Lunar Mining of Oxygen Using Fluorine

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Abstract

Experiments during the first year of the project were directed towards generating elemental fluorine via the electrolysis of anhydrous molten fluorides. Na_2SiF_6 was dissolved in either molten $NaBF_4$ or a eutectic (minimum-melting) mixture of KF-LiF-NaF and electrolyzed between $450°$ and $600°$ C to Si metal at the cathode and F_2 gas at the anode. Ar gas was continuously passed through the system and F_2 was trapped in a KBr furnace. Various anode and cathode materials were investigated. Despite many experimental difficulties, the capability of the process to produce elemental fluorine was demonstrated.

Introduction

We are engaged in experiments to produce fluorine by the electrolysis of anhydrous molten fluorides, with application to the mining of oxygen on the Moon. Fluorine, as the most reactive element, readily releases oxygen from all oxygen-bearing rocks and minerals. Stable isotope geochemists have carried out this reaction successfully for more than 30 years in Ni crucibles at a temperature of about 500° C.

Fluorine can only be produced by electrolysis. Conventionally, an HF-KF mixture is electrolyzed at moderate temperatures to yield H_2 at the cathode and F_2 at the carbon anode (e.g., Ellis and May, 1986). This route does not readily lend itself to recycling of the fluorine, all of which would have to be brought from Earth (as a stable inert salt, in the present process). The problem is that the hydrogen produced at the cathode is a relatively poor reducing agent.

An alternative fluorine-generating process, devised by D.M. Burt in 1989 (unpublished), produces by-product silicon (for solar cells) as well as oxygen, and results in all of the F_2 being recycled (in principle, at least). A lunar silicate rock is partially fluorinated by F_2 gas, yielding pure O_2 gas, then the residue is heated in the lunar vacuum to release gaseous SiF_4. The SiF_4 is trapped in NaF-bearing anhydrous molten salts as Na_2SiF_6, which is electrolyzed to Si metal at the cathode and F_2 gas at the anode, thus completing the cycle. Inasmuch as SiF_4 is the most volatile common fluoride, this process should work with any unbeneficiated lunar silicate rock.

Personnel

The apparatus was largely designed and set up this spring by Dr. Jeff Roberts, a former student of Prof. Jim Tyburczy. He left in June to accept a job at Lawrence Livermore Labs and was replaced by Mr. Rajan Balasubramanian, an ASU Chemical Engineering graduate student. Mr. Balasubramanian finished designing and assembling the apparatus in early July and has carried out the actual experiments since then. Prof. Tyburczy left for a sabbatical year at SUNY Stony Brook in August.

Progress

Since our progress report of May 28, 1992 we have finished setting up the electrolysis line and have carried out 16 experiments, the first 15 of which are summarized on the appended table. We have successfully prepared fluorine by electrolysis, beginning with our third try on July 23. Not

unexpectedly, we also have encountered many experimental difficulties.

We had, somewhat surprisingly, no problems with corrosion of the Inconel 601 electrolysis vessel, its water-coooled stainless steel top, or the inner alumina crucible in which we melted the electrolytes, at run temperatures up to 600 C (a technique used by Mamentov and Laher, 1989). The KBr furnace at about 200 C seemingly trapped nearly all of the F_2 formed as KF by releasing Br_2; we had no detectable releases of F_2 gas from the system.

Our initial few runs involved sheet graphite cathodes and anodes and low-melting $NaBF_4$ (M.P. 408° C) as the electrolyte (Mamentov and Laher, 1989). After run 4, we abandoned $NaBF_4$ in favor of a eutectic (minimum-melting) mixture of KF-LiF-NaF (M.P. 459° C: e.g., Minh and Redey, 1987) owing to the high volatility of the former. $NaBF_4$ releases gaseous BF_3 when heated, which gas was not trapped by our KBr furnace at 200° C, even with NaF placed at the downstream end. We detected this problem by the characteristic fuming of BF_3 when it contacted the water we had at the end of the line to measure gas flow via bubbling rate (Topchiev et al., 1959, p. 25). White borate deposits partly blocked the glass tube, which locally was etched by the HF formed by the reaction of BF_3 with the water.

We abandoned the graphite electrodes after 9 runs because of their relatively poor electrical conductivity (reducing the electrode spacing did not help much, revealing that salt conductivity was not the major problem). (We did produce some Si on the cathode by using long run times and small electrode spacing.) The metals that we tried later (inconel, copper, titanium, and nickel, to date) were much better conductors of electricity, although they suffered more severe anode corrosion.

Problems and Solutions

Our other experimental difficulties are summarized below, together with the measures we undertook to alleviate the problems. Many of these difficulties undoubtedly resulted from our inexperience in molten salt electrolysis.

1.   The KF-LiF-NaF mixture (especially KF) is highly hygroscopic. To minimize this problem, samples were weighed out rapidly just before a run, then placed in a stream of dry argon, and left to dry out at T > 300° C for an hour before proceeding with the run. Cell resistivity was then monitored as the salt was heated to melting.

2.   The maximum internal temperatures were much cooler (50-100° C) than those measured by the external thermocouple, as revealed by our initial failure to melt the charge. We placed an alumina-sheathed internal thermocouple in later runs.

3.   The closely- and evenly-spaced furnace windings, short length, and water-cooled top of our electrolysis vessel resulted in a undesirably high vertical temperature gradient in the electrolysis cell (100° C over a few cm, as revealed by raising and lowering the internal thermocouple). The alumina-sheathed thermocouple and especially the two cold metal electrode leads immersed in the salt made the problem worse, as did the cold stream of argon being directed downwards through the top. The only remedy was to carry out the experiments at much higher temperatures (more than 100° C greater) than initially planned. After run 9, we reshaped the furnace (removed the top) so as to place the bottom of the reaction vessel at the hot spot of the furnace, rather than above it. This slightly alleviated, but did not cure, the problem.

4.   The high vertical temperature gradient made the salts remain solid (crystalline) on top. They tended to form a impermeable crust on top of the molten electrolyte, clinging to and even climbing the metal electrode supports. In one run, #3, this crust trapped the first fluorine gas we produced as tiny fluid inclusions, which decrepitated "explosively" (in tiny gas puffs) after the run was opened and the adsorbed water began to dissolve the salts. The remedy was, again, to carry out the electrolysis at a high enough temperature (about 600° C) to make sure all of the salt was melted. The problem worsened when we began using metal electrodes; at this point we started preheating the furnace to over 700° C, then cooling it down for the actual electrolysis.

5.   Even with these measures, KF-LiF-NaF melts that were relatively rich in Na_2SiF_6 (up to 4%) tended to climb up the walls of the container and also up the electrodes. Placing a small ceramic cap or "protector" over the place where the electode joined the metal carrier, especially for the cathode, helped somewhat. In later runs we tried to retract the electrodes and thermocouple before cooling off the run, in order to facilitate their examination and cleaning (otherwise they were trapped in rock-hard frozen electrolyte and had to be laboriously chipped or dissolved free); vertical creep of the electrolyte made this impossible in some Si-rich runs (crystallized electrolyte crust "froze them in place" during the run).

6.   In runs with less Si or those electrolyzed for longer periods or at higher currents, all of the Si dissolved in the electrolyte was apparently used up (by deposition at the cathode) and at that

point the metallic anode became highly corroded. Fluorine produced at the anode reacted with it and the resulting fluoride dissolved in the melt; the metal reprecipitated at the cathode dendritically (and the fibrous dendrites eventually shorted out the cell). At this point the cell was producing no F_2 gas but was merely electrorefining the metal of the anode. This was especially visible in the runs with Cu electrodes (#12 and #13), but it also happened to Inconel (#14) and Ti (#15). TiF_4 is a gas at high temperatures, but much of it appears to have been reabsorbed by reaction with the melt.

7.   Our major problem was the failure of the cold trap (a simple U-tube) to trap the Br_2 released into the Ar gas stream by reaction of F_2 with KBr in our horizontal tube fluorine-trapping furnace. We tried switching from an ice-water bath to a dry ice bath, but this didn't help. Using a liquid nitrogen bath resulted in condensation of liquid argon from the argon gas stream; this rapidly blocked the U-tube and was abandoned. Our resident fluorine expert, Prof. Paul Knauth, tells us that a simple U-tube works for trapping diffuse Br_2 in a vacuum; apparently the thermal vibrations of all of the accompanying Ar atoms in our experiments prevent the Br molecules from condensing (they are "hustled on through" the cold U-tube, instead of sticking to its walls). We could try using dry N_2 in place of Ar as the gas stream, with liquid nitrogen bathing the U-tube, or could try using a vacuum (our present set-up is not vacuum tight). In order to measure fluorine production quantitatively, we shall have to come up with a different method of measurement, such as an ion-sensitive electrode.

We can, nevertheless, demonstate that we have been making considerable fluorine, if not exactly how much. Not only did tiny fluid inclusions of F_2 gas in salt crust react explosively with water after run #3, as mentioned above (the reaction $F_2 + H_2O = 2HF + O_2$), but also optical examination of the material filling the KBr furnace after 13 runs revealed that much of it had been converted to KF. This was accomplished by examining a crushed sample on a glass microscope slide under a cover slip using an oil of refractive index 1.555, which nearly matches that of KBr (1.559), making KBr grains appear nearly invisible. Any conversion to KF is detected by the much lower refractive index of the latter (1.363).

Results

1.   Fluorine *was* produced.
2.   KF-LiF-NaF eutectic better than $NaBf_4$ owing to volatility of latter.

3.   Graphite anode seemingly nonreactive with F_2, but such a poor conductor that only tiny currents could be maintained; some Si was produced.

4.   Metal anodes (Cu, Ti, inconel, Ni) corroded rapidly and metal reprecipated at the cathode (electrorefining) after Si in the melt was used up.

Major Discoveries

1.   Fluorine can be produced by anhydrous molten salt electrolysis; this can be carried out in alumina crucibles inside an inconel or nickel reaction vessel at temperatures up to 600 C.

2.   The eutectic (minimum melting) mixture of KF-LiF-NaF worked much better as the electrolyte than $NaBF_4$, owing to the high volatility of the latter.

3.   Sheet graphite anodes were less subject to corrosion than the metals we tried (inconel, Ni, Cu, and Ti) and conveniently broke off when it was time to free them from the electrolyte, but were such poor conductors of electricity that only long run times and close electrode spacing allowed visible production of Si at the cathode.

4.   The metal electrodes corroded rapidly at the anode and the metal reprecipitated dendritically at the cathode (electrorefining); this problem was probably caused by the low initial Si contents of the melts; all of the Si was precipitated at the cathode quite rapidly. Two differently-colored layers of precipitate were commonly observed on the cathode after these experiments, the inner one presumably being Si and the outer one the cathode metal.

5.   Many experimental problems remain to be solved.

Future Research

Continued funding is requested to carry out the following experiments:

1.   Continue electrolysis experiments with other metals and forms of carbon other than graphite as the anode material.

2.   Determine the composition of the metals deposited at the cathode by using electron microprobe microanalysis.

3.   Devise a different method of measuring fluorine production quantitatively, either by replacing Ar by N_2 in the gas stream, or by redesigning the apparatus to work in a vacuum, or by using an ion sensitive electrode to measure F in aqueous solution.

4.   Redesign the furnace and reaction vessel to minimize temperature gradients, thereby minimizing several experimental problems involving electrolyte crusts and vertical creep, and also minimizing anode corrosion by allowing electrolysis at lower temperatures. Two modifications that could be tried with our present set-up involve air instead of water cooling of the top of the reaction vessel and pre-heating of the argon stream before it enters the reaction vessel.

5.   Initiate experiments on partial fluorination of silicate rocks and on SiF_4 release by pyrolysis of partly fluorinated rocks.

References

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Run No	Composition	Wt. of Electrolyte	Max. Outside Temp.	Max. Inside Temp.	Resistance (Minimum)	Voltage Volts	Current Amp.	Electrode Material	Comments
1	NaBF4 = 90% Na2SiF6 = 10%	25.4 gms	490 C	-	28 k ohms	-	-	Graphite	Electrolyte not completely molten.
2	NaBF4 = 95% Na2SiF6 = 5%	25.256 gms	560 C	-	10.81 k ohms	-	-	Graphite	Electrolyte molten. Gray crystalline material on top of electrolyte.
3	NaF = 10 % KF = 44 % LiF = 44 % Na2SiF6 = 2%	22.462 gms	650 C	-	35 ohms	2.9 - 3.4 4.6 - 5.6 4.8 - 7.0 5.4 - 8.2	.1 .2 .3 .4	Graphite	Black material deposited on the cathode. Sparks of smoke observed while dismantling. Grayish material observed on the anode.
4	NaBF4 = 95% Na2SiF6 = 5%	22.39 gms	625 C	492.7 C	27.38 k ohms	15 - 25 V	.1	Graphite	KBr analysed microscopically. Abundant fluid inclusions present. No visual formation of KF.
5	NaF = 10 % KF = 44 % LiF = 44 % Na2SiF6 = 2%	21.232 gms.	656 C	552 C	0.43 k ohms	15 V 20 V 25 V	0.04 - 0 A 0.03 - 0 A 0.12-0.01 A	Graphite	1 M KI solution used as final trap in Run # 5.
6	NaF = 10 % KF = 44 % LiF = 44 % Na2SiF6 = 2%	24.82 gms.	640 C	516 C	128 k ohms	25 V	0.01 - 0.1 A	Graphite	Poor conductivity of electrodes.
7	NaF = 11 % KF = 41 % LiF = 44 % Na2SiF6 = 4%	27.895 gms.	600 - 675 C	446 - 476 C	34.68 k ohms	25 V	0 - 0.03 A	Graphite	No bubble on electrolyte surface. No visual depos. of Si on cathode. Electrolyte fully molten.
8	NaF = 11.5 % KF = 42 % LiF = 46.5 %	24.497 gms.	650 c	575 - 581 C	0.78 k ohms.	25 V 15 V	0.03 - 0.05 A 0.03 - 0.04 A	Graphite	Observed a major temperature gradient inside the cell. (summarized at end of report.) Very little electrolysis occurred.
9	NaF = 10.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =1 %	28.666 gms.	650 - 660 C	589 - 598 C	0.52 k ohms.	25 V	0.02 - 0.07 A	Graphite	Black Material (Si?) found around the cathode. Electrolyte surface was silvery (Na or K ?). Many bubbles on electrolyte surface. Electrolyte contained dendrites. Electrolyte melt crust found half-way up the crucible.

#	Composition	Weight	Temp (C)	Temp (C)	Resistance	Voltage	Current	Electrode	Observations
10	NaF = 10.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =1 %	28.581 gms.	660 C	575 - 580 C	0.347 k ohms.	2.2 V 2.3 V 2.4 V 2.2/2.5 V	0.10 A 0.2 A 0.30 A 0.40 A	Inconel	Good conductivity from use of metal electrode. White crust on top. Grayish white crust below. Anode was quite corroded. Much metal deposited on cathode.
11	NaF = 10.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =1 %	27.997 gms.	680 - 700 C	573 - 590 C	10.68 k ohms.	15 V 1.9 V	0.04 A 0.10 A*	Anode-Graphite Cathode - Ni	Reduced electrode spacing from 20mm to 6mm. Electrolyte fully molten. Preheated melt to 650 prior to electrolysis at 580 C. This avoided the formation of crust. * Reading after switching electrodes.
12	NaF = 9.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =2 %	27.14 gms.	675 C	605 C	0.8097 k ohms.	1.6 V 1.8 V 2.0 V 2.1 V 2.5 V	0.10 A 0.20 A 0.30 A 0.40 A 0.50 A	Copper	Electrode Spacing - 8mm. Preheated melt to 725 C before electrolysis. No crust. Electrolyte surface orange in color. Electrodes shorted by metal deposition. Anode was corroded. Si deposited on the cathode.
13	NaF = 8.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =3 %	29.314 gms.	675 C	-	.2 k ohms.	1.6/1.7 V 1.8	0.10 A 0.20 A	Copper	Electrodes shorted by metal deposition. Anode was corroded. Electrode spacing - 19mm. Tried to use liquid N2 to trap Br2. But froze argon instead. Hence used dry ice in cold trap. No success. Analysed KBr trap microscopically. Observed KF.
14	NaF = 8.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =3 %	30.611 gms.	675 C	-	12.23 ohms.	1.3 V 1.6/1.7 V	0.10 A 0.20 A	Inconel	Electrolyzed for only one hour to avoid shorting of electrodes, at low current. Cathode had large Si deposit. Anode was corroded. Cathode deposit had 3 layers. Innermost layer was black. (Si?) Second layer was brownish. (Ni?) Outermost layer appeared to be molten salt. Electrodes pulled out of the melt before cooling down.
15	NaF = 8.5 % KF = 42 % LiF = 46.5 % Na2SiF6 =3 %	31.6375 gms.	650 C	599 C	57 ohms.	0.8/1.0 V	0.20 A	Titanium	Electrode spacing - 19mm. The molten electrolyte had crept way up on the electrodes (due to 4% Si?). Corrosion of top plate (due to TiF4 vap?). Anodic deposit was purple.