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Chlorination Processing of Local Planetary Ores for Oxygen  
and Metallurgically Important Metals

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Abstract

The use of chlorine to extract, reclaim, and purify metals has attractive possibilities for extraterrestrial processing of local planetary resources. While a complete cyclic process has been proposed for the recovery of metallurgically significant metals and oxygen, this progress report focuses on the chlorination step of the cycle. An experimental apparatus for reacting refractory materials, such as ilmenite, in a microwave-induced plasma is being built. Complex equilibria calculations reveal that stable refractory materials can, under the influence of a plasma, undergo chlorination and yield oxygen as a by-product. These issues and the potential advantages for plasma processing in space are reviewed. Also presented in this report is a discussion of the complex equilibria program used in the analysis.

Introduction

On Earth, the use of chlorine to extract, reclaim, and purify metals has long been an attractive possibility.<sup>1-5</sup> In space, plasma chlorination has even greater possibilities. Those possibilities include the production of oxygen and chloride metal vapor. The latter can be either reduced or decomposed to its metal and chlorine states for recycling. In addition, a plasma chlorinator is versatile. It can be used to process a number of different ores, and it can also be used to decompose metal chloride vapor or waste products from other processes.

Our immediate goal is to complete construction of the plasma reactor and begin testing. The unit will, for the next year, be the center of focus for our experimental program. The reactor has been designed to meet both our immediate needs and to serve as a service facility for other investigators participating in Center activities who may wish to determine if a plasma can enhance their research.

In the same spirit of cooperation, we have assembled a software package for complex equilibria calculations and an extensive data base. The software package is based on Outokumpu's HSC program. The data base is oriented toward the extractive metallurgical industry and has already found considerable use in this work. The HSC program has been interfaced with LOTUS 123 for manipulation of data, Grapher and Energraphics for data plotting, and Inset to cut and insert results from any program into

another. The entire package is up and running, and we plan to put together a brief description regarding its operation.

### Background

The general advantages to chlorination processing are the large number of elements that form chlorides, the reactivity, volatility and solubility of metal chloride products, and the reducibility of metallurgically important chlorides to metal.<sup>1</sup> Almost all of the elements in the periodic table form chlorides, except for a few noble gases. In addition, chlorides tend to volatilize or have comparatively low melting points. Both physical phenomena provide a means for separation and subsequent refining.

Metal chlorides, while easily produced by reaction of chlorine with the metal, are difficult to form from metal oxides.<sup>2</sup> This difficulty is usually overcome by employing a CO-Cl<sub>2</sub> gas mixture or by reacting the oxide with Cl<sub>2</sub> in the presence of solid carbon. In carbochlorination, carbon monoxide acts as a reducing agent, forming CO<sub>2</sub>, while the chlorine oxidizes the metal, forming a volatile chloride. In this manner, a new surface is continually exposed for reaction. This process is certainly viable, and one worth considering for space application. However, there are technical complexities with carbochlorination that may be ignored on Earth, but cannot be overlooked with regard to space application.

A number of chlorinated oxy-carbon compounds are stable at elevated temperatures. Landsberg et al.<sup>6</sup> conducted an extensive study of the relationship between various metal oxide carbochlorination reactions and C-Cl-O compound by-products. They found and quantified 136 identifiable C-Cl-O by-product compounds produced during carbochlorination of oxides of titanium, zirconium, and aluminum at reaction temperatures between 600 and 1000°C. In an economic setting, such as that which can be anticipated for a space base, the loss of scarce reactants and oxygen in an unwanted by-product cannot be tolerated.

"Cold" plasma chlorination can eliminate this problem, enhance reaction rates, minimize reactor size, and yield oxygen as a by-product. In addition, a plasma chlorination reactor is versatile. A single reactor could be used to process more than one ore, and it could also be used in the thermal reduction of chloride vapor.

### Approach

"Cold" plasma processing of metallurgical materials is a natural progression of technological development within the extractive industry. High-temperature or "thermal" plasmas are used in many industrial applications in the extractive industry, including such areas as process heating and melting, thermal decomposition, smelting,

and refining.<sup>7,8</sup> Those applications rely primarily upon plasma heating to achieve conventional results that could be achieved with other heating sources. A "cold" plasma, unlike conventional heating sources, can significantly enhance reaction rates and form compounds, ions, and reactive species that cannot be produced by normal means.

In spite of their name, "cold" plasmas are not necessarily cold. Depending upon the gas composition and pressure, a "cold" plasma can exist at molecular temperatures up to 2000 K. The term "cold" is attached to those plasmas wherein there is a significant difference between the molecular and electron temperatures, the latter often being thousands of degrees greater than the former. The reactive nature of a "cold" plasma is a direct result of the difference in the two temperatures.

Both the reactive nature and the thermodynamic character of a "cold" plasma are represented by the sketch in Figure 1.16. In this sketch, the chemical potential of both reactants and products are plotted against an arbitrary variable to represent potential reactions. In a normal gas solid reaction, reactants combine to yield products and an overall reduction in the chemical potential of the system. In a "cold" plasma, energetic free electrons collide with gas molecules, leading to ionization and/or dissociation of those molecules. Depending on the initial gas composition, the excitation process can produce novel reactants, such as monatomic chlorine.<sup>9,10</sup> In addition, there occurs a substantial increase in the overall chemical potential of the reactants, which, in turn, allows a number of extra potential reactions, including the formation of metastable phases not attainable under non-plasma conditions.

Reaction rates can be substantially increased in a "cold" plasma. The high chemical potential of ionized and dissociated molecules reflects the reactive nature of these molecules. The presence of broken bonds, partially filled orbitals, and unbalanced charge makes these molecules highly reactive and can substantially enhance kinetic processes. It is these characteristics of a "cold" plasma, and how they can be used to enhance extractive processes, which are the focus of this investigation.

### Results to Date

*Experimental Apparatus.* The primary effort in the past eight months has involved design and construction of the experimental apparatus. A schematic diagram of the apparatus is presented in Figure 1.17. The system includes a microwave source, an applicator where the plasma is generated, a gas delivery system, a mass spectrometer for monitoring the extent of the reaction, an optical pyrometer for monitoring 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.

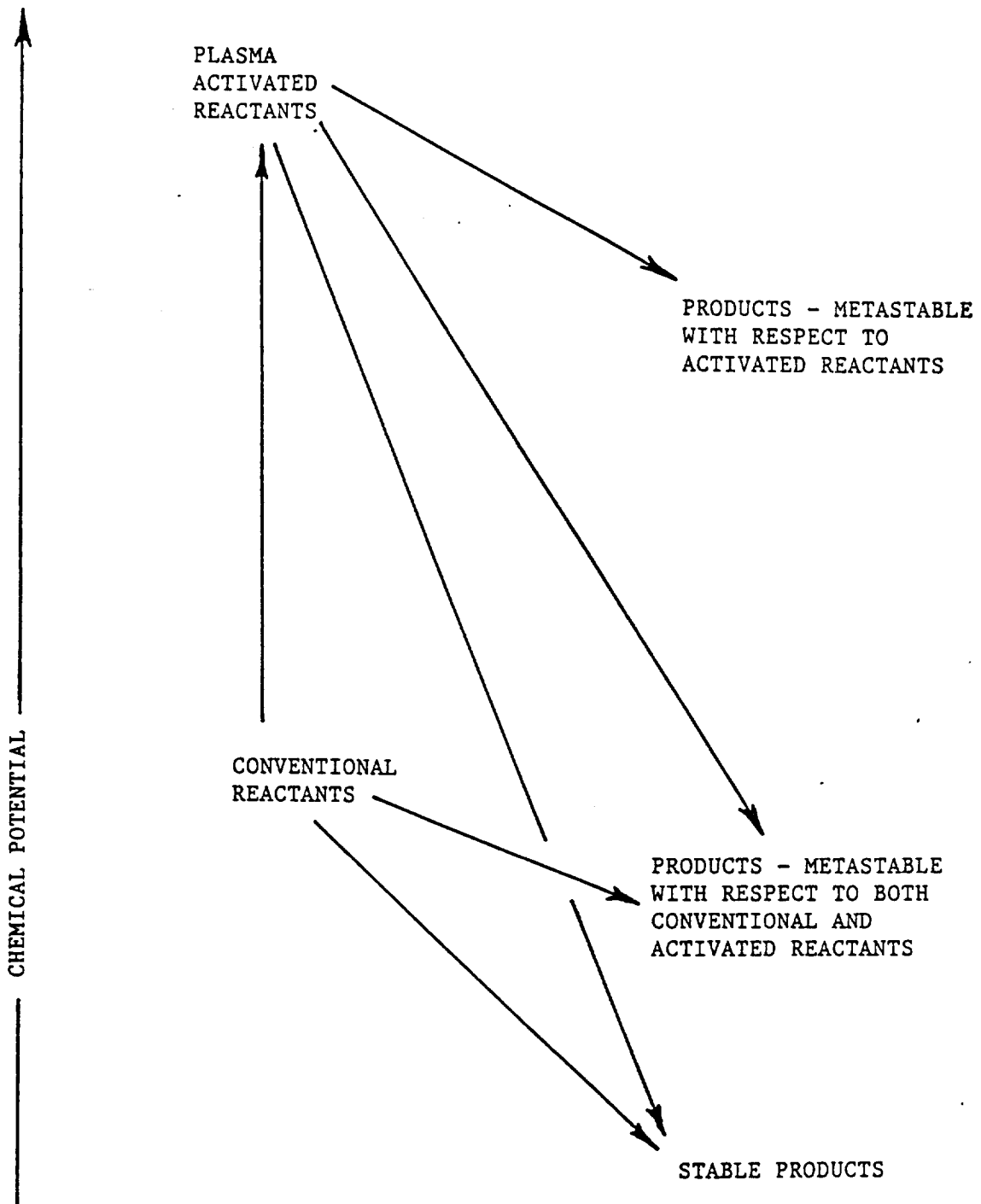


Figure 1.16. Schematic representation of chemical potential for conventional and plasma-assisted reactions.

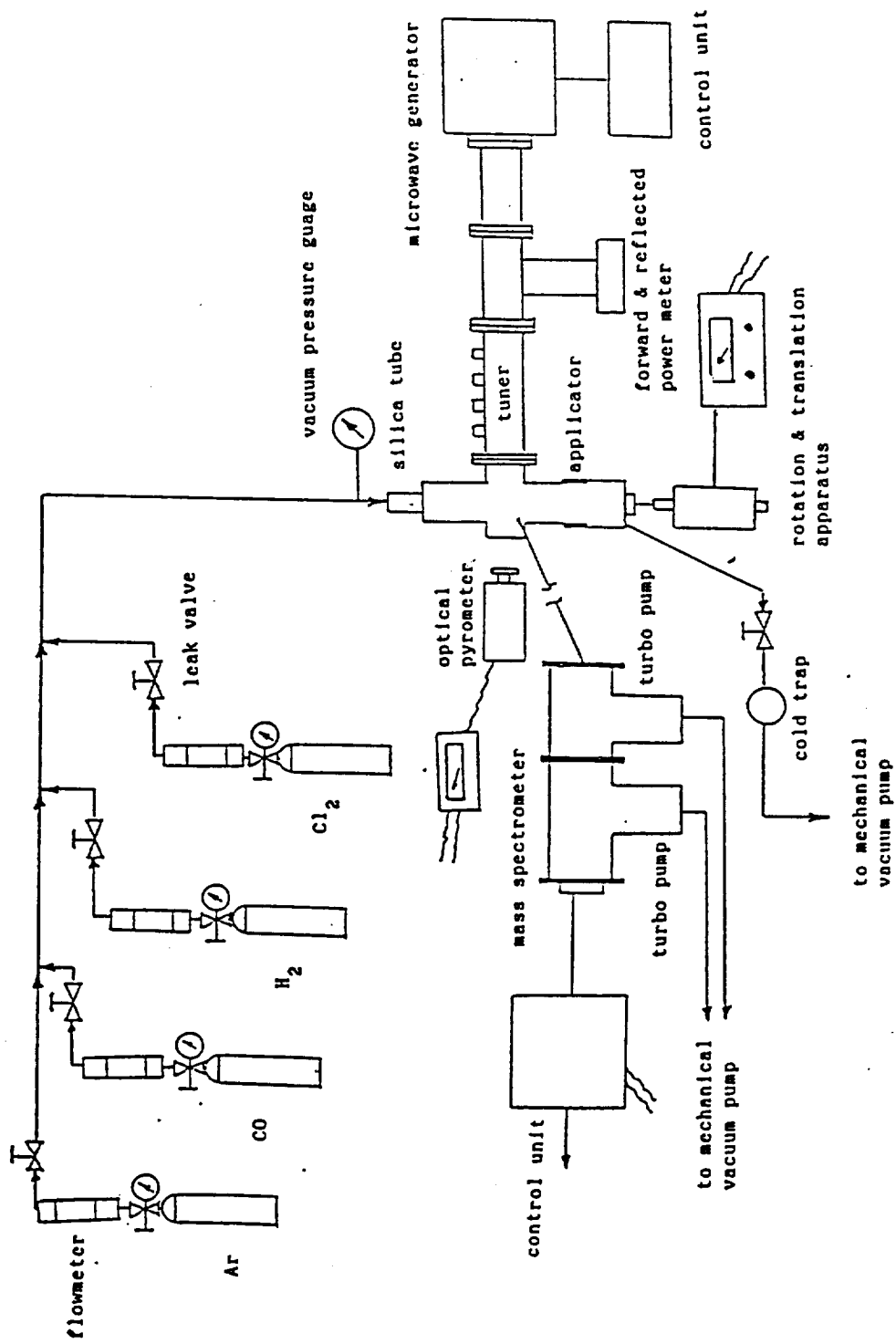


Figure 1.17. Experimental apparatus. Note: Mass spectrometer is rotated 90° and mass spec capillary sampling tube is not to scale.

The microwave generator was moved from a southside industrial site to the Arizona Material's Laboratory, where it has been set up and is now operational. The gas delivery system is in place; the specimen holder has been constructed, tested, and deemed operational. The reaction chamber, which is housed in the applicator, has been designed and built, while the applicator has been redesigned to accommodate the mass spectrometer.

In addition to these activities, we are in the process of completing arrangements for specimen preparation. This activity has involved construction of a vacuum system for sealing specimens in silica ampules and setting up a sintering furnace. Specimens prepared from powders will be isostatically pressed and then sealed in a silica ampule under vacuum before sintering at approximately 1000°C. The solid specimens formed in this manner will be characterized using a BET apparatus to determine surface area and pore volume, with visual confirmation of those results provided through use of a scanning electron microscope.

We are currently awaiting arrival of the mass spectrometer and mechanical pumps. The mass spectrometer, an EXTRELL C-50 Quadropole, was ordered last Fall. The instrument is currently being tested by the manufacturer, and the expected shipping date is March 17, 1989. Three corrosion-resistant pumps are on order and are expected to be shipped before the end of March 1989. Upon receipt of this equipment, we will complete construction of the apparatus and begin experimentation.

*Thermodynamic Calculations.* In many systems, chlorination is limited by the dissociation of diatomic chlorine. In Figure 1.18, the equilibrium partial pressure of monatomic chlorine in equilibrium with the diatomic species is plotted assuming the sum of the partial pressures of both the monatomic and diatomic species equals 1 atm. Also in Figure 1.18, the partial pressure is compared to the partial pressure of monatomic chlorine that can be achieved in a "cold" plasma. The latter value, based on a total plasma pressure of 0.1 atm and total dissociation of diatomic chlorine, intersects the equilibrium-calculated curve at 1560 K. Depending upon the concentration of monatomic chlorine in the plasma, it is possible to enhance the chlorination kinetics greatly.

The chemistry which takes place in a plasma is usually quite complex and involves a large number of elementary reactions which are initially generated by collisions between energetic free electrons and gas molecules.<sup>10,11</sup> While we cannot model the thermochemistry of the plasma at this early stage, we are in a position to estimate its potential impact on chlorination processing. The impact is estimated through complex equilibria calculations, using the computer program described earlier.

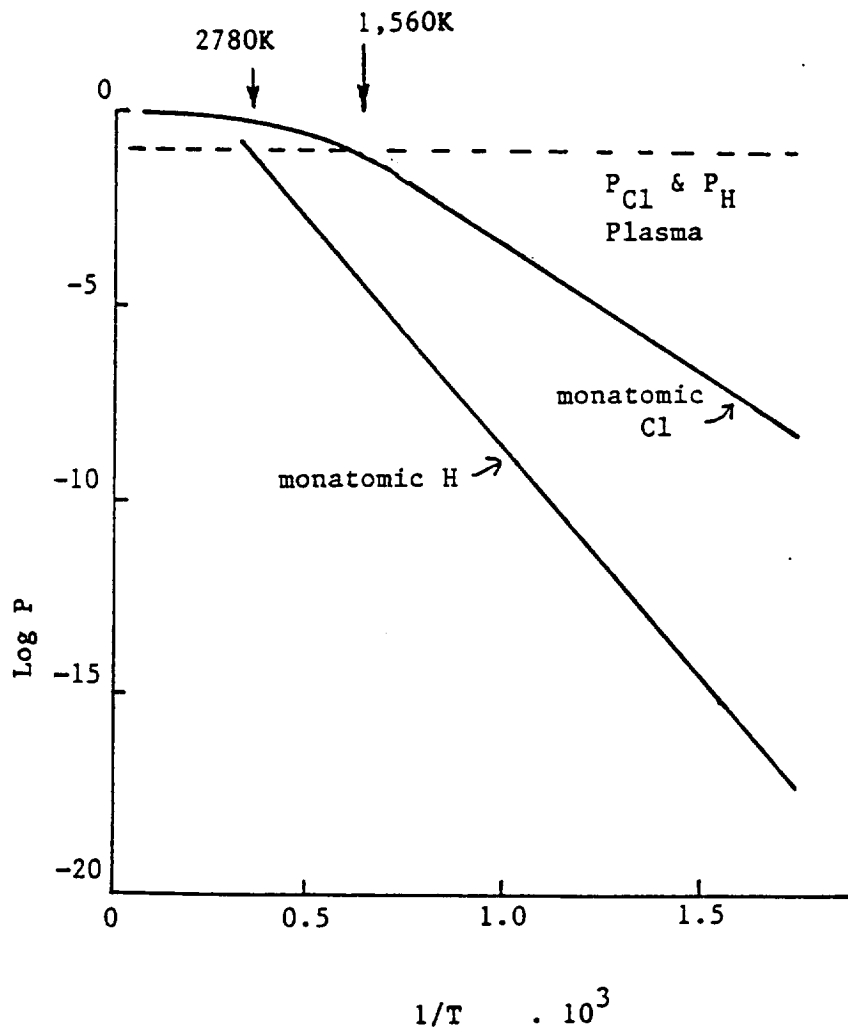


Figure 1.18. Comparison of the partial pressures of monatomic chlorine and hydrogen produced by thermal heating (total pressure 1 atm) and plasma (total pressure 0.1 atm).

The chlorination of ilmenite has been modeled using the system presented in Table 1.5. It has been assumed that, in plasma processing, diatomic chlorine is completely decomposed. Accordingly, the results presented below regarding the plasma represent the best-case scenario and do not take into consideration the effect of the plasma on other reactants and products. Moreover, it is important to remember that the results presented in this section are based on thermodynamic calculations and thus represent only what is energetically possible. Kinetic processes may also limit what can be achieved.

Table 1.5. System used for thermodynamic calculations.

Vapor Phase		
Cl <sub>2</sub> and/or Cl, O <sub>2</sub> , ClO, ClO <sub>2</sub> , FeCl, FeCl <sub>2</sub> , FeCl <sub>3</sub> , Fe <sub>2</sub> Cl <sub>6</sub> , TiCl, TiCl <sub>2</sub> , Ti <sub>2</sub> Cl <sub>6</sub> , TiCl <sub>4</sub> , TiOCl, TiOCl <sub>2</sub> , TiO		
Solids		
FeTiO <sub>3</sub>	TiO <sub>2</sub>	TiCl <sub>2</sub>
TiCl <sub>3</sub>	TiCl <sub>4</sub>	FeO
Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	FeCl <sub>2</sub>
FeCl <sub>3</sub>	FeOCl	

Ilmenite reacts with chlorine at 1100°C. The extent of this reaction is represented in Figure 1.19 as a function of the moles of chlorine available per mole of ilmenite. The results in the figure and the raw data reveal that the iron is volatilized as chlorides while elemental oxygen is released. The process continues until iron is eliminated, leaving only rutile (TiO<sub>2</sub>) remaining in the solid. At this point, the reaction stops for all practical purposes.

The extent of the chlorination of ilmenite in a plasma can be enhanced, as the results shown in Figure 1.20 reveal. Even after all the iron has been volatilized, the chlorination process continues. Titanium chlorides are volatilized and elemental oxygen is released. A comparison of Figures 1.19 and 1.20 reveals that the chlorine may be better utilized in a plasma reactor.

The potential for plasma chlorination is dramatically illustrated in Figure 1.21. Rutile, as noted earlier, is not readily chlorinated under standard conditions. The results in Figure 1.21 reveal that rutile, a highly refractory material, may readily be reacted in a plasma. It is this reactive nature that holds exceptional promise for the use of "cold" plasmas in the processing of local planetary resources.

#### Summary and Future Work

The investigation is in its initial stage. Considerable effort has been expended in the design and construction of the plasma reactor. This initial work is expected to continue for three to four months. Upon completion of the apparatus, a number of preliminary experiments will be undertaken.

The preliminary experiments will focus on the power absorbed by the plasma, which will be evaluated as a function of the gas content (chlorine versus inert gas content, as well as the choice of inert gas), the total pressure, reactor size, and power



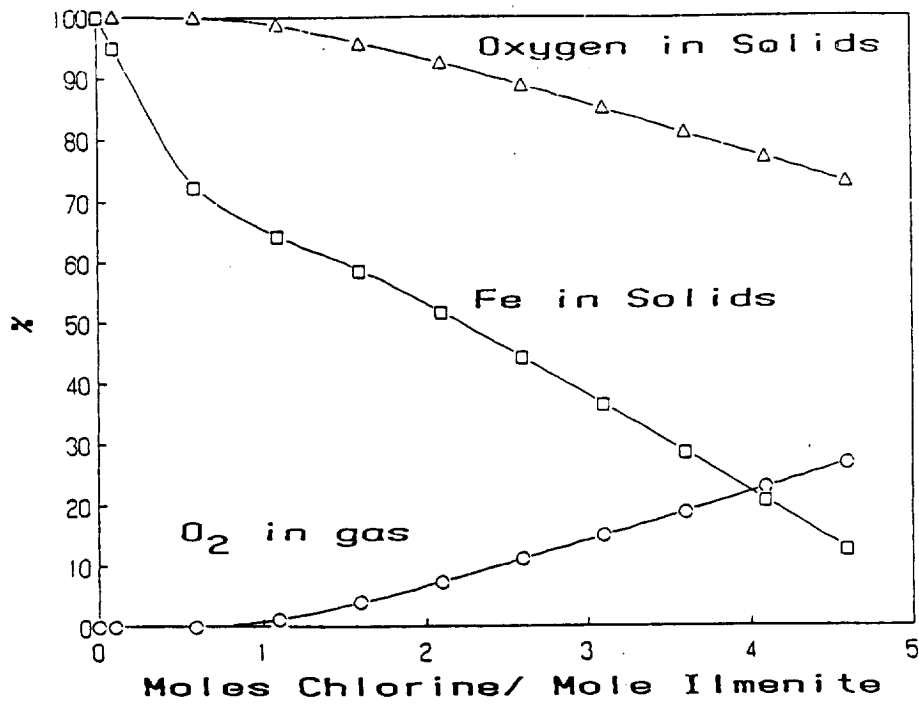


Figure 1.19. Extent of reaction of ilmenite with chlorine under conventional heating at 1100°C and total pressure of 0.1 atm.

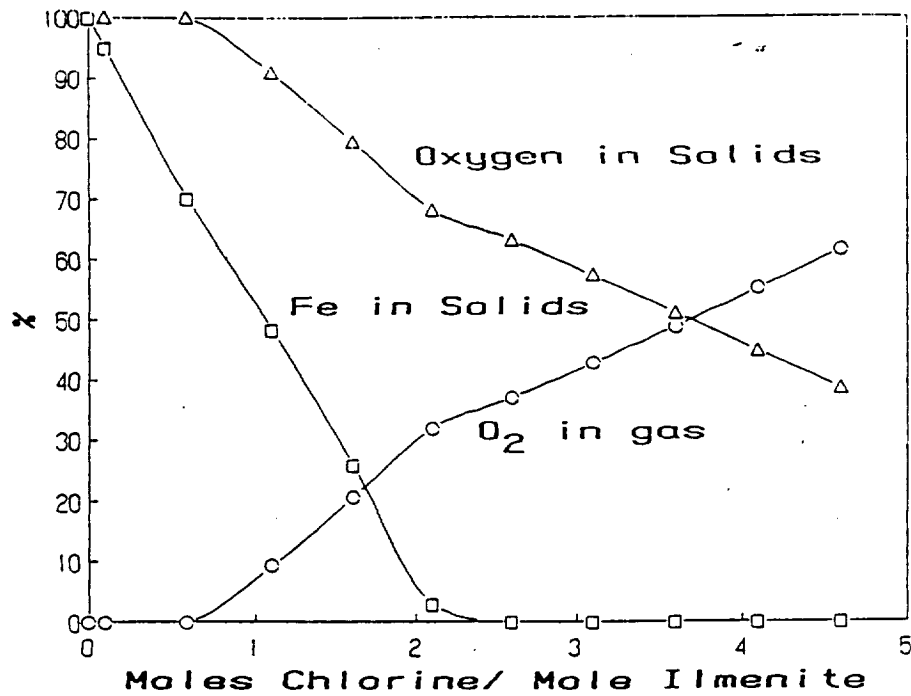


Figure 1.20. Monatomic chlorine in a plasma can readily react with ilmenite at 1100°C and a total pressure of 0.1 atm.

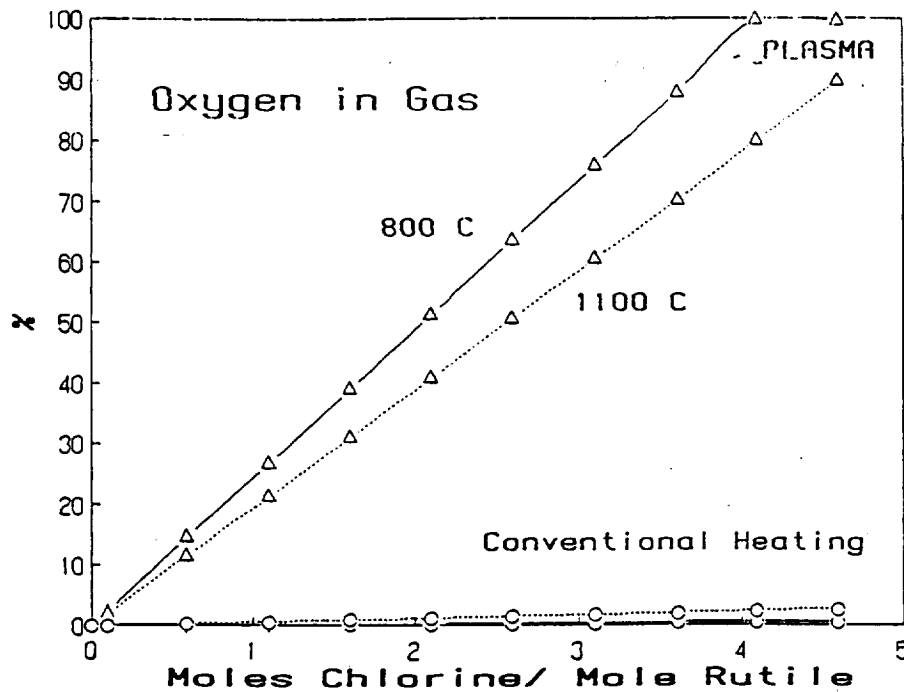


Figure 1.21. A plasma can effectively chlorinate refractory oxides.

provided. The apparatus is equipped with meters to measure both the forward and reflected power, the difference being the absorbed power. The level of absorbed power reflects the extent of radical formation. The results of this work will be used to identify optimum conditions for the chlorination reaction. This work is expected to take no longer than two months.

Chlorination studies will begin upon completion of the initial power studies. The kinetics of chlorination will be examined as a function of temperature, chlorine content in the gas, total pressure, power level, and plasma density. These experiments are expected to be in progress throughout the remainder of the year.

#### Student Participants

Mr. Daniel Bullard and Mr. Robert Ortega, both U.S. citizens, are working on this project. Daniel, who joined our research group in January, completed his undergraduate program at the University of Wisconsin at Milwaukee in December, where he received a double degree in Materials Engineering and Chemistry. Robert is in his last year of undergraduate study at the University of Arizona. Upon completion of his Bachelor's degree in May, he plans to commence graduate work. Robert began working on the project in December.

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