WPO 36214

Mass of MgO that could be added as backfill in theWIPP and the mass of MgO required to saturate the brine and react with the CO_2 generated by microbial processes.

WBS No:0517.110120

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SWCFA:WBS 1.1.01.2: Source Term:Backfill Calculations

Scope of Analysis

The objectives of this analysis is to calculate the mass of MgO backfill that could be emplaced in the total free volume of the WIPP, calculate the amount of MgO required to react will all the CO_2 generated from microbial processes, and calculate the amount of MgO that will be dissolved in Castile brine and a mixture of 90% Castile and 10% Salado Brine.

This analysis was performed by hand calculations using information from the literature.

Andrew C. Peterson performed these calculations.

The following assumptions are made.

The bulk density of MgO is 0.5 of the crystalline density.
The volume of brine to be chemically controlled is $1.0x10^6$ m^3.
(This assumption is based on personal communication from Kurt Larson)
The brine composition is (a) 100% Castile or (b) 90% Castile and 10% Solado.
The RH waste was not considered because of emplacement in walls of the disposal rooms above the room floor.

1.) Mass of MgO Backfill

The volume will be determined from the total volume less the air space above the waste and the volume of the waste.

Total volume of a room is equal to the width times the length times the height (less the 0.711 meters of air space). (Appendix A is pg. 3-13 from WIPP PA, 1991).

Width = 10.06 m
Length = 91.44 m
Height = 3.251 m

Room Volume = (10.06)*(91.44)*(3.251) = 2,990.55 m^3

Appendix A shows the dimensions of a 7-Pack. The length of each side of this regular 6 sided polygon is equal to

$l = (1.65/2)/\text{Cosine } 30° = 0.825/0.866 = 0.953$ m

The area of a regular 6 sided polygon is equal to

$\text{Area} = (1/4)*6*l^2*\text{Cot}(180°/6) = 0.25*6*0.953^2*1.7321 = 2.36\ m^2$

From Appendix A, the height of a 7 Pack is the height of the drum plus the height of two slip sheets.

height = 0.892 + 2 (0.004) = 0.900 m

7- Pack Volume =(2.36)*(0.900) = 2.124 m^3

From Appendix A the drum external diameter is 0.602 m and the height is 0.892 m. The external volume is equal to :

$\text{Volume} = (3.1416)*(0.602)^2*(0.892)/4 = 0.2539\ m^3$

Free Volume per 7- Pack = (7-Pack Volume)-Volume of 7 Drums - volume of slip sheets.

= (2.124 - 7*(0.2539)-2*0.004*2.36 = 0.3278 m^3

Number of 7-Packs per room = No. per length * No per Width * No per height
= 54*6*3=972 (Appendix A)

Free Volume per Room = Total volume-Total 7 Pack volume + Free volume per 7-Pack
=2,990.55-(972)*(2.124)+(972)*(0.3278)
= 1,245 m^3

The number of rooms is about 120. (WIPP PA, 1991, pg. 3-5)

The Total Free Volume in the WIPP = 120 * 1,245 = 149,400 m^3

Mass of MgO that could be emplaced in the Free Volume

The density of crystalline MgO is 3.58 gm/cm^3 (Lide, 1995)

Assume the bulk density of MgO is 50% of the crystalline density.

Bulk Density = $(0.5)*(3.58 g/cm^3)*(10^6\ cm^3/m^3) = 1.79 * 10^6\ gm/m^3$

Mass of MgO emplaced = Free Volume * Bulk Density
= $149{,}040\ m^3 * 1.79*10^6\ gm/m^3 = 2.67*10^{11}$ gms

The molecular wight of MgO is 40.3.

Total Moles of MgO emplaced = $2.67*10^{11}$ gm/(40.3 gm/mole)
= $6.62*10^9$ moles

2.) Moles of MgO dissolved in brines

Castile

The concentration in Castile brine was estimated from an EQ3NR calculation by Yifeng Wang. Appendix B contains the first page of the input file and the calculated concentration of Mg^{++}.

As shown in Appendix B, the maximum concentration of Mg^{++} was about 0.02 moles per kg of H_2O.

As is also shown in the input file in Appendix B, the initial Mg^{++} concentration was 0.019 moles per kg of H_2O

The initial concentration of total dissolved salts, as shown in Appendix B, was $3.33*10^5$ mg of salts/liter of brine (0.333 kg/l) and the density was 1.216.gms/cm^3 (1.216 kg/l).

The mass of salts per kg of brine = (0.333 kg of salt/l) /1.216 kg of brine/l) = 0.27 kg of salt/kg of brine.

Mass of H_2O per kg of brine = Total - mass of salt = 1.0 - 0.29 = 0.73 kg H_2O/ kg brine

The volume of the brine to be chemically controlled is 10^6 m^3.

The moles of MgO dissolved in Castile brine
=change in concentration*density *H_2O/kg brine*brine volume
= (0.020-0.019)mole/kg H_2O*1.216 kg brine/l*0.73 kg H_2O/kg brine*10*^{6} m^3 *10^3l/m^3
= $8.88*10^5$ moles

Salado

The concentration in Salado brine was also estimated from an EQ3NR calculation by Yifeng Wang. Appendix C contains the first page of the input file and the calculated concentration of Mg^{++}. As shown in Appendix C, the concentration was about 1 mole/kg of H_2O after the addition of MgO.

The initial concentration, as show in Appendix C, was 1.44 mole/kg of H_2O.

The addition of MgO resulted in a decrease in the final concentration Mg^{++}.

A mixture of 90% Castile brine and 10% Salado brine would dissolve 90% of the amount for Castile brine

The amount dissolve would equal
$=0.90*(8.88*10^5 \text{ moles})= 7.99*10^5$ moles

3.) Estimate of moles of CO_2 generated by microbial activity

Inventory Report (DOE, 1995) will be used to estimate the amount of cellulosics, rubbers, and plastics in the inventory. The method of Wang and Brush (1996) will be used to convert to weights of plastics and rubbers into moles of C produced.

DOE, 1995 reports the following weights for an average drum of CH TRU waste

Cellulosics	= 54 kg/m^3
Rubber	= 10 kg/m
Plastics	= 34 kg/m^3
Container Plastic	= 26 kg/m^3

Based on the method of Wang and Brush 1996 the total estimated weight of equivalent celluolosics is

Cellulosis = 54 kg/m^3
Rubber = 10 kg/m^3
Plastic = $1.7*(34\ kg/m^3) = 57.8\ kg/m^3$
Plastic/liner = $1.7*(26\ kg/m^3) = 44.2\ kg/m^3$
Total Cellulosics = $54 + 10 + 57.8 + 44.2 = 166\ kg/m^3$

The total volume of CH waste (DOE 1996, pg. 3-3) is $1.6*10^5\ m^3$

The total cellulosics in the WIPP = $(166\ kg/m^3)*(1.6*10^5\ m^3) = 2.656*10^7$ kg

A molecular weight of 162 was used by Wang and Brush (1996) for all cellulosics.

The total moles of C, based on the method of Wang and Brush (1996), pg. 15
= (weight of equivalent cellulosics /molecular weight of cellulosics)*number of C per mole
= $((2.656*10^7\ kg)*(1000\ gm/kg)/(162\ gms/mole))*(6) = 9.84 * 10^8$ moles of C.

The maximum amount of CO_2 generated would be one mole for each mole of C in the waste.

Total MgO required for dissolving in brine and reacting with CO_2 generated by microbial activity.

Castile Brine

Dissolved = $8.88*10^5$ moles.

The maximum CO_2 generated from microbial activity = $9.84*10^8$ moles

One mole of MgO is required for each mole of CO_2 generated.

Total MgO required = $8.88*10^5 + 9.84*10^8 = 9.85*10^8$ moles

Volume of MgO = ($9.85*10^8$ moles*40.3 gms/mole)/$1.79*10^6$ gms/m^3 = 22,176 m^3

Wang and Brush 1996a estimated that 0.04% of the cellulose would be converted by denitrification, 0.01% converted by sulfate reduction, and 95% converted by methanogenesis. Denitrification and sulfate reduction generate on mole of CO_2 for each mole of cellulose and methanogenesis generates one half mole of CO_2 for each mole of cellulose. Based on this estimate the total amount of CO_2 generated would equal

Moles of $CO_2 = (0.04 + 0.01 + 0.95/2)*9.84*10^8 = 5.17*10^8$ moles.

Total MgO required = $8.88*10^5 + 5.17*10^8 = 5.18*10^8$ moles

Volume of MgO = ($5.18*10^8$ moles* 40.3 gms/mole)/$1.79*10^6$ gms/m^3 = 11,662 m^3

Total MgO available if all of the 149,400 m^3 of free volume was fill with MgO was previously calculated to be $6.62*10^9$ moles.

Mixture of 90% Castile brine and 10% Salado Brine

Dissolved = $7.99*10^5$ moles

Maximum CO_2 generated = $9.84*10^8$ moles

Total MgO required = $7.99*10^5 + 9.84*10^8$ moles = $9.85*10^8$ moles

Volume of MgO = ($9.85*10^8$ moles*40.3 gms/mole)/$1.79*10^6$ gms/m^3 = 22,176 m^3.

Using the estimates of Wang and Brush for the expected microbial processes which resulted in $5.17*10^8$ moles of CO_2 being generated the

Total MgO required =$7.99*10^5$+ $5.17*10^8 = 5.18*10^8$ moles.

Volume of MgO = ($5.18*10^8$ moles*40.3 gms/mole)/$1.79*10^6$ m^3 = 11,662 m^3

References

Department of Energy (DOE), 1995. *Transuranic Waste Baseline Inventory Report (Revision 2).* DOE/CAO-95-1121. Carlsbad New Mexico.

Lide D. R. (1995) *Handbook of Chemistry and Physics.* CRC.

WIPP PA (Performance Assessment) Division 1991. *Preliminary Comparison with 40 CFR Part 191, Subpart B for the Waste Isolation Pilot Plant, December 1991. Volume 3: Reference Data.* SAND91-0893/3. Albuquerque, NM:Sandia National Laboratories.

Wang, Yifeng and Larry Brush, (1996). *Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment,* Sandia National Laboratories, Albuquerque, NM. (Memo to Martin Tierney, January 26, 1996).

Wang, Yifeng and Larry Brush. (1996a). *Modify the Stoichiometric Factor y in BRAGFLO to include the Effect of MgO Added to WIPP Repository as Backfill.* Sandia National Laboratories, Albuquerque, NM. (Memo to Martin Tierney, February 23, 1996).

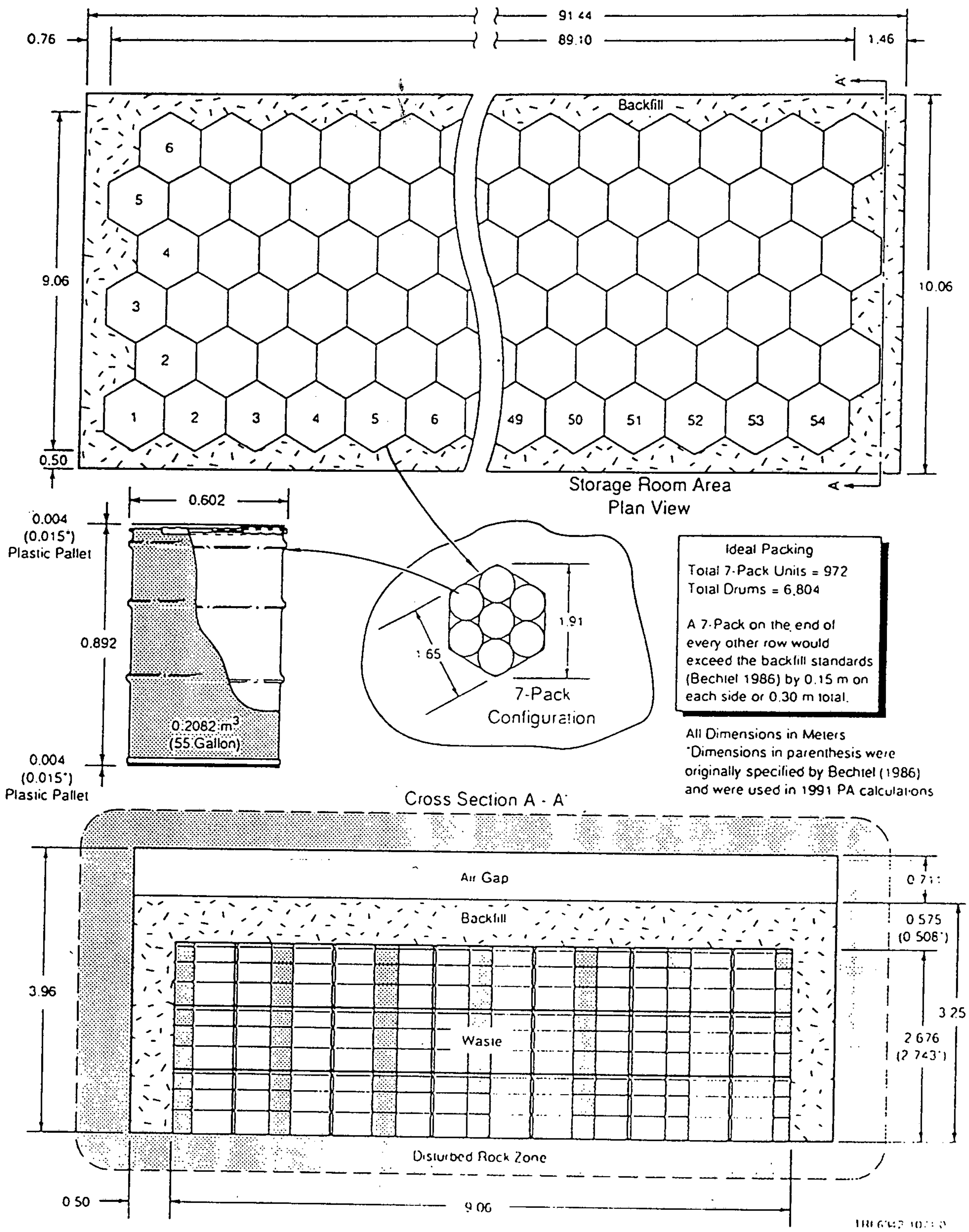
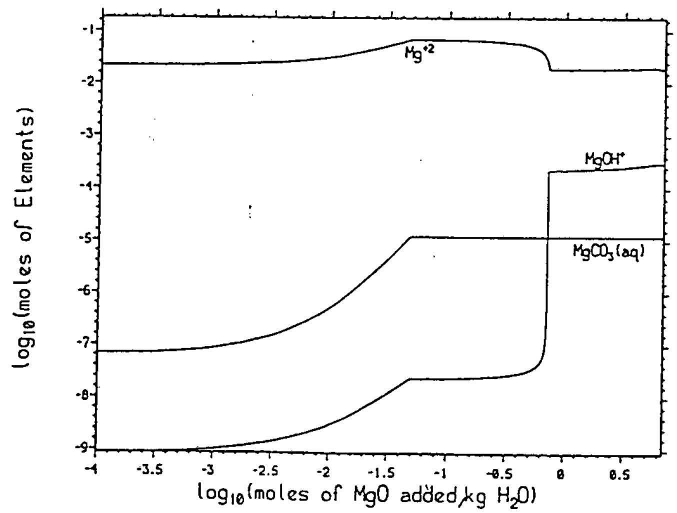
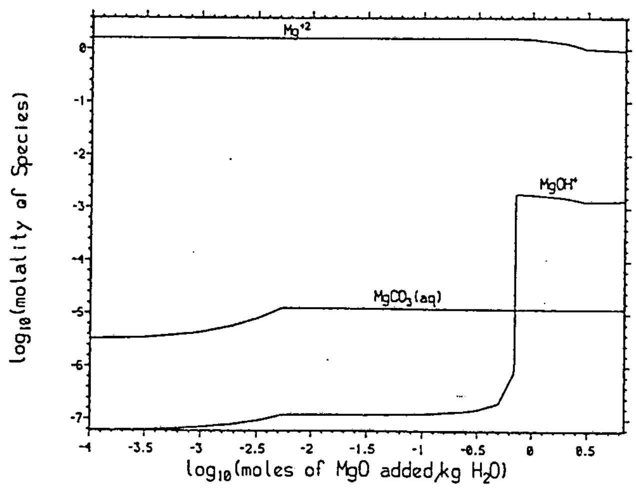


Figure 3.1-3. Ideal Packing of Drums in Rooms and 10-m-wide Drifts.

```
EQ3NR input file name= erda6.3i
Description= "erda6"
Version level= 7.2
Created 1/26/96      Creator= Yifeng Wang

   Purpose: to calculate total dissolved inorganic carbon in the brine
   for a given pH. The activity coefficient of the aqueous species
   are calculated from the HMW equation and related equations.
-----------------------------------------------------------------------------
Temperature (C)          | 25.00          |Density(gm/cm3)|  1.21600
-----------------------------------------------------------------------------
Total Dissolved Salts    |   3.33E+05     | mg/kg  |*mg/l   | not used
---------------------------------------------------------------------------------
Electrical Balancing on  |                          | code selects|*not performed
---------------------------------------------------------------------------------
 SPECIES                 | BASIS SWITCH/CONSTRAINT| CONC/ETC    | UNITS OR TYPE
---------------------------------------------------------------------------------
redox                    |                        |-.70000      |LogfO2
Na+                      |                        | 4.8700      |Molarity
K+                       |                        |0.09700      |Molarity
Ca++                     |                        |0.01200      |Molarity
Mg++                     |                        | 0.0190      |Molarity
H+                       |                        | 6.1700      |pH
HCO3-                    |                        | 0.0160      |Molarity
Cl-                      |                        | 4.8000      |Molarity
SO4--                    |                        |0.17000      |Molarity
---------------------------------------------------------------------------------
Input Solid Solutions
---------------------------------------------------------------------------------
 none                    |                        |             |
---------------------------------------------------------------------------------
SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value
-----------------------------------------------------------------------------
 Dolomite                | mineral                | suppress          | 0.       |
-----------------------------------------------------------------------------
OPTIONS
-----------------------------------------------------------------------------
 - SOLID SOLUTIONS -
    * ignore solid solutions
      process hypothetical solid solutions
      process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
    * does nothing
      lists species loaded into memory
 - ECHO DATABASE INFORMATION -
    * does nothing
      lists all reactions
      lists reactions and log K values
      lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
    * in order of decreasing concentration
      in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
    * all species
      only species > 10**-20 molal
      only species > 10**-12 molal
      not printed
 - LIST OF AQUEOUS SPECIES (by element) -
```


log₁₀(moles of Elements)
log₁₀(moles of MgO added/kg H₂O)
Mg+2
MgOH+
MgCO3(aq)
-1
-2
-3
-4
-5
-6
-7
-8
-9
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5

```
--------------------------------------------------------------------
EQ3NR input file name= BRN A.3i
Description= "Brine A"  Salado
Version level= 7.2
Created 1/26/96        Creator= Yifeng Wang

  Purpose: to calculate total dissolved inorganic carbon in the brine
  for a given pH. The activity coefficient of the aqueous species
  are calculated from the HMW equation and related equations.

--------------------------------------------------------------------
Temperature (C)          | 25.00        |Density(gm/cm3)|  1.20000
--------------------------------------------------------------------
Total Dissolved Salts    |  3.06E+05    | mg/kg |*mg/l  | not used
--------------------------------------------------------------------
Electrical Balancing on  |                          | code selects|*not performed
--------------------------------------------------------------------
 SPECIES                 | BASIS SWITCH/CONSTRAINT| CONC/ETC   | UNITS OR TYPE
--------------------------------------------------------------------
redox                    |                        |-.70000     |LogfO2
Na+                      |                        | 1.8300     |Molarity
K+                       |                        |0.77000     |Molarity
Ca++                     |                        |0.02000     |Molarity
Mg++                     |                        | 1.4400     |Molarity
H+                       |                        | 6.5000     |pH
HCO3-                    |                        | 0.0100     |Molarity
Cl-                      |                        | 5.3500     |Molarity
SO4--                    |                        |0.04000     |Molarity
--------------------------------------------------------------------
Input Solid Solutions
--------------------------------------------------------------------
 none                    |                        |            |
--------------------------------------------------------------------
SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value
--------------------------------------------------------------------
 Dolomite                | mineral                | suppress         0.
--------------------------------------------------------------------
OPTIONS
--------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
```


Mg+2
MgOH+
MgCO3(aq)
log10(molality of Species)
log10(moles of MgO added/kg H2O)
0
-1
-2
-3
-4
-5
-6
-7
-4
-3.5
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5