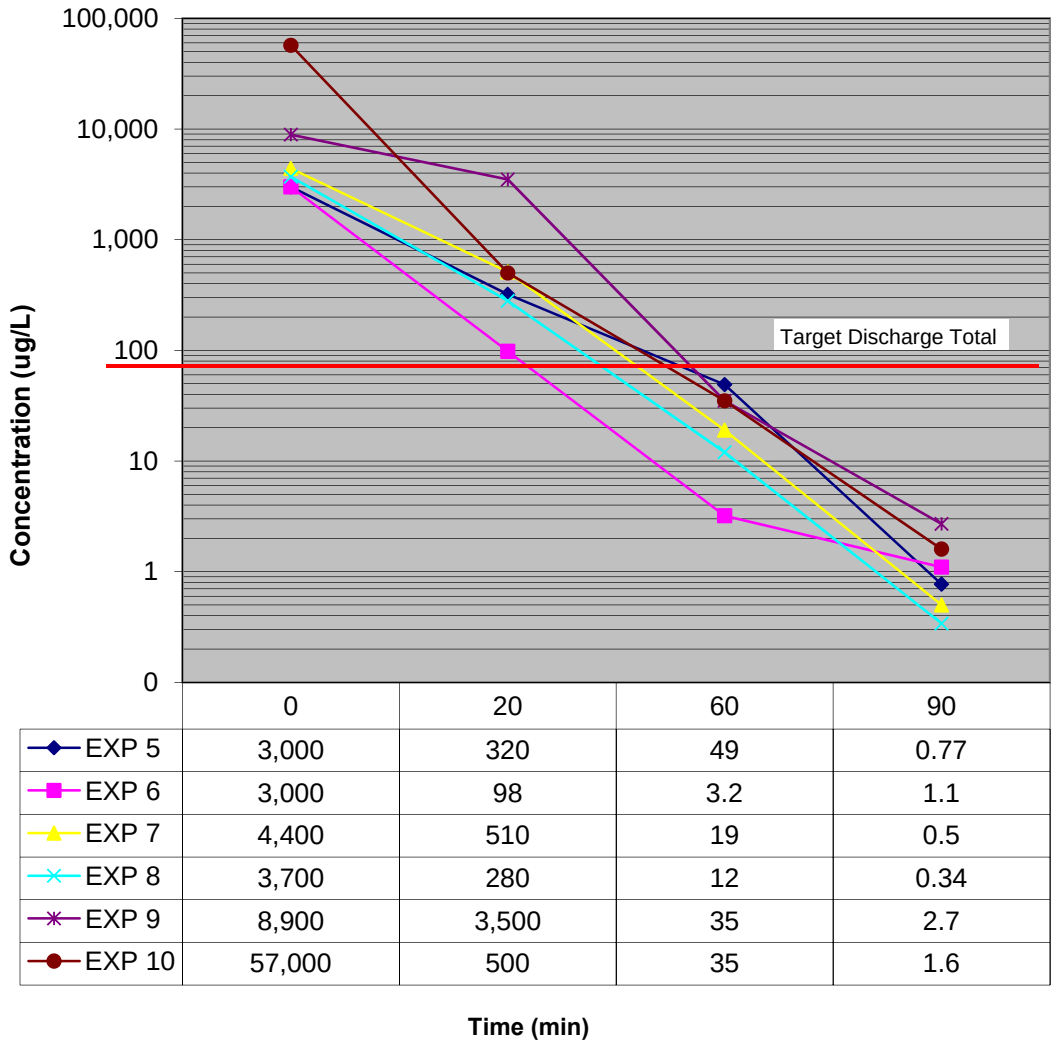
	0	20	60	90
EXP 5	69,200	7,720	5,550	178
EXP 6	69,200	337	831	16
EXP 7	71,300	804	1,520	25.1
EXP 8	68,000	564	1,280	28.9
EXP 9	70,400	717	1,940	73.3
EXP 10	5,410	457	570	12.3

Figure 3. Results of Main Stream AOP: Iron Removal



	0	20	60	90
EXP 5	1,200	940	40	4
EXP 6	1,200	850	20	2
EXP 7	1,240	1,290	320	10
EXP 8	1,300	1,310	470	10
EXP 9	1,260	1,250	440	10
EXP 10	1,200	1,130	140	20

Figure 4. Total CN Removal

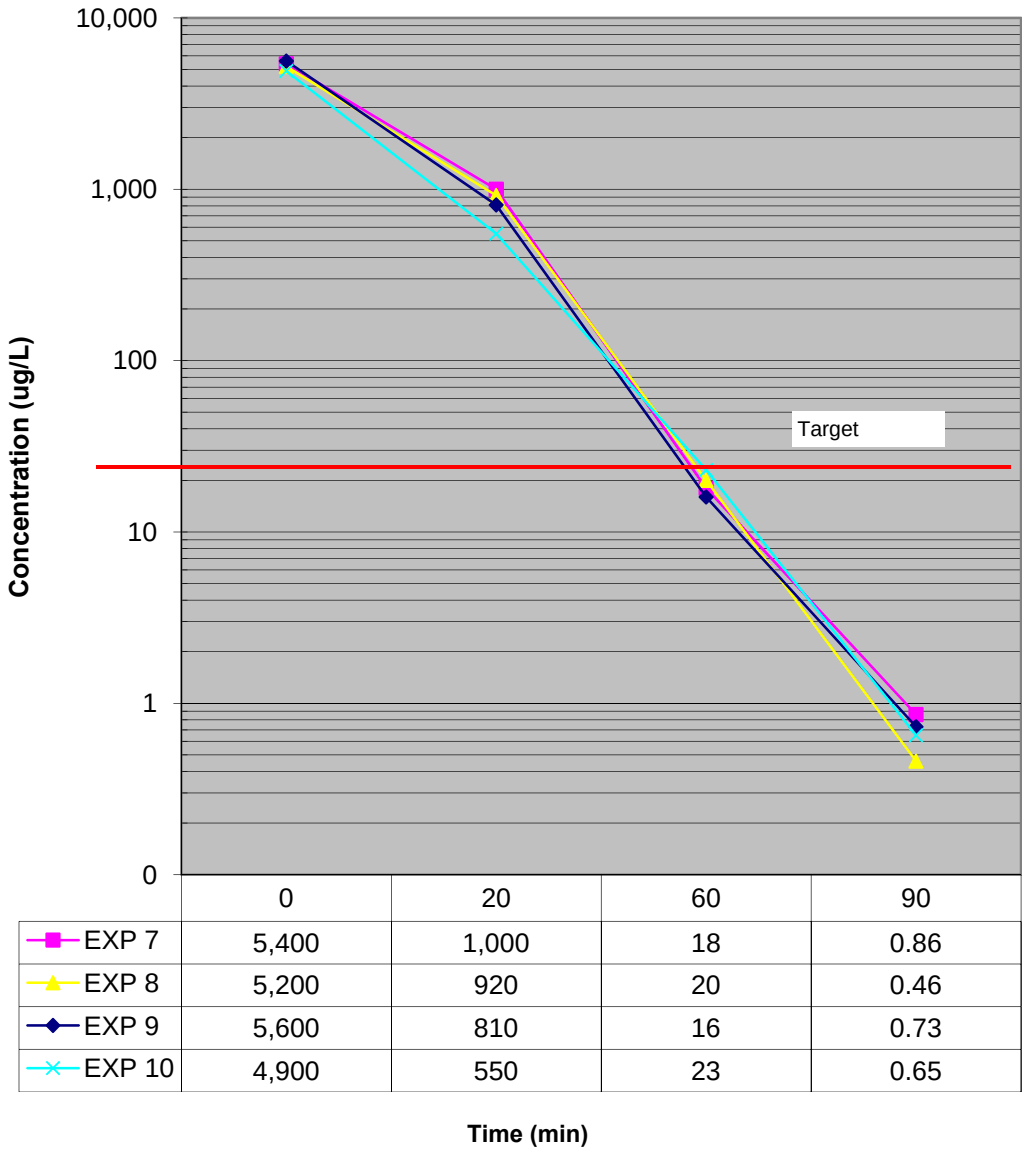


	0	20	60	90
EXP 5	3,000	320	49	0.77
EXP 6	3,000	98	3.2	1.1
EXP 7	4,400	510	19	0.5
EXP 8	3,700	280	12	0.34
EXP 9	8,900	3,500	35	2.7
EXP 10	57,000	500	35	1.6

Figure 5. Naphthalene Removal

3. CONCLUSION AND RECOMMENDATIONS

Based on the results of these AOP treatment experiments, it appears that the contaminated groundwater from this MGP site can be readily treated to achieve the surface water discharge limits as required by the governing regulatory agency. In order to further refine the treatment process and to determine the minimum required dosages of ozone, H_2O_2 and UV light intensity, further experiments could be carried out in a full-scale plant or a pilot plant could be could be constructed on site and operated to test the process under actual larger continuous



	0	20	60	90
EXP 7	5,400	1,000	18	0.86
EXP 8	5,200	920	20	0.46
EXP 9	5,600	810	16	0.73
EXP 10	4,900	550	23	0.65

Figure 6. Benzene Removal

flow conditions. The full scale plant or pilot plant could be run under continuous flow conditions while varying the dosages. For the treatment process experimentsdescribed herein there was no need for pH adjustment or the addition of other chemicals to treat the groundwater under continuous flow conditions. The full-scale pilot system would also allow for the gathering of additional information for solids handling and optimize filter design requirements. Shown

below is a conceptual full-scale process design based on the bench-scale results (Figure 7). It is sized for the treatment of a continuous flow of groundwater at the rate of up to 400 gpm.

The groundwater samples collected from the site for the subject study were analyzed and found to contain among others the following contaminants: Total Cyanide = 1,300 – 950ppb,, Benzene = 5,600 – 1,400 ppb, Naphthalene = 57,000 – 3,700 ppb, Iron = 452,000 – 69,200 ppb. The test results indicate that the subject "Pump and Treat" ozone process is superior to GAC (granular activated carbon) filtration in three respects: 1) It removes the contaminants by complete oxidation and does not transfer them from the water to another location such as to the GAC for further treatment. 2) The carbon footprint is at the theoretical minimum. No other materials than the contaminants are oxidized. 3) The estimated cost of treating a groundwater flow of 400 GPM with the subject three stage ozone process indicates that it is less than half of the estimated cost of GAC treatment.

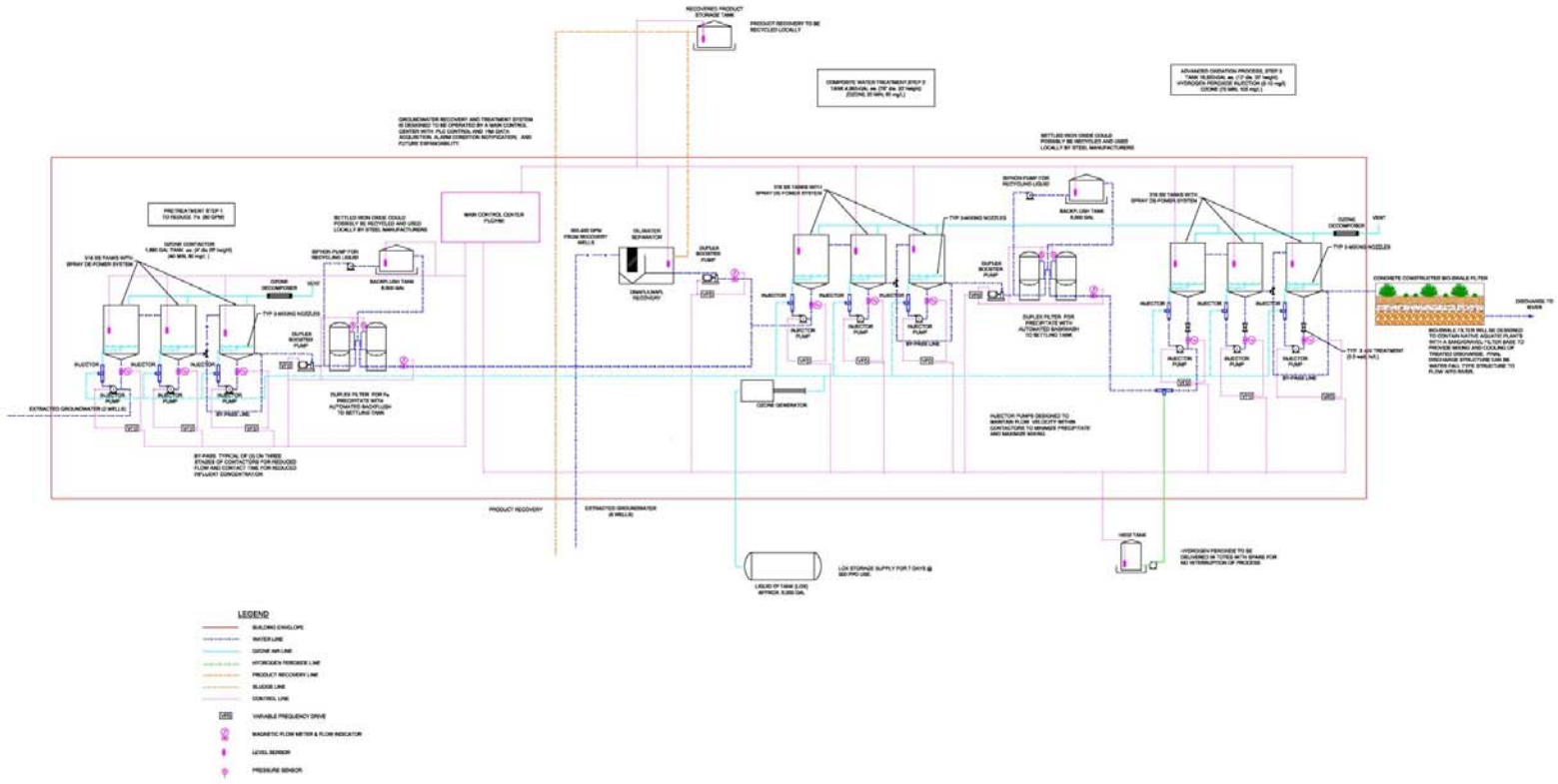


Figure 7. Conceptual full-scale process design based on the bench-scale results.