Thermochemical Modeling of Molten Regolith Electrolysis Supporting Assessment of Metallic Product Compositions and Dynamic Oxide Properties. B. Schneiderman[1], E. McMurchie[1], M. Lensing[1], J. Stokes[2], G. Brennecka[1], C. Dreyer[1], C. Brice[1], C. Henry[3], A. Ignatiev[4], M. Hinkel[4], Z. Yu[1], J. Kim[1]. [1]Colorado School of Mines, Golden, CO; [2]NASA Glenn Research Center, Cleveland, OH; [3]NASA Marshall Space Flight Center, Huntsville, AL; [4]Lunar Resources, Inc., Houston, TX. (Contact: jihyekim@mines.edu)

Introduction: As visions for lunar exploration continue to mature, the costs of launching all mission resources from Earth are unrealistic, requiring development of in-situ resource utilization [1]. Applying extractive metallurgy processes to reduce the constituent metal oxides in lunar regolith can produce both breathable oxygen and metals supporting construction. Molten regolith electrolysis (MRE) is an advantageous extraction technique in part because it avoids foreign reducing agents (hydrogen, methane, or sulfuric acid) [2-3], but high MRE operating temperatures and dynamic molten oxide composition and properties during reduction pose challenges to reactor vessel and flow-path design. This work aimed to extend the existing body of knowledge [4-5] pertaining to molten oxide composition trajectory and property evolution during MRE by developing a thermochemical process model using the integrated software package FactSage [6], in support of a larger project (Molten Aluminum Generation for Manufacturing Additively – MAGMA) aimed to advance MRE to TRL 6. FactSage streamlines the consideration of parallel oxide species reduction according to instantaneous chemical activity, rather than assuming fully discretized species reduction governed by the electrochemical series. This advantage allows quantification of prospective secondary element concentrations, either beneficial alloying additions or detrimental impurities, in reduced metallic products.

Methods: *Composition Trajectory*. Recursive governing equations were developed to define the contents of the thermochemical model system as electrolysis was incrementally simulated through the imposed liberation of oxygen from the system. Electrolysis progress was quantified by the oxygen extraction yield parameter λ_{O_2}, defined as the mass of molecular (diatomic) oxygen liberated normalized by the mass of input regolith. Electrolysis was modeled in increments no larger than $\Delta(\lambda_{O_2}) = 0.015$. As graphically depicted in Figure 1, it was assumed that any volatile metal-bearing vapor species were vented or deposited on cold surfaces and not reincorporated into the molten oxide pool; any oxygen contained in these species (e.g., that in gaseous SiO) was excluded from the λ_{O_2} calculation. The governing equations describe a progressively shrinking model system that is increasingly deficient in oxygen. Chemical equilibrium of this system was calculated in FactSage to determine the composition of the oxide and reduced molten metal phases. The kinetics of phase separation, while likely to impact deployed MRE, were not considered in the thermochemical model.

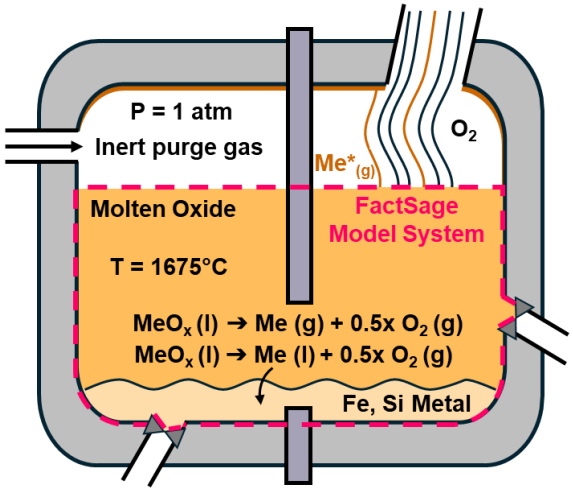

Figure 1. Schematic illustration of reactor vessel at an early stage of electrolysis, showing thermochemical modeling assumptions.

Property Evolution. For property modeling, the molten oxide phase was treated as an isolated system at each step. Chemical equilibrium was calculated as a function of temperature to determine the molten oxide liquidus, and FactSage's viscosity calculator simulated the oxide viscosity evolution.

Results: All specific results assume the input regolith has the chemistry of the lunar highlands regolith simulant CSM-LHT-1.

Composition Trajectory. Under the model assumptions, the composition trajectory of the system is pressure-dependent because of disparities in volatility among regolith constituents. In a hypothetical model case at 1 atm ullage pressure, the transition from primarily SiO_2 reduction to primarily Al_2O_3 reduction occurs at $\lambda_{O_2} \approx 0.30$, where a means of isolating previously reduced ferrosilicon may be considered to promote usability of separate metallic product streams. If such a strategy is implemented, predicted product ferrosilicon and aluminum compositions (see Table 1) can nearly meet

those of terrestrially employed materials in cases of ideal metallic product isolation.

Table 1: Compositions (wt. %) of ferrosilicon and aluminum metallic products if isolated from one another at λ_{O_2} = 0.30. Initial regolith chemistry is that of CSM-LHT-1 highlands simulant.

Elem / Prod.	Si	Al	Fe	Ti	Mg	Mn	Ca
Fe-Si ($\lambda \leq 0.30$)	84.8	3.09	11.0	1.13	Tr.	Tr.	Tr.
Al ($\lambda > 0.30$)	0.30	99.3	-	-	Tr.	-	0.43

Property Evolution. Figure 2 shows the calculated molten oxide liquidus evolution at 1 atm ullage pressure. The highest intermediate molten oxide liquidus temperature prior to the termination of feasible MRE is 1644°C, justifying a model reactor temperature of 1675°C. Termination of feasible MRE occurs near $\lambda_{O_2} \approx 0.37$ where a rapid rise in the oxide liquidus occurs, owing to the increased concentration of CaO in the oxide. Experimental validation by differential scanning calorimetry (DSC) showed that FactSage may improve predictions of molten oxide liquidus over predictions by other regression models. For example, Figure 2 indicates that a generalized regression equation for the liquidus of oxide slags [7] predicts values up to several hundred degrees higher than FactSage, but preliminary DSC measurements on two compositions (λ_{O_2} = 0 and 0.165) demonstrated liquidus values approximately equal to or below the corresponding FactSage prediction.

As highlighted by the select intermediate compositions in Figure 3, the molten oxide viscosity increases with reduction of FeO until $\lambda_{O_2} \approx 0.015$ and then progressively decreases. Figure 3 shows excellent agreement in value and temperature dependency between FactSage and spindle viscometry data until at least λ_{O_2} = 0.165. The agreement is better than any of five regression models in the literature. This accuracy is attributed to FactSage's incorporation of a quasichemical model for bridging oxygen concentration in silicate melts. After most SiO_2 is reduced and no longer present in the oxide melt, the advantages of using the quasichemical model are less relevant, and FactSage's accuracy consequently diminishes for the tested SiO_2-lean composition at λ_{O_2} = 0.35.

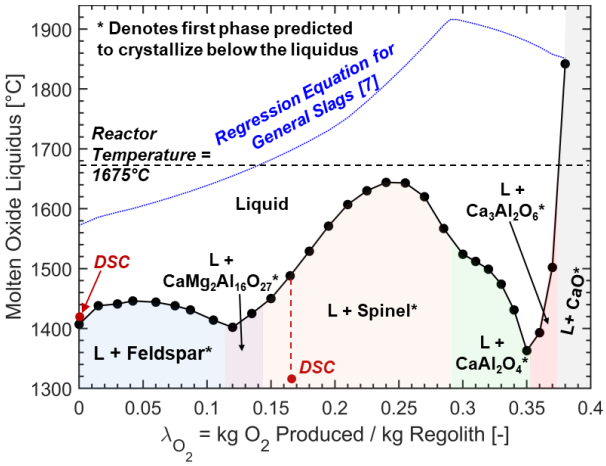

Figure 2. Evolution of the molten oxide liquidus temperature, calculated by FactSage (black curve) and the regression equation from [7] (blue curve). DSC liquidus data from λ_{O_2} = 0 and 0.165 shown.

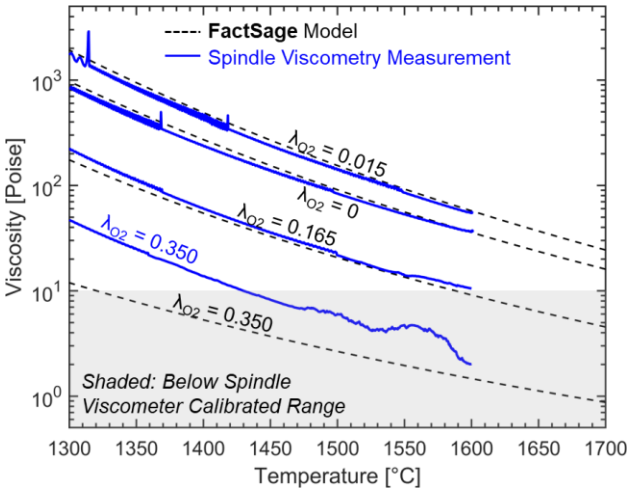

Figure 3. Comparison of calculated viscosity as a function of temperature from FactSage with experimental spindle viscometry data at four stages of MRE progress (λ_{O_2} = 0, 0.015, 0.165, 0.35)

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