Zero-Valent Zinc Shows Promise for Removing TCP from Groundwater

Studies Show Positive Results Removing Recalcitrant Compound from Pendleton Well

THE SOLVENT 1,2,3-TRICHLOROPROPANE (TCP), which is highly toxic to humans, is attracting increasing regulatory attention. As sampling and analytical methods improve, TCP detection in groundwater resources is on the rise. As of 2007, TCP had been detected in more than 200 samples at twenty or more Department of Defense sites.

At Marine Corps Base (MCB) Camp Pendleton, CA, TCP was detected at levels above California's action level, resulting in two groundwater wells being removed from service. MCB Camp Pendleton officials faced significant challenges in trying to address the contamination because TCP is difficult to degrade (i.e., breakdown into its chemical components). Recent studies at MCB Camp Pendleton, sponsored by the Navy Environmental Sustainability Development to Integration (NESDI) program, show promise for removing TCP from groundwater wells.

Background

TCP is a chlorinated volatile organic compound that has been used in a variety of chemical production processes, in agricultural chemicals, and as a solvent. Over time, point and non-point source releases of TCP have contaminated soil and groundwater in many places.

Because its toxicity to humans appears to be high relative to other chlorinated solvents, even low-level exposures to TCP could pose significant human health risk. Consequently, the California Department of Public Health (DPH, formerly the Department of Health Services (DHS)) has set a notification level of 0.005 micrograms per liter (µg/L) for TCP in drinking water (DHS, 2005), which is much lower than the corresponding level for other chlorinated solvents such as trichloroethene (TCE: 5 µg/L). California requires monitoring for TCP as an unregulated chemical and has specified an Action Level of 0.5 µg/L for removing a public drinking water well from service. In addition, the California Office of Environmental Health Hazard Assessment (OEHHA) has established a public health goal (PHG) of 0.0007 µg/L in drinking water based on recent re-evaluation of risk exposures. In 2009, the U.S. Environmental Protection Agency, which does not yet regulate TCP in drinking water, added the compound to its Contaminant Candidate List 3 (CCL3).

State Action Levels (Federal MCL anticipated)

STATE	CONCENTRATION	UNITS
CA	0.005[a] 0.0007[b]	µg/L
CT	0.05	µg/L
TX	0.13	µg/L
OR[c]	N/A	N/A

a—CA DPH notification level
b—CA OEHHA Public Health Goal
c—TCP designated an "Unregulated Organic"

Looking for TCP Treatment Alternatives at MCB Camp Pendleton

At MCB Camp Pendleton, TCP has been detected in three of nine groundwater production wells located within the Santa Margarita River valley, north and west of the portion of the site known as the 22/23 Area. These wells have been taken offline and MCB Camp Pendleton considered multiple options to replace the lost resource, including:

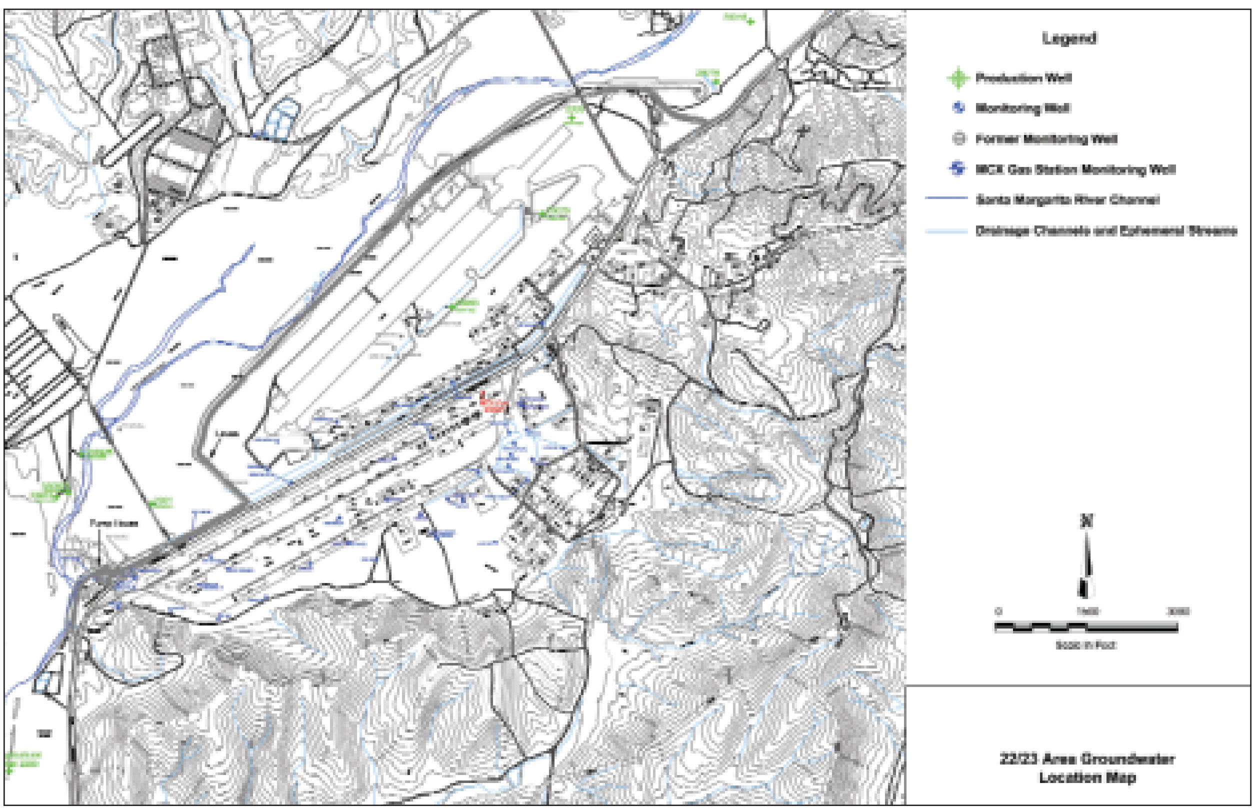
- Installing additional groundwater production wells
- Developing an approach to treat affected groundwater, either in situ or at the wellhead
- Purchasing drinking water from an outside source

Past research offered possibilities for finding a way to treat the affected groundwater. Results of work supported by the Secretary of Defense's Strategic Environmental Research and Development Program (SERDP) and conducted by Dr. Paul Tratnyek and his students at the Oregon Health and Science University (OHSU), showed the potential of using zero-valent metals (ZVM) to degrade organic compounds.

In 2009, personnel from the Naval Facilities Engineering Service Center (NAVFAC ESC), with resources and guidance provided by the NESDI program, began to evaluate two types of zinc and one proprietary form of iron for degrading TCP. The project took a step-wise effort beginning with Tratnyek conducting laboratory (bench scale) experiments then proceeding to a larger, two-phase on-site column test at MCB Camp Pendleton.

Specific objectives of the project included:

- Assess the ability of Zero-valent Zinc (ZVZ) and/or Zero-valent Iron (ZVI) to effectively degrade TCP in MCB Camp Pendleton groundwater
- Evaluate potential secondary water quality effects (e.g., changes in pH or dissolved zinc concentration) that could affect future implementation of a ZVZ or ZVI remedy
- Identify potential factors that may affect performance of ZVZ or ZVI as a remedy for TCP in groundwater
- Conduct a preliminary evaluation of the full-scale applicability of ZVZ or ZVI for treatment of TCP in groundwater at Camp Pendleton



The Basics About the NESDI Program

THE NESDI PROGRAM seeks to provide solutions by demonstrating, validating and integrating innovative technologies, processes, materials, and filling knowledge gaps to minimize operational environmental risks, constraints and costs while ensuring Fleet readiness. The program accomplishes this mission through the evaluation of cost-effective technologies, processes, materials and knowledge that enhance environmental readiness of naval shore activities and ensure they can be integrated into weapons system acquisition programs.

The NESDI program is the Navy's environmental shoreside 6.4 Research, Development, Test and Evaluation program. The NESDI technology demonstration and validation program is sponsored by the Chief of Naval Operations Energy and Environmental Readiness Division and managed by the Naval Facilities Engineering Command. The program is the Navy's complement to the Department of Defense's Environmental Security Technology Certification Program which conducts demonstration and validation of technologies important to the tri-Services, U.S. Environmental Protection Agency and Department of Energy.

For more information, visit the NESDI program web site at www.nesdi.navy.mil or contact Leslie Karr, the NESDI Program Manager at 805-982-1618, DSN: 551-1618 or leslie.karr@navy.mil.

Step One—Into the Laboratory

Results from the preceding SERDP research project (ER-1457) showed that although TCP was significantly harder to degrade than other chlorinated solvents, ZVMs showed promise for chemical reduction. ZVZ and one form of ZVI (a proprietary high reactivity, atomized iron powder) were of particular interest. These results provided the starting point for the new project.

Tratnyek's initial laboratory studies at OHSU were conducted to help identify which ZVM materials were most suitable for the MCB Camp Pendleton groundwater conditions. This would also provide information necessary for subsequent on-site testing to evaluate ZVM performance. The lab work included batch studies, using both deionized water and groundwater from MCB Camp Pendleton, to identify the best ZVM candidates, establish degradation rate constants and identify other factors that might affect on-site testing. Batch studies were followed by small-scale column experiments.

Based on the batch experimental results, two ZVZ materials advanced to the next step—zinc dust 64 (Zn64) and zinc powder 1210 (Zn1210).

The small-scale column experiments were conducted to assess the short-term performance of Zn64 and Zn1210 in flow-through systems and to identify an effective mixing ratio of Zn64 with sand for future on-site testing. The experiments were performed in columns packed with materials corresponding to specific batch experiments. The columns were packed with either pure ZVZ or a ZVZ/sand mixture and were operated in an up-flow manner, with the influent entering the bottom of the column and effluent exiting the top. The columns were operated until a steady-state concentration was reached (about 24 to 48 hours), after which an experimental observed rate constant for the column was determined.

Based on the column results, a 25% Zn64/sand mixture appeared to be a favorable choice for on-site testing. However, the Zn64 columns appeared to produce a larger amount of hydrogen gas relative to the Zn1210 columns. Since it was thought that this hydrogen gas production, along with other factors such as clogging, aging and inhibition by sand could affect the long-term performance of the Zn64/sand mixture, 100% Zn1210 was also retained as a material for on-site testing. Its long-term performance could then be compared to that of Zn64. Finally, the proprietary ZVI, was retained as a material for on-site testing in order to provide a baseline for comparing ZVZ performance to that of a ZVI material.

Step Two—On-Site for Column Testing

Following baseline testing of groundwater from a MCB Camp Pendleton well, researchers initiated the first of two column-testing phases. Three types of reactive media were used:

1. 25% Zn64 and 75% sand mixture
2. 100% Zn1210
3. 50% ZVI and 50% sand mixture

Data generated from the batch experiments were analyzed to develop estimated TCP degradation rates for the different media. These degradation rates then were used to develop design parameters for column volume based on a target TCP degradation of 95%, an initial TCP concentration of 5 µg/L, and a nominal groundwater flow rate of 5 milliliters per minute (mL/min).

Phase I

The Phase I column testing configuration is shown in the following figure. The influent reservoir contained groundwater from MCB Camp Pendleton monitoring well 6W-35B, spiked with TCP to a nominal concentration of 5 µg/L. The columns were operated as up-flow systems, with the groundwater influent entering the bottom of the columns.

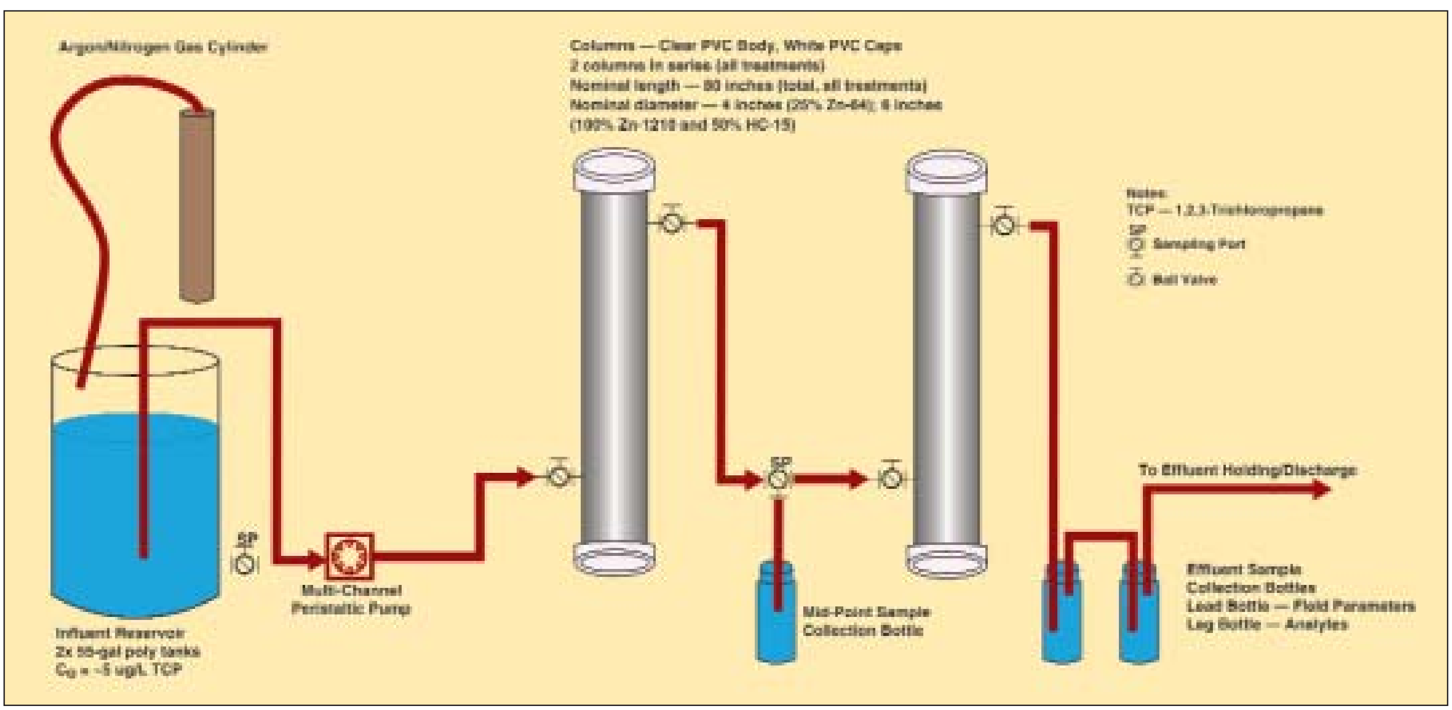
The three sets of columns were scheduled for a 12-week operation period. Every two weeks, samples were collected from the influent reservoir, the midpoint of each column, and the effluent of each column. The samples were tested for:

- Field parameters (pH, Oxidation-Reduction Potential, temperature, and Dissolved Oxygen)
- Propane and Propene
- TCP
- Dissolved Zinc
- Cations (Calcium, Iron, Magnesium, Potassium, and Sodium)
- Anions (Chloride, Nitrate, Nitrite, and Sulfate)
- Total Sulfide
- Silica
- Phosphate
- Alkalinity (Total, Bicarbonate, and Carbonate)

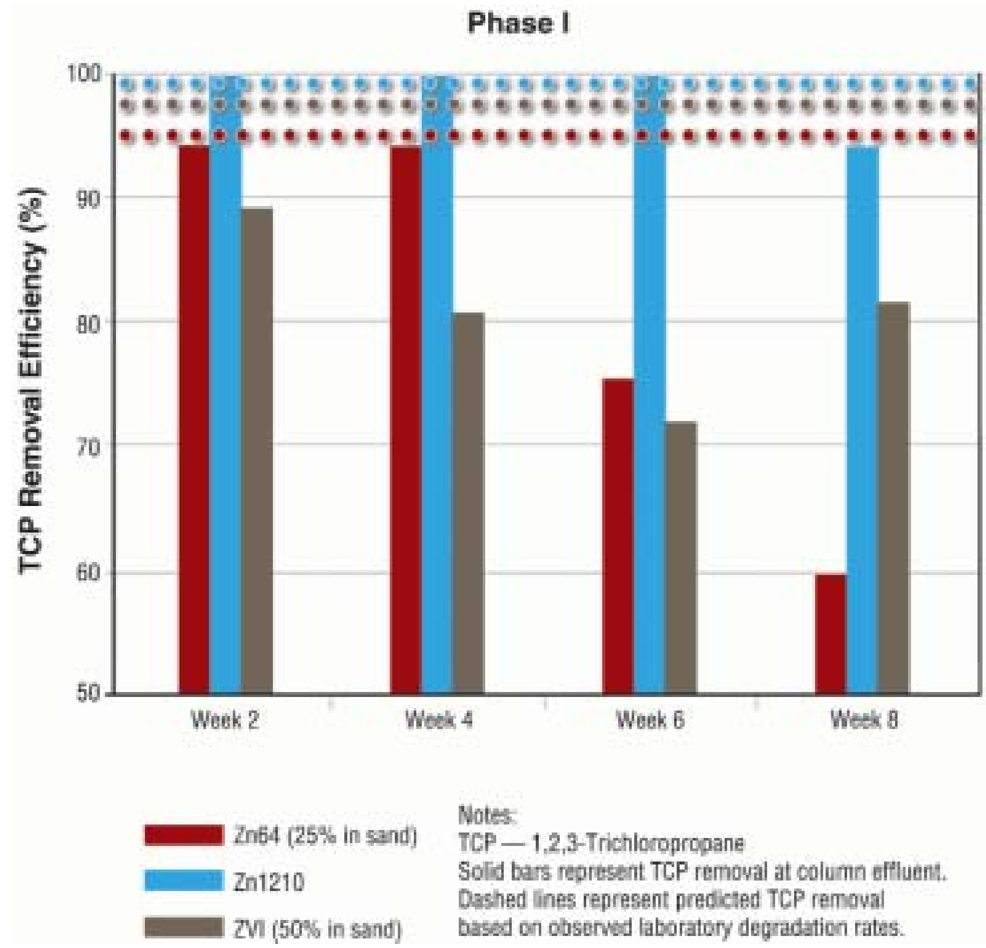
Column operations initially proceeded without event, although some problems did arise later in the testing period. First, the zinc columns developed leaks, which were attributed to increased pressure from hydrogen gas production. The columns were modified to address the issue and re-started. Following restart, upward flow through the second ZVI column could not be maintained (possibly due to cementing of the ZVI material at the column inlet). The ZVI column flows were reconfigured. All three columns again were restarted and operated for three more weeks, until the input tube to the Zn1210 column broke, draining the lead column. After additional issues following restart, the Zn1210 column was discontinued.

Based on the results of the Phase I column operations, it appeared that the selected materials performed relatively well with respect to reducing TCP concentrations in groundwater. (See the following page.) In particular, Zn1210 performed significantly better in reducing TCP than expected from laboratory studies.

During the first four weeks of column operation, TCP removal in both the



Zn64 and Zn1210 columns were similar to or exceeded predicted values. After week four, TCP removal efficiency in the Zn64 column decreased from approximately 95% to 60% and continued to decrease through the remainder of testing. In contrast, the Zn1210 column maintained a TCP removal efficiency of over 95% until it was taken offline. The ZVI column performance did not meet predictions for TCP removal. See the results of Phase I tests in the figure to the right.



Phase II

Based on the Phase I results, four types of media were selected for evaluation during the Phase II column testing:

1. 25% Zn64 and 75% sand mixture
2. 33% Zn1210 and 67% sand mixture
3. 67% Zn1210 and 33% sand mixture
4. 100% Zn1210

The first and fourth types of media were selected to confirm the Phase I TCP degradation results. The second and third media types were selected to evaluate the efficacy of TCP degradation by Zn1210 when mixed with sand, as might occur in a permeable reactive barrier (PRB)-style deployment.

The Phase II columns were redesigned to address the operational issues experienced during Phase I. The design also reflected the TCP degradation rates observed during the Phase I testing and the nominal target groundwater flow rate of 5 mL/min. As in Phase I, columns were operated for twelve weeks, with samples collected every two weeks from the influent reservoir, the midpoint of each column, and the effluent of each column. Phase II columns operated without problem. Phase II results are presented on the following page.

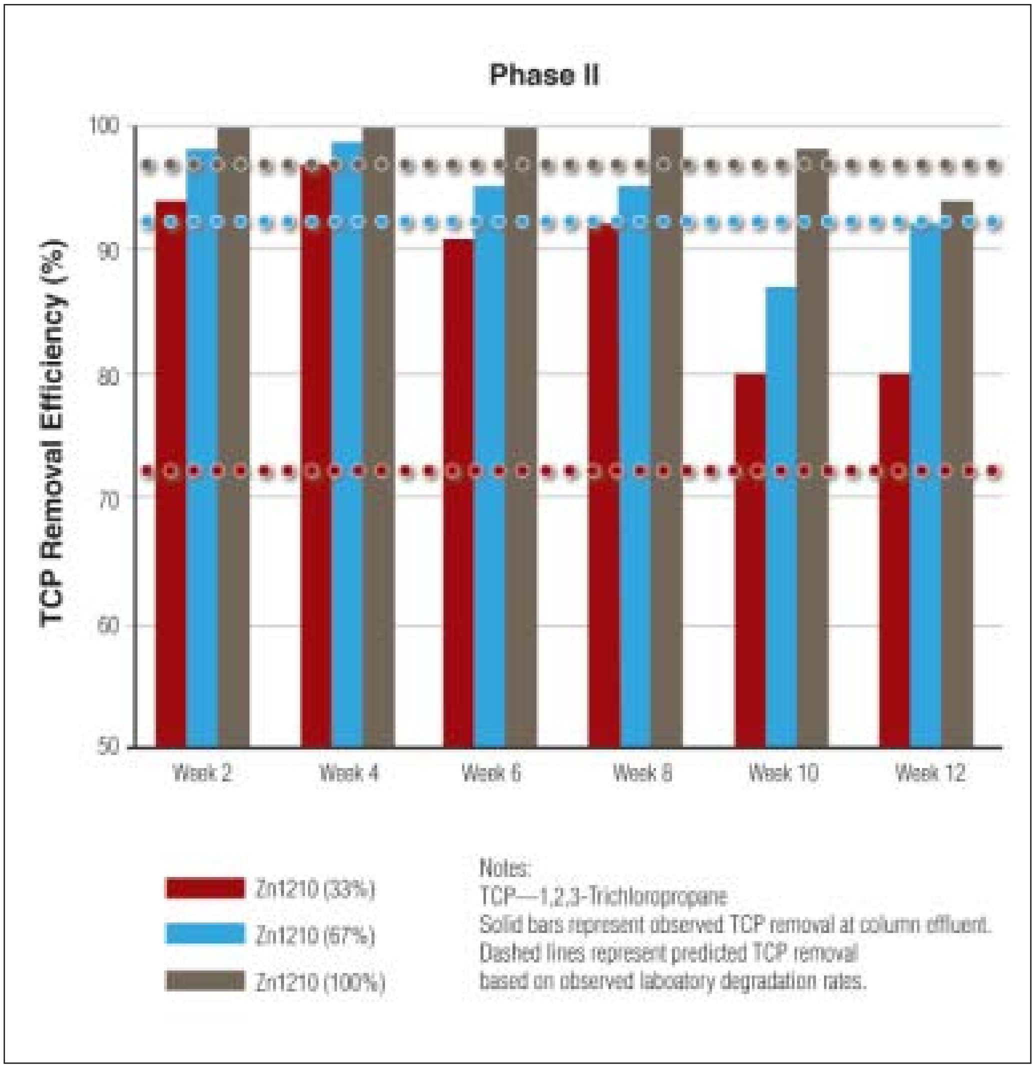
The Phase II Zn1210 columns met or exceeded the predicted TCP removal throughout the 12 weeks of column operations, confirming the Phase I column results. TCP removal efficiency after week 12 ranged from approximately 80% (the 33% Zn1210 and 67% sand column) to 95% (the 100% Zn1210 column). The high reactivity of the Zn1210 when combined with sand suggests that deployment of Zn1210/sand mixtures may be a viable remedial approach. TCP removal efficiency by the Phase II Zn64 column also remained high throughout the 12 weeks of operation, and was 90% at the conclusion of testing.

Other important parameters were sampled during column operation.

Propene, a byproduct of the TCP degradation, was detected in the effluent of each of the Phase II column throughout the 12 weeks of operation. The propene concentrations, however, were less than expected based on the amount of TCP removed. Concentrations of dissolved zinc in the Phase II column effluent were less than 0.5 mg/L.

During weeks 4 and 12 of Phase II operation, samples were collected for evaluating changes in groundwater geochemistry through the columns. Calcium, silica, and alkalinity concentrations decreased significantly between the influent and effluent of all four Phase II columns in week 4. Manganese concentrations also decreased in the columns to a lesser extent. The week 12 sampling of these analytes, observed at the column midpoints and effluent, were generally higher than those observed during week 4. It appears that the mechanisms operating within the columns to remove these compounds from groundwater became less efficient over the course of the 12-week operational phase.

After Phase II testing was completed, the columns were drained and tested for physical and chemical material changes. The zinc particles did not cement together as has been occasionally observed with ZVI. The moderate decreases in reactivity may be due to surface changes on the zinc particles that made them chemically passive.



Can It Scale?

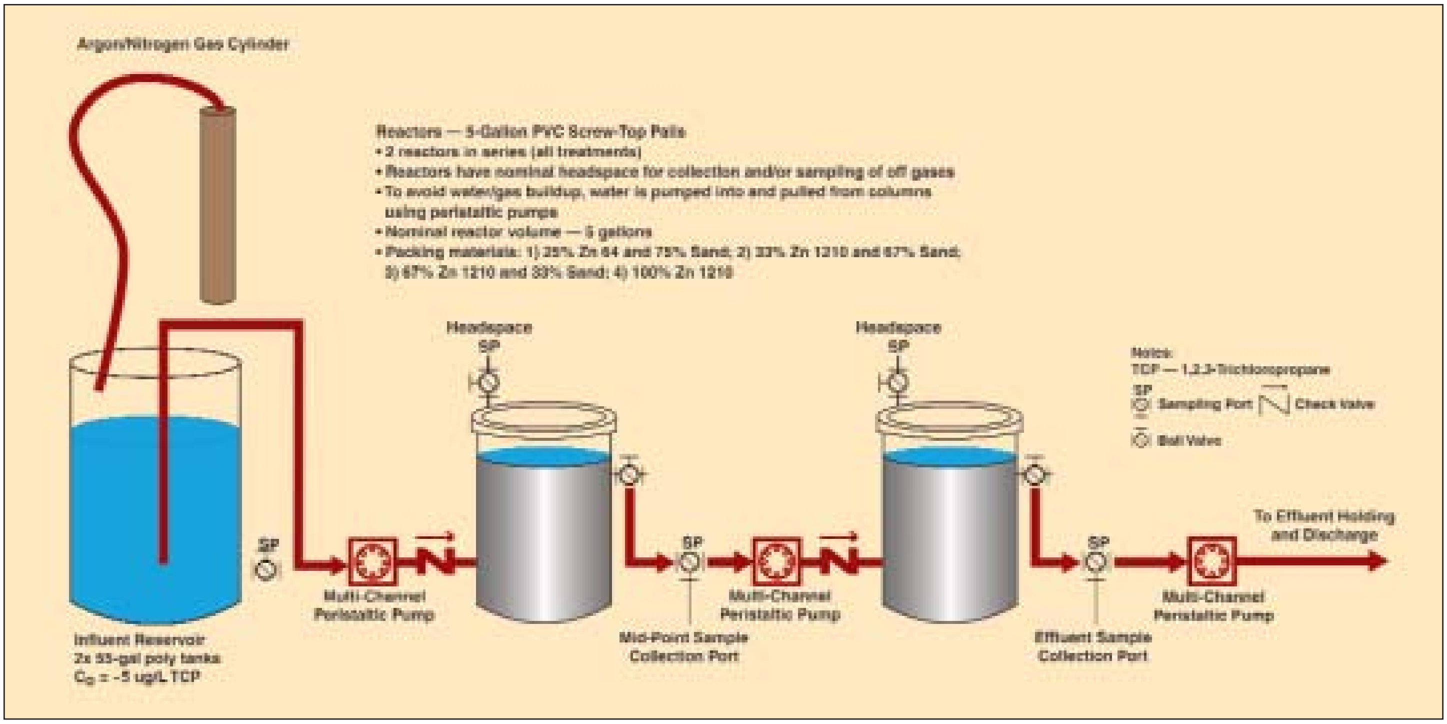
Based on the results of the preliminary laboratory studies and on-site column testing, ZVZ appears to be a viable technology for degrading 1,2,3-TCP. In particular, ZVZ appears to have the following technical advantages:

- Relatively high rates of TCP degradation, with predictable degradation behavior when transitioning from laboratory testing to field testing
- Limited changes to TCP degradation rates over time
- No identified secondary water quality effects

The on-site column testing identified Zn1210 as a promising material due to its better than expected TCP degradation performance and ease of handling relative to finer zinc materials such as Zn64.

The primary limitation of ZVZ as a remedial technology for TCP degradation is expected to be cost since ZVZ is significantly more expensive than other ZVMs such as ZVI.

Models were developed to evaluate the costs of applying this technology



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at scale both in situ (e.g., permeable reactive barrier) and ex situ (wellhead treatment of TCP at an affected water supply well). The results of the scale-up evaluation indicated that:

- Under current market conditions, the technology is not economically feasible for ex situ application due to the large reactor volumes required for treatment and high cost of ZVZ.
- The technology may be economically feasible for in situ application, particularly under the following site conditions:
  - The areal extent of TCP is limited. This would allow the length and height of a PRB application to be minimized, reducing the volume of material required.
  - The groundwater flow velocity is relatively low. This will reduce the volume of zinc required for PRB construction.
  - The cost for the in situ application is low relative to wellhead activated carbon treatment (e.g., low groundwater flow velocities and high groundwater extraction rates).

Conclusion

The NESDI-sponsored study demonstrated that it might be possible to remediate this difficult toxic compound. Based in part on these results, a pilot scale PRB is being considered to treat affected groundwater at MCB Camp Pendleton. As Theresa Morley from Naval Facilities Engineering Command Southwest noted, "I want to thank the NESDI program for sponsoring this study. We were really scratching our heads trying to figure out how to remediate such a toxic, emergent, recalcitrant compound." ⚓

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