THERMAL AND EVOLVED GAS ANALYSIS OF MAGNESIUM PERCHLORATE: IMPLICATIONS
FOR PERCHLORATES IN SOILS AT THE MARS PHOENIX LANDING SITE. H. V. Lauer Jr.,
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Introduction: Perchlorate salts were discovered in the soils around the Phoenix landing site on the
northern plains of Mars [1]. Perchlorate was detected by an ion selective electrode that is part of the MECA
Wet Chemistry Laboratory (WCL). The discovery of a mass 32 fragment (likely O2) by the Thermal and
Evolved-Gas Analyzer (TEGA) provided additional confirmation of a strong oxidizer in the soils around
the landing site. The purpose of this paper is to evaluate the thermal and evolved gas behavior of
perchlorate salts using TEGA-like laboratory testbed instruments. TEGA ovens were fabricated from high
purity Ni. Hence, an additional objective of this paper is to determine the effects that Ni might have on the
evolved gas behavior of perchlorate salts.

Materials and Methods: Mg-perchlorate was chosen as the test candidate because it is a leading
candidate for the perchlorate salt in the Phoenix soils [1]. The first set of perchlorate experiments utilized a
mixture of organic free SiO2 (i.e., quartz heated to 1000°C in O2 for 12 hrs) and reagent grade
Mg(ClO4)2*6H2O. The composition of this mixture was 90.14 wt. % SiO2 and 9.86 wt. %
Mg(ClO4)2*6H2O. Another set of experiments were conducted using high purity Ni (99.9 % Ni) mixed
with the Mg-perchlorate. The composition of the material was 50.17 wt. % organic-free SiO2, 47.00
wt. % Ni, and 2.83 wt. % Mg(ClO4)2*6H2O.

The thermal and evolved gas laboratory testbed consisted of a Setaram SENSYS EVO differential
scanning calorimeter (DSC) integrated with a Pfeiffer quadrapole mass spectrometer. The DSC has an
operating temperature range -120°C to 830°C. However the current set of experiments were run from ambient temperature to 820°C, 275 mbar oven pressure, ultrapure N2 carrier gas, 10 sccm gas flow rate, and 20°C/min temperature ramp rate. The mass spectrometer has a 300 AMU range. The mass spectrometer data was collected for a predetermined set of individual masses (i.e., mass hopping) and recorded as a function of time rather than a full range mass scan. The carrier gas was allowed to flow through the system for approximately one hour before starting the oven ramp to reach a steady gas state and remove any trace gas contaminants. Samples were reheated after the initial temperature ramp to 820°C to establish the baseline data for the DSC data.

Results: Reagent grade Mg-perchlorate has structural water and perchlorates are known to be
notorious water adsorption media. Water evolved at an onset temperature of 85°C, which, corresponds to
a well-defined endothermic peak (Fig. 1). Two additional water releases with corresponding
endothermic peaks had onset temperatures of 155°C and 195°C. A strong exothermic reaction had an
onset temperature at 435°C (Fig. 1). This exothermic reaction corresponds to the release of Cl species (Fig.
2) and O2 (Fig. 3). The release of the volatiles results in the formation of MgO and hence, the phase
transition responsible for the exothermic reaction.

![Figure 1: Thermal and evolved H2O analysis for Mg-perchlorate mixed with inert SiO2.](https://ntrs.nasa.gov/search.jsp?R=20090010369)

![Figure 2: Evolved gas analysis for Cl species. The dominant species evolved was HCl.](https://ntrs.nasa.gov/search.jsp?R=20090010369)
MgClO samples with & without Ni

I.0 0.01 CE z 7*
01.10 0.-TO 0
WI 160111 NI W11, Si
00.-TO 00.10 Ifl0. 15 4.0*-I1 C 441.-I1 0 124.10 -020-11 1'

Figure 3: Evolved O₂ for Mg-perchlorate with and without the addition of Ni. The large O₂ release (onset around 435°C) for the sample without the Ni addition corresponds to the exothermic reaction shown in Figure 1. Note that much less O₂ is released around 435°C in the sample with the Ni addition. The low temperature O₂ releases correspond to the evolution of H₂O (see Fig. 1).

The evolved Cl species were HCl, Cl and Cl₂ (Fig. 2). HCl was the dominant Cl species to evolve and somewhat unexpected was that less Cl₂ was evolved compared to HCl.

Nickel was added to the Mg-perchlorate to simulate the TEGA ovens, which were fabricated from high purity Ni metal. The strong exothermic peak around 435°C is not well-defined compared to Mg-perchlorate without the Ni addition.

No Cl species were observed in the Mg-perchlorate sample with the Ni addition (Fig. 5). The absence of Cl species and the reduction of evolved O₂ indicate that the Ni is reacting with these highly corrosive gases within the DSC oven. Volatile Cl compounds are very reactive (corrosive) on the surfaces of metals such as Ni [2].

Imperative for TEGA. Oxygen (mass 32) was detected by TEGA (325-625°C) for a surface soil sample dubbed “Baby Bear” at the Phoenix landing site. The evolved O₂ has been attributed to the thermal decomposition of a perchlorate salt [1]. This study supports that interpretation although the release of O₂ was higher in our laboratory test. An important difference between the TEGA and laboratory experiments is the oven pressure conditions of the two systems (≤30 mbar pressure for TEGA vs. 275 mbar for the laboratory system). Tests are currently underway to simulate the TEGA operating conditions in the laboratory testbed. We expect that the onset temperature for O₂ evolution will be lower at lower pressures [e.g., see 3].

A key finding in this study is that Ni reacts with evolved Cl species and O₂ that prevents their detection by the mass spectrometer. No Cl-bearing species were observed by TEGA. This observation indicates that the Cl species in the Martian soils reacted with the Ni ovens and therefore were not evolved to the mass spectrometer. Some TEGA runs experienced “plugging” of the ovens (i.e., no gas detection) that might be explained by the formation of Ni-Cl compounds on the Ni oven frits.

Acknowledgements. This work was supported by grants to DWM, RVM, and WVB through the NASA Mars Phoenix Scout Program