Production of Steel from Lunar Regolith through Carbonyl Iron Refining (CIR)

POWDER METALLURGY RESEARCH LAB

THE UNIVERSITY OF UTAH

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NASA BIG IDEA CHALLENGE

Motivation

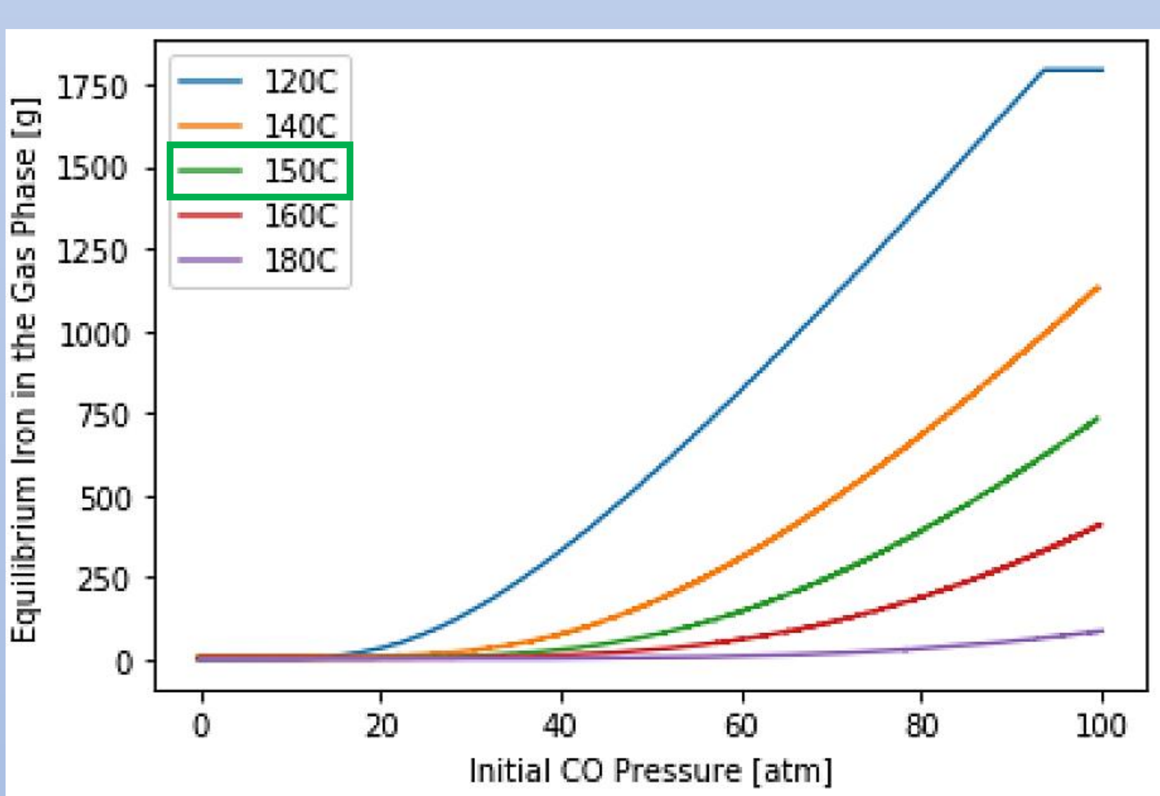
Transporting equipment to the moon is extremely cost-prohibitive, and competition is fierce over a limited cargo volume. Freight impediments are circumvented if the required material can be harvested, processed, and shaped at the destination. The hostile and remote environment constrains candidate technologies to establish a production pipeline with minimal equipment volume and a low dependence on consumables.

Approach

Carbonyl Iron Refining (CIR) has attributes especially conducive to these constraints. Our proposed CIR concept tailors existing iron refining technology into lunar-optimized apparatus. CIR uses a reactive gas phase to concentrate disparate iron particles into a high-purity (>98%) powder product with properties favorable for additive manufacturing. The process does not consume the reactive gas, making the apparatus nearly closed-loop.

Feasibility Calculations

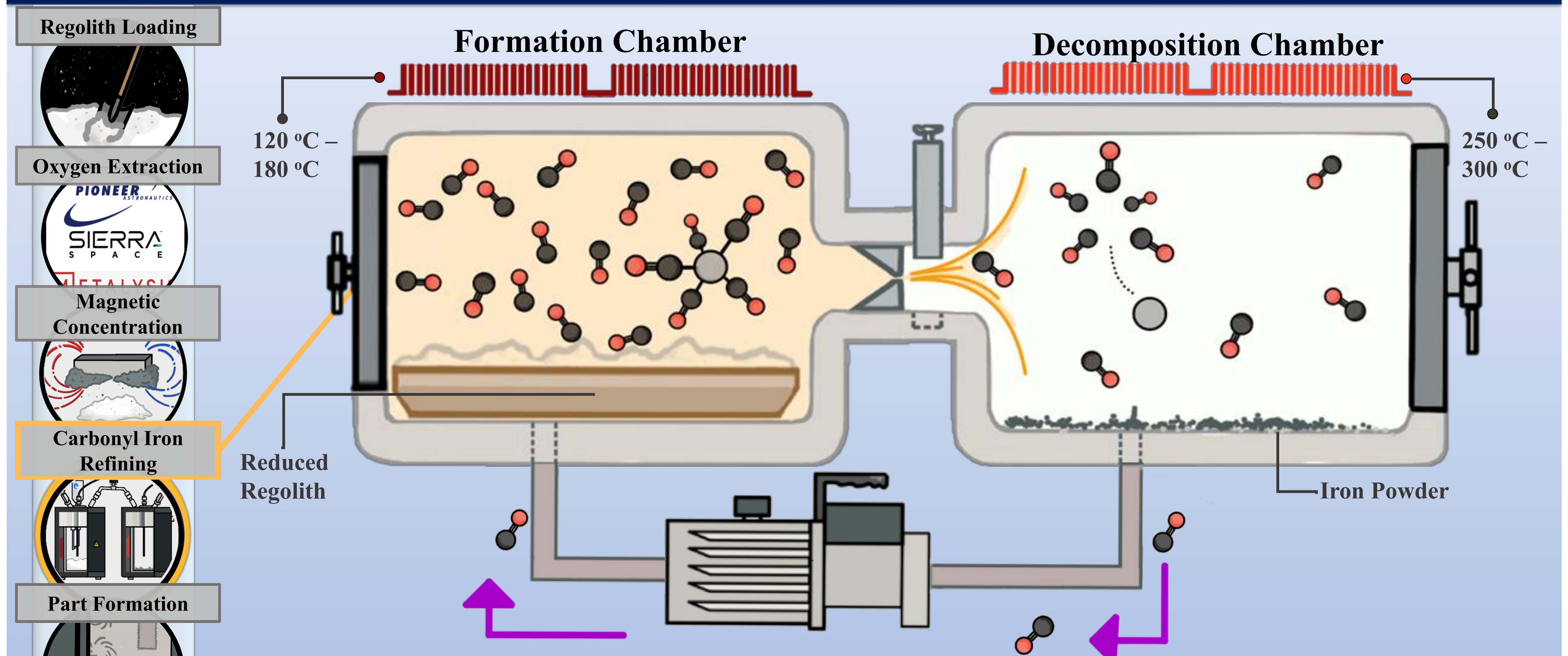
- Iron pentacarbonyl ($Fe(CO)_5(g)$) formation is favored at low temperatures and high pressure. However, operating at a low *T* introduces a kinetic limitation.
- Carbonylation is commercially done at high *P* (>200 atm) to maximize per-batch iron yield over the course of ~48 hours. Production at lower pressures has received relatively little research.
- Operating at lower pressures appears ideal for the lunar environment, where a curtailed throughput may be an acceptable tradeoff for a lighter vessel.
- Thermodynamic calculations suggest the feasibility of low-pressure equilibrium iron yield.



Pressure [atm]	Iron Yield per Cycle [g]	Cycles to Break Even
20	3.74	43,829
40	29	5,653
60	145	1,131
80	389	422
100	732	224

Temperature: 150 °C; Apparatus mass: 164 kg; Composition: 10 wt% Fe; Volume loading: 10%; Volume Reactor: 100 L

Proposed CIR Production on Moon: Two-chamber design



1) Reduced regolith is pressurized (50 – 100 atm) with carbon monoxide to form an iron-bearing gas

$Fe(s) + 5CO(g) \rightarrow Fe(CO)_5(g)$

2) Loaded gas thermally decomposes to iron powder and carbon monoxide in a second low-pressure (1 – 80 atm) chamber

$Fe(CO)_5(g) \rightarrow Fe(s) + 5CO(g)$

Dissociated CO(g) is immediately available for reuse. The occasional CO(g) regeneration from CO_2(g) can be accomplished using waste carbon or NH_3(g) from the Sabatier system.

Carbonylation and Decomposition Verification Testing

Lab-scale carbonylation system

- Built for verification testing under specific conditions of *T* and *P* for $Fe(CO)_5(g)$ formation and decomposition into iron.
- Formation chamber was a 0.6-liter titanium pressure vessel connected to a 19-liter stainless steel decomposition chamber.

Experimental conditions

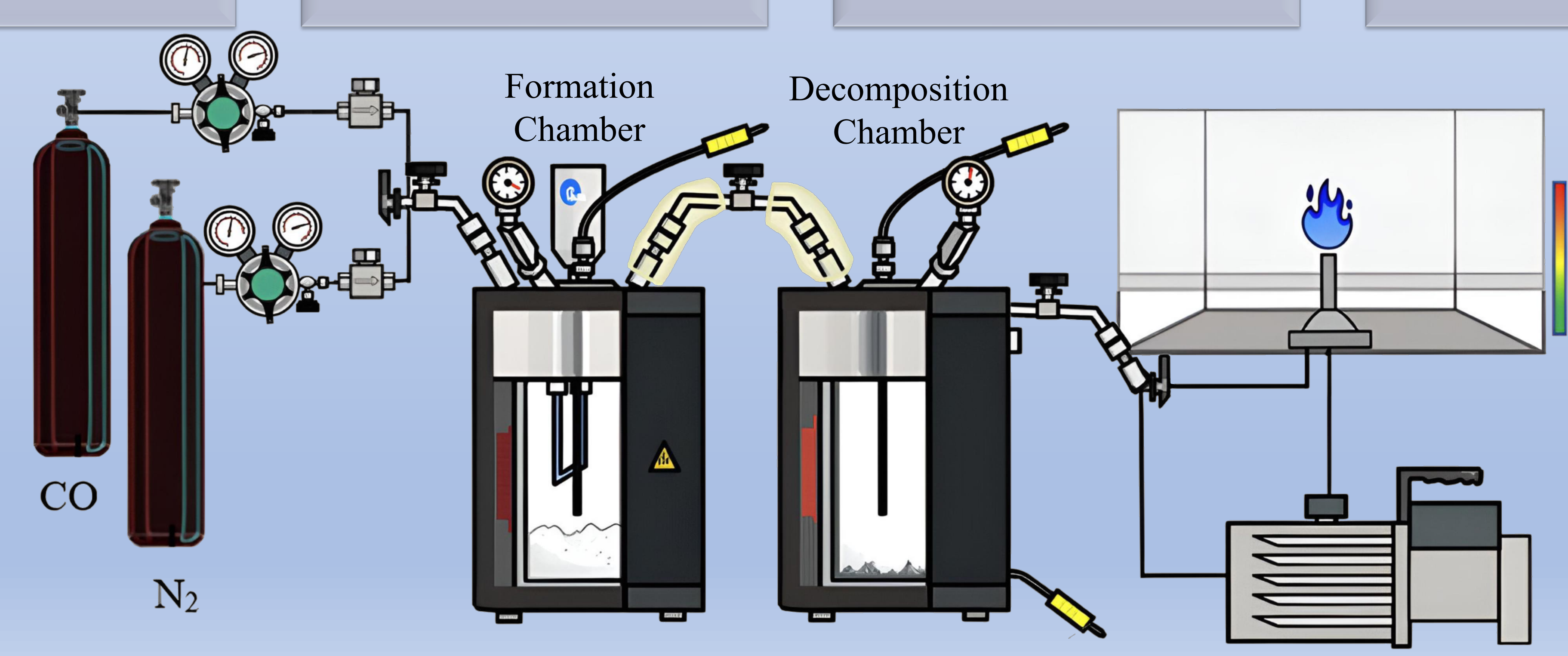
- *T* (120 – 150 °C) and *P* (50 – 55 atm) combinations were tested to find the optimal yield of $Fe(CO)_5(g)$ formation.
- The pressure was maintained between 180 to 410 minutes.

Verification testing

- Performed on 11 samples with different loading materials:
  - 6 with iron puriss
  - 4 simulant regolith from Pioneer Astronautics,
  - 1 simulant regolith reduced in-house.
- 7 of the 11 experiments produced a small quantity of powder product.

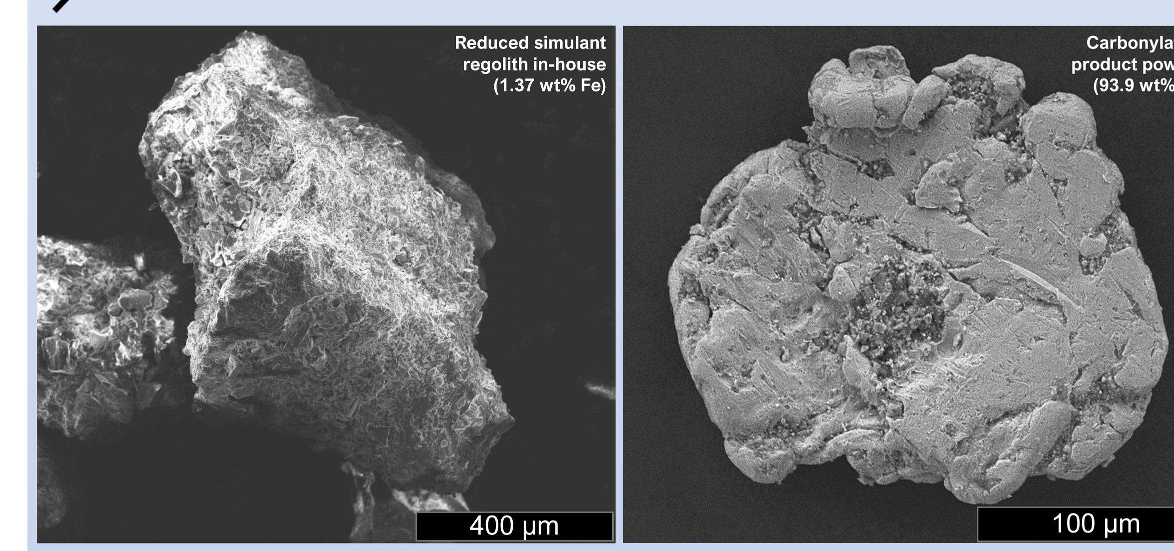
Further Experiments

- Two additional experiments with CO(g) were performed using a High-Pressure wire-mesh TGA up to 180°C and 80 bar to verify the $Fe(CO)_5(g)$ formation.
- A decrease in mass up to 0.9% mass decrease was observed for a 3 h 39 min experiment.

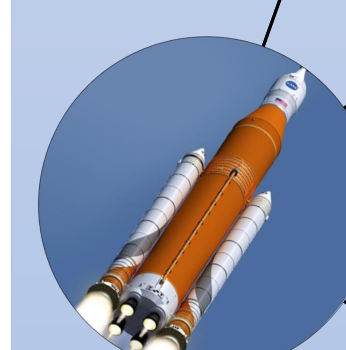


Results and Conclusions

1. Products were found to be >91 wt% iron, with balance oxygen (E3, E8, E11 contained ~99, 6.4, 1.37 wt% Fe in starting material).
2. XRD verification on E8 assuaged iron powder entrainment concerns, confirming the absence of Ti and Si peaks.
3. Carbonylation product was large in diameter (mean~200 μm) and of low density (~3.2 g/cm³) compared to puriss powder.
4. Feasibility of extracting and concentrating iron into a product powder from a reduced simulant regolith was demonstrated.



Future Research



1. Modify decomposition chamber variables to densify and shrink the product particles to meet the constraints of additive manufacturing.
2. Refine a kinetic model by maintaining formation conditions >8 hours to inform ultimate lunar viability.
3. Consider testing production at an intermediate pressure (80-120 atm).
4. Address yet unanswered questions pertinent to a closed-loop carbonylation system, such as monitoring and maintaining an effective CO/CO_2 ratio.
5. Test the merits of magnetically concentrating free iron directly from the lunar surface to remove the need for a prior reduction step.

Acknowledgments

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NASA's 2023 BIG Idea Challenge Lunar Forge: Producing Metal Products on the Moon

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Industry Partners: Powder Metallurgy Laboratory

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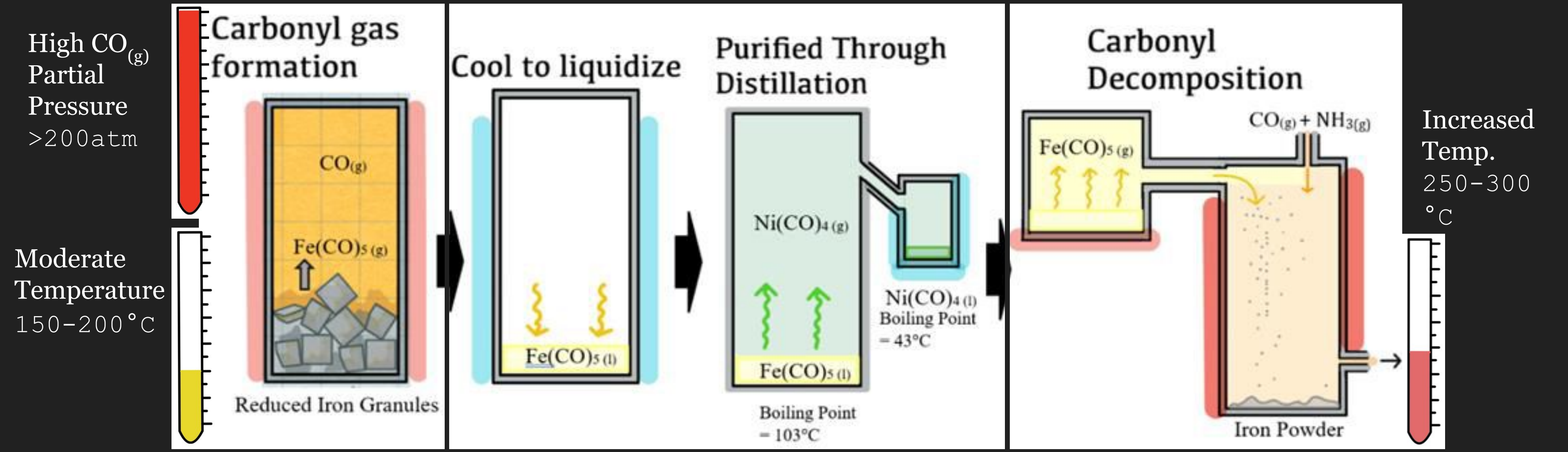
BIG IDEA CHALLENGE

Background and Motivation: Lunar Regolith

- **Prohibitive Transportation Costs**
  - It costs thousands of dollars per kilogram to get material into space (Roberts & Kaplan, 2022)
  - Transporting metal components is particularly expensive due to material weight.
- **Untapped Metal Underfoot**
  - Iron is relatively abundant on the lunar surface in the form of iron oxide. (Badescu 2016)
  - The concentration of iron oxide ranged from 0.7 to 22.5 wt% in Apollo and Luna samples.
- **Carbonyl Iron Refining (CIR)**
  - Technology has been commercially proven on Earth
  - Has a number of characteristics optimal to lunar environment
  - Could play a supporting role to oxygen-extraction technologies.

The Commercial Carbonyl Iron Refining Process



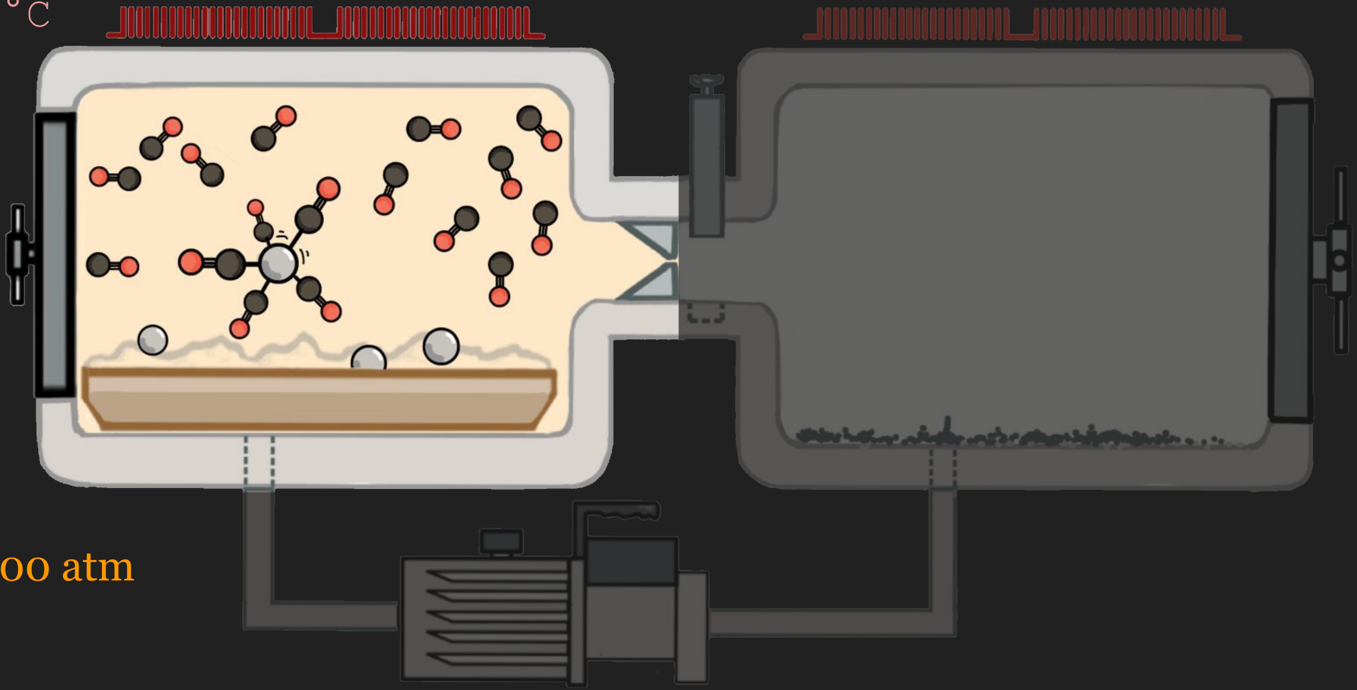
$Fe_{(s)} + 5CO_{(g)} = Fe(CO)_{5\,(g)}$ | $Fe(CO)_{5\,(l)}$ | $Fe(CO)_{5\,(g)} = Fe_{(s)} + 5CO_{(g)}$

- BASF extracts ~65% of Fe in 120 hours.
- Commercial production generates~29,000 metric tons/year Fe powder (Inovar 2017)

Formation Chamber

$$Fe_{(s)} + 5CO_{(g)} = Fe(CO)_{5\,(g)}$$

T= 120-180 °C

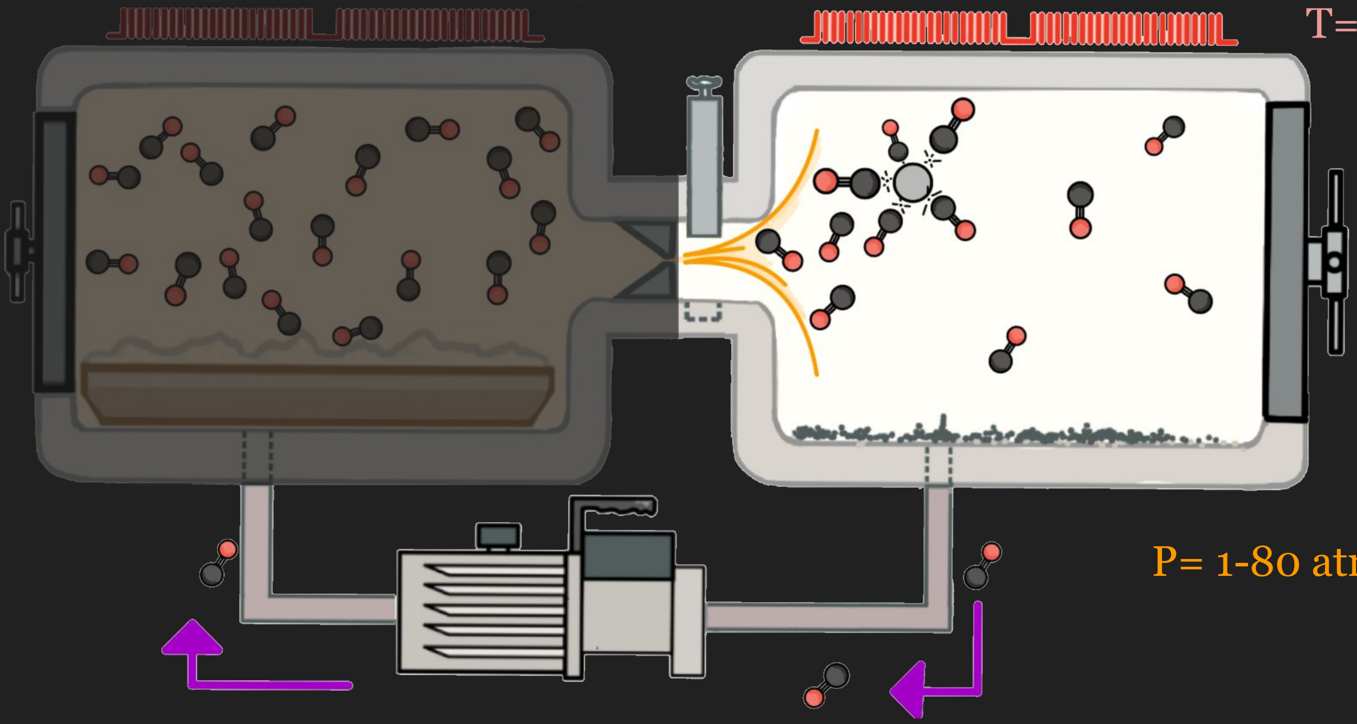


P= 60-100 atm

Decomposition Chamber

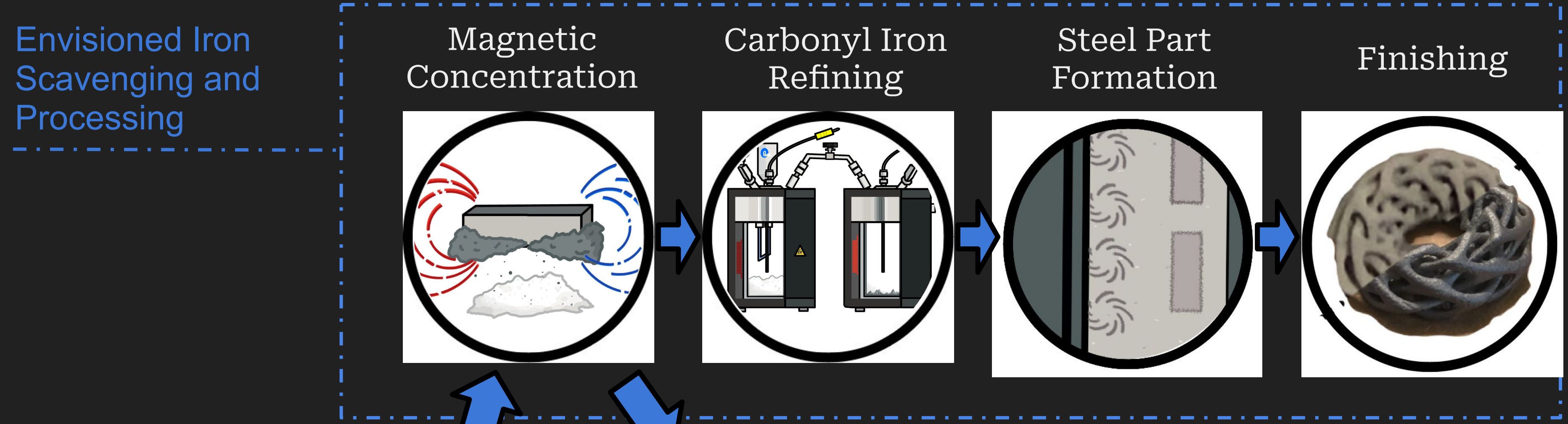
$$Fe(CO)_{5\,(g)} = Fe_{(s)} + 5CO_{(g)}$$

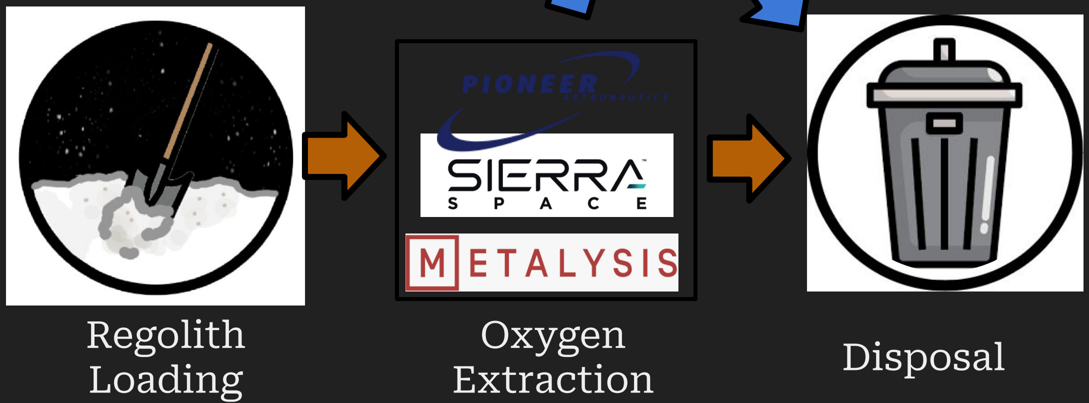
T= 250-300 °C



P= 1-80 atm

Regolith to Steel Component Flow





- Produces a high-purity, ultra-fine, spherical iron powder ideal for versatile additive manufacturing.
- Extracts, concentrates, and purifies iron simultaneously in a compact space. Chamber doubles as a carburization chamber.

Description of Concept: Carbonyl Iron Refining

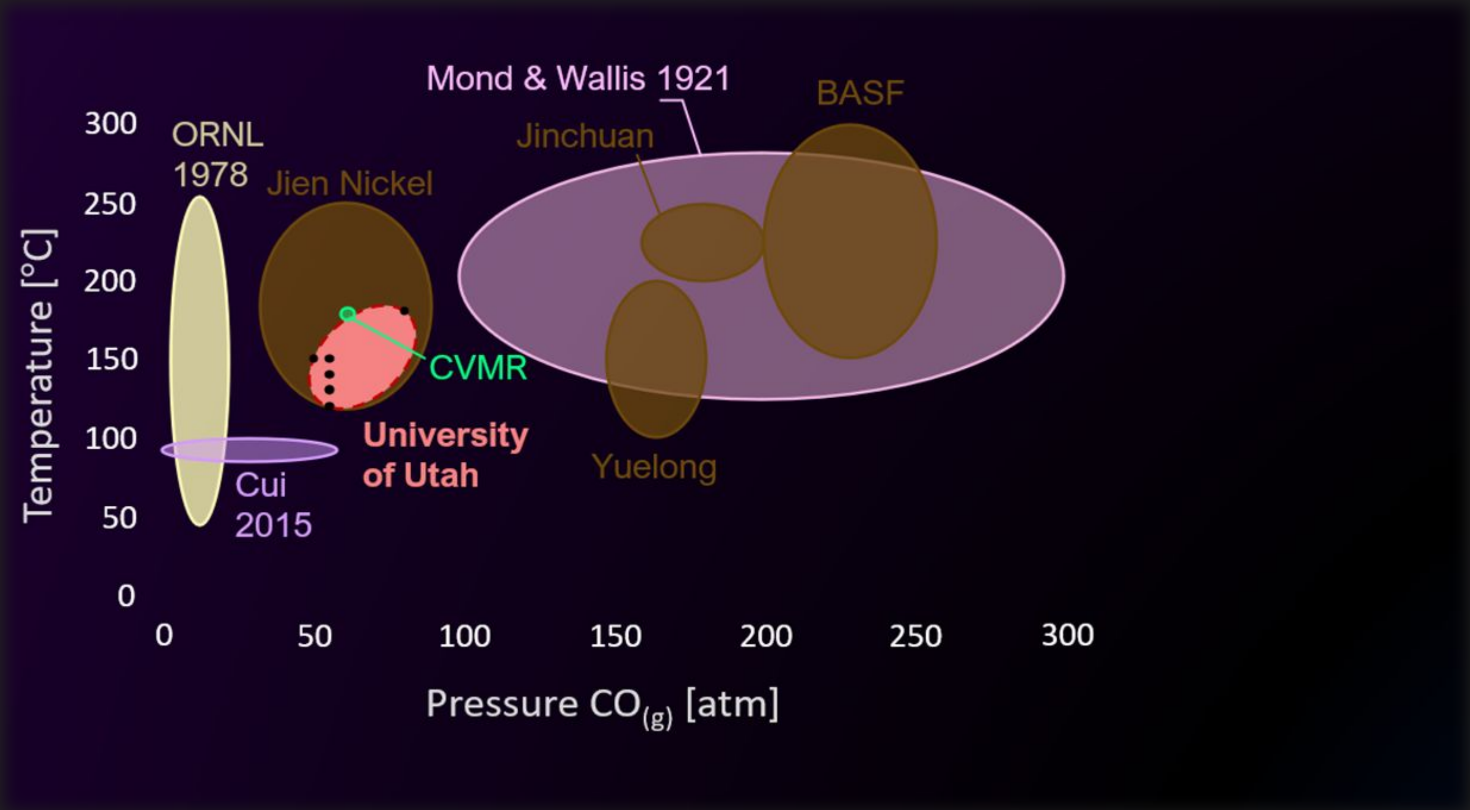
Advantages

- Process does not require a regular consumable
  - CO(g) is released upon disassociation
  - Immediately available for reuse
  - Many refining cycles can occur
- Affinity for additive manufacturing
  - Complex geometry parts can be generated
- Compatibility with existing life-support systems
  - Regolith reduction uses H_2(g) to produce water vapor to provide O_2(g) for the crew
  - CO(g) oxidized via Boudouard reaction can be periodically regenerated

Disadvantages:

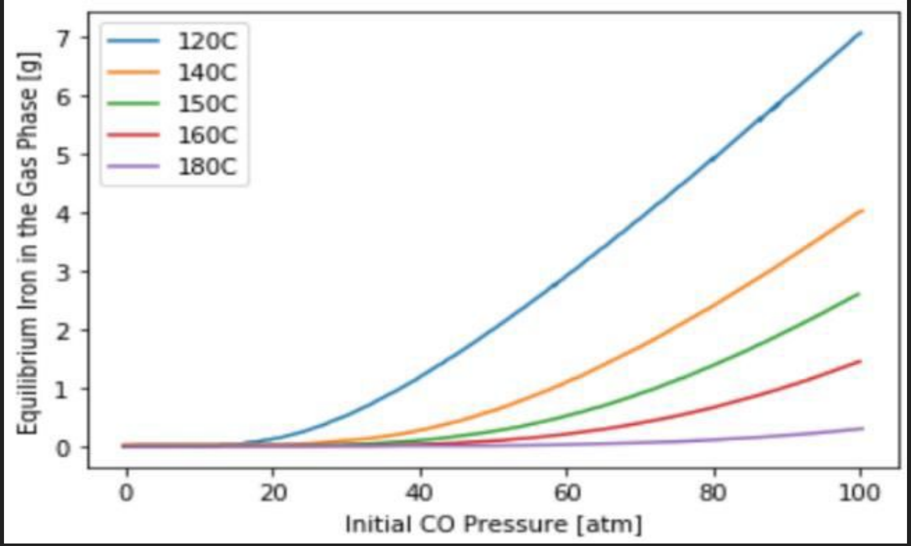
- Considerable formation pressure
  - Pressure >200 bar (Inovar 2017)
  - Vessel wall thickness would be substantial
- Iron carbonyl formation is exothermic
  - Equilibrium is not favorable if the balance between heating and cooling is not kept
- Iron pentacarbonyl may decompose and adhere strongly on reactor surfaces rather than forming a usable particle product
  - Not observed in our experiments, but could present challenges in some designs

Literature Review



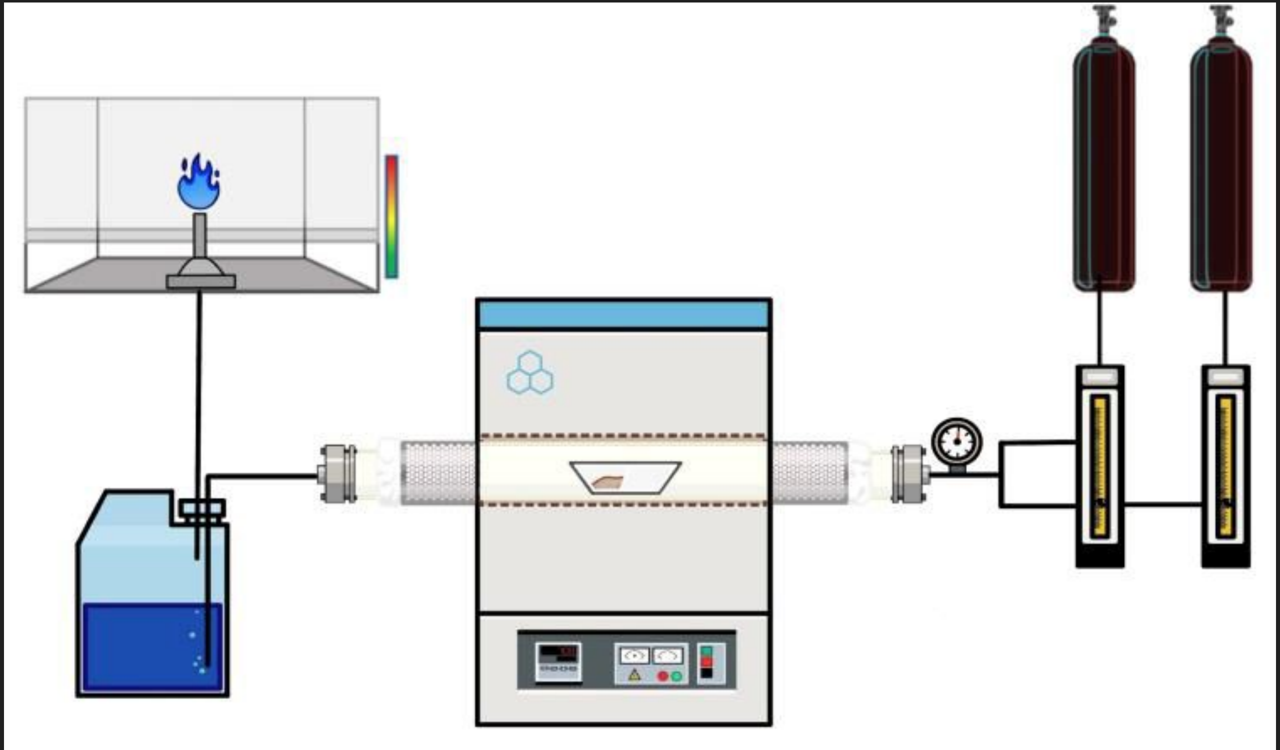
Predicting Equilibrium Conditions in a Physical System

- A predictive model was created in Python
  - Tailored equilibrium quantities to the physical parameters of the carbonylation and decomposition of carbonyl iron experiments
- Linking the equilibrium concentrations to the dimensions of the reactor vessel allowed for projections to be made concerning the number of complete formation cycles
  - Before the CIR apparatus breaks even and produces a greater mass than its weight



Verification Testing

Reduction of Iron Oxide in Lunar Regolith



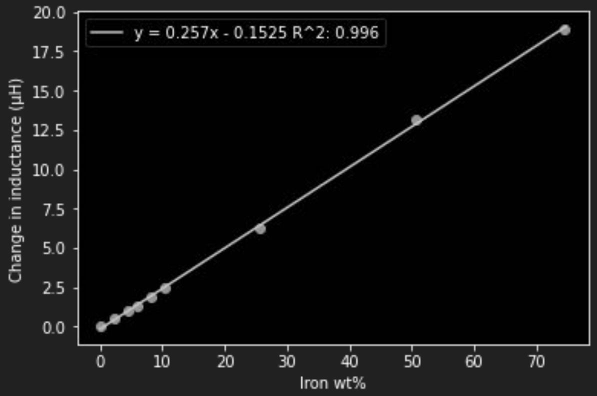
Iron oxide reduction in a Horizontal Tube Furnace

Reduction of Iron Oxide in Lunar Regolith

- Four different methods were selected
  - Dried lunar regolith (LR)
  - Dried lunar regolith mixed with carbon powder (LRC)
  - Oxidized lunar regolith (OLR)
  - Oxidized lunar regolith mixed with carbon powder (OLRC).
- A portion of each powder reduced was analyzed to determine iron concentration and extent of reduction
- Pioneer Astronautics generously sent 4 kg of their beneficiated regolith simulant
  - Eliminating the need to reduce our regolith
  - One carbonylation (E11) was performed on our in-house reduced sample.

Reduction Results - Induction Coil Method

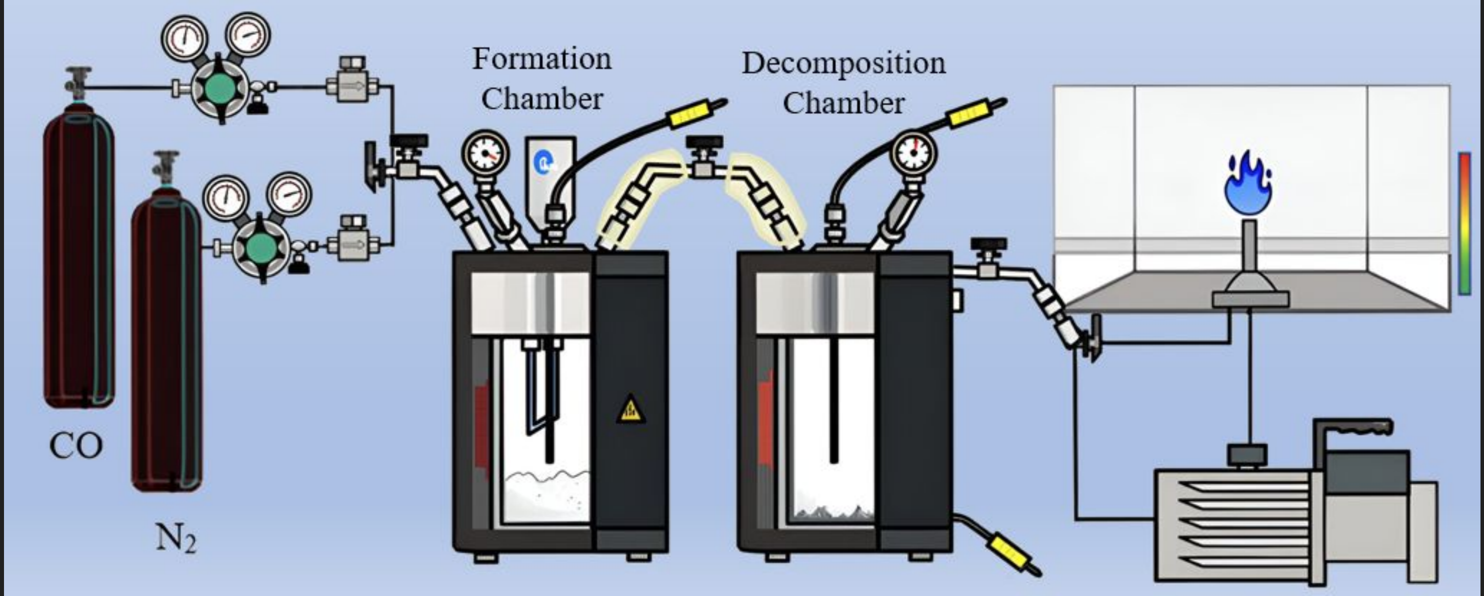
- Pioneer Astronautics used the inductance variable of a copper coil to determine the iron content in a powder sample
- The setup was calibrated with various 4-gram standards, each containing a specific weight percent of iron offset with silica
  - Inductance of a coil is directly proportional to the magnetic permeability of its core sample
  - As the amount of iron in the core material increases, the coil's measured inductance also increases



Reduction Results

- Highest reduction achieved was ~3.6 wt% of Fe after 6 hours under 100% $H_2(g)$ flow
  - May be due to the limited amount of Ilmenite in the lunar regolith sample along with the difficulty of Olivine and Pyroxene reduction
  - Pure Olivine was reduced and had a maximum metallic iron content of 2.15 wt%
  - Pure Pyroxene was reduced and had a maximum of 1.37 wt% metallic iron
- The limited amount of metallic iron produced from Olivine and Pyroxene is a contributing factor to the total limited amount of iron in the reduced regolith, as they are major components in the lunar regolith simulant
  - The limited ability of Olivine and Pyroxene to be reduced is probably due to the formation of silica shells and layers

Carbonylation of Reduced Iron

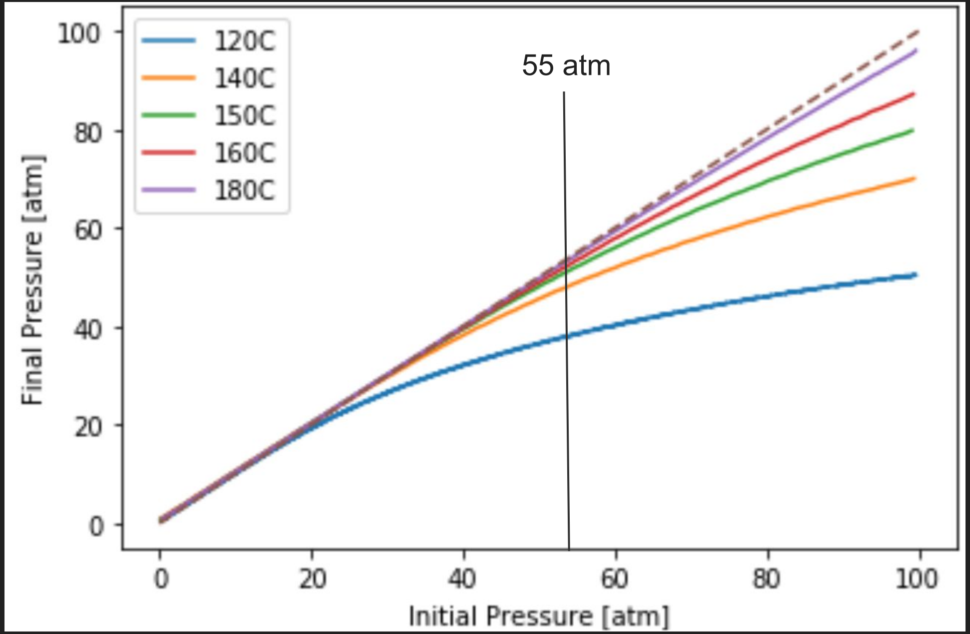


Carbonylation Experiments

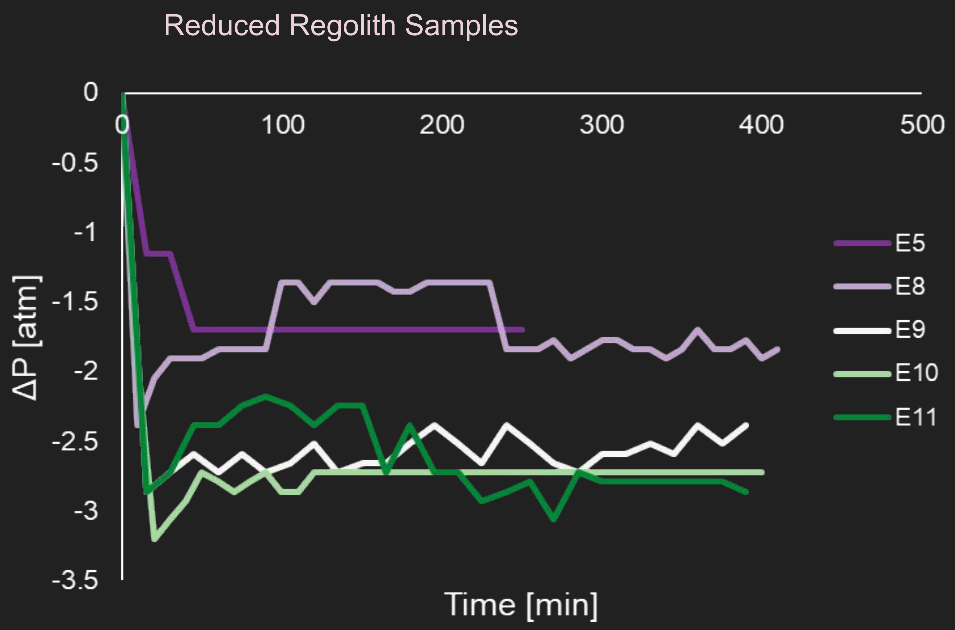
Experiment	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
Configuration	Batch	Continuous	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Non-Cooled Batch	Batch
Input Load Material	Synthetic Iron Powder	Synthetic Iron Powder	Synthetic Iron Powder	Synthetic Iron Powder	LR PA	Synthetic Iron Powder	Synthetic Iron Powder	LR PA	LR PA	LR PA	LR HTF
Pressure (atm)	50	50	55	55	55	55	55	55	55	50	55
Temperature (°C)	150	150	120	150	150	130	140	120	120	150	120

Pressure Monitoring to Approximate Reaction Progress

- Five moles of CO(g) are consumed for every mole of $Fe(CO)_5$ (g) produced. This results in a net loss in total pressure.
- The rate that pressure drops should approximate the carbonylation progress and kinetics.
- Additionally, pressure drop can be used to calculate the moles of $Fe(CO)_5$ (g) in the gas phase to provide a third corroborating data point to regolith mass loss and product mass.

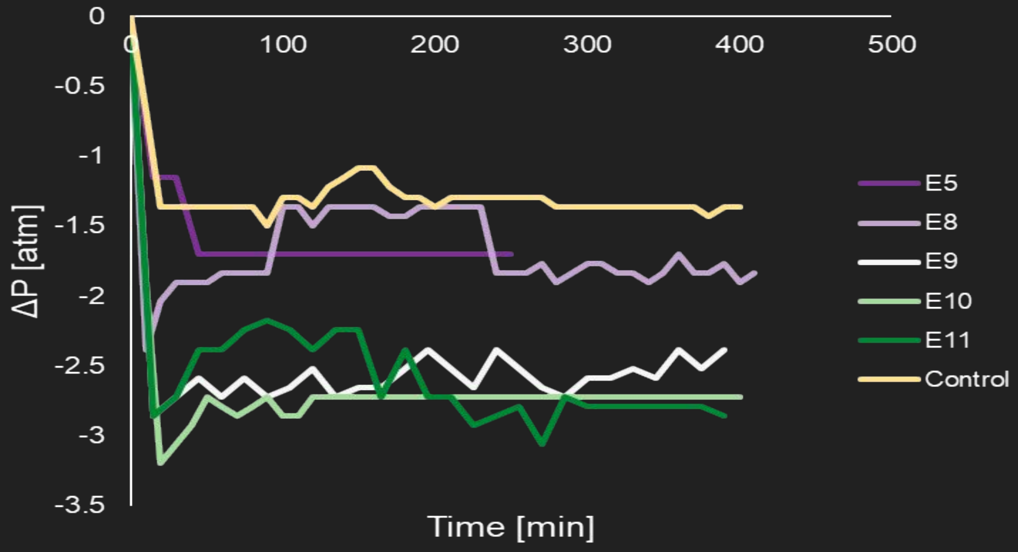


Tracking the Formation Rate



- Recording chamber pressure commenced when the temperature stabilized on the planned value.
- The pressure is seen to undergo a precipitous initial drop before flattening out.
- Not shown (for clarity) are the pressure profiles on the six iron puriss samples. These follow the same trend with some exceptions.

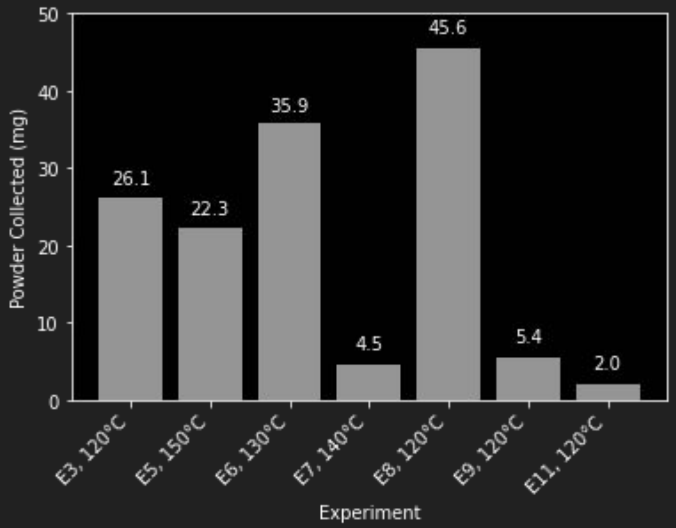
Tracking the Formation Rate (Continued)



- A control experiment performed with sand. It also displayed an initial pressure drop.
- The initial pressure drop is now thought to be attributable to pressure lagging the temperature after an initial heating overshoot.
- Unfortunately, the pressure gage was not sensitive enough, nor the experiments long enough, to determine reaction kinetics or confirm the Python model.

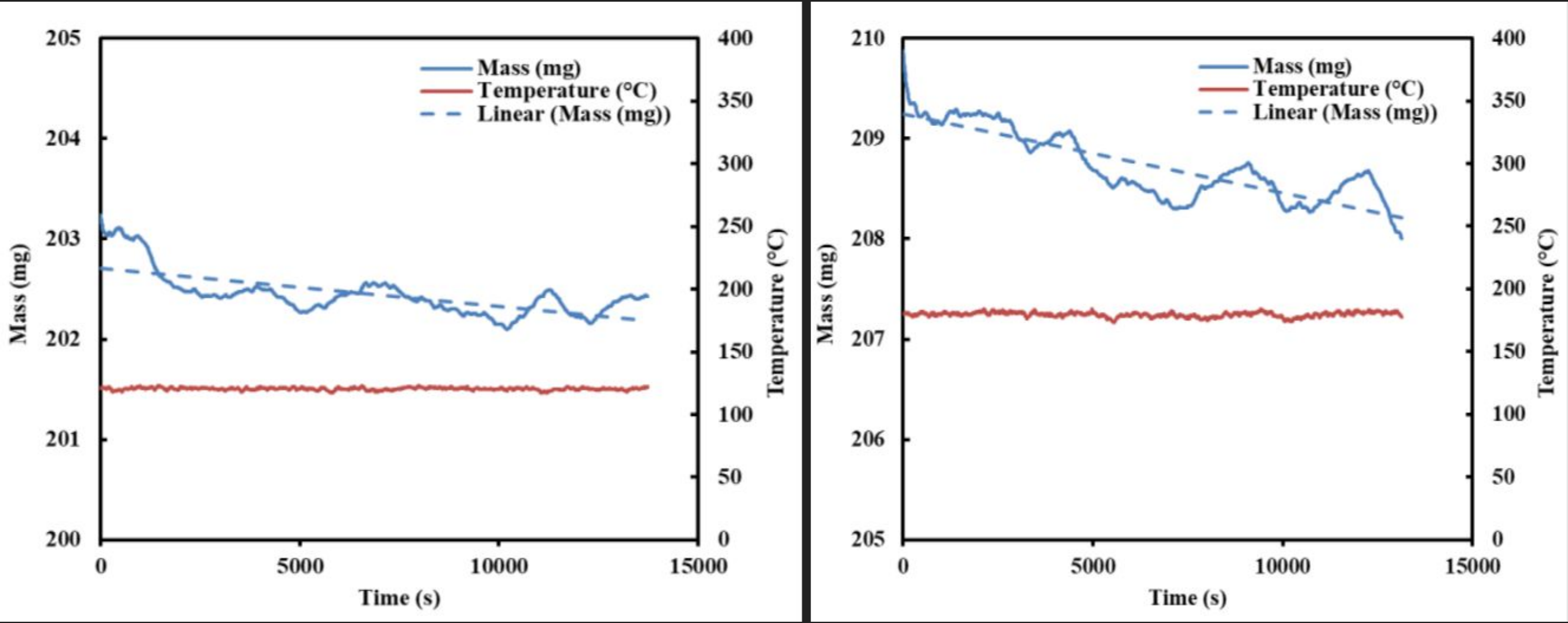
Carbonylation Results

- E3, E5, E6, E7, E8, E9, and E11 all produced product powder
- The largest amount of powder recovered was in E8
  - 120°C and 55 atm for ~410 minutes.
  - Reduced lunar regolith from Pioneer Astronautics with ~6.4 wt% Fe
- Experiment E11 had the loading of reduced simulant lunar regolith from the HTF with ~1.37 wt% Fe
  - similar conditions to experiment E8
  - Ability of the system to do so with lower iron content



Second High-Pressure Reaction System for Verification

- High-Pressure wire-mesh Thermogravimetric Apparatus (HTPA)
- Two experiments were performed with 99.5% purity CO(g)
  - 55 bar, 120ºC, under 0.2 SLPM flow for a duration of 3 hours 49 minutes
    - Decrease of 0.8mg (0.4 wt% loss)
  - 80 bar, 180ºC, under 1.5 SLPM flow for a duration of 3 hours 39 minutes
    - Decrease of 1.9mg (0.9wt% loss)
- If the weight loss is attributable to iron carbonyl formation, this would entail a conversion rate of 1.1 wt% Fe/hr
  - One possible explanation is that the condition of the feed material inhibited the formation rate
  - Another possible source of mass reduction is the formation of $Ni(CO)_4$(g) from nickel contained in the TGA sample holder (SS316)



Mass (mg)
Temperature (°C)
Linear (Mass (mg))
205
204
203
202
201
200
400
350
300
250
200
150
100
50
0
0
5000
10000
15000
Time (s)
Mass (mg)
Temperature (°C)
Linear (Mass (mg))
210
209
208
207
206
205
400
350
300
250
200
150
100
50
0
0
5000
10000
15000
Time (s)

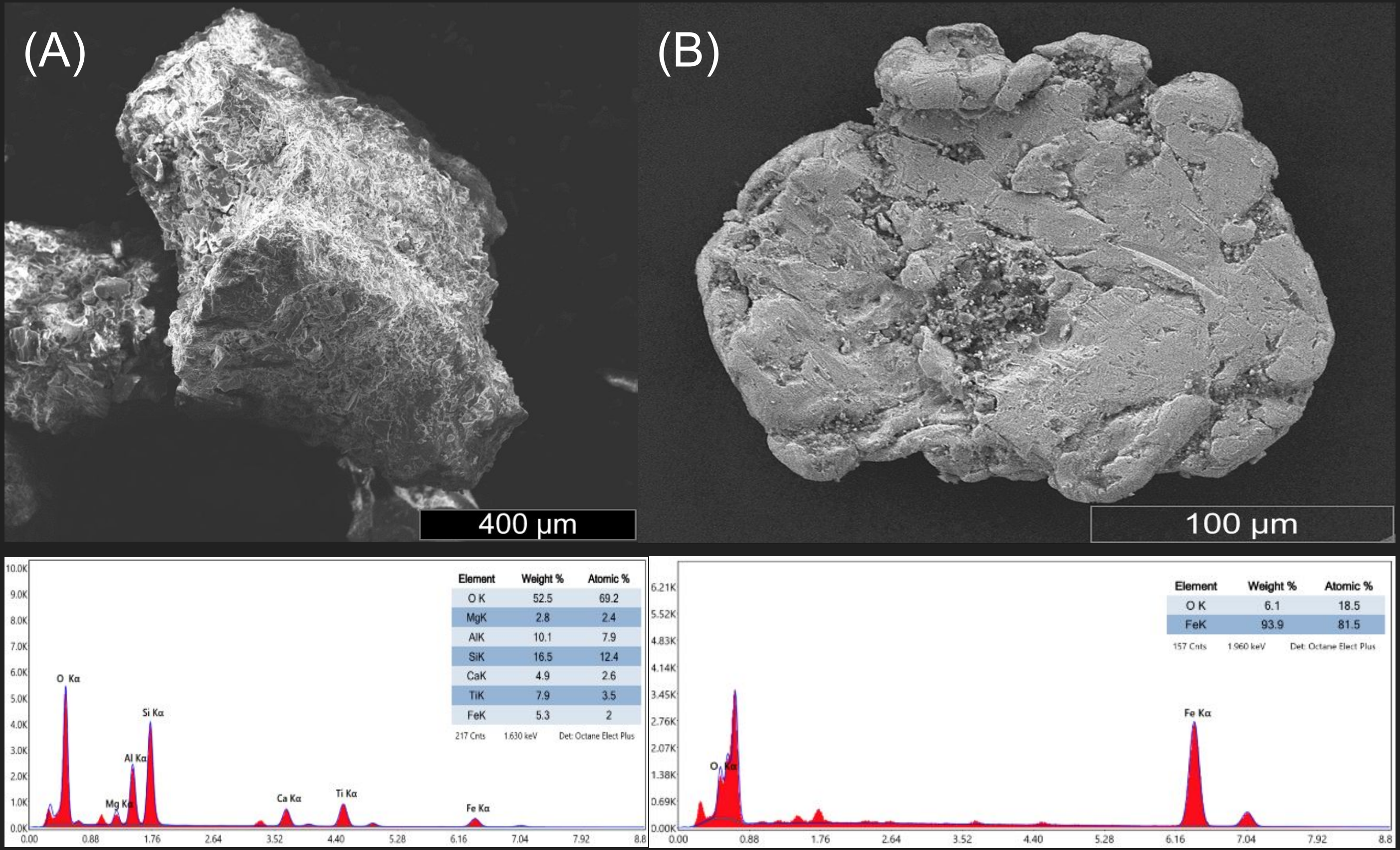
Results and Conclusions

Pycnometer and Particle Size Distribution

- Final products from the carbonylation experiments (E2 and E5) show different mean particle sizes compared with the Iron Puriss powder and HTF reduction powder
  - Standard deviation values are less than 0.28

Sample	HTF Reduction Product Powder	Iron Puriss Powder	E2 Product	E5 Product
Mean Particle Size (um)	297	95	223	213
Density (g/cm^3)	3.17	7.62	3.20	3.48

SEM/EDS

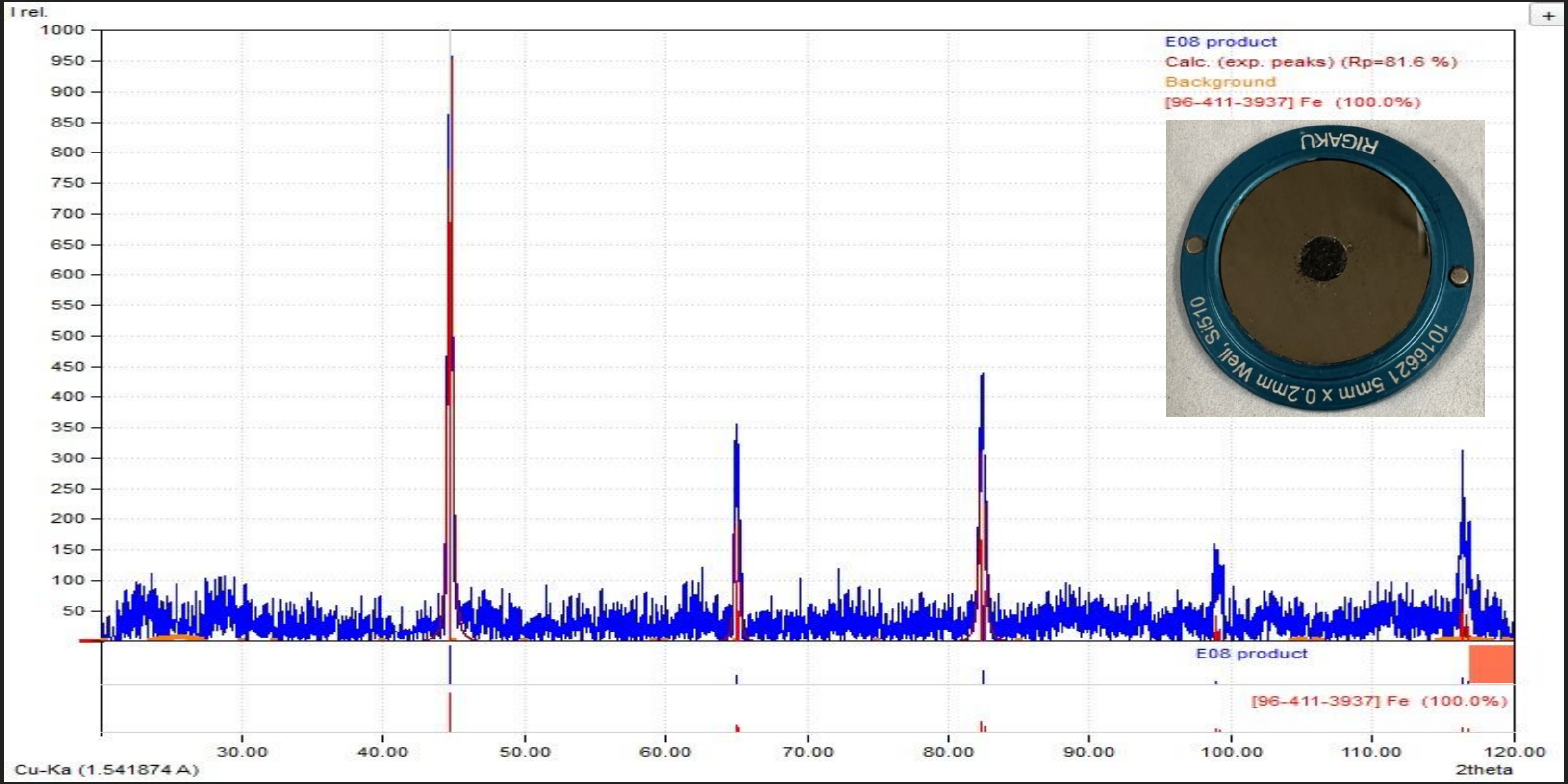


A) Sample LR HTF powder starting material; B) Fe product powder experiment E11

XRD

- Experiment E8 product powder indicated that iron was formed in the decomposition chamber
- Furthermore, no silicon or titanium peaks were identified
  - No blow-through from the carbonylation towards the decomposition chamber
  - Iron powder is being formed under the experimental tested conditions
- Two carbonylation/decomposition experiments with $CO(g)$ were performed using an HPTA, one at 55 bar and 120^{o}C and one at 80 bar and 180^{o}C
  - A decrease of 0.8 mg and 1.9 mg, respectively, indicating that $Fe(CO)5(g)$ formation is occurring
  - However, kinetics would suggest that a more extended investigation must be performed to obtain more significant weight loss

XRD


I rel.
E08 product
Calc. (exp. peaks) (Rp=81.6 %)
Background
[96-411-3937] Fe (100.0%)
RIGAKU
1016621 5mm x 0.2mm Well, Si510
E08 product
[96-411-3937] Fe (100.0%)
Cu-Ka (1.541874 A)
2theta

Overall Conclusions

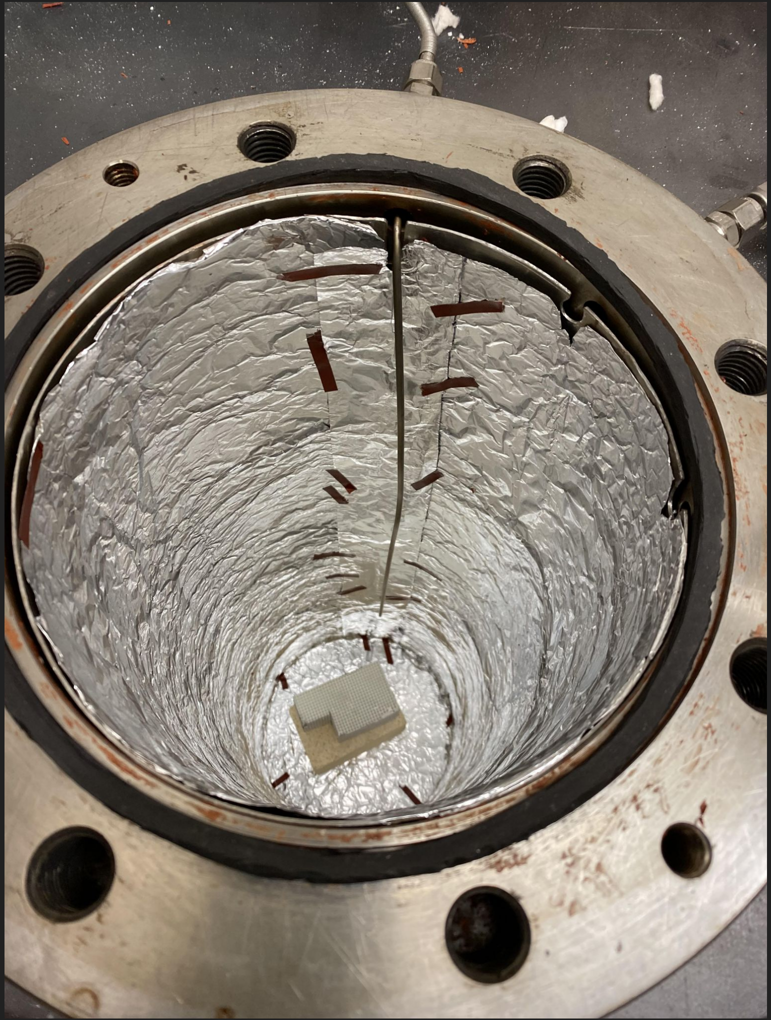
- Carbonyl iron refining can extract iron from reduced lunar regolith using a two-chamber process from starting material as poor as 1.37 wt% iron.
- Pressure monitoring was not sufficiently sensitive to monitor reaction progress and kinetics under our conditions.
- The carbonylation product was large in diameter (mean~200 μm) and of low density (~3.2 g/cm3) compared to commercial Puriss powder.

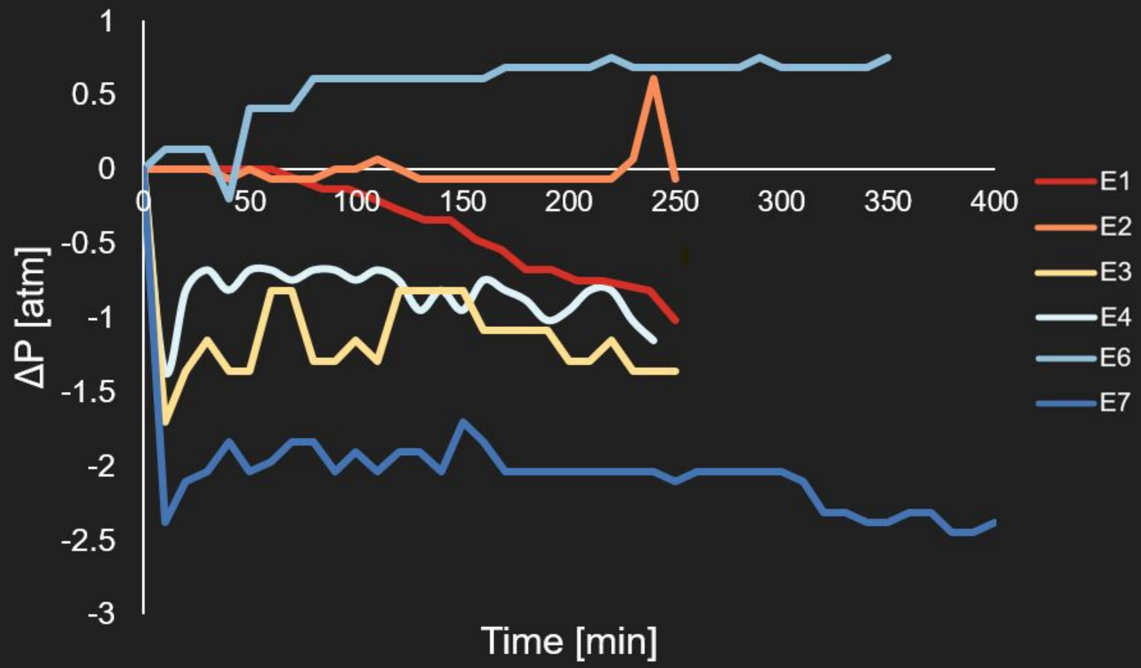
Future Work

- 1 wt% addition of sulfur increased yield
  - Could be combined with lunar sulfur capture system designed by Pioneer Astronautics
- Addition of mass flow controller for continuous flow
    - Guarantee ame conditions throughout system
    - Increase yield
- Scale-up of design
  - Square cube law suggests “break-even point” would be reached faster
  - Current process on Earth support that it can be scaled up
  - Dust related damage is a high risk
- Higher formation pressure to empower reaction monitoring and increase yield.

Additional Slides for Questions


Kimwipes





1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
ΔP [atm]
0
50
100
150
200
250
300
350
400
Time [min]
E1
E2
E3
E4
E6
E7