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Innovative Techniques for the Production of Energetic Radicals for Lunar Materials Processing Including Photogeneration Via Concentrated Solar Energy

D. E. Osborn, D. C. Lynch, and R. Fazzolari

Department of Materials Science and Engineering

and

Solar and Energy Research Facility, Department of Nuclear and Energy Engineering

The University of Arizona

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 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:

$$E = \frac{hc}{\lambda} = h\nu .$$

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

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

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 H_2O_2 or 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 Cl, F, O, H, and OH* for reduction and oxidation.

Table 1.5 Dissociation energies for chemical bonds (Legan 1982).

Bond	D (Kcal/mol)	λp (nm)
Cl-Cl	58	490
C-Cl	81	353
C-F	116	247
C-H	99	290
C-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.

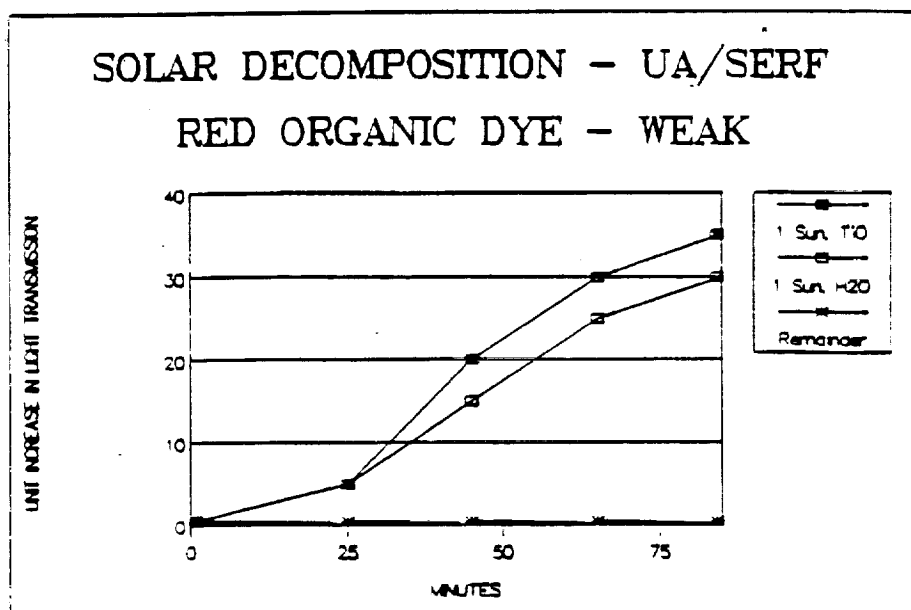| Reaction	λp (nm)	Resultant Radicals
$H_2O + hv = H^* + OH^*$	185	Atomic hydrogen and hydroxy
$H_2O_2 + hv = 2OH^*$	254	Hydroxy
$O_2 + hv = O_3$	254	Ozone
$Fe^{+2} + hv = Fe^{+3}$	254	Ferrous ion to ferric ion
$O_3 + hv = O_2 + O^*$	310	Atomic oxygen (Note: $O^* + H_2O = 2OH^*$)
$Cl_2 + hv = 2CL^*$	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 AM0, AM1, and AM4 (W/m^2).

	AM0	AM1	AM4
< 400 nm	118.1	88.4	11.1
< 310 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 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 (250-450°C). Simulated solar light should lead to the dissociation of 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 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
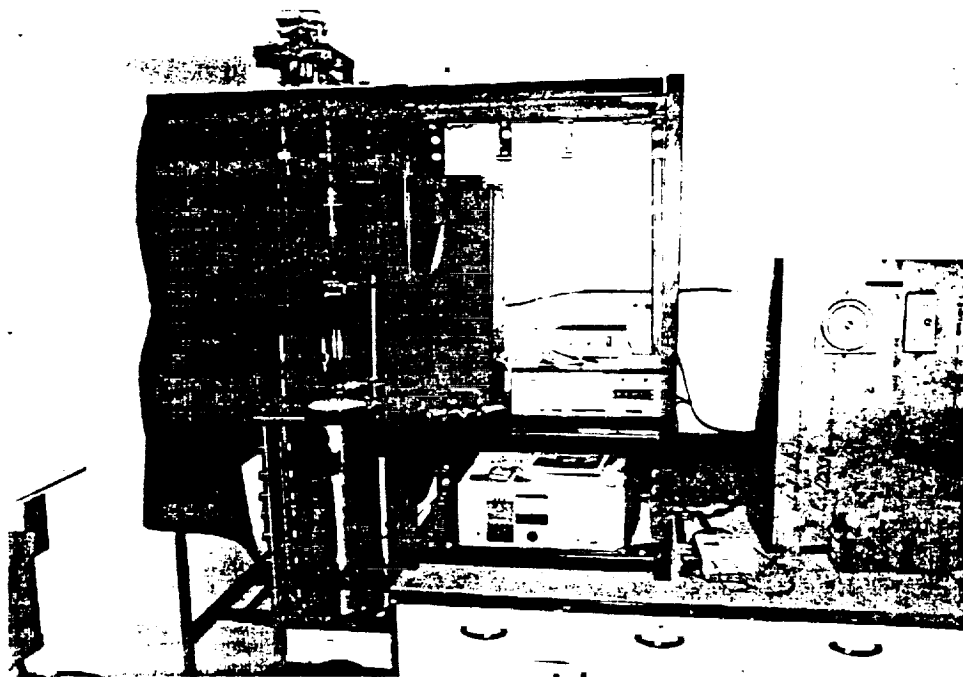
Figure 1.20   Experimental apparatus.

calibrated orifice-manometer.   An accuracy of ±2% is desired for gas flow rates.   A total gas flow rate of 500 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 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° and 450°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.

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