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Dessicant Materials Screening for Backfill in a Salt Repository

Technical Report

October, 1980

Dale R. Simpson

Lehigh University
Bethlehem, PA 18016

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Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed Copy: A05
Microfiche copy: A01

ONWI-214
Distribution Category UC-70

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Prepared by Lehigh University under Contract No. DE-AC-97-79 ET 4660 with the U.S. Department of Energy. Program direction was provided by the Office of Nuclear Waste Isolation, Battelle Project Management Division, Columbus, OH 43201, under Contract DE-AC06-76RLO 1830-ONWI with the U.S. Department of Energy.

ABSTRACT

Maintaining an anhydrous environment around nuclear waste stored in a salt repository is a concern which can be alleviated by using a desiccant material for backfilling. Such a desiccant should desiccate a brine yet be non deliquescent, the hydrated product should have moderate thermal stability, and the desiccant should have a high capacity and be readily available.

From a literature search MgO and CaO were identified for detailed study. These oxides, and an intimate mixture of the two obtained by calcining dolomite, were used in experiments to further determine their suitability. They proved to be excellent desiccants with a high water capacity. The hydrates of both have moderate thermal stability and a high water content.

Both MgO and CaO react in an alkaline chloride brine forming oxychloride compounds with different waters of crystallization. Some of these compounds are the Sorel Cements.

CaO hydrates to $Ca(OH)_2$ which carbonates with CO_2 in air to form $CaCO_3$ and release the hydrated water. Thus the intimate mixture of CaO and MgO from calcined dolomite may serve as a desiccant and remove CO_2 from the repository atmosphere.

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1.0 INTRODUCTION

Nuclear wastes from both the national defense program and commercial nuclear reactors have accumulated and safe disposal is an important national concern. Salt deposits are one setting considered as a repository for the packages containing the radioactive waste. Although such salt deposits are essentially dry, there are microscopic droplets of brine trapped in crystals of the salt. Most salts are cryophylic, or their solubility increases with increasing temperature. The nuclear wastes will generate some heat; therefore, the microscopic inclusions in the salt will migrate by solution on the warmed side of the inclusion and precipitation on the opposite side. The temperature gradient across the microscopic inclusion is very small, and consequently there is a very slow rate of migration. Studies concerning rates of migration have been presented by Olander and Machiel (1979) and Anthony and Cline (1974). The migration rates are low and the quantity of liquid involved is small. Nevertheless, the migrated brine could cause some corrosion and solution problems.

The anhydrous character of the disposal site can be easily re-established, or maintained, by backfilling around the containerized waste with a desiccant material. The duration over which the desiccant is effective is a function of its sorptive capacity, quantity, and nature. The dehydration temperature of a hydrated desiccant is important because heat generation from radioactive decay may elevate temperatures above the stability limit of the hydrated desiccant and thus release moisture to the environment.

The present research surveyed the literature to select candidate materials which are good desiccants for use as backfill. Along with an in-depth literature search of the best group of materials, experiments were conducted to further screen the candidate materials. Basically, a desiccant is desired which is so effective that it will hydrate by drawing water from a hypersaline brine, and essentially dry up the brine. The activity of water in such a brine may be less than half that of pure water; consequently the stability of the hydration product of the desiccant is affected. The experimental studies were aimed at establishing this stability and other reactions which may result from ions in the brine.

2.0 LITERATURE SEARCH APPROACH

2.1 Grouping of Candidate Materials

For the initial screening of materials, there were three major categories. The first category was material with a natural analogue, or equivalent mineral. The second was industrially synthesized materials, and the third was industrial byproducts and waste materials. The mineral type materials are further listed in the usual order following Dana's System, namely hydroxides, chlorides, carbonates, borates, sulfates, phosphates, and silicates.

2.2 Criteria

In screening the categories, it is necessary to consider the requirements for backfill desiccants. Two environments may be considered under which the desiccant should be effective. First the desiccant must be able to sorb water from air in equilibrium with the brine. In this case, the desiccant reacts only with water. With the second environment, the brine may actually come in contact with the desiccant. Brines contain large quantities of Na, K, Mg, Ca, Cl, and SO_4 ions. In this case, ions in the brine may also react with the desiccant. Consequently the anhydrous compound and the hydration product should be compatible with a hypersaline environment.

The rate of hydration is only a minor concern for a system where migration of brine is through crystalline material in response to a thermal gradient; however, since the desiccant must compete with saline brines for water, its effectiveness and water capacity must be extremely high.

The desiccant must also have a thermal stability greater than 200°C to withstand the heat from spent fuel. This requirement is a severe limitation but lower than some estimates of salt-and-canisters surface temperature for a spent fuel salt repository. This thermal stability requirement eliminates many materials such as silica gel, in which the water is poorly bound and with heating is expelled over a broad temperature range.

The hydrated material should also remain solid and have low solubility; otherwise it is likely to contribute to a brine problem. For example, a common and highly effective desiccant, P_2O_5, becomes a corrosive fluid with increased hydration and would contribute to the brine. For use as backfill, the desiccants need a long term stability.

The geological occurrences of the anhydrous and hydrous compounds would be strong evidence of sufficient stability for the backfill material.

Some materials which readily hydrate unfortunately have a limited life for the anhydrous material. An example is cement powder, which contains reactive phases. The reactive phases, however, are metastable at room temperature and ideally will invert to a stable form. Unfortunately, the stable form doesn't hydrate at a suitable rate. Although cement powder can be preserved for years, some of its phases are metastable relative to low temperature polymorphs; consequently its truely long term stability is questionable.

Until it is established whether the atmosphere about the repository will be open or closed, the stability of the desiccant in the presence of the CO_2 content of air will be a consideration.

A chemical simplicity is desired to decrease the likelihood of undesired subsidiary reactions with ions of the brine. If the anhydrous compound is to be synthesized, the technique should be known and plausible for large scale operations. The constituents of the material should be cheap, abundant, and preferably domestically available.

These requirements are somewhat general, but they are serving only to identify the most suited compounds and eliminate ones lacking some important characteristic. The following summarizes the working criteria:

1) the anhydrous compound and the hydration product should be compatible with a hypersaline environment.
2) the anhydrous compound should react readily with water and have a high water capacity.
3) the hydrous compound should have a thermal stability greater than 200°C, remain solid, and have low solubility.
4) there should be geological evidence of long term stability of the anhydrous and hydrous compounds.
5) the compound should have no, or limited, reactivity with carbon dioxide in air.
6) chemical simplicity of the compound is desired.
7) if the anhydrous compound is to be synthesized, the

techniques should be known and plausible for large scale operations.

8) constituents of the material should be cheap, abundant, and preferably domestically available.

2.3 Search Methods

A computerized search was completed on compounds which initially appeared to have appropriate properties. This search was by the Lockheed Dialogue-Chem Com System. Both the hydrous and anhydrous equivalents, with chemical and mineralogical designations, were cross referenced with various terms for brine and components of brine. The search covered the last eight years of Chem Abstracts. For the materials appearing superior at this stage of the study, systematic search of each Chem Abstract, using the same designation, was hand completed for the earlier years. The literature is voluminous, but little has a direct bearing on the compatibility and stability of the compounds in a hypersaline environment.

3.0 LITERATURE SEARCH RESULTS

3.1 Mineral Equivalents

3.1.1 Oxides→ Hydroxides

Periclase, MgO, readily hydrates to brucite, $Mg(OH)_2$, which contains 31% water. This reaction has been the subject of intense investigation over many years. In a very complete report, Giauque and Archibald (1937) used the reaction of periclase plus water reacting to brucite to determine the dissociation pressure, heat of reaction, and heat capacities of MgO and $Mg(OH)_2$. This early study was an introduction to the problem of obtaining true equilibrium when the reactants or products are prone to minute crystal size, or poor crystallinity. In this reaction, some MgO can be prepared such that it has moderate crystal size; however when $Mg(OH)_2$ decomposes, the MgO is a powder with minute crystal size. This difference in crystallinity of MgO yield different univariant curves for the reaction.

Later in 1955, MacDonald used the reaction to determine the Gibbs free energy of water at elevated temperature and pressure. In so doing, several univariant curves for the reaction were calculated depending on the crystallinity of the reactants and products. For example, the reaction of well crystallized brucite dehydrating to poorly crystallized periclase will occur at a lower temperature than well crystallized brucite decomposing to poorly crystallized periclase. These curves are based on the thermodynamic data for the well or poorly crystallized phases. Under a confining pressure of 200 bars, the difference is about 40°C, and it increases with increased confining pressure.

The highest temperature curve calculated by MacDonald is about 50° below a curve experimentally determined by Roy, Roy, and Osborn in 1953. A redetermination of the univariant curve was published by Roy and Roy (1957), and the results essentially confirm their earlier study. They conclude that strained MgO or $Mg(OH)_2$ was unlikely with their experimental setup. In 1956 Kennedy experimentally determined the conditions for the reaction, and his results are in agreement with the higher temperature curve calculated by MacDonald (1955). Fyfe (1957) redetermined the equilibria and was also in agreement with MacDonald. The univariant curve was extended to 40 Kbars by Yamaoka, Fukunaga, and Saito (1970). All of these curves are shown in Figure 1.

The decomposition of $Mg(OH)_2$ under one atmosphere is discussed by Webb (1970). The decomposition temperature is in the range of 350 to 450°C by differential thermal analysis (DTA). The exact temperature of the onset of the endothermic reaction was found to be affected by the history of the sample and the atmosphere. For example grinding produced a larger and sharper peak, and atmospheres of CO_2 or water vapor pressure.

Three studies have particular relevance. Weber and Roy (1965) used DTA under pressure to determine the temperature of dehydration of brucite as a function of water vapor pressure. Under one atmosphere, the dehydration temperature of brucite ranged from 350°C to 390°C, and the nine determinations averaged 375°C. Through a low pressure range they find

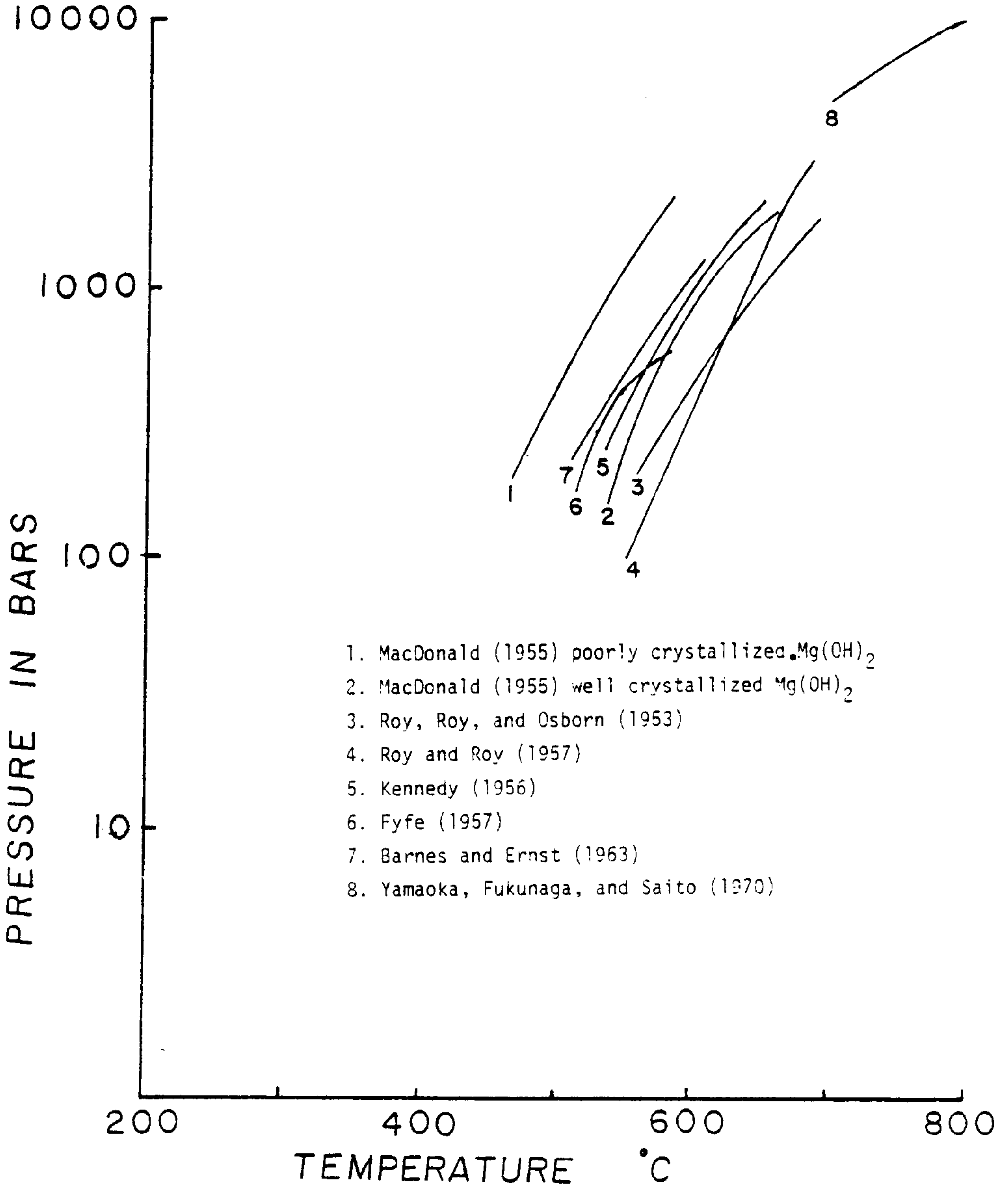

Figure 1. Comparison of the vapor pressure curves for the reaction $Mg(OH)_2 = MgO + H_2O$.

a subsidiary endothermic peak off of the main peak, and this subordinate peak decreases with increasing pressure. They suggest that at low pressures, the decomposition may be a two stage reaction. Their data showing the decomposition temperature as a function of pressure are shown in Figure 2. This study is one of the few providing data for the low pressure region.

Barnes and Ernst (1963) show the effect of NaOH on the decomposition temperature of brucite as a function of pressure. Under 1000 bars confining pressure, brucite in the presence of a 12.5 molal NaOH solution decomposes 50°C below its decomposition curve in the absence of the NaOH. This temperature difference decreases with decreased pressure and decreased concentration of NaOH.

Somiya, Nakamuro, Huario, and Saito (1977) reported the effects of salts on the decomposition temperature of $Mg(OH)_2$. Using a 5 mole % solution, the authors show that the decomposition temperature is lowered the most by LiCl, followed by KCl, and then NaCl. The effect of NaCl is especially strange because the decomposition curve with the NaCl solution appears to cross the decomposition curve in the absence of a salt. Thus at pressure below about 250 bars, the authors show that a NaCl solution raises the decomposition temperature. This peculiar behavior is not explained. Data on the lowering of vapor pressure of water by different salts, as published in the Smithsonian Tables, lead one to predict that the three salts would have about the same magnitude of lowering of the decomposition temperature per mole of salt. The slight differences would

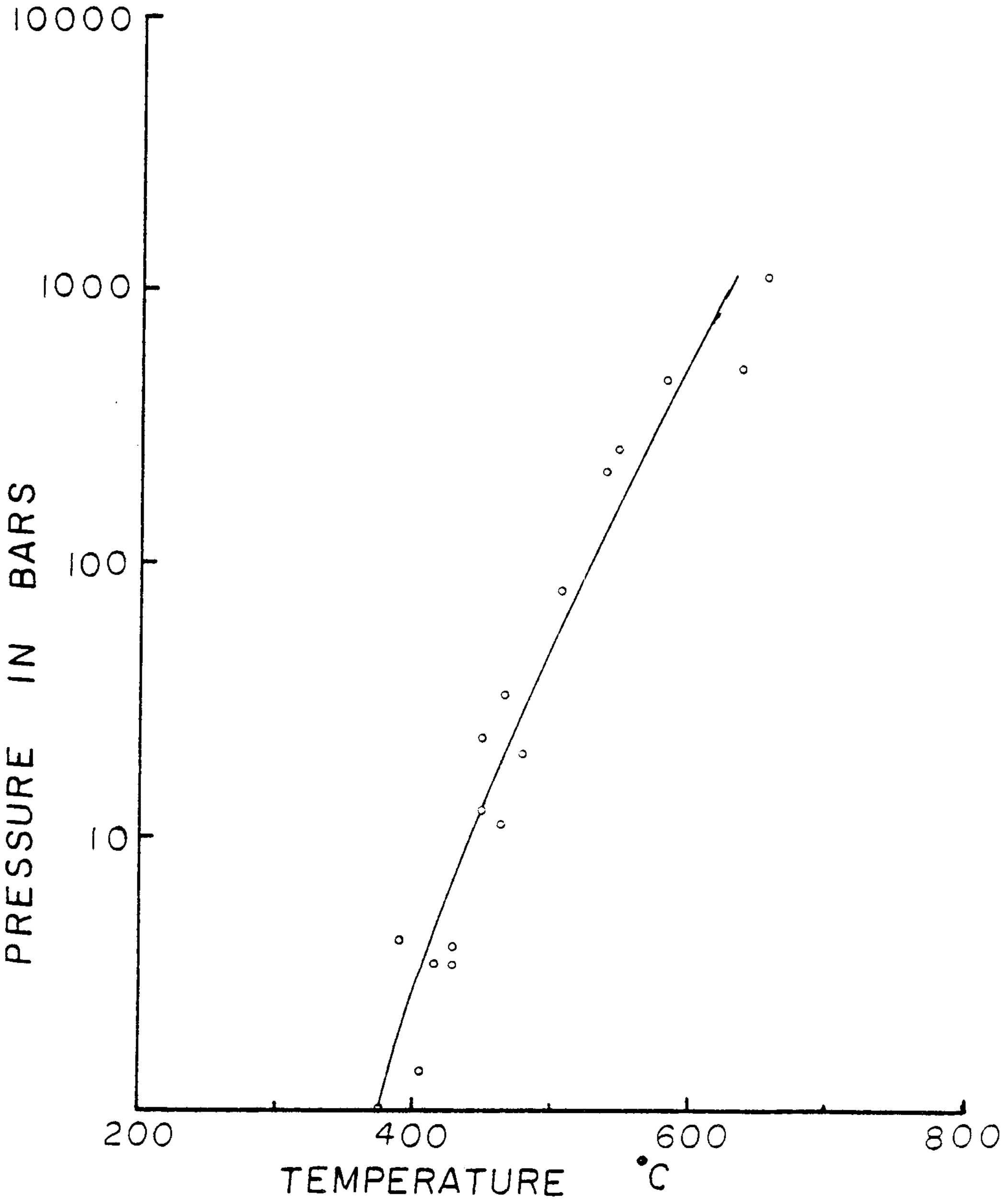

Figure 2. Vapor pressure curve for $Mg(OH)_2 = MgO + H_2O$ determined by DTA from Weber and Roy (1965).

indicate a reverse order for the decomposition curves shown by Somiya et al (1977). The reported results are unusual and should be verified.

Brucite can be precipitated from sea water by the addition of a base. This is an intermediate step in the production of MgO from sea water. Briefly, dolomite [$CaMg(CO_3)_2$] is calcined to $CaO \cdot MgO$. These oxides, stirred in sea water, yield a precipitate of $Mg(OH)_2$. Unfortunately, the precipitate is a flocculent mass of poor crystallinity. Consequently, it absorbs other ions and is difficult to separate from the solution. There is extensive literature bearing on improvement of crystallinity of the precipitate to facilitate separation from the liquor. Other techniques and procedures are concerned with lowering the boron content of $Mg(OH)_2$ precipitated from saline solutions. Many of the techniques for the improved crystallinity and purity are given in patent applications and lack application to the present study.

Precipitation of $Mg(OH)_2$ from sea water involves the addition of CaO and MgO obtained from calcined dolomite. This addition enriches the solution in calcium. In experiments concerned with the precipitation process, Phillips and Opperhauser (1977) conclude that with excess $Ca(OH)_2$ in the system, at 60°C, sheetlike crystals of brucite form. They suggest that this morphology is the result of calcium ions adsorping on the basal surfaces thus limiting further growth. Under other conditions, the calcium is desorbed yielding a different morphology of the brucite. These conclusions are supported by ESCA and Auger studies of calcium levels on the crystal surfaces. This study and the studies concerned with purification of brucite precipitated from sea water indicate that brucite has some sorptive capacity for other ions.

Desalination involves the distillation of water from sea water, leaving a heated brine. An alkaline scale precipitates from this brine. Dooly and Glater (1971) show that the amount and composition of the alkaline scale is a function of temperature, brine concentration, bicarbonate ion concentration, and flow conditions through the evaporator. They find $CaCO_3$ and $Mg(OH)_2$ in the scale formed from normal sea water; however, the $Mg(OH)_2$ is dominant, and the dominance increases with increased temperature. In solution enriched in bicarbonate ions both $CaCO_3$ and $Mg(OH)_2$ precipitated but the yield of $CaCO_3$ was greater than in the normal solution.

The coprecipitation of $CaCO_3$ and $Mg(OH)_2$ raises concern over the stability of $Mg(OH)_2$ in a system containing CO_2 in the gaseous atmosphere. It is well established that $Mg(OH)_2$ can be precipitated from sea water open to air. However, Lawrence (1970) shows that at 25°C, under an atmosphere containing 250 ppm of CO_2, brucite in sea water will partly convert to a hydrous magnesium carbonate. This carbonated compound is reported to be $MgCO_3 \cdot 3H_2O$, which has the mineral name nesquehonite. At higher temperature, there was less conversion to the hydrous magnesium carbonate, but greater conversion under increased concentration of CO_2 in the atmosphere. This greater conversion simply reflects the temperature-partial pressure of CO_2 effects on the carbonate and bicarbonate in the solution. The study raises a concern that MgO used as a desiccant backfill may carbonate if the atmosphere becomes enriched in CO_2 and/or the temperature is decreased.

It is concluded brucite can be easily formed by hydration of MgO or precipitation from a solution, and this brucite is stable to moderate temperature. Furthermore the constituents of typical saline solution have only a minor effect on the formation of brucite; however it may coprecipitate with calcium carbonate under the partial pressure of CO_2 typical of air. The reaction of MgO with water of a brine to form $Mg(OH)_2$ is considered for detailed study, and MgO is viewed as a potential backfill material.

Lime (CaO) readily hydrates to portlandite [$Ca(OH)_2$], which contains 24% water. Portlandite is reported to yield an endothermic peak on DTA over the temperature range of 480°- 620°C (Webb, 1970). This endothermic peak results from the formation of lime and water vapor, which is expelled. Berg and Rassonskaya (1951) show that $Ca(OH)_2$ heated in a CO_2 atmosphere undergoes an endothermic reaction at about 525°C followed by a strong exothermic reaction at about 620°C. This change of reactions corresponds to dehydration reaction followed by a carbonatization reaction forming $CaCO_3$. It is well established that $Ca(OH)_2$ exposed to air in a humid climate readily converts to $CaCO_3$. The decomposition of $CaCO_3$ is a function of the partial pressure of CO_2, but at the partial pressure of CO_2 in air the compound is stable to a temperature of roughly 550°C, and at one atmosphere CO_2 the stability is raised to nearly 900°C. Lime is an excellent desiccant, with the hydrated product stable to a high temperature in the absence of CO_2. In the presence of CO_2, the hydrated compound will liberate water and form a calcium carbonate. Thus it has potential for absorbing CO_2 from the atmosphere and may prove important if there is concern over CO_2 buildup in a repository.

Dolomite, $CaMg(CO_3)_2$, is a widespread mineral. If calcined it yields an intimate mixture of CaO and MgO. These alkaline oxides may be added to sea water forming a basic solution enriched in MgO. This yields a precipitation of $Mg(OH)_2$, which can be recovered for industrial purposes. The literature and patent literature bearing on this process are voluminous. A major focus of many of the reports is to improve the crystallinity of $Mg(OH)_2$ to facilitate separating it from the solution. In other reports, especially those concerned with boiler scale formation, it is shown that calcium carbonate and magnesium hydroxide coprecipitate.

In summary, CaO appears to be an ideal desiccant for use in a backfill operation if the system is closed to CO_2. If open to CO_2, the CaO reacts to form $CaCO_3$. Similarly the CaO component from the calcined dolomite will react with CO_2, even under low values, as typical of air. This identifies a possibility of using calcined dolomite as a backfill for a system to be closed to air, essentially sealed. If degradation of organic material in storage yielded moisture and CO_2, the CaO would react with the CO_2 to form $CaCO_3$ and the MgO would react with water vapor to form $Mg(OH)_2$. This could prevent a gas pressure buildup. Until the nature of the repository is established, the potential dual role of calcined dolomite make it a desirable material for further study.

Goethite [FeO(OH)] decomposes to hematite (Fe_2O_3) and water. Goethite heated in air undergoes an endothermic reaction at 380°C

(Mackenzie and Berggren, 1970). This corresponds to the loss of water and the formation of hematite. Goethite readily adsorbs many cations and anions on its surface, and it has served as a model for the adsorption processes (Parfitt and Russell, 1977; Grimme, 1968; Forbes, Posner, and Quirk, 1970; Parfitt and Smart, 1978). Although this adsorption is a very desirable property, Wefer (1966) experimentally determined the univariant curve for the reaction, and he found that the inversion occurred at less than 100°C even at pressure of several hundred bars. Bischoff (1969) calculated the relation between hematite and goethite and applied the finding to the conditions found for the Red Sea brines. These brines reach 56°C and a salt concentration such that the activity of water is less than 0.8. Goethite is stable under these Red Sea brine conditions, but in one core was found to have inverted to hematite. Thus, the 56°C is close to the boundary between hematite and goethite for a highly saline solution. Berner (1969) concluded that finely divided goethite was unstable relative to hematite under practically all geologic conditions.

Unless very low temperatures could be maintained in a respository, it appears that the goethite-hematite reaction is unsuitable. The same conclusion is drawn for lepidorrocite, another hydrated iron oxide. Even if the temperature is restricted, the rate of hydration is probably insufficient.

Iron may be used as the reactant rather than Fe_2O_3. Water would react with the iron forming Fe_2O_3, perhaps hydrated, and hydrogen gas.

If the atmosphere of the system is closed, or restricted, this gas buildup may present a problem. For these reasons iron or hematite were eliminated from further consideration.

Gibbsite $[Al(OH)_3]_2$ and boehmite and diaspore, two other hydrous alumina compounds, are found in clays and ores of aluminum. These compounds have a decomposition temperature above 250°C (Mackenzie and Berggen, 1970); however, the reactant Al_2O_3 has an unfavorable rate of hydration. The absence of the hydrated compound, even as rare minerals, in salt deposits, suggest that they are incompatible with hypersaline brines. The use of aluminum metal creates problems similar to the use of iron and additional problems of galvanic action. Consequently, aluminum or alumina appear to be unsuited.

Manganite $[MnO(OH)]$ appears similar to goethite $[FeO(OH)]$, which has a low temperature inversion. In addition the behavior of manganese in a hypersaline brine is unknown. Although manganese is a common material, it is on the Strategic Materials List and lacks the domestic availability of other materials. Hydrocalumite $[Ca_4Al_2(OH)_{14} \cdot 6H_2O]$ and hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O]$ are other hydrous oxides. The complexity of the compounds, the likelihood of secondary reactions with a brine, and the unknown nature of the anhydrous equivalent make these compounds poor candidate materials.

3.1.2 Chlorides → Hydrated Chlorides

In screening chloride compounds six were found to form hydrates containing appreciable water. A review showed that each held little promise.

These chloride compounds are all highly soluble, and decompose with the evolution of HCl. For example, the anhydrous equivalent of chloraluminate [$AlCl_3 \cdot 6H_2O$] is an extremely deliquescent material; it dissolves violently in water with the evolution of HCl. According to solubility data given by Linke (1965), $AlCl_3 \cdot 6H_2O$ is in equilibrium at 25°C with a solution containing roughly 2.8 molar in $AlCl_3$. The Smithsonian Tables, tabulations of lowering of vapor pressure by salts in aqueous solution, show that $AlCl_3$ would desiccate any other brine; unfortunately, it would form an aluminum chloride brine with the evolution of some HCl. This example illustrates that the reactant and the hydrous product must have low solubility otherwise they may contribute to a brine problem.

Cadwaladerite [$Al(OH)_2Cl \cdot 4H_2O$] and any other aluminum chloride bearing salts are dismissed from further consideration because the anhydrous reactants would necessarily contain aluminum chloride.

Magnesium chloride hydrates to $MgCl_2 \cdot 6H_2O$, the mineral bischofite, which is found in some salt deposits. Berg (1970) reports that with heating an endothermic reaction occurs at 116°-120°C. This corresponds to melting, and at about 155°C the solution boils followed by decomposition to MgO and HCl. These temperatures are low and the formation of HCl undesirable. In addition the reactant has a high solubility and its solution a low vapor pressure. Thus, the material could dissolve in its own liquor obtained by abstracting water from other brine. These problems will plague any system using $MgCl_2$ as one of the anhydrous components.

Carnallite ($KMgCl_3 \cdot 6H_2O$) and tachyhydrite ($CaMg_2Cl_6 \cdot 12H_2O$) are compounds for which their anhydrous component would necessarily contain $MgCl_2$ as one component. Carnallite melts at 160°- 165°C (Berg, 1970), a low temperature for desiccant backfill.

Tachyhydrite is a rather rare hydrous salt that occurs in large deposits in Brazil and Western Africa. Thermal data on tachyhydrite is unreported. Since it would seem that the anhydrous equivalent should readily hydrate and contain a high percentage of water, the thermal data was determined as part of this research effort. The results, presented in a later section, show it to decompose starting at 100°C. Unfortunately, these compounds have a high solubility.

Because of the solubility, evolution of HCl, low thermal stability of the hydrates, the chloride compounds lack the appropriate properties for a desiccant backfill.

3.1.3 Carbonates → Hydrated Carbonates

The suitability of carbonates as a desiccant backfill is in part a function of the nature of the atmosphere. If the repository is open to air, circulation of the system is under the partial pressure of CO_2 in the air. If the system is closed, intentionally, or through rock flowage over a long period, the partial pressure of CO_2 in the gaseous phase may increase if there is oxidation of organic material, or decrease if used in a reaction. Until these conditions are defined, the stability of the different carbonates cannot be judged.

Trona $[Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O]$ decomposition is discussed by Webb and Kruger (1970). At 170°C an endothermic peak is considered to result from the simultaneous loss of water from the bicarbonate component. Unfortunately, as the $NaHCO_3$ is decomposed with the liberation of water there is also a loss of CO_2. Consequently trona could not be dehydrated to form anhydrous reactants. Presumably mixed Na_2CO_3 and $NaHCO_3$ would hydrate in an appropriate environment, but the exact conditions are unknown. Trona is reported in Palache, Berman, and Frondel (1951) to not alter by exposure to dry air and to occur with many different salts in saline lakes. Thus trona forms in water of low activity and once formed it retains the water of crystallization to 170°C. Trona has appreciable solubility.

Thermonatrite ($Na_2CO_3 \cdot H_2O$) loses its water of crystallization at roughly 100°C (Webb and Kruger, 1970). This low temperature, and concern over the required carbon dioxide, makes the anhydrous material inappropriate for a desiccant backfill.

Nesquehonite ($MgCO_3 \cdot 3H_2O$) is reported to lose water at about 200°C (Webb and Kruger, 1970). Langmuir (1970) using thermochemical calculations showed the relations among $Mg(OH)_2$ and the hydrous and anhydrous carbonates. Lawrence (1970) using DTA concluded that nesquehonite is a stable phase between 25 and 104°C. Nesquehonite is of considerable importance because it may form instead of $Mg(OH)_2$ in an atmosphere slightly enriched in CO_2. Because of the plausity of the data, and the potential importance as a subsidiary reaction during the hydration of MgO, the stability of nesquehonite was a subject of investigation in the experimental studies.

Dawsonite $NaAl(CO_3)(OH)_2$ is stable to moderate temperatures. However the anhydrous components would likely contain Al_2O_3, which is inert or very slow in reacting.

None of the carbonates appear especially desirable for a desiccant backfill; however, complete evaluation requires information on the CO_2 content of the system. A major reservation with the alkali carbonates and bicarbonates is that a calcium chloride brine would react with an alkali carbonate yielding calcium carbonate and a sodium chloride brine. Nesquehonite is of concern because it may enter the reactions involving the hydration of MgO.

3.1.4 Borates → Hydrated Borates

Four common borates are: Kernite ($Na_2B_4O_7 \cdot 4H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), and hydroboracite ($CaMgB_6O_{11} \cdot 6H_2O$). Kernite and ulexite decompose at 140°C, or less (Berg, 1970; Palache, Berman, and Frondel, 1951). This is a low temperature for the desired purpose. Colemanite and hydroboracite, according to Berg (1970), decompose at temperatures above 300°C. Palache et al (1951) report colemanite associated with gypsum ($CaSO_4 \cdot 2H_2O$), calcite ($CaCO_3$), and other borate minerals. Hydroboracite is reported in the cap rock of a salt dome and with halite (Palache et al, 1951). The behavior of these calcium and magnesium borate in a typical brine is unknown, but the occurrence of hydroboracite with halite suggests that hydroboracite can form from a saline brine. The anhydrous equivalent of hydroboracite should be studied to determine its compatibility with ions of a brine and its effectiveness as a desiccant.

3.1.5 Sulfates → Hydrated Sulfates

Hydrated sulfate compounds of moderate thermal stability are the following:

Syngenite	$K_2Ca(SO_4)_2 \cdot H_2O$
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Natrojarosite	$NaFe_3(SO_4)_2(OH)_6$

All of these compounds have appreciable thermal stability, but unfortunately there are reservations. Syngenite and polyhalite contain less than 6% water; thus their capacity is low as a desiccant. According to Palache et al (1951) syngenite is a rare constituent of oceanic salt deposits, and it is precipitated from brines in part of a potash mine. Experimentally its formation required the solution to be greatly dominant in K_2SO_4. Berg (1970) reports that it dehydrates at 265°C.

The anhydrous components from which syngenite should form would be K_2SO_4 and $CaSO_4$. Unfortunately, $CaSO_4$, called anhydrite, is very sluggish in reacting with water. Anhydrite is an abundant mineral, or it can be formed by dead burning gypsum ($CaSO_4 \cdot 2H_2O$). The dehydration of gypsum proceeds in steps and can be stopped with a composition ($CaSO_4 \cdot \frac{1}{2}H_2O$). This is called plaster of Paris and is a material that hydrates. ($CaSO_4 \cdot \frac{1}{2}H_2O$) and K_2SO_4 may react with water to form syngenite, but since one of the components is partly hydrated, the already low capacity of the desiccant is further reduced.

Polyhalite is a common mineral of salt deposits. According to Nagler (1974) polyhalite is stable to 300 to 400°C, and many isotherms showing its relations with other phases have been published (Perova, 1973 a & b). It has the same deficiencies as syngenite concerning the rate of hydration of its anhydrous components and low water capacity.

Alunite and natroalunite are hydrous alkali aluminum sulfate phases which are stable to high temperatures. They are common minerals, but their occurrence in salt deposits is unreported by Palache et al (1951). This suggests that they are unstable in a saline environment. It appears likely that the aluminum bearing component of the anhydrous mix would oxidize yielding an unreactive material.

Jarosite and natrojarosite are iron equivalents of alunite and natroalunite and are unsuited for similar reasons.

3.1.6 Phosphates → Hydrous Phosphates

The most common phosphate mineral is apatite, but it is not a mineral found in salt deposits. It contains little water, and this is easily replaced by flouride ions. The anhydrous components of apatite and other phosphates are poor desiccants as shown by the anhydrous equivalents being stable over a wide range of conditions.

3.1.7 Zeolites

Zeolites, framework silicates with an open structure, have an aluminum plus silicon to oxygen ratio of 1:2 with charges balanced by alkali or alkaline ions. Because of the open structure and the alkali and alkaline ions, the zeolites behalve as if they have a large surface area with exchangable ions. Water can be loosely held in the holes of the open structure.

Zeolites can be classified into two groups on the basis of their dehydration behavior (Flanigen and Mumpton, 1977). The first group has no structural change and has continuous weight loss and dehydration as a function of increased temperature. The second group has a structural change during dehydration and shows discontinuities in the weight loss curve. This division identifies two problems with the use of zeolites as a desiccant. First, weight loss is continuous with increasing temperature, and second the compound may undergo a non-reversible structural change. Also, it appears unlikely that zeolites, in which water is loosely bound, will be able to desiccate a saturated brine, especially one containing calcium and magnesium.

Zeolites form in saline environments. Hay (1977) describes how a tuff bed in a saline lake deposit may be zoned. The outer zone is glass or glass altered to clay where the lake water was relatively fresh, a zeolitic zone where the water is saline, a more saline zone characterized analcime, and in the highly saline zone the tuff may be altered to potassium feldspar.

Breck (1974) summarizes data on the dehydration of zeolites. Most show a continuous water loss with increased temperature, and the initial weight loss is at a low temperature. In view of this limited thermal stability and uncertain chemical stability in a hypersaline environment, the zeolite appear to lack the ideal properties desired for a desiccant backfill. However there are many species and chemical variants of zeolites, and from this group some may be found to have suitable properties.

3.2 Synthesized Materials

Commercially synthesized desiccants and cements were considered, but there are reservations concerning their use as desiccant backfill. Many of the commercial desiccants, as phosphorus pentoxide, magnesium perchlorate, alkali hydroxides, and calcium chloride are highly effective as a desiccant, but they yield a soluble product. Unless the supply of moisture was limited, the desiccants could end up contributing to the brine. Silica gel, not a highly effective desiccant, has a further limitation of releasing its water with heating over a broad temperature range. Several other desiccants as $CaSO_4$ and $CuSO_4$ lack sufficient effectiveness to draw water from a saturated complex brine.

Commercial cement is available in five types which are described in ANSI/ASTM C 150-78a. These cements differ in the ratio of the principal phases, but all of the cements contain a high percentage of tricalcium aluminate, tricalcium silicate, and dicalcium silicate. One of the types is sulfate resistent; but according to Lea (1971), sulfates, especially magnesium sulfate, do attack cement.

The hydration products of the phases of cement are many and complex. Some of these products and the conditions for dehydration, are given by Lea (1971). The common hydrated calcium silicate is tobermorite, but its composition is variable, especially the water content. Some tobermorite loses water at roughly 140°C. The calcium aluminate of cement also hydrates, and again several compounds are possible. The specific compounds which will form and their nature and degree of hydration in a hypersaline brine are unknown. Many of the hydrated compounds lose water at relatively low temperatures, and the low hydration temperature is of concern if cement powder is used as a desiccant backfill.

Anhydrous cement powder is unstable. If kept dry, ordinary cement, or the hydrophobic cements, can be preserved for an extended period. Nevertheless the preservation of this metastable material over a very long period of time in a form that will not hydrate if exposed to a brine is questionable.

Cement may serve a purpose as a desiccant backfill in a brine atmosphere, but the long term stability of the powder, and dehydration temperature of its products create reservations concerning its use. Some experiments were conducted on cement powder and clinkers in the course of this study.

3.3 Industrial Byproducts

Three types of industrial byproducts were considered. These are fly ash, stack dust, and slag and red mud. Fly ash is dominantly SiO_2, Al_2O_3, and Fe_2O_3. It typically contains little CaO + MgO, thus there is very limited material in fly ash which will hydrate.

Stack dust from the cement industry typically shows about 45% CaO in its chemical analysis. The analysis reviewed show that it has an ignition loss of about 30%. This means that nearly all of the CaO has recombined with CO_2. Use of stack dust from the cement industry would require that the material be recalcined, probably a difficult process because of the extremely fine grained nature. After recalcining the sorptive material is CaO, which unless precautions are taken, could recarbonate. As discussed, even if the CaO hydrated a later carbonation would release the water.

Slags from the iron industry contain some high temperature minerals and glass. Some of these minerals are rich in calcium and magnesium, and one present in some slags is dicalcium silicate. This compound is also the principal constituent of Portland cement, and, if in the forms that will hydrate, it is metastable. Red mud is a byproduct of the aluminum industry, and it is principally dicalcium silicate. The problems with slags and red mud is that the reactive phase is metastable relative to a low temperature stable phase, which will not react with water, the hydration capacity is low, and the nature and thermal stability of the hydrated material is unknown.

3.4 Summary Results of the Literature Search

The literature search showed the best candidate materials to be MgO, CaO, or calcined dolomite. These materials have a large desiccant capacity, acceptable thermal stability, and are chemically simple and readily available. They are not deliquesce if exposed to excessive moisture. Because of these properties the experimental effort was concentrated on these compounds.

Cursory and feasibility experiments were conducted on some compounds because of a dearth of important data for evaluation of the compound or the compound has some particularly desirable feature. Tachyhydrite, for example, contains a high water content and forms in brines, but its thermal stability was unreported. Polyhalite contains little water but has a high thermal stability and is compatible with a saline environment; however the rate of hydration was of concern. Cement and the phase which constitute cement lack some desirable feature uniquely hydrate with the product providing mechanical strength. For this reason some rate studies were conducted with cement and the phases of cement.

4.0 APPROACH TO TESTING POTENTIAL CANDIDATES

4.1 Stock Materials for Experiments

4.1.1 Industrial Materials

Several types of cement powders and unground clinker were supplied by Lehigh Portland Cement Company. Types I, II, III, and an additional sample of powder aged ten years were used. The clinker was pellets about 1-2 cm in diameter.

A granular MgO was purchased. This material was marketed as an animal feed supplement. The producer is the Michigan Chemical Corp., Chicago, Illinois. This material was used because it is commercially available, cheap, and granular or pelletized, whereas reagent MgO is a powder of very low density. Reportedly the material has a minimum MgO content of 97.2%. Under the microscope, the pellets are found to be composed of coarse crystals of MgO, and no other material could be detected. X-ray diffraction showed only MgO, and the sharpness of the peaks indicates that it has excellent crystallinity.

4.1.2 Synthesized Materials

Unless otherwise specified, all materials were reagent grade. The planned experiments required the preparation of some stock material. MgO was heated to 900°C to assure the anhydrous nature before any experiments were conducted. $Mg(OH)_2$ was precipitated by mixing of boiling magnesium chloride and sodium hydroxide solutions. The product was $Mg(OH)_2$, brucite, with a distinct X-ray diffraction pattern, but the flocculent precipitate failed to improve its crystallinity even after aging in solution. The flocculent $Mg(OH)_2$ with its enormous surface area could yield some metastable reactions in further experiments. Therefore, as needed, brucite was synthesized under hydrothermal conditions or natural material of high purity and crystallinity was used.

Polyhalite, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ was formed by reaction and precipitation. Some of the synthesized polyhalite was dehydrated to $CaSO_4$ (anhydrite) and $K_2Mg_2(SO_4)_3$ (langbeinite) for starting material. Other material was a mixture of $CaSO_4 \cdot \frac{1}{2}H_2O$, K_2SO_4, and $MgSO_4$.

Mixtures of calcium carbonate and silicon dioxide having Ca/Si ratios of 3:1, 2:1, 1:1, were calcined and reacted at temperatures to 1300°C. Similar products of calcium aluminates were prepared. The calcined products are similar to some of the phases in Portland cement. Some of the reactions were incomplete and the products were lime (CaO) plus the calcium silicate or calcium aluminate.

Large cleavage fragments of dolomite were used as a source of $CaO \cdot MgO$. No impurities could be detected by optical examination, and the mineral ranged from light cream to light gray. X-ray diffraction showed it to be a well ordered dolomite. This dolomite was calcined by heating to 1300°C for 24 hours, after which it is dark brown. X-ray diffraction of the calcined powder show it to be CaO, MgO, and a trace of hematite.

Lime was obtained by calcining reagent grade $CaCO_3$ at temperatures over 1100°C. The industrial grade, pelletized MgO also was heated to a high temperature to insure that any surface layer of $Mg(OH)_2$ or $MgCO_3$ was removed. The weight loss with heating of this industrial grade MgO was trivial which supports the x-ray diffraction results showing the material to be MgO and lack detectible $Mg(OH)_2$ or $MgCO_3$.

4.2 Environments for Experiments

If waste is placed in a cavern excavated in salt, the pressure in the cavern is essentially one atmosphere of air. The pressure will remain one atmosphere as long as there is some open space and the cavern is vented to the surface. If the cavern contained a heat source, microinclusions of brine in the massive salt surrounding the cavern would slowly migrate. Finally, some microinclusions of brine would reach the cavern wall and weep from the surface. This brine which weeps from the salt is now under a pressure of one atmosphere, and the partial pressure of water in the brine is much less than one atmosphere. As a limiting case, a plethora of such inclusions could contribute water vapor to the air. For a system in equilibrium, the partial pressure of the water vapor in the air is equal to the activity of water in the brine times the saturation vapor pressure of water in air at the temperature of the system. As an example, the water in the atmosphere of a cavern at 100°C at equilibrium will have a vapor pressure of 760 mm of mercury, one atmosphere. If a similar cavern contained a 6 molar sodium chloride solution, the activity of water in the brine is about 76% of the pure water at 100°C. Therefore, the vapor pressure of water in the atmosphere over the brine is 76% of 760 mm of mercury. This is roughly 580 mm of mercury, or 0.76 of an atmosphere. The vapor pressure of water in the atmosphere is controlled by the temperature of the system and the composition of the brine. At this stage, it is desirable to dry up the brine. The brine supplies water at a low vapor pressure to the air in the cavern, and the desiccant backfill must be effective at removing this moisture. Because of this type of a setting, many experiments were conducted on candidate materials using a very low partial pressure of water under one atmosphere total pressure.

After the repository cavern is filled, backfilled, and sealed, perhaps after a very long period of time the pressure in the cavern may reach the pressure of the overlying rock. A slow migration of micro-inclusions of brine toward the backfill desiccant is still possible. When the brine reaches the backfill, the desiccant material hydrates with the reaction being at an elevated pressure. The pressure may be one atmosphere if there is pore space in the desiccant backfill, or the pressure may be equal to the weight of the overlying rocks. For this type of setting, it is important to know the effect of pressure and brines on the hydration reactions. Clearly a desiccant is desired that will retain water to a high temperature at pressures equal to the weight of the overlying rock. This leads to the experiments on the hydration reactions at elevated pressures and temperatures.

5.0 EXPERIMENTS

5.1 Experiments with Less than One Atmosphere

5.1.1 Tests for Hydration in Low Vapor Pressure

5.1.1.1 Background

The Smithsonian Tables gives the lowering of vapor pressure of water by different molar concentrations of various salts. These data are retabulated in the Handbook of Physics and Chemistry. The data for sodium, potassium, calcium, and magnesium chloride are plotted in Figure 3. The solid lines connect the data points and the dashed curve projects the vapor pressure data to the molar concentration of a saturated solution at 100°C. The data show that for solution of equal molar concentration calcium and magnesium chloride lower the vapor pressure about twice as much as sodium and potassium chloride do.

The molar concentration of salts in WIPP solution A and B, and NBT-6a are given in Table 1 and the total shown on Figure 3. Their molar concentration is roughly 4 to 5. If their composition was solely $MgCl_2$ and water, the vapor pressure of water in the atmosphere is roughly 400 mm of mercury. Under these conditions, for a desiccant to dry a brine in equilibrium with an atmosphere, the desiccant must react under a water vapor pressure of less than 400 mm of mercury. In other words, if MgO is to be a desiccant for a WIPP or NBT-6a type brine, the assemblage $MgO + Mg(OH)_2$ must be in equilibrium with a water vapor pressure of less than 400 mm of mercury at 100°C. At a given partial pressure of water vapor, a weight gain

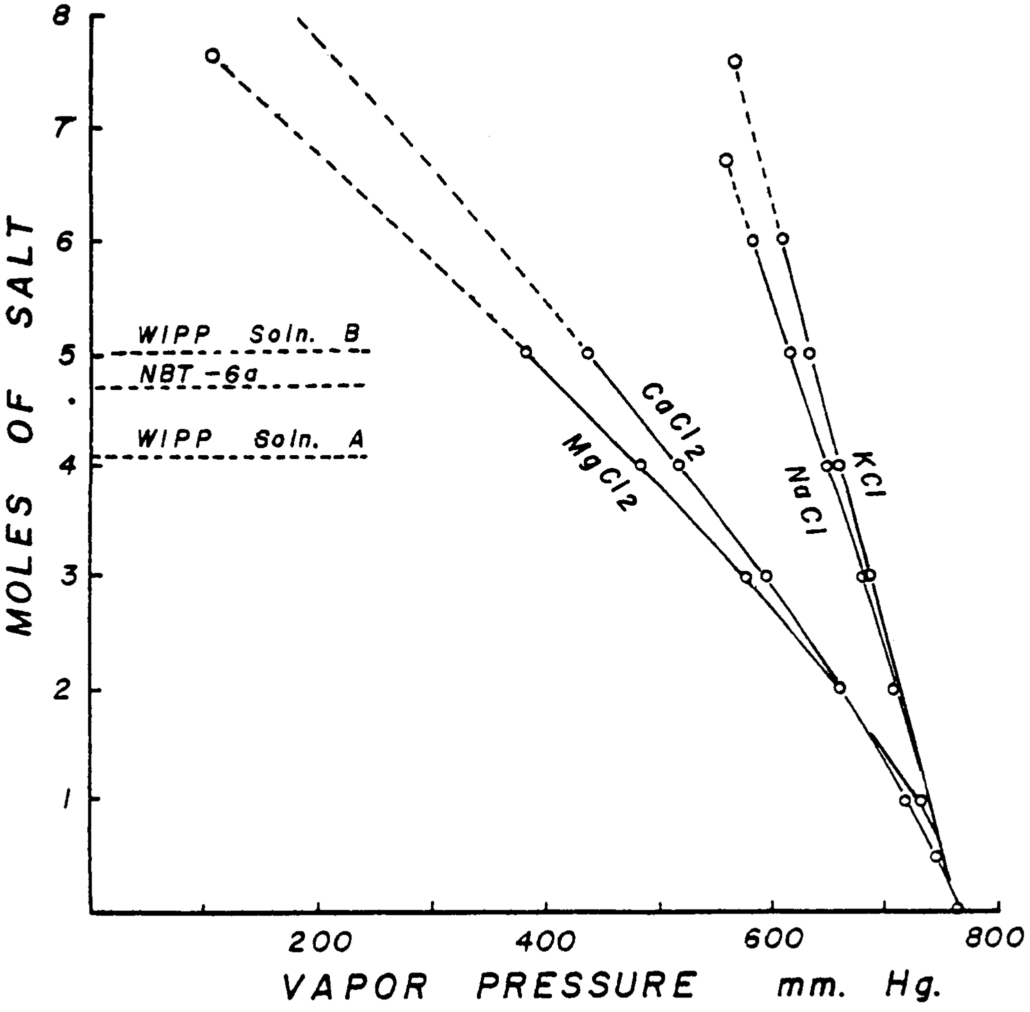

Figure 3. Change of vapor pressure with molar concentration of salts in solutions at 100°C. Molar concentrations of WIPP and NBT-6a shown by horizontal dashed lines. Dashed projections of curves, except $CaCl_2$, are terminated at the molarity of a saturated solution.

Table 1

Composition of Brines

	WIPP-Sol A		WIPP-Sol B	
	mg/L.	Moles/L.	mg/L.	Moles/L.
Na^+	42,000	1.826	115,000	5.000
K^+	30,000	0.769	--	
Mg^{++}	35,000	1.458	--	
Ca^{++}	600	0.015 4.068[1]	900	0.023 5.023[1]
Cl^-	190,000	5.352	175,000	4.930
$SO_4^=$	3,500	0.036	3,500	.365
$BO_3^\equiv$	1,200	0.020	--	
HCO_3^-	700	0.011	--	
Br^-	400	0.005	400	.005

NBT-6a

	wt %	Moles/L.[2]
$CaCl_2$	10	1.17
$MgCl_2$	10	1.37
NaCl	5	1.16
KCl	5	0.90
H_2O	70	
		4.60

1. Assuming simple salts or NaCl, $MgCl_2$, $MgSO_4$, etc., the moles of salt per liter is the same as the moles of cations.
2. The brine was considered to have a density of 1.3.

of MgO with time will establish that the vapor pressure of water is in excess of that necessary for hydration of MgO. A similar approach is usable with other anhydrous materials.

The vapor pressure of water as a function of temperature is well established (Handbook of Physics and Chemistry); a plot of this curve for the range of 0-100°C is shown in Figure 4. Also shown is the vapor pressure of various salt solutions at 100°C based on the data of Figure 3. The activity of water in a 6M NaCl solution at 25°C is reported by Robinson and Stokes (1965). This activity times the vapor pressure of pure water at 25°C gives the vapor pressure of the 6M NaCl solution at 25°C, as shown in Figure 4. The vapor pressure of other salt solutions at 25°C is also shown. Assuming only that the general form of the vapor pressure curve for a salt solution is similar to the vapor pressure curve for water, constant composition curves can be projected showing vapor pressure as a function of temperature for different salt solutions. Or, given a known salt solution at a certain temperature, the vapor pressure can be closely estimate.

Experimentally, the extent of hydration of a desiccant in air equilibrated with a salt solution can easily be determined by weight changes. The vapor pressure during the experiment is obtainable from Figures 3 and 4.

5.1.1.2 Reactants

MgO reagent grade powder was used after heating to 900°C, and CaO was obtained from reagent $CaCO_3$ by heating to a high temperature.

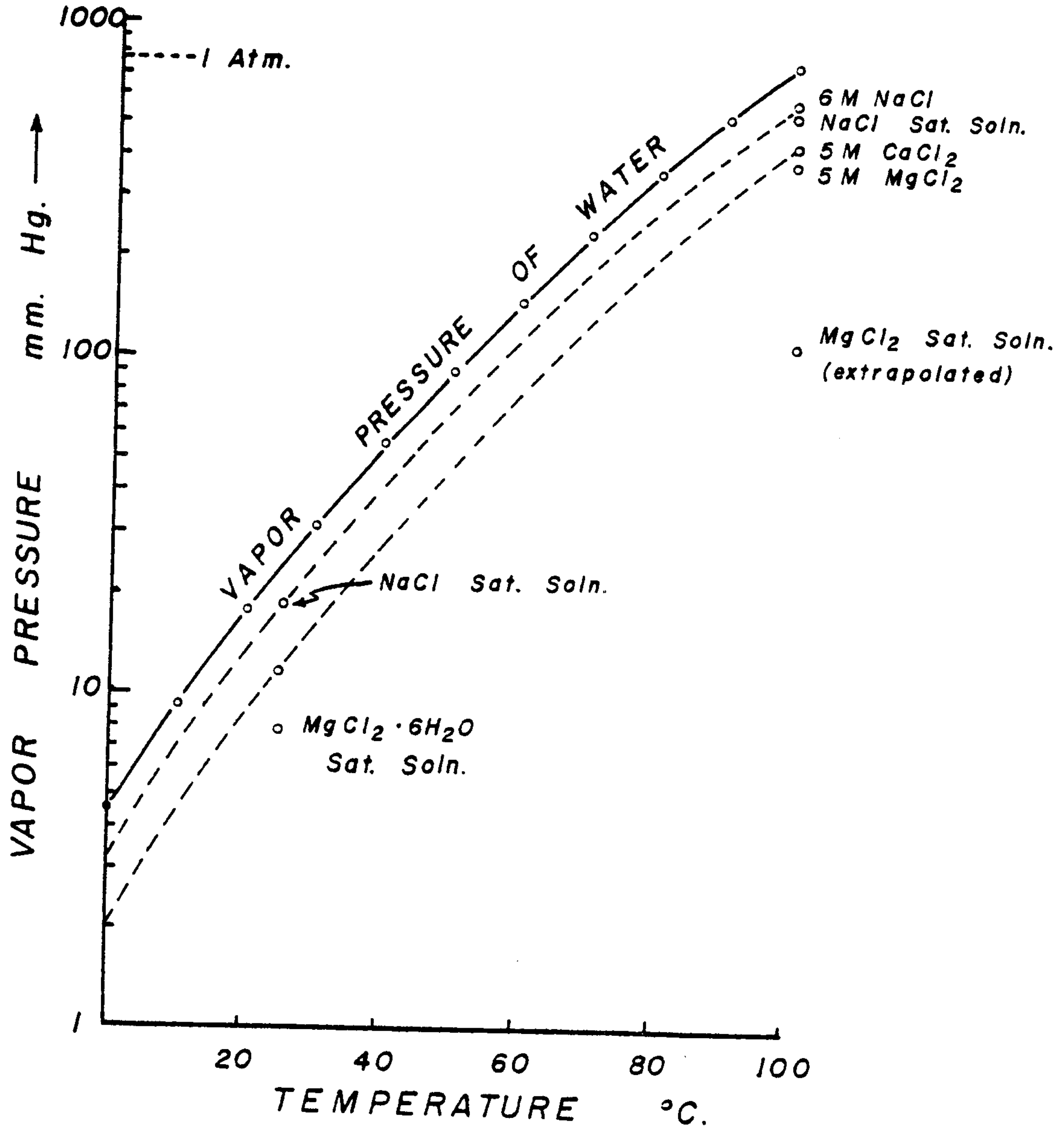

Figure 4. Vapor pressure of water and brines from 0-100°C. Data from the Smithsonian Tables and Robinson and Stokes (1965).

Calcined dolomite was a mixture of CaO and MgO obtained by heating crushed dolomite $CaMg(CO_3)_2$ to 1300°C. Polyhalite was synthesized and then partially dehydrated. With complete dehydration, polyhalite $[K_2Ca_2Mg(SO_4)\cdot 2H_2O]$ decomposes to K_2SO_4; $MgSO_4$; and $CaSO_4$. Anhydrite $(CaSO_4)$ reacts very slowly with water vapor, and therefore is to be avoided. With partial dehydration of polyhalite, $CaSO_4\cdot \frac{1}{2}H_2O$ forms. This compound, known as plaster of Paris, will hydrate.

5.1.1.3 Procedures

The reactants were exposed to controlled vapor pressure and temperature similar to those obtainable with the saline solution, as shown in Figure 4. For this type of experiment, the most effective desiccant would absorb or react with the greatest quantity of water at the lowest vapor pressure. These desiccants react only with the vapor. Later experiments will test whether desiccants react with ions in a brine.

Experiments at temperatures over 100°C involved flowing air saturated with water vapor at a designated temperature, but less than 100°C. Because of the system, long term experiments were difficult to maintain. Although a longer term was desirable for complete reaction, these experiments ranged from several days to a week.

For study of low water vapor pressure and samples above 100°C a different system was used. Air was passed through water at a controlled temperature and then into a furnace containing the samples at an elevated temperature. The desired partial pressure of water was obtained by controlling the temperature of the water bath. This dynamic system lacked the stability of the closed brine system.

5.1.1.4 Results

MgO powder readily reacts forming brucite in less than two weeks at a very low vapor pressure of water (Figure 5). For example, at 100°C, MgO will hydrate under a water vapor pressure of less than 150 mm of mercury, roughly 0.2 atmospheres of water vapor pressure. At 25°C, MgO will hydrate at less than 20 mm of mercury, about 0.027 atmospheres. At 60°C and at water vapor pressure of 19 mm of mercury, 0.025 atmospheres, reagent MgO showed no weight gain after 24 days. It is concluded that MgO is the stable phase under this partial pressure of water at 60°C. If the weight gain is accepted as evidence that the reaction has occurred, the kinetics of the reaction is a concern. To determine the kinetics of the MgO hydration reaction, a sample of the same magnesia powder was exposed to 0.1 atmospheres of water vapor pressure at 60°C. The weight of the sample increased rapidly for the first six days and reached a near steady value by 10 days (Figure 6). The steady weight is much lower than needed to account for complete conversion of MgO to $Mg(OH)_2$. Presumable surface area is important, and with reaction a hydrated surface partly armours the residual core of MgO, which sharply reduces the reaction rate. Thus the duration of the experiments is established by determining the number of days needed to stabilize weight gain.

For temperatures above 100°C, it is possible that with a longer duration some of the MgO would react; therefore, those apparently unreacted MgO samples are identified with a P on Figure 5. On the basis of this study,

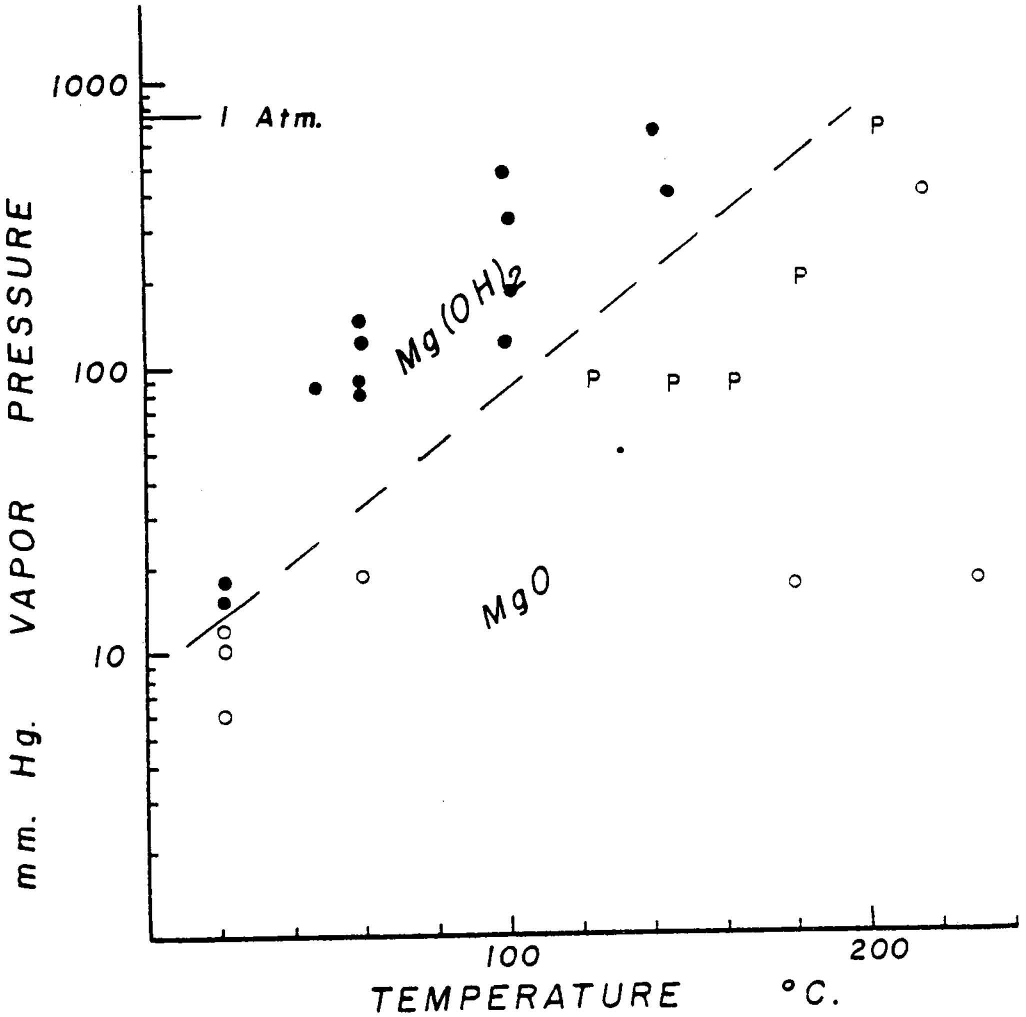

Figure 5. Formation of $Mg(OH)_2$ by the hydration of MgO at water vapor pressures less than 1 atmosphere.

- ○ MgO unreacted
- ● MgO hydrated to $Mg(OH)_2$
- P MgO appeared unreacted after a short term experiment

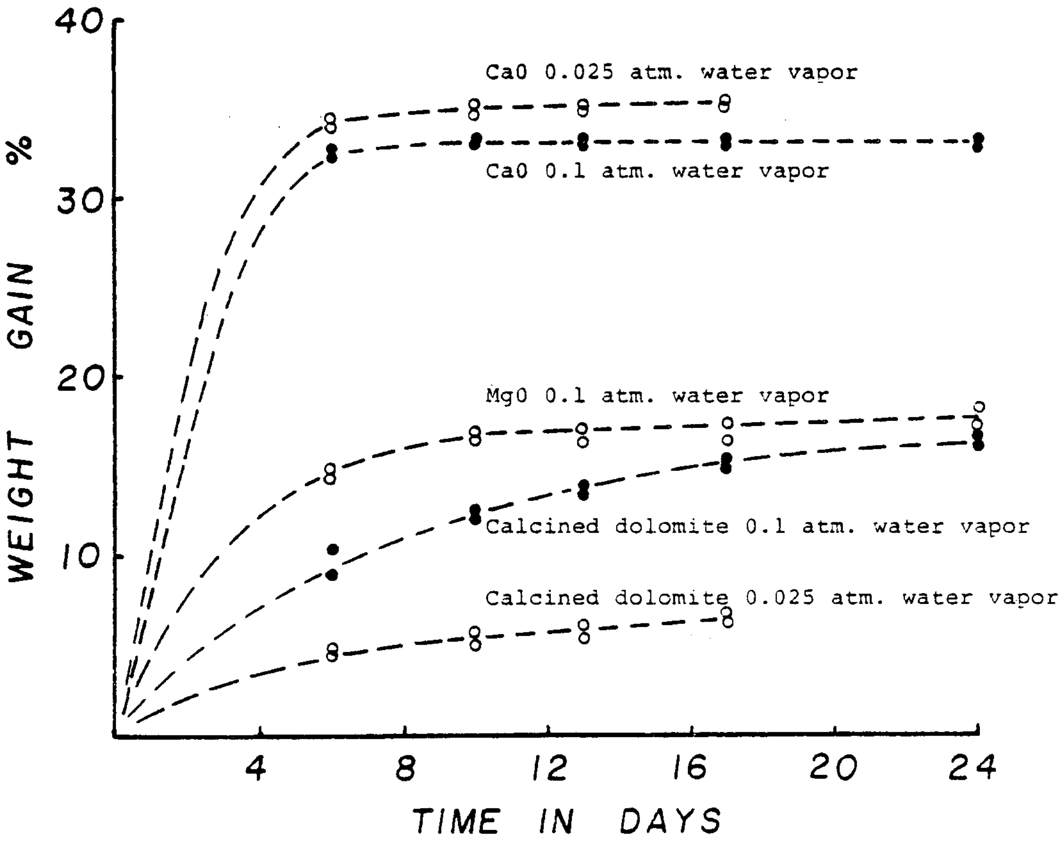

Figure 6. Kinetics of hydration of Ca0, Mg0, and calcined dolomite at 60°C and water vapor pressures of 0.025 and 0.1 atmospheres.

the boundary between $Mg(OH)_2$ and MgO under one atmosphere of water vapor pressure approaches 200°C.

Experiments were conducted using CaO instead of MgO. At 60°C and 0.025 atmospheres water vapor pressure, CaO showed a weight gain of 34% in six days and little further gain with increased time (Figure 6). The reaction of CaO going to $Ca(OH)_2$ involves a weight gain of 32%. Thus the anhydrous CaO completely hydrated and in fact may have sorbed a trace of CO_2 from the air to form $CaCO_3$.

Calcined dolomite, CaO + MgO, showed an increasing weight under the same condition (Figure 6). The product is poorly crystallized, but x-ray diffraction peaks of $Ca(OH)_2$, $Mg(OH)_2$, and MgO could be identified. The $Mg(OH)_2$ detected under both water vapor pressures is particularly interesting because reagent MgO failed to hydrate under the lower pressure condition. Apparently the MgO in the calcined dolomite is more prone to reaction than the reagent MgO.

Partially dehydrated polyhalite reacts with water under a higher vapor pressure than MgO or $CaO \cdot MgO$ as desiccants. The calcium silicates reacted with little water at a higher partial pressure than MgO. It is possible that the hydration results from reaction with free CaO in the samples. Consequently, further research on the polyhalite and the calcium silicates compounds will be deferred.

At 60°C and a higher water vapor pressure, 75 mm mercury or about 0.1 atmospheres, MgO, CaO, and calcined dolomite readily reacted (Figure 6). As shown, CaO has a slightly greater weight gain under the lower partial pressure of water. This may be due to some sorbed CO_2 from the air. At a lower water pressure, 0.025 atmospheres, CaO and calcined dolomite hydrate, but MgO was unreacted.

5.1.2 Tests for Hydration in Partial Vapor Pressure from Brines

5.1.2.1 Background

Three brines which have received attention in regard to storage in salt deposits are WIPP-A, WIPP-B, and NBT-6a. The composition of each of these brines was cast into the number of molar of salt. WIPP solution A was found to be slightly greater than 4 molar in salts and WIPP solution B about 5 molar. NBT-6a is in the range of 4-5 molar. The maximum lowering of vapor pressure from these solutions can be obtained from Figure 3. For example, a solution 5 molar in $MgCl_2$ or $CaCl_2$ would have a vapor pressure at 100°C of 400-500 mm of mercury. If the same solution in 5 molar in NCl or NaCl the vapor pressure is about 650 mm of mercury. In fact, the solutions contain nonovalent and divalent cations, and therefore the vapor pressure is intermediate.

WIPP, solutions A and B, and NBT-6a cannot have a vapor pressure lower than 400 mm of mercury at 100°C. Figure 5 shows that at 100°C MgO should readily hydrate to $Mg(OH)_2$. This approach to the problem of suitable desiccants was tested.

5.1.2.2 Materials

Solutions corresponding to WIPP-A and NBT-6a were prepared, and a second set of the same solution to which excess NaCl was added was prepared. This additional NaCl simply assure saturation of the salts in the solution.

5.1.2.3 Procedures

Reagent MgO, calcined dolomite, cement powder, and a mix of $CaSO_4 \cdot \frac{1}{2}H_2O + MgSO_4 + K_2SO_4$ (which hydrates to polyhalite) were exposed to controlled vapor pressure. The vapor pressure were those obtained from solutions having compositions equal to WIPP-A, WIPP-A plus excess NaCl, NBT-6a, and NBT-6a plus excess NaCl at 100°C. The rate and extent of reaction was determined by weight gain of the anhydrous samples as they draw water vapor from the controlled atmosphere at 100°C.

Experiments also were initiated to establish the rate and extent of hydration at 21°C. Containers of MgO, CaO, calcined dolomite, and polyhalite components were placed in the atmosphere over a brine in a closed vessel. The weight gain, and thus hydration was monitored after 17 days, 40 and 70 days.

5.1.2.4 Results

The results of these hydration experiments at 100°C are shown in Figures 7 and 8.

Reagent MgO and calcined dolomite in the water vapor pressure of WIPP-A and WIPP-A plus excess NaCl at 100°C readily hydrate. The weight gain for MgO and calcined dolomite are approaching the ideal for $Mg(OH)_2$ and $Ca(OH)_2 + Mg(OH)_2$. The weight gain for calcined dolomite clearly indicates that both its oxides are hydrating.

Portland cement powder hydrates more rapidly in vapors over WIPP-A than in vapors over WIPP-A plus excess NaCl. The components of polyhalite

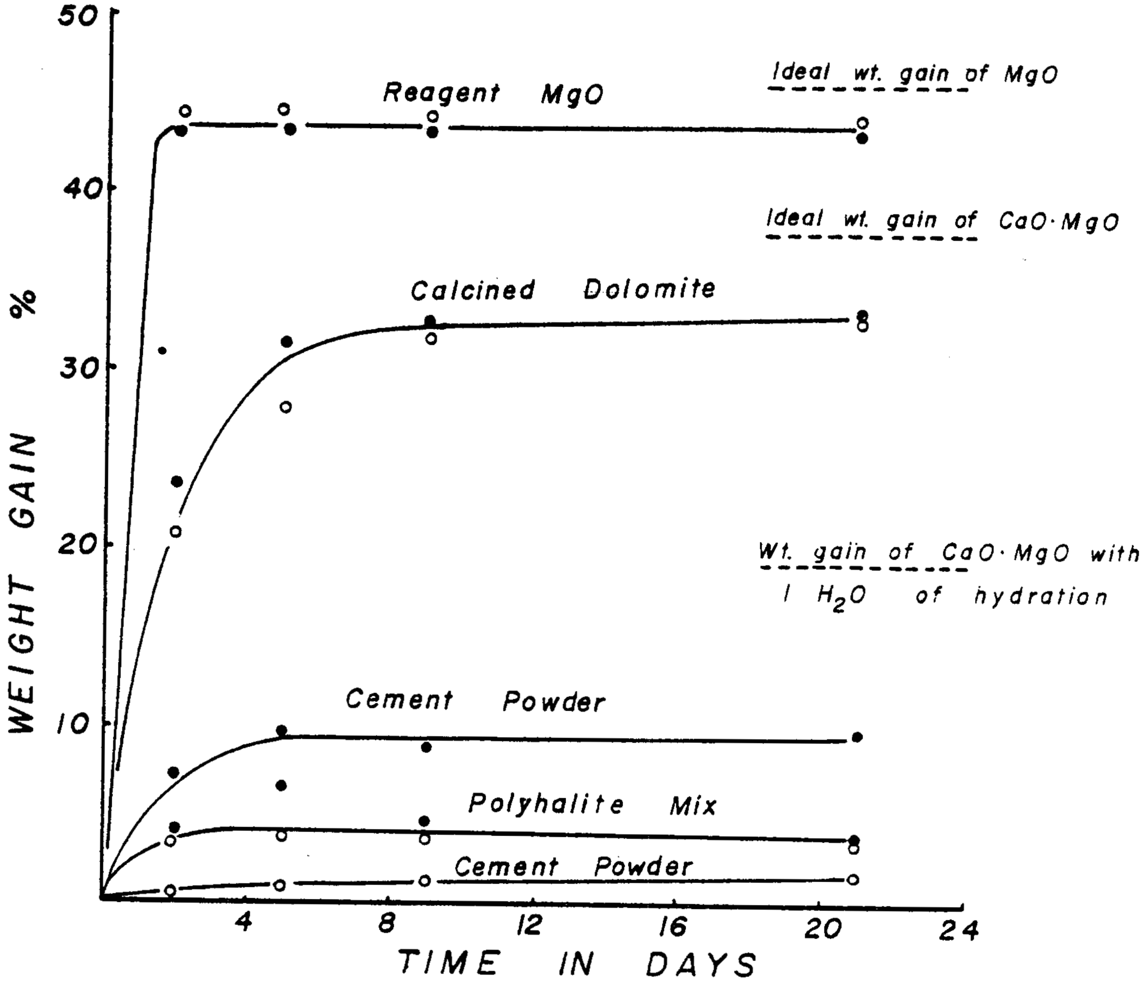

Figure 7. Hydration of desiccants at 100°C in water vapor pressure controlled by solution of WIPP-A composition and WIPP-A plus excess NaCl composition. Solid circles = WIPP-A, open circles = WIPP-A plus NaCl.

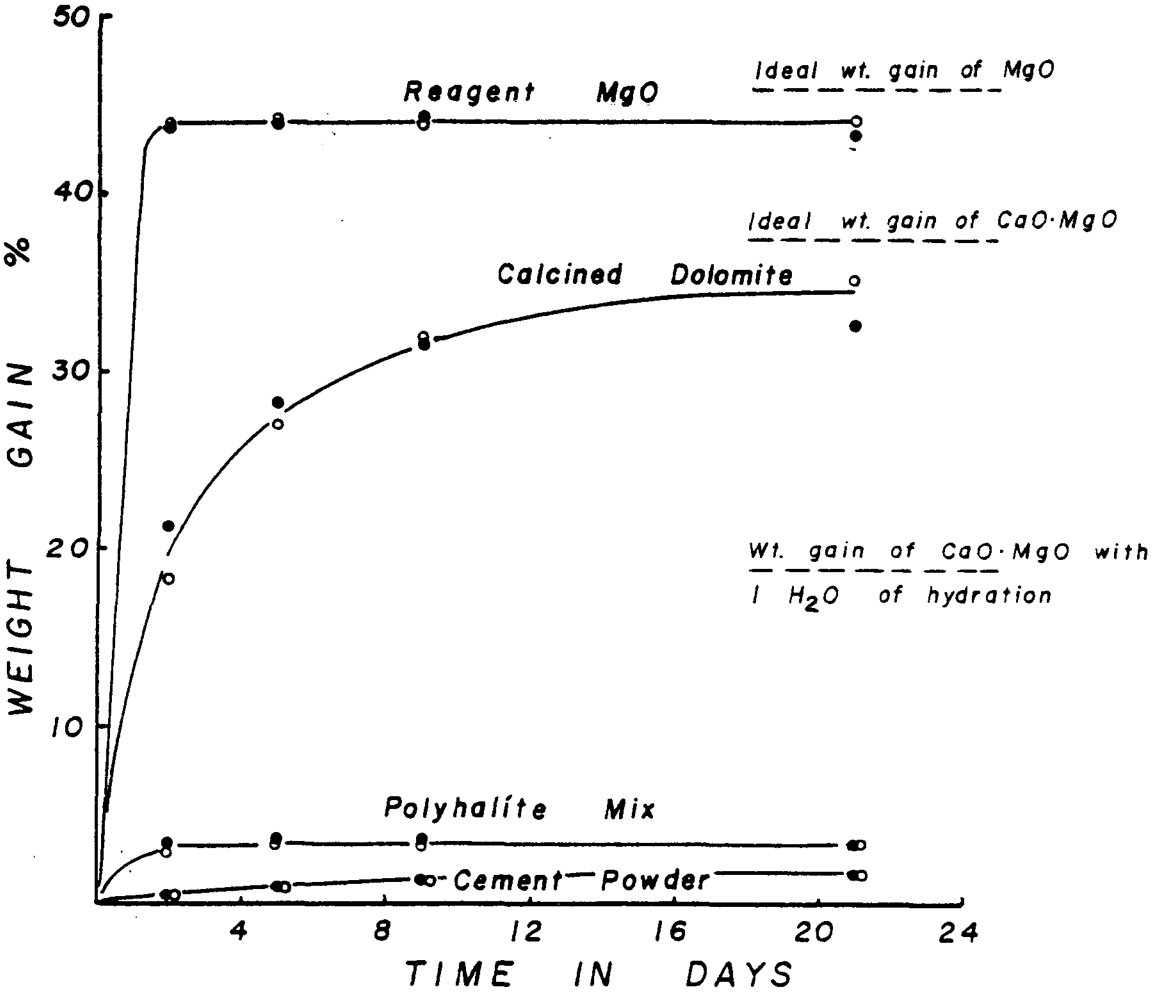

Figure 8. Hydration of desiccants at 100°C in water vapor controlled by solutions of NBT-6a composition and NBY-6a plus excess NaCl composition. Solid circles = NBT-6a and open circles = NBT-6a plus excess NaCl.

show some hydration in the vapors over both solutions (Figure 7).

The results of experiments with NBT-6a solutions shown in Figure 8, are similar to those obtained with the WIPP solution. The experiments with WIPP and NBT-6a at 100°C show the efficacy of reagent MgO or calcined dolomite in removing water vapor from an atmosphere controlled by WIPP-A or NBT-6a type brines. Cement powder and the components of polyhalite will similarily abstract water from the atmosphere, but the rate and capacity are inferior to MgO and calcined dolomite.

The results of experiments at 21°C after 17, 40, and 70 days are shown in Figures 9, 10, 11, and 12. The data clearly shows that all four desiccants are capable of drawing water vapor from the atmosphere at 21°C even though the partial pressure of the water vapor is lowered by the brines.

5.1.3 Tests for Reaction with Carbon Dioxide

5.1.3.1 Background

The gaseous atmosphere of the first two sets of experiments was air with the water vapor resulting from an underlying brine. This is similar to air in a cavern being supplied moisture by the brine inclusions which would weep from the salt wall. The air contains roughly 0.02% CO_2 and it is well known that MgO and especially CaO react with CO_2 to form calcium and magnesium carbonate minerals. Yet in most of the experiments, the vessel was closed or restricted to prevent the free exchange of air. Thus the initial quantity of CO_2 in the experiments was very limited, and

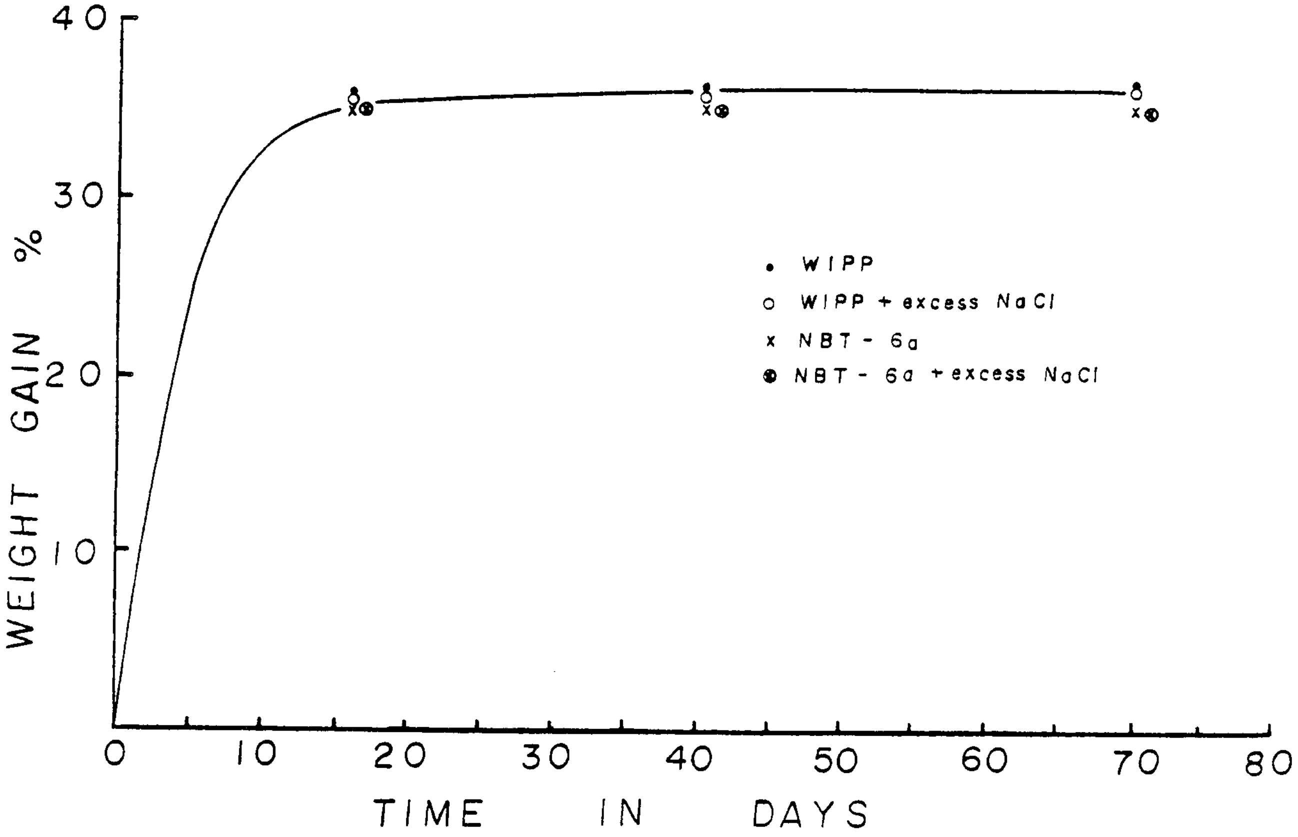

Figure 9. Rate of hydration of CaO in a closed system at 21°C with the vapor pressure of water controlled by the brines identified by the symbols.

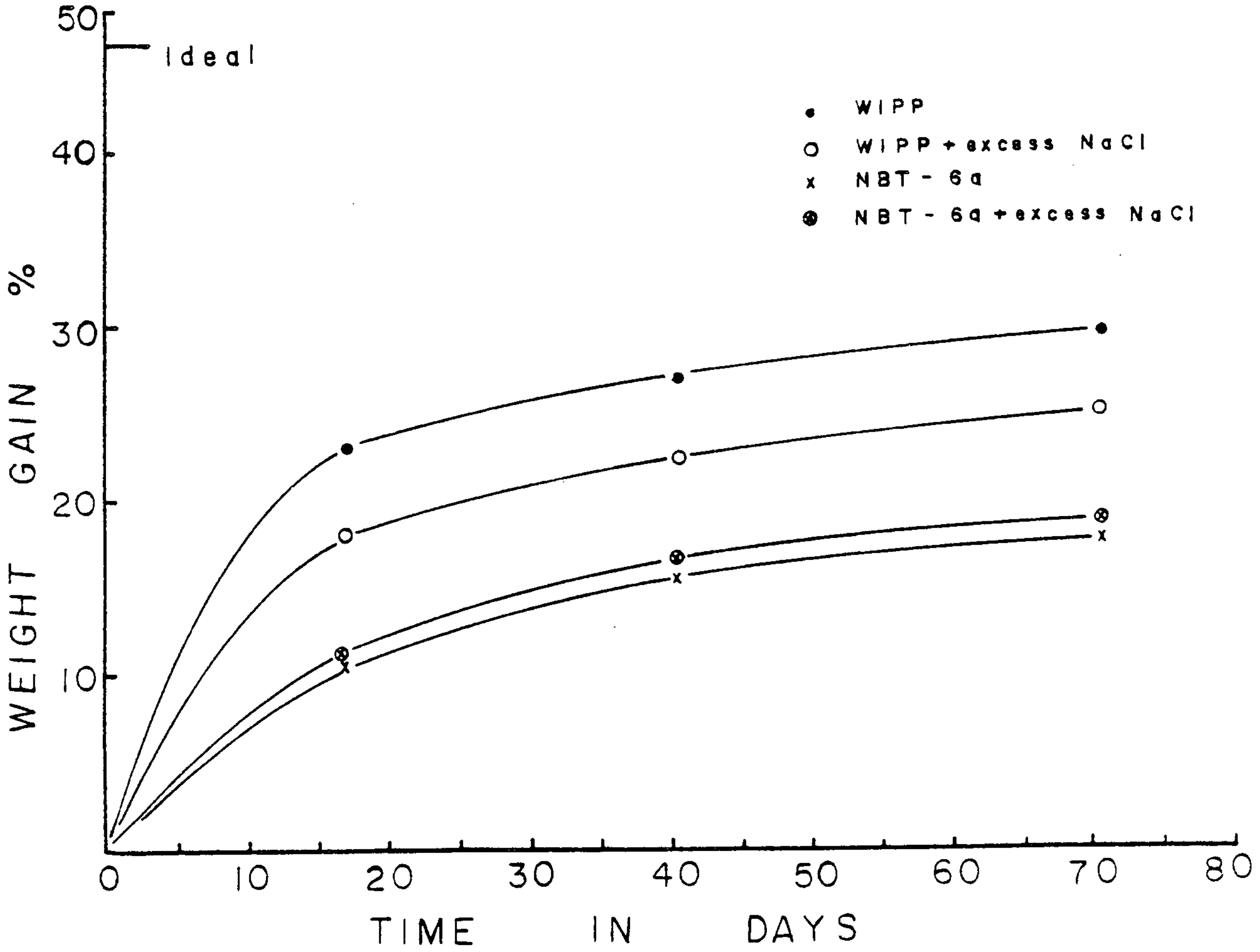

Figure 10. Rate of hydration of MgO in a closed system at 20°C with the vapor pressure of water controlled by the brine identified by the symbol.

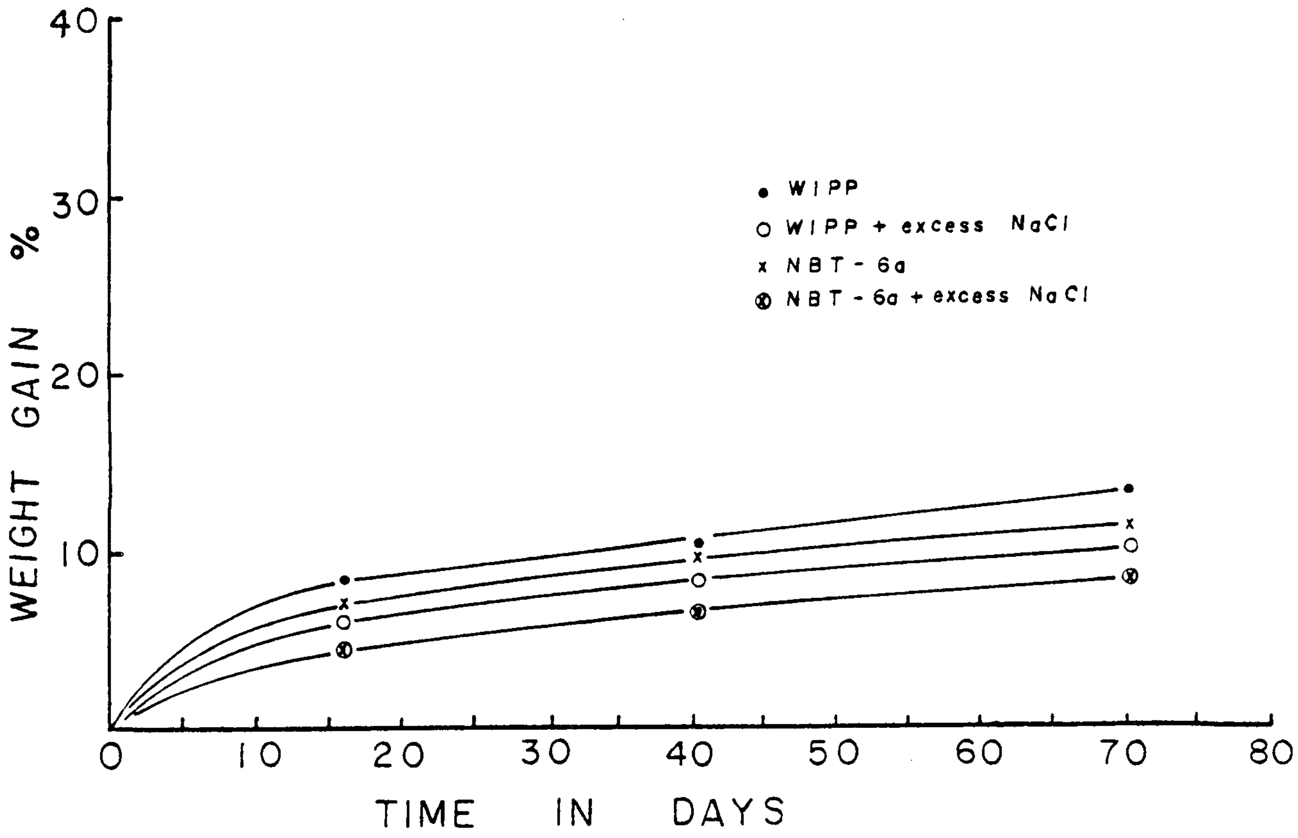

Figure 11. Rate of hydration of calcined dolomite (CaO + MgO) in a closed system at 20°C with the vapor pressure controlled by the brines identified by symbols.

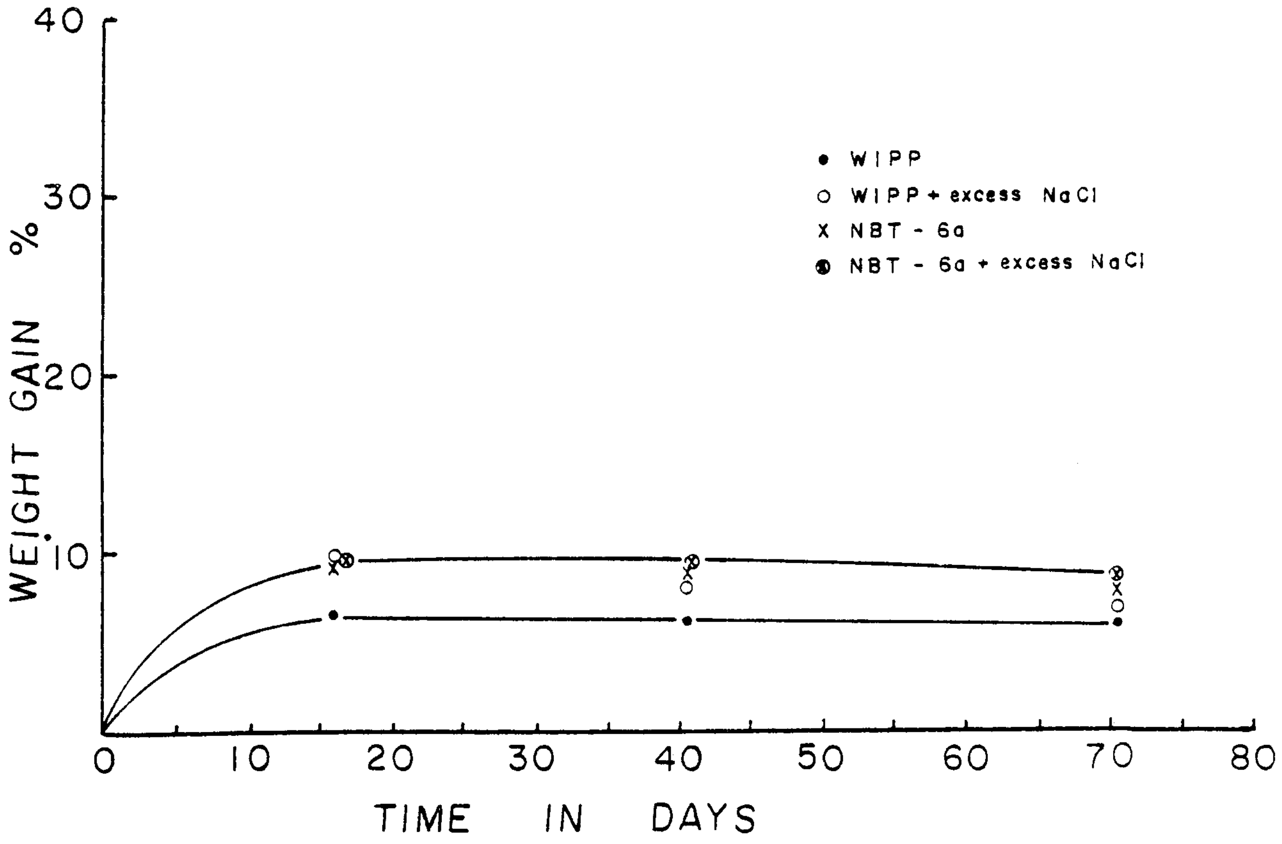

Figure 12. Rate of hydration of polyhalite components in a closed system at 21°C with the vapor pressure controlled by the brines identified by the symbols.

the resupply was prevented. As a result, calcium and magnesium carbonate compounds were prevented from forming, and none were found in the course of these experiments. Nevertheless, it is appropriate to determine whether the desiccants will form carbonate compounds with or without the hydrated compounds in an open air system. The concern in regard to carbonate formation is that if CO_2 from the air reacts with the hydroxide compounds, the water is again released to the atmosphere. Of the two oxides, CaO is of the greatest concern because of the propensity of $Ca(OH)_2$ to react with CO_2 yielding $CaCO_3$, a very common mineral. $Mg(OH)_2$ has greater stability and does not react with air containing a normal percentage of CO_2. However, some experiments show that $Mg(OH)_2$ will react with an atmosphere greatly enriched in CO_2, yielding a magnesium carbonate hydrate.

5.1.3.2 Results

In no hydration experiments using the CO_2 content of air was MgO found to carbonate during the course of the experiment at one atmosphere. There has been less experimentation in this program with CaO and calcined dolomite, at one atmosphere, in an open system. In several experiments at 0.025 atmospheres of water vapor pressure in air of normal CO_2 content, CaO and calcined dolomite reacted yielding products identified by x-ray diffraction as $Ca(OH)_2$ and $Ca(OH)_2 + Mg(OH)_2$ respectively. Calcium carbonate was searched for in the x-ray diffraction patterns, but not found. However, both products showed a very minor effervescence in acid indicating that a trace amount of a carbonate compound had formed. Perhaps more would have formed in an experiment of a longer duration.

5.1.4 Tests for Reaction with Ions in Brine

5.1.4.1 Background

It is important to determine whether the anhydrous desiccant or the hydrated compound reacts with ions of the brine. There is no evidence of a reaction product involving sodium or chloride in the MgO or $CaO \cdot MgO$ studies. At this stage, it seems that NaCl in the brine only controls the activity of water in the brine and the partial pressure of water in the vapor over the brine.

Reaction of the brine with the desiccant is a more important consideration for brines containing magnesium, calcium, and chloride ions. Magnesium and calcium oxychloride compounds are known. The magnesium compound is called Sorel cement. MgO in Portland cement hydrates to $Mg(OH)_2$ after the cement sets, and the increase in volume causes a spallation of cement. It was found that the addition of $MgCl_2$ to a MgO containing cement mix stopped the deleterious action by the formation of Sorel cement ($3MgO \cdot MgCl_2 \cdot 11H_2O$). A study by Demedink, Cole, and Hueber (1955) showed that a series of magnesium and calcium oxychlorides form, and some of the compounds form above 100°C.

5.1.4.2 Procedures

There are many different oxychlorides with different waters of hydration, and unfortunately the compounds are poorly defined and their stability poorly established. In some feasibility experiments $MgCl_2 \cdot 6H_2O$ was reacted in the presence of limited water with MgO, CaO, and calcined dolomite. These experiments were at 60°C, 40°, and 20°C.

5.1.4.3 Results

The products are calcium and magnesium oxychlorides. One product, $Mg(OH)_3Cl \cdot 4H_2O$ is of particular importance and is included in the later thermal stability study.

5.2 Experiments with Greater than One Atmosphere

5.2.1 Hydrothermal Experiments - $MgO\text{-}NaCl\text{-}H_2O$

5.2.1.2 Background

Many reports show the univariant curve for the reaction $MgO + H_2O \rightleftarrows Mg(OH)_2$, and there is a wide spread in the data. Data for low pressures is sparse and none of the reports consider highly saline solutions. Nevertheless, the reports present an important background to the problem. The wide spread in the data has been explained by lack of equilibrium, failure to recognize the true products synthesized over those formed during quencing, thermal gradients in the experimental apparatus, and a metastable or more reactive form of MgO perhaps resulting from the small grain size. The reactive MgO is of interest, but in fact is a beneficial aspect to the overall goal of this research. It is desired that MgO react with a brine and thus incorporate the water of the solution into a solid phase. If the hydrated material, $Mg(OH)_2$, became more reactive, and therefore less stable, there would be concern. Such reactive $Mg(OH)_2$ is not proposed to explain the spread of data by other. Therefore, the experiment effort was concerned with the stability of $Mg(OH)_2$, which under hydrothermal conditions can be rapidly formed by reaction of MgO and water.

5.2.1.2 Solution Materials

The need for experimental studies of the stability of $Mg(OH)_2$ in hypersaline solution is brought on by the marked decrease in the activity of water caused by the dissolved salts. In early experiments, a salt solution saturated at room temperature was used. It is obvious that such a solution would be undersaturated at elevated temperatures, but it would become saturated as the reaction proceeds and water is consumed. This change in extent of saturation is deemed undesirable and a poor model. Therefore, excess NaCl was added in all experiments so that the solution remains saturated at all temperatures and pressures, and it in fact models a brine migrating in a temperature gradient.

5.2.1.3 Procedures

Weighed mixtures of MgO, NaCl, and water were sealed by welding in a gold tube. These samples contained slightly less water than required to completely hydrate the MgO and excess NaCl over that required for a saturated solution if none of the water was used by hydration of MgO. Thus, if the hydration reaction occurred, the product would be $Mg(OH)_2$, NaCl, and some excess MgO. There would be an absence of a liquid or vapor phase. If hydration did not occur, the products would be MgO, NaCl, and a NaCl saturated solution, or supercritical gaseous phase.

The gold encased samples were subjected to hydrothermal conditions using standard cold-seal vessels. The samples were removed from the hydrothermal environment by first releasing the pressure and almost immediately lowering the temperature. In this quench procedure, the samples were removed from the conditions of the experiment to standard conditions in less than one minute. Because the samples were subjected to a pressure, the thin wall gold tube collapses tightly against the sample. If the hydration reaction occurred, the sample contains three solid phases, and the quenched charge shows the gold tube pressed tighly against the solid phases. If MgO did not hydrate, the sample contains a saline solution or gaseous phase. Under the conditions of the experiment, the solution or gas is contained by the gold membrane under the confining pressure at moderate temperature, for example 300 to 400°C. When the confining pressure is released before the temperature is lowered, the internal fluid or gas either bloats or ruptures the gold membrane. Thus, the nature of the gold membrane tube after the experiment immediately indicates whether the hydration reaction has occurred. If the gold tube is intact, its encased sample can be reused for subsequent experiments.

Some difficulty was experienced in using cold-seal vessel at moderate temperatures and low pressure. The pressure media in the vessel in water, and over a considerable pressure temperature range the vessel, with its closure out of the furnace, will act as a heat pipe. To prevent this, the closure was insulated.

5.2.1.4 Results

Using the hydrothermal quench method, the stability of $Mg(OH)_2$ in a saturated NaCl brine has been determined from 340 bars to 110 bars. At the higher pressure, the hydrate is stable to roughly 510° at the lower pressure the stability has decreased to about 475°C.

This hydrothermal quench approach was discontinued because of concern over the preservation and identification of the high pressure-temperature assemblage.

5.2.2 Differential Thermal Analysis

5.2.2.1 Background

The wide spread in the published stability curves for $Mg(OH)_2$ attest to difficulties investigations have encountered in interpretation of experimental results. As a second approach to determination of the stability of $Mg(OH)_2$ in a brine, a pressure vessel was modified so that it could be used for differential thermal analysis (DTA) under a confining pressure.

In DTA, both decomposition and rehydration can be studied. During the initial heating cycle, the MgO reacts with the water vapor forming $Mg(OH)_2$. This formation of $Mg(OH)_2$ is undetected by the DTA, but an endothermic reaction at higher temperature, marks the decomposition of $Mg(OH)_2$. With cooling of the DTA pressure vessel, the MgO reacts with water vapor to rehydrate. Thus decomposition of $Mg(OH)_2$ occurs on heating and crystallization of $Mg(OH)_2$ occurs during the cooling cycle.

5.2.2.2 Materials

Reagent grade MgO, which is a very finely divided powder, was used for most experiments; however, a commercial grade MgO was used for several determinations for comparison. This commercial grade MgO is much coarser grained, and it is also pelletized.

5.2.2.3 Procedures

A welded gold capsule contained MgO + NaCl + H_2O and a second gold capsule served as a reference. These capsules were inserted in a loose fitting ceramic block with sheathed thermocouples between the capsule and the block. A third thermocouple measured the internal vessel temperature. The ceramic block was the sample holder, but it also reduced the gas volume and convection of the system. The ceramic block and sample were in the pressure vessel and the thermocouples were inserted through a silver soldered seal.

Water pumped to the vessel supplied the pressure for values over 70 atmospheres. At lower pressure tank nitrogen was used. The temperature within the vessel and the differential temperature between the sample and reference material, both encased in gold, were continuously recorded. Heating rates were about 5-10°C/minute and cooling rates 10-15°C/minute.

5.2.2.4 Results

The DTA determination of the univariant curve for the reaction $Mg(OH)_2 \rightarrow MgO + H_2O$ vapor is shown in Figure 13. This data fits the curve extremely well and is highly consistent with the DTA data shown by Weber and Roy (1965). Three decomposition data points

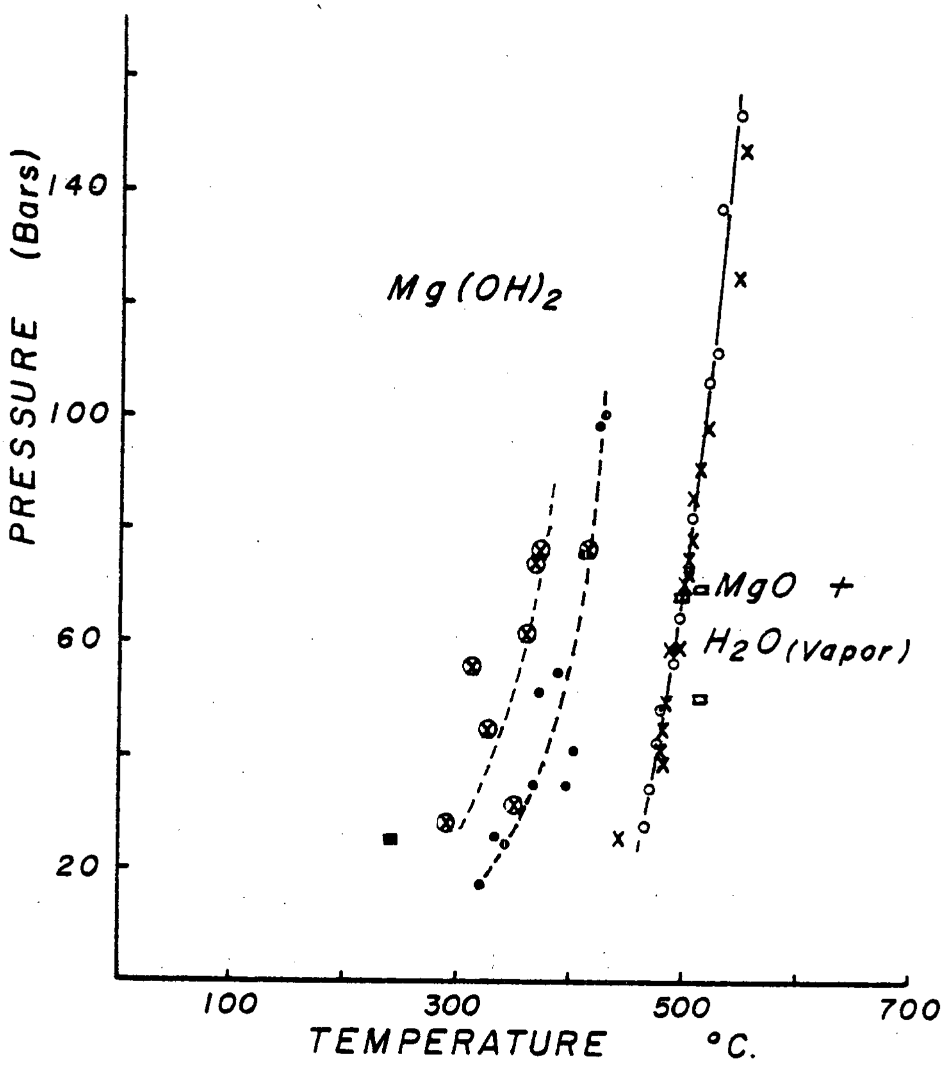

Figure 13. DTA determinations of decomposition of $Mg(OH)_2$ on heating cycle and crystallization of $Mg(OH)_2$ on cooling cycle.

- ○ Dehydration of $Mg(OH)_2$ synthesized from reagent MgO.
- × Dehydration of $Mg(OH)_2$ synthesized from MgO with excess NaCl.
- □ Dehydration of $Mg(OH)_2$ synthesized from commercial grade MgO. The sample contained excess NaCl.
- ● Rehydration of $Mg(OH)_2$ synthesized from reagent MgO.
- ⊗ Rehydration of $Mg(OH)_2$ synthesized from MgO with excess NaCl.
- ■ Rehydration of $Mg(OH)_2$ synthesized from commercial grade MgO. The sample contained excess NaCl.

were determined using $Mg(OH)_2$ hydrated from commercial grade MgO. These points are close to the well defined decomposition curve for $Mg(OH)_2$.

In the absence of NaCl the decomposition temperature of $Mg(OH)_2$ is roughly 100°C above its temperature of formation with cooling. Although there were variations in the heating rate and cooling rates, there is no consistent pattern which would support an overheating or undercooling hypothesis. Nevertheless one explanation of the different position of the two curves is that there is some undercooling and overheating before the reactions are initiated. Weber and Roy (1965) found evidence for a two stage reaction at low water pressure and mention the possibility that the "periclase" may actually be an oxy-hydroxide. If the reaction is two stage it is possible that a metastable phase enters the reaction. MacDonald (1955) calculates and discusses how there are several reaction curves. Namely, poorly crystallized $Mg(OH)_2$ will react to well crystallized MgO at a lower temperature than well crystallized $Mg(OH)_2$ reacting to poorly crystallized MgO. The present data does not uniquely support or refute any of the three possibilities. This point is of academic interest in regard to this research. It is important to note that $Mg(OH)_2$ forms in accord with the boundary at the lower temperature and once formed persists to the higher temperature. This is as desired if MgO is used as backfill in a heat generating area.

The samples of MgO and water which contained an excess of NaCl behaved similarly to those without NaCl. In fact, the two sets of data cannot be distinguished. The data indicate that the presence of NaCl has no, or an insignificant, effect on the decomposition temperature of $Mg(OH)_2$.

The MgO hydration curve, Figure 5, is the low pressure extension of the hydration curve Figure 13. Projections of both curves shows that MgO hydrates at about 200°C under a water vapor pressure of one atmosphere.

The Mgo sample containing NaCl tended to rehydrate at roughly 50°C lower than those lacking NaCl. Data from a commercial grade MgO, which was of excellent crystallinity before any thermal treatment, are consistent with this trend.

The commercial grade MgO, however, did rehydrate at a slightly lower temperature than reagent MgO. This lower temperature may result from the commercial material being coarser grained.

5.2.3 Thermal Stability Studies

5.2.3.1 Background

In the course of the experiments, hydrous compounds were synthesized by several methods. Some $Mg(OH)_2$ was crystallized in the presence of a brine under a confining pressure at more than 300°C. Other $Mg(OH)_2$ was formed by hydration with a lower partial pressure of water from an air atmosphere. Some MgO only partly hydrated because of low temperatures, insufficient time, and very low partial pressure of water in the air atmosphere. It was unknown whether such samples synthesized under different conditions, and therefore of different crystallinity, would decompose at different temperatures if simply heated in air. For this reason, experiments were conducted to establish the weight loss, or decomposition, of the samples with heating. This is referred to as thermogravimetric analysis (TGA).

The thermal stability of other materials needed to be determined. The hydration products from experiments with calcined dolomite and a product from the reaction with brines experiment, $Mg(OH)_3Cl \cdot 4H_2O$, were included. In addition, tachyhydrite was included since its thermal stability data were lacking.

5.2.3.2 Materials

Six samples were used for TGA. The first sample was $Mg(OH)_2$ synthesized under a confining pressure and with excess NaCl at a temperature above 300°C.

A second sample of $Mg(OH)_2$ was formed by hydration of reagent MgO in the vapor pressure of water in air at less than 100°C. The third sample was MgO only partly hydrated. Hydrated calcined dolomite was the fourth sample; $Mg(OH)_3Cl \cdot 4H_2O$, the fifth. The sixth sample, tachyhydrite, was prepared by precipitation and reaction.

5.2.3.3 Procedures

The heating rate for all $Mg(OH)_2$ and calcined dolomite samples was slow, typically 1-2°C/minute, and all heating was in air. The temperature was raised by steps with at least 24 hours between each step.

5.2.3.4 Results

The first sample, $Mg(OH)_2$ synthesized under a confining pressure and with excess NaCl at a temperature above 300°C, had the best crystallinity of the $Mg(OH)_2$ samples used for TGA. Figure 14 shows that this $Mg(OH)_2$ began to decompose at 300°C and decomposition was complete at 400°C with heating in air. Ideal $Mg(OH)_2$ contains over 30% water and would show a larger weight loss. This sample contained some unreacted MgO and considerable NaCl, but only the $Mg(OH)_2$ loses weight with heating.

TGA of the second sample, Figure 15, shows some weight loss beginning at roughly 250°C, and a sharp increase in weight loss at 300°C. The data show a weight loss of about 28% at 325°C and, although there is scatter in the data, a slight weight gain appears near 400°C as a minimum in the weight loss curve. The data are inconclusive concerning the weight gain, but a weight gain is consistent with the finding for hydrates of calcined dolomite, sample four. The incipient weight loss at temperature between 250 and 300°C (compare Figure 14 and 15) suggest that some of the water of this more poorly crystallized $Mg(OH)_2$ is sorbed and released at temperatures slightly below the true decomposition temperature of $Mg(OH)_2$.

The third sample, partially hydrated MgO, was heated to determine whether the product of limited hydration would behave different than when the reaction is carried more nearly to completion. The decomposition curve, Figure 15, shows less weight loss, but otherwise is similar to the form of the completely hydrated sample.

Thermogravimetric analysis data for the fourth sample, hydrated

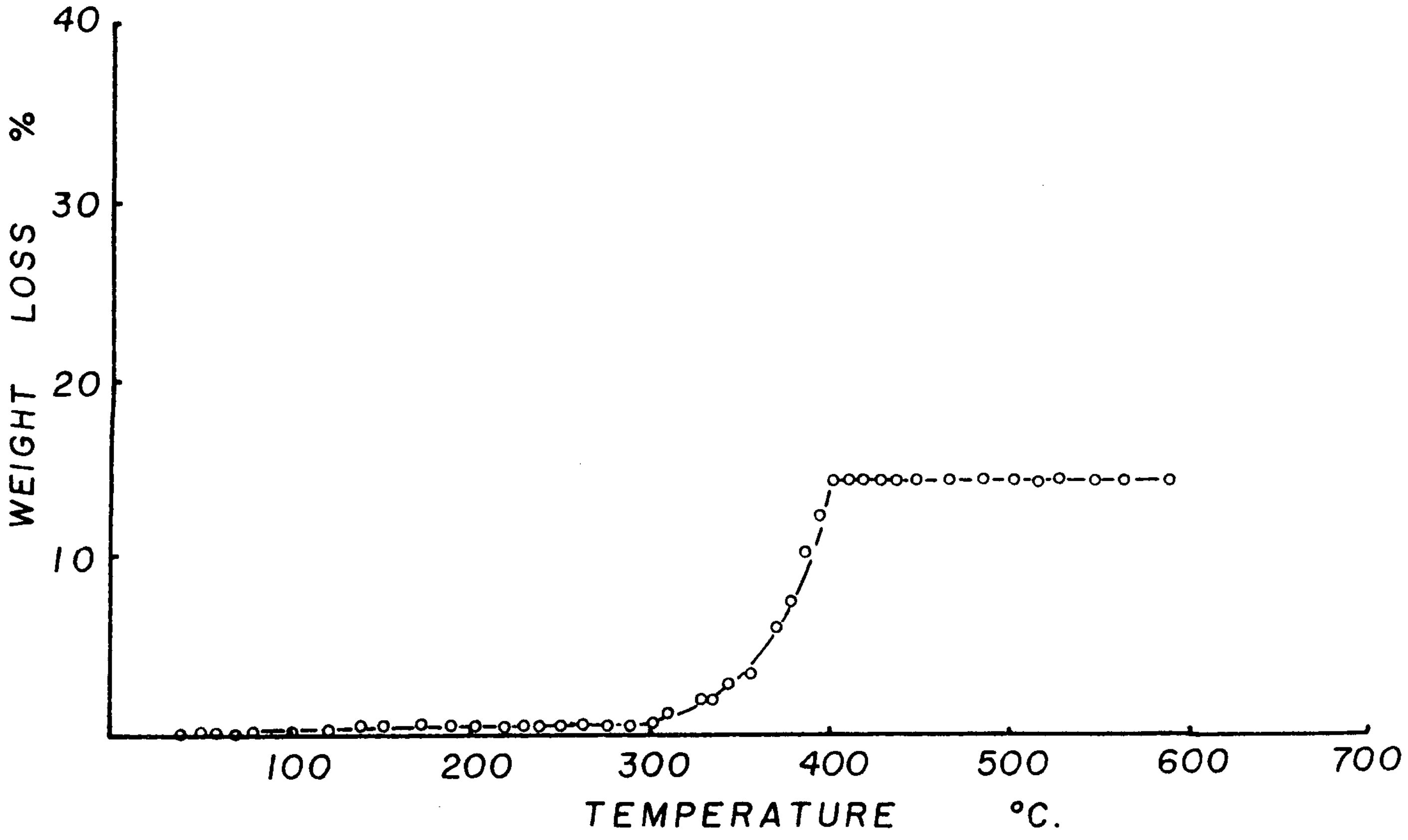

Figure 14. Thermogravimetric analysis of $Mg(OH)_2$ synthesized in the presence of NaCl under a confining pressure. The temperature of synthesis was above 300°C.

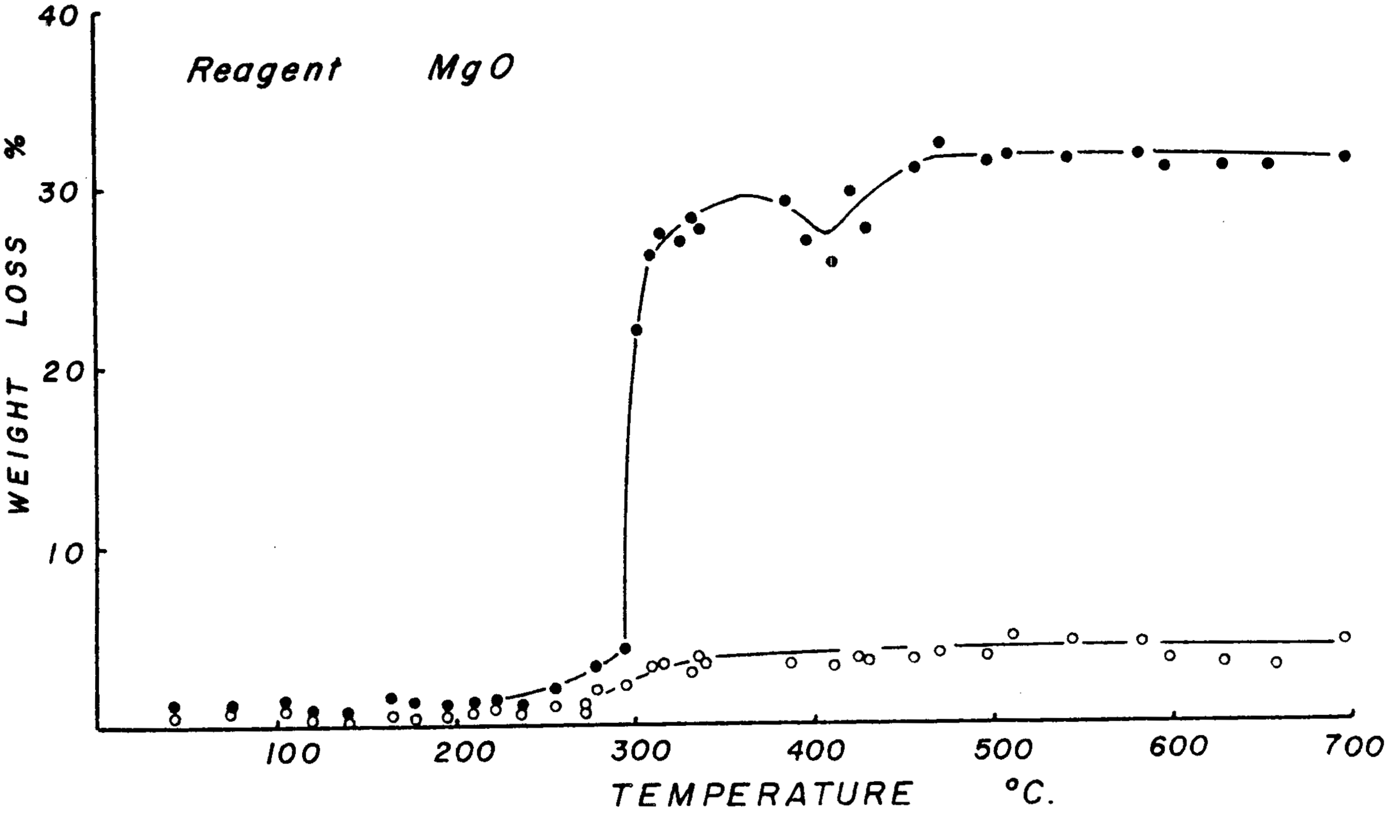

Figure 15. Thermogravimetric analysis of $Mg(OH)_2$ formed by hydration of reagent MgO in air with a controlled vapor pressure of water. Solid circles represent a sample of $Mg(OH)_2$ and the open circles represent a sample of MgO partly reacted to $Mg(OH)_2$.

hydrated products from the calcined dolomite, are shown in Figure 16. The upper curve of Figure 16 represents the TGA of a highly hydrated sample prepared from the calcined dolomite, and the lower curve represents a sample with limited hydration. With limited hydration, it is probable that the CaO of the calcined dolomite would hydrate before the MgO based on the kinetic data shown in Figure 6.

The extensively hydrated material from calcined dolomite shows weight loss beginning at roughly 300°C, reaching a maximum at about 360°. Then there is a weight gain, continuing to about 550°C, followed by a sharp weight loss. The partly hydrated material, represented by open circles on the figure, reacted similarly except the first weight loss at about 300°C is compensated by a weight gain.

The first weight loss for the hydrated samples from the calcined dolomite occurs at the temperature of decomposition of $Mg(OH)_2$. Considering that the heating was in air, the weight gain must result from a reaction involving CO_2. Either $CaCO_3$, $MgCO_3$, or dolomite $CaMg(CO_3)_2$ may have formed causing the weight gain. Resolution of this reaction is important because if a carbonate compound forms, it sacrifices some of the alkaline oxide which is to serve as a desiccant. A beneficial aspect is that the partly hydrated alkaline oxides may be an absorbent for CO_2 in the event of a buildup of CO_2 in the gaseous atmosphere.

The TGA curves, Figure 16, show a maximum weight gain at about 500°C. A sample of hydrated material from calcined dolomite was held

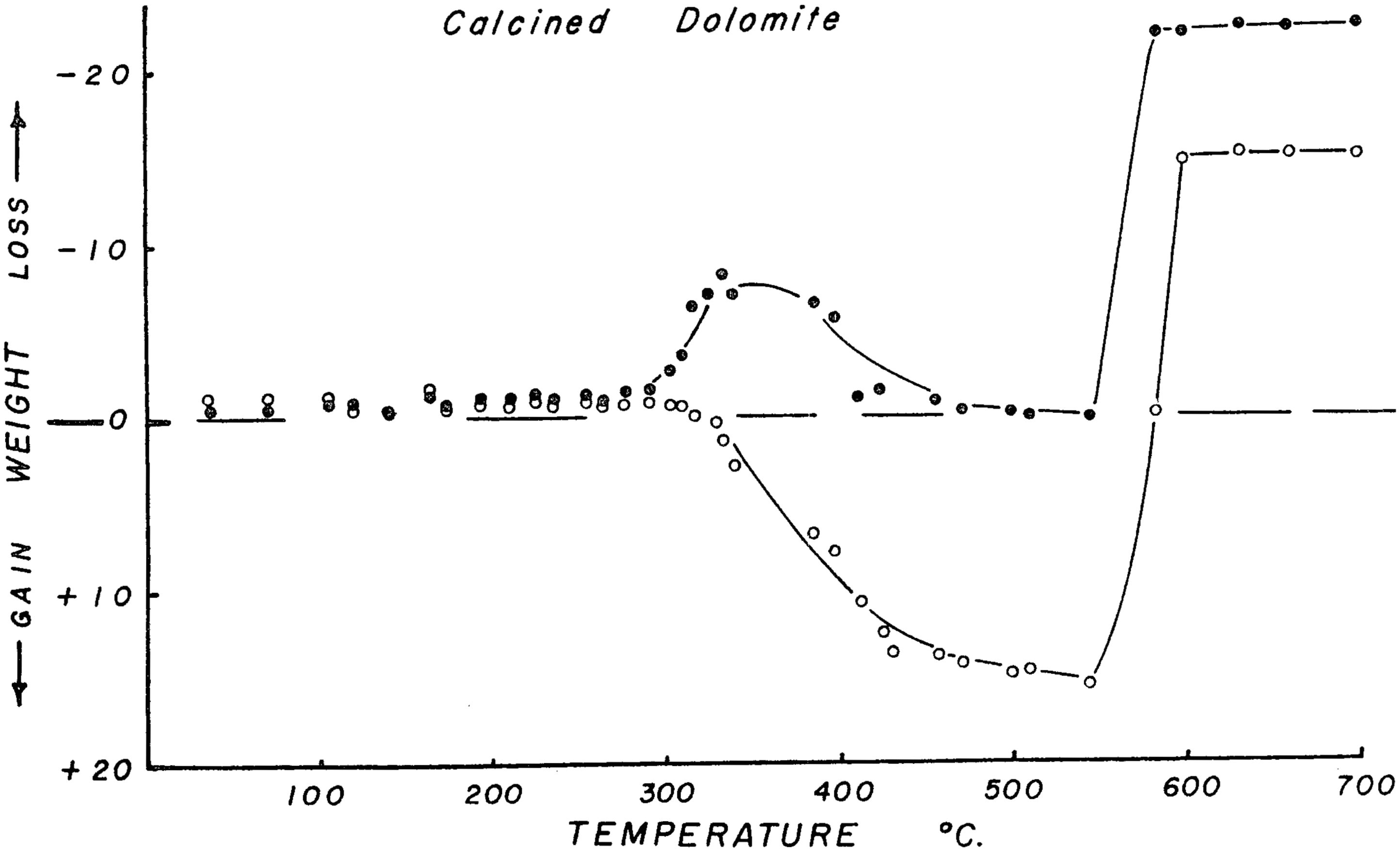

Figure 16. Thermogravimetric analysis of hydrated calcined dolomite. Solid circles represent a highly hydrated material and the open circles are a partly hydrated material.

at 460°C for several days. After the heat treatment MgO, CaO, and a trace of $CaCO_3$ was identified in an x-ray diffractogram of the product. The major diffraction peak for $MgCO_3$ overlaps a strong CaO peak; consequently the presence or absence of $MgCO_3$ could not be established. Thus, it is established that some $CaCO_3$ formed by reaction of the heated sample with CO_2 from the air.

A major weight loss occurs at roughly 550°C. It has been established that $Mg(OH)_2$ decomposes starting at 300°C, $Ca(OH)_2$ is reported to decompose at 580°C. On this basis, the major weight loss is concluded to be the loss of water from $Ca(OH)_2$. At temperature above the stability of $Mg(OH)_2$, and in the absence of CO_2 in the atmosphere, the heated sample would be MgO plus $Ca(OH)_2$. Such a sample could only lose 16% weight by expelling the water at temperatures above 550°C. The TGA curves shows losses above 20%. Thus, more than water is lost during the decomposition at temperatures above 550°C. The decomposition temperature of carbonate compounds is in part a function of the partial pressure of CO_2 in the atmosphere. Using the same apparatus and heating rate, a sample of dolomite $[CaMg(CO_3)_2]$ was found to undergo a large weight loss starting at 560°C.

The fifth sample, $[Mg_2(OH)_3Cl \cdot 4H_2O]$, has essentially a chloride substituted for a hydroxyl and additional water. The TGA is shown as Figure 17. Assuming that the weight loss below 100°C represents drying, two waters are lost between 100 and 200°C. Thus, from 200-300°C the stable compounds appears to be $Mg_2(OH)_3Cl \cdot 2H_2O$. At about

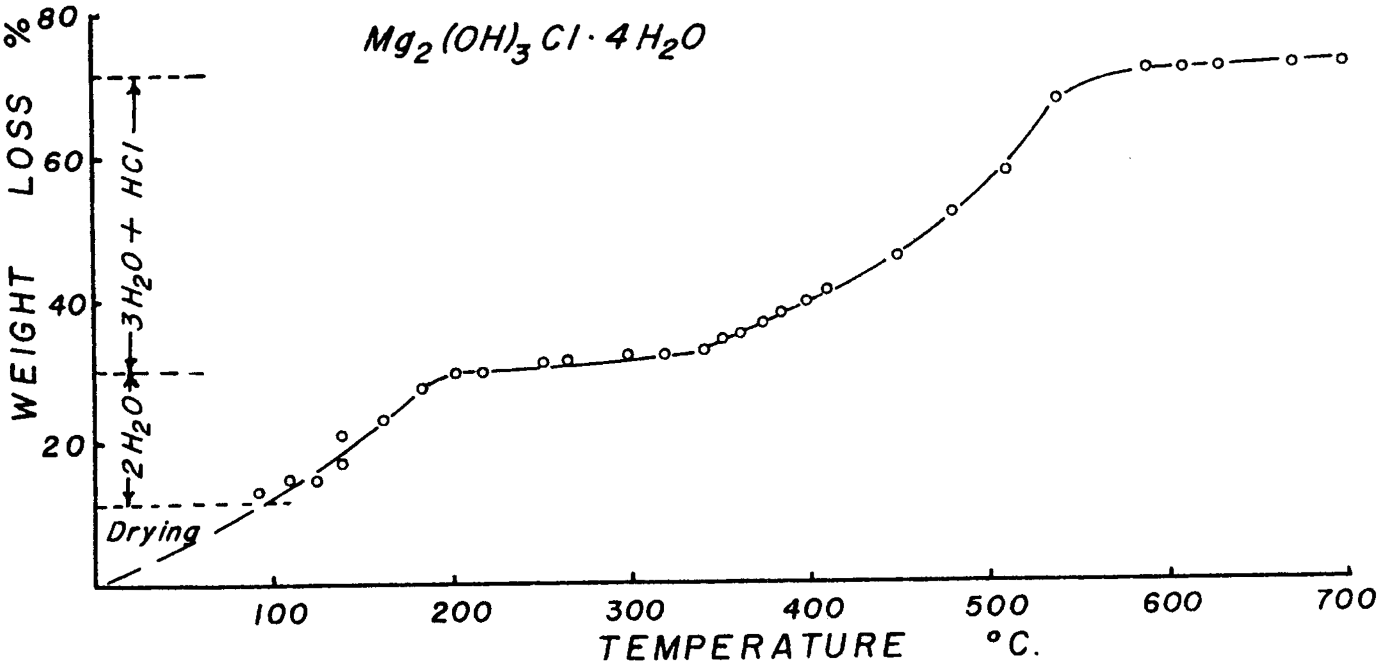

Figure 17. Thermogravimetric analysis of $Mg_2(OH)_3$ $Cl \cdot 4H_2O$ formed by reaction of $MgCl_2 \cdot 6H_2O$ and MgO in the presence of water.

350°C, additional weight loss commences. The total loss above 350°C corresponds to three waters plus HCl with the final solid being MgO. Once the first two waters are lost, the remaining compound has stability equal to $Mg(OH)_2$. At this stage, this magnesium oxychloride compound appears as desired as $Mg(OH)_2$ provided the system contains some excess MgO to react with the two waters released in the 100-200°C range. But the stability and nature of the oxychlorides is poorly established. A complex brine may react with MgO or CaO and yield some unknown phases.

Data from the sixth sample, tachyhydrite, show that there is rapid water loss at temperatures slightly over 100°C, and most water is lost at less than 160°C (Figure 18). Such low temperature stability limits the usefulness of the anhydrous equivalent of tachyhydrite as a desiccant material.

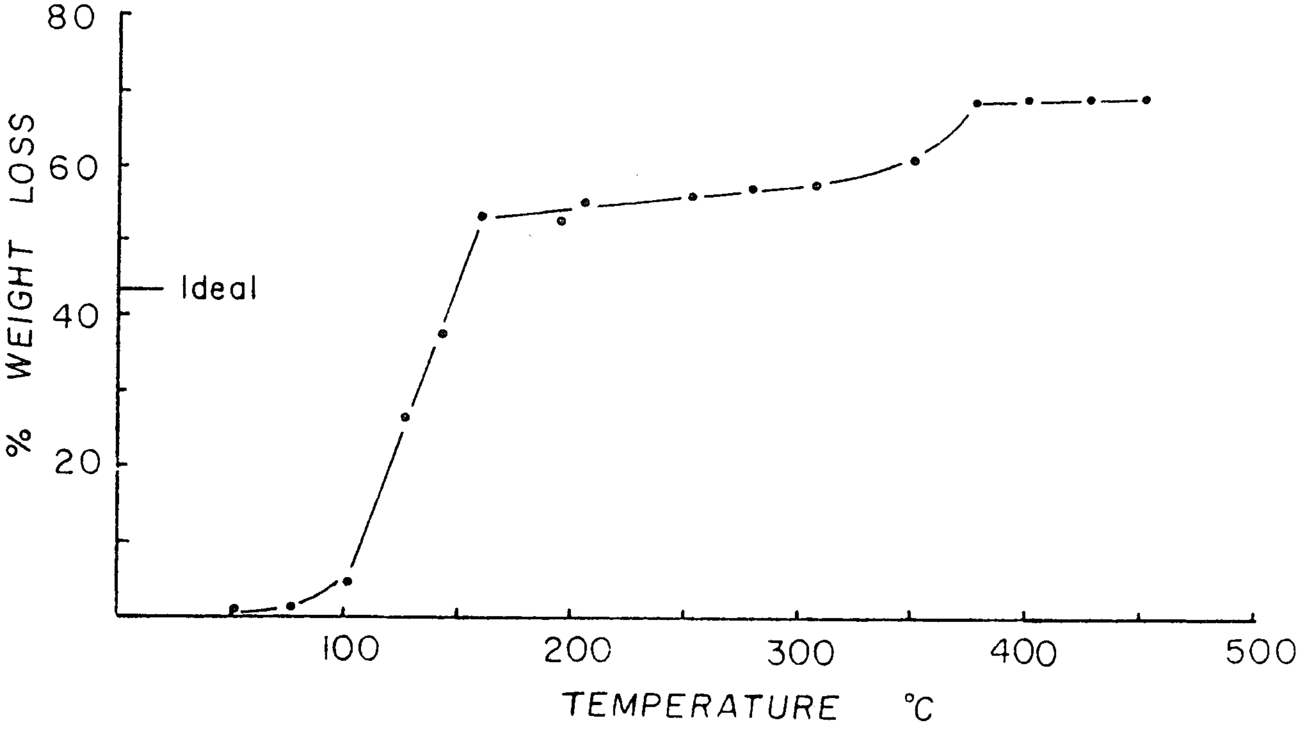

Figure 18. Weight loss of Tachyhydrite ($CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$), Heated in Air.

6.0 SUMMARY AND CONCLUSIONS

There are many anhydrous compounds which react with water vapor to form a hydrate which is stable to moderate temperature, and a large list of these compounds was established from the literature search. For the anhydrous compounds to be an effective desiccant, they must be able to desiccate the salt brine. The activity of the water in a sodium chloride brine, and consequently its vapor pressure, will be only about half the value of pure water. With such reduced water activity in a brine, many of the anhydrous compounds are stable and will not react to a hydrous compound. This problem of many compounds not being sufficiently effective as a desiccant is exacerbated when the brine contains a more soluble salt than sodium chloride. Because of the extreme solubility, magnesium and calcium chloride salts are especially effective at reducing the activity and vapor pressure of water in a brine. Consequently, an extremely effective desiccant is required if a magnesium or calcium chloride bearing brine is to be desiccated. For example, the anhydrous desiccant used for backfill for NBT-6a brine, which contains appreciable magnesium and calcium chloride, would need to be a better desiccant than one used with WIPP B, which is a sodium chloride rich brine.

The best desiccant material which form hydrates with appreciable thermal stability are:

1) MgO
2) Calcined $CaMg(CO_3)_2$ [dolomite] = $CaO \cdot MgO$
3) CaO

CaO, MgO, and the intimate mixture of the two obtained by calcining dolomite, are excellent desiccants, and they will absorb water from brines containing a high concentration of calcium and magnesium chloride. Their hydrate products are $Mg(OH)_2$ (brucite) and $Ca(OH)_2$ (portlandite). Both have moderate thermal stability and a high water content; yet neither is deliquescent with continued exposure to moisture. The anhydrous compounds have long term stability if dry, and with exposure to moisture they react readily with water. The present research has been focused on these compounds because of the desirable properties. Either would neutralize any hydrochloric acid produced by reaction of metal with the brine.

Both MgO and CaO hydrate in a sodium chloride brine or in the water vapor pressure of a magnesium or calcium chloride brine. However, CaO or MgO reacts in a magnesium or calcium chloride brine to form a magnesium or calcium oxychloride instead of brucite or portlandite. The reaction is of concern and requires more study. At this stage, the hydrated oxychloride compounds appear to have desirable thermal stability in air at one atmosphere, and they have a high water content. Some of the oxychlorides, of which there are many with different waters of crystallization, are termed Sorel Cement, and the most complete study is that of Demedink, Cole, and Hueber (1955). These phases should be reexamined with modern equipment in the light of the needed data for the present problem. The concern is not that the formation of these compounds negates the use of MgO or CaO as desiccant backfill, it is simply that the properties of the products are not fully established.

In the present study, the MgO and CaO used in the experiments was reagent grade material. This material, especially the MgO, is very fine grained and therefore has an enormous surface area and low bulk density. Such MgO is also used as a high temperature insulation This leads to a concern of whether backfilling with such insulating MgO would cause an undesirable temperature rise around waste canisters instead of a dissipation of heat. Some commercial grade MgO was obtained and it was found to be pellets 1-3 mm. in diameter with a high bulk density. Microscopically, the pellets were found to contain good crystals of MgO, roughly 10-60μ in diameter. Such crystals are very large compared to the reagent grade MgO. Feasibility experiments with this coarse grained MgO show that the rate of reaction is orders of magnitude less than that of the fine grained material. Thus, it appears that there will be a trade-off of the kinetics of the hydration reaction and the thermal conductivity of the reactants.

Two environments might be considered for the backfill material. In the first environment, the storage area is vented to the atmosphere. This might require that the desiccant backfill material hydrates in a brine under an atmosphere containing the CO_2 content of air. In a later environment, the system may be sealed and after a long period and be under the pressure of the lithostatic load of the overlying rock. In this environment, there would be moderate pressure, perhaps some brine, but no appreciable atmosphere bearing carbon dioxide. It is the presence of the carbon dioxide in air that may cause some other reactions with CaO and MgO. Both CaO and MgO form very stable carbonate compounds, and $Ca(OH)_2$ is known to go to $CaCO_3$ and water when left exposed to air. A number of magnesium carbonate-hydrate compounds are known; however, $Mg(OH)_2$ is stable under the partial pressure of CO_2 in air. Thus, calcined dolomite, which is CaO·MgO, may be a desiccant at a very low partial pressure of water because of the MgO, and a scavenger of carbon dioxide in the air, or from oxidation of organic material, because of the CaO. Thus the exact nature and design of the repository will be important in the final selection of the best desiccant.

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