

Resource Production on the Moon

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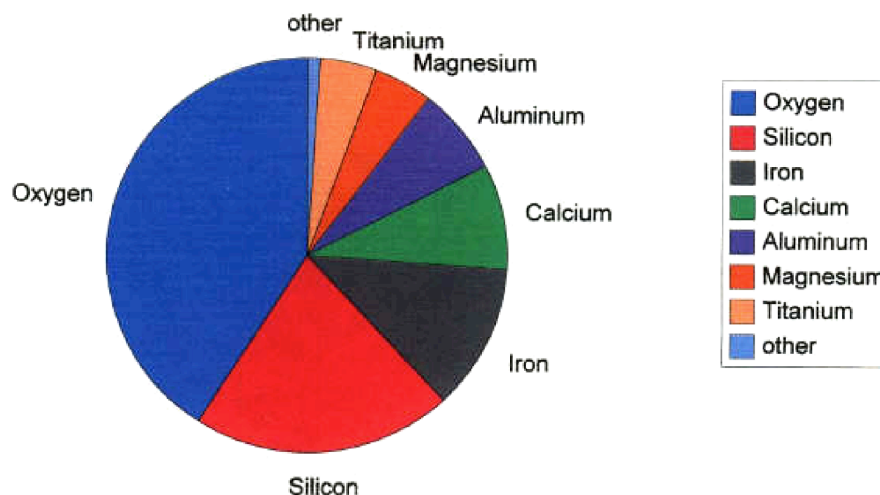
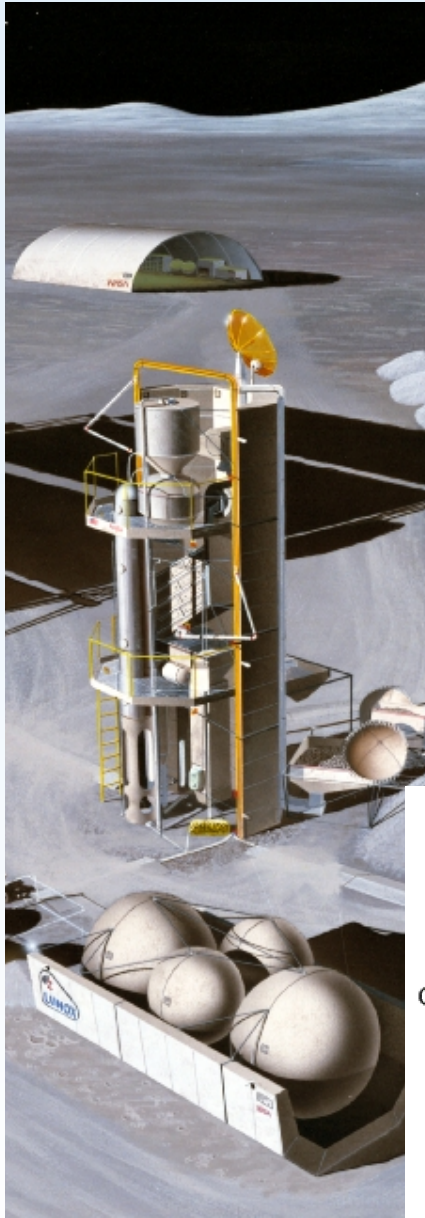


Lunar Resource Production

Oxygen will be the first element to be refined from lunar materials

- Main component (by mass) of lunar soil
- Main component (by mass) of rocket fuel
- Essential element for life support

It's present, it's abundant, and it's useful



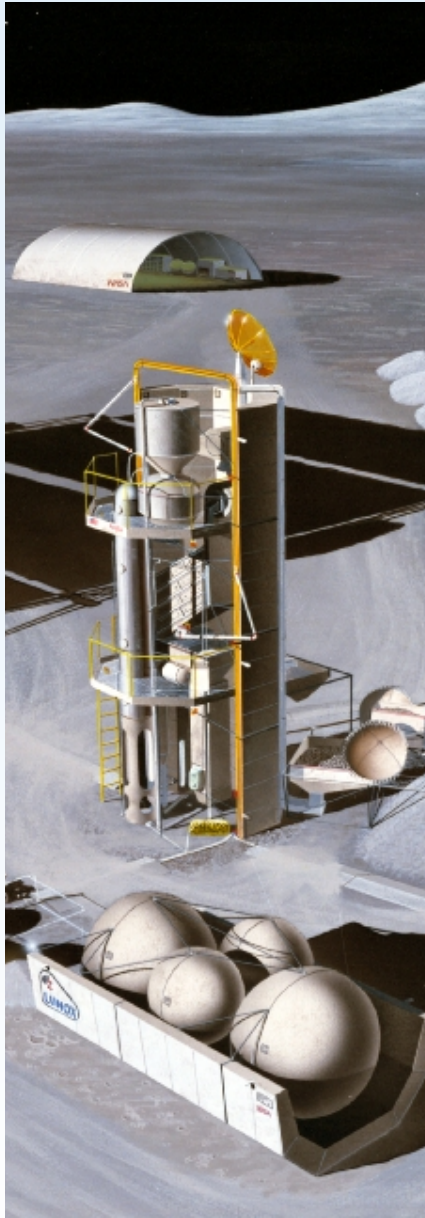
Lunar Resources: Beyond Oxygen

Oxygen will be the first element to be refined... but not the last

- **For space industrialization we want more**
- Goal: develop a production sequence that makes useful raw materials for production
- *Set up the basic infrastructure for space industrialization*

“Footsteps” philosophy:

- Start with the highest value product
- But do it in a way that allows step by step expansion



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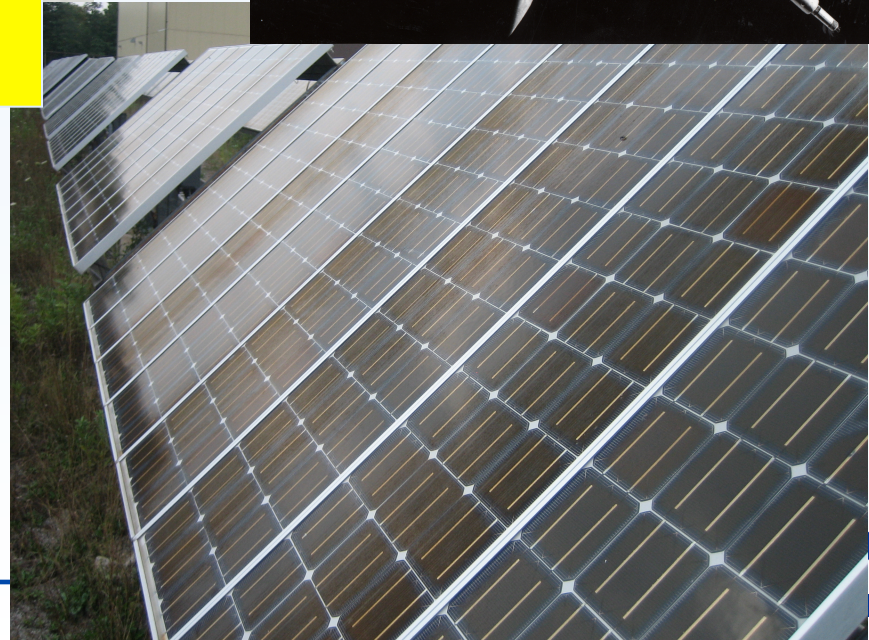
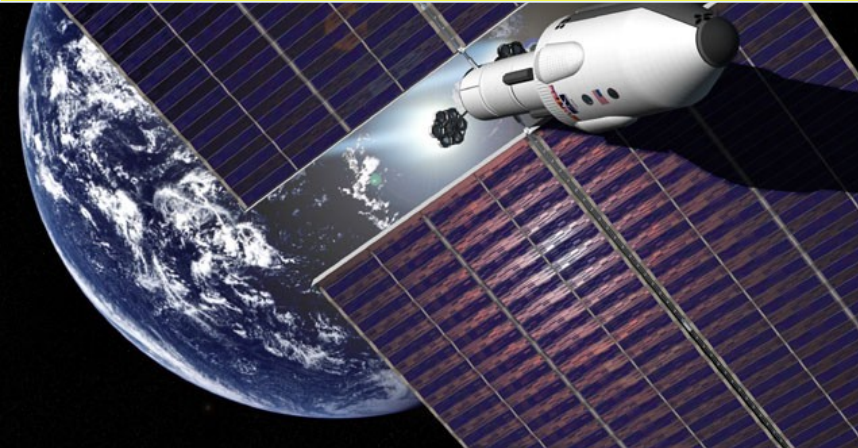
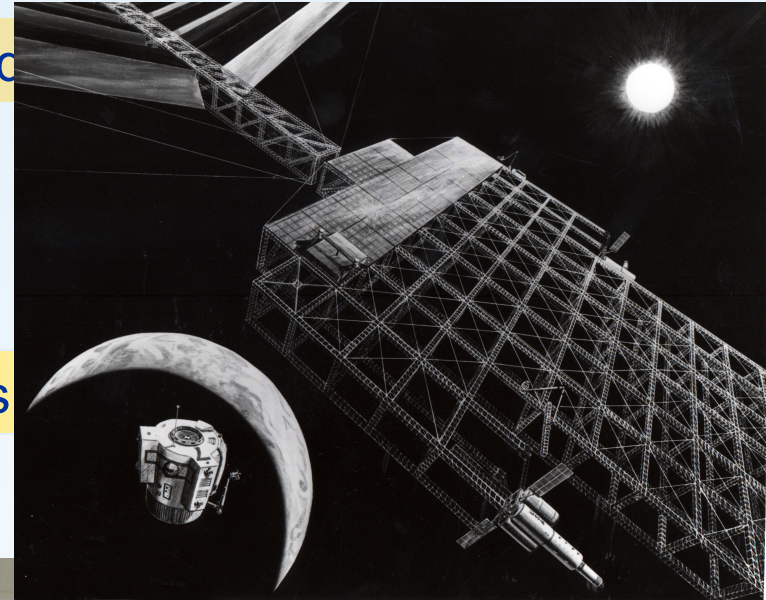
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An industrial product: Manufacturing solar cells on the Moon?

- Valuable to expand

- Valuable for other space applications

- Possible production of solar panels for space solar power?





Proposed before:

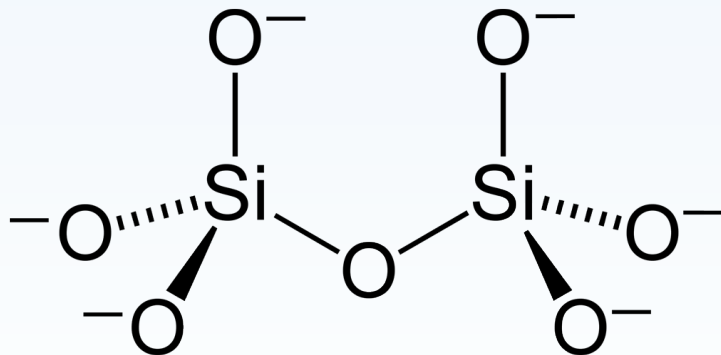
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- G. Landis, “Solar Array Production on the Moon,” *SPS-97: Space and Electric Power for Humanity*, Aug. 24-28, 1997, Montreal, Canada, pp. 311-318.
- G. Landis, “Materials Refining for Structural Elements from Lunar Resources,” *Workshop on Using In-situ Resources for Construction of Planetary Outposts* (M.B. Duke, ed.), Lunar and Planetary Institute Technical Report 98-01, p. 11 and pp. 43-46 (1998).
- G. Landis, “Technology for Solar Array Production on the Moon,” *Proceedings of the 29th IEEE Photovoltaic Specialists Conf.*, New Orleans LA, May 19-24 2002, pp. 796-798.
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- G. Landis, “Materials Refining on the Moon,” *Acta Astronautica*, Vol. 60, No. 10-11, 906– 915 (May-June 2007).

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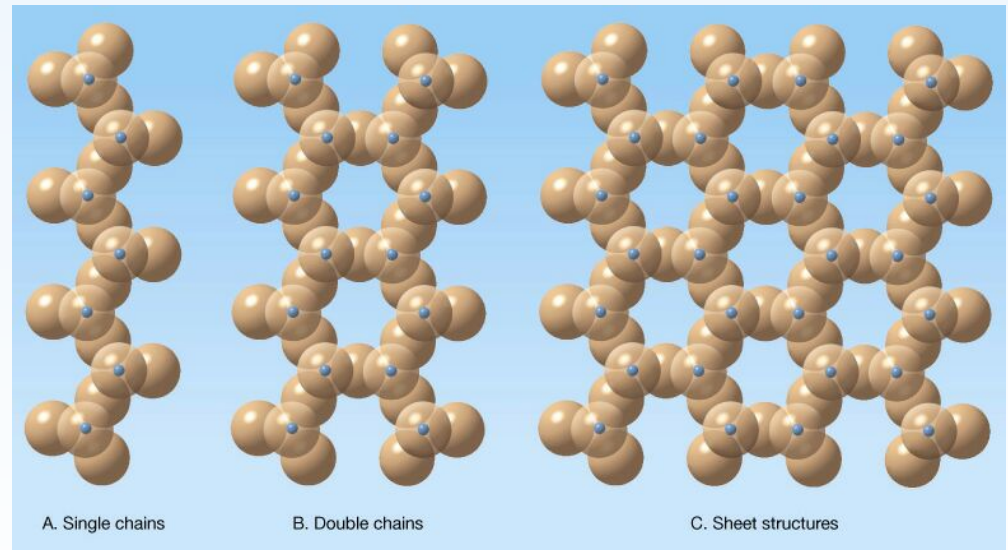
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Why is oxygen production hard?

- Oxygen is tightly bound in the form of silicates
- Silicates form networks
 - Strongly bonded, high melting point materials
- Oxygen production requires breaking up silicate networks



Silicate chain



Example silicate networks

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Desired process

The optimum regolith reduction process would have the following desirable properties:

1. Works on average lunar regolith, with minimum beneficiation
2. Produces large amounts of oxygen (should reduce the majority mineral constituents of regolith).
3. Recycles reactants (or uses reactants produced from lunar sources)*
4. Occurs at moderate temperature
 - Minimize need for exotic materials for reaction crucibles, electrodes, etc.
 - Reduce the complexity required of solar concentrators.
5. **Produces reduced byproduct in a form that may be easily refined for use in other manufacturing processes.**

Image Courtesy of NASA

NASA artwork by Pat Rawlings/SAIC

*and preferably both. Since real-world recycling of reactants will be less than 100% efficient, it is desirable that all reactants can be replenished from local materials.)

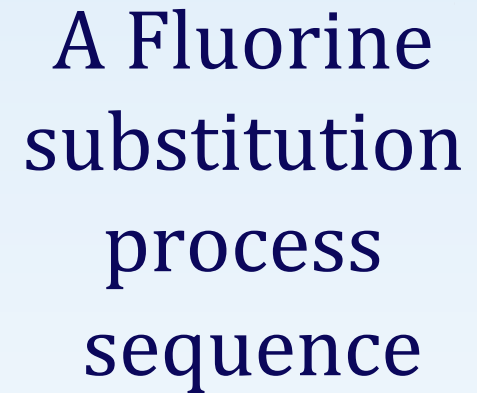
Anion Substitution Reaction

- Anion substitution: replace one negative ion with a different one
- If the new ion is further *down* on the electrochemical series (more electronegative), this is a forward reaction
- Proposed substitution: replace oxygen in lunar soil with fluorine
 - Uses up as fluorine as fast as you produce oxygen
 - But fluorides don't form networks: simpler to reduce



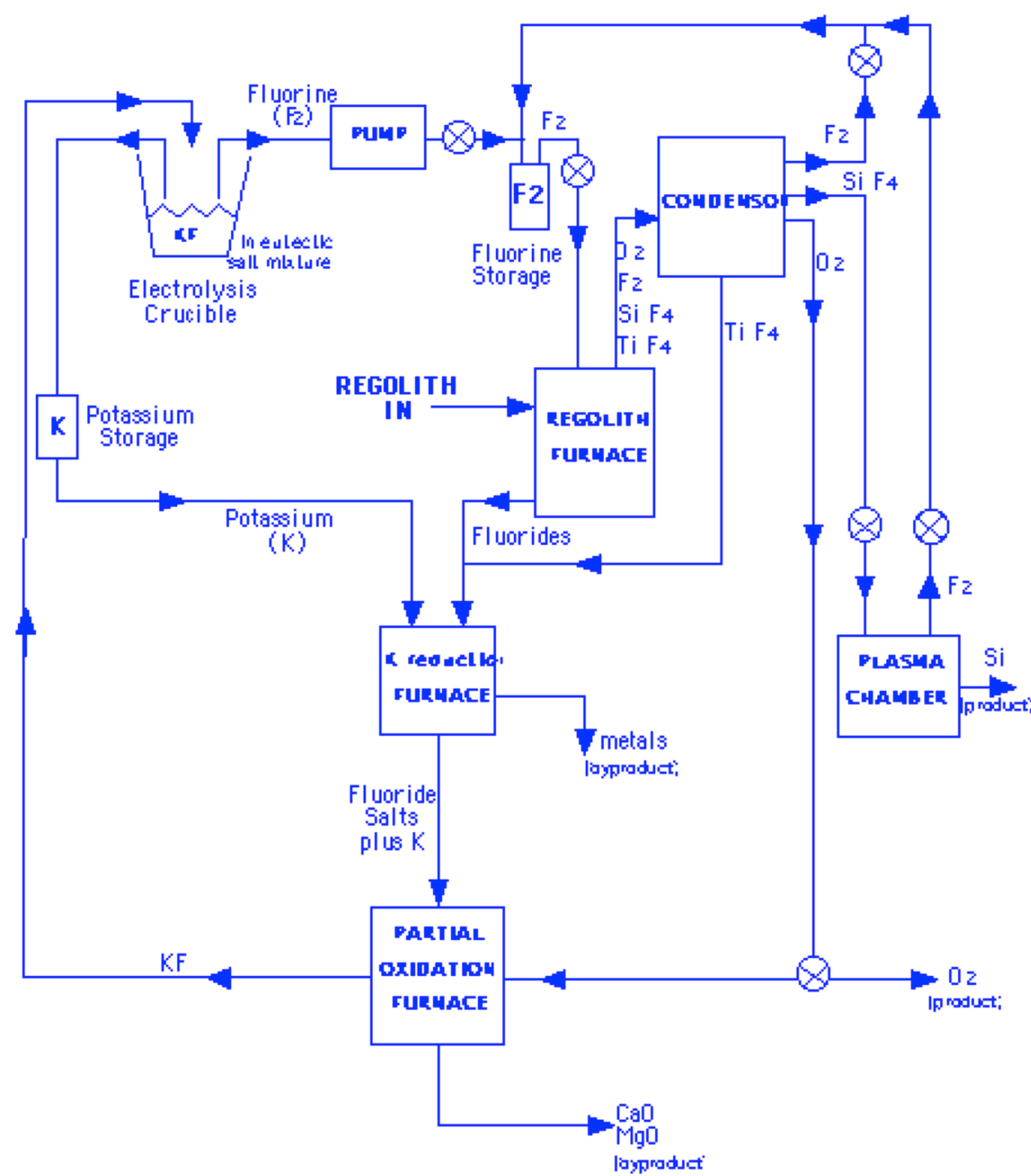
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- G. Landis, "Materials Refining on the Moon," *Acta Astronautica*, Vol. 60, No. 10-11, 906– 915 (May-June 2007).

- G. Landis, "Materials Refining for Solar Array Production on the Moon," *NASA Technical Memorandum TM-214014*, December 2005.





Reduction by Fluorine substitution

- Initial reactant: fluorine is brought to moon as a potassium fluoride eutectic salt
- **1. Potassium fluoride is electrolyzed from the salt at 676 °C** to form free fluorine and metallic (liquid) potassium.
- **2. The fluorine is reacted with heated lunar regolith at ~500 °C** to form SiF_4 , oxygen, and metal fluorides.



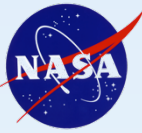
Reduction by Fluorine substitution

- **3. Gaseous SiF_4 is separated from oxygen by condensation at 178 °K.**
- **4. Potassium is added to the metal fluorides at 500 °C to produce metallic aluminum and iron, plus KF reactant. (CaF_2 & MgF_2 unreacted)**
- **5. Potassium oxide is reacted with CaF_2 and MgF_2 at 520 °C to produce potassium fluoride and calcium oxide, and MgO.**
 - the initial KF reactant is regenerated
 - CaO and MgO are byproduct



Silicon production

- Silicon is produced in the form of fluorosilane (SiF_4), which can be decomposed by a plasma process to produce elemental silicon.
- If elemental silicon is required, potassium can reduce the silicon to elemental form:
- **6. SiF_4 is reacted at 300 °C with potassium to form silicon.**



Advantages of Fluorine substitution

- Reactant brought to moon as fluoride salts
 - Inert, easy to transport
- Oxygen produced in first step
 - Si, Fe, Ti, Al reduced; CaO and MgO unreacted: high O₂ yield compared to other sequences
- Temperature of 650°C reasonable to achieve
 - but this is theoretical minimum- real world will be higher
- Silicon and Titanium produced as volatile gasses which are easily distilled
- Fe, Al are reduced to metal form
 - Can be refined as fluoride salts

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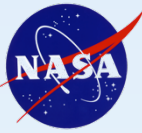
What materials do you need?

- 1. Metals: a ubiquitous structural material, and also used as wires.
 - Aluminum is the clear choice for wires.
 - Ca, not used on Earth because of high reactivity, is a possible conductor for vacuum.
- 2. Glass and ceramics.
 - Transparent glass for solar arrays
 - Ceramics for insulators.
 - Glass or ceramic fibers are also useful for structural composite materials.
 - The primary glass-forming material, silicon oxide, is abundant on the moon



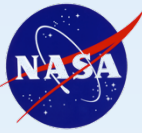
What materials do you need?

- 3. Silicon.
 - Optimal choice for in-situ solar cell production
 - Silicon suitable for semiconductor applications is a highly purified product (\sim ppb for some impurities).
- 4. Civil-engineering materials.
 - The equivalent of concrete, asphalt, and bricks.
 - Many possibilities for such bulk material exist, including sintered or melted regolith bricks, material produced from slag from other processes, or composite materials comprising aggregate fill cemented with a ceramic matrix.



Cation Substitution

- Cation substitution: replaces one positive ion (e.g., Al, Mg, Si) with another
 - This does not actually produce oxygen: it merely substitutes one oxide for another
 - However, if it breaks the tenacious silicate network, it leaves a new oxide that is much simpler to reduce
- When the substituted cations start out in metallic form, this is called *Metallothermic reaction*
 - Typically exothermic reactions
 - “thermite” is the most well known



Process

The process consists of two parts, first reducing the regolith, and then regenerating the metallic reactant:

(1) Metallothermic reduction

Heating of the regolith in the presence of (liquid) metallic calcium, to convert the silicates into metals plus calcium oxide.

(2) Molten Salt Electrolysis

Electrolyze the calcium oxide in a molten salt eutectic to produce metallic calcium and oxygen.

Metallothermic Reduction

- *Metallothermic reactions:*
 - Typically exothermic reactions
 - “thermite” is the most well known
- Metallothermic reaction has been used for production of metals on Earth.
- Production process for reduction of rare earth elements, as well as for production of Manganese, chromium, vanadium, zirconium, and niobium



• See: Armando Delgado, **Thermite Reactions in the Mixtures of Magnesium with Lunar and Martian Regolith Simulants**. 5th JOINT MEETING OF THE SPACE RESOURCES ROUNDTABLE and the PLANETARY & TERRESTRIAL MINING SCIENCES SYMPOSIUM, Golden, CO June 10-11, 2014



Metallothermic Reduction: *why calcium?*

- Examined many metals for reduction, including lithium, sodium, calcium, and others
- Calcium is high on the electromotive series
- Calcium can be produced from lunar materials
- Reduces all common elements except alkali metals (lithium, cesium, etc.)
 - not major components of lunar soil by mass
- Most important: **reactive enough to reduce the silicate bond**

Electromotive series

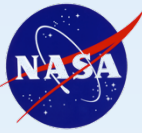
<u>element</u>	<u>E (Volts)</u>
Lithium	3.04
Cesium	3.03
Rubidium	2.99
Potassium	2.93
Barium	2.91
Strontium	2.89
Calcium	2.87
Sodium	2.71
Magnesium	2.37
Beryllium	1.7
Aluminum	1.66
Titanium	1.37
Iron (II)	0.44
Nickel	0.26
Iron (III)	0.04
Hydrogen	0
Silicon	-0.26

Most common
elements found in
lunar soil

- Each element on this list will reduce the elements below it, and be reduced by elements above it
- Reduction potential is the difference in electrochemical potential. The larger the value of ΔE , the more strongly the reaction will proceed.
- Data from *CRC Handbook of Chemistry and Physics*, 80th edition
- Some restrictions apply. Not valid in all media. See details.

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Example Calciothermic reactions

- For typical olivine composition MgFeSiO_4 :



- For typical anorthite composition $\text{CaAlSi}_2\text{O}_8$:





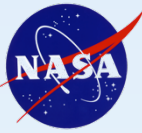
Metallothermic Reduction: calciothermic process

- Heat regolith in the presence of (liquid) metallic calcium at a temperature above melting point of calcium, 845°C.
- Calcium reacts with rock to convert the silicates into metals plus calcium oxide.
- Reaction rate enhanced with finely-ground reactants (or fine component of regolith)
- Reaction rate enhanced by excess of calcium.



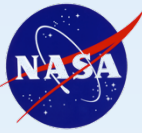
Reaction details

- Reaction product CaO is refractory
 - layer of oxide slag can limit the reaction.
 - This can be dealt with by addition of a flux to dissolve the slag.
- Since both calcium and calcium oxide are soluble in calcium chloride, CaCl_2 or a CaO/CaCl_2 eutectic mix can be used as a flux
 - calciothermic reaction done in a liquid solution.
- CaCl_2 flux is used for Ca reduction of titanium oxide
- $\text{CaCl}_2/\text{NaCl}$ melt used for Ca reduction of Rare Earths



Reaction temperature

- Minimum temperature set by melting point of calcium: **845°C.**
- Higher temperature increases rate and conversion fraction
- Terrestrial processes typically **900 to 1000°C**
 - Calciothermic reaction is exothermic, thus, the reaction is self-heating.
 - At higher temperature, the dense molten alloy byproduct settles to the bottom, where it can be decanted as a liquid, or separated mechanically



Molten Salt Electrolysis

- Following the reaction, the oxygen is in the form of the reaction product CaO.
- To generate oxygen and recover the reactant, this oxide is electrolyzed:





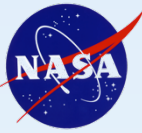
Molten Salt Electrolysis: temperature

- Calcium oxide (melt point 2580°C) is too refractory to be electrolyzed in its pure form.
- Solution: *electrolysis in a molten salt eutectic*
- Calcium chloride/calcium oxide mixture, with eutectic at 750°C .
- Electrolysis in CaO/CaCl_2 has been demonstrated at operating temperature 774°C
- More commonly done from 850 to 900°C



Combined reduction/electrolysis process

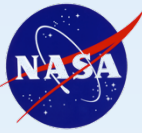
- Calciothermic reduction and molten salt electrolysis need not be separate steps
- With molten salt as reduction flux, both steps can be done in one crucible
 - Both processes can be done simultaneously
 - Calcium is regenerated by electrolysis as the reaction proceeds
- Combined processing is FFC ("Fray, Farthing, Chen") reduction process
 - used to produce titanium, molybdenum, and tungsten



Advantages of Ca Reduction process over other electrochemical reduction sequences

(*e.g.*, magma electrolysis)

- Does not require the regolith itself to be melted; thus can be done at temperatures as low as the CaO/CaCl_2 eutectic point of 750 °C.
- Does not require electrical conductivity of the regolith
- Process will reduce all the components of lunar regolith, up to magnesium and titanium.



Comparison of Processes

typical values from the literature

<i>Process</i>	<i>temperature</i>	<i>yield fraction</i>
Calcium reduction	825-900 °C	100%
Hydrogen reduction of ilmenite	800°C - 1100 °C	1.5%
Magma electrolysis	1300 °C - 1450 °C	30%
Carbothermal reduction	1625 °C - 1800°C	20% - 45%
Vacuum pyrolysis of ilmenite	>1200°C	1.5%
Vacuum pyrolysis of regolith	1400°C - 2500 °C	4% - 35%

“yield fraction” is defined here as the percentage of the oxygen content of regolith which is released in processing unbeneficiated soil .

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Byproducts

In addition to oxygen:

- Metallic calcium is produced as a byproduct
 - *This is the main reactant*
 - *Not required to take extensive steps to ensure high reactant recycling, since it is produced locally*
 - *Metal calcium may have other uses*
- Reduced byproduct is iron-aluminum silicide
 - *Incorporates magnesium and possibly titanium*
 - *Physical and chemical routes to refine this further*
 - *Iron aluminide may be useful as a structural material*

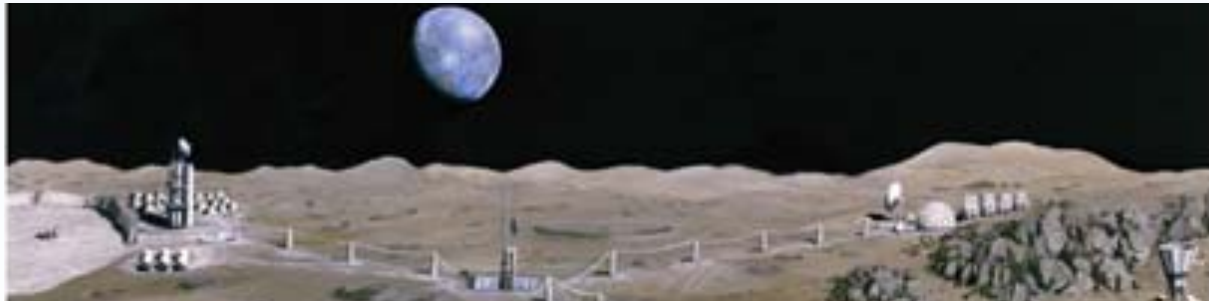
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Conclusions

Fluorine and Calcium reduction processes are proposed for lunar oxygen production

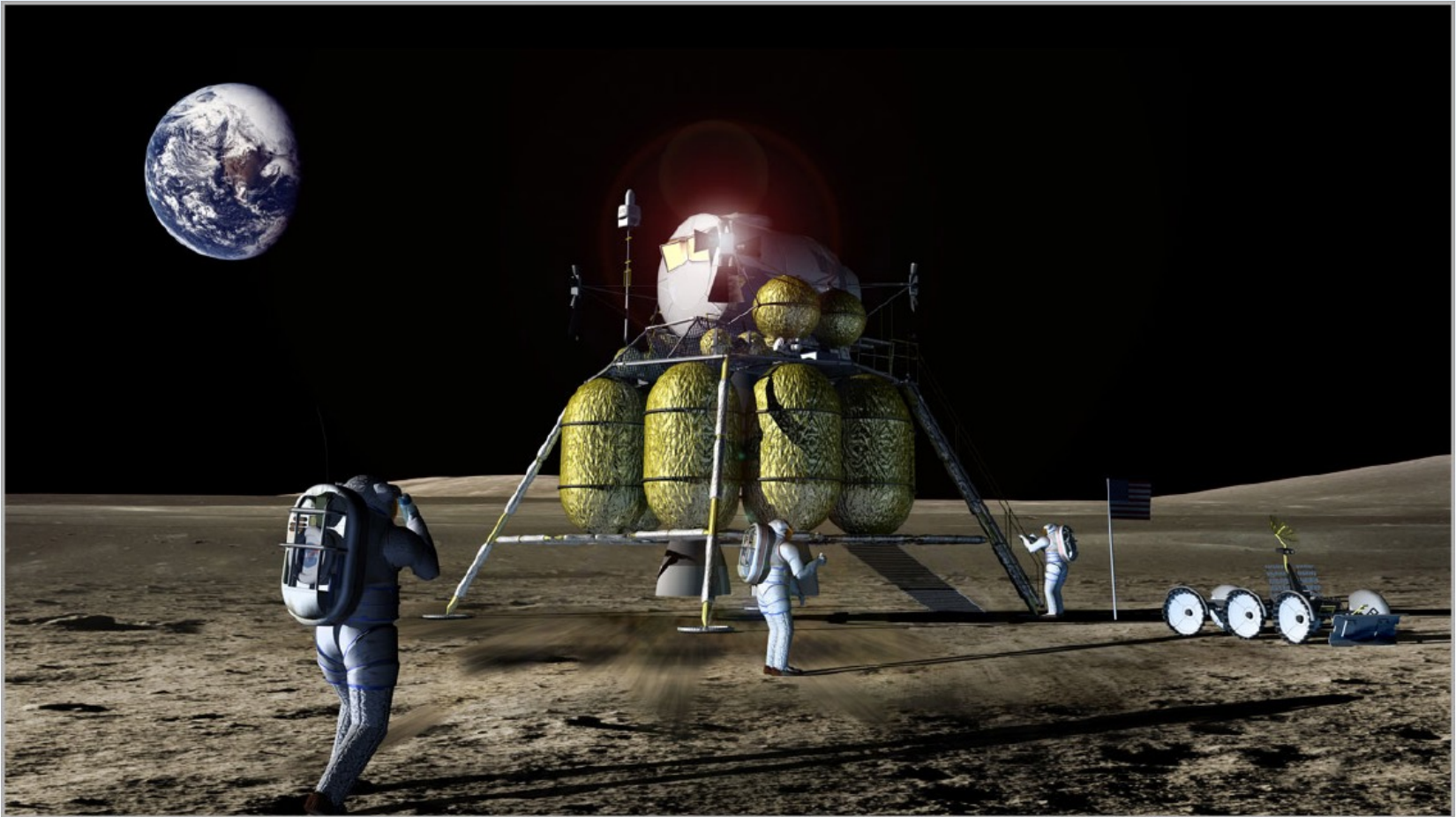
- High yield of oxygen per kilogram of soil
- Can be used as first step to other material refining
- Low temperature ($\sim 825\text{-}900^\circ\text{C}$) compared to many other proposed oxygen sequences
- Should work with unbeneficiated soil
 - some advantages to selecting the small particle-size component



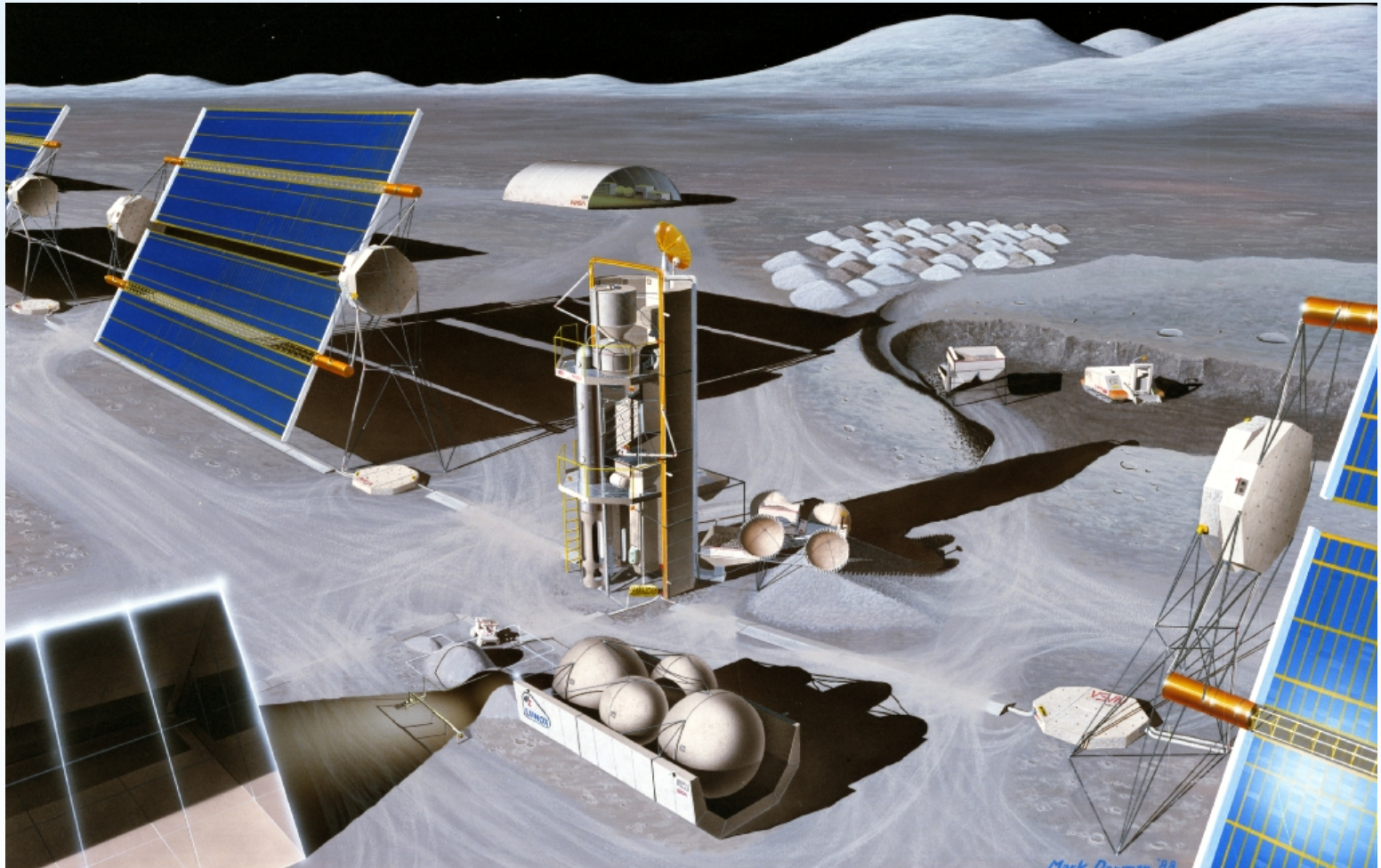
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Objective, near term: *lunar refueling*



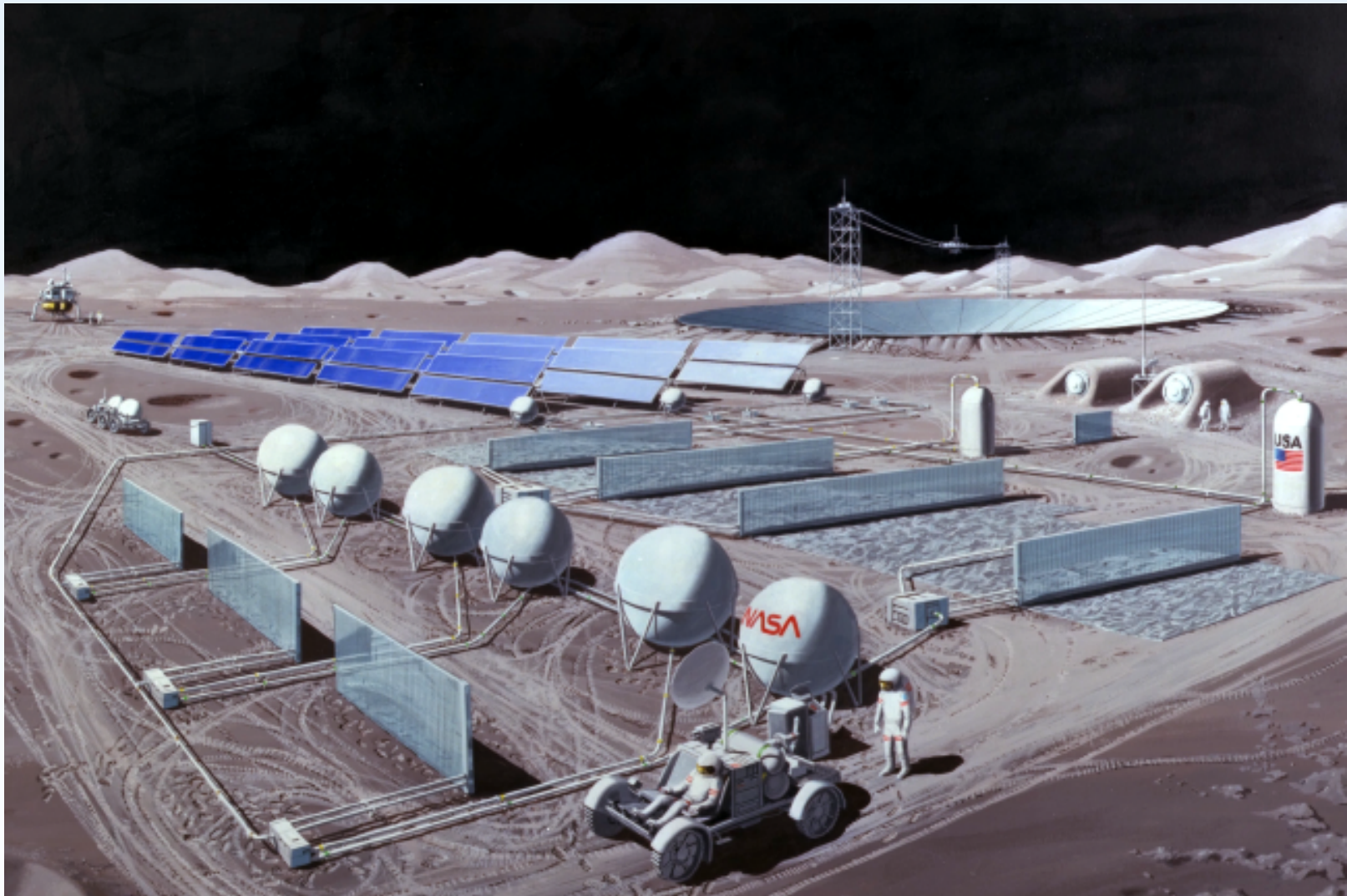
Objective, long term: Lunar industrialization



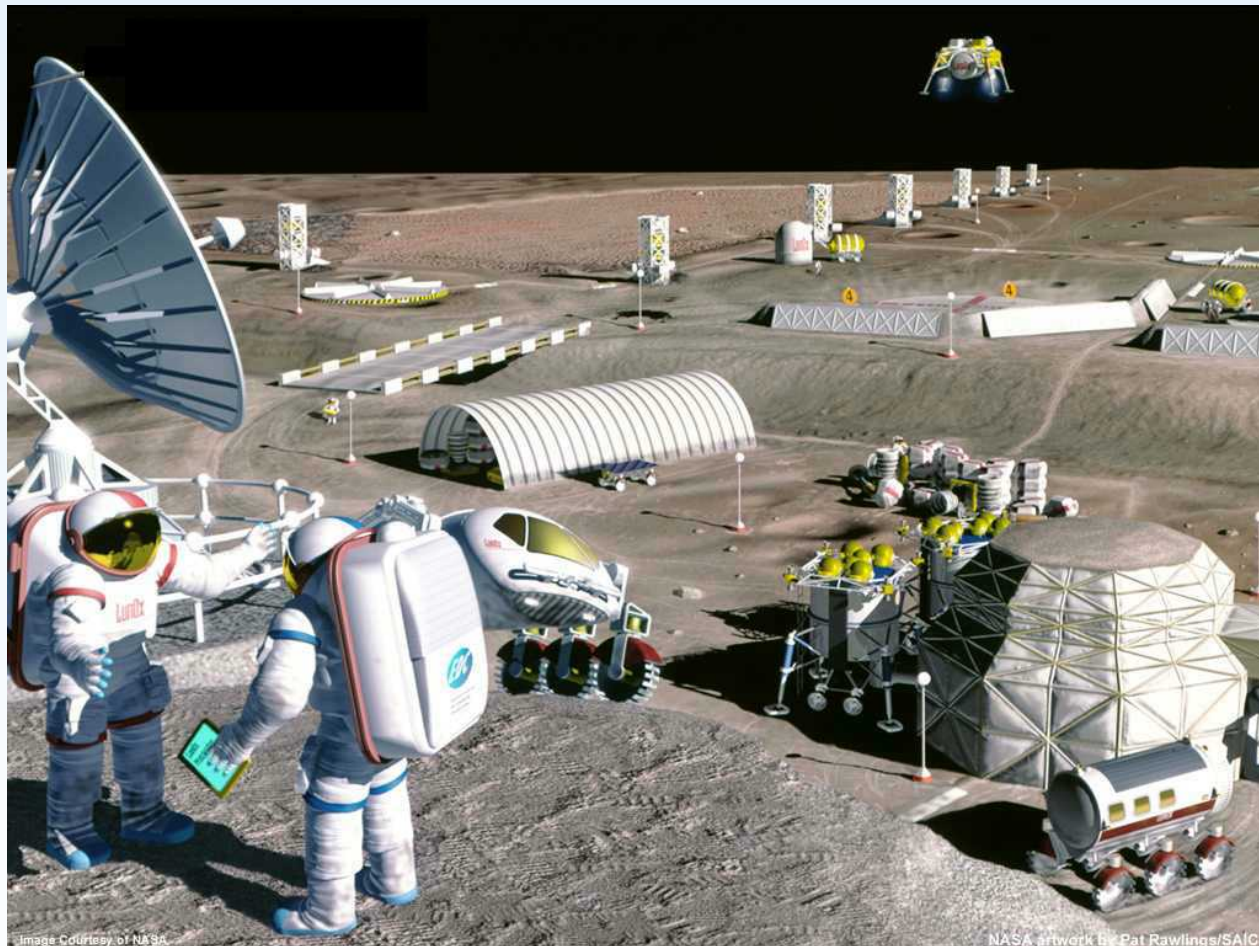
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Lunar industrialization



Lunar base

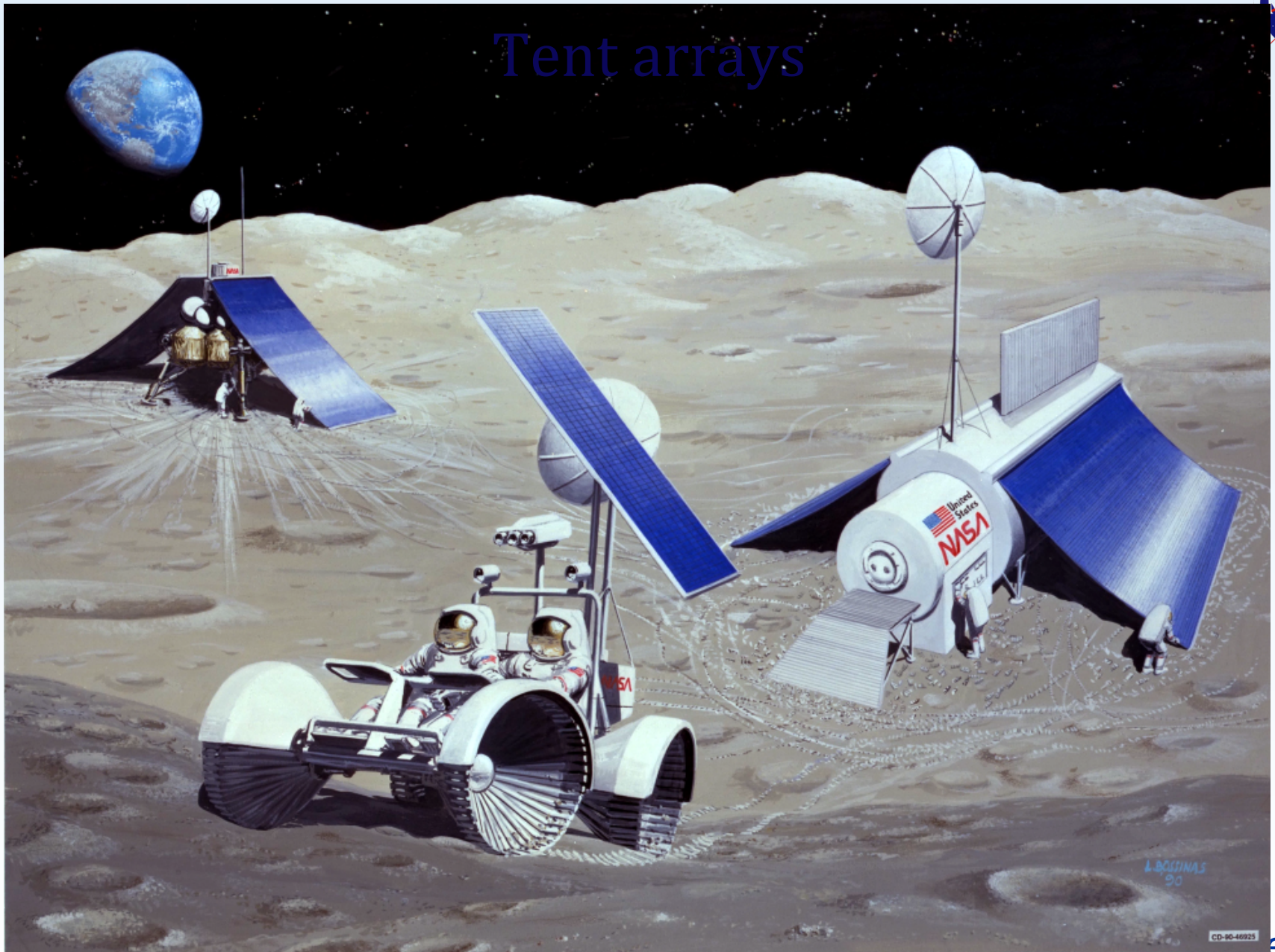




Lunar lander

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Tent arrays



CD-90-46925



Metallothermic reduction references

- Martirosyan and Luss 2005, Ti+B thermite on JSC 1A
- Corrias et al. 2012, FeTiO₃+Al on 30% JSC 1A
- Faierson et al 2020, Al on 67% JSC1A
- Armando Delgado, The University of Texas at El Paso, “Thermite Reactions in the Mixtures of Magnesium with Lunar and Martian Regolith Simulants, FIFTH JOINT MEETING OF THE SPACE RESOURCES ROUNDTABLE and the PLANETARY & TERRESTRIAL MINING SCIENCES SYMPOSIUM, Colorado School of Mines Golden, Colorado June 10-11, 2014 –Mg 30% reaction, with preheat