

NAOH-INJECTION EXPERIMENTS FOR IN-SITU REMEDICATION OF SURFACE-MINE SPOIL PRODUCING ACID-MINE DRAINAGE: PRELIMINARY RESULTS

DONOVAN, Joseph J. *
ZIEMKIEWICZ, Paul F.**
MORGAN, Jesse F. *
BARKER, R. Elizabeth*
SINCOCK, M. Jennifer*

* Department of Geology and Geography, West Virginia University

** National Mine Land Reclamation Center, West Virginia University

Perched aquifers form from resaturation of coal overburden and develop extremely-heterogeneous unconfined groundwater systems above the original pit floor. The hydraulic conductivity (K) distribution determined using well tests shows two distinct populations separated by 2 orders of magnitude, interpreted to reflect spoil matrix (weathered shales and claystone) and highly-porous zones (sandstone and rubble), respectively. To attempt acidity reduction and metals removal *in situ*, injection experiments using concentrated sodium hydroxide (NaOH, caustic soda) were recently performed at two West Virginia sites, representative of weakly-acidic and strongly-acidic mine discharge, respectively. The approach in both experiments was to inject strong base into the aquifer within the recharge area (upgradient portion) of the waste dump, inducing mixing of alkaline solutions with native acid waters during flow to downgradient springs. The goals of these pilot experiments were to evaluate efficiency and timing of metals and acidity removal, as well as to examine potential problems anticipated with alkaline injection designs. Such problems may include underdosing of base, overdosing of base, poor mixing and dispersion within the aquifer, and plugging by mineral precipitates causing permeability reduction. NaOH was used because of its ease of injection and handling and its high base solubility, and despite its relatively high cost in comparison to other sources of soluble base. NaOH may not be the ideal chemical for practical treatment.

Prior to injection, the weakly-acidic site had localized zones of acid production (aqueous pH 2.0-2.5), with alkaline or near-neutral groundwater (pH 3.9-6.3) in other portions of the spoil. Pre-treatment pH of spring discharge was 4.28 and dissolved acidity was relatively low, 140 mg/L as CaCO₃, mainly as dissolved manganese and aluminum (iron was relatively low). The aqueous geochemistry indicates that neutralization occurs *in situ* from dissolution of overburden calcite and from dilution by recharge. Manganese concentrations increase during flow across the dump, nearly doubling. Two additions of 50% caustic were made, in August. (40 liters) and October 1996 (240 liters). The caustic was added via a leaking ditch at the

upper recharge area for the dump. There was for both injections an approximate 2-week lag between caustic addition and changes in pH, metals, and acidity at the single spring at the toe of the dump. Both injections elevated pH for about a month, rising to ca. 4.2 for the August injection and 4.6 for the October one. Manganese values decreased from 50-60 mg/L to 15-40 mg/L and aluminum from 33-37 mg/L to 5-26 mg/L, reductions of over 50%. At periods of peak base breakthrough, iron was reduced to <0.3 mg/L, although it was not a major dissolved metal prior to injection.

At the strongly-acidic site, pH in groundwater ranged from 2.6 to 4.3 prior to injection, but acid and metals loads were extremely high (range 1700 to 10,000, average 3500 mg/L as CaCO₃). The dominant metal is aluminum, with lesser amounts of iron and manganese. Most iron is neutralized and precipitated *in situ* within the spoil due to dissolution of alkaline amendments and native carbonates, but the alkalinity is insufficient to fully neutralize the acid load, and acidity from iron hydroxide precipitation causes extensive clay dissolution. The metals load is extreme. Average groundwater velocities measured by tracer tests prior to injection range from 2 to 10 m/day, indicating preferential flow along highly-conductive channels. In October 1996, 7500 liters of 20% NaOH were injected into a recharge-area well approximately 480 feet (140 in) from the nearest downgradient spring. pH declined at this well from >14 to 6.3 over the following month as the NaOH "plume" moved downgradient. The injection-well pH then stabilized at >6 for an additional 2 months, while the center of the plume moved downgradient past two wells 80 and 180 feet downgradient, where pH values of over 7 were observed. Analysis of water indicated substantial reduction of acidity, although iron and manganese acidity remained as well as carbonate alkalinity. As of March 1997, the neutralization plume had still not reached the springs, but groundwater downgradient of the injection well remained extensively neutralized (pH>5.5). Average groundwater velocities indicated by plume movement are less than 1 meter/day, much slower than the tracer test results. While the experiment has not been repeated, a tentative hypothesis is that the flow-rate discrepancy may be attributed to precipitation of large fluxes of metals and resulting plugging of hydraulic pathways.

The two injection experiments yielded very different results. For the weakly-acidic system, flow rates through spoil remained rapid and partial reduction (20-70%) of aluminum and manganese was achieved, but only over short periods. Alkaline leakage or injection methods show substantial promise in amelioration of water chemistry here, but would require injection/leakage schemes that provide a fairly continuous supply of base. Alternate sources of base in addition to NaOH are being examined. For the acidic site, alkaline injection appears to have substantially altered both spoil hydraulics and groundwater chemistry, with the base moving through the aquifer but at much lower velocity than expected. The base dosage appears to have been dispersed and effective over a nearly 5 month time period even though the injection was instantaneous, not continuous. This time-dispersion of added base is considered to be a positive result. While it is considered unlikely that caustic injection will be cost-effective for long-term remediation, alternative sources of base may be very effective at ameliorating discharge quality and removing metals prior to their discharge at springs. The promise of alkaline-injection techniques is supported by preliminary experiments at both sites.