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Innovative Techniques for The Production of Energetic Radicals for Lunar Processing Including Cold Plasma Processing of Local Planetary Ores

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Abstract

Hydrogen reduction of ilmenite has been studied by a number of investigators as a potential means for recovery of oxygen from lunar soil. Interest in this process has always rested with the simplicity of the flow diagram and the utilization of established technology. Effective utilization of hydrogen in the reduction process at temperatures of 1200 °C and below has always been disappointing and, as such, has led other investigators to focus attention on other systems.

Effective utilization of hydrogen in the reduction of ilmenite can be significantly enhanced in the presence of a non-equilibrium hydrogen plasma. Ilmenite at solid specimen temperatures of 600 °C to 970 °C were reacted in a hydrogen plasma. Those experiments revealed that hydrogen utilization can be significantly enhanced. At a specimen temperature of 850 °C the fraction of H_2 reacted was 24% compared to the 7% theoretical limit calculated with thermodynamic theory for the same temperature.

An added advantage for a hydrogen plasma involves further reduction of TiO_2. Reduction of the iron oxide in ilmenite yields TiO_2 and metallic iron as by products. Titanium forms a number of oxides including TiO, Ti_2O_3, Ti_3O_5 and the Magneli oxides (Ti_4O_7 to $Ti_{50}O_{99}$). In conventional processing of ilmenite with hydrogen it is possible to reduce TiO_2 to Ti_7O_{13} within approximately an hour, but with poor utilization of hydrogen on the order of one mole of H_2 per thousand. In the cold or non-equilibrium plasma TiO_2 can be rapidly reduced to Ti_2O_3 with hydrogen utilization exceeding 10%. Based on design considerations of the plasma reactor greater utilization of the hydrogen in the reduction of TiO_2 is possible.
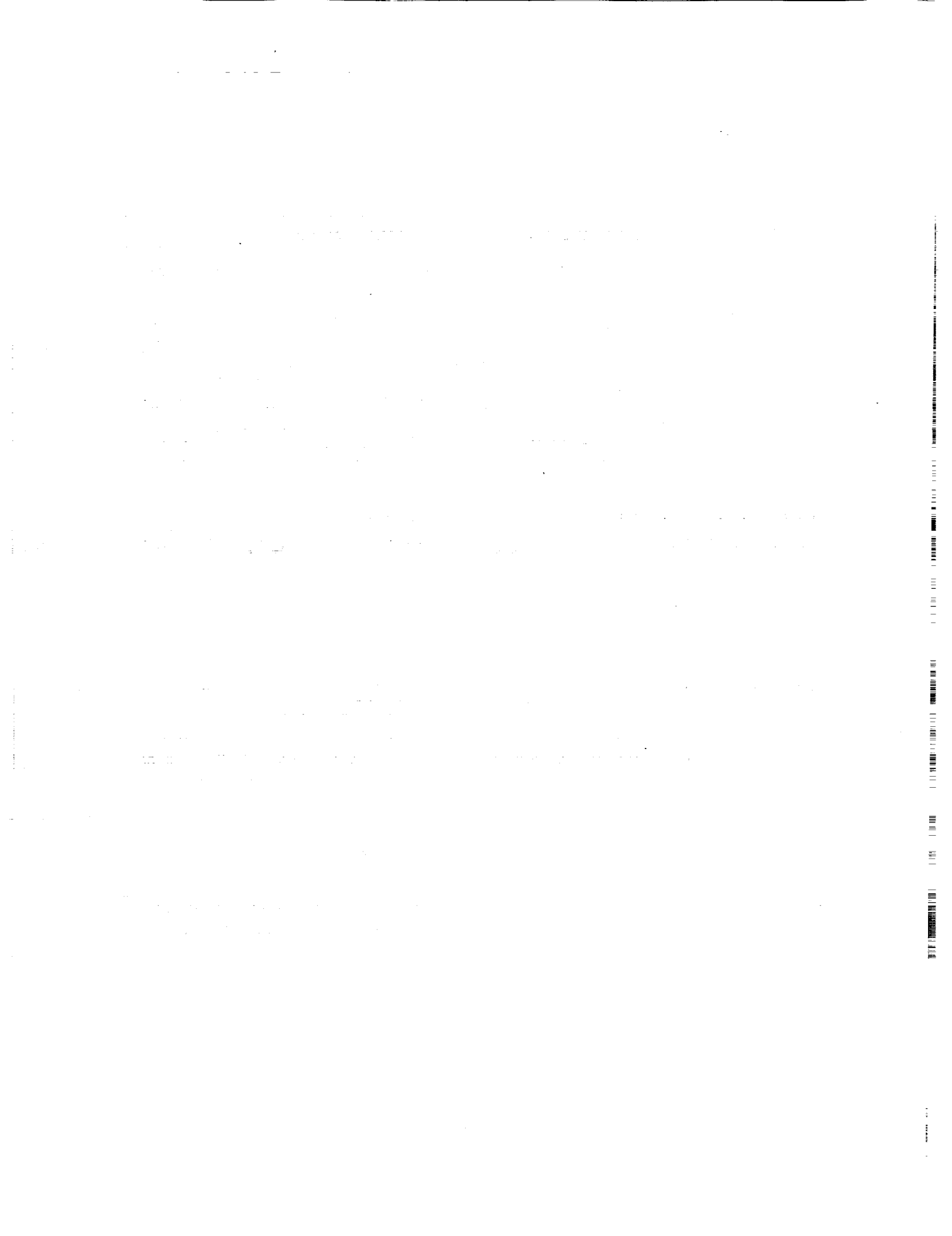
Introduction

The most attractive source of lunar oxygen from energy considerations is that associated with iron in the mineral ilmenite, $FeO \cdot TiO_2$. Investigators in their efforts to recover that oxygen, have primarily focused their attention on H_2, CO, and C reduction of the mineral. Carbon is a highly effective reducing agent. However, processes based on solid carbon are more complex than those involving H_2 and CO. While processes based on H_2 and CO are simpler, the thermodynamic equilibrium limits effective use of those reducing agents.

That limit, however, can be surpassed with the aid of electromagnetic energy in the form of a non-equilibrium plasma. It is not that the restrictions of thermodynamics are violated, but that the system be viewed as consisting of separate parts whose thermodynamic parameters can be adjusted separately. In a plasma-solid reactor there are atoms bound in the solid reactant, gaseous molecules, and free electrons all of which can have different temperatures. Electrons accelerated by a high frequency electro-magnetic field have temperatures between 10,000 to 40,000 K. Charged molecules, because of their mass, cannot respond to the applied high frequency radiation. In addition, physical procedures for transferring energy between free electrons and molecules in a cold plasma are inefficient. As a result, the cold plasma consists of high temperature electrons and molecules (including positive ions) at temperatures only a few hundred degrees above ambient temperature.

Reaction Chemistry -- In conventional heating reduction of ilmenite involves the reactions,

$$FeO \cdot TiO_2(s) + H_2(g) = Fe(s) + TiO_2(s) + H_2O(g) \tag{1}$$

$$TiO_2(s) + XH_2(g) => TiO_{2-x}(s) + XH_2O(g) \tag{2}$$
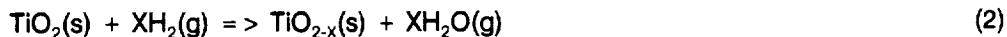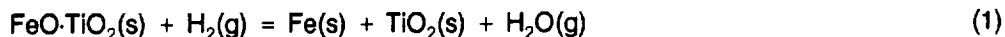
condensation and then electrolysis of the H_2O for release of the oxygen and recycle of the hydrogen as shown in *Figure 1*. The thermodynamic equilibrium for reaction 1 is represented graphically in *Figure 2*, where it can be seen that at 500°C the fraction of hydrogen that can be reacted amounts less than 1%. That percentage grows to only 15% at 1200 °C. In conventional processing the practical value of X that can be achieved in reaction 2 is 0.15.

In a non-equilibrium plasma both diatomic and monatomic hydrogen are available for reaction. The latter is formed as a result of inelastic collisions between H_2 and energetic electrons and positive
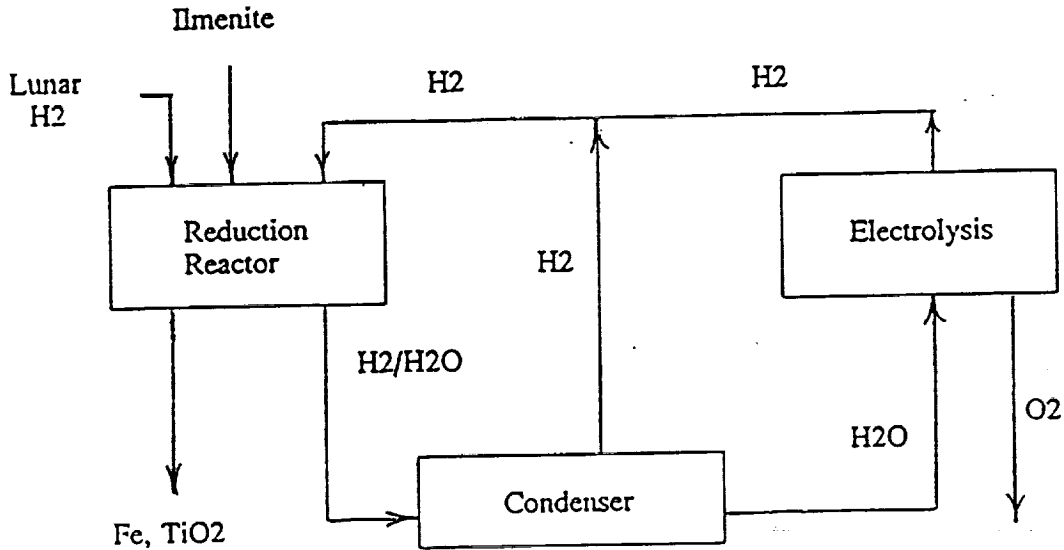
Figure 1.   Schematic Design of System for Recovery of Oxygen From Lunar Regolith Using Hydrogen Reduction
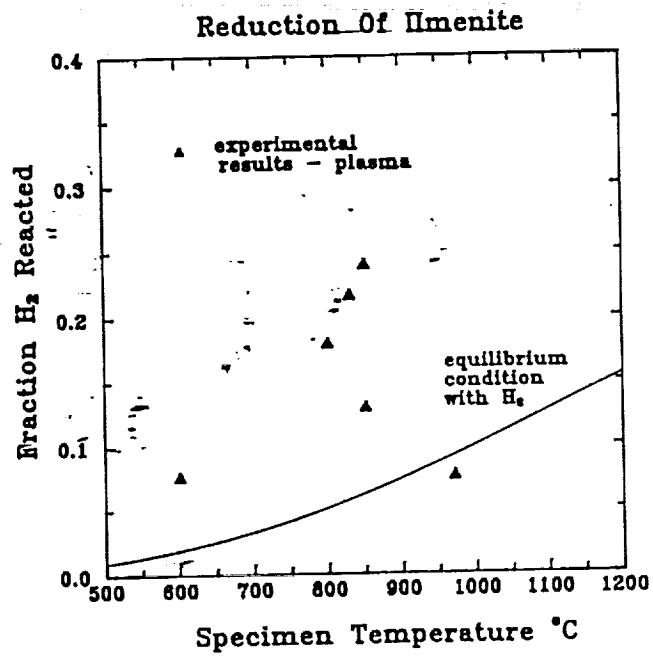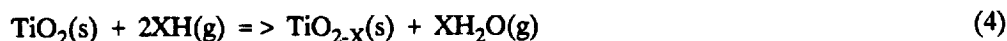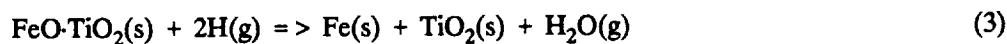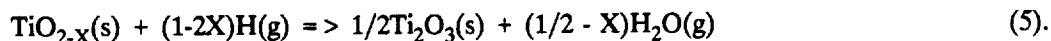

Figure 2.   Representation of the thermodynamic equilibrium for both the thermal and plasma processing of ilmenite. Thermal processing makes use of only a fraction of the hydrogen present, while plasma processing theoretically allows nearly 100 percent of the hydrogen available for reaction. The actual experimental results achieved with the plasma are indicated.

Ions. The latter are accelerated through the Debye sheath that surrounds the ilmenite particles. Reduction of ilmenite in a plasma follows the following sequence of reactions:

$$FeO \cdot TiO_2(s) + 2H(g) \Rightarrow Fe(s) + TiO_2(s) + H_2O(g) \tag{3}$$

$$TiO_2(s) + 2XH(g) \Rightarrow TiO_{2-X}(s) + XH_2O(g) \tag{4}$$

and

$$TiO_{2-X}(s) + (1-2X)H(g) \Rightarrow 1/2Ti_2O_3(s) + (1/2 - X)H_2O(g) \tag{5.}$$

Reactions 1 and 2 also occur as a result of sample heating. An additional 30% of oxygen can be recovered with the plasma in comparison to that achieved with conventional heating. Moreover it can be recovered in a substantially shorter period.

Experimental

The effectiveness of a cold plasma for reducing ilmenite and TiO_2 has been tested in the apparatus shown in *Figure 3*. That apparatus consists of a microwave generator which emits microwaves at 2.45 GHz along a waveguide to the applicator where solid specimens are reacted in a hydrogen plasma. A specimen is rotated during an experiment to ensure even heating. A mass spectrometer has been used to follow the rate at which water vapor is evolved, and to quantify results. X-ray diffraction (XRD) analysis was used to both identify solid products and quantify the extent of their formation.

Ilmenite reacted in a hydrogen plasma yielded improved efficiency in hydrogen utilization. As noted earlier, the extent of reaction 1 is thermodynamically limited. That is not the situation with reaction 3. The high chemical potential of monatomic hydrogen pushes reaction 3 to the right, the theoretical limit being near complete consumption of the hydrogen, as shown in *Figure 2*. Ilmenite reacted at a specimen temperature of 850 °C yielded hydrogen consumption rates of 13 to 24%. That value is substantially better than the 6% predicted in *Figure 2* for conventional heating at 850 °C. The enhanced utilization has been achieved even thou#h the reactor is not specifically designed for extensive interaction between the specimen and the plasma. Utilization of a fluidized bed reactor should improve plasma-solid contact.
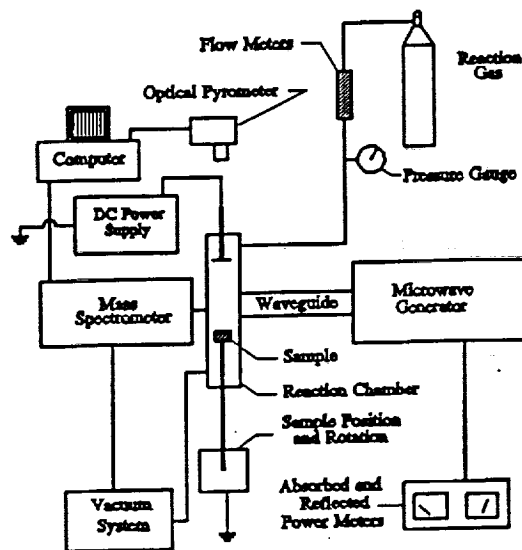
Figure 3.   Schematic of the plasma processing system. The sample holder can be directly inserted into the XRD for analysis of the solid product layer.
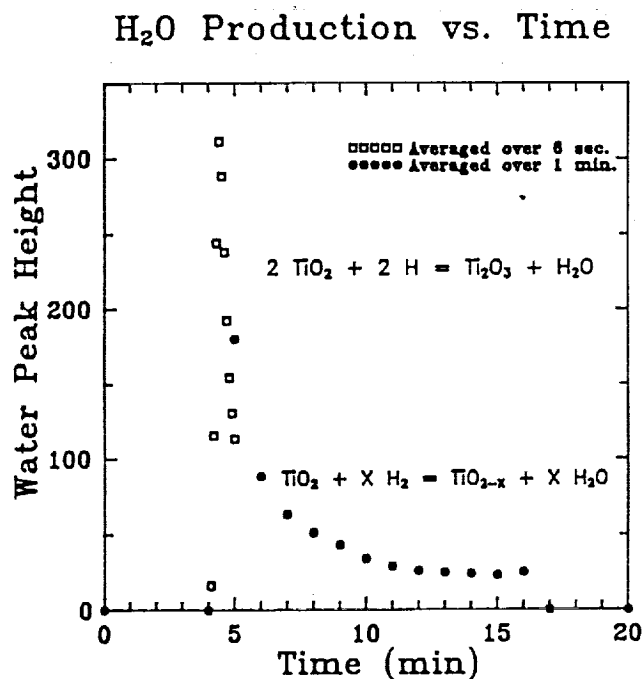

H₂O Production vs. Time

Figure 4.   A plot of the H_2O signal from the mass spectrometer as a function of reaction time. This signal is characteristic of a surface reaction.

Plasma-solid contact has to do with the Debye sheath than actual physical contact between the ilmenite and the plasma. Non-conducting particles and insulated particles in a high frequency plasma become negatively charged due to the mobility of the electrons. The electrons responding to the field are accelerated quickly as a result of their small mass. Some of those electrons will impact solid particles and since they are more mobile than the positive ions a negative charge builds up on the surface of the particle. The resulting potential difference between the particle and the plasma is referred to as the Debye sheath. Positive ions that enter the sheath due to random thermal motion are accelerated toward the particle surface where they can break bonds and thereby enhance reaction rates.

Achieving the appropriate conditions across the Debye sheath is not always reproducible. The wide variation in the fraction of hydrogen reacted at 850 °C and the low value at 970 °C is attributed to this condition. The fraction of hydrogen reacted at 970 °C is slightly less than the equilibrium condition for that temperature. It is suspected at that temperature that the low fraction of hydrogen reacted is associated with improper conditions at the sheath and thus the impact of the plasma is not experienced.

Experimentally it has been determined that the presence of a ground in the system has a significant impact on the Debye sheath and the acceleration of ions across the sheath. The extent of the impact of the ground has been demonstrated with the reduction of TiO_2. Selection of that compound is based on the fact that ilmenite can be reduced with both H_2 and H, whereas TiO_2 is only reduced in significant amounts with monatomic hydrogen. Use of TiO_2 allows us to evaluate the role plasma variables (pressure, power absorption, "etc.) have on the Debye sheath and the reduction process.

Figure 4 indicates that water vapor is evolved instantaneously with ignition of the plasma. Evolution of water peaks within the first minute of reaction, and then decreases to a steady state value after approximately 8 minutes. At the peak the mole fraction of water is on the order of 10 mole percent. At the same time the surface of the specimen changes from white (TiO_2) to black. The black product extends to a depth of 1 mm and is characteristic of both Ti_2O_3 and TiO_{2-x}.

XRD analysis of the solid product revealed it to be principally Ti_2O_3 with some residual TiO_2. The spectra for both of these phases showed excellent agreement with the standard spectra. Quantitative XRD analysis revealed that up to 60% of the specimen surface, to a depth of 5 l m, was converted to Ti_2O_3, as shown in *Figure 4*. Notice that in that figure the volume fraction of Ti_2O_3 remains constant with time. That information, coupled with the results in *Figure 4*, suggest that the

conversion of TiO_2 to Ti_2O_3 is complete after 8 minutes. According to reaction 2, the weight fraction of TiO_2 continues to decrease with time due to the continued production of TiO_{2-x}. The sum of the volume fractions in *Figure 5* do not add up to one at any specific time because experimental evidence indicates that TiO_{2-x} is amorphous.

A plasma and solid must have contact in order for a plasma-solid reaction to take place. Confinement of the black product layer to the surface in contact with the plasma strongly suggests that effective use of the plasma will require design of a reactor that has greater spacing between particles. A plasma cannot form or be maintained in the interstices of a powdered specimen if particles are too close because the sheaths overlap. A fluidized bed reactor is under construction to overcome this problem.

Energy Considerations

Energy, and in particular electrical energy, will be limited on the Moon and must be used effectively. A microwave-induced plasma is energy efficient. Energy in the form of electromagnetic radiation must be continuously applied to maintain the plasma. The efficiency of converting DC current to microwaves is reported as high as 90.4% at optimum conditions and 84% for extended periods. The plasma is highly efficient in the absorption of microwaves, with efficiencies approaching 100%. The extent to which the energy in the plasma can be utilized in chemical reaction is still under investigation.

Concluding Remarks

Processing of lunar regolith with a plasma offers more than just an increase in the amount of oxygen recovered per mass of soil. It offers a chemistry that can be used with both refractory and easily reduced oxides. In the case of the former the reduction process involves oxides that can be reduced to suboxides, such as TiO_2, Al_2O_3, and SiO_2. As a result, it may be possible to use the regolith without beneficiation.

Another advantage of cold plasma processing is that the only consumable resource is the electricity used to maintain the plasma. As the reactant, hydrogen can be recovered by electrolysis and any losses can be made up with lunar hydrogen.

An additional advantage of cold plasma processing involves reactor life and safety issues. Enhanced

reaction rates at reduced temperatures reduces thermal degradation of the containment vessel. An applied magnetic field to contain the plasma can eliminate chemical attack of the vessel by ions and radicals. In an emergency, the reduction process can be brought to a halt with the extinguishing of the plasma by eliminating electrical power, or either reducing or increasing the pressure.
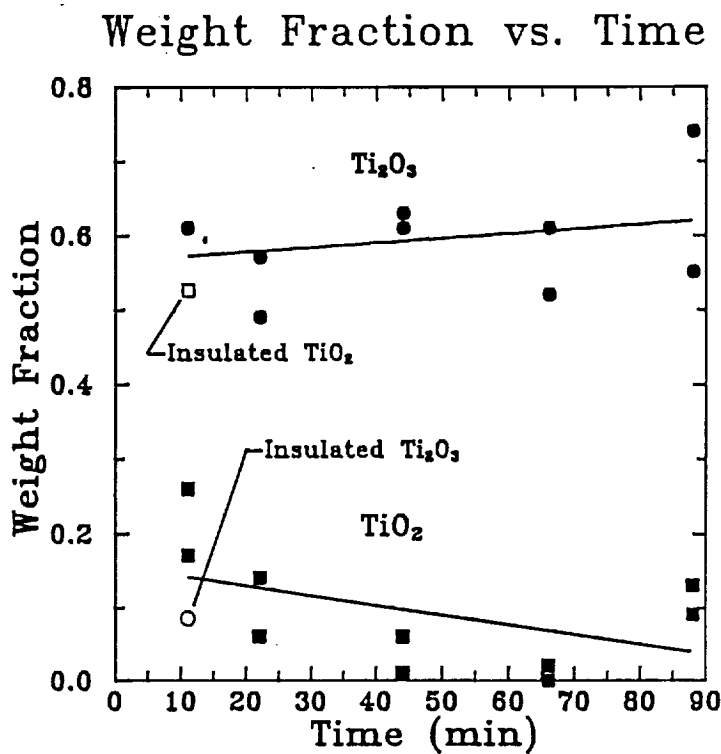
Weight Fraction vs. Time

Figure 5.   The production of Ti_2O_3 appears to be over after 8 minutes of reaction, while depletion of TiO_2 continues for longer periods. The data points labeled "Insulated" indicate the importance of a ground in the system in order the reaction to proceed.