

Use of MgO to Mitigate the Effect of Microbial CO₂ Production in the Waste Isolation Pilot Plant

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Introduction

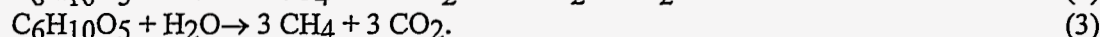
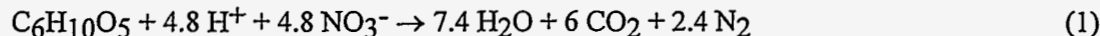
The Waste Isolation Pilot Plant (WIPP), located in a salt bed in southern New Mexico, is designed by U.S. Department of Energy to demonstrate the safe and permanent disposal of design-basis transuranic waste. WIPP performance assessment requires consideration of radionuclide release in brines in the event of inadvertent human intrusion. The mobility of radionuclides depends on chemical factors such as brine pH (-log molality of H⁺) and CO₂ fugacity. According to current waste inventory estimates, a large quantity (~ 10⁹ moles C) of organic materials will be emplaced in the WIPP (DOE/CAO, 1996). Those organic material will potentially be degraded by halophilic or halotolerant microorganisms in the presence of liquid water in the repository, especially if a large volume of brine is introduced into the repository by human intrusions. Organic material biodegradation will produce a large amount of CO₂, which will acidify the WIPP brine and thus significantly increase the mobility of actinides. This communication addresses (1) the rate of organic material biodegradation and the quantity of CO₂ to be possibly generated, (2) the effect of microbial CO₂ production on overall WIPP performance, and (3) the mechanism of using MgO to mitigate this effect.

Microbial CO₂ Production

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The occurrence of microbial gas generation in the repository will depend on: (1) whether microbes capable of consuming the emplaced organic materials will be present and active; (2) whether sufficient electron acceptors will be present and available; (3) whether enough nutrients will be present and available (Brush, 1995). Apparently, all these factors can not be evaluated accurately based on our current knowledge. Because of these uncertainties, we are not able to either eliminate the possibility of the occurrence microbial gas generation or propose that microbial gas generation will certainly occur in the repository. In order to bracket all the possibilities, we assume that only half realizations will have significant microbial gas generation in WIPP performance assessment calculations.

The biodegradation of organic materials follows the sequence of the following reaction pathways, according to the order of decreasing energy yield per carbon atom in each reaction (Berner, 1980; Brush, 1995; Wang and Van Cappellen, 1996):



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We ignore the reaction pathways of aerobic respiration, dissimilatory Mn(IV) and Fe(III) reduction, since the quantities of O₂, Mn(IV) and Fe(III) initially present in the repository will be negligible relative to the other electron acceptors. In Reactions (1) through (3), biomass accumulation is also not taken into account. This is because significant biomass accumulation seems unlikely in the WIPP repository and the accumulated biomass, if any, will be recycled by microbes after all biodegradable cellulose is consumed.

Cellulose, plastics, and rubber are identified as major components of organic materials to be emplaced in the WIPP (DOE/CAO, 1996). Cellulose is much more biodegradable than the other components and its biodegradation rates have been experimentally measured under anticipated WIPP conditions (Francis and Gillow, 1994; Francis et al., 1997). The rate of cellulose biodegradation was determined by incubating representative cellulosic materials (filter paper, paper towels, and tissue) in WIPP brine with microbes enriched from various WIPP environments (Francis & Gillow, 1994; Francis et al., 1997). The incubation experiments were conducted under various conditions: aerobic or anaerobic, inundated or humid, with or without bentonite, and amended or unamended with nutrients or NO₃⁻. Because the repository is expected to become anoxic shortly after waste emplacement and also because bentonite will not be added with the waste according to the current waste emplacement plan, the experimental data from anaerobic incubation without bentonite present are most relevant to expected WIPP conditions. Considering that the current experimental data are mostly for denitrification (Reaction 1), but not sulfate reduction (Reaction 2) and methanogenesis (Reaction 3) (Francis & Gillow, 1994; Francis et al., 1997), we assume that the range of denitrification rate can apply to sulfate reduction and methanogenesis.

CO₂ production data is used to estimate the rates of cellulose biodegradation, for two reasons: (1) there are experimental data available on the CO₂ dissolution in WIPP brine (Telander and Westerman, 1997) and, therefore, it is easy to correct the CO₂ production data for gas dissolved in the brine; (2) since cellulose biodegradation did not reach the stage of methanogenesis in the experiments, according to Reactions 1 and 2, the consumption of one mole carbon of cellulose will produce one mole of CO₂. This 1:1 relationship is independent of oxidation state of carbon in cellulose. Therefore, it is rather straightforward to determine the amount of cellulose biodegraded from the amount of CO₂ produced.

Experimental data show a strong dependence of CO₂ generation on the concentrations of nutrients and nitrate (Figure 1). The maximum CO₂ generation was observed in nitrate-and-nutrient-amended samples. In those experiments, after a short lag phase, CO₂ first linearly increased with time and then approached some limiting value as its production rate diminished (Figure 1). If we assume that biodegradation is nitrate- or nutrient-limited, the experimental data can be explained by Michaelis-Menten kinetics (Chapelle, 1993). Michaelis-Menten kinetics, which describes the dependence of microbial reaction rate on substrate concentration, can be expressed by:

$$V = \frac{V_{\max} S}{K_s + S} \quad (4)$$

where V is the microbial reaction rate; V_{\max} is the maximum value of the rate; S is the concentration of the limiting substrate; K_s is a constant. Equation (5) states that the microbial

reaction rate becomes independent of the substrate concentration, if the latter is high enough, i.e. $S \gg K_s$ and $V = V_{\max}$. In this circumstance, the reaction product accumulates linearly with time before the substrate is sufficiently depleted. In other words, in our cases, the linear part of CO_2 vs. time curve gives the estimate of the maximum rate of cellulose biodegradation.

From Figure 1 and with a correction for CO_2 dissolved in the brine in the experiments, we estimate the maximum and minimum rates of cellulose biodegradation under inundated conditions to be 0.3 and 0.01 mole C/kg/year, respectively. The maximum rate is estimated from the data obtained from both NO_3^- - and nutrients-amended experiments, whereas the minimum rate is derived from the data obtained from the inoculated-only experiments without any nutrient and NO_3^- amendment. Under humid conditions, experimental data show no clear correlation between CO_2 production and nutrient concentration (Francis et al., 1997). The best estimate of the maximum rate of cellulose biodegradation under humid condition is 0.04 mole C/kg/year. The minimum of the humid biodegradation rate is set to 0, corresponding to the cases where microbes become inactive due to nutrient and water stress. Under brine-inundated conditions, at the maximum rate, all organic materials will be biodegraded in ~ 200 years.

The rates of plastics and rubber biodegradation under expected WIPP conditions were measured by Francis et al. (1997). The experimental data show that plastics and rubbers are much less biodegradable than cellulose, although the data themselves are not sufficient for us to constrain the long-term biodegradation rate for plastics and rubbers. There are two factors that may potentially increase the biodegradability of those materials: long time scale and cometabolism. Over a time scale of 10,000 years, plastics and rubbers may change their chemical properties and therefore their biodegradability. Cometabolism means that microbes degrade an organic compound but do not use it as a source of energy or of their constituent elements, all of which are derived from other substrates (Alexander, 1994, p. 177-192). In the WIPP repository, plastics and rubbers, which are resistant to biodegradation, may still be cometabolized with cellulose and other more biodegradable organic compounds. Because of these uncertainties, we recommend a 50% chance for the biodegradation of plastics and rubbers in the event of significant microbial gas generation for the WIPP performance assessment. We further suggest lumping plastics and rubbers into cellulose and applying the ranges of cellulose biodegradation rate to plastics and rubbers. This treatment is conservative in respect of repository pressurization and actinide solubility.

Based on the inventory estimates for nitrate (2.6×10^7 moles) and sulfate (6.6×10^6 moles) (DOE/CAO, 1996), the fractions of individual biodegradation pathways (Reactions (1) through (3)) are estimated to be: denitrification - 4%, sulfate reduction - 2%, and methanogenesis - 94%. Note that methanogenesis produces one half mole of carbon dioxide per mole of organic carbon consumed. With total organic carbon inventory of 10^9 moles C, we estimate that about 5×10^8 moles of CO_2 will be generated in the repository, if organic materials are completely biodegraded.

Impact of CO_2 Production on Repository Chemistry

Although the actual CO_2 partial pressure in the repository is not easy to estimate without consideration of detail mass transfer between the repository and its surrounding geologic media, a simple thermodynamic calculation, based on the real gas model developed by Duan et al. (1992) for a pure CO_2 system, indicates that the CO_2 partial pressure can reach the lithostatic

pressure, if all CO₂ generated by microbial reactions is contained in the repository. The accumulation of CO₂ in the repository has two significant impacts on WIPP brine chemistry: (1) It will acidify the brine, through the dissolution of carbon dioxide and the dissociation of carbonic acid in the brine, and (2) it will increase the concentrations of carbonate species capable of forming stable complexes with actinides in the solution. Therefore, overall, the microbial production of CO₂ in the repository will significantly enhance the mobility of actinide in the brine release.

According to the human intrusion scenarios developed in WIPP performance assessment, in which boreholes will possibly penetrate the repository or the brine pockets in Castile formation below the repository, two types of brines will be involved in radionuclide release after a human intrusion: Salado brine and Castile brine. The former, represented by brine A, is derived from the geologic formation where the repository is located, whereas the latter, represented by brine ERDA-6, is derived from the brine pockets in the geologic formations below the repository. The composition of the two brines is listed in Table 1. The pH of the original brines is close to neutral values. In order to study the brine pH changes as the repository becomes pressurized with CO₂ gas, a reaction-path model calculation has been conducted with the computer code EQ3/6 v. 7.2a (Wolery, 1992; Wolery and Daveler, 1992). In the calculation, we have assumed that the CO₂ dissolution and dissociation in the brine is the main factor causing brine acidification. The calculation shows that the brine pmH can be as low as 4.5 and the CO₂ fugacity can be as high as 55 atm, if the repository is pressurized with CO₂ up to the lithostatic pressure of ~ 150 atm (Figure 2). Under such chemical conditions, the solubility of actinides in the brine is expected to be considerably high.

Chemical Control

In order to mitigate the detrimental effect of microbial CO₂ generation on the WIPP performance, a sufficient amount of MgO (2x10⁹ moles) will be added to the repository as a backfill. MgO will react with brine and CO₂ through the following reactions:



Reaction (6) will buffer CO₂ fugacity (f_{CO_2}) at ~ 10⁻⁷ atm. This low CO₂ fugacity implies that Reaction (6) will practically remove all CO₂ from both gaseous and liquid phases. The mineral formation and brine pH resulting from MgO reactions have been calculated with computer code EQ3/6 v. 7.2a. The calculation shows that the addition of sufficient MgO into the repository will buffer pmH at 9.2 for Salado brine and at 9.9 for Castile brines (Figure 3). Under those chemical conditions, actinide solubility becomes minimal (Novak and Moore, 1996). Therefore, MgO backfill can effectively mitigate the effect of microbial CO₂ generation and control the repository chemistry within a desired range.

The EQ3/6 v. 7.2a calculation indicates that the mineral equilibrium between Mg(OH)₂ and MgCO₃ constitutes a chemical invariant point. At this chemical invariant point, the brine pH is essentially determined, e.g. for the Castile brine, by the following equations describing reaction equilibria and charge balance:

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2} f_{\text{CO}_2} \quad (7)$$

$$a_{\text{HCO}_3^-} a_{\text{H}^+} = K_{\text{H}_2\text{CO}_3} a_{\text{H}_2\text{CO}_3} \quad (8)$$

$$a_{\text{CO}_3^{2-}} a_{\text{H}^+} = K_{\text{HCO}_3^-} a_{\text{HCO}_3^-} \quad (9)$$

$$a_{\text{H}^+} a_{\text{OH}^-} = K_w \quad (10)$$

$$a_{\text{Mg}^{2+}} a_{\text{OH}^-}^2 = K_{\text{Mg(OH)}_2} \quad (11)$$

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = K_{\text{CaCO}_3} \quad (12)$$

$$2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] = \text{constant} \quad (13)$$

where a_i is the activity of chemical species i ; K_i is the equilibrium constant of a dissociation or mineral dissolution reaction i . Note that f_{CO_2} in Equation (7) is constant and fixed by the equilibrium constraint on Reaction (6). Thus, Equations (7) through (13) constitute a closed system for $[\text{H}^+]$. A similar set of equations can be written for the Salado brine. The above equations show that the brine pmH depends on the activity coefficients of the involved chemical species, the charge balance constant appearing in the right hand side of Equation (13), and which stable mineral phases form. This is why the MgO reactions give rise to different pmH values for Castile and Salado brines, although the f_{CO_2} remains the same for both cases.

The presence of Ca(OH)_2 as cementitious materials in the waste can also affect WIPP brine pmH and f_{CO_2} . A thermodynamic calculation shows that a sufficiently high ratio of Ca(OH)_2 to water can shift the chemical system from the chemical invariant point of $\text{Mg(OH)}_2/\text{MgCO}_3$ to the chemical invariant point of $\text{CaCO}_3/\text{Ca(OH)}_2$. At the point of $\text{CaCO}_3/\text{Ca(OH)}_2$, the brine pmH is buffered at 13 for Castile brine and 12 for Salado brine. However, based on the current inventory estimate for Ca(OH)_2 , which is about 8×10^6 moles, the overall possibility for the WIPP chemistry to be controlled by the chemical invariant point of $\text{CaCO}_3/\text{Ca(OH)}_2$ is low. This is because the amount of Ca(OH)_2 present in the waste is relatively small and it can be easily consumed by reaction either with microbially generated CO_2 or with MgCl_2 in Salado brine. Considering that actinide solubility is higher at the chemical invariant point of $\text{Mg(OH)}_2/\text{MgCO}_3$ (Novak & Moore, 1996), we recommend using this actinide solubility for the WIPP performance calculations.

Conclusion

A large quantity of CO_2 may be generated by the microbial degradation of organic materials in the WIPP. The microbial production of CO_2 in the repository will significantly enhance the mobility of actinide in the brine release. This detrimental effect can be effectively mitigated by adding MgO backfill. The MgO backfill reactions will practically remove all CO_2 from both gaseous and liquid phases and buffer the brine pmH within a desired range, thus significantly improving the WIPP performance. Also, because the MgO reactions will maintain constant chemical conditions over the whole 10,000 year regulatory time period, adding MgO reduces uncertainties in the prediction of actinide mobility for the long-term WIPP performance assessment.

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Table 1. Major element composition of the representative WIPP brines (Brush, 1990, p. 20-22)

	Salado brine Brine-A	Castile brine ERDA-6
Ca ²⁺ (mM)	20	12
Cl ⁻ (M)	5.35	4.8
K ⁺ (mM)	770	97
Mg ²⁺ (M)	1.44	0.019
Na ⁺ (M)	1.83	4.87
pH	6.5	6.17
SO ₄ ²⁻ (mM)	40	170
TDS (mg/l)	306,000	330,000
TIC (mM)	10	16

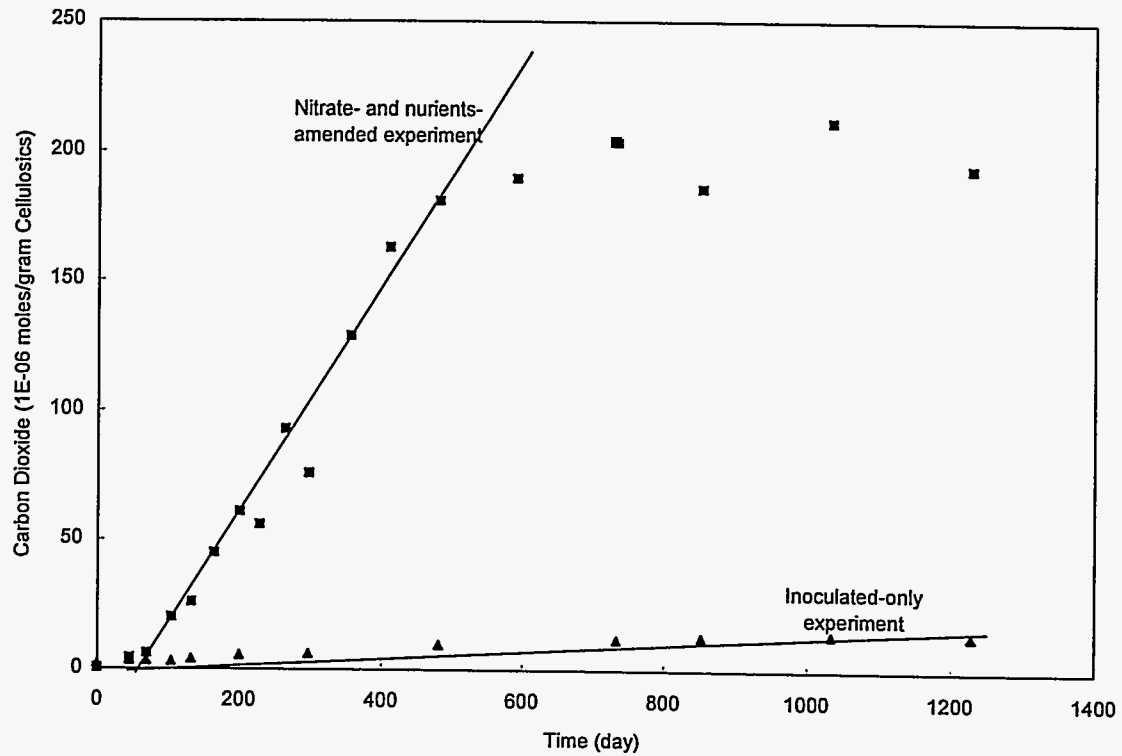


Figure 1. Amount of carbon dioxide accumulated in the head space in anaerobic and brine-inundated cellulotics biodegradation experiments (Francis et al., 1997).

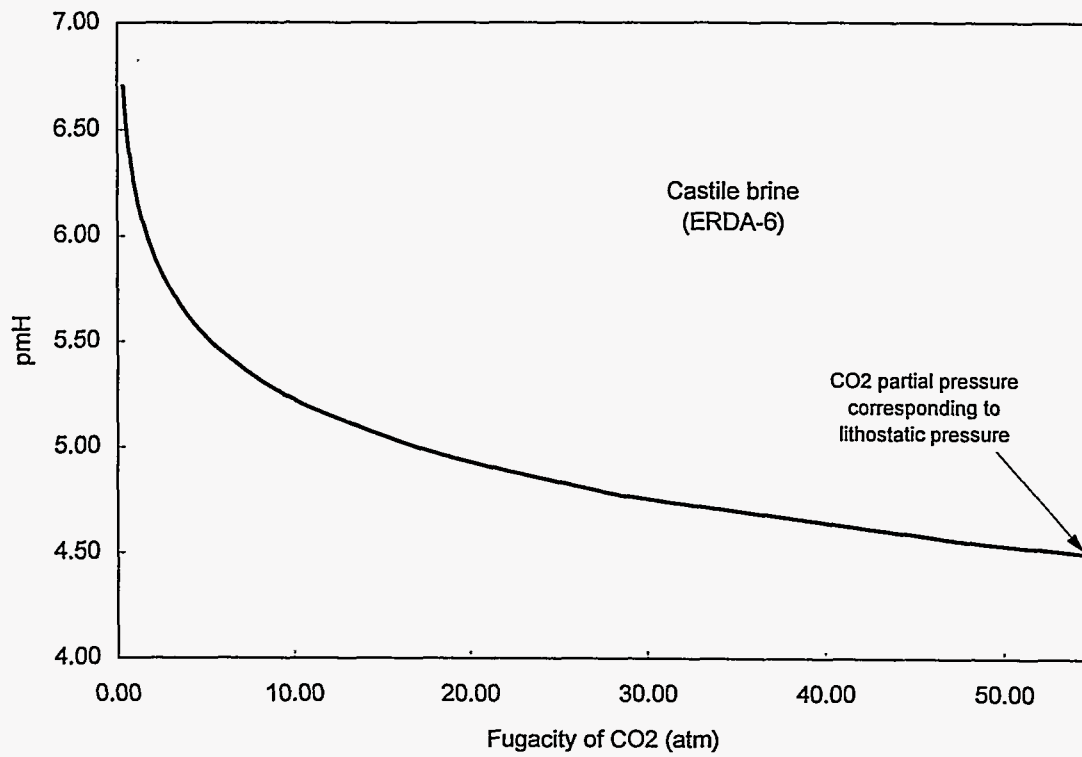
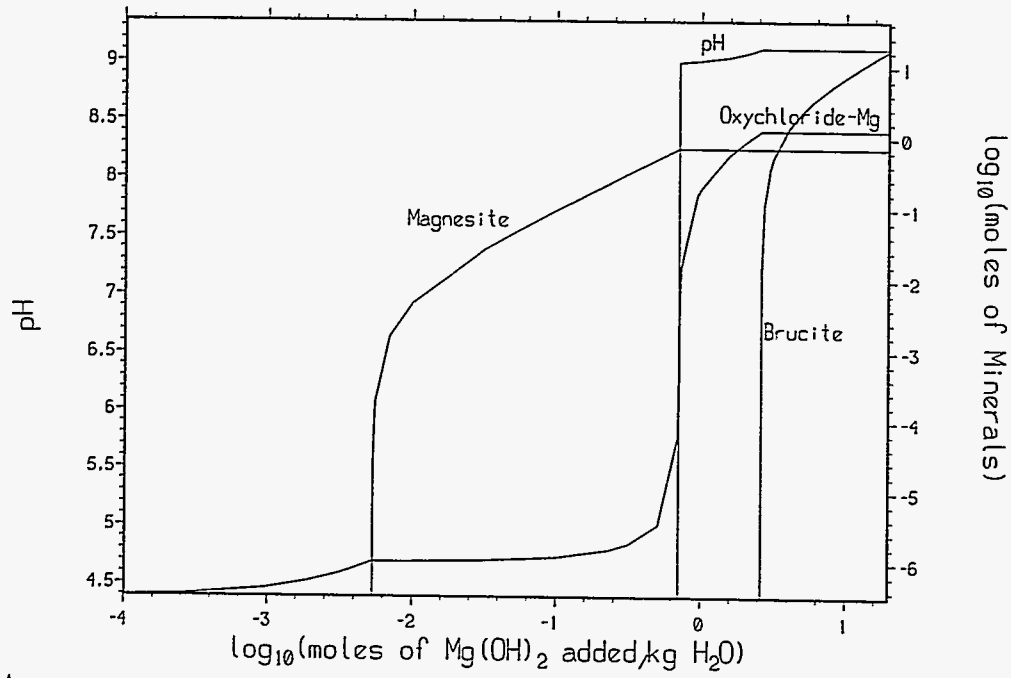
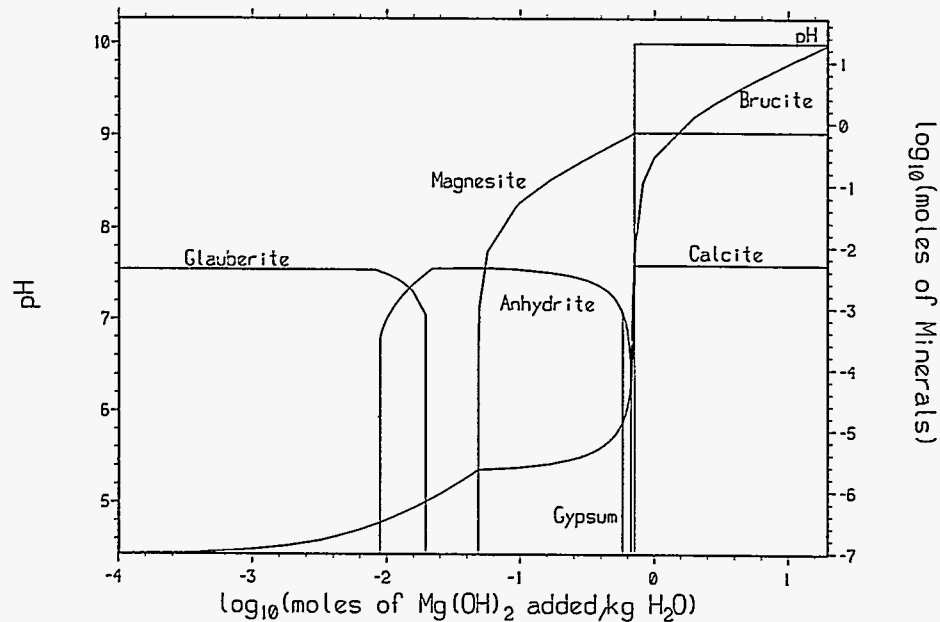


Figure 2. The pmH of Castile brine (ERDA6) as a function of CO₂ fugacity.



A



B

Figure 3. Mineral formation and pmH changes as $\text{Mg}(\text{OH})_2$ is added to WIPP brines: (A) Brine-A and (B) ERDA-6

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