Thermodynamics of the Conversion of Calcium and Magnesium Fluorides to the Parent Metal Oxides and Hydrogen Fluoride

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by

Mike H. West and Keith M. Axler

ABSTRACT

We have used thermodynamic modeling to examine the reaction of
calcium fluoride (CaF_2) and magnesium fluoride (MgF_2) with water (H_2O)
at elevated temperatures. The calculated, equilibrium composition
corresponds to the global free-energy minimum for the system. Optimum,
predicted reaction temperatures and reactant mole ratios are reported for the
recovery of hydrogen fluoride (HF), a valuable industrial feedstock.
Complete conversion of MgF_2 is found at 1000°C and a ratio of 40 moles of
H_2O per 1 mole of MgF_2. For CaF_2, temperatures as high as 1400°C are
required for complete conversion at a corresponding mole ratio of 40 moles
of H_2O per 1 mole of CaF_2. We discuss the presence of minor chemical
constituents as well as the stability of various potential container materials
for the pyrohydrolysis reactions at elevated temperatures. CaF_2 and MgF_2
slags are available as wastes at former uranium production facilities within
the Department of Energy Complex and other facilities regulated by the
Nuclear Regulatory Commission. Recovery of HF from these wastes is an
example of environmental remediation at such facilities.

INTRODUCTION

Calcium fluoride (CaF_2) and magnesium fluoride (MgF_2) slags from production of uranium metal

for Department of Energy and Department of Defense programs represent environmentally harmful

waste volumes at multiple sites throughout the United States. Disposal (burial) costs are becoming

prohibitively expensive, and, because of the radioactive content of the wastes, burial is

increasingly restricted as the result of legislative actions in many states. However, recovery

operations are viable since several chemical components in the slags have industrial applications.

Therefore, slag recovery is attractive from an economic as well as an environmental standpoint.

One slag component, CaF_2, is used as a reagent in the steel industry. It is also used industrially as

a source of hydrogen fluoride (HF) gas, a reactant used in the manufacture of aluminum trifluoride

(AlF_3), another industrial commodity. The MgF_2 slags can also potentially be used to produce

anhydrous HF for commercial distribution. Magnesium metal, another marketable quantity, can be

regenerated from the slag constituent MgF_2. Magnesium metal is combined with aluminum to produce lightweight alloys of industrial importance (e.g., Mg-Al-Zn-Mn, Mg-Al-Mn, Mg-Al-Si, or Mg-Al-lanthanide compounds).[1] Recovered uranium can be re-introduced into uranium metal production. By sufficiently removing uranium from the treated waste streams, final waste disposal options would become more viable. If uranium concentrations are below specifications of the Nuclear Regulatory Commission Branch Technical Position (NRC-BTP) or the more rigorous NRC NUREG-1500 (currently in draft form) unrestricted release guidelines, burial of the treated waste could be accomplished with no reasonable environmentally-based objections.

DESCRIPTION OF MODELING APPROACH

We used computer modeling to assist in the development of optimized processes and equipment selection for the recovery operations. The modeling was used to elucidate reaction tendencies in the complex chemical systems which constitute the waste streams. Specifically, we used robust computer codes to model the chemical reactions to recover Ca, Mg, HF, and U from CaF_2 and MgF_2 and the separate reactions of CaF_2 and MgF_2 with water (H_2O).

The mole ratio of H_2O to the respective alkaline earth fluoride and the system temperature were the variables most thoroughly examined during this phase of the study. This modeling technique is based on the thermodynamic principle that the equilibrium chemical composition for a complex heterogeneous system corresponds to the global minimum value for the system free energy.[2] Therefore, the computer-generated free-energy minimization corresponds to the system composition after all reaction sequences are completed. The approach to thermodynamic modeling used in this work has been described within a similar study we performed, and, therefore, a detailed description has not been reproduced herein.[3]

RESULTS OF THERMODYNAMIC MODELING

We first studied the reaction of MgF_2 with H_2O because the majority of the slags are high in this constituent (from depleted uranium production in the armor penetrator program).

At 1500°C, the highest temperature used in the calculations, only 41.5% of fluoride is released as HF under a nitrogen atmosphere. The results of this iteration of the computer model appear in Fig. 1. In the initial conditions, only 1 mole of H_2O was present to react with 1 mole of MgF_2. Based

on the modeling results, under equilibrium conditions and stoichiometric quantities of reactants, the conversion of MgF_2 to HF with H_2O is not favorable over the temperature range 800–1500°C.

We extended the model to consider the effects of other initial gas compositions. Some minor species such as $MgF_{2(g)}$, $H_{2(g)}$, $NO_{(g)}$, and $O_{2(g)}$ were observed in the nitrogen environment (see Fig. 2). Under an atmosphere of pure oxygen, the equilibrium distribution of species appears to be similar to a nitrogen atmosphere.
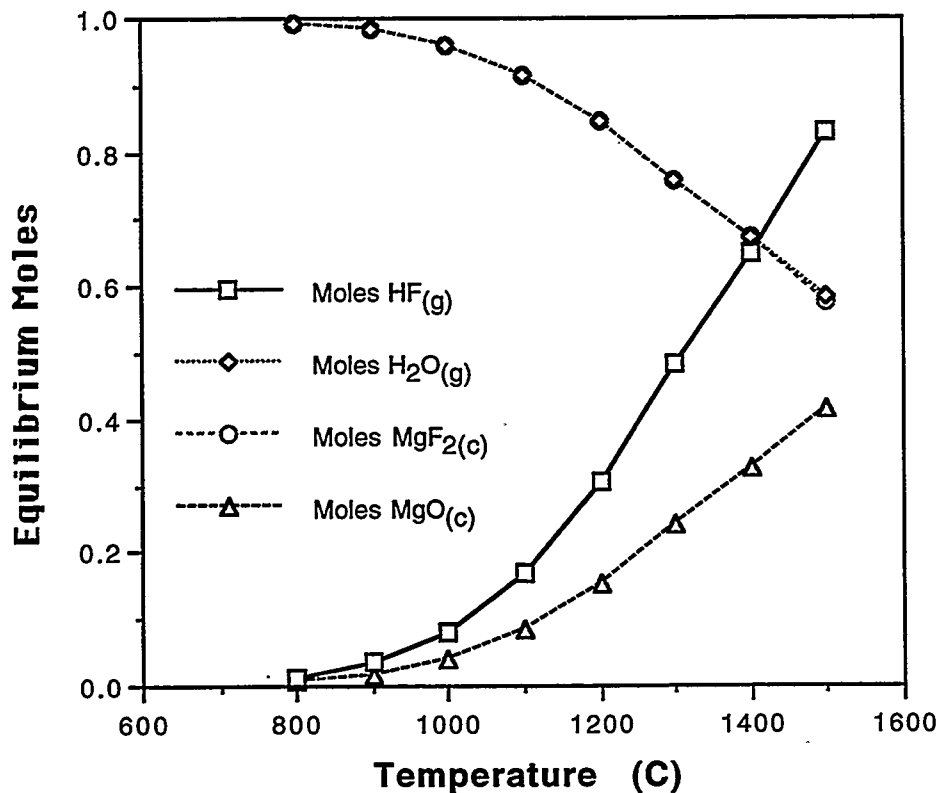

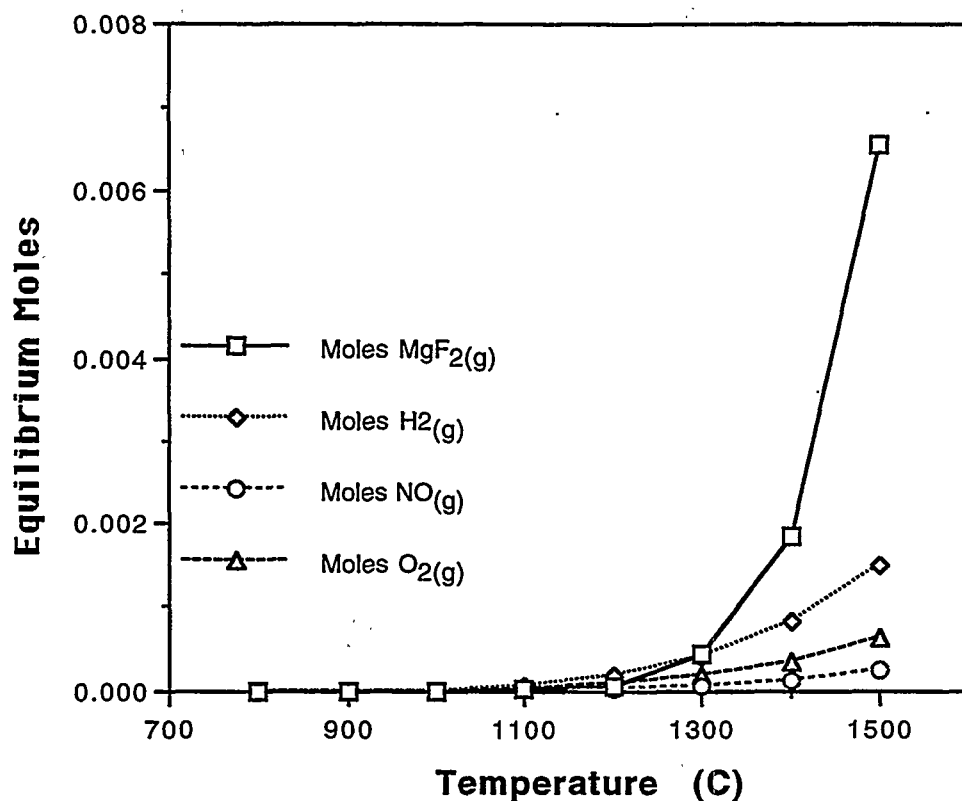Fig. 1. Modeling results of MgF_2-H_2O reaction in N_2.

Fig. 2. MgF$_2$-H$_2$O reaction in N$_2$ as a function of temperature (minor species included).

The reaction between CaF$_2$ and H$_2$O, with a 1:1 mole ratio, in a nitrogen atmosphere proved to be considerably less favorable than the corresponding reaction for MgF$_2$ discussed above. Over the temperature range 800–1500°C, only 4.3% of the fluoride content of CaF$_2$ was converted to HF (see Fig. 3). Minor quantities of CaF$_{2(g)}$, H$_{2(g)}$, OH$_{(g)}$, NO$_{(g)}$, and O$_{2(g)}$ were found at equilibrium (see Fig. 4).
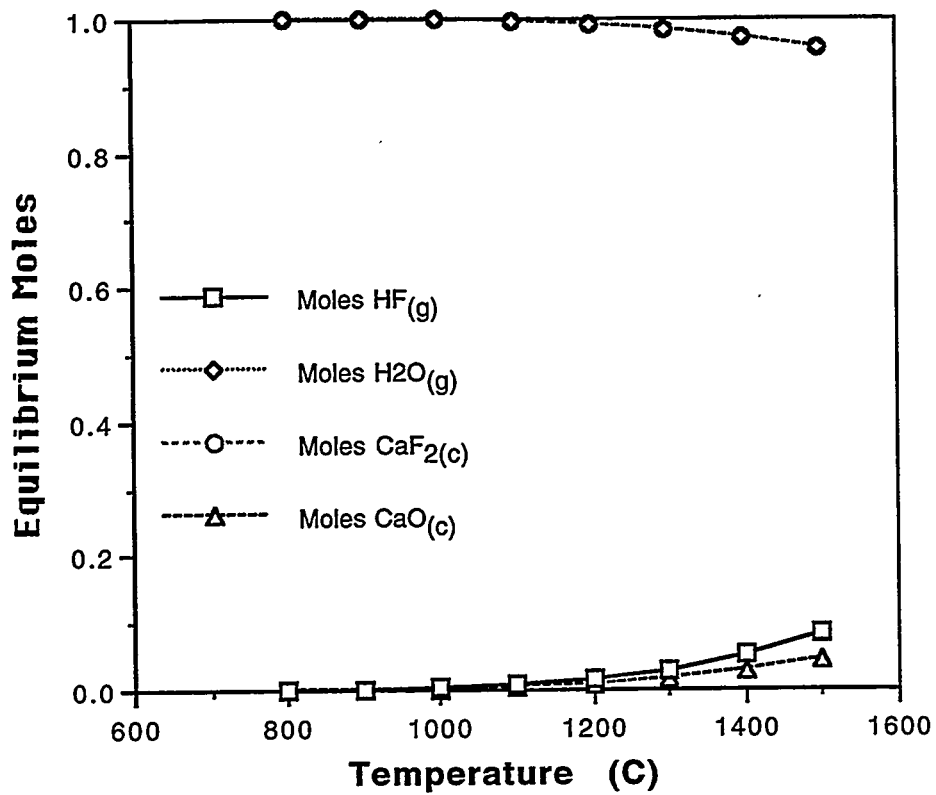
Fig. 3. CaF_2-H_2O reaction in N_2 as a function of temperature.

It is interesting to note that the reaction of CaF_2 with sulfuric acid (H_2SO_4) is considerably more thermodynamically favorable than the MgF_2-H_2SO_4 reaction.[2]
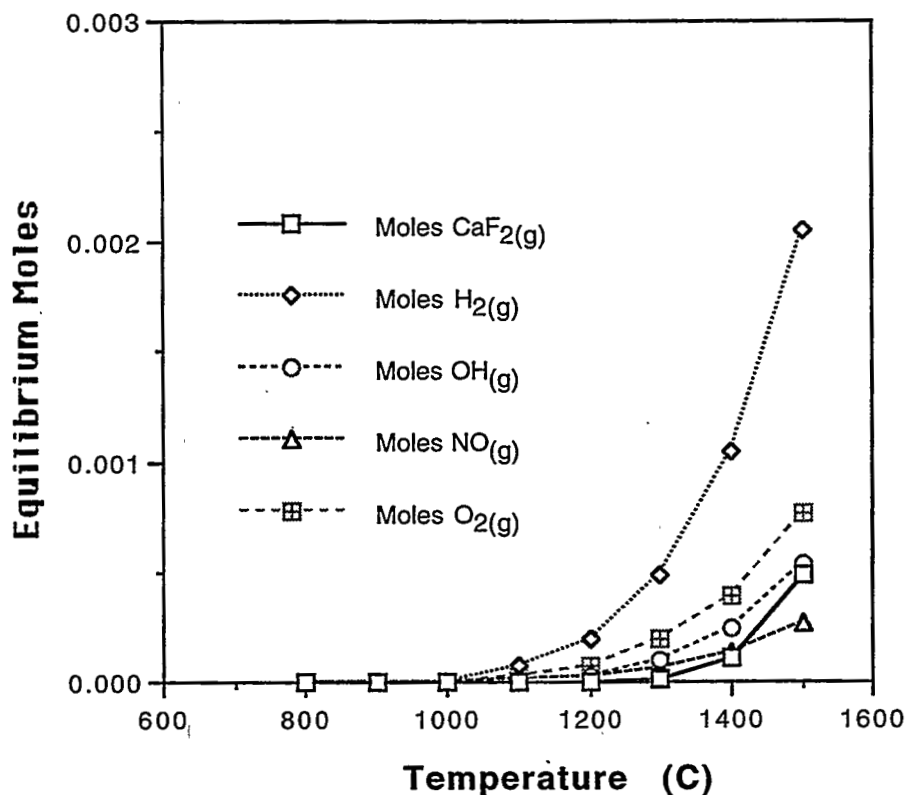
Fig. 4. CaF$_2$-H$_2$O reaction in N$_2$ as a function of temperature (minor species included).

As a result of the poor conversion of both MgF$_2$ and CaF$_2$ to HF in the presence of equimolar quantities of steam, we considered the use of excess steam to drive the reactions to completion. We discovered that 40 moles or more of H$_2$O in nitrogen would drive the former reaction to completion at temperatures as low as 1000°C (see Fig. 5). The temperature necessary for complete conversion might be somewhat lower under nonequilibrium conditions. For example, the removal of products in real time would drive the reactions towards completion.
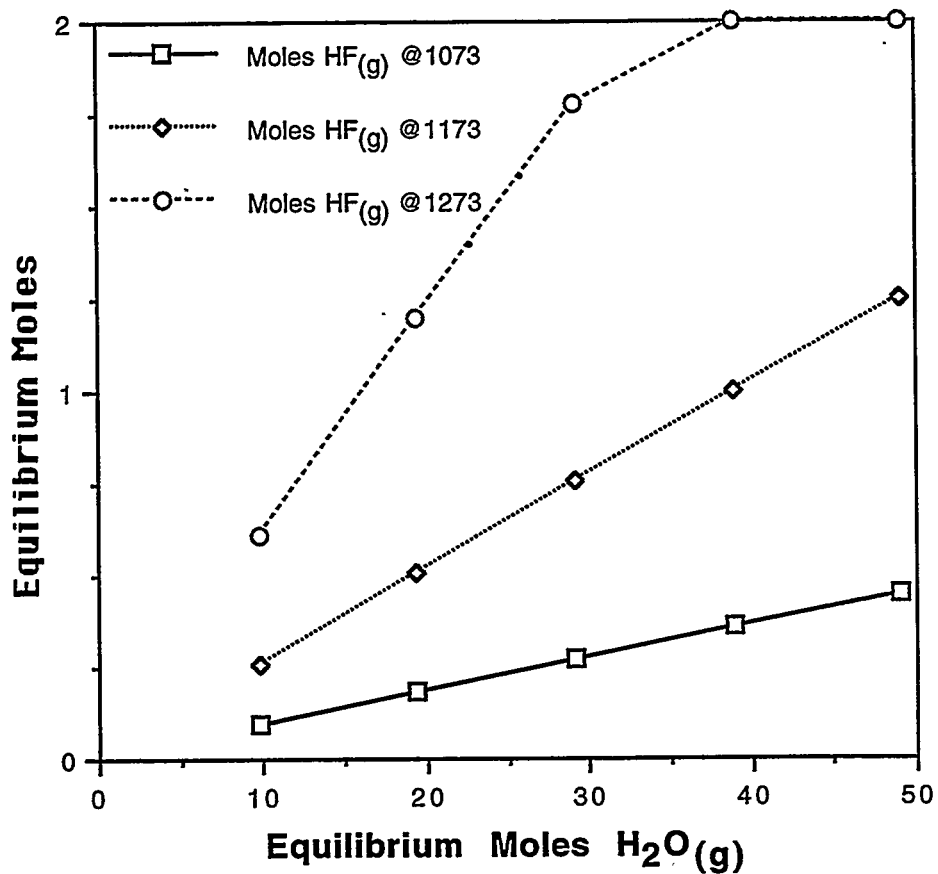
Fig. 5. MgF$_2$-H$_2$O reaction in N$_2$ as a function of temperature and moles H$_2$O$_{(g)}$.

Similarly, we explored the reaction of CaF$_2$ with excess steam under nitrogen and found complete formation of HF for 40 moles of H$_2$O per 1 mole of CaF$_2$ at 1400°C (see Fig. 6).
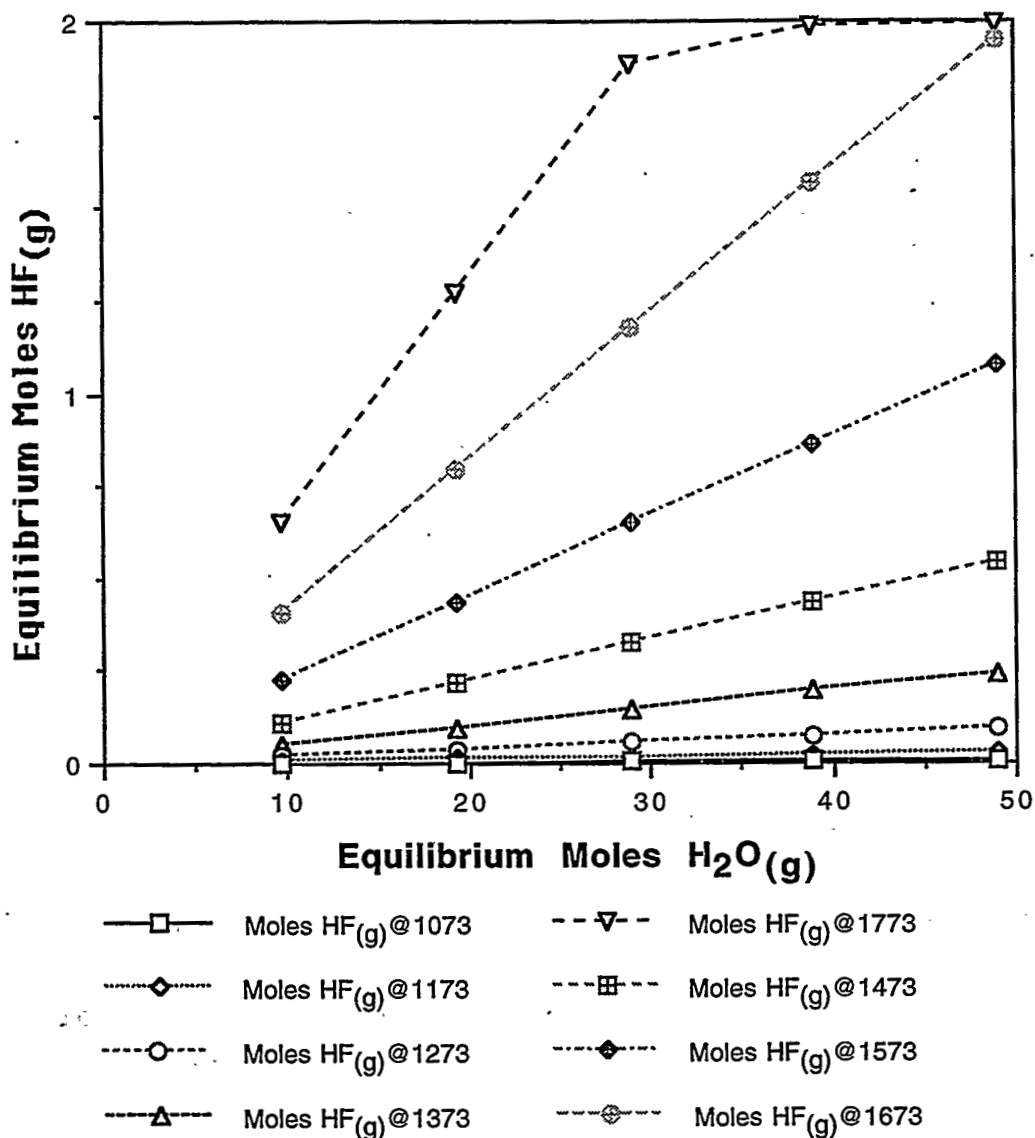
Fig. 6. CaF$_2$-H$_2$O reaction in N$_2$ as a function of temperature and moles H$_2$O$_{(g)}$.

Finally, one potential material of construction (nickel) was examined for its stability toward corrosion in the high-temperature environment, presented by the reaction between MgF$_2$ and H$_2$O, under nitrogen. The amount of elemental nickel changed to nickel oxide (NiO) does not change over the temperature range of this study (see Fig. 7). This suggests nickel is a viable construction material for reactor vessels. In that application, the reactions of alkaline earth fluorides with steam can be performed without anticipated corrosion of the nickel. Nickel and Monel™ (nickel-copper alloy) are both resistant to attack by anhydrous HF.
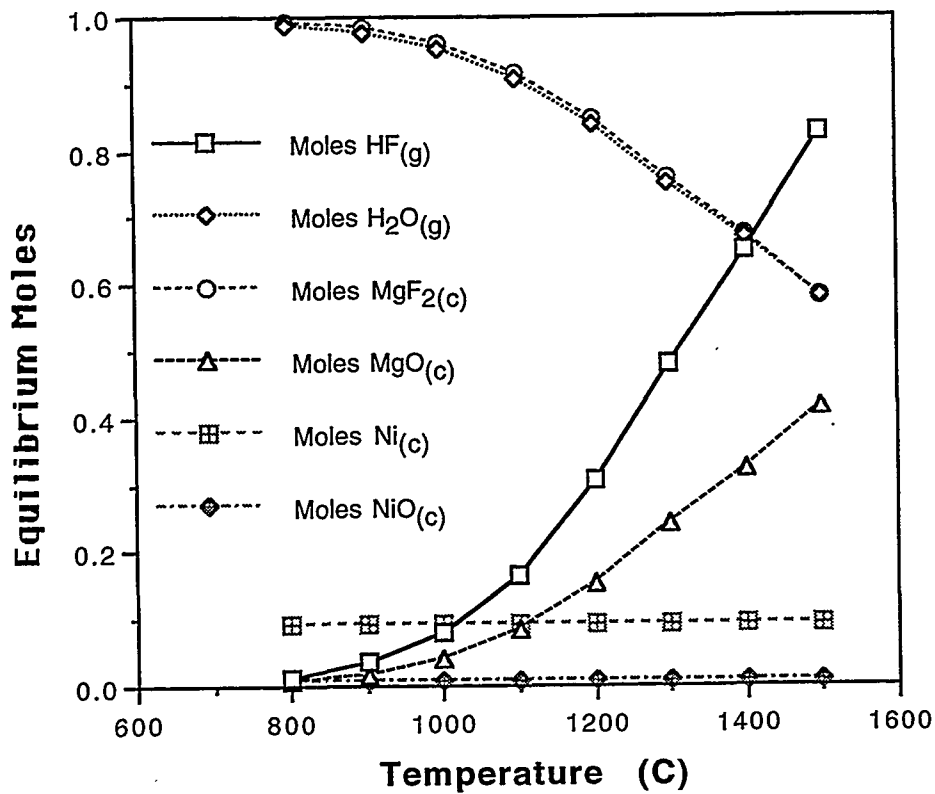
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Fig. 7. MgF_2-H_2O reaction in N_2 as a function of temperature (0.1 mol nickel).

The results of the calculations included a complete set of predicted equilibrium species. This includes the set of minor constituents $MgF_{2(g)}$, $H_{(g)}$, $H_{2(g)}$, $OH_{(g)}$, $NO_{(g)}$, and $O_{2(g)}$ (see Fig. 8).
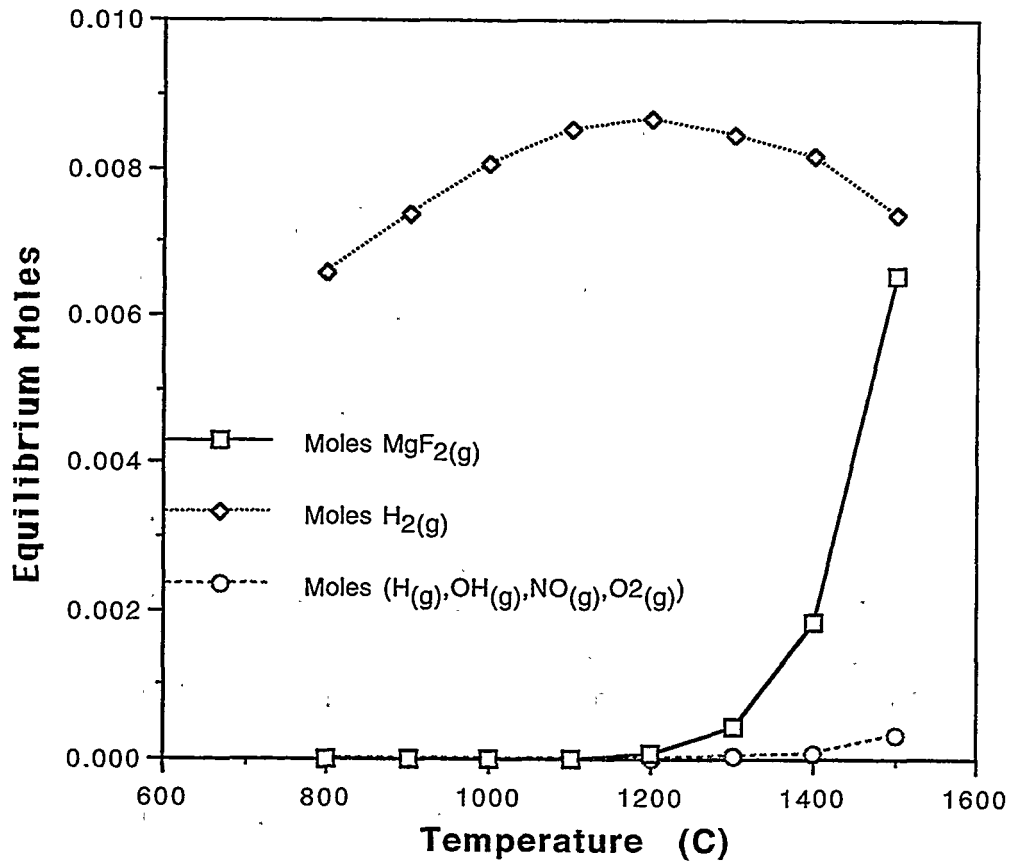
Fig. 8. MgF_2-H_2O reaction in N_2—composition vs. temperature (note 0.1 mol Ni provided).

FUTURE WORK

The present thermodynamic modeling effort can be extended to include common impurities found in MgF_2 and CaF_2. In the modeling completed to date, we included nickel as the containment material.

The equilibrium compositions could be extended to study the influence of other construction materials in the system such as Monel™ and alternative ceramics.

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