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P. 7

Extraction of Volatile and Metals From Extraterrestrial Materials

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Abstract

Since 1 March 1989, we have concentrated our attention on the extraction of ilmenite from extraterrestrial materials and on the planning and development of laboratory facilities for carbonyl extraction of ferrous metal alloys. Work under three subcontracts was administered by this project: electrolytic production of oxygen from molten lunar materials (L. Haskin, Washington University), microwave processing of lunar materials (T. Meek, University of Tennessee), and production of a resource-oriented space science data base (D. Davis, Planetary Sciences Institute).

Introduction

As the first principal target of SERC's research, the production of propellants from nonterrestrial materials, especially those found on the lunar surface, has necessarily been the focal point of much of our research activity. Since the large majority of the mass of an H/O propellant (89%) is liquid oxygen, and since programmatic considerations seem to favor relatively early operations on the Moon, the focus of efforts within this program has been the production of oxygen on the Moon. Our research group has participated in this program in two very different ways. First, we have studied the prospects for extracting reactive FeO-bearing minerals suitable for oxygen production from the lunar regolith, concentrating on the properties and extraction physics of ilmenite and the preparation of suitable stimulants for lunar-derived ilmenite. Second, we have searched for simple ways to coproduce other products along with oxygen, so as to maximize the total yield of useful products per unit energy expended. This latter search has exposed ferrous metals and refractory oxides as the most likely products to accompany lunar oxygen production. We have chosen to begin this effort with an experimental investigation of the use of the gaseous carbonyl process for recovery of ferrous metals in conjunction with the ilmenite reduction and melt electrolysis schemes for lunar oxygen production.

Lunar Ilmenite and Simulants

As the result of a continuing literature search, several major concerns regarding proposed schemes for oxygen production from lunar ilmenite have been identified. These are the effects of other minerals on oxygen production, the chemical nature of simulants of lunar ilmenite, procedures for beneficiation of ilmenite from lunar regolith

feedstocks, and the merits of using lunar fines versus lithic fragments as the source of ilmenite.

Effects of Other Minerals. Hydrogen reduction experiments by Williams (1985), using terrestrial ilmenite simulants containing trace amounts of iron sulfides, has demonstrated that small amounts of sulfur have dramatic effects on the ilmenite reduction process. During hydrogen reduction of the simulant, hydrogen sulfide formed along with water vapor in such quantity as to force the termination of the experiment. When such a mixture is electrolytically decomposed to regenerate hydrogen and oxygen, sulfur is oxidized to sulfur trioxide and forms sulfuric acid, which is highly corrosive. Since lunar soils typically contain approximately 0.5 wt% of the sulfide mineral troilite (stoichiometric FeS) (Vaniman et al. 1989), some method of removing sulfides from the feedstock must be devised. Because both troilite and lunar ilmenite are nonmagnetic (*stoichiometric* FeS is antiferromagnetic whereas familiar terrestrial pyrrhotite is ferrimagnetic), and since both minerals have nearly the same density, devising an adequate separation scheme is not trivial. Pre-oxidation of the sulfide by roasting to release sulfur dioxide is a possibility, but this necessitates more complexities: either (a) the SO₂ must be discarded, which wastes oxygen, or (b) it must be further reacted to make sulfuric acid *for process use*, which apparently requires the demonstration of a whole new family of processes in which some practical and profitable use can be made of the sulfuric acid, and in which the sulfuric acid can be recycled. This introduces a wholly unwanted set of complications into what was intended to be a simple, early processing scheme to make oxygen.

Simulants. Lunar ilmenite is almost stoichiometric FeTiO₃ and, hence, contains no ferric iron. Therefore, terrestrial ilmenite, which is a solid solution of Fe₂O₃ in FeTiO₃, is not a good thermodynamic or kinetic analogue of lunar ilmenite. Synthetic ilmenites are useful for determining the effects of minor substitution of other (lunar) constituents of the kinetics of ilmenite reduction. The most abundant solute in lunar ilmenite is MgTiO₃, which is never the dominant impurity in terrestrial ilmenites. Synthetic ilmenites, although useful for kinetic studies, do not suffice either for beneficiation experiments or for determining the effects of other native lunar minerals on the reduction process.

In the search for a better, more relevant analogue of lunar ilmenite, we have considered in some detail the use of many different types of meteorites. The closest analogue is found in the eucritic (basaltic) meteorites, ilmenite-bearing rocks with overall chemistry and oxidation state similar to lunar basalts. Indeed, with respect to oxidation state, the eucrites are known to be formed under conditions strikingly similar

(but not identical) to those under which lunar basalts formed, at far lower oxygen fugacities than terrestrial basalts. Table 1.4 compares the composition of lunar and eucritic ilmenite.

Table 1.4 Composition of natural lunar and eucritic ilmenites.^a

Moiety	Lunar		Eucritic	
	Mean	Range (wt%)	Mean	Range (wt%)
FeO	43.3	35.20 - 47.70	44.20	42.80 - 45.00
TiO ₂	52.7	49.90 - 55.50	52.80	52.50 - 53.00
Al ₂ O ₃	—	0.10 - 0.30	0.06	0.03 - 0.11
Cr ₂ O ₃	0.64	0.50 - 2.12	0.09	0.03 - 0.27
MgO	2.23	0.00 - 9.50	1.05	0.46 - 2.35
MnO	0.42	0.00 - 0.95	0.88	0.82 - 0.93
CaO	—	0.00 - 0.30	0.10	0.03 - 0.16

^aLunar data from a compilation of 133 ilmenites from high-Ti basalts (Vaniman et al. 1989), except for Al₂O₃ and CaO, which are Apollo 11 ilmenites (Masan and Nelson 1970). Ilmenite data for eight eucrites are from Bunch and Keil (1971).

Beneficiation. Due to its lack of ferric iron, lunar ilmenite has a low magnetic susceptibility, similar to that of the coexisting silicate phases. Attempts to beneficiate eucritic ilmenites (which also lack ferric iron) magnetically were unsuccessful. It appears that electrostatic separation is the most viable presently conceived technique for use with lunar feedstocks. The amount of recoverable ilmenite in the lunar soils (about 1-2% ilmenite) is far lower than in high-titanium basaltic rocks (8-16%) (Vaniman, personal communication). Moreover, experiments by William Agosto have shown that electrostatic separation experiments on terrestrial soil simulants *lacking agglutinates* (shock-fused glass and rock fragments) produced fairly satisfactory enrichments of ilmenite. This suggests that lithic fragments from high-titanium basalts may be a much better ilmenite source than soils.

Unfortunately, the use of rocks as a feedstock requires a crushing step before beneficiation, and crushing may not, by itself, efficiently liberate single ilmenite grains. During a recent attempt to separate ilmenite from a crushed eucrite, the rock did not disaggregate cleanly along grain boundaries and most of the ilmenite remained trapped in composite grains. In addition, a serious "static cling" problem was observed, in which individual mineral and composite grain-sized lithic fragments were coated with a fine adherent dust produced during crushing. This coating introduced a large amount

of contamination, including FeS, into even the "ilmenite grain" fraction. This problem is traditionally combated by passing moist air over the material, a solution most inappropriate for use on the Moon. Further, static (and van der Waals) adhesion of particles is likely to be much more severe in the lunar environment than in our laboratory, since lunar grains lack adsorbed multilayer coatings of "sticky" (high-dipole-moment, easily condensed, or highly polarizable) gases that, on Earth, inhibit the "welding" of these grains to each other at their points of contact. At the very least, study of a variety of methods of disaggregating strong rocks is needed.

Ferrous Metal Extraction

Extraction and use of nonterrestrial ferrous metals is very attractive for several reasons that are quite unrelated to the terrestrial mining experience. First, the iron-group elements are extremely abundant in the solar system. The terrestrial planets, their moons, and the asteroids are generally about 30% iron and nickel by mass. Further, these elements are often found as native metals, instead of being tied up in thermodynamically stable oxides and sulfides as they are in Earth-surface ore deposits. Indeed, some belt asteroids, and even one near-Earth asteroid, have reflection spectra characteristic of pure native metal. The amounts of ferrous native metals available in nearby space are not trivial; one of the metallic (M-type) asteroids in the belt, 16 Psyche, has a diameter of 250 km. If the surface composition is representative of its interior, Psyche contains about 6×10^{16} tonnes of ferrous native metals, equivalent to 200,000,000 years of global iron and steel production at present rates.

On a more modest scale, several opportunities for acquiring ferrous native metals for early use in space present themselves. First, there are native metals found in the lunar regolith, both tiny fragments of asteroidal metal from the explosion of impactors and nearly pure elemental iron made by reduction of lunar FeO-bearing minerals by solar wind-implanted hydrogen. These forms of native metals make up about 1000 ppm of the regolith, most of which is readily extractable by a magnetic rake. Second, the ilmenite reduction process leaves an intimate, partly sintered mixture of metallic iron and the titanium oxide rutile (TiO_2). Each ton of oxygen extracted leaves behind 4.5 tons of metallic iron, 5.7 tons of rutile, and an unknown amount of unreacted ilmenite and dross. Third, electrolysis of molten silicates produces a cathode deposit of metals, dominantly iron during the early stages of electrochemical reduction. The mixed metals in the cathode deposit also include nickel, cobalt, chromium, and manganese, all of which form gaseous carbonyls. Further electrolysis produces abundant silicon, leaving a refractory oxide melt rich in calcium, magnesium, titanium, and aluminum.

Beyond the Moon, asteroids are abundant, rich sources of ferrous native metals. Concentrations of 10 to 30% by weight of native metals are typically present in undifferentiated (chondritic) meteorites, and many asteroids in the inner part of the belt have metallic (M-type) reflection spectra. There is even a near-Earth asteroid that has an M-type spectrum. These bodies may be up to 99% native ferrous metal alloy. The concentration of free metals in the **average** meteorite is about 20%, some 200 times as high as in the lunar regolith.

In order to extract and purify these metals with minimal energy consumption, it is highly desirable to avoid forming intermediate compounds that are strongly bonded. Attractive schemes include physical separation by magnetic beneficiation and volatilization by the gaseous carbonyl process. Efficient magnetic separation, even in the case of the lunar regolith, requires crushing to a fine enough size to liberate particles of metal. Both native metal minerals, kamacite (alpha iron; 4 to 7% Ni content) and taenite (gamma iron; 20 to 60% Ni), are ferromagnetic, as are the widespread trace minerals schreibersite, $(\text{Fe,Ni})_3\text{P}$, and cohenite, $(\text{Fe,Ni})_3\text{C}$. The sulfide mineral troilite, FeS, is antiferromagnetic and, hence, follows free metals during magnetic extraction only because of the common textural association of FeS with metal in intergrowths. In carbonaceous chondrites, the metals are progressively oxidized, culminating in zero free metal and abundant magnetite in the highly oxidized, carbon- and volatile-rich Ci chondrites. Magnetite is ferrimagnetic and, hence, it is almost as easily extracted as free metal. Strong heating of CI chondrites leads to extensive autoreduction, with release of carbon oxides and water and the formation of metallic iron.

Gaseous carbonyl extraction is appealing for several reasons (Lewis et al. 1988): The only reagent necessary is carbon monoxide, which is released upon heating every known class of meteorite. The compounds formed, principally iron pentacarbonyl and nickel tetracarbonyl, are weakly bonded, can be readily separated from each other by distillation, and can also be readily separated into their component elements by gentle thermal decomposition (or by isothermal pressure reduction). Separation of ferrous metals is not practical in any operation involving melting of a metal mixture. It is indeed remarkable that the low-energy route to ironmaking also gives a natural and highly effective route to making pure metal separates. This is very desirable, because it permits the formulation of a wide variety of alloy compositions.

We have surveyed the literature on the thermodynamics and kinetics of gaseous carbonyl formation and developed several designs for extraction systems. We have acquired several of the crucial components and will be assembling them in the near

future, so we can resume the experimentation we originally began in 1982. The ideal materials for the system construction are brass and aluminum, which are completely invulnerable to carbonyl attack. The initial experiments will be aimed at validating the safety and functional design of the system. Safety is paramount in handling carbonyls, because they are highly toxic. The next step will be the volatilization of pure samples of iron and nickel (and possibly cobalt, if we are confident in the reliability of the system at the high pressures necessary for cobalt carbonyl formation). We may then move directly to volatilization of meteoritic iron. Iron meteorite samples are available in large quantities and at low prices, and nothing is to be gained by lengthy and expensive excursions into simulant production and validation. Indeed, magnetic separates from chondritic meteorite powders are themselves very good first-order stimulants of lunar regolith native free metals and will permit us to prepare for requesting lunar samples for similar study.

We will then use native iron produced in ilmenite reduction experiments and mixed-metal cathode deposits from Haskin's electrolysis project as feedstock for the carbonyl extraction. Analytic services will be provided by Boynton (neutron activation) and by Ruiz (inductively coupled plasma mass spectrometer). Platinum-group metal extraction from the carbonyl volatilization residues will be carried out by Freiser's group (Strategic Metals Recovery Research Facility).

We are not presently planning extensive experimentation on fabrication of metal products in our laboratory. However, we have already begun discussions with Vaporform Products regarding collaborative research on codeposition of Fe/Ni alloys. They have the greatest body of expertise in the world on fabrication of nickel products by chemical vapor deposition (CVD) from gaseous nickel carbonyl, but have no experience with the effects of admixtures of iron carbonyl as an "extender." It is, however, well established that pure nickel tetracarbonyl produces nickel deposits ("castings") of excellent quality, whereas pure iron pentacarbonyl produces only a fine black powder of ultra-high-purity iron. The intermediate compositional regime is ripe for exploration. The facilities required for large-scale experimentation with mixed-carbonyl CVD are available only at their facility in Pennsylvania.

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*See Appendix C.