

LUNAR MINING OF OXYGEN USING FLUORINE

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An important aspect of lunar mining will be the extraction of volatiles, particularly oxygen, from lunar rocks. Thermodynamic data show that oxygen could readily be recovered by fluorination of abundant lunar anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$. Fluorine is the most reactive element, and the only reagent able to extract 100% of the oxygen from any mineral, yet it can safely be stored or reacted in nickel or iron containers. The general fluorination reaction, $\text{mineral} + 2\text{F}_2 = \text{mixed fluorides} + \text{O}_2$, has been used for more than 30 years at a laboratory scale by stable-isotope geochemists. For anorthite, metallic Al and Si may be recovered from the mixed fluorides by Na-reduction, and CaO via exchange with Na_2O ; the resulting NaF may be recycled into F_2 and Na by electrolysis, using lanthanide-doped CaF_2 as the inert anode.

INTRODUCTION

Oxygen can be recovered from lunar rocks because they consist mostly of oxygen, by volume if not by weight. The minimum cost technology will probably be that which uses the least amount (by weight and volume) of Earth-derived plant components and reagents. The ideal reagent for oxygen recovery may be something light, reactive, and relatively nonvolatile (easily and safely storable). Hydrogen reduction of the FeO component in lunar ilmenite, FeTiO_3 , seems currently to be the "favorite" process (e.g., Gibson and Knudsen, 1988), although hydrogen is highly volatile, the thermodynamics are somewhat unfavorable, and the process recovers, at best, only one-third of the oxygen in ilmenite (as water, not oxygen). High-temperature (pyrometallurgical) processes that do not require difficult radiational cooling or easily lost hydrogen (or water) thus seem preferable. Any technology will require a great deal of energy (electrical or thermal) to break the very strong metal-oxygen bonds in rocks and minerals.

THE MOST POWERFUL REAGENT: FLUORINE

Of the variety of recyclable reagents that have been suggested for lunar minerals processing (mainly combinations of hydrogen, carbon, nitrogen, chlorine, and fluorine), only one is strong enough to break all metal-oxygen bonds, releasing oxygen gas, O_2 , from any rock or mineral. That reagent is simple fluorine gas, F_2 , which has been used for that purpose in stable isotope laboratories for nearly 40 years (Baertschi and Silverman, 1951; Taylor and Epstein, 1962); fluorination thus constitutes a proven technology. Commonly, BrF_5 (Clayton and Mayeda, 1963) or ClF_3 are used in place of F_2 . In either case, the fluorination of any mineral occurs rapidly at about 500°C and is safely carried out in nickel reaction vessels. The basic reaction is $\text{mineral} + 2\text{F}_2 = \text{mixed fluorides} + \text{O}_2$, as discussed below.

Some other properties of fluorine are that (1) it is the lightest halogen (roughly half the atomic weight of chlorine); (2) it is inexpensive, crustally abundant, and readily extractable on Earth (Kilgore et al., 1985), mainly from fluorite, CaF_2 (Ellis and May, 1986); (3) it is safely storable not only in Fe or Ni containers,

but also as stable fluorides (salts such as sodium fluoride, NaF, which I propose to use for transporting fluorine to the Moon); (4) the fluoride ion is about the same size as the oxide ion, and thus molten fluorides easily dissolve rock oxides; (5) among halogens, fluorine forms the most stable and least volatile crystal lattices (fluorite is especially stable and therefore CaO is of potential use in "scrubbing" minor F_2 from the O_2 product); (6) fluorides have half the average bond strengths of the corresponding oxides, and consequently have lower melting temperatures (making for much easier electrolysis); (7) fluoride melts are generally nonvolatile and are much less viscous than oxide or silicate melts (with better transport properties for electrolysis); (8) silicon tetrafluoride, SiF_4 , is a volatile gas (this property is useful for desilicating rocks or for concentrating Si for solar cells); (9) minor amounts of fluoride ion (as in drinking water or toothpaste) are not particularly toxic (although hydrofluoric acid, HF, and F_2 gas are); and (10) the chemistry of fluorine and of fluoride gases, crystals, and melts is well known. In particular, fluoride melts (molten cryolite) have long been used as the electrolytic solvent in aluminum production by the Hall-Heroult process (cf. Grjotheim et al., 1982; Burkin, 1987) and were thoroughly studied as possible high-temperature reactor coolants. Fluorine gas is widely used in the processing of uranium (e.g., Cochbet-Muchy and Portier, 1985), also a mature technology.

In sum, fluorine is the most reactive element. I believe it is indeed "the knife to cut the lunar cheese," which is a very tough and refractory one. Fluorine has been used to extract oxygen from lunar minerals for stable isotope studies since the very first (e.g., Taylor and Epstein, 1970; Epstein and Taylor, 1971). Why not extend this procedure to larger-scale oxygen extraction?

The possible use of fluorine for lunar oxygen and metal production was briefly reviewed by Dalton and Degelman (1972, pp. 219-220 and 225-226), but was apparently rejected essentially because "all of the reactions are very fast and difficult to control" and "because of the very corrosive nature of fluorides" (p. 220). To me, the first "disadvantage" is essentially an advantage, given proper systems design, and the second can be overcome by proper choice of container, electrode, and reagent materials, as discussed below. The above study did conclude (pp. 219 and 226) that, despite safety and corrosion problems,

the fluorination route was thermodynamically the most favorable and was the only method studied that was both anhydrous and allowed easy coproduction of metals. I might also add that it is the only one (besides direct electrolysis) that allows the direct production of oxygen as O₂ gas (instead of tied up in water, carbon monoxide, or carbon dioxide).

The direct fluorination method was considered about the same time by NASA and the U.S. Bureau of Mines (e.g., E. Schnitzer and M. James, unpublished data, 1972), but apparently has not been considered since. It is not even mentioned by *Waldron et al.*, (1979), *Waldron and Criswell* (1982), and *Waldron* (1985), who instead propose a more complex, lower temperature, hydrous procedure: the HF acid leach process, which depends on the corrosive nature of HF. Others (e.g., *Kesterke*, 1970; *Jarrett et al.*, 1980; *Anthony et al.*, 1988) have considered using molten fluorides merely as fluxes to dissolve refractory lunar oxides [property (4) above]. This parallels their 100-year use in the aluminum extraction industry. Although this use of fluorides as solvents rather than reagents also leads to the direct production of oxygen, the dry fluorination route offers many of the same advantages, and is potentially applicable to extracting oxygen from the full range of lunar minerals, including ilmenite (although I here consider only oxygen extraction from anorthite).

TYPES OF REACTIONS INVOLVING FLUORINE AND OXYGEN

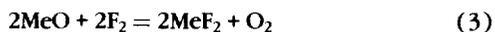
The simplest reaction type involves roasting an oxide or fluoride at high temperatures to produce a metal plus oxygen or fluorine, with dissociation reactions of the type (where Me is any metal)



or



Because metal-oxygen and metal-fluorine bonds tend to be very strong, this type of reaction must, in general, be done at extremely high temperatures, and even then the oxide or fluoride may just vaporize (without dissociation). Despite the advantageous lunar vacuum, this procedure has only rarely been proposed for oxygen production (e.g., *Steurer*, 1985). Oxygen production is more readily carried out by an exchange reaction between fluorine and oxygen, of the type



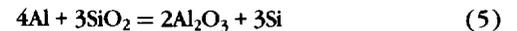
This type of reaction occurs readily over a wide range of temperatures (although Ni containment of fluorine is not practical above 500°-600°C). Note that two fluorines are needed to extract each oxygen. The shorthand notation for such an exchange operation is F₂O₋₁, where F₂O₋₁ is a component called an "exchange operator" (*Burt*, 1974). It tells you "put two fluorines in, get one oxygen out." The operator F₂O₋₁ has properties of an electronic or Lewis acid (*Burt*, 1974; cf. *Lewis*, 1938). The implication is that the more basic the metal oxide, the more easily it can be fluorinated, releasing oxygen. Moon rocks are mainly basic (silica-poor) and therefore easy to fluorinate (*Burt*, 1988; cf. *Taylor and Epstein*, 1970).

The above reactions all involve a gas phase, potentially a problem if you want to keep your plant small, closed, and

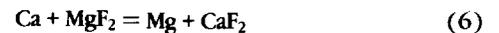
nonpolluting. Solid-solid (or solid-melt or melt-melt) reactions involving oxygen and fluorine should also be considered. The first type is an O-exchange reduction, such as



You can derive such a reaction from two gaseous dissociation reactions by subtracting them so that the gas molecules cancel. In the above reaction, Ca is the reducing agent, able to reduce Mg to its metallic form because Ca has a greater affinity for (less of a tendency to give up or more of a tendency to react with) oxygen than does Mg. A similar, but slightly more complicated, reaction is



This is part of a proposed dry process for producing aluminum and silicon using a molten fluoride bath as a solvent for anorthite (*Anthony et al.*, 1988); the Al₂O₃ produced by reduction of SiO₂ is electrolyzed to Al and O₂ in a process similar to that used for aluminum production on Earth (accumulation of unreduced CaO in the melt is a problem with this method). Analogous reactions can be written for fluorides, such as



We can similarly write



and



These represent the Na reduction of Al (the so-called Castner process) and of Si (*Sanjurjo et al.*, 1980) to native form, and are steps in the process proposed below.

We can also write fluorine-oxygen exchange reactions involving only condensed phases, such as



As above, the tendency for such "two fluorines for one oxygen" exchange processes can be expressed in terms of the exchange operator F₂O₋₁ (*Burt*, 1974). As mentioned, more basic oxides have a greater tendency to become fluorinated. Of particular interest is the reaction involving the basic oxide Na₂O



This reaction is proposed below for moving fluorine from fluorite, CaF₂, which has a very high melting point (1418°C) and is therefore unsuitable for direct electrolysis, to NaF, whose much lower melting point (990°C) makes it more suitable for electrolysis.

ELEMENT AND EXCHANGE AFFINITIES

The general affinities of some important lunar elements for oxygen are given as a bar chart at 1000 K (727°C) in Fig. 1 (data from *Pankratz et al.*, 1984). The order at other temperatures

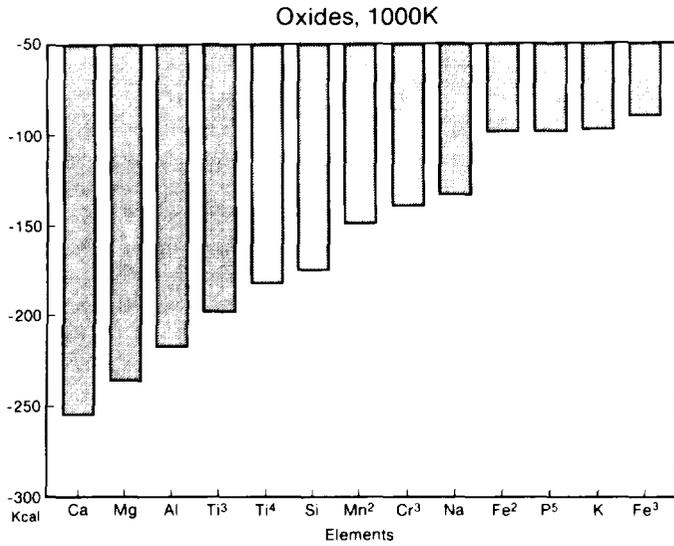


Fig. 1. Bar diagram for free energies of formation (kcal per mole of O₂) of lunar-element oxides, 1000 K. Diagram shows affinities of the lunar elements for oxygen (greatest for Ca).

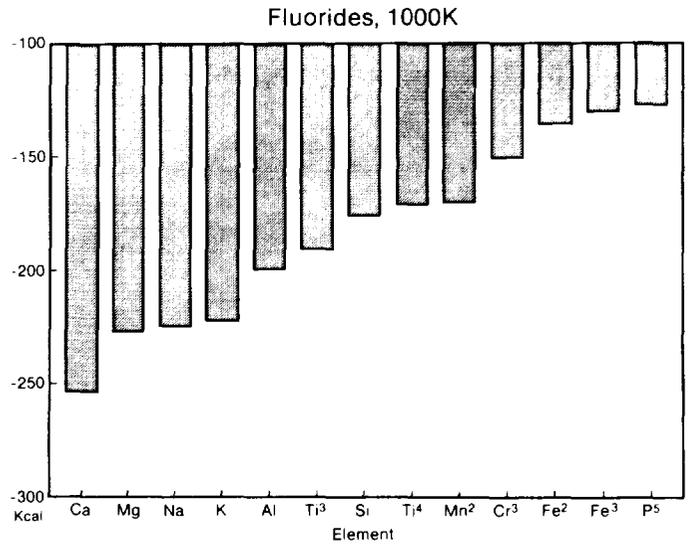


Fig. 2. Bar diagram for free energies of formation (kcal per mole of F₂) of lunar-element fluorides, 1000 K. Diagram shows affinities of the lunar elements for fluorine (greatest for Ca).

would be very similar (cf. the Ellingham or free energy vs. temperature diagrams used by extractive metallurgists; e.g., *Rosenqvist*, 1983). The general order is

$$\text{Ca} > \text{Mg} > \text{Al} > \text{Ti}^3 > \text{Ti}^4 > \text{Si} > \text{Mn}^2 > \text{Cr}^3 > \text{Na} > \text{Fe}^2 = \text{P}^5 = \text{K} > \text{Fe}^3 \quad (11)$$

Any element to the left will reduce an element to the right from its oxide (this treatment neglects possible mixed oxides). Note that iron is very easy to reduce (a major reason why it is so widely used on Earth), and that sodium is a very poor reducing agent for oxides of elements other than iron (e.g., it cannot reduce either aluminum or silicon). Calcium is the best reducing agent, but would be the most difficult element to produce as a metal.

Affinities for fluorine are given in Fig. 2 under the same conditions. Note the different order, namely

$$\text{Ca} > \text{Mg} = \text{Na} = \text{K} > \text{Al} > \text{Ti}^3 > \text{Si} > \text{Ti}^4 = \text{Mn}^2 > \text{Cr}^3 > \text{Fe}^2 > \text{Fe}^3 > \text{P}^5 \quad (12)$$

Sodium is now an excellent reducing agent (about the same as magnesium), and could easily reduce aluminum and silicon to metals from their fluorides (as noted above).

Affinities for F-O exchange are given in Fig. 3. Note that this is the only sequence whose order reflects position of the elements in the periodic table (e.g., the order K > Na > Li > Ca > Mg > Be) or periodic properties such as the charge-to-radius ratio of the cations (*Burt*, 1988). In fact, this is an order of increasing oxide acidity

$$\text{K} > \text{Na} > \text{Ca} > \text{Mg} > \text{Mn}^2 > \text{Ti}^3 > \text{Al} > \text{Si} > \text{Fe}^2 > \text{Fe}^3 > \text{Cr}^3 > \text{Ti}^4 > \text{P}^5 \quad (13)$$

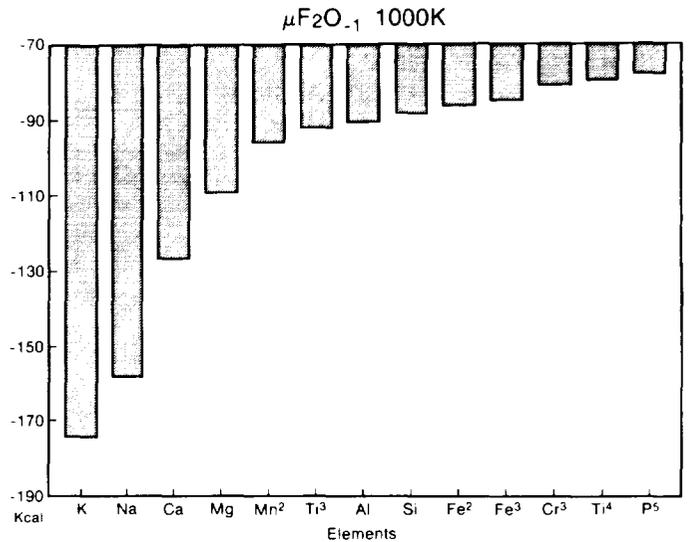


Fig. 3. Bar diagram for molar free energy differences ($\mu_{\text{F}_2} - 1/2 \mu_{\text{O}_2}$, where μ is the chemical potential) of lunar elements, 1000 K. Diagram shows affinities of the lunar elements for F-O exchange (greatest for K).

It implies, as mentioned above, that Moon rocks, being relatively basic, should fluorinate easily (releasing oxygen) and potassium or sodium oxides could be used to remove the fluorine from fluorite.

All the above information can be shown on a single μ_{F_2} vs. μ_{O_2} diagram, Fig. 4, where μ is the molar free energy (or chemical potential) of the gas in equilibrium with the element, fluoride, or oxide. The order of affinity for F₂ is given along the

vertical axis, that for O₂ along the horizontal axis, and that for the exchange operator F₂O₋₁ perpendicular to the diagonal lines (of slope + 1/2) from lower right to upper left.

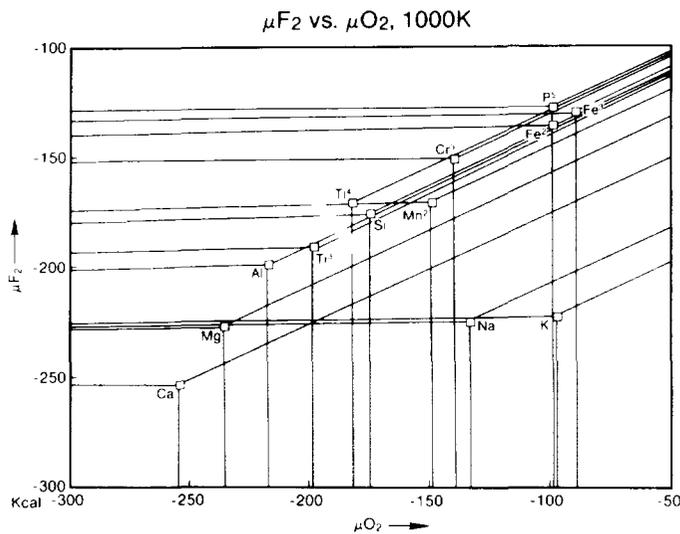
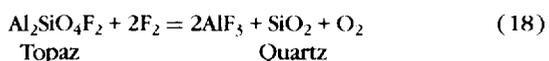
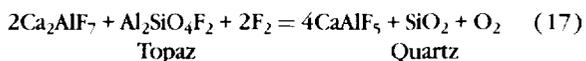
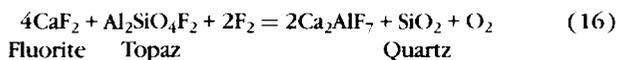
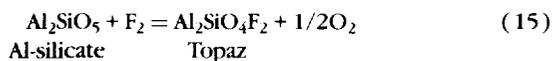
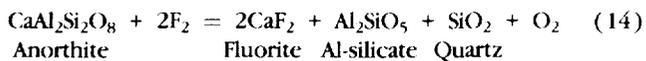


Fig. 4. μF₂ - μO₂ diagram for lunar elements, 1000 K.

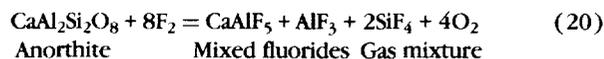
STEPWISE FLUORINATION OF ANORTHITE

Although fluorination of bulk lunar soil would be possible and would yield oxygen (e.g., Epstein and Taylor, 1971; Waldron, 1985), it seems preferable to use instead a single mineral of fairly simple constitution. This facilitates metal co-recovery and recycling of the fluorine. Anorthite from lunar anorthosites is abundant, presumably could be prepared as a uniform concentrate, and could supply as by-products CaO, Al, and Si. Its idealized formula is CaAl₂Si₂O₈ (with minor solid solution towards albite, NaAlSi₃O₈).

The details of fluorinating a single mineral are more complicated than simple element affinities might indicate. A possible sequence of fluorination reactions for anorthite (as deduced from available thermodynamic and phase equilibrium data) is given below (note that an "index fluoride" is produced at each step—fluorite, topaz, Ca₂AlF₇, CaAlF₅, AlF₃, and finally SiF₄ gas)



The overall (bulk) reaction is then



At equilibrium, the above would be the sequence of reactions occurring from top to bottom of a fixed- or fluidized-bed reactor in which sieved anorthite was fed into the top and F₂ gas into the bottom. Note that quartz is produced by each of the reactions except the last (which is the only reaction that produces a gas other than O₂) and that SiO₂, as the most acid oxide, is the most difficult to fluorinate (consistent with what was stated about exchange affinities above). The separation of SiF₄ and excess F₂ from the O₂ product, and the electrolytic recycling of the fluorides into F₂, are discussed below.

These reactions can also be seen on a barycentric triangular oxide diagram CaO-Al₂O₃-F₂O₋₁, which is projected through the composition of (shows phases in equilibrium with) SiO₂ or quartz (Fig. 5). The six reactions (equations 14-19) above correspond to the six numbered triangular fields of the main triangle. The arrows indicate the reaction path of increasing fluorination, from anorthite towards the F₂O₋₁ corner.

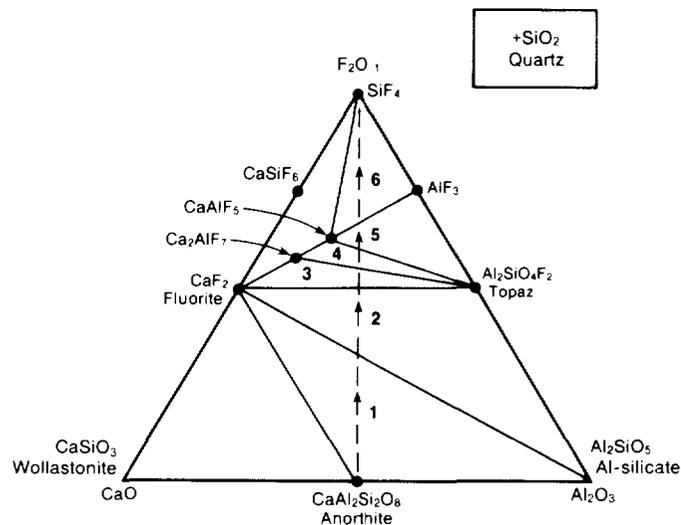
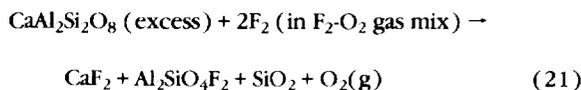


Fig. 5. Stepwise fluorination of anorthite. Triangular diagram showing phases in equilibrium with quartz. Numbered triangular fields 1 to 6 correspond to the six reactions in equations (14) to (19) in the text.

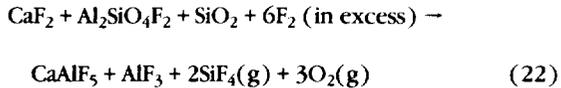
DETAILS OF THE PROPOSED PROCESS

The anorthite concentrate is fluorinated in at least two steps (probably in different parts of the same column reactor). The first step is partial fluorination of pure anorthite, using the F₂-O₂ mixture produced by the main stage of the process [equations (22) and (23) below]. Because this step removes excess F₂ from product O₂, it is a "scrubbing" step. A typical reaction is

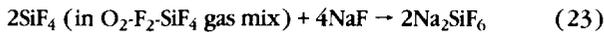


Final removal of trace F_2 , should it prove necessary to produce a breathable O_2 product (for propellant use the absolute purity would be unimportant), is done as in equation (28) below.

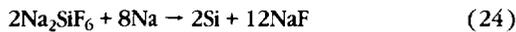
The next or main step is complete fluorination of the fluorite-bearing product of equation (21). By using excess F_2 , this step produces a mixture of leftover F_2 , O_2 , and SiF_4 . The reaction is



The SiF_4 from the product gas mixture of equation (22) is scrubbed using NaF to produce Na_2SiF_6 , then the partly purified gas mixture (no SiF_4) is fed back to fresh anorthite to scrub the F_2 [equation (21) above]. The SiF_4 -scrubbing reaction is

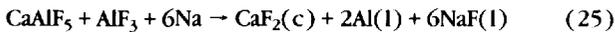


Next, Si is produced by Na-reduction of the Na_2SiF_6 (and used for, e.g., solar cells)



[Recycle four of the NaFs to equation (23) above; the eight remaining NaFs go to the electrolysis cell of equation (29) below.]

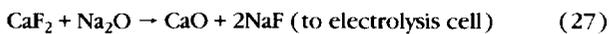
Analogously, Al is produced by Na-reduction of the $CaAlF_5$ - AlF_3 mixture given by equation (22)



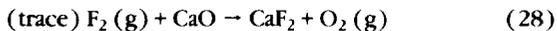
[Move the six NaFs to the electrolysis cell of the step in equation (29).] Some of the Na produced by electrolysis is reacted with O_2 to produce Na_2O



This Na_2O is used to recover F from CaF_2 , producing CaO

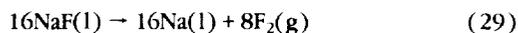


If necessary, some of this CaO is used to scrub the final traces of F_2 from the O_2 product of equation (21)



This CaF_2 is periodically recycled to the step shown in equation (27). Note that Na_2O itself should be even more effective than CaO at scrubbing traces of F_2 , but I am assuming that the process will yield "waste" CaO, easily spared for this purpose (unlike Na_2O).

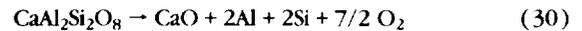
Finally, the NaF generated in the steps shown in equations (24), (25), and (27) above is recycled to Na and F_2 via electrolysis



This electrolysis step represents unproven technology; the main challenge is to find an electrode material that will not be attacked by the F_2 produced at the anode (fluorine will attack nearly any conventional conductor, including platinum and other precious metals). Lanthanide- or even sodium-doped fluorite, CaF_2 , is a fairly good electrical conductor (e.g., *Catlow*, 1985; *Tressaud*,

1985) and is therefore a potential inert electrode material (*Burt*, 1988). It has a high melting point and won't dissolve in the molten NaF if the bath is a mixture of CaF_2 at its saturation concentration and NaF, rather than pure NaF. This procedure would, moreover, lower the minimum bath temperature from 990°C for pure NaF to 818°C for the eutectic binary mixture, thereby assisting electrolysis. A bath consisting of a ternary eutectic with LiF could have an even lower temperature of 615°C (*Barton et al.*, 1959, reproduced in *Levin et al.*, 1964, Fig. 1544). Essentially pure Na should be produced at the cathode, inasmuch as Ca and Li are much better reducing agents than Na in fluoride baths. The process itself would result in the production of huge quantities of fluorite, CaF_2 , so that fluorite use as an electrode (and perhaps container) material is certainly appealing, if as yet untested.

Omitting recycled Na and F, the overall reaction is



For each mole of anorthite to be processed, the plant is required to contain 20 moles of NaF (16 for electrolysis, 4 for scrubbing SiF_4), plus a large electric capacity. From formula weights, each ton of anorthite to be treated per cycle would then require 3.02 tons of NaF to be brought from Earth. Also bringing LiF and CaF_2 would lower the temperature of the electrolysis cell; these components would afterward be nonparticipating.

One could save on weight (only 1.86 tons LiF per ton capacity of anorthite) and obtain a better reducing agent by using LiF and Li for all the above processes (*Burt*, 1988). Electrolysis of a CaF_2 -LiF eutectic mixture ($T = 773^\circ C$) would, however, probably produce a Ca-rich Li alloy at the cathode, inasmuch as Li is nearly as good a reducing agent as Ca. This might offer a route to obtaining Ca-metal rather than CaO as a product of the process, given a method of separating the Ca from the Li in the alloy. Also Li, unlike Na, will reduce Mg in fluorides obtained from olivine or pyroxene, and would therefore offer a route to obtaining oxygen and metals from these minerals.

SUMMARY AND CONCLUSIONS

The proposed process basically involves stepwise fluorination of anorthite to release O_2 , then Na-reduction of the mixed fluorides to the metals Al and Si, leaving CaO unreduced. In general, this is a dry, much simpler, high-temperature analog of *Waldron's* (1985 and earlier references) HF acid-leach process. The product gas is cleansed of SiF_4 by NaF and of excess F_2 by reaction with fresh anorthite (then CaO, if needed). From $CaAl_2Si_2O_8$, the process produces CaO, 2Al, 2Si, and $7/2O_2$ (i.e., 87.5% recovery of oxygen). Fluorine is brought from Earth as NaF. An unproven technology is the electrolysis of molten NaF to regenerate F_2 and Na, using doped CaF_2 as the anode. To save weight, or for treatment of Mg-bearing minerals, one could consider analogous processes with LiF in place of NaF. Gaseous F_2 produced by electrolysis is reacted immediately to produce oxygen and no fluorine need be stored or handled outside the plant.

The exact geometry and nature of the eight reaction vessels (one per numbered step) required for such a process are not yet worked out, and most of the reactions are untested, even in the laboratory, although the fluorination reactions of equations (21) and (22) are tested in stable isotope laboratories every day. Some of the reactions might best be carried out in molten fluoride

baths, others in the gas phase. Gas-solid reactions could be carried out in vertical fixed- or fluidized-bed reactors, with opposing ("counter-current") flows of gases and solids.

The main problem that I see with this process, other than its unproven technology, is that it requires considerable materials handling—multiple steps in up to eight different reaction vessels. Nevertheless, the steps might be fully automated, especially if the reactions occur fast enough. The first step in testing the feasibility of the process would be to investigate the electrolysis of molten NaF (and then of various eutectic compositions involving CaF₂ and LiF), using doped CaF₂ or finding other inert electrode (and container) materials.

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