LUNAR OXYGEN AND METAL FOR USE IN NEAR-EARTH SPACE: MAGMA ELECTROLYSIS

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Abstract

Because it is energetically easier to get material from the Moon to earth orbit than from the Earth itself, the Moon is a potentially valuable source of materials for use in space. The unique conditions on the Moon, such as vacuum, absence of many reagents common on the earth, and presence of very non-traditional "ores" suggest that a unique and non-traditional process for extracting materials from the ores may prove the most practical. With this in mind, we have begun an investigation of unfluxed silicate electrolysis as a method for extracting oxygen, Fe, and Si from lunar regolith.

The advantages of the process include simplicity of concept, absence of need to supply reagents from Earth, and low power and mass requirements for the processing plant. Disadvantages include the need for uninterrupted high temperature and the highly corrosive nature of the high-temperature silicate melts which has made identifying suitable electrode and container materials difficult.

Introduction

One consequence of Earth's relatively high gravity is a relatively high energy cost for launching material from Earth into space, even near-Earth space. Because of this, as the need for propellants and constructional materials in near-Earth space grows, materials available from extraterrestrial sources should become economically attractive. The Moon is the closest potential source of such material. Its gravity is only about one-sixth that of Earth, low enough to improve greatly the payload/liftoff mass ratio for conventional rockets but still high enough to facilitate separation and manufacturing processes.

We know from the Apollo missions what the compositions and physical states of common materials on the lunar surface are (see Heiken et al., 1990, for extensive information about the nature of the Moon and its materials and conditions). We can thus begin to design and develop processes for providing, from lunar sources, the

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propellants and constructional materials we expect to need in near-Earth space. In our laboratory, we have chosen to investigate electrolysis of (simulated) molten lunar soil, a technique sometimes called "magma electrolysis", as a means of producing oxygen, iron, and silicon (Oppenheim, 1968; Kesterke, 1971; Lindstrom and Haskin, 1979; Haskin et al., 1990). We have chosen to investigate this uncommon technique because lunar surface conditions are very different from Earth's. On the Moon there is no water, air, or fossil fuel to serve as inexpensive solvents, oxidizing and reducing agents, fuels, or heat transfer agents. There are no suppliers of chemicals and no infrastructure for living or transportation. This suggests that it may not be economical to transfer well understood terrestrial technologies to the Moon's surface.

The Moon has sunlight (half the time), hard vacuum, and plentiful clinging dust (lunar "soil"). Production of useful materials from lunar resources is likely to prove economical to the extent that we learn how to take advantage of these conditions. Also, we must require that little material be brought from Earth to the lunar surface in relation to the quantities of product obtained. This is true because the principal anticipated cost of using lunar materials is that of lifting the necessary factories and equipment to process them from the Earth to the lunar surface. Therefore, reduced costs of transportation from the Earth to low-Earth orbit (which is the energy-expensive portion of the journey from the Earth to the Moon) will almost equally reduce the cost of using lunar materials in near-Earth space.

Because the Moon is largely unexplored, we do not know what specialized resources may be available. The only abundant resource we can presently count on is the common surface soils (regolith), whose average depth is unknown but probably exceeds three meters (Heiken et al., 1990). These soils are a good resource, containing some 45% (wt.) oxygen and 21% silicon, and up to 15% iron, 14% aluminum, 10% calcium, 6.6% magnesium, and 4.8% titanium, with the highest values for iron, magnesium, and titanium being in mare soils and those for aluminum and calcium in highlands soils (Heiken et al., 1990). The soils also contain minor proportions of sodium, chromium, manganese, metallic iron-nickel alloy (of meteoritic origin), and large quantities (at very low concentrations) of hydrogen, nitrogen, carbon, and noble gases (of solar wind origin; these can be extracted by heating the soil) (Haskin, 1990). All of the chemical elements are present in the soils, but most are present at very low concentrations.

We suggest that the earliest technologies for extraction and processing of extraterrestrial materials for early use in near-Earth space will have the following characteristics (Haskin, 1985; Haskin and Colson, 1990): They will come from a nearby source, most likely the Moon. They will have few and simple steps. They will require minimal material from the Earth. They will be reasonably automated, requiring only occasional tending. They will use an easily mined material as feedstock (probably lunar soil) and be able to accommodate a range of feedstock compositions.

We chose silicate electrolysis for study because of its apparent simplicity. The electrolytic cell could operate in batch mode, or may operate efficiently in continuous mode. We anticipate that it may need no moving parts. It can use lunar soil as feedstock, with no more preprocessing of the soil than sieving out of gravel and cobbles that might damage the cell before they could melt. (The bulk of the lunar soil is quite fine grained; gravel will be a scarce commodity on the Moon and we probably cannot afford to melt it.) We believe that silicate electrolysis can

convert the feedstock to oxygen and metal with high efficiency, some 40% oxygen and metal by weight. Our best current estimate is that its operation will require about twice as much energy as the theoretical minimum necessary to enable the chemical separation. In principle, the cell could operate on solar power during the lunar day, but for initial simplicity nuclear power seems preferable. The main problems are the high operating temperature (1,200 - 1,600°C) and the materials problems associated with corrosive, molten magma.

Review of Process Theory

The process theory is described in detail by Haskin et al., 1990, but we provide a brief review here. The cathode reactions that produce metal are the following:

$$Fe^{2+} + 2e^- = Fe^o \tag{1}$$

$$Si(IV) + 4e^- = Si^o \tag{2}$$

There is a competing reaction if the oxygen pressure is allowed to build up above the cell:

$$O_2 + 4e^- = 2O^{2-} \tag{3}$$

However, this reaction is not significant for oxygen fugacity less than about 10^{-3}. Other competing reactions include the reductions of trace and minor metals, such as Cr, Ti, Mn, and Ni, in the silicate melt.

At the anode, the principal desired reaction is the reverse of equation (3). However, this reaction is not significant because of low O^{2-} concentration and slow kinetics of formation of O^{2-} from silicate polymer chains. Therefore, the actual reaction during electrolysis involves oxidation of silicate polymer chains to form oxygen in the neutral state (Haskin et al., 1990). This process increases the extent of polymerization of the silicate. A serious competing reaction at the anode in melts with high iron concentrations is oxidation of Fe^{2+}.

$$Fe^{2+} = Fe^{3+} + e^- \tag{4}$$

Other competing reactions at the anode include oxidation of other multivalent cations such as Ti and Cr. Because reaction (4) is the primary competing reaction at the anode, the efficiency of oxygen production (defined as moles O_2 produced/4·moles electrons passed through the melt) depends primarily on the concentration of Fe^{2+} cations. The dependence of oxygen production efficiency on Fe^{2+} concentration can be expressed as $\%O_2/(100-\%O_2) \approx 0.049/X_{FeO}$, where $\%O_2$ is the oxygen production efficiency in percent and X_{FeO} is molar fraction FeO in the melt. This has the consequence that electrolysis to produce oxygen as a main product is most efficiently carried out in melts with relatively low iron concentrations (<2%).

Power to drive the electrolysis equals E*I, where I is the current required to get oxygen at the desired rate and is proportional to oxygen production rate/oxygen production efficiency. This demonstrates the dependence of power requirements on oxygen production efficiency. E is the potential required to drive the electrolysis and is equal to $E_c-E_a - \eta_c-\eta_a -I(R_{cell})$, where E_c-E_a is the potential required to drive

the reaction(s) and is a function of the cation reduced ($|E_c-E_a|$ increases in the order Fe < Si,Ti <Mg,Al < Ca) and the concentrations of the cations in the melt. The quantity $-\eta_c-\eta_a$ is the overpotential required because of slow reaction kinetics or, as we use it in this paper, because of cation mobility problems (inability of cations to migrate to the cathode fast enough to yield the desired production rate). R_{cell} is the resistance of the electrolysis cell and is equal to $L/\kappa A$ where L is the distance between electrodes, A is the electrode surface area, and κ is the melt conductivity. This expression illustrates the dependence of power on both cell configuration and resistivity of the molten feedstock. Not unexpectedly, κ is found to increase as the average ionic mobility of the melt increases. That is, κ increases systematically as mobile cations such as Fe, Mg, and Ca increase relative to Si and Al in the melt.

The electrolysis scenario for batch cell operation would be as follows: At low values for E_c-E_a (-0.7 to -1.3V), Fe is reduced at the cathode. As Fe is removed from the silicate melt, oxygen production efficiency increases and conductivity decreases, with a combined effect of increasing power requirements for oxygen production. Then, once Fe is nearly depleted, E_c-E_a is increased to more negative potentials (<-1.4V) and Si and Ti are reduced at the cathode. Because Fe has already been removed, oxygen production efficiency is high, and conductivity increases as SiO_2 is removed from the melt, resulting in a sharp drop in power required to produce oxygen. Theoretically, Mg, Al, and Ca could also be reduced at even more negative potentials.

Evaluation of the silicate electrolysis process and comparison with alternatives

The silicate electrolysis method for extracting oxygen from lunar regolith has several advantages over alternative processes. These include the absence of any need for reagents that must be brought from earth or recovered from the products; the wide range of feedstock compositions that are acceptable, and the lack of need for preprocessing of the feedstock; and the conceptual simplicity of the process. The primary disadvantages include the need to find durable materials for containers and electrodes in these high-temperature (1200-1600°C), highly corrosive silicate melts, high startup temperatures, and the need to keep the cell hot during the lunar nights.

In order to place what we know about the silicate electrolysis method into a context readily compared with other processes, we have identified several key questions to address. These are the following: How much power is required to produce a given amount of oxygen? What plant mass is required to produce oxygen at a given rate? What feedstock is required; is it a common lunar material or will it require location and ore-body verification? What preprocessing of lunar material is necessary to prepare it? What fraction of the feedstock is converted into products? What reagents are required for the process and at what rate must they be replenished? How complex is the process and how many steps does it involve? What is the product(s) of the process? What technology must be developed before the process is viable? What must yet be learned about the theory of the process before any or all of the questions above can be answered?

The complex dependence of the answer to one question on answers to others makes comparisons among proposed processes difficult. For example, if one process yields a more pure product than another, or more products, what is this worth in terms of

power required, plant mass, or process complexity? Also, how do we judge a promising but undeveloped technology, or technologies at different stages of development? If a problem in developing a technology cannot be solved quickly enough, then the process is not viable however promising its other aspects may be. Alternatively, once the problem is solved then the relative worth of the process is measured in terms of its other aspects. Despite these difficulties, the discussion below gives some grounds for evaluating the silicate electrolysis process and comparing it to alternative processes.

Power requirements:
Power requirements for any of several proposed processes for extracting oxygen can be divided into two categories, thermal and electrical, with electrical power supplied by a power plant, either nuclear or solar, while thermal power can be supplied, at least for some applications, by direct solar power and therefore is somewhat cheaper in terms of plant cost, mass required, and plant upkeep. The power required by silicate electrolysis is entirely electrical, with resistance heating in the magma supplying sufficient heat to melt new feedstock which might have otherwise been melted by direct solar energy. (If a batch mode is utilized, then initial melting could possibly be done by direct solar energy.)

The power required for silicate electrolysis is a function of electrode surface area, distance between electrodes, and composition of the magma (effecting the oxygen production efficiency and magma resistivity). Therefore, the power required can be decreased as we accept a greater plant mass, a greater possibility of shorting the electrodes (as the electrodes are moved closer together), and a more specialized feedstock. By choosing a reasonable trade-off among these variables we can derive a reasonable value for energy required per unit oxygen produced. The value reported by Eagle Engineering (1988) is about 15.6 MWh/MT oxygen. The value reported by Haskin et al (1990) is somewhat less at 13 MWh/MT oxygen (but does not included energy to compress oxygen, acquire and handle feedstock, etc.).

This value is about twice the theoretical minimum energy to extract oxygen and reduced Fe and Si in basaltic silicate melts. This value compares favorably with energy values reported for extracting oxygen by other processes, most of which require 2 to 4 times the theoretical minimum (e.g. Eagle Engineering, 1988). Some reports for very low energy requirements of 5 MWh/MT oxygen for hydrogen reduction of ilmenite have been made (Table 4.1, Eagle Engineering, 1988). This is almost identical to the theoretical minimum and probably can not be practically achieved. We point out that the theoretical minimum for getting oxygen from ilmenite is about 25-35% less than that for getting oxygen from basaltic melt (assuming both Fe and Si in melt are reduced), but this difference is not large compared to the uncertainties intrinsic in estimating the power that will be required for any particular process. Also, this estimate does not include the energy to preprocess the starting material to produce the ilmenite.

Plant mass:
Because of the few processing steps involved in silicate electrolysis and the simplicity of the process, the plant mass compares favorably with those for other processes. If we consider that accessory masses such as oxygen collecting facilities, material handling facilities, power plant mass, etc. are common to most processes, then we can reduce the comparison to one of the processing plant masses only. Most of the mass for the silicate electrolysis process is in the electrodes, magma containers,

electric busses, and the insulation/heat radiators. We have estimated this to be on the order of 3-10MT for 1000 MT oxygen/year. This is considerably less than the 20-80 MT expected for most other processes. However, if facilities are included to separate the components of the Fe-Si-Ti-Cr alloy product of silicate electrolysis, mass requirements might be increased to values comparable to other processes. Also, a considerable portion of the plant mass for silicate electrolysis may be in the form of Pt, an exceptionally expensive material, because Pt is the proposed anodic material. However, the cost of the Pt is small compared to the launching costs of greater masses of material.

Feedstock requirements:
In theory, the silicate electrolysis process can accept feedstock of nearly any composition with little or no preprocessing. The primary constraints are the efficiency of oxygen production, which decreases with increasing Fe in the melt, increasing power requirements, and the resistivity, which increases with increasing SiO_2 and Al_2O_3 in the melt, again increasing power requirements. Also, if the liquidus temperature of the melt were to rise above the temperature at which the electrolysis is done, the presence of crystals in the melt would further increase resistivity. However, a steady state residual melt may be achievable, which would act as a fluxing agent to buffer the efficiencies, resistivities, and liquidus temperature of the melt, thus making the process nearly independent of feedstock within the limits of lunar regolith compositions. Minimal monitoring of feedstock or product composition might be necessary so that temperatures and electrode potentials could be varied to maintain the composition of the residual flux within reasonable limits.

Reagents required:
The silicate electrolysis process requires no reagents that need to be supplied from Earth or recovered from the process.

Complexity of process:
Magma electrolysis is essentially a one step process taking place in one reaction pot. As such, it is one of the simplest processes proposed. Keeping the process simple is important for several reasons, including being easier to automate, fewer replaceable parts needed, and fewer things to go wrong with the operation, leading to less down time and fewer people needed to operate the plant. Simplicity can also decrease development time and cost. Fewer processing steps is also an advantage in that it generally results in lower mass requirements. We also note that because theoretical energy requirements to extract oxygen from a given composition are the same regardless of the process chosen, fewer steps give fewer opportunities for energy loss. The simplicity of the process is generally recognized as one of the main advantages of the silicate electrolysis method over other approaches. However, as already pointed out above, if pure metal products such as pure Fe or Si are desired, additional purification steps need to be added to the process necessarily adding to its complexity.

Products:
We have identified several basic products of silicate electrolysis. The main products are oxygen, produced at the anode, and a suite of metals and metal alloys produced at the cathode and consisting of Si, Fe, or Fe-Si alloys containing 0.2-1% Ti and Cr. The metal compositions vary as a function of imposed potential and magma composition. (Theoretically, but not yet observed in our experiments, Al, Mg, and

Ca could be reduced at increasingly negative potentials and at higher melt temperatures.) The mineral spinel precipitates from the residual melt at sufficiently low temperatures or with sufficient removal of SiO_2. This material varies in composition from Fe-Cr rich spinel to Mg-Al rich spinel depending on the composition of the magma and extent of electrolysis.

The remaining molten silicate would be an important byproduct; it can be cast into bars, sheets, beams, etc., or its CaO-MgO enriched composition may make it suitable for use in cements. So-called "waste heat" carried off with the products or radiated by the cell is another potentially useful byproduct.

Status of technology development:
We have determined that the products and efficiencies of silicate electrolysis are sufficient to justify engineering demonstration of technological feasibility. Here, we mention several problems that such experiments must address. The most critical is to test materials to serve as container, anode, and cathode, as nearly all metals and ceramics are corroded by these high-temperature silicate melts. We have in mind four general types of possible electrode or container materials.

One type of material is simply inert to the silicate and its products. As an example, Pt has been used extensively in experimental petrology as inert containers for silicate melts at high temperature. However, Pt combines with Si to form an alloy that melts below 1,000°C and is unsatisfactory as a cathode or container. Pt appears to be a suitable anode material, however (Haskin et al., 1990).

The second type of material involves a steady-state equilibrium. An "iron skull" container or cathode could be formed by balancing the heat generated by the electrolysis with heat lost to the surroundings to form a solid skin of product or feedstock enclosing the silicate melt and metal product. High melt resistivities (Haskin et al, 1990) coupled with the large distance between electrodes that would seem to be required to make the approach robust might make power requirements prohibitive for cathodes, but the cell container might be made in this fashion.

The third type of material would be in thermodynamic equilibrium with the silicate melt and electrolysis products and would therefore not react with them. Because the product is Si-Fe metal, Fe-Si alloys might serve as the cathode material (Haskin, et al., 1990). Similarly, the presence of spinel $(MgAl_2O_4)$ on the liquidus of the residual silicate of the electrolysis process suggests the use of spinel as the containing material.

The fourth type of material would be destroyed by the process, but slowly. This option detracts from one of the intended advantages of unfluxed silicate electrolysis, the absence of any need to resupply reagents or other materials from Earth or to recover them from the products. Nevertheless, such an option may prove to be the most cost effective.

Theory:
We now understand in some detail the chemistry of the oxidation-reduction reactions involved in the electrolysis of silicate melts (Semkow and Haskin, 1985; Haskin et al., 1990). This includes identifying the reactions involved and studying their kinetics,

evaluating the dependence of oxygen production efficiency on melt composition, and determining the resistivities of melts as a function of composition.

We are now studying dynamic problems in the electrolysis and how they relate to overpotentials needed to drive reductions in the melt. We are studying whether material flow and thermal convection in a cell can keep fresh material at the electrodes or whether active mixing will be necessary. We are studying the effects of overpotential on product composition; preliminary experiments have yielded a metal with somewhat lower Si/Fe ratio than expected. Remaining uncertainties in activities of melt components still present a small but possibly significant uncertainty in estimating power requirements and product compositions.

Conclusions

Unfluxed silicate electrolysis offers several advantages over alternative processes. These include simplicity of the process and the absence of a need to supply reagents from earth. Power and mass requirements for the process are competitive. The main unsolved problems center around testing of materials to serve as cathode and container in high-temperature silicate melts. However, little work has been done in the way of engineering studies. This work needs to be done before we know whether the theoretical simplicity and efficiency of the silicate electrolysis process is also a practical simplicity.

Appendix I: References

Eagle Engineering, Inc (1988). *Conceptual design of a lunar pilot plant lunar base systems study (LBSS)*. EEI report No. 88-182.

Haskin, L. A. (1985). "Toward a Spartan scenario for use of lunar materials." In *Lunar Bases and Space Activities of the 21st Century*, (ed. W. W. Mendell), 435-443.

Haskin, L. A. (1990). "Water and cheese from the lunar desert: Abundances and accessibility of H, N, and C on the Moon. In *Lunar Bases and Space Activities of the 21st Century (II)*, (Ed. W.W. Mendell). (in press)

Haskin, L. A. and Colson, R. O. (1990). "Lunar resources: toward living off the lunar land." *Proceedings of the first annual invitational symposium of the UA/NASA Space Engineering Research Center for Utilization of Local Planetary Resources*. (Ed. T. Triffet) (in press).

Haskin, L. A., Colson, R. O., Lindstrom, D. J., Lewis, R. H., and Semkow, K. W. (1990). "Electrolytic smelting of lunar rock for oxygen and iron." In *Lunar Bases and Space Activities of the 21st Century (II)*, (Ed. W.W. Mendell). (in press)

Kesterke, D. G. (1971). *Electrowinning of oxygen from silicate rocks*. U.S. Bureau of Mines Report of Investigations 7587.

Lindstrom, D. J. and Haskin, L. A. (1979). "Electrochemical preparation of useful material from ordinary silicate rocks." In *Space Manufacturing Facilities*, (eds. J. Grey and C. Drop.) AIAA, 129-134.

Heiken G., Vaniman, D., and French, B (eds) (1990). *Lunar Sourcebook*. Oxford University Press. (Accepted for publication.)

Oppenheim, M. J. (1968). "On the electrolysis of molten basalt." *Mineral. Mag.* 36, 1104-1122.

Semkow, K. W. and Haskin, L. A. (1985). "Concentrations and behavior of oxygen and oxide ion in melts of composition $CaO \cdot MgO \cdot xSiO_2$." *Geochim. Cosmochim. Acta* 49, 1897-1908.