In Situ Groundwater MOP-UP

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**Topical Report
April 12, 1996 - May 11, 1998**

Work Performed Under Contract No.: DE-AR21-96MC33090

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In Situ Groundwater Cleanup of Heavy Metal Contaminants

EXECUTIVE SUMMARY

Groundwater dominates all other contaminated media in DOE's Environmental Restoration Program. Of the 792.8 million m³ total volume of contaminated media already known to require remediation, groundwater accounts for 89.3% (708.0 million m³). By contrast, soil, sediments, and ash together account for only 7% (58.5 million m³). Eight of the top 10 contaminants at DOE sites are heavy metals or radionuclides, i.e., chromium, lead, mercury, trichloroethylene, uranium, perchloroethylene, cesium-137, uranium-238, uranium-235, and strontium-90. Organics are found at only 150 of the DOE groundwater sites with remediation requirements, whereas 4,923 DOE groundwater sites require remediation for heavy metals and/or radionuclides. It is generally accepted that reactive barriers would offer significant improvements over conventional pump-and-treat technologies in life cycle costs, safety, and utilization of the land above the contaminated plume – provided that suitable reactive media can be developed. To be practical, these media must take a wide range of inorganic contaminants to extremely low levels, exhibit high loading capacities for these contaminants, function effectively under the widely fluctuating conditions found at contaminated sites, and be inexpensive as well.

Under this FETC-funded program, Biopraxis proposed to demonstrate the feasibility of using its new MOP-UP® technology for *in situ* treatment of metal-contaminated groundwater. The Savannah River Site (SRS) D-Area Coal Pile Runoff Basin was chosen for two reasons. It was contaminated by Pb and Cd, both of which are of very high concern throughout the DOE complex. More importantly, it represented an extremely challenging problem, because the groundwater was strongly acidic (pH 1.8-2.0) and contained parts per thousand levels of iron and sulfate; low pH and high iron or sulfate content will interfere with or prevent effective and economical treatment of heavy metal cations by conventional or emerging technologies. Two goals were established for this initial program. (1) At the end of the program, a laboratory demonstration with a sample of groundwater collected at a suitable site must show that > 90% of the Cd and Pb could be removed under the conditions (pH, temperature, and dissolved oxygen) found at that site. And (2) the data developed on the contract must indicate that the *in situ* groundwater MOP-UP® technology will either be more cost effective than conventional technologies while achieving the same degree of groundwater purification, or be at least as cost effective as conventional technologies while offering superior performance.

Due to a number of unexpected factors – most notably, a sharp rise in the pH of the SRS D-Area site groundwater and concomitant disappearance of the Cd and Pb contamination after the FETC program was well under way – coupled with the extraordinary performance of the MOP-UP® reagents, the first goal was changed. Instead of optimizing the technology to demonstrate the feasibility of its use at a single site, the final series of tests were designed to showcase the breadth and flexibility of the MOP-UP® technology by demonstrating its capabilities in as many different groundwater environments as possible. Sites that were contaminated with metal pollutants of wide-spread concern to DOE were located; and MOP-UP® reagents were screened for their ability to treat any or all of these metals – without any attempt to optimize the technology for use with the new target metals and/or for treating these metals under the diverse conditions found at the sites. Groundwater samples exhibiting a wide range of environments were generously provided by DoD, EPA, and private industry as well as DOE for use in these treatability tests. The tests showed that MOP-UP® can readily remove all detectable traces of a wide variety of metals, such as Hg, Pb, Cd, Cu, Cr(VI), As, Ba, Zn, and Al, and take U into the low parts per trillions, in heavily polluted groundwater, with little or no effort needed to optimize the reagent formulation.

The studies conducted on the FETC program demonstrated that MOP-UP® reagents take up as much as 4 to 5 times their own weight in metals, even when incubated in very dilute metal ion solutions. They are effective at pH extremes, taking up hundreds of milligrams per gram in

strongly acidic, low and sub-ppb solutions and thousands of milligrams per gram in heavily contaminated acid mine drainage at pH 2.8. They can treat complex mixtures of metal ions containing many other inorganics, such as iron, calcium, and sulfate. For example, when the pH of the SRS groundwater was spiked with 25 ppm each Cu, Cd, and Pb, and the pH adjusted, the Cu^{2+} was taken to nondetectable levels at pH 0.1. All detectable Cd and Pb as well as Cu were removed at pH 1.0. When ^{109}Cd and ^{210}Pb radiotracers were added to samples of the SRS groundwater that did not contain any detectable (< 0.002 ppm) Cd or Pb, MOP-UP® reagents removed all detectable radioactivity – i.e., the Cd and Pb were taken to very low- or sub-parts per trillion.

The treatability tests were very simple – and very challenging. They comprised a 2- or 4-hour incubation of the selected MOP-UP® reagents in the groundwater sample as received, without agitation, filtering, purging, or pH adjustment. The groundwaters ranged from those at neutral pH containing only trace levels of a single contaminant of concern, to those at strongly acidic pH containing high levels of metals, other inorganics, and organic contaminants as well. A handful of reagents were selected, on the basis of extremely limited information, for screening in each sample. Nevertheless, the MOP-UP® reagents performed so well that in almost all cases, the targeted metals were taken to nondetectable levels during the very first test with each of the groundwaters.

Kirtland Air Force Base (AFB) provided a sample of groundwater containing 0.07 ppm Ba. Although no testing had ever been done with Ba before, all three reagents chosen for screening took the Ba below the limits of detection by ICP-MS at the native pH of 7.85.

Hill AFB provided samples from two different sites. One of these, from Well U8-008, contained 0.35 ppm Cr(VI) and was at pH 7.58; three MOP-UP® reagents took the Cr(VI) to nondetectable levels. The second Hill AFB sample, pulled from Well U8-014, contained 0.064 ppm arsenic at pH 7.06; two of the reagents tested took the arsenic to nondetectable levels.

INEEL provided a sample of acid mine drainage containing 0.13 ppm arsenic and 0.15 ppm Cu, as well as 0.58 ppm Fe. Two reagents successfully removed all detectable arsenic and copper from this groundwater during the first treatability test.

The EPA provided a sample of acid mine drainage from the California Gulch CERCLA site. This strongly acidic (pH 3.17) groundwater typically contains 4,400 ppm sulfate and ~500 ppm each of iron, calcium, manganese, and magnesium. In the first test, without any treatment optimization or pH adjustment, one of the MOP-UP® reagents took 0.16 ppm Cd, 0.31 ppm Cu, and 0.26 ppm Pb to nondetectable levels. Two others showed high affinity for arsenic, taking the residual level as low as 0.002 ppm (91.7% removed), while simultaneously removing all detectable Pb.

The very first test ever conducted with acid mine drainage was done with water from the Berkeley Pit; in this test, 95% of the copper was removed from a pH 2.8 sample containing 222 ppm Cu, 552 ppm Zn, 290 ppm Al, 465 ppm Ca, 1,000 ppm Fe, 490 ppm Mg, 205 ppm Mn, 80 ppm Na, and 7,600 ppm SO_4 . In addition to 125 mg Cu/g, the reagents were also found to be simultaneously taking up high loadings of Zn (as much as 121 mg/g) and Mg (as much as 4,375 mg/g) – at this strongly acidic pH.

Groundwater at a private industrial site heavily contaminated with arsenic in both inorganic and organic forms [i.e., 20 ppm total arsenic, with ~ 50% being arsenic acid, ~ 40% As(V), and ~ 10% As(III)] has been found to be exceptionally difficult to treat; extensive studies found that only a very elaborate series of chemical treatments and separation steps could take out the mixture of arsenic species. Four reagents were screened in a preliminary test to determine whether treatment by the MOP-UP® technology would be feasible. The best of the four removed 97.6% of the total arsenic, at the sample's native pH, without any pre- or post-treatment. Even the reagent with the poorest performance removed 93% of the total arsenic on this very first try.

DOE is installing a funnel-and-gate treatment barrier test bed at the S-3 Ponds Area, Y-12 Plant, Oak Ridge. The groundwater in the area is heavily contaminated with a wide range of inorganic and organic pollutants, as well as high levels of other anions and cations. Therefore, this site appears ideal for demonstrating the unique capabilities of the MOP-UP® technology. Attempts to arrange for a shipment of a sample from the S-3 Ponds area in time for use on the current contract were unsuccessful. However, FETC has provided detailed information about the contaminants and the ranges of their concentrations that have been found throughout the site. Using this information, Biopraxis developed an S-3 Ponds groundwater 'simulant' containing all inorganics and organics found at more than half of the wells tested. The average concentrations of the groundwater constituents found in the wells were used in the simulant, with the exceptions of metals that are of wide-spread concern throughout the DOE complex, such as Cd, Cu, and Hg; for these high priority pollutants, Biopraxis used the maximum concentrations ever reported. The resulting mixture, which contains some 360ppm metals, 88ppm total organic pollutants (i.e., 3.8ppm TCE, 5.0ppm 2-butanone, 51.8ppm acetone, 7.0ppm chloroform, 3.2ppm toluene, and 17.3ppm methylene chloride), 1700ppm nitrate, and high levels of sodium, potassium, and chloride, was found to have a pH of 4.1; although this is considerably more acidic than the neutral groundwaters reported at most of the wells, Biopraxis elected not to adjust the pH, in order to challenge MOP-UP® to the maximum extent possible. The results were very exciting. A single screening run of five reagents was used to identify the most promising reagents. Formulations containing two of these were then used to treat the groundwater simulant. Analyses performed by an independent laboratory showed that, by using the mixed formulation, MOP-UP® was able to take the aluminum, cadmium, copper, zinc, and mercury all to nondetectable levels (the minimum level of detection for mercury was 500 parts per trillion); to remove 99.95% of the uranium, leaving a residual concentration of 180 parts per trillion; and remove 98% of the 15.2ppm barium. Since MOP-UP® reagents have taken barium to nondetectable levels in complex metal mixtures before, a slight adjustment of the process is expected take out the final 0.3ppm of that metal as well.

Under a matching Defense Conversion grant to evaluate adapting the MOP-UP® technology for treating electronics manufacturing effluents, all detectable Cd^{2+} , Pb^{2+} , and Cu^{2+} were removed from simulated semiconductor, printed circuit board, and cathode ray tube manufacturing rinsewaters containing solvents, other organics, and/or chelating agents, even at pH 2; and Cr(VI) and Ni were also taken to nondetectable levels readily by adjusting the pH to the neutral range at which these waters are approved for discharging.

Since the analysis of organics and nitrate are not covered under the FETC contract or matching DoD grant, the fate of these pollutants is not known. However, other studies indicate that the organics, and possibly the nitrate, may have been treated as well. A handful of simple, preliminary studies were conducted under an internally-funded project to evaluate the potential of the reagents for treating organic as well as inorganic pollutants. For example, one reagent was incubated for 24 hours with polyhalogenated and polyaromatic priority pollutants, including hexachlorobenzene, heptachlor and its *cis*-epoxide, aldrin, endosulphan and its sulfate, DDT and its analogs, carbetamide, chlorotoluron, fluoranthene, benzo(ghi)perylene, benzo(u)fluoranthene, indeno-(123cd)pyrene, benzo(b)fluoranthene, and benzo(a)pyrene; the reagent was then removed, and the water analyzed by GC-MS. The results showed that 15 of the 21 organics were below the minimum levels of detectability, less than 8% of 3 others remained, and less than half of each of the final 3 remained. There was evidence that the reagents were not just adsorbing, but degrading the organics; the concentration of chloride ion in solution rose sharply. Even if the solvents were simply being sorbed, the capacity of the reagent was extremely high, i.e., ~600 mg organics /g reagent. In another experiment, a handful of MOP-UP® reagents were incubated with a mixture containing 500 ppb each of fourteen halogenated solvents. Several reagents were found to remove the organics, being particularly effective with tetrachloroethene, carbon tetrachloride, trichloroethene, and 1,1,1-trichloroethane. One reagent, for example, took these solvents down to < 4 ppb, 13 ppb, 38 ppb, 40 ppb, respectively, while simultaneously removing more than half of each of the other organics. When the incubation period was extended, the residual levels of

organics continued to decrease. It should be noted that there was no attempt to optimize any of the conditions on either of these studies. In fact, on the latter study, a very limited amount of reagent was purposely added, to help determine whether adsorption or degradation phenomena might be involved. Very recently, Biopraxis evaluated the potential of MOP-UP® for treating explosives contamination, incubating four reagents in solutions containing 2,4,6-TNT, 2,4-DNT, and 2,6-DNT. Three of the reagents took TNT to nondetectable levels and significantly reduced the concentration of the DNT isomers, while the fourth reagent removed all detectable traces of all three pollutants. These results also provided direct evidence that chemical degradation processes, rather than simple adsorption phenomena, are involved, since traces of Am-DNT was found in all treated samples.

A handful of preliminary, internally-funded experiments indicate that the MOP-UP® reagents are just as effective at treating radionuclides as they are at treating heavy metal pollutants. These tests, done in "clean" laboratory solutions at neutral pH using a single MOP-UP® reagent, showed that ^{99}Tc , ^{137}Cs , and $^{239/240}\text{Pu}$ were taken to nondetectable levels from initial activities of 485.3, 1.415, and 202.2 Bq/ml, respectively. Radionuclide uptake was so rapid that residual ^{137}Cs was nondetectable by the time the first sample was collected for analysis, at 1 hour's incubation; and both ^{99}Tc and $^{239/240}\text{Pu}$ were at nondetectable levels within 2 hours. When $1/10$ th as much reagent was used, > 95% of the ^{57}Co and ^{60}Co and > 99% of the ^{63}Ni were removed from 0.26, 1.25, and 330 Bq/ml, respectively. Still lower reagent concentrations took up > 90% of ^{241}Am or ^{89}Y from an initial activity of 1.24 Bq/ml within the first hour of incubation. (No attempt was made to identify the most promising reagent for use in these studies, or to optimize treatment conditions.)

The second goal of the program was to show that the *in situ* groundwater MOP-UP® technology will either be more cost effective than conventional technologies while achieving the same degree of groundwater purification, or be at least as cost effective as conventional technologies while offering superior performance.

MOP-UP® has now been shown to be unusual in that it can be implemented in a variety of configurations, ranging from pump-and-treat to *in situ* reactive barriers, both permeable wall and treatment zone. MOP-UP® can therefore be compared as a pump-and-treat system against other pump-and-treat systems for use at locations where reactive barrier technology cannot be used; as a reactive barrier technology that can be substituted for conventional pump-and-treat; or as a reactive barrier that can be substituted for other emerging reactive barrier technologies.

The comparison that was originally proposed was *in situ* MOP-UP® versus conventional treatment technologies. It is generally accepted that, where such reactive barriers can be used, they offer significant improvements in life cycle costs, safety, and utilization of the land above the contaminated plume. As one example of the cost savings that can be achieved through the use of *in situ* permeable barriers, DOE Los Alamos National Laboratory estimated that the life cycle costs for a full-scale reactive barrier to treat one of its sites are expected to be 5 to 10 times less than those for excavation. A case study of the groundwater contamination problem at the Savannah River Site concluded that if conventional pump and treat remediation strategies were replaced with reactive barriers, savings of \$130 million, or 33%, of the current estimated costs for groundwater remediation could be saved. Longer range improvements to adapt reactive barrier for treating radionuclides would even more cost savings. The data developed under the FETC program indicate that *in situ* MOP-UP® will be highly competitive with emerging reactive barrier technologies – and, therefore, even more competitive by comparison against conventional treatment technologies.

Biopraxis elected to conduct an even more challenging evaluation, comparing MOP-UP® not just against conventional treatment systems, but also against emerging reactive barrier technologies. Two reactive barrier technologies for treating heavy metals and/or radionuclides have reached the commercialized stage, i.e., zero-valent iron for Cr(VI) and lime/limestone barriers for Pb. Reactive media that have been implemented in pilot and field-scale studies include ferric oxy-

hydroxide for the control of U and Mo, dithionite for the removal of Cr, V, Tc, and U, and zero-valent iron for the control of U. Hydroxyapatite for Pb and zeolites for ^{90}Sr , Pb, and Cd are considered to have shown good potential in laboratory studies. In general, the same types of barrier designs and the same barrier installation technologies can be used for MOP-UP® reagents as for any other reactive medium. Therefore, both performance and cost will be driven essentially by the performance of the reagents, and so the comparison was couched primarily in terms of the reactive media themselves.

Based on the findings in reports published by the EPA, the Federal Remediation Technologies Roundtable, the Ground-Water Remediation Technologies Analysis Center, and the company that is commercializing the zero-valent iron technology, MOP-UP® offers significant advantages over commercial and emerging reactive barrier technologies, in terms of both performance and cost.

One major difference between MOP-UP® reagents and other reactive media that quickly becomes clear is the number of heavy metals/radionuclides that can be treated effectively. Zero-valent iron is suitable only for metals such as Cr(VI) and U(VI) that are detoxified and immobilized by reduction processes. Limestone relies on chemical precipitation induced by raising strongly acidic pH in acid mine drainage, and is targeted at metals that are readily removed by pH adjustment without the need for careful control of the pH, such as Pb. Adsorbents such as iron oxyhydroxide typically have a much lower affinity for Cd and Ni than for other pollutants such as Cu and Pb; and parameters that optimize the uptake of U are very poor for the removal of Mo – both of which are found at UMTRA sites – and vice versa. Hydroxyapatite worked well for immobilizing Pb, but is inhibited from doing even this by the presence of other metals, including Al, Cu, Fe(II), Cd, Zn, and Ni. Although zeolites such as clinoptilolite exhibit reasonably high loadings for Pb and Cd, they take up no Hg or anions at all, even in clean laboratory solutions.

MOP-UP® reagents also take up exceptionally high loadings of heavy metals and radionuclides, and take residual contamination to far lower levels, by comparison with other reactive media. MOP-UP® has been shown to have far more promise for treating complex mixtures of contaminants, especially those containing both heavy metals/radionuclides and organics, than any other reactive barrier technology. And, finally, it has been shown to be far more effective at pH extremes.

A simple cost model has been used to estimate the costs for MOP-UP® reagents to be \$750-\$1500 per ton, depending on the particular reagent, when produced in 1-ton lots. (The costs plummet when production is in the 5-10 ton range.) A formulation for treating a complex groundwater environment is estimated to cost in the range of ~ \$1200 per ton. If one compares costs solely on a per-ton basis, therefore, MOP-UP® reagents appear to rank in the middle to high end of the spectrum of commercial and emerging permeable barrier reactive media. Activated charcoal costs ~ \$3,000 per ton. Zero-valent iron runs as high as \$1,200 per ton for some installations, with others in the ~ \$440-550 per ton range. (The "enhanced iron" needed at many sites, since it is doped with an expensive metal such as palladium, can be expected to cost substantially more.) The cost of the anhydrous FeCl_3 used to generate ferric oxyhydroxide *in situ* for treatment zones is \$250 per tonne; effective immobilized iron oxyhydroxide preparations have not yet been developed. Estimates for clinoptilolite have been as low as \$200 per ton, although this is, apparently, for the as-mined material, and not zeolite that has been sized and/or sodium-enhanced, either or both of which are needed for maximum efficiency.

Costs for *using* MOP-UP® reagents, however, are expected to be extremely attractive by comparison with other reactive media, because MOP-UP® reagents exhibit much higher loadings and selectivity for toxic groundwater constituents. The difference is perhaps best illustrated by comparing MOP-UP® with what appears to be the least expensive reactive medium, i.e., clinoptilolite. Clinoptilolite does not have the innate capacity of MOP-UP® reagents for removing cations from solution and, moreover, has a very high affinity for ubiquitous cations such as Na^+ and Ca^{2+} . When tested in acid mine drainage, clinoptilolite was found to have a loading value of

0.4 meq/g for all ions combined. Because the Ca^{2+} was taken up preferentially, the amount of zeolite required to treat the Al, Cu, Mg, and Zn in the groundwater was found to be 25 lb per 10 gallons. MOP-UP® reagents, on the other hand, have been shown to have loading values of ≥ 184 meq/g when incubated in Berkeley Pit water. Although the Pit has roughly the same amount of calcium and 10 times as much Cu, 50 times as much Zn, and 4 times as much Al, Mg, and Fe as the acid mine drainage used in the clinoptilolite studies, preliminary results indicate that only ~0.25 lb of MOP-UP® reagents would be needed to treat 10 gallons of Pit water. Costs for the MOP-UP® reagents needed to treat the highly contaminated Berkeley Pit water would therefore be $< 6\%$ those for the clinoptilolite needed to treat the far less contaminated Nevada mine water.

MOP-UP® promises to offer additional cost savings as well. For example, costs for construction of a barrier wall are typically much higher than those for the reactive media with which the wall is charged. The thickness of the treatment wall that is needed, which will be determined by the amount of contamination in the water, the groundwater flow rate, the loading capacity of the reactive media, and the time it takes for the reactive media to take the contaminants to the targeted levels, will, in turn, drive the construction costs. MOP-UP® reactive media not only exhibit high loadings but also very rapid reaction rates. All other factors being equal, the costs for a MOP-UP® barrier will be much lower than those for a barrier exploiting other reactive media because the width of the treatment wall needed to take contaminants to the targeted level by MOP-UP® reagents will be much narrower than the width needed by other reactive media. In addition, walls that exploit reactive media with very high loadings do not have to be recharged as often as those with low-load media. Replacing "spent" media more frequently will cost more, not just for the additional reactive media that will be needed, but also for the additional labor involved in performing the maintenance more often. When the reactive media has to be replaced, the "spent" media will require disposal. The higher the loadings that can be achieved by the reactive media, the lower the volume of hazardous sludge requiring disposal and, therefore, the lower the shipping and disposal costs. The loadings that MOP-UP® reagents take up are far higher than those of all reactive media for which loadings are known – often by orders of magnitude. Therefore, the maintenance and disposal costs for a MOP-UP® permeable barrier are expected to be much lower than those for a barrier exploiting any of the other reactive media identified to date.

Sites with plumes below 10-30 m cannot currently be treated with reactive barrier technology, since there is currently no way to emplace the barrier. Pump-and-treat systems utilizing chemical precipitation dominate the metal-contaminated groundwater treatment market, with a handful of "innovative" systems utilizing ion exchange or activated charcoal. The data produced under the FETC program show that pump-and-treat MOP-UP® also has the potential to offer performance that is orders of magnitude better than that offered by conventional pump-and-treat systems, taking residual contamination to much lower levels while treating much more complex contaminant mixtures. Capital costs for a MOP-UP® treatment system capable of producing a moist solid are projected to be roughly equivalent to or less than those provided by the Federal Remediation Technologies Roundtable for a system to accomplish just the chemical precipitation itself, without dewatering and drying. Chemical precipitation systems are far less expensive than ion exchange. Assuming a very conservative loading of 500 mg/g at neutral pH for the MOP-UP® reagents (which have been shown to take up $> 4,550$ mg/g at pH 3), and an average cost of \$1,200/ton for a formulation produced in relatively small lots (1 ton of each reagent), operating costs are projected at ~\$0.02 - \$0.15/1,000 L, which is very favorable by comparison with chemical precipitation, and even more so by comparison with ion exchange. Activated charcoal costs roughly twice as much as estimates for even the most expensive MOP-UP® reagents. Additional cost savings can be realized through the very high loadings taken up by the MOP-UP® reagents, which results in much lower volumes of sludge requiring transportation and disposal than conventional treatments.

In short, MOP-UP® far surpassed the goals established for this initial feasibility demonstration. This new technology promises to be extremely effective and very economical whether used in a permeable barrier for treating shallow plumes, or a direct injection or pump-and-treat configuration for treating deep-subsurface plumes of heavy metal, radionuclide, or mixed contamination.

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TOPICAL REPORT

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1. PROGRAM OVERVIEW

The top three environmental pollutants found most widely throughout the United States are the metals Pb, As, and Hg; trichloroethylene, the subject of so much attention, ranks a distant #13. However, while there are many alternatives for treating organic contaminants, metals (including radionuclides) comprise a significantly greater challenge and there are, accordingly, far fewer treatment alternatives.

In terms of sheer volume, groundwater dominates all other contaminated media in DOE's Environmental Restoration Program – of the 792.8 million m³ total volume of contaminated media already known to require remediation, *groundwater accounts for 89.3%* (708.0 million m³). Surface water and wastewater/liquids account for another 2% (14.4 million m³) and 1% (8.1 million m³), respectively, of contaminated DOE media requiring remediation. By contrast, soil, sediments, and ash together account for only 7% (58.5 million m³) of DOE's environmental remediation problem. These volumes may grow larger still, as characterization activities continue – information about the extent of contamination at many of the installations listed still is incomplete.

Eight of the top 10 contaminants at DOE sites are heavy metals or radionuclides, i.e., chromium, lead, mercury, trichloroethylene, uranium, perchloroethylene, cesium-137, uranium-238, uranium-235, and strontium-90. Metal- and radionuclide-contaminated plumes constitute the lion's share of the total number of groundwater sites requiring remediation. Organics are found at only 150 of the DOE groundwater sites with remediation requirements, whereas heavy metals are found at 1,597 sites, radioactive contaminants at 1,556 sites, mixed low-level waste (LLW) at 1,747 sites, and metal/organic contaminants at 23 sites, for a total of 4,923 DOE groundwater sites requiring remediation for heavy metals and/or radionuclides. Surface water containing radioactive, heavy metal, mixed LLW, or metal/organic contaminants are found at another 110 DOE sites requiring remediation.

Heavy metal contamination in surface- and groundwaters is a significant problem not only throughout the DOE complex, but also throughout DoD and EPA sites, and many polluted sites under the control of other Federal, state, and local agencies, and private industry. Radionuclide contaminants are found predominantly, although not totally exclusively, at DOE sites; otherwise, groundwater contamination problems throughout the Federal sector are very similar, and a technology suitable for treating heavy metal pollution at DOE facilities will be equally effective for use at other Federal facilities. Environmental remediation problems tend to be similar across all of these major market sectors, with groundwater being the most prevalent contaminated medium at NPL (76% of sites), RCRA Corrective Action (82% of sites), and DoD (71% of sites), and metals being prevalent in almost all media. Metals are found in 1,872 (59%) of DoD groundwater sites known to require cleanup, with lead, zinc, barium, and aluminum among the top eight contaminants found in groundwater. Of the 944 National Priorities List (NPL) sites with Records of Decision, 76% (721 sites) have contaminated groundwater; half of the dozen contaminants most commonly found to need remediation at NPL sites are metals, including lead, arsenic, chromium, cadmium, nickel, and zinc. EPA estimates that more than 80% ($\geq 2,100$ sites) of RCRA Corrective Action sites still remaining to be remediated have groundwater requiring remediation; the predominant constituents projected to be above action levels in these groundwater plumes include chromium, arsenic, and lead among the top five (with chromium at 47% of facilities, and arsenic and lead at 20% each), as well as cadmium, nickel, and selenium. One particularly significant source of heavy metal contaminated surface water and groundwater is acid mine

drainage. The runoff from over 300,000 abandoned hard rock mines has contaminated more than 12,000 miles of rivers and streams and over 180,000 lakes and reservoirs throughout the United States.

Reactive barriers that can accomplish both *in situ* containment and *in situ* treatment are considered a very promising approach for treating many such sites – provided that:

- (a) the reactive media can tolerate the range of conditions found at contaminated sites, and
- (b) a way can be found to ensure that the reactive media used in the barriers can be replaced as it becomes "spent."

Under this FETC-funded program, Biopraxis proposed to demonstrate the feasibility of using its new MOP-UP® reactive barrier approach for treating two heavy metal pollutants of widespread concern to all Federal environmental market sectors (i.e., cadmium and lead) under the conditions found at a single DOE site, i.e., the Savannah River Site (SRS) D-Area Coal Pile Runoff Basin. As the program progressed, MOP-UP® not only achieved the success criteria of demonstrating $\geq 90\%$ removal of both pollutants from SRS groundwater samples, but achieved $\geq 99\%$ removal of a wide range of heavy metal pollutants from diverse DOE, DoD, EPA, and private industrial groundwater sites, taking contaminants such as Hg, Cd, Pb, Cu, Cr(VI), As, Zn, Ba, and Al to levels nondetectable by ICP-MS (or cold vapor) and U down to 180 parts per trillion, in complex groundwater samples containing a wide range of metals, other inorganics, and organic pollutants.

1.1. The Original Proposal

Under this initial contract for DOE's Federal Energy Technology Center, Biopraxis proposed to demonstrate the feasibility of adapting MOP-UP® for the *in situ* containment and treatment of metal-contaminated groundwater. In one concept described in the proposal to FETC, a MOP-UP® reagent formulation would be pumped into the "gate," i.e., the filter wall, of a funnel-and-gate barrier. The formulation was expected to comprise select additives and microbial preparations, tailored to induce the microorganisms to produce a heavy coating of extracellular metal precipitates. After the reagents had taken up high loadings of heavy metals, they would be pumped to the surface and separated from the water by a proprietary separation technology called VCS; the water would be returned to the filter wall with a fresh batch of MOP-UP® reagents, while the solids fraction would be processed for disposal or the recycling of valuable metals.

The proposal to FETC called for Biopraxis to optimize the technology for treating groundwater under the conditions found at a single site; develop concepts for an *in situ* system, including process flow diagrams, materials balance sheets, and cost estimates, for treating the water at that site; and then compare the projected cleanup efficiency and cost estimates for the *in situ* groundwater treatment concept against those projected for conventional technologies to determine the performance and/or cost benefits of the MOP-UP® approach. According to the success criteria established for *in situ* groundwater MOP-UP®, the selected MOP-UP® formulation must be shown to be capable of removing $\geq 90\%$ of the targeted heavy metal pollutants from groundwater samples. In addition, the processing concept and the cost estimates developed on the contract must indicate that the *in situ* groundwater MOP-UP® technology will either (a) be more cost effective than competing technologies while achieving the same degree of groundwater purification, or (b) be at least as cost effective as competing technologies while offering superior performance.

At the Go/No-Go Decision Point, FETC was to determine whether the MOP-UP® technology appeared promising enough to warrant further development and demonstration. If determined feasible, based on the suitability of the technology as a solution for the problem as well as economic and environmental considerations, FETC would request Biopraxis to prepare recommendations for the additional effort needed to prepare for and conduct an on-site demonstration, first with a bench-scale, aboveground treatment system and then with an *in situ*

reactive barrier.

In preparing its proposal to FETC, Biopraxis elected to target the Savannah River Site (SRS) D-Area Coal Pile Runoff Basin for a number of reasons. First, and most importantly, this site is representative of the most difficult groundwater pollution problem facing Government and private entities, i.e., groundwater contaminated by acid leachates. Acid leachates (e.g., from coal pile runoff or mine drainage) create groundwater conditions that are strongly acidic (pH 2-4) and contain high levels of iron, aluminum, and sulfate, as well as a variety of heavy metal priority pollutants, and often contain other contaminants such as nitrate. Since the majority of the heavy metal pollutants of concern are cations, treatment of strongly acidic groundwater is particularly difficult. Iron interferes with many conventional and innovative approaches to groundwater treatment – most notably ion exchange resins and biosorbents – and sulfate complexes with many heavy metals, making it even more difficult to treat them. A technology shown to be effective at treating cation pollutants in the SRS groundwater would readily transition to many other sites, both Federal and private. Furthermore, the groundwater at the D-Area Coal Pile Runoff Basin was reported to contain lead, cadmium, and chromium, which are among the contaminants found most widely throughout the DOE complex, as well as other Federal and private remedial action market sectors. Finally, SRS had reported that a state-of-the-art funnel-and-gate barrier had been installed at this site, with an extensive network of wells that provide a 3-dimensional “picture” of the groundwater throughout the area, designed to demonstrate promising surface and *in situ* groundwater treatment technologies. Therefore, Biopraxis selected the SRS funnel-and-gate barrier at the D-Area Coal Pile Runoff Basin as the perfect site for showcasing the capabilities of its MOP-UP® technology; and designed this initial feasibility demonstration program to optimize *in situ* groundwater MOP-UP® for treating Pb, Cd, and Cr(VI) under the conditions reported at the gate of the barrier. Westinghouse Savannah River Company (WSRC) joined Biopraxis in preparing the proposal to FETC, and agreed to provide support on the initial feasibility demonstration program, as well as on any follow-on project for an on-site demonstration that DOE might fund.

1.2. Program Modifications

Due to a number of unexpected factors, the proposed program had to be changed after the program was already under way. The most significant of these factors, in terms of their impact on the technical approach used to demonstrate the MOP-UP® technology, were:

- Biopraxis originally proposed to utilize native microorganisms, enriched from samples collected from the funnel-and-gate barrier site. WSRC activities on this program, which included providing support to Biopraxis personnel in collecting suitable inocula, were to be funded directly through DOE. Various programmatic issues delayed such funding being in place until the program was into its sixth month – one-third of the way through the original 18 month period of performance. In order to minimize the impact on the schedule as much as possible, Biopraxis obtained samples from other suitable sites such as Edgar Mine in Colorado through contacts and friends, and obtained some isolates through culture collections. A single trip to SRS was subsequently arranged, and additional samples collected.

Some of the most promising MOP-UP® reagents have been developed with inocula from sites other than the SRS D-Area Coal Pile Runoff Basin.

- The barrier at SRS is not a funnel-and-gate, as originally reported. Instead, it is a hanging curtain with lateral pipes used to pump groundwater from the plume to the surface through an interceptor well. The only feasible approach that was conceived by the joint efforts of FETC, Biopraxis and its teammates, and WSRC personnel for using the hanging curtain as an “*in situ*” reactive barrier was to pump MOP-UP® reagents into the distal ends of the laterals, so the reagents could interact with the groundwater as it was pumped to the interceptor well, and then accomplish the separation step as the groundwater was pumped to the surface from the

interceptor well. This configuration decreased the reagent contact time with groundwater from the several days originally anticipated to, at most, 2-4 hours. The viable MOP-UP® reagent formulations could not be expected to accumulate enough metal in such a short period of time for subsequent separation by VCS to be efficient. Two alternatives were considered, i.e., switching from VCS to another proprietary MOP-UP® separation technology called "MSS"; and exploring the idea of changing focus from the viable microbial formulations emphasized in the proposal to a new type of nonviable microbial reagent briefly discussed but not considered to be a technology mature enough to be relied upon for the DOE program.

Biopraxis had already demonstrated the potential of this proprietary (patents pending) method of preparing new types of nonviable reagents for treating organic as well as heavy metal contamination before FETC awarded the contract; and studies had already shown these reagents to be capable of taking metals to extremely low residual levels even when incubated in the contaminated medium for a short period of time. The nonviable MOP-UP® microbial preparations are expected to be much more economical and "user-friendly" than the viable microbial formulations emphasized in the proposal; and, since they are nonviable, can be used in groundwater containing high concentrations of toxic constituents, both inorganic and organic. However, they are also a much more recent development; far less was known about their chemistries or about the impact of production parameters on their pollutant treatment properties, and there was very little basis for predicting they would be effective with the targeted heavy metal cations under the strongly acidic conditions of the SRS D-Area groundwater. Nevertheless, the many practical advantages associated with these reagents indicated that conducting "quick and dirty" experiments on the FETC program to determine whether Cd^{2+} and Pb^{2+} could be removed from strongly acidic solutions was warranted as a potential solution to the problem of adjusting to the very short groundwater contact time possible at the Savannah River hanging curtain barrier.

These "quick and dirty" experiments were a resounding success. For example, in the very first test conducted with the very first such nonviable reagent produced on the FETC program, 98% of the Cd was removed from a pH 3 solution within 30 minutes (the first time point at which a sample was analyzed). Emphasis was therefore shifted from viable to nonviable MOP-UP® reagents.

- Several months after the program was started, the groundwater at the SRS D-Area began to change dramatically in its composition. The pH of the water, which had remained steady in the 1.8 - 2.0 range for some 8-10 years, abruptly rose to ~4.0 - 4.2 and stayed there. Sulfate reducing activity increased, as evidenced by the strong smell of sulfide. The composition of the groundwater changed dramatically, with Cd and Pb disappearing completely, and the levels of iron, sulfate, and aluminum dropping sharply. The chromium and nickel concentrations rose, presumably due to sulfide leaching the metals from steel in the barrier and associated piping, pumps, and support structures.

Since the reason for the sharp change in the groundwater environment was unknown, the possibility remained that the groundwater would revert to its former set of conditions. For most of the remainder of the program, therefore, studies were performed with groundwater samples supplemented with spikes of Cd and Pb and with the pH adjusted to a more acidic level, to simulate the earlier composition. These studies showed that even when ^{109}Cd and ^{210}Pb radiotracers were added to SRS groundwater containing < 0.002 ppm Cd and Pb, all detectable radioactivity was removed, i.e., both Cd and Pb were taken to < 0.002 ppb in the presence of hundreds of parts per million each iron, sulfate, and aluminum, at pH < 3.

- As part of its support for Biopraxis, WSRC began providing additional information about the groundwater at the site. A paper on metal speciation was unearthed in August 1997 that reported the chromium in the groundwater at the site is exclusively in the trivalent form, presumably due to the highly acidic and strongly reducing nature of the groundwater. Trivalent

chromium is not nearly as mobile or as toxic as hexavalent chromium; and a number of emerging environmental remediation technologies rely on reducing Cr(VI) and leaving the Cr(III) in place. This narrowed the number of high-priority pollutants at the site to Cd and Pb.

- Sixteen months into the program, the SRS D-Area site showed no sign of reverting to its earlier status – both Cd and Pb continued to stay at nondetectable levels, and the pH remained in the 3.8 - 4.2 range. Due to the acidic, strongly reducing environment, the chromium was entirely in the trivalent form, and therefore in little need of treatment. This left nickel as the only heavy metal pollutant at the site – but present at artificially high concentrations due to the steel pumps and structures in the barrier. Since an on-site demonstration of Cd and Pb treatment obviously could not be held at the site unless the Cd and Pb concentrations rose to their earlier levels, Cr(III) removal is of little interest, and the source/speciation of the nickel contamination was questionable, the goals of the program clearly had to be modified. However, there was little time or money remaining on the program.

Although the only tests conducted to date had been with the pollutants found at the SRS D-Area site, Biopraxis proposed a bold move, i.e., to change the objective of the program from optimizing the technology for use at a single site, to showcasing the breadth and flexibility of the MOP-UP® technology by demonstrating its capabilities in as many different groundwater environments as possible. Biopraxis proposed to locate groundwater sites that were contaminated with metal pollutants of wide-spread concern to DOE; and to evaluate the ability of the MOP-UP® reagents to treat any or all of these metals – without any attempt to optimize the technology for use with the new target metals and/or for treating them under the diverse conditions found at the various sites. FETC agreed.

In December 1997, Biopraxis began treatability testing, using groundwater samples generously provided by DOE, DoD, EPA, and private industry. The simple tests showed that MOP-UP® can readily remove all detectable traces of a wide variety of metal pollutants, such as Hg, Pb, Cd, Cu, Cr(VI), As, Ba, and Zn, in a wide range of groundwater environments, with little or no effort needed to optimize the reagent formulation.

- FETC notified Biopraxis that a funnel-and-gate barrier was being installed at the S-3 Ponds Area, Y-12 Plant at Oak Ridge, which could be considered as an appropriate site for demonstrating the MOP-UP® technology. The groundwater at this site is contaminated with radionuclides, nitrate, and organics – none of which were included or had been studied in this initial contract – as well heavy metals. Oak Ridge was not able to arrange for a shipment of the groundwater in time for it to be included in the treatability tests. However, FETC provided information on the water at the site that could be used to prepare an S-3 Ponds Area groundwater 'simulant' for demonstrating the feasibility of treating the targeted heavy metals in the presence of the organic and nitrate contaminants found at the S-3 Ponds Area site. The simulant contains some 360 ppm metals, 88 ppm total organic pollutants, 1700 ppm nitrate, and high levels of sodium, potassium, and chloride. The treatability test showed the MOP-UP® reagent formulation removed all detectable Al, Cd, Cu, Zn, and Hg (the minimum level of detection for mercury was 500 parts per trillion); removed 98% of the Ba; and took the U down to 180 parts per trillion – at the native pH of 4.1. Since the analysis of organics and nitrate are not covered on the FETC contract, the fate of these pollutants is not known. However, earlier, Biopraxis-funded studies indicate that the organic contaminants, and possibly the nitrate, may have been treated simultaneously as well.
- MOP-UP® has not only met but significantly surpassed the go/no-go success criteria established for the program. FETC has therefore formally requested a proposal to demonstrate the MOP-UP® technology at a suitable site. Cognizant DOE and Oak Ridge site personnel have agreed to help Biopraxis prepare a proposal to demonstrate MOP-UP® at the S-3 Ponds Area funnel-and-gate installation.

The following sections provide more details on the relevant studies performed on the new, nonviable MOP-UP® reagents. These include tests with 'clean' solutions containing a single metal or mixtures of metals, natural and simulated Savannah River groundwater, groundwater samples provided by DOE, DoD, EPA, and private industry, and simulated S-3 Ponds Area, Y-12 Plant, Oak Ridge groundwater.

Since the nonviable MOP-UP® reagents have proven to be extremely effective at treating heavy metal pollutants in a wide range of groundwater environments, and are expected to be much more user-friendly, reliable, and economical than viable preparations, studies on the use of viable preparations for treating the Savannah River D-Area groundwater are not discussed in this report. Biopraxis would be pleased to provide the data, however, if DOE so desires.

2. SCREENING AND TREATABILITY TESTING

A wide variety of different nonviable MOP-UP® reagents can be produced. These reagents and the methods for producing them, which are the subject of a number of invention disclosures and patent applications, are proprietary to Biopraxis. Under the FETC program, Biopraxis worked primarily with two different categories of MOP-UP® reagents, dubbed "class O" and "class S". Some preliminary studies were conducted with "class P" as well; however, although this latter category of reagents was found to be superior to most reactive media being developed for groundwater remediation (in terms of the pH range under which they are effective and the loadings of metals that are taken up), class O and S reagents performed even better, and the class P reagents were therefore not tested as extensively.

For each category of reagent, Biopraxis evaluated the effects of using of a variety of different microorganisms and production techniques on the metal uptake capabilities of the reagent produced. Tests to evaluate reagent metal uptake capabilities evolved as the program evolved. Initially, reagents were screened in 'clean' laboratory solutions containing a single metal and/or in samples of 'real' or 'simulated' groundwater from the Savannah River D-Area site. As the Savannah River site changed, groundwater samples were spiked with metals of interest and/or the pH was adjusted (usually acidified). Once it became clear that the changes in the subsurface environment might be permanent, and the decision was made to begin working with samples from other sites, screening was done with 'clean' solutions containing standard mixtures of metals of high priority to DOE, i.e., Cd, Pb, Cu, Hg, As, Zn, and Cr(VI). The final series of tests were performed with samples of groundwater provided by other DOE sites, as well as DoD, EPA, and private industrial sites.

Unless otherwise noted, 'clean' laboratory solutions were made up with MilliQ water that had been deoxygenated by boiling and/or purging with N₂ prior to the addition of the metal ions. The pH was adjusted with HCl or NaOH before the incubation was initiated; buffers were not used, because a buffer has the potential to affect test results in a variety of different ways, e.g., can complex with the metal ions and/or interact directly with the reagent. Savannah River groundwater was deoxygenated by purging with N₂ and, if needed, acidified with HCl and/or supplemented with metal ion or radiotracer spikes prior to treatability testing. All other groundwater samples were used as received.

Tests were performed by incubating the MOP-UP® reagent in a sample in a sealed glass vial at room temperature without agitation, typically for 2 or 4 hours. The reagent was then separated from the sample by centrifugation and/or filtration or by removing the sample from the vial by needle. The residual metal concentration was determined by liquid scintillation or gamma counting (for radioisotope tracers), ICP (for non-radioactive isotopes of all metals except U or Hg; limits of detection typically 0.002 to 0.010 ppm), ICP-MS (for U, limit of detection 1 part per trillion), or cold vapor (for Hg, limit of detection generally 500 parts per trillion.) Samples from some of the earlier screening tests were analyzed by AAS. Aliquots of the untreated sample were analyzed at the same time as the treated samples were analyzed, for all experiments. Analyses involving

radioisotopes or AAS were performed in-house. All ICP, ICP-MS, and cold vapor analyses were performed by independent contract laboratories using EPA-approved protocols.

2.1. Preliminary Studies with Clean Laboratory Solutions

Before submitting the original proposal to FETC, Biopraxis had conducted preliminary, internally-funded studies that indicated class S and class O reagents are capable of taking up very high loadings of heavy metals, taking residual metal concentrations to very low (low- to sub-parts per billion) levels, and treating a wide variety of organic pollutants. All of these studies were conducted at neutral pH, with the single exception of testing performed on a class S reagent with lanthanide (La^{3+}) ions. This last testing series had shown, unexpectedly, that La^{3+} could be taken to nondetectable levels at the most acidic pH level tested, i.e., pH 1.5. The results were so surprising that they were assumed to be unique to lanthanide and, possibly, related metals. Biopraxis therefore expected to work primarily with viable microbial preparations under this initial feasibility demonstration contract for FETC.

However, the design of the hanging curtain barrier installation at the Savannah River D-Area Coal Pile Runoff Basin was, as discussed above, significantly different from the funnel-and-gate reported in various publications. Instead of the reasonably long (2-4 days) time expected for the MOP-UP® reagents to be in contact with the groundwater, the hanging curtain would only permit a few hours' contact at most. Because the nonviable MOP-UP® reagents take up heavy metals and radionuclides very quickly, they were considered to be more suitable for demonstration at the SRS site – provided that they would prove to be effective at taking up Cd and Pb at acidic pH. Therefore, Biopraxis decided to conduct a "quick and dirty" test with a class S reagent prepared from a readily available microbial strain and test this preparation for its ability to remove Cd^{2+} from 'clean' laboratory solutions under acidic conditions. A reagent (ME30-L7RXWS) was prepared and 1.2 g/L of the reagent was incubated in 0.2 mM (22.5 ppm) ^{109}Cd solutions at pH 3, 6, and 10. Within 30 minutes at room temperature, 1.2 g/L of the reagent had taken up $\geq 98\%$ of the Cd^{2+} at all three pHs. A $\gamma\text{-Al}_2\text{O}_3$ adsorbent which has been very well characterized was run as a control; it exhibited classical adsorbent behavior, taking up no detectable Cd at the acidic pH, 50% at the neutral pH, and 99% at the alkaline pH.

This test indicated that results in the earlier, internally-funded studies involving La^{3+} and a different class S reagent were not unique to lanthanide; and that the nonviable MOP-UP® reagents did indeed have the potential to treat at least some cationic heavy metal contaminants at acidic pH. The results were particularly interesting since researchers developing other types of metal treatment technologies have found that adsorbents such as iron oxyhydroxide – considered to be very promising for groundwater remediation – typically have a much lower affinity for Cd than for other pollutants such as Cu, Pb, and Zn¹.

The mechanisms whereby the nonviable MOP-UP® reagents take up heavy metals have not been elucidated. Some preliminary data indicates there are probably a number of different phenomena that can come into play. However, since the reagents are nonviable, they 'function' as adsorbents and, therefore, comparing their properties against those of conventional adsorbents is appropriate.

Several different factors are known to affect metal ion uptake by conventional adsorbents, including the initial concentrations of the metal ion and the concentration of the adsorbent, the oxidation state of the metal ion, the degree and type of complexation of the metal (if any), solution pH, ionic strength, the presence of competing adsorbates, and the contact time. When comparing adsorption in clean systems to real systems with more complex solution composition, it is important to keep in mind the major factors affecting trace metal adsorption, which are solution pH, metal ion concentration, adsorbent concentration, ionic strength, and the presence of metal-complexing ligands such as Cl^- and SO_4^{2-} . Solute/solid ratio and overall solution composition, in particular, are factors which will strongly affect adsorption. For example, studies with hydrous iron oxyhydroxide have found:

- There is a narrow pH range where the adsorption of a cation goes from near-zero to near-100% adsorption. This pH range, typically 1 to 2 pH units wide, is commonly called the 'pH-adsorption edge'. Adsorption of a cation increases as the pH is increased; anion adsorption is a mirror image of cation adsorption, i.e., anion adsorption increases with decreasing pH.
- In clean systems, metal cation adsorption capacities of hydrous iron oxyhydroxides are equivalent to or better than those of conventional adsorbents used for heavy metal treatment, including activated carbons, other metal oxides such as zeolites, and some chelating polymer exchangers. For example, at an initial concentration of 5 ppm metal ion, capacities are on the order of 10 mg Cd, 20 mg Zn, and 50 mg Pb per gram of adsorbent².
- When several potential adsorbates are present in a solution, adsorption of any adsorbate reduces the number of binding sites available to the ions remaining in solution. Adsorption of some ions may limit the availability of sites so much that adsorption of other ions is severely inhibited. This inhibition can take two forms, i.e., either the entire adsorption edge can be shifted; or adsorption may be suppressed in such a way that 100% removal of the poorly competing ion is prevented regardless of pH.
- When metal cations combine with dissolved ligands to form soluble complexes, adsorption of the cation can be affected in several ways. Complexation may reduce the tendency of the cation to adsorb, as apparently is the case when cadmium ions form complexes with chloride or sulfate. Alternatively, if the ligand is an anion that adsorbs strongly at low pH, the ligand may bind to the surface at low pH as the complex, thus taking the cation with it.
- In general, at a given pH, decreasing the adsorbent concentration at a fixed metal concentration decreases the fractional adsorption. For cations, this has the overall effect of shifting the adsorption edge towards a higher pH. Likewise, increasing the metal concentration at a fixed adsorbent concentration will decrease the fractional adsorption, also shifting the adsorption edge towards a higher pH.
- If a contaminated medium such as groundwater or wastewater has a fairly constant solution composition, the two feasible parameters to control adsorption in a treatment process are adsorbent concentration and solution pH.

Accordingly, a number of studies on metal uptake properties of the ME30-L7RXWS reagent were performed to confirm the initial test, and to develop additional information about the factors affecting metal ion removal by the nonviable MOP-UP® reagent. The studies were very simple, designed only to develop a means to conduct a crude comparison of this reagent against adsorbents known to be promising for use in groundwater remediation, in order to determine whether the approach of using nonviable MOP-UP® reagents warranted more extensive evaluation. In evaluating the results, it should be kept in mind that, despite the exceptional capabilities demonstrated by ME30-L7RXWS during these early tests, subsequent studies indicated that this particular reagent is not as promising for metal removal as a number of other class S and class O MOP-UP® reagents that were prepared and evaluated later in the program.

Results from tests to evaluate the impact of pH, metal ion concentration, and reagent concentration on Cd²⁺ uptake by ME30-L7RXWS are shown in Figures 1 - 4. Figure 1 shows tests comparing Cd removal when different reagent concentrations (i.e., 0.6, 0.06, and 0.006 g/L) were incubated in ¹⁰⁹Cd solutions ranging from 0.001 to 1.0 mM (0.11 to 112.4 ppm) Cd. It should be noted that the reagent was incubated for only 2 hours, without agitation, in the Cd solutions in these tests. The initial pH was 6.5. At the "high" concentration (0.6 g/L), the reagent took up >97% of the Cd for all starting concentrations tested (0.11 - 56.2 ppm Cd). At 0.006 g reagent/L, the reagent took up all detectable radioactivity from the 0.11 ppm starting concentration; and by the time the initial Cd concentration was raised as high as 1.0 mM (112.4 ppm), the reagent was taking up 533 mg

Cd/g reagent within the two hour incubation period at this pH.

Figure 2 shows the results from a test to evaluate the impact of changing the pH on metal cation uptake. In this case, 0.006 g reagent/L was incubated for 2 hours without agitation in ^{109}Cd solutions at initial pH levels of 2.7, 6.5, and 10.3 and ranging in concentration from 0.001 to 1.0 mM (0.11 to 112.4 ppm) Cd. The concentration of the reagent was selected to be low enough that the reagent should not have been able to remove all of the Cd from any but the most dilute solutions, so that the impact of pH would be clear. As expected, at the alkaline pH, the ME30-L7RXWS MOP-UP® reagent took up more Cd than at the neutral or acidic pH. As the starting concentration of the Cd was increased, the metal loading on the reagent increased, reaching as high as 4,953 mg Cd/g reagent during this 2-hour incubation. Even at the lowest initial Cd concentration of 0.11 ppm, the reagent took up > 95 mg Cd/g at pH 10.3. The metal loadings taken up in these tests are given in Table 1.

The results at pH 2.7 were *not* as expected – the reagent took up far more ^{109}Cd than predicted. Even in the most dilute solution tested (0.11 ppm Cd), the reagent removed nearly half of the Cd, taking up 44 mg Cd/g. As the starting concentration of the Cd was increased, the metal loading on the reagent increased, reaching as high as 394 mg Cd/g during a 2-hour incubation at this strongly acidic pH.

In general, at a given pH, increasing the metal concentration at a fixed adsorbent concentration will decrease the fractional adsorption. For cations, this has the overall effect of shifting the adsorption edge towards a higher pH. Figure 3 shows the results from a test in which the reagent concentration was held constant at 0.006 g/L and was incubated in 0.01 and 0.1 mM (1.12 and 11.2 ppm) Cd over the pH range of 2 - 12. To some extent, the MOP-UP® reagent showed classical behavior in that the pH adsorption edge shifted as the metal ion concentration was increased. However, the Cd^{2+} removal did not ever approach 0% at the acidic end of the pH edge from the higher initial metal concentration. Instead, the reagent removed a steady ~17% of the ^{109}Cd throughout the pH range 2.00 - 5.30. It would therefore appear that more than one type of metal removal mechanism may be involved, one that is based on classical adsorbent phenomena and one that is not. The metal loadings taken up from the 11.2 ppm Cd solutions are given in Table 2. Even at the most strongly acidic pH (pH 2.00), the reagent took up 321 mg Cd/g.

Only a single sample was processed and analyzed at each pH tested. In the tests conducted in the 11.2 ppm solutions, the samples tested at pH 2.00, 2.06, and 2.29 all showed removal of 17% of the Cd. In the tests conducted in the more dilute 1.12 ppm solutions, only one sample was run at a pH below 3.02. At pH 3.02, the reagent was still taking up 117 mg Cd/g. It is therefore not known whether the apparent sharp drop in Cd removal at pH 2.02 is real, or an aberrant data point. However, numerous subsequent tests showed that other class S MOP-UP® reagents are able to take up relatively high loadings of Cd from dilute solutions even at pH levels below 2.0.

Finally, the impact of contact time (i.e., incubation period) at different pH levels is shown in Figure 4. As before, 0.006 g/L of the reagent was incubated at ambient temperature without agitation in a Cd solution, this time at a concentration of 0.01 mM (1.12 ppm) Cd, and samples analyzed periodically during the next 168 hours. At both the neutral (pH 7.2) and alkaline (pH 10.3) initial pH levels, Cd uptake was extremely rapid, with more than 80% of the Cd removed within 10 minutes from the neutral solution and more than 90% removed within 10 minutes from the alkaline solution. At 99% Cd removal – which occurred within 4 hours at pH 7.2 and 10.3 – the reagent had taken up 194 mg Cd/g. Cd removal from the acidic solution (pH 2.8) exhibited a different pattern. Approximately 48 hours were needed for the maximum loading seen at this pH (112 mg Cd/g) to be reached. However, initial uptake was very rapid, with more than half of that amount (i.e., 70 mg Cd/g) taken up within the first 4 hours. Thereafter, Cd removal was more gradual. At all three pH levels, the MOP-UP® reagent retained the Cd once it had been removed.

As mentioned above, adsorbents such as iron oxyhydroxide typically have a much lower affinity for Cd than for other pollutants such as Pb, which is also found in the groundwater at the Savannah River site. Therefore, a simple set of tests was also run with Pb, to determine whether the trend would hold true for the MOP-UP® reagent. The results are shown in Figure 5. Two different concentrations of the ME30-L7RXWS reagent were incubated for 2 hours without agitation in 0.1 mM (20.7 ppm) solutions of ^{210}Pb at initial pH levels ranging from 2.11 to 10.43. At the "high" reagent concentration, 87% of the ^{210}Pb was removed from the most strongly acidic pH solution tested (i.e., 2.22), with the reagent taking up 300 mg Pb/g; more than 90% was removed at pH 3.57; and Pb removal was essentially complete by pH 6.3. The reagent behaved in a "classical" fashion in that a decrease in reagent concentration resulted in a shift of the "adsorption edge" to a higher pH. However, as with the Cd, Pb removal did not ever approach 0. Instead, although the "edge" appeared to be in the pH 5.5 - 7.5 range, the reagent was still taking up exceptionally high loadings at pH 2.11, i.e., 232 mg Pb/g reagent. By the point the pH was in the neutral range, the reagent was taking up nearly $3\frac{1}{2}$ times its own weight in Pb (3,451 mg Pb/g reagent at an initial pH of 7.00.) Since the reagent was taking up all available Pb before the pH ever got into the alkaline range, it is unknown how much Pb could have been taken up at higher pH levels. At the low reagent concentration (Table 3), ME30-L7RXWS was taking up 232 mg Pb/g of reagent at pH 2.11, and 3,563 mg Pb/g reagent at pH 9.08.

Hexavalent chromium exists as an anion, and should therefore exhibit "mirror image" behavior if the nonviable MOP-UP® reagent is a conventional adsorbent. A "quick and dirty" experiment was performed to determine whether this were true, i.e., the reagent was incubated in solutions of $^{51}\text{Cr(VI)}$ at acidic, circumneutral, and alkaline pH levels (i.e., 3.0, 6.0, and 10.0.) For this experiment, different ratios of mM Cr(VI) : mg/L reagent were used (Fig. 6). It is important to remember that Cr removal was being determined by measuring radioactivity, i.e., total ^{51}Cr removal was determined. The results were far from those expected. At the acidic pH - where the anionic Cr(VI) should be totally taken up - the reagent removed 12-18% of the total Cr. However, because both the reagent concentrations and the initial Cr(VI) concentrations were low, metal loadings were still high. For example, when 0.006 g/L reagent was incubated in 0.1 mM Cr(VI), it took up 150 mg Cr/g reagent at pH 3. Cr(VI) removal was essentially complete at pH 6 at all ratios tested, with the exception of the sample in which the ratio was the highest, i.e., when 0.006 g/L reagent was incubated in 0.1 mM Cr(VI). Under these conditions, the reagent took up 198 mg Cr/g, which appears to be the maximum loading possible within a 2-hour incubation under these conditions. At the alkaline pH - the pH range in which the hexavalent chromium removal should be the lowest - the reagent took up as much as 63 mg Cr/g (0.06 g/L reagent incubated in 0.01 mM Cr(VI).)

One possible explanation for these unusual results is that the nonviable MOP-UP® reagents are reducing the hexavalent chromium to the trivalent form, but has little or no affinity for Cr(III) under acidic conditions. However, determination of the species of the chromium in solution and on the MOP-UP® reagent was beyond Biopraxis' current capabilities.

A second experiment was performed, in which 0.06 g/L of the reagent was incubated in 0.01 or 0.1 mM (0.52 or 5.2 ppm) Cr(VI) solutions in the pH range 2.18 - 10.41 (Fig. 7.) At the lower Cr : reagent ratio, the same trend was observed, i.e., total Cr removal was higher in the neutral range than in either the acidic or the alkaline ranges. At the higher Cr : reagent ratio, total Cr removal was lower in the acidic range, and essentially complete throughout the pH range 6.50 - 10.11. It should be noted that this profile is exactly the opposite of what would be expected for adsorption of an anion - again, suggesting that the reagent may be reducing Cr(VI) to Cr(III).

Finally, a simple test to evaluate the impact of contact time on total Cr removal under acidic, neutral, and alkaline conditions was performed (Fig. 8.) For this test, 0.06 g/L of the reagent was incubated in 0.1 mM (5.2 ppm) Cr solution, without agitation, and samples analyzed periodically over a period of 96 hours. As expected, Cr removal at neutral (7.2) pH was excellent, with more than 80% removed within 5 minutes, more than 90% within 2 hours, and more than 99% within

4 hours. All detectable radioactivity was removed within 72 hours, and Cr was still completely retained on the MOP-UP® reagent at 96 hours. Results at the pH extremes are very interesting. Again, data from the test under strongly alkaline conditions support the idea that the reagent is reducing the Cr(VI). When the reagent was incubated in Cr(VI) solutions at an initial pH of 10.8) – in which an anion should not be taken up at all – total Cr removal is slow and steady; the reagent achieves 97% removal within 48 hours and >99.9% removal within 96 hours, under the conditions used. When the reagent was incubated in solutions at pH 3.1, ~30% of the Cr was removed very quickly. A very small percentage of this material was gradually released over the next 2 hours; thereafter, Cr retention stayed at a very steady 23-24% over the remainder of the experiment. The reason for this behavior is unknown, although it does support the concepts that the Cr(VI) is reduced by the reagent, and that the reagent exhibits multiple metal ion removal mechanisms.

Finally, a handful of studies were conducted on Ni²⁺ removal. In clean systems, Cd²⁺ and Ni²⁺ behavior with amorphous iron oxyhydroxide adsorbent tend to be similar. The same cannot be said for their behavior with the ME30-L7RXWS reagent. Figure 9 shows a quick-and-dirty test of ⁶³Ni removal at acidic, neutral, and alkaline pH, using different Ni : reagent ratios. In general, the reagent appeared to exhibit a classical pH adsorption edge, with neutral to alkaline pH for complete Ni removal to be achieved. However, behavior was quite atypical when it came to the amount of Ni taken up by the reagent, especially under acidic conditions. At the highest Ni : reagent ratio, for example, 127 mg Ni / g reagent was taken up at pH 2.74. As the pH was raised, the Ni loading was raised, so that the reagent was taking up its own weight (1,027 mg Ni / g reagent) at pH 10.45 under the conditions used. As before, it should be noted that these results were achieved with a 2-hour incubation under ambient temperature without agitation.

Figure 10 shows the pH “adsorption” edge more clearly. In this test, 0.06 g/L of the reagent was incubated for 2 hours in solutions of 0.1 mM (5.87 ppm) Ni at pHs ranging from 2.22 to 10.02. The classical edge appears to be in the range pH 5.5 - 7.5. However, Ni removal does not drop quickly to 0 as the pH becomes more and more acidic. Instead, there appears to be a biphasic metal ion removal, possibly – as above – due to more than one metal ion removal mechanism. Even at pH 2.22, the reagent was taking up almost 10% of the Ni. By the time the pH approached neutral, more than 90% of the ⁶³Ni was removed. At alkaline pH (10.02), all detectable radioactivity had been removed from solution. Because the ratio of Ni : reagent was low, there was insufficient metal present for the reagent to take up its maximum loading of Ni in this experiment.

Finally, the impact of contact time was evaluated. As before, 0.06 g/L reagent was incubated in a 0.1 mM (5.87 ppm) Ni solution, without agitation, at acidic, circumneutral, and alkaline pH, and samples analyzed periodically during a period of 144 hours (Fig. 11.) Initial metal cation removal was very rapid at pH 6.5 and 9.5, with 56% being taken up within the first hour at pH 6.5 and 89% within the first hour at pH 9.5. At the more alkaline pH, the reagent continued to remove more and more of the metal, taking up 99.6% of the Ni by 72 hours and continuing to retain the metal for the remainder of the test. At pH 6.5, however, cation removal is in the middle of the pH adsorption edge, and Ni is never completely taken up. Results at the acidic pH (3.2) are again interesting; under these conditions, the reagent quickly removes 8% of the metal cations (within 2 hours) and then slowly and steadily continues to take up more and more of the metal throughout the remainder of the experiment, attaining a loading of more than 13 mg Ni / g reagent under these strongly acidic conditions.

In short, the ME30-L7RXWS reagent exhibited very unusual properties by comparison with some of the conventional adsorbents, most notably extremely high loadings for heavy metals of high concern to DOE, even under strongly acidic conditions. The approach of using nonviable reagents therefore appeared promising enough to warrant shifting attention from viable preparations for a more extensive evaluation.

2.2. Preliminary Studies with Savannah River Groundwater

As mentioned above, metal ion removal from "real" waters containing more complex constituents can be very different from metal ion removal in clean systems to real systems. In particular, ionic strength, the presence of other metal anions and cations that compete for binding sites, and the presence of metal-complexing ligands such as Cl^- and SO_4^{2-} can have a significant impact on treatment efficacy. The groundwater at the Savannah River D-Area Coal Pile Runoff Basin site, of course, was especially high in SO_4^{2-} content, and had extremely high levels of iron – which compete very effectively for binding sites on adsorbents such as ion exchange resins – as well. Accordingly, Biopraxis proposed to work with "real" samples as early in the program as possible, in order to ensure that reagents that appeared promising in "clean" solutions would also be promising when transitioned to the "real world."

Having determined that nonviable MOP-UP® reagents were promising, studies were initiated in which a range of different reagent production techniques were used, so that – hopefully – a range of different reagents would be produced. As noted above, this technology is very new, and little is known about the impact of using different microorganisms and/or different production techniques on the properties of the resulting reagents. Therefore, some of the tests were targeted at evaluating reagents in which the production techniques were held constant but different microorganisms were used; and in others, different production techniques were used with a single microbial culture.

At this point in time, it is still very premature to attempt to draw any firm conclusions about the impact of altering any of the reagent production parameters on reagent metal removal efficacy. What became clear very quickly, however, was that a range of different reagents exhibiting a range of different metal ion removal properties could be prepared.

Many different groundwater constituents can play a role in metal ion removal, by many different mechanisms. Savannah River had been monitoring the metal ion content, pH, temperature, and dissolved oxygen content of the groundwater for some 8 years; however, very little was known about other potential contaminants such as cyanides, nitrates, and organic acids. WSRC had expected to complete an elaborate analysis of the site by the time a contract was awarded to Biopraxis; however, the work was delayed in favor of higher-priority efforts, so that methods to do the analyses were not even available in time for the program. At first, Biopraxis attempted to at least evaluate the potential impact of "unknown" sample constituents by running side-by-side tests with "artificial Savannah River water (ASRW)" containing all known groundwater constituents and "natural Savannah River water (NSRW)" samples provided by WSRC. Unfortunately, the composition of the groundwater at the site changed rapidly; analyses of the groundwater from the contract laboratory hired by WSRC were provided to WSRC months after the samples were received and used by Biopraxis; and it was apparent that sample collection upset the balance of the groundwater chemistry, causing precipitates to form steadily in some samples, which was not prevented by filtering the precipitates upon receipt. (Tests were conducted to determine the stability of the bulk groundwater samples pulled by WSRC for shipment to Biopraxis, by analyzing the content of a sample pulled in November 1996 shortly after it was pulled and again a few weeks later. These analyses showed that the concentrations of dissolved inorganics such as B, Ba, Cd, Co, Cr, Cu, Fe, La, Li, Mo, P, Pb, Ti, V, and Zr decreased with time, several by more than 50%, e.g., Ba, Cu, La, Mo, Ti, V, and Zr. Other dissolved inorganics – i.e., Al, Ni, Si, Sn, and Zn – appeared to increase in concentration, possibly through dissolution of suspended fines. A handful remained essentially the same in concentration, e.g., Mg, Mn, Na, and Sr.) The composition of the ASRW, therefore, rarely if ever coincided with the composition of the NSRW, and therefore never served adequately as controls. The results from the ASRW samples, however, were very useful in that the composition of the water was known, was very complex, and was a reasonably representative simulant for an acid-leachate-contaminated groundwater site.

A typical 'recipe' for the 'artificial' SRS water used in these studies is: 3.5 mg/L NiSO_4 , 750 mg/L FeSO_4 , 25 mg/L MnSO_4 , 15 mg/L $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 0.2 mg/L CuSO_4 , 200 mg/L AlSO_4 , 200 mg/L CaSO_4 , 0.1 mg/L CdSO_4 , 0.7 mg/L CoSO_4 , 100 mg/L MgSO_4 , 25 mg/L Na_2SO_4 , 0.2 mg/L $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 1.0 mg/L $\text{Pb}(\text{NO}_3)_2$, 50 mg/L $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 1.0

mg/L ZnSO₄, and 1.0 mg/L K₂HPO₄.

In general, tests with ASRW and NSRW were conducted in the same manner as those with "clean" laboratory samples, i.e., MOP-UP® reagents were added to the solution and incubated at ambient temperature without agitation; the reagents were then separated from the sample by centrifugation and/or filtering, or by using a needle to withdraw the water for analysis. Most of the analyses were done through the use of the radioactive tracers ¹⁰⁹Cd, ²¹⁰Pb, ⁵¹Cr, and ⁶³Ni, since Biopraxis did not have access to analytical instrumentation capable of measuring residual metal ion concentrations in such complex samples at the desired sensitivities. Because the different metal radioisotopes could not be mixed – for reasons of safety and disposal – it was necessary to run four different vials for each set of samples – one for each metal pollutant of interest. Because the purpose of the tests was to screen a variety of reagents, with several different reagents being tested during each "run," because of the safety precautions needed when working with the radiotracers, and because the preliminary tests with the ME30-L7RXWS indicated that at least some nonviable MOP-UP® reagents should take up the bulk of the metal pollutants within 4 hours, it was decided to use a 4-hour incubation period for these tests. The tests were done at ambient pH which, for the most part, was at pH 2.8 - 3.0, but on occasion was as low as pH 2.0 or as high as pH 4.0. (For any bulk groundwater samples that had a pH higher than 4.0, the pH was adjusted to the 2.8 - 3.0 range with HCl before a given test was initiated.) Buffers were never used to control the pH, because they can have a wide range of effects on metal ion removal.

Since the results with the ME30-L7RXWS reagent were so promising, initial efforts focused on preparing additional class S MOP-UP® reagents for screening with the artificial and natural Savannah River groundwater.

It should be noted that the nonviable MOP-UP® reagents are particulate in nature. Therefore, if one reagent exhibits a high affinity for some of the contaminants of interest while others exhibit high affinity for different contaminants, the various reagents can be mixed together in a "formulation" capable of treating a complex mixture of contaminants. Accordingly, while it may be preferable to identify a single reagent capable of treating a wide range of heavy metals, it is not essential to find any single reagent that is capable of treating the full range of contaminants found at a given site.

For the most part, these new class S reagents also showed extraordinary affinity for the two metals of concern, i.e., Cd and Pb. Even when the initial concentrations of these metals in the groundwater were below the limits of detection by ICP-MS (i.e., below 0.002 ppm), many reagents were found to be capable of removing all detectable radioactivity when tracer levels of ¹⁰⁹Cd or ²¹⁰Pb was added. This meant that the residual levels of Cd and Pb were at least 2 to 3 orders of magnitude lower than the starting concentrations, i.e., ≤ 0.02 to ≤ 0.002 ppb.

Chromium removal from the SRS water is of far less concern, since the metal is reported to be entirely in the trivalent form under the strongly reducing, highly acidic conditions found at the site. Nevertheless, radiotracer ⁵¹Cr was used to evaluate chromium uptake under the conditions used in the tests. In general, the reagents screened on this study tended to remove reasonably high percentages of the contaminant, i.e., 85 - 98%, from the "artificial" groundwater but lower – sometimes dramatically lower – percentages from the "natural" groundwater. Since the "natural" water often had a lower pH, the difference may have been due to pH rather than "unknown" groundwater constituents. It should also be noted that these were crude, screening experiments designed at determining whether the different production techniques affected heavy metal pollutant removal properties of the resulting reagents – i.e., no attempt was made to optimize the treatment process.

Nevertheless, three of the reagents tested were found to take up very high percentages of Cr(III) at pH 2.7 - 3.0 from SRS groundwater samples as well as from the "artificial" mix – at the same time they removed very high percentages of the Cd and Pb.

Based on the preliminary results in the "clean" solutions, it was anticipated that treatment of Ni in strongly acidic groundwaters would be more difficult than treatment of Cd or Pb, i.e., that higher concentrations of class S reagents would be needed. In general, this proved to be the case with the reagents produced and screened during this part of the program. Nevertheless, three class S reagents were found to remove 91-95% of the Ni from the ASRW at pH 4.0, and two others were shown to remove 76-79% of the Ni from NSRW as well as ASRW at pH 2.8-3.0, under the conditions used.

In short, some of the new class S reagents showed high affinity for one or two of the heavy metals tested, while two or three of the reagents showed high affinities for all four of the heavy metals in complex, acidic water. One of the latter reagents, SRT09-A7RSIS, for example, removed all detectable traces of Cd, 98% of the Cr, 95% of the Ni, and 97% of the Pb from ASRW at an initial pH 4.0.

2.3. Screening with Metal Ion Mixtures

As mentioned earlier, the groundwater at the SRS D-Area site began changing after the program got under way. Within a few months of start of the FETC contract, the pH of the groundwater began to go up; and then the Cd and Pb concentrations began to go down. Twelve months into the program, the NSRW samples had to be spiked with Cd and Pb in order for the initial metal concentrations to be detectable. Sixteen months into the program, the SRS D-Area site showed no sign of reverting to its earlier status – both Cd and Pb continued to stay at nondetectable levels, and the pH remained in the 3.8 - 4.2 range. Since an on-site demonstration of Cd and Pb treatment obviously could not be held at the site unless the Cd and Pb concentrations rose to their earlier levels, and since the reason for the change was unknown, the goals of the program clearly had to be modified. However, there was little time or money remaining on the program.

Although the only tests conducted to date had been with the pollutants found at the SRS D-Area site, Biopraxis suggested changing the objective of the program from optimizing the technology for use at a single site, to showcasing the breadth and flexibility of the MOP-UP® technology by demonstrating its capabilities in as many different groundwater environments as possible. Biopraxis proposed to locate groundwater sites that were contaminated with metal pollutants of wide-spread concern to DOE; and to evaluate the ability of the MOP-UP® reagents to treat any or all of these metals – without any attempt to optimize the technology for use with the new target metals and/or for treating them under the diverse conditions found at the various sites. FETC agreed.

First, Biopraxis evaluated all of the information readily obtainable on groundwater contamination throughout the DOE complex, in order to identify the heavy metal pollutants of highest concern. To some extent, preference was given to metals that are also prominent in DOE waste/wastewater treatment requirements, since a MOP-UP® system can readily be configured for "industrial" as well as environmental remediation applications. Based on the information gleaned from this research, it was decided to focus on Cd, Pb, Cr(VI), Cu, Hg, As, Zn, Ba, and, if it were possible to obtain suitable samples, U.

Locating sites that were willing and able to provide groundwater samples was far more difficult and time-consuming. In the interim, a new screening protocol was developed, so that candidate reagents could be screened for their ability to take up this wider range of metals. It should be noted that the purpose of this new screening protocol was to identify the reagents expected to be promising for treating a given metal in a complex mixture, so that by the time groundwater samples were available, Biopraxis would have some idea which reagents might be superior for use in a given groundwater environment. I.e., there was no attempt made to optimize metal ion removal – in fact, the screening test was deliberately designed to be very challenging, in order to be able to compare different reagents with each other.

The new screening protocol called for testing candidate reagents in two sets of standards, one at pH 2 and the other at pH 5. These two pHs were chosen for three reasons: (a) Biopraxis hoped to be able to locate samples of acid mine drainage to test, in keeping with the earlier plans to develop a treatment for highly acidic groundwaters; (b) most of the contaminants of interest are cations, and therefore much more difficult to treat at acidic pH; and (c) all tests conducted to date had indicated that metal removal at neutral pH would be relatively easy for the MOP-UP® reagents, i.e., the differences among many of the reagents would become clear only at pH extremes.

The pH 2 standard contained 10 ppm each of Cd, Cr(VI), Ni, Pb, Cu, Hg, and As(V). The pH 5 standard contained 10 ppm each of all these except Pb, which precipitated out of solution at pH 5. In order to challenge the MOP-UP® reagents, ~0.5 g/L reagent was added to a given standard, so that a high metal ion capacity would be required for a high percentage of all the metals to be taken up – and so that competition among the various metals for available binding sites would therefore be much more apparent. As before, the reagents were incubated in these solutions for 4 hours, at ambient temperature without agitation, before being separated from the water. Analyses of the controls and treated samples were performed by independent contract laboratories using EPA-approved protocols. In general, detection limits were on the order of 0.002 - 0.01 ppm (depending on the quantity of sample available) except for Hg; the detection limit for Hg was usually 0.0005 ppm (0.5 ppb).

The new screening protocol was used to evaluate some of the reagents that appeared promising for treatment of Cd, Pb, Cr, and/or Ni for their ability to take up a wider range metals, while suitable groundwater samples located for the treatability tests. A range of reagents was screened, i.e., some were chosen on their ability to treat all four metals, while others were chosen because they appeared to be selective for a given metal. The results were interesting, far from predictable, but still extremely promising.

For example, as mentioned above, SRT09-A7RSIS was one of the reagents considered to be more promising for broad-spectrum heavy metal treatment in acidic media, since it removed all detectable traces of Cd, 98% of the Cr(III), 95% of the Ni, and 97% of the Pb from ASRW at an initial pH 4.0. When subjected to the new screening protocol, it continued to exhibit excellent metal ion removal capabilities. At pH 2, the reagent took up 99.5% of the Cd, 98.7% of the Pb, 99.0% of the Cu, and 96.8% of the Hg, plus 20% of the As and 5.6% of the Ni. Interestingly, no detectable Cr(VI) was removed under these conditions – whereas in the testing conducted to date, it had been unusual for a class S reagent to show higher affinity for Ni than Cr (whether hexavalent or trivalent) at strongly acidic pH. Under the conditions used in this screening protocol, SRT09-A7RSIS took up a total loading of > 47 mg metals/g reagent at pH 2. When screened in the pH 5 standard, this reagent exhibited very broad-spectrum metal treatment properties, taking up 99.0% of the Cd, 98.6% of the Cr(VI), 55.1% of the Ni, 96.9% of the Cu, 95.5% of the Hg, and 95.7% of the As(V), for a total loading of 89 mg metals/g reagent. It was interesting to note that the relative affinities for Cr and Ni changed at the higher pH (and, it should be noted, in the absence of Pb.) It was also interesting that the relative affinity for the As(V) rose as the pH rose; since As(V) should be present as an anion, its removal should be better at the more acidic pH if the MOP-UP® reagent were functioning as a conventional adsorbent. On the other hand, the As(V) might have been in direct competition with Pb for binding sites in the pH 2 solution.

In addition to using the new screening protocol to evaluate some of the more promising reagents that had already been developed, efforts to produce new reagents were continued.

Generally speaking, the class S reagents showed extremely high affinities for Cu and Hg as well as Cd and Pb, even at pH 2; and, especially at the low pH, lower affinities for Cr(VI) and Ni. However, one of the more interesting new class S reagents produced, SRT06-M7EMWS(Mn), exhibited a higher affinity for Cr(VI) and As(V) at pH 2 than for Cd or Cu (45.6% and 76.7% vs 8.6% and 23.1% removal, respectively.) At pH 5, this reagent showed high removal rates for all

contaminants save Ni, taking up > 95% of Cd, Cr(VI), Cu, and Hg, and 83% of the As(V), as well as taking up 39% of the Ni.

Some new production techniques resulted in class S preparations that had a very sharp sensitivity to pH for some metals but not for others. Two such preparations, for example, readily took up 90-99% of the Cd, Pb, Cu and Hg but no Cr(VI), Ni, or As(V) at pH 2; and, in addition to removing high levels of the Cd, Pb, Cu and Hg at pH 5 also took up 95% of the Cr, ~90% of the Ni, and 50-65% of the As(V). In fact, the Ni and the two anions were beginning to compete effectively against the other cations at the higher pH, with removals of Cd, Cu, and Hg decreasing slightly in comparison with removals at pH 2.

The new class S reagent SRT09-W7ESWS showed pH sensitivity to all metals except Cu and Pb – but took up very high loadings (96.3 - > 99.9%) for all contaminants save Ni at pH 5. Such reagents might prove very useful for selective metal ion removal applications. It was interesting that when a different production technique was used with this same microorganism, the resulting class S reagent had very high affinities for Cd (99.5% removal) and Hg (96.8% removal) at pH 2.

Although a variety of new production techniques for class S reagents were tried, emphasis began to switch to producing and screening class O and class P reagents, to determine whether these new types of reagents would be as effective as hoped and/or would exhibit different properties that would make them more suitable for treating metals against which the class S reagents are less effective. In particular, it was hoped that the various classes of reagents would exhibit such different properties that by mixing class O or class P with class S reagents, treatment of complex mixtures could be optimized.

As mentioned earlier, class P reagents produced on the program showed excellent metal removal properties by comparison with conventional adsorbents, but the class S and class O reagents were clearly better for broad-spectrum removal of the targeted contaminants. On the other hand, some of the class P reagents offered interesting specificities for some of the metals. FRT03-M7ESWP, for example, did not remove any detectable Cd, Cr, Pb, or As(V) at pH 2 but showed a relatively high affinity for Hg, removing > 30% of this cation while taking up low levels of Ni (4.5%) and Cu (5.4%). Another class P reagent, prepared by the same production technique but using a different microorganism, exhibited a different specificity at this strongly acidic pH, removing no detectable Cd, Cr, Ni, Pb, or Cu while taking up 25% of the Hg and 10% of the As(V). A third class P reagent removed no detectable Cu, Hg, or As(V) at pH 2 but took up 17% of the Pb. Yet another took up traces of most metals save Cd at pH 2 but exhibited its highest affinity for As(V).

In general, when the class P reagents were incubated in the pH 5 standard solution, metal uptake increased across the board. Total metal loadings reached as high as > 65 mg/g. This is outstanding performance by comparison with many conventional adsorbents used for heavy metal treatment. Nevertheless, the greatly superior performance of the class S reagents dictated that efforts be directed toward their development for this particular application.

It should be noted, however, that there is reason to believe class P reagents may prove particularly effective with certain radionuclides, such as strontium.

A modest amount of effort (by comparison with the class S reagents) was also spent on producing and screening class O reagents. Class O, as hoped, exhibited metal removal properties that were often very different from those of the class S reagents. For example, class S reagents tended to take up higher loadings of As(V) from these solutions at pH 5 than at pH 2. The class O reagent FRT01-M7HSWO, on the other hand, took up 2 1/2 times as much As(V) at pH 2 as at pH 5. FRT09-S7RSWO exhibited this property even more markedly, removing 97.7% (25.2 mg/g) of the As(V) at pH 2 but only 34% at pH 5. Surprisingly, this same trend was not seen with Cr(VI). For hexavalent chromium to be taken up in preference to other metals such as Cd, Cu, and/or Hg, the pH had to be at the higher level. At pH 5, however, the class O reagents often removed >99%

of the Cr(VI). One class O reagent, FRT03-P3ESWO, showed a higher affinity for Cr(VI) at pH 5 than any other contaminant in the mixture save As(V).

As mentioned above, it was assumed that because the nonviable MOP-UP® reagents are particulate in nature, it would be possible to mix different reagents that exhibited different metal uptake properties to optimize treatment of a complex groundwater environment. Therefore, one or two very simple tests were done in which a mixture of two different reagents was screened using the standard heavy metal ion mixture protocol. When mixtures were incubated in the standard solutions, a ratio of 1:1 by dry weight was used, for the same total g/L concentration of MOP-UP® reagent added to the standard solution. The general trend observed in these tests was the mixing two reagents – whether mixing two class S reagents with different properties together or mixing a class S reagent with a class O – did indeed improve overall metal removal in terms of average mg metal/g reagent, particularly improving the results from the more problematic challenges, such as Ni at pH 2.

Arsenic, like chromium and uranium, can exist as different species in the environment. Unlike Cr and U, however, As is likely to exist in organoarsenicals as well as in inorganic species, due to metabolic activities of microorganisms that attach alkyl or phenyl groups to inorganic arsenic as well as the use of organoarsenicals in various industrial processes. A small handful of experiments were therefore conducted in which some of the MOP-UP® reagents were screened against “clean” laboratory solutions containing As(III) or arsanilic acid. Several of the class S reagents were found to be extremely effective with As(III), removing 95-99% at pH 2 under the conditions used. They were less effective with arsanilic acid, taking up ~40-60% at either pH 2 or pH 5. The class O reagents, for the most part, were ineffective at treating As(III) even when they had been found to be very effective with As(V) in the standard mixtures containing other metals. On the other hand, a class O reagent was found to be the most effective at treating arsanilic acid of any reagent of either class tested, removing 70-75% at pH 2 and 5 under the conditions used.

2.4. Treatability Testing with Groundwater Samples

Locating sites that were willing and able to provide groundwater samples proved to be difficult. Although many contacts at suitable sites within DOE, DoD, EPA, and private industry were eventually located and expressed strong interest in helping out, quite a few were unable to do so simply because winter weather was making it impossible for their crews to reach the site to collect samples and/or because rainfall had been so low that the wells were not producing enough water for them to pull samples. Nevertheless, Biopraxis was eventually able to arrange for shipments of groundwater samples representing a wide range of environments, from those containing trace levels of a single heavy metal contaminant to those containing concentrated, complex mixtures of many different inorganics, and from those at circumneutral pH to those collected from acid mine drainage sites.

The tests with these samples were very simple screening tests, designed to (a) evaluate the range of groundwater environments for which the MOP-UP® technology has the potential to be effective, and (b) evaluate the amount of “fine-tuning” and tailoring that will be needed to optimize MOP-UP® for use at a given site. Due to the extremely short period of time remaining on the program, treatability testing had to be done concurrently with tests to screen the reagents in the standard heavy metal solutions. Therefore, there was very little data on which to base selection of the MOP-UP® reagents to be used in the treatability tests. In addition, due both to the timing and the fact that funds were rapidly running out, it was not possible to do a large matrix of tests. Instead, a handful of reagents were chosen for treatability tests with a given groundwater sample, and a single set of parameters used. Since there was not nearly enough time or money to optimize treatment for each and every groundwater sample received, the goal was to evaluate the technology's potential, not attempt to identify the conditions under which all of the targeted heavy metals could be removed from each sample. As at the beginning of the program, it was expected that Biopraxis would select a single site for use in the “go/no-go” demonstration, i.e., that

the treatability testing would culminate in the selection of a single site for which MOP-UP® appeared well-suited, tailor the treatment for that site, and demonstrate the removal of > 90% of the targeted heavy metals from a groundwater sample collected at that site under the conditions (pH, dissolved oxygen, and temperature) found there.

Unless otherwise noted, the treatability tests comprised a 2- or 4-hour incubation of the selected MOP-UP® reagents in the groundwater sample as received, without agitation, filtering, purging, or pH adjustment. The reagents were then separated from the sample by centrifugation and/or filtering, and the sample stabilized and sent out for analysis at one or more independent contract laboratories. Two types of controls were analyzed simultaneously, i.e., a sample of the groundwater collected and stabilized at the beginning of the treatability test and a second aliquot incubated and then centrifuged and/or filtered side-by-side with the treated samples. There was no significant difference between the two controls on any of the tests.

As before, results were unexpected – the MOP-UP® reagents performed so well that in almost all cases, the targeted metals were taken to nondetectable levels during the very first test with each of the groundwater samples.

Several of the groundwater samples contained only trace levels of a single contaminant of concern. Kirtland Air Force Base (AFB), for example, provided a sample of groundwater containing 0.07 ppm Ba. (This site has shown traces of selenium and arsenic contamination from time to time, but both of these contaminants were below the limits of detection in the sample provided for use on the DOE program.) Since Biopraxis had never worked with Ba before, three reagents, one each from class S, class O, and class P, were chosen for the “screening” test (Fig. 12.) All three reagents took the Ba below the limits of detection by ICP-MS at the native pH of 7.85.

Hill AFB provided samples from two different sites. One of these, from Well U8-008, contained 0.35 ppm Cr(VI) and was at pH 7.58. Class O reagents were expected to be superior for treating Cr(VI); three class O and one class S reagents were therefore screened (Fig. 13.) As with the Kirtland AFB sample, this first test with the Hill Cr(VI) sample was successful, with all three class O reagents taking the Cr(VI) to nondetectable levels. The class S reagent removed 80% of the Cr(VI) under the conditions used.

The second Hill AFB sample, pulled from Well U8-014, contained 0.064 ppm arsenic at pH 7.06. No attempt was made to determine whether the arsenic was present as As(III) or As(V), or in inorganic and/or organic species. Three class O and one class S reagents were screened (Fig. 14.) This first test was also very successful, with the class S reagent and one of the class O reagents being shown to be capable of taking the arsenic to nondetectable levels.

INEEL provided a sample of acid mine drainage containing 0.13 ppm arsenic and 0.15 ppm Cu, as well as 0.58 ppm Fe. Two class O and two class S reagents were screened for their ability to treat this groundwater (Fig. 15.) One reagent from each class successfully removed all detectable arsenic and copper from this groundwater during this first treatability test.

The class O reagent FRT01-M7sp appeared to show high affinity and excellent specificity for arsenic in the INEEL sample. The production technique used to prepare this reagent was unusual by comparison with most of the others. Very little work has been done with this particular reagent. However, it appears to offer some extremely interesting properties; for example, when incubated in Berkeley Pit water at the native pH of 2.85, it took up little or no copper, aluminum, or manganese, but a high loading of magnesium (800 mg Mg/g reagent.)

The EPA provided a sample of acid mine drainage from the California Gulch CERCLA site. This strongly acidic groundwater typically contains 4,400 ppm sulfate and ~500 ppm each of iron, calcium, manganese, and magnesium. Two class O and two class S reagents were chosen for treatability screening (Fig. 16.) In the first test, without any treatment optimization, pretreatment,

or pH adjustment, one of the class S reagents took 0.16 ppm Cd, 0.31 ppm Cu, and 0.26 ppm Pb to nondetectable levels at the native pH 3.17. Both of the class O reagents, which were equally effective at treating lead, also showed high affinity for arsenic, taking the residual level as low as 0.002 ppm (91.7% removed.) None of the reagents removed any significant levels of manganese, which was expected. This is a promising attribute, since Mn – which is the fifth most abundant element in the earth's crust – is not considered to be a toxic metal. Selective removal of Cd, Cu, Pb, and/or As, therefore, will result in the production of far less hazardous sludge. If removal of the Mn and/or Fe is desired, however (e.g., to make drinking water more palatable), another category of nonviable MOP-UP® reagent (class M) is already well-characterized and has been shown to be very effective at removing Mn and Fe, taking both to extremely low (low- to sub-ppb) residual levels in a wide range of solutions and under a wide range of conditions. (See, for example, Figure 17 which shows the results from an earlier test in which the reagent was incubated for less than 1 hour in seawater, with its complex mixture of ions, where it was shown to be capable of taking Mn at least as low as 1.5 ppb, Zn at least as low as 0.75 ppb, and Co at least as low as 10^{-3} ppb.) The class M reagents can be used in series after treatment by class S and/or class O, thereby producing two separate sludges and preventing Fe and/or Mn from contributing to the amount of hazardous sludge that is produced.

The EPA also provided acid mine drainage from the Summitville site Reynolds Adit. This groundwater, which had a pH of 3.07, contained 229 ppm Al, 88.8 ppm Cu, 16.3 ppm Zn, and ~380 ppm Fe, as well as low levels of Cd and Ni. A single treatability test was performed with three class S and one class O reagents. Too little reagent was added for all of the targeted metals to be removed from such concentrated solutions at this pH. However, the reagent that performed the best – a class S reagent, as expected – took up 76.5 mg Cu/g, which would be an extremely high loading at a neutral or alkaline pH, let alone a strongly acidic solution. None of the reagents took up appreciable amounts of iron under these conditions. Some were beginning to take up relatively modest amounts of aluminum; the class S reagent that took up so much copper also removed 13 mg Al/g, while a second class S reagent took up 21 mg Al/g as well as 51.4 mg Cu/g. (Note that other test results indicate a higher reagent concentration would in all likelihood remove the aluminum. See, for example, the results with the S-3 Ponds Area simulant, discussed below.) There was insufficient time or funding to conduct a second treatability test on this water; however, the objective of the treatability study was amply achieved, in that the reagents were clearly shown to be very effective at taking up high priority heavy metal cations from strongly acidic groundwaters in the presence of high levels of iron and sulfate, without pretreatment or pH adjustment.

The very first test ever conducted with acid mine drainage was done with water from the Berkeley Pit; in this test, 95% of the copper was removed from a pH 2.8 sample containing 222 ppm Cu, 552 ppm Zn, 290 ppm Al, 465 ppm Ca, 1,000 ppm Fe, 490 ppm Mg, 205 ppm Mn, 80 ppm Na, and 7,600 ppm SO_4 . In addition to copper, the class S reagents were also found to be taking up high loadings of Zn simultaneously. One (B-M5RSWS) took up 86.3 mg Cu and 61.9 mg Zn per gram of reagent, for example.

A second test was done in order to determine whether other metals are being taken up as well. Although neither aluminum nor manganese was removed at pH 2.8, the reagents were found to be very effective at treating magnesium. One class S reagent, A-M5RMWS(thio), for example, took up 64.3 mg Cu, 36.3 mg Zn and a whopping 4,375 mg Mg per gram, for a total loading of 4,531 mg metals/g at this strongly acidic pH.

Chester Engineers provided a groundwater sample from a private industrial site heavily contaminated with arsenic in both inorganic and organic forms (i.e., containing a total of 20 ppm arsenic, with ~50% of that being organoarsenicals). This groundwater has been found to be exceptionally difficult to treat; extensive studies to develop a treatment system for this site found that only a very elaborate series of chemical treatments and separation steps can take out the mixture of arsenic species. Four different reagents, two class S and two class O, were screened in a preliminary test to determine whether treatment by the MOP-UP® technology would be feasible

(Fig. 18.) The best reagent of the four removed 97.6% of the total arsenic, i.e., took the total arsenic content down to 0.49 ppm, at the sample's native pH – without any pretreatment. (Even the reagent with the poorest performance removed 93% of the total arsenic.) Studies with As(III), As(V), and arsanilic acid in standard solutions showed that each of the arsenic species can be taken to much lower residual levels by MOP-UP® reagents; therefore, a minor modification to the treatment is expected to take the total arsenic in this highly problematic groundwater to drinking water levels quickly, easily, and economically.

Mercury is of widespread concern throughout the DOE complex. Earlier studies, in which mercury was spiked into the Savannah River Site groundwater and the Berkeley Pit water, had indicated MOP-UP® reagents have an extremely high affinity for this pollutant, even in complex media at low pH. However, neither of these groundwaters actually contains mercury, and so the environment of such a sample may be vastly different from that of a site that normally is contaminated with mercury. Therefore, Biopraxis made numerous attempts to obtain a sample of mercury-contaminated groundwater. The contractor at the S-3 Ponds Area, Y-12 Plant, Oak Ridge, had hoped to be able to provide a sample from this site, which typically contains mercury. However, it was difficult to arrange for a shipment of a sample from the S-3 Ponds area in time for use on the current contract, since the groundwater is very heavily contaminated with numerous pollutants and typically contains a number of radionuclides. The contamination at this site is much more complex than the others studied under the MOP-UP® program; contains a number of metals against which MOP-UP® has never been tested (and certainly was never designed to treat); and also contains high levels of organics and nitrate. Therefore, it seemed unlikely that MOP-UP® could be shown to be capable of treating this site without substantial additional development work. Studies conducted to date, however, indicate that some MOP-UP® reagents have such a strong affinity for mercury that this priority pollutant should be readily treated even in the presence of numerous other contaminants. In order to evaluate the potential for using MOP-UP® to treat mercury in a complex environment, therefore, FETC provided detailed information about the contaminants and the ranges of their concentrations that are found throughout the site. Using this information, Biopraxis developed an S-3 Ponds groundwater 'simulant' containing all inorganics (except radioactive isotopes) and organics found at more than half of the wells. The average concentrations found in the wells were used in the simulant, with the exceptions of metals that are of wide-spread concern throughout the DOE complex, such as Cd and Cu as well as Hg; for these high priority pollutants, Biopraxis used the maximum concentrations ever reported. The resulting mixture, which contains some 360 ppm metals, 88 ppm total organic pollutants (i.e., 3.8 ppm TCE, 5.0 ppm 2-butanone, 51.8 ppm acetone, 7.0 ppm chloroform, 3.2 ppm toluene, and 17.3 ppm methylene chloride), 1700 ppm nitrate, and high levels of sodium, potassium, and chloride, was found to have a pH of 4.1; although this is considerably more acidic than the circumneutral groundwaters found throughout most of the site, Biopraxis elected not to adjust the pH, in order to challenge MOP-UP® to the maximum extent possible.

The results were very exciting. An initial screening run (Fig. 19) confirmed that class S reagents were generally better at treating Cd, Cu, Hg, and Zn, whereas class O were superior when it came to uranium; and both were very effective at treating Ba in this particular environment. On the basis of this test and the results from some of the screening tests with the "clean" pH 2 and pH 5 standard solutions being performed concurrently, two formulations were chosen, each comprising a 1:1 ratio of one class O and one class S reagent.

The second and final test with the S-3 Ponds Area water (Fig. 20) was designed to accomplish several goals. First, in order to confirm that the use of higher reagent concentrations would indeed take contaminants to lower and lower levels in a given groundwater environment, three different concentrations were used (0.5, 1, and 2 mg reagent/L, with the reagents used in a 1:1 ratio, dry weight.) This experimental design also revealed the metals for which the reagent formulations have the highest affinities. Preliminary experiments had indicated that the reagents can be used in a mixture; however, the second S-3 Ponds Area test was designed to determine whether using the reagents in sequence would provide superior performance. Three different sets of samples were

run for a given formulation, i.e., one in which both reagents were added simultaneously to the water and incubated for 4 hours; one in which the class S reagent was added first and incubated for 2 hours before the class O was added and the incubation continued another 2 hours; and the third in which the class O reagent was added first and incubated for 2 hours before the class S was added and the incubation continued another 2 hours. (There was too little left of the reagents selected for use in the second formulation for the full matrix of samples to be run, so only part of the matrix was run.) And finally, of course, the experiment was designed to demonstrate removal of > 90% of all the targeted heavy metals, in this case, Hg, Cd, Cu, Zn, Ba, and U.

The only work that had been done with uranium by this point in time was the first S-3 Ponds Area screening test. It was therefore essentially impossible to select reagents that were known or expected to be optimal for uranium treatment. Nevertheless, this contaminant is one of the most commonly found throughout the DOE complex, and analyses were performed to determine the extent of uranium removal. The laboratory that conducted the bulk of the analyses on these samples was not able to detect levels below ~0.25 ppm. Therefore, select samples (i.e., those that were expected to have the lowest residual levels of all contaminants) were sent to a second laboratory that offered 0.000001 ppm sensitivity (at, of course, a much higher cost per sample!)

The S-3 Ponds Area simulant contains 1.8 ppm nickel. At this point in the development of the MOP-UP® technology, Biopraxis is producing the nonviable reagents in gram batches. There was not enough of the reagents left over from previous testing to enable testing with large volumes of S-3 Ponds Area water, i.e., the number of metal analyses that could be performed was limited. Therefore, uranium analysis was given priority, and nickel analyses were done only on a few samples.

The data showed:

- MOP-UP® was able to take the mercury, cadmium, copper, zinc, and aluminum all to nondetectable levels (the minimum level of detection for mercury was 500 parts per trillion), take uranium to 180 parts per trillion, and remove 98% of the 15.3 ppm barium – at pH 4.1, in the presence of high levels of other inorganics such as nitrates as well as high levels of organic contaminants. Since MOP-UP® reagents have taken barium to nondetectable levels in complex metal mixtures before, a slight adjustment of the process is expected take out the final 0.3 ppm of that metal as well.
- This experiment readily achieved its initial goal of demonstrating MOP-UP®'s ability to treat mercury in contaminated groundwater!
- Very simple tests can be used to select a MOP-UP® reagent formulation capable of treating even highly complex, heavily contaminated groundwater.
- By using two different reagents that exhibit different affinities for the contaminants, it is possible to design a formulation that can treat a complex mixture of contaminants. It is therefore expected that by tailoring the relative amounts of each reagent, metal removal from a complex mixture can be even more efficient.
- It appears that the treatment system can be optimized (i.e., reagent loading can be maximized) by using reagents in sequential layers that exploit each reagent's relative affinity for metals found in a complex mixture, rather than by combining the reagents in a single, homogeneous bed.
- Metal removal is selective; i.e., the formulations tested in this S-3 Ponds Area simulant showed much higher affinity for Hg, Cd, Cu, and Zn than for Al.
- Even at pH 4.1, significant levels of nickel were taken up by nonviable MOP-UP®

reagents; and the higher the reagent concentration, the more nickel removed. Fractional nickel removal was parallel to and slightly less than fractional barium removal in the samples analyzed, with 1 g/L Formulation 1 taking up ~42% of the Ni. Since the objective of the groundwater treatment system at Oak Ridge is to raise the pH to neutral levels during treatment, the data produced on this program indicate that simple pH adjustment will not only improve Ni removal to the desired target of >90% but also raise the reagents' capacity for metal pollutants by an order of magnitude or more.

- Since the analysis of organics and nitrate are not on the contract, the fate of these pollutants is not known. However, earlier Biopraxis-funded studies indicate that the organics, and possibly the nitrate, may have been treated as well. (See section 2.7 below.)

And, most importantly, the data showed:

- MOP-UP® passed the success criteria established for groundwater MOP-UP®, – i.e., that a selected MOP-UP® formulation must be shown to be capable of removing $\geq 90\%$ of the targeted heavy metal pollutants from the “chosen” groundwater sample – with flying colors.
- MOP-UP® can be demonstrated on-site at the funnel-and-gate test bed being installed at the S-3 Ponds Area – and with much less development effort than was originally expected.
- MOP-UP® appears to be capable of readily achieving – and often far surpassing – U.S. goals for cleaning up heavy metal contamination in groundwater. The goals include, for example, 50 ppb for As, 5 ppb for Cd, as low as 5 ppb for Pb, as low as 50 ppb for Cr, and 0.05 - 2 ppb for Hg (Table 4)³; and the EPA-proposed standard of 20 ppb for U in drinking water⁴.

In short, the findings under the FETC program have been far better even than hoped. The results obtained to date show that MOP-UP reagents have the ability to treat a wide range of metals; have extremely high capacities for heavy metals, even in very dilute solutions, in complex mixtures, and/or at pH extremes; have the ability to take a wide range of metals to nondetectable (by ICP or cold vapor) levels; and have the ability to treat metals in the presence of organics, and possibly even to treat organics as well as metals. Rather than merely achieving the established success criterion with a single groundwater sample after extensive studies to optimize treatment for the chosen site, MOP-UP® surpassed the success criterion with a wide range of groundwater samples with little or no need for treatability testing.

2.5. Testing with Electronics Manufacturing Wastewaters

The California Office of Strategic Technology awarded a matching Defense Conversion grant designed to evaluate adapting the DOE in situ groundwater MOP-UP® technology for treating electronics wastewaters contaminated with heavy metals. This application was chosen because (a) the electronics industry produces huge amounts of metal-contaminated wastewater, (b) the wastewater is extremely difficult and expensive to treat, and (c) the composition of the electronics wastewaters is similar in many respects to the composition of acid-leachate-contaminated groundwater, and so a technology developed for the treatment of one can transition relatively easily to the treatment of the other. The bulk of the work performed under the Defense Conversion grant was associated with market analysis and strategic planning rather than laboratory studies. Nevertheless, the limited laboratory work that was authorized provided interesting data that confirm MOP-UP®'s ability to treat heavy metals in complex solutions containing high levels of organics, surfactants, and other contaminants.

Methods, processes, chemicals, and components used in the production of electronics equipment is sensitive commercial information. Certain aspects of electronics manufacturing processes can be gleaned from the constituents found in rinsewater wastes produced by the manufacturing

processes. Therefore, electronics companies, in general, will not provide information about or samples of their rinsewater wastes without first seeking the protection of a Secrecy and Nondisclosure Agreement. The "recipes" for the simulant rinsewaters used on the matching grant were developed through a combination of access to such protected, proprietary information provided by electronics companies and a market survey. Five recipes, designed to simulate the wastewaters that are produced in high volume by targeted sectors of the electronics industry, were developed (Fig. 21.) Each of these types of rinsewaters has been found to be very difficult to treat, due to the high concentrations of solvents, chelating agents, and constituents such as sulfate that form complexes with heavy metals.

As promising reagents were developed under the DOE program, they were transitioned to the matching grant program for evaluation as potential treatment reagents for use by the electronics industry. The same basic testing protocol was used, i.e., the MOP-UP® reagents were added to the contaminated water, incubated for 2 or 4 hours under ambient conditions without agitation, and then separated. There was one significant difference. Industry is required to adjust wastewater to near neutral pH prior to discharge. If the pH is adjusted before the MOP-UP® reagents are added, some metals – notably lead – will precipitate, forming a high volume of sludge that is difficult to separate and dry. Biopraxis predicted that by adding the MOP-UP® reagents first, metals such as Pb would be taken up and therefore not available for precipitation; and not only would a smaller volume of sludge would be formed, but a smaller amount of chemicals would be needed to adjust the pH before discharge. Therefore, the tests with the electronics rinsewater simulants were usually done in parallel at pH 2, and at pH 7 minus any metals that tended to precipitate at this pH.

The same general trends were observed for metals removal in the presence of solvents and chelating agents under the matching grant as in the "clean" laboratory solutions and/or groundwater under the DOE program:

- Promising class S reagents showed very high affinities for lead in all the Pb-containing simulants at pH 2. Loadings as high as 91 mg Pb/g reagent were seen at this pH in the semiconductor positive lithography wastewater, for example, in the presence of 32 ppm TCE, 43 ppm acetone, 5 ppm each acrylate, polyalkyl aldehyde, ethyl acetate, and ethanol, 16 ppm isopropyl alcohol, and 12 ppm phosphate, which is a strong metal complexing agent. Using a minimal amount of reagent and without any attempt to optimize the treatment, the MOP-UP® reagents consistently removed 90-98% of the Pb from the three Pb-containing electronics wastewater simulants.
- Cr(VI) and Ni were not as amenable to treatment of these wastewaters at pH 2 as Pb. However, when the pH was raised to ~7, both metals were readily removed by MOP-UP® reagents, even in the presence of solvents, surfactants, and chelating/complexing agents. The class S reagent DV-W7ESIS, for example, removed 97% of the Cr(VI) and 95% of the Ni from the semiconductor final layering and cleaning wastewater, even in the presence of a part per thousand of sulfate, as well as high levels of xylene and acetone, taking up 64 mg metals/g reagent. Interestingly, the class O reagent FRT04-M5RSAS took up even higher loadings in this same wastewater, i.e., 93 mg metals/g; and showed the extraordinary capacity of 141 mg/g for Ni in the cathode ray tube interior panel coating wastewater at neutral pH. Two other class S reagents were shown to be capable of removing ≥95% of both the Cr(VI) and Ni from the semiconductor final layering and cleaning wastewater as well.
- Since the analysis of organics and complexing/chelating agents were not on the grant, the fate of these pollutants is not known. However, there is some indirect evidence that at least some of the organics may have been treated as well. Certain organics, such as xylene, mask the presence of Pb when analyses are done by AAS. Once the printed wire board assembly process wastewater had been treated with a MOP-UP® reagent, low levels of Pb were readily detected, indicating the xylene was no longer present to any appreciable extent. This

is consistent with some very simple, internally-funded studies on the use of nonviable MOP-UP® reagents to treat organic pollutants (see section 2.7 below.)

Biopraxis has contacted several major semiconductor manufacturers to ask for samples of problematic wastewaters so that treatability tests to evaluate MOP-UP®'s potential can be conducted with "the real thing." As mentioned above, the companies are leery of providing such samples. However, the results obtained on the matching grant sparked sufficient interest that one facility sent a sample of an arsenic-containing wastewater that has consistently gone over the permissible discharge limitations despite an elaborate and costly treatment train. In the first treatability test to identify promising reagents – i.e., without any attempt to optimize the process – > 90% of the arsenic was removed. Delighted with these results, the company subsequently sent a sample of water from another facility that contains Pb, Cu, Zn, and Ni. At the native pH of 3, the MOP-UP® reagents chosen for screening readily took the Pb and Cu to nondetectable levels – at least an order of magnitude lower than the facility's treatment plant can achieve after pretreatment and adjustment to alkaline pH. Ni and Zn were below the required discharge limits. As a result of these extraordinary tests, the company is now considering providing samples of wastewater from its extremely valuable, highly sensitive, new manufacturing process in which copper has been substituted for aluminum. The company has not yet found a treatment capable of taking copper to the desired discharge levels in this water. Biopraxis has also been put into contact with SEMATECH, a consortium of the top electronics manufacturers dedicated to the development of technologies that will benefit the entire industry, to discuss the possibility of a project to develop MOP-UP® for treating wastes from emerging copper-based manufacturing processes.

2.6. Internal Research and Development (IR&D) Studies with Radionuclides

A handful of preliminary, company-funded experiments, performed by Biopraxis Ltd in Great Britain, indicate that the nonviable MOP-UP® reagents are just as effective at treating radionuclides as they are at treating heavy metal pollutants. A simple series of tests have been conducted to evaluate the residual levels to which radionuclides can be taken, and the amounts of reagent needed to achieve extremely low (nondetectable) concentrations. These tests, done in "clean" laboratory solutions at neutral pH using a single class S MOP-UP® reagent, were designed to evaluate the effect of contact time and reagent concentration on radionuclide removal.

The results showed that ^{99}Tc , ^{137}Cs , and $^{239/240}\text{Pu}$ were taken to nondetectable levels from initial activities of 485.3, 1.415, and 202.2 Bq/ml, respectively, using 5 g reagent/L (Fig. 22). Radionuclide uptake was so rapid that residual ^{137}Cs was nondetectable by the time the first sample was collected for analysis, at 1 hour's incubation; and both ^{99}Tc and $^{239/240}\text{Pu}$ were at nondetectable levels within 2 hours.

When 0.5 g/L was used, the class S reagent readily removed > 95% of the ^{57}Co and ^{60}Co and > 99% of the ^{63}Ni from 0.26, 1.25, and 330 Bq/ml, respectively (Fig. 23.)

And when using a mere 0.05 g/L of reagent (Fig. 24), > 90% of ^{241}Am or ^{89}Y were removed from an initial activity of 1.24 Bq/ml within the first hour of incubation. (Tests have not yet been done to confirm that all detectable ^{241}Am or ^{89}Y can be removed with slightly higher levels of the reagent.)

It should be noted that no attempt was made to identify the most promising reagent for use in these studies; this particular class S reagent was optimized for its magnetic properties, rather than its radionuclide scavenging capabilities.

Although little work has been done to determine the Mn-scavenging abilities of the nonviable MOP-UP® reagents produced and evaluated on the DOE program, the few analyses that have been performed indicate that they have little if any affinity for Mn. However, this magnetic class S reagent showed a high affinity for ^{54}Mn , with 5 g/L removing more than 92% of the ^{54}Mn from a

neutral solution containing 17.3 Bq/ml within the first hour of incubation.

2.7. Internal Research and Development (IR&D) Studies with Organics

Since the analysis of organics and nitrate are not covered under the FETC contract, the fate of these pollutants is not known. However, other studies indicate that the organics, and possibly the nitrate, may have been treated as well. As mentioned above, there was indirect evidence in the studies performed under the matching Defense Conversion grant that the reagents were removing organics such as xylene from the simulated rinsewaters.

Much more direct evidence was produced under an internally-funded project, in which a handful of simple, preliminary studies were conducted to evaluate the potential of the reagents for treating organic as well as inorganic pollutants.

For example, a class S reagent was incubated for 24 hours with polyhalogenated and polyaromatic priority pollutants, including hexachlorobenzene, heptachlor and its *cis*-epoxide, aldrin, endosulphan and its sulfate, DDT and its analogs, carbetamide, chlorotoluron, fluoranthene, benzo(ghi)perylene, benzo(u)fluoranthene, indeno(123cd)pyrene, benzo(b)fluoranthene, and benzo(a)pyrene; the reagent was then removed, and the water analyzed by GC-MS. The results (Fig. 25) showed that 15 of the 21 organics were below the minimum levels of detectability, less than 8% of 3 others remained, and less than half of each of the final 3 remained. There was evidence that the reagents are not just adsorbing, but degrading the organics; i.e., the concentration of chloride ion in solution rose sharply. (It should be noted that even the most effective bioremediation and 'zero valent' metal catalyst technologies measure half-lives for these highly refractory pollutants in terms of weeks and sometimes even months.) Even if the solvents were simply being sorbed, the capacity of the reagent was extremely high, i.e., ~600 mg organics /g reagent.

In another experiment (Fig. 26), a handful of class O and class S MOP-UP® reagents were incubated with a mixture containing 500 ppb each of fourteen halogenated solvents. Several reagents were found to remove the organics, being particularly effective with tetrachloroethene, carbon tetrachloride, trichloroethene, and 1,1,1-trichloroethane. One reagent, for example, took these solvents down to < 4 ppb, 13 ppb, 38 ppb, 40 ppb, respectively, while simultaneously removing more than half of each of the other organics. When the incubation period was extended, the residual levels of organics continued to decrease.

It should be noted that there was no attempt to optimize any of the conditions on either of these studies. In fact, on the latter study, a very limited amount of reagent was purposely added, to help determine whether adsorption or degradation phenomena might be involved.

Many DOD as well as several DOE sites are contaminated with explosives. Very recently, Biopraxis conducted a simple study (Fig. 27) to evaluate the potential of its reagents for treating explosives contamination, incubating four reagents for 18 hours in solutions containing 1,000 µg/L 2,4,6-TNT, 150 µg/L 2,4-DNT, and 200 µg/L 2,6-DNT. Three of the reagents took TNT to nondetectable levels and significantly reduced the concentration of the DNT isomers, while the fourth reagent removed all detectable traces of all three pollutants. These results also provided direct evidence that chemical degradation processes, rather than simple adsorption phenomena, are involved, since traces of Am-DNT was found in all treated samples.

(Note: Biopraxis recently received a major DoD contract to evaluate the use of nonviable MOP-UP® reagents for the removal and/or destruction of chemical warfare agents.)

3. IN SITU MOP-UP® TREATMENT SYSTEM CONFIGURATIONS

MOP-UP® is an unusual technology in that it can be implemented in a variety of configurations,

ranging from pump-and-treat to *in situ* reactive "barriers". The initial goal of the FETC program was to develop a design compatible with a funnel-and-gate barrier installation that involved a modest amount of periodic pumping to remove spent reagents and replace them with fresh reactive material. Preliminary sizing experiments conducted under the FETC program with several of the more promising nonviable reagents (representatives of classes S, O, and M) indicated that the VCS is readily able to separate the reagents from the treated water, and the approach that was originally proposed is therefore quite viable.

However, the results developed under the program indicate that MOP-UP® can be deployed in an even more promising approach. The extremely high capacities of the MOP-UP® reagents for a wide variety of heavy metal pollutants even in solutions containing very low metal concentrations, other inorganics, and/or organics and even in strongly acidic groundwater, and the tolerance of the MOP-UP® technology for a wide range of groundwater environments indicate that the MOP-UP® reagents can serve as reactive media for use in completely passive reactive barriers.

Passive reactive barriers can be designed in a variety of configurations. For large-scale remediation projects, *in situ* systems may either be constructed as a continuous, permeable treatment zone or as a funnel-and-gate configuration. In a continuous permeable reactive wall (PRW) system, the whole width of the contaminant plume flows through the emplaced wall under natural gradient conditions. The contaminant is treated by reactive material as it flows through the wall. For funnel-and-gate designs, low permeability barrier wall "funnels" (impermeable slurry walls, sheet piles, or soil admixtures applied by soil mixing or jet grouting) channel the plume through the reactive material in a gate or multiple gates. Gates must be proportionately thicker (longer flow path) than a comparable permeable wall, due to the amount of flow diverted by the adjacent funnels. Contact time between groundwater and the reactive medium is primarily controlled by the thickness of the layer of reactive medium and by the flow rate. The design of the reactor is site-specific. The required contact time depends on the half-lives and concentrations of the contaminants in the influent water, and the target limits for effluent concentrations. Generally, higher influent contaminant concentrations require greater contact time for treatment and, therefore, wider walls or thicker gates.

MOP-UP® appears to be very well suited for use with either configuration. Very simple column tests conducted under the FETC program indicate that the particulate MOP-UP® reagents can be held in place via mixing with fine sand (or, presumably, soil). Sand or soil can help ensure continuous, even flow of the groundwater through the wall, allow for porosity changes due to installation of the reactive medium, and enable the construction of walls with practical dimensions yet minimum reactive medium, and is therefore typically mixed with other types of reactive media, such as zero-valent iron. Note, however, that there was not enough time or funding remaining on the program to evaluate a permeable barrier approach more fully. One major question that needs to be addressed during future testing is the impact of the extremely high metal capacities these reagents exhibit; although water flowed freely through columns packed with a mixture of sand and reagents, and even through columns packed with reagents only, MOP-UP® reagents take up such extraordinary amounts of metal that they may eventually clog.

On the other hand, most (if not all) reactive media are expected to have a limited lifetime, and to require periodic replacement. This requirement is already receiving attention, and several solutions have been demonstrated and/or are under development. For example, an *in situ* reactor can be placed in a container such as a well screen that facilitates removal when the reactor must be rejuvenated. For example, a container has been constructed by modifying a well screen to allow connection to sealable joint sheet piling. The container was made by cutting a series of windows in opposite sides of a 24-inch diameter steel pipe and welding pieces of stainless steel continuous slot well screen into the openings. The container was oriented with one set of screened windows facing upstream and the opposite set facing downstream, allowing ground water to easily flow through the reactive medium inside. A funnel-and-gate system that includes this type of gate has been installed at Borden Ontario. In the U.S., the problem has been addressed by developing a

construction approach whereby the reactive media is placed in the subsurface in removable cassettes. A temporary sheet pile box or a large diameter caisson is installed into the subsurface and the screen panels are placed on the up- and downgradient sides, while impermeable panels are placed on the lateral sides. Steel rail guides for the cassettes are installed within this interior compartment and the temporary sheet piles or caisson are removed. The cassette is a steel frame box (2.5 m long, 1.5 m wide and 0.5 m thick) with two opposing screened sides and two impermeable sides which is filled with the reactive media and lowered into the cavity. By replacing cassettes containing depleted reactive media with cassettes containing fresh media, the full-scale remediation system operation life can be extended essentially indefinitely. MOP-UP® reagents should be very compatible with such designs.

At sites where the installation of permeable walls may be impractical for technical or financial reasons, treatment zones can be created with arrays of unpumped wells. Convergence and divergence of naturally flowing groundwater through the wells provides hydraulic control and downgradient mixing. An array of wells, installed within or without a funnel-and-gate, can serve either as a set of *in situ* reactors or as a means to release reagents that promote metal uptake/stabilization downgradient. Sophisticated two-dimensional flow and transport modeling algorithms are already being developed by other organizations to evaluate the impacts on hydraulic performance of the wells and thus the required spacing of wells to achieve various remedial goals⁵. MOP-UP® reagents may simply be flushed out of the wells once they have become "spent." Alternatively, the EPA has suggested exploiting a new approach in which a "sock" full of reactive media is inserted into the well; once the media becomes "spent", the sock can be withdrawn and replaced⁶.

Creation of treatment zones, in place of treatment walls that are confined within strict boundaries, can be accomplished with injection wells or by hydraulic fracturing. Well systems typically involve injection of fluids or fluid/particulate mixtures for distribution into a treatment zone within the target area of the aquifer. Potential advantages of this approach are that there is no need to construct a trench and that it is possible to access aquifers at greater depths. Direct injection of the MOP-UP® reagents appears extremely appealing for applications in which the aquifer is far below ground. DOE Grand Junction, which has funded a number of studies to evaluate direct injection approaches, is encouraging Biopraxis to explore this alternative. Certainly, from a cost standpoint, with the data that are currently available, direct injection appears to be the least expensive by far. However, additional testing will be required to ensure that MOP-UP® can address regulatory issues, notably whether the reagents will upset the subsurface environment through some unforeseen mechanism (although, given what is currently known about the chemistries of the proprietary nonviable MOP-UP® reagents, this is considered to be highly unlikely), and whether the reagents will remain stable *in situ*. Another consideration, which is being addressed by other researchers, is a question of the reliability of injection for creating homogeneous treatment zones. Horizontal hydraulic fracturing is capable of creating propped fractures generally less than 2.5-cm thick and 7 to 12 m in diameter that can be filled with reactive material. However, this technology is typically used at shallower depths (3 to 12 m), and there is no current record of a field application to treatment zones. On the other hand, depending on the soil type, vertical hydrofracturing can create fractures up to 20 cm wide, which may be suitable for treatment wall applications.

4. COMPETING TECHNOLOGIES

Two goals were established for the FETC program. One was to demonstrate that MOP-UP® is capable of removing > 90% of the targeted heavy metal contaminants; this goal has been more than achieved.

The second goal was to demonstrate that MOP-UP® is competitive by comparison with conventional groundwater treatment technologies. However, because data produced on the FETC program indicate that MOP-UP® is particularly well-suited for use in reactive barrier configurations, and because reactive barriers offer so many potential advantages over conventional

remediation technologies, Biopraxis has elected to include a much more challenging evaluation, i.e., comparing MOP-UP® against emerging reactive barrier technologies.

The information that is included in the following comparison has been compiled from reports in the open literature, primarily those published by the EPA, the Ground-Water Remediation Technologies Analysis Center, the Federal Remediation Technologies Roundtable, and EnviroMetal Technologies, Inc., the company that is commercializing the most thoroughly demonstrated reactive medium, i.e., the "zero-valent iron" technology. Opinions regarding the competing technologies and interpretations of data produced during their development are those of the authors of these reports.

4.1. Conventional Groundwater Treatment

Pump and treat systems, typically involving chemical precipitation, currently dominate the groundwater treatment market. Despite their prevalence, they suffer from many disadvantages. These may include⁷, for example:

- As with any pump and treat process, if the source of contamination is not removed (as in metals absorbed to soil), treatment of the groundwater may be superfluous.
- The presence of multiple metal species may lead to removal difficulties as a result of amphoteric natures of different compounds (i.e., optimization on one metal species may prevent removal of another.)
- As discharge standards become more stringent, further treatment may be required.
- Metal hydroxide sludges must pass TCLP prior to land disposal.
- Reagent addition must be carefully controlled to preclude unacceptable concentrations in treatment effluent.
- Efficacy of the system relies on adequate solids separation techniques (e.g., clarification, flocculation, and/or filtration.)
- Process may generate toxic sludge requiring proper disposal.
- Process can be costly, depending on reagents used, required system controls, and required operator involvement in system operation.
- Dissolved salts are added to the treated water as a result of pH adjustment.
- Polymer may be added to the water to achieve adequate settling of solids.
- Treated water will often require pH adjustment.

The Federal Remediation Technologies Roundtable provided performance information on three sites (Fig. 28.) At the Coakley Landfill, 330 ppb Cr, 122-200 ppb Ni, and 10-90 ppb As were taken to 50, 100, and 50 ppb, respectively, by conventional hydroxide precipitation with lime. At the Stringfellow's Acid Pit Site, conventional precipitation technology took 1.5-270 ppm Cr, 0.32-9.3 ppm Cd, 2.2-300 ppm Zn, and 1.7-20 ppm Cu to 0.5, 0.11, 2.61, and 2 ppm, respectively. And at the Winthrop Landfill, a pilot test of the conventional pump-and-treat chemical precipitation technology took 0.1-0.8 ppm As, 0.04 ppm Ni, and 0.2-0.6 ppm Zn to 0.05, 0.04, and 0.18 ppm, respectively. The typical levels that can be achieved with other metals, in industrial wastewaters, is shown in Figure 29.

The primary capital cost factor is design flow rate. Capital costs for 75 and 250 L/min (20 gpm and 65 gpm) packaged metals precipitation systems are ~ \$85,000 and \$115,000, respectively. The primary factors affecting operating costs are labor and chemical costs. Operating costs (excluding sludge disposal) are typically in a range from \$0.08 to \$0.18 per 1,000 liters (\$0.30 to \$0.70 per 1,000 gallons) of groundwater containing up to 100 mg/L metals. Pumping costs average \$0.07/1000 liters (\$0.25 per 1000 gallons). Sludge disposal may be estimated to increase operating costs by approximately \$0.13 per 1,000 liters (\$0.50 per 1,000 gallons) of groundwater treated. Actual sludge disposal costs (including fixation and transportation) have been estimated at approximately \$330 per metric ton (\$300 per ton) of sludge. Costs for performing a laboratory treatability study for metals precipitation may range from \$5,000 to \$20,000. Depending on the

degree of uncertainty or other requirements, a pilot or field demonstration may be needed. Associated costs may range from \$50,000 to \$250,000, depending on scale, analytical requirements, and duration.

Reactive barrier technology is considered to be an extremely promising approach to groundwater remediation. However, a major potential limitation of treatment wall technology is the difficulty of constructing the wall at depths greater than 10 m. Wall installation at depths of 10 to 30 m is significantly more difficult and escalates construction costs to the point that they may become limiting for the implementation of this technology. Installations at depths greater than 30 m are only theoretically possible with current technologies. Therefore, pump-and-treat remains the only semi-viable approach to the treatment of deep subsurface plumes.

4.2. Commercialized and Emerging Heavy Metal Treatment Reactive Barriers

Water permeable treatment walls are installed as permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume, allowing the plume to move passively through the wall while retaining heavy metal or radionuclide contaminants. Reactive barriers can adopt many forms. These include the continuous permeable wall, the funnel-and-gate, and treatment zones comprised of unpumped well arrays or reactive media injected directly into the aquifer. Several different types of reactive media have been identified for use in barrier technologies⁸ for heavy metal contaminants. Reactive media that modify the pH or Eh conditions in the subsurface can affect the solubility of pH or redox sensitive species and cause their precipitation. For example, Blowes and Ptacek⁹ describe a reactor that causes chromium precipitation by generating reducing conditions in the subsurface. Another type of *in situ* reactor contains a material capable of dissolving and causing the precipitation of a mineral phase that immobilizes the contaminant. For example, Xu and Schwartz¹⁰ describe a reactor that contains hydroxyapatite (calcium phosphate), which dissolves to release phosphate, which in turn causes precipitation of lead phosphate minerals. A third type of *in situ* reactor removes materials from solution by sorption, e.g., through the use of activated carbon, zeolites or synthetic ion exchange resins. The reactions that take place in barriers are dependent on parameters such as pH, oxidation/reduction potential, concentrations, and kinetics. Thus, successful application of the technology requires characterization of the contaminant, groundwater flux, and subsurface geology¹¹.

Reactive barriers – whether in permeable wall or treatment zone configurations – offer many potential advantages over conventional pump-and-treat and impermeable barrier containment methods for groundwater remediation.

- Actual *in situ* contaminant remediation, rather than simple migration control as with impermeable barriers
- No requirement for continuous input of energy, because a natural gradient of groundwater flow is used to carry contaminants through the reaction zone
- Not susceptible to failure due to mechanical breakdown or power outage
- Limited maintenance (e.g., only periodic replacement or rejuvenation of the reactive medium) following installation
- No required surface structures other than monitoring wells following installation; enables maximum land utilization while minimizing environmental impact
- Comparatively quick installation and containment of contaminants
- Ability to remediate plumes even when the source term of the plume cannot be located
- Overall groundwater flow pattern is not altered as much as with approaches involving high-volume pumping
- Greatly minimizes or eliminates disposal requirements or disposal costs for treated wastes
- Does not involve removal of groundwater or air from the subsurface, and therefore does not require permits for discharges of groundwater or air to the environment
- Avoids the mixing of contaminated and uncontaminated waters that occurs with pumping, thereby significantly minimizing the volume of water that must be treated

- Minimizes exposure of workers to hazardous substances during installation and operation of the wall, due to lack of direct contact with contaminated materials
- Contaminants are not brought to the surface; i.e., no potential cross-media contamination
- Groundwater resources are not wasted by being brought to the surface for treatment and discharge
- Permeable barriers may also be used as landfill liners, thereby providing *in situ* treatment of leachate

It is therefore generally accepted that, where such reactive barriers can be used, they offer significant improvements in life cycle costs, safety, and utilization of the land above the contaminated plume. As one example of the cost savings that can be achieved through the use of *in situ* permeable barriers, field tests of the zero-valent iron technology were conducted at DOE Los Alamos National Laboratory. The installation had an initial capital cost of \$1,200,000 and an O&M cost of \$670,000 in FY93 (the year before the tests were scheduled for completion.) Life cycle costs for operational systems are expected to be 5 to 10 times less than excavation¹².

The main concern about treatment wall technology is the question of long-term performance under variable conditions that are commonly associated with groundwaters (e.g., seasonal variations in groundwater flow velocity and patterns, variations in the contaminant speciation and concentration). Loss of permeability over time as a result of particle invasion, chemical precipitation, or microbial activity, and possible gradual loss of media reactivity as the reactant is either depleted or coated by reaction by-products, need to be resolved before this technology can be applied with wider confidence. Currently planned field-scale tests and many ongoing laboratory studies are designed to address some of these issues.

Since the first commercial application of zero-valent iron using a funnel-and-gate system for the removal of chlorinated hydrocarbons in February 1995, several field- and pilot-scale studies have been implemented to evaluate the feasibility of reactive barrier technologies for treatment of both organic and inorganic contaminants. The emerging reactive barrier technologies and their current commercial status¹³ are summarized in Figure 30. The technologies that are targeted at heavy metals and/or radionuclides include various types of sorbents (peat, ferric oxyhydroxide, bentonite, zeolites and modified zeolites, and chitosan beads) and precipitating reagents (hydroxyapatite, zero-valent iron, dithionite, and lime/limestone.) Of these, only zero-valent iron and lime/limestone have been commercialized. It should also be noted that only zero-valent iron and dithionite are targeted at both heavy metals and organics, although zeolites and bentonites are capable of being modified for treating both.

Zero-Valent Iron: Trenches filled with elemental iron have shown promise for the practical, inexpensive remediation of contaminated sites. This "zero-valent iron" technology is primarily known for the extensive studies that have been conducted on treatment of halogenated organic compounds. However, studies to assess its applicability to remediation of select heavy metals have been initiated recently.

Low oxidation-state chemical species can serve as electron donors for the reduction of higher oxidation-state contaminants. This ability can be exploited to remediate metals that are more toxic and mobile in higher oxidation states, such as Cr(VI). Results of column experiments performed by Powell *et al*¹⁴ and batch experiments performed by Cantrell *et al*¹⁵ showed that chromate reduction was enhanced in systems containing iron filings in addition to the natural aquifer material. Accordingly, a field experiment was initiated in 1994 by the U.S. EPA National Risk Management Research Laboratory to investigate the use of zero-valent iron for chromium remediation at the U.S. Coast Guard air support base near Elizabeth City, NC. The mixed waste contaminant plume was between 4.2 and 6 m below the surface, and the water table ranged from 1.5 to 2 m below the surface. A treatment wall was constructed from a series of large-diameter augered holes in a staggered 3-row array. Twenty-one 20-cm columns were installed to a depth of 6.7 m throughout a 5.5 m² area. Columns were charged with a mixture of 50% iron filings (two

types), 25% clean coarse sand, and 25% aquifer material to a depth between 3 and 8 m below the surface. (One iron type was shown to be an effective reductant for chromate in a two-year laboratory study, while the other iron was shown to be more effective in the reductive dechlorination of the organics.) Untreated groundwater contained between 1 and 3 mg/L of chromate, while the treated groundwater contained < 0.01 mg/L. Dissolved iron in the groundwater increased from 0.05 mg/L to 1-20 mg/L, while dissolved oxygen decreased from 0.6 mg/L to 0.1 mg/L with a slight increase in alkalinity. There was also greater than 75% reduction in initial TCE concentrations and vinyl chloride concentrations were taken to less than 1 μ g/L. Longer residence times were planned to enable more complete remediation of the organics in the full field scale test. A full-scale reactive iron wall (150 ft long, 2 ft wide, and 26 ft deep) was installed in June 1996. This was the first application of the continuous wall configuration in a full-scale system. The wall begins about 3 feet below the ground surface and consists of 450 tons of granular iron. The system was designed to remediate a plume containing 10 ppm of trichloroethene (TCE) and 10 ppm of hexavalent chromium. Installation of the wall was complete in less than a day. According to EnviroMetal Technologies, Inc., the total installation cost \$500,000, with the iron costing slightly under \$400/ton.

In developing this chromium treatment process¹⁶, numerous stirred batch reactor and shaken batch bottle experiments to test chromate reduction were performed using two different aquifer sediments and a silica sand, seven types of iron, titanium, magnesium, aluminum, various metal pretreatments and seven aluminosilicate minerals. Aluminosilicate dissolution in these systems was also evaluated. Chromate adsorption and desorption studies as well as electron probe microscopic analyses of the reacted materials were carried out. The results showed that the rate and completeness of chromate reduction are dependent on a complex interaction between metal type, mass, surface area, pretreatment, and aquifer material mineralogy. The corrosion reactions involved in reducing and precipitating the chromium can only proceed when suitable e^- acceptors, such as protons, are present to form an appropriate couple and prevent the accumulation of electric charge. Some types of iron, particularly impure and partially corroded forms, are far more reactive than others for reducing CrO_4^{2-} . Certain aquifer materials contribute more significantly to these reactions due to their mineralogy. Aluminosilicates appear able to provide e^- accepting protons through dissolution, maintaining the corrosion process. A cycle can develop in which rust formation through corrosion promotes additional aluminosilicate dissolution.

The oxidation-reduction reaction that drives the metal-enhanced dechlorination process creates physical and chemical conditions (high pH and low Eh) that may cause precipitation of ferrous hydroxide [$Fe(OH)_2$], siderite ($FeCO_3$), calcium carbonate ($CaCO_3$), and other minerals when influent groundwater contains soluble metal compounds. Precipitation of these minerals may eventually reduce the porosity of the granular iron, decreasing volumetric flow through the system and possibly inducing channelized flow in the reactor; precipitates may also block the available surface area of the reactive iron, increasing the half-lives of chlorinated compounds in the system and potentially resulting in incomplete dechlorination¹⁷. Due to the potential for precipitation, groundwater containing high concentrations of dissolved metal compounds, inorganic carbon, or other compounds may impact operation and maintenance (O&M) requirements.

Clogging or coating that inhibits the performance of the system necessitates replacement or flushing of the granular iron every few years in areas where groundwater may have high mineral content. Porosity losses due to inorganic mineral precipitates from 2 to 15 percent per year have been predicted based on laboratory column results¹⁸. Rehabilitation or replacement costs can be calculated by assuming that a percentage of the original iron costs will need to be spent every five to ten years. The percentage and frequency are site-specific; for example, for very high TDS (carbonate) groundwaters, 75% of the iron costs might be expended at five-year intervals; for lower TDS groundwater, one might assume expenditures of only 25% of the iron costs every ten years. High concentrations of suspended solids in influent groundwater may "blind" or accumulate and physically block the reactive iron medium, reducing flow. Blinding of the top of the reactive iron layer occurred early in the SITE demonstration¹⁹.

If the iron has to be replaced, the spent iron would constitute a process residual. Disposal options for the spent reactive iron have not been evaluated. It is possible that the iron may require management as a hazardous waste²⁰. Additional process residuals may be generated depending on site-specific conditions. If required, use of secondary treatment (e.g., for mixed contaminants in which some are not entirely amenable to treatment by granular iron) could also generate process residuals, e.g., spent carbon. For some sites, it may be necessary to periodically replace the pea gravel, well sand, or other pretreatment filtration devices if they become completely blocked with sediments.

Figure 31 summarizes capital costs for treatment walls that are already built or for which costs have been estimated.

One of the most critical issues that must be considered in the design of permeable reactive barriers is selection of an appropriate barrier width²¹. The barrier width must provide sufficient contact time to ensure that contaminants are degraded to target levels. The necessary contact time is a function of the reactive surface area of the iron; degradation rate constants for the contaminants by iron; reaction pathways that lead to formation and degradation of hazardous reaction products; and the degree of contaminant degradation required to reduce effluent concentrations to regulatory limits. By modeling the net contribution of these four factors, it is possible to derive some quantitative guidelines for the preliminary design of reactive barriers.

The cost of the impermeable sections of the treatment wall system can be obtained from experiences with slurry walls or sheet pile installations. The cost of the zero-valent iron can be estimated based on the density of about 2.83 kg/m³ and a cost of approximately \$440-550/tonne²². (Note, however, that costs as high as \$1,200 per ton have been reported by EnviroMetal Technologies, Inc., for the treatment wall installed at an industrial facility in Mountainview CA. The construction cost of the iron treatment zone at this site was \$100,000 including \$60,000 for 50 tons of iron. In addition, the cost for the reactive medium can be driven substantially higher still if certain types of recalcitrant organics are present, necessitating the use of palladized iron.) A recent review²³ suggested that installation costs between \$2,500 and \$8,000 per L/min of treatment capacity can be used as a rule-of-thumb for estimating the capital cost of these systems. Since zero-valent iron treatment walls is patented technology, a site licensing fee, which has been typically 15% of the capital costs (materials and construction costs), may also be required.

A principal advantage of the permeable treatment walls technology over other groundwater remediation approaches is the reduced operation and maintenance (O&M) costs. Other than groundwater monitoring, the major factor affecting operating and maintenance costs is the need for periodic removal of precipitates from the reactive media or periodic replacement or rejuvenation of the affected sections of the permeable wall. It is currently difficult to predict the magnitude of inorganic precipitate formation prior to site-specific trials. A recent review by DuPont²⁴ suggested O&M costs between \$1.3 and \$5.2 per 1,000 L of treated water can be used as a rule-of-thumb for estimating the O&M costs of these systems.

At the Intersil site in Sunnyvale, CA, it was estimated that the total O&M costs associated with groundwater monitoring and replacement of the entire reactive media in a 12 m long, 3.6 m deep and 1.2 m wide treatment wall every 10 years could be about \$2 million over a 30-year period²⁵.

To date, all of the plumes treated with zero-valent metal have been at depths less than 15 m. EnviroMetal Technologies, Inc., is currently evaluating innovative approaches for sites requiring deeper emplacements. The emplacement methods selected for preliminary design and costing were slurry wall, driven/vibrated beam, deep soil mixing and hydrofracturing and injection. For each of these methods, the iron must be slurried for ease of pumping and placement using biodegradable polymer viscosifiers that leave the iron reactive²⁶. This will add significantly to the costs of the reactive medium and/or its emplacement. The two primary types of viscosifier available are natural

biodegradable polymers derived from plant polysaccharides (cellulose or starch) and synthetic polymers of long chained organic molecules. For permeable zone emplacement, the advantage of the natural polysaccharides (such as those derived from xanthum or guar bean) is that they can be biodegraded by premixed enzymes, whereas the synthetic polymers require post-emplacement flushing with chemicals appropriate to the bonds to be broken. To suspend iron particles in a viscous but pumpable gel, it is necessary to "cross-link" the polysaccharide chains, forming covalent bonds between adjacent chains. Enzyme products are also available to break these bonds. Thus, a blend of enzymes appropriate to the polymer and cross-linker used can first "de-link" the cross-linked gel, then break down the polysaccharide chains to glucose and/or mannose molecules.

Work is underway at the University of Waterloo on the development of an enhanced iron material that gives a half life on the order of 3 min for PCE, or at least 10 times lower than commercial iron. The granular iron is enhanced by deposition of an alloy containing nickel metal. This enhanced iron had potential uses in above ground canisters for pump-and-treat applications, and would also have significant implications for deep *in situ* remediation – in that the more highly reactive material could be mixed into the ground at lower iron:soil ratios, or could be implaced in walls at a fraction of the thickness of commercial granular iron, and therefore potentially reduce the costs of such emplacements significantly – provided that the cost of the enhanced iron is reasonable.

Limestone Barriers: The use of limestone treatment walls has been proposed for certain types of sites with metals contamination, in particular former lead acid battery recycling sites which have lead and acid contamination in groundwater and soil. In such cases, a limestone trench that neutralizes acidic groundwater can promote immobilization of dissolved lead through precipitation and/or adsorption onto minerals.

There is some experience in the coal mining industry with use of limestone for metal contamination control. Most of this experience has been acquired since 1990, when the concept of "anoxic limestone drains" was introduced. Since that time, limestone drain systems have been installed at Appalachian coal field sites (primarily in Kentucky, West Virginia, and Pennsylvania) in an attempt to control acid mine drainage. Design and operating guidelines for the anoxic limestone drains have for the most part been developed from trial and observation. The systems in use employ fairly large, #3 or #4 (baseball size) limestone rocks. Anoxic mine water is directed to the limestone drain, which is installed with a soil cover to inhibit contact with air. Some systems constructed with limestone powder and gravel have failed, apparently because of plugging problems²⁷. The primary concern with this technology is maintenance of anoxic conditions in the drains. If high dissolved concentrations of iron are present and aerobic conditions develop, insoluble ferric hydroxide can form and coat the limestone, rendering it ineffective. High concentrations of aluminum are also a concern, whether or not anoxic conditions can be maintained, since aluminum hydroxide can precipitate and yield the same kind of coating problems. Plugging is minimized through use of large diameter stones; however, if precipitation occurs, the coated stones do not treat the contamination effectively even though plugging is avoided.

Available operating data for anoxic limestone drains indicate that they can be effective in raising the pH of strongly acidic water. Hedin and Watzlaf²⁸ compiled operating data for 21 limestone drain systems that showed fairly consistent increases in pH of highly acidic mine drainage (at pH 2.3 to 3.5) to pH values in the range of 6.0 to 6.7. Thus, there is clearly precedent for employing the limestone drain approach with some confidence of success in raising pH of highly acidic water. Long term (i.e., greater than 10 years) performance cannot be predicted with confidence as there has been relatively short duration operating experience. However, experience to date indicates that limestone drain systems can operate effectively under appropriate conditions, especially anoxic or low-oxygen groundwater, for at least several years²⁹.

No data on the residual concentrations of the heavy metals was readily available.

Pilot- and Laboratory-Scale Studies: A number of emerging reactive barrier technologies

are at the pilot- or laboratory-scale stage (Fig. 32.) Reactive media that have been implemented in pilot and field-scale studies for the treatment of heavy metal/radionuclide contaminants include ferric oxyhydroxide for the control of U and Mo, dithionite for the removal of Cr, V, Tc, and U, and zero-valent iron for the control of U and Cr. Among other reactive media that have been investigated in laboratory studies, zeolites and hydroxyapatite are considered to have shown a good potential for field applications³⁰.

Iron Oxyhydroxide: Uranium mill tailings commonly contain a wide variety of contaminants, including U, Mo, ²²⁶Ra, ²³⁰Th, Pb, Se, As, Cu, Zn, and Cr, that potentially could be released to the groundwater. Uranium and molybdenum are the most mobile elements at uranium mill tailings sites; and molybdenum is often mobile under high-pH conditions in which uranium is immobile and vice versa. Combined, these two elements are probably the most difficult to stabilize. The addition of hydrate lime decreases the concentration of dissolved uranium and other contaminants, for example, but increases the concentration of molybdenum. A number of industrial materials already known to be effective at taking up U and/or Mo were evaluated for use in chemical barriers for uranium mill tailings remediation³¹. These two major contaminants were therefore the focus of the studies. Batch experiments involving a single additive (with no pH adjustment) in synthetic pore fluid were run for 14 days. These experiments used a relatively large concentration of the test material to maximize extraction results. Dissolved uranium concentrations were lowered from 30.0 mg/L to less than 0.5 mg/L by lignite, peat, hydrated lime, fly ash, barium chloride, titanium oxide, and hydroxyapatite. Dissolved molybdenum concentrations were lowered from 8.9 mg/L to less than 0.4 mg/L by ferrous sulfate, calcium chloride, ferric sulfate, ferric nitrate, hematite, peat, and barium chloride. [The U.S. EPA has proposed standards for uranium and molybdenum of 30 pCi/L (0.043 mg/L, based on natural isotopic abundances) and 0.1 mg/L, respectively, for groundwater at uranium mill tailings sites.] As much as 45 g/L of the sorbent was required to reach these residual contaminant concentrations. In these experiments, only peat and barium chloride extracted significant amounts of both uranium and molybdenum. Removal efficiency was sensitive to pH in all cases, with maximum removal of uranium taking place in strongly alkaline (e.g., pH 10.27-11.22) solutions and maximum removal of molybdenum taking place under acidic conditions; only hematite lowered molybdenum concentrations to less than 1 mg/L in a broad pH range of 2.15-7.91.

Iron oxyhydroxide is also under study as a potential reactive medium. As with virtually all other adsorbents, the extent of sorption of metal cations and anions onto iron oxyhydroxide has been shown to be a function of pH for a particular background electrolyte composition (Fig. 33)³². Lead sorbs extensively at much lower pH values than zinc or cadmium. Morrison *et al*^{33,34,35} investigated its use for the adsorption of uranium(VI) from mill tailings at the former uranium mill site in Monticello, UT. Uranium adsorption behaved similarly to that of cations, adsorbing more strongly at high pH, while molybdenum adsorption behaved similarly to that of anions, adsorbing more strongly at low pH. Because the adsorption of U(VI) onto amorphous ferric oxyhydroxide is less efficient at high pH (in the presence of dissolved carbonate), however, no U(VI) retardation occurred in tailings with alkaline pore fluids. The adsorbent was effective for treating U(VI) at neutral pH. The cost of anhydrous FeCl₃ (the raw material used to make amorphous ferric oxyhydroxide) is \$250 per tonne (10³ kg)³⁶. The cost for the amount required for the 3x10⁶ yard³ (2.3x10⁶ m³) Monticello repository was estimated at \$150,000 or 1% of the estimated cost for the repository, with an effective barrier (concentrations limited to 0.05 mg/L U(VI) to within 88 ft of the repository boundary).

For many applications, a vertical wall or funnel-and-gate configuration are needed. Iron oxyhydroxide must be immobilized on a suitable support for use in such systems. To date, efforts to develop immobilized preparations have resulted in reactive media with significantly degraded performance^{37,38}.

Dithionite: The possibility of injecting sodium dithionite into the subsurface (2-day half-life) to reduce structural iron in clay-sized layer silicate minerals and in sediment from the Hanford

formation has been investigated^{39,40}. The reducing conditions created in the subsurface would transform metals to less soluble forms. Using a sonic drilling technology, the reagent (120,000-150,000 L) can be injected into the aquifer to create 18- to 30-m diameter zone where it would be allowed to react from 5 to 30 days. After the reaction period, water containing the reaction byproducts and any remaining reagent would be pumped out (three times the injection volume) to create a permeable reaction zone in advance of a contaminant plume. Preliminary results of the ongoing laboratory investigations in support of the planned field trials indicated that a chromate concentration of 0.1 mg/L can be reduced to 0.005 mg/L, which is well below the treatment goal of 0.011 mg/L.

The primary problem associated with *in situ* chemical treatment is the nonspecific nature of the chemical reagents⁴¹. Oxidizing/reducing agents added to the matrix to treat one metal will also interact with other metals (and organics) and can make them more toxic and/or mobile. Chemical agents must therefore be carefully selected so that they do not further contaminate the treatment area. Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions.

Zero-Valent Iron: Technologies that are suitable for the treatment of Cr(VI) are often also useful for treating uranium contamination. Bi-metallic iron/copper, zero-valent iron steel wool, and Cerona zero-valent iron foam are being evaluated for the remediation of U, Mo, and nitrate at the UMTRA Site in Durango, CO. Four different treatment zones were installed below surface in the path of the uranium mill tailing drainage. Two were in baffle style boxes and two were horizontal beds of 0.3 m of steel wool. Influent concentrations were in the range of 2.9-5.9 mg/L for U, 0.9 for Mo, and 27-32 for NO₃. The first test started in May 1996 with Cerona iron foam in the baffle design as the first media to be tested. The earliest results showed a decrease in U concentration to 0.4 mg/L and NO₃ to 20 mg/L. The results after 3 months of operation showed a decrease in U and nitrate to below detection limits, while Mo decreased to 0.02 mg/L. Although not confirmed, it is suspected that biological reduction enhanced by the high hydrogen environment produced by the contact between iron and water has resulted in the removal of nitrate from the system⁴².

A variation on the zero-valent iron technology underwent testing at Valley Wood Treating, Turlock CA. In this process, contaminated groundwater is brought to the surface and treated using ferrous iron. A reductant is added to the treated water, which is reinjected around the plume margin, where it reacts and reduces residual levels of chromium, forming a precipitate. Such reinjection creates a "barrier" of elevated water levels around the plume, enhancing the gradient and associated hydraulic control. The reinjection also allows for *in situ* reduction and subsequent fixation of residual chromium.

Zeolites and Modified Zeolites: Fuhrmann *et al*⁴³ conducted laboratory studies to support the design of a full-scale *in situ* sorbent barrier for intercepting a strontium plume within a surficial water-bearing sand and gravel layer. Initial screening of the sorbent materials included natural zeolites Na-chabazite, clinoptilolite, and mordenite and various metal oxides (alumina and iron and manganese oxides). Based on the results of laboratory experiments, a simulation of the performance of a 1.2 m thick treatment wall containing 20x50 U.S. mesh size clinoptilolite, using a dispersivity of 5% and a seepage velocity of 4.6×10^{-6} cm/s, indicated that it would take more than eight years for the effluent strontium concentration to increase to 100 pCi/L if the influent concentration was maintained at 5000 pCi/L. Because the clinoptilolite is a natural aluminosilicate mineral, no adverse environmental impacts are expected; and it is available at a relatively low cost (approximately \$200 per ton). Bench-scale development of this technology has been completed and design of a field-scale demonstration was expected to begin construction in the summer of 1996. The purpose of the field demonstration is to determine if a reactive barrier composed of clinoptilolite can be successfully emplaced using available technology, such as conventional backhoe trenching or drilling with 4-foot diameter augers, and to determine the effectiveness of this technology in an actual field setting. If the field demonstration is successful, this technology can be considered as a final remediation alternative at Hanford Site's 100-N Area or other sites with

⁹⁰Sr contamination. At the 100-N Area, the clinoptilolite is expected to reduce ⁹⁰Sr migration by more than 99.7% using a one-meter thick barrier.

Ouki *et al*⁴⁴ investigated the ability of chabazite and clinoptilolite, both containing significant amounts of exchangeable potassium, calcium, and sodium, to remove lead and cadmium from contaminated waters. Both Pb and Cd were effectively removed by as-received zeolites (approximately 50 mg/g at aqueous concentration of 250 mg/L), with particle size having no impact on the exchange process. At Pb and Cd concentrations above 250 mg/L, pretreatment of these zeolites with NaCl (conversion to homo-ionic state in the Na form) greatly enhanced their capacity for the exchange of these metals; exchange capacities exceeded 200 mg/g at optimal conditions.

The Bureau of Mines⁴⁵, however, found that zeolites have severe limitations. Extensive studies with several samples of clinoptilolite, and more limited studies with mordenite, chabazite, erionite, and phillipsite, showed that zeolites exhibit a wide range of affinities (or lack thereof) for cations. The selectivity series was determined to be Pb > Cd > Cs > Cu > Co > Cr(III) > Zn > Ni > Hg, with heavy metal ion exchange loading values on clinoptilolites ranging widely, i.e., 330 mg Pb, 134 mg Cd, 126 mg Cs, 53 mg Cu, 42 mg Co, 17 mg Cr(III), 16 mg Zn, 14 mg Ni, and 0.0 mg Hg per gram of zeolite in single ion tests. Like mercury, anions were not adsorbed by the zeolites.

More importantly, metal uptake was strongly affected by common cations such as Na⁺, Ca²⁺, and NH₄⁺. Calcium and NH₄ were adsorbed preferentially to all heavy metal cations except Pb. When testing turned to studies with real world samples, such as acid mine drainage from an abandoned copper mine in Nevada, this fact had enormous impact on overall performance. In column tests with the mine water containing 73 ppm Al, 550 ppm Ca, 27 ppm Cu, 210 ppm Fe, 22 ppm Mn, 120 ppm Mg, 0.43 ppm Ni, 1.4 ppm Pb, and 11 ppm Zn, only a small amount of metal ions were removed during each cycle due to the presence of calcium which is also taken up by the zeolite. Calcium was eventually almost completely removed. The Bureau's findings did not agree that because clinoptilolite is a natural aluminosilicate mineral, there would not be any adverse environmental impacts; the removal of calcium is expected to have an adverse impact on aquatic life. Even when calcium was decreased to < 3 ppm, the zeolite did not remove the metal ions completely; Al, Fe(III), Cu, and Zn were removed to below drinking water standards (i.e., were taken to < 1 ppm, < 0.5 ppm, < 0.6 ppm, and 4.8 ppm, respectively), but Mn and Ni were not (i.e., were still at 0.35 ppm and 0.05 ppm, respectively). Based on test results, the Bureau calculated that 25 lb of zeolite would be needed to treat 10 gal of the acid mine drainage. At \$200 per ton, this equates to \$66.05 per 1,000 L, for the reactive media alone.

Experiments with montmorillonite and clinoptilolite with synthetic pore fluid in the studies on uranium mill tailing containment cited above⁴⁶ show low sorption potential by both these adsorbents for both uranium and molybdenum.

The possible use of surfactant-modified zeolites for treating arsenic, cadmium, chromium and lead has been studied^{47,48,49}. Surfactant-modified zeolites, which remained stable in a variety of aggressive solutions, sorbed chromate, selenate, and sulfate, apparently through surface precipitation of a surfactant-oxyanion complex, as well as lead. Costs of the modified zeolites was estimated at \$330-\$550/tonne.

Hydroxyapatite: The ability of phosphate minerals (apatites) to immobilize lead *in situ* has been studied^{50,51}. Hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] reduced an initial Pb concentration of 5 - 500 mg/L to 0.18 - 19.7 µg/L. Aqueous Pb in Pb-contaminated soil materials was reduced from 2273 to 36 µg/L. The immobilization process was rapid and near completion in 30 min. In addition, natural apatite was shown to be effective in removing Pb from aqueous solution. Effective lead immobilization by apatites was accomplished only when the solution pH was low enough (5 - 6) to dissolve apatite and supply phosphate to react with Pb, yet high enough to keep the solubility of hydroxypyromorphite low. However, the presence of various other metals in

solution inhibited Pb immobilization through precipitation of amorphous to poorly crystalline metal phosphates, thereby decreasing the amount of dissolved P available for precipitation with dissolved Pb ions. The order of inhibition was $\text{Al} > \text{Cu} > \text{Fe(II)} > \text{Cd} > \text{Zn} > \text{Ni}$, and $\text{Cu} > \text{Fe(II)} > \text{Cd} > \text{Zn} > \text{Al} > \text{Ni}$, at high and low initial Pb concentrations, respectively.

Chitosan Beads: The effectiveness of porous chitosan beads to remove different metallic ions from contaminated waters has been evaluated^{52,53,54}. The capacity of naturally occurring chitosan was dependent on particle size, with chitosan particles of mean diameter below 250 μm adsorbing as much as 500 mg vanadium(IV)/g at pH 4 and equilibrium aqueous phase V(IV) concentration of 50 mg/L. However, the rate of vanadium uptake was slow, and it took almost 24 hours to reach equilibrium even for the smallest particle size studied ($D_p < 125 \mu\text{m}$). Gelled chitosan beads crosslinked by glutaraldehyde possessed surface areas exceeding 150 m^2/g and were insoluble in acid media at pH 2. However, the capacity of the beads varied with diameter, with 1 mm beads adsorbing as much as 518 mg Cd^{2+}/g , while 3 mm beads adsorbed 188 mg Cd^{2+}/g for an aqueous phase concentration of 1690 mg Cd^{2+}/L . On the other hand, polyaminated chitosan beads exhibited appreciable chelating properties with the selectivity at pH 7 on the order: $\text{Hg} > \text{UO}_2 > \text{Cd} > \text{Zn} > \text{Cu} > \text{Ni}$; while Mg(II), Ca(II), Ga(II), As(III) and Sr(II) were not adsorbed onto the resin at all. In all cases, the saturation capacities were close to the concentrations of amino groups fixed on the resin, and low pH (500 mmol/L H_2SO_4) was appropriate for resin regeneration.

Although regenerability is often touted as an advantage, it also means that the adsorbent is very sensitive to fluctuations in pH. In addition, it has been estimated by industries utilizing regenerable adsorbents for wastewater treatment that for every one dollar of operating cost in the adsorption part of the treatment system, about 3 to 6 dollars are spent in regeneration.

Bentonite: Oscarson *et al*⁵⁵ established that the ability of bentonite to adsorb cesium was greatly affected by the extent of bentonite compaction. Using a novel test cell, the distribution coefficient, K_d , for the compacted bentonite with a density ranging from 0.5 to 1.5 mg/m^3 , was about one-half to one-third of the distribution coefficients measured for the loose bentonite.

Peat: Humic materials, such as sawdust, peat, lignite, and subbituminous coal, often exhibit high extraction efficiencies for a range of heavy metals⁵⁶. As mentioned above, for example, only peat and barium chloride extracted significant amounts of both uranium and molybdenum from synthetic pore fluid. Ho *et al*⁵⁷ established that the ability of sphagnum peat moss to remove nickel from contaminated water is best realized at pH 4-7, but is still relatively poor in comparison with other metals. Sphagnum peat moss can adsorb as much as 119 mg Cr(VI)/g at pH 1.5 and 16.5 mg Cu/g at pH 5.0, while the maximum capacity for nickel was only 9.18 mg Ni/g at pH 7.0. Equilibrium for nickel adsorption was established after 25 min for an initial Ni concentration of 50 mg/L, while it took 90 min to reach equilibrium for an initial Ni concentration of 400 mg/L.

Other researchers⁵⁸ have noted that peat – and sawdust, under consideration for treating nitrates – are less promising for reactive barrier applications than other reactive media, as they will biologically degrade.

Microbial Treatment: Bioremediation is being evaluated for the treatment of acid mine drainage. For example, acid rock drainage from a closed gold-mining operation in northern California was treated on the pilot-scale level to determine the technical feasibility of passive microbial treatment⁵⁹. The drainage has a pH of 3.8, and concentrations of Cu, Fe, Mn, Ni, and Zn of 140, 290, 28, 0.93, and 40 mg/L, respectively. Based on laboratory results, a pilot system was constructed that consisted of a steel container filled with a substrate volume that measured 2x3x12m. The substrate mixture was equal amounts by weight of cow manure, fine-grained soil, and limestone gravel. Loading of the system was based on the estimate that 0.3 moles of sulfide per m^3 of substrate per day would be generated by sulfate reducing bacteria, and the inflow of heavy metals should not exceed the sulfide generated. Using these principles, the flow was set at approximately 800 mL/min. Over the course of 10 months, the pilot system achieved removal of Cu and Ni

below the effluent standards of 1.0 and 0.7 mg/L. Zn concentrations averaged approximately 0.1 mg/L, compared with an effluent standard of 0.02 mg/L. For a majority of the operation time, the cell was overloaded because the sulfide production rate of the substrate was lower than expected.

5. COMPARISON OF MOP-UP® WITH COMPETING TECHNOLOGIES

The criteria established for comparing MOP-UP® with conventional groundwater remediation technologies were that the *in situ* groundwater MOP-UP® technology should either (a) be more cost effective than competing technologies while achieving the same degree of groundwater purification, or (b) be at least as cost effective as competing technologies while offering superior performance.

The data produced under the FETC program indicate that MOP-UP® will be far more effective than either conventional pump-and-treat technologies or commercialized and emerging reactive barrier media – and will be very economical by comparison as well.

5.1. Comparison of MOP-UP® with Conventional Groundwater Treatment

Conventional pump-and-treat, with the pumped groundwater being treated by chemical precipitation, dominates the groundwater remediation market. For example, conventional pump-and-treat, using chemical precipitation, has been selected for 98% of the over 600 NPL sites where groundwater is to be treated⁶⁰. A few “innovative” systems exploit ion exchange resins and/or activated charcoal. The Federal Remediation Technologies Roundtable also cites *ex situ* chemical precipitation/flocculation as by far the most widely-used and well-established treatment technology for heavy metals and radionuclides in groundwater, sometimes coupled with ion exchange and/or filtration to improve performance. (Predominance of chemical precipitation with a few percentage of systems exploiting ion exchange – typically in combination with chemical precipitation – is also the case in industrial wastewater treatment systems.)

To determine whether MOP-UP® offers performance and/or cost benefits over conventional groundwater treatment technologies, therefore, MOP-UP® was compared against chemical precipitation/pump-and-treat systems. Because costs for any remediation technology are site-specific, and because MOP-UP® has not yet been optimized for remediation of a given site, the comparison had to be done with a top-level analysis.

Performance: The data produced under the FETC program show that MOP-UP® has the potential to offer performance that is orders of magnitude better than that offered by conventional pump-and-treat systems, such as those cited by the Federal Remediation Technologies Roundtable (Fig. 28.)

Using conventional technologies, Cr was taken from 330 ppb to 50 ppb (< 85% removed) at the Coakley Landfill and from 1.5-270 ppm to 0.5 ppm at the Stringfellows site, whereas in the first treatability tests – without any attempt at optimization – MOP-UP® reagents took Cr to nondetectable levels (< 10 ppb) in the groundwater from Hill AFB containing 350 ppb Cr. Cr(VI) was readily removed from simulated electronics rinsewaters, with 97% of the metal removed from wastewaters containing 22 ppm Cr and 13 ppm Ni, as well as ppm levels of organics and parts per thousand of complexing agents.

Using conventional technologies, As was taken from 90 to 50 ppb (44% removed) in the Coakley Landfill, and from 0.1-0.8 ppm to 0.05 ppm (94% removed) at the Winthrop Landfill. In the first MOP-UP® treatability tests – without any attempt at optimization – As was taken to nondetectable (< 0.002 ppm) levels in the Hill AFB groundwater containing 0.064 ppm arsenic, and in the acid mine drainage provided by INEEL containing 0.13 ppm arsenic and 0.15 ppm Cu. Even in the highly recalcitrant industrial site groundwater containing a complex mixture of As(III), As(V), and

arsanilic acid, MOP-UP® reagents removed 97.6% of the 20 ppm total arsenic at the sample's native pH, without any pretreatment, in the very first treatability test. Studies with As(III), As(V), and arsanilic acid in standard solutions showed that each of the arsenic species can be taken to much lower residual levels by MOP-UP® reagents; therefore, a minor modification to the treatment is expected to take the total arsenic in this highly problematic groundwater to drinking water levels quickly, easily, and economically.

At the Stringfellow's Acid Pit Site, conventional precipitation technology took Cd from 0.32-9.3 ppm to 0.11 ppm, and Cu from 1.7-20 ppm to 2 ppm, in the presence of Cr and Zn. MOP-UP®, on the other hand, took Cd and/or Cu to nondetectable (< 0.002 ppm) levels – without pH adjustment or any other form of pretreatment – in the first treatability tests with the acid mine drainage provided by INEEL containing 0.15 ppm Cu as well as 0.13 ppm As; with pH 3.17 acid mine drainage from the California Gulch CERCLA site containing 0.16 ppm Cd, 0.31 ppm Cu, and 0.26 ppm Pb as well as 4,400 ppm sulfate and ~500 ppm each of iron, calcium, manganese, and magnesium; with the Savannah River D-Area Coal Pile Runoff Basin site groundwater at pH 2; and even with the heavily contaminated and complex S-3 Ponds Area simulant at a pH of 4.1.

Conventional technology took Ni from 0.2 to 0.1 ppm at the Coakley Landfill, and left 0.04 ppm Ni untouched at the Winthrop Landfill. In early development testing with natural and simulated Savannah River groundwater, MOP-UP® removed as much as 95% of 1.9 ppm Ni at pH 4, > 76% of 3.6 ppm Ni from natural SRS groundwater at pH 3, and > 84% from 1.9 ppm Ni from simulated water at pH 2.8. When the pH was adjusted to neutral or acidic levels, MOP-UP® removal of Ni was greatly enhanced, with ≥ 95% of the Ni being removed from electronics rinsewaters containing as much as 33 ppm Ni in complex mixtures containing Cr or Pb, plus surfactants, complexing agents, and organics. Studies with a single class S reagent in “clean” solutions, designed to evaluate the impact of raising pH on MOP-UP® removal of heavy metals, showed that adjusting the pH has a dramatic effect on Ni treatment. These studies repeatedly showed that by taking the pH into the alkaline range, all traces of radioactivity were removed from 5.87 ppm and 0.587 ppm solutions of ⁶³Ni – i.e., the residual ⁶³Ni concentration was in the parts per trillion range – with the MOP-UP® reagent taking up as much as 1,027 mg ⁶³Ni/g reagent.

Performance data about “innovative” pump-and-treat systems utilizing *ex situ* ion exchange treatment is not readily available. However, given that groundwater is typically much more difficult to treat than industrial effluents, ion exchange performance in groundwater should be equivalent to, or worse than, ion exchange performance with industrial effluents. Typical wastewater discharge concentrations that are achieved with chemical precipitation are shown in Figure 29, and those achieved with ion exchange are shown in Figure 34. As with chemical precipitation, MOP-UP® performance in preliminary treatability tests without any attempt at optimization has been shown to be far better than ion exchange performance in optimized wastewater treatment systems. Ion exchange systems rely on a complicated series of pretreatment steps and often utilize post-treatment polishing as well, yet yield concentrations of arsenic, barium, lead, mercury, uranium, and zinc that are one or more orders of magnitude higher than the residual levels achieved by MOP-UP® reagents without any pretreatment – even pH adjustment – in complex groundwater samples. And, of course, the residual concentrations of Cr and Cu shown for ion exchange were achieved only after extensive pretreatment steps, whereas MOP-UP® performed as well or better without pretreatment, in the case of Cu taking the metal to nondetectable levels at pH 0.1.

Cost: With any groundwater remediation technology, costs are very site-specific. As noted above, however, reactive barrier technologies are expected to offer significant cost savings over conventional technologies. For example, a case study of the groundwater contamination problem at the Savannah River Site concluded that if conventional pump and treat remediation strategies were replaced with reactive barriers inserted in the aquifer to intercept the contaminant plumes, savings of \$130 million, or 33%, of the current estimated costs for groundwater remediation could

be saved. These technologies are anticipated to be available sometime between the years 2000 and 2015. Longer range improvements to reactive barriers would employ engineered sequestrants to trap specific radionuclides in their molecular structure and achieve even more cost savings⁶¹. Preliminary analyses indicate that MOP-UP® will be highly competitive with emerging reactive barrier technologies (see below.)

Sites with plumes below 10-30 m cannot currently be treated with reactive barrier technology, since there is currently no way to emplace the barrier. MOP-UP®, of course, is very readily configured for sites requiring pump-and-treat systems. (Interestingly, much of the recent work that has been done by organizations developing these reactive barrier technologies, such as EnviroMetal Technologies, Inc., has been targeted at adapting the reactive material treatment system so that it can be used in pump-and-treat configurations! Their interest in pump-and-treat is presumably driven by the EPA estimate that only some 10 to 20 percent of sites can be treated by barrier technologies.) The hardware needed for pump-and-treat MOP-UP® is already available, commercially and/or in prototype form. Capital costs for the MOP-UP® treatment system are projected to be roughly equivalent to or less than those provided by the Federal Remediation Technologies Roundtable. Assuming averages of 1 and 50 ppm metals contamination, a very conservative loading of 500 mg/g at neutral pH for the MOP-UP® reagents (which have been shown to take up > 4,500 mg/g at pH 3), and an average cost of \$1,200/ton for a formulation containing class O and class S reagents in a 1:1 ratio, operating costs are projected at ~\$0.02 - \$0.15/1,000 L, which is equivalent to or lower than the operating costs cited by the Roundtable for chemical precipitation.

Additional cost savings can be realized through the very high loadings taken up by the MOP-UP® reagents, which results in much lower volumes of sludge requiring transportation and disposal. Note that separating MOP-UP® reagents from the treated water does not require the use of any flocculants or coagulants, the way chemical precipitation treatment systems do.

The EPA has noted that the adsorbents such as carbon, zeolites, or ion exchange resins are sometimes used instead, but these approaches have a number of undesirable drawbacks⁶². Each of these is based on the concept of regenerating the adsorbents by acid leaching for reuse. The metals in the aqueous stream are then isolated by precipitation. The precipitate sludge is further treated, then disposed in a hazardous waste landfill. Even with regeneration, these adsorption processes tend to be very expensive for large dilute matrices. Moreover these adsorbents do not possess high adsorption capacity (mostly a fraction of a percent), which imparts two undesirable effects on process economics, i.e., adsorbent cost and eventual dilution of the metals on regeneration. In addition, it has been estimated that for every one dollar of operating cost in the adsorption part of this technology, about 3 to 6 dollars are spent in regeneration. Their conclusion was that inexpensive, high capacity adsorbents that could be disposed without regeneration would be a much more cost-effective approach to groundwater remediation.

Since these conventional adsorbent-based systems are far more expensive than chemical precipitation (as has also been found to be the case in industrial use of ion exchange resins for wastewater treatment), MOP-UP® will be far more attractive economically than conventional, regenerable adsorbents. As noted above, the cost for even the most expensive MOP-UP® reagents is currently estimated to be half that of activated charcoal, while the loading capacities of the MOP-UP® reagents are orders of magnitude higher. MOP-UP® therefore appears to fit the requirement described by the EPA perfectly. MOP-UP® sludges will contain a much higher percentage of metals by comparison with flocced precipitates; therefore, significant savings should be achieved in sludge transportation and disposal. It would appear, from the data produced under the FETC program, that treatability testing can be very simple and inexpensive with MOP-UP®, which offers another source of significant cost savings over conventional chemical precipitation and/or ion exchange.

Overall: Therefore, in comparison with the conventional groundwater remediation technology

that is predominant throughout the Federal and private sectors, data produced under the FETC program indicate MOP-UP® will both be significantly more cost effective than current groundwater remediation technologies and will offer substantially superior performance.

5.2. Comparison of MOP-UP® with Reactive Barrier Technologies

In general, the same types of barrier designs and the same barrier installation technologies can be used for MOP-UP® reagents as for any other reactive medium. Therefore, cost will be driven essentially by the performance of the reagents, and so the following comparison will be couched primarily in terms of the reactive media themselves.

Performance: There are several factors that need to be addressed when comparing the performance of MOP-UP® reagents against the performance of commercialized and emerging reactive media, including (1) the range of heavy metals/radionuclides that can be treated, (2) the pH range that can be treated, (3) the loadings of heavy metals that can be taken up, and (4) the ability to treat mixtures of contaminants.

Zero-Valent Iron: The difference between MOP-UP® reagents and other reactive media quickly becomes clear when comparing the number of heavy metals/radionuclides that can be treated effectively (Fig. 32.) Zero-valent iron has been shown to be effective for the treatment of Cr(VI) and promises to be effective for treating U(VI) as well. However, because the technology relies on the reduction and subsequent precipitation of metal contaminants, it is therefore very limited in the number of metals and radionuclides that can be treated. It should be noted, of course, that if the corrosion reactions raise the pH, other metals will probably precipitate to some extent; and also that a variety of metals will adsorb onto the iron oxides that are formed. However, it is unlikely that such generic metal removal phenomena can be optimized to the point that zero-valent iron will prove to be an effective technique for broad-spectrum heavy metal treatment, or can ever hope to achieve the extremely low residual concentrations that are needed for the treatment of radionuclides. Nor has the technology been proposed for use at sites containing metals other than Cr(VI) and U.

By comparison, MOP-UP® has already been shown to be extremely effective at treating a wide range of heavy metals and radionuclides, taking them to nondetectable levels – even when radioisotopes are used – from complex solutions containing both cation and anion contaminants.

The pH over which zero-valent iron is effective at treating Cr and U has not been published; it is not known whether this question has even been addressed. In addition, the “capacity” of zero-valent iron for Cr or U has not been established *per se*. Laboratory studies showed that the rate and completeness of chromate reduction are dependent on a complex interaction between the type of “zero-valent metal” that is used and aquifer material mineralogy. High concentrations of dissolved metal compounds, inorganic carbon, or other compounds can result in excessive precipitate formation, which in turn can result in clogging and/or degraded reactivity – i.e., effectively lower the “capacity” of the zero-valent iron for Cr(VI) and/or U. These factors are not easily modeled for determining the “capacity” of the reactive medium. Therefore, there is no established basis for comparison with MOP-UP® reagents.

Zero-valent iron was originally developed for treating select organic contaminants; and the installations at which chromium is being remediated contain one or more of the targeted organics. MOP-UP® was originally proposed for treating heavy metals and radionuclides. However, as discussed above, the reagents appear to be capable of treating a wide range of organics as well as inorganics, although it has not yet been established definitively whether the processes involved in the disappearance of the organics are adsorption and/or degradation. It is interesting to note, however, that several of the organics that have been shown to be amenable to treatment by MOP-UP® reagents cannot be treated by zero-valent iron. 1,2-dichloroethane and 1,1-dichloroethane, for example, are not degraded by zero-valent iron⁶³; other compounds that are expected to be

resistant to treatment by zero-valent iron⁶⁴, but have been shown to be treated by MOP-UP®, include hexachlorobenzene and DDT.

EnviroMetal Technologies, Inc., is actively pursuing several areas where they hope the commercial application of reactive iron walls can be enhanced⁶⁵. One is the integration of zero-valent iron technology with others to treat groundwater plumes containing a mixture of contaminants, such as heavy metals, radionuclides, and organics that are not amenable to treatment by corrosion processes. In addition, a variety of methods of enhancing the iron degradation rates are being investigated, so that the technology will be more applicable to aboveground treatment systems. MOP-UP® has already been shown to be capable of treating a wide range of contaminants, including heavy metals, radionuclides, and organics that cannot be treated effectively by zero-valent iron – and to do so very quickly, with rates that can readily be used in aboveground treatment systems.

Therefore, MOP-UP® appears to offer significant advantages over zero-valent iron, in terms of the range of contaminants and groundwater environments that can be treated.

Limestone: Limestone barriers are under consideration for a very limited range of applications, primarily strongly acidic, lead-contaminated groundwaters found at former lead acid battery recycling sites and abandoned mines. Metal removal is promoted exclusively by pH adjustment; and, in general, pH adjustment is ineffective with many metals and is especially ineffective with complex mixtures of metals. The need to control the dissolved oxygen content in the presence of iron is also a very limiting factor; iron is the fourth most abundant element in the earth's crust, and it is difficult to find metal-contaminated sites that do not have high concentrations of dissolved iron. The technology is also limited to sites that have low concentrations of aluminum – another metal that is prevalent in the environment. It is not under consideration for use with groundwaters containing radionuclides and/or mixtures of inorganics and organics.

The question, of course, is how effective metal precipitation will be in taking the contaminants of concern to the targeted residual levels. As could be seen in the operating data from conventional pump-and-treat systems, chemical precipitation is often only marginally effective in separating the heavy metals from the groundwater, particularly in streams containing mixtures of different metals.

MOP-UP®, on the other hand, is extremely effective with a wide range of heavy metals and radionuclides; can be used in treating very complex solutions containing a variety of cation and anion inorganics, and organics as well as; and can be used in neutral and/or alkaline waters as well as acidic. Heavy metals and radionuclides have been taken to nondetectable levels under extremely adverse conditions. To date, oxygen has been found to reduce the capacities of some class S reagents slightly for select heavy metals; however, once the metals had been taken up, exposure to oxygen did not cause their release.

Therefore, MOP-UP® appears to offer many significant advantages over limestone, in terms of the residual levels that can be achieved as well as the range of contaminants and groundwater environments that can be treated.

Pilot- and Laboratory-Scale Studies: Far less information is available about most of the emerging reactive barrier technologies, since these are still primarily in the laboratory stage, with a few having made it to pilot-scale testing. Nevertheless, several obvious advantages that MOP-UP® offers are readily apparent.

Most of the emerging reactive media for treating heavy metals and radionuclides are adsorbents – and, as such, suffer from the conventional problems associated with using adsorptive materials when treating complex, fluctuating aqueous streams. For example, although iron oxyhydroxide is one of the more promising reactive media under evaluation, it is still a typical adsorbent in terms of the fact that pH strongly affects its performance. When a given groundwater contains only a few

heavy metals or radionuclides with similar properties, it is possible to optimize conditions so that the removal of most or all is optimized. When, however, a mixture of dissimilar contaminants is present, the conditions that are the best for some are the worst for the others, as was found under the studies on simultaneous treatment of U and Mo in uranium mill tailings cited above. Generally speaking, any water containing both anionic and cationic contaminant species will be difficult, if not impossible, to treat by iron oxyhydroxide, as has been found in a series of extensive studies funded by the Electric Power Research Institute (EPRI). Not only does pH affect contaminant removal, but so does the relative concentration of metal to oxide (Fig. 35.) Ionic strength will also affect heavy metal treatment efficacy, as will the presence of species capable of acting as complexing agents, such as sulfate, chloride, ammonia, cyanide, and simple organic acids such as acetate. Both of the complexing ligands Cl^- and SO_4^{2-} form complexes which affect Zn adsorption by iron oxyhydroxide, for example; and sulfate anion also suppresses Cr(VI) adsorption.

In fact, the removal efficiencies of all of the reactive media expected to be optimal for the treatment of uranium or molybdenum were sensitive to pH, with maximum removal of uranium taking place in strongly alkaline (e.g., pH 10.27-11.22) solutions and maximum removal of molybdenum taking place under acidic conditions; only hematite lowered molybdenum concentrations to less than 1 mg/L in a "broad" pH range of 2.15-7.91. Peat is an inexpensive adsorbent expected to have high affinity for a variety of metals; the impact of pH on peat treatment is typical, with pH 1.5 needed for optimum treatment of Cr(VI) , pH 5.0 for optimum treatment of Cu, and 7.0 for optimum treatment of Ni.

In addition, emerging reactive media tend to be optimal for treating only a handful of inorganic contaminants; and are also limited in the residual levels of contaminants that can be achieved, and have relatively low metal loading capacities. Of the many different types of reactive media tested with uranium or molybdenum, for example, only peat and barium chloride removed what the researchers considered to be "significant" amounts of both contaminants. In simulated pore waters, large amounts of barium chloride and peat (~ 30 and 5 g/L, respectively) were required to lower the uranium concentration to less than 1.0 mg/L, i.e., the adsorbents took up ~1 and 6 mg U/g, respectively, at the optimum treatment condition of strongly alkaline pH. Although peat can adsorb as much as 119 mg Cr(VI) /g and 16.5 mg Cu/g under optimum conditions, the maximum capacity for nickel was only 9.18 mg Ni/g. Similarly, iron oxyhydroxides typically have a much lower affinity for Cd than for other pollutants such as Cu and Pb.

Although pH has an effect on loading capacity, it does not prevent MOP-UP® reagents from taking many heavy metal and radionuclide contaminants to nondetectable levels over a wide pH range. Metals such as Cu, Hg, Cd, and Pb have been taken to nondetectable levels over an extremely wide range in pH (i.e., $\geq$ pH 0.1 for Cu and Hg, and $\geq$ pH 1.5 for Cd and Pb). Nor do mixtures of heavy metals/radionuclides or even mixtures containing organics prevent MOP-UP® reagents from removing essentially all the heavy metals/radionuclide contaminants. Even in very complex groundwaters containing high levels of organics and nitrates, MOP-UP® has been shown to be capable of taking Hg, Cd, Cu, Zn, and Al all to nondetectable levels (residual Hg being < 500 parts per trillion) and U to 180 parts per trillion, as well as simultaneously removing 98% of 15.3 ppm Ba – at pH 4.1, without any attempt to optimize the treatment. And even though pH affects loading capacity, MOP-UP® reagents have been shown to take up extraordinarily high loadings under extremely adverse conditions. Optimum conditions for metal uptake have not been established for any of the MOP-UP® reagents; yet one class S MOP-UP® reagent has already been shown to take up as much as 198 mg Cr(VI) /g, 1,027 mg Ni/g, 3,563 mg Pb/g, or 4,953 mg Cd/g. Loadings as high as 125 mg Cu/g plus 121 mg Zn, and as high as 4,531 mg total metal cations/g have been observed at pH 2.8 in acid mine drainage with MOP-UP®. In short, the loadings achieved by MOP-UP® reagents under extremely adverse conditions are far higher than the loadings achieved by adsorbent reactive media under optimum conditions.

Therefore, by comparison with adsorbents proposed for use as reactive media, MOP-UP® offers

significantly superior performance in the range of contaminants that can be treated, the loadings that can be achieved, the range of groundwater environments that can be remediated with high loadings and excellent efficacy, and in the degree and range of fluctuations that can be tolerated at a site without encountering contaminant breakthrough.

Like iron oxyhydroxide and peat, zeolites have also been found to be very limited in their useful applications. Even in clean laboratory solutions containing single ions under optimum treatment conditions, loading values on zeolites such as clinoptilolite ranged widely, i.e., 330 mg Pb, 134 mg Cd, 126 mg Cs, 53 mg Cu, 42 mg Co, 17 mg Cr(III), 16 mg Zn, 14 mg Ni, and 0.0 mg Hg per gram of zeolite in single ion tests. Anions were not adsorbed by any of the zeolites. More importantly, the zeolites showed high affinities for ubiquitous cations such as calcium, sodium, and ammonia, which has an extremely negative impact on their use in groundwater treatment. In tests with groundwater, only a small amount of metal ions were removed during each cycle due to zeolite uptake of calcium. This (a) limited zeolite removal of the metal ions to the point that some could not be taken below drinking water levels, (b) greatly increased the amount of zeolite needed to take the hazardous ions to acceptable levels (25 lb of zeolite would be needed to treat 10 gal of this particular groundwater, for example) and thereby affected the costs for any barrier system negatively, (c) results in the production of extremely high levels of hazardous waste when the reactive medium in the barrier has to be replaced, (d) and has an adverse impact on aquatic life. At \$200 per ton, 25 lb to treat 10 gallons equates to \$66.05 per 1,000 L, for the reactive media alone – i.e., does not factor in the increased costs associated with installing the much larger barrier needed to hold so much material and/or the need to replace the reactive media much more often and dispose of much larger quantities of sludge. Therefore, the use of zeolites must be limited to sites which have metals that are readily taken up – such as Pb and Cd – but do not have any significant levels of calcium, sodium, or ammonia.

Although zeolites exhibited reasonably high loadings for Pb and Cd, they took up no mercury or anions at all, even in clean laboratory solutions. In clean laboratory solutions, MOP-UP® reagents took up more than ten times the loadings in Pb or Cd; and in complex solutions containing 10 ppm each Hg, Cd, Cu, Pb, Cr(VI), As(V), and Ni, 0.5 g/L of reagents removed all detectable Hg – as well as all detectable Cd, Cu, and Pb, and high loadings of Cr, As, and Ni. None of the studies conducted to date have shown any adverse impact on MOP-UP® reagent performance due to the presence of commonly-found innocuous ions such as calcium, sodium, ammonia, or sulfate. For example, loadings as high as 4,531 mg metals/g reagent have been observed at pH 2.8 in Berkeley Pit acid mine drainage, in the presence of 465 ppm Ca, 80 ppm Na, and 7,600 ppm SO₄. Although the Berkeley Pit water has 10 times as much Cu, 50 times as much Zn, and 4 times as much Al and Mg, preliminary results indicate that ~0.25 lb of MOP-UP® reagents would be needed to treat 10 gallons – i.e., 1/100 the amount of zeolites needed for treating 10 gallons of the far less contaminated Nevada mine drainage. Loading values have been obtained with MOP-UP® reagents that were more than 10 times higher for Pb or Cr, or 37 times higher for Cd, than those observed with clinoptilolite. Even when comparing loadings under maximum conditions in clean solutions for zeolites versus adverse conditions in acid mine drainage for MOP-UP®, a MOP-UP® reagent achieved loadings 8 times higher for Zn plus more than twice as high for Cu – while simultaneously taking up massive amounts of Mg as well.

Since iron and manganese are the fourth and fifth most commonly found elements in the earth's crust, contaminated groundwaters are very likely to contain relatively high concentrations of one or both. Zeolites tend to take up iron and manganese as readily as or more readily than toxic heavy metals. Therefore, any waste produced by zeolite-based treatments used for groundwater containing Fe and/or Mn will comprise a mixture of these metals and the toxic metals; and the entire volume of sludge will have to be disposed as hazardous waste.

The studies conducted to date indicate that, in general, class O and class S MOP-UP® reagents do not remove significant levels of iron or manganese, which is expected. If removal of the Mn and/or Fe is desired, class M reagents have been shown to be extremely effective. The class M

reagents can be used in series after treatment by class S and/or class O, thereby producing two separate sludges that can be disposed separately – and thereby preventing Fe and/or Mn from contributing to the amount of hazardous sludge that is produced.

Zeolites are minerals that must be mined for use in groundwater treatment. Bulk density and loading values must be considered when selecting a zeolite based on performance at the lowest possible cost. As zeolite capacity is measured per unit weight, bulk density is important for process design. The Bureau of Mines study found that clinoptilolite and mordenite, for which there were several samples, showed a wide range of bulk densities. They also showed a very wide range in loading capacities. Loading capacities of clinoptilolite samples from 13 different locations, for example, ranged from 120 to 319 mg/g in 100 mL of 828 ppm Pb solution – i.e., differed by a factor of > 2.65.

MOP-UP®, on the other hand, utilizes nonviable microbial preparations – i.e., as much reagent as is needed for any given application can be prepared, reproducibly, with consistent properties and reproducible treatment efficacy.

MOP-UP®, therefore, offers many significant advantages over zeolites for use in reactive barriers.

Hydroxyapatite acts by inducing precipitate formation rather than by adsorbing the targeted metal. As such, it suffers from the typical problems of all precipitating agents, i.e., it is very sensitive to pH and/or the presence of other ions, especially Fe(II). Since iron is ubiquitous in the environment, its impact on hydroxyapatite immobilization of Pb will severely limit the use of this otherwise promising approach to environmental remediation. The narrow pH range that can be tolerated, and the limited number of metals that can be treated under any circumstances, will also limit the use of hydroxyapatite. MOP-UP® does not suffer from any of these limitations; in particular, it has already been shown to be extremely effective in the presence of parts per thousand levels of iron, and to be effective with a wide range of contaminants over a wide range in pH. MOP-UP® also offers the potential for simultaneously treating organic contamination; if anything, organics should interfere strongly with the efficacy of Pb treatment by hydroxyapatite.

Dithionite has been proposed for direct injection into the subsurface, to create reducing conditions that would transform metals such as Cr(VI) to less soluble forms. Initial tests showed that a chromate concentration of 0.1 mg/L can be reduced to 0.005 mg/L. There are two primary problems associated with injection of a reducing agent, i.e., (1) reduction of some contaminants can make them *more* toxic and/or mobile, thereby increasing contamination; and (2) changes in soil and water chemistry might reverse the selected reactions. MOP-UP® offers superior attributes in that (a) Cr(VI) can be taken to much lower levels than those achieved with dithionite; (b) a mixture of MOP-UP® reagents can be used to treat a wide range of contaminants, both those that are redox sensitive and those that are not; (c) MOP-UP® does not act by affecting the subsurface environment, and therefore is far less likely to have an adverse environmental impact; and (d) because MOP-UP® is effective over a wide range in pH, it is far less likely that changes in the subsurface environment will reverse the treatment process. (Obviously, however, substantial testing remains to be done before subsurface injection of MOP-UP® reagents should be attempted in the field.)

Cost: A number of factors will affect the economics of using reactive media in barriers, including (1) the cost of the reactive medium, (2) the rate at which metal removal is accomplished, (3) the metal loadings that can be achieved, (4) any adverse impact of other environmental constituents or parameters on the performance/lifetime of the reactive medium, and (5) the amount of hazardous waste that is produced. When a site is contaminated with a mixture of pollutants, then the range of contaminants that can be treated will also have a major impact on cost, since the need for a treatment train to accomplish complete remediation can be expected to be far more expensive than the use of a single component in that train.

MOP-UP® reagents are expected to be very competitive with commercialized and emerging reactive media, since they are nonviable microbial preparations. Using a crude cost model based on the commercial production of xanthum, the most expensive of the MOP-UP® reagents are estimated to cost ~ \$1500 per ton when produced in one-ton lots, and substantially less when produced in 5- or 10-ton lots. This is roughly half the cost of activated charcoal, which is an adsorbent used in many groundwater pump-and-treat systems. Other MOP-UP® reagents are currently expected to cost ~ \$750-\$1,000 when produced in one-ton lots. For general comparative purposes, therefore, the following discussion assumes that a formulation containing two reagents mixed in a 1:1 ratio will cost ~ \$1200 per ton.

If one compares the cost of the reactive medium solely on a per-ton basis, MOP-UP® reagents rank in the middle to high end of the permeable barrier reactive media spectrum. Activated charcoal costs ~ \$3,000 per ton. Zero-valent iron runs as high as \$1,200 per ton, with some installations costing ~ \$440-550 per ton. Cost estimates for the "enhanced iron" needed at many sites are not readily available but, since the enhanced iron is doped with an expensive metal such as palladium, can be expected to cost substantially more than the undoped iron, on a per-ton basis. The cost of anhydrous FeCl_3 (the raw material used to make amorphous ferric oxyhydroxide) is \$250 per tonne. Estimates for clinoptilolite have been as low as \$200 per ton, although this is, presumably, for the as-mined material, and not the sodium-enhanced zeolite and/or zeolite that has been sized, either or both of which are needed for maximum efficiency. Costs of surfactant-modified zeolites for treating anions (chromate, selenate, and sulfate) were estimated at \$330-\$550/tonne.

Costs for *using* MOP-UP® reagents, however, are expected to be extremely attractive by comparison with other reactive media. This is because MOP-UP® reagents exhibit much higher loadings and selectivity for toxic groundwater constituents. The difference is perhaps best illustrated by comparing MOP-UP® with what appears to be the lowest cost reactive medium, i.e., zeolites. Clinoptilolite, the zeolite most widely studied for use in barrier systems, appears to cost $1/6$ th as much as a MOP-UP® reagent formulation (\$200 vs \$1200 per ton.) However, clinoptilolite does not have the innate capacity of MOP-UP® reagents for removing cations from solution and, moreover, has a very high affinity for ubiquitous cations such as Na^+ and Ca^{2+} . When tested in acid mine drainage, clinoptilolite was found to have a loading value of 0.4 meq/g for all ions combined, including Ca^{2+} . Because the calcium was taken up preferentially, the amount of zeolite required to treat the Al, Cu, Mg, and Zn in the groundwater was found to be 25 lb per 10 gallons. At \$200 per ton, 25 lb to treat 10 gallons equates to \$66.05 per 1,000 L.

MOP-UP® reagents, on the other hand, have been shown to have a loading value of at least 184 meq/g when incubated in Berkeley Pit water. Although the Pit has roughly the same amount of calcium and 10 times as much Cu, 50 times as much Zn, and 4 times as much Al, Mg, and Fe as the acid mine drainage used in the clinoptilolite studies, preliminary results indicate that only ~0.25 lb of MOP-UP® reagents would be needed to treat 10 gallons of Pit water – i.e., $1/100$ the amount of zeolites needed for treating 10 gallons of the far less contaminated Nevada mine drainage. At \$1200 per ton, MOP-UP® reagents would cost \$3.96 per 1,000 L to treat the extremely contaminated Berkeley Pit water – less than 6% of the cost of treating the far less contaminated Nevada mine water with clinoptilolite.

This comparison takes into account the costs for the reactive media alone. However, the costs for treating a site involve a great deal more. For example, costs for construction of the wall are typically much higher than those for the reactive media (see, e.g., Fig. 31.) The thickness of the treatment wall needed for complete remediation of the contaminated groundwater will typically, in turn, drive the construction costs. The thickness of the treatment wall (or reactor in the "gate") will be determined by the amount of contamination in the water, the groundwater flow rate, the loading capacity of the reactive media, and the time it takes for the reactive media to take the contaminants to the targeted levels (i.e., the half-life of the contaminants in the groundwater.) If all other factors are equal, construction costs for a wall that requires 25 lb reactive media per 10 gallons will be far higher than those for a wall requiring 0.25 lb per 10 gallons.

The residual levels to which the contaminants were taken by the various reactive media described in Section 4 above were typically measured after 1 - 3 days of incubation with agitation. The residual levels to which the contaminants were taken by MOP-UP® reagents, on the other hand, were those observed within 2-4 hours of incubation without agitation. I.e., MOP-UP® reactive media not only exhibit high loadings but also very rapid reaction rates. All other factors being equal, then, the width of treatment wall needed to take contaminants to the targeted level by MOP-UP® reagents will be much narrower than the width needed by other reactive media. This, too, will help keep the costs for a MOP-UP® barrier much lower than those for a barrier exploiting other reactive media.

Loading capacities affect life cycle costs of permeable barriers in other ways as well. For example, sooner or later, reactive media used to treat inorganic contaminants will require replacement. Walls that exploit reactive media with very high loadings do not have to be recharged as often as those with low-load media. Replacing "spent" media more frequently will cost more, not just for the additional reactive media that will be needed itself, but also for the additional labor involved in performing the maintenance more often. When the reactive media has to be replaced, the "spent" media will require disposal. The higher the loadings that can be achieved by the reactive media, the lower the volume of hazardous sludge requiring disposal and, therefore, the lower the shipping and disposal costs.

Once again, MOP-UP® reagents are superior to all those reactive media for which loadings are known – often by orders of magnitude. Therefore, the maintenance and disposal costs for a MOP-UP® permeable barrier are expected to be much lower than those for a barrier exploiting any of the other reactive media that have been identified to date.

Finally, the Federal Remediation Technologies Roundtable noted that treatability studies for metals precipitation may range from \$5,000 to \$20,000; it is likely that treatability studies for reactive media can typically be expected to run higher. Costs associated with a pilot or field demonstration, if needed, may range from \$50,000 to \$250,000, depending on scale, analytical requirements, and duration. Studies conducted to date indicate that treatability studies with MOP-UP® can be very short, simple, and inexpensive, even when the groundwater to be treated is a very challenging remediation problem – such as the S-3 Ponds Area at the Oak Ridge Y-12 Plant.

Overall: The FETC program targeted development of a technology that was either (a) more cost effective than conventional technologies while achieving the same degree of groundwater purification, or (b) at least as cost effective as conventional technologies while offering superior performance. The studies conducted to date indicate MOP-UP® will be more cost effective than either conventional pump-and-treat or commercialized/emerging permeable barrier technologies while offering substantially superior performance.

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Impact of Reagent Concentration and Initial Metal Ion Concentration on Cadmium Removal

Figure 1. ME30-L7RXWS incubated 2 hours in cadmium ion solutions at pH 6.5

Impact of Initial Metal Ion Concentration and pH on Cadmium Removal

Figure 2. 0.006 g/L of ME30-L7RXWS incubated 2 hours in cadmium ion solutions

Impact of Initial Metal Ion Concentration and pH on Cadmium Removal

Figure 3. 0.006 g/L of ME30-L7RXWS incubated 2 hours in cadmium ion solutions

Impact of pH on Cadmium Removal Rate

Figure 4. 0.006 g/L of ME30-L7RXWS incubated in 0.01 mM (1.12ppm) cadmium ion solutions

Impact of Reagent Concentration and pH on Lead Removal

Figure 5. ME30-L7RXWS incubated 2 hours in 0.1 mM (20.8ppm) lead ion solutions

Impact of Reagent Concentration, Initial Metal Ion Concentration, and pH on Chromium Removal

Figure 6. ME30-L7RXWS incubated 2 hours in hexavalent chromium solutions (Metal loadings for ratio of 17.2 given in italics)

Impact of Initial Metal Ion Concentration and pH on Chromium Removal

Figure 7. 0.06 g/L of ME30-L7RXWS incubated 2 hours in hexavalent chromium solutions

Impact of pH on Chromium Removal Rate

Figure 8. 0.06 g/L of ME30-L7RXWS incubated in 0.1 mM (5.2ppm) hexavalent chromium ion solutions

Impact of Reagent Concentration, Initial Metal Ion Concentration, and pH on Nickel Removal

Figure 9. ME30-L7RXWS incubated 2 hours in nickel ion solutions (Metal loadings for ratio of 17.2 given in italics)

Impact of pH on Nickel Removal

Figure 10. 0.06 g/L of ME30-L7RXWS incubated 2 hours in 0.1 mM nickel ion solutions

Impact of pH on Nickel Removal Rate

Figure 11. 0.06 g/L of ME30-L7RXWS incubated in 0.1 mM (5.87ppm) nickel ion solutions

<i>Sample</i>	<i>Barium</i>	
	<i>ppm</i>	<i>% removed</i>
Untreated	0.07	
SRM03-W7ESWS (Class S)	ND	>85.7
FRT02-P3ESWO (Class O)	ND	>85.7
FRT02-P3ESWP (Class P)	ND	>85.7

Figure 12. First treatability test with barium-contaminated groundwater at pH 7.85 from Kirtland Air Force Base.

<i>Sample</i>	<i>Cr(VI)</i>	
	<i>ppm</i>	<i>% removed</i>
Untreated	0.35	
<i>Class O</i>		
– FRT09-S7RSWO	ND	>94.3
– FRT02-P3ESWO	ND	>94.3
– FRT03-P3ESWO	ND	>94.3
<i>Class S</i>		
– SRT02-S7ESAS	0.07	80.0

Figure 13. First treatability test with Cr(VI)-contaminated groundwater at pH 7.58 from Hill Air Force Base.

<i>Sample</i>	<i>Arsenic</i>	
	<i>ppm</i>	<i>% removed</i>
Untreated	0.064	
<i>Class O</i>		
– FRT09-S7RSWO	0.056	12.5
– FRT02-P3ESWO	0.006	90.6
– FRT03-P3ESWO	ND	>92.9
<i>Class S</i>		
– SRT02-M5RSAS	ND	>92.9

Figure 14. First treatability test with arsenic-contaminated groundwater at pH 7.06 from Hill Air Force Base.

Sample	Arsenic		Copper	
	ppm	% removed	ppm	% removed
Untreated	0.13		0.15	
Class O				
- FRT09-S7RSWO	ND	>98.5	ND	>93.3
- FRT01-M7sp	0.01	92.3	0.15	0
Class S				
- SRM02-W7RSIS	ND	>98.5	ND	>93.3
- SRM04-W7ESIS	0.07	46.2	0.03	76.9

Figure 15. First treatability test with acid-mine drainage provided by INEEL.

Sample	Cadmium		Copper		Lead		Arsenic		Mn ppm
	ppm	% rmvd	ppm	% rmvd	ppm	% rmvd	ppm	% rmvd	
Untreated	0.16		0.31		0.26		0.024		219
Class O									
- FRT09-S7ESWO	0.16	0	0.32	0	ND	>96.2	0.002	91.7	214
- FRT02-P3ESWO	0.16	0	0.23	28.1	ND	>96.2	0.005	79.2	217
Class S									
- SRM01-W7ESWS	0.15	6.2	0.04	87.1	ND	>96.2	0.020	16.7	224
- SRT04-W7ESWS	ND	>93.8	ND	>93.8	ND	>96.2	0.017	29.2	221

Figure 16. First treatability test with California Gulch acid mine drainage at pH 3.17 from the EPA.

Ion	Initial ppm in seawater	% Removed	Final ppm in < 1 hr
Mn ²⁺	0.054	97.3	0.0015
Mn ²⁺	0.54	96.4	0.019
Zn ²⁺	0.107	97.2	0.00075
Zn ²⁺	0.757	99.3	0.021
Co ²⁺	0.0057	75.1	0.0014
*Co ²⁺	6x10 ⁻⁶	82.5	1x10 ⁻⁶

*Co reduced to 0.06 parts per trillion
in distilled water

Figure 17. Nonviable class M MOP-UP® reagent incubated in seawater spiked with metals and/or radiotracers.

Sample	Arsenic	
	ppm	% removed
Untreated	20.0	
Class O		
- FRT02-P3ESWO	0.46	97.6
- FRT03-P3ESWO	1.1	94.5
Class S		
- SRM03-W7ESWS	1.2	94.0
- SRT09-W7ESWS	1.4	93.0

Figure 18. Second treatability test with groundwater from private industrial site contaminated by arsenic [5-10% as As(III), 40-50% as As(V), and 50-40% as arsanilic acid.]

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Sample	Cadmium		Copper		Mercury		Aluminum		Zinc		Barium		Uranium	
	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd
Untreated	3.90		0.43		1.54		67.1		0.51		0.98		2.7	
Class O														
- FRT09-S7RSWO	3.90	0	0.43	0	1.14	25.9	62.5	6.8	0.60	0	0.17	82.7	1.5	44.4
- FRT01-M7ESWP-01	3.94	0	0.42	2.3	1.08	29.8	55.6	17.1	0.55	0	0.12	81.8	1.1	59.2
- FRT02-P3ESWO-03	3.65	6.4	0.17	60.4	0.0312	97.97	49.5	26.2	0.56	0	0.09	90.8	1.0	63.0
Class S														
- SRM01-W7ESWS	ND	>99.74	ND	>97.7	0.0011	99.93	64.6	3.7	0.34	33.3	0.10	89.8	2.4	11.1
- SRM02-W7RSIS	ND	>99.74	ND	>97.7	0.0005	99.96	46.9	30.1	0.01	98.0	0.10	89.8	2.0	25.9
- SRT07-M7RMWS	3.75	3.8	ND	>97.7	0.0198	98.70	63.0	6.1	0.52	0	0.10	89.8	1.3	51.8

Figure 19. Selection of reagents to be used in the Oak Ridge Y-12 Plant S-3 Ponds Area treatability test.

Sample	Cadmium ppm % rmod	Copper ppm % rmod	Mercury ppm % rmod	Aluminum ppm % rmod	Zinc ppm % rmod	Barium ppm % rmod	Uranium ppm % rmod
Untreated	3.87	0.35	1.16	76.0	0.51	15.3	0.36
<u>Formulation 1</u>							
- 0.5 g/L each							
Mix	0.01	ND	0.0028	38.3	0.04	10.4	32
Class S first	ND	ND	ND	28.9	0.04	10.2	33
Class O first	ND	ND	ND	27.8	ND	10.0	34
- 1 g/L each							
Mix	ND	ND	ND	2.8	ND	7.26	52
Class S first	ND	ND	ND	3.0	0.02	6.96	54
Class O first	ND	ND	ND	13.8	ND	8.90	41
- 2 g/L each							
Mix	ND	ND	0.0011	0.08	ND	0.61	96
Class S first	ND	ND	ND	ND	ND	0.55	96
Class O first	ND	ND	ND	ND	ND	0.30	98
<u>Formulation 2</u>							
- 0.5 g/L each							
Mix	ND	ND	ND	45.5	0.04	12.9	15
Class S first	ND	ND	ND	44.7	0.04	13.2	13
Class O first	ND	ND	ND	41.0	ND	12.8	16
- 1 g/L each							
Mix	ND	ND	ND	21.6	0.08	10.4	32
Class S first	ND	ND	ND	24.5	0.02	12.3	19
- 2 g/L each							
Mix	ND	ND	ND	0.07	ND	2.12	86
							99.9

Mix: both reagents added to S-3 Ponds water simultaneously in a 1:1 ratio by dry weight and incubated 4 hours without agitation

Class S first: class S reagent added to S-3 Ponds water and incubated 2 hours; an equal weight of class O added and incubation continued for another 2 hours

Class O first: class O reagent added to S-3 Ponds water and incubated 2 hours; an equal weight of class S added and incubation continued for another 2 hours

Figure 20. Treatability test with Oak Ridge Y-12 Plant S-3 Ponds
Area groundwater simulant at pH 4.1.

Semiconductor
Positive Lithographic

Hydrofluoric acid	8 *
Trichloroethane	32
Acetone	43
Acrylate	5
Polyalkyl aldehyde	5
Sodium silicate	5
Potassium phosphate	12
Isopropyl alcohol	16
Ethyl acetate	5
Ethanol	5
Pb	50

Printed Wire Board
Imaging Process

Isopropyl alcohol	2.6 *
Trichloroethane	12
Glycol ether	8.5
Amine	5
Methylene chloride	5
Ammonium sulfate	16
Sodium citrate	5
Pb	10

Semiconductor
Final Layering & Cleaning

Xylene	72 *
Acetone	55
Ammonium sulfate	1000
Ni	8
Cr	10

CRT
Coating to Panel Interior

H ₂ SO ₄	2.2 *
Surfactant (Tween 80)	0.1
Sodium citrate	20
Methanol	35
Ammonium sulfate	10
Ni	33
Cr	1

Printed Wire Board
Assembly Process

Acetone	18 *
Xylene	36
Ni	10
Pb	17

* mg/L except Tween 80 in mL/L

Figure 21. Recipes used to simulate wastewaters from major electronics manufacturing processes

Figure 22. Class S MOP-UP® reagent treatment of radionuclides at neutral pH

Figure 23. Class S MOP-UP® reagent treatment of radionuclides at neutral pH

Figure 24. Class S MOP-UP® reagent treatment of radionuclides at neutral pH

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	SUBSTANCE	Initial ng / L	Final ng / L	% Rmvd / Destroyed (< 24 hr)
Hexachlorobenzene	1000	60.0	94
	Heptachlor	1000	<10.0	>99
	Heptachlorepoxyde (cis)	1000	20.0	98
Aldrin	1000	<10.0	>99
	Endosulphan A	1000	<10.0	>99
	Endosulphan B	1000	<10.0	>99
	op DDE	1000	<10.0	>99
	pp DDE	1000	80.0	92
op DDD	1000	<20.0	>98
	pp DDD	1000	260	74
	op DDT	1000	<20.0	>98
	pp DDT	1000	<20.0	>98
Endosulphan Sulphate	1000	<20.0	>98
	Carbetamide	1000	340	66
	Chlortoluron	1000	370	63
	Fluoranthene	100	<5.0	>95
	Benzo(ghi)perylene	20	<2.0	>90
	Benzo(u)fluoranthene	20	<2.0	>90
	Indeno(123 cd)pyrene	20	<2.0	>90
Benzo(b)fluoranthene	20	<2.0	>90
	Benzo(a)pyrene	20	<2.0	>90

Figure 25. Class S MOP-UP® reagent treatment of organic pollutants

Organic *	CLASS O REAGENTS				CLASS S REAGENTS									
	#1		#2		#1		#2		#3		#4		#5	
	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd	ppm	% rmd
Bromoform	130	74	220	56	470	6	420	16	420	16	420	16	400	20
Carbon tetrachloride	20	96	13	97.4	80	84	65	87	62	88	54	89	55	89
Chloroform	140	72	140	72	260	48	250	50	270	46	260	48	260	48
1,1-Dichloroethane	120	76	110	78	210	58	210	58	230	54	210	58	220	56
1,2-Dichloroethane	200	60	180	64	310	38	290	42	300	40	300	40	290	42
1,2-Dichloropropane	160	68	160	68	300	40	280	44	300	40	300	40	290	42
1,1,2,2-Tetrachloroethane	110	78	180	64	330	34	300	40	280	44	300	40	290	42
Tetrachloroethene	12	98	ND	>99.2	83	83	54	89	42	92	42	92	51	90
1,1,1-Trichloroethane	54	89	40	92	120	76	110	78	120	76	100	80	100	80
1,1,2-Trichloroethane	170	66	220	56	350	30	330	34	330	34	340	32	330	34
Trichloroethene	36	93	38	92.4	160	68	110	78	140	72	130	74	100	80

* The standard solution also contained dibromomethane, 1,2,3-trichloropropane, and 1,1,1,2-tetrachloroethane. Analyses were not done for these pollutants.

Figure 26. Screening nonviable MOP-UP® reagents for treatment of organic pollutants. (Starting concentrations of 500 ppb each of 14 halogenated solvents.)

<i>Reagent</i>	<i>% TNT removed</i>	<i>% DNTs removed</i>	<i>% Conversion to Am-DNT</i>
Class S #1	>97.2%	73.5	8.3
Class S #2	>97.2%	>96.9	2.4
Class O #1	>97.2%	26.5	14.2
Class O #2	>97.2%	51.0	10.0

Figure 27. Preliminary screening test for MOP-UP® reagent treatment of nitroaromatic explosives

<i>Site</i>	<i>Summary</i>	<i>Beginning Levels</i>	<i>Levels Attained</i>
<i>Coakley Landfill New Hampshire</i>	Pretreatment of groundwater by hydroxide precipitation with lime, then air stripping for removal of VOCs	330 ppb Cr 122-200 ppb Ni 10-90 ppb As	50 ppb Cr 100 ppb Ni 50 ppb As
<i>Stringfellows Acid Pit Site, California</i>	Pretreatment for removal of metals and organics, then POTW	1.5-270 ppm Cr 0.32-9.3 ppm Cd 2.2-300 ppm Zn 1.7-20 ppm Cu	0.5 ppm Cr 0.11 ppm Cd 2.61 ppm Zn 2 ppm Cu
<i>Winthrop Landfill Winthrop, ME</i>	Pilot test of metals from the groundwater by precipitation	0.1-0.8 ppm As 0.04 ppm Ni 0.2-0.6 ppm Zn	0.05 ppm As 0.04 ppm Ni 0.18 ppm Zn

Taken from Federal Remediation Technologies Roundtable

Figure 28. Performance of Conventional Pump-and-Treat Systems Utilizing Chemical Precipitation

<i>Metal</i>	<i>pH range for hydroxide treatment</i>	<i>Typical effluent discharge following sedimentation, mg/L</i>
Aluminum	6-7	0.10
Cadmium	>10	0.5
Chromium	7-8	0.10
Copper	9-10	0.50
Nickel	10-11	>1.0
Zinc	8-11.5	>1.0
Lead	9.5-10.5	>10
Silver	10.5-11.5	0.50

Figure 29. Typical Wastewater Discharge Concentrations from Metal Hydroxide Precipitation Processes

<i>Contaminant</i>	<i>Barrier Type</i>	<i>Reactive Media</i>	<i>Status</i>
Organics <ul style="list-style-type: none"> • DCE, TCE, PCE • BTEX • Nitrobenzene • DCA, TCA • PCBs, PAHs 	Degradation	zero-valent iron iron(II) porphyrins resting-state microorganisms oxygen-releasing compound dithionite	commercial laboratory field field field
	Sorption	zeolite surfactant modified silicates organobentonites activated carbon	laboratory laboratory laboratory laboratory
Inorganics <ul style="list-style-type: none"> • Heavy metals (Ni, Pb, Cd, Cr, V, Hg) • Radioactive (U, Ra, Sr, Cs, Tc) • Nitrate 	Sorption	peat ferric oxyhydroxide bentonite zeolites and modified zeolites chitosan beads	laboratory field laboratory laboratory laboratory
	Precipitation	hydroxyapatite zero-valent iron dithionite lime or limestone	laboratory commercial field commercial
	Degradation (nitrate)	saw dust	field

Taken from RD Vidic and FG Pohland, Treatment Walls, GWRTAC E Series Technology Evaluation Report TE-96-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh PA (1996).

Figure 30. Commercialized and Emerging Treatment Wall Technologies

Location	Dimensions	Contaminants	Construction	Costs	
				Media	Total
Sunnyvale, CA <i>full-scale, built</i>	7m slurry wall on either side of 12m long treatment section; 6m deep; 3.5m vertical and 1.2m flow-through thickness of iron	1-2 mg/L VC, cis-1,2-DCE, & TCE	\$550.0K	\$170.0K	\$720.0K
Moffet Federal Air Field, CA <i>full-scale, built</i>	6.5m long interlocking sheet piles on either side of a 3.2m wide, 3.2m thick, and 8.2m deep reaction cell	1 mg/L TCE			\$300.0K
Coffeyville, KS <i>pilot-scale, built</i>	150m slurry wall on either side of 6m long gate; 9m deep; 3.8m vertical and 1m flowthrough thickness of iron	100's µg/L TCE	\$350.0K	\$50.0K	\$400.0K
Elizabeth City, NC <i>full-scale, built</i>	45m long, 5.5m deep, and 0.6m wide zero-valent iron wall	TCE, chromium	\$220.0K	\$200.0K	\$420.0K*
Lowry AFB, CO <i>pilot-scale, built</i>	3.5m wide, 1.6m thick, and 2.9m deep gate with 5m long cutoff walls on each side of the reaction zone	850 µg/L TCE 220 µg/L cis-1,2-DCE	\$105.0K	\$32.5K	\$137.5K
New Hampshire <i>full-scale, estimate</i>	400m long wall with several gates; 9m deep	100's µg/L TCE, VC, cis-1,2-DCE	\$1200.0K	\$9000.0K	\$2100.0K
Michigan <i>full-scale, estimate</i>	90m long with 3 gates; 6m deep	10-100 mg/L TCE	\$300.0K	\$135.0K	\$435.0K
Canada <i>full-scale, estimate</i>	45m long with 2 gates; 4.5m deep	50-100 µg/L TCE	\$130.0K	\$52.5K	\$182.5K

Taken from RD Vidic and FG Pohland, *Treatment Walls*, GWRTAC E Series Technology Evaluation Report TE-96-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh PA (1996).

* Promotional literature provided by EnviroMetal Technologies, Inc., list the cost of this barrier as "just under \$500K"

Figure 31. Construction Costs of Reactive Barrier Treatment Walls

<i>Reactive Media</i>	<i>Contaminant</i>	<i>Study Type</i>	<i>Location / Comments</i>
<i>Zero-Valent Iron</i>	Cr	commercial	Elizabeth City, NC
	Cr	field	Elizabeth City, NC
	U	field	UMTRA Site, Durango, CO
<i>Peat</i>	Ni, Cr, Cd	laboratory	low pH enhances capacity, equilibrium reached in less than 2 hours
	U, Mo	laboratory	
<i>Bentonite</i>	Cs	laboratory	clay composition decreases sorption capacity
<i>Ferric oxyhydroxide</i>	U, Mo	laboratory	requires neutral pH; effluent below 0.05 mg U/L
	U, Mo	pilot	Monticello, UT
<i>Zeolite</i>	Pb, Cd	laboratory	pretreatment of chabazite and clinopitohite with NaCl or surfactants enhances capacity
	Sr	laboratory	
<i>Modified zeolites</i>	As, Cr, Cd, Pb	laboratory	
<i>Chitosan beads</i>	V, Cd, Hg	laboratory	slow rate of uptake; capacity = 500 mg V/g
<i>Hydroxyapatite</i>	Pb	laboratory	complete removal in 30 min; pH 5-6; other metals inhibit removal of Pb
<i>Dithionite</i>	Cr, V, Tc, U	field	18-30 m treatment zone to react for 5-30 days at Hanford 100H Area, WA
<i>Lime/limestone</i>	Acid mine drainage	commercial	various sites; oxygen, Fe and/or Al causes clogging, loss of reactivity
<i>MOP-UP®</i>	Cd, Pb, Hg, Cu, Cr, Zn, Ba, As, Al, Ni, Se, Mg, Ru, Rh, U, Pu, Tc, Cs, Co, Am, Y, La, B	laboratory	demonstrated with wide range of groundwaters & wastewaters; high capacities in dilute or complex solutions and/or at pH extremes; removal of Mn, Fe if desired; simultaneous treatment of organics

Adapted from RD Vidic and FG Pohland, *Treatment Walls, GWRTAC E Series Technology Evaluation Report TE-96-01*, Ground-Water Remediation Technologies Analysis Center, Pittsburgh PA (1996).

Figure 32. Current Status of Treatment Wall Technologies for Inorganic Contaminants

Taken from CR Evanko and DA Dzombak, *Remediation of Metals-Contaminated Soils and Groundwater*, GWRTAC E Series Technology Evaluation Report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh PA (1997).

Figure 33. Metal adsorption to amorphous iron oxyhydroxide (a) metal cations and (b) metal anions

<i>Metal</i>	<i>Treatment operation type</i>	<i>Ion exchange type</i>	<i>Influent concentration mg/L</i>	<i>Effluent concentration mg/L</i>
Arsenic ¹	Laboratory	Anion	2.3	0.52
Barium	Commercial	Cation	11.7	0.17
Chromium(VI) ²	Commercial	Anion	44.8	0.025
Copper	Commercial	Cation	45.0	ND
Lead	Pilot-plant	Cation	126.7 - 144.8	0.02 - 0.053
Mercury	Commercial	Cation	5.0 - 25	0.001
Uranium ³	Laboratory	Anion	84.8	0.03
Zinc	Pilot-plant	Cation	6.0	0.4

1. Present as arsenite (AsO_3^{2-}) or arsenate (AsO_4^{3-})

2. Present as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$)

3. Present as uranyl carbonates [$\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$]

Figure 34. Ion Exchange Effectiveness in Electroplating Wastewater

Taken from CR Evanko and DA Dzombak, *Remediation of Metals-Contaminated Soils and Groundwater*, GWRTAC E Series Technology Evaluation Report TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh PA (1997).

Figure 35. Metal adsorption to amorphous iron oxyhydroxide (a) metal cations and (b) metal anions. Arrows indicate direction of increasing sorbate/sorbent ratio.

<i>Initial mM Cd</i>	<i>mg Cd / g reagent</i>		
	<i>pH 2.7</i>	<i>pH 6.5</i>	<i>pH 10.3</i>
0.005	44	97	96
0.01	63	189	186
0.03	189	310	523
0.1	281	364	1777
0.2	320	389	3574
0.4	394		4732
0.5		448	
0.6	390		4953
0.8	394		4694
1.0	391	533	4849

Table 1. Metal loadings taken up by 0.006 g ME30-L7RXWS / L incubated at room temperature for 2 hours.

<i>Initial pH</i>	<i>mg Cd / g reagent</i>
2.00	321
2.06	323
2.29	323
2.43	324
2.80	362
5.30	384
7.40	548
9.40	1538
10.15	1746
10.38	1865
11.35	1924

Table 2. Cd²⁺ loadings taken up by 0.006 g ME30-L7RXWS / L incubated in 11.24 ppm Cd solutions at room temperature for 2 hours.

<i>Initial pH</i>	<i>mg Pb / g reagent</i>
2.11	232
2.95	252
3.47	237
3.60	342
3.65	481
4.23	700
5.80	878
6.51	2800
7.00	3451
7.56	3558
9.08	3563
10.43	3541

Table 3. Pb²⁺ loadings taken up by 0.006 g ME30-L7RXWS / L incubated in 20.7 ppm Pb solutions at room temperature for 2 hours.

Table 4. Examples of U.S. Cleanup Goals/Standards for Selected Metals in Groundwater

<u>Description</u>	<u>As</u>	<u>Cd</u>	<u>Cr</u>	<u>Hg</u>	<u>Pb</u>
	<u>Metals (µg/L)</u>				
Maximum Contaminant Level (MCL) ^a	50	5	100	2	15
Superfund Site Goals ^b	50	—	50	0.05 - 2	50
Pennsylvania Standard for Groundwater in Aquifers (<2500 mg/L TDS) ^c	50	5	100	2	5
Wisconsin Groundwater Quality Enforcement Standards	50	5	100	2	15

a MCL = the maximum permissible level of contaminant in water delivered to any user of a public system, established under the Safe Drinking Water Act.

b from U.S. EPA, Contaminants and Remedial Options at Selected Metals-Contaminated Sites, EPA/540/R-95/512, U.S. Environmental Protection Agency, Office of Research and Development, Washington DC, 1995

c PA DEP Health-Based Standards, 1996

d WI Department of Natural Resources (DNR) Groundwater Quality Standards tables, 1996