STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
1250 W Alder St • Union Gap, WA 98903-0009 • (509) 575-2490

TECHNICAL MEMO

Assessment of Hydrogen Sulfide Release from Sodium Hydrosulfide Solutions

Holden Mine Water Treatment Plant (MWTP)

Chris Wend, PhD, PE
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Table of Contents

Sodium Hydrosulfide – Holden MWTP

Summary

The mine water treatment plant located at Holden Mine will utilize a 30% sodium hydrosulfide (NaHS) solution as a source of sulfide for a supplemental metals removal process in the event conditions do not allow the main process to remove metals below the required effluent levels. The possible release of hydrogen sulfide (H_2S) gas from the bulk solution storage tank has been identified as an issue of concern and this document outlines an analysis of different release scenarios. Only three plausible release scenarios are outlined in this technical memo, largely because the requirements necessary to produce H_2S gas from the 30% NaHS solution are extremely limiting. Ultimately, there is little support for a release of H_2S in quantities that would impact offsite (outside MWTP site boundary) receptors (e.g., people at Holden Village).

NOTE: Although this technical memorandum, in outlining release scenarios, finds little risk for a H_2S release from a 30% NaHS solution to Holden Village, it should not be interpreted as implying that 30% NaHS solution is not dangerous. In all cases, proper safety protocols, and standard operating procedures should be followed. Onsite personnel at the MWTP are most at risk, given their close proximity, and should be properly trained in handling the chemicals present as well as emergency response procedures.

The three plausible H_2S release scenarios for a 30% NaHS solution that were considered are:

1. Rapid contact and mixing with sufficient quantities of a strong (>10 molar) acid, causing the generation of H_2S gas.

2. High solution temperatures. (This scenario could include a fire similar to the 2015 Wolverine Fire at Holden Village).

3. Dilution with water in a spill/fire situation. This scenario envisions a spill (perhaps during transport), release from secondary containment to storage pond, or localized fire in the immediate vicinity of the tank.

The results for these release scenarios are summarized below.

1. Rapid contact and mixing with sufficient quantities of a strong acid will cause the production and release of H_2S gas. However, given the lack of bulk acid at the site, this scenario is not likely.

2. High temperatures from a scenario like a long-burning, close proximity fire, could cause the NaHS solution to off-gas H_2S. However, there are two very important limiting factors:

    a. The first is the quantity of H_2S within the NaHS solution, which is a negligible (< 0.0001%) portion of the total sulfide mass in solution. The maximum amount of release would be limited to the quantity of H_2S in solution only.

    b. The second limiting factor is heat. First, the temperature required to off-gas H_2S requires elevating tank temperatures above 80°C which would take a minimum of three days with a consistent, close proximity heat source > 800°C. Although fires can burn for a long time, they tend to move around. Another important point is that the autoignition temperature for H_2S is 260°C. In a forest fire situation, the H_2S would oxidize (essentially, burn up into the air).

3. Given that water is often the remedy for spills and small fires, this scenario contemplates diluting the solution with water. This would drop the pH, but also dilute the solution, keeping the H_2S dissolved (in liquid versus gas).

The results of chemical calculations below show that 30% NaHS solution chemistry at pH = 11.5 has very little H_2S in the solution compared to the total sulfides in solution. There is still, however, sufficient mass of H_2S to impact onsite receptors. The concentrations were found to be in the following amounts:

$[H_2S] = 8.8e\text{-}6 \ \frac{moles}{L}$

$[HS^-] = 8.6 \ \frac{moles}{L}$

$[S^{2-}] = 1.59 \ \frac{moles}{L}$

The solution is strongly basic having been produced with a strong solution of sodium hydroxide greater than 10 $\frac{moles}{L}$. This prohibits the production of H_2S from the sulfide species and is why the concentration of H_2S is so low. The concentration of the H_2S is well below the solubility of H_2S even at elevated temperatures which will further restrict releases under elevated temperature conditions.

In conclusion, release of sufficient amounts of H_2S from the MWTP that might impact offsite receptors does not appear to be possible under the scenarios investigated in this technical memorandum.

Introduction

As part of the mine water treatment plant design at Holden Mine, there is a final process that will use sulfide addition to remove additional metals if the main process does not meet operating effluent metals concentrations. The main process is lime and flocculant addition followed by aeration to produce metal hydroxides around a neutral pH. The resulting flocs are removed in a high density sludge clarifier. With enough iron oxides and contact time the main process should remove most of the metals. However, with certain conditions created by mixing of groundwater, mine water and flow rates, the addition of sulfide is necessary.

NaHS Chemistry

The source of sulfide for the mine water treatment plant is a 30% sodium hydrosulfide (NaHS) solution with an anticipated maximum daily usage of 8 gallons. The 30% NaHS solution is a good storage formulation for a sulfide source since the high pH effectively prohibits the formation of the H_2S species and leaves the sulfide available for reaction with metals in solutions.

General NaHS Information

NaHS may be produced by dissolving H_2S in a strong sodium hydroxide solution. The solution is typically available in concentrations ranging from 20-59 % by weight. These solutions have a freezing point between 0 and 80 °F with boiling points ranging from 220 to 260 °F.

The proposed 30% solution will have a freezing point of ~ 0°F and a boiling point of ~ 235°F.

Oxygen can react with the sulfide in solution turning the solution yellow to dark green. Weak (3-5%) hydrogen peroxide solution will oxidize the sulfides and can be used to mitigate H_2S in a spill situation.

A confined head space can accumulate levels of H_2S gas which has a wide flammable range of 4% to 44% by volume in air.

NaHS is a strong base with a pH between 11.5 and 12.5.

Sources: Wireless Information System for Emergency Responders (WISER) created by the National Library of Medicine. http://wiser.nlm.nih.gov

Version: 5.0.9

Database Version: 5.0.2

and “Technical Guide for Solutions of Sodium Hydrosulfide” TDC, LLC, www.tdc-home.com, 800-422-6274.

Hydrogen Sulfide Chemistry

H_2S is a diprotic acid in solution with the following reactions.

$$H_2S + H_2O \leftrightarrow H^+ + HS^- \qquad pK_1 = 7.04$$

$$HS^- + H_2O \leftrightarrow H^+ + S^{2-} \qquad pK_2 = 11.96$$

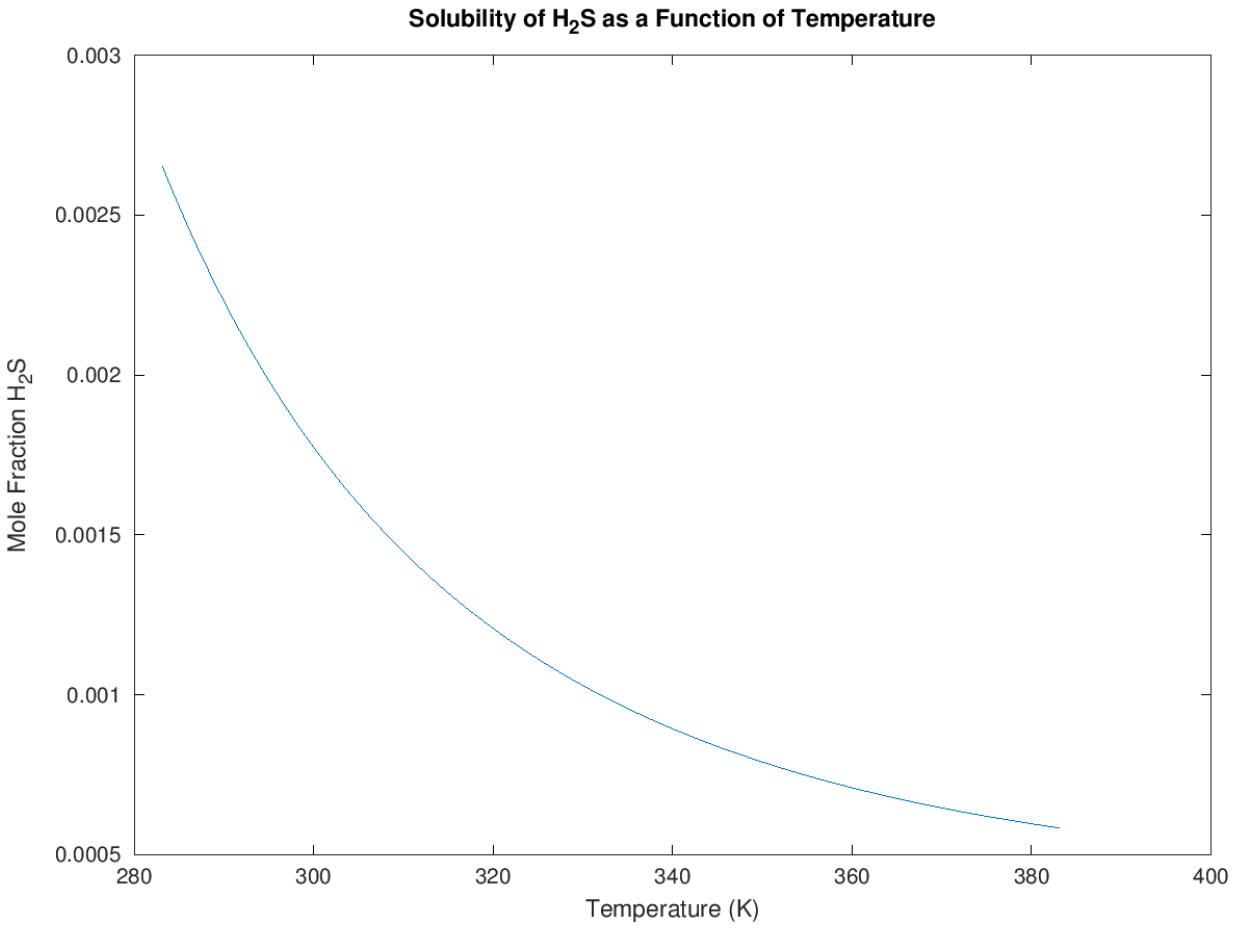
Henry's law constant = 9.8 L atm/mole at 25°C

Note that pK_2 will vary with concentration of NaOH and production conditions pertaining to CO_2 levels and temperature. See Mamrosh, D., Beitler C., Fisher, K., and Stem, S., 2008,"Consider Improved Scrubbing Designs for Acid Gases: Better application of process chemistry enables efficient sulfur abatement", Hydrocarbon Processing, January 2008. www.hydrocarbonprocessing.com

H_2S Solubility and Temperature

A temperature increase can reduce the solubility of the H_2S and release that species but the dissolved phase of H_2S in a 30% NaHS solution is well below the solubility even at higher temperatures. The following graph was produced using the solubility equation for H_2S from "Solubility of Selected Gases in Water" by L.H.Geventman. Here the solubility at 100°C (373.15 K) is above 0.0005 (5e-4) mole fraction. The liquid phase mole fraction of the 30% NaHS solution is 1.6e-7 which is well below the solubility (5e-4) at 100°C.

In addition to having concentrations below the maximum solubility, the process will be limited once the concentration has been exhausted since the high pH does not allow for more sulfide to form H_2S to be available for off-gassing. Also, without agitation of the liquid, the release of gas at the gas-liquid interface will rapidly become diffusion limited on the liquid side and will take many days to fully release the dissolved gas.



30% Sodium Hydrosulfide (NaHS) Chemistry

NaHS solutions represent a storage chemistry for sulfide via strong base solutions such as sodium hydroxide (NaOH). To determine the chemistry of a 30% by weight solution of NaHS produced with NaOH, it was useful to perform chemical equilibrium calculations for solutions with pH = 11.5 and pH = 12.5. This pH range is described in a typical safety data sheet (SDS) for NaHS solutions.

Preliminary chemical equilibrium modeling was performed using PHREEQC Version 3.0 by USGS. Documentation and computer programs may be downloaded at the link below. All output with input conditions are in Appendices A and B.

https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

The purpose of the modeling was to

1. Understand sodium and sulfide solution chemistry of a 30% by weight NaHS solution at a pH of 11.5 to 12.5.

2. Develop a preliminary estimate of species distribution due to temperature increase.

3. Develop a preliminary estimate of species distribution as the solution is diluted and pH approaches 7.0.

The tables below summarize the results for the conditions in the tank. The 30% NaHS solution volume was assumed to be 14,939 L (3946.5 gal). This is based upon a 4385 gallon tank capacity at 90% fill. The 4385 gallon tank capacity is described in subsection 2.9A.1.1 Sulfide Reagent Storage System of section 2.9A System 900A – Sulfide Reagent Storage and Feed in Operating and Maintenance Manual Mine Water Treatment Plant, Holden Mine, March 2016.

pH	11.5		
Species	mole/L	Mole Fraction	Total Moles
H2S	8.88E-06	1.60E-07	1.33E-01
HS-	8.36E+00	1.51E-01	1.25E+05
S2-	1.59E+00	2.87E-02	2.38E+04
pH	12.5		
Species	mole/L	Mole Fraction	Total Moles
H2S	5.80E-08	1.05E-09	8.67E-04
HS-	3.72E+00	6.70E-02	5.56E+04
S2-	7.45E+00	1.34E-01	1.11E+05

The model calculations also estimated that the solution would be a strong base equivalent to a 12 molar NaOH solution for pH of 11.5 and a 19 molar NaOH solution for a pH of 12.5.

As can be seen from the mole fraction calculations, the mass of sulfide as H_2S in solution is negligible compared to the total mass of sulfide in the system. There is, however, sufficient mass in this state to produce a gas phase concentration in a head space that would present a risk to nearby workers (onsite receptors). There is not, however, sufficient mass to produce a plume to threaten offsite receptors.

See appendix B for complete model input and output for chemical speciation and other physical parameters of a pH = 11.5, 30% NaHS solution that is diluted with water through 3 orders of magnitude. It is important to note here that PHREEQC performs solution mixing on a mass basis. Hence the dilution reported in the table is on a mass basis and when converted to a volume basis it is not direct due to changes in fluid density. The table below summarizes the results of the dilutions.

					Total Volume	
Species	Dilution	mole/L	Total Moles	pH	Liters	Gallons
H2S	0	8.88E-06	1.33E-01	11.5	14939	3946.5
HS-	0	8.36E+00	1.25E+05	11.5	14939	3946.5
S2-	0	1.59E+00	2.38E+04	11.5	14939	3946.5
H2S	1.00E-01	6.67E-06	9.96E-01	11.616	1.49E+05	39465
HS-	1.00E-01	6.99E-01	1.04E+05	11.616	1.49E+05	39465
S2-	1.00E-01	1.21E-01	1.80E+04	11.616	1.49E+05	39465
H2S	1.00E-02	1.69E-06	2.52E+00	11.455	1.49E+06	394650
HS-	1.00E-02	7.42E-02	1.11E+05	11.455	1.49E+06	394650
S2-	1.00E-02	5.22E-03	7.79E+03	11.455	1.49E+06	394650
H2S	1.00E-03	1.82E-05	2.72E+02	9.515	1.49E+07	3946500
HS-	1.00E-03	7.73E-03	1.15E+05	9.515	1.49E+07	3946500
S2-	1.00E-03	4.29E-06	6.41E+01	9.515	1.49E+07	3946500

Here it can be seen that diluting the mass with 100 times the original mass in water does not change the pH much but does lower the corresponding concentrations as would be expected. The total moles of sulfide change slightly as sulfate species are in play with the dilution.

This also demonstrates the strength of the high pH solution and the need for a strong acid (> 10 molar) to affect pH with a comparable volume.

Heat Transfer

Heat transfer calculations were performed to estimate energy and time requirements needed to increase the temperature of the tank. In the specifications found on page 63 section 2.9A.1.1 of the Operating and Maintenance Manual, Mine Water Treatment Plant, Holden Mine, Revision 0, March 2016, the tank has a factory-applied spray-on foam insulation polyurethane foam with a minimum “R” value of 6.3/inch.

The tank dimensions are also listed here as 10 feet 2.5 inches in diameter and a height of 10 feet. From this the radius can be calculated to be 155.6 cm and the height is 304.8 cm. Top surface area is 7.6e4 cm^2 and the lateral surface area is 2.98e5 cm^2. For this analysis it was assumed that the top of the tank contributes to the heat transfer at the same rate as the lateral sides. This is conservative since the top will have some head space between the top of the tank and the liquid which would provide an additional heat transfer resistance to the calculation. The total surface area is estimated to be 3.74e5 cm^2.

The standard heat transfer equation can be written below as

$$q = UA\Delta T$$

Where

$$q = heat\ transfer\ rate\ (watts, W)$$

$$U = overall\ coefficient\ of\ heat\ transfer\ \left(\frac{W}{m^2 K}\right)$$

$$A = area\ (m^2)$$

$$T = absolute\ temperature\ (K)$$

Insulated Tank

R_{US} in US units is equal to 5.678 times R_{SI} in SI units which yields R_{SI} = 2.22 using the R value reported above and assuming 2 inches of insulation. Assuming a wildfire with a temperature of 800° C = 1073K and assuming a beginning temperature of 20°C = 293K yields ΔT = 780K. With a surface area of 3.74e5 cm^2 = 37.4 m^2 the resulting heat transfer rate is 13,141 W.

The specific heat capacity for a 30% solution of NaOH ranges from about 0.84 to 0.88 $\frac{cal}{g°C}$. Using a middle value of 0.86 $\frac{cal}{g°C}$ and a density of 1.25 g/L for a 30% NaHS solution yields a specific heat capacity of 4.5 $\frac{J}{mL°C}$. To raise the temperature of 14,939L (tank capacity) of 30% NaHS from 20°C to 80°C will require 4.0033x10^9 J. With the calculated 13,141W heat transfer rate it will take approximately 3.5 days to raise the temperature 60°C from 20°C to 80°C.

Uninsulated Tank

There is one more thing to consider with this scenario. Application of such an intense external heat source will consume the externally applied polyurethane foam insulation since the polyurethane foam will decompose above 180°C and has a flash ignition point of between 315°C and 370°C and an autoignition point between 370°C and 427°C.

Without the insulation the tank material will be the only heat transfer material to consider. Note that this was neglected in the insulated tank calculation above making the time estimate conservative. R values were difficult to obtain for cross-linked high density polyethylene and a fiberglass sheet value of R_{US} = 2.5/in was selected. Assuming a tank wall thickness of 0.5 in. an R_{SI} = 0.22 was calculated. The resulting heat transfer rate was found to be 1.3e5 W which corresponds to an 8.6 hour heat up period to 80°C.

The difficulty with both of the above scenarios is that cross-linked high density polyethylene is not rated for use above 60°C to 65°C. At some point the tank will fail and the contents will flow into the secondary containment which is concrete on the ground. This will essentially stop the heating process since the secondary containment will provide adequate heat transfer to the ground to prevent additional temperature increases.

Mass Transfer

Mass transfer describes the movement of the constituent of concern in liquid and gas phases and across the gas-liquid interface. In this discussion the transport of H_2S in the liquid phase will be examined. With no mixing only diffusion processes will be considered. This will be a limiting case since in many situations there may be advection as well such as convective currents during a heating process.

Fourier Number

The liquid side mass transfer resistance was investigated through a quick check with the Fourier number. When mass transfer has gone on for a sufficient amount of time the process approaches equilibrium and the Fourier number is approximately equal to one.

$$1 = \frac{z^2}{\sqrt{\mathcal{D}t}}$$

$$z = length\ (cm)$$

$$\mathcal{D} = diffusion\ coeffient\ \left(\frac{cm^2}{sec}\right)$$

$$t = time\ (sec)$$

From this equation a time to diffuse to a certain depth or the depth of diffusion for a given time may be estimated. The Fourier number indicates 6 months to go 17.6 cm or 16 years to go 100 cm for diffusion in water.

Diffusion Models

Two models were also investigated to determine H_2S mass transport in the liquid phase. One was diffusion into a semi-infinite domain which represents unsteady diffusion and the other was decay of a pulse. Both of these models give some indication of the diffusion transport speed in solution. The comparison of these models to the tank situation is based upon the hypothesis that when the upper layer near the gas-liquid interface is depleted of H_2S, the diffusion from the lower volume will proceed at a rate similar to those estimated in these models for a semi-infinite domain.

See the following sections for a description of the partial differential equation, boundary conditions, and analytical solution. Computer script for the output was written in language that can be run in Matlab or Octave. See Appendix C for a copy of the scripts.

Semi-infinite

The partial differential equation along with the appropriate spatial and temporal boundary conditions is listed below. For the semi-infinite case, the following graph shows the concentration of H_2S versus depth for various times up to 190 years. Two of these profiles were selected and were used to predict a velocity of the front where there is zero concentration. See the second graph. This velocity was calculated to be 0.18 cm/day.

$$\frac{\partial c}{\partial t} = \mathcal{D}\frac{\partial^2 c}{\partial z^2}$$

$$c(z,0) = c_\infty = 0 \text{ where } z \in [0,\infty)$$

$$c(0,t) = c_\circ \; where \;\; t \in (0,\infty)$$

$$c(\infty,t) = c_\infty = 0 \; where \; t > 0$$

$$c(z,t) = c_\circ - \; c_\circ erf\left(\frac{z}{\sqrt{4\mathcal{D}t}}\right) = \; c_\circ erfc\left(\frac{z}{\sqrt{4\mathcal{D}t}}\right)$$

$$erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-s^2} ds$$

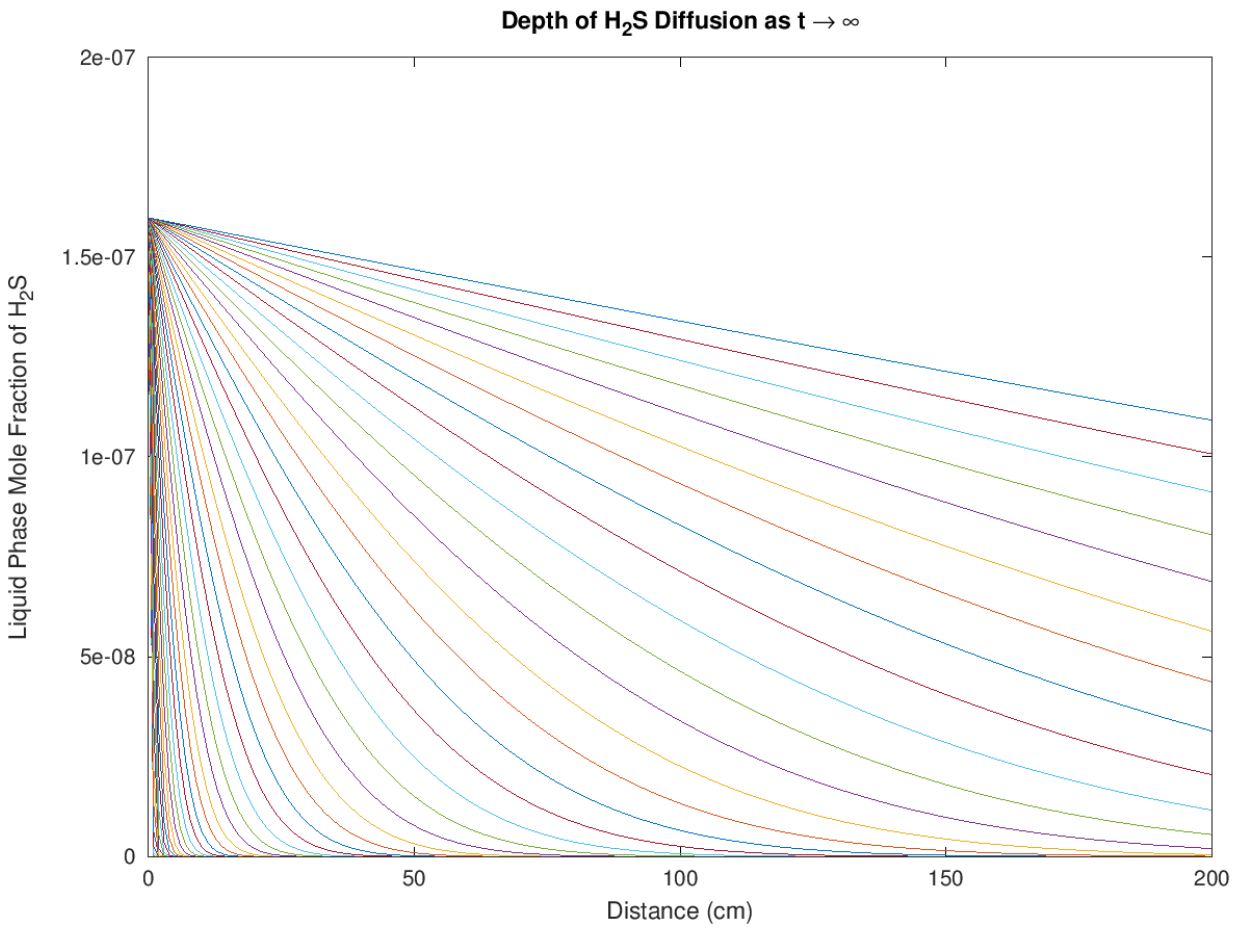
$$erfc(x) = 1 - erf(x)$$

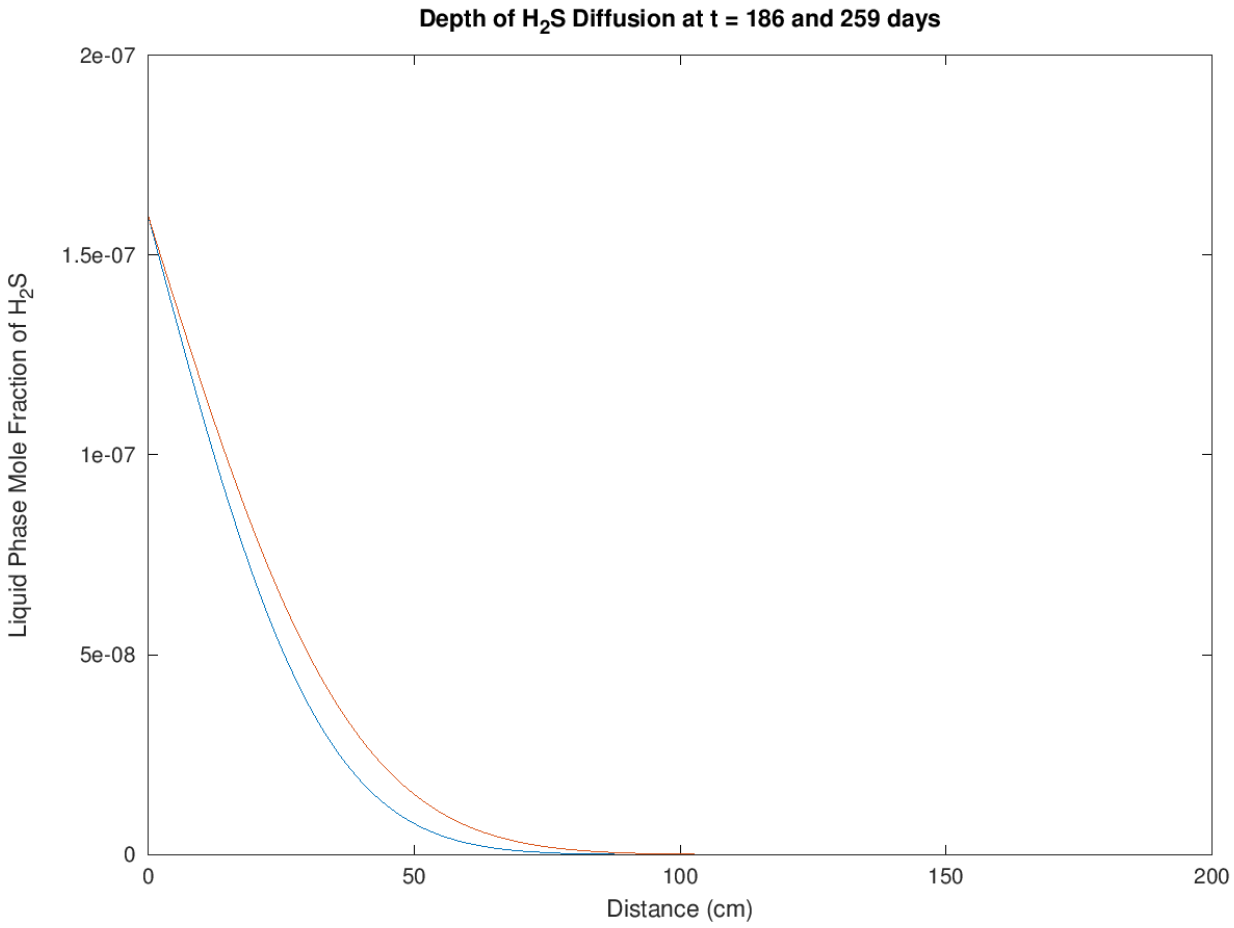
$$c(z,t) = concentration \; as \; a \; function \; of \; position \; and \; time$$

$$z = length \; (cm)$$

$$\mathcal{D} = diffusion \; coeffient \left(\frac{cm^2}{sec}\right)$$

$$t = time \; (sec)$$


Depth of H_2S Diffusion as $t \rightarrow \infty$
2e-07
1.5e-07
1e-07
5e-08
0
Liquid Phase Mole Fraction of H_2S
0
50
100
150
200
Distance (cm)



Pulse Decay Model

Using the pulse decay model, the profiles from selected times ranging from 134 to 6944 days are graphed. From this graph two profiles were selected to calculate a velocity for the diffusion front. See the second graph. The velocity was found to be about 0.25 cm/day.

$$\frac{\partial c}{\partial t} = \mathcal{D}\frac{\partial^2 c}{\partial z^2}$$

$$c(\infty, t) = c_\infty = 0 \; where \; t > 0$$

$$c(0,0) = \frac{M}{A}\,\delta(z)$$

$$\left.\frac{\partial c}{\partial z}\right|_{z=0} where \; t > 0$$

$$c(z,t) = \frac{\frac{M}{A}}{\sqrt{4\pi\mathcal{D}}} e^{\frac{-z^2}{4\pi\mathcal{D}}}$$

$$\delta(z) = Dirac \; delta \; function$$

$$M = total \; mass$$

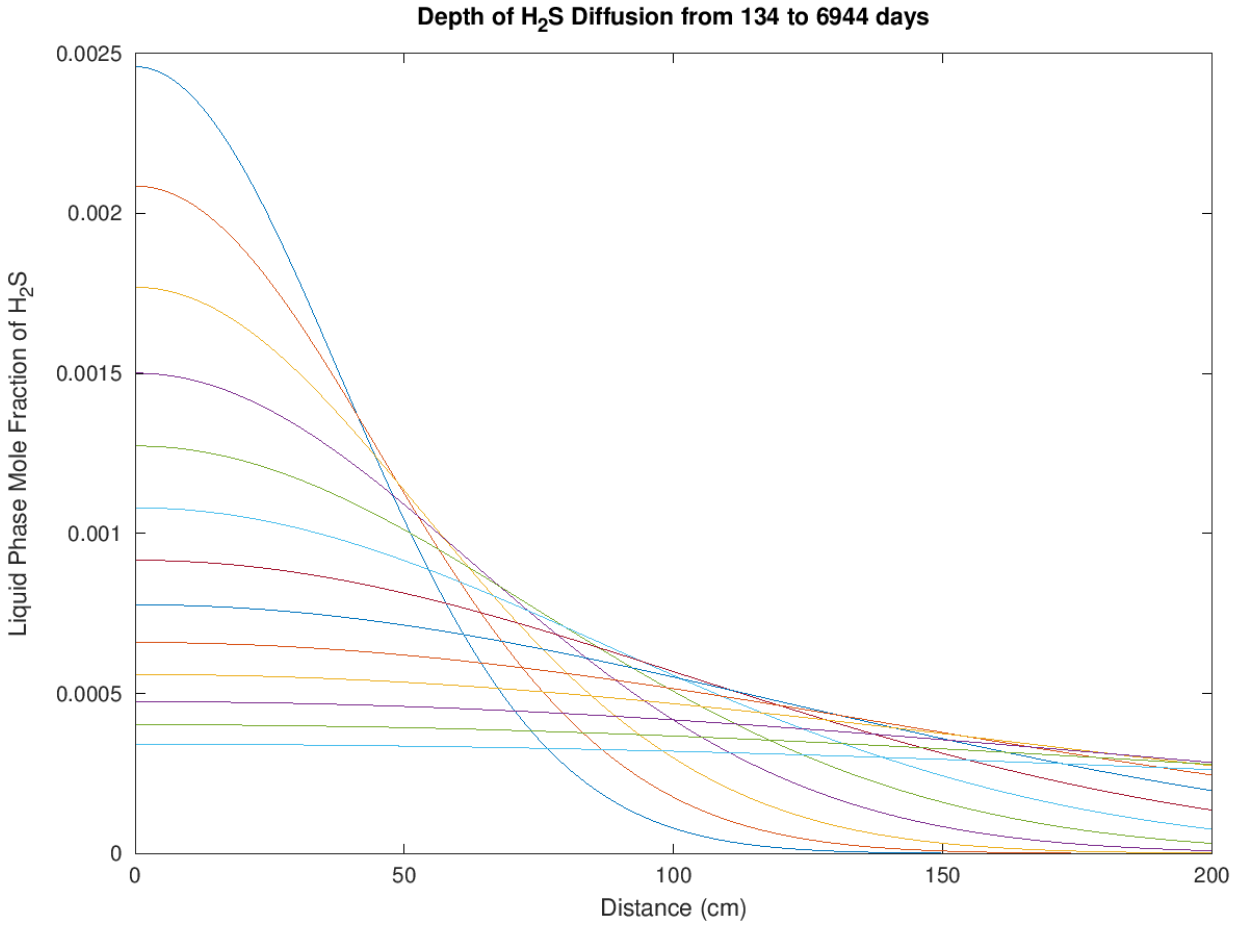
$$A = cross - sectional\ area\ for\ diffusion$$

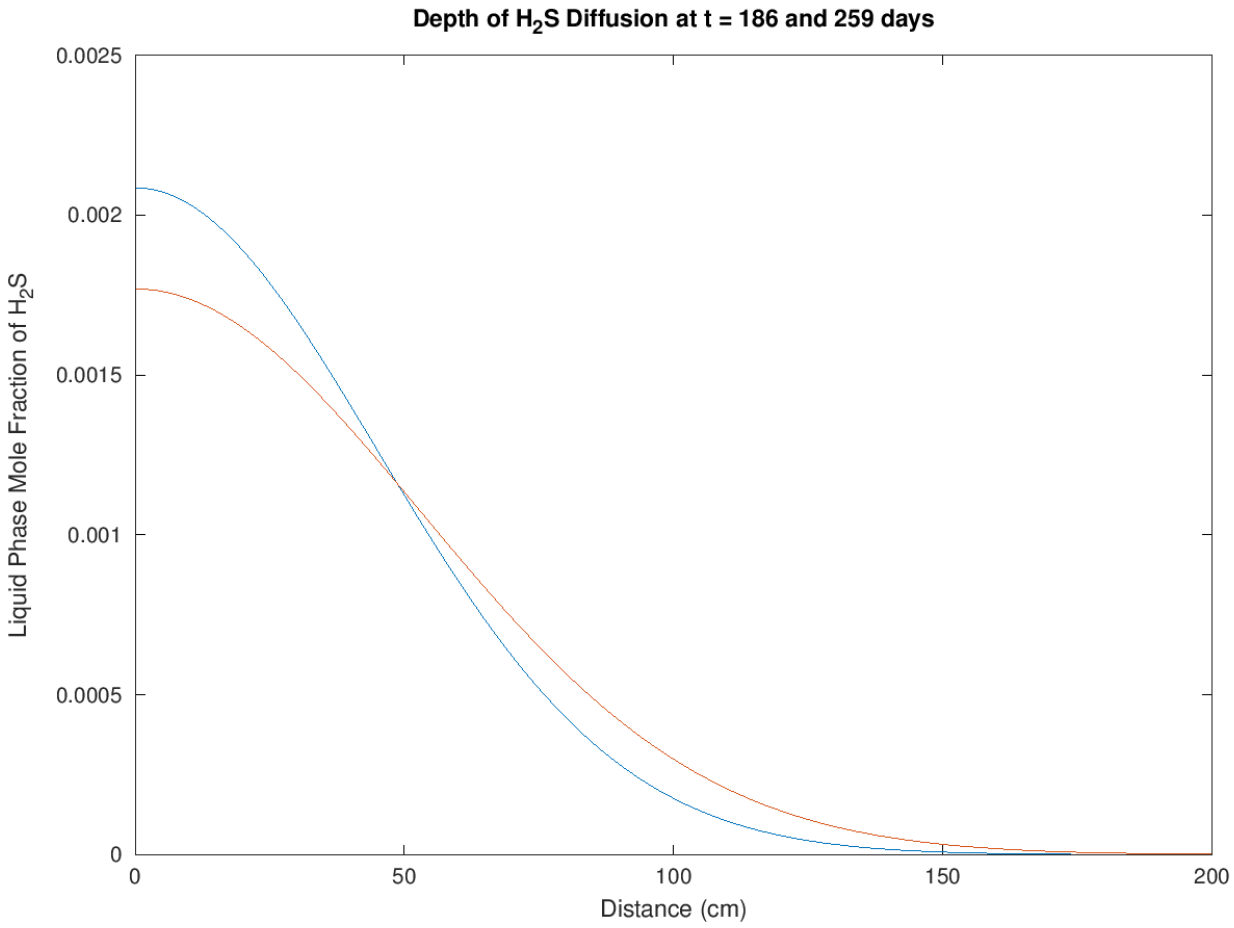
$$c(z,t) = concentration\ as\ a\ function\ of\ position\ and\ time$$

$$z = length\ (cm)$$

$$\mathcal{D} = diffusion\ coeffient\ \left(\frac{cm^2}{sec}\right)$$

$$t = time\ (sec)$$





Plume Model

To examine the threat from the H_2S in a 30% NaHS solution at pH = 11.5, the total amount of dissolved H_2S was assumed to be instantaneously released. It should be noted here that the previous section demonstrates that this is not likely.

The Pasquil-Gifford puff model in one dimension was used to determine downwind concentrations. A 12 m/s wind with stable (little mixing) condition was selected. The dispersion coefficients were derived from a linear regression of the figures 8.8 and 8.9 pages 416 and 417 found in *Air Pollution* Control by Cooper and Alley. See Appendix D for the script used to generate the graphs below.

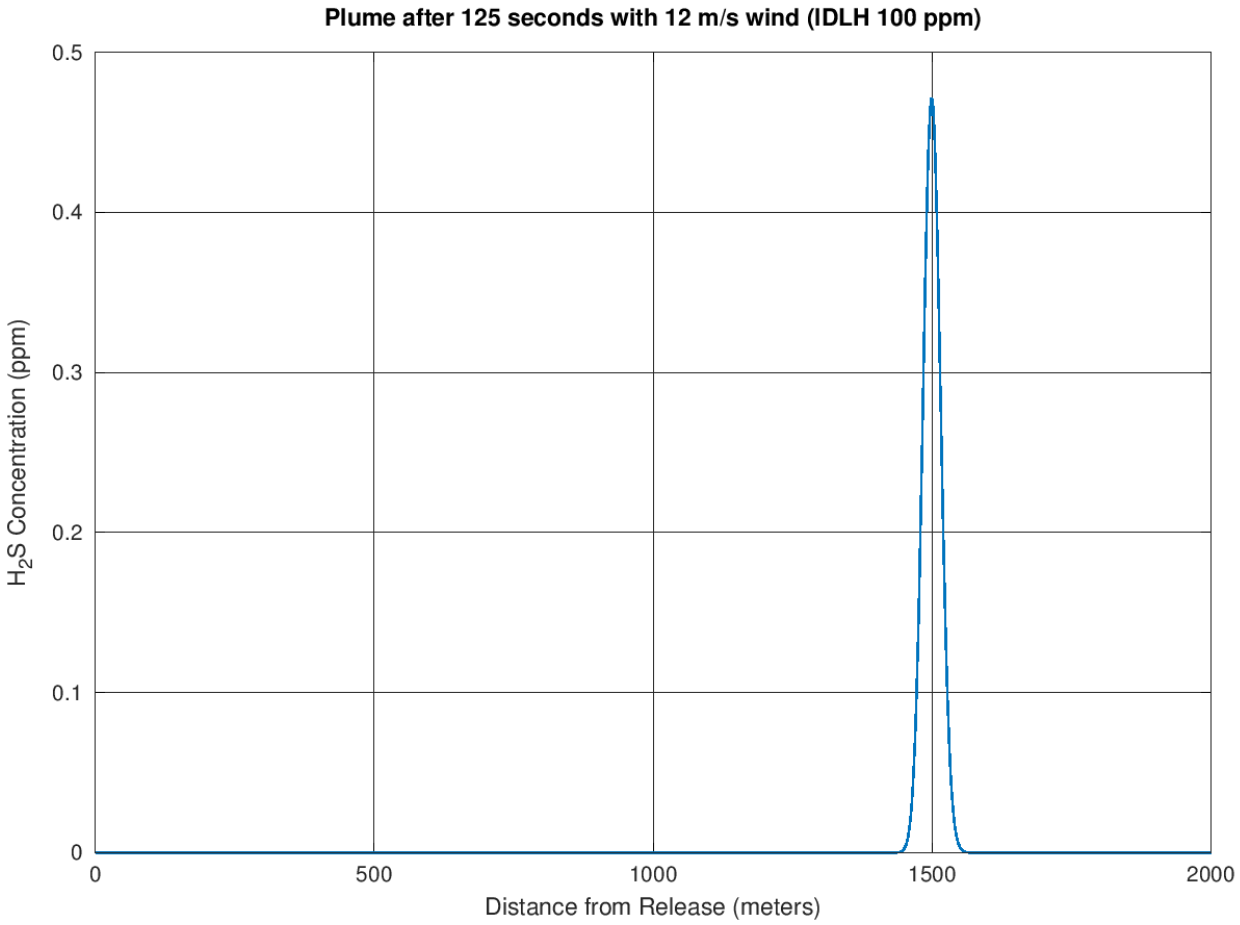
$$C(x,t) = \frac{Q_m}{\sqrt{2}\pi^{2/3}\sigma_x\sigma_y\sigma_z} e^{\left\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)^2\right]\right\}}$$

$$C(x,t) = concentration\ \left(\frac{mg}{m^3}\right)$$

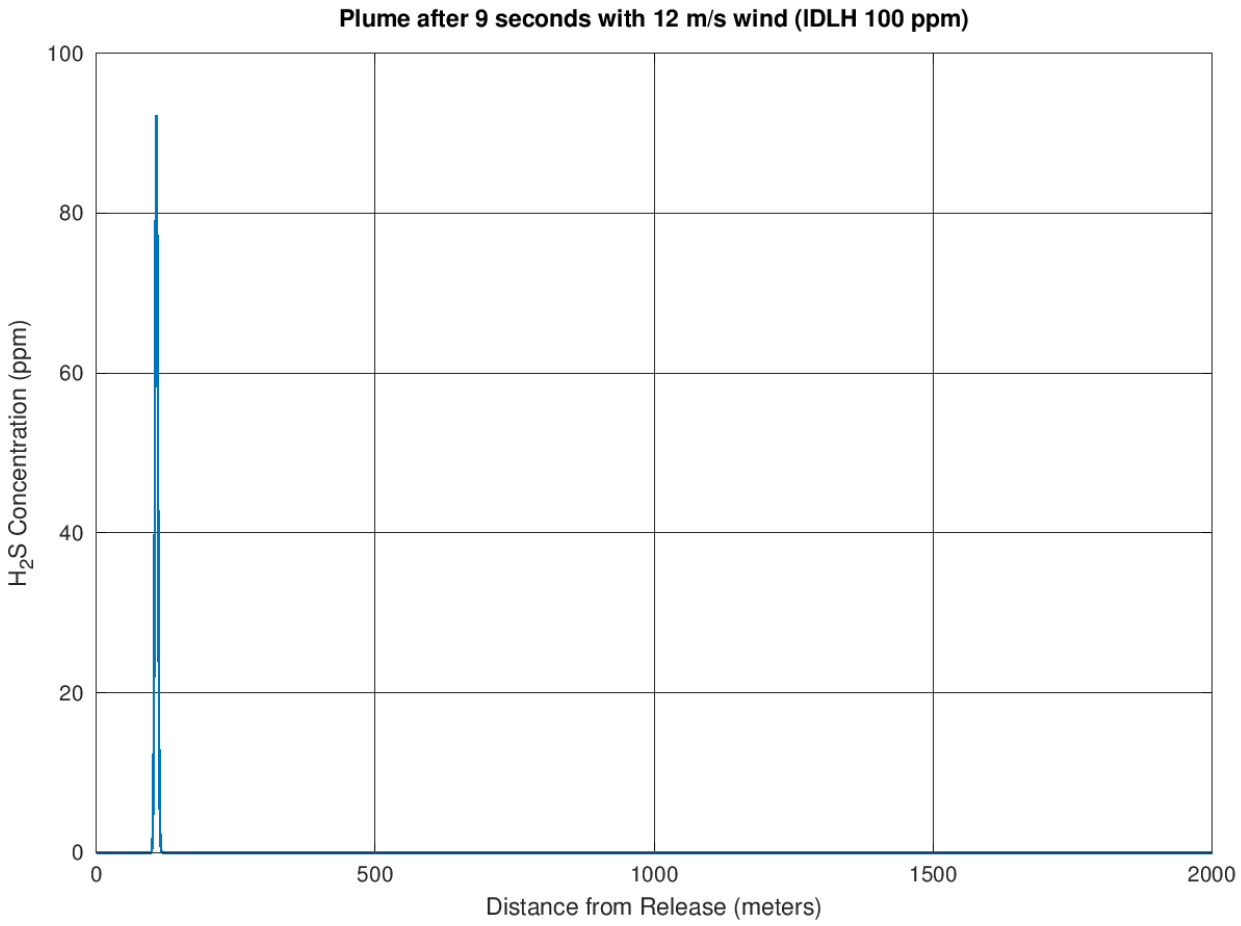
$$\sigma_x = \sigma_y = 9.44x + 1.5\ (x\ in\ km)$$

$$\sigma_z = 3.2z + 0.75\ (z\ in\ km)$$

The graph below shows the concentration profile at 1500m with a maximum concentration of less than 0.5ppm. This concentration is less than the threshold value for an 8 hour time weighted average of 1ppm.



For the onsite exposure situation, the release will be below the IDLH within 200m of the release which will occur in less than 10 seconds. See the following graph.



Discussion

Using the understanding of species distribution from the NaHS chemistry section, estimates of release mass and rate under changes in condition could be considered. The case with strong acid was not considered since there is no source for this at the site.

For a 30% by weight NaHS solution at a pH of 11.5, there will be approximately 8.88e-6 $\frac{\text{moles}}{L}$ of H_2S in solution while there are 9.95 $\frac{\text{moles}}{L}$ of sulfide in solution. With the given Henry's Law constant a concentration of 87 ppm is estimated for a closed headspace such as the storage tank. The total mass of H_2S available in the tank is 0.133 moles H_2S or 5.42 g H_2S. The volume of air needed to dilute this amount down to the IDLH of 100ppm is approximately 35m^3 (46 yd^3 or 10,000gal). This volume would not have sufficient radius to reach the boundaries of the plant site.

The ability to release this total amount in a reasonable time frame such as an hour is not feasible due to liquid side mass transfer resistance. Diffusion times for a meter below the surface can be on the order of years if no advection is present.

Heating the tank will not be successful in releasing this amount very fast either since the heating time to raise the tank temperature from 20°C to 80°C using an 800° C heat source is more than 3 days. In addition, the solubility of H_2S is 3.74 $\frac{g}{L}$ at 21°C while the concentration of H_2S in the 30% solution is 3e-4 $\frac{g}{L}$ at 21°C which means there is little chance that the solution will become supersaturated.

NaHS solutions may also be a byproduct of caustic scrubbers in the oil industry where H_2S removal occurs using the caustic solutions at temperatures as high as 100°C. This helps illustrate the robustness of the solution as an absorbent of H_2S and storage chemistry of sulfides.

Release scenarios 2 and 3 may both have localized releases that are close to the IDLH (100ppm) for near tank workers exposed to the head space of a closed tank but the majority of the sulfide will remain in solution as HS^- and S^{2-} and cannot be released as H_2S. An analysis of the chemistry of the NaHS solution reveals that under conditions that lower the pH either by strong acid addition or dilution it will retain greater than 90% of sulfide in solution until pH drops below 7. In the event of lower pH from dilution, the volume of water necessary to reduce the pH will allow for any H_2S produced to remain in solution. Also, any production of H_2S from sulfides will result in the consumption of H^+ which will raise the pH slowing the production, and subsequent release, of H_2S. This significantly reduces the mass of H_2S that can be produced and there is little threat to offsite receptors.

Under release scenario 2, heat transfer calculations indicate that there is a period of days needed to raise the temperature of the tank contents to sufficient levels required for off-gassing of H_2S. The total amount of H_2S that could off-gas would be less than 6 grams which would impact at most 35 cubic meters (1236 cubic feet) of local air space before being diluted below the IDLH of 100ppm. In the absence of mixing or significant convective currents in the liquid phase, diffusional mass transfer on the liquid side of the gas-liquid interface will limit release due to liquid side mass transfer limitations. This will further reduce the release rate of any dissolved H_2S.

A 30% solution of sodium hydrosulfide (NaHS) can only release large amounts of H_2S gas if mixed with sufficient amounts of a strong acid. Other release scenarios such as heating will take much longer (on the order of days for the insulated tank) and in the case of open flame or high temperature any produced H_2S gas will autoignite at 260° C. With the absence of acid at the plant, the use of NaHS is considered safe from this scenario.

In the event of an accidental release such as an accident during transport, the main threat to emergency responders is from the high pH since the 30% solution is also greater than a 10 molar sodium hydroxide solution and represents a strong base. Emergency response would follow accepted guidelines for NaHS spills as outlined by a standard SDS or more specific instructions from the manufacturer. Residual reactive sulfides can be oxidized with a weak (3-5%) hydrogen peroxide solution. This will prevent further generation of H_2S from the solution but the amount of hydrogen peroxide to sulfide needs to be at a 4:1 molar ratio. This would require 27L of 5% hydrogen peroxide for every liter of 30% NaHS.

If an emergency scenario includes excess water such as from firefighting, drainage of secondary containment to the storage pond, or release to the lake, the dilution of the 30% solution is sufficient to maintain the hydrogen sulfide in solution as the pH drops. While H_2S is of concern for emergency response personnel on the scene, the development of a significant plume that can affect offsite receptors is unlikely to occur.

Conclusions

The three plausible H_2S release scenarios for a 30% NaHS solution that were considered are:

1. Rapid contact and mixing with sufficient quantities of a strong (>10 molar) acid, causing the generation of H_2S gas.

2. High solution temperatures. (This scenario could include a fire similar to the 2015 Wolverine Fire at Holden Village).

3. Dilution with water in a spill/fire situation. This scenario envisions a spill (perhaps during transport), release from secondary containment to storage pond, or localized fire in the immediate vicinity of the tank.

The results for these release scenarios are summarized below.

1. Rapid contact and mixing with sufficient quantities of a strong acid will cause the production and release of H_2S gas. However, given the lack of bulk acid at the site, this scenario is not likely.

2. High temperatures from a scenario like a long-burning, close proximity fire, could cause the NaHS solution to off-gas H_2S. However, there are two very important limiting factors:

    a. The first is the quantity of H_2S within the NaHS solution, which is a negligible (< 0.0001%) portion of the total sulfide mass in solution. The maximum amount of release would be limited to the quantity of H_2S in solution only.

b. The second limiting factor is heat. First, the temperature required to off-gas H_2S requires elevating tank temperatures above 80°C which would take a minimum of three days with a consistent, close proximity heat source > 800°C. Although fires can burn for a long time, they tend to move around. Another important point is that the autoignition temperature for H_2S is 260°C. In a forest fire situation, the H_2S would oxidize (essentially, burn up into the air).

3. Given that water is often the remedy for spills and small fires, this scenario contemplates diluting the solution with water. This would drop the pH, but also dilute the solution, keeping the H_2S dissolved (in liquid versus gas).

The results of chemical calculations below show that 30% NaHS solution chemistry at pH = 11.5 has very little H_2S in the solution compared to the total sulfides in solution. There is still, however, sufficient mass of H_2S to impact onsite receptors. The concentrations were found to be in the following amounts:

$[H_2S] = 8.8e\text{-}6 \ \frac{moles}{L}$

$[HS^-] = 8.6 \ \frac{moles}{L}$

$[S^{2-}] = 1.59 \ \frac{moles}{L}$

The solution is strongly basic having been produced with a strong solution of sodium hydroxide greater than 10 $\frac{moles}{L}$. This prohibits the production of H_2S from the sulfide species and is why the concentration of H_2S is so low. The concentration of the H_2S is well below the solubility of H_2S even at elevated temperatures which will further restrict releases under elevated temperature conditions.

Heat transfer calculations were performed on the tank with the specified insulation. The results reveal that to raise the tank temperature to 80°C from 20°C with an 800°C external heat source it will take more than 3 days. During this time, any H_2S that would escape will oxidize since the autoignition temperature for H_2S is 260°C.

Calculations and models were examined to estimate liquid mass transport of H_2S in solution. Results indicate that if conditions are quiescent the release of gas phase H_2S will be reduced quickly due to diffusional resistance to H_2S transport in the liquid phase. Estimates from the Fourier number indicate that only the top 20 cm of the tank would be depleted of H_2S in 6 months. More detailed analyses indicate a transport velocity of 0.18 to 0.25 $\frac{cm}{day}$ in the liquid phase. All of this demonstrates the inability of the 30% NaHS solution to release the amount of H_2S in solution instantaneously.

A puff release model was evaluated to consider whether the mass of H_2S in solution could impact offsite receptors if all of it could be released at once (which is not plausible). The results show with a strong wind and stable conditions that the concentrations will be below the 100 ppm IDLH limit within 200m of the tank. With no wind or air movement, the amount of H_2S that could theoretically be released could not occupy a volume of air greater than 35 m^3 and still be above the IDLH of 100ppm.

The assumptions and calculations in this document attempt to provide a conservative estimate for the production and transport of hydrogren sulfide in a 30% sodium hydrosulfide solution. More rigorous calculations could be investigated, however the results indicating limited production of hydrogen sulfide from the sulfide solution and minimal release to the gas phase are unlikely to change.

In conclusion, release of sufficient amounts of H_2S from the MWTP that might impact offsite receptors does not appear to be possible under the scenarios investigated in this technical memorandum.

NOTE: Although this technical memorandum, in outlining release scenarios, finds little risk for a H_2S release from a 30% NaHS solution to Holden Village, it should not be interpreted as implying that 30% NaHS solution is not dangerous. In all cases, proper safety protocols, and standard operating procedures should be followed. Onsite personnel at the MWTP are most at risk, given their close proximity, and should be properly trained in handling the chemicals present as well as emergency response procedures.

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Appendix A: 30% NaHS PHREEQC model results

pH 11.5


```
Input file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs_ph_11_5

Output file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs_ph_11_5.out

Database file: /home/cwend/get/usgs/phreeqc/phreeqc-3.3.5-10806/database/phreeqc.dat


Initializing...

End of Run after 0 Seconds.

    EXCHANGE_MASTER_SPECIES
    EXCHANGE_SPECIES
    SURFACE_MASTER_SPECIES
    SURFACE_SPECIES
    RATES
    END
------------------------------------
Reading input data for simulation 1.
------------------------------------

    TITLE Sodium hydrosulfide equilibrium test.
    SOLUTION 1  Tank Contents of 30% sodium hydrosulfide solution
        pH  11.5 #charge
            density 1.3
            temp    25.0
            redox   O(0)/O(-2)
            Na              1.103e+04  charge
           S(-2)            7.95e+3   #charge
        C       1e+02
            O(0)             7     O2(g) -0.7
    SOLUTION_MASTER_SPECIES
    SOLUTION_SPECIES
    EQUILIBRIUM_PHASES 1
    END
-----
TITLE
-----

 Sodium hydrosulfide equilibrium test.

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Tank Contents of 30% sodium hydrosulfide solution

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                1.000e-01   1.000e-01
    Na               9.423e+00   9.423e+00  Charge balance
    O(0)             4.419e-05   4.419e-05  Equilibrium with O2(g)
    S(-2)            7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.500
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 504414
                           Density (g/cm³)  =   1.25224
                                Volume (L)  =   1.18537
                        Activity of water  =   0.704
```

```
                                Ionic strength  =   1.063e+01
                                Mass of water (kg)  =   1.000e+00
                            Total alkalinity (eq/kg)  =   9.423e+00
                                Total CO2 (mol/kg)  =   1.000e-01
                                  Temperature (°C)  =  25.00
                               Electrical balance (eq)  =   6.198e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                        Iterations  =   7
                                           Total H  = 1.176993e+02
                                           Total O  = 5.581131e+01

-----------------------------------Redox couples----------------------------------

    Redox couple             pe  Eh (volts)

    O(-2)/O(0)           9.1980      0.5441

----------------------------Distribution of species-----------------------------

                                                      Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             5.048e-03   2.254e-03    -2.297    -2.647    -0.350     10.52
   H+              4.532e-12   3.162e-12   -11.344   -11.500    -0.156      0.00
   H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          0.000e+00
   CH4             0.000e+00   0.000e+00  -150.788  -149.725     1.063     35.46
C(4)           1.000e-01
   NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
   CO3-2           2.051e-02   2.145e-03    -1.688    -2.669    -0.981     11.96
   HCO3-           2.544e-04   1.446e-04    -3.595    -3.840    -0.245     52.21
   NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
   CO2             1.262e-10   1.460e-09    -9.899    -8.836     1.063     34.43
   (CO2)2          3.384e-21   3.915e-20   -20.471   -19.407     1.063     68.87
H(0)           0.000e+00
   H2              0.000e+00   0.000e+00   -45.609   -44.546     1.063     28.61
Na             9.423e+00
   Na+             9.344e+00   3.410e+01     0.971     1.533     0.562      2.14
   NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
   NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
   NaOH            6.644e-13   7.686e-12   -12.178   -11.114     1.063      (0)
O(0)           4.419e-05
   O2              2.209e-05   2.556e-04    -4.656    -3.592     1.063     30.40
S(-2)          7.950e+00
   HS-             6.681e+00   2.983e+00     0.825     0.475    -0.350     23.65
   S-2             1.269e+00   1.139e-01     0.103    -0.943    -1.047      (0)
   H2S             7.129e-06   8.248e-05    -5.147    -4.084     1.063     37.16

--------------------------------Saturation indices--------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)         -146.92   -149.72   -2.80  CH4
  CO2(g)           -7.37     -8.84   -1.47  CO2
  H2(g)           -41.44    -44.55   -3.10  H2
  H2O(g)           -1.66     -0.15    1.50  H2O
  H2S(g)           -3.03    -11.03   -7.99  H2S
  O2(g)            -0.70     -3.59   -2.89  O2   Pressure   0.2 atm, phi 1.000
  Sulfur           32.43     37.31    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-----------------------------------------
```

```
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 1.   Tank Contents of 30% sodium hydrosulfide solution
Using pure phase assemblage 1.

-----------------------------Solution composition------------------------------

     Elements           Molality       Moles

     C                 1.000e-01   1.000e-01
     Na                9.424e+00   9.423e+00
     S                 7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.501      Charge balance
                                       pe  =  -9.342      Adjusted to redox
                                       equilibrium
        Specific Conductance (µS/cm,  25°C)   = 504293
                             Density (g/cm³)  =   1.25232
                                  Volume (L)  =   1.18530
                          Activity of water   =   0.704
                             Ionic strength   =   1.064e+01
                          Mass of water (kg)  =   9.999e-01
                 Total alkalinity (eq/kg)     =   9.417e+00
                          Total CO2 (mol/kg)  =   9.680e-02
                            Temperature (°C)  =  25.00
                   Electrical balance (eq)    =   6.203e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)     =   0.00
                                  Iterations   =  22
                                     Total H   = 1.176993e+02
                                     Total O   = 5.581131e+01

----------------------------Distribution of species----------------------------

                                                  Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             5.066e-03   2.262e-03    -2.295    -2.646    -0.350     10.53
   H+              4.517e-12   3.151e-12   -11.345   -11.501    -0.156      0.00
   H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          3.209e-03
   CH4             3.209e-03   3.716e-02    -2.494    -1.430     1.064     35.46
C(4)           9.680e-02
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   CO3-2           1.986e-02   2.077e-03    -1.702    -2.683    -0.981     11.97
   HCO3-           2.455e-04   1.396e-04    -3.610    -3.855    -0.245     52.22
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   CO2             1.213e-10   1.405e-09    -9.916    -8.852     1.064     34.43
   (CO2)2          3.127e-21   3.621e-20   -20.505   -19.441     1.064     68.87
H(0)           5.879e-09
   H2              2.940e-09   3.403e-08    -8.532    -7.468     1.064     28.61
Na             9.424e+00
   Na+             9.344e+00   3.412e+01     0.971     1.533     0.562      2.14
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   NaSO4-          2.931e-03   1.667e-03    -2.533    -2.778    -0.245     46.53
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   NaOH            6.665e-13   7.717e-12   -12.176   -11.113     1.064       (0)
O(0)           0.000e+00
   O2              0.000e+00   0.000e+00   -78.812   -77.748     1.064     30.40
S(-2)          7.947e+00
```

```
      HS-              6.675e+00   2.980e+00     0.824      0.474     -0.350      23.65
      S-2              1.272e+00   1.142e-01     0.104     -0.942     -1.047      (0)
      H2S              7.093e-06   8.212e-05    -5.149     -4.086      1.064      37.16
S(6)           3.220e-03
      NaSO4-           2.931e-03   1.667e-03    -2.533     -2.778     -0.245      46.53
      SO4-2            2.891e-04   9.748e-06    -3.539     -5.011     -1.472      26.70
      HSO4-            1.730e-16   2.987e-15   -15.762    -14.525      1.237      42.41

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)             1.37     -1.43   -2.80  CH4
  CO2(g)            -7.38     -8.85   -1.47  CO2
  H2(g)             -4.37     -7.47   -3.10  H2
  H2O(g)            -1.66     -0.15    1.50  H2O
  H2S(g)            -3.03    -11.03   -7.99  H2S
  O2(g)            -74.86    -77.75   -2.89  O2
  Sulfur            -4.65      0.23    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------

-----------------------------------
Reading input data for simulation 2.
-----------------------------------

---------------------------
End of Run after 0 Seconds.
---------------------------
```

pH 12.5


```
Input file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs_ph_12_5

Output file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs_ph_12_5.out

Database file: /home/cwend/get/usgs/phreeqc/phreeqc-3.3.5-10806/database/phreeqc.dat


Initializing...

End of Run after 0 Seconds.

    EXCHANGE_MASTER_SPECIES
    EXCHANGE_SPECIES
    SURFACE_MASTER_SPECIES
    SURFACE_SPECIES
    RATES
    END
------------------------------------
Reading input data for simulation 1.
------------------------------------

    TITLE Sodium hydrosulfide equilibrium test.
    SOLUTION 1  Tank Contents of 30% sodium hydrosulfide solution
        pH  12.5 #charge
            density 1.3
            temp    25.0
            redox   O(0)/O(-2)
            Na              1.103e+04  charge
           S(-2)            7.95e+3   #charge
        C       1e+02
            O(0)             7     O2(g) -0.7
    SOLUTION_MASTER_SPECIES
    SOLUTION_SPECIES
    EQUILIBRIUM_PHASES 1
    END
-----
TITLE
-----

 Sodium hydrosulfide equilibrium test.

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Tank Contents of 30% sodium hydrosulfide solution

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                1.000e-01   1.000e-01
    Na               1.350e+01   1.350e+01  Charge balance
    O(0)             6.759e-06   6.759e-06  Equilibrium with O2(g)
    S(-2)            7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  12.500
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 681117
                           Density (g/cm³)  =   1.40581
                                Volume (L)  =   1.12017
                          Activity of water  =   0.634
```

```
                                Ionic strength  =   1.879e+01
                                Mass of water (kg)  =   1.000e+00
                            Total alkalinity (eq/kg)  =   1.350e+01
                                Total CO2 (mol/kg)  =   1.000e-01
                                  Temperature (°C)  =  25.00
                               Electrical balance (eq)  =  -1.722e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                                      Iterations  =   9
                                         Total H  = 1.137075e+02
                                         Total O  = 5.585372e+01

-----------------------------------Redox couples-----------------------------------

    Redox couple             pe  Eh (volts)

    O(-2)/O(0)           8.2209       0.4863

----------------------------Distribution of species----------------------------

                                                      Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             4.750e-02   2.029e-02    -1.323    -1.693    -0.369     20.41
   H+              4.571e-13   3.162e-13   -12.340   -12.500    -0.160      0.00
   H2O             5.551e+01   6.338e-01     1.744    -0.198     0.000     18.07
C(-4)           0.000e+00
   CH4             0.000e+00   0.000e+00  -153.374  -151.495     1.879     35.46
C(4)            1.000e-01
   NaCO3-          5.774e-02   1.666e+01    -1.239     1.222     2.460     91.29
   CO3-2           4.217e-02   4.048e-03    -1.375    -2.393    -1.018     19.88
   HCO3-           4.904e-05   2.730e-05    -4.309    -4.564    -0.254     71.97
   NaHCO3          4.485e-05   3.392e-03    -4.348    -2.470     1.879      1.80
   CO2             4.049e-13   3.062e-11   -12.393   -10.514     1.879     34.43
   (CO2)2          2.275e-25   1.721e-23   -24.643   -22.764     1.879     68.87
H(0)            0.000e+00
   H2              0.000e+00   0.000e+00   -46.470   -44.592     1.879     28.61
Na              1.350e+01
   Na+             1.344e+01   2.210e+02     1.128     2.344     1.216      3.34
   NaCO3-          5.774e-02   1.666e+01    -1.239     1.222     2.460     91.29
   NaHCO3          4.485e-05   3.392e-03    -4.348    -2.470     1.879      1.80
   NaOH            5.927e-12   4.483e-10   -11.227    -9.348     1.879       (0)
O(0)            6.759e-06
   O2              3.380e-06   2.556e-04    -5.471    -3.592     1.879     30.40
S(-2)           7.950e+00
   S-2             5.303e+00   4.319e-01     0.724    -0.365    -1.089       (0)
   HS-             2.647e+00   1.131e+00     0.423     0.053    -0.369     24.66
   H2S             4.134e-08   3.126e-06    -7.384    -5.505     1.879     37.16

-----------------------------Saturation indices-----------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)         -148.69   -151.49    -2.80  CH4
  CO2(g)           -9.05    -10.51    -1.47  CO2
  H2(g)           -41.49    -44.59    -3.10  H2
  H2O(g)           -1.70     -0.20     1.50  H2O
  H2S(g)           -4.45    -12.45    -7.99  H2S
  O2(g)            -0.70     -3.59    -2.89  O2   Pressure   0.2 atm, phi 1.000
  Sulfur           31.05     35.94     4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

---------------------------------------
```

Beginning of batch-reaction calculations.

Reaction step 1.

Using solution 1. Tank Contents of 30% sodium hydrosulfide solution
Using pure phase assemblage 1.

----------Solution composition----------

Elements	Molality	Moles
C	1.000e-01	1.000e-01
Na	1.350e+01	1.350e+01
S	7.950e+00	7.950e+00

----------Description of solution----------

pH	= 12.500	Charge balance
pe	= -10.565	Adjusted to redox equilibrium
Specific Conductance (µS/cm, 25°C)	= 681091	
Density (g/cm³)	= 1.40580	
Volume (L)	= 1.12018	
Activity of water	= 0.634	
Ionic strength	= 1.879e+01	
Mass of water (kg)	= 1.000e+00	
Total alkalinity (eq/kg)	= 1.350e+01	
Total CO2 (mol/kg)	= 9.919e-02	
Temperature (°C)	= 25.00	
Electrical balance (eq)	= -1.658e-11	
Percent error, 100*(Cat-|An|)/(Cat+|An|)	= -0.00	
Iterations	= 24	
Total H	= 1.137075e+02	
Total O	= 5.585372e+01	

----------Distribution of species----------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm³/mol
OH-	4.753e-02	2.030e-02	-1.323	-1.692	-0.369	20.43
H+	4.568e-13	3.160e-13	-12.340	-12.500	-0.160	0.00
H2O	5.551e+01	6.338e-01	1.744	-0.198	0.000	18.07
C(-4)	8.068e-04					
CH4	8.068e-04	6.102e-02	-3.093	-1.215	1.879	35.46
C(4)	9.919e-02					
NaCO3-	5.727e-02	1.652e+01	-1.242	1.218	2.460	91.36
CO3-2	4.183e-02	4.016e-03	-1.379	-2.396	-1.018	19.89
HCO3-	4.861e-05	2.706e-05	-4.313	-4.568	-0.254	72.01
NaHCO3	4.446e-05	3.362e-03	-4.352	-2.473	1.879	1.80
CO2	4.010e-13	3.033e-11	-12.397	-10.518	1.879	34.43
(CO2)2	2.232e-25	1.688e-23	-24.651	-22.773	1.879	68.87
H(0)	2.521e-09					
H2	1.261e-09	9.535e-08	-8.899	-7.021	1.879	28.61
Na	1.350e+01					
Na+	1.344e+01	2.210e+02	1.128	2.344	1.216	3.34
NaCO3-	5.727e-02	1.652e+01	-1.242	1.218	2.460	91.36
NaSO4-	7.813e-04	4.349e-04	-3.107	-3.362	-0.254	58.08
NaHCO3	4.446e-05	3.362e-03	-4.352	-2.473	1.879	1.80
NaOH	5.932e-12	4.486e-10	-11.227	-9.348	1.879	(0)
O(0)	0.000e+00					
O2	0.000e+00	0.000e+00	-80.613	-78.735	1.879	30.40
S(-2)	7.949e+00					

```
      S-2              5.303e+00   4.319e-01     0.725     -0.365     -1.089      (0)
      HS-              2.646e+00   1.130e+00     0.423      0.053     -0.369     24.66
      H2S              4.128e-08   3.122e-06    -7.384     -5.506      1.879     37.16
   S(6)           8.085e-04
      NaSO4-           7.813e-04   4.349e-04    -3.107     -3.362     -0.254     58.08
      SO4-2            2.720e-05   3.927e-07    -4.565     -6.406     -1.841     30.75
      HSO4-            4.181e-20   1.206e-17   -19.379    -16.919      2.460     42.72

   ------------------------------Saturation indices-------------------------------

     Phase               SI** log IAP   log K(298 K,   1 atm)

     CH4(g)             1.59     -1.21   -2.80  CH4
     CO2(g)            -9.05    -10.52   -1.47  CO2
     H2(g)             -3.92     -7.02   -3.10  H2
     H2O(g)            -1.70     -0.20    1.50  H2O
     H2S(g)            -4.45    -12.45   -7.99  H2S
     O2(g)            -75.84    -78.73   -2.89  O2
     Sulfur            -6.52     -1.63    4.88  S

   **For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
     For ideal gases, phi = 1.

   -------------------
   End of simulation.
   -------------------

   -----------------------------------
   Reading input data for simulation 2.
   -----------------------------------

   ---------------------------
   End of Run after 0 Seconds.
   ---------------------------
```

Appendix B. 11.5% NaHS solution dilution runs with PHREEQC

1e-1 dilution


```
Input file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7

Output file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7.out

Database file: /home/cwend/get/usgs/phreeqc/phreeqc-3.3.5-10806/database/phreeqc.dat


Initializing...

End of Run after 0.01 Seconds.
XCHANGE_MASTER_SPECIES
    EXCHANGE_SPECIES
    SURFACE_MASTER_SPECIES
    SURFACE_SPECIES
    RATES
    END
------------------------------------
Reading input data for simulation 1.
------------------------------------

    TITLE part 1 Sodium hydrosulfide solution pH 11.5
    SOLUTION 1  Tank Contents of 30% sodium hydrosulfide solution
        pH  11.5 #charge
            density 1.3
            temp    25.0
            redox   O(0)/O(-2)
            Na               1.103e+04  charge
           S(-2)             7.95e+3   #charge
        C        1e+02
            O(0)             7     O2(g) -0.7
    SOLUTION_MASTER_SPECIES
    SOLUTION_SPECIES
    EQUILIBRIUM_PHASES 1
    SAVE solution 1
    END
-----
TITLE
-----

 part 1 Sodium hydrosulfide solution pH 11.5

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Tank Contents of 30% sodium hydrosulfide solution

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                 1.000e-01   1.000e-01
    Na                9.423e+00   9.423e+00  Charge balance
    O(0)              4.419e-05   4.419e-05  Equilibrium with O2(g)
    S(-2)             7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.500
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 504414
                           Density (g/cm³)  =   1.25224
                                Volume (L)  =   1.18537
                       Activity of water    =   0.704
```

```
                                Ionic strength  =   1.063e+01
                                Mass of water (kg)  =   1.000e+00
                            Total alkalinity (eq/kg)  =   9.423e+00
                                Total CO2 (mol/kg)  =   1.000e-01
                                  Temperature (°C)  =  25.00
                               Electrical balance (eq)  =   6.198e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                        Iterations  =   7
                                           Total H  = 1.176993e+02
                                           Total O  = 5.581131e+01

--------------------------------Redox couples--------------------------------

    Redox couple             pe  Eh (volts)

    O(-2)/O(0)           9.1980      0.5441

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             5.048e-03   2.254e-03    -2.297    -2.647    -0.350     10.52
   H+              4.532e-12   3.162e-12   -11.344   -11.500    -0.156      0.00
   H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          0.000e+00
   CH4             0.000e+00   0.000e+00  -150.788  -149.725     1.063     35.46
C(4)           1.000e-01
   NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
   CO3-2           2.051e-02   2.145e-03    -1.688    -2.669    -0.981     11.96
   HCO3-           2.544e-04   1.446e-04    -3.595    -3.840    -0.245     52.21
   NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
   CO2             1.262e-10   1.460e-09    -9.899    -8.836     1.063     34.43
   (CO2)2          3.384e-21   3.915e-20   -20.471   -19.407     1.063     68.87
H(0)           0.000e+00
   H2              0.000e+00   0.000e+00   -45.609   -44.546     1.063     28.61
Na             9.423e+00
   Na+             9.344e+00   3.410e+01     0.971     1.533     0.562      2.14
   NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
   NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
   NaOH            6.644e-13   7.686e-12   -12.178   -11.114     1.063       (0)
O(0)           4.419e-05
   O2              2.209e-05   2.556e-04    -4.656    -3.592     1.063     30.40
S(-2)          7.950e+00
   HS-             6.681e+00   2.983e+00     0.825     0.475    -0.350     23.65
   S-2             1.269e+00   1.139e-01     0.103    -0.943    -1.047       (0)
   H2S             7.129e-06   8.248e-05    -5.147    -4.084     1.063     37.16

----------------------------Saturation indices----------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)         -146.92   -149.72   -2.80  CH4
  CO2(g)           -7.37     -8.84   -1.47  CO2
  H2(g)           -41.44    -44.55   -3.10  H2
  H2O(g)           -1.66     -0.15    1.50  H2O
  H2S(g)           -3.03    -11.03   -7.99  H2S
  O2(g)            -0.70     -3.59   -2.89  O2   Pressure   0.2 atm, phi 1.000
  Sulfur           32.43     37.31    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-----------------------------------------
```

```
Beginning of batch-reaction calculations.
-------------------------------------------

Reaction step 1.

Using solution 1.   Tank Contents of 30% sodium hydrosulfide solution
Using pure phase assemblage 1.

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                 1.000e-01   1.000e-01
    Na                9.424e+00   9.423e+00
    S                 7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.501      Charge balance
                                       pe  =  -9.342      Adjusted to redox
                                       equilibrium
       Specific Conductance (µS/cm,  25°C)  = 504293
                            Density (g/cm³)  =   1.25232
                                 Volume (L)  =   1.18530
                          Activity of water  =   0.704
                             Ionic strength  =   1.064e+01
                         Mass of water (kg)  =   9.999e-01
                 Total alkalinity (eq/kg)  =   9.417e+00
                       Total CO2 (mol/kg)  =   9.680e-02
                         Temperature (°C)  =  25.00
                  Electrical balance (eq)  =   6.203e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                 Iterations  =  22
                                    Total H  = 1.176993e+02
                                    Total O  = 5.581131e+01

----------------------------Distribution of species----------------------------

                                                 Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             5.066e-03   2.262e-03    -2.295    -2.646    -0.350     10.53
   H+              4.517e-12   3.151e-12   -11.345   -11.501    -0.156      0.00
   H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          3.209e-03
   CH4             3.209e-03   3.716e-02    -2.494    -1.430     1.064     35.46
C(4)           9.680e-02
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   CO3-2           1.986e-02   2.077e-03    -1.702    -2.683    -0.981     11.97
   HCO3-           2.455e-04   1.396e-04    -3.610    -3.855    -0.245     52.22
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   CO2             1.213e-10   1.405e-09    -9.916    -8.852     1.064     34.43
   (CO2)2          3.127e-21   3.621e-20   -20.505   -19.441     1.064     68.87
H(0)           5.879e-09
   H2              2.940e-09   3.403e-08    -8.532    -7.468     1.064     28.61
Na             9.424e+00
   Na+             9.344e+00   3.412e+01     0.971     1.533     0.562      2.14
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   NaSO4-          2.931e-03   1.667e-03    -2.533    -2.778    -0.245     46.53
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   NaOH            6.665e-13   7.717e-12   -12.176   -11.113     1.064       (0)
O(0)           0.000e+00
   O2              0.000e+00   0.000e+00   -78.812   -77.748     1.064     30.40
S(-2)          7.947e+00
```

```
    HS-              6.675e+00   2.980e+00     0.824      0.474     -0.350      23.65
    S-2              1.272e+00   1.142e-01     0.104     -0.942     -1.047      (0)
    H2S              7.093e-06   8.212e-05    -5.149     -4.086      1.064      37.16
S(6)          3.220e-03
    NaSO4-           2.931e-03   1.667e-03    -2.533     -2.778     -0.245      46.53
    SO4-2            2.891e-04   9.748e-06    -3.539     -5.011     -1.472      26.70
    HSO4-            1.730e-16   2.987e-15   -15.762    -14.525      1.237      42.41

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)             1.37     -1.43   -2.80  CH4
  CO2(g)            -7.38     -8.85   -1.47  CO2
  H2(g)             -4.37     -7.47   -3.10  H2
  H2O(g)            -1.66     -0.15    1.50  H2O
  H2S(g)            -3.03    -11.03   -7.99  H2S
  O2(g)            -74.86    -77.75   -2.89  O2
  Sulfur            -4.65      0.23    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 2.
------------------------------------

    TITLE --Part 2 water
    SOLUTION 2 water
         pH 7.0
         Temp   25.0
    EQUILIBRIUM_PHASES
        CO2(g)  -2.0
        Calcite 0.0
    SAVE solution 2
    END
-----
TITLE
-----

 --Part 2 water

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 2. water

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    Pure water

----------------------------Description of solution----------------------------

                                       pH  =   7.000
                                       pe  =   4.000
       Specific Conductance (µS/cm,  25°C)  = 0
                            Density (g/cm³)  =   0.99704
```

```
                                Volume (L)  =   1.00297
                           Activity of water  =   1.000
                              Ionic strength  =   1.007e-07
                           Mass of water (kg)  =   1.000e+00
                     Total alkalinity (eq/kg)  =   1.217e-09
                        Total carbon (mol/kg)  =   0.000e+00
                           Total CO2 (mol/kg)  =   0.000e+00
                             Temperature (°C)  =  25.00
                      Electrical balance (eq)  =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.60
                                  Iterations  =   0
                                     Total H  = 1.110124e+02
                                     Total O  = 5.550622e+01

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log     mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             1.013e-07   1.012e-07    -6.995    -6.995    -0.000     -4.14
   H+              1.001e-07   1.000e-07    -7.000    -7.000    -0.000      0.00
   H2O             5.551e+01   1.000e+00     1.744     0.000     0.000     18.07
H(0)          1.416e-25
   H2              7.079e-26   7.079e-26   -25.150   -25.150     0.000     28.61
O(0)          0.000e+00
   O2              0.000e+00   0.000e+00   -42.080   -42.080     0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  H2(g)           -22.05    -25.15    -3.10  H2
  H2O(g)           -1.50      0.00     1.50  H2O
  O2(g)           -39.19    -42.08    -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 2.   water
Using pure phase assemblage 1.

-------------------------------Phase assemblage--------------------------------

                                                        Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)          -2.00    -3.47     -1.47    1.000e+01   9.998e+00  -1.976e-03
Calcite          0.00    -8.48     -8.48    1.000e+01   9.998e+00  -1.646e-03

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                3.622e-03   3.622e-03
    Ca               1.646e-03   1.646e-03

----------------------------Description of solution----------------------------
```

```
                                        pH  =   7.297      Charge balance
                                        pe  =  -1.575      Adjusted to redox
                                        equilibrium
        Specific Conductance (µS/cm,  25°C)  = 306
                             Density (g/cm³)  =   0.99726
                                  Volume (L)  =   1.00300
                          Activity of water  =   1.000
                             Ionic strength  =   4.826e-03
                         Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   3.291e-03
                         Total CO2 (mol/kg)  =   3.622e-03
                           Temperature (°C)  =  25.00
                  Electrical balance (eq)  =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                                Iterations  =  17
                                   Total H  = 1.110124e+02
                                   Total O  = 5.551511e+01

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             2.162e-07   2.005e-07    -6.665    -6.698    -0.033     -4.07
   H+              5.401e-08   5.048e-08    -7.268    -7.297    -0.029      0.00
   H2O             5.551e+01   9.999e-01     1.744    -0.000     0.000     18.07
C(-4)           1.401e-25
   CH4             1.401e-25   1.403e-25   -24.854   -24.853     0.000     35.46
C(4)            3.622e-03
   HCO3-           3.224e-03   2.998e-03    -2.492    -2.523    -0.032     24.73
   CO2             3.399e-04   3.403e-04    -3.469    -3.468     0.000     34.43
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342    -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255     0.000    -14.60
   CO3-2           3.724e-06   2.785e-06    -5.429    -5.555    -0.126     -5.13
   (CO2)2          2.123e-09   2.125e-09    -8.673    -8.673     0.000     68.87
Ca              1.646e-03
   Ca+2            1.591e-03   1.189e-03    -2.798    -2.925    -0.126    -18.02
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342    -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255     0.000    -14.60
   CaOH+           4.213e-09   3.910e-09    -8.375    -8.408    -0.032      (0)
H(0)            5.090e-15
   H2              2.545e-15   2.548e-15   -14.594   -14.594     0.000     28.61
O(0)            0.000e+00
   O2              0.000e+00   0.000e+00   -63.193   -63.192     0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  Aragonite         -0.14     -8.48   -8.34  CaCO3
  Calcite            0.00     -8.48   -8.48  CaCO3
  CH4(g)           -22.05    -24.85   -2.80  CH4
  CO2(g)            -2.00     -3.47   -1.47  CO2  Pressure   0.0 atm, phi 1.000
  H2(g)            -11.49    -14.59   -3.10  H2
  H2O(g)            -1.50     -0.00    1.50  H2O
  O2(g)            -60.30    -63.19   -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------
```

```
383   ------------------------------------
384   Reading input data for simulation 3.
385   ------------------------------------
386
387       TITLE -- Part 3 mix the two
388       MIX 1
389           1   0.1
390           2   0.9
391       SAVE solution  3
392       END
393   -----
394   TITLE
395   -----
396
397    -- Part 3 mix the two
398
399   ----------------------------------------
400   Beginning of batch-reaction calculations.
401   ----------------------------------------
402
403   Reaction step 1.
404
405   Using mix 1.
406
407   Mixture 1.
408
409        1.000e-01 Solution 1  Solution after simulation 1.
410        9.000e-01 Solution 2  Solution after simulation 2.
411
412   -----------------------------Solution composition------------------------------
413
414       Elements           Molality       Moles
415
416       C                 1.326e-02   1.326e-02
417       Ca                1.481e-03   1.481e-03
418       Na                9.425e-01   9.423e-01
419       S                 7.951e-01   7.950e-01
420
421   ----------------------------Description of solution----------------------------
422
423                                       pH  =  11.616      Charge balance
424                                       pe  =  -9.368      Adjusted to redox
                                          equilibrium
425         Specific Conductance (µS/cm,  25°C)  = 65380
426                              Density (g/cm³)  =   1.03096
427                                   Volume (L)  =   1.01717
428                           Activity of water  =   0.970
429                              Ionic strength  =   1.057e+00
430                           Mass of water (kg)  =   9.998e-01
431                  Total alkalinity (eq/kg)  =   9.447e-01
432                        Total CO2 (mol/kg)  =   1.290e-02
433                          Temperature (°C)  =  25.00
434                   Electrical balance (eq)  =  -1.089e-09
435    Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
436                                  Iterations  =  17
437                                     Total H  = 1.116811e+02
438                                     Total O  = 5.554473e+01
439
440   ----------------------------Distribution of species----------------------------
441
442                                                  Log       Log       Log    mole V
443     Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol
444
445     OH-             7.052e-03   4.055e-03    -2.152    -2.392    -0.240     -2.02
```

446	H+	3.266e-12	2.422e-12	-11.486	-11.616	-0.130	0.00
447	H2O	5.551e+01	9.703e-01	1.744	-0.013	0.000	18.07
448	C(-4)	3.638e-04					
449	CH4	3.638e-04	4.641e-04	-3.439	-3.333	0.106	35.46
450	C(4)	1.290e-02					
451	NaCO3-	9.362e-03	7.491e-03	-2.029	-2.125	-0.097	4.87
452	CO3-2	3.246e-03	5.869e-04	-2.489	-3.231	-0.743	-1.01
453	CaCO3	2.339e-04	2.984e-04	-3.631	-3.525	0.106	-14.60
454	HCO3-	4.648e-05	3.031e-05	-4.333	-4.518	-0.186	28.06
455	NaHCO3	9.159e-06	1.168e-05	-5.038	-4.932	0.106	1.80
456	CaHCO3+	1.744e-07	1.170e-07	-6.758	-6.932	-0.173	9.99
457	CO2	1.333e-10	1.701e-10	-9.875	-9.769	0.106	34.43
458	(CO2)2	4.163e-22	5.310e-22	-21.381	-21.275	0.106	68.87
459	Ca	1.481e-03					
460	Ca+2	1.221e-03	3.026e-04	-2.913	-3.519	-0.606	-16.43
461	CaCO3	2.339e-04	2.984e-04	-3.631	-3.525	0.106	-14.60
462	CaOH+	2.515e-05	2.012e-05	-4.600	-4.696	-0.097	(0)
463	CaSO4	1.288e-06	1.643e-06	-5.890	-5.784	0.106	7.50
464	CaHCO3+	1.744e-07	1.170e-07	-6.758	-6.932	-0.173	9.99
465	CaHSO4+	3.268e-17	2.615e-17	-16.486	-16.583	-0.097	(0)
466	H(0)	3.549e-08					
467	H2	1.775e-08	2.264e-08	-7.751	-7.645	0.106	28.61
468	Na	9.425e-01					
469	Na+	9.329e-01	6.855e-01	-0.030	-0.164	-0.134	-0.28
470	NaCO3-	9.362e-03	7.491e-03	-2.029	-2.125	-0.097	4.87
471	NaSO4-	1.608e-04	1.049e-04	-3.794	-3.979	-0.186	23.27
472	NaHCO3	9.159e-06	1.168e-05	-5.038	-4.932	0.106	1.80
473	NaOH	2.179e-13	2.780e-13	-12.662	-12.556	0.106	(0)
474	O(0)	0.000e+00					
475	O2	0.000e+00	0.000e+00	-77.222	-77.116	0.106	30.40
476	S(-2)	7.948e-01					
477	HS-	6.776e-01	3.896e-01	-0.169	-0.409	-0.240	21.54
478	S-2	1.171e-01	1.943e-02	-0.931	-1.711	-0.780	(0)
479	H2S	6.468e-06	8.251e-06	-5.189	-5.084	0.106	37.16
480	S(6)	3.649e-04					
481	SO4-2	2.028e-04	3.052e-05	-3.693	-4.515	-0.822	18.27
482	NaSO4-	1.608e-04	1.049e-04	-3.794	-3.979	-0.186	23.27
483	CaSO4	1.288e-06	1.643e-06	-5.890	-5.784	0.106	7.50
484	HSO4-	8.982e-15	7.187e-15	-14.047	-14.143	-0.097	41.13
485	CaHSO4+	3.268e-17	2.615e-17	-16.486	-16.583	-0.097	(0)

```
487 -------------------------------Saturation indices--------------------------------
488
489   Phase               SI** log IAP   log K(298 K,   1 atm)
490
491   Anhydrite         -3.76     -8.03   -4.28  CaSO4
492   Aragonite          1.59     -6.75   -8.34  CaCO3
493   Calcite            1.73     -6.75   -8.48  CaCO3
494   CH4(g)            -0.53     -3.33   -2.80  CH4
495   CO2(g)            -8.30     -9.77   -1.47  CO2
496   Gypsum            -3.48     -8.06   -4.58  CaSO4:2H2O
497   H2(g)             -4.54     -7.65   -3.10  H2
498   H2O(g)            -1.52     -0.01    1.50  H2O
499   H2S(g)            -4.03    -12.03   -7.99  H2S
500   O2(g)            -74.22    -77.12   -2.89  O2
501   Sulfur            -5.47     -0.59    4.88  S
502
503 **For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
504   For ideal gases, phi = 1.
505
506 ------------------
507 End of simulation.
508 ------------------
509
```

```
510   ------------------------------------
511   Reading input data for simulation 4.
512   ------------------------------------
513
514   ----------------------------
515   End of Run after 0.01 Seconds.
516   ----------------------------
517
518
```

1e-2 dilution


```
Input file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7

Output file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7.out

Database file: /home/cwend/get/usgs/phreeqc/phreeqc-3.3.5-10806/database/phreeqc.dat


Initializing...

End of Run after 0 Seconds.

    EXCHANGE_MASTER_SPECIES
    EXCHANGE_SPECIES
    SURFACE_MASTER_SPECIES
    SURFACE_SPECIES
    RATES
    END
------------------------------------
Reading input data for simulation 1.
------------------------------------

    TITLE part 1 Sodium hydrosulfide solution pH 11.5
    SOLUTION 1  Tank Contents of 30% sodium hydrosulfide solution
        pH  11.5 #charge
            density 1.3
            temp    25.0
            redox   O(0)/O(-2)
            Na               1.103e+04  charge
           S(-2)             7.95e+3   #charge
        C        1e+02
            O(0)              7     O2(g) -0.7
    SOLUTION_MASTER_SPECIES
    SOLUTION_SPECIES
    EQUILIBRIUM_PHASES 1
    SAVE solution 1
    END
-----
TITLE
-----

 part 1 Sodium hydrosulfide solution pH 11.5

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Tank Contents of 30% sodium hydrosulfide solution

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                 1.000e-01   1.000e-01
    Na                9.423e+00   9.423e+00  Charge balance
    O(0)              4.419e-05   4.419e-05  Equilibrium with O2(g)
    S(-2)             7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.500
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 504414
                           Density (g/cm³)  =   1.25224
                                Volume (L)  =   1.18537
```

```
                          Activity of water  =   0.704
                             Ionic strength  =   1.063e+01
                          Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   9.423e+00
                          Total CO2 (mol/kg)  =   1.000e-01
                            Temperature (°C)  =  25.00
                       Electrical balance (eq)  =   6.198e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                  Iterations  =   7
                                     Total H  = 1.176993e+02
                                     Total O  = 5.581131e+01

--------------------------------Redox couples--------------------------------

    Redox couple             pe  Eh (volts)

    O(-2)/O(0)           9.1980       0.5441

----------------------------Distribution of species----------------------------

                                                  Log       Log       Log    mole V
    Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

    OH-             5.048e-03   2.254e-03    -2.297    -2.647    -0.350     10.52
    H+              4.532e-12   3.162e-12   -11.344   -11.500    -0.156      0.00
    H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          0.000e+00
    CH4             0.000e+00   0.000e+00  -150.788  -149.725     1.063     35.46
C(4)           1.000e-01
    NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
    CO3-2           2.051e-02   2.145e-03    -1.688    -2.669    -0.981     11.96
    HCO3-           2.544e-04   1.446e-04    -3.595    -3.840    -0.245     52.21
    NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
    CO2             1.262e-10   1.460e-09    -9.899    -8.836     1.063     34.43
    (CO2)2          3.384e-21   3.915e-20   -20.471   -19.407     1.063     68.87
H(0)           0.000e+00
    H2              0.000e+00   0.000e+00   -45.609   -44.546     1.063     28.61
Na             9.423e+00
    Na+             9.344e+00   3.410e+01     0.971     1.533     0.562      2.14
    NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
    NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
    NaOH            6.644e-13   7.686e-12   -12.178   -11.114     1.063     (0)
O(0)           4.419e-05
    O2              2.209e-05   2.556e-04    -4.656    -3.592     1.063     30.40
S(-2)          7.950e+00
    HS-             6.681e+00   2.983e+00     0.825     0.475    -0.350     23.65
    S-2             1.269e+00   1.139e-01     0.103    -0.943    -1.047     (0)
    H2S             7.129e-06   8.248e-05    -5.147    -4.084     1.063     37.16

-----------------------------Saturation indices-----------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)         -146.92   -149.72    -2.80  CH4
  CO2(g)           -7.37     -8.84    -1.47  CO2
  H2(g)           -41.44    -44.55    -3.10  H2
  H2O(g)           -1.66     -0.15     1.50  H2O
  H2S(g)           -3.03    -11.03    -7.99  H2S
  O2(g)            -0.70     -3.59    -2.89  O2   Pressure   0.2 atm, phi 1.000
  Sulfur           32.43     37.31     4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.
```

```
129  ----------------------------------------
130  Beginning of batch-reaction calculations.
131  ----------------------------------------
132
133  Reaction step 1.
134
135  Using solution 1.   Tank Contents of 30% sodium hydrosulfide solution
136  Using pure phase assemblage 1.
137
138  -----------------------------Solution composition------------------------------
139
140      Elements           Molality       Moles
141
142      C                 1.000e-01   1.000e-01
143      Na                9.424e+00   9.423e+00
144      S                 7.950e+00   7.950e+00
145
146  ----------------------------Description of solution----------------------------
147
148                                       pH  =  11.501      Charge balance
149                                       pe  =  -9.342      Adjusted to redox
                                          equilibrium
150        Specific Conductance (µS/cm,  25°C)  = 504293
151                             Density (g/cm³)  =   1.25232
152                                  Volume (L)  =   1.18530
153                          Activity of water  =   0.704
154                             Ionic strength  =   1.064e+01
155                          Mass of water (kg)  =   9.999e-01
156                 Total alkalinity (eq/kg)  =   9.417e+00
157                          Total CO2 (mol/kg)  =   9.680e-02
158                            Temperature (°C)  =  25.00
159                       Electrical balance (eq)  =   6.203e-11
160   Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
161                                  Iterations  =  22
162                                     Total H  = 1.176993e+02
163                                     Total O  = 5.581131e+01
164
165  ----------------------------Distribution of species----------------------------
166
167                                                    Log       Log       Log    mole V
168      Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol
169
170      OH-             5.066e-03   2.262e-03    -2.295    -2.646    -0.350     10.53
171      H+              4.517e-12   3.151e-12   -11.345   -11.501    -0.156      0.00
172      H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
173  C(-4)           3.209e-03
174      CH4             3.209e-03   3.716e-02    -2.494    -1.430     1.064     35.46
175  C(4)            9.680e-02
176      NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
177      CO3-2           1.986e-02   2.077e-03    -1.702    -2.683    -0.981     11.97
178      HCO3-           2.455e-04   1.396e-04    -3.610    -3.855    -0.245     52.22
179      NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
180      CO2             1.213e-10   1.405e-09    -9.916    -8.852     1.064     34.43
181      (CO2)2          3.127e-21   3.621e-20   -20.505   -19.441     1.064     68.87
182  H(0)            5.879e-09
183      H2              2.940e-09   3.403e-08    -8.532    -7.468     1.064     28.61
184  Na              9.424e+00
185      Na+             9.344e+00   3.412e+01     0.971     1.533     0.562      2.14
186      NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
187      NaSO4-          2.931e-03   1.667e-03    -2.533    -2.778    -0.245     46.53
188      NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
189      NaOH            6.665e-13   7.717e-12   -12.176   -11.113     1.064       (0)
190  O(0)            0.000e+00
191      O2              0.000e+00   0.000e+00   -78.812   -77.748     1.064     30.40
```

```
S(-2)          7.947e+00
   HS-             6.675e+00   2.980e+00     0.824     0.474     -0.350     23.65
   S-2             1.272e+00   1.142e-01     0.104    -0.942     -1.047     (0)
   H2S             7.093e-06   8.212e-05    -5.149    -4.086      1.064     37.16
S(6)           3.220e-03
   NaSO4-          2.931e-03   1.667e-03    -2.533    -2.778     -0.245     46.53
   SO4-2           2.891e-04   9.748e-06    -3.539    -5.011     -1.472     26.70
   HSO4-           1.730e-16   2.987e-15   -15.762   -14.525      1.237     42.41

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)             1.37     -1.43   -2.80  CH4
  CO2(g)            -7.38     -8.85   -1.47  CO2
  H2(g)             -4.37     -7.47   -3.10  H2
  H2O(g)            -1.66     -0.15    1.50  H2O
  H2S(g)            -3.03    -11.03   -7.99  H2S
  O2(g)            -74.86    -77.75   -2.89  O2
  Sulfur            -4.65      0.23    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 2.
------------------------------------

    TITLE --Part 2 water
    SOLUTION 2 water
         pH 7.0
         Temp   25.0
    EQUILIBRIUM_PHASES
        CO2(g)  -2.0
        Calcite 0.0
    SAVE solution 2
    END
-----
TITLE
-----

 --Part 2 water

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 2. water

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    Pure water

----------------------------Description of solution----------------------------

                                       pH  =   7.000
                                       pe  =   4.000
       Specific Conductance (µS/cm,  25°C)  = 0
```

```
                              Density (g/cm³)  =   0.99704
                                   Volume (L)  =   1.00297
                            Activity of water  =   1.000
                               Ionic strength  =   1.007e-07
                           Mass of water (kg)  =   1.000e+00
                  Total alkalinity (eq/kg)     =   1.217e-09
                     Total carbon (mol/kg)     =   0.000e+00
                        Total CO2 (mol/kg)     =   0.000e+00
                          Temperature (°C)     =  25.00
                   Electrical balance (eq)     =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)     =  -0.60
                                  Iterations   =   0
                                     Total H   = 1.110124e+02
                                     Total O   = 5.550622e+01

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             1.013e-07   1.012e-07    -6.995    -6.995    -0.000     -4.14
   H+              1.001e-07   1.000e-07    -7.000    -7.000    -0.000      0.00
   H2O             5.551e+01   1.000e+00     1.744     0.000     0.000     18.07
H(0)          1.416e-25
   H2              7.079e-26   7.079e-26   -25.150   -25.150     0.000     28.61
O(0)          0.000e+00
   O2              0.000e+00   0.000e+00   -42.080   -42.080     0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  H2(g)           -22.05    -25.15    -3.10  H2
  H2O(g)           -1.50      0.00     1.50  H2O
  O2(g)           -39.19    -42.08    -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 2.   water
Using pure phase assemblage 1.

-------------------------------Phase assemblage--------------------------------

                                                      Moles in assemblage
Phase               SI  log IAP  log K(T, P)    Initial       Final       Delta

CO2(g)          -2.00    -3.47     -1.47    1.000e+01   9.998e+00  -1.976e-03
Calcite          0.00    -8.48     -8.48    1.000e+01   9.998e+00  -1.646e-03

----------------------------Solution composition-----------------------------

    Elements           Molality       Moles

    C                3.622e-03   3.622e-03
    Ca               1.646e-03   1.646e-03

---------------------------Description of solution---------------------------
```

```
                                        pH  =   7.297      Charge balance
                                        pe  =  -1.575      Adjusted to redox
                                        equilibrium
        Specific Conductance (µS/cm,  25°C)  = 306
                             Density (g/cm³)  =   0.99726
                                  Volume (L)  =   1.00300
                           Activity of water  =   1.000
                              Ionic strength  =   4.826e-03
                          Mass of water (kg)  =   1.000e+00
                 Total alkalinity (eq/kg)  =   3.291e-03
                          Total CO2 (mol/kg)  =   3.622e-03
                            Temperature (°C)  =  25.00
                   Electrical balance (eq)  =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                                  Iterations  =  17
                                     Total H  = 1.110124e+02
                                     Total O  = 5.551511e+01

----------------------------Distribution of species----------------------------

                                                  Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             2.162e-07   2.005e-07    -6.665    -6.698    -0.033     -4.07
   H+              5.401e-08   5.048e-08    -7.268    -7.297    -0.029      0.00
   H2O             5.551e+01   9.999e-01     1.744    -0.000     0.000     18.07
C(-4)          1.401e-25
   CH4             1.401e-25   1.403e-25   -24.854   -24.853     0.000     35.46
C(4)           3.622e-03
   HCO3-           3.224e-03   2.998e-03    -2.492    -2.523    -0.032     24.73
   CO2             3.399e-04   3.403e-04    -3.469    -3.468     0.000     34.43
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342    -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255     0.000    -14.60
   CO3-2           3.724e-06   2.785e-06    -5.429    -5.555    -0.126     -5.13
   (CO2)2          2.123e-09   2.125e-09    -8.673    -8.673     0.000     68.87
Ca             1.646e-03
   Ca+2            1.591e-03   1.189e-03    -2.798    -2.925    -0.126    -18.02
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342    -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255     0.000    -14.60
   CaOH+           4.213e-09   3.910e-09    -8.375    -8.408    -0.032      (0)
H(0)           5.090e-15
   H2              2.545e-15   2.548e-15   -14.594   -14.594     0.000     28.61
O(0)           0.000e+00
   O2              0.000e+00   0.000e+00   -63.193   -63.192     0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  Aragonite         -0.14     -8.48    -8.34  CaCO3
  Calcite            0.00     -8.48    -8.48  CaCO3
  CH4(g)           -22.05    -24.85    -2.80  CH4
  CO2(g)            -2.00     -3.47    -1.47  CO2  Pressure   0.0 atm, phi 1.000
  H2(g)            -11.49    -14.59    -3.10  H2
  H2O(g)            -1.50     -0.00     1.50  H2O
  O2(g)            -60.30    -63.19    -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------
```

```
383
384   ------------------------------------
385   Reading input data for simulation 3.
386   ------------------------------------
387
388       TITLE -- Part 3 mix the two
389       MIX 1
390           1   0.01
391           2   0.99
392       SAVE solution  3
393       END
394   -----
395   TITLE
396   -----
397
398    -- Part 3 mix the two
399
400   ----------------------------------------
401   Beginning of batch-reaction calculations.
402   ----------------------------------------
403
404   Reaction step 1.
405
406   Using mix 1.
407
408   Mixture 1.
409
410         1.000e-02 Solution 1  Solution after simulation 1.
411         9.900e-01 Solution 2  Solution after simulation 2.
412
413   -----------------------------Solution composition------------------------------
414
415       Elements           Molality       Moles
416
417       C                 4.586e-03   4.585e-03
418       Ca                1.629e-03   1.629e-03
419       Na                9.424e-02   9.423e-02
420       S                 7.951e-02   7.950e-02
421
422   ----------------------------Description of solution----------------------------
423
424                                       pH  =  11.455      Charge balance
425                                       pe  =  -9.078      Adjusted to redox
                                          equilibrium
426          Specific Conductance (µS/cm,  25°C)  = 9468
427                               Density (g/cm³)  =   1.00082
428                                    Volume (L)  =   1.00427
429                            Activity of water  =   0.997
430                               Ionic strength  =   1.034e-01
431                           Mass of water (kg)  =   9.999e-01
432                  Total alkalinity (eq/kg)  =   9.726e-02
433                           Total CO2 (mol/kg)  =   4.466e-03
434                             Temperature (°C)  =  25.00
435                      Electrical balance (eq)  =  -1.286e-09
436    Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
437                                  Iterations  =  19
438                                     Total H  = 1.110793e+02
439                                     Total O  = 5.551807e+01
440
441   ----------------------------Distribution of species----------------------------
442
443                                                 Log       Log       Log    mole V
444     Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol
445
```

	OH-	3.792e-03	2.878e-03	-2.421	-2.541	-0.120	-3.72
	H+	4.255e-12	3.506e-12	-11.371	-11.455	-0.084	0.00
	H2O	5.551e+01	9.969e-01	1.744	-0.001	0.000	18.07
C(-4)		1.199e-04					
	CH4	1.199e-04	1.228e-04	-3.921	-3.911	0.010	35.46
C(4)		4.466e-03					
	CO3-2	2.290e-03	8.750e-04	-2.640	-3.058	-0.418	-4.13
	NaCO3-	1.518e-03	1.183e-03	-2.819	-2.927	-0.108	-0.27
	CaCO3	5.722e-04	5.860e-04	-3.242	-3.232	0.010	-14.60
	HCO3-	8.320e-05	6.541e-05	-4.080	-4.184	-0.104	25.19
	NaHCO3	2.608e-06	2.671e-06	-5.584	-5.573	0.010	1.80
	CaHCO3+	4.192e-07	3.327e-07	-6.378	-6.478	-0.100	9.84
	CO2	5.051e-10	5.172e-10	-9.297	-9.286	0.010	34.43
	(CO2)2	4.795e-21	4.911e-21	-20.319	-20.309	0.010	68.87
Ca		1.629e-03					
	Ca+2	1.030e-03	3.986e-04	-2.987	-3.399	-0.412	-17.42
	CaCO3	5.722e-04	5.860e-04	-3.242	-3.232	0.010	-14.60
	CaOH+	2.414e-05	1.881e-05	-4.617	-4.726	-0.108	(0)
	CaSO4	2.560e-06	2.621e-06	-5.592	-5.581	0.010	7.50
	CaHCO3+	4.192e-07	3.327e-07	-6.378	-6.478	-0.100	9.84
	CaHSO4+	7.751e-17	6.041e-17	-16.111	-16.219	-0.108	(0)
H(0)		2.434e-08					
	H2	1.217e-08	1.246e-08	-7.915	-7.904	0.010	28.61
Na		9.424e-02					
	Na+	9.270e-02	7.260e-02	-1.033	-1.139	-0.106	-1.09
	NaCO3-	1.518e-03	1.183e-03	-2.819	-2.927	-0.108	-0.27
	NaSO4-	1.711e-05	1.345e-05	-4.767	-4.871	-0.104	16.36
	NaHCO3	2.608e-06	2.671e-06	-5.584	-5.573	0.010	1.80
	NaOH	2.040e-14	2.090e-14	-13.690	-13.680	0.010	(0)
O(0)		0.000e+00					
	O2	0.000e+00	0.000e+00	-76.584	-76.574	0.010	30.40
S(-2)		7.939e-02					
	HS-	7.417e-02	5.630e-02	-1.130	-1.249	-0.120	20.88
	S-2	5.212e-03	1.940e-03	-2.283	-2.712	-0.429	(0)
	H2S	1.685e-06	1.726e-06	-5.773	-5.763	0.010	37.16
S(6)		1.200e-04					
	SO4-2	1.003e-04	3.698e-05	-3.999	-4.432	-0.433	15.61
	NaSO4-	1.711e-05	1.345e-05	-4.767	-4.871	-0.104	16.36
	CaSO4	2.560e-06	2.621e-06	-5.592	-5.581	0.010	7.50
	HSO4-	1.617e-14	1.260e-14	-13.791	-13.899	-0.108	40.54
	CaHSO4+	7.751e-17	6.041e-17	-16.111	-16.219	-0.108	(0)

------------------------------Saturation indices-------------------------------

Phase	SI**	log IAP	log K(298 K, 1 atm)	
Anhydrite	-3.55	-7.83	-4.28	CaSO4
Aragonite	1.88	-6.46	-8.34	CaCO3
Calcite	2.02	-6.46	-8.48	CaCO3
CH4(g)	-1.11	-3.91	-2.80	CH4
CO2(g)	-7.82	-9.29	-1.47	CO2
Gypsum	-3.25	-7.83	-4.58	CaSO4:2H2O
H2(g)	-4.80	-7.90	-3.10	H2
H2O(g)	-1.50	-0.00	1.50	H2O
H2S(g)	-4.71	-12.70	-7.99	H2S
O2(g)	-73.68	-76.57	-2.89	O2
Sulfur	-5.89	-1.01	4.88	S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
. For ideal gases, phi = 1.

End of simulation.

```
510
511   -------------------------------------
512   Reading input data for simulation 4.
513   -------------------------------------
514
515   ---------------------------
516   End of Run after 0 Seconds.
517   ---------------------------
518
519
```

1e-3 dilution


```
Input file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7

Output file: /home/cwend/get/usgs/phreeqc/work/holden/nahs/nahs7.out

Database file: /home/cwend/get/usgs/phreeqc/phreeqc-3.3.5-10806/database/phreeqc.dat


Initializing...

End of Run after 0.01 Seconds.
XCHANGE_MASTER_SPECIES
    EXCHANGE_SPECIES
    SURFACE_MASTER_SPECIES
    SURFACE_SPECIES
    RATES
    END
------------------------------------
Reading input data for simulation 1.
------------------------------------

    TITLE part 1 Sodium hydrosulfide solution pH 11.5
    SOLUTION 1  Tank Contents of 30% sodium hydrosulfide solution
        pH  11.5 #charge
            density 1.3
            temp    25.0
            redox   O(0)/O(-2)
            Na              1.103e+04  charge
           S(-2)            7.95e+3   #charge
        C        1e+02
            O(0)             7     O2(g) -0.7
    SOLUTION_MASTER_SPECIES
    SOLUTION_SPECIES
    EQUILIBRIUM_PHASES 1
    SAVE solution 1
    END
-----
TITLE
-----

 part 1 Sodium hydrosulfide solution pH 11.5

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Tank Contents of 30% sodium hydrosulfide solution

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                1.000e-01   1.000e-01
    Na               9.423e+00   9.423e+00  Charge balance
    O(0)             4.419e-05   4.419e-05  Equilibrium with O2(g)
    S(-2)            7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.500
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 504414
                           Density (g/cm³)  =   1.25224
                                Volume (L)  =   1.18537
                          Activity of water  =   0.704
```

```
                                Ionic strength  =   1.063e+01
                                Mass of water (kg)  =   1.000e+00
                            Total alkalinity (eq/kg)  =   9.423e+00
                                Total CO2 (mol/kg)  =   1.000e-01
                                  Temperature (°C)  =  25.00
                               Electrical balance (eq)  =   6.198e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                      Iterations  =   7
                                         Total H  = 1.176993e+02
                                         Total O  = 5.581131e+01

-----------------------------------Redox couples-----------------------------------

    Redox couple                pe  Eh (volts)

    O(-2)/O(0)              9.1980      0.5441

----------------------------Distribution of species----------------------------

                                                      Log       Log       Log    mole V
    Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

    OH-             5.048e-03   2.254e-03    -2.297    -2.647    -0.350     10.52
    H+              4.532e-12   3.162e-12   -11.344   -11.500    -0.156      0.00
    H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)           0.000e+00
    CH4             0.000e+00   0.000e+00  -150.788  -149.725     1.063     35.46
C(4)            1.000e-01
    NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
    CO3-2           2.051e-02   2.145e-03    -1.688    -2.669    -0.981     11.96
    HCO3-           2.544e-04   1.446e-04    -3.595    -3.840    -0.245     52.21
    NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
    CO2             1.262e-10   1.460e-09    -9.899    -8.836     1.063     34.43
    (CO2)2          3.384e-21   3.915e-20   -20.471   -19.407     1.063     68.87
H(0)            0.000e+00
    H2              0.000e+00   0.000e+00   -45.609   -44.546     1.063     28.61
Na              9.423e+00
    Na+             9.344e+00   3.410e+01     0.971     1.533     0.562      2.14
    NaCO3-          7.899e-02   1.362e+00    -1.102     0.134     1.237     51.99
    NaHCO3          2.397e-04   2.774e-03    -3.620    -2.557     1.063      1.80
    NaOH            6.644e-13   7.686e-12   -12.178   -11.114     1.063       (0)
O(0)            4.419e-05
    O2              2.209e-05   2.556e-04    -4.656    -3.592     1.063     30.40
S(-2)           7.950e+00
    HS-             6.681e+00   2.983e+00     0.825     0.475    -0.350     23.65
    S-2             1.269e+00   1.139e-01     0.103    -0.943    -1.047       (0)
    H2S             7.129e-06   8.248e-05    -5.147    -4.084     1.063     37.16

----------------------------Saturation indices----------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)          -146.92   -149.72   -2.80  CH4
  CO2(g)            -7.37     -8.84   -1.47  CO2
  H2(g)            -41.44    -44.55   -3.10  H2
  H2O(g)            -1.66     -0.15    1.50  H2O
  H2S(g)            -3.03    -11.03   -7.99  H2S
  O2(g)             -0.70     -3.59   -2.89  O2   Pressure   0.2 atm, phi 1.000
  Sulfur            32.43     37.31    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-------------------------------------------
```

```
Beginning of batch-reaction calculations.
-------------------------------------------

Reaction step 1.

Using solution 1.   Tank Contents of 30% sodium hydrosulfide solution
Using pure phase assemblage 1.

-----------------------------Solution composition------------------------------

     Elements           Molality       Moles

     C                 1.000e-01   1.000e-01
     Na                9.424e+00   9.423e+00
     S                 7.950e+00   7.950e+00

----------------------------Description of solution----------------------------

                                       pH  =  11.501      Charge balance
                                       pe  =  -9.342      Adjusted to redox
                                       equilibrium
       Specific Conductance (µS/cm,  25°C)  = 504293
                            Density (g/cm³)  =   1.25232
                                 Volume (L)  =   1.18530
                          Activity of water  =   0.704
                             Ionic strength  =   1.064e+01
                          Mass of water (kg)  =   9.999e-01
                 Total alkalinity (eq/kg)  =   9.417e+00
                       Total CO2 (mol/kg)  =   9.680e-02
                         Temperature (°C)  =  25.00
                  Electrical balance (eq)  =   6.203e-11
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                                 Iterations  =  22
                                    Total H  = 1.176993e+02
                                    Total O  = 5.581131e+01

----------------------------Distribution of species----------------------------

                                                  Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             5.066e-03   2.262e-03    -2.295    -2.646    -0.350     10.53
   H+              4.517e-12   3.151e-12   -11.345   -11.501    -0.156      0.00
   H2O             5.551e+01   7.042e-01     1.744    -0.152     0.000     18.07
C(-4)          3.209e-03
   CH4             3.209e-03   3.716e-02    -2.494    -1.430     1.064     35.46
C(4)           9.680e-02
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   CO3-2           1.986e-02   2.077e-03    -1.702    -2.683    -0.981     11.97
   HCO3-           2.455e-04   1.396e-04    -3.610    -3.855    -0.245     52.22
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   CO2             1.213e-10   1.405e-09    -9.916    -8.852     1.064     34.43
   (CO2)2          3.127e-21   3.621e-20   -20.505   -19.441     1.064     68.87
H(0)           5.879e-09
   H2              2.940e-09   3.403e-08    -8.532    -7.468     1.064     28.61
Na             9.424e+00
   Na+             9.344e+00   3.412e+01     0.971     1.533     0.562      2.14
   NaCO3-          7.646e-02   1.320e+00    -1.117     0.120     1.237     52.02
   NaSO4-          2.931e-03   1.667e-03    -2.533    -2.778    -0.245     46.53
   NaHCO3          2.313e-04   2.678e-03    -3.636    -2.572     1.064      1.80
   NaOH            6.665e-13   7.717e-12   -12.176   -11.113     1.064      (0)
O(0)           0.000e+00
   O2              0.000e+00   0.000e+00   -78.812   -77.748     1.064     30.40
S(-2)          7.947e+00
```

```
      HS-              6.675e+00   2.980e+00     0.824     0.474    -0.350     23.65
      S-2              1.272e+00   1.142e-01     0.104    -0.942    -1.047     (0)
      H2S              7.093e-06   8.212e-05    -5.149    -4.086     1.064     37.16
S(6)           3.220e-03
      NaSO4-           2.931e-03   1.667e-03    -2.533    -2.778    -0.245     46.53
      SO4-2            2.891e-04   9.748e-06    -3.539    -5.011    -1.472     26.70
      HSO4-            1.730e-16   2.987e-15   -15.762   -14.525     1.237     42.41

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  CH4(g)             1.37     -1.43   -2.80  CH4
  CO2(g)            -7.38     -8.85   -1.47  CO2
  H2(g)             -4.37     -7.47   -3.10  H2
  H2O(g)            -1.66     -0.15    1.50  H2O
  H2S(g)            -3.03    -11.03   -7.99  H2S
  O2(g)            -74.86    -77.75   -2.89  O2
  Sulfur            -4.65      0.23    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 2.
------------------------------------

    TITLE --Part 2 water
    SOLUTION 2 water
         pH 7.0
         Temp   25.0
    EQUILIBRIUM_PHASES
        CO2(g)  -2.0
        Calcite 0.0
    SAVE solution 2
    END
-----
TITLE
-----

 --Part 2 water

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 2. water

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    Pure water

----------------------------Description of solution----------------------------

                                       pH  =   7.000
                                       pe  =   4.000
      Specific Conductance (µS/cm,  25°C)  = 0
                           Density (g/cm³)  =   0.99704
```

```
                                  Volume (L)  =   1.00297
                           Activity of water  =   1.000
                              Ionic strength  =   1.007e-07
                           Mass of water (kg)  =   1.000e+00
                     Total alkalinity (eq/kg)  =   1.217e-09
                        Total carbon (mol/kg)  =   0.000e+00
                           Total CO2 (mol/kg)  =   0.000e+00
                             Temperature (°C)  =  25.00
                      Electrical balance (eq)  =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.60
                                  Iterations  =   0
                                     Total H  = 1.110124e+02
                                     Total O  = 5.550622e+01

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol

   OH-             1.013e-07   1.012e-07    -6.995    -6.995    -0.000     -4.14
   H+              1.001e-07   1.000e-07    -7.000    -7.000    -0.000      0.00
   H2O             5.551e+01   1.000e+00     1.744     0.000     0.000     18.07
H(0)          1.416e-25
   H2              7.079e-26   7.079e-26   -25.150   -25.150     0.000     28.61
O(0)          0.000e+00
   O2              0.000e+00   0.000e+00   -42.080   -42.080     0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  H2(g)           -22.05    -25.15    -3.10  H2
  H2O(g)           -1.50      0.00     1.50  H2O
  O2(g)           -39.19    -42.08    -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 2.   water
Using pure phase assemblage 1.

-------------------------------Phase assemblage--------------------------------

                                                      Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)           -2.00    -3.47     -1.47    1.000e+01   9.998e+00  -1.976e-03
Calcite           0.00    -8.48     -8.48    1.000e+01   9.998e+00  -1.646e-03

-----------------------------Solution composition------------------------------

    Elements           Molality       Moles

    C                 3.622e-03   3.622e-03
    Ca                1.646e-03   1.646e-03

----------------------------Description of solution----------------------------
```

```
                                        pH  =   7.297      Charge balance
                                        pe  =  -1.575      Adjusted to redox
                                        equilibrium
        Specific Conductance (µS/cm,  25°C)  = 306
                             Density (g/cm³)  =   0.99726
                                  Volume (L)  =   1.00300
                          Activity of water   =   1.000
                             Ionic strength   =   4.826e-03
                         Mass of water (kg)   =   1.000e+00
                 Total alkalinity (eq/kg)     =   3.291e-03
                       Total CO2 (mol/kg)     =   3.622e-03
                         Temperature (°C)     =  25.00
                  Electrical balance (eq)     =  -1.217e-09
 Percent error, 100*(Cat-|An|)/(Cat+|An|)     =  -0.00
                                  Iterations  =  17
                                     Total H  = 1.110124e+02
                                     Total O  = 5.551511e+01

----------------------------Distribution of species----------------------------

                                                    Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity  Gamma   cm³/mol

   OH-             2.162e-07   2.005e-07    -6.665    -6.698   -0.033     -4.07
   H+              5.401e-08   5.048e-08    -7.268    -7.297   -0.029      0.00
   H2O             5.551e+01   9.999e-01     1.744    -0.000    0.000     18.07
C(-4)          1.401e-25
   CH4             1.401e-25   1.403e-25   -24.854   -24.853    0.000     35.46
C(4)           3.622e-03
   HCO3-           3.224e-03   2.998e-03    -2.492    -2.523   -0.032     24.73
   CO2             3.399e-04   3.403e-04    -3.469    -3.468    0.000     34.43
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342   -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255    0.000    -14.60
   CO3-2           3.724e-06   2.785e-06    -5.429    -5.555   -0.126     -5.13
   (CO2)2          2.123e-09   2.125e-09    -8.673    -8.673    0.000     68.87
Ca             1.646e-03
   Ca+2            1.591e-03   1.189e-03    -2.798    -2.925   -0.126    -18.02
   CaHCO3+         4.887e-05   4.549e-05    -4.311    -4.342   -0.031      9.70
   CaCO3           5.559e-06   5.565e-06    -5.255    -5.255    0.000    -14.60
   CaOH+           4.213e-09   3.910e-09    -8.375    -8.408   -0.032      (0)
H(0)           5.090e-15
   H2              2.545e-15   2.548e-15   -14.594   -14.594    0.000     28.61
O(0)           0.000e+00
   O2              0.000e+00   0.000e+00   -63.193   -63.192    0.000     30.40

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  Aragonite         -0.14     -8.48   -8.34  CaCO3
  Calcite            0.00     -8.48   -8.48  CaCO3
  CH4(g)           -22.05    -24.85   -2.80  CH4
  CO2(g)            -2.00     -3.47   -1.47  CO2  Pressure   0.0 atm, phi 1.000
  H2(g)            -11.49    -14.59   -3.10  H2
  H2O(g)            -1.50     -0.00    1.50  H2O
  O2(g)            -60.30    -63.19   -2.89  O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------
```

```
383   ------------------------------------
384   Reading input data for simulation 3.
385   ------------------------------------
386
387       TITLE -- Part 3 mix the two
388       MIX 1
389           1   0.001
390           2   0.999
391       SAVE solution  3
392       END
393   -----
394   TITLE
395   -----
396
397    -- Part 3 mix the two
398
399   ----------------------------------------
400   Beginning of batch-reaction calculations.
401   ----------------------------------------
402
403   Reaction step 1.
404
405   Using mix 1.
406
407   Mixture 1.
408
409         1.000e-03 Solution 1  Solution after simulation 1.
410         9.990e-01 Solution 2  Solution after simulation 2.
411
412   -----------------------------Solution composition------------------------------
413
414       Elements           Molality       Moles
415
416       C                 3.718e-03   3.718e-03
417       Ca                1.644e-03   1.644e-03
418       Na                9.424e-03   9.423e-03
419       S                 7.950e-03   7.950e-03
420
421   ----------------------------Description of solution----------------------------
422
423                                       pH  =   9.515      Charge balance
424                                       pe  =  -6.726      Adjusted to redox
                                          equilibrium
425         Specific Conductance (µS/cm,  25°C)  = 1217
426                              Density (g/cm³)  =   0.99763
427                                   Volume (L)  =   1.00312
428                           Activity of water  =   1.000
429                              Ionic strength  =   1.362e-02
430                           Mass of water (kg)  =   1.000e+00
431                  Total alkalinity (eq/kg)  =   1.235e-02
432                           Total CO2 (mol/kg)  =   3.536e-03
433                             Temperature (°C)  =  25.00
434                    Electrical balance (eq)  =  -1.215e-09
435    Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
436                                   Iterations  =  19
437                                      Total H  = 1.110191e+02
438                                      Total O  = 5.551540e+01
439
440   ----------------------------Distribution of species----------------------------
441
442                                                 Log       Log       Log    mole V
443     Species          Molality    Activity  Molality  Activity     Gamma   cm³/mol
444
445     OH-             3.738e-05   3.312e-05    -4.427    -4.480    -0.052     -4.01
```

```
      H+              3.382e-10   3.055e-10    -9.471    -9.515    -0.044      0.00
      H2O             5.551e+01   9.996e-01     1.744    -0.000     0.000     18.07
C(-4)              1.818e-04
      CH4             1.818e-04   1.824e-04    -3.740    -3.739     0.001     35.46
C(4)               3.536e-03
      HCO3-           2.480e-03   2.214e-03    -2.606    -2.655    -0.049     24.79
      CO3-2           5.353e-04   3.399e-04    -3.271    -3.469    -0.197     -4.95
      CaCO3           4.262e-04   4.276e-04    -3.370    -3.369     0.001    -14.60
      NaCO3-          5.929e-05   5.269e-05    -4.227    -4.278    -0.051     -0.89
      CaHCO3+         2.364e-05   2.115e-05    -4.626    -4.675    -0.048      9.73
      NaHCO3          1.033e-05   1.037e-05    -4.986    -4.984     0.001      1.80
      CO2             1.516e-06   1.521e-06    -5.819    -5.818     0.001     34.43
      (CO2)2          4.233e-14   4.247e-14   -13.373   -13.372     0.001     68.87
Ca                 1.644e-03
      Ca+2            1.180e-03   7.488e-04    -2.928    -3.126    -0.198    -17.88
      CaCO3           4.262e-04   4.276e-04    -3.370    -3.369     0.001    -14.60
      CaHCO3+         2.364e-05   2.115e-05    -4.626    -4.675    -0.048      9.73
      CaSO4           1.367e-05   1.371e-05    -4.864    -4.863     0.001      7.50
      CaOH+           4.576e-07   4.067e-07    -6.340    -6.391    -0.051      (0)
      CaHSO4+         3.098e-14   2.753e-14   -13.509   -13.560    -0.051      (0)
H(0)               3.730e-09
      H2              1.865e-09   1.871e-09    -8.729    -8.728     0.001     28.61
Na                 9.424e-03
      Na+             9.349e-03   8.326e-03    -2.029    -2.080    -0.050     -1.36
      NaCO3-          5.929e-05   5.269e-05    -4.227    -4.278    -0.051     -0.89
      NaHCO3          1.033e-05   1.037e-05    -4.986    -4.984     0.001      1.80
      NaSO4-          4.814e-06   4.297e-06    -5.318    -5.367    -0.049     14.47
      NaOH            2.749e-17   2.758e-17   -16.561   -16.559     0.001      (0)
O(0)               0.000e+00
      O2              0.000e+00   0.000e+00   -74.926   -74.924     0.001     30.40
S(-2)              7.768e-03
      HS-             7.746e-03   6.864e-03    -2.111    -2.163    -0.052     20.68
      H2S             1.828e-05   1.833e-05    -4.738    -4.737     0.001     37.16
      S-2             4.299e-06   2.714e-06    -5.367    -5.566    -0.200      (0)
S(6)               1.818e-04
      SO4-2           1.633e-04   1.030e-04    -3.787    -3.987    -0.200     14.83
      CaSO4           1.367e-05   1.371e-05    -4.864    -4.863     0.001      7.50
      NaSO4-          4.814e-06   4.297e-06    -5.318    -5.367    -0.049     14.47
      HSO4-           3.441e-12   3.058e-12   -11.463   -11.515    -0.051     40.36
      CaHSO4+         3.098e-14   2.753e-14   -13.509   -13.560    -0.051      (0)

------------------------------Saturation indices-------------------------------

  Phase               SI** log IAP   log K(298 K,   1 atm)

  Anhydrite         -2.84     -7.11   -4.28  CaSO4
  Aragonite          1.74     -6.59   -8.34  CaCO3
  Calcite            1.89     -6.59   -8.48  CaCO3
  CH4(g)            -0.94     -3.74   -2.80  CH4
  CO2(g)            -4.35     -5.82   -1.47  CO2
  Gypsum            -2.53     -7.11   -4.58  CaSO4:2H2O
  H2(g)             -5.63     -8.73   -3.10  H2
  H2O(g)            -1.50     -0.00    1.50  H2O
  H2S(g)            -3.69    -11.68   -7.99  H2S
  O2(g)            -72.03    -74.92   -2.89  O2
  Sulfur            -4.04      0.84    4.88  S

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
  For ideal gases, phi = 1.

------------------
End of simulation.
------------------
```

```
510   -----------------------------------
511   Reading input data for simulation 4.
512   -----------------------------------
513
514   ------------------------------
515   End of Run after 0.01 Seconds.
516   ------------------------------
517
518
```

Appendix C. Diffusion Models Script

C:\cygwin64\home\cwen461\work\octave\nahs\h2s_diff.m 1

```
# h2s_diff.m will calculate diffusion through liquid and gas phases along with
volatilization fluc rate of hydrogen sulfide from water.
clear all;

t = [0:100];   #seconds
z = [0:200];   # cm

MW = 34.076;  #g/mol
sol = 5.66; # g/L
Vp = 13376; # vapor pressure mmHg  (17.6 atm)
Hl = 9.8;  # Henry's Law constant atm/mole/L


diffw = 2e-5;  # diffusion coefficient water  (cm^2/sec) 25C
diffa = 0.166;  # diffusion coefficient air (cm^2/sec) 25C

volw = 3946.5;  #volume of water (gallons)
volw = volw * 3.7854;  # (L)
#sa = 8*43; # water surface area in tank (ft^2)
#sa = sa * 929.0304;  # surface area (cm^2)
sa = 7.6e4;     #(cm^2)

conc = 8.88e-6;  # (mole/L)  calcluted with PHREEQC NaHS soln at pH = 11.5 25C
concg = conc * MW;  # g/L
tmass = conc*volw;  #(grams)


x = conc/55.55; # mole fraction (moles h2s / mole water)
y = conc * Hl;  #mole fraction gas phase (equals partial pressure (atm))

xl = conc/1000;  # mole/cm^3 liquid phase
yl = y/24400;  # mole/cm^3 gas phase  mole air = 24.4L at 25C 1000cm^3/L


##########################################
#  flux calculations in gas phase
# t = 60 seconds flux at surface z=0

jxt60 = (diffa/(pi*60))^(0.5)*yl    # flux mole/(cm^2 sec) at 60 seconds
jxt600 = (diffa/(pi*600))^(0.5)*yl    # flux mole/(cm^2 sec) at 600 seconds
jxt6000 = (diffa/(pi*6000))^(0.5)*yl    # flux mole/(cm^2 sec) at 6000 seconds
jxt60000 = (diffa/(pi*60000))^(0.5)*yl    # flux mole/(cm^2 sec) at 60000 seconds

# concentration calculations

eta60 = (4*diffa*60)^(-0.5)*z;
eta600 = (4*diffa*600)^(-0.5)*z;
eta6000 = (4*diffa*6000)^(-0.5)*z;
eta60000 = (4*diffa*60000)^(-0.5)*z;
eta600000 = (4*diffa*600000)^(-0.5)*z;
eta6000000 = (4*diffa*6000000)^(-0.5)*z;
eta60000000 = (4*diffa*60000000)^(-0.5)*z;


cz60 = y*ones(size(z)) - y * erf(eta60);
cz600 = y*ones(size(z)) - y * erf(eta600);
cz6000 = y*ones(size(z)) - y * erf(eta6000);
cz60000 = y*ones(size(z)) - y * erf(eta60000);
cz600000 = y*ones(size(z)) - y * erf(eta600000);
cz6000000 = y*ones(size(z)) - y * erf(eta6000000);
cz60000000 = y*ones(size(z)) - y * erf(eta60000000);

figure(1)

```

Monday, July 10, 2017 3:18 PM

```
64  plot(z,cz60,z,cz600,z,cz6000,z,cz60000,z,cz600000,z,cz6000000,z,cz60000000), xlabel(
    "Diffusion into Headspace (cm) "),...
65   ylabel("Gas Phase Mole Fraction H_2S "), title("Gas Phase Diffusion of H_2S
     t=(1,10,100,1000,..1e6) minutes)")
66
67  print -dpdf fig1.pdf
68  print -dpng fig1.png
69
70
71   ##################################################
72  # consider constant liquid diffusion to ss
73
74  t1 = 6*logspace(2,9);
75
76  i=0;
77  for j = 1:length(t1);
78  i=i+1;
79  eta(i,:) = ((4*diffw*t1(j))^(-0.5))*z;
80  cz(i,:) = x*erfc(eta(i,:));  # x is mole fraction
81  end;
82
83  figure(2)
84  mesh(cz), xlabel("Distance (cm)"),ylabel("Time (sec)"), zlabel("Liquid Phase Mole
    Fraction of H_2S"), title('Depth of H_2S Diffusion as t \rightarrow \infty')
85  print -dpdf fig2.pdf
86  print -dpng fig2.png
87
88  figure(3)
89  plot(z,cz),xlabel("Distance (cm)"), ylabel("Liquid Phase Mole Fraction of H_2S"),
    title('Depth of H_2S Diffusion as t \rightarrow \infty')
90
91  print -dpdf fig3.pdf
92  print -dpng fig3.png
93
94  figure(4)
95  plot(z,cz(32,:),z,cz(33,:)), xlabel("Distance (cm)"), ylabel("Liquid Phase Mole
    Fraction of H_2S"), title("Depth of H_2S Diffusion at t = 186 and 259 days")
96
97  print -dpdf fig4.pdf
98  print -dpng fig4.png
99
100 front_speed1 = (90-77)/(t1(33)-t1(32))*(3600*24)   # cm/day
101 cz(32,77)
102 cz(33,90)
103
104 dist_180_1 = front_speed1 * 180
105
106 depth = 1000*volw/sa
107
108 # check fourier number  z^2/(diff*time)
109 #  assume 100 cm
110
111 diff_time = 100^2/diffw     # 100cm  time for 100cm saturation
112 diff_depth_6_mo = (diffw*1.555e7)^(0.5)     # diffusion depth in 6 months using
    Fourier number
113
114 ########################################
115 # consider pulse solution
116
117 t2 = 6*logspace(1,8);
118
119 i=0;
120 for j = 1:length(t2);
121 i=i+1;
```

```
122   c(i,:) = (tmass*(4*pi*diffw*t2(j)).^(-0.5)).*exp(-z.^2/(4*pi*diffw*t2(j)));  # (
      grams/cm^3)
123   end;
124
125   figure(5)
126   mesh(c), xlabel("Distance (cm)"),ylabel("Time (sec)"), zlabel("Liquid Phase Mole
      Fraction of H_2S"), title('Pulse Release Depth of H_2S Diffusion as t \rightarrow
      \infty')
127
128   print -dpdf fig5.pdf
129   print -dpng fig5.png
130
131   figure(6)
132   plot(z,c),xlabel("Distance (cm)"), ylabel("Liquid Phase Mole Fraction of H_2S"),
      title('Pulse Release Depth of H_2S Diffusion as t \rightarrow \infty')
133
134   print -dpdf fig6.pdf
135   print -dpng fig6.png
136
137   figure(7)
138   plot(z,c(38:50,:)), xlabel("Distance (cm)"), ylabel("Liquid Phase Mole Fraction of
      H_2S"), title("Depth of H_2S Diffusion from 134 to 6944 days")
139
140   print -dpdf fig7.pdf
141   print -dpng fig7.png
142
143   figure(8)
144   plot(z,c(39,:),z,c(40,:)), xlabel("Distance (cm)"), ylabel("Liquid Phase Mole
      Fraction of H_2S"), title("Depth of H_2S Diffusion at t = 186 and 259 days")
145
146   print -dpdf fig8.pdf
147   print -dpng fig8.png
148
149   c(39,112)
150   c(40,130)
151
152   front_speed2 = (130-112)/(t2(40)-t2(39))*(3600*24)    # cm/day
153   dist_180_2 = front_speed2 * 180
154
155   t2(39)/2.592e6     # months
156
157   c(39,1)
158
159
160
161
162
163
164
165
166
167
168
```

Appendix D. Pulse Release Air Model Script

C:\cygwin64\home\cwen461\work\octave\nahs\air.m 1

```
% air.m    air modeling for nahs release at holden
%  graphics_toolkit gnuplot
clear all;
clf();

s_x=14.9;  % dispersion coefficient (meters)
s_y = s_x;  % table 8.8 s_x = 9.44*x/1000 + 1.5
s_z = 3.5;  % at 1500 m table 8.9 for stable s_z = 3.2x/1000+0.75
u = 12;  % wind speed (m/s)
q_m = 6000;  %  release mass (mg)
x1 = 0;
  %for x=1:10:2000
  for x=1:1:2000
    x1 = x1+1;
      for t=1:200

          s_x = 9.44*x/1000+1.5;
                s_y = s_x;
                s_z = 3.2*x/1000+0.75;
          c(x1,t) = (q_m/(2^(0.5)*pi^(3/2)*s_x*s_y*s_z))*exp(-0.5*(((x-u*t)/s_x)^2
          ));  % mg/m^3

end;
end;

figure(1)

plot(c(:,125),"linewidth",3), xlabel('Distance from Release (meters)'), ylabel(
'H_2S Concentration (mg/m^3)'), ...
  title('Plume after 125 seconds with 12 m/s wind (IDLH 100 ppm)')
  grid

print -dpdf air.pdf
print -dpng air.png
%print -deps -color air.eps

  c_max = max(c(:,125))
c_max_ppm = c_max*24.4/29    %  24.4 L/mole at 25C and air 29 g/mole

figure(2)

plot(24.4/29*c(:,125),"linewidth",3), xlabel('Distance from Release (meters)'),
ylabel('H_2S Concentration (ppm)'), ...
  title('Plume after 125 seconds with 12 m/s wind (IDLH 100 ppm)')
  grid

print -dpdf air_ppm.pdf
print -dpng air_ppm.png
%print -deps -color air_ppm.eps

figure(3)

plot(24.4/29*c(:,9),"linewidth",3), xlabel('Distance from Release (meters)'), ylabel
('H_2S Concentration (ppm)'), ...
  title('Plume after 9 seconds with 12 m/s wind (IDLH 100 ppm)')
  grid

print -dpdf air_ppm_nearby.pdf
print -dpng air_ppm_nearby.png
%print -deps -color air_ppm_nearby.eps


```

Monday, July 10, 2017 3:17 PM