LUNAR PRODUCTION OF OXYGEN AND METALS USING FLUORINE:
CONCEPTS INVOLVING FLUORITE, LITHIUM, AND ACID-BASE THEORY;
Donald M. Burt, Dept. of Geology, Arizona State Univ., Tempe, AZ
85287-1404 and Lunar and Planetary Institute, 3303 NASA Road 1,
Houston, TX 77058-4399

The sequence of affinities of some common lunar elements
for O₂ (data at 1000K from [1]) is Ca>Mg>Al>Ti³>Si>Mn²>Cr³>
Na>Fe²=P⁵=K>Fe³. Ca is the strongest reducing agent, and Na and
K are incapable of reducing major metals from their oxides. The
quite different sequence of affinities for F₂ is Ca>Mg=Na-K>Al>
Ti³>Si>Ti⁴=Mn²>Cr³>Fe²=Fe³>P⁵. Ca is still the strongest
reducing agent, but Na and K are able to reduce the metals
(other than Mg) from their fluorides. This is the basis of the
anhydrous fluorine-exchange process of [2] and the hydrous HF
acid leach process of [3], which depend on K- [2] or
Na-reduction [3] of metals from their fluorides. In the
anhydrous process (preferable given the lack of lunar H₂O), K or
Na, along with F₂, are regenerated (recycled) by electrolysis of
their low-melting molten fluorides, an unproven technology made
difficult by corrosion of the F₂-electrode.

The high melting point of CaF₂ discourages its direct
electrolysis. Why not take advantage of this property and use
lanthanide-doped fluorite, a good conductor [4], as a
non-corroodable electrode material for the electrolysis of
eutectic (CaF₂-saturated) molten fluorides?

Thermodynamic data [1] indicate that Li, although not
common on the Moon, is nearly as good a reducing agent as Ca
(better than Mg) and that LiF has a lower melting point than
NaF, an advantage for electrolysis. In addition, it is 38%
lighter than NaF, so that less of it would have to be brought
from Earth to establish the same size of plant. Consideration
should therefore be given to LiF-based metal production.

Lunar oxygen for propellants and life support is more
important than metals are. Although O₂ production via H₂
reduction of the FeO-component of lunar ilmenite is being
investigated [5,6], H is a rather poor reducing agent, and would
probably have to be brought from Earth. Fluorine, brought from
Earth as NaF or LiF, offers the advantage [7] of being able to
extract oxygen from ANY mineral, a fact long known to stable
isotope geochemists [8,9], who use Ni or Fe vessels at about
500°C. The generalized reaction is 0-mineral + 2F₂ = fluorides +
O₂; that is, 2 F’s are added for each O evolved. Such reactions
can be expressed in terms of the exchange operator F₂O⁻₁, which
has properties of a Lewis acid [10] (think of it as the acid
anhydride of HF). The sequence of affinities [1] of common lunar
elements for F₂O⁻₁ is K>Na=Ca>Mg=Mn²>Ti³>Al>Si=Fe²=Fe³>Cr³>Ti⁴>
P⁵. Unlike the irregular affinity sequences for O₂ and F₂ alone,
the sequence for F₂O⁻₁ is periodic (e.g. K>Na>Li>Ca>Mg>Be) and
is, in fact, a sequence of increasing oxide acidity. In other
words, the more basic the oxide, the greater its susceptibility
to fluorination. Lunar minerals are basic (silica-poor), and
therefore should be amenable to O₂ production using F₂.
Although an oxygen-producing fluorination plant could work with most lunar minerals, including ilmenite, anorthite seems like a good initial feed. It is abundant, reactive, able to be made into a pure nonmagnetic concentrate, and could supply CaO (for cement or for scrubbing F from the O₂ product), Al (for structural and electrical purposes), and Si (for solar cells). A possible sequence of fluorination reactions is as follows:

\[
\begin{align*}
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{F}_2 &= 2\text{CaF}_2 + \text{Al}_2\text{Si}_0\text{O}_8 + \text{SiO}_2 + \text{O}_2 \\
\text{Al}_2\text{Si}_0\text{O}_8 + \text{F}_2 &= \text{Al}_2\text{Si}_0\text{F}_2 + \text{SiO}_2 + 2\text{O}_2 \\
4\text{CaF}_2 + \text{Al}_2\text{Si}_0\text{F}_2 + 2\text{F}_2 &= 2\text{Ca}_2\text{AlF}_7 + \text{SiO}_2 + \text{O}_2 \\
2\text{Ca}_2\text{AlF}_7 + \text{Al}_2\text{Si}_0\text{F}_2 + 2\text{F}_2 &= 4\text{CaAl}_2\text{F}_5 + \text{SiO}_2 + \text{O}_2 \\
\text{Al}_2\text{Si}_0\text{F}_2 + 2\text{F}_2 &= 2\text{AlF}_3 + \text{SiO}_2 + \text{O}_2 \\
\text{SiO}_2 + 2\text{F}_2 &= \text{SiF}_4 + 2\text{O}_2
\end{align*}
\]

or, overall, \( \text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{F}_2 = \text{CaAl}_2\text{F}_5 + 4\text{AlF}_3 + 2\text{SiF}_4 + 4\text{O}_2 \).

The SiF₄ produced could be scrubbed from the product gas by NaF, yielding Na₂SiF₆, which could be Na-reduced to Si; Na-reduction of the mixed Ca-Al halides would yield Al plus CaF₂, which could be reacted with Na₂O to yield CaO plus 2NaF. Li could replace Na in these reactions, at least initially (Na in plagioclase would replace Li-losses).

References: