Fate of Isolated Spills on Savannah River Site Soils

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Spills of acids and bases onto Savannah River Site soils will generally be neutralized to acceptable pH levels by passage through the soils. Contact of SRS soils with concentrated acids or bases causes reactions that tend to neutralize the pH of the reagent. Initial and relatively rapid reactions are those that involve adsorption and desorption from surfaces of minerals in the soil. These are generally most important in neutralizing pH values that are relatively close to that of the soil. When soils contact solutions that have pH values vastly different from that of the soil, dissolution/precipitation reactions tend to neutralize the pH. Thus, isolated spills of contaminant free acids and bases onto the ground are rarely threats to the environment at SRS.

Acid Spills

Adsorption-desorption reactions affect pH of a solution when hydronium or hydroxyl ions are adsorbed or desorbed from mineral surfaces. For example, a sulfuric acid spill may cause desorption of hydroxyl ions because the sulfate from the acid will tend to exchange with hydroxyl ions on the surfaces of minerals. The additional hydroxyl ions in solution raise the pH of the acidic fluid as it passes through the soil. These reactions are relatively rapid, but are more limited in the amount of acid they can neutralize than dissolution/precipitation reactions.

SRS soils contain several phases that may contribute to neutralization of acids and bases. Ferric iron and aluminum hydroxides [e.g., $(\text{Fe,Al})(\text{OH})_3$] and oxyhydroxides [e.g., $(\text{Fe,Al})\text{OOH}$] are common in SRS soils. Likewise, kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ is an abundant clay mineral in SRS soils. The amphoteric nature of the ferric iron and aluminum cations allow dissolution of these minerals to neutralize both concentrated acids and bases. Figure 1 shows the solubility curves for kaolinite, gibbsite $(\text{Al}(\text{OH})_3)$, and goethite (FeOOH) . The solubility increase of these minerals at pH extremes ($\text{pH} < 3$ and $\text{pH} > 8$) controls their ability to neutralize concentrated acids and bases.

Acidic spills will be neutralized by reaction with aluminosilicate minerals. Figure 2 shows a titration curve of nitric acid by kaolinite. Dissolution of approximately 340 grams of kaolinite will buffer the pH to a value of about 1.8. At pH 1.8 the titration curve intersects the solubility curve of kaolinite and no more kaolinite can be dissolved. However, gibbsite can continue to be dissolved and the slow nucleation kinetics of

kaolinite will allow continued neutralization of the acid. The titration of an acid with $\text{pH}=1.8$ by gibbsite is shown in Figure 3. Only a small amount of gibbsite, about 450 mg, will neutralize the acid to a pH of 2.30 where the solubility limit of gibbsite is reached. Thus, for most isolated spills of concentrated acid, the dissolution of soil minerals can be expected to neutralize the acid to a pH of approximately 2.3 or above. This does not account for complexing of aluminum by the acid anion. Such complexing will increase the solubility of kaolinite and gibbsite, and thus will increase the final pH .

At a pH of 2.3 the hydronium ion activity is low enough that neutralization by adsorption and anion exchange can significantly raise the pH . For example, sulfate introduced by a spill of concentrated sulfuric acid will tend to adsorb onto mineral surfaces. The adsorption process is actually an anion exchange reaction in which hydroxyl ions are released from the mineral surface and react to neutralize the acid. At a pH of 2.3 the concentration of hydronium ions is about 0.005 moles/liter. Thus, in a spill of concentrated sulfuric acid that has been neutralized to a pH of 2.3 by mineral dissolution, the exchange of a small fraction of the sulfate with hydroxyl ions will raise the pH significantly higher than 2.3. This phenomenon is illustrated in the results of experiments on the interactions of coal leachate (similar to a sulfuric acid solution of $\text{pH}=2.1$) with SRS soils by Anderson et al. (1993). When pH 2.1 sulfuric acid was passed through 25 cm x 2.5 cm columns packed with SRS soils, the first two pore volumes of solution were buffered to $\text{pH}>4.5$. The molar quantity of hydronium ion neutralized was approximately equal to sulfate adsorbed to the soil.

Hence, isolated spills (point sources as opposed to continuous sources) of concentrated acid will be neutralized by reaction with soil minerals. Dissolution of kaolinite and gibbsite will raise the pH to a value of 2.3 or above. As the acid continues to move through the soil, adsorption and anion exchange reactions will raise the pH further. This analysis is consistent with experiments on SRS soils by Hoeffner (1985) from which the conclusion was drawn "that a strongly acidic spill will be neutralized within a short distance from the spill site".

To assess the travel distance required to neutralize an acid spill in SRS soil, consider a spill of 50% nitric acid solution having a pH of about -0.18. Figures 2 and 3 show that it would take about 340 grams of dissolved kaolinite and a minor amount of gibbsite (about 450 mg) to neutralize each liter of acid solution to a pH of 2.3. At 100% saturation in a soil with a porosity of 0.26 (Looney et al., 1987) each liter of solution would be contained in a unit soil volume of 3846 cm^3 . The mass of soil minerals in that volume would be about 7542 grams $[(3846-1000\text{cm}^3) \times 2.65 \text{ g/cm}^3]$. If the soil consisted of 5 wt.% kaolinite then each unit soil volume would contain 377 grams of kaolinite. If, on average, 5 % of the kaolinite present is dissolved from each unit volume of soil as acid passes through, then the acid must pass through about 18 unit soil volumes to become neutralized to a pH of 2.3. Assuming each unit soil volume is a cube 15.7 cm on a side,

for neutralization by dissolution of kaolinite and gibbsite and does not consider anion exchange. The experimental results of Anderson et al. (1993) suggest that anion exchange could drive the pH to above 4 within another 16-32 cm (1-2 unit soil volumes). The assumptions in this analysis are conservative and actual distances required for neutralization may be less.

After neutralization of the acid, the main environmental concern is the fate of the acid anion. The anions of sulfuric and phosphoric acids, sulfate and phosphate, will be attenuated by adsorption and precipitation. Phosphate forms relatively insoluble phases with cations such as aluminum, ferric iron, and calcium. Thus, high concentrations of phosphate can not be maintained in groundwater at SRS. Likewise, sulfate forms relatively insoluble phases with aluminum and ferric iron, as well as adsorbs to mineral surfaces in acidic soils. Chloride, from hydrochloric acid, forms few insoluble phases and is generally less strongly adsorbed than sulfate and phosphate. Thus, it can migrate through SRS soils more rapidly than sulfate and phosphate. Likewise, nitrate is not strongly sorbed to soils, but it can be attenuated by microbiological processes. In addition, the concentration of anions in isolated spills would be diluted by the process of dispersion during migration. Thus, it is unlikely that anions of acids in point source type spills would become significant environmental threats.

Sodium Hydroxide/Caustic Spills

Chemical and physical processes affect the migration of highly alkaline solutions spilled onto SRS soils. Experiments on SRS soils (Fenimore and Horton, 1968; Cook, 1981) show that high ionic strength and high pH solutions cause dispersal of clays that clog soil pores, reducing permeability. Cook (1981) found that above pH of 10 there was a substantial decrease in permeability of H-Area Seepage Basin soils. This suggests that a spill of sodium hydroxide onto SRS soils would cause a similar decrease in permeability, thus limiting the initial infiltration of the spill to a few centimeters.

Chemical reactions that neutralize the pH at the spill site would begin to occur during initial infiltration and would continue over time as the spill site was leached by rainfall. By stoichiometry alone the pH of a 50% sodium hydroxide solution is approximately 15. At this pH and with exposure to atmospheric CO₂, calcium and magnesium carbonate could precipitate by the reaction:

This reaction would decrease the pH if sufficient calcium and magnesium were available. Strom et al. (1994) reported that an F-Area soil contained 0.0123 meq/100g of exchangeable calcium and 0.0914 meq/100g exchangeable magnesium. Assuming a soil porosity of 30%, then a total of approximately 6.5 meq of calcium and magnesium are

available for exchange with sodium per 1 liter pore volume. Thus, much of the base could be neutralized in a short migration length during leaching of the spill site.

Other base neutralizing reactions may also occur. Langton (1985) found that exposure of soil to saltstone caused dissolution of kaolinite and precipitation of hydrated sodium aluminum silicates. Braney et al. (1993) found that calcium hydroxide solutions passed through sandstone were neutralized by precipitation of hydrated calcium silicate phases. These reactions are very similar to those that occur during the curing of Portland cement. Because of the similarity in chemistry, saltstone and portland cement provide good analogues to the spills of concentrated sodium hydroxide. Thus, it is likely that the long term environmental impact of an isolated sodium hydroxide spill would be similar to that caused by injection of grout into a soil.

Aluminum Nitrate Spills

Though the exact nature of the spilled aluminum nitrate solutions is unclear, there should be no environmental threat associated with these spills. A 34% aluminum nitrate solution would have a pH of about 3.3, and thus would not be hazardous because of low pH. The nitrate associated with these solutions would have the same fate as nitrate associated with nitric acid spills. It would be diluted by rainfall and dispersion and some would be degraded by biological processes. As pH is raised by dilution and reaction with soil materials, the aluminum would precipitate. Thus, these spills pose no danger to the environment.

Potassium Permanganate Spills

Potassium permanganate is a relatively strong oxidizing agent. In soils it will react predominantly with organic matter to produce carbon dioxide, potassium ions, water and solid MnO_2 . Surface soils contain abundant organic matter because of vegetation. Looney et al. (1990) found a median total organic carbon concentration of 644 $\mu\text{g/g}$ in SRS near surface soils. Thus, a 6% solution of potassium permanganate spilled onto such soils will be degraded before infiltrating deeply into the soils.

Alcohol Spills

Small spills of alcohol do not pose a danger to the environment. Alcohol is miscible in water and will become diluted during migration. In addition, low molecular weight alcohols are readily biodegraded in soils.

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Figure 1: Solubility curves for gibbsite, goethite, and kaolinite vs. pH. Solubility expressed as the log [M] where [M] is the total dissolved concentration of the metal ion (Al(III) or Fe(III)) in units of moles/liter.

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Figure 2: Estimated titration curve of a 50 wt.% HNO_3 solution (initial pH=-0.18) by kaolinite. Dashed line is the solubility limit of kaolinite.

Figure 3: Estimated titration curve of a solution of HNO_3 with pH=1.8. Dashed line represents solubility limit of gibbsite assuming solubility limit for kaolinite at pH = 1.8 (340 grams/liter) has been reached.