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# NASA Space Engineering Research Center for Utilization of Local Planetary Resources 

Annual<br>Progress Report 1989-90

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## EXECUTIVE SUMMARY

## EXECUTIVE SUMMARY

The University of Arizona and NASA have joined to form the UA/NASA Space Engineering Research Center. In its second year, the Center has successfully brought together leaders in the engineering fields and many space sciences to assemble the knowledge and develop the systems necessary for man to find a home in space.

The purpose of the Center is sharply focused: To discover, characterize, extract, process, and fabricate useful products from the extraterrestrial resources available in the Inner Solar System (the Moon, the Mars system, and nearby asteroids). During this reporting period, important progress has been made on the evolution of the "big picture" through a quantitative interdependent matrix that enables a visual display of the overall space mission when the components are specified. This development enables not only quick evaluations of the various candidates, but also provides quick guidance for promising avenues of research in order to reap the maximum benefit. For the first time, we now have a quantitative tool for evaluating the overall "Figure of Merit" of emerging technologies.

Early emphasis has been placed on minerals and the methods for processing them to provide propellants and life-support volatiles. At the same time, investigations into using the direct coproducts from these processes, such as metals and refractories, are underway. Manufacturing propellants near to where they will be used saves a significant percentage of the cost of space travel; local production of life-support volatiles saves in transportation costs and also lends greater flexibility to missions. The goal is to become self-sufficient for both these classes of materials.

Later projects must serve the long-range goal of investigating all potential lowtechnology, high-demand products for use in space, including not only propellants and life-support materials, but also construction materials (such as anhydrous "cements," metals, etc.), and refractory materials for furnaces and aerobrake construction.

Following this summary, individual progress reports covering each of these areas are included as updates on each group's work. They represent the current status of the field of space resources. The summary here includes highlights of our activities in the past year.

In an engineering sense, the first step in developing extraterrestrial sources of propellants is acquiring a firm understanding of the tradeoffs involved in making and using propellants under specific, realistic conditions compatible with foreseeable national plans in space. Dr. Kumar Ramohalli is leading this effort. Mario Rascon in Dr. Ramohalli's group has carried out a broad assessment of the performance characteristics of a wide range of fuel-oxidizer combinations using both frozen-kinetic and equilibrium models of the combustion process. This work provides a valuable reference point for a very wide range of future scenarios for use of non-terrestrial propellants.

Underlying these efforts are certain essential scientific investigations. Proceeding sequentially with the results of these, Dr. Tom Gehrels, from the Lunar and Planetary Laboratory at the University of Arizona, and his Spacewatch group have greatly improved their ability to find comets and asteroids through the permanent installation of a $2048 \times 2048$ CCD. During an early test of the equipment, team member Dr. David Rabinowitz visually discovered a new, fast-moving asteroid, 1989UP. Dr. Gehrels is
also working with SERC and ASPERA on the production of a book on space resources in the highly regarded University of Arizona Press Space Sciences Series.

Dr. Robert Singer's group, also from the Lunar and Planetary Laboratory, has been observing the full Moon using a Tucson-based telescope and lunar CCD-image processing to estimate concentrations of $\mathrm{TiO}_{2}$ on the lunar surface. Areas of high concentration may make good landing sites; for example, high titanium dioxide concentration should be a good indicator of high abundances of lunar ilmenite, potentially a rich source of oxygen on the Moon.

Dr. Larry Lebofsky and Dr. Marcia L. Nelson at LPL have made spectral studies of several asteroids to determine their composition. They have also studied Mars' smaller moon Deimos, the asteroid Vesta, and the Moon to determine whether the Hapke reflectance theory can be applied to compositional analysis using these well-known bodies. Early results look promising.

Once useful bodies are found and characterized, propellants and volatiles can be derived from them. The first step is the actual mining and extraction of useful materials. Dr. Charles Glass is working with GPR (ground-penetrating radar) to see if it might prove useful in finding water on the Moon and Mars. GPR has a greater depth of penetration than do other radar techniques.

The next important step is production. Several techniques are being investigated for oxygen production, including several schemes for reduction of lunar ilmenite. The most widely discussed scheme for manufacture of oxygen on the Moon, hydrogen reduction of ilmenite, and several other related processes, such as carbothermal ilmenite reduction, are under broad study within SERC. The first challenge, to characterize lunar ilmenite and find or develop satisfactory simulants for it, is being addressed by Melinda Hutson in Dr. John S. Lewis' research group. After a lengthy search, she has found and purchased a large quantity of material from a basaltic achondrite meteorite, very similar to lunar basalt, that contains abundant ilmenite. These samples are the basis of experimentation on ilmenite beneficiation by Dr. Ruiz.

Dr. Joaquin Ruiz in the Geosciences Department is developing techniques for extracting the ilmenite. Some of these techniques are only for use in the laboratory for separation of ilmenite simulant used in the experiments conducted by Dr. Farhang Shadman's group. Dr. Ruiz is also working on both magnetic (ineffectual) and electrostatic (promising) separation techniques for beneficiation of ilmenite from crushed lunar (and meteoritic) basalts. The great difficulty of extracting pure (and FeS-free) ilmenite from the agglutinate-rich lunar regolith has led Dr. Ruiz into a more serious examination of the extraction of ilmenite from basaltic lithic fragments rather than directly from regolith fines.

Dr. Shadman's laboratory in the Chemical Engineering Department has refined the techniques for measuring the rate of reduction of ilmenite, both synthetic and natural meteoritic simulants, in preparation for the use of small samples of actual lunar ilmenite to verify the validity of the simulant behavior. They have successfully built and operated two reactor systems for these studies, and have already gained some insight into the kinetic factors limiting the reduction rate. Hydrogen, carbon monoxide, methane, mixtures of these gases, or carbon can be used as reducing agents.

Dr. Larry Haskin, of the Center for Earth and Planetary Sciences at Washington University in St. Louis, has made considerable progress on refining the conditions necessary to optimize production of oxygen through electrolysis of a molten sample of lunar regolith. Some interesting and complex chemistry seems to be occurring at the
anode and cathode; nonetheless, early results seem promising; for example, the energy cost per ton of oxygen produced by electrolysis now appears similar to that for reduction of ilmenite.

Dr. Jibamitra Ganguly of the Geosciences Department is developing the computational tools for modeling the equilibrium chemistry and kinetic behavior of heated carbonaceous chondrite material. These calculations are supported by experimental work on the dehydration kinetics of relevant OH -silicate phases. A goal is to develop a computational model that reproduces experimental results on volatile release from carbonaceous meteorites and their component minerals. Such a model can then be used for preliminary process design for the extraction of volatiles from carbonaceous asteroids and the Martian moons Phobos and Deimos.

Dr. David C. Lynch in the Department of Materials Science and Engineering is investigating another innovative process for extraction of oxygen from ilmenite by plasma-enhanced chlorination. An apparatus has been built and experiments have been conducted that clearly demonstrate benefits of chlorination of ilmenite. Similar reduction of ilmenite by a hydrogen plasma is also under study.

A promising scheme for the production of an atomic chlorine plasma by absorption of highly concentrated sunlight is also under study by Dr. Lynch, Donald E. Osborn, and Dr. Rocco Fazzolari of the Solar Energy Research Facility of the Department of Nuclear and Energy Engineering. Their experimental apparatus has been designed and built, and will be ready for use in the immediate future.

In a final project concerning lunar volatiles, Dr. Timothy Swindle of LPL and Dr. Charles Glass are carrying out a study of the distribution and extraction of Helium-3 from the lunar regolith. This is contract work not supported by NASA, but indicates an important interest and potential future direction for SERC research.

Dr. P. E. Nikravesh has developed a numerical model for mixing the components of propellants in rockets. In a closely related study, Dr. T. L. Vincent's group has also studied the automatic control of temperature during propellant processing for the purpose of making propellant processing hardware more amenable to automation.

Investigations concerning structural materials are also progressing well. A team at SAIC (San Diego) has studied the feasibility of producing large solar reflectors from endogenous lunar materials.

Dr. C. S. Desai, from the Department of Civil Engineering at the University of Arizona, is in the process of determining if concrete-like materials can be made without water from lunar-type soils. Applications of various vacuums and cyclic loading are being used to find if particles of these materials can combine in such a way as to yield a material with adequate strength and deformation properties.

Dr. Tom Meek, from the Department of Materials Science and Engineering at the University of Tennessee, has also been working with simulated lunar material. He is carefully trying to reproduce as many properties as possible of actual lunar material from the Apollo program in order to have a supply of material with which to test a microwave-sintering process he has developed. The sintered material may be useful for construction.

Dr. Henry Freiser, from the University of Arizona's Department of Chemistry and the Strategic Metals Recovery Facility, is working on the recovery in space of precious metals in the platinum group. He is currently using Earth-derived materials to refine his
methods; he has also established a data base on solvent extraction methods of metals separation. Eventually, his work could be used for extracting precious-metal byproducts from oxygen production on asteroids and the Moon.

Another major pursuit might best be called "major enabling technology." Each of these individual processes must be optimized within the overall constraints of the location and its resources, the energy cost of transportation, and the properties of the processing equipment and support systems. As mentioned, a Figure-of-Merit scheme dedicated to the assessment of the relative overall merits of different competing schemes for using those resources to make propellants is developed. In some cases, low-performance propellants have sufficiently modest equipment demands (such as no need for refrigeration of liquid hydrogen) that they are, overall, preferable to schemes that make higher performance propellants at the same site.

Dr. Rocco Fazzolari and Belinda Wong-Swanson have investigated a particular scheme for lunar oxygen production (hydrogen reduction of ilmenite) for the purpose of developing the tools for analyzing energy use and flow and total energy demand for the process. This is an essential prelude to the specification of energy sources for industrial use at the lunar base.

Finally, SERC is working on several fronts to develop data bases on the scientific data on space resources and the technology for processing them. Leo Masursky in Dr. Lewis' group, Dr. Andrew H. Cutler of SERC, the Planetary Sciences Institute, and Dr. David Criswell of the California Space Institute are all working on different aspects of the development of these data bases.

On the educational front, SERC has recently passed a significant education milestone with the award of its first Master of Science degrees. The Center actively participated, through an invited paper, at the 40th Congress of the International Astronautical Federation. A "first" in education has been achieved through the development of a senior/graduate-level course in space technologies, as was promised in the original proposal. This course has proved to be extremely popular and has the largest enrollment (51) of any elective course in the department. The structure is given in Appendix A.

This summary illustrates the intimate interrelatedness of the functions of SERC, spanning activities from the discovery of new space resources through development of new principles for the assessment of resource-related technologies.

## I. PROPELLANTS AND VOLATILES

 better, was also used.

## Background

With the high cost of putting payloads into orbit, the ability to reduce the size and weight of the payload is highly beneficial. Since the largest part of any space vehicle consists of propellant, it is hoped that the overall size and weight of the vehicle can be reduced by finding near-Earth-orbit materials suitable for use as fuels.

To this end, this work seeks to find propellants that will give acceptable performance, yet be producible or readily available in near-Earth orbit. Another possibility for fuels is the use of materials, such as nylon and rubbers, that would be taken for other purposes. Also considered is the need for the propellant to be easily stored over long periods of time while, ideally, avoiding the use of heavy refrigeration systems.

Although extensive research has been done on Earth-transported propellants that give high performance characteristics, very little work is available on propellants that give less than ideal performance. In addition to studying such overlooked propellants, low chamber pressures need to be considered to help reduce weight and high-pressure ratios, which can be achieved in atmospheres such as that of Mars. Some propellants considered unacceptable for use on Earth could be ideal for use since tradeoffs of performance for availability; storability, and cost are acceptable within the scope of this research.

[^0]
## Approach

We identified propellants that might be suitable for our purposes. These propellants have been divided into three areas: low-Earth orbit, the Moon, and Mars. The propellants were divided this way due to the availability of materials in these areas, such as $\mathrm{CO}_{2}$ in the Martian atmosphere. A range of chamber pressures was also determined for each of the above areas, along with a range of expansion ratios.

The CET 86 program was first set up on a mainframe so that the two personal computer versions could be compared for accuracy. One version was obtained from the University of Minnesota, and the second was obtained from AVCO. Both proved to give results identical to those of the mainframe version.

## Results to Date

Personal computer versions of the Gordon and McBride CET 86 program were obtained from the University of Minneosta and AVCO and set up on an IBM PS/2 Model 80. These two versions were compared to the mainframe version and were found to give identical results.

The Lockheed/Air Force Solid Propellant Theoretical Performance program was obtained and set up on an IBM PS/2. Since no mainframe version of this program was available for comparison, the CET 86 program was used to test the accuracy of the program. The Lockheed/Air Force program also proved to give accurate results.

Computer programs were written to help organize the data obtained from the CET 86 and Lockheed/Air Force programs into more useful forms. A commercially available plotting program, GRAPHER, was obtained for this purpose.

Twenty-one propellant combinations were analyzed using the CET 86 and Lockheed/Air Force programs. This generated over 1000 sets of data. Graphs were made of $\mathrm{I}_{\mathrm{sp}}$ versus oxidizer-to-fuel ratio for various pressure ratios for each of the propellants. The data were organized into presentable formats. Some samples are shown in Appendix B.

Summary
This work involves analyzing propellants at various operating conditions and determining which give acceptable performance, yet can be easily stored for long periods of time and are readily available in near-Earth orbit. We have found that a number of the propellants studied would give acceptable performance for space missions. Another graduate student is using the data obtained in this work to develop a method for identifying the propellants and operating conditions that are best for a

## I-3

particular space mission. So far, conditions in excess of 30,000 separate sets have been calculated.

## Participants

Jennifer Kares and Yamel Caquias, both undergraduate students, helped in analyzing the propellants. Jeff Kahl, also an undergraduate student, assisted in developing the various computer programs needed to process the data.
$52-75$
"Cold" Plasma Processing of Local Planetary Ores for Oxygen and Metallurgically Important Metals
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## Abstract

In the previous progress report for 1988-89, the utilization of a "cold" plasma in chlorination processing was described. This report is a continuation of that discussion, but is focused on the progress that has been achieved in the past 12 months. During that period, essential equipment and instruments were received, the experimental apparatus assembled and tested, and preliminary experiments conducted. The results of the latter lend support to the original hypothesis, namely, that a "cold" plasma can both significantly enhance and bias chemical reactions.

In two separate experiments, a "cold" plasma was used to reduce $\mathrm{TiCl}_{4}$ vapor and chlorinate ilmenite. The latter, reacted in an argon-chlorine plasma, yielded oxygen. The former experiment reveals that chlorine can be recovered as HCl vapor from metal chlorides in a hydrogen plasma. Furthermore, the success of the hydrogen experiments has lead to an analysis of the feasibility of direct hydrogen reduction of metal oxides in a "cold" plasma. That process would produce water vapor and numerous metal byproducts.

## Introduction

Those who read last year's report will note a change in title. This change reflects an expansion of the investigation as a result of supplementary funding (received October 1, 1989) from the U.S. Bureau of Mines. A focal point of that investigation involves hydrogen reduction of refractory oxides in a "cold" plasma. The results of that work are significant from both a terrestrial and extraterrestrial viewpoint and, thus, the results from the Bureau study are included in this report and will be included in all future reports.

The advantages associated with a "cold" plasma were discussed in the previous progress report. That material, although focused on chlorination processing, is applicable to hydrogen reduction. While there is no intention to repeat that material here, this report offers an opportunity to at least identify both the advantages and disadvantages associated with "cold" plasma hydrogen reduction in an extraterrestrial environment.

That discussion is followed by a description of the activities during the past year. The discussion includes a description of building activities, as well as a review of
preliminary experimental results. The progress report is concluded by a review of activities planned for the coming year.

## Hydrogen Reduction With a "Cold" Plasma



A "cold" plasma can generate a substantial concentration of monatomic hydrogen at low molecular temperatures. With conventional heating, the same effect can only be achieved at temperatures approaching $3000^{\circ} \mathrm{K}$ (see $1988-89$ progress report). The reduction of rutile with $\mathrm{H}_{2}$ is, for practical purposes, impossible, as the following thermodynamic data indicate:

$$
\mathrm{TiO}_{2}(\mathrm{~s})+2 \mathrm{H}_{2}(\mathrm{~g})=\mathrm{Ti}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}), \quad \Delta \mathrm{G}^{\circ}\left(1100^{\circ} \mathrm{C}\right)=83,962 \text { cal. }
$$

For all reasonable values for the partial pressures of $\mathrm{H}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$, the reaction involves an increase in the chemical potential of the system. In a "cold" plasma, monatomic hydrogen can react with rutile according to the reaction,

$$
\mathrm{TiO}_{2}(\mathrm{~s})+4 \mathrm{H}(\mathrm{~g})=\mathrm{Ti}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}), \quad \Delta \mathrm{G}^{\circ}\left(1100^{\circ} \mathrm{C}\right)=-53,750 \mathrm{cal} .
$$

The large negative standard Gibbs' energy for this reaction favors reduction of the metal oxide. Similar conditions exist for other lunar oxides.

The evolved water vapor leaves the reactor with the bulk gas, which is continually passed through the reactor. Removal of the water vapor prevents any back reaction. The water vapor can be condensed and purified for human consumption or electrolysis can be used to recover $\mathrm{O}_{2}$ and $\mathrm{H}_{2}$. The advantages and problems associated with the process are summarized in Table 1.1.

Table 1.1 Hydrogen reduction in a "cold" plasma.
Advantages

- Highly reactive environment Near $100 \%$ theoretically efficient use of $\mathrm{H}_{2}$
- No beneficiation of ore required
- Minimal equipment

Plasma reactor, condenser, and electrolytic cell

- Continous operation
- Numerous metal by-products


## Disadvantages

[^1]
## Results to Date

Experimental Apparatus. Construction of the experimental apparatus was completed during the past year. The apparatus, shown in Figure 1.1, consists of a microwave source; an applicator, where the plasma is generated, as shown in Figure 1.2; a gas delivery system; a mass spectrometer for monitoring the extent of reaction; an optical pyrometer for recording the temperature of the solid specimen in the plasma; a specimen holder that both rotates and allows for vertical translation of the solid specimen; and a vacuum system. The microwave unit, mass spectrometer, optical pyrometer, and vacuum system have been tested. As a result of testing, modifications have been incorporated in the system design and faulty equipment was returned to the manufacturer for repair.

Experimental Results. Equipment problems, unfortunately, delayed the experimental program. Some experimental results have been obtained, even with the delay. These results, although preliminary, lend support to the general hypothesis that a "cold" plasma can be used to enhance reactions and bias thermodynamics such that products can be formed from reactants that otherwise would not react.

Ilmenite heated in a plasma releases oxygen. Ilmenite was heated in both an inert and argon-chlorine plasma.* The results of those experiments are compared in Table 1.2, where the intensity of signal for $\mathrm{O}_{2}$ is tabulated as a function of power absorbed by the plasma. The results indicate that oxygen is evolved upon heating of the mineral in a plasma, but that significantly more oxygen is evolved with the chlorine present.

At an absorbed power level of 1 kw , rapid chlorination took place. At this power level, the reaction chamber was rapidly coated with metal chlorides. The results in Table 1.3 indicate that the chlorine was readily consumed.

These results are very encouraging, but preliminary. We are developing both proficiency and experience in operating the mass spectrometer and in evaluating the resulting data. In future reports, we expect to give all results in more meaningful terms, either as normalized intensities or mole fractions.

In another experiment, hydrogen was used to reduce $\mathrm{TiCl}_{4}(\mathrm{~g})$ for reaction with $\mathrm{Al}(\mathrm{I})$ in a "cold" plasma. The reaction involved formation of titanium aluminides and $\mathrm{HCl}(\mathrm{g})$. Thermodynamically, the reaction is impossible unless monatomic hydrogen is the reducing agent. These experiments revealed that radicals generated in a plasma can be used to bias a reaction and that ungrounded metal pieces can be placed in a

[^2]
# ORIGINAL PAGE COLOR PHOTOGRAPH 



Figure 1.1 Experimental apparatus.

(a) With Plasma

(b) Connected to Mass Spectrometer

Figure 1.2 Applicator where plasma is generated.

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Table 1.2 Experimental results for ilmenite: oxygen generation.

|  | Signal Intensitya |  |  | $\mathrm{O}_{2}$ (Arbitrary Units) |
| :--- | :---: | :---: | :---: | :---: |
| Power <br> (kw) | Nitrogen Plasma | Argon-Chlorine ${ }^{\text {b }}$ Plasma |  |  |
|  | $\mathrm{O}_{2}$ | O | $\mathrm{O}_{2}$ | O |
| 0 | 0 | 0 | 0 | 0 |
| 0.2 | 1 | 0 | 60 | 7 |
| 0.4 | 0 | 0 | - | - |
| 0.6 | 3 | 0 | 53 | 6 |
| 0.8 | 24 | 0 | - | - |
| 1.0 | 25 | 0 | 1384 | 4900 |
| 1.4 | 29 | 0 | - | - |
| 1.6 |  | - | - |  |

[^3]Table 1.3 Experimental results for ilmenite: chlorine consumption.

| Power (kw) | Signal Intensitya $\mathrm{O}_{2}$ (Arbitrary Units) Argon-Chlorine ${ }^{\mathrm{b}}$ Plasma |  |
| :---: | :---: | :---: |
|  | Cl | $\mathrm{Cl}_{2}$ |
| 0 | 1045 | 585 |
| 0.2 | 603 | 329 |
| 0.6 | 276 | 79 |
| 1.0 | -- | -- |
| ${ }^{\text {a }}$ Sign ginal. b 10\% | aged | ground |

microwave-induced plasma without charge buildup. It was feared that charge buildup would lead to electrical discharge and damage to the reactor vessel. As a result of the success of this work, the program was expanded to include the hydrogen reduction of lunar oxides.

## Future Work

Kinetic studies of plasma-enhanced reactions involving both chlorination and hydrogen reduction of lunar ores will continue throughout the coming year. The purpose of this work is to both demonstrate the feasibility of oxygen recovery using a "cold" plasma and to refine our understanding of the role plasma power and plasma
density play in mass transfer, heat transfer, and chemically controlled processes in gassolid reactions.

Coupled with the experimental program during the coming year will be an analysis of the applicability of plasma processing of lunar ores. That analysis will draw heavily on the experimental information developed throughout the investigation. Scaling up of "cold" plasmas to the size required for a lunar base will be examined. Finally, the cost of the process will be estimated to determine the applicability of the experimental work in establishing a lunar base.

## Student Participation

Mr. Daniel Bullard and Mr. Robert Ortega, both U.S. citizens, are working on this project. Daniel has generally been responsible for the construction of the experimental apparatus. He is currently in our M.S. degree program, but plans to petition the department to have his standing changed to the Ph.D. program in January. Dan is doing an excellent job, both academically and in his research.

Robert Ortega joined our research group in July. He has assisted Mr. Bullard and is now engaged in setting up a second plasma unit. Robert is seeking an M.S. degree.



#### Abstract

This research work deals with the autonomous production of propellants. Because, typically, $80 \%$ to $90 \%$ of a spacecraft's mass is propellants, it is advantageous to produce propellants in strategic locations en route to, and at, the desired mission destination. This will then reduce the weight of the spacecraft and the cost of each mission. Since one of the primary goals of the space program is safety, a totally automated propellant production system is therefore desirable. This system would thereby remove, from hostile, high-risk extraterrestrial environments, the constant human intervention currently required in the production of many propellants. This enables the exploration of space to be more than the search for and production of fuel. As a proof-of-concept demonstration, one specific case was chosen for this study, that of composite propellant processor; the principle is more important than the application, and the specific processor used saved SERC the considerable cost of acquiring a new liquid propellant processor that would also have required similar automation.


## Background

Currently, most space propellant production is done with constant human intervention. Using a control room, man has total control over all aspects of the propellant production. This is fine on Earth, but it is too costly in space. Thus, the need for automated composite propellant production exists.

## Approach

During the last year, we have completed testing on a heating system, which was designed by a graduate student (Paul Schallhorn), for the 1-pint mixer that is to be used for this project. Because propellant production requires mixing the ingredients at two constant temperatures ( 160 and $140^{\circ} \mathrm{F}$ ), a self-contained water heating system is required for space-based operation. This system provides the required temperatures and only needs an electric power source to drive the pump motor and to heat the water in the heaters. This is not unrealistic, considering that electricity is also required for the mixer and controlling computer.

One approach, therefore, is to use a personal computer to control the introduction and mixing of the composite propellant ingredients (making sure that temperature is
constant on the walls of the bowl, detecting local "hot spots" within the mixture, and taking in-situ measurements of the viscosity of the mixture to check if it is within an acceptable range) in the mixer. Then, the mixture is pumped, via a computer program, into a cast, which will be placed into an oven for curing and then stored for future use.

## Results to Date

The major results for 1989 are as follows:

1. During the spring of the year, the heating system for the propellant mixer was thoroughly tested for its ability to achieve the design requirements. The system not only achieved, but greatly exceeded these requirements. The system was able to maintain a negligible temperature drop across the bowl of the mixer (the $1^{\circ} \mathrm{F}$ temperature drop for which the system was designed had easily been reached). The temperature of the system was easily changed from $160^{\circ} \mathrm{F}$ to the required $140^{\circ} \mathrm{F}$ in a short amount of time, even without the aid of the computer. The automatic control work performed by Richard Wilson has allowed the system to easily maintain the required temperature within a $\pm 2^{\circ} \mathrm{F}$ tolerance, with this tolerance continually decreasing.
2. An IBM PS/2 Model 80 was purchased for use on this project. This model has an Intel 80386 microprocessor operating at 20 MHz , a 115-megabyte hard disk drive, 4 megabytes of RAM, and a 1.44 -megabyte 3.5 -inch internal floppy disk drive. The computer was ordered with the following peripherals: a 14 -inch VGA monitor, an 80387 math coprocessor, a 1200-baud internal modem, two 5.25 -inch external diskette drives ( 360 Kb and 1.2 Mb ), a mouse, and a Hewlett Packard Laserjet II printer. The computer arrived in January, and the peripherals arrived in early February. The computer system was operational by the middle of February. This computer system is also being used on various other SERC projects.
3. An Inframetrics infrared camera, Model 600L, has been purchased for this project. It will be used for direct surface temperature measurement of the propellant slurry. It will be mounted (not permanently) at the entrance of one of the mixer's view ports. It will eventually be integrated into the computer system for aiding the temperature control process of the automation.
4. A prototype hopper is currently being built for the injection of the propellant ingredients. This work is being done by undergraduate students under the supervision of Paul Schallhorn. This portion of the project has a projected completion date of May 1990. The hopper consists of a series of chambers containing the required ingredients, a means of weighing the solid ingredients, an
injection system for the liquid ingredients, a thermal jacket to preheat the ingredients, and a port to inject the ingredients.
5. An in-situ viscometer is being designed for placement within the mixing bowl. This would give more accurate viscosity measurements of the slurry at any point in time, and it is the only way in which an automated system could check for viscosity problems.

## Summary

In summary, this task has shown that there is a need for automatic space-based production of propellants. We have also shown that there is no current system to produce composite propellants without human intervention. Work has begun on achieving this task. The heating system (previously designed) for a 1-pint vertical propellant mixer has been thoroughly tested. The result is that the heating system meets or exceeds the design criteria. A prototype hopper is being built for the injection of the required ingredients. It consists of a measuring system (for solid particles), a liquid injection system, a series of containers for the solid particles, a thermal jacket, and a delivery system. An IBM personal computer has been acquired. An Inframetrics infrared camera has been procured for temperature measurements of the propellant slurry. An in-situ measuring device is being developed for future integration in the system.

## Participants

We would like to take this opportunity to thank Gary Hopkins and Milton Schick for their help in assembling and maintaining the entire system. We would also like to acknowledge Richard Wilson, who is doing the automatic controls portion of the heating system.

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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 resourceoriented 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 lunarderived 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 Simulant
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 $0.5 \mathrm{wt} \%$ 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 $\mathrm{SO}_{2}$ 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 $\mathrm{FeTiO}_{3}$ and, hence, contains no ferric iron. Therefore, terrestrial ilmenite, which is a solid solution of $\mathrm{Fe}_{2} \mathrm{O}_{3}$ in $\mathrm{FeTiO}_{3}$, 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) constitutents of the kinetics of ilmenite reduction. The most abundant solute in lunar ilmenite is $\mathrm{MgTiO}_{3}$, 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. ${ }^{\text {a }}$

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

a Lunar data from a compilation of 133 ilmenites from high-Ti basalts (Vaniman et al. 1989), except for $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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-fitanium 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 irongroup 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 $6 \times 10^{16}$ 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 $\left(\mathrm{TiO}_{2}\right)$. 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 $7 \% \mathrm{Ni}$ content) and taenite (gamma iron; 20 to $60 \% \mathrm{Ni}$ ), are ferromagnetic, as are the widespread trace minerals schreibersite, $(\mathrm{Fe}, \mathrm{Ni})_{3} \mathrm{P}$, and cohenite, $(\mathrm{Fe}, \mathrm{Ni})_{3} \mathrm{C}$. 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, carbonand 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 lengthly 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 $\mathrm{Fe} / \mathrm{Ni}$ 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 mixedcarbonyI CVD are available only at their facility in Pennsylvania.

## References

Bunch, T. E. and Keil, K., 1971, "Chromite and ilmenite in nonchondritic meteorites," Amer. Mineral. 56, 146-157.

Lewis, J. S., Jones, T. D., and Farrand, W., 1988, "Carbonyl Extraction of Lunar and Asteroidal Metals," pages 111-122 in Space 88, AIAA, New York.*

Mason, B. and Nelson, W. G., 1970, The Lunar Rocks, J. Wiley and Sons, N. Y.
Vaniman, D., Heiken, G., and Muhich, T., 1989, "Lunar Ilmenite," preprint.
Williams, R. J., 1985, "Oxygen Extraction From Lunar Materials: An Experimental Test of an Ilmenite Reduction Process," in Lunar Bases and Space Activities of the 21st Century, LPI, Houston.

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During the past year, our group has worked on characterizing lunar material that has the potential of becoming ilmenite lunar ore. The important aspects of any such material are that it has abundant ilmenite and that the ilmenite be easily separated. The final result sought is a pure (greater than $99 \%$ ilmenite) concentrate that will be used as feed for the ilmenite reduction process.

There are two types of starting material available on the Moon. Solid rock (basalt or anorthosite) and regolith. We have not done any ilmenite separation experiments on either of these materials, but have done extensive literature reviews and have separated simulants (meteorites). We have tentatively concluded that, because of the large amounts of agglomerates, regolith may not be the best starting material for ilmenite beneficiation and either basalts or anorthosites may be better. This is because no matter how finely the regolith is ground, it would not be possible to efficiently separate all the ilmenite. This hypothesis, however, needs to be tested with lunar material. We propose, for the next year, to obtain some lunar regolith, which will be used to separate the ilmenite. Since our separation process will be nondestructive, we will be able to return all the regolith to NASA.

We separated meteoritic ilmenite so that Professor Shadman had extraterrestrial simulant for his reduction experiments. Ms. Melinda Hutson and I ground the sample, sieved it, and used conventional separation techniques to separate the ilmenite. It was found that extraterrestrial ilmenite cannot be separated by electromagnetic separators, because of the complete absence of ferric iron in the ilmenite. We used heavy liquid separation procedures to obtain a reasonably pure separate (about $70 \%$ ilmenite). Final purification needs to be done by hand picking. The final concentrate will be analyzed by Hutson using XRD before turning the sample over to Shadman. The possible impurities in the concentrate are pyroxens and sulfides. Our work with the meteorite samples clearly shows that magnetic separators will not work with lunar material and that the most likely separation technique that will work on these samples is electrostatic. We will build an electrostatic separator that can be subjected to high vacuum, and we start performing realistic separations on simulant next year. After we have successfully installed the electrostatic separator and have performed some separations with extraterrestrial simulants, we will need to ask NASA for lunar material.

In addition to the separation experiments, we have obtained all the isotopic spikes to make isotope dilution spikes for analyses of trace elements in extraterrestrial material using an induced coupled plasma quadropole mass spectrometer. Our aim is to very accurately analyze elements that might be commerically recoverable from extraterrestrial material and then be brought back to Earth. The elements of interest are mostly platinoids, and the necessary analytical techniques have been developed to analyze small amounts (ppb levels) of these elements. We have already made some of the spikes and plan on finishing the calibration of all spikes and standards next year. Our lab will be among the best laboratories in the country actively analyzing extraterrestrial material for a large number of trace elements at very low abundances. Already, other planetary scientists are interested in analyzing a variety of types of meteorites in this lab.

Production of Oxygen From Lunar Ilmenite<br>- Y. Zhao and F. Shadman<br>Department of Chemical Engineering The University of Arizona

Oxygen is a consumable material that needs to be produced continuously in most space missions. Its use for propulsion, as well as life support, makes oxygen one of the largest volume chemicals to be produced in space. Production of oxygen from lunar materials is of particular interest and is a very attractive possibility.

Among the proposed processes, the hydrogen and carbothermal reductions of ilmenite appear very promising. Hydrogen reduction has a relatively simple process configuration; the individual steps are relatively well studied. However, the major problem is the large heating and cooling loads required to condense the water and then heat the hydrogen to its reaction temperature. Handling and storage of large amounts of hydrogen are also a problem. Hydrogen reduction of lunar ilmenite has been studied by several investigators. Carbothermal reduction of terrestrial ilmenite has also been extensively studied, but its application to lunar ilmenite is still an open area for investigation.

The overall objectives of this study can be described as follows:

- Study of the mechanism and kinetics of carbothermal reduction of simulated lunar ilmenite using carbon and, particularly, CO as reducing agents; determination of the rate-limiting steps; investigation of the effect of impurities, particularly magnesium; search for catalysts suitable for enhancement of the rate-limiting step.
- Comparison of the kinetics of carbothermal reduction with those of hydrogen reduction; study the combined use of CO and hydrogen as products of gasification of carbonaceous solids.
- Development of new reduction methods that are based on the use of waste carbonaceous compounds for the process; development of a novel carbothermal reaction path that utilizes gasification of carbonaceous solids to reducing gaseous species (hydrocarbons and carbon monoxide) to facilitate the reduction reaction kinetics and make the process more flexible in using various forms of carbonaceous feeds.
- Development of advanced gas separation techniques, including the use of hightemperature ceramic membranes.
- Development of an optimum process flow sheet for carbothermal reduction, and comparison of this process with the hydrogen reduction scheme, as well as a general comparison with other leading oxygen production schemes; use of new and advanced material processing and separation techniques.


## Experimental Method

Two reactor systems have been designed, fabricated, and put into operation: A small fluidized bed reactor for quick response times and a thermo-gravimetric reactor system with an electronic microbalance for the continuous measurement of the rate and the sample conversion. A unique method is developed for preparation of two types of ilmenite samples used in the experiments. The first type was pure synthetic ilmenite with impurity less than $0.1 \%$. The second was synthetic ilmenite in which known and controllable amounts of impurities are introduced to simulate actual impurities found in lunar samples. A series of tests, including X-ray diffraction experiments and Mossbauer spectroscopy, were performed on synthetic ilmenite to ensure that the iron in these samples was $\mathrm{Fe}^{++}$.

In each experiment, a known amount of ilmenite was exposed to the reducing gas, and the rate of conversion was monitored using both gravimetric response and continuous monitoring of the gases produced. The starting samples were fully characterized by particle size, porosity, surface area, and composition. The important reaction parameters are temperature, reducing gas composition, and flow rate.

Results and Conclusions
A typical temporal profile of conversion is shown in Figure 1.3. The results indicate the presence of three stages:

- Induction stage during which reaction is very slow. Detailed microprobe analysis of samples quenched during this stage indicate that the formation of iron nuclei is the rate-controlling step. The presence of small amounts of impurities can affect this stage.
- Acceleration stage during which rate increases progressively. The reaction rate during this stage is influenced by diffusion of reducing gas into the particles and diffusion of iron away from the reaction front.
- Deceleration stage which is primarily due to depletion of ilmenite.

The effect of temperature on the rate and the activation energies at different levels of conversion are shown in Figure 1.4. The effect of CO concentration on the rate is shown in Figure 1.5. Partially converted samples were probed using high-resolution energy dispersive X-ray analysis; the micrographs and concentration maps show the importance of iron nuclei formation and growth in controlling the rate. Sample results are shown in Figures 1.6 and 1.7.

An important finding during this phase of the project has been the determination of the rate-limiting step and the mechanism of impurities action. These results are
important in developing reaction conditions and selecting catalysts to enhance the rate and lower the reaction temperature. The experimental work on the effect of magnesium, an important impurity, on kinetics is currently in progress. The reactor system is being prepared for experimental runs with hydrogen and mixtures of hydrogen and carbon monoxide as reducing gases.


Figure 1.3 Temporal profile of synthetic ilmenite reduction by carbon monoxide.


Figure 1.4 Apparent activation energy at 10,30, and $50 \%$ conversions.


Figure 1.5 Effect of CO concentration on the rate of reduction.

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Figure 1.6 SEM backscattered electron micrograph of the polished cross section of a synthetic ilmenite flake after partial reduction at $1000^{\circ} \mathrm{C}$.


Figure 1.7 SEM secondary electron micrograph of two grains of the sample shown in Figure 1.6.

# Volatile-Bearing Phases in Carbonaceous Chondrites: Compositions, 

 Modal Abundances, and Reaction KineticsJ. Ganguly

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The spectral and density characteristics strongly suggest that the Phobos and Deimos (the two small natural satellites of Mars) and a significant fraction of the nearEarth asteroids are made of carbonaceous chondrites, which are quite rich in volatile components and, thus, could serve as potential resources for propellants and lifesupporting systems in future planetary missions. However, in order to develop energy efficient engineering designs for the extraction of volatiles, we must have a good knowledge of the nature and modal abundances of the minerals in which the volatiles are structurally bound and appropriate kinetic data on the rates of the devolatilization reactions.

The grain size of the volatile-bearing phases in carbonaceous chondrites are often too small ( 100 to 1000 A ) to permit identification under optical microscopes and are best observed under high-resolution transmission electron microscopy (HRTEM). We have, therefore, carried out theoretical calculations to predict the modal abundances and compositions of the major volatile-bearing and other mineral phases that could develop in the bulk compositions of C 1 and C2 classes as functions of pressure and temperature. These are the most volatile-rich classes among carbonaceous chondrites. The results suggest that talc and antigorite $\pm$ magnesite are the major volatile-bearing phases and are stable below $\sim 400^{\circ} \mathrm{C}$ at 1 bar in these chondritic compositions. The phyllosilicates are fairly iron rich, with about $25-30 \mathrm{~mol} \%$ of $\mathrm{Fe}^{2+-}$ end-member components in solid solution.

Simulated equilibrium heating of a kilogram of C2 chondrite at fixed bulk composition between 400 and $800^{\circ} \mathrm{C}$ at 1 bar yields about 135 gm of volatile, which is made primarily of $\mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2}, \mathrm{CH}_{4}, \mathrm{CO}_{2}$, and CO . The relative abundances of these volatile species change as functions of temperature and, on a molar basis, $\mathrm{H}_{2}$ becomes the most dominant species above $550^{\circ} \mathrm{C}$. Hydrogen is a very good propellant and reducing agent, which may be preferentially extracted, according to the above results, by heating the C 2 chondritic material to $\mathrm{T}>550^{\circ} \mathrm{C}$. In contrast to the C 2 chondrite, the volatiles given off by C 1 material under equilibrium conditions at $1 \mathrm{bar}, \mathrm{T}>400^{\circ} \mathrm{C}$, consist essentially of $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}$. Per kilogram of material, the total yield of volatile is about 306 grams, of which nearly $60 \mathrm{wt} \%$ is $\mathrm{H}_{2} \mathrm{O}$.

The theoretical study summarized above has been published recently in a paper entitled "Theoretical Predictions of Volatile Bearing Phases and Volatile Abundances in

Carbonaceous Chondrites" (pages 97-105 in Space Manufacturing 7, American Institute of Aeronautics and Astronautics, 1989). A copy is included as Appendix. D.

Having identified the most likely mineralogical source of volatiles in the carbonaceous chondrites, we have begun a program of systematic kinetic study of devolatilization reactions. The results will provide the framework for optimal engineering designs for the extraction of volatiles from the mineral phases. These will also help resolve the problems concerning the process and condition of formation of the volatile-bearing phases, especially the phyllosilicates, in the carbonaceous chondrites, which are of fundamental importance to our understanding of the planetary processes.

We have determined the rates of dehydration of talc at $585,600,637$, and $670^{\circ} \mathrm{C}$, $P($ total $)=1$ bar, according to the reaction

$$
\text { Talc }=3 \text { Enstatite }+ \text { Quartz }+\mathrm{H}_{2} \mathrm{O} .
$$

The dehydration kinetics was studied before by Greenwood (1963) at $\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}=2 \mathrm{~Kb}$. However, the available data were inadequate to permit reliable extrapolation to lower pressure. The "process condition" for the extraction of volatiles is likely to be set at a pressure of the order of 1 bar.
-The starting material talc is nearly pure Mg-end member. The weight loss of a known quantity of material was determined continuously as a function of time at the above temperatures by the thermogravimetric (TG) method. The results are illustrated in Figure 1.8 in terms of fractional weight of talc remaining versus time. The sample was suspended within the reactor in open platinum containers shaped from Pt-foils. The TG setup used in this study has the drawback that it does not permit introduction of the sample within a reactor that has been preheated to the desired run temperature. Thus, corrections have to be made for the weight loss through the induction period to the run temperature. The corrections, however, are quite straightforward. Another drawback of this particular TG setup is that the change of weight as a function of time is recorded in a strip-chart recorder, but it is not available in the form of a digitized output. Thus, the curves in the strip-chart recorder have to be visually read to compute fractional weight loss, which has led to the irregularities seen in the curves in Figure 1.8. The raw data show a very smooth relation of weight of talc versus time. We are in the process of developing a TG setup that would permit direct introduction of the sample into a preheated reactor and also provide digitized output of the data.

We have not yet carried out detailed analyses of the experimental data to obtain the kinetic parameters and to understand the mechanism of reaction. These analyses


Figure 1.8 Weight fraction of talc remaining as a function of time at different temperatures. Reaction: talc $\rightarrow 3$ enstatite + quartz $+\mathrm{H}_{2} \mathrm{O}$ (Talc: $\mathrm{Mg}_{3} \mathrm{Si}_{4} \mathrm{O}_{10}(\mathrm{OH})_{2}$; Enstatite: $\mathrm{MgSiO}_{3}$; Quartz: $\mathrm{SiO}_{2}$ )
will eventually be carried out after we gather a larger body of experimental data and refine the experimental techniques. However, we find that the dehydration reaction does not seem to follow the first-order mechanism, which is in contrast to the highpressure results of Greenwood (1963).

It is important for the kinetic study, especially for understanding the mechanism of reaction, to be able to determine the modal abundance of phases at various stages of reactions. In the only work of this nature to date involving phyllosilicates, Greenwood (1963) determined the abundances of the various phases in the run products by the extremely laborious technique of petrographic modal analysis, i.e., by "point counting" the amount of phases under an optical microscope. We have conducted a scanning electron microscopic (SEM) study to see if the relative abundance of phases can be determined on the basis of the spectral identification and $X$-ray mapping. On standard samples made up of known amounts of talc, anthophyllite, and quartz, X-ray mapping
and software processing of the data resulted in the determination of quartz to talc-plusanthophyllite combined, but the latter two could not be distinguished separately. However, once the amount of quartz is known, the proportions of talc and anthophyllite can be estimated by mass balance, assuming that no other phase is present. The latter can be checked by microprobe and X-ray analysis. In the analysis of the standard samples, we have, however, systematically overestimated the amount of talc by about $6 \%$. With further work, we hope to be able to refine the method to yield better estimates of phases in a standard mixture.

## Reference

Greenwood, H. J., 1963, "The Synthesis and Stability of Anthophyllite," Journal of Petrology, Vol. 4, pp. 317-351.
*91-25231
Quantitative Computer Representation of Propellant Processing
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With the technology currently available for the manufacture of propellants, it is possible to control the variance of the total specific impulse obtained from the rocket boosters to within approximately $5 \%$. Though at first inspection this may appear to be a reasonable amount of control, when we consider that any uncertainty in the total kinetic energy delivered to the spacecraft translates into a design with less total usable payload, even this degree of uncertainty becomes unacceptable. There is strong motivation to control the variance in the specific impulse of the shuttle's solid boosters. Any small gains in the predictability and reliability of the boosters would lead to a very substantial payoff in Earth-to-orbit payload. The purpose of this study is to examine one aspect of the manufacture of solid propellants, namely, the mixing process. We attempt to introduce a unique methodology to enable understanding of this process.

The traditional approach of computational fluid mechanics is notoriously complex and time consuming. We wish to make certain simplifications, yet be able to investigate certain fundamental aspects of the mixing process as a whole. It is possible to consider a mixing process in a mathematical sense as an operator, $F$, which maps a domain back upon itself (Figure 1.9). An operator which demonstrates good mixing should be able to spread any subset of the domain completely and evenly throughout the whole domain by successive applications of the mixing operator, $F$.

A two-dimensional model was first developed using this approach. The differential equations of motion were designed to satisfy conditions of continuity and incompressibility for two-dimensional flow in a unit circle. These equations of motion were designed by Arthur Maser and are given as:

$$
\begin{align*}
\dot{x} & =[1+\sin (t)]\left\{\frac{2 y\left[4 x-2+\left[(2-x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}\right]}{3\left[(2-x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}}+2 y\right\} \\
& +[1-\sin (t)]\left\{\frac{\left.2 y\left[4 x+2-\left[(2+x)^{2}-3\left(1-x^{2}-y^{2}\right)\right)\right]^{1 / 2}\right]}{3\left[(2+x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}}+2 y\right\} \tag{1}
\end{align*}
$$



Figure 1.9 Application of mixing operator in a two-dimensional domain.

$$
\begin{align*}
& \dot{y}=[1+\sin (t)]\left\{\frac{2}{9}\left[2 x-2-\left[(2-x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}\right]\right. \\
&\left.\times\left[2+\frac{4 x-2}{\left[(2-x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}}\right]\right\} \\
&+[1-\sin (t)]\left\{\frac{2}{9}\left[2 x-2+\left[(2+x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}\right]\right.  \tag{2}\\
&\left.\times\left[4+\frac{4 x-2}{\left[(2+x)^{2}-3\left(1-x^{2}-y^{2}\right)\right]^{1 / 2}}\right]\right\} .
\end{align*}
$$

If we examine the streamlines generated by this velocity function, we can see that the flow consists of two superimposed eccentric vortices, rotating in opposite directions. The two vortices lie along the $x$-axis at $x \pm 0.5$. The two components of the flow are modulated by sinusoidal forcing functions that are $180^{\circ}$ out of phase. It is the periodic forcing function that gives rise to the chaotic behavior of the flow by perturbing the regular flow field set up by the nested eccentric vortices. Equation (1) is therefore an attempt to design a mapping that will give random mixing from completely nonrandom functions.

Numerical methods were employed to investigate these equations in order to determine if they can give rise to mixing. The computational process and the animation of the results were conducted on a Silicone Graphics IRIS workstation. One objective was to determine if any small region within the domain can spread itself more or less evenly throughout the whole domain given sufficient applications of the mixing operator. To demonstrate this, we defined small clusters of points within the
domain and integrated the equations of motion with the initial conditions being the starting locations of each of these particles. The path of each individual particle could then be followed across successive iterations of the mixing cycle. The period of the mixing cycle is defined as the period of the sinusoidal forcing functions. This approach mimics a traditional approach for studying flow fields.

In laboratory experiments, highly localized amounts of tracer dyes are introduced, via injection, into the fluid, and the position and the distribution of these dyes can be followed as the flow develops. In the numerical experiment; each group or species of particles is branded with its own particular color so that the species can be followed throughout the experiment and its interaction with other species can be studied visually. To be consistent with the mapping approach, the position of each of the particles was updated after each completion of a mixing cycle. In several simulations of the mixing process, five sets of particles, initially very tightly spaced together, were considered. Each block of particles represents a $30-$ by -30 set of particles, and we ran the simulations across 20 iterations of the mixing cycle. Figure 1.10 documents the graphical animation derived for these simulations. Each successive frame in the sequence represents the application of one or more mapping operations onto the previous frame and, thus, we are able to study how the flow field evolves through time. We can see how very quickly all apparent structure to the species distribution becomes lost, and we state that our original mapping can give rise to good mixing of the domain within a few iterations of the mixing cycle. We recall a theorem in set theory that states that for any two-dimensional mapping of a domain back upon itself, there must be at least one invariant set or, in terms of the mixing process, at least one dead zone. We therefore seek to find this invariant set. If we animate the same data set such that each successive mapping of the species is superimposed on top of the previous ones, then any region of the domain that remains unmixed should become apparent. We find that when we graph the data with this approach, one dead zone can be found in the lower right-hand corner (Figure 1.11).

Another test of mixing can be outlined as follows. We partition the domain into many elements of equal area. We begin with a particle in some initial position within the domain and follow the particle as it takes many cycles through the mixing operator. A measure can be defined as the number of times the particle falls within an element divided by the total number of iterations. A necessary but not sufficient condition for perfect mixing is that this measure must go to a mean value for each partition as the number of iterations becomes very large. When we apply this test to our operator, we can see that the invariant set becomes apparent as a trough in the plot of the density function (Figure 1.12).


Figure 1.10 Graphical visualization of a two-dimensional mixing process.

Figure 1.10 (Continued).


ORIGINAL PAGE<br>BLACK AND WHITE PHOTOGRAPH



Figure 1.11 Two-dimensional model after 20 iterations.


Figure 1.12 Probability density function for two-dimensional mapping.

Later work expanded this approach to investigate mixing in three dimensions. Here, the domain was a torus that was cut and mapped to a unit cube. Particles would flow across the domain and, upon impinging upon the boundary, would be mapped to a point on the opposite face. The mapping function chosen for this experiment was the well-known Baker's transformation. This transformation is an example of a discontinuous mapping that can be used to investigate mixing due to its action of stretching and folding a domain back upon itself (Figure 1.13). We are guaranteed ergodicity through successive iterations of the mapping due to its discontinuity. Real mixers can be designed to mimic this action of splitting, stretching, and refolding the flow without the traditional use of paddles. As in the two-dimensional case, an initially small, very tightly spaced group of particles was carried along by the flow field and the graphical visualization of the results showed the presence of mixing (Figure 1.14). In the three-dimensional case, it was also observed that pseudorandom behavior can be induced from completely nonrandom functions.


Figure 1.13 Baker's transformation in base two.


Figure 1.14 Graphical visualization of three-dimensional mixing process.

Temperature Automation for a Propellant Mixer
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This past year has been spent analyzing and installing an automatic temperature controller on a propellant mixer. Ultimately, the entire mixing process will come under automation. Automation is not only important for producing a uniform product, but it will be necessary for envisioned space-based propellant production.

The propellant mixer was obtained from the Jet Propulsion Laboratories. It was installed on campus for the purpose of studying and improving the mixing process. In its installed configuration, the mixer was not automated. Control of mixing time, speed, and temperature profile was provided by the operator. Each of these factors is important in providing a reliable and predictable product. Since precise adherence to the temperature profile is very difficult to sustain manually, this was the first component to be automated.

Figure 1.15 illustrates the water circulation system for the installed system. It was a closed system in which water could be drawn from one of two hot water tanks that were set at $140^{\circ} \mathrm{F}$ and $160^{\circ} \mathrm{F}$. The water was circulated around the system by means of a pump. The storage tank provided for fluctuations in the flow. The actual mixing bowl is surrounded by a jacket through which the water flows. By operating valves at the outlet of the hot water tanks, the operator is able to vary the water temperature in the jacket and thus influence the temperature of the components in the mixing bowl. The temperature profile desired during the mixing process is one in which the components are held at $160^{\circ} \mathrm{F}$ (for the first 35 minutes) and then at $140^{\circ} \mathrm{F}$ (for an additional 165 minutes). The manual operation involved simply drawing water from the $160^{\circ} \mathrm{F}$ tank for the first 35 minutes and then drawing water from the $140^{\circ} \mathrm{F}$ tank for the remaining time. However, this procedure did not provide an accurate profile, as illustrated in Figure 1.16. This figure illustrates (for the first 65 minutes) the desired temperture profile, the water temperature in the jacket, and the temperature at the inside of the jacket in contact with the materials being mixed. This latter temperature (jacket temperature) is taken to be representative of the temperature of the components.

In order to improve the jacket temperature profile, as well as to automate the process, a control system (Figure 1.17) was designed and implemented. The system uses the same water circulation system as before, except now water is drawn from the two tanks by means of a control valve. Rather than having the tanks at the two set-point


Figure 1.15 Original water circulation system.


Figure 1.16 Temperature profile for the manual control system.


Figure 1.17 Automatic control system.
temperatures, one tank (hot tank) is set for a temperature greater than $160^{\circ} \mathrm{F}$ and the other tank is turned off (cold tank). The control valve that regulates the amount of water drawn from each tank is set using a stepper motor according to a control algorithm. Temperature measurements are made using a thermocouple, which scans the inside jacket temperature. An 8-bit A/D converter is used in conjunction with an Apple computer to implement the control algorithm. The control algorithm uses open-loop command feed-forward in conjunction with closed-loop error feed-back.

Figure 1.18 illustrates the desired temperature profile, as well as the actual temperature profile of the jacket obtained under this control system for the first 65 minutes. Compared with Figure 1.16, this represents a considerable improvement. Two factors prevented even better results. First, the 8 -bit A/D converter limited the resolution of the temperature readings to $0.4^{\circ} \mathrm{F}$. This is about the extent of the chatter about the nominal profile. Second, there is very little temperature control available at the hot end. The highest temperature that the hot water tank can be set to is $170^{\circ} \mathrm{F}$. This is very close to the higher command temperature. As water is circulated through the system, the heat loss is greater than the heating element in the hot water tank can


Figure 1.18 Temperature profile using automatic control.
replace, hence, the system is started hot $\left(165^{\circ} \mathrm{F}\right)$ to give enough reserve to last the first 35 minutes. At the jump point in command temperature, the temperature of the cold water tank is not known with sufficient accuracy to allow for a proper setting of the control valve. This accounts for the discrepancy in jacket temperature for about the first 5 minutes after the jump. This problem can be eliminated by installing a thermocouple in the tanks so that these temperatures can be used in the control algorithm.

This first design was implemented with minimal change to the existing system and with some older equipment (Apple computer, A/D converter) in order to demonstrate the feasibility of the procedure. Our intent now is to replace this older equipment and to modify the water circulation system. With these changes, it should be possible to precisely maintain any desired temperature profile. The new design will also consider minimizing the energy required to heat the water.

A complete description of this project is contained in a Master's report submitted by R. G. Wilson to the Department of Aerospace and Mechanical Engineering, dated November 20, 1989.
D. E. Osborn, D. C. Lynch, and R. Fazzolari

$$
\begin{gathered}
\text { Department of Materials Science and Engineering } \\
\text { and } \\
\text { Solar and Energy Research Facility, Department of Nuclear and Energy Engineering } \\
\text { The University of Arizona }
\end{gathered}
$$

## Introduction

The Department of Materials Science and Engineering (MSE), with funding from the NASA Space Engineering Research Center (SERC) for Utilization of Local Planetary Resources, is investigating use of monatomic chlorine produced in a "cold" plasma to recover oxygen and metallurgically significant metals from lunar materials (Lynch 1989). Development of techniques for the production of the chlorine radical (and other energetic radicals for these processes) using local planetary resources is a key step for a successful approach.

It has been demonstrated terrestrially that the use of UV light to energize the photogeneration of $\mathrm{OH}^{*}$ radicals from ozone or hydrogen peroxide in aqueous solutions can lead to rapid reaction rates for the breakdown of toxic organic compounds in water (Osborn et al. 1988). A key question is how to use the expanded solar resource at the lunar surface to generate process-useful radicals. This project is aimed at investigating that question as a joint effort of MSE and the Solar and Energy Research Facility (SERF) of the Department of Nuclear and Energy Engineering (NEE). It is being conducted by Donald E. Osborn under the supervision of Dr. David Lynch.

## Approach

Sunlight provides useful energy for processing in the forms of both thermal and quantum energy. While the use of thermal energy is well accepted, the use of quantum energy of the solar photons (photonic processes) for chemical reactions presents new and exciting possibilities.

Photonic Processing. Sunlight is electromagnetic radiation that is normally divided into three major bands: Ultraviolet (UV) ranges from about 180 nm to 380 nm , visible ranges from 380 nm to 780 nm , and infrared (IR) ranges from 780 nm to about 10,000 nm . The energy of a photon varies inversely with wavelength as follows:

$$
E=\frac{h c}{\lambda}=h v
$$

where $E$ is energy, $h$ is Planck's constant, $\lambda$ is wavelength, and $v$ is frequency. If one considers a gram-mole (gmol) of photons, the energy associated with a given wavelength is

$$
\mathrm{E}=\frac{28591}{\lambda} \mathrm{kcal} / \mathrm{gmol} .
$$

The shorter wavelengths are the most energetic.
Light can affect material in two basic ways: thermally or through photonic processes. The absorption of light can lead to an increase in the vibrational, rotational, and translational energy of the atoms of the material. Macroscopically, this shows up as an increase in temperature and, once absorbed, the effectiveness of the energy is not dependent on the wavelength of the light. Photonic processes are wavelength dependent and are characterized by a threshold wavelength that is specific for each process and material.

If light is absorbed by a molecule and if it has sufficient energy (i.e., short enough wavelength), it can cause a transition of electrons from one orbital to another. If the electron belongs to a chemical bond, the bond may be broken by this transition. UV and near UV, as the most energetic wavelengths, can break a wide variety of bonds, as seen in Table 1.5. While it may not be possible with the wavelengths available to break the bonds of the material of interest directly, a photocatalytic process may be used, or energetic free radicals that can break the bonds can be photogenerated. Some of the photochemical reactions that can lead to such free radicals are shown in Table 1.6.

It has been demonstrated that the combination of ozone and UV photons produces rapid reactions in the form of photochemical oxidation of halogenated organic compounds (Fletcher 1987). Ozone and hydrogen peroxide decomposition to free radicals is accelerated by absorption of UV light. Free radicals, having a considerably higher oxidation potential than molecular ozone, produce the favorable reaction rates. Experiments by Osborn et al. (1988) demonstrate the increased reaction rate for the decomposition of a red organic dye using UV from natural sunlight in combination with $\mathrm{H}_{2} \mathrm{O}_{2}$ or $\mathrm{TiO}_{2}$. The process produces free radicals that lead to bond breaking and reduction of the color of the dye solution (Figure 1.19). Further experiments at a concentration of 6 suns show greatly enhanced reaction rates over the 1 -sun case.

The concentrated solar irradiation could be used in materials processes by using the UV and near-UV photons to form free radicals desired for "cold" plama processing (Lynch 1989). These radicals could include monatomic $\mathrm{Cl}, \mathrm{F}, \mathrm{O}, \mathrm{H}$, and $\mathrm{OH}^{*}$ for reduction and oxidation.

## I-44

| Table 1.5 | Dissociation energies for chemical bonds (Legan 1982$).$ |  |
| :--- | :---: | :---: |
| Bond | $\mathrm{D}(\mathrm{Kcal} / \mathrm{mol})$ | $\lambda \mathrm{p}(\mathrm{nm})$ |
| $\mathrm{Cl}-\mathrm{Cl}$ | 58 | 490 |
| $\mathrm{C}-\mathrm{Cl}$ | 81 | 353 |
| $\mathrm{C}-\mathrm{F}$ | 116 | 247 |
| $\mathrm{C}-\mathrm{H}$ | 99 | 290 |
| $\mathrm{C}-\mathrm{O}$ | 86 | 334 |
| C-C | 83 | 346 |
| C=C | 146 | 196 |
| C=C | 200 | 143 |
| H-H | 104 | 274 |
| O-O | 119 | 240 |
| O-H | 118 | 243 |
| H-Cl | 103 | 279 |
| F-F | 37 | 780 |

Table 1.6 Photochemical reactions leading to free radicals.

| Reaction | $\lambda p(n m)$ | Resultant Radicals |
| :--- | :--- | :--- |
| $\mathrm{H}_{2} \mathrm{O}+\mathrm{hv}=\mathrm{H}^{*}+\mathrm{OH}^{*}$ | 185 | Atomic hydrogen and hydroxy |
| $\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{hv}=20 \mathrm{H}^{*}$ | 254 | Hydroxy |
| $\mathrm{O}_{2}+\mathrm{hv}=\mathrm{O}_{3}$ | 254 | Ozone |
| $\mathrm{Fe}^{+2}+\mathrm{hv}=\mathrm{Fe}^{+3}$ | 254 | Ferrous ion to ferric ion |
| $\mathrm{O}_{3}+h v=\mathrm{O}_{2}+\mathrm{O}^{*}$ | 310 | Atomic oxygen (Note: $\left.\mathrm{O}^{*}+\mathrm{H}_{2} \mathrm{O}=20 \mathrm{H}^{*}\right)$ |
| $\mathrm{Cl}_{2}+h v=2 \mathrm{CL}^{*}$ | 490 | Atomic chlorine |



Figure 1.19 Effect of solar light on red dye.

Extraterrestrial Radiation. While the UV content of the solar spectrum at the Earth's surface is very limited in quantity and decreases rapidly with decreasing wavelength, sunlight at the Moon's surface or in Earth orbit contains both greatly increased levels of total UV and the shorter wavelengths. For Earth-based systems, we have little UV below 320-340 nm. Extraterrestrial solar radiation, however, extends below 240 nm , with significantly higher levels throughout the UV band (see Table 1.7). The use of Al reflectors would permit the concentration of this energy, with good reflectance throughout the solar UV band. Appropriate spectrally selective filters could remove excess energy at unwanted wavelengths if excess thermal energy is a problem (Osborn 1986).

Table 1.7 UV content in sunlight for AMO, AM1, and AM4 ( $\mathrm{W} / \mathrm{m}^{2}$ ).

|  | AMO | AM1 | AM4 |
| :--- | ---: | ---: | ---: |
| $<400 \mathrm{~nm}$ | 118.1 | 88.4 | 11.1 |
| $<310 \mathrm{~nm}$ | 22.5 | 0.5 | 0.0 |

## Chlorination Kinetics

Extensive studies of chlorination kinetics of several materials were undertaken by the Bureau of Mines (Landsberg and Block 1965). The experiment being conducted under this project extends the Bureau of Mines' work and seeks to determine the effect of concentrated solar energy on the chlorination kinetics of iron and molybdenum. Those metals were chosen because the rate of chlorination of Mo is known to be limited by the dissociation of $\mathrm{Cl}_{2}$, while that for Fe is not. Furthermore, the rate constants for reactions are well established. In addition, the reaction products are volatile at reasonable temperatures $\left(250-450^{\circ} \mathrm{C}\right)$. Simulated solar light should lead to the dissociation of $\mathrm{Cl}_{2}$ and thereby enhance the rate of chlorination of Mo . The increase should, initially, be linear with the intensity of the simulated solar energy. The solar energy should have no effect on the chlorination rate of Fe , unless a new reaction path is created with the presence of monatomic chlorine.

The objective of these experiments is to test the hypothesis that solar energy can be used to produce reactive radicals. If the experiments are successful, an attempt will be made to use solar energy in the chlorination of metal oxides and thereby the liberation of $\mathrm{O}_{2}$.

Experimental Setup. The experimental apparatus is shown in Figure 1.20. The sample to be chlorinated will be suspended by a fiber resistant to the chlorine environment. The fiber is attached to one arm of the Cahn R-100 electrobalance. A tare weight is suspended from the other arm. The balance is enclosed by a bell jar and base plate. The balance will be flushed with argon gas to protect it from the corrosive environment. A 1 -inch fused silica tube extends from the balance into a resistance wound furnace. The tube is $U$-shaped so that an argon-chlorine gas mixture is preheated in the electric furnace before it contacts the metallic specimen. The specimen will be positioned just above the electric furnace, where the simulated solar light can be absorbed by the specimen and gas mixture near the specimen. A solar reflector will be used to concentrate the light around the specimen. During an experiment, the region of the silica tube above the furnace will be insulated with ceramic wool to minimize heat loss.

A thermocouple will be extended down the tube to a position near or in contact with the specimen to record its temperature during an experiment. The thermocouple will be placed in contact with the specimen when it is necessary to determine how much addtional heating the simulated solar energy provides.

The chlorine-argon gas mixture is supplied from a pressure-regulated cylinder with a needle valve. If deemed necessary, the gas mixture can be scrubbed in concentrated sulfuric acid and passed over calcium chloride pellets before being metered by a


Figure 1.20 Experimental apparatus.
calibrated orifice-manometer. An accuracy of $\pm 2 \%$ is desired for gas flow rates. A total. gas flow rate of $500 \mathrm{cc} /$ minute or greater will be used with chlorine concentrations ranging from 0 to $12 \%$.

The metal specimens will be both annealed and cold rolled. They will be rubbed with abrasive powder and rinsed with acetone to remove scale and thereby provide a uniform surface. The surface area should be about 4-5 $\mathrm{cm}^{2}$.

Results to Date. The primary effort in the past 5 months has involved design and construction of the experimental apparatus. A photograph of the nearly completed unit is shown in Figure 1.20. The system includes a Cahn microbalance, resistance wound furnace, solar simulator, gas delivery system, reaction chamber, furnace control unit, and associated electronics. The apparatus is undergoing initial testing at this time.

## Future Work

Three major experimental tests will be performed. The first seeks to confirm the Bureau of Mines' results and to determine the chlorination rates without UV light. The second set of experiments will determine the reaction rates under the same conditions, but with UV light. The third stage of the experimental program will extend those tests to lower reaction temperatures and varying concentrations of light. Chlorine levels will vary from $0 \%$ to $12 \%$, and the reaction temperature between $300^{\circ}$ and $450^{\circ} \mathrm{C}$.

These experiments will help to establish the experimental and theoretical basis for the direct production of energetic radicals from solar energy and the use of those radicals in the processing of lunar materials.

## References

Fletcher, D. B., 1987, "UV/Ozone Process Treats Toxics," Water World News, Vol. 3, No. 3, pp. 25-27.

Glaze, W. H., Kang, J. W., and Chapin, D. H., 1987, "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultra Violet Ratiation," Ozone Science and Engineering, Vol. 9, pp. 335-352.

Landsberg, A. and Block, F., 1965, "A Study of the Chlorination Kinetics of Germanium, Silicon, Iron, Tungsten, Molybdenum, Columbium, and Tantalum," Report 6649, U.S. Bureau of Mines.

Legan, R. W., 1982, "Ultraviolet Light Takes on CPI Role," Chemical Engineering, Vol. 89, No. 2, pp. 95-100.

Lynch, D. C., 1989, "Chlorination Processing of Local Planetary Ores for Oxygen and Metallurgically Important Metals," Annual Progress Report 1989-99, NASA Space Engineering Research Center, University of Arizona, pp. 1-25-35.

Osborn, D. E., 1986, "Spectrally Selective Beam Splitters Designed to Decouple Quantum and Thermal Solar Energy Conversion in Hybrid Concentrating Systems," Final Report, SERI Contract XK-4-04070-01 and Sandia Contract 04-5348, University of Arizona.

Osborn, D. E., Sierka, R., and Karpiscak, M., 1988, "Solar Thermal Water Reclamation and Toxic Waste Destruction," Final Report SERI Contract XX-7-07199-1, University of Arizona.

# Oxygen Production by Electrolysis of Molten Lunar Regolith 

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## Introduction

Previous work has shown that FeO and $\mathrm{O}_{2}$ can be derived by electrolysis from silicate melt of a composition typical of lunar soils. (Oppenheim 1968, Lindstrom and Haskin 1979). In the present study, we attempt to further refine the conditions necessary to optimize production and to determine efficiencies of production (how much product is derived for a given current) and purity of products.

Our goal in this study has been threefold. First, we want to define the theoretical energy requirements of the process. This includes studies of the relevant oxidationreduction reactions in the melt, their kinetics and energies of reaction, and experimental determination of production efficiencies and melt resistivities as functions of melt composition and applied potential.

Second, we want to characterize the products) of silicate electrolysis. This includes evaluating the phase relationships in the systems $\mathrm{SiO}_{2}-\mathrm{TiO}_{2}-\mathrm{Al}_{2} \mathrm{O}_{3}-\mathrm{MgO}-\mathrm{FeO}-$ CaO and $\mathrm{Fe}-\mathrm{Si}$; estimating the compositions of the metal products as a function of applied potential and feedstock composition based on phase equilibria in the $\mathrm{Fe}-\mathrm{Si}$ system and free energy values for $\mathrm{SiO}_{2}$ and FeO reported in the literature; definition of compositions of products in actual experiments; and definition of the form the product takes, whether phases separate or remain fixed, whether crystals settle or float in the remaining melt, and how large crystals form.

Third, we want to identify materials that can serve as electrodes and container materials for these highly corrosive high-temperature silicate melts. This includes identifying materials that may be either inert or thermodynamically stable in these melts, and experimental testing of the materials to confirm that they do not deteriorate. The ensuing report discusses our results within this framework.

## Theory

We now understand in some detail the chemistry of the oxidation-reduction reactions involved in the electrolysis of silicate melts. 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. Much of this work is currently in final revision before publication (Haskin et al. 1990).

We have identified the cathode reactions that produce melt as the following:

$$
\begin{align*}
\mathrm{Fe}^{2+}+2 \mathrm{e}^{-} & =\mathrm{Fe}^{\circ}  \tag{1}\\
\mathrm{Si}(\mathrm{IV})+4 \mathrm{e}^{-} & =\mathrm{Si}^{\circ} . \tag{2}
\end{align*}
$$

Based on comparison with reductions of other cations such as $\mathrm{Ni}, \mathrm{Co}$, and Zn , these reactions are fast and will present no kinetics problems at current-densities needed to produce oxygen at a sufficiently high rate. Competing reactions at the cathode include the reductions of trace and minor melts, such as $\mathrm{Cr}, \mathrm{Ti}, \mathrm{Mn}$, and Ni , and the reduction of oxygen dissolved in the silicate melt.

At the anode, the principal reaction is

$$
\begin{equation*}
4\left(\mathrm{SiO}^{-}\right)=2(\mathrm{Si}-\mathrm{O}-\mathrm{Si})+\mathrm{O}^{2-}+4 \mathrm{e}^{-} \tag{3}
\end{equation*}
$$

The kinetics of this reaction are also fast.
A serious competing reaction at the anode in melts with high iron concentrations is oxidation of $\mathrm{Fe}^{2+}$

$$
\begin{equation*}
\mathrm{Fe}^{2+}=\mathrm{Fe}^{3+}+\mathrm{e}^{-} \tag{4}
\end{equation*}
$$

Other competing reactions at the anode include oxidation of other multivalent cations such as Ti and Cr .

We identify the variables important in calculating the energy required by the electrolysis process as follows: 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 $E_{c}-E_{a}-\eta_{c}-\eta_{a}-I\left(R_{c e l l}\right)$, where $E_{c}-E_{a}$ is the potential required to drive the reaction(s) and is a function of the cation reduced $\| E_{c}$ $\mathrm{E}_{\mathrm{a}} \mid$ increases in the order $\mathrm{Fe}<\mathrm{Si}, \mathrm{Ti}<\mathrm{Mg}, \mathrm{Al}<\mathrm{Ca}$ ) and the concentrations of the cations in the melt. The quantity $-\eta_{\mathrm{c}}-\eta_{\mathrm{a}}$ 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). $R_{\text {cell }}$ 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 surfac area, and $\kappa$ is the melt conductivity. This expression illustrates the dependence of power on both cell configuration and resistivity of the molten feedstock. Not unexpectedly, $\kappa$ is found to increase as the average ionic mobility of the melt increases. That is, $k$ increases systematically as mobile cations such as $\mathrm{Fe}, \mathrm{Mg}$, and Ca increase relative to Si and Al in the melt.

We have now determined values for most of the variables identified in the discussion above. Because reaction (4) is the primary competing reaction at the anode, the efficiency of oxygen production (defined as moles $\mathrm{O}_{2}$ produced/4-moles electrons passed through the melt) depends primarily on the concentration of $\mathrm{Fe}^{2+}$ cations. The dependence of oxygen production efficiency on $\mathrm{Fe}^{2+}$ concentration can be expressed as $\% \mathrm{O}_{2} /\left(100-\% \mathrm{O}_{2}\right) \cong 0.049 / \mathrm{X}_{\mathrm{FeO}}$, where $\% \mathrm{O}_{2}$ is the oxygen production efficiency as a percentage and $\mathrm{X}_{\mathrm{FeO}}$ is molar fraction FeO in the melt (see Figure 1.21). 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\%).

We have reported conductivities of molten silicates with compositions similar to those of molten lunar rocks and soils in the temperature range 1420-1550 ${ }^{\circ}$ (Haskin et al. 1990). The values lie in the range $0.08-40 \mathrm{ohms}^{-1} \mathrm{~cm}^{-1}$. These values appear adequate for robust cell design. A systematic variation in conductivity with composition is observed. The theoretically expected variation of conductivity with composition at


Figure 1.21 Diagram from Haskin et al. (1990) showing the dependence of oxygen production efficiency (defined in text) on concentration of ferrous iron in the melt.
constant temperature can be expressed by

$$
\text { Conductivity } \propto \Sigma X_{i} D_{i} Z_{i}^{2},
$$

where $X_{i}$ is the molar concentration of $i, D_{1}$ is diffusivity of $i$, and $Z_{i}$ is the charge of $i$ (Reiger 1987, p. 160). This expression is similar to the relationship we observe between composition and conductivity, permitting conductivity to be predicted for any given composition.

We have found no kinetic problems associated with either anodic or cathodic reactions (both reactions being fast at the expected current-densities) and therefore expect low overpotentials arising from kinetic problems. 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.

New experiments are currently underway that will extend some of these results to compositions more typical of lunar soils. These experiments include a study of redox reactions for various cations in silicate melts of basaltic composition (similar to Apollo 12 soil) and compositions along the join Diopside $\left(\mathrm{Mg}_{2} \mathrm{Si}_{2} \mathrm{O}_{6}\right)$-Anorthite ( $\mathrm{CaAl}_{2} \mathrm{Si}_{2} \mathrm{O}_{8}$ ). These studies will demonstrate how the potential required to reduce various species changes as a function of composition [extending the results of Semkow and Haskin (1985) to more realtistic soil compositions], as well as confirm that there are no kinetic problems with the reactions in these more realistic melts. Figure 1.22 shows preliminary results of these experiments illustrating the shift in Ni reduction potential as a function of silicate melt polymerization.

## Characterization of Products

Based on known phase equilibria in basaltic systems; on phase equilibria in the system $\mathrm{Fe}-\mathrm{Si}$; on thermodynamic data for the reduction of the cations of $\mathrm{Fe}, \mathrm{Si}, \mathrm{Al}, \mathrm{Ti}$, Mg , and Ca ; and on our experiments already reported (Lindstrom and Haskin 1979, Semkow and Haskin 1985, Colson and Haskin 1990a,b), we expect the products of silicate electrolysis to be as follows (at a temperature of, for example, $1350^{\circ} \mathrm{C}$ and at a reduction potential of about -1.5 volts):

Predictions From Theory: Two or three metal phases form at the cathode (depending on the $\mathrm{Si} / \mathrm{Fe}$ ratio of the bulk metal). These metal phases will contain varying amounts of $\mathrm{Si}, \mathrm{Fe}, \mathrm{Cr}, \mathrm{Mn}$, and Ti (and small amounts of trace constituents such as Ni ), with the $\mathrm{Si} / \mathrm{Fe}$ ratio of each phase


Figure 1.22 Diagram showing the dependence of Ni reduction potential on polymerization of the melt. $X_{n b o}$ and $X_{b o}$ are fraction non-bridging ( Si O ) and bridging ( $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$ ) oxygens, respectively. Trend is opposite of that expected and that reported by Semkow and Haskin (1985).
roughly defined by the Si-Fe phase diagram. Oxygen is liberated at the anode. Depending on the temperature and extent of $\mathrm{SiO}_{2}$ removal, spinel $(\mathrm{Mg}, \mathrm{Fe})(\mathrm{Al}, \mathrm{Cr})_{2} \mathrm{O}_{4}$ is expected to precipitate from the residual melt.

We have now begun a new set of experiments designed to test these predictions. These experiments are designed so that current and cell resistance can be measured and potential controlled simultaneously. This permits results to be interpreted in light of a known value for $E_{c}-E_{a}$. All measurements are made and instruments controlled by an AT-type personal computer attached to the instruments by an IEEE-488 bus. A diagram of the experimental circuitry is shown in Figure 1.23.

Results of these experiments should define product compositions as a function of feedstock, applied potential, and extent of electrolysis, thereby testing theory. They should give a qualitative idea of how cell resistance changes with extent of electrolysis, again testing theory. They should give a semi-quantitative estimate of the overpotentials required to drive the electrolysis and how the required overpotentials


Figure 1.23 Diagram of circuit designed to measure cell resistance (via the $10000-\mathrm{Hz}$ waveform generator and voltmeters) and control the DC potential (via the PAR 176/276 for current <1A, or the HP6033A for higher currents). IEEE488 bus lines go to an AT-type computer that controls the experiment.
affect product composition. They should define the behavior of the products, whether the products float or sink, whether they separate or mix with other products, and what size of crystals or crystal aggregates are formed. As discussed below, these experiments also give a handle on the durability of the chosen electrode materials.

Preliminary experiments (each sample about 80 mg , mounted on a small Pt wire loop with temperature, atmosphere, and electrode potential controlled) show that the phase equilibria and metal phase compositions vary in a manner similar to that predicted from theoretical calculations, with $\mathrm{Si} / \mathrm{Fe}$ ratio in the product melt increasing
with increasing potential and spinel crystallizing as $\mathrm{SiO}_{2}$ removed from the melt (at $1350^{\circ} \mathrm{C}$ ). The metal has a somewhat lower $\mathrm{Si} / \mathrm{Fe}$ ratio than expected, possibly reflecting the lower mobility of Si in the melt relative to Fe.

Microprobe analyses of products from two experiments are reported in Table 1.8, illustrating the effects of applied potential and initial magma composition on metal composition, oxygen production efficiency, and spinel composition. The difference in composition between the two is that the second is like the first, with Si and Fe removed in the proportions expected to be removed by the electrolysis. Therefore, to some degree, these two illustrate how compositions change with extent of electrolysis.

Experiment A12_1, an electrolysis of an Apollo 12-soil-iike composition, contains Fe-Cr-rich spinel and nearly pure Fe metal, and has a low oxygen production efficiency (28\%). Experiment A12_1cb, which was at a higher potential with lower Si and Fe in the initial melt, contains Mg-Al-rich spinel, three distinct Fe-Si phases that contain significant amounts of Ti and Cr (the presence of Ir is due to use of Ir as the cathode material in these experiments), and somewhat higher oxygen production efficiency (45\%). A backscattered electron image of the three metal phases is shown in Figure 1.24 .

## Testing of Electrode and Container Materials

We have suggested that Si may make a suitable cathode material (Haskin et al. 1990). We have made several efforts to test Si experimentally, but have run into difficulty mounting the Si as a cathode in our experiments. The Si cannot be mounted to Pt because of the low Si-Pt eutectic. We have tried welding the Si to Ir but, so far, the Si has either broken away from the weld-joint or has reacted with C in the reducing acetylene flame. We have tried mounting the Si to tungsten, but the tungsten oxidizes under our experimental conditions.

We have suggested the use of Pt as anode material (Haskin et al. 1990). There are also some experimental difficulties with testing the Pt as an anode, linked primarily to the small scale of our experiments. Even if the Pt lost from the anode was $10 \%$ of the amount of oxygen generated, it would not necessarily be apparent from looking at the electrode after the experiment that any Pt was lost, because the total Pt mass is large compared to the mass of oxygen generated. However, we have taken an alternative approach to estimating the Pt lost from the anode. We note that any Pt lost would be dissolved in the silicate melt and ultimately reduced to metal at the cathode. We have analyzed for Pt in the silicate glass and metal product of our electrolysis experiments (by electron microprobe) and have detected a Pt peak (Figure 1.25 ), suggesting that

Table 1.8 Microprobe analyses of metals and glasses in two experiments in Apollo 12-like melts. ${ }^{\text {a }}$
a. Metal Phase(s).

|  | A12_1 | A12_1cb |  |  |
| :--- | ---: | :---: | :---: | :---: |
| Si | 0.024 | 2.471 | 6.999 | 7.389 |
| Ti | 0.040 | 0.142 | 0.464 | 0.581 |
| Cr | -0.007 | 0.567 | 0.370 | 0.356 |
| Mn | -0.037 | 0.231 | 0.041 | 0.037 |
| Fe | 9.13 | 33.12 | 29.28 | 30.06 |
| Ir | 0.000 | 56.40 | 56.50 | 56.40 |
| Pt | -0.021 | - | - | - |

b. Glass and Spinel+Glass ( $\mathrm{S}+\mathrm{G}$ ).

|  | A12_1 |  | A12_1cb |  |
| :--- | ---: | ---: | ---: | ---: |
|  | Glass | $\mathrm{S}+\mathrm{G}$ | Glass | $\mathrm{S}+\mathrm{G}$ |
| $\mathrm{SiO}_{2}$ | 49.48 | 0.13 | 49.21 | 48.07 |
| $\mathrm{TiO}_{2}$ | 2.34 | 1.16 | 2.76 | 2.78 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 10.78 | 9.10 | 18.92 | 19.31 |
| FeO | 13.23 | 42.37 | 0.69 | 0.41 |
| MgO | 10.09 | 12.63 | 14.23 | 14.69 |
| CaO | 9.96 | 0.31 | 12.48 | 11.99 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.12 | -0.01 | 0.82 | 0.70 |
| $\mathrm{~K}_{2} \mathrm{O}$ | 0.10 | 0.00 | 0.08 | 0.08 |

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Figure 1.24 Backscattered electron image of the three metal phases in A12 1cb showing differences in density (white is more iron-rich, black is more Si rich) and the mixed nature of the phases.


Figure 1.25
Microprobe profile across the Pt L-alpha peak illustrating the absence of Pt in the glass of experiment A 12 1, suggesting significant Pt does not erode from the anodes during electrolysis. The peak observed at the left of the profile is a higher order Zn peak (although Zn was not added to these experiments, it exists as a contaminant in the reagents used to make the synthetic composition).
significant Pt is not lost from the anode. Shown as a function of oxygen generated, this is expressed as: Pt lost (mass)/oxygen produced (mass) $<1.8 \times 10^{-3}$ (2 sigma uncertainty).

Papers and abstracts describing many of these results in more detail are given in the list of references. Haskin et al. (1990) is in final revision before publication, as is Haskin (1990). The papers by Colson and Haskin (1990b) and Haskin and Colson (1990) are included as Appendices $D$ and $E$, respectively.

## References

Colson, R. O. and Haskin, L. A., 1990a, "Lunar Oxygen and Metal for Use in Near-Earth Space: Magma Electrolysis,". ASCE/AIAA Space 90 Engineering, Construction, and Operations in Space (abstract).

Colson, R. O. and Haskin, L. A., 1990b, "Lunar Oxygen and Metal for Use in Near-Earth Space: Magma Electrolysis," Engineering, Construction, and Operations in Space (S. W. Johnson and J. P. Wetzel, eds.) (in review)."

Haskin, L. A., 1990, "Water and Cheese From the Lunar Desert: Abundances and Accessibility of H, N, and C on the Moon," Lunar Bases and Space Activities of the 21 st Century (II) (W. W. Mendell, ed.) (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 (T. Triffet, ed.) (in preparation)."

Haskin, L. A., Colson, R. O., Lindstorm, D. J., Lewis, R. H., and Semkow, K. W., 1990, "Electrolytic Smelting of Lunar Rock for Oxygen and Iron," Lunar Bases and Space Activities of the 21st Century (II) (W. W. Mendell, ed.) (in press).

Lindstrom, D. J. and Haskin, L. A., 1979, "Electrochemical Preparation of Useful Material From Ordinary Silicate Rocks," pages 129-134 in Space Manufacturing Facilities J. Grey and C. Drop, eds.), AIAA, New York.

Oppenheim, M. J., 1968, "On the Electrolysis of Molten Basalt," Mineral. Mag., Vol. 36, pp. 1104-1122.

Reiger, P. H., 1987, Electrochemistry, Prentice-Hall, Englewood Cliffs, N.J.
Semkow, K. W. and Haskin, L. A., 1985, "Concentrations and Behavior of Oxygen and Oxide Ion in Melts of Composition $\mathrm{CaO} \cdot \mathrm{Mg} \times \mathrm{xSO}_{2}, "$ Geochim. Cosmochim. Acta, Vol. 49, pp. 1897-1908.

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## Helium -3 in the Lunar Regolith ${ }^{*}$ T. Swindle

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We have completed a preliminary assessment of ${ }^{3} \mathrm{He}$ distribution in lunar soils, including variations with soil location, depth, composition, grain size, and other parameters that might be useful in developing mining scenarios. One of the primary tools is a compilation of available analyses of ${ }^{3} \mathrm{He}$ in lunar samples. The compilation includes analyses of more than 250 numbered samples (plus duplicates and subsamples in many cases) from the American and Russian lunar programs, reported in nearly 100 publications. In addition, we have computed average abundances for soils from each of the Apollo landing sites. These have been coupled with models and measurements of other pertinent parameters.

The distributions of ${ }^{3} \mathrm{He}$ within grains, and hence variations of ${ }^{3} \mathrm{He}$ concentration with grain size, are well-understood. Solar-wind-implanted gases, including ${ }^{3} \mathrm{He}$, are concentrated near the surfaces of grains, in a region less than $10^{-7} \mathrm{~m}$ thick. Therefore, smaller grains, which have a larger ratio of surface to volume, contain more ${ }^{3} \mathrm{He}$ per gram than larger grains. Whether the enhancement is sufficient to warrant grain-size separation before extraction is less certain, particularly when losses during separation are considered.

Variations with soil composition are also well-understood. For grains with comparable exposure histories, ${ }^{3} \mathrm{He}$ concentration correlates with Ti concentration. This is because Ti is primarily found in the mineral ilmenite, which is far more resistant to He loss than any other common mineral. In this case, it is clear that beneficiation is not economical, since only a small fraction of the ilmenite can be readily separated.

Regional variations in ${ }^{3} \mathrm{He}$ concentration depend both on Ti concentration and exposure history. They can be estimated, though with some uncertainty, by using remote sensing techniques. Estimates based on presently available remote-sensing data suggest that the areas richest in Ti , and hence in ${ }^{3} \mathrm{He}$, are likely to be the nearside maria, with Mare Tranquillitatis probably the most promising site. It might be possible to refine these estimates, but it would require work (in particular, improving techniques for remote determinations of soil "maturity" or bombardment history) beyond the scope of this project.

By far the largest uncertainty stems from our lack of knowledge of variations with depth in the structure and ${ }^{3} \mathrm{He}$ content of the regolith. Only three drill cores with depths of more than 1 m have been returned from the Moon, and the deepest of these sampled less than 3 m . Furthermore, the depth to which the regolith extends is largely
unknown, although there are experimental techniques (based on seismic data and analyses of the morphology of photographed craters) and models that address the question. Since the range of reasonable assumptions gives total lunar ${ }^{3} \mathrm{He}$ abundances that vary by a factor of about 10, our estimates are based on the extreme values of reasonable assumptions. We calculate total lunar ${ }^{3} \mathrm{He}$ contents ranging from about $4 \times$ 105 metric tons to $4 \times 106$ metric tons. Even from the few drill cores available, it is clear that the ${ }^{3} \mathrm{He}$ distribution with depth is variable from one location to another, a factor that has to be considered in designing the mining system.

## II. STRUCTURAL MATERIALS



Summary
Science Applications International Corporation (SAIC) has investigated the . feasibility of producing solar reflectors from indigenous lunar materials for solar power production on the Moon. First, lunar construction materials and production processes were reviewed, and candidate materials for reflector production were identified. At the same time, lunar environmental conditions were reviewed for their effect on production of concentrators. Next, conceptual designs and fabrication methods were proposed and studied for production of dish concentrators and heliostats. Finally, fabrication testing was performed on small-scale models using Earth analogues of lunar materials. Findings from this initial investigation indicate that production of concentrators from lunar materials may be an attractive approach for solar energy production on the Moon. Further design and testing are required to determine the best techniques and approaches to optimize this concept.

Four materials were identified as having high potential for solar reflector manufacture. These baseline materials were foamed glass, concrete with glass-fiber reinforcement, a glass-fiber/glass-melt composite, and an iron-glass sintered material. Lunar-produced metals were generally expected to be too costly and their production too energy intensive for large-scale use in solar reflector fabrication. Two exceptions to this conclusion are the use of very thin foils for heliostat membranes (like terrestrial membrane heliostats) and the use of aluminum for reflective surfaces. Vacuumsputtering of aluminum onto the front surface of concentrators was selected as the best approach for production of all reflective surfaces.

Molding of dish reflectors on male molds was chosen as the preferred method of fabrication over free-forming techniques using membrane technology or spin molding. The main advantage of molding is reduced risk. Techniques for focusing heliostat concentrators using static electricity were identified. A passive tracker drive for dish concentrators was also proposed.

Testing of fabrication techniques is being carried out for the four baseline materials. Small-scale models of lunar dishes are being fabricated. The foam glass material is being simulated by polyester resin containing glass microspheres. This allows testing to be conducted at room temperature. Lunar concrete is being simulated with high-alumina cement and ground terrestrial anorthite aggregate, and chopped glass fibers are being used for reinforcement. Fabrication tests with the glass-glass composite and iron-glass sintered material are being conducting using high-lead glass,
with a low melting temperature for the molten glass portion, in order to reduce temperature requirements for the tests.

## Introduction

Dependence upon the Earth for materials and power makes a space colony very vulnerable to supply problems. Also, the cost of transport of materials out of the Earth's gravitational potential well is very high. Finally, the most available form of long-term power is solar energy. Therefore, production of a solar collection system in which large portions of the system are constructed of indigenous materials has promise for increasing the autonomy and security of such colonies. Lunar colonies are of particular interest at present, due to the Moon's proximity and its likelihood as a starting point for colonization and as a debarkation point for extended excursions into space.

In this project, Science Applications Interational Corporation (SAIC) has studied the feasibility of using materials produced from lunar soil to form reflectors for distributed or central concentrating solar power systems for lunar settlements. These systems may employ photovoltaic or solar thermal receivers to produce electric power or provide high-temperature thermal energy for the needs of the lunar colony.

## Lunar Materials Evaluation

The lunar surface is unique in comparison to terrestrial soils. One effect of meteorite impacts is to mix and homogenize surface constituents through great depths of soil. This fact, together with the lack of a hydraulic cycle on the Moon, means that no ore deposits or mineral concentrations due to evaporation are to be found. Another effect of meteorite impacts is the lithification of various components of the soil into lunar rocks called breccias. Thermal cycling and micrometeorite impacts contribute to the comminution of surface materials into a very fine dust, which forms the "lunar soil," or regolith. The lack of life-forms eliminates the presence of organic compounds, and many common terrestrial constituents such as $\mathrm{C}, \mathrm{Na}$, and Cl are also rare. Finally, the lunar surface environment, consisting of a high vacuum, means that the only gases present in the surface materials are those captured from the solar wind.

The lunar surface may be broadly divided into mare and highland regions. Mare regions are characterized by being low-lying areas consisting mainly of basalts that were ejected from the Moon's core. The highlands are, physically, about a kilometer above the maria and consist mainly of feldspar-rich plutonic material, with minor amounts of aluminum and trace-element-rich basaltic minerals. Table 2.1 (taken from

Table 2.1 Chemical compositions (Wt. \%) for the major minerals.
a. High-Titanium Basalts

|  | Modal Abundance (Volume \%) |  |  |  |
| :--- | :---: | :---: | :---: | :---: |

b. Low-Titanium Basalts

|  | Modal Abundance (Volume \%) |  |  |  |
| :--- | ---: | ---: | :---: | :---: |

c. Highlands Rocks

|  | Modal Abundance (Volume \%) |  |  |  |
| :--- | :---: | ---: | :---: | :---: |
|  | Pyroxene | Olivine <br> $0-35 \%$ |  | Plagioglase <br> $45-95 \%$ |
| $5-35 \%$ | Opaques <br> (Mostly Ilmenite) <br> $0-5 \%$ |  |  |  |
| $\mathrm{SiO}_{2}$ | $51.1-55.4$ | $37.7-39.9$ | $44.0-48.0$ | $0.0-0.1$ |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | $1.0-2.5$ | $0.0-0.1$ | $32.0-36.0$ | $0.8-65.0$ |
| $\mathrm{TiO}_{2}$ | $0.45-1.3$ | $0.0-0.1$ | $0.02-0.03$ | $0.4-53.0$ |
| $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | $0.3-0.7$ | $0.0-0.1$ | $0.0-0.02$ | $0.4-4.0$ |
| $\mathrm{FeO}^{\mathrm{MgO}}$ | $8.2-24.0$ | $13.4-27.3$ | $0.18-0.34$ | $11.6-36.0$ |
| CaO | $16.7-30.9$ | $33.4-45.5$ | $0.0-0.18$ | $7.7-20.0$ |
| $\mathrm{Na}_{2} \mathrm{O}$ | $1.9-16.7$ | $0.2-0.3$ | $19.0-20.0$ | $0.0-0.6$ |
| $\mathrm{~K}_{2} \mathrm{O}$ | - | - | $0.0-0.6$ | - |

Waldron et al. 1979) summarizes the ranges of chemical compositions for the major minerals that are found in these regions.

The metal-bearing silicates, pyroxene, anorthite, and olivine are the primary minerals available from the lunar surface. The oxide ilmenite is also present to a lesser extent. These mineral groups contain oxygen, silica, and the metals iron, magnesium, titanium, and aluminum. The lunar regolith also contains a high concentration of glass from micrometeorite bombardment. To exploit these natural resources, the raw material must be heated to allow certain chemical reactions to occur. The amount of thermal energy required to process these minerals depends largely on the specific heats and melting points of the minerals. These data are shown in Table 2.2 (taken from SAIC 1989).

Table 2.2 Thermal properties of various lunar materials.

| Mineral | $C_{p}$ <br> $(\mathrm{~kJ} / \mathrm{kg} / \mathrm{K})$ | $\mathrm{C}_{\mathrm{p}}$ <br> $(\mathrm{kWh} / \mathrm{kg} / \mathrm{K})$ | Melting <br> Point $(\circ \mathrm{K})^{\mathrm{a}}$ |
| :--- | :---: | :---: | :--- |
| Ilmenite $\left(\mathrm{FeTiO}_{3}\right)$ | 0.687 | 0.000190 | 1640 |
| Anorthite $\left(\mathrm{CaAl}_{2} \mathrm{Si}_{2} \mathrm{O}_{8}\right)$ | 0.755 | 0.000209 | 1823 |
| Olivine $\left[\left(\mathrm{Mg}_{2}, \mathrm{Fe}_{2}\right) \mathrm{SiO}_{4}\right]$ | 0.790 | 0.000219 | $1478-2163$ |
| Pyroxene $\left[(\mathrm{Mg}, \mathrm{CA}, \mathrm{Fe}) \mathrm{SiO}_{3}\right]$ | 0.766 | 0.000213 | $1813-1830$ |

${ }^{\text {a }}$ From Williams and Jadwick (1980).

Many useful products can be generated from lunar minerals via various chemical and physical processes. Some of the processes being considered are hydrogen reduction, carbothermal reduction, carbochlorination, hydrofluoric acid leaching, magma electrolysis, and vapor phase reduction. These processes extract oxygen, metals, and silicates from the lunar regolith. For the purposes of this study, the materials of particular interest are structural materials for solar reflector support structures and surfaces and materials that can be used for coatings (particularly aluminum for reflective surfaces). Table 2.3 shows that high-strength metals, glasses, ceramic materials, and concrete-like materials form the basic possibilities for lunar structural materials. The production, abundance, and characteristics of each of these types of materials are discussed in the following subsections.

Metals. Metals found on the Moon in significant quantities include iron, aluminum, magnesium, and titanium. Processes to extract these elements from lunar soil have been

Table 2.3 Possible useful products from lunar sources.

## Structural Materials

Metals: Steels, aluminum, magnesium, titanium
Reinforced Metals: Aluminum, magnesium reinforced with silica, steel, or alumina Glasses, fused silica
Ceramics, alumina, magnesia, silica, compounds
Hydraulic cements (need water
Thermal Materials
Refractories plus chromia, titania, titanium silicide
Same as ceramics above, plus castables, ramming cements, insulation, fiberglass, fibrous or powdered ceramics

## Electrical Materials

Conductors: Aluminum, iron, resistance alloys ( FeCrAl )
Electrodes: Graphite, $\mathrm{Fe}_{3} \mathrm{O}_{4}$
Magnetic materials, iron alloys, magnetic ceramics
Insulation, glass, ceramics
Fibrous Materials
Glass, silica (for apparel, paper, filters, etc.)
Plastics, Elastomers, and Sealants
Soluble silicates, silicone resins (contain some C)

## Adhesives and Coatings

Anodized aluminum, magnesium, titanium electroplating (Cr)
Sputtered coatings, etc.
Lubricants, Heat-Transfer Fluids
Sulfides, $\mathrm{SO}_{2}$, He
Industrial Chemicals
Detergents, cleansers, solvents, acids, bases, $\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{H}_{3} \mathrm{PO}_{4}, \mathrm{CaO}, \mathrm{NaOH}$

## Biosupport

Oxygen (breathing), 16/18 of water by mass
$\mathrm{SiO}_{2}$ : Soil component (includes many trace nutrients)
Constituent Elements of Life-Forms: $\mathrm{O}, \mathrm{Ca}, \mathrm{C}, \mathrm{Fe}, \mathrm{Mg}, \mathrm{K}, \mathrm{P}, \mathrm{N}, \mathrm{Na}, \mathrm{H}$, and others
developed (Waldron et al. 1979, AIAA 1988) and their use as structural elements needs no explanation. However, there are constraints in both their absolute quantities in lunar soils and in other materials needed to utilize these materials effectively. For instance, some important alloying materials for the production of steel, such as $\mathrm{C}, \mathrm{Ni}, \mathrm{Mo}, \mathrm{W}, \mathrm{V}$, and Nb , are not readily available on the Moon. Likewise, production of high-strength alloys of aluminum, magnesium, and titanium require elements (particularly Zn and Mo ) not found in abundance on the Moon. Thus, although many commercial alloys can be
made solely from lunar materials, importation of small amounts of some materials from Earth is almost certain.

Metals are not found in large concentrations in lunar materials, although elemental iron is found in the form of small particles in some lunar materials. In any case, significant processing must be done to obtain useful structural alloys. Therefore, in comparison to some of the other structural materials available, such as glass, it may require more effort to produce the large quantities of metallic materials needed for large solar reflectors from lunar materials. Also, metallic materials have many uses for which other materials cannot easily be substituted, such as electrical conductors. Thus, their use may be, to a large extent, dictated by other needs of the lunar colony. For these reasons, metals are expected to be less attractive than other lunar materials for use in solar reflectors. One probable use for metals in solar reflectors is vacuumdeposited aluminum to produce highly reflective surfaces. This is expected to be attractive because the process uses very little material, it requires a vacuum environment anyway, and it produces high-quality reflective surfaces.

Glasses. All lunar materials form glasses easily upon being melted. In fact, the presence of small glass spheres is common in lunar samples (although they constitute only a tiny percentage of the total mass) due to vitrification from meteorite impacts. Lunar mare materials consist of a material very similar to terrestrial basalt. Here on Earth, cast basalt is already used for chemical process components, including pipes, tees, Y -sections, and cyclones. Thus, the technology for processing this material is already developed. Although normal lunar glass is brown due to impurities, glass produced from anorthite can be made colorless by the removal of iron contamination.

In earlier studies (NASA n.d., Lunar and Planetary Institute 1980), glass from lunar materials was proposed as the structural material from which most of a space power system could be constructed. The proposed process, shown in Figure 2.1 (from Lunar and Planetary Institute 1980), takes normal lunar soil, removes metallic iron particles magnetically, and then melts the remainder to form a glass melt from which fiberglass and glass sheet are produced. In addition, it was proposed to electrolyze oxygen from the melt for the production of foamed glass. Other studies performed at Los Alamos National Laboratory proposed that lunar soil could be melted in-place by an electrically heated molybdenum or tungsten mandrill to form a glass-like material that would form the walls and ceilings of a lunar habitat (Rowley and Neudecker 1980).

Another factor in favor of the use of glass over metals is the amount of energy required to produce it. Table 2.4 (from Friedlander and Cole 1989) summarizes the energy and power requirements for lunar glass and metals processing. Glass products

Figure 2.1 Schematic process for production of lunar glass products.

Table 2.4 Energy and power requirements for lunar glass and metal production.

|  | Product |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Fiberglass | SilicaGlass | Aluminum | Titanium/Iron | Iron |
| Beneficiated Feedstock | Anorthite | Bulk soil slag, CoO | Anorthite | Ilmenite | Ilmenite |
| Process Technique | Meltdown | Meitdown | ----Car | rination------ | Carbothermal |
| Process Energy (kWh/ton) |  | : |  | - |  |
| Thermal | 878 | 534 | 9890 | 2080/4910 | 3500 |
| Electric |  |  | 9000 |  |  |
| Throughput (tons/yr) | 10,000 | 10,000 | 1000 | 860/1000 | 1000 |
| Total Power (kW) |  |  |  |  |  |
| Thermal | 1000 | 610 | 1129 | 765 | 400 |
| Electrical | 55 | 17 | 1049 | 25 | 41 |

require far less energy to produce than any of the metals listed. In addition, they are amenable to far larger production volumes.

Since glass can be easily produced from lunar materials in large quantities, it appears a very promising material for solar reflectors. Glass has many desirable characteristics for production of solar reflectors, including high strength, low chemical activity, excellent surface finish, and ease of forming. Clear glasses could also have applications as lenses or cover glasses for optical components.

Ceramic Materials. Along with components that form glasses, lunar materials contain a high fraction of ceramic materials and ceramic pre-cursors. In particular, alumina $\left(\mathrm{Al}_{2} \mathrm{O}_{3}\right)$, silica $\left(\mathrm{SiO}_{2}\right)$, and magnesia are all present, or can be produced in significant quantities. It is possible to produce a glass-ceramic product from lunar materials that has a tensile strength greater than $345 \mathrm{MPa}(50,000 \mathrm{psi})$ (MacKenzie and Claridge 1979). Ceramics may be useful in the production of glass (e.g., melt tanks can be made of.silica), and they can be used as refractory components of solar collectors (e.g., thermal receivers). Finally, pure silicon produced from lunar materials can be used to make photovoltaic cells.

Cementitious Materials. Little consideration has been given to cement-like lunar materials until very recently, when the Construction Technology Laboratory (CTL) associated with the Portland Cement Institute began to study the production and use of concrete from lunar materials (Lin 1987a, 1987b). These studies have shown that lunar soils can serve as aggregate and that the residue from a simple high-temperature
evaporation process performed on lunar basalt materials may serve as a high-alumina cement. A small block of concrete was, in fact, produced by CTL using Apollo 16 lunar sample materials as aggregate. This concrete sample was tested at CTL to determine its properties, which are summarized in Table 2.5.

Table 2.5 Physical properties of concrete with lunar aggregate.
Compressive Strength: 75.7 MPa
Modulus of Rupture: $\quad 8.3 \mathrm{MPa}$
Modulus of Elasticity: $21,400 \mathrm{MPa}$
Thermal Expansion Coefficient: $5.4 \times 10^{-6} \mathrm{~cm} / \mathrm{cm} /{ }^{\circ} \mathrm{C}$

Normal concrete has a flow flexural strength (about $10 \%$ of its compressive strength). Reinforcement of lunar concrete with glass or steel fibers can greatly increase its flexural strength, strain energy capacity, and ductility. For instance, reinforcement with $4 \%$ steel fibers by weight nearly doubles the flexural strength. Both glass and steel can be produced from lunar materials for use as fiber reinforcements.

Lunar concrete has many good characteristies as a construction material. Concrete strength is retained at temperatures as low as $-150^{\circ} \mathrm{C}$; in fact, its strength actually increases at low temperatures if the humidity is high. Similarly, strength is nearly constant to temperatures of $250^{\circ} \mathrm{C}$ or more, and concrete is thermally stable to $600^{\circ} \mathrm{C}$ or more. Another useful characteristic of concrete is its high resistance to abrasion, which protects against micrometeorite damage. Finally, concrete is resistant to radiation damage and is stabile in a vacuum environment.

One possible complication in the use of lunar concrete is that water is required for the formation of concrete (about 4\% by mass). Since water is essentially non-existent on the Moon, it would probably need to be imported from Earth. The impact of this can be reduced by shipping only hydrogen, which saves $16 / 18$ in the mass that needs to be transported. The hydrogen would be combined with oxygen produced from the lunar soil to form the needed water. Using this approach, the material that would need to be transported from Earth is $0.4 \%$ of the final concrete mass.

## Lunar Conditions and Constraints

In considering the production of solar reflectors on the Moon, consideration of the characteristics of the lunar environment is essential. The lunar environment affects the design, the fabrication, and the operation of any solar reflectors that are produced.

Salient characteristics of the lunar environment are listed in Table 2.6. These include both atmospheric and geologic factors.

Table 2.6 Characteristics of the lunar environment.

```
Atmosphere
    Pressure: <10-14 torr
    Surface Temperatures:
    Solar Insolation:
    Solar Wind:
    Length of Lunar Day:
    Inclination of Axis to Ecliptic:
Daytime up to }11\mp@subsup{0}{}{\circ}\textrm{C
Night down to -170}\textrm{C
1350 W/m
Charged particles of H,O, and other species
708 hours
1/20
Geology
    Gravitational Constant: }\quad1.62\textrm{m}/\mp@subsup{\textrm{s}}{}{2}+\mathrm{ perturbations in maria
    Magnetic Field:
    Moonquakes--Frequency:
                            Energy Release:
                    Average Severity:
            Maximum Severity:
    Surface Heat Flux:
<4.4 \times 10 ' tesla/cm }\mp@subsup{}{}{3
Several thousand per year
<3.6 \times 105 MW
< 2 on Richter Scale
4 on Richter Scale
0.02 W/m}\mp@subsup{}{}{2
```

In the present study, the most important characteristics related to the production and operation of solar reflectors are micrometeorite impacts, temperature variations, gravity, and atmospheric pressure on the lunar surface. Of secondary importance are the solar wind components and the effects of moonquakes. Finally, magnetic field and heat flux effects are expected to be negligible.

Summary of Lunar Concentrator Meeting of 21 November
Materials. Several additional potential structural materials were identified in the course of the meeting:
-Relatively low-temperature $\left(1000^{\circ} \mathrm{C}\right)$ sintering of iron-enriched (i.e., magnetically separated) lunar soil to produce a structural material. This would be a simpler process than either glass or concrete production from lunar soil.

- Use of foamed glass in the same way as concrete to form structural shapes. This would have the additional advantage that the front surface could be made to form a smooth skin for application of the reflective coating. Also, compared to a thin sheet of glass, a foam would be more resistant to fracturing from micrometeorite impacts.
- A glass-glass composite consisting of high-temperature glass fibers in a lowtemperature glass "cement" matrix. This would give a composite with good tensile, as well as compressive, strength for dishes, etc.
- Lamination of glass layers to achieve improved strength.

Vacuum-deposited aluminum as a reflective surface was adopted as a baseline. Because of the difficulty in obtaining an optically smooth surface on concrete, it will require a surface coat of glass or some other substance. This adds another step to the fabrication process.

One possible disadvantage identified for glass collectors is their susceptibility to fracture once cracked (for instance, by micrometeorite impact). Thermal cycling causes stresses that would tend to propagate cracks through a sheet of glass. Some approaches to mitigate this problem are to use foamed glass instead of sheet glass, to design the collector as a faceted dish so that failure of one facet would not put the entire dish out of commission, and to attach the glass surface to another material that would support it (e.g., concrete).

Fabrication Techniques. Several techniques and conceptual design approaches were presented for producing concentrators from lunar materials (see Figure 2.2). A consensus was that molding techniques were preferred to free-forming techniques to reduce the risks in the production process. Several methods, including blow molding, spin molding, injection molding, stamping, and gravity sagging of a sheet into a mold, were determined to be applicable to glass production. Gravity sagging has the disadvantage of requiring production of glass sheet first. Spray-up on a male mold is the preferred technique for concrete collector production. Spin molding of concrete is not likely to be successful, because the concrete will have minimum water and will therefore be quite stiff. Material to be sintered could be placed onto a male mold, then pressed and sintered in place.

Use of solar energy as a heat source is attractive because of its availability and ability to be directed where desired by simple reflectors. The vacuum atmosphere makes heat loss reduction simple, since only radiative heat transfer is possible and, therefore, layers of thin foils will work as excellent thermal insulation.

Conceptual Designs. As mentioned above, free-forming of concentrators was felt to be more risky, so molded methods were preferred. Based upon the designs that were discussed at the meeting, the following are proposed as baseline designs to be examined initially:

- Foam glass over male mold. The approach is to form a glass foam that can be poured/draped over a mold. As the front surface contacts the mold, the foam will coalesce to form a solid glass surface on which the reflective aluminum


## Parabolic Dishes

Blow-mold glass sheet into a spherical shape like a soap bubble: gravity sagging at the bottom would make it more nearly parabolic; extrude glass beams for the edge support ring.


Blow-mold glass sheet into parabolic mold.


Gravity-sag glass sheet into mold.


Spin molding: rotating mold in which a thin layer of glass is melted as it rotates. When the glass cools, it takes on a perfect parabolic shape.


Concrete sprayed over parabolic mold, with glass fiber or iron fiber reinforcement: excess water removed by vacuum pumping and condensation; front surface coated with thin glass and aluminum to form reflective surface.

GNENT


Squirt liquid glass into the air; the liquid will follow a parabolic path, solidifying as it goes, to form parabolic shapes. A single nozzle could produce parabolic ribs, a slotted distributor could make parabolic trough shapes, or a central distributor (like a sprinkler head) could produce a parabolic dish shape.


Figure 2.2 Solar collector manufacturing processes.

Figure 2.2 (Continued).

## Heliostat

Concrete poured into mold or sprayed over forms to make a ring; iron or steel foil, or very thin glass, for membrane. These heliostats would have to be unfocused, which would mean small sizes, or else the membranes would have to be self-supporting.


## Support Structures

Glass beams, with glass foam core for compressive loads and glass fibers for tensile loads.


Zomeworks-type passive trackers, based upon liquid-vapor balance system. This requires the system be supported very near the CG, and that an appropriate liquid be chosen.


## Miscellaneous

Sputtered aluminum first-surface mirror surface on glass substrates. The aluminum will oxidize slightly on the surface due to impingement of oxygen ions from the solar wind. This oxide layer will eliminate the dip in reflectance at about 880 nm that is present for a pure aluminum reflective surface, yielding an excellent reflector.


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layer can be deposited. The back of the dish will remain foam, for structural support and for protection against micrometeorites.

- Concrete applied over male mold. After molding, the concrete shell will be inverted and a thin glass layer applied, possibly by spin-molding. Finally, a reflective layer of aluminum will be applied to the glass surface.
- Iron-ore concentrator formed on male mold by sintering.
- Glass-glass composite. High-temperature fibers will be laid out on a mold, and low-temperature binder glass will be melted and forced to flow onto the mold to bind the fibers together, and form a composite.
- Heliostat ring of concrete, glass-glass composite, or foam glass-cored glass tube, with thin metal or microsheet glass membranes. Focusing via electrostatic forces (see below).
- Multi-faceted dish structure with foam-glass/glass beam construction to support mirror facets.
More designs can be added along the way if we come up with improvements.
Miscellaneous. Use of static electricity to focus heliostats was proposed. By placing opposite charges on the front and rear membranes, the attractive force between them will cause the membranes to deform to a shape approximating a parabola. This approach has been used in some satellite systems. An advantage over pressurefocusing is that pinholes due to micrometeorites will not affect the focusing system.

Due to the lack of wind loads, a very simple tracking device for parabolic dishes may be possible. A design similar to the passive tracker sold by Zomeworks for terrestrial photovoltaic systems might be appropriate. This tracker relies on a mechanical balance between two partially shaded accumulators that are partially filled with liquid. If the collector gets off-track, one of the accumulators becomes more exposed to the sun, increasing the vapor pressure in the accumulator and forcing more fluid to the other accumulator. The shift in the system's center of gravity causes the collector to rotate back to its proper tracking position. Since the lunar rotation axis is very close to perpendicular to the ecliptic, no seasonal adjustment for declination would be necessary, and a very simple polar mount would be sufficient.

Testing. It may be possible to simulate foam glass fabrication techniuqes at room temperature, using a standard polyurethane foam or an adhesive/glass microsphere mixture. As soon as we identify materials that duplicate as well as possible the lunar materials, we can begin some fabrication tests.

## References

American Institute of Aeronautics and Astronautics, 1988, Commercial Opportunities in Space--Progress in Astronautics and Aeronautics, Vol. 110, AIAA.

Friedlander, A. and Cole, K., 1989, "Power Requirements for Lunar and Mars Exploration Scenarios," Report No. SAIC-89/1000, SAIC, San Diego.

Lin, T. D., 1987a, "Concrete for Lunar Base Construction," Commercial Opportunities in Space--Progress in Astronautics and Aeronautics, Vol. 110, AIAA.

Lin, T. D., 1987b, "Physical Properties of Concrete Made With Apollo 16 Lunar Soil Sample," Commercial Opportunities in Space--Progress in Astronautics and Aeronautics, Vol. 110, AIAA.

Lunar and Planetary Institute, • 1980, Extraterrestrial Materials Processing and Construction: Final Report, Lunar \& Planetary Institute.

MacKenzie, J. D. and Claridge, R. C., 1979, "Glass and Ceramics From Lunar Materials, Commercial Opportunities in Space--Progress in Astronautics and Aeronautics, Vol. 110, AIAA.

NASA, n.d., Publication SP-482.
Rowley, J. C. and Neudecker, J. W., 1980, "Melted In-Place Lunar Soil for Construction of Primary Lunar Surface Structures," Extraterrestrial Materials Processing and Construction: Final Report, Lunar \& Planetary Institute.

Science Applications International Corporation, 1989, "Use of Thermal Energy From Nuclear Power Systems for Lunar Materials Processing," Report No. SAIC89/1001, SAIC, San Diego.

Waldron, R. D., Erstfeld, T. E., and Criswell, D. R., 1979, "The Role of Chemical Engineering in Space Manufacturing," Chemical Engineering, February, pp. 80-94.

Williams, R. J. and Jadwick, J. J. (Eds.), 1980, Handbook of Lunar Materials, NASA Reference Publication 1057.

Investigation of Mechanical and Thermal Properties of MicrowaveSintered Lunar Simulant Material Using 2.45 GHz Radiation T. T. Meek Department of Materials Science and Engineering University of Tennessee
During the past year, the focus of our research was in two areas. While they may appear to be different, they are closely related. One project investigated the mechanical and thermal properties of lunar simulant material. The current status of this research is given in the following. An alternative method of examining thermal shock in microwave-sintered lunar samples is being researched. At present, a computer code has been developed that models how the fracture toughness of a thermally shocked lunar simulant sample is related to the sample hardness as measured by a microhardness indentor apparatus. This technique will enable much data to be gathered from a few samples. To date, several samples have been sintered at different temperatures and for different times at temperature. During the past year, a technical presentation was made on this work and a paper submitted for publication (Nehls et al. 1989). During this investigation, photomicrographs of microwave-heated samples showed what appear to be glassy regions in between grains (Figures 2.4 and 2.5). Currently, these samples are being examined using TEM techniques to determine if, indeed, the intergranular regions are amorphous. If they are, then this may help explain the apparently enhanced thermal shock resistance of microwave-sintered lunar simulant materials. Figures 2.4 and 2.5 show the fractured surface of simulant material, which is compositionally the same as Apollo 11 lunar material. Note the apparently melted intergranular regions. This phenomenon was first observed by Meek et al. (1986) in earlier microwave sintering of conventional ceramics. Earlier work on the diffusion of various metal cations in pyrex also revealed unusual nucleation characteristics when the system was heated and cooled in a microwave field (Meek et al. 1988).

It was decided to investigate (along with the above work) the melting and recrystallization characteristics of a well-studied binary system to see if the thermodynamic barrier for the nucleation of a crystalline phase may be affected by the presence of a microwave field. The system chosen was the albite (sodium alumino silicate)-anorthite system (calcium alumino silicate). Table 2.7 shows the design of the experiment. Mixtures of albite and anorthite were melted at $1400^{\circ} \mathrm{C}$ and then cooled to $1200^{\circ} \mathrm{C}$ and held for specific lengths of time in both a conventional furnace and a microwave furnace (frequency 2.45 GHz ). Heating duration varied from 1 hour to 128 hours, and thermally processed samples were investigated using X-ray, microprobe, and optical polarized light techniques to determine if differences resulted from the two

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Figures 2.3 SEM photomicrograph of 2A11XLB sample heated at $56,070^{\circ} \mathrm{C}$ per hour using 2.45 GHz radiation. Note the apparent melt regions located in between grains. Magnification 650X.


Figure 2.4 Same as Figure 2.3, but with magnification 2960X.

Table 2.7 Sample compositions and duration time at constant holding temperature in a microwave field.

| Sample Composition | Holding Temperature (Degrees C) | Duration Time (Hours) |
| :---: | :---: | :---: |
| $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \% \mathrm{An}$ | 1200 | 1 |
| 90 wt\% Ab-10 wt\% An | 1200 | 2 |
| $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \% \mathrm{An}$ | 1200 | 4 |
| $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \% \mathrm{An}$ | 1200 | 8 |
| 90 wt\% Ab-10 wt\% An | 1200 | 16 |
| $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \% \mathrm{An}$ | 1200 | 32 |
| $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \% \mathrm{An}$ | 1200 | 64 |
| 90 wt\% Ab-10 wt\% An | 1200 | 128 |
| 81 wt\% Ab-19 wt\% An | 1200 | 1 |
| 81 wt\% Ab-19 wt\% An | 1200 | 2 |
| 81 wt\% Ab-19 wt\% An | 1200 | 4 |
| 81 wt\% Ab-19 wt\% An | 1200 | 8 |
| 81 wt\% Ab-19 wt\% An | 1200 | 16 |
| 81 wt\% Ab-19 wt\% An | 1200 | 32 |
| 81 wt\% Ab-19 wt\% An | 1200 | 64 |
| 81 wt\% Ab-19 wt\% An | 1200 | 128 |
| $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \% \mathrm{An}$ | 1200 | 1 |
| 72 wt\% Ab-28 wt\% An | 1200 | 2 |
| 72. wt\% Ab-28 wt\% An | 1200 | 4 |
| 72 wt\% Ab-28 wt\% An | 1200 | 8 |
| 72 wt\% Ab-28 wt\% An | 1200 | 16 |
| 72 wt\% Ab-28 wt\% An | 1200 | 32 |
| $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \% \mathrm{An}$ | 1200 | 64 |
| $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \% \mathrm{An}$ | 1200 | 128 |

heating techniques. Figure 2.5 shows the portion of the albite-anorthite system investigated in this work.

All three conventionally heated compositions of albite and anorthite showed the presence of the crystalline $\alpha$ phase as shown by X-ray diffraction analysis in Figures $2.6-2.8$. For the samples heated in a $2.45-\mathrm{GHz}$ electromagnetic field, all compositions heated for 64 hours and the $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \%$ An heated for 128 hours showed no trace of crystalline phase (Figures 2.9 and 2.10). For the 128 -hour runs heated in the microwave field, only the $81 \mathrm{wt} \% \mathrm{Ab}-19 \mathrm{wt} \% \mathrm{An}$ and the $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \% \mathrm{An}$ showed a trace of crystallinity (Figures 2.11 and 2.12).

The above results show that a $2.45-\mathrm{GHz}$ field affects the nucleation of the plagioclase phase in the albite-anorthite system. This effect results from the different dielectric constants of the crystalline phase and the liquid phase, respectively.

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Figure 2.5 Albite-anorthite phase diagram.


Figure 2.6 X-ray diffraction pattern of the $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \%$ An heated in a conventional furnace at $1200^{\circ} \mathrm{C}$ for 128 hours.


Figure 2.7 X-ray diffraction pattern of the $81 \mathrm{wt} \% \mathrm{Ab}-19 \mathrm{wt} \%$ An heated in a conventional furnace at $1200^{\circ} \mathrm{C}$ for 128 hours.


Figure 2.8 X-ray diffraction pattern of the $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \%$ An heated in a conventional furnace at $1200^{\circ} \mathrm{C}$ for 128 hours.


Figure $2.9 \quad$ X-ray diffraction patterns of the (a) $90 w t \% A b-10 w t \%$ An, (b) $81 w t \% A b-$ $19 \mathrm{wt} \% \mathrm{An}$, and (c) $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \%$ An heated in a microwave overn at $1200^{\circ} \mathrm{C}$ for 64 hours.


Figure 2.10 X-ray diffraction pattern of the $90 \mathrm{wt} \% \mathrm{Ab}-10 \mathrm{wt} \%$ An heated in a microwave oven at $1200^{\circ} \mathrm{C}$ for 128 hours.


Figure 2.11 X-ray diffraction pattern of the $81 \mathrm{wt} \% \mathrm{Ab}-19 \mathrm{wt} \%$ An heated in a microwave oven at $1200^{\circ} \mathrm{C}$ for 128 hours.


Figure 2.12 X-ray diffraction pattern of the $72 \mathrm{wt} \% \mathrm{Ab}-28 \mathrm{wt} \%$ An heated in a microwave oven at $1200^{\circ} \mathrm{C}$ for 128 hours.

Electromagnetic field theory predicts that more power will be deposited into the lower dielectric constant region (crystalline phase) than into the higher dielectric constant region (liquid phase). This phenomenon results in the inhibition of the nucleation of the crystalline phase in the crystal-liquid two-phase region in the albite-anorthite system.

The results of this investigation suggest that all oxide-phase systems may be different when heated in a microwave field. Thus, we may expect that processing extraterrestrial materials using microwave radiation will possibly result in some different microstructures that exhibit different mechanical and thermal properties from those that are processed using conventional heating techniques.

## References

Meek, T. T., Brooks, M. H., Blake, R. D., Petrovic, J. J., Jory, H., and Milewski, J. V., 1986, "Microwave Processing of Ceramics," Journal of Microwave Power and Electro Magnetic Energy, Vol. 21, pp. 193-194.

Meek, T. T., Blake, R. D., Katz, J. D., Bradberry, J. R., and Brooks, M. H., 1988, "Cation Diffusion in Glass Heated Using 2.45 GHz Radiation," Journal of Materials Science Letters, Vol. 7, pp. 928-931.

Nehls, M. K., Park, S. S., and Meek, T. T., 1989, "Processing Lunar Simulant Materials Using 2.45 GHz Radiation," Proceedings of the Ninth Princeton/AIAA/SSI Conference, May 10-13, pp. 94-96.
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#### Abstract

The development of construction materials such as "concrete" from lunar soils without the use of water requires a different methodology than that used for conventional terrestrial concrete. At this time, this research project involves two aspects: (1) liquefaction of lunar simulants with various additives in a furnace so as to produce a construction material like an intermediate ceramic, and (2) cyclic loading of simulant with different initial vacuums and densities in a specially designed new device leading to a compacted material with different final densities with respect to the theoretical maximum densities (TMD). In both cases, bending, triaxial compression, extension, and hydrostatic tests will be performed to define the /stress-strain-strength response of the resulting materials. In the case of the intermediate ceramic, bending and available multiaxial test devices will be used, while for the compacted case, tests will be performed directly in the new device. The tests will be performed by simulating in situ confining conditions. A preliminary review of high-purity metal is also conducted.


## Introduction

Significant progress has been made in the area of space exploration in the past three decades. However, little has been done for development of construction materials for long-term shelters, work stations, pavements, excavation, and shielding materials for man on the Moon and other planets. For large-scale productivity on other planets, buildings and other structures are indispensable. Because of payload limitations on spacecrafts and the high cost of transportation, a prudent and efficient approach to construction on other planets requires that every effort be made to utilize the materials available on the planets themselves. The technique that is being developed in the Department of Civil Engineering and Engineering Mechanics is intended to utilize extraterrestrial "soils" to develop construction materials for building safe and serviceable structures and other systems.

## The Lunar Soil Simulant

The simulant used in this study was crushed basalt rock from the Pomona Flow near Hanford, Washington. The chemical composition of the simulant and that of some
returned lunar soils are quite similar. Although the composition of the simulant did not exactly match that of lunar soil, the differences were not deemed significant enough to affect this investigation.

Every attempt was made to accurately simulate the grain size distribution of returned lunar soil. The crushed basalt rock was shaken through a stack of U.S. Standard sieves to separate the constituents by size. By re-combining the differentsized particles in the correct proportions, a satisfactory lunar soil simulant has been produced.

## Progress to Date

The new test device for compression testing is ready. Two photographs showing the device are given in Figure 2.13.

The new furnace has been acquired. Preliminary molds made of tungsten are prepared for bending tests.

A draft report on high-quality purity metal is almost ready.

## Planned Research

A series of laboratory tests will be performed in the new compression testing device with different initial vacuums and densities. Then, stress-strain behavior of each specimen will be obtained with different confining pressures.

The furnace will be used to obtain a number of specimens for bending and multiaxial tests.

The literature review of high-purity metals will be finalized.

## Approach and Test Procedure

The locally developed lunar simulant with additives will be placed in molds of different sizes for bending and multiaxial tests and will be liquefied in a furnace with Argonne environment around a temperature of about $1100^{\circ} \mathrm{C}$. A number of combinations of simulant and additives will be tried, and the resulting specimens will be tested for their stress-strain-strength properties.

For the cyclic loading in the new test device (Figure 2.13), specimens (under different initial vacuums and densities) of about $3^{\prime \prime}$ diameter and 6 " height will be subjected to cycles of loading until an equilibrium compaction is achieved. The resulting density will be compared with the TMD. Then, a specially designed sleeve will be extracted and the specimen will receive a rubber membrane around it. A confining pressure will be applied, and the specimen will be subjected to increasing shear stress until failure.


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Figure 2.13 New device for cyclic compression testing with initial vacuums, densities, and confining pressures.

## Expected Results

In both cases, the test results will lead to stress-strain-strength response including pre-failure, failure, and ultimate response. These results will be used to evaluate deformation parameters such as modulus of elasticity, Poisson's ratio, cohesive and frictional constants, and other plasticity constants. These constitutive constants will permit evaluation of the applicability and use of the resulting materials for construction such as shielding, structures, pavements, and excavation systems.

Participants
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\text { Strategic Metals Recovery Research Facility } \\
\text { The University of Arizona }
\end{gathered}
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This program is proceeding along the lines compatible with the objective of developing feasible separation and recovery processes for precious metals in a space environment. We are exploring efficient, compact, solvent extraction systems, both single- and multistage, capable of high selectivity and rapid equilibration, based on chelate and ion pair complexes. During the current reporting period, two research projects were undertaken: (a) study of the time-dependent aspects of the formation of Pd (II) extractable chelate complexes, and (b) development of a multistage countercurrent distribution process for the separation and recovery of $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ ions.

Kinetics of Chelate Formation of Pd (II) Ions
Using the stopped-flow kinetics system, the rate of formation of the 8-quinolinol ( HOx ) chelate of $\mathrm{Pd}\left(\mathrm{PdOx}_{2}\right)$ from the extractant and a solution of $\mathrm{PdI}_{4}^{2-}$ was found to be first order in both Pd and HOw, but independent of pH in the range 5-7. We are now investigating the effect of surfactants of varying charge type, in order to explore the possibility of significantly increasing the rate of chelate formation, which is desirable to enhance separation efficiency.

## Countercurrent Distribution Separation of Pd and Pt

We have obtained a 2400-stage centrifugal partition "chromatograph (CPC) and tested a number of solvent extraction systems for their suitability to separate precious metals efficiently. We found that the neutral phosphorus extractant tri-n-octylphosphine oxide dissolved in heptane provided sufficient selectively to accomplish total separation of Pt and Pd by extraction from hydrochloric acid. We are planning to extend this system to the other precious metal ions and, with the acquisition of higher capacity CPC modules, developed scaled-up separation processes.

Finally, a data base system is being developed that will make the vast literature on metals separation of solvent extraction processes more accessible to the research group working on this project. The work to date has proven to be of great utility in the location and selection of the extraction systems employed above.

## III. RESOURCE DISCOVERY AND CHARACTERIZATION

# Search for Near-Earth Asteroids With the Spacewatch Camera 

 T. GehrelsLunar and Planetary Laboratory
The University of Arizona
The Spacewatch program began as an engineering development for the discovery of near-Earth asteroids and comets, with the first observations starting in 1983 using an RCA CCD that has $320 \times 512$ pixels. We wrote extensive software to scan the sky and learned how to do astrometry for precise orbits of newly discovered objects. The merit of the concept was proven, with many observations reported in the Minor Planet Circulars and recovery of comets in the Circulars of the International Astronomical Union. We improved the precision of astrometric observations for comets and asteroids (T. Gehrels, B. G. Marsden, R. S. McMillan, and J. V. Scotti, "Astrometry With a Scanning CCD," Astron. J., Vol. 91, pp. 1242-1243, 1986). For efficient scanning and discovery of new objects, however, one needs a larger CCD, for which we have obtained a Tektronix $2048 \times 2048$ CCD.

This type of pioneering work has not been done before with such a large CCD in the scanning mode. We have defined most of the problems: For instance, what is the best scanning routine to find near-Earth asteroids and comets? Which are the best scan regions for this goal? In addition to the automatic detection that we have done before with the computer system in Tucson, it may be possible to inspect the data already on the mountain in order to recognize fast-moving objects with the new computer equipment. How to recognize fast-moving objects on the screen already at the telescope? How to interpret the data on that screen, and next on the tapes for further analysis with our computer on the campus in Tucson? Should the data be partially pre-processed or compressed before being sent to Tucson, or should we attempt to concentrate all the data-reduction capability at one site?

Since 1981, we have obtained some of the answers to these questions through various exercises that usually resulted in the accomplishment of useful research on various objects, with publication of the results. This is all summarized in a paper entitled "Various Modes of Using Charge-Coupled Devices" that Gehrels, McMillan, Scotti, Perry, and Rabinowitz have submitted to the Astrophysical Journal. Its abstract reads:

This paper describes a new discipline in astrophysics, "scannerscopy," of scanning the sky with charge-coupled detectors (CCD) and computerized reduction. Usually we turn the drive off, and the scanning motion of the sky is precisely followed by slaving the charge-transfer of the CCD to the sidereal drift rate. The CCD is read out during the observing, and flat-fielding corrections are not needed. In this paper, a comparison is made with photographic surveying of Schmidt telescopes,

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showing that the CCD-scanning is to be preferred, especially for the detection of fast-moving objects. With the "Spacewatch Telescope" of the Steward Observatory of The University of Arizona on Kitt Peak, we have developed new modes of using the CCD for searches of gamma-ray bursters, space debris, satellites, comets, cometesimals, the tenth planet, and various types of asteroids. Routine astrometry is done for moving objects, with a precision of $\pm 0.6$ arcsecs. We are presently using a Tektronix $2048 \times 2048$ CCD, which appears to be successful also in the discovery of near-Earth asteroids. The goal is to study magnitudefrequency relations of asteroids, comets, and satellites, as well as to develop new techniques for surveying; the need for a $1.8-\mathrm{m}$ CCDscanning reflector, and for surveying with CCD cameras on spacecraft that pass through the asteroid belt, is apparent.

The $2048 \times 2048$ CCD is now permanently on the Spacewatch Telescope. A Solbourne computer has arrived and is being programmed by Dr. David Rabinowitz, who joined us for postdoctoral study in September. It will take at least half a year to complete these programs, but every month we test the next step in this work with observations at the telescope. During one of these tests, Rabinowitz discovered the trail of a fast-moving asteroid, 1989 UP. Its perihelion distance is near 0.9 AU, which seems to indicate that it is dynmaically under the influence of the Earth and will eventually impact it. The aphelion distance is in the asteroid belt, which seems to indicate that it is a fragment of collisions there. A lightcurve obtained by Dr. Wieslaw Wisniewski yielded an amplitude near 1 magnitude, and this seems to confirm that it is an elongated fragment.

We have taken the first organizational steps towards a text and source book on Space Resources in the Space Science Series of The University of Arizona Press. The book will be based on an international conference to be held in Tucson in January 1991. The leading scientific editor is $P$. Lewis.



#### Abstract

The mapping of ilmenite on the surface of the Moon is a necessary precursor to the investigation of prospective lunar base sites. Telescopic observations of the Moon using a variety of narrow bandpass optical interference filters are being performed as a preliminary means of achieving this goal. Specifically, ratios of images obtained using filters centered at $0.40 \mu \mathrm{~m}$ and $0.56 \mu \mathrm{~m}$ provide quantitative estimates of $\mathrm{TiO}_{2}$ abundances. Analysis of preliminary distribution maps of $\mathrm{TiO}_{2}$ concentrations allows identification of specific high- Ti areas. Investigations of these areas using slit spectra in the range $0.30-0.85 \mu \mathrm{~m}$ are underway to search for discrete spectral signatures attributable to ilmenite.


## Introduction and Background

An important criterion during selection of lunar base sites will be the availability of ilmenite $\left(\mathrm{FeTiO}_{3}\right)$ for use as a local resource. The distribution of ilmenite across the surface of the Moon must therefore be well known. Earth-based telescopic remote sensing of the lunar surface in combination with laboratory spectral reflectance measurements of returned lunar samples has proven to be a valuable tool, both in discerning relative differences between lunar material and in establishing more quantitative estimates of surface compositions (e.g., Head et al. 1978).

Lunar ilmenites most often contain greater than $50 \mathrm{wt} \%$ titanium dioxide ( $\mathrm{TiO}_{2}$ ), making ilmenite the dominant titanium-bearing mineral on the surface of the Moon. Surface distribution maps of $\mathrm{TiO}_{2}$ abundances are consequently valuable in determining regions of probable high-ilmenite concentrations.

Charente et al. (1974) measured $\mathrm{TiO}_{2}$ contents of sampled bulk lunar soils and compared their spectral reflectivities in the laboratory. An empirical relation between weight percent $\mathrm{TiO}_{2}$ and the reflectance slope between $0.40 \mu \mathrm{~m}$ and $0.56 \mu \mathrm{~m}$ was established (Figure 3.1). The slope of the lunar reflectance spectrum in this region is primarily affected by the absorptions due to Fe and Ti in the lunar soil, ie., the agglutinates and glasses. The relation is therefore more accurate for mature soils (those that have been extensively reworked by micrometeorite impacts), particularly in the lunar maria. Charente et al. also found the relation to hold for telescopic spectra of lunar landing sites (Figure 3.2).


Figure 3.1 Plot of $\mathrm{TiO}_{2}$ percentage of the bulk lunar soils as a function of $0.40 \mu \mathrm{~m}$ to $0.56 \mu \mathrm{~m}$ slope. (From Charette et al. 1974.)


Figure 3.2 Plot of $\mathrm{TiO}_{2}$ percentage versus $0.40 \mu \mathrm{~m}$ to $0.56 \mu \mathrm{~m}$ slope for telescopic spectra. The $\mathrm{TiO}_{2}$ contents of telescopic areas are averages of sampled soils used in Figure 3.1. (From Charette et al. 1974.)

Johnson et al. (1977) used a silicon vidicon imaging system to obtain multispectral images of the Moon through narrow bandpass interference filters centered at $0.38 \mu \mathrm{~m}$ and $0.56 \mu \mathrm{~m}$. An abundance map of $\mathrm{TiO}_{2}$ for the northern maria was produced by converting the $0.38 / 0.56 \mu \mathrm{~m}$ ratio (normalized to a standard area in Mare Serenitatis named MS-2) to weight percent $\mathrm{TiO}_{2}$ (Figure 3.3).

Figure 3.4 shows the most recent version of the relation between the $0.40 / 0.56 \mu \mathrm{~m}$ ratio and weight percent $\mathrm{TiO}_{2}$ (Pieters 1978). At values of $\mathrm{TiO}_{2}$ less than about $4 \mathrm{wt} \%$, the absorbing effects of the Ti-Fe opaque phases can be obscured by the effects of other contaminants such as Fe-metal, plagioclase, and non-opaque (homogeneous) glass compositions in the soil. Thus, a ratio value of 1.00 may correspond to a range of $0-2.5 \mathrm{wt} \% \mathrm{TiO}_{2}$.

## Multispectral Image Acquisition and Results

Previous efforts to obtain multispectral images of the Moon used television-type silicon vidicon tubes (e.g., McCord et al. 1976, 1979). These images possessed spatial resolutions of about 2 km per picture element (pixel) but covered relatively small areas on the lunar surface. Mosaicking of photographs taken of the individual vidicon images was necessary to achieve greater areal perspective. Contrast differences between the mosaic frames suffer from some uncertainties, which discourage comparison of apparently similar gray-level intensities between frames not contiguous.

Newer imaging technologies use charge-coupled device (CCD) systems that provide better stability and higher photometric precision. For our project, an RCA 320 $\times 512$-pixel CCD chip has been used at The University of Arizona Tumamoc Hill Station $0.5-\mathrm{m}$ telescope. In October 1989, multispectral images of the Moon were obtained at the f/4 Newtonian focus using a variety of narrowband interference filters (Table 3.1). In addition to the $0.40 \mu \mathrm{~m}$ and $0.56 \mu \mathrm{~m}$ filters, ultraviolet filters were used to discern reflectance differences in that interesting but seldom-imaged portion of the lunar spectrum. The near-infrared filters can be used to investigate additional surface properties; for example, the 0.95/0.56 $\mu \mathrm{m}$ ratio can be used as a relative indicator of surface maturity (McCord et al. 1976).

Five images are necessary to cover the full Moon (Figure 3.5). The spatial resolution of the images is about 5.3 km per pixel on the Moon. Figure 3.6 shows four of the image ratios obtained by dividing the $0.40 \mu \mathrm{~m}$ images by the $0.56 \mu \mathrm{~m}$ images in which the brighter areas correspond to higher ratio values. Full-size versions of the $0.40 \mu \mathrm{~m}$ image and $0.40 / 0.56 \mu \mathrm{~m}$ ratio for the eastern section of the Moon are shown in Figures 3.7 and 3.8. Using an average of the plot in Figure 3.4 (dotted line) to calibrate


Figure 3.3 Weight percent $\mathrm{TiO}_{2}$ versus $0.40 / 0.56 \mu \mathrm{~m}$ ratio (relative to MS-2). (From Pieters and McCord 1976.)


Figure 3.4 Relationship between weight percent $\mathrm{TiO}_{2}$ in lunar mare soils and the the $0.40 / 0.56 \mu \mathrm{~m}$ ratio for telescopic spectra relative to MS-2. The stippled area is the estimated range of $\mathrm{TiO}_{2}$ that can be derived from a $0.40 / 0.56$ $\mu \mathrm{m}$ ratio measurement of mature mare regions. Dotted curve approximates the curve used for calibration of ratio values to $w t \% \mathrm{TiO}_{2}$ in present study. (After Pieters, 1978.)

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Figure 3.5 Images of the Moon obtained with bandpass interference filter centered at $0.40 \mu \mathrm{~m}$. (Reduced-size postscript laser printer copies.)

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(Reduced-size postscript laser printer copies.)


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Figure 3.7 Image of eastern section of Moon taken through $0.40 \mu \mathrm{~m}$ filter. (Full-sized postscript laser printer copy).

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Figure 3.8 Preliminary $0.40 / 0.56 \mu \mathrm{~m}$ ratio image of the eastern section of the moon. (Full-sized postscript laser printer copy.)

Table 3.1 Bandpass interference filters.

| Center Wavelength (nm) | Bandwidth [FWHM] $(\AA)$ |
| :---: | :---: |
| 309 | 75 |
| 319 | 102 |
| 338 | 106 |
| 365 | 80 |
| 389 | 48 |
| 400 | 95 |
| 427 | 80 |
| 560 | 95 |
| 729 | 128 |
| 902 | 289 |
| 948 | 184 |

images, a $\mathrm{TiO}_{2} \mathrm{wt} \%$ abundance map can be constructed (Figure 3.9). The value for MS-2 was taken from the eastern ratioed image section in Figure 3.8.

Variability in observed $\mathrm{TiO}_{2}$ concentrations in some overlapping areas between adjacent image ratio sections rarely exceeds $2 \mathrm{wt} \%$ but is nevertheless problematic. Investigations are underway to calibrate the MS-2 standard to areas common to the overlapping portions of individual images in order to provide a standard ("tied" to MS2) for those images in which MS-2 is not in view.

## Spectroscopic Studies

Those areas highest in $\mathrm{TiO}_{2}$ content (as determined from analysis of the preliminary maps of $\mathrm{TiO}_{2}$ concentration) are being studied spectroscopically as well. Initial attempts were made in November 1989 (again at Tumamoc Hill) to obtain slit spectra for several regions of interest using the CCD spectrograph/camera designed by one of us (S.M.L.). It includes two blue-blazed gratings, one giving a spectral range from $0.30 \mu \mathrm{~m}$ to about $0.88 \mu \mathrm{~m}$ with $11 \AA$ per pixel and the other providing spectra from $0.30 \mu \mathrm{~m}$ to about $0.56 \mu \mathrm{~m}$ at $5 \AA$ per pixel. The $6 \times 0.2 \mathrm{~mm}$ slit used corresponded to $130.0 \times 4.3 \mathrm{~km}$ on the Moon. In December 1989, further spectra were obtained using a $20 \times 0.25 \mathrm{~mm}$ slit with the spectrograph, corresponding to $442.3 \times 5.5$ km on the Moon. For the December run, a new reflecting slit allowed the image of the spectrographic slit on the Moon to be simultaneously videotaped for all lunar spectra so that the precise region being analyzed could be recorded accurately.

For both the November and December observations, each spectral observation was followed immediately by acquisition of spectra for the MS-2 area. In this way, relative reflectance spectra (ratioed to MS-2) free from instrumental and atmospheric effects were collected.

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Figure $3.9 \quad \mathrm{TiO}_{2}$ abundance map of the eastern section of the Moon based on $0.40 / 0.56 \mu \mathrm{~m}$ ratio image. Dark gray areas correspond to $<5 \mathrm{wt} \%$. Light gray areas correspond to $5-8 w t \%$. Brightest areas correspond to $>8 w t \%$.

Figure 3.10 shows relative reflectance plots obtained in December with the lower resolution grating for four lunar areas. The spectra have been normalized to unity at $5600 \AA$. The Tranquillitatis and Iridium mare regions show a characteristic upturn in slope toward the near-UV and a noticeable upturn in the near-IR (longward of about 7800 A). From preliminary maps, Tranquillitatis was shown to have larger $\mathrm{TiO}_{2}$ concentrations than Iridium. The relative reflectance spectra are consistent with this comparison, as the slope of the spectrum for Tranquillitatis is steeper than that for Iridium, i.e., Tranquillitatis has a greater $0.40 / 0.56 \mu \mathrm{~m}$ ratio and a corresponding higher $\mathrm{TiO}_{2}$ value (Figure 3.4). For comparison with mature mare areas, the craters Tycho (located in the southern highlands) and Aristarchus (located in northern Oceanus Procellarum) show a more constant relative reflectance in the near-UV and a steady decrease toward the near-IR. These two spectra also exhibit an abrupt downturn in relative reflectance at about $4800 \AA$

The relative reflectance spectra can be more readily compared to laboratory spectral reflectance measurements of lunar soils by calibrating them to absolute reflectance. In order to accomplish this, further spectra were obtained at The University of Arizona Catalina Observatory 1.54-m telescope in January 1990. Spectra were recorded for a solar analog star (i.e., one with spectral characteristics indistinguishable from the Sun) and then ratioed to spectra of the MS-2 region for the same air mass in order to provide an absolute spectrum for MS-2. This can be applied to the December relative reflectance ratios in order to provide absolute reflectance spectra for specific lunar areas. Reduction of the spectra to this form is presently underway.

## Conclusions

The multispectral image data set taken in October 1989 is of sufficient quality to be used for analysis of both $\mathrm{TiO}_{2}$ variations in the lunar maria and relative maturity differences of the lunar surface. Initial results from the October images show most of western Mare Tranquillitatis to be a region of high $\mathrm{TiO}_{2}$ concentrations ( $>8 \mathrm{wt} \%$ ) (Figure 3.10 ); this region is being investigated more fully with high-resolution spectra. Other smaller areas that show high concentrations, such as the "dark spots" east of the crater Copernicus and in the region of Sinus Aestuum (south of Mare Imbrium), are also under spectral scrutiny.

The $0.95 / 0.56 \mu \mathrm{~m}$ maturity index may be of interest to other SERC investigators when used in conjunction with the $\mathrm{TiO}_{2}$ abundance map. M. Hutson, J. Ruiz, and J. Lewis conclude that high-Ti soils with low agglutinate content (immature soils) are best for processing and separation of ilmenite grains. T. Swindle and C. Glass note that the
 Figure 3.10 Relative reflectance spectra scaled to MS-2 and normalized to unity at $5600 \AA$ The relative reflectance for Iridium (a large flooded crater in northern Mare Imbrium) shows a shallower slope in the 4000-5600 $\AA$ region than does the spectrum for western Mare Tranquillitatis. The craters Tycho (in the highlands) and Aristarchus (in Oceanus Procellarum) are shown for comparison.


highest Ti soils are apparently the best sites for ${ }^{3} \mathrm{He}$ implantation. Since ${ }^{3} \mathrm{He}$ will be more abundant in soils that have been long exposed to the solar wind, they prefer high-Ti soils with abundant agglutinates (mature soils).

Final products of this project will be $\mathrm{TiO}_{2}$ abundance maps of the entire lunar near-side maria. Other ratio images [including the relative maturity index (0.95/0.56 $\mu \mathrm{m})$ ] may be of enough interest in comparison with each other to warrant additional analysis. Qualitative analysis of relative and/or spectral reflectance measurements of several areas will provide further details regarding the mineralogical and chemical makeup of high-Ti regions. The Apollo 15 and 16 orbital gamma-ray data set for titanium is also being used as an additional resource. Comparisons of the two methods' estimates of Ti concentrations will give further insight to the precision of the spectral studies.

## References

Charette, M. P., McCord, T. B., Pieters, C., and Adams, J. B., 1974, "Application of Remote Spectral Reflectance Measurements to Lunar Geology Classification and Determination of Titanium Content of Lunar Soils," J. Geophys Res., Vol. 79, p. 1605.

Head, J. W., Pieters, C., McCord, T., Adams, J., and Zisk, S., 1978, "Definition and Detailed Characterization of Lunar Surface Units Using Remote Observations," Icarus, Vol. 33, pp. 145-172.

Johnson, T. V., Saunders, R. S., Matson, D. L., and Mosher, J. A., 1977, "A TiO Abundance Map for the Northern Maria," Proc. Lunar Sci. Conf. 8th, pp. 1029-1036.

McCord, T. B., Pieters, C., and Feierberg, M. A., 1976, "Multispectral Mapping of the Lunar Surface Using Groundbased Telescopes," Icarus, Vol. 29, pp. 1-34.

McCord, T. B., Grabow, M., Feierberg, M., Maclaskey, O, and Pieters, C., 1979, "Lunar Multispectral Maps: Part II of the Lunar Nearside," Icarus, Vol. 37, pp. 1-28.

Pieters, C. and McCord, T. B., 1976, "Characterization of Lunar Mare Basalt-Types: Luna 24 Landing Areas as Derived From Remote Observations," Geophys. Res. Lett., Vol. 3, pp. 697-700.

Pieters, C., 1978, "Mare Basalt Types on the Front Side of the Moon: A Summary of Spectral Reflectance Data," Proc. Lunar Planet. Sci. Conf. 9th, pp. 2825-2849.


Lunar and Planetary Laboratory<br>The University of Arizona

This year we have continued observational studies of near-Earth asteroids and development of techniques for determining their compositions. The analysis techniques have been applied to the spectra of several bodies in preparation for their application to near-Earth asteroids.

In mid-November 1989, we made near-IR observations of three near-Earth asteroids: 1865 Cerberus, 1989 VA, and 1989 VB. We were able to observe these asteroids in 6 broad-band visual and near-IR filters ( 0.4 to $2.5 \mu \mathrm{~m}$ ). We were also able to obtain a few narrow-band measurements in the IR, but the asteroids were too faint to measure beyond $2.5 \mu \mathrm{~m}$. Simultaneous, high-resolution visual CCD spectra were measured for these objects, but the data have not yet been reduced to determine their quality.

In collaboration with Jeff Bell at the University of Hawaii, we have obtained narrow-band spectra of the Martian satellite Deimos in the $1-$ to $3-\mu \mathrm{m}$ spectral region. Both satellites of Mars have spectra similar to C-class asteroids; therefore, this was an opportunity to test the models developed for main-belt asteroids on an object closer to the Sun. Our preliminary analysis indicates that there is little or no water present in the surface silicates. We hope to obtain spectra of Phobos from the infrared spectrometer on the Soviet Phobos mission to analyze next year.

Simultaneous with the observing project, we are also continuing our laboratory studies (funded by NASA) of meteorites and meteorite analogs which are used in spectral analysis of our telescopic data. These spectra will also be used in compositional modeling of some of the asteroid spectra, using Hapke reflectance theory.

Extensive work has been done developing applications of Hapke reflectance theory to compositional analysis. Hapke theory is an adaptation of radiative transfer theory to particulate surfaces. The surface is assumed to be composed of irregularly shaped, randomly oriented particles that are large compared with the wavelength of the light. The particles are in contact, but coherent effects are assumed to average out due to the random orientation and irregularity of the particles. Diffraction is also not included in the derivation because the light diffracted by one particle in the surface encounters another particle before it has dispersed sufficiently to be distinguished from the incident light. By definition, all of the light striking a particle is either scattered or absorbed; therefore, the maximum extinction efficiency of a particle in a surface is one.

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In the derivation, the light reflected from the surface is separated into singly and multiply scattered components. The term for the singly scattered component includes all the geometric information, and the multiply scattered component is approximated by the isotropic solution.

The principal equation is an expression for the bidirectional reflectance:

$$
\mathrm{r}=\frac{\mathrm{w}}{4 \pi} \frac{\mu_{0}}{\mu_{0}+\mu}\left\{[1+\mathrm{B}(\mathrm{~g})] \mathrm{P}(\mathrm{~g})+\mathrm{H}\left(\mathrm{mu}_{0}\right) \mathrm{H}(\mathrm{mu})-1\right\},
$$

where

$$
\begin{aligned}
\mathrm{w} & =\text { the single scattering albedo }, \\
\mu_{0} & =\text { the cosine of the incidence angle }, \\
\mu & =\text { the cosine of the emission angle }, \\
\mathrm{g} & =\text { the phase angle } \\
\mathrm{B}(\mathrm{~g}) & =\text { the backscatter function, } \\
\mathrm{P}(\mathrm{~g}) & =\text { the phase function, and } \\
\mathrm{H}(\cdot) & =\text { the Chandrasekhar } H \text {-function for isotropic multiple scattering. }
\end{aligned}
$$

The single scattering albedo is the percentage of total light encountering a grain that is scattered out of the grain. The backscatter function describes the magnitude and extent of the opposition effect observed at low phase angles. The phase function describes the average angular scattering behavior of the grains in the surface. This basic equation can be manipulated to calculate other quantities, such as the radiance coefficient, the directional hemispherical reflectance, and the normal albedo.

The reflectance of an intimate mineral mixture can be calculated from this equation by substituting average quantities for the single scattering albedo and phase function. The average single scattering albedo is an average of the single scattering albedos of the components, weighted by their relative cross-sectional areas. The average phase function is weighted both by cross-sectional area and single scattering albedo because bright grains contribute a higher portion of the light that strikes them to the total surface reflectance. These equations can be used to determine the relative abundances of minerals in a mixture if the end members are known or can be inferred.

Two applications of relevance to near-Earth asteroids were initiated by Marcia Nelson in her graduate work at the University of Hawaii. The composition of Vesta was determined by fitting a mixture equation to telescopic spectra of Vesta and, in collaboration with Paul Lucey at the University of Hawaii, the theory was used to calculate many lunar analogue spectra to aid in the interpretation of lunar telescopic spectra.

High-resolution, visible, and near-infrared spectra of Vesta have been available for many years. The spectra have been interpreted repeatedly, and a consensus has emerged that the majority of Vesta's surface is very similar, if not identical, to the eucrite meteorites. The eucrites are basalts, which are composed of plagioclase and pyroxene, with little to no olivine or metal. Hapke's equations can be fit to a spectrum to determine the relative abundances of the components, given spectra of the end members. The theory has matched laboratory spectra well, so Vesta was chosen for the first unconstrained test because its spectrum is already so well analyzed.

Spectra of actual eucrite mineral separates are not available, so spectra of the most chemically similar pyroxene, plagioclase, and olivine available were chosen as end members. The single scattering albedos of the end members were determined by fitting the directional hemispherical reflectance equation to the end-member spectra. Then, the abundances of the end members were determined by fitting the normal albedo of a mixture equation to the spectrum of Vesta using the single scattering albedos of the end members as input. The abundances determined were $65 \%$ plagioclase $/ 35 \%$ pyroxene, which is essentially eucritic. This is an extremely good result, considering the large uncertainties and known approximations in the inputs. Efforts will be made to improve the inputs and the fitting techniques this year so they can be used to analyze other asteroids.

A different approach was used in applying Hapke theory to the analysis of lunar spectra. Instead of analyzing individual telescopic spectra, the theory was used to calculate synthetic mixture spectra from which spectral trends were determined. The eventual goal of the project is to construct actual calibration plots using parameters derived from the synthetic spectra. It was sidetracked this year when it was discovered what a powerful tool this is for investigating the systematics of spectra of intimate mineral mixtures. It is possible to calculate any mixture that can be defined, containing as many components as desired, providing spectra of the end members are avaiable. It is also possible to quickly calculate mixture series, holding components fixed, or varying them as desired. The mixture series calculated to date have explored orthopyroxene, clinopyroxene, olivine, and plagioclase mixtures, and have begun to explore the spectral effects of ilmenite and agglutinates. The effect of shocked plagioclase has yet to be included.

This has proven to be an important, general-purpose tool for quickly investigating the spectra of mineral mixtures. It will be particularly useful in testing the validity of the end members chosen before more time-consuming fits are run to determine absolute abundance. It is also an excellent tool for directing laboratory investigations,
aiding in testing end members, and determining the relevant mixtures to actually create. It will undoubtedly be used regularly in work on near-Earth asteroids next year.

## Presentations

The following papers were presented at the American Astronomical Society Division of Planetary Sciences meeting, October 31-November 3, 1989:
J. F. Bell, P. G. Lucey, J. C. Gradie, J. C. Granahan, D. J. Tholen, J. R. Piscitelli, and L. A. Lebofsky, "Reflection Spectroscopy of Phobos and Deimos."
L. A. Lebofsky and T. D. Jones, "The Nature of Low Albedo Asteroids From 3- $\mu \mathrm{m}$ Multi-Color Photometry and Spectrophotometry."
M. L. Nelson and J. F. Bell, "Modal Mineralogy of Vesta From Hapke Theory." Processing of Rover Geophysical Data

A proposal submitted by the Laboratory for Advanced Subsurface Imaging (LASI) to the Center for Utilization of Local Planetary Resources entitled "Continuous Monitoring of the Lunar or Martian Subsurface Using On-Board Pattern Recognition and Neural Processing of Rover Geophysical Data" includes research using the groundpenetrating radar (GPR) and seismic systems. The ultimate goal of this research is to create an extraterrestrial unmanned system for subsurface mapping and exploration. Neural networks are to be used to recognize anomalies in the profiles that correspond to potentially exploitable subsurface features.

The GPR signal patterns are analogous to seismic patterns, and the preprocessing techniques are likewise identical. Hence, our preliminary research focus on GPR systems will be directly applicable to seismic systems once such systems can be designed for continuous operation. The original GPR profile may be very complex due to electrical behavior of the background, targets, and antennas, much as the seismic record is made complex by multiple reflections, ghosting, and ringing. Because the format of the GPR data is similar to the format of seismic data, seismic processing software may be applied to GPR data to help enhance the data. A neural network may then be trained to more accurately identify anomalies from the processed record than from the original record.

## Advantages to Designing a GPR System

Earth-based radar has been used to determine statistical descriptions of the surface and near-subsurface properties of the Moon and the near planets since the development of radar during World War II (Evans et al. 1968). The deductions of the lunar surface and subsurface from Earth-based radar were verified by experiments carried out by the Apollo missions. Therefore, it is believed that radar measurements of the planets should give reliable estimates for planetary electrical properties. The data from these measurements can be used in designing the proper parameters for an extraterrestrial radar survey system.

GPR is sensitive to the water content of the soils being surveyed. Although water creates good radar reflectors, it also attenuates the transmitted and reflected signals, seriously limiting the depth of investigation of the system. Lunar samples have shown
that the soils have the electrical properties of very good dielectric insulators and have an absence of water. The mean atmospheric pressure and temperature of Mars is far below the triple point of water. Venus has surface temperatures and pressures that are far above the critical point of water. Therefore, water will most likely not contribute to the dielectric properties of these planets (Strangway and Olhoeft 1977). It may be expected that GPR will have an excellent depth of penetration, as well as excellent responses to changes between the dielectric constants of subsurface anomalies and the dielectric constants of the surrounding regolith.

## Past Lunar Experiments

Lunar profiles were collected by the Apollo 17 astronauts during the surface electrical properties (SEP) experiment in December 1972. SEP was designed to perform the same functions through interferometry that LASI is trying to perform with GPR, i.e., to detect electrical layering, discrete scattering bodies, and the possible presence of water.

A single model to fit all of the SEP data was not found. Resolution was not great enough to detect near-surface anomalies (Strangway et al. 1975). High-frequency GPR has excellent resolution, and GPR's use of pulses instead of continuous waves facilitates interpretation as long as the profiles are not saturated with noise. Conclusions and results from the SEP experiment should be utilized in the planning and construction of a new extraterrestrial electrical experiment. LASI is presently corresponding with Dr . Peter Annan, who was a co-scientist of the SEP experiment and is a developer of digital GPR systems, for insight into developing the extraterrestrial GPR system.

## Potential Earth Test Sites

The closest terrestrial approximations of the lunar and near-planet surface conditions are the Sahara Desert and the Poles, where there is either very little water present in the wind-blown sands or the water is frozen and therefore not detrimental to the radar wave. The space shuttle Columbia performed shuttle imaging radar (SIR-A) experiments over the Eastern Sahara in November 1981. Although very high frequencies were used, calculated depths of penetration of dry sand based on laboratory experiments were greater than 5 m , while field studies have verified depths greater than 2 m (McCauley et al. 1982). The University of Munster and the Free University of Berlin have worked together with the General Petroleum Company of Egypt in using GPR to survey the groundwater system of Southern Egypt. Frequencies of 20 and 50 MHz were used to survey depths up to 45 m (Blindow et al. 1987). The extremely dry sands are similar to conditions that will be found on lunar and Martian
surfaces. Comparisons between shuttle radar and surface radar over the Sahara sites should help in the design of GPR systems that will work on the surface of planets that already have high-frequency radar data.

## Processing Radar Data

Current research at LASI includes using commercial seismic data-processing software to enhance the radar returns. MIRA, from the Oklahoma Seismic Corporation, is the software being used presently. The following figures demonstrate what may be done with the data to make anomalies more easily recognizable for neural networks.

Figure 3.11 is the standard printout from the profile recorder purchased as part of a commercial GPR system from Geophysical Survey Systems, Inc. This profile was taken over a pipe buried at The University of Arizona School Mine GPR test site. The pipe is buried at a known depth of 38 cm . The sweep rate of the recorder was set at 16 scans per second and the 500 MHz antenna was pulled over the pipe at a slow walking pace. Marks on the record were made at meter intervals along the profile line.

After recording the analog signals, another traverse was made with a Tektronix scope digitizing the analog signal, the results of which are shown in Figure 3.12. Traces were recorded every 10 cm along the profile line. Trace 1 on the digital record corresponds to the first mark on the left of Figure 3.11, trace 10 corresponds to the second, trace 20 to the third, and so on. By having the antenna fixed in one position during a sampling, a real-time stacking may be performed by the Tektronix scope in order for coherent signals to add and incoherent noise to cancel, thereby increasing the signal-to-noise ratio.

Because the traces have been digitized, computer algorithms may be applied to the traces to enhance the returns. All trace-attribute data of Figures 3.13 to 3.19 are the same data presented as profile traces in Figure 3.12. The basic assumption of MIRA is that any periodic function, such as a GPR trace $s(t)$ can be considered as the real part of a complex function $S(t)$, which has both a real part and an imaginary part:

$$
S(t)=s(t)+i s^{*}(t) .
$$

$s^{*}(t)$ can be calculated from the trace $s(t)$ with a Hilbert Transform. Any complex number can also be written as

$$
S(t)=A(t) e^{i \Theta(t)}
$$

so that

$$
A(t) e^{i \theta(t)}=s(t)+i s^{*}(t),
$$

where $A(t)$ is called the instantaneous amplitude and $\theta(t)$ is called the instantaneous phase.


Figure 3.11 Output of analog profile over pipe buried 38 cm deep. Vertical axis is time ( $2.5 \mathrm{nsecs} /$ div.); horizontal axis is distance ( $1 \mathrm{~m} / \mathrm{div}$.).


Figure 3.12 Output of digitized profile of same target as that of Figure 3.11. Each CDP represents a $10-\mathrm{cm}$ shift such that 10 CDP's equal a $1-\mathrm{m}$ horizontal shift.


Figure 3.13 Instantaneous amplitude from digitized traces of Figure 3.12. Traces were left on the plot for reference.


Figure 3.14 Instantaneous power from digitized traces of Figure 3.12.


Figure 3.15 Instantaneous phase from digitized traces of Figure 3.12.

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Figure 3.16 Instantaneous frequency from digitized traces of Figure 3.12.


Figure 3.17 Reflection strength from digitized traces of Figure 3.12.


Figure 3.18 Real polarity from digitized traces of Figure 3.12.


Figure 3.19 Amplitude-weighted imaginary part of the phase difference of adjacent traces of Figure 3.12.

MIRA uses the instantaneous amplitude and the instantaneous phase to calculate all other attributes. The individual traces are plotted in MIRA by a color spectrum; with low values represented by violet and high values represented by red. Instantaneous amplitude is plotted in Figure 3.13, and instantaneous phase in Figure 3.15.

A few examples of some other attributes calculated by MIRA are given in Figures 3.14 to 3.19. Figure 3.14 is the instantaneous power display that is computed by squaring the instantaneous amplitude. Power displays tend to accentuate highamplitude events. Figure 3.16 is the instantaneous frequency, which is calculated by taking the time derivative of the instantaneous phase attribute. Figure 3.17 is the reflection strength, or decibel display, which is a normalized logarithmic display of the instantaneous amplitude. This function tends to equalize the low- and high-amplitude events. Figure 3.18 is the real polarity, which is simply a color-coded display of the real seismic trace weighted by its amplitude. Figure 3.19 is an amplitude-sine-phase difference plot created by taking two adjacent traces, calculating the phase difference between them, and then weighting the resulting imaginary part of the phase difference by the instantaneous amplitude.

From these examples, it may be seen that MIRA can be very useful, enhancing the returns from a subsurface feature. However, most features are found with a much lower signal-to-noise ratio that the example shown. The algorithms used by MIRA are not powerful enough to increase the signal-to-noise ratio significantly for many of these features. For this reason, LASI is reformatting the GPR data for a more powerful dataprocessing package. Routines such as deconvolution, various filters, and migration will be applied to these data to determine which sequence of operations will best increase the signal-to-noise ratio, so that subsurface anomalies will be more distinct from the surrounding background.

Once signal patterns are considered optimal, neural network pattern recognition will be applied to permit rapid recall of pattern associations. Our research on neural network pattern recognition of other EM geophysical patterns has demonstrated, for the first time (see, for example, Poulton et al. 1989), that our pattern recognizers can not only recall known patterns accurately, but can generalize and form abstractions when faced with patterns that are not part of the training suite.

## Selected Bibliography

Annan, A. P. and Davis, J. L., 1977, "Radar Range Analysis for Geological Material: Report of Activities," Geol. Surv. Can. Paper 77-1B, pp. 117-124.

Blindow, N., Ergenzinger, P., Pahls, H., Scholz, H., and Thyssen, F., 1987, "Continuous Profiling of Subsurface Structures and Groundwater Surface by EMR Methods in Southern Egypt, Subproject B11;" pages 575-627 in Research in Egypt and Sudan, Results of the Special Research Project Arid Areas Period 1984-1987 (E. Klitzsch and E. Schrank, eds.), Verlag von Dietrich Reimer, Berlin.

Daniels, J. J., 1988, "Fundamentals of Ground Penetrating Radar," Department of Geology and Mineralogy, Ohio State University, Columbus.

Elachi, C., Brown, W. E., Cimino, J. B., Dixon, T., Evans, D. L., Ford, J. P. Saunders, R. S., Breed, C., Masursky, H., McCauley, J. F., Schaber, G., Dellwig, L., England, A., MacDonald, H., Martin-Kaye, P., and Sabins, F., 1982, "Shuttle Imaging Radar Experiment," Science, Vol. 218, pp. 996-1003.

Evans, J. V. and Hagfors, T., 1968, Radar Astronomy, McGraw-Hill Book Company, New York.

McCauley, J. F., Schaber, G. G., Breed, C. S., Grolier, M. J., Haynes, C. V., Issawi, B., Elachi, C., and Blom, R., 1982, "Subsurface Valleys and Geoarchaeology of the Eastern Sahara Revealed by Shuttle Radar," Science, Vol. 218, pp. 1004-1020.

McDonald, H. C., 1980, "Techniques and Applications of Imaging Radars," pages 297-336 in Remote Sensing in Geology (B. S. Seigal and A. R. Gillespie, eds.), John Wiley and Sons, New York.

McGill, J. W., Sternberg, B. K., and Glass, C. E., 1989, "Applications of Ground Penetrating Radar in Southern Arizona," LASI-89-2, The University of Arizona, Tucson.

Poulton, M. M., Glass, C. E., and Sternberg, B. K., 1989, "Recognizing EM Elipticity Patterns With Neural Networks," SEG 59th Annual Meeting, Expanded Abstracts, Vol. 1, EM38, pp. 208-212.

Strangway, D. W., Annan, A. P., Redman, J. D., Rossiter, J. R., and Watts, R. D., 1975, "Electrical Structure at Taurus-Littrow," NASA Techical Publications N-75-16308.

Strangway, D. W. and Olhoeft, G. R., 1977, "Electrical Properties of Planetary Surfaces," Phil. Trans. Roy. Soc. Lond. A, Vol. 285, pp. 441-450.

# IV. SYSTEMS OPTIMIZATION 

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Abstract
A concept is developed for interrelated optimizations in space missions that utilize extraterrestrial resources. It is shown that isolated (component) optimizations may not result in the best mission. Overall economics in the broadest sense must include the "costs" of transportation, storage, continuous monitoring, and corrective actions in situ. When all of these needs are quantitatively considered, it is shown that substantial benefits can be had through less-than-the-best propellants, propellant combinations, propulsion hardware, and, actually, some waste in the traditional sense. One ready example is the possibility of discarding hydrogen produced extraterrestrially by water splitting and using only the oxygen to burn storable fuels. The gains in refrigeration and leak-proof equipment mass (elimination) outweigh the loss in specific impulse.

After a brief discussion of this concept, the synthesis of the four major components of any future space mission is developed. The four components are: orbital mechanics of the transportation; performance of the rocket motors; support systems that include power, thermal and process controls, and instruments; and in-situ resource utilization plant equipment. State-of-the-art numbers are used for the components' performances; each is studied in depth elsewhere, but those studies are beyond the scope of this paper, whose main aim is the development of the concept of a figure-of-merit for the mission. One specific example is used to illustrate the new concept; this is the Mars Sample Return mission. At this time, a popular spreadsheet is used to quantitatively indicate the interdependent nature of the mission optimization. Future prospects are outlined that promise great economy through extraterrestrial resource utilization and a technique for quickly evaluating the same.

## Introduction

The remarkable potential for cost reduction in space missions that use extraterrestrial resources, as contrasted with more traditional missions that depend exclusively on all-Earth-transported resources, has been amply discussed elsewhere (Ash and Cuda 1984; Ash et al. 1978, 1982; Carroll 1983; French et al. 1985; Frisbee and Jones 1983; Ramohalli et al. 1987a, 1987b, 1989; (Presidential) National Commission on Space 1986). Every pound, or kilogram, that can be saved in the initial liftoff mass from Earth can pay back several pounds, or kilograms, because of the leverage effect
of the mass ratio equation. In this regard, it is obvious that we should specifically target those fractions of the liftoff mass that have the maximum impact on the mission. Even a cursory glance at the state-of-the-art spacecraft indicates that a very large fraction of the overall mass is the propellant mass. Thus begun the studies that explored the possibilities of manufacturing propellants in situ on extraterrestrial bodies to "refuel" out there, instead of from Earth-transported precious propellants. These ISPP studies concluded that it is definitely advantageous to manufacture propellants extraterrestrially. The pioneering paper by Ash et al. (1978) showed the first technical aspects of such an ISPP mission. More recent studies (Ramohalli et al. 1987a, 1987b, 1989) not only looked at specific missions, but also explored the general class of extraterrestrial resources instead of just resources to be used as propellants. These results were sufficiently promising for NASA to establish a Center devoted to utilization of extraterrestrial resources. In addition to the all-important propellants, structural materials, shield materials, and other useful materials are being seriously considered. The fundamental goal is to render large-scale space operations economically feasible without depending upon a fleet of dedicated heavy-lift launch vehicles and upon Earthtransported repair, relief, and support supplies. It is also of utmost importance to evolve a long-range ecologically acceptable plan to minimize contamination, and subsequent cleanup, of space.

After this recognition of the significant merits of extraterrestrial resource utilization, some of the more traditional thoughts on space missions may have to be re-examined. For example, many of the components and systems that are used almost routinely for their superior performance may not be the best ones in light of the overall mission impact. Simple examples will illustrate the point. Oxygen-hydrogen rockets have been used almost exclusively because of their excellent specific impulse, years of accumulated design experience, contingency margins, and reliability. In fact, use of the LOX $-\mathrm{H}_{2}$ system for primary, and even secondary, propulsion seems beyond question for future space missions. And yet when one considers the cryogenics, refrigeration, leaks, long-term material compatibility, power needs in simple storage, and safety of remote operations, several important questions arise. It is necessary to consider the full support equipment, too, in space missions. When one adds these support masses to the primary LOX $-\mathrm{H}_{2}$ propulsion system, the desirability picture changes. It may be better to utilize a propellant system that is far less demanding in terms of refrigeration, leaks, and other related aspects, even if the specific impulse performance is inferior. The point is that what we lose in specific impulse can be more than made up in the Earth-transported mass. Some of the storable propellant combinations are seen to offer several advantages.

Expanding on these simple thoughts, we next consider several other aspects, such as long-term reliability, repairability, ease of resupply, and multiple use of components (e.g., Can an empty propellant tank become the chamber for the next-stage rocket? Can the TVC injector for the first stage become the main propellant injector for the third stage?). Also, what are the implications of using some of the unconventional propellants in rocket hardware? Will injector nozzle buildup and blockage become a serious problem? Will some of the highly solids-laden flow cause excessive erosion of the nozzle throats? With the less energetic propellants, can we use a simple nozzle and not worry about replacing critical nozzle throats? What is the overall gain to the mission?

By now, it is obvious that future space missions, especially those designed to utilize extraterrestrial resources, will have to be designed from an overall mission advantage point of view rather than in a simple component-optimized fashion. This may seem simple enough, but we must evolve a quantitative engineering design methodology that reflects this new design philosophy. We term this the figure-ofmerit (FoM) approach. Although it may seem like an over-simplification; one number may be useful, purely for the purposes of initial screening of a myriad of concepts, in characterizing the overall merits of a space mission The figure-of-merit considers the specific impulse, mass ratio, reliability, inverse risk, repairability, ease of autonomous controls, scalability, and adaptability. We recognize that this is only the first step; more involved considerations will be added later. Here, the idea is to introduce a new methodology that is quantitative and considers the known engineering facts and technologies for future space missions.

The next section gives a brief overview of the components of the space missions of interest. These missions are largely the recommendations of the Sally Ride report and the Space Commission report. To render some of these thoughts more concrete, it is important to consider some specific missions. We have chosen one of the most popular missions of the next century, namely, Mars Sample Return (MSR). An advantage of this mission is that it has been extensively studied both in the USA and the USSR, including some joint-effort possibilities. Thus, it is easy to see the advantages of the FoM approach over the conventional approach. The basic mission "ground rules" are mentioned in order to provide a meaningful basis for comparisons. Whenever hard numbers are not readily available, the best estimate has been used based upon conversations with experts; it is an easy matter to change these numbers as they become more exact.

The heart of this paper considers the development of a quantitative, interrelated, color-coded program that enables the FoM to. be readily examined for all mission
variations. This was first accomplished through the use of simple manual entry into one of the popular spreadsheets (Lotus 1-2-3). After checking for consistency and simple verifications, the program is now being upgraded to use one of the expert systems. While other researchers may have taken similar approaches to this interrelated "spreadsheet" development, our main contribution has been the detailed quantitative considerations of the ISPP itself. Since the ISPP modules represent the most critically important components of the entire mission, it is very important to treat them in detail. The results indicate the definite advantages of this FoM approach.

It is concluded that the FoM approach may provide a powerful and yet easy and simple tool to design future space missions that can introduce great economy (and ecology) through the utilization of local planetary (extraterrestrial) resources.

## The Concept of "Figure-of-Merit"

It is very important to have a clear understanding of what is meant by the figure-of-merit. The FoM could be different for different missions and should be different for different priorities. The simplest definition appears to be simply the payload ratio as the most easily understood form of FoM. In some circles, the specific impulse ( $\mathrm{I}_{\mathrm{sp}}$ ) is good enough as the FoM. In the context of the more complex missions that we need in order to utilize extraterrestrial resources, several possible definitions are indicated in Table 4.1.

Table 4.1. Possible definitions of a figure-of-merit.

1. $\frac{m_{\text {pl }}}{m_{\text {launch }}}=\frac{m_{\text {payload }}}{m_{\text {launch }}}$
2. $\frac{\text { A Standard "Cost" }}{\text { Total Life-Cycle Cost of This Mission }}$
3. $\frac{\text { State-of-the-Art Launch Cost of This Payload }}{\text { Launch Cost of the Payload in This Mission }}$
4. Mass of the Sample Returned to LEO
5. Total Useful Mass
6. Any of the above, modified by factors for Reliability ( $\mathrm{R}_{\mathrm{el}}$ ), Repairability ( $\mathrm{R}_{\mathrm{ep}}$ ), Inverse Risk (1/Risk), . . .

Note: Definition 1 will not consider the shuttle external tank in the numerator, but Definition 5 may include the ET in the numerator if it can be usefully employed in the space operation, such as ISRU.

For the purposes of introducing the concept of the FoM approach in extraterrestrial resource utilization and for the purposes of this paper, we have chosen definition number four (4), modified by factors for reliability, repairability, and inverse risk (Table 4.2); also, a factor of $10^{4}$ is used as a multiplier for reasons of convenience. We recognize the limitations of the above definition. For example, it gives no indication of the relative ease, or difficulty, of getting to LEO in the first place. It also gives no indication of the ease, or difficulty, of assembling the spacecraft in LEO to be launched towards its destination. If the main intention of the mission is an extended duration settlement on Mars, the return of a small sample to LEO is no indication of the FoM. The main point is to start with an FoM that is easily modified subsequently while retaining the meaning and spirit of the quantitative interpretation and the flexibility to accommodate the modifications. Our present choice of the FoM-definition possesses that capability. Thus, for the purposes of this initial introduction,

$$
\text { FoM }=\frac{m_{\text {pl.returned }}}{m_{\text {launch.LEO }}} R_{\text {el }} \cdot R_{\text {epr }} \cdot(1 / \text { Risk }) \cdot 10^{4}
$$

In this specific example of MSR, the assembled spacecraft is launched from LEO on a Hohmann ellipse. The craft is made to enter a circular Mars parking orbit (MPO) approximately 200 km above the Martian surface. The orbiting craft is decelerated by aerobreaking (through the thin atmosphere of $\mathrm{CO}_{2}$ ). Soft landing is achieved through retrorockets. The craft spends several months on Mars, until the time is right for a minimum energy transfer and travel to Earth. The Mars ascent vehicle (MAV) is propelled to the MPO, from which the vehicle is sent on a Hohmann ellipse towards Earth. Upon approaching Earth, the craft is captured in a highly elliptic orbit around Earth, instead of the more energy-consuming circular LEO. The design, configuration, and operation of the MAV is critical, and the entire mission FoM is extremely sensitive to changes in the MAV design. The energy requirement calculations ( $\Delta v$ 's) are straightforward and, after verification with two reliable sources (Irving and Blum 1959, Bursard and deLauer 1965), we used the numbers given in Table 4.3.

Table 4.2. The modifier factors. ${ }^{\text {a }}$

|  | Cases |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | 2 a | 2 b | 3 | 4 |  |
| Risk/Inverse <br> Repairability | 0.9 | 0.7 | 0.7 | 0.6 | 0.2 |  |

[^7]Table 4.3. The $\Delta v$ 's for the Mars Sample Return mission.


Four different scenarios, to accomplish an identical MSR, are considered in detail. The first is the base line (case 1) and involves state-of-the-art, Earth-transported resources; LOX $/ \mathrm{H}_{2}$ propulsion; and the associated cryogenic storage both en route and on Mars. Variation 1 (case 2) considers Earth-transported resources, but employs storable propellants in order to clearly reveal the influence of refrigeration as distinct from the influences of in-situ resource utilization (ISRU); here, a fairly routine oxidizer $\left(\mathrm{N}_{2} \mathrm{O}_{4}\right)$ and a slightly unconventional oxidizer in space missions $\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)$ are considered as cases $2 a$ and $2 b$. Variation 2 (case 3) considers Earth-transported fuel (hydrocarbon) and the production of the oxidizer from the Martian atmosphere; the ISRU equipment to produce oxygen on Mars is Earth-transported. Variation 3 (case 4) considers only ISRU propellants; oxygen is manufactured on Mars through Earth-transported equipment. In variations 2 and 3, the Earth-transported ISRU equipment is left behind on Mars and is not part of the MAV. In variation 3, the fuel is a hydrocarbon derived from the spent case of the Mars lander vehicle (Kevlar or Nylon). The specific impulse of the MAV is highest in the base line case and lowest in variation 3. The specific cases considered
in this paper are shown in Table 4.4. It is a simple matter to consider various other combinations of fuel/oxidizer, chamber pressures, nozzle expansion ratios, rocket chamber and propellant container cases, and all related equipment.

Table 4.4. Comparative study.

| Base Line (case 1) | All Earth-transported resources, LOX $/ \mathrm{H}_{2}$ propulsion, cryogenic storage |
| :---: | :---: |
| Variation 1 (case 2a;b) | All Earth-transported resources, storable propellants $\left(\mathrm{CH}_{4} / \mathrm{N}_{2} \mathrm{O}_{4}\right.$; $\mathrm{CH}_{4} / \mathrm{H}_{2} \mathrm{O}_{2}$ ) |
| Variation 2 (case 3) | Earth-transported fuel (HC), in-situ resource utilization (ISRU) of LOX from atmosphere ( $\mathrm{CH}_{4} / \mathrm{LOX}$ ) |
| Variation 3 (case 4) | All ISRU propellants (fuel is the spent case; Nylon/LOX) |

## A Brief Description of Components

The overall system to accomplish the mission depends upon the performance of the individual components. It is important to understand the nature of the components that comprise the integrated system. Such an understanding also enables us to change the components, almost in a modular fashion, to see the influences of variations and the sensitivity to changes, and to incorporate advances in technology. It is the specific intention of this FoM approach to refain the flexibility to incorporate any change in any component in a clearly understandable manner. Thus, this approach is distinctly different from complex programs and software "packages" that frequently fail to reveal the component influences individually. The fundamental essence of this FoM approach is shown in Figure 4.1. The components are fairly straightforward and have been discussed in the literature. For the purposes of this paper, we give only a brief description of the components that make up the FoM system.

The Mission. As was stated earlier, the mission we chose as a case study is the Mars Sample Return. The high-thrust propulsion technique is employed. The incremental velocities needed are broken up into different stages, as shown in Table 4.3. Some midcourse corrections, $\Delta v$ 's needed to account for the noncircular nature of orbits of the Earth and Mars (around the Sun) and the non-coplanar nature of the two orbits, are all taken as incidentals and amount to a total of approximately 1 to $2 \mathrm{~km} / \mathrm{s}$. The return journey is on a Hohmann ellipse, but the Earth capture is in an energyefficient, highly elliptical orbit rather than a circular orbit. The main variations are not so much in the value of the $\Delta v$ 's necessary, but in the way one could choose to split


Figure 4.1 The essence of the figure-of-merit concept.
the stages. Our choice is by no means the best, but is consistently used, so the comparisons are meaningful.

Rocket Performance. The performance of the rocket(s) at various stages of the mission are needed in order to calculate the mass ratios. The main program used here is CET86, which is an improvement over the highly popular CEC72 program, from NASA Lewis Research Center. The PC version of this program was obtained from the University of Minnesota, and the results were verified with the mainframe version of the program at the University of Arizona. Another version of this program was obtained from a private company. This version has the specific capability of handling large fractions of charged species, or plasmas. Yet another program has been independently developed by a private company in California for the specific purpose of handling large fractions of solid particles in the products. This program is also installed on a PC (with a 386 board) at the University of Arizona. Thus, two versions of the NASA Lewis program, a variation with plasma capability enchancement, and an independent thermochemical program were used. After satisfactory verifications, the CET86 output was used as the input in this FoM study. More than 30,000 data sets were generated and covered various fuels, oxidizers, fuel/oxidizer ratios, chamber pressures, and
expansion ratios in the nozzle. Both equilibrium and frozen cases were run, and usually the mean was taken as the reliable number. The output includes the usual matrix of specific impulse, temperatures, and species concentrations, along with a myriad of parameters. Unconventional propellants and combinations were specifically studied, as were the more conventional ones. LOX/ $\mathrm{H}_{2}$ formed the standard basis for comparisons. Its performance is illustrated in Figure 4.2. Some of the unconventional combinations involved highly fuel-rich and highly oxidizer-rich cases; some unconventional fuels included Nylon and Kevlar burned with oxygen; some unconventional oxidizers included hydrogen peroxide. These unconventional propellant studies are intrinsically important, and are important to space missions, but the details are beyond the scope of this paper. They are the subject of a Master's thesis (Rascon 1989), the extensive calculations of which will be published shortly.


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Figure 4.2 Typical performance contour for $\mathrm{LH}_{2} / \mathrm{LOX}$.

The "Support" Components. These include the power, thermal control, radiation shield, pumping, storage, and monitoring equipment. Again, these are very important to the FoM calculations, but do not form the mainstream of our discussions here. We have used the state-of-the-art numbers for nuclear, radioisotopic, solar photovoltaic, solar dynamic, and solar thermal power sources. The sources of these are shown in Table
4.5. These "support" components are likely to undergo rapid advances in the next few years and will ultimately translate into lower masses and costs.

Table 4.5. The "support" energy data.

| RTG | $333 \mathrm{~kg} / \mathrm{kW}_{\mathrm{e}}$ |
| :--- | :--- |
| Nuclear | $340 \mathrm{~kg} / \mathrm{kW}_{\mathrm{e}}$ |
| Solar PV | $300 \mathrm{~kg} / \mathrm{kW}$ |
| Solar Dynamic | $100 \mathrm{~kg} / \mathrm{kW}_{\mathrm{e}}$ |

The In-Situ Resource Utilization Components. The in-situ resource utilization (ISRU) components represent the very core of the present study to the extent that the ISRU influences upon space missions are brought out by this FoM approach. The NASA Center at the University of Arizona is devoted to the development of ISRU. Various schemes are being considered for the manufacture of propellants and other useful materials from extraterrestrial resources. Associated with these are innovative concepts for energy utilization, separation of species in microgravity, reactor designs, and storage. The details, as of early 1989, are available in the University of Arizona, NASA Space Enginering Research Center "Annual Progress Report 1988-89." The idea of ISRU is relatively new, and the available studies have taken a somewhat traditional(!) approach. This statement is not as paradoxical as it may seem at first glance. The advantages of ISRU have been well recognized indeed; the approaches toward ISRU have involved ideas of transporting terrestrially used processing plants to extraterrestrial sites in order to manufacture useful substances "out there." Some innovation, a little high technology, some reductions in mass, and smaller safety margins have been the recipe of such proposed ISRU missions. At the NASA SERC of the University of Arizona, a fundamentally different approach is being taken. Here, the aim is to design the ISRU systems as one would design them from local resources, using the information bank from terrestrial and previous space missions. The details used in this paper are shown in Table 4.6. The numbers and technologies will certainly change and will be incorporated in future calculations.

Table 4.6. The ISRU plant data for LOX production on Mars.

```
70 kg (Zr cells)
    10 kg/day
425 kg support mass
```


## The Development of the Interdependent Matrix

The purpose of this section is to develop the fundamentals of the interdependent matrix that can evaluate the influences of various components upon the overall system. Mathematically, the problem can be formulated as an optimization problem with constraints. The use of Lagrange multipliers may seem natural. When one considers that there are at least twenty constraints at a time and that the nature of the mass equation is highly nonlinear (exponential), the use of analytical methods may not be straightforward. There are many modern techniques that could be used for such a problem. At the present time, we have used a popular spreadsheet (Lotus 1-2-3) to represent the interdependent matrix. The actual technique of quantitatively interrelating the variables and calculating the optimum is not critically important for the purposes of this paper, although the evolution of the optimum technique could be as important as the evolution of the optimum itself in terms of the economy of arriving at the solution. The use of this spreadsheet has the advantages of simplicity, popularity and ease of use at various locations, ready color graphing capability, and the ease of interfacing with other software. There is certainly room for improvement, and that is the subject of the graduate thesis of the junior author.

## The Evolution of the Spreadsheet

The spreadsheet was used to build the relationship between the initial mass and final mass in a single-stage rocket. The usual approach is to select a propellant and make an estimate of the structural mass. In this study, the structural mass was separated into different system masses, starting with the most general case. The different options included the aeroshell, nozzle, guidance and control, fuel tankage, oxidizer tankage, and a structural mass (pumps, valves, lines, etc.). The refrigeration needs of the propellant were then addressed. An interesting problem arose in the evaluation of the refrigeration needs. The propellant and the refrigeration masses are dependent upon each other. In transit, the dominant effect was assumed to be the solar radiation introducing a heat flux. The spreadsheet was used to solve the equations without attempting to linearize the highly nonlinear expression. The result is the solution of a cubic. Each stage then served as input for the previous stage. The masses for each category were then summed and the FoM was calculated for each case.

## Sample Results

These are shown in Table 4.7 and Figures 4.3 and 4.4. The liquid oxygen needs refrigeration on Mars. The heat transfer is taken to be a combination of natural

Table 4.7. Summary of masses from low Earth orbit $(\mathrm{kg})$ and figures of merit.

| Masses | Case 1 | Case 2a | Case 2b | Case 3 | Case 4 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Aeroshell | $2.48 \mathrm{E}+04$ | $5.86 \mathrm{E}+01$ | $6.16 \mathrm{E}+01$ | $2.56 \mathrm{E}+01$ | $1.01 \mathrm{E}+03$ |
| Fuel | $4.74 \mathrm{E}+05$ | 4.72E+03 | $9.44 \mathrm{E}+03$ | $1.52 \mathrm{E}+03$ | $1.62 \mathrm{E}+04$ |
| Fuel leaked | $2.12 \mathrm{E}+04$ | - | - | -- |  |
| Fuel tanks | 6.63E+04 | 7.73E+01 | $1.57 \mathrm{E}+02$ | $2.39 \mathrm{E}+01$ | $2.76 \mathrm{E}+02$ |
| Guidance and control | $6.63 \mathrm{E}+05$ | $4.04 \mathrm{E}+03$ | $4.37 \mathrm{E}+03$ | $1.06 \mathrm{E}+03$ | 1.17E+04 |
| Nozzle | $6.63 \mathrm{E}+05$ | $4.04 \mathrm{E}+03$ | $4.37 \mathrm{E}+03$ | $1.06 \mathrm{E}+03$ | $1.17 \mathrm{E}+04$ |
| Nylon factory | -- | - | -- | -- | $1.42 \mathrm{E}+02$ |
| Oxidizer | $3.79 \mathrm{E}+06$ | $2.30 \mathrm{E}+04$ | $2.01 \mathrm{E}+04$ | $6.04 \mathrm{E}+03$ | $6.50 \mathrm{E}+04$ |
| LOX refinery | - | -- | - | $1.84 \mathrm{E}+01$ | $3.59 \mathrm{E}+01$ |
| Oxidizer leaked | $1.69 \mathrm{E}+05$ | -- | - | $2.30 \mathrm{E}+02$ | $2.49 \mathrm{E}+03$ |
| Oxidizer tanks | $2.65 \mathrm{E}+05$ | $2.42 \mathrm{E}+03$ | 2.62E+03 | $4.26 \mathrm{E}+02$ | $4.66 \mathrm{E}+03$ |
| Refrigeration (fuel) | $4.20 \mathrm{E}+05$ | - | - | -- | -- |
| Rover | $1.50 \mathrm{E}+02$ | $1.50 \mathrm{E}+02$ | $1.50 \mathrm{E}+02$ | $1.50 \mathrm{E}+02$ | $1.50 \mathrm{E}+02$ |
| Refrigeration (oxidizer) | $4.42 \mathrm{E}+04$ | -- | - | -- | - |
| Structural | $2.65 \mathrm{E}+05$ | $2.02 \mathrm{E}+03$ | $2.62 \mathrm{E}+03$ | $4.26 \mathrm{E}+02$ | $4.66 \mathrm{E}+03$ |
| Sample | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ |
| Sample support | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ | $1.00 \mathrm{E}+00$ |
| Total | $6.86 \mathrm{E}+06$ | $4.05 \mathrm{E}+04$ | $4.39 \mathrm{E}+04$ | $1.10 \mathrm{E}+04$ | $1.18 \mathrm{E}+05$ |
| Modification factor ( $\mathrm{R}_{\text {el }}, \mathrm{R}_{\text {ep }}$, inverse risk, ...) | $9.00 \mathrm{E}-01$ | 7.00E-01 | 8.00E-01 | 5.90E-01 | $1.94 \mathrm{E}-03$ |
| Figure-of-merit (FoM) | 2.62E-03 | $3.46 \mathrm{E}-01$ | $3.65 \mathrm{E}-01$ | $1.07 \mathrm{E}+00$ | 3.28E-02 |

MARS SAMPLE RETURN MISSION (1 kg)


Figure 4.3 Figure-of-merit results.


Figure 4.4 Mission mass summaries.
convection and solar radiation. The $\mathrm{LH}_{2}$ needs refrigeration always. During space travel, it is assumed that the infinite heat sink (space) can be used to keep the LOX cool and that no active refrigeration is used. Further innovations may alter some of these numbers. The rest of the results are straightforward solutions to the governing equations.

## Preliminary Findings

As was expected (Ramohalli et al. 1987a, 1987b), the LOX/H ${ }_{2}$ case is not the best for this mission. In order of merit, the options should be:

1. ISRU LOX/Earth-transported $\mathrm{CH}_{4}$
[BEST]
2. All-Earth-transported $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{CH}_{4}$
3. All-Earth-transported $\mathrm{N}_{2} \mathrm{O}_{4} / \mathrm{CH}_{4}$
4. Spent case as fuel/ISRU LOX
5. All-Earth-transported LOX/H2

Discussion
The preliminary results of these studies indicate two important facts. One is that it is feasible to attempt a figure-of-merit approach to space missions that utilize extraterrestrial resources. The other is that the ISRU plant (hardware, equipment, controls, . . .) per se is not very taxing in terms of mass penalties, but the refrigeration needs of the liquid oxidizer (LOX) produced extraterrestrially can impose a very heavy penalty on the entire mission. Nevertheless, the decisive advantages of the ISRU mission are brought out, once again, in relation to all-Earth-transported resources. However, the demands of refrigeration prompts one to seriously consider the prospects for non-cryogenically storing the valuable oxidizer produced extraterrestrially. The production itself is quite simple, if not easy, through the use of modern high-tech zirconia oxygen cells. The necessary duration of 9-12 months on Mars, dictated by the orbital mechanics of minimum energy transfers of interplanetary travel, provides us with the important opportunity of carrying a small oxidizer plant that has a small output per hour, but produces a large quantity over the 9-12 months. The main issue is to find a means of economically storing the oxidizer for that length of time.

In this regard, one scheme that may seem very radical is to think of storing the oxidizer as a solid. Many powerful oxidizers are solids, and many of these possess a fairly low (negative) enthalpy of formation, $\Delta h_{f}^{0}$. A ready example is ammonium perchlorate that has been extensively used as an oxidizer in rocket propellant over a wide temperature range. While we are not suggesting making AP on Mars, the concept of a solid oxidizer, such as ammonium nitrate, may be worth some consideration. Nitrogen is found in the Martian atmosphere, and there are indications that the polar regions of Mars may have as much as $10-14 \%$ nitrogen in the atmosphere because of some differential diffusional effects [Source: Prof. John Lewis, University of Arizona]. The point to note is that some innovation in storing and end-use of the extraterrestrially produced oxidizer may make ISRU schemes orders-of-magnitude better than they are now through the elimination of refrigeration. On other planets and moons, where very low-temperature (< melting point of oxygen) regions are present, the concept of oxygen bricks has been suggested by James Burke. Some work on these schemes is proceeding at the UA NASA Space Engineering Research Center at the University of Arizona.

## Future Work

Further study will include variations in the overall mission and additional testing of the propellant options. The MSR mission needs testing for an orbiting craft left in MPO, where the sample could be transferred from the MAV and propelled on towards LEO.

Other options would be to investigate how ISRU could be used to enhance missions to Phobos and Deimos. Other possibilities include long-term refueling stations. Propellant selection will prove vital to future analyses. Refrigeration requirements have proved to be a dominant factor in the analysis. In this light, the use of solids must also be evaluated. The mission requirements and propellant selection will determine the role of ISRU.

## Summary

The approach to extraterrestrial resource utilization through the concept of an overall mission figure-of-merit leads to more realistic designs than through individual component performance maximizations. Simple examples show that the much studied LOX/ $/ H_{2}$ propulsion system may be capable of specific impulses in the 460 to 462 sec range, but the necessary refrigeration systems, leak-proofing, extended storage, cryogenic handling, pumping, and safety hazards all translate into excessive mass. This mass increase can easily exceed the mass ratio advantage gained through the superb specific impulse. Generalizing these thoughts, several variations were considered. It was shown that some of the less spectacular components can add up to a better system, overall. Conservative assumptions were made where specific numbers were not available. The actual numbers, although critically important for the final mission, are not critical for the purpose of this paper, which is advancing a new concept of extraterrestrial resource utilization rather than precise delineation of mission design numbers. A popular spreadsheet was used to demonstrate quantitatively the interrelationships among the various parameters. The approach is flexible. A specific MSR mission was considered to illustrate the approach at this time. It is easy to consider more involved Mars missions, such as those described by Nock and Friedlander (1987), as the mission component, instead of the very simple mission mechanics we have considered here to develop the FoM concept. Some of the unconventional propellant combinations were compared with the all-Earth-transported LOX $/ \mathrm{H}_{2}$ system. In summary, this new approach using a figure-of-merit may be more revealing, helpful, and meaningful than the conventional approaches of individual optimizations. An FoM approach may well become the key to economical utilizations of extraterrestrial resources to the benefit of all mankind.

[^8]Ash, R. L., et al., 1978, "Feasibility of Rocket Propellant Production on Mars," Acta Astronautica, Vol. 5, pp. 705-734.

Ash, R. L., et al., 1982, "Autonomous Oxygen Production for a Mars Return Vehicle," IAF (Paris) Paper 82-210.

Ash, R. L. and Cuda, V., Jr., 1984, "Technology Status Report for In Situ Propellant Production," Report to Jet Propulsion Lab., Pasadena, California.

Bursard, R. W. and deLauer, R. D., 1965, Fundamentals of Nuclear Flight, $2^{\text {nd }}$ Ed., McGraw Hill, New York, pp. 40-44.

Carroll, W. F. (Ed.), 1983, "Research on the Use of Space Resources, JPL Publication 83-86.

French, J. R., et al., 1985, "Mars Sample Return Options," Aerospace America, Vol. 23, pp. 50-53.

Frisbee, R. H. and Jones, R. M., 1983, "An Analysis of Propulsion Options for Transport of Lunar Materials to Earth Orbit," AIAA Paper 83-1344.

Irving, J. H. and Blum, E. K., 1959, "Comparative Performance of Ballistic and LowThrust Vehicles for Flight to Mars," pages 191-218 in Vistas in Astronautics, Vol. II (Alperin and Gregory, eds.), Pergamon Press, New York.

Nock, K. T. and Friedlander, A. L., 1987, "Elements of a Mars Transportation System," Acta Astronautica, Vol. 15, pp. 505-522.
(Presidential) National Commission on Space, Pioneering the Space Frontier, Bantam Books, New York, 1986.

Ramohalli, K. N., et al., 1987a, "Novel Extraterrestrial Processing for Space Propulsion, Acta Astronautica, Vol. 15, pp. 259-273.

Ramohalli, K. N., et al., 1987b, "Some Aspects of Space Propulsion With Extraterrestrial Processing," AlAA J. Spacecraft \& Rockets, Vol. 24, pp. 236-244.

Ramohalli, K. N., et al., 1989, "Recent Concepts in Missions to Mars--Extraterrestrial Processing," AlAA J. Propulsion \& Power, Vol. 5, pp. 181-187.

Rascon, M., 1989, "Performance Calculations for Unconventional Propellants and Combinations," M.S. Thesis, University of Arizona, Tucson.

Energy Management Analysis of Lunar Oxygen Production

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#### Abstract

Energy load models in the process of hydrogen reduction of ilmenite for lunar oxygen production are being developed. The load models will be used as a first step to ultimately determine the optimal energy system needed to supply the power requirements for the process.


## Introduction

The goal of this project this year is to determine the energy requirements in the process of hydrogen reduction of ilmenite to produce oxygen. The general approach is shown schematically in Figure 4.5. Our objectives are to determine the energy loads of the processes in the system. Subsequent energy management studies will be made to minimize the system losses (irreversibilities) and to design optimal energy system power requirements.

A number of processes are being proposed as possible candidates for lunar application as outlined in the recent study by Eagle Engineering (1988). Some detailed experimental efforts are being conducted within this project at The University of Arizona. Our priorities are directed toward developing the energy models for each of the proposed processes being considered. Our immediate goals are to identify the variables that would impact energy requirements and energy sources of supply.

## Objective

The objective of this study is to develop a preliminary comprehensive energy load model of the lunar oxygen production plant processes. The model, when refined, will be used to help identify energy management opportunities and optimal energy supply source (s).

## Research Status

Figure 4.6 is a block diagram of the five component processes in a lunar oxygen production plant that is based on the hydrogen reduction of ilmenite. The subprocesses are: mining, mineral processing, ilmenite reduction, water decomposition, and oxygen liquefaction. Those identified with an asterisk are items for which preliminary models have been developed. Beneath each process block in the diagram are listed the probable energy users associated with each process. The following is a


Figure 4.5 Study flow diagram.

*Preliminary energy models developed.

Figure 4.6 Energy consumers in lunar oxygen production.
summary of these models and their associated variables that impact energy supply and demand.

- Energy Isuses Related to Mining. Lunar mining devices will probably be electrically powered to operate in a vacuum. Thus, power requirements of terrestrial mining devices, which are mostly powered by internal combustion engines, could not be used to extrapolate power requirements on the Moon.

The choice of an energy source will depend on the power demands of the mining devices, which depend on the grade of the haul path, the shear strength of the regolith being cut, the size (boulders vs. gravels vs. fines) of the regolith being excavated, and the depth.

Use of modified terrestrial mining technology vs. specialized lunar mining technology, e.g., lunar rovers that mine and process the ores on location and haul only concentrated ilmenite to the oxygen production plant, needs to be studied. This would affect energy loads and distribution.

- Energy Issues Related to Mineral Processing. The particle size of the mined regolith will affect the type of mineral processing equipment (for sorting and size reduction) needed to reduce the ilmenite to specified size. For example, the energy demand of revolving screens is represented by

$$
E=D L(k w)
$$

where $D$ is the trommel diameter in meters and $L$ is the trommel length in meters. The energy demand of plane screens is given by

$$
E=k F(k w)
$$

where $k$ (in $K W / M^{2}$ ) equals 1.5 for a screen-surface area $F$ of 1 to $2 M^{2}$ and $k$ equals 1.2 for $F$ of 2 to $7 \mathrm{M}^{2}$.

Energy consumption in size-reduction machines is related to the hardness of the particles, the initial size, and the reduction achieved. A general model for the work required for size reduction is

$$
d E=-c \frac{d x}{x \eta}
$$

where x is the particle size, $\eta=1$ for crushing and fine impact pulverizing (coarse particles), $\eta=2$ for fine grinding and ball milling (fine particles), $\eta=1.5$ for rough milling of in-between-sized particles, and $c$ is a constant that depends on material strength and brittleness.

- Energy Requirement for Hydrogen Reduction of Ilmenite.
$\mathrm{FeTiO}_{3}(\mathrm{~s})+\mathrm{H}_{2}(\mathrm{~g})=\mathrm{Fe}(\mathrm{s})+\mathrm{TiO}_{2}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$


$$
\Sigma\left(h_{0}-h_{i}\right)=h_{\mathrm{Fe}}\left(T_{0}\right)+h_{\mathrm{TiO}_{2}}\left(T_{0}\right)+h_{\mathrm{H}_{2} \mathrm{O}}\left(T_{0}\right)-h_{\mathrm{Fe} \mathrm{TiO}_{3}}\left(T_{i 1}\right)-h_{\mathrm{H}_{2}}\left(T_{i 2}\right),
$$

where
$\mathrm{T}_{\mathrm{i} 1}=$ temperature of ilmenite entering the reactor
$\mathrm{T}_{\mathrm{i} 2}=$ temperature of hydrogen entering the reactor
$T_{0}=$ temperature of the streams leaving the reactor

$$
\Delta h_{h_{r}}=\Delta h_{f}\left(\mathrm{TiO}_{2}\right)+\Delta h_{f}\left(\mathrm{H}_{2} \mathrm{O}\right)-\Delta h_{f}\left(\mathrm{FeTiO}_{3}\right)
$$

where $h_{f}$ are the enthalpy of formation for the substances at temperature $T$.
$\mathrm{q}_{\text {loss }}=\epsilon A \sigma T^{4}$ (radiation loss from the reactor to the environment)
where
$\epsilon=$ reactor emissivity
$A=$ exterior surface area of reactor
$\sigma=$ Stefan-Boltzmann constant
$\mathrm{T}=\mathrm{exterior}$ surface temperature of reactor

- Energy Requirement for Water Decomposition.

$$
\mathrm{H}_{2} \mathrm{O} \Rightarrow \mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2}
$$

For the reversible process at constant temperature and pressure, the useful work required is

$$
W=\Delta G=\Delta H-T \Delta S .
$$

The heat (thermal energy) required is $q=T \Delta S . \Delta G, \Delta H$, and $\Delta S$ are changes in the Gibbs free energy, the enthalpy, and the entropy for the reaction. $\Delta G$ is the minimum amount of electrical energy for the process to take place endothermally, with an additional amount of heat $T \Delta S$ being added. When the energy supplied to the process is greater than $\Delta H$, the process takes place exothermally and excess
heat is given off. . Therefore, $\Delta H$ is the amount of energy required by the process. This energy can be supplied electrically or thermally. Assuming an efficiency $\eta$ for the energy source, the total energy required is $E=\Delta H / \eta$.

- Energy Issues Related to Water Decomposition. It has been suggested that hightemperature thermal decomposition should be used to decompose water to minimize heating of the recycled hydrogen to the reactor. An energy load model for both electrolysis and thermal decomposition will be developed to evaluate the merits of each.


## Problems Encountered

A major uncertainty in lunar oxygen production modeling efforts is the applicability of terrestrial mining techniques to the lunar surface. Power and energy estimates based on terrestrial mining devices must be used at this time, but they may not be appropriate for lunar applications. The lunar mining mechanisms need to be refined in order to develop an appropriate energy load model. The ongoing efforts in lunar mining studies at The University of Arizona and the Colorado School of Mines should be able to provide more insight into the problem.

## Future Work

The goal of the upcoming year is to complete the energy load models for the last three process blocks shown in Figure 4.6: ilmenite reduction, water reduction, and oxygen liquefaction. A secondary goal is to develop energy load models for mining and mineral processing.

## References

Casper, M. S. (Ed.), 1978, "Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques," Noyes Data Corporation,

Eagle Engineering, Inc., "Conceptual Design of a Lunar Oxygen Pilot Plant, Lunar Base Systems Study (LBSS), Task 4.2," EEI Report 88-182, NASA Contract No. NAS9-17878, Houston, Texas, 1988.

Engineering, Construction, and Operations in Space, Proceedings of Space 88, American Society of Civil Engineers, 1988.

Justi, E. W., 1987, A Solar-Hydrogen Energy System, Plenum Press.
Lynch, A. J., 1977, Mineral Crushing and Grinding Circuits, Elksevier Scientific Publishing Company.

Magerowski, A. J., 1984, "Energy Utilization in a Comminution Circuit," paper presented at the International Conference on Mineral Processing and Extractive Metallurgy.

Perry, J. H., Chemical Engineer's Handbook,
Trajan, G., 1981, Mineral Processing, Vol. 1, Fundamentals, Comminution, Sizing and Classification, Akademiai Kiado, Budapest.

Turkdogan, E. T., 1980, Physical Chemistry of High Temperature Technology, Academic Press,

## V. DATA BASE DEVELOPMENT

Data Base on Physical Observations of Near-Earth Asteroids and Establishment of a Network to Coordinate Observations
of Newly Discovered Near-Earth Asteroids
D. R. Davis, C. R. Chapman, and H. Camping

The University of Arizona
This programs consists of two tasks: (1) development of a data base of physical observations of near-Earth asteroids and establishment of a network to coordinate observations of newly discovered Earth-approaching asteroids and (2) a simulation of the surfaces of low-activity comets. Significant progress was made on Task 1, and Task 2 was completed during the period covered by this progress report.

## Task 1: Astromical Data Bank on Local Space Resources

(D. R. Davis and C. R. Chapman)

In the past six months, work continued on the development of the data base of near-Earth asteroids. Specific items accomplished in this period were:

- Completion of the initial data base as an ASCII file containing data from: (i) Russian ephemeris on orbit elements, (ii) McFadden review paper for the forthcoming Asteroids II book on physical observations of near-Earth asteriods, and (iii) IRAS data files. A printout of the ASCII file is given in Appendix G.
- Installation and familiarization with dBase IV at PSI. The ASCII data base described above was tranferred into a dBase IV file for evaluation of the dBase software for scientific use. A major defect in dBase is the inability to produce plots in any convenient fashion. Generally, one has to create an ASCII file containing the data to be plotted, exit ABase, and go to a separate plotting program in order to generate graphical output.
- We started work to extend the data base to include reference to the scientific literature for all entries. This subtask will be completed by the end of the current contract period (February 1, 1990).
- All entries in the data base were verified against original sources.

The second part of the Astronomical Data Bank task is to establish and operate a coordination/communication network to inform astronomical observers worldwide of newly discovered asteroids and to encourage them to make physical observations of such bodies. In the past six months, we sent a participation request form to 87 individual astronomers and 24 observatories (Appendix H). The individuals and observatories were selected based on their having done asteroid work previously. To date, we have received 20 positive responses from individuals (23\%) and 8 responses
from observatories (30\%), with 1 refusal of participation from an observatory. Only 3 individual responses and 1 observatory response came from outside the United States. Further effort will be made to expand the global availability of participating observers.

Following the relocation of PSI to our new quarters at 2421 East 6th Street in early October, we prepared a master schedule of observers that we can consult immediately upon receiving word of newly discovered asteroids. We have re-established the electronic IAU circular service and will notify teams searching for near-Earth asteroids (Shoemakers, Helin, Spacewatch, etc.) in the next few weeks requesting that they alert us as soon as new objects are found. The network is anticipated to be operational by the end of the year. A telephone-answering machine will be installed so that messages can be left regarding discoveries and observations outside of normal business hours.

Task 2: Modeling of the Surface Properties of Cometary Nuclei

## H. Campins

This task was aimed at characterizing the surface and subsurface properties of cometary nuclei, particularly to characterize regoliths and reveal indications of surface ice and water of hydration. Such studies are vital in order to plan how to utilize asteroidal resources. An analysis of the surface characteristics of the nuclei of periodic Comets Arend-Rigaux and Tempel 2 has been completed. We have used extensive visible and infrared observations of the nuclei of these two Earth-approaching comets to constrain a nonspherical thermal model developed by Dr. R. H. Brown (1985, Icarus, Vol. 64, p. 53). Our results indicate that the albedo and emissivity (at $10 \mu \mathrm{~m}$ ) of the nuclear surface of both comets is constant within the uncertainties. We interpret such constancy as due to a uniform mantle of dust that covers the surface of each nucleus. It appears that the source of volatiles is buried sufficiently deep that it does not significantly affect the surface temperature. We estimated how deep inside the nucleus the ice must be to be consistent with our results.

Meanwhile, we are preparing to publish our results. A paper by A'Hearn et al. describing our preliminary analysis of nuclear properties of Comet Tempel 2 . has been accepted for publication in the Astrophysical Journal (Appendix I).

## APPENDICES

## APPENDIX A

## AME 464/564 COURSE DESCRIPTION

# AN INTRODUCTION TO SPACE TECHNOLOGIES (AME 464/564) 

Instructor: Dr. Kumar Ramohalli (office in Aero Bldg room 200A)
Teaching Assistant: Paul Schallhorn
a senior/graduate credit course: Spring, 1990; M.W.F. 11:00 a.m. Social Sciences 206

OFFICE HOURS: M.W.F. 9:00 a.m.

AIM The principal aim of this course is to familiarize interested students with the mutifaceted disciplines that constitute space missions. Missions to/in Low Earth Orbit (LEO), Geosynchronos Orbit (GEO), the Moon, Mars, Phobos, Deimos, Asteroids, or the outer planets, all have many common features. These include the initial launch, the space environment, best use of trajectories, best use of available resources, and the maximum "returns" for our investment in the mission; these returns could include scientific data, weather/climate patterns, earth resource maps, colonization, platforms for further missions, to name only a few possibilities. It is also the specific aim to introduce students to the synthesis/design of space missions from these component technologies, results from a study of the individual disciplines will have to be combined in an efficient manner in order to tailer-fit the missions. This synthesis has frequently evolved into an art; however, the students will be introduced to some modern tools that are attempting to introduce scientific methodology to evolve the "best" design. The course will also indicate important terrestrial applications of the modern space technologies.

Throughout the course the emphasis is on synthesis of technologies for engineering space missions (rather than the details of component disciplines; i.e., orbital mechanics or advanced propulsion will be covered to the extent that they provide useful information on space technologies, but will not be covered in-depth, since such in-depth treatments are available in separate courses).

## CONTENTS

1. The Space Environment: the "atmosphere" out there, the chemical composition of the available species, plasma belts, solar and other radiation, microgravity, meteorites, space debris, levels of "vacuum",....
2. A Little Orbital Mechanics: Newton's law of gravitation, the two-body problem, simple $\Delta v$ calculations, orbit, escape, capture, mid-course corrections, some practical considerations,...
3. Elements of Rocketry and Space Flight: the high-thrust and low-thrust options, typical state-of-the-art and projected specific impulses, thrust-to-weight ratios, available vehicies, ELV's, STS, Buran, Hermes, and the NASP,....
4. Introduction to Planetary Sciences: composition of inner planets, surface features, atmospheres, simple theories of evolution, characterization of resources,....
5. Control, Command and Communications: the typical time lag, introduction to system analyses, telescience possibilities, stability of control systems.....
6. Materials and Structures: space-age materials, metals, plastics, ceramics, composites, strength-to-weight ratios, thermal behavior, long-term space exposure, effects of space environment on performance of materials, innovative space structures,....
7. Robotics and Man-Machine Systems: introduction to theory of robotics, degrees of freedom, available hardware, projections,....
8. The Thermal Design Issue: introduction to heat transfer, conduction, radiation, microgravity-convection, simulations under 1 g conditions, thermal cycting in orbit, the thermai lag and equilibration,....
9. System Synthesis: design of a complete mission (possibilities include earth-watch satellites, ozone-monitoring satellites, return-to-the-Moon, Mars Sample Return, Asteroidal
Missions,....)

## EVALUATION AND FEEDBACK

$\begin{array}{ll}\text { Homework assignments: } & \begin{array}{l}1 \text { each on the first } 8 \text { chapters.............. } 80 \text { points } \\ 1 \text { on the } 9 t h \text { chapter, synthesis.......... } 20 \text { points }\end{array}\end{array}$
Tests: (50 minutes each)
\#1 on February 16. $\qquad$ 100 points
\#2 on the third week on March (TBA). 100 points \#3 on April 13. .100 points
Final Examination. $\qquad$
Grades will be determined by the distribution of cummulative points.

## REQUIRED READING IN THE FIRST TWO WEEKS

1. Paine, Dr. Thomas O., "The Next 40 Years in Space", Plenary Paper given at the 40 th Congress of the International Astronautical Federation, Malaga, Spain, October, 1989 (copy on file at the UA NASA Space Engineering Research Center). Also, Dr. Paine, who was the NASA Administrator during its heyday, will visit the AME Department and give a seminar on this topic on February 22. You are strongly urged to attend.
2. Ride, Dr. Sally K., "Leadership and America's Future in Space", NASA, August, 1987
(copy on file at the UA NASA SERC).

In addition, "Report of the 90-Day Study on Human Expioration of the Moon and Mars", November, 1989, will be a useful reference throughout the course.

## OPEN FORUM/QUESTIONS AND ANSWERS

On Monday, January 29, the class will be conducted in an open forum format with questions
and answers. and answers.

## A NOTE ON THE LOGISTICS OF THE COURSE

January 10: Distribution of course structure material; student survey; video
January 12: The STS and project Moon-base (two videos) January 15: NO CLASSES.

January 17 and 19: Chapter 8: Thermal Design Issues in Space; introduction to heat transfer, conduction, radiation, convection, microgravity influences in convection, simple problems (guest professor, Dr. K.R. Sridhar).

## APPENDIX B

## THEORETICAL ROCKET PERFORMANCE DATA

IHEORETICAL ROCKET PERFORMAFCE ASSUMING EQUILIBRIUM COMPOSITION OURING EXPANSION

| CIIEMICAL I |  |  | FORPMIIA |  | WT FRACIIDH （SEE NOIE） | ENERGV CAL／MOL | STATE | TEMJ <br> DEG K |
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| 1）．000（1） | 0．00004 | 0.110004 | 0.00001 | 0． 110000 | 0.00000 | 0．（1）000 | 0．（1）000 | 0．00000 | 0．00000 | 0.00000 |
| （1）．03976 | 0．03136 | 0.02929 | $0.01 / 18$ | 0.010993 | 0.00475 | 0．00112 | 0． 110023 | 0.00003 | 0.00000 | 0.00000 |
| 11．91179 | （1）．93165 | 0． 93644 | 0．96．1．36 | （1）． 97856 | 0.98893 | 0.99590 | 0． 99763 | 0.99805 | 0.99814 | 0.99814 |
| （1．001．0） | d．（10001 | 0．00001 | O．O0， 110 | 1． 000000 | 0．00000 | 0． 110000 | 0．110000 | 0．00000 | 0.00000 | 0．0（）いい） |
| 0.00159 | 0.00102 | 0.00090 | 0．00034 | 0．00013 | 0.00004 | 0.00001 | 0．00000 | 0.00000 | 0.00000 | 0．00010） |
| 0.02847 | 0.02122 | 0.01951 | 0．01035 | 0.00559 | 0.00259 | 0.00073 | 0.00023 | 0.00006 | 0.00001 | 0.00000 |
| 0.01462 | 0.01225 | 0.0116 .4 | 0.00788 | 0． 00543 | 0.00358 | 0.00223 | 0.00191 | 0.00186 | 0.00186 | 0.00186 |




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PERFORMANCE PARAMETERS
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IVAC.LB-SEC/LB
ISP, LB-SEC/IB





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|  | CHEMICAL FORMULA |  |  |  |
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\begin{array}{r}
E \times 1 T \\
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0.06805
\end{array}
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1.2272 \\
1078.4 \\
3.0<7
\end{array}
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| 1.000000 | -3102.000 | l. | 90.18 |

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1014.3 \\
3.3 .19
\end{array}
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1.2164 \\
1166.7 \\
2.538
\end{array}
$$

3.3 .13



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& 10.04 .76 \%
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\text { E11: } 9
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& 6-1596 \\
& 6.9 E 8 t \\
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& 11 \times 7
\end{aligned}
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& 210 \sim 0 \\
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\end{aligned}
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THEORETICAL ROCKET PERFORMANCE ASSUMING EQUILIBRIUM COMPOSITIOH DURING EXPANSION



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19.60 .3
0.4551
1.2850
712.7
4.7 .6

| AE：${ }^{\text {a }} 1$ |  | 1．1006＂ | 1．H1096 | 1．4／113 | $\therefore 24.30$ | 3． $3 \% 24$ | 6． 13.11 | 11 ． $1 .=$ | 111．36： |  | 37.4711 | 6．2． $8: 1$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| CSIAR．I I／SES． |  | 6081 | 6081 | 6，7e1 | 6081 | 6081 | 6081 | 1，081 | 6081 |  | 6081 | OOB1 |
| CF |  | 11.678 | 11.742 | 1． 188 l | 1． 261 | 1．． 406 | 1．549 | 1．630 | 1．708 |  | 1.785 | 1.03 .1 |
| IVAC．U SEC／LU |  | 234.7 | 2.15 .7 | 201． 5 | 841.9 | 299.4 | 318.7 | 3.30 .6 | 340.6 |  | 351.5 | 358．2 |
| ISP．L．B SEC／LB |  | 128．1 | 140.2 | 20：5．9 | 239.5 | 265.7 | 2．32．8 | 309.1 | 322.7 |  | 331.4 | 346.4 |
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| 1 | 0.11012 | 111 |  | 1. |  | 112 |  | 0．110．3： |  | 1120 |  | （1． $00 \rightarrow 20$ |
| H20． | 0.00006 | 0 |  |  | 91 | OH |  | 0.10137 |  | 02 |  | 0.17364 |

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13.66 .3
1.4998
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134.7
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3.0 .31
19663
 コ． $6 \times 11$
5.0000
13.609
2605.0
1.2518 .3
-658.62
-922.09
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3.1344 1


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$\begin{array}{lll}\text { CF．CAI／（G）（K）} & 0.0128 & \text { O．604 } \\ \text { GAMMA（ } \\ \text { G）} & 1.1375 & 1.2007\end{array}$


T，DEG K
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S．CAL．$/(\mathrm{i})$
$\begin{array}{lrr} & \text { CHAMBER } & \text { THROAT } \\ \text { PL／P } & 1.0000 & 1.7722 \\ \text { P．AIM } & 6 B .046 & 38.396 \\ \text { T，DEG K } & 3415.5 & 3105.9 \\ \text { RIH，G／CC } & 4.7740 .3 & 2.9622 .3 \\ \text { H．CAL／G } & -171.68 & -360.13 \\ \text { II．CAL／G } & -516.86 & -674.03 \\ \text { G．CAL／G } & 10677.1 & 10095.3 \\ \text { S．CAI．／（L）（K）} & 3.134 .7 & 3.1344\end{array}$
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\begin{aligned}
\text { CHAMBER } & \text { IHROAT } \\
\text { I.OOOU } & 1.7722
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$4.7740 \cdot 3 \quad 2.9622 \cdot 3$ $3.1347 \quad 3.1344$
0.00006

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1.0000 & 1.7239
\end{array}
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1.1213
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\text { FERCENT FUEL }=10.5263
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| 100．0 rら1A |  |  |  |  |  | WT FRACIIUII （SEE NOTE） | $\begin{aligned} & \text { ENERGV } \\ & \text { CAL/MOL } \end{aligned}$ | SIAIE | $\begin{aligned} & \text { TEMO } \\ & \text { DEG K } \end{aligned}$ |
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-1661.21 \\
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\end{array}
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& 1.7404 \\
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|  | $\begin{array}{r} 1.0000 \\ 6090 \\ 4.660 \\ 1.35 .6 \\ 104.5 \end{array}$ | $\begin{array}{r} 1.0135 \\ 5098 \\ 0.735 \\ 196.7 \\ 116.4 \end{array}$ | $\begin{array}{r} 1.1191 \\ 4119 \mathrm{H} \\ 1.11117 \\ 260.0 \\ 11 \because \because \end{array}$ | $\begin{array}{r} \because 3250 \\ 1.098 \\ 1.270 \\ 238.1 \\ \because 101.2 \end{array}$ | $\begin{array}{r} 3.7312 \\ 5098 \\ 1.414 \\ 253.7 \\ 224.1 \end{array}$ | $\begin{array}{r} 7.1999 \\ 6090 \\ 1.565 \\ 270.7 \\ 247.9 \end{array}$ | $\begin{array}{r} 1.0102 \\ 5098 \\ 1.656 \\ 281.4 \\ 262.4 \end{array}$ | $\begin{array}{r} 11.141 \\ 5098 \\ 1.732 \\ 290.4 \\ 274.4 \end{array}$ | $\begin{array}{r} 411.118 \\ 5098 \\ 1.815 \\ 300.2 \\ 287.5 \end{array}$ | $\begin{array}{r} 61.642 \\ B 098 \\ 1.060 \\ 306.3 \\ 295.6 \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| （1）110！ 101 | （1）（111）${ }^{\text {a }}$ | 11．1027！ | （1）．1111）$/ 2$ | （1）11011） 8 | （1）1）100103 | （1）．11）1000 | （1）．1131）d | 1）．（1）1001） | （1）．（1）01）（1） | （1）．110111111 |
| 11．11s272 | （1）． 119568.1 | （1）．119623 |  | （1）11939！ 1 | （1）． 19974 | （1．11997！ | （）． 139383 | （1）．09580 | （1． 195 （3） | （1）．11） 1 （1） 1 |
| 0．01106 | （1）．110054 | （1）．10044 | O．（0）1）い） | （1）010） | （0．00000 | （1）．00000 | （1）（）0）（f）（） | （1．000）0 | O． 000000 | （）．（1）（1）（1） |
| （）．（1）（1） 17 | 11．00004 | （1）．00004 | O．（1）1111 | 11．0000） | 0．00000 | 0．00000 | O．000000） | （1．00）000 | 0.00000 | （1）．000（）0） |
| （1）．1）（17：1！ | 11．00450 | 11．00390 | O．001113 | （1）．00035 | 0.00007 | 1）．0000） | O． 0 （）00） | （1）．00000 | （）．0U（）U0） | （1．0000） |
| 11． $1(\mathrm{i} 7 \mathrm{5} 0$ | （1．77875 | （1．78116 | 0．79さ11 | （1． 79703 | 0.79848 | 0． 19960 | 0.79971 | 0． 79973 | 0．75973 | （1． 79913 |
| （1）002：31 | U．U0137 | 0．00118 | 0．000：35 | （1．00010 | 0．00002 | 0.00000 | U． 000000 | 1）．00000 | 0.00000 | 0．000（1） |
| 1）． 02503 | （1．01747 | 0． 01577 | 0．006839 | （1）．00298 | 0.00104 | （3）．00018 | 0．001）04 | （1． 00000 | 0.00000 | 0．00000） |
| （1）．1151811） | （1）．09845 | （1．09852 | （1）． 0909 ？ | 11． 119983 | 0． 10022 | 0．1010 4 ？ | （）．lil）ati | （1）．10147 | 0.10047 | 0． $100.1 \%$ |

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-489.25
-761.90
9807.63
2.9980
22.648
.05188
2.0529
2.4064
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1127.0
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| (1. 1298 | 0.141 | 0.14450 | 0.16523 | 0.18156 | 0.19835 | 0.22099 | 0. 23820 | 0. 25525 | 0.27701 | 8 |
| 0. 1132 Bl | 0. | 0.028 | 0.112259 | 0.01881 | 0.01537 | 0.01135 | 0.00870 | 0.00638 | 0.00385 | 36 |
| 0.100016 | 0.000 | 0.0001 | 0.10006 | 0.00004 | 0.00002 | 0.00001 | 0.00001 | 0 | 0.00000 | 0.00000 |
| . 136296 | 0.0590 | 0.05793 | $0.1)$ | 0.0 .16 | 0.041 | 0.03507 | 0.03026 | 0.0255 | 0.01933 | 0.01480 |
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| CF |  | 0.652 | 0.732 | 1.088 | 1.277 | 1.430 | 1.595 | 1.698 | 1.786 | 1.883 | 1.944 |
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| CO | 1.0186 E |
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| CO |  |
| （1） | 1.6862 O |

$\begin{array}{ll}11 & 48320 \mathrm{E} \cdot \mathrm{O} \\ 11 & 2.235 \mathrm{E} \cdot \mathrm{O}\end{array}$
$\begin{array}{ll}1110 & 2.9635 \mathrm{E} \\ 110 & 2181 \mathrm{E}\end{array}$
 12960 E
$3 \mathrm{aj40E}$ 333401
$\begin{array}{ll}6 & 58 \\ 5 & 5496 E \\ 2 & 8.3451 \\ 0 & 0000\end{array}$ 2.
0
0
0






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EOUIIIBRIIIM COMPOSIIION
PRESSURE LB／SQ IN
IEMPERATIRE（K）
FNIHAIPY．KCAI．／10）GM ENT CONT．CAI．／GAMMIKI MOI WT P．GM／MOI． MOLES GAS
$\begin{array}{ll}\text { TOIAI．MOI．ES } \\ \text { CPP } & \text { BTH／（MOI）（R）}\end{array}$ CPG．Bill／（MOL）（R）
$C P P$
$C P G$
BIIN／（IB）（R） ISP，SEC
ISP（V）．
CSIAR．
 EXII VELOCIIY IG／CII IN AREAS SO IN
IXPANSION RAIIO

MUII＇；PROHOCIS／ION GRAMS PROPIIIANI




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0 \omega-\infty n-m-\infty-\infty \infty 0
$$







$$
\begin{aligned}
& \text { TEMP } \\
& \text { DEG K } \\
& 298.15 \\
& 20.27 \\
& 90.18
\end{aligned}
$$

|  |  <br>  <br>  000000000000c |
| :---: | :---: |
|  |  <br>  <br>  0000000000000 |
|  |  <br>  <br>  0000000000000 |
|  |  <br>  <br>  $000000000000=$ |
| $\begin{aligned} & 008 \\ & 0.0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \end{aligned}$ |  |
|  |  <br>  <br>  0000000000000 |
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| $\begin{aligned} & 00 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & 0 \\ & \sim \end{aligned}$ |  |
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$$
\begin{aligned}
& n \\
& 0 \\
& -0 \\
& N
\end{aligned}
$$




$E \times I I$
2.0000
1.34023
2797.4
$.9068-5$
-369.93
-653.39
10262.9
3.5365

$$
\begin{aligned}
& N \\
& 0 \\
& 0 \\
& 0 \\
& 0 \\
& 0 \\
& 0 \\
& -0 \\
& -0 \\
& 0 \\
& 0 \\
& 0 \\
& 0
\end{aligned}
$$



$$
\begin{aligned}
& 9.533 \\
& 04712 \\
& .0306 \\
& .9120 \\
& .1073 \\
& 154.5 \\
& 1.000
\end{aligned}
$$

IIAMEER

$$
\begin{aligned}
& \text { PC: P } \\
& P, \quad A T M \\
& T . \quad D E G K \\
& \text { RFIU, G/CC } \\
& H 1 . ~ C A L / G \\
& U . ~ C A L / G \\
& G . ~ C A L / G \\
& S . ~ C A I /(G)(K)
\end{aligned}
$$

$$
\begin{array}{r}
1.60000 \\
0.68046
\end{array}
$$

$$
\begin{array}{r}
2938.8 \\
5.4336-5
\end{array}
$$

$$
\begin{array}{r}
19.256 \\
1.05327 \\
2.1202 \\
3.0550 \\
1.1093 \\
1106.4 \\
10.1000
\end{array}
$$


$P H I=0.6616$

$$
\begin{aligned}
& \stackrel{\square}{\square}
\end{aligned}
$$

$$
\begin{aligned}
& \left.\begin{array}{llllll}
-0 & 0 & 0 & n & 0 & 0 \\
\hline
\end{array}\right) \\
& \therefore \cdot 1 T \\
& 1.1 \times 3
\end{aligned}
$$

$$
\begin{aligned}
& \begin{array}{l}
10.0 \text { PSIA } \\
\text { CIIEMICAL } \\
\text { AL. 1.OOOOO } \\
\text { H } 2.00000 \\
O \\
2.0 O O O O
\end{array} \\
& \begin{array}{l}
\text { FC: } \\
\text { FUEL } \\
\text { FUEL } \\
\text { OXIDANT }
\end{array} \\
& \begin{array}{l}
\text { FC : } \\
\text { FUEL } \\
\text { FUEL } \\
\text { OXIDANT }
\end{array}
\end{aligned}
$$




## 






$$
\begin{array}{ll}
11 & 11111111 \\
11 & 1151011 \\
11 & 17130
\end{array}
$$

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\underset{y}{V}
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$$
\begin{aligned}
& \text { A1 (1..11 } \\
& \text { H20 } \\
& \text { AL } 20.3(1)
\end{aligned}
$$

$\qquad$


$$
\begin{array}{r}
14.241 \\
4.6927 \\
1.2108 \\
1 \therefore 365 \\
0.11,0
\end{array}
$$




H．／
H．AIM
T．DEG K

6817
7.896
$9 / 99$
11111


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ORIGINAL FAGE 13 OF POOR QUAITYY

$$
\begin{aligned}
& \begin{array}{rr}
1180.3 & 1160.7 \\
1.11110 & 1.111
\end{array}
\end{aligned}
$$



HII $=0.9924$





| $\leftarrow$ |
| :--- |
| $\times 0$ |
| 0 |


 5.4
991
$\begin{array}{lll}-0 m \infty & 0 \\ \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{array}$
0
0
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0
0


$\omega \times-\infty$





MOI E FRACTIONS
AE／AI
CSIAR，FI／SEI
CF
IVAC．IB－SEC／LB
ISM．LB－SEC／IB
0.00000
0.00000
0.00000
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0.00649
0.00000
0.03681
0.91252
0.00180
0.01397
0.01944
0.00896
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\begin{aligned}
& \text { M. MOL WI } \\
& \text { (DIV/DL.P)T } \\
& \text { ([HV/DLI)F } \\
& \text { CP. CAL/(Ci) }(K) \\
& \text { GAMIAA (S) } \\
& \text { SON VEL.M/SFC } \\
& \text { MACII HNABFR }
\end{aligned}
$$

$$
\begin{array}{r}
15.721 \\
1.107665 \\
2.5513 \\
4.7338 \\
1.1076 \\
1328.5 \\
11.0110
\end{array}
$$

WFRYGFMAISCF WAKAMFIIF：

StATE

$1+11=0.3969$
wt fraction
WT FRACTION
(SEE NOTE)
皃
$00-$





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\begin{array}{r}
E \times 1 \dot{1} \\
00.00
\end{array}
$$ 0

-00
$\times 00$
$\times 00$
40 5292.00
$2.95: 35$

$$
\begin{array}{r}
23.266 \\
111842 \\
1.4394 \\
1.3867 \\
1.1226 \\
11139.2 \\
11.11411
\end{array}
$$

FERI ORMANCE FARAME IERS

$$
\begin{array}{rr}
1 \dot{1} & \text { EXIT } \\
\text { OnO OO }
\end{array}
$$








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$\stackrel{\sim}{\square}$

 $E \times 1 T$
4.0000
11.136119
2308.2
$7187-5$
.480 .67
-672.42
7297.89
2.95 .35



CHAMBER

$$
\begin{array}{r}
\text { CHAMBER } \\
1.0000 \\
11.6 B 046 \\
2692.0 \\
7.1669 .5 \\
-141.93 \\
-.171 .86 \\
13012.89 \\
\therefore .9435
\end{array}
$$

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MOL WI
10.0 PS1A

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& 1118 .
\end{aligned}
$$


14 PC：H
P．AHI
T．DEG
RIUU．
H．CAI
II．CAI
I．CAI
S．CAI


[^10]FEKYOGGIAME FAKARLILK．
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11.685
150.0
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\begin{aligned}
& 0.745 \\
& 131.4
\end{aligned}
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\]

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\begin{aligned}
& 131 \\
& 117
\end{aligned}
$$

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$$
\begin{aligned}
& \begin{array}{l}
60 \\
56
\end{array} \\
& \begin{array}{r}
0.4656 \\
1.2247 \\
1019.3 \\
1.098
\end{array} \\
& \begin{array}{r}
\therefore 613 \\
46 \% 3 \\
2236 \\
29.4 \\
.040
\end{array} \\
& \begin{array}{l}
2.1 \\
0 . \\
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\end{array}
\end{aligned}
$$



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三5u0
$\begin{array}{rr} \\ & \\ .010010 & 1.0175 \\ 1.624 & 6624 \\ 0.645 & 0.729 \\ 253.0 & 254.9 \\ 132.9 & 150.1\end{array}$
 HAMHER
 S．（AI／（G）（K）

16.11
.05609

$\begin{array}{lr}\text { M．MOL WI } & 15.412 \\ \text {（DIV／DLP）} & 1.07332 \\ \text {（DLV／OLI）P } & 2.4932 \\ \text { CP．CAL／（I．）（K）} & 4.6929 \\ \text { GAMMA（S）} & 1.1080 \\ \text { SON VEL．M／SFI } & 13.18 .4 \\ \text { MACH NUMBER } & 1)(1) 0\end{array}$
15.651

 ..... 92.6
.139 ..... 139

$=$

$$
\begin{aligned}
& \text { M. MOL WI } \\
& \text { (DIV/DLP)I } \\
& \text { (DL.V/OLI)P } \\
& \text { CP. CAL/(C;)(K) } \\
& \text { GAMMA (S) } \\
& \text { SON VEL.M/SFC } \\
& \text { MACH NIMBER }
\end{aligned}
$$




$$
\begin{array}{r}
\text { IFAMBER } \\
1.10000 \\
11.68046 \\
2996.7 \\
4.2648-5 \\
-201.27 \\
-537.66 \\
.12988 .3 \\
4 . \because 670
\end{array}
$$


81.06
$\angle 2.02$
51.862
$4.0 \exists 0$
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20.27
96.10
 CAL/MC1
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2164.0011
3102.000




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617.

| $\square$ |
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| 0 |
| 0 |



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\begin{aligned}
& \bar{a} \\
& \frac{1}{4}=
\end{aligned}
$$

FEKHOMPIAHEL FAKAMEILK,

O. (11,1)

ェuvin = -C/P
P. AII

1. DE
RIIC.
2. CAI
3. CAI
4. CAI
j. CAI
 CP. (:A1/(L) (N)
GAMMA (S)

SON VII M/SEC
MACII HIMEER
MACII MIMEER
(1.151)
(1. 59671
0.00243

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OF POOR QUALISY

10.0 ISIA
$\begin{array}{ll} & \text { CIIEMICAI FOKMII.A } \\ \text { FIIEI } & \text { AL 1.0OOOO } \\ \text { OXIUAIII } & 0 \\ 2.00000\end{array}$

## $0 / F=1.3330$



IHEOREIICAL ROCKEI PERTORMANCE ASSUMING EQUILIBRIUM COMPOSIIION DURING EXPANSION
$\backsim \perp$

$$
\begin{aligned}
& P C= \\
& \text { FUEL } \\
& \text { DXIDANT }
\end{aligned}
$$

$$
10.0 \text { PSIA }
$$

$$
\begin{array}{ll} 
& \text { CIIEMICAL F } \\
\text { FUEL } & \text { AI. } 1.00000 \\
\text { DXIDANI } & 0 \\
\hline
\end{array}
$$

CIIEMICAL FORMUI.A

$$
\begin{array}{rl}
\text { CHAMBER } & \text { IIROAI } \\
1.0000 & 1.6983
\end{array}
$$

$$
\begin{array}{r}
\text { EXII } \\
5.0000 \\
0.13609 \\
3595.6 \\
86915 \\
241.74 \\
-356.61 \\
6066.13 \\
1.6199
\end{array}
$$

62.202 63.051 63.891

$$
\begin{array}{r}
* * * * \\
1.0733 \\
701.1 \\
2.159
\end{array}
$$

$$
\begin{array}{r}
1.0708 \\
684.2 \\
2.494
\end{array}
$$

$$
64.990
$$

$$
1.0005
$$

$$
\begin{array}{r}
3122.4 \\
1.7478-6
\end{array}
$$

$$
\begin{array}{r}
1.7478-6 \\
-553.31
\end{array}
$$

$$
66.624
$$

$$
\begin{array}{rr}
* * * * * * * * * * * * * * \\
1.0657 & 1.0637 \\
648.4 & 634.3 \\
3.179 & 3.448
\end{array}
$$


state
L
 PHI＝ 1.0005

$$
\begin{aligned}
& \text { WT FRACTION } \\
& \text { (SEE NOTE) } \\
& 1 \text { OOOOOO }
\end{aligned}
$$

$$
\begin{array}{r}
E \times 1 T \\
1000.00 \\
0.00068 \\
2837.7 \\
2.0013-7 \\
-756.13 \\
-838.47 \\
-5352.86 \\
1.6199
\end{array}
$$

$$
68.484
$$

$$
\begin{aligned}
& 67.688 \text { 68.484 } \\
& \text { 6. }
\end{aligned}
$$

$$
\begin{aligned}
& 00^{\circ} 001 \\
& 1 I \times 3
\end{aligned}
$$

$$
\begin{aligned}
& 968 \tau \\
& \tau \subset 9 \\
& B \angle 90
\end{aligned}
$$

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$11 \times 3$

$$
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PERI ORMANCE PARAMEIERS

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MOI T TRACIIONS


$\stackrel{\text { 를 }}{\stackrel{\text { ® }}{=}}$
ORICHAL PRGE IS OF POOR QUALITY

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\begin{array}{r}
\infty \\
m \times N \\
-\infty
\end{array}
$$




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PC- 10.0 PSIA
$\begin{array}{ll} & \text { CIIEMICAI FORMIIIA } \\ \text { 1H1 } & \text { AL } 1.00000 \\ 0 X 10 \text { DAIII } 0 \quad 2.00000\end{array}$
$(1 / 1)=$
GIAMBER
1.0000
0.68046
3918.3
2742.4
45.622
-17.4 .95
6392.72
1.6199

FLRIGIMAFN:L PARAMLILK:
AE/AI
CSIAR. $11 /: E C$
IVAC. 1 IS-SEC/IB
ISP. 1 B-SEC/IB
MULE IRACJIONS
120

$$
\begin{array}{r}
3835 \\
0.645 \\
146.4 \\
76.9
\end{array}
$$

$$
\begin{array}{r}
.0175 \\
3835 \\
0.729 \\
147.5 \\
86.9
\end{array}
$$

$$
\begin{aligned}
& 116.9 \\
& 129.6
\end{aligned}
$$

$$
\begin{aligned}
& 1.21298 \\
& 0.00729
\end{aligned}
$$

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$$

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\begin{aligned}
& \text { Al } 0 \\
& \text { Al } 202
\end{aligned}
$$


theoretical rocket performance assuming equilibrium composition during expansion
10.0 PSIA

$$
2.00000 \quad l
$$

$$
\begin{array}{ccc}
\text { WT FRACTION } & \text { ENERGY } & \text { STATE } \\
\text { (SEENOTE) } & \text { CAL/MOL } & \\
1.000000 & 7300.000 & S \\
1.000000 & -3102.000 & L
\end{array}
$$

$$
0.3985, \quad P H I=0.39
$$

$$
P H I=0.3985
$$

$$
\begin{aligned}
& \text { TEMP } \\
& \text { DEG K } \\
& 298.15 \\
& 90.18
\end{aligned}
$$


 EXIT 100.00
0.00680
$\infty$
1
$\infty$
$\cdots$
$\cdots$
$\cdots$ 0
0
0
0
0
0
0 2.3592




## PC/P P. ATM T. DEG K RHO. G/CC $H . C A L / G$ U. CAL/G G. CAL/G S. CAL/(G)




-


"

$$
\begin{array}{r}
30.943 \\
-1.25441 \\
6.3335 \\
7.5736 \\
1.0938 \\
922.4 \\
0.000
\end{array}
$$

PERFORMANCE PARAMETERS




$\infty$



.0190
4617
0.727
177.5
104.4
$\begin{array}{lll}0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & - \\ 0 & 0 & \sigma\end{array}$

CP. CAL/(G)(K)
GAMMA (S)
SON VEL,M/SEC
SON VEL,M/SEC
MACH NUMBER
AE/AT
CSTAR. FT/SEC
CF
IVAC. LB-SEC/LB
ISP. LB-SEC/LB
$\begin{array}{ll}00705 & 0.00530 \\ 00001 & 0.00000\end{array}$

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10.0 PらIA

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## 


$I H I=0.6642$
WT FRACTION
（SEE NOTE）
1.000000

## 

WT FRACTION CNERGY


$11 \times 7$

## CHEMICAL FORMULA SI 1．00000 H 4.00000 <br> PC $=$ 1 FUEL OXIDAN

$\begin{array}{rr}\text { CHAMEER } & \text { IHROAT } \\ 1.0000 & 1.7045 \\ 0.68046 & 1.39922 \\ 2945.2 & 2866.6 \\ 7.7958-5 & 4.7841-5 \\ -15.883 & -126.09 \\ -227.26 & -328.18 \\ -7603.28 & -7510.86 \\ 2.5762 & 2.5762\end{array}$
－

WERCENT FUEL =
EXIT
$0 / ト=$

$$
25.0000
$$

$E \times 1 T$
1000.00
0.00068
2171.4
$1.2942-7$
-1147.22
-1274.54
-6740.96
2.5762

EQUIVALENCE RATIO $=0.6642$

E×1

| $\vdash 0 円 \infty ぃ の-m N$ －ON：－ 0 M <br>  <br>  <br>  －NーーツサN |  |
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ONNM
$0 N N$
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$\cdots \sigma$
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#### Abstract





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## APPENDIX C

## CARBONYL EXTRACTION OF LUNAR AND ASTEROIDAL METALS

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John S．Lewis＇，Thomas D．Jones ${ }^{2}$ ，and william ：i．Parrand ${ }^{2}$
The century－old Hond process for carbonyl extraction of
metals from ore shows great promise as an efficient，low

 carbonyl processing of the metallic alloy by－producta of such operations．The native metal content of steroidal High－purity，corrosion resistant Fe and Ni can be extracted

 Introduction
The exploitation of extraterrestrial natural resources
will be essential to the successful economic development of
 materials，propellants，and life support ilujiss－－that we cannot afford to ignore if we are to sustain a growing remote，low－g vacuum environment of the lunar or asteroid surface，we should emphasize the use，whenever possible，of
simple，proven terrestrial refinement schemes in our simple，proven terrestrial refinement schemes in our
lunar and asteroidal mining，the Hond process for carbonyl
extraction of iron and nickel（as well as other valuable
 technique．capable of producing high purity metals from the
local regolith or other feedstock．In this paper we
 its advantages and drawbacks，show its application to lunar The Carbonyl Process
The groundwork for the gaseous carbonyl process was
1 Professor，Department of Planetary Sciences，Univ．of
2 Space sciences Bldg．．Univ，of Arizona，Tucson，Az 85721

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## Albuquerque．New Mexico

August 29－31． 1988
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CARISONYI. I:XIRACTION OF METAIS

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Ieliations for ition caibonyl.


favors the best yield of carbonyls at the lowest temper-
atures. If, for other reasons (kinetic factors, or limited atures. If, for other reasons (kinetic factors, or inmited
reactor volume). it is found desirable to operate at much higher gas densities and preasures, higher temperatures can be tolerated: a pressure of 10 bars of co is sufficient to
keep nickel carbonyl stable and obundant fa partial keep nickel carbonyt stable and obundant fa partial pressure of carbonyl gas in Eqn.
power of the co pressure, and that the iron and nickel carbonyls have different equilibriua stabilities.
Therefore, passing the reaction product gas through a collecting bed with the samo temperature but 10 times lower
 co released can be recycled through the reaction chamber Indefinitely.

The some principles apply to the formation of the yaseous carbonyls of many other alements (e.g. Os, Co, lr, Ru, Rh, Pt, and Pd). Stability data for a number are avaliable
(See the JANAF Thermochemical rables; Robie et al., 1978:

A forther tmpl icatlon of the datagiven in Flg.
A further implication of the data given in fig. 1 and 2 is separate very pure fe while retaining all the Ni in the gas phase. The commorcial Mond process can produce fe and Ni With puritiea of about 99.951 in a single step by taking ideal for making tough, corrosion-resistant single crystais of very high tensile strength, cannot be made by eithor
 mutual solubilty of solld and iiquid re and Ni. (The eutectic composition in the Fe-Ni is near 607 Ni , not near the pure end-meraber compos
similar vapor pressures.)

An entirely aeparate approach to carbonyl separation is avallable: the vapor pressures of the liquid carbonyls are large enough ot and near room cemperature to permit their Illustrate this alternative. By holding an Pe-Ni carbonyl liquid mixture at, say, 300 K , Ni carbonyl will have about
lo times the vapor pressure of fe cartionyl, allawing 10 times tha Vapor pressure of fe cartuonyl, allowing
preferential separation of the former. This process is even more effective at lowar temperatures.

For process design, the kinetics of carbonyl formation and decomposition are just as laportant as thermadynamic
atability. literature daca for Fe and $H i$ are avaliable (Garratt and Thompson, 1934a,b; Carlton and Oxley, 1965, valatilization of metallic feedstocks is striking, as is

Ianar-specific Applications
Any scheme for producing oxygen from the lunar regolith could be enhanced by applying the Nond prong the sulte of minerala in the lunar regolith, the one which acemioj).
amenable to oxygen extraction would be llmenite (feTioj).
Ground and orbital studies from the Apollo misgions indicate that flmenite cancentrationa are highest in and
lunar marla, particularly in mare manguilifatis and southern Mare. Sorenitatis, where Apollo 11 and 17 , respectively, found ilmenite making up to somection of electrontic techniques for benoriciation of lunar ilimenite trom auch aolis indicate that grades and (Agosto, 1984).
CARIGNYI. I:XIRACTION OF METAIS IIS gaseous carbonyls. Rhee et al. (1973) have shown that the

 of the net torward reaction varias as about $1 / \mathrm{T}^{2}$. hisins,

 greater stablishend. 1955 ).
 application are numarous. The only reactant requition and
co, recoverable at the tine of motal deposition very co, recoverable at indefinitaly. The basic process uses very
recyclable ind can

 automatic operation. As the are wall-understood for the


 disadvantages. Nickel and Iron carbonyls are extreaely
toxic. so contaminatlon of any workers and their jiving
 applications ls that co will
from Earth, but tha gas is recyclable, and can be
supplemented by combustion of organic wastea. In the
 asteroidal case, as we shait every asteroid type suitable for metals extraction. - $\qquad$ $\longrightarrow$
117
$\mathrm{FeTlO}_{3}+\mathrm{H}_{2} \rightarrow \mathrm{Fe}+\mathrm{TlO}_{2}+\mathrm{H}_{2} \mathrm{O}$. The $\mathrm{H}_{2} \mathrm{O}$ can then be broken down to $\mathrm{H}_{2}$ and $1 / 2 \mathrm{O}_{2}$ via electrolysis with the hydrogen being recycied and the later shipment. Some hydrogen wili be lost in thla process, but some solar ind implanted hyd
released from the ilmenite fedstock.

 is 58 or less (williams, 1984 ). The energy cost of the process is 5000 calories per gram of ory Running the process at higher temperatures wili produce higher yields, but that ralses the associated problems of increased hydrogen loss rates through diffusion, sintering
of solid reactants and products and, of course, higher energy usage.
 needed. Specifically, it must be determined how efficient
the process is when the ilmenite feedstock contains no Fe ${ }^{3+}$. Extraterrestrial inmenites used In such teatis could
 The solid residue of the hydrogen reduction proce proceas
a mass of native Fe and ruthe (rio $)$ The Hond cumid be effectively used to separato this residue int ich can then be thermaliy decomposed to yield high-purity iron for use in structural meabers. The left-over rutile can be used in products that require a rerractory consti.

Another promising technique for winning oxygen from Another
ifrenite is che carbothermal reduction process (cutler and
Krag. 1984). In this process. ilmenite feedstock is mixed Krag, 1984). In this process, ilmenite feedstock is mixed
with a carbon reductant and an anorthite fluxing agent and with a carbon reductant causing the following endothermic reaction: $\mathrm{FeTiO}_{3}+\mathrm{C} \rightarrow \mathrm{Fe}+\mathrm{CO}+\mathrm{THO}_{2}$

The resulting iron is contaminated with carbon and can be subjected to the Hond procese to purify the iron. When
reacted with $H_{2}$, the co sonc of which could be removed for use as the Mond process reactant) can be converted to $\mathrm{yCO}+(2 y+1) \mathrm{H}_{2} \rightarrow \mathrm{yH}_{2} \mathrm{O}+\mathrm{C}_{\mathbf{y}} \mathrm{H}_{2 \mathrm{y}+2}$


Fig. A. The hydrogen-reduction of ilmenite produces oxygen
with an fe-tion residue.


Fig. 5 . Electrolysis of molten silicates produces oxygen
at the anode while various metalis plate out on tha cathode.
Tabla I．）The parent bodies of these meteorites have not undergone the melting and geochenical ditiorentiation concentrated most of their metals in inaccessible cores． Because of the very low oxygen fugacity in matal－bearing meteoritels，al direct extraction from the metal phase，not
 fe／Ni cartionyl extraction，tha reasining metallic reaidue

 process．

TABLE I：Fe and Ni concentrations in ordinary chondrites

| 1．075．0 | 1．07\％ 0 | 2．0ir．t | tejam ul toljerjuajuma on |
| :---: | :---: | :---: | :---: |
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| ¢991 | $2 \overline{76}$ | じ。 |  |
| $\mathrm{n}^{-}$ | ss975 | IT |  |


 （NEA）population．Spectral analogs of ordinary chondrites are rare in the feu dozen near－Earth asterolds the sheer









 perhaps magnetic beparation．

The major advantage of asteroldal feedstocks for the
carbony process is the low energy required to deliver
mining equipment to the NEA and return useful ore to LEO．

Oxygen can then be recovered via electrolysis and the
originai carbon reactant can be recovered via hydrocarbon


Although carbothermal reduction is on involved process， It doas have some bignlificant advantages over hydrogen than 1.25 times lts mass of oxygen per pass while hydrogen only temoves o． 1 to 0.9 times its mass per pass．Also， carbon can be recovered from garbage and co $_{2}$ waste gases
and should be an easler reducing agent to handie than hydrogen．Disaduantages of the process are that it is mora
energy Intensive than hydrogen－reduction and requires more processing eteps

While $11 m e n i t e ~ m a k e s ~ u p, ~ a t ~ b e s t, ~$
108
of lunar solls， while liberating oxygen from ailicates is an energy Intensive process，one proposed extraction scheme stands out because of ita conceptual，if not practical，
slrapllcity．hindstroa and haskin（ig7s）have experimented with a aystem of magma olectrolysis（Fig．5）．A feedstock of silicates is melted and two electrodes are inserted into liberated at the anode while the cathorle is ploted with a mixture of Fe，Cr．Hn．Ti and possitily si．The process
requires jooo calorles of tharmal and electrical energy per
 the nass of solids）the cost per gram of oxygen is 30,000
calories．Note that instead of meiting bulk lunar sillicates，the readstock could Just os easily be ilmenite．
 constituent metals can be volatillized and extracted．

Ot the hydrogen reduction，carbothermal and magma
electrolyeis methods，the firat appears more viable．It operates at lowar temperatures，does not require massive be provided by icalar furnace），and is more energy－ efticient than oither the carbotherral process or
 product are produced，then the additional expense of the atter process may be justified．

Application to Asteroldal metals
 extraction，separation，and refinement of the native metal
alloys plentiful in the regoliths of certain types of asteroids，those corresponding to the unequilibrated


Not only are many Nen more acceasible from leo than the lunar suriace in terms of av, but the return energy $1 i k e 1982 \mathrm{DB}$, the $\Delta V$ required is leas than $100 \mathrm{~m}_{\mathrm{s}} \mathrm{s}^{-1}$.) These asteroldal ores can be subjected 1 mmediately to the required for lunar feedatocks. Further, Bimple heating of any class of chondritic meteorite can supply all the
necessary co.

The major drawback to the exploitation of asterold
targets is the long elight-time associated with the low launch and return energies, typlcally on the order of 1 to 3 years. Moreover. the most energeticaliy attractive asteroids have the longest synodic parlods; launch windows
occur for a given asterold occur at typical intervals of about 5 years. As a result. dozens of energeticaliy favorable asteroids would have to be discovere Usea of Carbonyl-Derived Ketals
yet another attractive feature of carbonyl processing
that the separated metals are ovallable as very pure is that the eeparated metals are avallable as very pure

powders, or in the gas phase as carbonyla. In the iatter came the metal can be deposited directly onto a heated mold or mandrel that causes the carbonyl gas to decompose on contact. Nickel "vaporforming," as the process is called, marketu ror precision nickel components previously supplifed by machining, electroplating, cauting, and other vapor deposition techniques (Meinel, 1985). Vaporformed nickel | produced by a division of Forbative Products co. has : |
| :--- |
| tensile strength of over $200,000 \mathrm{psi}$ |
| 1400 Mpa ): | surfaces of optlial quality can be produced directiy fiom

In perhape the moat demanding application tried to rockotu have bean vaporformed in an analagous process from Theniun carbonyl. Carbonyl deposition is also widely used iike razor blades. Another technique for production of thin tllas is laser chemical vapor doposition, where metal bean dwall tline and focius determine the fllimed thickinest. The space, this technique could produce lightwaight flims for
solar collectors, solar power satellite structures, and alectrical componenta.
 asteroldal oren, vaporforming of pure Fa as well as Fe-N1 as a high priority. Even if auch processes prove energy costs.
concluslons
The gaseous carbonyl proces offere aigniticant advantages in lunar and a pring the method to e practical level of developient for


 of the process an the hutile or space atation using actual meteorite samples: (4) evaluation of lunar and asteroidai
ores through space-based geochemical observations and
 autonatad processor in the selocted
observations could bagin with lunar survey miasions
degigned by Japan's NASDA far the mid-1990 E. The Sovieta




 based carbonyl extraction program.

Agosto. W.N. (2984) Electrostatic concentration of lunar
 Lunar and planetary Institute, Hounton. Van Nostrand.
Boldt (1967) The Ninninge Nickel. Van carlton, H.E.. and oxley, J.II. (1965). Klnetlcs of the Inst, Chem. J. 11, 79-84. (1967). Kinatice of the neterogeneoue decomposition of nickal tetracarbonyl.

 pp. 559-569. Lunar and Planetary Institute, Houston.
Garratt, A.p.. and Thompson, H. W. (1934a), The thermal decomposition and oxidation of nickel carbonyl. I.


Janar Thermochenical Tablee (1971). Second edition,
Hational grandard Roference Servica, U.S. Nationai
 Recovery of matallila iron from flotation tailings by
pneuaolytic transport I. Reduction by carbon monox ide

 and $\mathbf{C}$. Krop, da.). pp.129-134. American Institute o
Aeronautica and Aetronautice, Now York.
 carinesing with wnar and asteroldal Materlale. 88 . Faughnan and G. Marynlak, eds.), pp.150-159. American Mond, L. Hirtz, H., and Cowap, H.D. (1910). Liv. Some new oxiey. J.H. (1966). High-purity metals. in yapor

Rhee. C.5.. Kim, C.s.iilit K., and Rothfus, R.R. (1973). Recovary of metaliic iron from tlotation tallinge by
pneumalytic tranaport. II. Formation of iron pentacarbonyl from partiolily reduced iron in fixed bed.
Rny. Giche. Tech. 7, $730-735$. Robiax R.A. Heninguay, B.S.. and Fisher, J.R. (1978).
 and at higher temperaturas. W. S. Geological Suryey
Bulletin_lisia u.s. Governeent printing office, Shoemaker, E.M. (19a3). Asterold and conet bombardment of the Earth. Ann. Rey, of Earth and Planet, Sche 11,
 Tripatni, s.c., Ehrivastava, s.c., Mani, R.p., and Shrimal,
 Inorg, Chia, Acta 15, 249-290.
Tripathi, S.C., shrivastive, s.C., Mani, p. P., and Shrimal, A.K. (1976b). Advancea in platinum motal carbonyla and

whilams R.J.
 reduction procesa. In Lunar bages and apace activisies Lunar and pianetary inatitute, Houston.

## APPENDIX D

## THEORETICAL PREDICTION OF VOLATILEBEARING PHASES AND VOLATILE RESOURCES IN SOME CARBONACEOUS CHONDRITES


theoretical predictions of volatile bearing phases and volatile resources in some carbonaceous chondrites

jibamatra Ganguiy<br>Department $r$ Geosciences<br>Haiversity of icizona，Zicson，ذ̇z 2572l

Eurencra $\mathrm{K}_{\text {．}}$ ： $\operatorname{axena}$<br>2epartment が くeolog<br>Erookiyn Coliece，：＝cokivn，$\because \because$ ！ 1280

## Abstract

Caroonaceous cacnazites 三re uミuall！ belleved to be the $\because=1 m a r y$ constituents of near－Earth asteroios ano jnobos ino Diemos，and are eotential resources of suels wnich may be exploited for future planetary missions．In this work we have calculated the nature and abundances of the major volatile bearing and other phases，including the vapor phase，that snouid form in Cl and C2 type caroonaceous chondrites as functions of pressure ana cemperarure．The results sucgest irat talc，antigorite $=$ magnesite are the major volatile bearing pinases and are stable below $400^{\circ} \mathrm{C}$ at 1 sar in these cnoncritic compositions．Simulated teating oE a kilcoram of c2 choncrite at fixed sulk composition between 400 and $800^{\circ} \mathrm{C}$ at 1 Dar vielics adout 135 gm of volatile，wnich is ：nade primarily of $\mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2} \mathrm{O}, \mathrm{CH}_{4}, \mathrm{CO}$ anc co．The relative abundances of Finese volatile species change as functions ot temperature，and on a molar zasis，it？ becomes the most dominanc species aDove $550^{\circ} \mathrm{C}$ ．in contrast，Cl chondrites yield about 306 gm et volatile uncer the same condition，which consist almost completely of 60 wti $\mathrm{H}_{2} \mathrm{O}$ and 40 wts $\mathrm{CO}_{2}$ ．Freliminary kinetic considerations suggest that ģui－ librium dehydration of hyorous phyllosili－ cates should be attainavle witnin a Eew hours at $600^{\circ} \mathrm{C}$ ．These results provide the framework for further analyses of the $\because$ latile and economic resource petentiais of carbonaceous chondrites．

## Introduction

The near－Eartn asteroids are goten－ tial resources of volatiles which can de used as propellants and life supporting purposes for planetary missions．As emphasized by Lewis and Lewis（1），these asteroids are at times the nearest bodies to Earth，and many of them can bass between Earth and Moon．These authors have also shown that within any arditrary rhree－year period，tnere are roughly 300 and 90,000 launch opportunities to respec－ tiveiy kilometer and loo－meter sized asteroidal bodies as compared to 39 lunar launch wincows．These tacts and the fotentiai volatile resources make the asterolds important candidates Eor cetailed anaiyses tor supporting tuture zianetary missions．

Cost－effective or energy－etticient extraction of volatiles from the asterolds reculre knowiedge of the nature and modal Copyright ci 1989 by SSI and AIAt． All rights reserved．
souncances of the constatuenc minerals in
 ：Oraily zounc．There nss zeen several stuoies on reflectance syectroscopy ot near－Earch astercios to craracterize the nature of tho volatile seariny minerals （2，3）．$\because$ hile these stuales $=$ port ansorp－ tion band near $3-m$ suggesting $\ddot{\text { besence }}$ ot bydrous Ghyllosilicates，－ore irecise characterizations were fudvocal．An obvicus alternative approach to the reso－ lution of tie jroslem ：s to examine cirectly sne asteroical maceriais．

The spectrai and density cnaracter－ istics strongly sưgest chat $\equiv$ sionificant sract：on of the near－Earch asternias are rade ot carionaceous snonarites（l，t）． The most voiatile＝icn ot trose meteorites三re wnat $\equiv$ re connoni $\because$ bnown $\# 5 C l$ or（CI）
 grain size of the voletily gearing phages まre oteen too small（！1）0 te if00 $\therefore$ ）（5）to permit identification under ostical micro－ scope，anc are best onserven uncer high essolution transmissun flectron micro－
 have racently gresentea a sumary ot vola－ ：ile bearing phases toencitien in the carbonacous chondrites．

The 玉eimary objective of chis work is ：o carry uut theorecical aicuiations to predict modal anuncances and compositions ＂f tre maior mineral rasos，jlong with the abunuance anc compostition ot tin co－ existing vạor finase，that ：ould jevelno in the aulk rompositions ：E $C l$ and $\mathrm{C}_{2}$ znoncrites as Eunctions az Eressure and temperature．the rusults andid rovice the Eramework Eor englnetering gesiuns tor the extraction of volarile conpontents from asteroids as well as pnobos and Deimos． the two small natural satellites of ilars， which are also likely to be made of car－ bonaceous chondrites（1）．

## Theoretical Method

## Principles

Accoraing to Duncm＇s rheorem in ：lassical thermodynamics $: \pi, \bar{l}$ ，the equi－ ibrium stace or a closer $\equiv \because \mathrm{stem}$ i i．e．，a system of fixed composicion and mass）is compietely determined it any two variables are fixed regardiess ot wherher these are intensive，extensive，or a combination of both．Ganculy and Saxena（7）have recent－ －$\because$ reviewea sne varlous mernods by which one may carry out the actual computation ot the rauilibrium assemolages．The

Table 1 Bulk chemical compositions of Cl and C 2 carbọnaceous chondrites

|  |  |  |
| :--- | ---: | ---: |
|  | Cl | C 2 |
| Si | 10.40 | 12.96 |
| Ti | 0.04 | 0.06 |
| Al | 0.84 | 1.17 |
| Cr | 0.23 | 0.29 |
| Fe | 18.67 | 21.56 |
| Mn | 0.17 | 0.16 |
| Mg | 9.60 | 1.72 |
| Ca | 1.01 | 0.42 |
| Na | 0.55 | 0.06 |
| K | 0.05 | 0.13 |
| p | 0.14 | 1.25 |
| Ni | 1.03 | 0.06 |
| CO | 0.05 | 3.38 |
| S | 5.92 | 1.42 |
| H | 2.08 | 2.30 |
| C | 3.61 | 41.74 |
| O | 45.61 |  |

method used in this study obtains the compositions and abundances of the equilibrium phase assemblages by minimizing the Gibbs Eree Energy (G) DE the system at fixed P-T conditions. The minimization is constrained to conserve the various elemental masses of the system through the method of Lagrangian multipliers ( 7 ). Because of the extremely small grain size of the phyllosilicates observed in carmonaceous chondrites, one should consider the effects of surtace iree eneroy on the formation of these Enases. As a first auproximation, we have, however, ignored this effect. Thereiore, the actual equilibrium temperatures of volatile bearing phases could be lower than those predicted by our calculations.

## System, Phases and Data Base

Table 1 shows the bulk compositions of Cl and C 2 carbonaceous chondrites. These compositions are based on analyses of a number of tragments or orgueil and

Table 2 Phases in the system Mg-Fe-Si-C-H-O-S consicered in this work

The sources of thermochemical data are shown by reference numbers within parentheses. The Heat of formation of the ferent members of the nydrous phyllosilicates are derived in this work.

Anhydrous Silicates and Oxides

| Olivine | $(\mathrm{Mg}, \mathrm{Fe})_{2} \mathrm{SiO}_{4}$ | $(3)$ |
| :--- | :--- | :--- |
| Orthopyroxene | $(\mathrm{Mg}, \mathrm{Fe}) \mathrm{SiO}_{3}$ | $(8)$ |
| Periclase | $(\mathrm{Mg}, \mathrm{Fe}) \mathrm{O}$ | $(23)$ |
| Ouartz | $\mathrm{SiO}_{2}$ | $(17)$ |
| Cristobalite | $\mathrm{SiO}_{2}$ | $(17)$ |
| Hematite | $\mathrm{Fe}_{2} \mathrm{O}_{3}$ | $(23)$ |
| Magnetite | $\mathrm{Ee}_{3} \mathrm{O}_{4}$ | $(23)$ |

Hydrous and Carbonate Phases


Talc
Antigorite
Chrysotile
Brucite
Magnesite
$(\mathrm{Mg}, \mathrm{Fe})_{7} \mathrm{Sig}_{2} \mathrm{O}_{2}(\mathrm{OH})_{2}$
$(\mathrm{Mg}, \mathrm{Fe})_{3}=\mathrm{S}_{4} \mathrm{O}_{10}(\mathrm{OH})$
$(\mathrm{Mg}, \mathrm{Fe})_{48} \mathrm{Si}_{34 \mathrm{O}_{85}(\mathrm{OH})_{52}}$
$(\mathrm{Mg}, \mathrm{Fe})_{3} \mathrm{Si}_{2} \mathrm{O}_{5}(\mathrm{OH})_{4}$
$(\mathrm{Mg}, \mathrm{Fe})(\mathrm{OH})_{2}$
$(\mathrm{Mg}, \mathrm{Fe}) \mathrm{CO}_{3}$
fes
$\mathrm{FeS}_{2}$
Fe
5
C
$\mathrm{C}-\mathrm{O}-\mathrm{H}=\mathrm{S}$
(8)
$(17,24)$
(17,25)
Sulfides and Elements

| Troilite | fes | $(17)$ |
| :--- | :--- | :--- |
| Pyrite | $\mathrm{FeS}_{2}$ | $(17)$ |
| Iron | Fe | $(26)$ |
| Sulfur | S | $(17)$ |
| Graphite | C | $(17)$ |
| yapor phase | $\mathrm{C}-\mathrm{O}-\mathrm{Hi=S}$ | $(15.16,17)$ |

Species: $\mathrm{H}_{2} \mathrm{O}, \mathrm{CO}_{2}, \mathrm{CH}_{4}, \mathrm{CO}, \mathrm{O}_{2}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{~S}_{2}, \mathrm{SO}, \mathrm{COS}$

## D-4

Aurchison meteorites, respectively, ano are summatized in Dodd (22). It can be easily seen ram this taible that the subsystem Moffe-si-(C-H-O-S (:HfCHOS) constitutes almost ybs by welunt of the bulk compositions of Cl and Cl chonarites. in srcer to somewnat simplify the computational problem, we have confined the $G$ Ginimization $\quad$ alcuiation $\mathrm{t} \cdot \mathrm{o}$ this subsystem, but evidently the phases whose :umpositions form outsice ot this subsystem cannot be major constituents af these chonarites.

Table 2 shows the list of phases that we have consiuered as possible cevstallizing phases within che above subsystem along with the sources of the chermochemical data. The. choice of these phases have been guided by the puolisined reports of the mineralojy of carbonaceous chondrites whose compositions lie within the system MFCHOS (e.g., Zolensky and McSween (5)). The selection of thermochemical data in the system Mg-Si-O-H is based on the critical analysis of Chatterjee $(8,11)$ tor consistency with both calorimetric and experimentally determined phase equilibrium measurements. These data are similar to those of Berman (?). However, unlike those in German, the data are also consistent with high $P-T$ experimental data involving distribution of Fe and Mg among coexisting silicates.

The heat capacities ( $C_{5}$ ) and entropies ( $S^{\text {D }}$ ) of the phases, if not available in any of the recent systematizations of self-consistent data set, are estimated by stoichiometric summation of the properties of oxides and structuraily analogous compounds, as discussed in a number of publications $(13,14)$.

There are no thermochemical data for the fe-end members of the phyllosilicates listed in Table 2 . The enthalpies of these phases are estimated according to the known relative properties of Fe - and My-end members of biotite, which is also a phyllosilicate. The data derived by Chatterjee (3) and pobie pand femingway (10) Sor the Mg- and $\mathrm{F} \mathrm{e}^{2+}$-end members (phlogopite and annite, cespectively) yield an enthalpy difference of -359.566 KJ per mole of divalent cation at 1 bar, 298 K . We have used these values to estimate the enthalpies of formation from elements of fe-end members of phyllosilicates at 1 bar. 298 K from the available data for the Mg-end memoers. The results are as follows ( $\mathrm{KJ} / \mathrm{mol}$ of Fe). Fe-talc: -1606.80: Fe-antigorite: -1127.53 and Fechrysotile: -i094.87. The corresponding values of the free energy of formation from elements ( $\Delta G_{f}^{\circ}$ ) for Fe-talc and Feantigorite at 1 bàr, $29 \% \mathrm{~K}$ are -4477.18 and $-4784.0 \mathrm{KJ} / \mathrm{mol}$ of $\mathrm{Fe}^{2+}$, sespectively.

The validity of the estimated thermochemical properties of the $F e-e n d$ members of the phyllosilicates may be tested as follows. The Fe-end memoers of talc and
antigorite are unstable. Instead, the stable phases are closeiy analogous compounds, namely, minnesotite, which has a stoichiometry at Fe275i36ig6(UH) 26 as
 Fe-taic, and yreenaiite witn a stoichiometry ef re48डi $22^{\circ} \mathrm{Co}(\mathrm{OH})_{54}$ compared to Fe4gSi?40j(OH) 52 EOF Fe-anticorite. Anovitz at. (!2) have recently decermined $-\therefore$ of minnesotite and greenalite from そ̌ase ecuilibrium cata. Their results, $\therefore \mathrm{G}_{\mathrm{f}}($ minnesotite) $=-4577.73 \mathrm{KJ}$ and $-\hat{B}$ (.treenalite) $=-4799.50 \mathrm{~kJ}$, differ in the =ight direction from the corresponding values of fe-taic and feanticorite, considering the relative stabilities of the phases.

The stereochemical environments of divalent astions in biotite are quite similar to those in talc, both being 2:1 (TOT) layer silicates, and partly similar to those in antigorite, winich is an l:l (TU) layer silicate (28). Thus, these phyllosilicates siould have similar differences between the enthalpies of formation of the 5 fe- and Ag -end mempers. Further, since on the Dasis of observaEional data, the predicted compositions of the mineral pnases in carbonaceous chonarices are expected to be Mg-rich, the effects of errors in the se-end member thermochemical groperties and solid solution model will be relatively small. This can be easily uncerstood by considering the form of $G-X$ curve of a stable solution and evaluating the effects of errors in above properties near Mg-terminal segment.

The fhermodynamic mixing properties of the $\mathrm{Fe}^{\tilde{L}^{+}}$- and Mg-end member components of the annydrous silicates are taken from the self-consistent summary of Chatterjee (8), while those of the pinyllosilicates are assumec to be icieal for the lack of any data. The latter assumption is likely to be approximately valid at $T \geq 600^{\circ} \mathrm{C}$, since at these conditions biotite solid solution is found to behave approximately ideally (7). At lower temperature, the phyllosilicates may deviate from ideal solution venavior, but jerhaps not too dissimilariy to significancly atfect their relative stabilities. Magnesite is also assumed to be an ideal solution of Fe-Mg components. As emphasized by Ganguly and Saxena (7), the computed dehydration conditions are not very sensitive to errors in activity-composition relations since the devolatilization equilibria are characterized by large enthalpy changes. The iron oxides and sulfides are considered to be stoicniometric phases since the solid solutions of Mg are around a few percent at the temperatures of interest.

The fluid properties are taken from Saxena and Fei $(15,16)$ and Robie et al. (17). The "corresponding state method" of estimating $P-V-T$ reiation, as discussed by these authors, is extended to include the sulfur species. For mixing data, we have assumed that $\mathrm{H}_{2} \mathrm{~S}$ behave as $\mathrm{H}_{2} \mathrm{O}, \mathrm{S}_{2}$ as

## D-5



Eig. Calculated mocial abundances of minerals per kilogram of rock in (a) Cl and (b) C2 carDonaceous chondritic bulk compositions as functions of temperature at 2 kb . The steps in the caiculations are shown by symools.

```
i, and SO}2\mathrm{ and COS as CO2, anc used the
equivalent binary interaction jaramecers
from Saxena and Fei (i5).
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## Results

At 1 bar, the Eree encegy minimization calculations do not yield any volarile oearing phase at $T \geq 400^{\circ} \mathrm{C}$. At the oresent state of the thermochemicai tata, - co not selieve that vur こもiculaticns
are reliable at lower temperatures. Inceed, we find results at lower temperatures winich do not seem to tollow the systematics ot the results obtained at ingher temperatures. Thus, we have calculated the equilibrium pnase assemolaqes at 3 pressure of 2 kD so that the volatile bearing phases appear at higiner temperatures. This procedure at loast permits recognition of the major volatile bearing ziases. Some ot tnese pilases may de rem

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Eig. 2 Calculaced compositions of the silicate phases in $C l$ and C2 carDonaceous chondrites as functions of temperature at 2 kb .
placed by more stable assemolages at lower temperature, but should reappear during heating experiment. The results, wich are illustrated in Figure 1 , show that the frimary volatile bearing phases in the Cl and $C 2$ bulk compositions are talc, antigorite $\pm$ inagnesite. Talc is stable to around $650^{\circ} \mathrm{C}$ at 2 KD , and dehvdrates to orthopyroxene (OPX) at higner temperature according to $\mathrm{Ic}-\mathrm{DL}=5 \mathrm{OPx}+\mathrm{H}_{2} \mathrm{O}$. Anticorite and magnesite crystallize at $T$ く $550^{\circ} \mathrm{C}$, but magnesite is aosent in C2 bulk composition at $T \geqslant 400^{\circ} \mathrm{C}$. $\because e \mathrm{~S}$ is a stable эnase ar all temperatures investigated in shis work. Ne, nowever, did not consicer the formation of sulfate or pyrrhotite. sagnetite becomes a stable phase at ? $\leq 500^{\circ} \mathrm{C}$. Elemental sulfur founa in Cl shondrite is invariably associated with Fyrfhotite (Fel-xs) (5). This suggests decomposition of troilite (FeS) to pyrrhotite and sulfur.

Figure 2 shows the compositions of the ferromagnesian phases as function of temperature at 2 Kb for the Cl and C 2 bulk comoositions. Calculations at l bar also yield similar compositions. The observed compositions of these phases in the carbonaceous chondrites vary widely in Fe/mg ratio. One way to achieve this diverse Ee/Mg ratio is by aqueous alteration which seems to be a characteristic of the carbonaceous choncrites. F'e fractionates very strongly into an aqueous phase relative to the silicates (18). Thus, varying degrees of equilibration with an aqueous shase could lead to a spectrum of $\mathrm{Fe} / \mathrm{Mg}$ compositions of the ferromagnesian silif
cates. Aqueous aiteration may not be the sole reason, but is likely to be an important contributing factor in the development of variable fe/mg ratio of the ferromagnesian silicates in carbonaceous chondrites.

The abundances of volatile species in equilibtium with the solids per kilogram of total mass of $C 2$ chondrites are illustrated in Eigure 3 . Figures $3 a$ and $3 b$ illustrate the molar and mass abundances. cespectively, as functions of cemperature at 1 bar. It should be noted that the total mass of the volatiles do not change above 400 C , which means that under equilibrium condition $C 2$ chondritic material will completely devolatize it heated above $400^{\circ} \mathrm{C}$. The total yield of the volatile is about 1 is of the initial mass of C2 chondrites. The change in the abundance of various species above $400^{\circ} \mathrm{C}$ is due to homogeneous reactions within the fluid phase. Above 550 C , nyorogen has the highest molar concentration in the vapor phase. Hydrogen is a very good propellant and reducing agent which may thus be preferentiaily extracted by heating the C 2 chondricic material to $T>550^{\circ} \mathrm{C}$.

In contrast to the C 2 chondrites, the volgtiles given off by $C l$ material above 400 C consist essentially of $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}$ at 1 bar pressure. Per kilogram of mate rial, the cotal yield of volatile is about 306 grams of which nearly 60 wtit is $\mathrm{H}_{2} \mathrm{O}$.

The above results are subject to consideraple uncertainties owing to the


Fig. 3 Calculated equilibrium (a) molar and (b) mass abundances of the volatile species per kilogram of $C 2$ chondritic material.
approximate nature of the thermochemical properties of the phyllosilicate solid solutions, and also since we have ignored the effects of surface free energy on the formation of extremely fine grained crystals. Further, carbonaceous chondrites of any given type do not have homogeneous compositions, but instead probably represent agglomeration of materials formed at cifferent conditions at different parts of the solar system. However, these calculations are still useful in oroviding an cea of che relative stabilities, as well
as upper stabilities of the volatile bearing phases and their average abundance. It is interesting to note that recent reflectance spectroscopic studies of carbonaceous chondrites seem to corroborate the predictions made above as to the nature of the most abundant hydrous phases (Gaffey, pers. comm.).

## Kinetics of Devolatilization

The ?quilibrium calculations presented above provide a framework for the


Fig. 4 Dehyciration of talc as functions of time, temperature and extent of overstepping above the equilibrium dehydration boundary at $l \mathrm{~Kb}$. Volume fraction is that of talc remaining after reaction. Experimental data points, shown by asterisks, are from Greenwood (19).


Eig. 5 Equilibrium relations of talc, antigorite and orucite along with other minerals in the system MgO-SiO $\mathbf{N H}_{2} \mathrm{O}$. Peproduced from Evans and Guggenneim (21).
evaluation of the volatile as well as some mineralogical resource potential of Cl and C2 carbonaceous chondrites. The actual extraction of volatiles as a function of temperature and heating rate, however, depends on the $k$ inetics of the devolatilization process. For kinetic analysis, it is essential to identify the minerals in which the volatiles are most likely to be structurally bound. The above results suggest that talc, antigorite and magnesite are likely to be the major volatile bearing phases in carbonaceous chondrites.

Except for pure Mg-talc, there are no kinetic data for the other volatile bearing phases. The dehydration kinetics of talc was determined by Greenwood (19). At a given temperature, the rate of reaction depends on the rate constant, $K$, and the extent of departure from the equilitioum boundary. This is expressed in transition state theory $\{20)$ according to the relation Rate $=K^{+}(1-\exp (n \Delta G / R T))$, where $n$ is a constant, commonly assumed to be unity, and $A G$ is the Gibbs free energy of the reaction at the $P, T$ condition of interest. Figure 4, which is constructed from Greenwood's experimental data, illustrates the dehydration kinetics of talc as functions of time, temperature and extent of overstepping ( $\Delta T$ ) above the equilibrium dehydration boundary at $l \mathrm{~kb}$. It is evident from this figure that essentially complete cehydration of talc can be achieved within

6 hours at about $160^{\circ} \mathrm{C}$ above the equilib－ rium boundary．

The stability fields of the pure $\mathrm{Mg}-$ end members of various phyllosilicates of interest in this study are summarized for the condition of $P_{\text {total }}={ }^{P_{H 2 O}}$ in Figure 5．which is reprocuced from Evans and Guggenheim（21）．According to our re－ sults，talc and other phyllgsilicates com－ pletely dehydrate at $\geq 400^{\circ} \mathrm{C}$ at $l$ bar in C1 and C2 bulk compositions．This is com－ patible with the phase relations shown in Figure 5 ．Thus，based on the results shown in figure 4 ，one would anticipate that essentially complete dehydration of all phyllosilicates in Cl and C 2 chondrit－ ic material is likely to be achieved in a matter of a few hours at $T \geq 600^{\circ} \mathrm{C}$ ． Detailed studies of the devolatilization kinetics of both phyllosilicates and car－ bonates as functions of temperature，Eluid composition，and grain size are currently under way to evaluate the practical limi－ tations of the extraction of volatiles from carbonaceous chondritic materials．

## Acknowledgments

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## References

1．Lewis，J．S．，ana Lewis，R．A．（1987） Space resources：Breaking the bonds of Earth．Columbia University Press， New York．

2．Jones，T．，Lebofsky，L．，and Lewis． J．S．（1989）Asteroidal $\mathrm{H}_{2} \mathrm{O}$ and the hydration state of terrestrial raw materials．EOS Trans．Amer．Geophys． Union 70， 379 ．

3．Gaftey，M．J．，and McCord，T．B．（1979） Mineralogical and petrological char－ acterizations of asteroid surface materials，in Gehrels，T．（ed．）Aster－ oids，ep．588－723，University of Acizona，Tucson．

4．Lewis，J．s．，and Prinn，R．G．（1984） planers and their atmospheres． Academic press．

5．2olensky，M．，and McSween，H．S．（1988） Aqueous alteration，in Kerriage，J．$火$ ．， and Matnews，i．s．（eds．）Meteorites
and the early solar system，University of Arizona press，Tucson．

5．Prigogine，I．，and Defay，R．（1954） Chemical thermodynamics．Longman， London．

7．Ganguly，J．，and Saxena，S．K．（1987） Mixtures and minerai reactions． Springer－Verlag．

3．Chatterjee，N．（1989）An internally consistent thermodynamic data base on minerals．Ph．D．thesis，City Univers－ ity of New York．

9．Berman，R．G．（1988）internally con－ －sistent thermodynamic iata for min－ erals in the system $\mathrm{Na}_{2} \mathrm{O}-\mathrm{K}_{2}(1-\mathrm{CaO}-1 \mathrm{AO}-$ $\mathrm{FeO}-\mathrm{Fe}_{2} \mathrm{O}_{3}-\mathrm{Al}_{2} \mathrm{O}_{3}-\mathrm{SiO}_{2}-\mathrm{TiO} 2-\mathrm{H}_{2} \mathrm{O}-\mathrm{CO}_{2}$ ．J． Petrology 29．445－552．

10．Robie，R．A．，and demingway，B．S． （1984）Heat capacities and entropies of phlogopite and paragonite between 5 and 900 K and estimates ot enthalpies and Gibbs free energy of formation． Amer．Mineralogist 67，858－868．
il．Chatterjee，$\because$ ．（1987）Evaluaton of thermochemical data on re－Mg olivine， otchoyyroxene，spinei and Ca－Fe－Mg－Al garnet．Geochim．Cosmochim．Acta 51, 2515－2525．

12．Anovitz，L．M．，Essene，E．，and Heming－ way，S．S．（1989）Self－consistent thermodynamic data tor the system fe－ Si－C－O－H：Applications to metamor－ phosed banded tron formations and iron－rich blueschists．Geochim． Cosmochim．Acta，in submission．
：3．Lewis，G．N．，and Randall，M．（1961） Thermodynamics．McGraw－Hill．
！t．Helgeson，H．C．，Delaney，J．m．， Vesbict，H．W．．ana sira，D．K．（1978） Summary and critique $J f$ the thermoay－ namı proverties of rock－forminu minerals．mimer．J．Sci．278A，1－229．

15．Saxena，．K．，and t゚ei，そ．（1988）fluid mixtures in the $\mathrm{C}-\mathrm{H}-\mathrm{U}$ system ar high pressure and temperature．reochim． Cosmochim．Acta 52．505－512．

16．Saxena，S．K．，ミna Fei，Y．（1987）High oressure ana nigh tomperature fluia tucuacities．Geochim．Cosmocnim．Acta 51．733－791．
：7．Robie．R．A．，Hemıneway，s．S．，and Eisher，J．R．（19？3）Fhermodynamir \＃roperties of minesals and related substances at $298 .!5: i$ and 1 bar $\left(10^{2}\right.$ अascals）bressury and higher tempera－ tures．戶．S．Geol．Survey kull．i i S2．

18．Eugster，H．P．，and［lton，E．S．（1983） Mg－fe tractionation ：$n$ metamorpnic environments，in saxena，s．k．（en．）

Kinetics and equilibrium in mineral ractions. Springer-Verlag.

ị. Greonwood, H.J. (1963) The synthesis and stability of anthophyllite. J. petrology 4, 317-351.
:O. Easaga, A.C. (1981) Transition state tineory, in Lasaya, A.C., and Kirkpatrick, R.J. (eds.) kinetics of geochemical processes, Reviews in ilineralogy 8, 135-169.
21. Evans, S.W., and Guggenheim, S. (1998) -alc, pyrophyllite, and relaced minerals, in Bailey; S.W. (ed.) Hydrous phyllosilicates (exclusive of micas), Reviews in Mineralogy 19, 225-294.
22. Dodd, R.T. (1981) Meteorites: A jetrological-chemical synthesis. Cambridge University Press.
23. tei. Y., and Saxena, S.K. (1986) A therinochemi=al data base for phase equilibrium in the system Fe-My-Si-O at high yressure and temperature. Phys. Chem. Minerals 13, 311-324.
24. Babushkin, V.I., Matreyev, G.M. Mohedlov-Petrossyan, O.P. (1985) Thermodynamics of silicates. Springerverlag.
25. Barin, I., and Knacke, O. (1978) Thermochemical properties of inorganic suustances. springer-verlag.
26. Gustafsson, P. (1984) A thermodynamic evaluation of fe-C system. TRITA-MAC, Royal Inst. of Tech., Stockholm, Sweden.
27. Anovitz, L.M., Essene, E.J., Hemingway, B.S., Komada, N.L., and Westrum, E.E. (1988) The heat capacities of grunerite and deerite: phase equilibria in the system $\mathrm{Fe}-\mathrm{Si}-\mathrm{C}-\mathrm{O}-\mathrm{H}$ and implications for the metamorphism of banded iron formations. EOS Trans. Amer. Geophys. Union $69,515$.
28. Bailey, S.W. (1988) Introduction, in Bailey, S.W. (ed.) Hydrous phyllosilicates (exclusive of micas), Reviews in Mineralogy $19,1-8$.

## APPENDIX E

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

## N91-25※48

## LUNAR OXYGEN AND METAL FOR USE IN

 NEAR-EARTH SPACE: MAGMA ELECTROLYSISRussell O. Colon and Larry A. Gaskin ${ }^{1}$


#### 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 oi many reagents common on the earth. and presence of very non-traditionai "ores" suggest that a unique and nontraditional process for extracting materials from the ores may prove the most practical. With this in mind. we have begun an investigation of unfixed silicate electrolysis as a method for extracting oxygen. Fe. and Si from lunar regolith. The advantages of the process include simplicity oi 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, :ow enough io 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 rise Heiken et ai., 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, for lunar sources. the

[^11]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 transter 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 energyexpensive 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 wiil 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 soii 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 ( $1,200-1,600^{\circ} \mathrm{C}$ ) 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:

$$
\begin{align*}
& \mathrm{Fe}^{2+}+2 \mathrm{e}^{-}=\mathrm{Fe}^{\circ}  \tag{1}\\
& \mathrm{Si}(\mathrm{IV})+4 \mathrm{e}^{-}=\mathrm{Si}^{\circ} \tag{2}
\end{align*}
$$

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

$$
\begin{equation*}
\mathrm{O}_{2}+4 \mathrm{e}^{-}=2 \mathrm{O}^{2-} \tag{3}
\end{equation*}
$$

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 $\mathrm{Cr}, \mathrm{Ti}, \mathrm{Mn}$, 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 $\mathrm{O}^{2-}$ concentration and slow kinetics of formation of $\mathrm{O}^{2-}$ 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 $\mathrm{Fe}^{2+}$.

$$
\begin{equation*}
\mathrm{Fe}^{2+}=\mathrm{Fe}^{3+}+\mathrm{e}^{-} \tag{4}
\end{equation*}
$$

Other competing reactions at the anode inciude 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 $\mathrm{O}_{2}$ produced $/ 4 \cdot$ moles electrons passed through the meit) depends primarily on the concentration of $\mathrm{Fe}^{2+}$ cations. The dependence of oxygen production efficiency on $\mathrm{Fe}^{2+}$ concentration can be expressed as $\% \mathrm{O}_{2} /\left(100-\%_{2}\right) \approx 0.049 / \mathrm{X}_{\mathrm{Fe}}$, where $\% \mathrm{O}_{2}$ is the oxygen production efficiency in percent and $\mathrm{X}_{\mathrm{FeO}}$ 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 meits 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 $E_{e}-E_{3}-\eta_{c}-\eta_{a}-I\left(R_{\text {cell }}\right)$, where $E_{e}-E_{a}$ is the potential required to drive
the reaction(s) and is a function of the cation reduced. ( $\left|E_{c}-E_{a}\right|$ increases in the order $\mathrm{Fe}<\mathrm{Si}, \mathrm{Ti}<\mathrm{Mg}, \mathrm{Al}<\mathrm{Ca}$ ) and the concentrations of the cations in the melt. The quantity $-\eta_{c}-\eta_{\mathrm{a}}$ 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). $\mathrm{R}_{\text {cell }}$ 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 $\kappa$ is the melt conductivity. This expression illustrates the dependence of power on both cell configuration and resistivity of the molten feedstock. Not unexpectedly, $\kappa$ is found to increase as the average ionic mobility of the meit increases. That is, $\kappa$ increases systematically as mobile cations such as $\mathrm{Fe}, \mathrm{Mg}$, 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 $E_{e}-E_{\mathrm{a}}$ ( -0.7 to -1.3 V ), Fe is reduced at the cathode. As Fe is removed from the silicate meit, oxygen production efficiency increases and conductivity decreases, with a combined effect of increasing power requirements for oxygen production. Then, once Fe is nearly depleted, $\mathrm{E}_{2}-\mathrm{E}_{3}$ is increased to more negative potentials ( $<-1.4 \mathrm{~V}$ ) 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 , is removed from the melt, resulting in a sharp drop in power required to produce oxygen. Theoretically, $\mathrm{Mg}, \mathrm{Al}$, 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 $\left(1200-1600^{\circ} \mathrm{C}\right)$, 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 difficuities, 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 cheaperin 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 meiting 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 speciaiized 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 $15.6 \mathrm{MWh} / \mathrm{MT}$ oxygen. The value reported by Haskin et al (1990) is somewhat less at $13 \mathrm{MWh} / \mathrm{MT}$ 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 $5 \mathrm{MWh} / \mathrm{MT}$ 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 $3-10 \mathrm{MT}$ 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 $\mathrm{Fe}-\mathrm{Si}-\mathrm{Ti}-\mathrm{Cr}$ 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 materiai, 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 meit, increasing power requirements, and the resistivity, which increases with increasing $\mathrm{SiO}_{2}$ and $\mathrm{Al}_{2} \mathrm{O}_{3}$ 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 meit, thus making the process neariy 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 $\mathrm{Si}, \mathrm{Fe}$, or $\mathrm{Fe}-\mathrm{Si}$ alloys containing $0.2-1 \% \mathrm{Ti}$ 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 meit temperatures.) The mineral spinel precipitates from the residual melt at sufficiently low temperatures or with sufficient removal of $\mathrm{SiO}_{2}$. This material varies in composition from $\mathrm{Fe}-\mathrm{Cr}$ rich spinel to $\mathrm{Mg}-\mathrm{Al}$ 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 $\mathrm{CaO}-\mathrm{MgO}$ 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 neariy 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 meits below $1,000^{\circ} \mathrm{C}$ 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 $\mathrm{Si}-\mathrm{Fe}$ metal, $\mathrm{Fe}-\mathrm{Si}$ alloys might serve as the cathode material (Haskin, et al., 1990). Similarly, the presence of spinel $\left(\mathrm{MgAl}_{2} \mathrm{O}_{4}\right)$ 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 meit 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 $\mathrm{Si} / \mathrm{Fe}$ 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.

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## 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), 435443.

Haskin, L. A. (1990). "Water and cheese from the lunar desert: Abundances and accessibility of $\mathrm{H}, \mathrm{N}$, 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 $\mathrm{CaO} \cdot \mathrm{MgO} \cdot \mathrm{xSiO}_{2} . "$ Geochim. Cosmochim. Acta 49, 1897-1908.

## APPENDIX F

## LUNAR RESOURCES-TOWARD LIVING OFF THE LUNAR LAND

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LUNAR RESOURCES -- TOWARD LIVING OFF IEEE LUNAR LAND

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Space is now an accessible part of the human environment. and it behooves us to learn in the broadest sense what's out there. how it got there. and how it works. In the narrower context of modes oi exploration that place men and women in space. we should also barn how to keep ourselves healthy and safe, how to carry out activities in space. and how io use what we find there. Whatever the reasons may be for our activities in space, we should learn through those activities what the practical importance of space may be.

Why the Moon?

We can particularly improve our assessment of the value of space for human activities through
 indigenous materials. The nearest body appropriate for this is the Moon. which has properties and resources suitable for such exploration. The Moon. like low-Earth orbit. geostationary orbit, and lunar orbit, is part of near-Earth space, part of the Earth-orioit environment. Because it is close. in the near term it is the easiest and safest body outside of Earth to use. We know more about it than we know about any other planet except Earth. A. Moonoase will build on the experience of the Apollo missions. Even with these advantages of proximity and our knowledge of its surface, the Moon still offers substantial technological challenge in engineering, mining, manufacturing, construction, and life support.

Esonomics will witimateiv die:ate where and what kincs of materiai we will iuse in space bur, if we take a conservarive approach. we might zonciucie that for near-term use in aear-Earth space there are oniy roo choices. Coe is the Earth and the other is the Moon. Because the Moon is the most likely ooject :or testing and developing ine iirst iesinoiogies yor sustaining human presence on another pianet. it is aiso the most likely economical near-ierm suppiier of extraterrestrial materiai for use in near-Earth space. In the longer run. we may find it economical to use fiar more distant bodies such as near-Earth asteroids or Phobos to supply materiais to near-Earin space (e.g., Lきwis and Lewis. 1987). As we do nor know what specific materiais any of these codies has to ofier or winat the gnysicai states of their suriaces are, we cannot readily design technoiogies to use on inem: we theretore assume that their use is deades in the furure.

The Earth as a source for materiais to use in space has the advantage of weil developed recnnoiogies and manuracturing eapabiities. It has the disaduantage of reiativety high gravity and a consequent. unavoidable penalty in energy for lifting materiais from its suriace into orbit. The Moon has the advantage of intermediate gravity. low enough to enhance the
 use in separating froducts from residues. Transport of lunar material :o :ow-Earth orbit is particuiariy artractive if aerobraking suppiants rocket energy for achieving that oricit. Whatever the acrual cost of using a lunar materiais may be. provided they do not require extensive crew time to produce. the largest part of that cost is for hauling the lunar factory from Earth to the Moon (e.g., Simon. 1985). Forseenble rechnologies that would reduce the cost of transporting materials from Earth. 2ven to low-Earth oribir. wouid almost equally reduce the cost of operations on the lunar suriace.

Technoiogicaily, the Moon is underdeveloped. Earth tecinnologies cannor readily be transpianted to the iunar suriace because conditions and starting materials there are not those found or used

On Earth. The Moon aiso remains iargeiy underexpiorec. It is underexpiored ghysicaily, so that we have no satisiactory assessment of the range oi materiais it has to orifer. It is underexplored conceptually, in that we have not devoted enough eifort or funds to learn how we might make use of what we already know is there. Slany uses and technologies have been proposed, but Sew have been tested and none has been fuily devetoded. The lead time tor research and development is ten to fifteen years ior the simplest proposed technologies. and we need serious iaboratory work on them now if we are to test them. let alone hode :o use them, at the proposed lunar outpost.

Lunar Resources and Suriace Conditions

So, what is abundant on the Moon. and how might we use it? Here, we take a conservative view and acceot as resources oniy those materials we know itom tooilo experience to be sommon and present in such targe quantities that we wouid not require turther on-surface expioration to verify their existence as ore bodies. Abundant materiais in the lunar highlands are breceias (rocks that consist of fragments of eariier rocks. produced on the Moon by the
 unconsolidated. Fulverized products of the ctatering impacts. in the ithar maria, prevalent mareriais are basaitic lavas and soiis. and there may be substantai deposits or pyroctastic glasses (lunar volcanic ash). (The lavas and pyrociastic deposits would require on-suriace verification as ore bodies because: thicknesses and continuity of lavas with speciric characteristics, e.g., high proportions oi iimenite. would need to be demonstrated and thicknesses of pyroclastic deposits would need to be determined.)

In addition to these materiai resources, the lunar suriace offers intermediare gravity, high vacuum. and dependable sunigigt (half the time). It also orfers exrreme temperatures ( $120^{\circ} \mathrm{C}$ in
the sun. - : $70{ }^{\circ} \mathrm{C}$ in the shadel, no amosphere to transier heat or scatter tignt. ciinging dust. 3nd two-week-long days and nigits.

The most likely material for initial use is lunar soii. The principai chemicai constituents of the soils (e.g., Haskin and Warren. 1990) are oxygen (acout $45 \%$ c $\because$ wt.), silicon (abour 21\%), aluminum (about $13 \%$ in highland soiis. $5 \%$ in mare sois). calcium (in most soils $8-10 \%$ ), iron (some $15 \%$ in mare soils. $6 \%$ in highland soiisi, and magnesium labout $5 \%$ ), plus some sodium and. in some mare soiis. significant titanium (up to about $6 \%$ ). Of course, ail of the chemical elements are present in the soiis. but most are present in minor or trace acncentrations. There may be ores for some of the minor or trace eiements: cerminiy, Extensive amounts of chemical separation took piace. as incicared by smail. specialized iragments in the lunar sample collections. However. cecause the Moon lacks internal water. ores oi most types we find on Earth are uniikely to be found there.

## Guidelines for Eariy Lunar Technologies

Overail. simple sanspiantasion oi :arrectrial iechnoiogies io the fonar suriace seems inappropriate. Sateriais that are common on the lunar suriace would be uncompetitive as starting materiais for most terrestriai extraction processes. We especiaily would discain them as sources of air and water, which we regard as free and abundant on Earth. Lunar surface conditions would also be unsuitable for most terrestrial technologies. Because of this, we tend to regard them (and conditions on the suriaces of other objecrs in the solar system) as impediments. However, with new ideas and proper understanding, we shouid be able to turn ar least some of these conditions into advantages.

Initially, all operations on the lunar suriace (as elsewhere in space) wiil be awkward and expensive. Thus. the simpiest technologies that can produce crucial products will presumably be
the first technologies deveioped (e.g.. Faskin. :985). We can spenuiate that zaracteristics of Sesiracie initial lunar technologies wouid inciuce the following: Such tesmoiogies would have few and simple steps. inciuding minimai preparation of feedstock and minimai atiort to recycle reagents. They would require minimai materiai (reagents pius iactory) to be brought from Earin. They would make arificient use of energy, or at least of power other than direct sunlight. They wouid be easy to instail. have iew moving parts. and be ensy to maintain and operate. and thus require little astronaut time. They should be robust with respect to physical jarring during transport and installation. They shouid be rocust with respect to feedstock somposition: the ore cody shouid te $22 s \%$ io mine and batches of teartock shouid not require extensive compositionai monitoring.

However unusuai lunar soils may seem when compared with-terrestrial ores, they are an excellent resource in terms of their chemical compositions and. for some purposes, their physical sharacteristics. It is convenient to illustrate this in the sort oi ayaryday ierms one mignt use if one were a pioneer sertler on the Moon. Our pioneer settler must have the perspective of a chemist. however. to recognize much of the porential of the soil as a resource.

The Lunar Water Works: As pioneers. our tirst concern might be tood and water. especially since the Moon has the reputation of being very dry and carren or carbon. It is proposed that there may (e.g., Arnold. 1979) or may not (e.g., Lanzerotti and Brown, 1981) be water at the lunar poles, but we ignore that possibility in our conservative scenario. Instead of water, let us consider the abundance of its chemical components. oxygen and hydrogen. The lunar suppiy of oxygen is enormous: oxygen is the most abundant chemical eiement (by weight. some $45 \%$ ) in the lunar soils and rocks. It is chemicaily combined in those materiais and must be extracted, as discussed below.

## F-6

In contrast. soncentrations of hedrogen are vary low. tut the rotai anantiry avaiable is nevertheiess great. Lavas erupted from the Moon's interior contain such low amounts of hydrogen (and carcon and nitrogen) that we have ceen unable to ooserve them even with modern sensitive instruments. in contrast to terrestriai lavas. winich ypicaily contain at least $0.5 \%$ water. The iunar suriace. however. has been bathed for biilions of $\because$ ears in the solar wind, a flux or ionized atoms from the exterior of the sun. These ions emoed themseives in the suriaces of the grains of soii thar lie on the Moon's suriace. The lunar suriace is repeatedy "zardened" by iniailing meteorites. so oid. soiar-wind-rici grains are ouried and fresh grains zxposed. In this way. arge amouns of hydrogen have become curied ta the soii. enough to produce (if comoined with lunar ox:gen) about one milion C . S. gations tajout 3.3 milion liters) of water per square mile ( $2.5 \mathrm{~km}^{-}$) oi soii to a depth or two yards (1.3 mı (Haskin. 1990). This hydrogen can ce extracted by heating the sori to about $700^{\circ} \mathrm{C}$. Suppiving the Lunar Water Works is a matter of tecnnology and esonomics. but not a matter oi avaiiacility of hydrogen and oxygen on the Moon.

The Lunar Farm: Like nydrogen. carbon and nitrogen are abuncant in the lunar soil. Like そdrogen. hey are derived fom the soiar wind and are mresent in $\because \because \because$ ix woncentrations. They are ootained aiong with hydrogen orien lunar soil is heated. fil the other nutrients necessary to life are likewise present in the soii. In principie, just as they do on Earth, plants should be able to extract these nurrients directiy from the soil. once we have provided them with adequate lunar water. carbon dioxide, oxygen. and nitrogen. In praciice, such soils would procably not be very tertile untii their minerals had reacied with water, and hydroponic means oi farming might te needed initially.

The Lunar Filling Station: At least initiaily, an important mode of iransportation to and from the Moon base wiil be rockers. Hauling the tuel and oxidizer tor these from Earth wiil be expensive. It may prove cheaper to provide them irom lunar soil. The iuel of choice might be

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iydrogen. For persdecrive, consicier the production of to tonnes of Byorogen per year, as reasonable estimate of the amount needed for ail transportation irom low-Earth orbit in the
 :0 a deprh oi one mever (Haskin. !900).

Alternatively, lunar transport venicies might burn a metal such as iron. aiuminum. or silicon, aven though these are less efficient rocket fuels than hydrogen. All three are major constituents of lunar soiis. trom which they can be extracted from chemical combination with oxygen. Each is a oyproduc: oi one or more proposed processes for extraction oi oxygen.

We need an oxidizer for the tuel. and oxygen is very abundant, although it is not trivial to extract it from the soiis. Severai techniques have been proposed. inciuding extraction of oxygen from imenite by using hydrogen gas (e.g., Gioson and Knudsen. i985: Williams, 1985), extraction by using caricon monoxide gas (e.g.. Rosencerg et al., 1965: Cualer and Krag, 1985), extraction ty processing with hyorotluoric acid or iluorine (e.g., Waldron. 1985; Burt, 1990), and extraction by electrolysis. either with a flux (Keller et al.. 1989) or withour a flux (e.g., Haskin er ai.. : ©ç. Giscussed below.

The Lunar Lumber Yard: Suppose we decide we need a new structure on the Moon or in space; what will the Lanar Lumber Yard have to offer? A case can be made that the "boards" of space construction will be made of glass. Molten lunar soil can be cast into silicare beams, rods, and sheets. be extruded as tubes. and be spun into fibers. These may have greater strength than similar products on Earth because in the space environment there is no water to reacr with their polymer conas.

Iron, aluminum. and silicon are byproducts of oxygen extraction from lunar soils. Iron and aluminum can ce fabricated into beams and rods for structural support. They can be drawn
into wires, both for structural use and for use as electricai and hear concuctors. All three can be used as mirrors or mirror coatings to reflect sunlight.

The unprocessed soil itself can serve as therimai shieiding to moderate habitars and other environments against the broad, diurnal temperature fluctuations at the lunar suriace. It can also serve as radiation shielding against cosmic rays and solar flares. Partiaily distilled in a solar furnace, it seems possible that the residue from the soil might take on the composition of a good cement, and the water to turn it into concrete could be ootained from local sources, as mentioned above. Distilled further, the residue would be very retractory and could serve for hear shielding.

The Lunar Power Company: The Moon receives plentiful and predictable amounts of sunight, and sunlight will sureiy be the eventual source of neariy all electrical power and hear used by the lunar pioneer. Except at very restricted locations at the lunar poles. sunlight is locally available oniy half the time, however, and for some purposes, the temporal distribution of sunlight is inconvenient. Storing energy derived from the sun over the two-week-long lunar night seems difficuit, and might have to be done in the form of hyarogen. metals, and oxygen whose extraction was powered by solar energy. Thus. a strong case can be made that the power used initially on the Moon should be nuclear.

Initially, it may be economical to bring high yield solar panels to the Moon from Earth. Evenrually, elecrricai power wiil probably be derived from lunar silicon. a byproduct of oxygen production, or from lunar ilmenite, recently shown to be photovoitaic. Conversion need not be efficient if a local material simply obtained is used as the photovoitaic.

Elecrrical power may be the first major import to the Earth from the Moon (once the souvenir market has been satisfied). Large arrays of relatively low-yield solar cells can be placed on the

Moon to supply large amounts of power for transmission to Earth (Crisweil and Waldron, 1985). Also, lunar ${ }^{3} \mathrm{He}$ has been proposed for use as a fusion fuel superior to tritium $\left({ }^{3} \mathrm{H}\right)$ in that is is not radioactive, does not have to be made in nuclear fission reactors. and yields a.proton instead of a more destructive neutron when it fuses with deuterium ( ${ }^{2}$ H) (Wittenioerg et al., 1987). The use of iron, aluminum, and siiicon to coat mirrors to move suniight around was indicated above.

## "Magma Electrolysis," a Proposed Lunar Technology*

We are investigaring eiecrrolysis of molten siiicare as a means oi producing oxygen and metals for use on the Moon and in near-Earth space. (See also Oppenheim. 1968; Kesterke, 1971; Lindstrom and Haskin. 1979). Most oi our effort so far has been to determine the nature and kinetics of the electrochemical reactions and the conductivities and other parameters necessary for design of a test cell. We have not yet designed a production-scaie cell. but we have a rough idea of its characteristics (Haskin et al., 1990).

We envision a steady-state operation. The feedstock for the cell would be lunar soil that had been sieved to remove the smail proportion of materiai larger than 0.3 cm . is the soil was fed into the ceil, it would meit; the heat for meiting would be furnished by "excess" electrical heat released into the melt owing to its resistance. The cell would have a volume of about one cubic meter and anode and cathode areas of about thirty meters each. Oxygen would be produced at the anode, and iron, siiicon, or an alloy of the two would be produced at the cathode,

[^12]depending on the composition of the siiicate melt in the cell. The operating temperature of the cell would be between 1,200 and $1.400^{\circ} \mathrm{C}$.

We estimate that the power required to produce one tonne of oxygen gas per 24 hours would be about 0.54 Mw , of which some 0.11 Mw would be used to meit and heat the feedstock, 0.19 Mw would be used to separate the oxygen and metal from chemical combination, and 0.24 Mw would be "excess" resistance heat, some of which would be needed to make up for radiation losses from the hot ceil, and the rest of which would be available for other uses. In addition to the one tonne of oxygen gas, the cell would produce (for an average meit composition) some 0.64 tonne or iron and 0.62 tonne of silicon. Abour 4.3 tonnes of soil would pass through the ceil per 24 hours. so some 2.5 tonnes of spent siiicate melt would have to be removed along with the oxygen and metal. All products of the ceil would be usefui; nothing would need to be discarded. Potential uses are discussed above.

This process would satisfy many of the criteria set forth above for eariy lunar technologies. The cell proper would have no moving parts.althougn the equipment to mine, sieve, and introduce the lunar soil wouid and that to remove and store the oxygen might. Producing the oxygen, metals. and spent silicate wouid be a one-step process: we have not considered how to handle the products, an activity common to all proposed processes. The mass and size of the cell would be modest compared to the equipment for most proposed aiternate processes (e.g., Eagle Engineering, 1988).

The power requirements would also be comperitive with those of proposed alternate processes, if we include in the comparison the ancillary steps required by those processes such as ore refinement and reagent recycling that would not be needed for siiicate electrolysis. The cell would need continuous electrical power, however, so that its contents would not freeze during the lunar night, initially, this requirement may best be met by use of nuclear power.

The process would use common lunar soil; any common soil found by the Apollo or Luna missions would be acceprable, aithough prior knowledge of the general type of soil might enable oprimization of cell design or startup protocols. Different feedstocks would require somewhat different initiai conditions of temperature and eiectrical potencial but, once the bulk composition of the melt had been established in the cell, probable variations in feedstock composition wouid not greatiy affect cell temperature or operating potential.

The main identified and unsoived problems of the process center around finding suitable materials for the eiectrodes and container. Iron and silicon form alloys with most metals. Molten silicate is very corrosive. Anodes can probably be made of platinum or coated with it, and cathodes can probably be made of high-temperature iron-silicon ailoys. The container may have to be made of spinel, which would be brought into equilibrium with the silicate melt.

## Conclusions

Lunar soils contain in abundance the materiais required for life support. construction, and transportation. The high cost in energy of lifting material from the Earth's suriace suggests that, in the near term, lunar material shouid be considered for use both on the Moon and in low-Earth orbit. However, most conventional technologies are not suited to efficient processing of lunar material, so new technologies need to be developed. Additional ideas are needed, but most crucial is investment in thorough testing of existing ideas on a laboratory bench scale. Development of those that prove promising in the laboratory should be begun immediately, because of the long lead time to prepare robust units for testing or use on the Moon.

Acknowiedgements
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## MOONUSE

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## References

Armold J. R. (1979) Ice in the lunar polar regions. J. Geophys. Res. 84, 5659-5668.

Burt, D. (1990) Lunar mining of oxygen using fluorine. In Lunar Bases and Space Activities of the 21 st Century II, W. Mendell, ed. Lunar and Planetary Institute, Houston. (Accepted for publication).

Criswell, D. R. and Waldron R. D. (1985) Concept of the lunar power system. In Space Solar Power Review 5, 53-75.

Cutler A. H. and Krag P. (1985) A carbothermal scheme for lunar oxygen extraction. In Lunar Bases and Space Accivities of the 21st Century, W. Mendell, ed. Lunar and Planetary Instirute, Houston. pp. 559-569.
du Fresne, E. and Schroeder J. E. (1983) Magma elecrrolysis, in Research on the Use of Space Resources, W. F. Carroll, ed. JPL publication 83-86.

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

Gibson M. A. and Knudsen C. W. (1985) Lunar oxygen production from ilmenite. In Lunar Bases and Space Activities of the 21 st Century, W. Mendell, ed. Lunar and Planetary Institute, Houston. pp. 543-550.

Haskin, L. A. (1985) Toward a spartan scenario for use of lunar materiais. In Lunar Bases and Space Activities of the 21st Century, W. Mendell, ed. Lunar and Planetary Institute, Houston. pp. 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 21 st Century II, W. Mendell, ed. Lunar and Planetary Institute, Houston. (Accepted for publication).

Haskin, L. A., Colson R. O., Lindstrom D. J., Lewis R. H., and Semkow K. W. (1990) Electrolytic smelting of lunar rock for oxygen, iron, and silicon. In Lunar Bases and Space Activities of the 21 st Century II, W. Mendell, ed. Lunar and Planetary Institute, Houston. (Accepted for publication).

Haskin L. A. and Warren P. H. (1990) Chemistry. In Lunar Sourcebook, G. Heiken, D. Vaniman, and B. French, eds. Lunar and Planetary Science Institute, Houston. (Accepted for publication.)

Keiler, R. (1989) Dry extraction of silicon and aluminum from lunar ores. EMEC Consultants final report to Johnson Space Center.

Kesterke D. G. (197i) Electrowinning of oxygen from silicate rocks. U.S. Bureau of Mines Report of Investigations 7587.

Lanzerotti L. J. and Brown W. L. (1981) Ice in the polar regions of the moon. J. Geophys. Res. 86, 3949-3950.

Lewis J. S. and Lewis R. A. (1987) Space Resources, Columbia U. Press, N.Y. 418 pp.

## F-15

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

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

Rosenberg S. D., Guter G. A., and Miller S. F. (1965) Manufacture of oxygen from lunar materials, Annals New York Acad. Sci. 123, 1106-1122.

Simon M. C. (1985) A parametric analysis of lunar oxygen production. In Lunar Bases and Space Activities of the 2Ist Century, W. Mendell, ed. Lunar and Planerary Institute, Houston. pp. 531-541.

Waldron R. W. (1985) Total separation and refinement of lunar soils by the HF leach process. Space Manufacturing 7, ALAA, New York. pp. 132-149.

Williams R. J. (1985) Oxygen extraction from lunar materials An experimental test of an ilmenite reduction process. In Lunar Bases and Space Activities of the 21 st Century, W. Mendell, ed. Lunar and Planetary Institute, Houston. pp. 551-558.

Wittenberg L. J., Sarantius J. F., and Kulcinski G. L. (1987) Lunar source of ${ }^{3} \mathrm{He}$ for commercial fusion. Fusion Technology 10, 167-178.

## APPENDIX G

## NEAR-EARTH ASTEROID DATA BASE



## G-2



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| 1379] | 2.12095610 .1405951 | 3.3514 | 41.87948 11.75 | 328.12972 | 1.505/19.0/85 |  |  |  |  |
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| 18813 | 1.1152998 1.8211948 | 2.2145 | \$1.67299 19.90659 | 1.5118 | 1.21 91/05.0/41 |  |  |  |  |
| 18814 | 2.235072 8.5181129 | 37. 188 | 184.01212 288.10652 | 11.38831 | 1.38 81/19.9/82 |  |  |  |  |
| 15124 | 1.805714 0.6972581 | 31.5792 | 263.16231143 .63185 | 18.25108 | 1.18 10/81.9/8 |  |  |  |  |
| 1 1\% ${ }^{\text {a }}$ | 2.909115 0.1766159 | 2.60018 | 10.91719 220.12595 | 11.1918 | 1.1981/23.0/ts |  |  |  |  |
| 188184 | 8.2231101 0.5070001 | 12.1371 | 161.1445114 .10113 | 11.1118 | 1.38 10/21.0/11 |  |  |  |  |
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## APPENDIX I

## THE NUCLEUS OF COMET P/TEMPEL 2

THE NUCLEUS OF COMET P/TEMPEL 2<br>Michael F. A'Hearn ${ }^{1,2}$<br>Astronomy Program. University of Maryland<br>Humberto Camping ${ }^{1,3}$<br>Planetary Science Institute<br>David G. Schleicher ${ }^{2}$ and Robert L. Millais<br>Lowell Observatory<br>Received 1989 April 6: accepted 1989 June I7


#### Abstract

We present the results of simultaneous optical photometry and infrared radiometry of comet P/Tempel 2. Periodic variations of brightness, previously detected in the optical by others, are present and in phase at all wavelengths in our data. Because the optical and thermal rotational light curves are in phase, we conclude that the variations are caused by the changing apparent cross section of an elongated nucleus rotating with a period near 8.9 hr . The variation of flux with aperture allows us to separate the contributions of the nucleus and the coma. In the apertures with which we monitored the light curve. the contribution by the coma is $\sim 25 \%$ at maximum light in the optical and undetectable at the level of $10 \%$ at all times in the thermal infrared. By applying the standard thermal model for asteroids, we have determined the following nuclear properties: effective radius at maximum light, 5.9 km ; visual geometric albedo, 0.022 ; and projected axial ratio near 2. The nucleus is very red but there is evidence that the reflectivity in the ultraviolet increases toward shorter wavelengths. Based on the observed rate of outgassing, $\sim 1 \%$ of the surface is active. Properties common to all nuclei of periodic comets appear to include the very low albedo and the high-axial ratio. The fraction of the surface which is active appears to vary significantly among nuclei, as does the character of the reflection spectrum.


Subject headings: comets - rotation

## I. INTRODUCTION

Over the last 10 years or so, a resurgence of interest in measuring the properties of cometary nuclei has occurred. This resurgence is motivated by a desire to better understand the relationship between the nucleus and the more readily observed phenomena in the coma and to explore the relationship between cometary nuclei and Aten-Amor-Apollo (AAA) asteroids. The comas of comets have been conceptualized for many years as the product of outgassing from a dirty snowball (Whipple 1950) but the detailed nature of that snowball has remained elusive. Even the dramatic results from the Vega and Giotto spacecraft have left many questions unanswered concorning the nature of cometary nuclei, not the least of which is the degree to which P/Halley is typical of all comets. The possible relationship of comets to asteroids is based on the long-standing idea, originally suggested by Oik (1963), that a significant fraction of the AAA asteroids are extinct cometary nuclei. Current estimates from dynamical arguments suggest. with very large error bars. that roughly half the AAA asteroids are derived from comets (Wetherill 1988).
Unfortunately, it is very difficult to observe cometary nuclei. The least ambiguous observations are those from spacecraft. but ground-based observations have been made which, with varying degrees of certainty, appear to refer to a cometary nucleus rather than to material of the coma. These results have

[^13]been reviewed recently (A'Hearn 1988; Weissman et al. 1989) and will not be discussed in detail here. In general, there are two possible approaches to the problem of studying cometary nuclei from Earth. Jewitt and Meech (1988) have concentrated on observing comets optically at large heliocentric distances when the activity of the comet is expected to be small. We, on the other hand, have concentrated on observing comets which are relatively inactive even at small heliocentric distances which permits us to study the nuclei in the thermal infrared as well as in the optical (Camping et al. 1987, hereat er CAM87: Mills et al. 1988, hereafter MAC88). With both approaches there is always some uncertainty about the contamination of the measurements by coma although observers universally argue that their own measurements are relatively free from this problem.

Comet $\mathrm{P} /$ Temped 2 is a particularly interesting object. It has been considered repeatedly as a potential target for a cometary mission, but none of these has yet come to fruition. Nevertheless, because of this possibility, the comet has been the object of ground-based study by numerous astronomers. It is known from the orbital lightcurve (Sekanina 1979) ${ }^{4}$ that for much of the preperihelion arc the brightness of the coma is negligible. Similarly, the nongravitational acceleration is very small (Marsden 1985) suggesting low activity per unit mass of the nucleus (although a fortuitous geometry could also lead to a small nongravitational effect even with significant outgassing). P/Tempel 2 is, therefore, one of the few comets, the nuclei of which might be observable with Earth-based telescopes near

[^14]perihelion. Accordingly, we planned an observational program of simultaneous optical and infrared photometry similar to those we carried out earlier on comets P/Neujmin 1 (CAM87) and P/Arend-Rigaux (MAC88). Other groups aiso observed P/Tempel 2 at this apparition. Jewitt and Luu (1988) determined a rotational period from CCD photometry in 1988 April, before the onset of outgassing, while Wisniewski (1988) confirmed their value for the period and determined the rotational light curve from conventional broad-band photometry in 1988 May. Wisniewski's rapid distribution of his light curve to other observers was invaluable in planning our observing strategy. In particular, after the first few observations we were able to predict the times of subsequent maxima and minima in order to optimize the observations.

## I. OBSERVATIONS

The observations were scheduled for 1988 June near the time of the comet's closest approach to Earth. Although this time was somewhat after the predicted onset of activity, the light curve of Sekanina (1979) implied that activity would still be weak and the advantage to be gained by observing at minimum geocentric distance was significant. The infrared observations were carried out at the NASA Infrared Telescope Facility (IRTF) to measure the thermal emission from the comet on 1988 June 10 and 11 UT. The optical measurements were made with the University of Hawaii 2.2 m telescope during the same two nights and during a small portion of the night of June 9 UT. Subsequent nights were cloudy. The observing circumstances at the midpoint of the two full nights are as follows:

$$
\begin{aligned}
r_{\mathrm{H}} & =1.72 \mathrm{AU} \\
\Delta & =0.79 \mathrm{AU} \\
\text { phase } & =20^{\circ} \\
\dot{r}_{\mathrm{H}} & =-9.9 \mathrm{~km} \mathrm{~s}^{-1}
\end{aligned}
$$

In the infrared, the standard $N$ filter (reference waveiength $=10.1 \mu \mathrm{~m}$; Tokunaga 1986) and IRTF bolometer with a 4 mm aperture were used most frequently to define the light curve. On a few occasions, observations were made near maximum and minimum light (phases chosen to minimize the temporal variations) in four apertures, $3,4,5$, and 6.5 mm , for which drift scans on stars yielded effective angular diameters of 5 ".3, 7"0, 7"8 and 8".7, respectively. The chopper throw was 30" north-south. Based on the photometry with different apertures, we estimate that the coma contribution to the reference beam was less than $0.5 \%$ of the comet's peak brightness. Measurements with the standard $M(4.8 \mu \mathrm{~m})$ and $Q(20.0 \mu \mathrm{~m})$ filters were also made to determine color temperatures. The star $\alpha$ Bootis was used as a primary standard with adopted magnitudes $M=-2.12 . N=-3.17$, and $Q=-3.13$ (Tokunaga 1986). Two stars near the comet in the sky, $\alpha$ Serpentis and 110 Virginis. were observed frequently and used as local standards to monitor extinction and check for any instrumental variations. Neither of the local standards showed intrinsic variability although some changes in extinction were detected and corrected for. The observations were reduced and calibrated using the procedure and absolute fluxes discussed by Tokunaga (1986).

The optical observations were made with a photometer and pulse-counting electronics from Lowell Observatory and the standard International Haliey Watch (IHW) filters which
isolate various emission bands and portions of the reflected continuum. These filters are described in detail in an appendix to the IHW Archive of Observations of P/Giacobini-Zinner (Sekanina 1989). On June 9 an EMI 6256S photomultiplier was used completing the identical system to that which was used previously for comet P/Arend-Rigaux (MAC88). On June 10 and 11, we used an RCA 31034A photomultiplier which allowed use of filters at longer wavelengths than were used in the previous study. Since most of June 9 was devoted to another project, only $\sim 1.5 \mathrm{hr}$ were spent observing P/Tempel 2. Consequently, the data from that night were not well calibrated. The temporal variations were monitored using the two filters for the continuum at $4845 \AA$ and $6840 \AA$ and an aperture of 10.1 diameter. Sky was observed far from the comet (usually several tens of arcmin) after each set of observations of the comet (usually three 30 s integrations in each of the two continuum filters). The stars HD 149363 and HD 120086 were used for absolute calibration via the standard magnitudes defined by the IHW, while observations of two nearby comparison stars were interspersed between every set of cometary observations to monitor any variations in transparency or instrumental sensitivity or both. There was no indication of intrinsic variability in the brightness of the nearby comparison stars or in the extinction coefficients. Mean extinction coefficients for the two nights were used in reducing the data. Two or three times each night-usually near the times of maximum and minimum light when the brightness of the comet was changing most slowly-observations were made in apertures of $14.2,20^{\prime \prime} 0$, and $28^{\prime \prime} .5$ in order to determine the radial brightness profile of the coma. An accurate measurement of this profile is required if the contributions of the nucleus and the coma to the observed signal are to be disentangled. The comet was also observed a few times through other filters of the IHW set in order to estimate production rates of various gases, gas-to-dust ratio, and so on.

## a) Brightness Variations

The 4845 and $6840 \AA$ observations taken through the 10.1 aperture and the $N$ magnitudes measured through the $7^{\prime \prime}$ aperture are listed in Tables 1 and 2 for the nights of June 10 and 11. respectively. It was soon evident during our observing that both the reflected optical and the thermal infrared brightnesses of the comet were varying in phase. The peak-to-peak amplitude of the variation was 0.4 mag in the optical and 0.8 mag in the infrared. The existence of this variation was, in fact, no surprise. Jewitt and Luu (1988) had reported cyclic variations in April with an $\sim 9$ hour period and a peak-to-peak ampiitude of 0.7 mag in the $R$ passband, in good agreement with the amplitude we observed at $N$, while Wisniewski (1988), from $V$-filter observations in late May, had produced a convincing rotational light curve for Tempel 2 having a period of 8 hr .58 minutes, and an amplitude of 0.5 mag . Wisniewski's observations were made through photometer apertures of $17^{\prime \prime}$ and $12^{\prime \prime}$ diameter: Jewitt and Luu observed with a CCD. The difference in optical amplitude reported by these investigators and our still smaller optical amplitude of $\sim 0.4$ mag very probably can be attributed to greater dilution by the coma of the signal from the nucleus as the comet became more active because, based on Sekanina's (1987) determination of the polar orientation. we all observed the comet at nearly identical projections. On the other hand. the observations of P/Tempel 2 in 1987 by Jewitt and Meech (1988). which exhibited a much smaller amplitude ( $<0.3 \mathrm{mag}$, given our present knowledge of the period), were

TABLE 1
Optical Light Curve Data

| 4845 A |  |  |  | 6840 A |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { U.T. } \\ & \text { (hour) } \end{aligned}$ | Observed Magnitude | Nuclear Magnitude | Phase $(\mathrm{P}=3.9 \mathrm{hr})$ | $\begin{aligned} & \text { U.T. } \\ & \text { (hour) } \end{aligned}$ | Observed Magnitude | Nuclear Magnitude | Phase $(P=3.9 \mathrm{hr})$ |
| 1988 June 10 |  |  |  |  |  |  |  |
| - | - ${ }^{-1}$ | - | - | - 1.134 | 14.300 | 15.074 | 0.627 |
| -. 207 | 15.879 | 16.220 | 0.636 | 7.256 | 14.751 | 15.024 | 0.641 |
| 7.833 | 15.903 | 16.253 | 0.706 | 7.788 | 14.818 | 15.097 | 0.701 |
| 8.084 | 15.978 | 16.358 | 0.734 | 8.048 | 14.836 | 15.120 | 0.730 |
| 8.400 | 16.042 | 16.450 | 0.770 | 3.345 | 14.377 | 15.174 | 9.763 |
| 8.950 | 16.128 | 16.578 | 0.831 | 3.915 | 15.051 | 15.409 | 0.323 |
| 9.060 | 16.186 | 16.667 | 0.844 | 9.103 | 15.082 | 15.452 | 0.349 |
| 9.399 | 16.162 | 16.630 | 0.882 | 9.433 | 15.128 | 15.518 | 0.886 |
| 9.708 | 16.216 | 16.714 | 0.917 | 9.746 | 15.116 | 15.500 | 0.921 |
| 9.931 | 16.199 | 16.687 | 0.942 | 9.895 | 15.095 | 15.471 | 0.938 |
| 10.116 | 16.132 | 16.584 | 0.962 | 10.082 | 14.993 | 15.329 | 0.959 |
| 10.284 | 16.047 | 16.457 | 0.981 | 10.245 | 14.920 | 15.231 | 0.977 |
| 10.755 | 15.910 | 16.263 | 0.037 | 10.741 | 14.784 | 15.053 | 0.031 |
| 11.022 | 15.852 | 16.183 | 0.064 | 11.056 | 14.726 | 14.979 | 0.068 |
| 11.353 11.532 | 15.891 15.809 | 16.237 16.125 | 0.101 | 11.321 | 14.704 | 14.952 | 0.098 |
| 11.890 | 15.797 | 16.109 | 0.122 | 11.498 | 14.660 | 14.897 | 0.118 |
| 12.066 | 15.869 | 16.206 | 0.182 | 11.351 | 14.658 14.115 | 14.894 14.966 | 0.159 |
| 12.220 | 15.902 | 16.252 | 0.199 | 12.186 | 14.738 | 14.995 | 0.125 |
| 12.398 | 15.853 | 16.185 | 0.219 | 12.330 | 14.76 | 15.047 | 0.211 |
| 12.844 | 16.058 | 16.473 | 0.269 | 12.388 | 14.942 | 15.250 | 0.274 |
| 13.196 | 16.126 | 16.575 | 0.309 | 13.163 | 14.971 | 13.299 | 0.305 |
| 1988 June 11 |  |  |  |  |  |  |  |
| 6.278 | 15.956 | 16.189 | 0.228 | 5.221 | 1.4.714 |  |  |
| 0.726 | 16.025 | 16.425 | 0.278 | 6.537 | 14.372 | 15.167 | 0.221 |
| 5.844 | 16.053 | 16.466 | 0.291 | 6.308 | 14.905 | 15.211 | 0.287 |
| 7.078 | 16.091 | 16.522 | 0.318 | 7.126 | 15.001 | 15.340 | 0.323 |
| 7.350 | 16.231 | 16.738 | 0.348 | 1. 314 | 15.079 | 15.448 | 0.344 |
| 7. 340 | 16.267 | 16.796 | 0.403 | $\bigcirc .798$ | 15.107 | 15.488 | 0.399 |
| -. 983 | 16.220 | 16.720 | 0.419 | 7.349 | 15.077 | 15.445 | 0.416 |
| 8.142 | 16.187. | 16.668 | 0.437 | 8.109 | 15.058 | 15.419 | 0.416 0.434 |
| 8.287 | 16.188 | 16.670 | 0.454 | 8.254 | 15.020 | 15.366 | 0.434 0.450 |
| 8.429 | 16.185 | 16.665 | 0.470 | 3.396 | 15.010 | 15.352 | 0.466 |
| 8.723 | 16.046 | 16.456 | 0.503 | 8.689 | 14.897 | 15.200 | 0.499 |
| 3.920 | 15.988 | 16.372 | 0.525 | 8.954 | 14.905 | 15.211 | 0.529 |
| 9.093 | 15.988 | 16.372 | 0.544 | 9.127 | 14.829 | 15.111 | 0.548 |
| 9.544 | 15.844 | 16.173 | 0.595 | 9.506 | 14.762 | 15.1025 | 0.591 |
| 9.751 9.395 | 15.818 15.916 | 16.137 | 0.618 | 9.679 | 14.737 | 14.993 | 0.610 |
| 9.395 10.046 | 15.816 15.74 | 16.135 | 0.634 | 9.862 | 14.689 | 14.933 | 0.631 |
| 11.050 | 15.075 | 16.079 16.499 | 0.651 0.764 | 10.013 11.009 | 14.695 | 14.340 | 0.648 |
| 11.326 | 15.965 | 16.340 | 0.695 | 11.009 | 14.332 14.859 | 15.115 15.150 | 0.759 |
| 11.554 | 15.976 | 16.355 | 0.321 | 11.531 | 14.954 | 15.26 | 0.324 |
| 11.874 | 16.109 | 16.549 | 0.351 | 11.837 | 15.029 | 15.379 | 0.352 |
| 12.274 | 16.057 | 16.472 | 0.902 | 12.238 | 15.101 | 15.479 | 0.398 |
| 12.535 | 16.075 16.050 | 16.499 16.462 | 0.922 | 12.488 | 15.013 | 15.357 | 0.926 |
| 12.838 | 16.018 | 16.415 | 0.965 | 12.895 | 14.959 | 15.351 15.233 | 0.935 0.960 |

obtained when the sub-Earth and subsolar points were at cometographic latitudes such that the variation of cross section should have been approximately half that for the later observations if the nucleus is basically prolate. Consequently, the smaller optical amplitude in 1987 is likely due to the different aspect.

Although our observations do not extend over a sufficient time interval to permit a precise period determination, we have estimated the period using the method of phase dispersion minimization (Stellingwerf 1978). This technique was previously applied to comet P/Arend-Rigaux by MAC88 and the reader is referred to that paper for details of the method. We performed separate period searches on the $4845 \AA .6840 \AA$, and $10 \mu \mathrm{~m}$ data for P/Tempel 2 from June 10 and 11 . The statistic $\theta$ (see MAC88) for each of these sets of data is shown plotted
against period in Figure 1. Possible periods in the data are those for which there is a local minimum in this plot. The increase in depth of the minima toward shorter periods is. to some degree, an artifact of the method. In computing $\theta$, the data are divided into phase bins and the dispersion of the data points within each bin computed. The shorter the period. the narrower is each bin in time. and the less the intrinsic brightness variation of the comet wiil contribute to the dispersion within a bin. Note that the plots for all three data sets show a sharp minimum at a period of 4.45 days. The two adjacent minima, at 2.7 and 5.5 hr . are aliases of the strongest minimum with the 24 hr sampling interval between nights. The 4.45 hr period corresponds to a light curve having one maximum and one minimum per cycle but we believe, based on evidence which will be presented later in this paper, that the true rota-

TABLE 2
Infrared Light Curve Data ( $10.1 \mu \mathrm{~m}$ )

| U.T. <br> (hour) | Magnitude | Phase $(P=8.9 \mathrm{hr})$ | U.T. <br> (hour) | Magnitude | Phase $(\mathrm{P}=8.9 \mathrm{hr})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1988 June 10 |  |  | 1988 June 11 continued |  |  |
| 7.200 | 3.630 | 0.635 | 6.883 | 4.048 | 0.296 |
| 7.317 | 3.663 | 0.648 | 6.933 | 4.063 | 0.301 |
| 7.400 | 3.607 | 0.657 | 7.117 | 4.107 | 0.322 |
| 7.600 | 3.658 | 0.680 | 7.367 | 4.244 | 0.350 |
| 7.783 | 3.710 | 0.700 | -. 517 | 4.377 | 0.367 |
| 8.150 | 3.733 | 0.742 | i. 667 | 4.312 | 0.384 |
| 8.450 | 3.862 | 0.775 | 7.767 | 4.357 | 0.395 |
| 8.550 | 3.884 | 0.787 | 7.883 | 4.367 | 0.408 |
| 8.717 | 4.016 | 0.805 | 7.983 | 4.378 | 0.419 |
| 8.800 | 4.031 | 0.815 | 8.083 | 4.288 | 0.431 |
| 9.133 | 4.230 | 0.852 | 8.217 | 4.254 | 0.446 |
| 9.217 | 4.403 | 0.861 | 8.383 | 4.099 | 0.464 |
| 9.383 | 4.361 | 0.880 | 8.533 | 4.075 | 0.481 |
| 9.600 | 4.320 | 0.904 | 8.883 | 3.838 | 0.521 |
| 9.767 | 4.299 | 0.923 | 9.050 | 3.825 | 0.539 |
| 9.933 | 4.106 | 0.942 | 9.350 | 3.768 | 0.573 |
| 10.200 | 4.039 | 0.972 | 9.433 | 3.748 | 0.582 |
| 10.550 | 3.884 | 0.011 | 9.533 | 3.743 | 0.594 |
| 10.617 | 3.820 | 0.019 | 9.700 | 3.785 | 0.612 |
| 10.767 | 3.743 | 0.036 | 9.850 | 3.801 | 0.629 |
| 10.867 | 3.743 | 0.047 | $\bigcirc$ | 3.807 | 0.635 |
| 11.083 | 3.568 | 0.071 | 10.017 | 3.745 | 0.648 |
| 11.233 | 3.614 | 0.088 | 10.117 | 3.696 | 0.659 |
| 11.383 | 3.604 | 0.105 | 10.200 | 3.736 | 0.669 |
| 11.600 | 3.584 | 0.129 | 10.300 | 3.721 | 0.680 |
| 11.700 | 3.562 | 0.140 | 10.417 | 3.712 | 0.693 |
| 11.817 | 3.470 | 0.154 | 10.617 | 3.699 | 0.715 |
| 12.550 | 3.750 | 0.236 | 10.783 | 3.735 | 0.734 |
| 12.717 | 3.890 | 0.255 | 10.917 | 3.766 | 0.749 |
| 12.950 | 3.929 | 0.281 | 11.167 | 3.946 | 0.777 |
| 13.117 | 3.961 | 0.300 | 11.200 | 3.897 | 0.781 |
| 13.167 | 4.220 | 0.305 | 11.283 | 4.042 | 0.790 |
| 13.433 | 4.359 | 0.335 | 11.400 | 3.939 | 0.803 |
|  |  |  | 11.467 | 3.958 | 0.811 |
| 1988 June ll |  |  | 11.633 | 3.996 | 0.830 |
|  |  |  | 11.750 | 3.996 | 0.843 |
|  |  |  | 12.000 | 4.246 | 0.871 |
| 5.733 | 3.562 | 0.167 | 12.200 | 4.209 | 0.893 |
| 5.783 | 3.582 | 0.172 | 12.317 | 4.112 | 0.906 |
| 5.950 | 3.650 | 0.191 | 12.433 | 4.177 | 0.919 |
| 6.167 | 3.638 | 0.215 | 12.533 | 4.272 | 0.931 |
| 6.300 | 3.725 | 0.230 | 12.650 | 4.125 | 0.944 |
| 6.483 | 3.790 | 0.251 | 12.900 | 4.119 | 0.972 |
| 6.550 | 3.759 | 0.258 | 12.950 | 4.014 | 0.978 |
|  |  |  | 13.267 | 3.893 | 0.013 |

tional light curve must have two maxima and two minima per cycle and thus a period of 8.9 hr corresponding to the broad minimum in Figure 1 centered at $\sim 9 \mathrm{hr}$. This is in good agreement with the results of Jewitt and Luu (1988. 1989) and Wisniewski (1988). Light curves phased according to the periods corresponding with all the prominent minima in $\theta$ were plotted and confirm that a period of 8.9 hr yields the best light curve. We note that this is the shortest photometrically determined rotational period for a cometary nucleus except for the very first period so determined. Fay and Wisniewski (1978) determined a period of 5.2 hr for $\mathrm{P} / \mathrm{d}$ Arrest although the rather small amplitude of the variation yielded poor signal-to-noise ratio in the resultant power spectrum. All other rotational periods recently determined are substantiaily longer (Weissman et al. 1989).

Figure 2 shows the observations from June 10 and 11 phased according to a period of 8.9 hr and plotted as open circles and filled circles, respectively. In addition, the observations from June 9 have been included (as filled triangles) in the piot of the
$4845 \AA$ data. Zero phase arbitrarily has been set at 7.75 hr . UT. on June 9 . Since the observations from June 9 are poorly calibrated, we have simply shifted those data arbitrarily to the same mean brightness as the data at the same phase from the other nights. Note that the apparent peak in the abbreviated light curve from June 9 at phase 0.1 is coincident with a maximum in the light curve from the other two nights, confirming the periodicity.

It is apparent in Figure 2 that the reflected optical and thermal infrared light curves are closely in phase as was also the case for P/Arend-Rigaux (M.AC88). Now, as in the earlier paper, we interpret the alignment of the visible and infrared light curves to mean that the brightness variations result from the changing apparent cross section of an elongated. rotating nucleus. If the brightness variations were due to albedo features on the nucleus, the visible and IR light curves should be $180^{\circ}$ out of phase. The large difference in amplitude between the visible and infrared light curves results at least in part from greater dilution of the optical observations by the signal from


Fig. 1.-Phase-dispersion-measure for the light curve of comet P/Tempel 2 as a function of period. The statistic is shown for each of the three wavetengths at which light curves were obtained. 4845 A (dotted line), $6840 \AA$ (dashed line), and $10.1 \mu \mathrm{~m}$ (solid line). All show their deepest minimum at 4.45 hr which vieids a singie-peaked light curve. We betieve that the correct rotational period is the one indicated by the broad but shallower minimum at twice that period. 8.9 hr
the coma. In order to derive the size. shape, and albedo of $P_{\text {/ Tempel }}$ 2's nucleus. it is necessary to first remove this contamination by the coma.

## b) Removal of Coma

As noted above, observations were made of the aperturedependence of the flux several times at the three monitoring wavelengths $4845 \AA, 6840 \AA$ and $10.1 \mu \mathrm{~m}$. These observations were usually made near maximum or minimum light in order to minimize the temporal variation of the comet's brightness during the interval required to make measurements through all


Fig. 2.-Phased light curves for comet $\mathrm{P} /$ Tempel 2 assuming a period of 8.9 hr including data from 1988 June 9 ( 4845 A only; filled triangles), June 10 (open circies), and June 11 (filled circles). Zero phase is at 1988 June $9,7.75 \mathrm{hr}$ UT.
apertures. The sequence of these measurements was such that an observation with the monitoring aperture 110.11 and 7.0 diameter in the optical and infrared. respectively) was interspersed between each of the observations with the other apertures. This procedure took up to an hour, so it was necessary to use smooth curves through the data in Figure 2 to correct the observations to a common time assuming that the variation in flux was the same in all apertures (an assumption justified a posteriori). These corrections were as large as $6 \%$.
A simple radial outflow model for the dust predicts a surface brightness which varies as $\rho^{-1}$, where $\rho$ is the projected distance from the nucleus, which in turn implies that the fux in a centered aperture varies linearly with the diameter. Although this is clearly an oversimplification since the coma may be varying, it provides a convenient reference point. In Figures 3 and 4 we have plotted the flux from $\mathrm{P} /$ Tempel 2 as a function of diameter of the aperture in the infrared and the optical, respectively. An examination of the variation with aperture size at $10.1 \mu \mathrm{~m}$ shows that on average a horizontal straight line adequately describes the data. Fitting straight lines by least squares and comparing the value of those lines at 7.0 and $0^{\prime \prime}$ shows that the contribution by the coma to the monitoring aperture is $10 \% \pm 10 \%$ at maximum light. Thus, there is not a statistically significant detection of the coma at this wavelength. and we assume that the contribution is nil for our reductions, allowing for the possible contribution in our later discussion of uncertainties. There was not enough signal to even attempt to measure the variation with aperture size with the $M$ and $Q$ filters, and therefore we have assumed that the contribution by the coma at those wavetengths is also negligible. At least for $Q$, this assumption is supported a posteriori by the models discussed below.
At optical wavelengths, however, there is cleariy a contribution by the coma. In Figure 4, the straight lines have been fitted by least squares to observations through the $10.1,14.2,20^{\prime \prime} 0$, and 28.5 apertures. The standard deviations of the slopes are $\sim 10 \%$, and the variation in slope from one set of observations


Fic. 3.-Variation of flux with aperture at $10.1 \mu \mathrm{~m}$. The data are consistent with the absence of any coma.
to the next is not statistically significant. Based on the average slopes from Figure 4, the contribution by the coma to the flux in the $10^{\prime \prime} .1$ aperture at maximum light is $25 \%$ of the total flux at $4845 \AA$ and $20 \%$ of the total flux at $6840 \AA$. At minimum light, the contributions are $35 \%$ and $28 \%$, respectively.

The lack of significant temporal variation in the optical brightness profiles, it should be noted. argues strongly that the coma is not contributing significantly to the observed variations of brightness. For one thing, the amplitude of the observed variations is markedly greater than the variation in the coma contribution to the signal in the 10.1 aperture. Second, since the estimated time for dust to cross our apertures is comparable to the rotational period. any substantial variation in coma production would produce readily apparent distortions of the coma brightness profiles.

The coma contribution to the observations of the comet in the 10.1 aperture has been calculated on the basis of these
values of the slope and subtracted from the observed signal to give the brightness of the nucleus alone. Columns (3) and (7) of Table 1 contain these nuclear magnitudes on the standard system defined by the IHW. These values are plotted as a function of light curve phase in Figure 5 . The observed magnitudes at $N$, given in Table 2, are also plotted in Figure 5 since we have already argued that these $10.1 \mu \mathrm{~m}$ observations refer solely to the nucleus and do not require correction for coma.

A careful comparison of the panels in Figure 5 shows that the amplitude of the optical light curves is $\sim 0.55 \mathrm{mag}$ while that in the infrared is near 0.80 mag , a difference which is greater than the peak-to-peak scatter in the individual light curves. There are two possible explanations of this difference. One is that we have underestimated the amount of coma contamination of the optical measurements. In fact examination of Figure 4 does suggest a tendency for the observed variation with aperture to deviate from linearity in the sense of being


Fig. 4.-Variation of flux with aperture in the optical region. Straight lines have been fitted by least squares and indicate that a contribution from the coma is definitely present. The average siope for each filter was used for removat of coma from the daal.


Fic. 5.-Rotational light curve of the nucleus of comet P.Tempel 2. The optical observations have been corrected for the contribution by the coma. The difference in amplitude between the optical and infrared could be due to incomplete correction for coma but could also be an effect due to the enhanced amplitude of a prolate spieroid in its thermal emission. Zero phase is 1988 June 9, 7.75 hr UT.
convex upward. Curvature of this type has been seen in some other comets and has been attributed to the effects of radiation pressure (Jewitt and Meech 1987) or evaporation of grains (Baum and Kreidl 1986). To explore the impact of possible curvature in the brightness profile of the coma, quadratic fits to the data in Figure 4 were performed. These fits yielded nuclear fluxes at maximum light $10 \%-50 \%$ smaller than deduced from the linear fits and. therefore, gave light curve amplitudes closer to that observed in the infrared. However, a reduced $\chi^{2}$ analysis indicates that the improvement in the quality of the quadratic fits over that of the linear fits is not signinicant. Accordingly, we see no compelling justification for adopting the quadratic fits in computing the contribution by the coma but allow for that possibility in our later discussion of the uncertainties.
An alternative explanation of the difference in amplitude berween the optical and IR light curves comes from the work of Brown (1985). Brown has shown that for elongated bodies, the ampiitude of the thermal signal will be a function of wavelength as well as aspect. Because we have only the $10.1 \mu \mathrm{~m}$ light curve for P/Tempel 2, we are unable to confirm whether this effect is actually present in this comet. If it is, then it is by no means clear that the optical and IR light curves should have the same amplitude. In addition to the variation of the thermal amplitude with wavelength, there is also the possibility that the nucleus does not have uniform albedo. In any case, it is important to emphasize that if the coma contribution has been underestimated, the result will be an overestimate of the albedo of the nucleus but, because the albedo turns out to be so low, the determination of the nuclear effective radius, which varies as $(1-A)^{-0.5}$, will be essentially unaffected.

## c) Emission by the Coma

The observations of the coma. aimed at deriving rates of outgassing of the various molecular species, had to be interspersed among the observations of the light curve. just as with the observations to measure the dependence of fux on aperture size. These observations were. therefore, much less complete than would have been the case if determination of the outgassing had been our primary goal. The only species measured with large fields of view were OH and CN , the former because it is the best measure of the total gaseous outtow and the latter because it is usually the easiest species to measure in comets. $C_{2}$ and $C_{3}$ were measured only in the 10.11 diameter aperture used for monitoring the variability. Of these, $C_{2}$ was measured numerous times because, if strong, it could contaminate the measurements of the continuum at $4845 \AA$. Fortunately, the emission by $C_{2}$ was weak enough that the contamination of the $4845 \AA$ fux in the 10 ". 1 aperture was negligible, although still strong enough that we were abie to detect the emission reliably with the filter centered on the emission band ( $5140 \AA$ ).

The observations of OH required special treatment because of the noniinearity of atmospheric attenuation with airmass in the filter used to isolate this band. The IHW has calculated models of the atmospheric attenuation in this filter (U. Carsenty, private communication) using the actual transmission curve of this filter, stellar and cometary spectra. and atmospheric parameters suitable for Mauna Kea. The extinction can be linearized for these specific conditions by using an effective airmass:

$$
\begin{aligned}
X_{\text {eff }} & =X-0.07257 \times X^{2}(B-\text { stars }) \\
X_{\text {eff }} & =X-0.0348 \times X^{2}(\text { comets }) \\
k_{\text {comet }} & =0.9234 \times k_{\mathrm{g}} .
\end{aligned}
$$

Conversion to fluxes, both for OH and for the other species. was carried out using the transformations provided by the IHW (see appendices to the Giacobini-Zinner archive. Sexanina 1989). These formulae require continuum measurements which are used to remove the continuum that underlies the emission bands. In all cases the measurements of the continuum were sufficiently close in time that no correction was needed for the rotational variation. The resultant fluxes in the emission bands are given in Table 4 below.

The dust in the coma was measured as a byproduct of the removal of the brightness of the coma from the nuclear brightness as described above. This process is subject to all the uncertainties discussed in the previous section to an even higher degree since the desired component is now the smaller of the two components being separated. A single measurement at $4845 A$ in an aperture of $56^{\prime \prime} 8$ is less susceptible to these problems (only $28 \%$ of the light was due to the nucleus) but even in this case the result is somewhat uncertain.

## III. MODELING AND INTERPRETATION

a) Coma

We interpret the observed emission-band fluxes in the coma in terms of molecular production rates as is common in cometary studies. The fluorescence efficiencies ( $g$-factors) used to convert fluxes to column densities are given in Table 3. The column densities are then converted to production rates using a Haser model with the parameters given in Table 3. From the abundances of OH , we also calculate the production rate of

- TABLE $3^{\circ}$
A. Haser Model Parameters

| Species | $\mathrm{L} / \mathrm{N}$ <br> $\left(\mathrm{erg} \mathrm{s}^{-1}\right)$ | Parent Scale <br> $(\mathrm{km})$ | Daughter Scale <br> $(\mathrm{km})$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{OH} \ldots \ldots$ | $8.23 \times 10^{-16}$ | $1.20 \times 10^{5}$ | $3.41 \times 10^{5}$ |
| $\mathrm{CN} \ldots \ldots$ | $1.16 \times 10^{-13}$ | $3.60 \times 10^{4}$ | $8.83 \times 10^{5}$ |
| $\mathrm{C}_{2} \ldots \ldots$ | $1.53 \times 10^{-13}$ | $4.71 \times 10^{4}$ | $3.24 \times 10^{3}$ |
| $\mathrm{C}_{3} \ldots \ldots$ | $3.39 \times 10^{-13}$ | $2.94 \times 10^{3}$ | $1.77 \times 10^{5}$ |

- At $r=1.72 \mathrm{AU}$.


## B. Vectorial Model Parameters

| $(\mathrm{H}, \mathrm{O})=82400 \mathrm{~s} \ldots \ldots \ldots$ | $\mathrm{r}(\mathrm{OH})=200.000 \mathrm{~s}$ |
| :--- | :---: |
| $\mathrm{r}(\mathrm{OH})=1.15 \mathrm{~km} \mathrm{~s}^{-1} \ldots \ldots$ | fraction $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{OH}=0.93$ |

$\mathrm{H}_{2} \mathrm{O}$ using a vectorial model (Festou 1981) with the parameters given in Table 3. For the species for which we have multiple measurements, there is no statistically significant variation with time so we have averaged all measurements to give an average production rate for June $10-11$ for a given aperture. These results are given in Table 4. An examination of the reiative abundances of the various gaseous species shows that the ratio of other species to $\mathrm{H}_{2} \mathrm{O}$ is somewhat lower than typical of active comets but not by a large factor.

The production of dust is given by the quantity Af $\rho$ (A'Hearn et al. 1984), a directly observable (i.e.. model independent) quantity which. for pure radial outflow at constant velocity and for constant scattering, is proportional to the production of those grains dominating the optical scattering. Since it was shown above that the coma was constant to within our precision, we quote only a single value for each aperture. A few measurements were made with a filter at $3650 \AA$ (see Table 5 below) through the 10 ". 1 diameter aperture but. as with $M$ and $Q$, there was not sufficient signal-to-noise ratio to separate the coma from the nucleus directly. On the other hand, these data cleariy show that the amplitude of the light curve at this wavelength is $\sim 0.7 \mathrm{mag}$, noticably greater than that found at longer optical wavelengths. These data will be discusssed in more detail below but, since all evidence points to a constant
coma, the amplitude suggests that the contribution by the coma is less than $20 \%$, thereby allowing us to set an upper limit on the brightness of the coma at this wavelength.

We note that all our models assume spherical symmetry whereas it is well known that the coma of P/Tempel 2 is not circularly symmetric (e.g., Sekanina 1987). In many cases the lack of spherical symmetry will not materially affect the conclusions since, e.g., a set of jets in the plane of the sky can be approximated by fractions of the spherically symmetric case. Deviations from spherical symmetry become systematically less important as the field of view increases and in the limiting case in which one observes the entire comet the discrepancies vanish. For this reason we place much heavier weight on the observations with the large ( 56.8 ) aperture. Temporal variability is not included in any of our models and one must remember that any " production rates" represent an average rate over some appropriate interval depending on the transmit time of material in the field of view and the lifetimes of the relevant species and their parents.

The ratio of gas to dust is conveniently parameterized by the ratio $Q\left(\mathrm{H}_{2} \mathrm{O}\right) / \mathrm{Af} \rho$. This ratio is independent of the effects due to the finite field of view of the instruments although it differs from the true ratio of gas to dust both by a conversion of units (Af $\rho$ has the units of cm ) and by parameters of the dust and the gas which may vary from time to time and from comet to comet. In particular, it varies with the wavelength of the light used to determine Af $\rho$ due to the variation of reflectivity with wavelength. Nevertheless, we believe that this is the most observationally reasonable parameter for monitoring the ratio of gas to dust. Feldman and A'Hearn (1985) showed that the parameter did exhibit a correlation with heliocentric distance, which might indicate a variation of the parameters of the models but might also indicate real physical differences with heliocentric distance. At a given distance. the comets considered there showed rather little scatter. Comet P/Halley exhibited significant variation with heliocentric distance and closer than 1 AU did deviate noticeably from the usual relationship with distance (Feidman et al. 1987). Typical values of this ratio in P/Halley are in the range $10^{25}$ to $10^{26}\left(\mathrm{~cm} \mathrm{~s}^{-1}\right)$ using ultraviolet light and these numbers would be very roughly $\frac{2}{3}$ that value if the continuum were measured at 4845

TABLE 4
Production of the Coma. June 10-11
A. Gas

A. Comets generally considered to be dust-poor, like P/Encke and Bradfield 1979 X . have values near $2 \times 10^{26}$ using the continuum at $4845 \AA$. The value for $P /$ Tempel 2 is $\sim 1 \times 10^{26}$ $(\mathrm{cm} \mathrm{s})^{-1}$. a very typical value for comets at this heliocentric distance. The only comet of which we are aware that exhibits a substantiaily higher value of this parameter is $\mathrm{P} /$ Neujmin 1 (CAM87) for which the dust was undetectable and for which we estimate a lower timit of $1 \times 10^{27}(\mathrm{~cm} \mathrm{~s})^{-1}$.

## b) Nucleus

The nucleus was modeled using the "standard" thermal modeling program described by Lebofsky et al. (1986) as in the previous modeling of comets $\mathrm{P} /$ Neujmin 1 (CAM87) and $\mathrm{P} /$ Arend-Rigaux (MAC88). The input parameters used were the following: thermal phase coefficient 0.01 mag degree ${ }^{-1}$, visible phase coefficient 0.035 mag degree ${ }^{-1}$, thermal emissivity 0.9 , and thermal beaming factor 0.9 . The visible phase coefficient is consistent with but not strongly constrained by the data at phases smaller than $30^{\circ}$ presented by Sekanina (1987, Fig. 11). None of the other coefficients are known for this or for any comet but are taken from the standard model for asteroids. Because the observations were made at a relatively small phase angle (see § II), the results of the model are not very sensitive to assumptions about phase coefficients. This type of thermal modeling is appropriate for comets that are relatively inactive, such as P/Tempel 2, because the amount of energy that goes into sublimation is negligible compared to the total incident radiation (CAM87). The calculated effective radius at maximum light, which depends only on the infrared measurements as long as the optical albedo is low, is $5.90_{-0.68}^{+0.24} \mathrm{~km}$. In this calculation a $10.1 \mu \mathrm{~m}$ mag at maximum light of 3.532 was used. This value includes the monochromatic correction of -0.043 mag for 270 K , given by Tokunaga (1986). The larger uncertainty toward smaller radii is due to the possibility that the coma contributes as much as $20 \%$ of the $10.1 \mu \mathrm{~m}$ flux at maximum light (see § II).

The axial ratios obtained from the amplitude of the visible light curve corrected for coma ( 0.55 mag ) and from the $10.1 \mu \mathrm{~m}$ light curve amplitude ( 0.80 mag ) were averaged to determine a minimum axial ratio for the nucleus of $1.9_{-0.2}^{+0.6}$; the larger uncertainty toward a more elongated nucleus is again due to the possiblity of a larger contribution by the coma. At the time of our observations, Earth was nearly in the equatorial plane of the comet according to the model of Sekanina (1987); if so, and assuming that the nucleus of this comet can be approximated by a prolate spheroid rotating about a minor axis, the observed light curve amplitude and effective radius are consistent with overall nuclear dimensions of $16.3 \times 8.6 \times 8.6 \mathrm{~km}$. The geometric albedo is 0.022 with an estimated uncertainty of ${ }_{-0.006}^{+0.004}$. The effects of departures from sphericity on the resuits of the standard thermal model have been discussed by Brown (1985). We estimate the error in the calculated effective radius introduced by ignoring sphericity to be $\pm 5 \%$. Brown's nonspherical thermal model predicts that the amplitude of the rotational light curve will be larger in the thermal infrared than in the visible. This effect could explain the different amplitudes observed in the visible and at $10.1 \mu \mathrm{~m}$; on the other hand, this difference could also be due to an incomplete removal of the coma contribution in the visible (see § II). A more refined analysis of our observations and those of MAC88 aimed at improving our knowledge of the shape of the nuclei of comets $P /$ Tempel 2 and $P /$ Arend-Rigaux is in progress.
The observations at $M(4.8 \mu \mathrm{~m})$ and $Q(20 \mu \mathrm{~m})$, presented in

TABLE 5
addimonal Thermal Data

| ADDITIONAL Thermal Data |  |  |
| :---: | :---: | :---: |
| UT <br> (hr) | $m$ <br> (mag) | $Q$ <br> (mag) |
| June $10:$ <br> $12.48 \ldots \ldots$ | 8.56 | $\ldots$ |
| $13.05 \ldots \ldots$ | $\ldots$ | 1.98 |
| June 11. |  |  |
| $07.60 \ldots \ldots$ | $\ldots$ | 2.34 |
| $08.98 \ldots \ldots$ | $\ldots$ | 1.99 |
| $09.63 \ldots \ldots$ | $\ldots$ | 1.73 |
| $10.25 \ldots \ldots$ | 8.28 | $\ldots$ |
| $10.72 \ldots \ldots$ | $\ldots$ | 1.94 |
| $11.58 \ldots \ldots$ | $\ldots$ | 2.13 |

Table 5, provide a check on the thermal modeling. Several measurements at $Q$ were made at different points in the light curve in search of possible temperature variations predicted by the nonspherical thermal model. We detected only statistically marginal $N-Q$ color variations; a mean $N-Q=1.85$ was observed, consistent with the brightness temperatures of 270 K at $N$ and 256 K at $Q$, predicted by the standard thermal model. The comet was considerably fainter at $M$, hence the fluxes in this bandpass were not as well determined as those for $Q$. Only single values for $M$ were obtained for each day near a maximum in the light curve: the resultant fluxes are slightly higher than predicted by the standard thermal model. This excess in the $M$ flux is qualitatively similar to that observed in comet P/Arend-Rigaux (MAC88), where a significant contribution ( $\sim 33 \%$ of the flux) from the dust was observed in the $M$ bandpass. In the case of comet P/Tempel 2, however, the signal was too weak to obtain reliabie aperture photometry in the $M$ filter to quantify the contribution by the dust coma at this wavelength.

The albedo of the nucleus derived here is an effective visual albedo but some additional information is available on the variation of albedo with wavelength. The narrow-band magnitudes given in Table 1 yield directly the color of the nucleus (averaging many values near maximum light), CI(48-$68)=m(4845)-m(6840)=1.20$ with rms scatter of the individual points of 0.05 mag , whereas the solar color in this system is 0.87 based on observations of solar analogs. The nucleus of comet P/Tempel 2 is therefore rather red, with reflectivity gradient, $(d s / d \lambda) / s=15 \%$ per $k A$. There is some indication of a difference in color between the two maxima of the light curve; averaging several points near the separate maxima in Table 1, we find $1.226 \pm 0.015$ and $1.157 \pm 0.014$ (error of the mean based on scatter) but the true error bars are larger than the error bars based on scatter because of systematic effects due to the removal of coma. The differences between the two maxima could be due to either a true difference in color between the two observed faces of the nucleus or they could be due to differences in the contribution by the coma. Combining all sources of error, the uncertainty in the color is 0.06 mag.
Although we have data at $3650 \AA$, we cannot reliably remove the coma from those data because the signal-to-noise ratio is inadequate. Our data for the combined nucleus and coma at four different times are given in Table 6. Uncertainties are $\sim 0.02 \mathrm{mag}$ at the two longer wavelengths. At $3650 \AA$. the uncertainty due to photon statistics on the comet and on the sky amounts to 0.07 mag . Other errors, including extinction and the transfer to standard stars. combine quadratically with

TABLE 6
Color of P/Tempel 2*

| Date UT | $m(3650)$ <br> $(\mathrm{mag})$ | $m$ (4845) <br> $(\mathrm{mag})$ | $\mathrm{Cl}(36-48)$ <br> (mag) | $\mathrm{Cl}(48-68)$ <br> (mag) |
| :---: | :---: | :---: | :---: | :---: |
| Jun $10.475 \ldots \ldots$. | 16.97 | 15.90 | 1.07 | 1.20 |
| Jun $11.333 \ldots \ldots$. | 17.56 | 16.23 | 1.33 | 1.15 |
| Jun $11.404 \ldots \ldots$. | 16.73 | 15.82 | 0.91 | 1.08 |
| Jun $11.471 \ldots \ldots$. | 17.36 | 15.97 | 1.39 | 1.11 |
| Solar color $\ldots \ldots$. | $\ldots$ | $\ldots$ | 1.17 | 0.87 |

- 10 "1 aperture.
this and imply a total error of no more than 0.09 mag. The color index between 3650 and 4845 A , however, varies from bluer than the sun at maximum light to slightly redder at minimum light. Since all data at longer wavelengths imply that the coma is constant, and since the amplitude at $3650 \AA$ is 0.7 mag (averaging the two maxima and comparing with the single minimum), significantly greater than at longer optical wavelengths, we conciude that the contribution by the coma at maximum light is less than $20 \%$. We can therefore set a lower limit to the nuclear brightnesses at the two maxima: $m_{\mathrm{nuc}}(3650)<17.21$, 16.97. This yields colors $\mathrm{CI}(36-48)$ $=m(3650)-m(4845)<1.01,0.82$ compared to the corresponding solar color of 1.17 , i.e., much bluer than the Sun. It should be noted that the bluer of the two colors occurs during the same maximum during which the other color index, $\mathrm{Cl}(48-68)$, is less red than the average.

In Figure 6 we have plotted our data for the two maxima separately. The error bars on our data do not include all the uncertainty in the subtraction of coma because a portion of that uncertainty (the choice between linear and curved profiles) is coherent between the two filters at the longer wavelengths. Although the brightness at 4845 and $6840 \AA$ might be significantly fainter than we have deduced if indeed the profile of the coma is curved. the effect is comparable in the two filters so that the uncertainty in the color is only marginally increased. On the other hand, we believe that we have removed the maximum possible amount of coma from the data at $3650 \AA$, suggesting that the error bars for those two points might be extended upward significantly. The error bars for the data from Spinrad, Stauffer, and Newburn (1979) are taken directly from their paper. The agreement between the observations of Jewitt and Luu (1989), of Spinrad et al., and of ourselves at 4845 and $6840 \AA$ is very good. Note that the data of Spinrad et al. show
fine structure which results from combining data taken on two different observing runs at slightly different wavelengths. This is also easily understood if opposite faces of the nucleus have different colors as suggested by our data.
The very red color at visible wavelengths is characteristic of both $S$ asteroids and the reddest $D$ asteroids (although $S$ asteroids have much higher albedos than does comet $\mathrm{P} /$ Tempel 2 ), and it is among the reddest cometary nuclei measured (Weissman et al. 1989). At our shortest wavelength, our results are consistent with those of Spinrad et al. in showing a significant increase of reflectivity giving some confidence that the result is not spurious. This result, if it truly refers to the nucleus and not to some very blue dust in the coma. makes the nucleus of comet P/Tempel 2 very unusual. The only other object in the solar system which shows this behavior is comet $P /$ Schwassmann-Wachmann 1, for which the albedo clearly does not decrease at these wavelengths but which may be fiat rather than increasing. Other objects do seem to have albedos which increase in the ultraviolet beyond $3000 \AA$ but no others increase in this spectral range. We do not wish to discuss explanations for this effect in detail, however, because it is still possible that the blue color arises from a very large population of very blue, perhaps Rayleigh scattering, particles in the coma which vary with the rotation of the nucleus.

It is also significant that the color of the nucleus is quite different from the color of the grains in the coma. Examination of Table 4 shows that the grains in the coma have a very neutral color, whereas the nucleus is distinctly red except at the shortest wavelengths. Jewitt and Luu (1989) have reached a similar conclusion based on their long-slit spectra of the comet. There is no way of determining, from either our data or those of Jewitt and Luu, whether the difference is due to selective ejection of grains or to differences in scattering properties between the grains on the optically thick surface and grains in the optically thin coma.

We can combine the outgassing rate observed in the coma and the size of the nucleus to estimate the fraction of the surface of the nucleus which is active. Determination of that fraction of the surface of the nucleus which is active. Determination of that fraction depends. of course, on where the active area is on the nucleus since that determines the effective insolation. We have used the methods described by Cowan and A'Hearn (1979) to estimate the outgassing of water molecules per unit area for an isothermal nucieus (rapid rotation and high thermal conductivity), for a model which is everywhere in


Fic. 6.-Spectral refectivity of the nucleus of comet P/Tempel 2. Data from Spinrad et al. (1979) and from Jewitt and Luu (1989) as well as from the present work. See text for discussion of error bars and possible differences between the two faces of the nucleus.
local equilibrium (low thermal inertia), and for a model in which parallels of latitude are isotherms (rapid rotation). The range of rates of outgassing is from $2 \times 10^{16}$ to $5 \times 10^{17} \mathrm{~cm}^{-2}$ $\mathrm{s}^{-1}$. According to the nuciear model of Sekanina (1987), the vent is at a high cometographic latitude. For this latitude and obliquity $90^{\circ}$ and each latitude line being an isotherm. a typical rate of outgassing would be of order $3 \times 10^{16} \mathrm{~cm}^{-2} \mathrm{~s}^{-1}$. This is a lower limit to the outgassing per unit area since concentration of the heating to the daytime side nonlinearly increases the outgassing so that the average over the day is higher. Thus if the outgassing is from a single active vent vaporizing in equilibrium, its maximum area is $11 \mathrm{~km}^{2}$ or $3 \%$ of the total surface. Much smaller areas are likely since the outgassing per unit area increases if the active area is more nearly normal to the direction to the Sun or if a latitude line is much hotter on the dayside than on the nightside as we would expect. It is clear from this discussion that comet $\mathrm{P} /$ Tempel 2 , like comets $\mathrm{P} /$ Arend-Rigaux and $P /$ Neujmin 1, has an almost totally inactive nucleus. The fraction of the surface which can be active in all three comets is at least an order of magnitude less than the fraction for $P /$ Halley which itself has activity from no more than $30 \%$ of the surface (based on $15 \%$ in the sunlit hemisphere and an assumed comparable area on the dark hemisphere).

We also note that the geomerry of Sekanina's model predicts that the vent should be alternating between daylight and darkness at the time of our observations so that some variability might be expected (Sekanina 1988). Because the lifetimes of $\mathrm{H}_{2} \mathrm{O}$ and OH are both longer than the rotational period of the nucleus, the observed variation will be much less than the true variation in outgassing. A variation of the outgassing from one day to the next has been reported (A'Hearn et al. 1988) and will be discussed in more detail elsewhere. On the other hand, the constancy of the coma contributed by the dust argues against significant fluctuations in the outgassing unless the velocity of the dust leads to a transit time in our aperture much longer than the rotational period. If the velocity of the dust was less than $0.1 \mathrm{~km} \mathrm{~s}^{-1}$ this would be the case. and we should not see significant fluctuations.

The combination of the red slope of the reflectivity at long optical wavelengths with a possible increase in the near ultraviolet is unusual. The only similar curve of spectral reflectivity for a small body of which we are aware is that of comet $\mathrm{P} /$ Schwassmann-Wachmann 1 (S-W1). Although we cannot be sure that at quiescent phases the bare nucleus of this comet is visible, such a situation is often advocated and seems not unreasonable. Cochran, Cochran, and Barker (1982) measured the reflectivity of S-W 1 in its quiescent phase (mag $\sim 18.5$ ) and found a reflectivity similar to that of $\mathrm{P} /$ Tempel 2 , red at the longer optical wavelengths and gray or possibly bluish shortward of $4000 \AA$. Also as for P/Tempei 2. they found that the

TABLE 7
Summary of Nuclenr Properties

| Property | Value |
| :---: | :---: |
| $R_{\text {eff }} \ldots \ldots \ldots \ldots \ldots \ldots \ldots$ | 5.9 km |
| P .................... | 8.9 hr |
| $p_{1}$, $\ldots \ldots \ldots \ldots \ldots \ldots \ldots .$. | 0.022 |
| $\mathrm{T}_{\mathrm{B}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. | 270 K |
| Axial ratio ............ | $>1.9$ |
| Active fraction ........ | <3\% |
| Prolate spheroid ...... | $16.3 \times 8.6 \times 8.6 \mathrm{~km}$ |

coma of S-W 1 (measured during a subsequent outburst) was of a different color. The two comets are not, however, identical since the albedo of S-W1 was found by Cruikshank and Brown (1983) to be 0.13 , very much higher than found here for P / Tempel 2.

The reflectivities of these two comets appear unlike those of any standard types of asteroids. They are aiso significantly different from the reflectivities of other recently measured cometary nuclei: P/Neujmin 1 (CAM87) was very red even at the shortest wavelengths; P/Arend-Rigaux (MAC88) was almost neutral in color; P/Halley (Thomas and Keller 1989) was significantly less red at optical wavelengths. These other comets are similar in visual albedo and axial ratio and show a range of active surface fractions including the fraction found above for P/Tempel 2. The present results for P/Tempel 2 thus support the contention that cometary nuclei form a diverse group with no clear-cut match among the AAA asteroids:

We note finally that the results found here bear on models of cometary nuclei. Our results are generally consistent with the model of Sekanina (1987) in regard to the polar orientation and the general geometric description of the outgassing as being from a vent at high cometographic latitude. The combination of these results with similar results on the fraction of the surface which is active on other cometary nuclei qualitatively supports the widely discussed picture involving a mantle which gradually builds up on the surface of the nucleus. thereby choking off the vaporization.

## IV. SUMMARY AND DISCUSSION

Simultaneous photometry at infrared and optical wavelength has ailowed us to determine the albedo. size. and projected shape of the nucleus of comet P/Tempel 2. In gross size and shape it appears to be neariy identical to the nucleus of $\mathrm{P} /$ Halley, a prolate spheroid with axes $16 \times 8 \frac{1}{2} \times 8 \frac{1}{2} \mathrm{~km}$. The nucleus of $\mathrm{P} / \mathrm{Tempel} 2$ differs from that of $\mathrm{P} / \mathrm{Halley}$ in that the active portion of the surface is much less on P/Tempel 2. of order $1 \%$ as opposed to an estimated $15 \%-30 \%$ for P/Halley. The rotational period of $P /$ Tempel 2 's nucleus is near 9 hr , the second shortest of the photometrically determined rotationai periods for comets. The outgassing and the changes around the orbit (1987-88) in the observed amplitude of the rotational modulation appear to be consistent with the nuclear model for this comet by Sekanina (1987) given that Sekanina (1988) has already pointed out that the nucleus is likely prolate rather than oblate. The spectral reflectivity of the nucleus is red in the optical. but there is a suggestion that in the ultraviolet the reflectivity increases toward shorter wavelengths. In the optical the redness is significantly greater than for $\mathrm{P} /$ /Halley and comparable to the reddest of the other cometary nuclei measured and $S$ as well as the reddest $D$ asteroids. The increase at ultraviolet wavelengths, if real. is similar only to that seen for $\mathrm{P} /$ Schwassmann-Wachmann 1.

Observations of the nuclei of several periodic comets in recent years have shown that they are ail dark and usually very aspherical. This is consistent with simple models for the growth - of nuclei as fractal bodies by random accretion (Donn and Hughes 1986: Jewitt and Meech 1988). Furthermore, most of the surface is inactive on the nuclei of all periodic comets for which the relevant data exist. There is a selection effect in this conclusion because nuclei active over their entire surface are much harder to detect inside the coma. Nevertheless, a picture of gradual development of a mantle culminating in extinction of activity qualitatively firs all the available data on cometary
nuclei. It is still premature to make statements regarding the distribution of sizes or rotational periods because the sampie of objects is too small and, at least as far as sizes are concerned, subject to very strong selection effects. Finally, it seems clear that nuclei differ significantly from one another in their spectral reflectivity. Although there are many spectral similarities to $D$ and $C$ asteroids, no pattern is yet clear in the reflectance spectra of cometary nuclei. For this reason, there is as yet no physical connection that can be directly established between cometary nuclei and Aten-Amor-Apollo asteroids.

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REFERENCES

A'Hearn. M. F. 1988, Ann Rev. Earth Planet. Sci. 16, 273.
A'Hearn. M. F. Feldman, P. D., Roettger, E., and Schleicher, D. 1988. IAU Circ. No. 4622.
A'Hearn. M. F. Schleicher. D. G., Feldman, P. D., Millis, R. L., and Thompson. D. T. 1984, A.J. 89, 579.
Baum, W. A., and Kreid. T. J. 1986, in Asteroids, Comets. Meteors II, ed. C.-I. Lagerkvist. B. A. Lindbald. H. Lundstedt, and H. Rickman (Uppsaia: Uppsala Universitet), p. 397.
Brown. R. H. 1985, Icarus, 64. 53.
Campins. N. A'Hearn. M. F., and McFadden, L.-A. 1987, Ap. J. 316, 847 (CAM87).
Cochran. A. L. Cochran. W. D., and Barker, E. S. 1982 Ap. J.. 254.816.
Cochran. A. L.. Cochran, W. D., and Barker, E. S. 1982 A Ap. J., 254,
Cowan. J. J.. and A'Hearn. M. F. 1979 , Moon and Planets, 21, 155.
Cowan. J. J.. and A'Hearn. M. F. 1979, Moon and Planets,
Cruikshank. D. P., and Brown. R. H. 1983. Icarus. 56.377.
Donn. B.. and Hughes. D. 1986. in Exploration of Hailey's Comet, Voi. 3. ed.
B. Battrick. E. J. Rolfe. and R. Reinhard (ESA SP-250), p. 523.

Fay, Jr.. T. D., and Wisniewski. W. 1978. Jcarus. 34. 1.
Feidman. P. D., and A'Hearn. M. F. 1985, in Ices in the Solar System. ed.
J. Klinger, D. Benest, A. Dolifus, and R. Smoluchowski (Dordrecht: Reidel), p. 453.

Feldman. P. D. et al. 1987, Astr. Ap., 187. 325.
Festou. M. C. 1981 , Astr. Ap., 95.69.
Jewith. D.. and Luu. J. 1989, A.J., 97, 1766.
Jewitt. D. C., and Luu. J. 1988, IAU Circ., No. 4582.

Jewitt, D. C. and Meech, K. J. 1987, Ap. J., 317, 992.
L-be. 1988, Ap.J. 328, 974.
Leboisky, L. A., et al. 1986, Icarus. 68, 239.
Marsden, B. G. 1985, in Dynamics of Comets: Thier Origin and Evolution ed. A. Carusi and G. B. Valsecchi (Dordrecht: Reidel), p. 343.

Millis. R. L., A'Hearn, M. F., and Campins, H. 1988, Ap. J., 324, 1194 (MAC88).
Opik, E. J. 1963, Adv. Astr. Ap., 2, 219.
Sekanina. Z. 1979, Icarus, 37, 420.
-_-1987, in Symposium on the Diversity and Similarity of Comets. ed. E. J. Roife and B. Batrick (ESA SP-278), p. 323.

- 1988. IAU Circ. No. 4624.

ROM \# USA-NASA-IHW-GZ-0001 Test Disc, NASA Disc, NASA CD ROM \# USA-NASA-IHW-GZ-0001.
Spinrad.H_Stauffer, J., and Newburn. Jr.. R. L. 1979, Pub. A.S.P., 91, 707.
Stellingwer. R. F. 1978, Ap. J. $224,953$.
Thomas, N. and Keller, H. U. 1989, Astr. Ap., in press.
Tokunaga. A. T. 1986 . Photometry Manual, NASA Infrared Telescope Facility.
Weissman. P. A'Hearn. M. F.. McFadden. L.-A.. and Riciman. H. 1989 in Asteroids M. ed. R. Binzel and M. S. Matthews (Tucson: University of Arizona Press), in press.
Wetherill. G. W. 1988. Icarus, 76. 1.
Whipple. F. L. 1950. Ap. J.. 111. 375.
Wisniewski, W. 1988. IAU Circ. No. 4603.


[^0]:    'This work is independently funded by NASA Code XEU.

[^1]:    - Plasma reduction process unproven technology
    - Electrical energy utilized
    - Problems in handling and storage of hydrogen

[^2]:    *All future experiments will be conducted with either $\mathrm{N}_{2}, \mathrm{Cl}_{2}$, or a mixture of these gases. Nitrogen produces a more stable plasma than can be achieved with Ar.

[^3]:    ${ }^{\text {a Signal }}$ intensity is time averaged and corrected for background $\mathrm{O}_{2}$ signal.
    b $10 \% \mathrm{Cl}_{2}$.

[^4]:    *See Appendix C.

[^5]:    ${ }^{\text {a A }} 12 \mathrm{Icb}$ has lower initial Fe and Si and a higher applied potential than A 121. Metal in $\overline{\mathrm{A}} 121$ is nearly pure Fe (the low totals $<100 \%$ is likely due to oxidation of the Fe during quenching of the experiment). Metal in A 121 cb contains significant $\mathrm{Si}, \mathrm{Ti}$, Cr , and possibly Mn. The presence of Ir in metals of ${ }^{-}$A12 1 cb is due to use of Ir as the cathode material. Otherwise, the compositions correspond to the phases $\gamma-\mathrm{Fe}, \alpha-\mathrm{Fe}$, and melt in the system $\mathrm{Fe}-\mathrm{Si}$. Spinel grains were too small to analyze and, therefore, the analyses of spinel include glass as well. In the case of A12 1cb, the glass constitues the major portion of the analysis. Spinel in $\mathrm{A} 12 \_1$ is $\mathrm{Fe}-\mathrm{Cr}^{-}$rich; spinel in A 12 _1cb is apparently $\mathrm{Mg}-\mathrm{Al}$ rich.

[^6]:    *See Appendix E.
    " See Appendix F.

[^7]:    ${ }^{\text {a }}$ These numbers represent the total effects of all the factors. They have not been reviewed individually as yet.

[^8]:    Acknowledgments
    The authors are grateful to Steve Hartman for support and the Advisory Committee of the Center for constructive criticisms on an earlier version of this study.

[^9]:    WEHI ORMARCE WARAMEIERS
    AE／AT
    AE／AI
    CSIAR，II／AIC
    CF
    IVAC．IB－SEC／LB
    ISO．I．B－SEC／IB

[^10]:    

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[^12]:    *The term "magma e!ectrolysis" is catchy (e.g., du Fresne and Schroeder (1983); because to geoscientists the term "magma" indicates naturaily occurring meits. we generaily use the term "molten silicate electrolysis."

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[^14]:    4 An updated version of the orbital light curve. including data from the apparition of 1983, was widely distributed by the International Halley Watch

