Materials Refining for Solar Array Production on the Moon

Geoffrey A. Landis
Glenn Research Center, Cleveland, Ohio

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Geoffrey A. Landis
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center

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Refining Lunar Materials for Solar Array Production on the Moon

Geoffrey A. Landis
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Abstract

Silicon, aluminum, and glass are the primary raw materials that will be required for production of solar arrays on the moon. A process sequence is proposed for producing these materials from lunar regolith, consisting of separating the required materials from lunar rock with fluorine. The fluorine is brought to the moon in the form of potassium fluoride, and is liberated from the salt by electrolysis in a eutectic salt melt. Tetrafluorosilane produced by this process is reduced to silicon by a plasma reduction stage; the fluorine salts are reduced to metals by reaction with metallic potassium. Fluorine is recovered from residual MgF and CaF_2 by reaction with K_2O.

1. Background

Oxygen, a major component of rocket fuel and also critical for human life support, is a high priority resource to be produced on the moon. Many processes have been proposed to manufacture oxygen from lunar regolith. In the longer term, sustained habitation and industrialization of the moon will require the ability to produce other raw materials from lunar materials. It would be desirable to produce industrial materials as a co-product of oxygen production by reduction of lunar regolith.

Production of solar arrays on the moon could have many uses for space industrialization (Refs. 1 to 4). This would allow increasing the power available for lunar facilities with a minimum of material required from the Earth. Increased power availability could be useful in ramping up the production of lunar resources (for example, oxygen) or for other industrial-scale operations, such as powering a mass-driver to deliver resources. Lunar production could also be useful for manufacture of solar arrays for other space applications, including satellites and solar-electric propulsion vehicles, since the ΔV of launching from the lunar surface is considerably less than that of launching from the surface of the Earth, and hence lunar-produced solar arrays could be lower in cost than Earth produced arrays.

In the longer term, lunar produced solar arrays would be useful for the proposed production of solar power satellites to produce power in orbit for transmission to other users in space, or ultimately for transmission to the Earth's surface (Ref. 3). An alternate version of the orbital power concept is to produce the electricity by solar arrays directly on the lunar surface, using the moon itself as a large-area platform for beaming the power to the Earth (Refs. 4 to 5).

These applications have been widely discussed elsewhere. The details of the process of lunar production of solar cells, on the other hand, have been less widely addressed. Earlier work on this subject is in references (Refs. 1 to 4 and 6).

This paper will focus on developing workable production systems to reduce the lunar soil and produce the refined feedstock materials for making solar arrays from materials available on the lunar surface, including both the photovoltaic cell, and also the associated electrical connections and structural elements of the array. Table 1 shows the elements present in the lunar soil at abundances of 0.1 percent (by weight) or higher (Refs. 7 to 9). The processing sequence chosen should optimally recycle all reagents and waste products that are not available on the lunar surface.

Since the lunar surface comprises oxides, any reduction process chosen to manufacture purified feedstock materials will simultaneously produce oxygen.

2. Solar Cell Production

2.1 Lunar Silicon Production

Of the many materials used to make solar cells, only silicon is found in abundance on the moon. As shown in figure 1, after oxygen, silicon is the most abundant component of the lunar soil. Fortunately, silicon solar cells have the largest manufacturing base of any of the solar cell materials. For solar array production from lunar materials, the first requirement would be to demonstrate manufacture of relatively pure silicon from lunar resources. Since this is the major mass component of a solar cell, Si production would be the first step to showing solar cell manufacture is possible. In addition, silicon is the main component for glass.

For solar cell operation, it is necessary that the silicon produce be of high purity. "Metallurgical grade" silicon is not acceptable. The allowable impurity level depends on the nature of the impurity atoms. Transition metals such as Fe and Cr serve as recombination centers in silicon, as well as nucleating growth defects, and reduce the efficiency if they are present in significant quantities (Ref. 10). Since iron is the highest mass fraction of the lunar soil after silicon and oxygen, it will be necessary that the silicon production process be adaptable to a method to refine and purify the silicon produced.

Silicon can be used to produce several kinds of solar cells, including amorphous, polycrystalline, and conventional and unconventional single-crystal silicon cells.

2.1.1 Amorphous Silicon

Amorphous silicon solar cells are normally produced by a plasma deposition process exactly like the one proposed below. This will require a small amount of hydrogen to make the electrical properties acceptable (in fact, the material is more accurately labeled amorphous silicon:hydrogen, or a-Si:H). This will also require a substrate or superstrate for deposition, discussed later. Conversion efficiency will be in the range of 5 to 10 percent for cells using existing processes; up to 18 percent efficiency may be possible with advances in cell technology.

Amorphous silicon has the advantage of being highly radiation tolerant compared to other cell technologies (Ref. 11) (although sensitive to degradation by low-energy electrons and by ultraviolet light). It may also be possible to make extremely low mass a-Si arrays (Ref. 12), although this will require a lightweight substrate, which is not produced by the process sequences discussed here.

The hydrogen incorporation in amorphous silicon solar cells is typically in the range of 5 to 10 atomic percent. 5 atomic percent of hydrogen corresponds to about 0.2 percent composition by mass, so this is not a large fraction. The average mass fraction of hydrogen in Apollo lunar soil samples is 50 micrograms per gram, representing a hydrogen-to-silicon ratio of 0.02 percent by mass. Since the primary silicon usage in manufacturing a-Si:H cells will probably be for the glass superstrates, the hydrogen content of the soil is probably sufficient for solar cell production, if the entire hydrogen contained in the soil can be captured and conserved for use.

If the lunar base is situated on or near the pole, it is likely that hydrogen will not be a problem, since recent spacecraft measurements indicate large amounts of hydrogen available in permanently shaded polar locations. Alternately, the required amounts of hydrogen are so small that it is probably feasible to bring the hydrogen from Earth, or to scavenge waste hydrogen, for example, from residual propellants left in the tanks of transfer vehicles after landing of the moon.

Because of its ability to be deposited in thin films directly from gaseous feedstock without the requirement for wafering, amorphous silicon was the preferred technology for lunar production of solar arrays in earlier work (Refs. 1 and 2).

2.1.2 Polycrystalline Thin-Film Silicon

Polycrystalline thin-film solar cells involve deposition (and possibly recrystallization) of the silicon on a foreign substrate (Refs. 13 to 19). Because of their low thickness, they will also be more tolerant to radiation exposure than single-crystal cells. Possible deposition processes that could be adapted to lunar production include using a thermally-activated chemical-vapor deposition, or a plasma deposition process. Unlike amorphous silicon, in this plasma deposition of polycrystalline Si the silicon may be recrystallized after deposition (Ref. 14) to improve the size and quality of the microcrystallites. Using a solar furnace at 1500 suns, recrystallization has been demonstrated with a time required of 5 seconds (Ref. 19). No hydrogen is needed, but to date very few methods for producing thin-film silicon cells on foreign substrate cells have resulted in high efficiencies. The difficulty is due to the interaction of the silicon with the substrate material at the high temperatures requires to produce good crystalline quality. Several researchers have produced efficiencies of roughly 10 percent. The best efficiencies reported are about 15 percent under terrestrial (AM1.5) illumination conditions, equivalent to roughly 12 percent AM0, for cells deposited on a proprietary ceramic substrate (Ref. 13). Another group reports efficiency of 8.2 percent (equivalent to about 6.5 percent AM0 efficiency) on large-area modules in pilot production (Refs. 15 to 17).

Theoretical models (Ref. 21) indicate that thin silicon solar cells have the potential for both extremely high efficiency, and for extremely good radiation tolerance. However, because of the material quality of recrystallized polycrystalline silicon, it is unlikely that efficiencies anywhere near the theoretical limit of 24 percent could be achieved. Ten percent efficiency is a more reasonable goal.

It is reasonable that, in the future, multijunction solar cells combining both crystalline and amorphous silicon may be practical (Ref. 17), which would improve the efficiency by more efficient use of the solar spectrum. Yamamoto (Ref. 17) reports AM1.5 conversion efficiencies of 14.5 percent (equivalent to roughly 11.6 percent under AM0 illumination) for two-layer amorphous silicon/polycrystalline silicon cells on foreign substrates. Because of the higher efficiencies that can be achieved, a two-layer cell is assumed as the baseline technology for lunar cell production.

2.1.3 Conventional Crystalline Silicon

The "conventional" process for silicon is to produce the cells from high-quality, single-crystal wafers. This will require an additional step to produce wafers. The vacuum float-zone process produces single crystal material of the highest quality. This requires producing the initial silicon in the form of a rod. This can be done by plasma decomposition onto a thin wire in the conventional Siemens process. The rod is then melted in a traveling zone from one end to the other. This recrystallized rod is then sliced into wafers. The disadvantage of this process is that the crystal growth, wafering, and polishing are difficult, energy intensive steps that require heavy machinery and also result in significant wastage of material.

Terrestrial production of solar cells often uses polycrystalline silicon with large crystal grains. This is also sometimes (inaccurately) called "semi-crystalline" by some of the manufacturers. I use the term multicrystalline here to distinguish the material from the thin-film polycrystalline material discussed earlier. Multicrystalline material is produced by allowing molten silicon to cool under controlled conditions in a mold (Ref. 21). This is a lower cost and faster process than single crystal growth, but nevertheless is energy intensive and requires slicing and polishing of wafers, which results in waste.

2.1.4 Ribbon and Web Silicon

Considerable research was done in the 1970s and early 1980s to produce "ribbon" and "web" materials for silicon. These processes were designed to pull a flat sheet of silicon out of a melt without the requirements for wafering (Ref. 21).

While none of the ribbon or web productions processes went into large-scale commercial production, it may be possible in the future to revive these processes to avoid the slicing and polishing requirements. The requirement for a 1410 °C silicon melt, however, means that the technology which is both energy-intensive and may require frequent replacement of crucibles.

2.1.5 Silicon Baseline Choice

Because of the added difficulty and mass of wafer production machinery, the single- and multi-crystalline technologies are considered less desirable for lunar production. Direct ribbon technologies, although they do not require wafering, have the difficulties of being comparatively less well developed, requiring high mass machinery, and requiring an intermediate high-temperature silicon melt to produce solar substrates. For these reasons, it is suggested that either amorphous silicon, or polycrystalline Si on a foreign substrate, will be preferable technologies. Both of these technologies do not require an intermediate melt, but can be deposited directly from the gas phase. The slightly lower resulting efficiency will be an acceptable trade-off for the increased simplicity.

2.2 Solar Cell Raw Materials

Once silicon has been refined, it is necessary to refine the additional materials required to make solar cells and to form these solar cells into arrays. The photovoltaic blanket is typically less than 25 percent of the mass of a completed space solar array. In addition to the semiconductor, solar array production will require a superstrate or substrate for mechanical support, doping materials to produce a p-n or a Schottky junction, an ohmic contact material to electrically contact the silicon, radiation protective cover, interconnects, and wiring.

2.2.1 Substrate or Superstrate

The substrate or superstrate is the material upon which a thin-film semiconductor is deposited, and provides structural support. For a substrate, a lunar-derived glass or ceramic can be used. For a superstrate, the glass will have to be transparent. Note that it is a significantly more difficult task to produce transparent glass than it is to simply produce glass; this is discussed later. For both approaches, it is highly desirable that the thermal expansion coefficient of the superstrate or substrate should be close to that of the silicon.

a-Si solar cells have also been made with a stainless-steel substrate. This may be relatively simple to make on the moon, since iron and nickel are deposited into the lunar soil in reduced form from the impact of nickel-iron meteoroids. A metallic substrate will require use of an insulator between the semiconductor and the metal if the commonly used monolithic-interconnection process is used to integrally connect individual sub-cells into a series string to increase the voltage.

Ignatiev and co-workers (Ref. 23) propose that solar cells can be deposited directly onto the lunar surface by melting the regolith (with a solar concentrating mirror) and allowing it to refreeze, and using the refrozen surface as a substrate to deposit silicon cells by vacuum deposition. Since the conversion efficiency of silicon cells on foreign substrates is very sensitive to the substrate composition and surface properties, it is unlikely that melted lunar surface would produce a substrate of the uniformity and quality sufficient to allow solar cells with good conversion efficiency to be produced. Since the objective of this study is to design a process that can produce arrays that can be used in many applications, including arrays which can be shipped elsewhere, direct processing of the lunar surface is not a desirable option.

2.2.2 Doping Materials

To produce a solar cell, it is necessary to be able to dope the semiconductor to both p and n type conductivity.

P-type doping uses elements from group III of the periodic table. Boron is most commonly used. Of the p-dopants choices from lunar materials, Al is the most abundant. Since this is also used for other portions of the process, this will be assumed here.

N-type doping requires a group V element, which may be difficult to produce from lunar material. The n-type dopants for silicon are P, As, and Sb, all of which are relatively uncommon on the moon. Phosphorus is a "minor" constituent of the lunar surface, present in greatest concentration in KREEP materials, where concentration of 0.1 to 0.3 percent is typical. Small fragments of material have up to 2 percent concentration. Fortunately, the phosphorus requirement as a silicon dopant is very small. P doping is typically on the order of 10 (Ref. 19) per cm^3, or about 0.02 at.%. It is needed only in the emitter layer of a silicon solar cell, typically only 0.1 to at most 1 micrometer thick. For a silicon cell of 100 micrometer thickness, this makes the phosphorus requirement only one part in a million of the silicon requirement. This is low enough that for small production, it is probably worth bringing the phosphorus from Earth.

An alternative is to make a Schottky-barrier cell, although Schottky cells have not demonstrated the high efficiency possible with p-n junctions.

2.2.3 Ohmic Contact Material

Solar cells will need metal ohmic contacts for both the p and the n-type material, and a conductive metal to serve as the electrical contact.

Aluminum, which is a p-type dopant, will work well as a p-type contact.

For crystalline silicon, aluminum can also be used as an ohmic contact to n-type silicon, but the process sequence must keep the cell below the 577 °Al-Si eutectic point at all times after contact deposition. A better alternative may be use of titanium silicide. The classic space solar cell contact for silicon solar cells is titanium/palladium/silver. The titanium forms titanium silicide, which contacts the cell, the palladium forms a humidity barrier that prevents oxidation of the titanium, and the silver serves as a solderable conductor. In space, the palladium would be unnecessary.

A conductor metal will be needed on top of the contact metal, Any conductive metal will work for this purpose. For lunar produced cells, the best choice will be aluminum.

For an amorphous silicon cell, a front transparent conductor is typically used rather than connecting directly to the silicon. ZnO, SnO$_2$, In$_2$O$_3$ and CdS are typical choices. None of these are abundant on the moon. If a-Si is chosen, a microcrystalline silicon front layer, with an Al or TiSi contact layer, will substitute for the transparent conductor.

2.2.4 Coverglass for Front Surface Radiation Protection

Even radiation-tolerant a-Si cells will require at least a thin protection layer, or "coverglass," to keep low-energy electrons and protons away. Glass is the best choice. SiO$_2$, TiO$_2$ and/or Al$_2$O$_3$, are possible alternative choices.

A difficulty is that in conventional processes, the cell is attached to the coverglass with an adhesive layer, typically either a silicone, used for space applications, or ethylene-vinyl acetate (EVA), for terrestrial applications. Adhesive technologies require organic materials not easily available from lunar sources. One alternative technology is "electrostatic bonding", also known as field-assisted bonding or "direct glassing" (Ref. 23). This technology, however, requires solar cells with a flat surface, an ohmic contact system which will not degrade with heat, and a glass composition which closely matches the expansion coefficient of the silicon and which allows ionic conduction.

The front surface radiation protection can be same as superstrate, if the cell is produced by a technology that deposits the silicon directly on glass in an inverted configuration. This production process will have the advantage that the cell will be directly adhered to the glass, eliminating the requirement of adhesive. For the direct deposition technologies discussed, this option is the most preferable one.

2.2.5 Interconnects and Wiring

In addition to the photovoltaic arrays themselves, a practical solar array manufacturing plant will have to also manufacture the metals for electrical wiring. Interconnects are used to connect one cell to the next in series, for processes manufacturing separate cells. (Interconnection is often integral with the cell contacts for thin-film technologies.) Space solar arrays typically use silver-coated molybdenum interconnects, with either silver or copper used as alternate choices. In addition, solar arrays require wires to conduct the power to the user. In some applications, a considerable length of transmission wire may be required.

The primary requirement for the interconnects and wiring is high electrical conductivity. For space, corrosion by oxygen is not an issue. Most reasonable products to manufacture on the moon for electrical conductors will be aluminum. Calcium could also be used for electrical conductors, but the present process does not produce calcium in metallic form

3. Silicon Production: Refining of Regolith

3.1 Regolith Refining Strategies

Extraction of silicon from the lunar regolith cannot be done using the industrial silicon production processes currently in use on Earth. Terrestrial silicon production uses as a raw material high-silica sand, while lunar regolith is primarily igneous silicates such as anorthosites. Also, the terrestrial production method reduces the Si to elemental form by carbon reduction with coal, using up one mole of carbon for each mole of silicon produced. Any production process for the moon must use no reactants that are not completely recycled.

Unbeneficiated lunar soil ("regolith") is powdered igneous rock. Table 1 shows an "average" composition of regolith. It consists primarily of iron, calcium, aluminum, and magnesium silicates, with small amounts of chromium, titanium, and manganese. In places, the soil contains also sodium, potassium, and rare-earth oxides. The exact composition varies from site to site, and possibly from sample to sample at a given site. Regolith composition and mineralogy is discussed in detail in the Lunar Sourcebook (Ref. 7).

Several different production processes were examined. Good reviews are found in References 9 and 25 to 26. Many of the commonly proposed processes for reduction of regolith to produce oxygen from lunar resources, such as hydrogen reduction of ilmenite, were not applicable, since they did not produce reduced silicon. Others were discarded because reduced silicon, although a byproduct, was not separated from other materials reduced in the oxygen production process. Finally, processes were selected based on a requirement that the silicon be produced in a form that would allow easy purification.

Since the site of the lunar base is likely to be chosen on the basis of other criteria, it is desirable that the process chosen should be suitable for use on "average" lunar regolith, that is, the process should not require prospecting for a particular ore or a soil which is high in concentration in a particular mineral. For simplicity in materials handling, raw lunar regolith used in the production sequence should be able to be used with no pre-processing or beneficiation to concentrate particular mineral compositions in the soil.

3.2 Fluorine Process for Silicon Production

Fluoride extraction (Ref. 27) was chosen as the primary method to remove the oxygen from the rock and produce the raw material for reduction and refining. It has the advantage that the silicon is produced in the form of tetrafluorosilane, which can be easily purified of contaminating traces of the other metals by distillation. In fact, the process can be adapted in a straightforward manner to production of other relatively pure products, including titanium, aluminum, and iron.

Fluorine is brought to the moon in the form of potassium fluoride (KF). The KF is then electrolyzed to produce potassium and fluorine. The potassium and the fluorine are both used as reactants in the process.

The basic silicon reduction process is to heat the regolith in the presence of fluorine. The fluorine will displace the oxygen, which is collected as a useful byproduct. Silicon is produced in the form of tetrafluorosilane (silicon tetrafluoride), which is a gas at standard temperature. The net silicon process sequence is:

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$
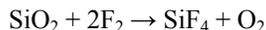
The tetrafluorosilane produced is liquefied at –86 °C and distilled to purify the resultant product and remove trace contaminants. This distillation process is similar to that used industrially to purify silane for semiconductor production.

One way to recover elemental silicon from the tetrafluorosilane is by potassium reduction:

$$SiF_4 + 4K \rightarrow Si + 4KF$$
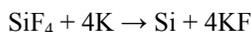
Potassium reduction is not typically employed in the terrestrial semiconductor industry, since for CMOS devices, alkalai ions are undesirable contaminants. It is not clear whether potassium is an unacceptable trace contaminant in silicon for solar cell applications. Unless solar cell tests show that potassium contamination is acceptable, an alternate process is direct decomposition:

$$SiF_4 \ (+ \ energy) \rightarrow Si + 2F_2$$
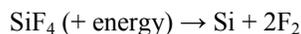
Both plasma deposition processes (primarily producing amorphous silicon) and chemical vapor deposition processes (direct thermal decomposition producing either amorphous or polycrystalline Si) are commonly used in the solar cell industry to produce elemental silicon from silane (SiH_4). Silicon production has also been demonstrated by plasma decomposition of tetrafluorosilane instead of silane. If silane is preferable to tetrafluorosilane for reasons of silicon properties, successive disproportionation of tetrafluorosilane to silane can be done. This is a multi-step chemical replacement of fluorine with hydrogen at high pressure and temperature, or could be done by disproportionation of the tetrafluorosilane with lithium-aluminum hydride ($LiAlH_6$) to produce lithium-aluminum fluoride and silane.

3.3 Other Raw Materials

In addition to the tetrafluorosilane and oxygen, the regolith will produce metal fluorides ("fluorine salts"). The primary products are:

$$2FeO + 3F_2 \rightarrow 2FeF_3 + O_2$$
$$2MgO + 2F_2 \rightarrow 2MgF_2 + O_2$$
$$2CaO + 2F_2 \rightarrow 2CaF_2 + O_2$$
$$Al_2O_3 + 3F_2 \rightarrow 2AlF_3 + 3/2 \ O_2$$
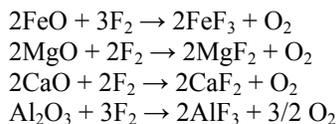
Since these product salts are solid at room temperature, it is easy to separate these from the gasses oxygen and tetrafluorosilane. Small amounts of other fluoride salts will also be formed from the trace components of the regolith; these will not be abundant enough to serve as raw materials, but must be accounted for in the fluorine recovery step.

It is necessary to recover the fluorine from these salts in order to make a closed-cycle process (and also to produce useful byproducts). The iron and aluminum fluorine salts are directly reduced with potassium to recycle the fluorine into potassium fluoride:

$$FeF_3 + 3K \rightarrow 3KF + Fe$$
$$AlF_3 + 3K \rightarrow 3KF + Al$$
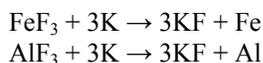
The same reaction will also be used to recover titanium. The calcium and magnesium fluoride is not so easily reduced, however, the fluorine can be recovered by oxidation of the potassium followed by a substitution reaction:

$$CaF_2 + K_2O \rightarrow 2KF + CaO$$
$$MgF_2 + K_2O \rightarrow 2KF + MgO$$
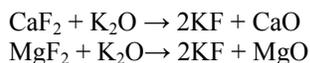
This is possible because potassium has a higher chemical exchange potential for the oxygen/fluorine substitution reaction than any of the metals that are not directly reduced by potassium. Fluorine can also be recovered in this ways from the trace sodium and lithium salts. This nominal temperature of this reaction is 520 °C. Therefore, if potassium is oxidized to K_2O, the metal fluorides can be returned to the metal oxide and the potassium converted to potassium fluoride. This can likely be done in a single step of adding oxygen to the mixture of metallic potassium with magnesium and calcium fluoride.

This potassium reduction is a significant improvement over the alternative of direct electrolysis of the salts to recover the fluorine, since direct electrolysis will require an electrolysis temperature as high as the calcium fluoride melt temperature of 1423 °C, which presents a difficult materials problem.

The net result is that FeO and Al_2O_3 are reduced to metals and oxygen, while the CaO and MgO remain in the form of oxides. These oxides are retained as a feedstock for glassmaking (discussed later).

Note that this fluorine process is different from that suggested in earlier work (Ref. 1), which suggested a fluxed aluminothermic reduction. The fluoride process suggested here is insensitive to the composition of the regolith source material, and thus a better one for a production process that will operate at a site without extensive prospecting to find "good" rock types, and without extensive beneficiation processing to isolate the desirable type of source material. The only useful beneficiation would be to separate the smallest particle size fraction for use as feedstock. This has no effect on the ultimate reaction endpoint, but use of small particle sizes will increase the reaction rate, since small particles have the highest surface area to mass ratio.

In addition to silicon, the process sequence produces oxygen from the lunar regolith with high yield, produces byproduct metals such as aluminum, titanium, and iron, and byproduct oxides of magnesium and calcium, which are either already purified or are relatively easy to separate in pure form. As discussed later, these byproducts are expected to be useful for other manufacturing processes.

At the end of this step, all of the fluorine is in the form of potassium fluoride, therefore, only a single salt needs to be electrolyzed to recover the initial reactants, instead of a mixture of salts. The potassium fluoride is electrolyzed back into the reactants potassium and fluorine, as discussed in the following section.

3.4 Eutectic Fluoride Salts for Electrolysis

It might be argued that fluorine is extremely reactive, and it will be difficult to find materials in which to do the initial electrolysis. However, electrolysis of molten fluoride salts is a high-throughput industrial process, used in the production of many materials. The most well-known fluoride electrolysis process is the Hall process for production of aluminum, in which molten sodium-aluminum fluoride ("cryolite") is electrolyzed at 1000 °C. Seboldt and co-workers (Ref. 27) discuss some of the materials issues involved in the electrolysis of fluoride salts.

It is desirable to reduce the electrolysis temperature below the 858 °C melting point of KF by as much as possible. Lower temperatures result in less corrosion of the electrodes, and it is desirable to avoid the need for frequent replacement of electrodes. Likewise, lower temperatures allow a wider range of materials for the crucible, and decrease the frequency of replacement of the crucible.

Reducing the electrolysis temperature is done by performing the electrolysis in a eutectic salt with a lower melt temperature than that of pure KF. The choice of salt is limited by the requirement that the electrolysis products are to be potassium and fluorine, and so the salt to be added to the KF to form a eutectic must not be electrolyzed more easily than KF. Since fluorine is the most electronegative element on the electromotive series, there is no choice available to replace fluorine as the anion. Because K is extremely low on the electromotive series, only a few cation choices are available which will reduce potassium at the cathode. Na, Ca, Sr, and Ba are lower on the electromotive series at 700 °C (Ref. 28), and will not be reduced from the salt. Hence, the possible choices are NaF, CaF_2, SrF_2, and BaF_2. In small quantities, other components may also be possible.

Na, Ca, Sr, and Ba fluorides all form eutectics with KF. The NaF/KF eutectic salt mixture at a molar ratio 60:40 NaF:KF, with a melt temperature of 710 °C, seems to be the best choice. An admixture of LiF will lower the temperature further, although a significant Li component will result in lithium instead of potassium electrolysis. A maximum of 5 percent (molar) admixture of LiF, which will lower the temperature to 700 °C, should be possible.

Ternary eutectics have even lower melt temperatures. A potassium/sodium/calcium fluoride eutectic mixture, with molar ratio approximately 0.6:0.3:0.1 KF:NaF:CaF_2, will have a melt temperature as low as 676 °C.

The electromotive series in molten salts has a dependence on temperature and on the composition of the salt (Ref. 27). Further research may make it possible to find a temperature and a salt mixture with a lower electrolysis temperature.

A 676 °C molten salt electrolysis temperature is assumed here. A solar dynamic ground-test demonstration demonstrated melting a LiF/CaF_2 eutectic salt at 800 °C (Ref. 29), well above the 676 °C electrolysis temperature. This test operated for extended period without corrosion. This design serves as a demonstration of the materials compatibility of fluoride salts at temperatures of interest.

An alternative reduction strategy is to use lithium fluoride. Lithium can be separated from fluorine by electrolysis in a KF/LiF eutectic salt mixture at a temperature of 492 °C. Lithium metal will reduce magnesium, sodium, and potassium fluoride to metal, but will leave calcium fluoride unreacted. By use of LiF, the temperature is reduced, but the fluorine recovery now includes both lithium and calcium fluoride. If lithium oxide can be used to drive the reaction $CaF_2 + Li_2O \rightarrow CaO + 2LiF$, reducing the electrolysis required to a single electrolysis. However, this reaction exploits only a small difference in chemical potential, instead of the large difference exploited in the potassium substitution reaction. It is worth exploring to see whether the calcium/lithium oxide exchange occurs at a fast enough rate, and with a high enough recovery of lithium fluoride, for use as a production reaction.

The use of gaseous fluorine presents some materials compatibility issues for the chemical engineer; however, fluorine chemistry is used industrially, and a body of work exists on materials handling properties, as summarized by Granec and Lozano (Ref. 30). Nickel and Monel crucibles, using copper gaskets, are compatible with the fluorine gas. Teflon is appropriate for gaskets and tubing at lower temperatures. Quoting from Granec and Lozano, "Fluorine handling at low pressures is not very dangerous, provided that a few precautions are taken" (Ref. 30).

3.5 Candidate Process for Demonstration of Production on the Moon

A block diagram of the basic mass flow process for the silicon production is shown in Figure 2. As a result of the partial-oxidation step required for recycling the KF, the process returns the magnesium, calcium, sodium, and lithium content of the lunar rock in their original condition as oxides. Sodium and lithium are only minor components of the lunar soil, and can be neglected. Calcium and magnesium oxides makes up about 20 percent of typical lunar soil, and leaving these unreduced results in about 15 percent reduction in oxygen production over a process which reduces these oxides. These oxides are not significantly valuable in reduced form. Calcium will be required in oxide form for glass manufacture (discussed in a later section). It has also been proposed to make concrete out of lunar material; this also requires calcium oxide. Thus, it is not of great significance that the process does not reduce calcium and

magnesium. It may be desirable to be able to separate these oxides in order to produce an optimum mixture for glass production, however, this is not discussed here.

3.6 Process Sequence

The process sequence is divided into seven steps.

(1) Fluorine is brought to moon in the form of potassium-fluoride/sodium fluoride/calcium fluoride salt mixture. 2 moles of fluorine are required for each mole of oxygen in regolith.
(2) Potassium fluoride is electrolyzed from eutectic salt to form free fluorine and metallic potassium at a temperature of 676 °C.
(3) The fluorine reacted with heated lunar regolith to form SiF4, oxygen, and metal fluorides at a temperature of 500 °C. Electrical power required: none.
(4) Gaseous SiF4 is separated from oxygen by condensation at a temperature of 178 K.
(5) SiF4 is reacted in plasma to form silicon at a temperature of 300 °C.
(6) Potassium metal is added to metal fluorides to produce metallic aluminum, titanium, and iron at a temperature of 500 °C. Required electrical power: none
(7) Oxygen is added to mixture of potassium metal with calcium fluoride to produce potassium fluoride and calcium oxide at a temperature of 520 °C. Required electrical power: none
(8) The KF is returned to step 2 to electrolyze potassium fluoride back to fluorine gas and metallic potassium.

3.7 Overall Requirements and Output Products

The overall processing plant will require:

(1) electrical power
(2) solar furnace with capability of 676 °C operation
(3) condenser stage with capability of 178 °K refrigeration
(4) crucibles, gas chambers, and plumbing

The output products from the demonstration are:

(1) Oxygen
(2) Silicon
(3) Aluminum/titanium/iron mixture
(4) Calcium and magnesium oxides (unseparated mixture)

A demonstration system would be designed so that only one chamber is in use at any one time. Thus, only a single solar furnace is required; the required reaction chamber is simply rotated into the hot zone when it is in use. The solar dynamic ground-test demonstration, based on a power system originally designed for the Space Station Freedom, demonstrated the technology for melting fluoride eutectic under simulated space conditions (Ref. 29). This design could easily be adapted to serve as the solar furnace required to produce the temperatures required for this process.

3.8 Discussion

The initial regolith heating step will also outgas volatiles, primarily materials implanted from the solar wind, out of the regolith. These will include hydrogen, oxygen, carbon monoxide, water, etc. These may be valuable, and can be captured after the heating but before the fluorine reaction is initiated by use of condensors.

For the fluorination step, there may be some unreacted oxide if the reaction is done at the lowest temperatures. As long as these do not contain fluorine, these can be considered slag and discarded.

The condenser must separate the tetrafluorosilane from the oxygen evolved from the sample, and must recover unreacted fluorine. This is done by fractional liquefaction (distillation). Tetrafluorosilane will liquefy at –86 °C, oxygen at –183 °C, and fluorine at –188 °C. Since any manufacturing sequence to produce silicon for solar cells would undoubtedly also manufacture liquid oxygen for rocket fuel and other applications, liquefaction equipment will be present in any case, and it is only necessary to adapt the equipment to allow progressive liquefaction of the individual gasses. This liquefaction process will require radiators to reject the waste heat to space (Ref. 31). Since the boiling points of fluorine and oxygen are close, it may be necessary to repeat the distillation process to adequately purify the product gasses and recover the fluorine reactant.

The only other volatile fluoride which is likely to be produced is titanium fluoride, TiF_4. With a sublimation point of 284 °C, TiF_4 will be a gas at the reaction temperatures of interest. The TiF_4 vapor must be condensed on a cold finger before the vapors enter the main condenser. If it is desirable to produce purified titanium out, this would be easy to do. The titanium fluoride will also include trace amounts of other volatile fluorides, as discussed later; if it is necessary to produce titanium free of even trace contaminants, it may have to be purified further, probably by additional fractional distillation.

4. Material Production for Structures and Wiring

4.1 Structures and Wiring

Other than silicon, the two primary raw materials needed for solar arrays are aluminum and glass. Glass is needed as the radiation-protecting cover, as the substrate or superstrate for cell deposition, and may also be used as a structural material in the form of glass-fiber composite material. Aluminum will be useful for electrical contacts and for the structural elements of a solar array. Titanium and steel are other materials produced by the process which could also be used for structure.

4.2 Aluminum Production

Aluminum is a byproduct of the candidate process, but not in pure form. If the titanium fluoride is separated in vapor form at the initial fluoridation stage, then the product from step 6 will be an aluminum/iron mixture. There are roughly 2 atoms of iron for every three atoms of aluminum in the lunar soil. Since the lowest temperature liquid phase of metallic aluminum and iron mixtures is liquid aluminum plus iron aluminide (Al_3Fe), the aluminum/iron resultant phase will be iron aluminides, primarily Al_3Fe. If the feed material is a high-aluminum/low-iron soil such as the Apollo 16 soil (27% Al_2O_3, 5% FeO), metallic aluminum will be a product.

If the main goal of the processing sequence is oxygen production, then once the oxygen has been separated out, the iron aluminide can be discarded as an unused byproduct. For applications as a structural metal, the intermetallic iron aluminide can be used directly. Iron aluminide is a weldable (Ref. 33) intermetallic ceramic with properties similar to stainless steel, although lower density and somewhat more brittle (Ref. 34).

Purifying the aluminum can be done by a number of processes, either by separating the aluminum fluoride by chemical means, by making an aluminum-enriched alloy and removing aluminum by melting, or by other means of removing the aluminum at the alloy stage.

A simple physical method for separating out the aluminum is by vacuum distillation. This process exploits the higher vapor pressure of aluminum over iron; it is a convenient method for lunar application since it requires only heat and vacuum. This requires heating the alloy mixture to a temperature at which aluminum vapor is evolved, and then exposing a cooled surface for the vapor to condense upon. The

relatively pure film of aluminum produced is then removed for use by heating the condensing surface to melt the aluminum.

Vacuum distillation could also be used to separate the aluminum fluoride from the fluoride salt mixture in the same way, first subliming aluminum salt AlF_3 away from the iron salt at 1291 °C. This has the disadvantage that, since the fluorine must be recovered to be reused as reactant, the distillation cannot allow any wasted material. Loss of aluminum metal, on the other hand, is of little concern, since aluminum is abundant on the moon. Thus, if high-aluminum soil cannot be easily found to use as feedstock, vacuum distillation will be used to separate the aluminum from the alloy mix.

An alternative material for electrical conduction is metallic calcium. This is not used on the Earth because of the extremely high reactivity of calcium in an oxygen atmosphere, but this may not be a problem on the moon. Calcium has the property of having one of the highest conductivity to density ratios of any easily-available metal, that is, metallic calcium makes the lightest wires. However, aluminum is adequate for wire use, and aluminum technology is well developed. Therefore I have not baselined calcium for use in the production sequence discussed.

4.3 Glassmaking

After silicon, the next most useful material for formation of a solar array on the moon will be glass. This can be used as a structural substrate (for a-Si or poly-Si cells), as a structural superstrate (for a-Si cells), and as a radiation protection layer for all cell types. It may also be usable to make fresnel lenses or to make mirrors, if a concentration system is required. Finally, glass could be used as fiberglass for structural elements. It is also, of course, has many uses other than solar cells.

Glassmaking is considered such a low-technology, bulk thermal process that it is hard to realize that it may be difficult on the moon. It is desirable to design a process that can use unbeneficiated regolith.

Glass is an amorphous mixture of silicon dioxide with typically alkaline and alkaline-earth oxides. The silicon dioxide forms the structural network of the glass; the other oxides modify the properties to the desirable form. On earth, the most commonly produced glass is soda-lime glass. "Soda" indicates sodium, in the form of Na_2O; lime indicated calcium oxide, in the form CaO. The typical proportions are SiO_2 75%, Na_2O 15%, and CaO 10%, plus 2 to 3 percent other materials. Soda lime glass is produced in large amounts on Earth because its low melt temperature makes it easy to work with. Unfortunately, sodium is not a common material on the moon. A second disadvantage of soda-lime glass is that it has a very high thermal expansion coefficient, making it vulnerable to the temperature excursion of the lunar day-night cycle.

An alternative glass to use would be fused silica, which consists of silicon dioxide plus trace components. While silicon is abundant on the moon, the melt temperature of fused silica makes it extremely difficult to work with. Typically laboratory silica is mixed with other components to lower the working temperature.

A useful laboratory glass is borosilicate glass, such as Pyrex, where boron oxide B_2O_3 is the primary additive, however, boron is also not a commonly available material on the moon.

For this reason, I have selected aluminosilicate glass as the baseline for lunar glass. (Similar considerations led to choice of aluminosilicate glass by Tillotson and co-workers (Ref. 3).) A typical aluminosilicate glass formula is 57% SiO_2, 20% Al_2O_3, 12% MgO, 5% CaO, 4% B_2O_3, 1% Na_2O, and 1% trace oxides. Of these constituents, silicon, aluminum, magnesium and calcium are common on the moon (in fact, calcium-magnesium aluminosilicate is virtually the definition of the anorthositic material that is the primary constituent of the moon, with some iron substituting for magnesium). I will assume here that the boron and sodium oxides can be left out. This will have the unfortunate effect of raising the softening temperature of the glass, but will allow it to be made from lunar material.

Aluminosilicate glasses have an intermediate melt temperature, typically around 1130 °C, which is well above the 860 °C melt temperature of soda-lime glass, but well below the almost unworkable 1710 °C of fused silica. In terms of working temperature, it has an annealing temperature of typically 715 °C, and softening temperature 915 °C (although note that the boron-free formulation discussed here

will probably have a slightly higher temperature). It also has a low thermal expansion coefficient, comparable to borosilicates.

A second difficulty is that for most uses our glass will have to be transparent. This turns out to be a significant difficulty. Glass darkening is primarily due to transition metal oxides, in particular, iron oxide (FeO). FeO is a significant component of lunar rock, ranging from roughly 3 to 23 percent of the rock weight fraction. This is why lunar rock is black. Producing a transparent glass will require reducing the iron content to nearly zero. On Earth, this is done by selecting iron-free source materials; however, this is not likely to be an option on the moon, and removal of the iron will probably have to be done by chemical or physico-chemical means. Another step used on Earth is to add manganese dioxide to neutralize some of the green color of the iron, however, on the moon, manganese is a low abundance mineral (<0.25 percent), and is found typically in exactly the same rocks that contain Fe, with a Fe:Mn ratio of ~80:1. Thus, this is not a good option.

In principle, in the procedure outlined here, most (if not all) of the iron is segregated in the form of an iron/aluminum/titanium mixture by potassium reduction. Of this, only the aluminum component is needed as a raw material for the glassmaking. Thus, the question of removal of the iron is equivalent to the problem of purifying the aluminum, discussed in the aluminum section.

Thus, there seems to be no real barrier to production of glass from lunar materials. Once the raw oxides have been refined, the glassmaking process requires melting the component materials, producing the required form (plate, cast ingots, etc), and, for stress-free glass, holding the glass at the annealing temperature for an extended period to allow internal thermal stress to relax. Conventional glass plate produced by the "float glass" method is done by spreading the melt on a bed of liquid tin; this may not be the optimum process for lunar production. The melting temperature for the aluminosilicate glass, on the order of 1130 °C, is significantly higher than the temperatures required in any other parts of the solar cell production process. This is an incentive for refining of boron, sodium, and lithium oxides despite the relatively low mass fraction of these materials in lunar soil, to lower the glass melting temperature.

An alternative approach to lunar glassmaking, discussed by Mackenzie and Claridge (Ref. 32), is to form glass out of anorthite purified from the lunar plagioclase. They note that anorthite (calcium aluminosilicate) is naturally low in iron, and hence can be used as a material to form a transparent glass. Their approach requires purification of the feedstock to separate out essentially pure anorthite, then melting this to make glass. The melting point of anorthite, approximately 1550 °C, is relatively high, making it difficult to work with. They suggest addition of calcium oxide, to form a composition of roughly 46% CaO, 42% SiO_2, 11% Al_2O_3, and 1% trace, to reduce the melting point to 1350 °C, and sketch a design for an electric furnace for processing the glass into both sheet and fiber. Even this modified composition results in a very high melt temperature of the glass, though, which will make it difficult to work. Nevertheless, if beneficiation of the input material to purify anorthosite proves to be easy, this may be a good approach.

4.4 Other Products

An additional advantage of the candidate process sequence is that it produces oxygen from the lunar regolith with high yield. Oxygen, of course, is probably the most important material which can be manufactured on the moon, important both as breathing oxygen, and also as the major component of rocket fuel. The process also produces byproduct metals such as aluminum, titanium, and iron, and byproduct magnesium and calcium oxide, which are either already purified or are relatively easy to separate in pure form. These byproducts are expected to be useful for other manufacturing processes. The silicon or light metals may also be used as fuel for a fully lunar-derived rocket propellant.

Hydrogen, nitrogen, fluorine, sulfur, carbon monoxide, helium, and other volatiles will be produced from the lunar soil in small quantities on the initial heating. The hydrogen will be useful for solar cell production, and the evolved fluorine (which will be released as hydrogen fluoride, HF) may be useful for replacement of process losses. The other evolved volatiles may also be valuable, and can be captured from the soil by use of condensors.

The fluorine processing of regolith may produce some quantities of other volatile fluorides, including fluorides of hydrogen, phosphorus, boron, arsenic, germanium, carbon, some platinum group elements, sulfur, tungsten, antimony, bromine, iodine, vanadium, uranium, niobium, and others. All of these boil (at 1 bar) below the processing temperature for the fluoridation step. While the abundances of these elements are rather low (<<0.01 percent for all except sulfur, ~0.07 percent, and carbon, 0.01 percent), production of rare-element fluorides must be taken into account for three reasons: the volatile fluorides will clog the plumbing or contaminate the product output if the process sequence is not designed to account for their production, they will represent a sink for fluorine if not recycled, and finally, many of these represent important resources which are in scant supply, and may have other processing uses.

In the process sequence discussed here, the oxygen appears as a byproduct of the silicon manufacture. In an actual lunar base, however, it is likely that the development will be in the opposite direction. The economic value of lunar oxygen, both for rocket propellant and for life support, is so high that oxygen will almost certainly be the primary product, with silicon and the other components required for solar array manufacture appearing as a welcome secondary product. The value of lunar oxygen is discussed in Reference 25.

5. Conclusions

There seems to be no insurmountable barriers to producing the main raw materials required for solar array manufacture on the moon, including both the primary semiconductor material and the structural materials required to manufacture arrays. Materials to produce silicon, aluminum, and glass can be refined directly from the regolith using fluorine, and a multi-stage reduction process can separate out and purify the required materials. This refining process, as a byproduct, also produces oxygen, and many other refined materials of possible economic value.

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TABLE 1.—AVERAGE COMPOSITION
OF MAJOR MATERIALS ON THE
LUNAR SURFACE
(PERCENT BY WEIGHT)
[From "Bulk Moon" data from
Taylorand Carrier (Ref. 24).]

Element	Amount
	(wt %)
0	43.4
Si	20.3
Mg	19.3
Fe	10.6
Ca	3.22
Al	3.17
Cr	0.42
Ti	0.18
Mn	0.12
H	(*)

(*) Hydrogen: while hydrogen is present in
surface soil at approximately 50 ppm by
weight, it is a major soil component in
high-latitude (near polar) craters only.
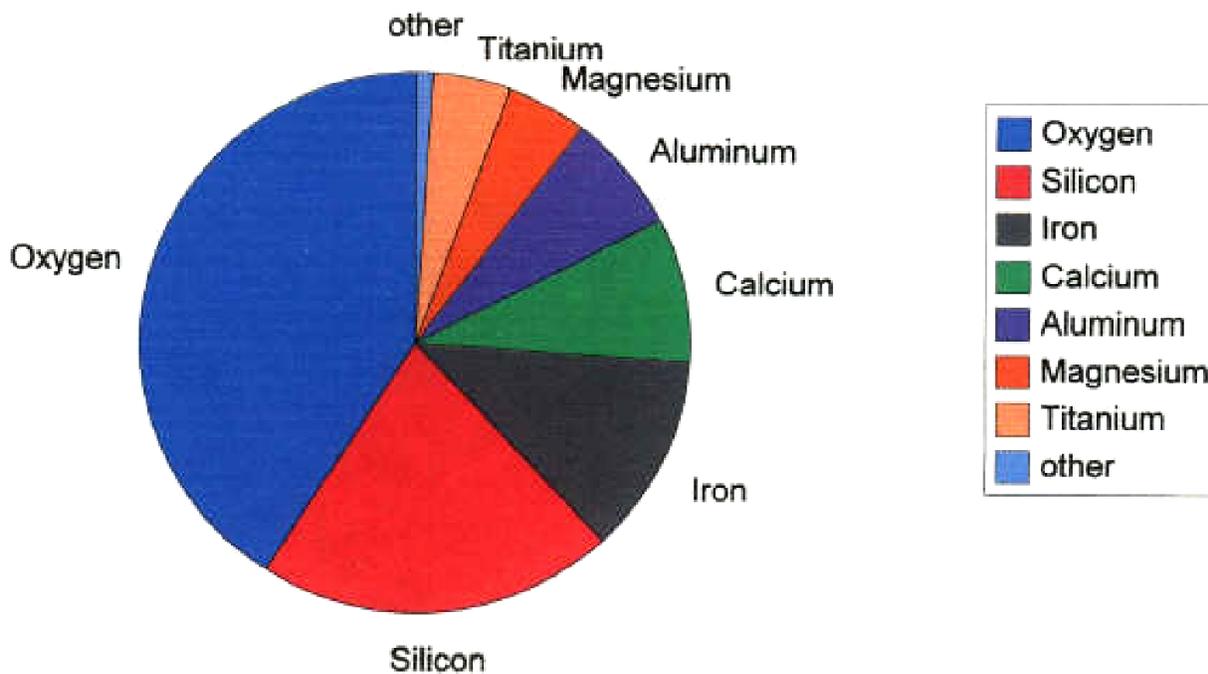
Figure 1.—Composition of the lunar regolith.
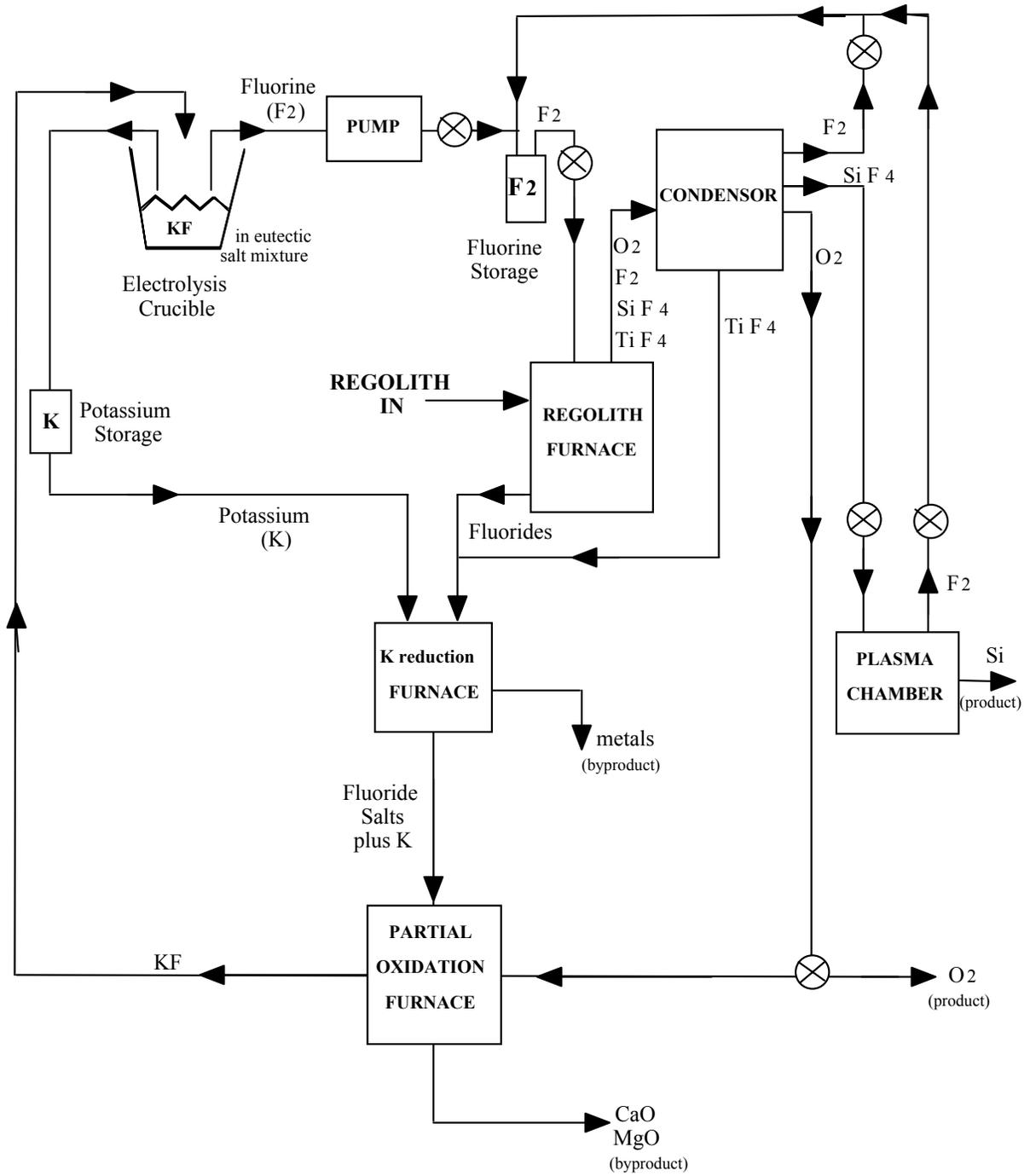
Figure 2.—Block diagram of silicon and oxygen production steps.

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Silicon, aluminum, and glass are the primary raw materials that will be required for production of solar arrays on the moon. A process sequence is proposed for producing these materials from lunar regolith, consisting of separating the required materials from lunar rock with fluorine. The fluorine is brought to the moon in the form of potassium fluoride, and is liberated from the salt by electrolysis in a eutectic salt melt. Tetrafluorosilane produced by this process is reduced to silicon by a plasma reduction stage; the fluorine salts are reduced to metals by reaction with metallic potassium. Fluorine is recovered from residual MgF and CaF_2 by reaction with K_2O.

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