PERCHLORATE RECOVERY BY DISSOLUTION FROM MARTIAN SOIL SIMULANTS: IMPLICATIONS FOR HUMAN EXPLORATION OF MARS. C. T. Adcock[1], E. M. Hausrath[1], E. B. Rampe[2], V. Cruz[1], L. Wright[1], [1]University of Nevada Las Vegas, 4505 S. Maryland Pkwy, Las Vegas, NV, 89154, [2]NASA Johnson Space Center, Houston, TX 77058, (Christopher.Adcock@unlv.edu)

Introduction: Extended human missions to Mars will be among the most ambitious ever undertaken by NASA. Among the many challenges that these missions present is the provision of sufficient energy and material resources to support operations. The energy required to escape planetary gravity is immense, and payloads are limited to a few percent of an overall launch mass. Apollo era launch vehicles from Earth to the Moon, for example, were <3% payload mass with the remainder being propellant and the vehicle [1]. Similar vehicles intended for Mars are predicted to have necessarily similar ratios [2]. In addition, part of the payload on a Mars human mission is the return ascent vehicle, itself predicted to be approximately 80% propellant by mass [3], further limiting other payload materials. To address this, *In Situ* Resource Utilization (ISRU) has been proposed. ISRU is the practice of supplementing or replacing vital resources at a mission destination (such as Mars) rather than transporting them from Earth, thus freeing payload mass for other needed supplies [4, 5].

One resource potentially available on Mars is perchlorate (ClO_4^-). Perchlorate is a strong oxidizer that is both a natural and manufactured product on Earth. Although considered a toxin and contaminant when found in groundwater or soil on Earth, it also has a broad range of industrial applications, including use as an oxidizing agent in rocket propellant [6]. Confirmation of Martian perchlorate first came from the *Phoenix* Mars lander which detected the compound in the northern polar region of Mars at 0.4 to 0.6 wt% [7]. The ion was later indicated at Rocknest (near the Martian equator) in similar concentrations (up to 0.5 wt%) by the Sample Analysis at Mars instrument aboard the *Curiosity* rover [8, 9]. These polar and equatorial indications suggest perchlorate may be widely present on the Martian surface in recoverable concentrations. Perchlorate could therefore represent an ISRU target for rocket propellent, and the removal of it from Martian soils could act as a long-term hazard mitigation [10] and remediation, benefiting potential agricultural efforts on Mars [11]. In this work we use dissolution experiments on Na-perchlorate spiked Martian soil simulants to investigate perchlorate recovery from Martian soils by water-rock interactions.

Methods: Water-rock interaction experiments, including blanks and duplicates, are being conducted at 25°C and 4°C using four Martian regolith simulants [12-14] as solids (Figure 1, Table 1). Each experiment consists of 1.5 grams of Na-perchlorate spiked simulant in contact with solution in a sealed reaction bottle with an N_2 atmosphere (Figure 1).

Figure 1. Dissolution experiment set. RT denotes 25°C experiments. Second (back) row of bottles are duplicates. An identical set of experiments were also made for 4°C. Red scale is 15cm long.

Table 1. Simulant sources/names and ID used in this study.

Source & Name	ID
Exolith Labs, MGS-1 Mars Global Simulant	MGS1
Exolith Labs, MGS-1C Clay ISRU	MGS1C
Johnson Space Center, Mars-1	JSCM1
Johnson Space Center, Mars Rocknest	JSCRN

To construct the experiments, simulants are first spiked with approximately 1 wt% desiccated Na-perchlorate (i.e. $NaClO_4$) to approximate Martian conditions. This excludes JSCRN which contains approximately 1 wt% Na-perchlorate as received [14]. Then 1.50 grams of each simulant/perchlorate mix is distributed into the appropriate 200ml acid washed, autoclaved, UV sterilized, PSF high-temperature resin bottle, including duplicates. Blanks (two for each temperature) receive no solids. The bottles are then heat sterilized for 2 hours at 160°C, transferred to an N_2 glove box to purge the headspaces, and capped with autoclaved and UV sterilized septa lids. To start the experiments, the bottles are removed from the box, injected with 120ml each of a 0.01 molar KNO_3 solution made with 18MΩ water sparged with N_2 for 1 hour and acidified to pH 4.85 with high purity (Aristar Plus) HNO_3. Injections are done using sterile needles and sterile 0.20µm syringe filters. Bottle headspaces are vented during solution injections into an N_2 gas sampling bag to prevent any backflow of oxygen from the atmosphere during venting. The experiments are then hand agitated for 1 minute and are placed at 4°C on

an oscillating table or in a 25°C shaker bath. Both are set to 100 "shakes" per minute. On days 1 (just after starting), 2, and 5, samples are taken though the septa using sterile needles and submitted for perchlorate analysis by Ion Chromatography (IC) (Dionex ICS-2000 series). Additional samples of the low temperature duplicate experiments taken on day 30 are also submitted for IC analysis to check for long-term perchlorate concentration changes at low temperature.

Results: Results from Exolith and JSCM1 simulants are ongoing. High variation in duplicates, likely due to inhomogeneous spiking, require they be re-run. The JSCRN simulant, however, is Na-perchlorate spike and homogenized as received and not affected by this. Preliminary results from these experiments appear in Table 2. For a given experiment, results from samples taken on days 1, 2, and 5 are generally similar and fall within 10% of each other. There are no overall indications of increasing or decreasing trends. The sample taken at 30 days from low temperature JSCM1-D experiment does show elevated perchlorate concentration, but it is within analytical error (10%) of the average analyses from Days 1 and 5.

Table 2. Preliminary analysis results (ppm) for perchlorate in solution after 1, 2, 5, and 30 days in JSCRN experiments

25°C Experiment Results

Day	JSCRN	JSCRN-D
1	104	95
2	103	103
5	99	99

4°C Experiment Results

Day	JSCRN	JSCRN-D
1	101	93
2	103	na[a]
5	98	99
30	-	105

note: "-D" = duplicate. [a]Sample lost during sampling.

Discussion: The relatively high concentrations and similar results for a given experiment from the first 3 sampling events indicate that much of Na-perchlorate goes into solution within the first day. The theoretical maximum concentration in the experiments is ~100 ppm perchlorate, and the JSCRN results average 99-102ppm. Thus, the dissolution for perchlorate under these conditions for simulant JSCRN appears to be complete or near complete just after the start of the experiments on day 1. Temperature does not appear to have a measurable affect at the sampling rates used.

The slightly higher concentration (highest of any of the JSCRN experiments) measured at 30 days for sample JSCRN-D at 4°C might suggest some residual perchlorate remains, at least after the first few days, and therefore dissolves at a much slower rate. However, the measured value is within 10% of the average analyses from Days 1 and 5 of that experiment (and the other experiments) and could be explained as analytical error. Results from ongoing experiments with the other simulants may clarify this. Nevertheless, these results suggest significant recovery of perchlorate as a potential propellent resource for extended Martian missions may be straight forward. The up to 0.6 wt% perchlorate concentrations indicated on Mars equate to 6 kg of perchlorate per metric ton of Martian regolith. Depending on the formulation used, this could represent 10 kg of solid rocket propellent per ton of regolith [e.g. 15, 16]. However, in regard to completely clearing Martian soil material of perchlorate, the JSCM1-D 30-day results caution that extended time or different conditions may be required. This may have implications for remediating the Martian materials for potential agricultural efforts on Mars [11], and ongoing research may clarify this.

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