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"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 $TiCl_4$ 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 by-products.

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.

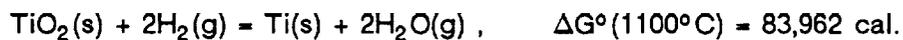
The advantages associated with a "cold" plasma were discussed in the previous progress report. That material, although focused on chlorination processing, is applicable to hydrogen reduction. While there is no intention to repeat that material here, this report offers an opportunity to at least identify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

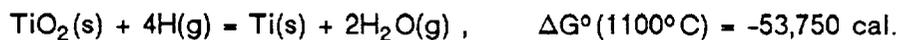
preliminary experimental results. The progress report is concluded by a review of activities planned for the coming year.

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°K (see 1988-89 progress report). The reduction of rutile with H₂ is, for practical purposes, impossible, as the following thermodynamic data indicate:



For all reasonable values for the partial pressures of H₂ and H₂O, 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,



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 O₂ and H₂. The advantages and problems associated with the process are summarized in Table 1.1.

Table 1.1 Hydrogen reduction in a "cold" plasma.

Advantages
<ul style="list-style-type: none"> • Highly reactive environment Near 100% theoretically efficient use of H₂ • No beneficiation of ore required • Minimal equipment Plasma reactor, condenser, and electrolytic cell • Continous operation • Numerous metal by-products
Disadvantages
<ul style="list-style-type: none"> • Plasma reduction process unproven technology • Electrical energy utilized • Problems in handling and storage of hydrogen

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 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 $TiCl_4(g)$ for reaction with $Al(l)$ in a "cold" plasma. The reaction involved formation of titanium aluminides and $HCl(g)$. 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

*All future experiments will be conducted with either N_2 , Cl_2 , or a mixture of these gases. Nitrogen produces a more stable plasma than can be achieved with Ar.

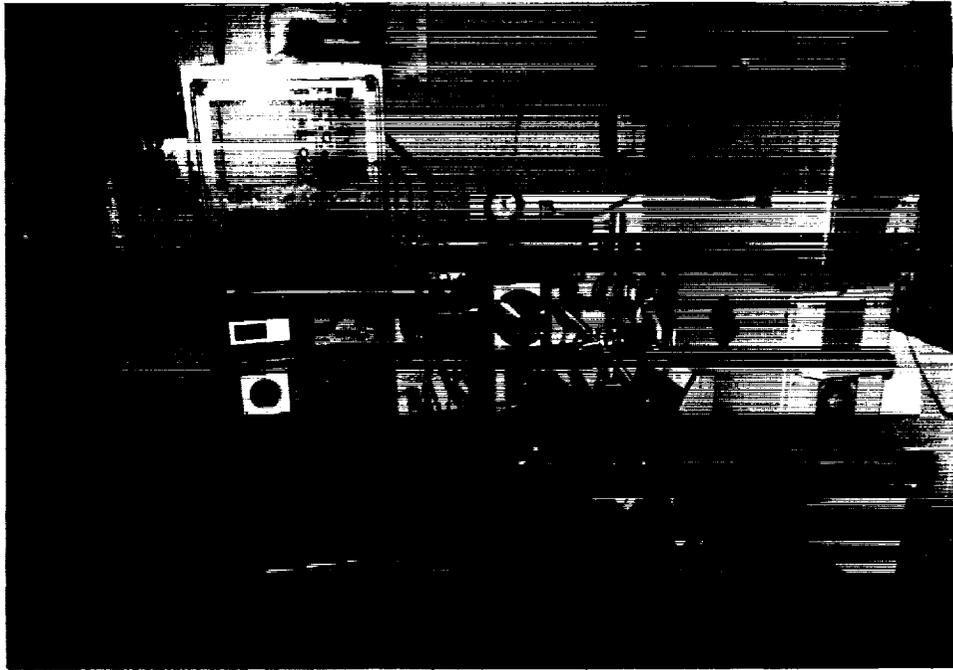
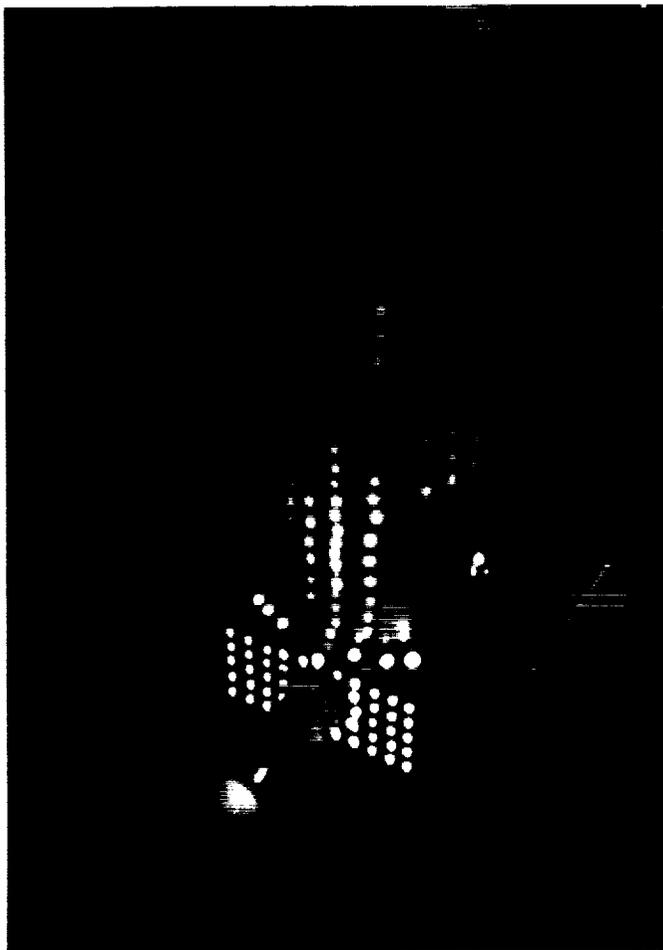
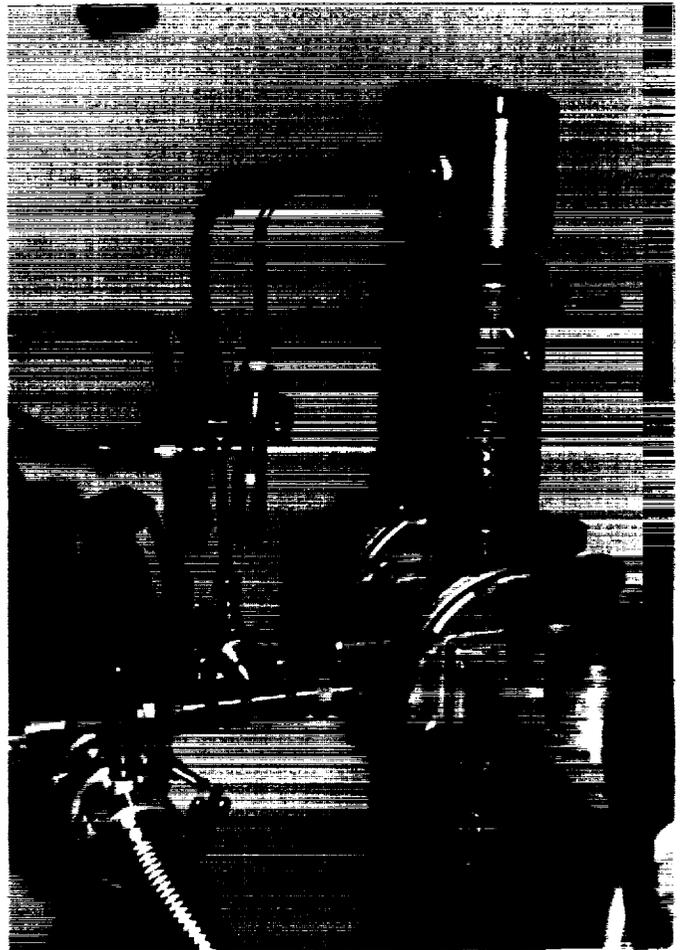


Figure 1.1 Experimental apparatus.



(a) With Plasma



(b) Connected to Mass Spectrometer

Figure 1.2 Applicator where plasma is generated.

Table 1.2 Experimental results for ilmenite: oxygen generation.

Power (kw)	Signal Intensity ^a O ₂ (Arbitrary Units)			
	Nitrogen Plasma		Argon-Chlorine ^b Plasma	
	O ₂	O	O ₂	O
0	0	0	0	0
0.2	1	0	60	7
0.4	0	0	--	--
0.6	0	0	53	6
0.8	3	0	--	--
1.0	24	0	1384	4900
1.4	25	0	--	--
1.6	29	0	--	--

^aSignal intensity is time averaged and corrected for background O₂ signal.

^b10% Cl₂.

Table 1.3 Experimental results for ilmenite: chlorine consumption.

Power (kw)	Signal Intensity ^a O ₂ (Arbitrary Units) Argon-Chlorine ^b Plasma	
	Cl	Cl ₂
0	1045	585
0.2	603	329
0.6	276	79
1.0	--	--

^aSignal intensity is time averaged and corrected for background O₂ signal.

^b10% Cl₂.

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 gas-solid 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.