GEOCHEMICAL BEHAVIOR OF COPPER, CHROMIUM AND ARSENIC IN GROUND WATER: CONSIDERATION INFLUENCING IN-PLACE CLEANUP

R. Z. Pyrih, Ph.D., and W. R. Bond
GEOCHEM, Inc., 12265 W. Bayaud Ave., Ste 140
Lakewood, Colorado 80227 USA
(303)988-8902

ABSTRACT

Copper, chromium and arsenic (CCA) preservation solutions have emerged as an outstanding water-borne wood preservative. It is important for the wood preservative industry to recognize that there are stringent environmental controls associated with their use and disposal in the environment. When acidic CCA treatment solutions percolate into soil or subsurface material, geochemical reactions are initiated which can act to attenuate or limit the mobility of copper, chromium, and arsenic in the seepage. These geochemical reactions can be the basis for cost effective and environmentally sound remediation of soil and ground-water contamination caused by seepage of CCA preservation solutions.

INTRODUCTION

Copper, chromium and arsenic (CCA) preservation solutions have emerged after over half a century of trials as an outstanding water-borne wood preservative. CCA formulation solutions undergo complex reactions during the treatment process in which the active chemical ingredients are fixed in the wood without being rendered inactive. Similar fixation reactions occur when CCA solutions encounter soil and geological materials. It is important for the wood preservation industry to recognize that the degree of fixation of the chemical constituents of CCA solutions varies as a function of soil properties. It is also important to recognize that copper, chromium, and arsenic all have stringent environmental controls associated with their use and disposal in the environment.

All three of the CCA elements are covered by U.S. EPA Drinking Water Standards. Arsenic and chromium are limited by Primary Drinking Water Standards of 0.05 mg/liter each; copper has a Secondary Drinking Water Standard of 1 mg/liter. The relatively high copper standard is a recognition of the fact that copper is not toxic to people in this concentration range; in fact it, is an important trace element required for human metabolism. By contrast, fresh and salt water aquatic life are severely affected by copper concentrations, as well as by concentrations of arsenic and chromium. For example, the Canadian fresh-water aquatic guideline for copper is a function of the hardness of the water, but ranges from 2 to 6 micrograms/liter. This guideline for copper is generally lower than the fresh water aquatic guidelines cited for both arsenic and chromium. The impact of the three elements varies depending on the organism and the uptake mechanism.

When acidic metal-bearing solutions such as CCA treatment solutions enter the subsurface, a complex series of geochemical reactions can occur between the constituents of the solutions and the soil or geological material. Numerous studies have been published from mining operations throughout Canada and the United States which provide insight into the geochemical processes that are at work. These processes are extremely dynamic. Some processes tend to remove potential ground-water contaminants, while others exchange one contaminant for another; still others actually introduce new contaminants into the system. These dynamic processes must be understood and appreciated before water-quality data can be correctly interpreted or effectual remedial measures can be designed.

GEOCHEMICAL ATTENUATION

Soils and geological materials have the ability to interact geochemically with chemical constituents of ground water. The results of this interaction can lead to the partial or total immobilization of potential ground-water contaminants. This process of immobilizing and restricting the chemical constituents from moving with ground-water flow is called attenuation.

When acidic CCA treatment solutions percolate into soil or rock material, geochemical reactions are initiated which can act to attenuate the movement of copper, chromium, and arsenic that are present in the seepage. To understand the reactions and to interpret any resultant data, it is helpful to visualize a conceptual geochemical model that describes the movement of copper, chromium, and arsenic in the subsurface. Such a conceptual geochemical model of contaminant migration is illustrated in Figure 1.

By far, the most significant geochemical process that takes place between acidic seepage and earthen materials is the reaction and dissolution of carbonate minerals. Hydrogen ions in the acidic solution react with calcite or other carbonate minerals which may be present in underlying soil, sediment, or bedrock. In the course of the reaction, hydrogen ions are consumed which neutralize the acidity of the seepage. Neutralization of the acidic seepage establishes pH conditions which are more favorable to the functioning of geochemical mechanisms such as ion exchange, sorption, and precipitation. Precipitation of metal hydrous-oxide is one mechanism which can be initiated by calcite dissolution and acid neutralization. Metal precipitation is pH dependent and results in the sequential removal of metals as a function of increasing pH. Iron is the earliest metal to precipitate, followed in turn by aluminum, copper, zinc, and finally manganese. Other metals and trace elements are co-precipitated along with the metal hydrous-oxides on geologic materials in aquifers.

As the acidic solutions percolate into the subsurface, geochemical processes occur as the reaction front advances. Depending upon the calcite content of the subsurface material, the acid front is retarded in its down-gradient movement relative to the rate of ground-water advance. The advance of the acid front is controlled by the number of pore volumes of acidic seepage that will react with a given volume of earthen material.

As the contaminant plume migrates down gradient, a total of three distinct zones develop (Figure 1). The first zone, which may be termed the "core" zone, consists of ground water with a quality which is virtually identical to that of the source of the seepage. The water is characterized by extremely low pH, very high dissolved solids concentrations, and elevated concentrations of metals. In the case of CCA solutions, high concentrations of copper, chromium, and arsenic would be expected to be presented in fluids of the core zone. In the core zone, virtually all the carbonate minerals in the soil or geological material have been consumed by chemical reaction.

The second zone in the conceptual model is termed the "active" zone, and is the area of active calcite dissolution and the formation of chemical precipitates including gypsum and metal hydrous-oxides. Water in this zone is characterized by high levels of some dissolved metals, in accordance with the sequence of metal hydrous-oxide removal. Arsenic and copper are generally removed within the active zone, in response to the formation of iron hydrous-oxides and iron coprecipitaiton.

The down gradient of the three zones is termed the "neutralized" zone. Water in this zone is characterized by high concentrations of total dissolved solids, and is frequently saturated with respect to gypsum. Very low concentrations of arsenic and copper would generally be present within the neutralized zone.

For any conceptual model, there are certain exceptions to the rule. Unfortunately for the wood treating industry, hexavalent chromium is the exception. The mobility of hexavalent chromium is very "conservative" in soil and ground-water environments; hexavalent chromium moves at the same rate as the ground water and is usually not attenuated to any significant extent by naturally-occurring geochemical reactions.

CHROMIUM ATTENUATION

Chromium has a somewhat unique geochemical behavior in natural water systems. Trivalent chromium is the most common form of naturally-occurring chromium, but is largely immobile in the natural environment, with natural waters having only traces of chromium unless the pH is extremely low. Under strong oxidizing conditions chromium is present in the hexavalent state, and persists in anionic from as hexavalent chromium. The use of hexavalent chromium in CCA solutions can introduce high concentrations of a very mobile chromium species into the ground water regime.

Typically, chromium in the trivalent form is sparingly soluble, but shows virtually limitless solubility in the oxidized hexavalent form. This behavior is very similar to the geochemical behavior of uranium, which is readily soluble in the oxidized (+6) form and insoluble in the reduced (+3) form. Such geochemical behavior has previously been used to advantage in solution mining of uranium. Similar geochemical behavior of chromium can be used to advantage in remediating soil and ground-water contamination by hexavalent chromium.

Cleanup of hexavalent chromium can be achieved in place (below the land surface) by introducing a chemical reagent capable of reducing hexavalent chromium to the trivalent state, and allowing the trivalent chromium to geochemically react with natural soil or geological material. If the geochemical properties of the earthen materials are favorable for this interaction, the trivalent chromium will be "fixed" and immobilized in geochemical traps below the surface.

IN-PLACE CLEANUP OF CCA SOLUTION SEEPAGE

Experience gained from the cleanup of in-place uranium leaching operations has been utilized to develop a phased approach for evaluating the feasibility of in-place remediation of soil or ground water which are contaminated with copper, chromium, and arsenic. As noted, copper and arsenic mobility is largely controlled by the pH of the migrating seepage. Thus, it is possible to achieve in-situ remediation of copper and arsenic by modification to the pH regime, so long as other conditions such as redox conditions are maintained within an appropriate range. In some cases, it may be necessary to form a co-precipitate of iron hydrous-oxide and iron arsenate, where the natural subsurface materials do not have adequate geochemical sorbtive capacity. It is best to take a phased approach when evaluating the feasibility of in-place chromium remediation. In the first phase, representative earthen materials are analyzed for geochemical properties which experience has shown can limit the mobility of trivalent chromium. These properties include soil pH, acid neutralizing potential, iron and manganese hydrous-oxides content, organic carbon content, and cation-exchange capacity. Based on the result of these analyses, a preliminary decision is made whether a contaminated site would be suitable for attempting in-place geochemical remediation.

Subsequent to the evaluation of the geochemical properties, laboratory testwork utilizing sequential batch-contact test and column test procedures are usually required to define the degree of chromium mobility at a particular site. Figure 2 presents the results of a paired column tests utilizing actual chromium-contaminated aquifer material from a wood-treating facility in the Central Valley of California. In the figure, the upper curve represents ground-water chromium concentrations that would be expected using a clean-water sweep (pump-and-treat) approach to achieve ground-water quality standards. The lower curve reflects the results from a duplicated test wherein an innocuous reagent was added in order to reduce the hexavalent chromium to the trivalent form, and, which in turn, immobilized the chromium by geochemical interaction with the aquifer material.

Upon completion of the laboratory evaluations described above, actual field tests must be conducted. Typical field evaluation most commonly uses the "push-pull" approach. The purpose of the push-pull field test is to ascertain restoration feasibility under field conditions having significant vertical variability.

ADVANTAGES OF IN-PLACE CLEANUP

Capital costs for in-place cleanup of contamination utilizing the geochemical attenuation approach are generally equivalent to the capital costs for cleanup by means of the "clean-water sweep" approach. Capital costs associated with recovery wells and surface treatment systems are common to both. The in-place remediation systems are often slightly less expensive since they do not have to operate for as long as does the equipment required in pump and treat options. This saving is offset by the need for reinjection wells and/or pits which are required for in-place remediation. Monitoring costs for the in-place remediation approach are more expensive; however, the tests indicate that the monitoring program need not be operated for as long as in the case of conventional clean-water sweep treatment.

The major cost saving of in-place remediation, relative to conventional techniques, comes in the area of operating cost. Such costs are directly related to the volume of water which must be pumped under each technique. Where the clean-water sweep approach may require pumpage of 20 to 30 pore volumes of water to effect ground-water quality restoration, in-place treatment may reduce required pumpage to only 5 pore volumes.

In-place remediation also has significant environmental advantages over conventional techniques. As described above, the in-place approach would involve much less pumping and subsequent surface discharge, an advantage in areas of water scarcity. Secondly, since much less treatment is required, less treatment-plant sludge is produced for disposal. In the case of chromium treatment, the sludge must be disposed into secure landfills, which are under increasing demand for receiving waste. Disposal costs are directly related to the quantity of sludge produced. Sludge disposal also carries a significant future liability which can be directly related to the quantity of material disposed.

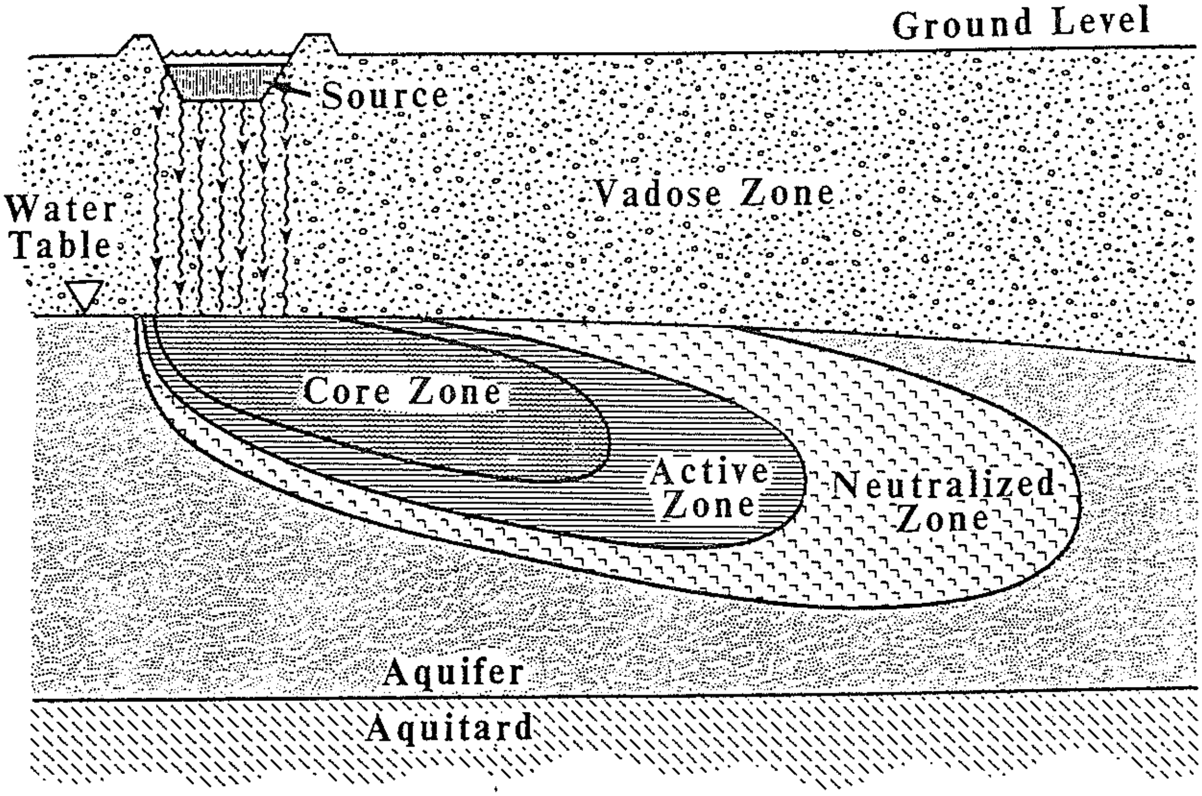

FIGURE 1
CONCEPTUAL GEOCHEMICAL MODEL OF
ZONES IN A CONTAMINANT PLUME

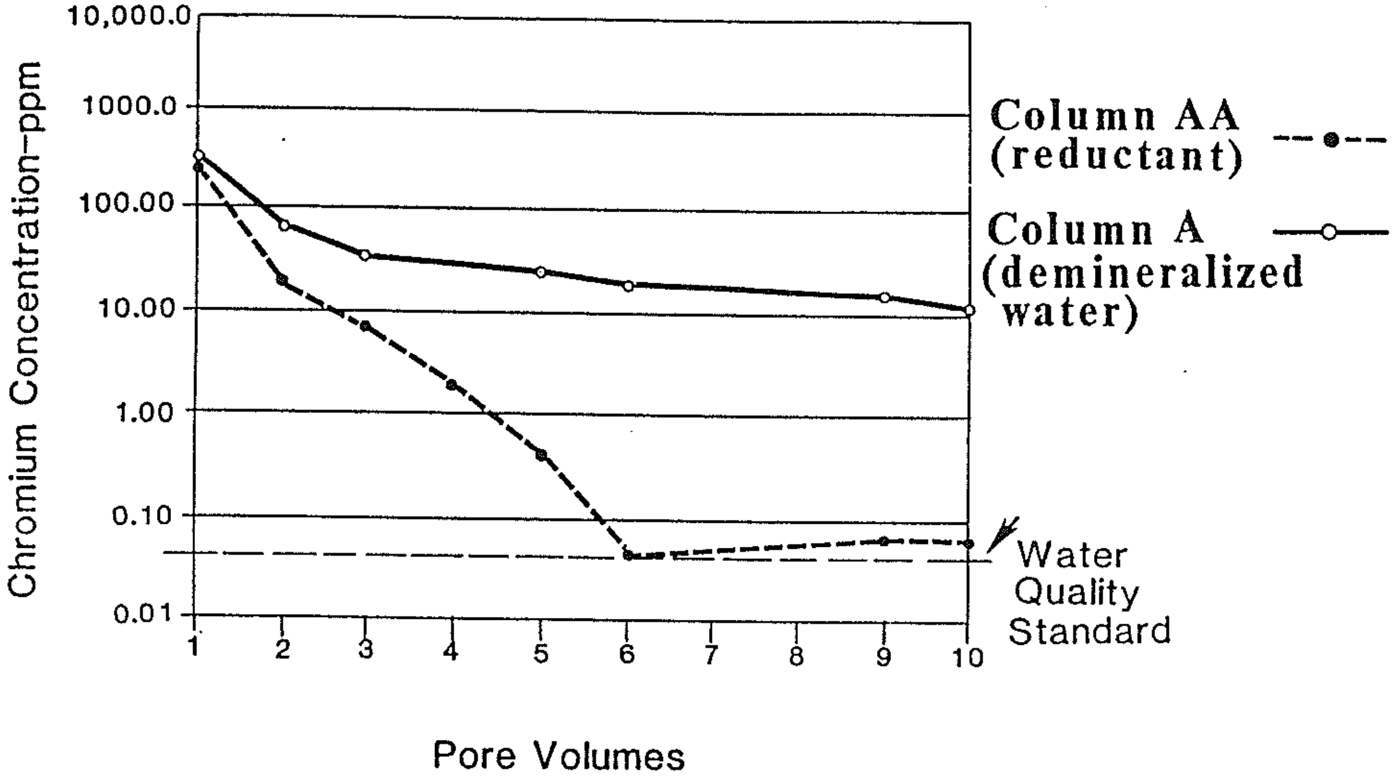

FIGURE 2
CHROMIUM CONCENTRATION IN PAIRED COLUMN EFFLUENTS
AS A FUNCTION OF PORE VOLUME THROUGHOUT