

Subsurface Fate and Transport of Cyanide at MGP Sites

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INTRODUCTION

Formation of cyanide complexes at MGP sites

The final step in the production of manufactured gas was its purification. Carburetted water gas plants, oil gas plants, and coal carbonization plants commonly used boxes filled with iron oxide (e.g. iron filings) and wood shavings as a final gas purification step for removing hydrogen sulfide from the manufactured gas. The process of gas purification was based on inorganic chemical reactions involving hydrogen sulfide, hydrogen cyanide and ammonia in the gas with the iron oxide. Spent oxide was regenerated by contact with air, producing reactivated iron oxide and sulfur dioxide. Cycles of fouling and regeneration were continued until the oxide eventually became irreversibly spent from accumulation of sulfur, fouling by traces of tar in the gas, and reaction of the iron with cyanide to produce ferrocyanides. At this point, the spent oxide was discarded and replaced with fresh material. The spent oxide box waste was typically used as fill on site, or off site (EEI 1984). Spent oxide box wastes are high in sulfur and contain significant amounts of various complex iron cyanides. They have a characteristic blue color resulting from the presence of ferrocyanide salts, known as Prussian blue.

Nature of the cyanide contamination

The presence of spent oxide box waste at MGP sites can result in the presence of cyanide in soil, and groundwater, due to the leaching process associated with the infiltration of rain or surface water. Due to its typical blue color, cyanide-containing box waste is easily identifiable at MGP sites. In addition, the 'perceived' risk of cyanide is high among the public and regulators, and has driven several remedial actions at MGP sites. As examples, in Lowell, MA, several homes were purchased by a utility due to the presence of spent oxide box waste; in Attleboro, MA, an emergency response action involved the removal of approximately 5000 yd³ of cyanide-contaminated soil at a cost of \$2.1 million.

Given these conditions, it is important for utilities to gain a better understanding of the potential for exposure to cyanide at MGP sites, as well as the toxicological characteristics of the various species of cyanide.

TOXICITY OF CYANIDE COMPLEXES

Not all forms of cyanide exhibit the acute toxicity associated with the hydrogen cyanide gas. In fact, many forms of cyanide are non-toxic to humans and are common in products that are used in the marketplace. In the case of MGP sites, cyanides exist in complex forms, iron complexes being the dominant species, with lesser quantities of copper and nickel complexes (GRI 1995). The toxicity of these complexes is negligible compared to the toxicity of hydrogen cyanide (Wilson and Stevens 1981). In general, the toxicity of cyanide complexes is related to the degree with which free cyanide is released (or dissociated) from the complex.

FATE AND TRANSPORT OF CYANIDE IN GROUNDWATER AT MGP SITES

Cyanide chemistry in groundwater

Cyanide in groundwater can occur in a number of forms. The most relevant ones for MGP sites are the following:

- Free cyanide. The sum of molecular hydrogen cyanide (HCN) and the cyanide anion (CN⁻).
- Simple cyanides. Compounds that dissociate directly to the cyanide anion (CN⁻) and a cation with no intermediaries. Examples are sodium cyanide (NaCN) and potassium cyanide (KCN).
- Complex cyanides. Compounds with the cyanide anion (CN⁻) incorporated into a molecular inorganic complex. Examples are ferrous ferrocyanide (Fe₂[FeCN₆]) and ferric ferrocyanide (Fe₄[FeCN₆]₃).
- Organic cyanides. Organic compounds containing the cyanide group, e.g. toluene diisocyanate.

At MGP sites, very little free and simple (weak acid dissociable) cyanide is typically found, and most cyanide is found in its complex form.

Cyanide fate in the subsurface environment

Cyanide is commonly found in groundwater underlying MGP sites, however, little is presently known about the geochemistry and transport of cyanide in groundwater systems.

In a recent study of the chemical composition of leachate from MGP oxide box wastes by Theis *et al.* (1994), it was found that most of the cyanide exists in the form of metal complexes, predominantly as iron cyanide complexes. This is consistent with the findings of other recent experimental work by Meeussen *et al.* (1992), who studied the dissolution behavior of iron cyanide in soils. It is also consistent with predictions of chemical equilibrium models (Meeussen *et al.* 1992).

It has been demonstrated that in the absence of exposure to light, iron cyanide in aqueous systems is stable with respect to many abiotic and biotic degradation reactions. Thus, iron cyanide may be expected to persist in the groundwater environment. The physicochemical processes governing possible sorption or precipitation reactions of iron cyanide are not well known, although a conservative assumption is that these reactions may not be significant. This supposition needs to be evaluated by experiment and modeling. Further, the extent to which cyanide may exhibit sorption or precipitation reactions in groundwater suggests possible opportunities for manipulation of the hydrogeological environment to retard the movement of iron cyanide.

While free cyanide is biodegradable, iron-cyanide complexes are resistant to biodegradation. This has been demonstrated many times in the context of wastewater treatment. Because iron-cyanide complexes appear to dominate the speciation of cyanide in leachates from oxide box wastes, and because iron-cyanide complexes are not biodegradable, adsorption (and, perhaps precipitation) onto soil and aquifer material is the most likely mechanism of 'natural attenuation' in the subsurface environment. While information on adsorption of iron-cyanide complexes onto minerals is very limited, the available information indicates that iron-cyanide complexes adsorb significantly onto oxidic minerals only at relatively low pH (less than 6) (Theis and West 1986).

In summary, available data indicate that cyanide in groundwater plumes emanating from oxide box disposal areas is likely to be primarily in the form of iron-cyanide complexes, which do not biodegrade and may have little tendency to adsorb to soil and aquifer materials. It is thus expected that cyanide in groundwater at MGP sites is likely to move with the bulk groundwater as a non-reactive species. At many sites, dilution might be the only attenuation process.

THE PLANNED CYANIDE RESEARCH PROJECT

A joint research project between Wisconsin Power and Light (WP&L), the Electric Power Research Institute (EPRI), and the Civil and Environmental Engineering Department of Carnegie Mellon University (CMU) has been initiated. The project is aimed at gaining a better understanding of the fate and transport of cyanide at MGP sites, to assess the potential for natural attenuation of cyanide concentrations in groundwater, and to evaluate the feasibility of potential *ex-situ* and *in-situ* treatment processes for cyanide in groundwater. It should be noted that the Wisconsin Department of Natural Resources (WDNR), which is the regulatory agency overseeing the environmental management of the site where this

research is being conducted, is familiar with the research project and is cooperating with the research team by providing regulatory guidance and oversight.

The research project will consist of field, laboratory and modeling studies of cyanide concentrations in groundwater at the MGP site in Portage, WI, which is owned by WP&L. The Portage site is underlain by a phreatic sand aquifer, which is relatively uniform, and possesses good hydraulic conductivity. These characteristics facilitate the development and validation of computer models of groundwater transport of cyanide. In addition, while at most MGP sites the presence of cyanide in groundwater is coupled to that of organic compounds (typically PAHs and BTEX), at the Portage site the leaching of the latter constituents to groundwater has been prevented by the presence of a concrete foundation. As such, the only chemical present in groundwater at relevant concentrations is cyanide. The cyanide source has been identified, characterized and removed from the site as part of remedial activities focused on site soils. In addition, a groundwater monitoring program has been started, and initial cyanide data are already available.

The above described conditions are considered to be favorable for the development and validation of a groundwater transport model for cyanide, and for the study of natural attenuation and *in-situ* treatments, both in the field and in the laboratory. The primary components of the research project to investigate these areas are discussed below.

Subsurface investigation

Additional field studies will be conducted to better define the hydrogeologic conditions at the Portage site, and to better characterize the extent of cyanide contamination in groundwater. A relatively dense network of monitoring wells will be established at the site. Multi-level wells will be employed to allow vertical as well as horizontal resolution of cyanide concentrations.

Laboratory investigation

Laboratory studies will be conducted to study the fate and transport of cyanide through soil/aquifer materials under controlled conditions. Batch adsorption tests and column tests will be conducted with site soils and model mineral phases in contact with synthetic solutions and site groundwater samples. The goal of this work is to explore the effects of solution and soil chemistry on the partitioning of cyanide species to the solid phase under static, equilibrium conditions in batch tests, and under dynamic conditions in continuous flow column tests. The laboratory work will also include a detailed evaluation of the speciation of cyanide in groundwater at the Portage site.

Modeling of the subsurface fate and transport of cyanide

To interpret the subsurface cyanide transport to date, and to estimate future fate and transport of the cyanide plume at the Portage site, a solute transport model will be developed. A preliminary version of the model will be used to initially locate the monitoring wells, and field data will be gathered and used to validate and/or calibrate the final version of the model.

Investigation of iron cyanide precipitation

With supplementary funding from the Aluminum Company of America (ALCOA), laboratory studies will be performed to develop basic information about the formation and solubility of iron cyanide solids: Prussian blue, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$, and Berlin green, $\text{Fe}_2(\text{CN})_6$. These solids, or some closely related variants, form readily upon addition of ferrous sulfate to aqueous solutions bearing Fe(III) and cyanide at low to neutral pH. Precipitation of iron cyanide solids has been used in the steel industry for treatment of wastewaters containing cyanide, and ALCOA is employing such processes for *ex-situ* treatment of cyanide contaminated groundwater at one of its sites. Precipitation of iron cyanide solids offers promise for low cost *ex-situ* and perhaps *in-situ* treatment of cyanide contaminated groundwater. However, the chemistry of the precipitation process needs to be better understood to enable assessment of its effectiveness under a range of conditions.

CONCLUSIONS

Oxide box waste, containing various species of cyanide compounds, is commonly found at MGP sites. As a consequence, cyanide contamination is often found in soils and groundwater. Presently, little is known about the geochemistry of cyanide, and the fate and transport characteristics of cyanide in groundwater. This knowledge gap will be addressed as part of a jointly sponsored research project, based on field data collected at the Portage MGP site, and on a combination of labo-

ratory and modeling studies. The results of this work will be used to improve prediction of the fate and transport of cyanide at MGP sites, and to suggest possible strategies to treat cyanide contaminated groundwaters both *ex situ* and *in situ*.

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