THERMAL AND EVOLVED GAS ANALYSIS OF MAGNESIUM PERCHLORATE: IMPLICATIONS FOR PERCHLORATES IN SOILS AT THE MARS PHOENIX LANDING SITE. H. V. Lauer Jr.[1], D. W. Ming[2], B. Sutter[3], D. C. Golden[4], R. V. Morris[2], and W. V. Boynton[5], [1]ESCG/Barrios Technology, Houston, TX 77258, [2]ARES NASA/JSC, Houston, TX 77058 (douglas.w.ming@nasa.gov), [3] ESCG/Jacobs, Houston, TX 77258, [4] ESCG/Hamilton Sundstrand., Houston, TX 77258, [5] University of Arizona, Tucson, AZ 85721.

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 O_2) 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 SiO_2 (i.e., quartz heated to 1000°C in O_2 for 12 hrs) and reagent grade $Mg(ClO_4)_2 \cdot 6H_2O$. The composition of this mixture was 90.14 wt. % SiO_2 and 9.86 wt. % $Mg(ClO_4)_2 \cdot 6H_2O$. 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 SiO_2, 47.00 wt. % Ni, and 2.83 wt. % $Mg(ClO_4)_2 \cdot 6H_2O$.

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 N_2 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 O_2 (Fig. 3). The release of the volatiles results in the formation of MgO and hence, the phase transition responsible for the exothermic reaction.

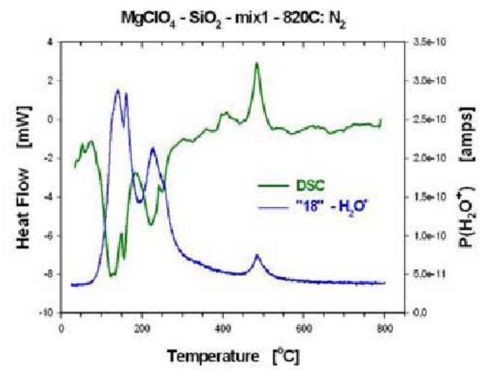

Figure 1: Thermal and evolved H_2O analysis for Mg-perchlorate mixed with inert SiO_2.

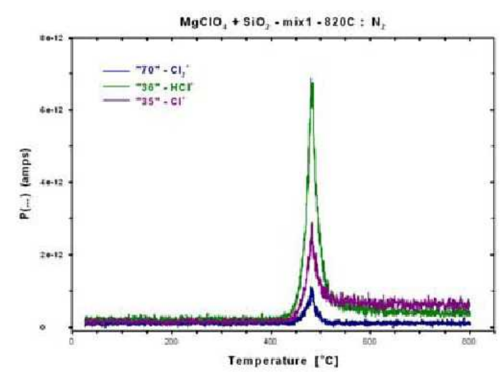

Figure 2: Evolved gas analysis for Cl species. The dominant species evolved was HCl.

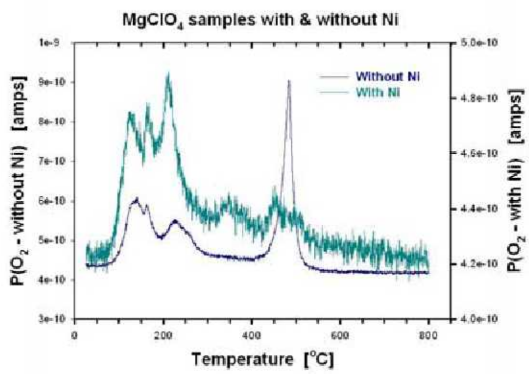

Figure 3: Evolved O_2 for Mg-perchlorate with and without the addition of Ni. The large O_2 release (onset around 435°C) for the sample without the Ni addition corresponds to the exothermic reaction shown in Figure 1. Note that much less O_2 is released around 435°C in the sample with the Ni addition. The low temperature O_2 releases correspond to the evolution of H_2O (see Fig. 1).

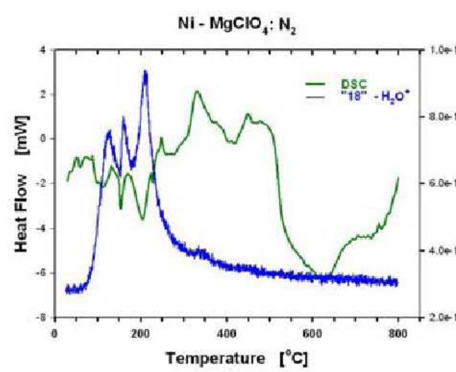

Figure 4: Thermal and evolved H_2O analysis for Mg-perchlorate with the addition of Ni to simulate the TEGA ovens. The exothermic peak around 435°C is not well-defined compared to Mg-perchlorate without the Ni addition.

The evolved Cl species were HCl, Cl and Cl_2 (Fig. 2). HCl was the dominant Cl species to evolve and somewhat unexpected was that less Cl_2 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 for Mg-perchlorate with the Ni addition (Fig. 4). Oxygen release around 435°C is much less in the Mg-perchlorate sample with 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 O_2 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].

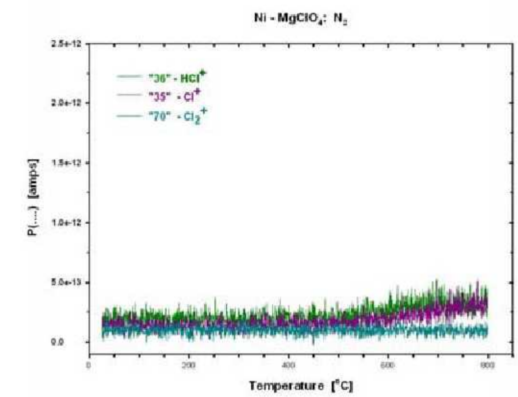

Figure 5: Evolved Cl for Mg-perchlorate with the addition of Ni to simulate the TEGA ovens. No Cl species evolved around 435°C as compared to Mg-perchlorate without the Ni addition (Fig. 2).

Implications 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 O_2 has been attributed to the thermal decomposition of a perchlorate salt [1]. This study supports that interpretation although the release of O_2 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 O_2 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 O_2 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.

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