0001140

Estimated Concentrations of Released Chemicals Entering the Hanford Site Ground Water

I. Discussion of the January 18, 1985, Occurrence

A. Event

On January 18, 1985, ~965 gal of 12M HNO_3 was released in the Plutonium-Uranium Extraction Plant (PUREX). The HNO_3 entered the 216-A-29 and 216-B-3-3 ditches and mixed with other waste streams, which resulted in an approximate reduction of concentration by a factor of ten. Negligible infiltration and evaporation occurred in these ditches. From the ditches, the solution entered B Pond and mixed with 1.8×10^7 gal of pond water, which resulted in an additional reduction. (B Pond has been in operation for several years, and infiltration and evaporation into the sediments from the pond surface is negligible.) From B Pond, the acid sequentially entered the other 63-acre lobes of the B Pond complex where further mixing and reduction in concentration occurred. (The B Pond complex consists of B Pond and three lobes). From B Pond, the solution percolates the 150 ft to ground water through partially saturated sediments.

For calculational purposes, the following conservative assumptions are made:

- The solution percolates only through a volume of sediments equal to sediments directly between B-Pond and ground water (i.e., no lateral migration).
- All mixing of other waste streams and with water in the B-Pond lobes is ignored in the calculations.

As the solution percolates through calcite containing sediments to ground water, it reacted with the solid base, $CaCO_3$, according to the reaction:

$$CaCO_3 + 2H^+ = H_2O + CO_2\uparrow + Ca^{+2}$$

All the solution is neutralized and there is no significant impact on the ground water. There is conservatively enough $CaCO_3$ in the sediment beneath B Pond to neutralize 1.6×10^4 releases of the size and composition of this release (table 1).

In summary the soils ability to buffer an acid solution added to it is many order of magnitude greater than the acidity of the released acid. Due to the production of CO_2 the neutralization reaction goes to completion and the solution contacting the ground water will be buffered to a pH of approximately 8.2.

B. Evaluation

There is no known impact to the ground water from the January 18, 1985, HNO_3 release. An example calculation supporting the data provided in Section A is given in Section C based on the data and assumptions provided and referenced at the end of this document.

C. Calculations

Volume of sediment (V) below the first lobe of B Pond:

$$V = SD$$

where

S = surface area of the first lobe of B Pond
D = depth ground water
$V = 39 \text{ acres} \times 43{,}560 \text{ ft}^2/\text{acre} \times 150 \text{ ft} = 2.5 \times 10^8 \text{ ft}^3 =$
$7.2 \times 10^9 \text{ l} = 7.2 \times 10^{12} \text{ cm}^3$.

Weight of sediment (W) below B Pond:

$$W = V\rho$$

where

ρ = bulk density of the Hanford Site soil

$W = 7.2 \times 10^{12}\ cm^3 \times 1.6\ g/cm^3 = 1.2 \times 10^{13}$ g of sediment.

$CaCO_3$ content of sediment (B) (minimum):

$$B = WP$$

where

P = minimum $CaCO_3$ percentage

$B = (0.003)(1.2 \times 10^{13} g) = 3.6 \times 10^{10} g$ of $CaCO_3$.

Equivalents of $CaCO_3$ available to neutralize acid below B Pond (E):

$$E = \frac{2B}{\underline{M}}$$

where

$\underline{M}$ = molecular weight of $CaCO_3$ (100)

$E = \frac{2(3.6 \times 10^{10})}{10^2} = 7.2 \times 10^8$ gram-equivalents of base available for neutralization.

Equivalents of acid released E^1:

$$E^1 = C^1 V^1$$

where

C^1 = concentration of acid released

V^1 = volume of acid released

$E^1 = (12\underline{M})(965\ gal)(3.785\ l/gal) = 4.4 \times 10^4$ gram-equivalents of acid.

II. Discussion of February 8, 1985, Occurrence

A. Event

On February 8, 1985, ~192 gal of 1.45M NO_2^- was released in the PUREX Plant. The solution entered the 216-A-29 and 216 B-3-3 ditches and mixed with other waste streams, which resulted in an approximate reduction in concentration by a factor of 10. Negligible infiltration and evaporation occurs in these ditches. From the ditches, the solution entered B Pond where it mixed with 1.8×10^7 gal of pond water, which resulted in a reduction of concentration by a factor of 1.2×10^3 to 1.2×10^{-3}M. (B Pond has been operational for several years and infiltration into the sediments and evaporation from the surface is negligible.) From B Pond the solution sequentially entered the other lobes of the B Pond complex where further mixing and reduction in concentration occurred. From B Pond, the solution percolated the 150 ft to the ground water through partially saturated sediments.

For calculational purposes, the following conservative assumption is made:

- The only mixing occurred in B Pond.

As the solution percolated to ground water, microorganisms in the partially saturated soil oxidized the NO_2^- to NO_3^- (Bitton and Gerba 1984). The maximum concentration of NO_3^- entering the ground water was 5.8 ppm. Additional dilution occurred in the ground water by a factor of approximately ten (table 2).

B. Evaluation

There is no known significant impact on the groundwater from the February 8, 1985, $NaNO_2$ release. An example calculation supporting the data stated in Section A is provided in Section C, based on the data and assumptions provided and referenced at the end of this document.

C. Calculations

Concentration after mixing in B Pond (C^1):

$$C^1 = \frac{C}{R}$$

where

C = concentration of $NaNO_2$ in the spill

R = ratio volume of B Pond to the volume of the spill

$$C^1 = \frac{1.45\ 1}{1.8 \times 10^7} = \frac{1.5 \times 10^{-5}\ M}{1.92 \times 10^2} = 0.93\ PPM\ (NO_3^-)$$

IV Discussion of the June 25, 1985 Occurrence

A. Event

On June 25, 1985, ~3800 gal of 12M HNO_3 was released in the PUREX Plant. The HNO_3 entered the 216-A-29 and 216-B-3-3 ditches and mixed with other waste streams, which resulted in an approximate reduction in concentration by a factor of ten. Negligble infiltration and evaporation occurred in these ditches. From the ditches, this solution entered B-Pond and mixed with 1.8×10^7 gal of pond water, which resulted in a reduction in concentration. (B Pond has been operational for several years. Infiltration into the sediments and evaporation from the surface is negligible.) From B Pond, the solution sequentially entered the other 63-acre B Pond lobes where further mixing and reduction in concentration occurred. From B Pond, the solution percolated the 150 ft to ground water through partially saturated sediments.

For calculational purposes, the following conservative assumptions are made:

- The solution percolated only through a volume of sediments equal to the sediments directly between the B Pond and ground water.

- All mixing with other waste streams and the water in the B Pond lobes is ignored in the calculations.

As solution percolated to ground water it reacted with the solid base, $CaCO_3$, according to the reaction:

$$CaCO_3 + 2H^+ = H_2O + CO_2\uparrow + Ca^2$$

All of the solution was neutralized and there was no impact on the ground water. There is conservatively enough $CaCO_3$ in the sediments beneath B Pond to neutralize 1.6×10^6 releases of the size and composition of this release (table 1).

In summary the soils ability to buffer an acid solution added to it is many order of magnitude greater than the acidity of the released acid. Due to the production of CC_2 the neutralization reaction goes to completion and the solution contacting the ground water will be buffered to a pH of approximately 8.2.

B. Evaluation

There is no known significant impact on the ground water from the June 25, 1985, release. An example calculation supporting the data provided in Section A is provided in Section C, based on the data and assumptions provided and referenced at the end of this document.

C. Calculation

The equivalent of base available for acid neutralization (E_B) below B Pond is provided in Section A of the January 18, 1985, occurrence, (7.2×10^{10} gram-equivalents.).

The equivalent of acid released (E_A) is the molarity (M) of the nitric acid released times the volume of nitric acid released:

$$E_A = (12\,M)(3800\text{ gal})\ 3.875\text{ l/gal} = 1.8 \times 10^5 \text{ gram-equivalents.}$$

The number of releases of the size and composition of the June 25, 1985 release that could be neutralized by the soil column is the equivalent of acid divided by the equivalent of base:

$$\text{Number} = \frac{E_B}{E_A} = \frac{7.2 \times 10^8}{1.8 \times 10^5} = 4.0 \times 10^3 \text{ release.}$$

III. Discussion of April 4, 1985, Occurrence

I. Event

On April 4, 1985, ~1,866 gal of 0.023M $FeHSO_3$, 0.27M HNO_3, and 0.08M H_3NSO_3 solution was released from the PUREX Plant. The solution entered the 216-A-29 and 216 B-3-3 ditches and mixed with other waste streams, which resulted in an approximate reduction in concentration by a factor of ten. Negligible infiltration and evaporation occurred in these ditches. From the ditches, the solution entered B Pond and mixed with 1.8×10^7 gal of pond water, which resulted in a reduction in concentration of the $FeHSO_3$ to 2.4×10^{-6} M. (B Pond has been operational for several years and infiltration into the sediments and evaporation from the surface is likewise negligible.) From B Pond, the solution sequentially entered the other lobes, where further mixing and reduction in concentration occurred. From B Pond, the solution percolated the 150 ft to the ground water through partially saturated sediments. Upon entering B Pond, the Fe^{+2} spontaneously oxidized to Fe^{+3} according to the equation (Pourbaix 1966):

$$Fe^{+2} = Fe^{+3} + e^-$$

The Fe^{+3} reacts with water to form an insoluble hydroxide-oxide according to the equation (Pourbaix 1966):

$$Fe^{+3} + (3+x)\ H_2O = Fe(OH)_3 \cdot xH_2O\downarrow + +3H^+$$

The insoluble hydrous oxide was almost totally filtered from the soil when the solution percolated to the ground water. The sulfamate ion (HSO_3^-) is also unstable in water and spontaneously forms SO_4^{-2} according to the equation.

$$HSO_3^{-2} + H_2O = + SO_4^{-2} + H^+$$

For calculational purposes the following conservative assumptions are made:

- The only mixing occurred in B Pond.
- The solution percolated only through a volume of sediments equal to the sediments directly between B Pond and ground water.
- All mixing with other waste streams and water in B Pond lobes is ignored in the calculations.

As the solution percolated to ground water, it reacted with the solid base, $CaCO_3$, according to the reaction:

$$CaCO_3 + 2H^+ = H_2O + CO_2\uparrow + Ca^{+2}$$

All the acid was neutralized and there was no impact upon the ground water from the solution. There is, conservatively, enough $CaCO_3$ in the sediment beneath B Pond to neutralize 1.4×10^8 releases of the size and composition of this release (table 1). The maximum concentration of SO_4^{-2} entering the ground water was 23 ppm. An additional minimum mixing reduction by a factor of about ten occurred in the ground water (table 2).

In summary the soil's ability to buffer an acid solution added to it is many order of magnitude greater than the acidity of the released acid. Due to the production of CO_2 the neutralization reaction goes to completion and the solution contacting the ground water will be buffered to a pH of approximately 8.2. The concentration of other chemical components entering the ground water are all below significant concentrations.

B. Evaluation

There is no known significant impact of the solution on the ground water from the April 4, 1985, solution release. An example calculation supporting the data provided in Section A is given in Section C, based on the data and assumptions provided and referenced at the end of this document.

C. Calculations

The concentration, reduction ratio (R) due to mixing is the volume of B Pond divided by the volume of the release:

$$R = \frac{VB}{VR}$$

where

V_B = volume of B Pond

V_R = volume of release

$$R = \frac{1.8 \times 10^7}{1.866 \times 10^3} = 9.5 \times 10^3$$

The concentration (CR) in B Pond after mixing is the solution concentration in the release divided by the mixing reduction ratio (R):

$$C_R = \frac{C1}{R}$$

$$CR\Big|_{HSO_3} = \frac{0.023\ M}{9.5 \times 10_3} = 2.4 \times 10^{-6}\ \underline{M} = 0.23\ ppm\ (SO_4^{-2})$$

The equivalent of acid released (E_A) is 2 times the moles of H_3SO_3 plus the moles of nitric acid release times the volume released:

$$E_A = [2(H_3SO_3) + (HNO_3)]\ V_R$$

where

$$E_A = [(2)(0.087)+(0.27)](1900)(3.785)$$
$$= 3.3 \times 10^3 \text{ eq. of acid release}$$

The calculation for the equivalents of $CaCO_3$ available in B Pond is provided in Section C of the January 18, 1985, occurrence (Ec) (7.2×10^8) gram-equivalents.

The number of releases of the size and composition of this release is the gram-equivalents of base divided by the gram-equivalents of acid:

$$\text{Number} = \frac{Ec}{E_A} = \frac{7.2 \times 10^8}{3.3 \times 10^3} = 2.1 \times 10^5 \text{ releases}$$

VI Discussion of the August 6, 1985, Ocurrence

A. Event

On August 6, 1985, ~6,529 gal of 19M NaOH base was released in the PUREX Plant. The solution entered the 216-B-3-3 ditches and mixed with other waste streams, which resulted in an approximate reduction in concentration by a factor of tne. Negligible infiltration and evaporation occurred in these ditches. From the ditches, the solution entered B Pond and mixed with 1.8×10^7 gal of pond water, which resulted in a reduction of concentration by a factor of 2.8×10^3 to 156 ppm. (B Pond has been in operation for several years. Infiltration into the sediments and evaporation from the surface is negligible.) From B Pond, the base sequentially entered the other 63-acre lobes where further mixing and reduction in concentration occurred. From B Pond, the solution peroclated the 150 ft to the ground water through partially saturated sediments.

For calculational purposes, the following conservative assumptions are made:

- The solution percolated only through a volume of soil sediment equal to the sediments directly between B Pond and ground water.
- All mixing with other waste streams in the ditches and B-Pond lobes is ignored in the calculations.

As the solution percolated to ground water, the OH^- ion in the waste reacted with the sediments and was neutralized to a pH of about 8.2. The concentration of Na^+ ion entering the ground water was less than 156 ppm.

B. Evaluation

There is no known significant impact on the ground water from the August 6, 1975, base release. An example calculation supporting the data provided in Section A is given in Section C, based on the data assumptions provided and referenced at the end of this document.

C. Calculations

The concentration reduction ratio (R) due to mixing is the volume of B Pond first lobe divided by the release volume:

$$R = \frac{V_B}{V_R}$$

where

V_B = volume of B-Pond
V_R = volume of release

$$R = \frac{1.8 \times 10^7 \text{ gal}}{6.529 \times 10^3 \text{ gal}} = 2.8 \times 10^3$$

The concentration (C_R) in B Pond after mixing is the release concentration divided by the concentration reduction ratio due to mixing (CR):

$$C_R = \frac{C_X}{R}$$

where

C_X = release concentration

$C_R = \frac{19\ \underline{M}}{2.8 \times 10^3\ \underline{M}} = 6.8 \times 10^{-3}\ \underline{M} = 156$ ppm (Na^+)

V Discussion of the July 1, 1985 Occurrence

A. Event

On July 1, 1985, ~1,548 gal of 10M NH_4F and 0.25M NH_4NO_3 was released in PUREX Plant. The solution entered the 217-A-29 and 216 B-3-3 ditches and mixed with other waste streams, resulting in an approximated reduction in concentration by a factor of ten. Negligible infiltration and evaporation occurred in these ditches. From the ditches, the acid entered B Pond and mixed with 1.8×10^7 gal of pond water, which resulted in a reduction of concentration to 31 ppm of NH_4F and 0.32 ppm of NH_4NO_3. (B Pond has been operation for several years and infiltration into the sediments and evaporation from the surface is negligible.) B Pond, the solution sequentially entered the other 63-acre lobes where further mixing and reduction in concentration occurred. From B Pond, the solution percolated the 150 ft to the ground water through partially saturated sediments.

For calculational purposes, the following conservative assumptions are made:

- The only mixing occurred in B Pond.
- The solution percolated only through a volume of sediments equal to the sediments directly between B Pond and ground water.

As the solution percolated, the F^- ion reacted with $CaCO_3$ in the sediment to form CaF and essentially non entered the ground water (Ames 1960). The NH_4 ion was oxidized first to NO_2 and finally to stable NO_3 by soil micro-organisms (Bitton and Gerba 1984). The concentration of NO_3 entering the ground water was conservatively no higher than 6.6 ppm.

B. Evaluation

There is no known significant impact on the ground water from the July 1, 1985, solution release. An example calculation supporting the data provided in Section A is given in Section C, based on the data and assumption provided and referenced at the end of this document.

C. Calculation

The concentration reduction ration (R) is volume of B Pond divided by the volume of the release:

$$R = \frac{V_B}{V_R}$$

where

V_B = volume of B Pond
V_R = volume of the release

$$R = \frac{1.8 \times 10^7 \text{ gal}}{1.548 \times 10^3 \text{ gal}} = 1.2 \times 10^4$$

The concentration (CR) in B Pond following mixing is the release solution concentration (Cx) divided by the concentration reduction ration (R):

$$C_R = \frac{C_X}{R}$$

where

C_X = concentration of solution released

$$C_R\Big|_{NH_4F} = \frac{10\ \underline{M}}{1.2 \times 10^4} = 8.3 \times 10^{-4}\ \underline{M} = 15\ \text{ppm}\ (F^-) = 12$$

$$C_R\Big|_{NO_3} = \frac{(2)\ (0.24)}{1.2 \times 10^4} = 4.0 \times 10^{-5}\underline{M} = 0.25\ \text{ppm}\ (NO_3)$$

Table 1. Disposition of Acid Released from the PUREX Plant

Release	Release (Equivalents)	$CaCO_3$ (Equivalents)	Possible Neutralizations
January 18, 1985 12M HNO_3	4.4E + 04	7.2E + 8	1.6E + 04
April 4, 1985 0.27M HNO_3 0.087M H_3SO_3	3.3E + 03	7.2E + 8	2.1E + 05
June 25, 1985 12M HNO_3	4.6E + 04	7.2E + 8	1.6E + 04

Table 2. Disposition of Nonacid Chemicals Released from the PUREX Plant

	Concentration			
Release	Release	216-A-29 and 216-B-3-3 Ditched (ppm)	B Pond (ppm)	Ground Water (ppm)
February 8, 1985				
$NaNO_2$	1.45	33,000	0.93	<1
April 4, 1985				
$FeHSO_3$	0.023	1,800	0.23(SO_4^{-2})	<1
H_3SO_3	0.087	7,200		
July 1, 1985				
NH_4F	10	370,000	31(F^-)	~0(F^-)
NH_4NO_3	0.24	70,000	0.3	<1
August 1, 1985				
NaOH	19	440,000	156(Na^+)	16

Data and Assumptions

1. Volume of B Pond - 1.8×10^7 gal = (Dillon 1985).

2. Surface area of B Pond - 39 acres = 1.7×10^6 ft^2 (Dillon 1985).

3. Depth to ground water under B Pond - 150 ft (Dillon 1985).

4. Sediment density- 1.6 g/cm^3 (Routson and Fecht 1980).

5. $CaCO_3$ content of sediments beneath B Pond - 0.3-2.2% (Fecht and Price 1977).

6. Mixing fraction in the ground water beneath B Pond - 8-100:1 (calculated by the author).

7. Mixing fraction in 216-A-29 and 216 B-3-3 ditches- 10:1.

8. Evaporation from B Pond - assumed negligible (data below) (Dillon 1985).

   January 18, 1985 - <0.1 in/day
   February 8, 1985 - <0.1 in/day
   April 4, 1985 - <0.1 in/day
   June 25, 1985 - 0.2 in/day
   July 1, 1985 - 0.3 in/day
   August 6, 1985 - 0.25 in/day

9. Infiltration in the 216-A-29 and 216 B-3-3 ditches is negligible (Dillon 1985).

10. Infiltration in B Pond - <1% (Dillon 1985).

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