<u>INTERNATIONAL PHD IN ENVIRONMENTAL SCIENCE AND ENGINEERING</u>

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Development of new processes for ISRU (In Situ Resource Utilization) and ISFR (In Situ Fabrication and Repair) applications on Moon and Mars

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1 Introduction

From several decades Space Exploration has been one of the most fascinating and important scientific field to be developed.Due to the difficulty in exploring the outer space, indeed, only during the early 20th century large and relatively efficient rockets allowed physical space exploration became a reality. On the other hand, the observation of various objects in space started thousand of year ago, and it keeps to represent on of the most interesting issue for thousand of people and scientists. Brodly speaking, Space Exploration consists on improuving knowledge about exterrestrial environments by means of both human spaceflight and robotic spacecraft and rockets. The main results of this activity involve scientific, technologic and economic aspects. The scientific issues allow mankind, by means of the observation performed during space missions, to better understand lot of terrestrial phenomena, connected to climate change, terrestrial axis shifting, etc. The technological aspects related to Space exploration are, in addition, strongly connected to the technical solutions used to handle particular problems during Space activities and that, through the technological transfer, became an important part of our dayly life. Finally, the economic returns are related to the new technologies developed and involve also other activities, both scientific –as parabolic or suborbital flights- and divulgative as Space Tourism.

Nowadays main Space Agencies all over the world have set common space exploration goals defined collectively, that will be briefly summarized:

Search for Life consists on the determination if life is or was present outside of Earth and understand the environments that support or supported it. Pursuing this goal, indeed, continues the cultural quest of humankind to determine whether we are alone in the universe and answers deeply rooted questions about our origin and evolution. The question of whether life exists beyond Earth has great philosophical and scientific significance.

Extend Human Presence: Explore a variety of destinationsbeyond low-Earth orbit with a focus on continuallyincreasing the number of individuals that can be supported at these destinations, the duration of time that individuals can remain at these destinations, and the level of self-sufficiency. This enables humankind to live and work in space, to harness solar system resources for use in space and on Earth, and eventually to settle on other planets. Pursuing this goal expands the frontiers of humanity, opens doors to future utilization of space, and reshapes how we think of ourselves and our place in the universe.

Develop Exploration Technologies and Capabilities: Develop the knowledge, capabilities, and infrastructure required to live and work at destinations beyond low-Earth orbit through development and testing of advanced technologies, reliable systems, and efficient operations concepts in an off-Earth environment. This goal establishes the fundamental capabilities to extend and sustain space exploration missions. Pursuing this goal also yields spinoff products, new materials and manufacturing processes, and various technologies that can address major global challenges.

Perform Science to Support Human Exploration: Reduce the risks and increase the productivity of future missions in our solar system by characterizing the effect of the space environment on human health and exploration systems. This is essential for human exploration and will enable a human presence across the solar system. Pursuing this goal also yields innovationfor Earth-based health care.

Stimulate Economic Expansion: Support or encourage provision of technology, systems, hardware, and services from commercial entities and create new markets based on space activities that will return economic, technological, and quality-of-life benefits to all humankind. Pursuing this goal generates new industries, spurs innovation in fields such as robotics and energy systems, and creates high-technology employment opportunities. As space activities evolve from government research to exploration to utilization, new economic possibilities may extend beyond low-Earth orbit to the Moon and elsewhere in the solar system.

Anyway, the implications that Space exploration has played in the hystory has been really different, also not directly linked to the research and Human development. For instance Space exploration has been used as a proxy competition for geopolitical rivalries. During the Cold War the space exploration was driven by a "Space Race" between the Soviet Union and the United States: the launch of the first man-made object to orbit the Earth, the USSR's Sputnik 1, on October 4, 1957, and the first Moon landing by the American Apollo 11 craft on July 20, 1969 are often taken as the boundaries for this initial period. Anyway, obviously, in this thesis the hystorical and political issues related to Space Exploration will be not discussed. Specifically, this thesis consists on four chapters, in the second chapter the most important challenges and results achieved in Space Exploration, with particular reference with ISRU (In-Situ Resources Utilization) and ISFR (In-Situ Fabrication and Repair) paradigms on Moon and Mars will be brefly sumed up. ISFR and ISRU paradigms focus on the utilization of in-situ extraterrestrial resources and, as a consequence, will result in a strong reduction of transport costs and in a significant increasing of the efficiency of the corresponding operations. In the third chapter, the development of a new process potentially useful for future manned Lunar and/or Martian space missions in the framework of the so-called ISRU and ISFR concepts is described and discussed. Finally, in the fourth chapter, one of the steps of the process described in the third chapter, based on the occurrence of the highly exothermic self-propagating thermite reduction of ilmenite ($FeTiO_3$) for the in-situ fabrication of composite ceramics in Lunar environment is systematically investigated.

2 State of the art of the most important ISRU and ISFR applications for the Space exploration

2.1 Space Exploration current scenario and future settlement

2.1.1 Space Exploration Overview

Space Exploration is a research field that involves different scientific aspects. The main investigation's topics that have been developed from the beginning are related to the propulsion, the communication between Earth and crew, mobility on extraterrestrial environments and the energy production in Space.

To give an omnicomphensive review of Space exploration it would be necessary to examine each mission in deep detail, but -as discussed also in the previous chapter-, Space exploration hystory is not the key topic of this thesis work. Anyway, to better understand the processes described in what follows a brief timeline of the most relevant Space Exploration discoveries and results isreported in a schematic way in **Tables 2-1, 2-2, 2-3 and 2-4**.

2.1.1.1 <u>1957–1961</u>

TABLE 2-1: Relevant Milestones Of Space Exploration Between 1957 And 1961

Date	Mission Achievements	Country/Organization	Mission Name
4 October 1957	First artificial satellite First signals from space	USSR	Sputnik 1
3 November 1957	First animal in orbit, the dog Laika	USSR	Sputnik 2
31 January 1958	Confirmed the existence of the Van Allen belts	USA (ABMA)	Explorer 1
2 January 1959	First firing of a rocket in Earth orbit First reaching Earth escape velocity or Trans Lunar Injection First detection of solar wind	USSR	Luna 1
4 January 1959	First artificial satellite in heliocentric orbit	USSR	Luna 1
7 August 1959	First photograph of Earth from orbit	USA (NASA)	Explorer 6
13 September 1959	First impact into another world (the Moon) First delivery of national (USSR) pennants in a celestial body	USSR	Luna 2
4 October 1959	First photos of far side of the Moon	USSR	Luna 3

Date	Mission Achievements	Country/Organization	Mission Name
19 August 1960	First plants and animals to return alive from Earth orbit	USSR	Sputnik 5
1961	First launch from orbit First mid-course corrections First spin-stabilisation	USSR	Venera 1

2.1.1.2 1961–1969

TABLE 2- 2: Milestones Of Space Exploration Between 1961 And 1969

Date	Mission Success	Country/Organization	Mission Name
12 April 1961	First human spaceflight–(Yuri Gagarin) First human-crewed orbital flight	USSR	Vostok 1
7 March 1962	First orbital solar observatory	USA (NASA)	OSO-1
14 December 1963	First planetary flyby (Venus closest approach 34,773 kilometers)	USA (NASA)	Mariner 2
16 June 1963	First woman in space (Valentina Tereshkova)	USSR	Vostok 6
19 July 1963	First reusable crewed spacecraft (*suborbital*)	USA (NASA)	X-15 Flight 90
18 March 1965	First extra-vehicular activity	USSR	Voskhod 2
14 July 1965	First Mars flyby (closest approach 9,846 kilometers)	USA (NASA)	Mariner 4
15 December 1965	First orbital rendezvous (parallel flight, no docking)	USA (NASA)	Gemini 6A/Gemini 7
3 February 1966	First soft landing on another world (the Moon) First photos from another world	USSR	Luna 9
1 March 1966	First impact into another planet (Venus)	USSR	Venera 3
16 March 1966	First orbital docking between two spacecrafts	USA (NASA)	Gemini 8/Agena target vehicle
3 April 1966	First artificial satellite around another world (the Moon)	USSR	Luna 10
2 June 1966	Soft landing on the Moon photos from the Moon	USA (NASA)	Surveyor 1
30 October 1967	First automated (crewless) docking	USSR	Cosmos 186/Cosmos 188
7 December 1968	First orbital ultraviolet observatory	USA (NASA)	OAO-2
21 December 1968	First piloted orbital mission of another celestial body (Moon), First-ever Trans-Earth injection (25 December)	USA (NASA)	Apollo 8
21 July 1969	First human on the Moon and first space launch from a celestial body	USA (NASA)	Apollo 11
19 November	First rendezvous on the surface of a	USA (NASA)	Apollo 12/Surveyor 3

Date	Mission Success	Country/Organization	Mission Name
1969	celestial body		

2.1.1.3 1970–1980

TABLE 2- 3: Milestones Of Space Exploration Between 1970 And 1980

Date	Mission Success	Country/Organization	Mission Name
24 September 1970	First automatic sample return from the Moon	USSR	Luna 16
23 November 1970	First lunar rover	USSR	Lunokhod 1
12 December 1970	First X-ray orbital observatory	USA (NASA)	Uhuru (satellite)
15 December 1970	First soft landing on another planet (Venus) First signals from another planet	USSR	Venera 7
23 April 1971	First space station	USSR	Salyut 1
June, 1971	First Manned orbital observatory	USSR	Orion 1
14 November 1971	First to maintain orbit around another planet (Mars)	USA (NASA)	Mariner 9
27 November 1971	First impact into Mars	USSR	Mars 2
2 December 1971	First soft Mars landing First signals from Mars surface	USSR	Mars 3
3 March 1972	First human made object sent on escape trajectory away from the Sun	USA (NASA)	Pioneer 10
15 July 1972	First mission to enter the asteroid belt and leave inner solar system	USA (NASA)	Pioneer 10
15 November 1972	First orbital gamma ray observatory	USA (NASA)	SAS 2
3 December 1973	First Jupiter flyby (at 130,000 km)	USA (NASA)	Pioneer 10
5 February 1974	Venus flyby at 5768 kilometers, first gravitational assist manoeuvre	USA (NASA)	Mariner 10
29 March 1974	First Mercury flyby at 703 kilometers	USA (NASA)	Mariner 10
15 July 1975	First multinational manned mission	USSR USA (NASA)	Apollo-Soyuz Test Project
20 October 1975	First orbit around Venus	USSR	Venera 9
22 October 1975	First photos from the surface of another planet (Venus)	USSR	Venera 9
20 July 1976	First photos and soil samples from the surface of Mars	USA (NASA)	Viking Lander
26 January 1978	First real time remotely operated ultraviolet orbital observatory	USA (NASA) ESA UK-SERC	International Ultraviolet Explorer
5 March 1979	Jupiter flyby (closest approach	USA (NASA)	Voyager 1

Date	Mission Success	Country/Organization	Mission Name
	349,000 km)		
1 September 1979	First Saturn flyby at 21,000 km	USA (NASA)	Pioneer 11
12 November 1980	Saturn flyby (closest approach 124,000 kilometers)	USA (NASA)	Voyager 1

2.1.1.4 1981–PRESENT

TABLE 2- 4: Milestones Of Space Exploration Between 1981 And 2012

Date	Mission Success	Country/Organization	Mission Name
12 April 1981	First Reusable manned spacecraft (*orbital*)	USA (NASA)	STS-1
1 March 1982	First Venus soil samples & sound recording of another world	USSR	Venera 13
25 January 1983	First Infrared orbital observatory	USA (NASA) UK-SERC Netherlands-NIVR	IRAS
23 March 1983	Ultraviolet orbital observatory	USSR France	Astron
13 June 1983	First spacecraft beyond the orbit of Neptune (first spacecraft to pass beyond all Solar System planets)	USA (NASA)	Pioneer 10
7 February 1984	First untethered spacewalk, Bruce McCandless II	USA (NASA)	STS-41-B
24 January 1986	First Uranus flyby (closest approach 81,500 kilometers)	USA (NASA)	Voyager 2
19 February 1986	First consistently inhabited long-term research space station	USSR	Mir
25 August 1989	First Neptune flyby	USA (NASA)	Voyager 2
18 November 1989	First orbital cosmic microwave observatory	USA (NASA)	COBE
1 December 1989	Ultraviolet to gamma ray spectrum orbital observatory	USSR France Denmark Bulgaria	Granat
14 February 1990	First photograph of the whole solar system[3]	USA (NASA)	Voyager 1
24 April 1990	Optical orbital observatory	USA (NASA) ESA	Hubble Space Telescope
21 October 1991	First asteroid flyby (951 Gaspra closest approach 1,600 kilometers)	USA (NASA)	Galileo
8 February 1992	First polar orbit around the Sun	USA (NASA) ESA	Ulysses
22 March 1995	record longest duration spaceflight (437.7 days) set by Valeri Polyakov	Russia	Mir
7 December 1995	First orbit of Jupiter	USA (NASA)	Galileo
7 December	First mission into the atmosphere of	USA (NASA)	Galileo's

Date	Mission Success	Country/Organization	Mission Name
1995	a gas giant (Jupiter)		atmospheric entry probe
14 February 2000	First orbiting of an asteroid (433 Eros)	USA (NASA)	NEAR Shoemaker
12 February 2001	First landing on an asteroid (433 Eros)	USA (NASA)	NEAR Shoemaker
4 January 2004	Free ranging Mars rover	USA (NASA)	Spirit rover
25 January 2004	Free ranging Mars rover	USA (NASA)	Opportunity rover
1 July 2004	First orbit of Saturn	USA (NASA) ESA ASI	Cassini–Huygens
14 January 2005	First soft landing on Titan	ESA USA (NASA) ASI	Cassini–Huygens
7 May 2006	First extended (multi-year) orbital exploration of Venus	ESA	Venus Express
24 October 2007	First stage of China's lunar probe program, the satellite Chang'e I	China	Chang'e I
6 March 2009	Kepler Mission is launched, first space telescope designated to search for Earth-like exoplanets[4]	USA	Kepler Mission
18 March 2011	First orbit of Mercury	USA (NASA)	MESSENGER
16 July 2011	First orbit of Vesta	USA (NASA)	Dawn
18 July 2011	Radio orbital observatory. Largest observatory ever launched.	Russia (Astro Space Center)	RadioAstron
26 November 2011	Nuclear-powered NASA rover toward Mars to seek out life clues.	USA (NASA)	Curiosity rover

As reported in the previous Tables, the first celestial body involved in space exploration was theMoon. While the Soviet Union's Luna programme was the first to reach the Moon with unmanned spacecraft in 1959, the United States' NASA Apollo program achieved the only manned missions, beginning with the first manned lunar orbiting mission by Apollo 8 in 1968, and six manned lunar landings between 1969 and 1972. In 1969 the Apollo 11 mission marked the first time humans set foot upon another world. Manned exploration of the Moon did not continue for long, however. The Apollo 17 mission in 1972 marked the most recent human visit to another world, and there is no further planned human exploration of an extraterrestrial body, though robotic missions are still pursued vigorously. Apollo missions returned over 380 kg of lunar rocks, which have been used to develop a detailed geological understanding of the Moon's origins. In subsequent years, anyway, also Japan, China, India, the United States, and the European Space Agency have each sent lunar orbiters. These spacecraft have contributed for instance to confirming the discovery of lunar water ice in permanently shadowed craters at the poles and bound into the lunar regolith. From the begining of space activities, in a parallel way of political and jurisdictional issues **(Zhokov et al., 1974, Kolman et al., 1974, Gaggero et al., 1981)** economical analysis outlined the high cost associated with space activities **(Ayres et al., 1979)**. Basically speaking it has been calculated that the cost associated to the transport of a kg of payload on orbit is about 20000 $, and depending on the destination only from the propellant it is necessary to take into account about 10000 kg for lunar ascent vehicles and 35000 kg for martian ascent vehicles **(Shrunk et al., 2008)**. As a consequence of these extimations from the beginningSpace missions scenarios design have taken into account the use of extraterrestrial resources to the production of materials in extraterrestrial environments**(Segal et al., 1965, Vasilik et al., 1965, Novosad, 1978)**. Specifically **Segal et al. (1965)** performed an economic analysis of oxygen and fuel production with and without lunar resources; with the same approach **Novosad et al. (1978)** analysed the integration of extraterrestrial resources into design of space transportation systems. This approach has been transposed in the formulation of two paradigms already mentioned and known as ISRU and ISFR.Indeed, the use of ISRU and ISFR technologies provides back up support for the Martian mission could reduce the mass of vehicles of about 20000 kg. **Gillespie et al. (1965)** investigated the possibility of exploit extraterrestrial resources to supply propellants for refueling rockets at various stations during interplanetaryflights with particular reference on Moon, Mars andVenus. In subsequent years **Heppenheimer et al. (1965)** studied the feasibility of transport of lunar material to colonies in space. This preliminary studies confirmed that the concept of space exploration cannot be based on the total material supply from the Earth, because of the costs and risks associated with this kind of approach. The possibility of extracting and utilizing extraterrestrial material has been, indeed, developed in subsequent years by various authors **(Criswell et al. 1977, Bock et al., 1978, Williams et al., 1981, Carrol et al., 1983, Sadin et al., 1985, Graham et al., 1992)**.

More particular –as a preminary study- **Criswell et al. (1977)** prospected the utilization of lunar resources as materials for spaceborne construction. That use of lunar materials has been considered economically justifiable in the case of large scale projects as space power stations. The same result has been obtained by **Bock et al. (1978)**, that demontsrated that the use of lunar resources is potentially more cost-effective than earth-derived material utilization, due to significant reductions in both transportation and manufacturing costs. **Carrol et al. (1983)** analyzed the various technologies proposed to obtain oxygen on the lunar surface, to be used as a propellants.

In the same period, due to the availability of more accurate data from Space probes, lot of authors have investigated the possibility of designing a first colony of human presence in Space utilizing extraterrestrial resources in an integrated way to guarantee habitat structures and human wellness. Lot of knodlegde that had been developed until that period have been classified and integrated by **McKay et al. (1992)** with respect to Moon and Mars. The aim of that work was to offer an omnicomphensive analysis of space resources and the design of a colony on Moon and Mars, dividing the main topic into 4 sub-topic that represent, also nowdays, the main topics to be covered in Space exploration field: (a)Scenario's analysis, (b) Energy, Power, and Transport, (c)Materials and Social Concerns. From that period Space Agencies all over have collaborated in formulating new processes and solutions by organizing their results and analysis in periodical meetings in which different experiences are bounded **(Kaplan et al., 1997, Kaplan et al., 1999, Sanders et al., 1999a, Sanders et al., 1999 b, Mankins et al., 2000)** covering both technical and economic issues **(Criswell et al., 1978, Mankins et al., 2000)**: that will be discussed in deep detail in the following sections of this document.

As discussed also in what follows, future manned missions to the Moon have been planned, including government as well as privately funded efforts and lot of plans for lunar future outposts have been proposed **(Taylor et al., 1992, Roberts et al., 1992, Connolly et al., 1993, Albus et al., 1992, Haskin et al., 1989, Harper et al., 1990, Duke et al., 1990, Hypes et al., 1990, Staehle et al., 1991)**. **Connolly et al. (1992)** described the requirements and the design concepts for the First Lunar Outpost (FLO), while **Albus et al. (1992)** focused their attention on the robotic aspects of the future missions with particular reference on sensors' design to perform excavation, grading and other exploration activities. In this contest **Hypes et al. (1990)** proposed the fabrication of lunar-base structures and shelters using lunar materials. **Taylor et al. (1992)** outlined the importance of a preliminary robotic mission on the Moon in order to acquire more accurate geologic data for resource utilization. **Roberts et al. (1992)** analized a lunar base architecture able to to extract useful materials from the indigenous resources able to support a crew of up to twelve. This results was obtained exploting two major process: one produces oxygen, ceramics, and metals; the other produces hydrogen, helium, and other volatiles. In that paper is presented one of the most controverse ideas in Space exploration: the use of Moon for a simulation of a Mars mission. According to some scientists, indeed, the two environments are so different that this investigation would be useless **(Zubrin, 1996)**.

Immediately after the Lunar challenge the attention of the scientific community has been focused to Mars and more recently to the asteroids.The exploration of Mars has been an important part of the space exploration programs of the Soviet Union (later Russia), United States, Europe, and Japan. Dozens of robotic spacecraft, including orbiters, landers, and rovers, have been launched toward Mars since the 1960sand lot of plans for future martian outposts have been proposed in the literature **(Barker et al., 1998, Ming et al., 1993, Finn et al., 2000)**.

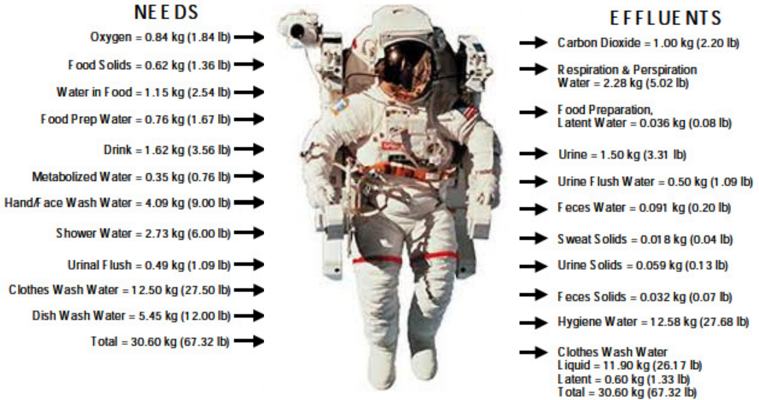
Barker et al. (1998) examined the potential for supporting the first manned mission with the objective of achieving self-sufficiency through resource utilization integrated in a program of rigorous scientific research aimed at extending that capability. In particular they examined the potential for initially extracting critical resources from the martian environment, and discussed the scientific investigations required to identify additional resources in the atmosphere, on the surface, and within the subsurface. **Finn et al. (2000)** proposed a unified mars exploration program, outlining the scientific and technological links between the robotic-only missions that have been flown and planned the robotic + human missions that will come in the future. With respect to automatic Space exploration, instead, the first objects to successfully landed on the surface were two Soviet probes: Mars 2 on November 27 and Mars 3 on December 2, 1971, but both ceased communicating within seconds of landing. The 1975 NASA launches of the Viking program consisted of two orbiters, each having a lander; both landers successfully touched down in 1976. Viking 1 remained operational for six years, Viking 2 for three. The Viking landers relayed color panoramas of Mars and the orbiters mapped the surface so well that the images remain in use. Until the first flyby of Mars occurred in 1965, by Mariner 4, many speculated about the presence of liquid water on the planet's surface. This was based on observed periodic variations in light and dark patches, particularly in the polar latitudes, which appeared to be seas and continents; long, dark striations were interpreted by some as irrigation channels for liquid water. These straight line features were later explained as optical illusions, though geological evidence gathered by unmanned missions suggest that Mars once had large-scale water coverage on its surface. Anyway, in 2005, radar data revealed the presence of large quantities of water ice at the poles, and at mid-latitudes. The Mars rover Spirit sampled chemical compounds containing water molecules in March 2007.

As said previously space probes have been sent during last decades all over th Solar system, and also on Asteroids, that could represent –currently- a key solution for Space exploration.Several asteroids have now been visited by probes, the first of which was Galileo, which flew past two: 951 Gaspra in 1991, followed by 243 Ida in 1993. Both of these lay near enough to Galileo's planned trajectory to Jupiter that they could be visited at acceptable cost. The first landing on an asteroid was performed by the NEAR Shoemaker probe in 2000, following an orbital survey of the object. In the literature near-Earth asteroids have been recently analyzed in terms of composition **(Lebofsky et al., 1990)**, and materials extraction **(Westfall et al., 1991, Oleary et al., 1997)**.

2.1.2 Controlled life support system

One of the biggest difficulties in performing Human Space exploration is that each crew member need to consume somequantities of materials that have to be transported from Earth.

In the following **Figure 2-1** the physiological human needs and effluents estimated per day for each crew member are reported. As it is apparent, being human evolution Earth-based, in Space environment or in Space Station it is necessary both to transport the needed life consumablesand/or to recreate the conditions to produce biological materials (as water, oxygen, food etc.).



According to this approach each crew member could be seen as a biological reactor that transform some inputs in byproducts that could be recycled and/or re-used.

FIGURE 2- 1: Human Needs And By Products

2.1.3 Controlled Ecological Life-Support System (ECLSS)

Basically speaking the essential operations to be faced by the Life-Support System inside the crew cabin in the Space Station consists on:

- Removal of both metabolic and non-metabolic wastes (dirty water, urine, feces, solid wastes, nitrogen from breathing and sweating)
- Production of breathing atmosphere with appropriate content of constituents
- Availability of water for both hygenic and drinkable needs
- Availability of food

The system that provides the solution to all of this needs is generally known as ECLSS (Controlled Ecological Life-Support System). In addition this system allows to obtain values of temperature, pressure and humidity in a range coherent with crew physiological needs.More specifically, the ECLSS consists of an air revitalization system, water coolant loop systems, atmosphere revitalization pressure control system, active thermal control system, supply water and waste water system, waste collection system and airlock support system.

In what follows, while different technologies and solutions to adress these problems have been designed,a brief explaination of most common ECLSS systems is reported. Frequently the water necessary for the crew is obtained by recycling urine, hygenic water and atmospheric humidity by means of chemico-physical processes as distillation, condensation, filtration and disinfection. Some of the recycled water could be also fed to an electrolyzer that allows the production of hydrogen (useful for energetic purposes) and oxygen, that could be used as life consumable product or as a propellant. In addition human breathing leads also to an increase of carbon dioxide partial pressure inside the cabin, that it is necessary to be removed in order to avoid health problems for the crew.In the ECLSS systems different techniques are used to achieve this goal: assorbtion, adsorbtion into zeolites, osmosys, membrane separation, or biological techniques as fixation by photosynthesis in algae strains grown inside photobioreactors. From a general point of view for short missions carbon dioxide is removed by absorption on lithium hydroxide panels while for longer missions the absorption on zeolites is preferred. In some cases in the ECLSS the carbon dioxide is electrolized to produce carbon monoxide –that could be used as a propellant- and breathable oxygen. The atmosphere humidity and the temperature are maintaned inside a physiological range by means of filters and condensers and cooling/heating systems fed by photovoltaic arrays, place in the external wall of the Space Station. For the metabolic solid wastes currently the recycle is not foreseen, but they are simply dewatered and stored, evan if are under investigation biological treatment for the wastes. Specifically pilot plant units for the anaerobic enzimatic degradation of solid wastes with the aim to produce methane and other useful materias. In the more modern design of ECLSS these wastes could be employed to produce fertilizers for the cultivation of of plants or algae, that represent edible food for crew members.

In any case the current ECLSS plants have not yet achieved the goal of the closed cycle, because it is not possibile to recover and recycle the materials with 100% efficiency. Specifically, without external supply it is not possibile to produce the necessary amount of water food and oxygen. For these reason the Space Station must utilize lot of materials brought from Earth, in particular when long term missions are foreseen. The necessity of these materials from Earth leads, anyway, to the necessity of lot of extremely expensive trips, that could invalidate the economic sustainability of the missions. With the aim to address to these problems the European Space Agency has designed and tested from 1988 the so-called MELISSA project. MELiSSA (Micro-Ecological Life Support System Alternative) is a multidisciplinary project which has been conceived as a micro-organisms and higher plants based ecosystem intended as a tool to gain understanding of the behaviour of artificial ecosystems, and for the development of the technology for a future regenerative life support system for long term manned space missions - for example: a lunar base or a mission to Mars. The driving element of MELiSSA is the recovery of edible biomass from waste, carbon dioxide and minerals, using light as source of energy to promote biological photosynthesis. As reported in **Figure 2-2**, MELiSSA has five compartments colonised respectively by thermophilic anoxygenic bacteria, photoheterotrophic bacteria, nitrifying bacteria, photosynthetic bacteria and higher plants, and the crew.

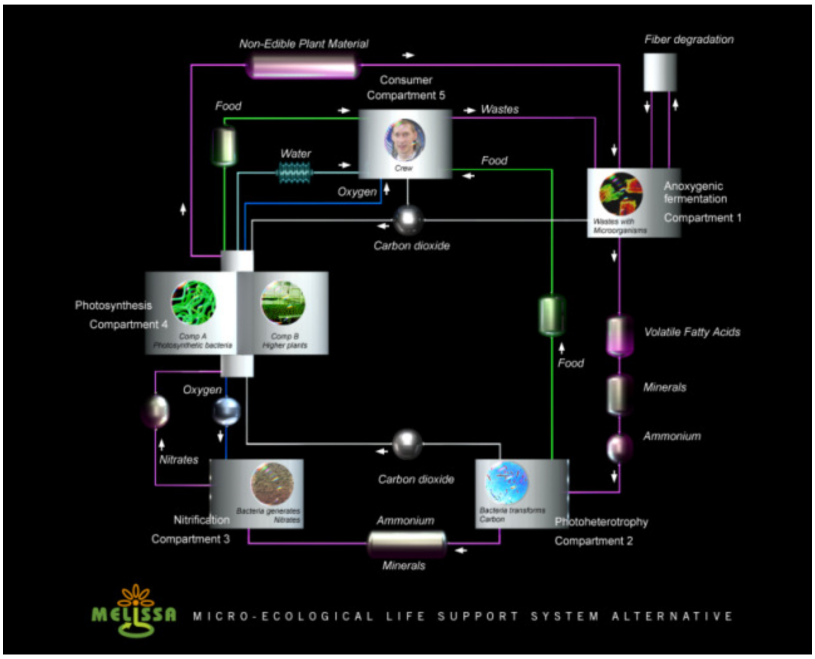


FIGURE 2- 2: Melissa Compartments

In what follows a brief description of the compartment is reported:

2.1.3.1 THE LIQUEFYING COMPARTMENT (COMPARTMENT 1)

This compartment is the collection pool for the waste produced by the consumer (i.e faeces, urine, paper) and also the non-edible output of the higher plant compartment (straw, roots,..) and the non-edible microbial biomass.

Its essential task is to anaerobically transform this waste to ammonium, H_2, CO_2, volatile fatty acids and minerals. For biosafety reasons, as well as degradation efficiency, the compartment operates in thermophilic conditions (i.e. 55°C). In terms of degradation, three main functions are expected in this compartment: proteolysis, saccharolysis, and cellulolysis.

During the early years of MELiSSA, it was expected that a proper selection of a restricted number of mesophilic bacteria could reach a reasonable level of degradation. However, despite interesting results, among them the identification of a new proteoloytic bacteria (i.e. protelyticus thermocellum), a percentage of degradation higher than 15% has never been obtained. Therefore it was rapidly decided to extend the number of bacteria and to work with a consortium of autochthonous strains. Now, the overall biodegradation efficiency by the selected inoculum allows the reaching interesting values (i.e.proteolysis 70%, fibre 44%). Better degradation values are currently limited by two factors: the very slow degradation of fibrous material (i.e cellulose, xylan, lignin) and the mechanical difficulty of extracting these non-degraded compounds for a specific and more adapted treatment.To improve this degradation level, several technologies are currently being studied (subcritical oxydation, fungi, rumen bacteria, hyperthermophilic bacteria,…).

2.1.3.2 *THE PHOTOHETEROTROPHIC COMPARTMENT (COMPARTMENT 2)*

The function of this compartment is the elimination of the terminal products of the liquefying compartment. In the MELiSSA concept, it is divided into two separate and independent compartments (i.e a photoautotrophic and an photoheterotrophic compartment).

This separation was mainly due to an expectation of high H_2 production from the first compartment. Although the specific treatment of hydrogen is still being kept in mind, the very wide results for substrate degradation obtained with R.rubrum lead to simplifcation of the loop to only one second compartment (that is, a photoheterotrophic one). Regarding the current researches on this compartment, they are driven by two major factors: the demonstration of the validity of the preliminarily established stoichiometries in presence of one or several carbon sources and the improvement of the light transfer model. As the quality of microbial biomass is always questionable for man, specific studies have been performed with R.rubrum and have demonstrated its acceptance at low level concentrations.

2.1.3.3 THE NITRIFYING COMPARTMENT (COMPARTMENT 3)

The nitrifying compartment's main function is to cycle NH_4^+ evolved from waste to nitrates, which is the most favourable source of Nitrogen for higher plant as well as Arthrospira platensis.

The compartment is composed of a mix Nitrosomas and Nitrobacter which oxidise NH_4^+ to NO_2^- and NO_2^- to NO_3^- respectively. As this compartment is a fixed bed reactor, the importance of the hydrodynamic factors is slightly more important as well as more complicated. Therefore the activity on this compartment has been focused on two areas: the physical characterisation of the reactors (i.e. Kla , RTD) and numerous bench tests to establish the proper kinetics and stoichiometries for different configurations.

2.1.3.4 THE PHOTOAUTOTOPHIC COMPARTMENT (COMPARTMENT 4):

As already explained the fourth compartment is split into two parts:

the algae compartment colonised by the cyanobacteria Arthrospira platensis and the Higher Plant(HP)compartment

These compartments are essential for the regeneration of oxygen and the production of food.The algae compartment(4A) has been extensively studied in the MELiSSA project, stoichiometries have been validated in optimal and several limitation conditions. A specific photobioreactor has been built to support investigations in the MELiSSA pilot plant, and a predictive model has been validated during continuous experiments.The higher plant compartment (HPC: 4B): The activities on this compartment have been initiated with eight crops: wheat, tomato, potato, soybean, rice, spinach, onion and lettuce. Simulations of this HPC require a description of biomass production rates as well as their mineral and proximate compositions. A third aspect of the investigations on the HPC is the study of the hardware necessary for higher plants. Studies have been initiated for the light sources and nutrients sensors.Other technologies are under development for utilize and convert human bioproducts during space missions: for instance **Cheng et al. (2006)** proposed a method for the removal of carbon dioxide from air by microalgae using a photobioreactor.

2.1.4 EVA (Extra-vehicular activity)

Extra-vehicular activity (EVA) is work done by an astronaut away from the Earth, and outside of a spacecraft. The term most commonly applies to an EVA made outside a craft orbiting Earth, but also applies to an EVA made on the surface of the Moon. In the later lunar landing missions (Apollo 15, 16, and 17) the command module pilot (CMP) did an EVA to retrieve film canisters on the return trip; he was assisted by the lunar module pilot (LMP) who remained at the open command module hatch. These trans-Earth EVAs were the only spacewalks ever conducted in deep space. A "Stand-up" EVA (SEVA) is where the astronaut does not fully exit a spacecraft, but is completely reliant on the spacesuit for environmental support.Its name derives from the astronaut "standing up" in the open hatch, usually to film or assist a spacewalking astronaut. EVAs may be either tethered (the astronaut is connected to the spacecraft; oxygen and electrical power can be supplied through an umbilical cable; no propulsion is needed to return to the spacecraft), or untethered. The metabolic assessment during extra-vehicular activity has been analyzed and quantified by lot of biomedical studies as **Osipov et al. (1998)**.

2.1.5 Energy and propellantsforSpace missions

In planning the development of a space out post, one of the first consideration is power – for operating machinery and for transportation. Getting to and from the lunar or martian surface is currently expensive, and the expenses could be reduced if the vehicles that go there did not have to carry enough fuel for return trip. There is also a need for power for robot and machinery on extraterrestrial surface. Again, if their power must be completely supplied by batteriesthat are sent with them, the cost of transportation is much greater than if they can generate some or all of their power from sunlight. Electrical, thermal, and chemical power have advantages over nuclear and hydraulic power on the Moon. Historically, it has been possible to power small space craft with RTG (radioisotope thermoelectric generators); however, RTGs are no longer being made because there is no plutonium available from which to make them. Other types of nuclear plants have been discussed, but it is difficult to gain pubblic support for nuclear energy, and it is also expensive to transport the equipment to the extraterrestrial surface. Hydraulic power requires a working fluid, and Moon and Mars don’t have any known source for the fluidsthat are tipycally used in these systems. For these reasons, mission planners are focusing on electrical power from solar cells, thermal power from solar collectors, and the production of rocket fuel from indigenous materials.

On the other hand, another key point of Space mission is the propellant production. Propellant is the chemical mixture burned to produce thrust in rockets and consists of a fuel and an oxidizer. A fuel is a substance which burns when combined with oxygen producing gas for propulsion. An oxidizer is an agent that releases oxygen for combination with a fuel. The ratio of oxidizer to fuel is called the mixture ratio. Propellants are classified according to their state - liquid, solid, or hybrid. The gauge for rating the efficiency of rocket propellants is specific impulse, stated in seconds. Specific impulse indicates how many kilograms of thrust are obtained by the consumption of one kilogramof propellant in one second. Specific impulse is characteristic of the type of propellant, however, its exact value will vary to some extent with the operating conditions and design of the rocket engine.

2.1.5.1 LIQUID PROPELLANTS

In a liquid propellant rocket, the fuel and oxidizer are stored in separate tanks, and are fed through a system of pipes, valves, and turbopumps to a combustion chamber where they are combined and burned to produce thrust. Liquid propellant engines are more complex than their solid propellant counterparts, however, they offer several advantages. By controlling the flow of propellant to the combustion chamber, the engine can be throttled, stopped, or restarted.

A good liquid propellant is one with a high specific impulse or, stated another way, one with a high speed of exhaust gas ejection. This implies a high combustion temperature and exhaust gases with small molecular weights. However, there is another important factor which must be taken into consideration: the density of the propellant. Using low density propellants means that larger storage tanks will be required, thus increasing the mass of the launch vehicle. Storage temperature is also important. A propellant with a low storage temperature, i.e. a cryogenic, will require thermal insulation, thus further increasing the mass of the launcher. The toxicity of the propellant is likewise important. Safety hazards exist when handling, transporting, and storing highly toxic compounds. Also, some propellants are very corrosive, however, materials that are resistant to certain propellants have been identified for use in rocket construction.

Liquid propellants used in rocketry can be classified into three types: petroleum, cryogens, and hypergols.

Petroleum fuels are those refined from crude oil and are a mixture of complex hydrocarbons, i.e. organic compounds containing only carbon and hydrogen. The petroleum used as rocket fuel is a type of highly refined kerosene, called RP-1 in the United States. Petroleum fuels are usually used in combination with liquid oxygen as the oxidizer. Kerosene delivers a specific impulse considerably less than cryogenic fuels, but it is generally better than hypergolic propellants.

Specifications for RP-1 where first issued in the United States in 1957 when the need for a clean burning petroleum rocket fuel was recognized. Prior experimentation with jet fuels produced tarry residue in the engine cooling passages and excessive soot, coke and other deposits in the gas generator. Even with the new specifications, kerosene-burning engines still produce enough residues that their operational lifetimes are limited. Liquid oxygen and RP-1 are used as the propellant in the first-stage boosters of the Atlas and Delta II launch vehicles. It also powered the first-stages of the Saturn 1B and Saturn V rockets.

Cryogenic propellants are liquefied gases stored at very low temperatures, most frequently liquid hydrogen (LH_2) as the fuel and liquid oxygen (LO_2 or LOX) as the oxidizer. Hydrogen remains liquid at temperatures of -253 °C and oxygen remains in a liquid state at temperatures of -183 °C.

Because of the low temperatures of cryogenic propellants, they are difficult to store over long periods of time. For this reason, they are less desirable for use in military rockets that must be kept launch ready for months at a time. Furthermore, liquid hydrogen has a very low density (0.071 g/ml) and, therefore, requires a storage volume many times greater than other fuels. Despite these drawbacks, the high efficiency of liquid oxygen/liquid hydrogen makes these problems worth coping with when reaction time and storability are not too critical. Liquid hydrogen delivers a specific impulse about 30%-40% higher than most other rocket fuels.

Liquid oxygen and liquid hydrogen are used as the propellant in the high efficiency main engines of the Space Shuttle. LOX/LH_2 also powered the upper stages of the Saturn V and Saturn 1B rockets, as well as the Centaur upper stage, the United States' first LOX/LH_2 rocket in 1962.

Another cryogenic fuel with desirable properties for space propulsion systems is liquid methane (-162 ^oC). When burned with liquid oxygen, methane is higher performing than state-of-the-art storable propellants but without the volume increase common with LOX/LH_2 systems, which results in an overall lower vehicle mass as compared to common hypergolic propellants. LOX/methane is also clean burning and non-toxic. Future missions to Mars will likely use methane fuel because it can be manufactured partly from Martian in-situ resources. LOX/methane has no flight history and very limited ground-test history.

Liquid fluorine (-188 °C) burning engines have also been developed and fired successfully. Fluorine is not only extremely toxic; it is a super-oxidizer that reacts, usually violently, with almost everything except nitrogen, the lighter noble gases, and substances that have already been fluorinated. Despite these drawbacks, fluorine produces very impressive engine performance. It can also be mixed with liquid oxygen to improve the performance of LOX-burning engines; the resulting mixture is called FLOX. Because of fluorine's high toxicity, it has been largely abandoned by most space-faring nations.

Some fluorine containing compounds, such as chlorine pentafluoride, have also been considered for use as an 'oxidizer' in deep-space applications.

Hypergolic propellants are fuels and oxidizers that ignite spontaneously on contact with each other and require no ignition source. The easy start and restart capability of hypergols make them ideal for spacecraft maneuvering systems. Also, since hypergols remain liquid at normal temperatures, they do not pose the storage problems of cryogenic propellants. Hypergols are highly toxic and must be handled with extreme care.

Hypergolic fuels commonly include hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH). Hydrazine gives the best performance as a rocket fuel, but it has a high freezing point and is too unstable for use as a coolant. MMH is more stable and gives the best performance when freezing point is an issue, such as spacecraft propulsion applications. UDMH has the lowest freezing point and has enough thermal stability to be used in large regeneratively cooled engines. Consequently, UDMH is often used in launch vehicle applications even though it is the least efficient of the hydrazine derivatives. Also commonly used are blended fuels, such as Aerozine 50 (or "50-50"), which is a mixture of 50% UDMH and 50% hydrazine. Aerozine 50 is almost as stable as UDMH and provides better performance.

The oxidizer is usually nitrogen tetroxide (NTO) or nitric acid. In the United States, the nitric acid formulation most commonly used is type III-A, called inhibited red-fuming nitric acid (IRFNA), which consists of HNO_3 + 14% N_2O_4 + 1.5-2.5% H_2O + 0.6% HF (added as a corrosion inhibitor). Nitrogen tetroxide is less corrosive than nitric acid and provides better performance, but it has a higher freezing point. Consequently, nitrogen tetroxide is usually the oxidizer of choice when freezing point is not an issue; however, the freezing point can be lowered with the introduction nitric oxide. The resulting oxidizer is called mixed oxides of nitrogen (MON). The number included in the description, e.g. MON-3 or MON-25, indicates the percentage of nitric oxide by weight. While pure nitrogen tetroxide has a freezing point of about -9 ^{o}C, the freezing point of MON-3 is -15 ^{o}C and that of MON-25 is -55 ^{o}C.

USA military specifications for IRFNA were first published in 1954, followed in 1955 with UDMH specifications.

The Titan family of launch vehicles and the second stage of the Delta II rocket use NTO/Aerozine 50 propellant. NTO/MMH is used in the orbital maneuvering system (OMS) and reaction control system (RCS) of the Space Shuttle orbiter. IRFNA/UDMH is often used in tactical missiles such as the US Army's Lance (1972-91).

Hydrazine is also frequently used as a monopropellant in catalytic decomposition engines. In these engines, a liquid fuel decomposes into hot gas in the presence of a catalyst. The decomposition of hydrazine produces temperatures up to about 1,100 ^{o}C and a specific impulse of about 230 or 240 seconds. Hydrazine decomposes to either hydrogen and nitrogen, or ammonia and nitrogen.

Other propellants have also been used, a few of which deserve mentioning:

Alcohols were commonly used as fuels during the early years of rocketry. The German V-2 missile, as well as the USA Redstone, burned LOX and ethyl alcohol (ethanol), diluted with water to reduce combustion chamber temperature. However, as more efficient fuels where developed, alcohols fell into general disuse.

Hydrogen peroxide once attracted considerable attention as an oxidizer and was used in Britain's Black Arrow rocket. In high concentrations, hydrogen peroxide is called high-test peroxide (HTP). The performance and density of HTP is close to that of nitric acid, and it is far less toxic and corrosive, however it has a poor freezing point and is unstable. Although HTP never made it as an oxidizer in large bi-propellant applications, it has found widespread use as a monopropellant. In the presence of a catalyst, HTP decomposes into oxygen and superheated steam and produces a specific impulse of about 150 s.

Nitrous oxide has been used as both an oxidizer and as a monopropellant. It is the oxidizer of choice for many hybrid rocket designs and has been used frequently in amateur high-powered rocketry. In the presence of a catalyst, nitrous oxide will decompose exothermically into nitrogen and oxygen and produce a specific impulse of about 170 s.

2.1.5.2 SOLID PROPELLANTS

Solid propellant motors are the simplest of all rocket designs. They consist of a casing, usually steel, filled with a mixture of solid compounds (fuel and oxidizer) which burn at a rapid rate, expelling hot gases from a nozzle to produce thrust. When ignited, a solid propellant burns from the center out towards the sides of the casing. The shape of the center channel determines the rate and pattern of the burn, thus providing a means to control thrust. Unlike liquid propellant engines, solid propellant motors can not be shut down. Once ignited, they will burn until all the propellant is exhausted.

There are two families of solids propellants: homogeneous and composite. Both types are dense, stable at ordinary temperatures, and easily storable.

Homogeneous propellants are either simple base or double base. A simple base propellant consists of a single compound, usually nitrocellulose, which has both an oxidation capacity and a reduction capacity. Double base propellants usually consist of nitrocellulose and nitroglycerine, to which a plasticiser is added. Homogeneous propellants do not usually have specific impulses greater than about 210 seconds under normal conditions. Their main asset is that they do not produce traceable fumes and are, therefore, commonly used in tactical weapons. They are also often used to perform subsidiary functions such as jettisoning spent parts or separating one stage from another.

Modern composite propellants are heterogeneous powders (mixtures) which use a crystallized or finely ground mineral salt as an oxidizer, often ammonium perchlorate, which constitutes between 60% and 90% of the mass of the propellant. The fuel itself is generally aluminum. The propellant is held together by a polymeric binder, usually polyurethane or polybutadienes, which is also consumed as fuel. Additional compounds are sometimes included, such as a catalyst to help increase the burning rate, or other agents to make the powder easier to manufacture. The final product is rubberlike substance with the consistency of a hard rubber eraser.

Composite propellants are often identified by the type of polymeric binder used. The two most common binders are polybutadiene acrylic acid acrylonitrile (PBAN) and hydroxy-terminator polybutadiene (HTPB). PBAN formulations give a slightly higher specific impulse, density, and burn rate than equivalent formulations using HTPB. However, PBAN propellant is the more difficult to mix and process and requires an elevated curing temperature. HTPB binder is stronger and more flexible than PBAN binder. Both PBAN and HTPB formulations result in propellants that deliver excellent performance, have good mechanical properties, and offer potentially long burn times.

Solid propellant motors have a variety of uses. Small solids often power the final stage of a launch vehicle, or attach to payloads to boost them to higher orbits. Medium solids such as the Payload Assist Module (PAM) and the Inertial Upper Stage (IUS) provide the added boost to place satellites into geosynchronous orbit or on planetary trajectories.

The Titan, Delta, and Space Shuttle launch vehicles use strap-on solid propellant rockets to provide added thrust at liftoff. The Space Shuttle uses the largest solid rocket motors ever built and flown. Each booster contains 500,000 kg of propellant and can produce up to 14,680,000 Newtons of thrust.

2.1.5.3 HYBRID PROPELLANTS

Hybrid propellant engines represent an intermediate group between solid and liquid propellant engines. One of the substances is solid, usually the fuel, while the other, usually the oxidizer, is liquid. The liquid is injected into the solid, whose fuel reservoir also serves as the combustion chamber. The main advantage of such engines is that they have high performance, similar to that of solid propellants, but the combustion can be moderated, stopped, or even restarted. It is difficult to make use of this concept for vary large thrusts, and thus, hybrid propellant engines are rarely built.

SpaceShipOne, which won the Ansari X-Prize, was powered by a hybrid engine burning nitrous oxide as the liquid oxidizer and HTPB rubber as the solid fuel.

As it will be apparent in following paragraphes, due of the different distancesbetween Earth and Moon and Earth and Mars, the propellant production using in-situ resources will result in strong cost reduction in particular on Martian surface.

2.2 Strategies and current paradigms of Space Exploration

In the 2000s, the People's Republic of China initiated a successful manned spaceflight program, while the European Union, Japan, and India have also planned future manned space missions. China, Russia, Japan, and India have advocated manned missions to the Moon during the 21st century, while the European Union has advocated manned missions to both the Moon and Mars during the 21st century. In 2010 President Obama presented the American space exploration program, a new concept of space exploration with respect to the Augustine committee program based on the return to the Moon. Indeed, according to very recent news from the USA administration, future human space exploration scenarios are consistent with the following perspectives: utilization of ISS (International Space Station) until 2020 and beyond, assembly of post ISS infrastructures, the design and development of long-cruise stages to get to other destinations, and the implementation of human activities on near a planetary body surface (Moon, near Earth asteroids, Mars and its moons).

To this aim, as of 2015 it is foreseen the building of new rocket useful for Earth-Mars missions and it is programmed in the next 30 years a manned missions first to an asteroid and finally on Mars.

The main future goal to be handled by Space Agencies are briefly drawn. The ESA, European Space Agency, is planning to send a space probe on Jupiter, in cooperation with NASA, the American space agency. In addition, currently, ESA is involved in the design of new space vectors.The Russian Space agency is collaborating with ESA in the building of new space transportation system as KLIPER and is setting up a manned mission on the Moon.The Japan has focused its attention a little more far, planning a manned mission on Mars by 2030, in a similar way as China, that have planned to land on Mars in the next 40 years. To complete this brief overview, the Indian Space agency is planning a human mission on the Moon by 2020.The importance of the exploitment of In-Situ Resources in the development of tecnical processes and solutions has been transposed in two paradigms: ISRU (In Situ Resource Utilization) and ISFR (In Situ Fabrication and Repair). ISRU and ISFR are the two paradigms that have been proposed recently in order to extent the manned mission time and -more generally- to make more economically sustainable space activities. Indeed in-situ production of propelleants, life support consumables, and fuel cell reactants significantly reduces the mass to be transported on the extraterrestrial surface. Specifically, ISRU and ISFR paradigms are related to the possibility of extracting and utilizing extraterrestrial resources necessary for human survival, without being equipped with huge amount of supplies from the Earth. In particular, this ability will significantly reduce the cost, mass, and risk of sustained human activities beyond Earth.

They are aimed to establish, evaluate and assess the in situ resources available on the Moon and Mars and the technologies needed to utilize and exploit these resources. More specifically ISRU approach will focus on technologies necessary to extract consumables (O_2, H_2O, N_2, He, etc.) for human life-support system replenishment, source materials for ISFR technologies, and source materials for In-Situ Fabrication and Repair applications. ISFR, is aimed to satisfy others human needs and in particular focus its attention in three main areas:

- Fabrication Technologies that is aimed to provide a means of building new parts or replacing existing parts or tools.

- Repair & NDE Technologies that provide a means of repairing systems during transport and while on the Moon, Mars, and other extraterrestrial bodies.
- Habitat Structures that focuses on the development of lunar and Martian habitat structures with environmental protection features.

In the framework of these approaches lot of scientific efforts have been used up**(i.e: Atchinson et al., 1966, Johnson et al., 1970, Bock et al., 1979, Hoffman et al. 1983, Staehle et al. 1983, Simon et al. 1992, Sastri et al., 1992, Duke et al., 1998, Ignatiev et al. 2000, Kaplan et al. 2000, Baird et al. 2003)** both with respect to the lunar environment and to the martian one: the main results obtained will be summarized in the following paragraphes.

The most recent common program of future Space exploration for the future Space has been drawn by the ISECG (International Space ExplorationCoordination Group) that coordinates the global interests of 14 space agencies.Indeed, by developing a common roadmap, agencies hope to coordinate their preparatory investments in ways that maximize return on investments and enable earlier realization of their goals and objectives.

The common human exploration strategy begins with the ISS as the first important step toward Mars and human expansion into space. It recognizes that human missions to both asteroids and the Moon are also important destinations that contribute to preparing for a future human mission to Mars.

This first iteration of the roadmap identifies two feasible pathways for human missions after ISS: (1) Asteroid Next (See **Figure 2-3** and **2-4**) and (2) Moon Next. They differ primarily with regard to the sequence of sending humans to the Moon and asteroids, and each reflects a stepwise development and demonstration of the capabilities ultimately required for human exploration of Mars. Alternatively, pursuing the “Asteroid Next” pathway aggressively drives advancements in deep space exploration technologies and capabilities such as advanced propulsion or habitation systems. As relics of the solar system formation, near-Earth asteroids are worthy of further study and takea major step toward readiness for Mars missions.

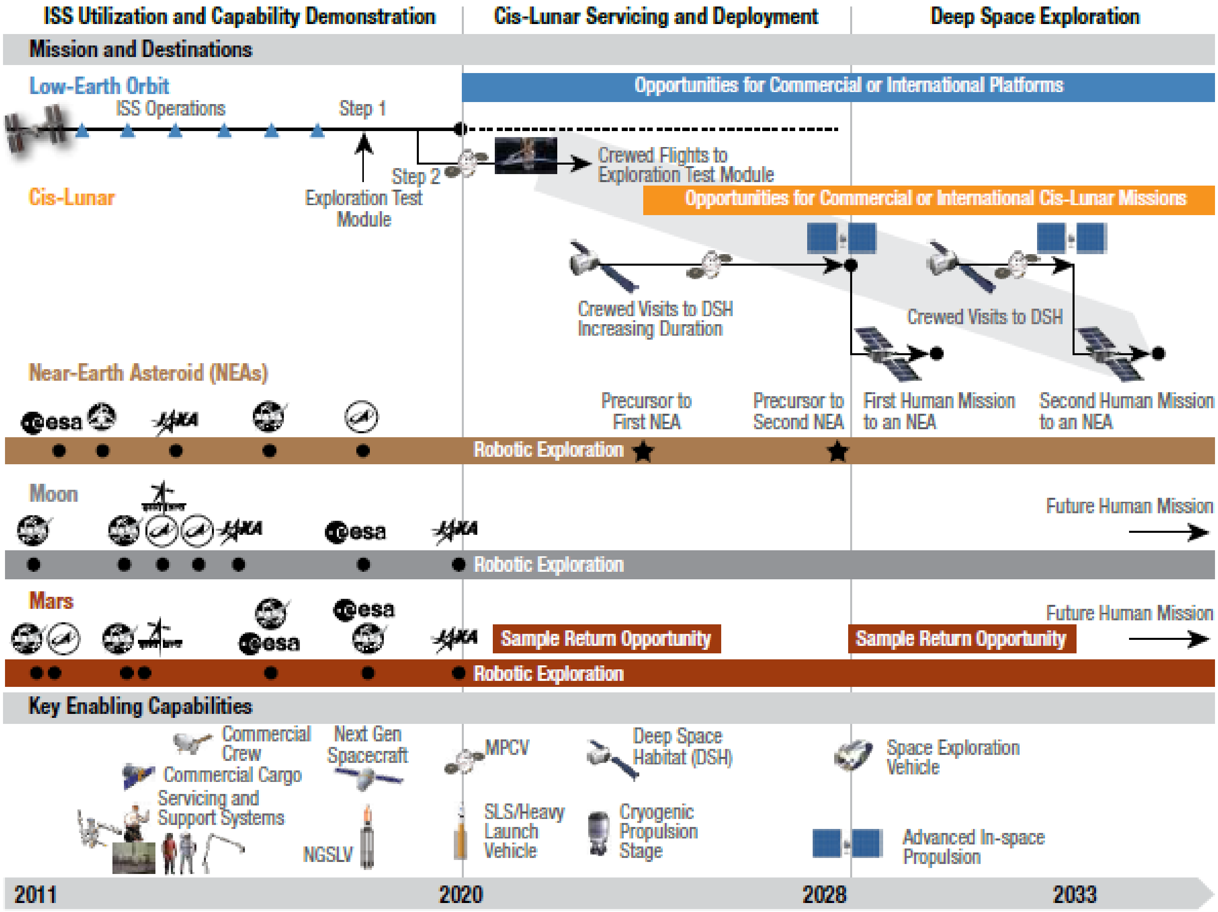


FIGURE 2- 3: Mission Scenario: Asteroid Next

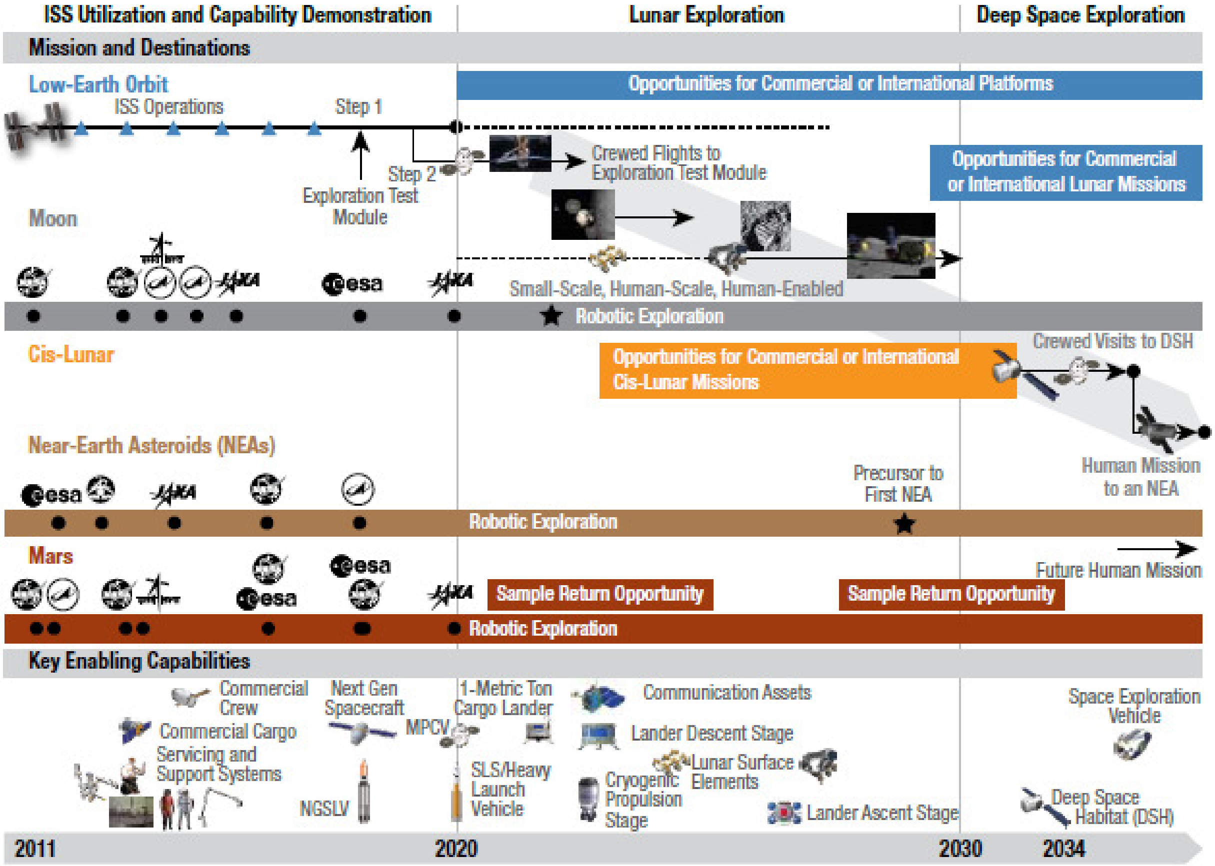


FIGURE 2- 4: Mission Scenario: Moon Next

Each pathway is elaborated by development of a representative mission scenario — a logical sequence of missions over a 25-year horizon — which is considered technically feasible and programmatically implementable.

Space agencies participating in ISECG have defined a longrange human exploration strategy that begins with the ISS and expands human presence throughout the solar system, leading to human missions to explore the surface of Mars. Unquestionably, sending humans to Mars in a manner that is sustainable over time will be the most challenging and rewarding objective of human space exploration in the foreseeable future. These missions will require new technologies and significant advances in the capabilities, systems, and infrastructure we have today.

The main Mars Mission challenges could be summarized in what follows:

- Radiation protection and measurement techniques
- Subsystem reliability and in-space repair capability
- Entry, descent, and landing of large payloads
- Utilization of local resources, such as oxygen, water, and methane
- Advanced in-space propulsion
- Long-term storage and management of cryogenic fluids (H_2, O_2, CH_4, Xe)
- Surface mobility, including routine extravehicular activity capability

Transforming this strategy into a roadmap involves identification of feasible pathways and the definition of mission scenarios that build upon capabilities we have today, drive technology development, and enable scientific return.

One of the other key points underlined by ISECG is the importance of robotic precursor in Space exploration. Indeed, Robotic missions have always served as the precursors to human exploration missions. Starting with Project Apollo, precursor robotic missions such as Rover, Surveyor, and Lunar Orbiter defined the boundary conditions and environments necessary to inform future human exploration of the Moon. These robotics missions identified potential hazards and characterized areas of the lunar surface for subsequent human exploration and scientific investigation. Similarly, several robotic missions have been sent to Mars in the recent years and these have consisted of remote sensing orbital spacecraft, landers, and exploration rovers. Much like the robotic missions to the Moon, these missions have obtained critical data on the Martian surface and atmospheric environment that will guide the development and operational concepts of exploration systems.

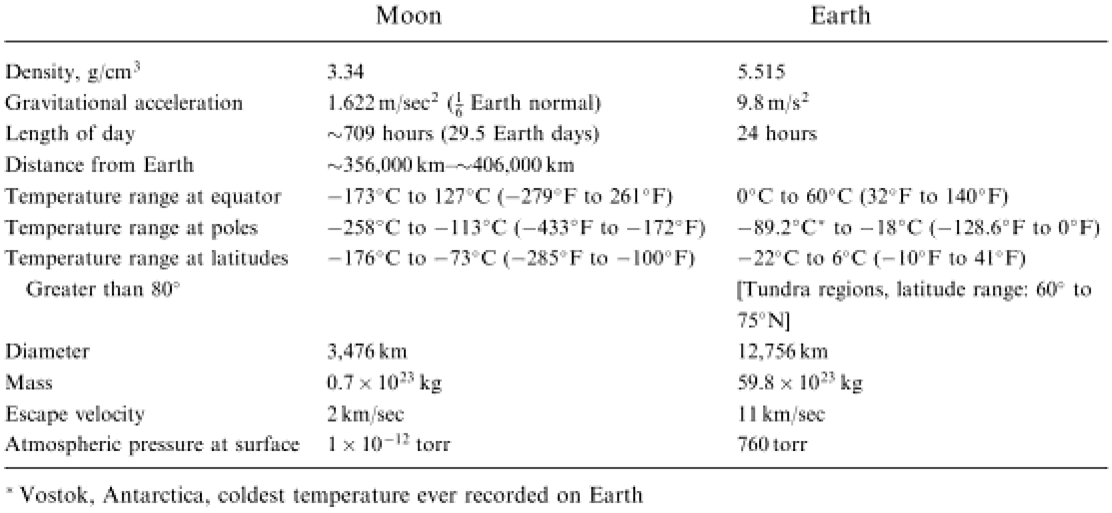
2.3 ISRU and ISFR processes on the Moon

In this chapter the most relevant processes related to the utilization of lunar resources to make more feasible the lunar colonization of our satellite are reported. Anyway to sake of simplicity firstly a brief description of our satellite is stated. It is worth noting, anyway, that only the most relevant characters related to the ISRU /ISFR technologies are reported. More details about lunar soil characteristics are reported elsewhere **(Heiken et al., 1993).**

2.3.1 Moon: Main physical features and exploitable resources

The Moon is Earth's only known natural satellite It is the largest natural satellite of a planet in the Solar System relative to the size of its primary, having a quarter the diameter of Earth and ⅟81 its mass. In the following **Table 2-5** the most relevant physical and geological charactics about our satellite are reported.

TABLE 2-5: Properties Of The Moon Compared With Earth (Heiken Et Al., 1993)

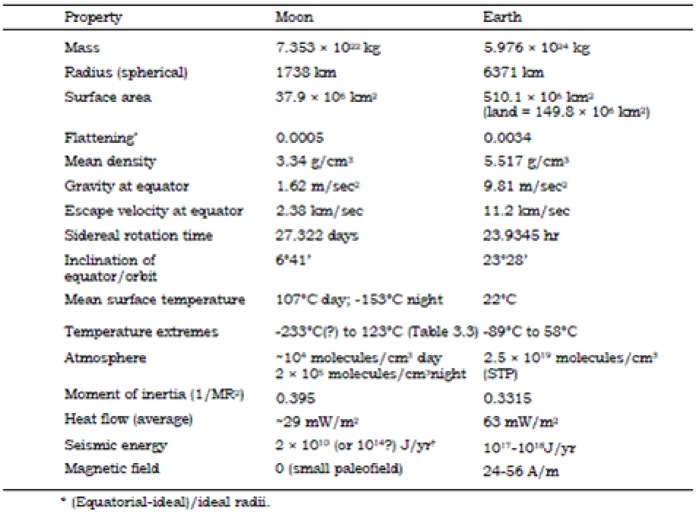


	Moon	Earth
Density, g/cm^3	3.34	5.515
Gravitational acceleration	$1.622\ m/sec^2$ ($\frac{1}{6}$ Earth normal)	$9.8\ m/s^2$
Length of day	~709 hours (29.5 Earth days)	24 hours
Distance from Earth	~356,000 km–~406,000 km	
Temperature range at equator	−173°C to 127°C (−279°F to 261°F)	0°C to 60°C (32°F to 140°F)
Temperature range at poles	−258°C to −113°C (−433°F to −172°F)	−89.2°C* to −18°C (−128.6°F to 0°F)
Temperature range at latitudes Greater than 80°	−176°C to −73°C (−285°F to −100°F)	−22°C to 6°C (−10°F to 41°F) [Tundra regions, latitude range: 60° to 75°N]
Diameter	3,476 km	12,756 km
Mass	0.7×10^{23} kg	59.8×10^{23} kg
Escape velocity	2 km/sec	11 km/sec
Atmospheric pressure at surface	1×10^{-12} torr	760 torr

* Vostok, Antarctica, coldest temperature ever recorded on Earth

The relationships between the Earth and Moon in origin, composition, and orbital dynamics are as important for the basing of people and equipment on the Moon as they are for scientific understanding. Differences between the Earth and the Moon appear clearly in comparisons of their physical characteristics, as shown in **Table 2-6**.

TABLE 2- 6: Comparison between Moon and Earth characteristics



Property	Moon	Earth
Mass	7.353×10^{22} kg	5.976×10^{24} kg
Radius (spherical)	1738 km	6371 km
Surface area	37.9×10^{6} km^2	510.1×10^{6} km^2 (land = 149.8×10^{6} km^2)
Flattening*	0.0005	0.0034
Mean density	3.34 g/cm^3	5.517 g/cm^3
Gravity at equator	1.62 m/sec^2	9.81 m/sec^2
Escape velocity at equator	2.38 km/sec	11.2 km/sec
Sidereal rotation time	27.322 days	23.9345 hr
Inclination of equator/orbit	6°41'	23°28'
Mean surface temperature	107°C day; -153°C night	22°C
Temperature extremes	-233°C(?) to 123°C (Table 3.3)	-89°C to 58°C
Atmosphere	~10^{4} molecules/cm^3 day 2×10^{5} molecules/cm^3 night	2.5×10^{19} molecules/cm^3 (STP)
Moment of inertia (1/MR^2)	0.395	0.3315
Heat flow (average)	~29 mW/m^2	63 mW/m^2
Seismic energy	2×10^{10} (or 10^{14}?) J/yr*	10^{17}-10^{18} J/yr
Magnetic field	0 (small paleofield)	24-56 A/m

* (Equatorial-ideal)/ideal radii.

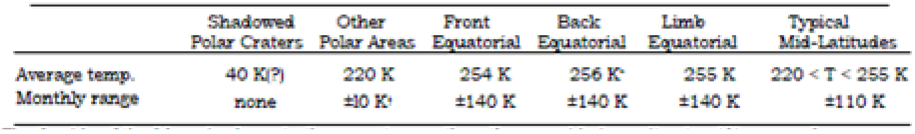
While differences represent in general a disadvange for human colonization, some of these also provide unique opportunities for using lunar environment and its resources in future space exploration. According to this viewpoint in this report it will be reported the most significant parameters useful for the full comprension of what follows.

- On the Moon the most clear environmental characteristics are extreme temperature fluctuations, low gravity, and –from a practical point of view- the absence of any atmosphere.
- The vacuum of space extends to the surface of the Moon, and is a valuable asset that has multiple applications, including:
- Telescope for attenuating the atmosphere
- Separation elements is more efficient in a vacuum environment (ion sputtering)
- Manufactoring of lot of technical devices as microelectronics, carbon nano-tubes and film solar cells requires vacuum
- Lunar vacuum allow trapped gases to escape from molten materials, making the producton of highly refined materials, glasses and other elements
- Rusting of external iron and other metal structures will not occur

- Buildings and towers will not be subjected to aerodiiynamics forces, and it will thus require far less structural length than their Earth counterpart
- Rockets and mass drivers will be able to deliver payload between tha lunar surface and lunar orbit without concern the weather delays or aerodynamics loads on launch vehicles
- Atom smaschers require a vacuum for their operations, so the Moon could represent a suitable place to build them.
- Laser communication and power-beaming system will be able to operate effectively at all times on the Moon because of the lack of atmospheric distorption and attenuation.

Lunar surface temperatures increase about 280 K from just before lunar dawn to lunar noon. Heat flow measurements within the upper several meters of the lunar regolith were made during Apollo missions, in particular at Apollo 15 and Apollo 17 where surface temperatures were also monitored by thermocouples several centimeters above the lunar surface. At the Apollo 15 site (26°N, 3.6°E), the maximum temperature was 374 K (101°C) with a minimum of 92 K (-181°C), while during Apollo 17 mission (site: 20°N, 30.6ºE) were about 10° higher. These observed temperatures are quite close to those determined by Earth-based instruments (maximum = 390 K, minimum = 104 K). At the Apollo 15 site, the meantemperature at a depth of 35 cm is 45 K higher than that of the surface; at the Apollo 17 site, the difference is 40 K. This increase in the mean temperature is related mostly to the temperaturedependence of thermal conductivity of the topmost 1 to 2 cm of lunar soil. Estimated average surface temperatures and temperature extremes for different areas of the Moon were made by the Lunar Colony Study Group **(Dalton and Hoffman, 1972)** and are summarized in **Table 2-7**.

TABLE 2- 7: Estimated Lunar surface temperatures



	Shadowed Polar Craters	Other Polar Areas	Front Equatorial	Back Equatorial	Limb Equatorial	Typical Mid-Latitudes
Average temp.	40 K(?)	220 K	254 K	256 K	255 K	220 < T < 255 K
Monthly range	none	±10 K	±140 K	±140 K	±140 K	±110 K

In addition the temperature at lunar noon varies throughout the year because of varying distance from the sun: this difference from aphelion to perihelion has been quantified in 6 K.

The Moon is a small planetary body, and there is good reason to believe that it has lost most of itsinitial heat during its 4.6-b.y. history. Most of the present heat flux is probably generated by radioisotopes(mainly 40K, 232Th, 235U, and 238U) present in the interior to a depth of about 300 km. During the Apollo missions, heat-flow probes were emplaced in the holes left after extracting cores from the regolith. Before the in situ measurements at the Apollo 15 and 17 landing sites, lunar heat-flow measurements were based on Earth-based observations of thermal emissions from the Moon in the microwave band.

Using electrical and thermal properties deduced from microwave observations in the 1-mm to 3-cm range, they interpreted this gradient has been quatified in terms of a heat flow of 3×10^{-6} W/cm2 to 4×10^{-6} W/cm2. This estimated heat flow is very close to that actually measured on the Moon.

Conductivity measurements were made by means of heaters energized at 0.002 W and the temperature rise was recorded as a function of time. The temperature rise and rate of temperaturerise was interpreted in terms of the conductivity of the surrounding lunar regolith. The upper 1 to 2 cm of lunar regolith must have extremely low thermal conductivities (1.5×10^{-5} W/cm2), with conductivity increasing 5 to 7 times at a depth of 2 cm. At the Apollo sites, mean temperatures 35 cm below the lunar surface are 40 to 45 K above those at the surface. This is primarily related to the temperature dependence of thermal conductivity in the topmost 1 to 2 cm of lunar regolith. Thermometers buried 80 cm below the lunar surface show no perceptible variation in temperature related to the lunar day/night temperature cycle. Below these depths, thermal gradients should reflect heat flow from the lunar crust. An insulating blanket of only about 30 cm of regolith is sufficient to dampen out the ~280 K lunar surface temperature fluctuation to ±3 K variation. From an ISFR point of view this indicates that a lunar habitation buried beneath a thick regolith radiation shield will not be subjected to monthly temperature extremes, but rather will have to find an efficient method for dissipating its waste heat.

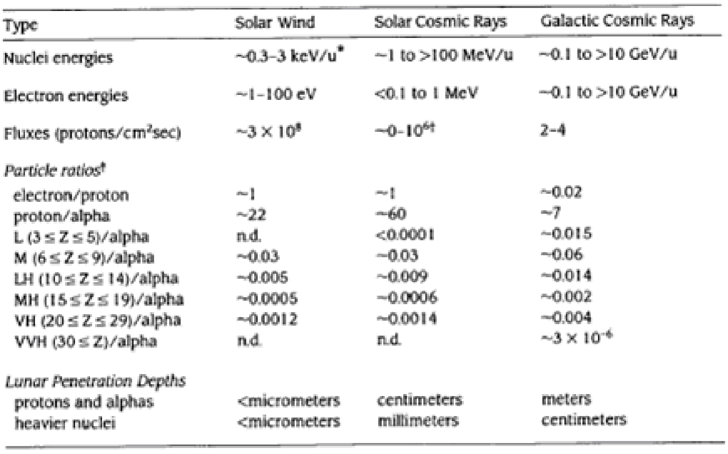
The lunar atmosphere is extremely tenuous: the undisturbed gas concentration is only about 2×10^5molecules/cm^3 during the lunar night, falling to perhaps 10^4 molecules/cm^3 during the lunar day

This is about 14 orders of magnitude less than Earth's atmosphere, a difference so extreme that the Moon is often said to have no atmosphere at all.

The Lunar surface is subject to large fluxes of low-energy solarwind particles, smaller fluxes of high-energy galactic cosmic rays, and rare but occasionally intense particle fluxes emitted by solar flares. The radiation fluxes and energies typically span at least eight orders of magnitude.

The lunar radiation environment also changes with time, usually reflecting the level of solar activity, suchas the modulation of galactic cosmic rays and the irregular emission of energetic particles from the sun.Three major types of radiation at the Moon are discussed here: the solar wind, solar-flare-associatedparticles (also called solar energetic particles or solar cosmic rays), and galactic cosmic rays. The radiation consists mainly of protons and electrons with some heavier nuclei. These particles interact with the Moon in different ways, depending on their energy and composition, resulting in penetration depths that vary from micrometers to meters. The results of interactions with exposed lunar rocks and soils alsovary considerably; the effects include solar-wind implantation, heavy-nuclei tracks, spallation reactions,and the generation of secondary neutrons and gamma rays. A summary of the three radiation typesin terms of their energies, fluxes, compositions, and lunar interaction depths is given in **Table 2-8**. Thenumbers in this Table are averages or more probable ranges, and most of the values can vary widely withtime and/or energy.

TABLE 2-8: Summary of the three major types of radiation in Lunar environment



Type	Solar Wind	Solar Cosmic Rays	Galactic Cosmic Rays
Nuclei energies	~0.3–3 keV/u*	~1 to >100 MeV/u	~0.1 to >10 GeV/u
Electron energies	~1–100 eV	<0.1 to 1 MeV	~0.1 to >10 GeV/u
Fluxes (protons/cm^{2}sec)	~3 × 10^8	~0–$10^{6‡}$	2–4
Particle ratios†			
electron/proton	~1	~1	~0.02
proton/alpha	~22	~60	~7
L ($3 \leq Z \leq 5$)/alpha	n.d.	<0.0001	~0.015
M ($6 \leq Z \leq 9$)/alpha	~0.03	~0.03	~0.06
LH ($10 \leq Z \leq 14$)/alpha	~0.005	~0.009	~0.014
MH ($15 \leq Z \leq 19$)/alpha	~0.0005	~0.0006	~0.002
VH ($20 \leq Z \leq 29$)/alpha	~0.0012	~0.0014	~0.004
VVH ($30 \leq Z$)/alpha	n.d.	n.d.	~3 × 10^{-6}
Lunar Penetration Depths			
protons and alphas	<micrometers	centimeters	meters
heavier nuclei	<micrometers	millimeters	centimeters

Not discussed below are other types of gamma, electron, antimatter, and other charged-particle radiation that have been observed in space around the Earth-Moon system. These particles are present in such low fluxes or low energies that their interactions with the Moon are very difficult to detect, and some have not been well characterized. The gamma rays that come from galactic sources or that are emitted from the sun in large solar flares have low fluxes.

There also are several varieties of low-energy particles (usually <0.1 MeV for electrons and <1 MeV forprotons) that have been seen near the Earth-Moon system or that have been inferred from studies oflunar samples. Some particles near the Moon have origins other than the sun or the "galaxy." Theseinclude electrons emitted by Jupiter's magnetosphere or nuclei like 40Ar that have diffused from the lunar surface and then been ionized and carried along with plasmas near the Moon. In addition, during the rare times that the Moon is in the Earth's magnetotail, even some terrestrial particles can reach the lunar surface. The majority of the observations about radiation presented here were collected by instruments onspacecraft beyond the

Earth's magnetosphere; these observations are representative of what hits the Moon. The Earth's strong magnetic field and thick atmosphere make it hard to use Earth-based methodsto study these radiations, even though observations on Earth led to their discovery.

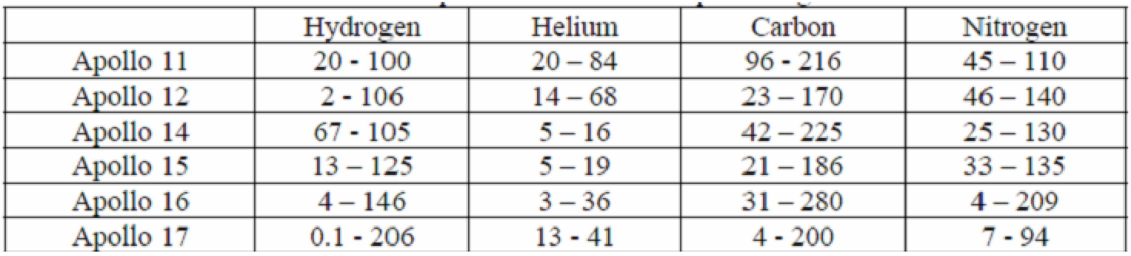
The Earth's magnetic field scatters particles back into space, except near the magnetic poles where evenlow-energy solar particles reach the Earth's atmosphere. The ionization at the top of the Earth's atmosphere by large fluxes of particles absorbs cosmic radio noise ("polar cap absorption" or PCA).

The solar wind represents a plasma of chemical elements, expelled as ionized atoms from the atmosphere of the sun. It bombards all objects in the solar system. Earth's magnetic field and atmosphere deflect and absorb the solar wind and prevent it from reaching the Earth's surface and interacting with it. The Moon has no such protection; ions from the solar wind strike the lunar surface with kinetic energies of about 1 keV per nucleon and embed themselves to depths of up to a few hundredths of a micrometer in exposed materials. Solar cosmic rays (associated with solar flares) consist of similar particles with megaelectron volt and higher energies, which penetrate farther (**Table 2-8).** The solar wind, however, supplies about 2 orders of magnitude more particles than solar cosmic rays, and is therefore the more significant source of solar-wind-implanted elements.Besides the radiant energy continuously emitted from the sun, there is also a steady plasma emission. This plasma consists of an equal number of ions and electrons with an embedded magnetic field thatexpands from the solar corona. The solar wind streams outward from the sun through the solar system creating interplanetary magnetic field lines that have spiral shapes because of the sun's rotation. The solar wind is electrically neutral, and the composition of the nuclei in it is approximately that of the sun. At a distance of 1 A.U. from the sun, the mean energy of the, solar-wind ions is ~1 keV/u (keV/atomic-mass-unit or, for nuclei, keV/nucleon), and all particles move at nearly the same velocity. The solar-wind velocity typically ranges from 300 to

700 km/s, and its particle concentrations normally range from 1 to 20 per cm^3. The solar-wind proton flux generally ranges from $1×10^8$ to $8×10^8$ protons/ cm^2 s. As noted previously, the solar wind is the main source for several volatile elements in the lunar atmosphere and on the lunar surface, such as H, He, C, and N, that are otherwise rare on the Moon. The principal component of the solar wind is H, and there is relatively less deuterium (D) present in the solar wind than in the Earth. The solar-wind isotopic ratio D/H is at least 3 orders of magnitude less thanthe terrestrial value ($1.5×10^{-4}$), and for practical purposes is essentially zero because D that may haveoriginally been present in the sun has been destroyed by nuclear reactions there. The second most abundant component of the solar wind is He, with an isotopic ratio of 3He/4He = $4×10^{-4}$. This impacts ratio is substantially higher than the value for terrestrial atmospheric He (1.4×10–6), which has been strongly affected by addition of 4He from the radioactive decay of U- and Th-series elements within the Earth. Next most abundant in the solar wind are C, N, and O, with concentrations an order of magnitude lower than that of He. Heavier elements are also present, most at concentrations too low to observe in lunar soil grains. The fundamental character of the solar-windimplanted elements is evident in the concentrations and behavior of the noble gases He, Ne, Ar, Kr, and Xe. These gases, and their various isotopes, can be measured in incredibly small amounts with very high precision by mass spectrometry. These measurements provide unique and extensive information about a broad range of fundamental questions: the chronology of earliest solar-system development; the surface exposure and radiation histories of lunar rocks and soils; the outgassing histories of planets; the nature of the solar wind; and the composition of the sun. The importance of this information and the interest in obtaining it has generated such an extensive literature on noble gases as to create the impression that these gases must be far more abundant in lunar materials than is actually the case.

Concentrations of noble gases in lunar materials drown during Apollo missions are shown in **Table 2-9**.

TABLE 2- 9: Solar Wind Implanted Volatiles in Apollo Regolith



	Hydrogen	Helium	Carbon	Nitrogen
Apollo 11	20 - 100	20 – 84	96 - 216	45 – 110
Apollo 12	2 - 106	14 – 68	23 – 170	46 – 140
Apollo 14	67 - 105	5 – 16	42 – 225	25 – 130
Apollo 15	13 – 125	5 – 19	21 – 186	33 – 135
Apollo 16	4 – 146	3 – 36	31 – 280	4 – 209
Apollo 17	0.1 - 206	13 - 41	4 - 200	7 - 94

Although the Moon has no atmosphere, 0xygen is overwhelmingly the most abundant element in Lunar surface materials. As reported in technical literature, on a weight percent basis Oxygen is the most abundant elements (45% by weight) and Si is the second (21 %). All the oxygen atoms are tightly bound to other elements in thermodynamically stable minerals.In particular silicate minerals, especially pyroxene, plagioclase feldspar, and olivine, are the most abundant minerals in rocks of the Lunar crust and mantle, making up over 90% by volume of most Lunar rocks. These silicate minerals, along with other minerals and glasses, make up the various mare basaltic lavas and the more complex suite of highland rocks (melt rocks, breccias and plutonic rocks).

The oxide minerals, composed chiefly of metals and oxygen, are next in abundance after silicate minerals. They are particularly concentrated in the mare basalts, and they make up as much as 20% by volume of these rocks. The most abundant oxide mineral is ilmenite, a black, opaque mineral that reflects the high $Ti0_2$ contents of many mare basalts.As stated in the literature **(Sibille et al., 2005)** the content of TiO_2 oxyde could be taken into account to evaluate the content of ilmenite ($FeTiO_3$), one of the key minerals that composes the lunar bulk soil. As an example the percentage of TiO_2 in the bulk is in the range of 7.4-8.5 wt% **(Sibille et al., 2005)**. Seeing as the molar weight of $FeTiO_3$ is 151.71 g/mol and the one of TiO_2 is 79.866 g/mol; considering that all the TiO_2 found is bound to FeO; the content of ilmenite is 7.4*1.89=14.06 wt% and 8.5*1.89=16.14 wt%. Similar results are stated by **Shrunk et al. (2008)** who stated that percentage of over 25 wt% of Ilmenite could be found in maria regions.

A remarkable aspect about this soil is the presence of a layer of dust due of the continuous process of breakdown worked by meteoric impacts; in **Figure 2-5** the chemical composition of lunar dust has been reported.

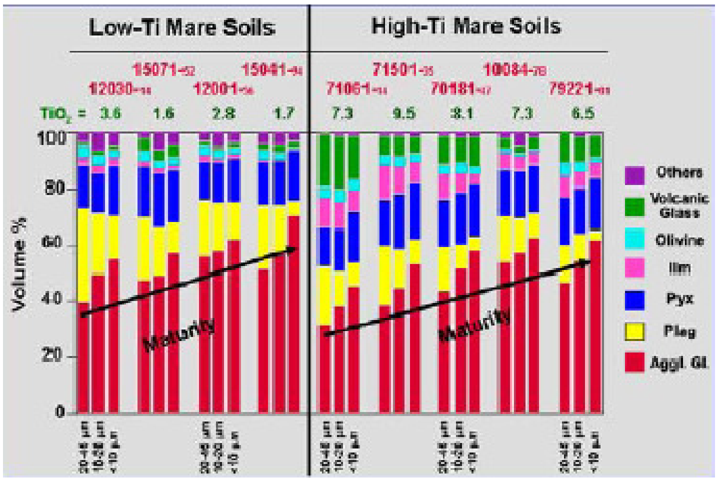
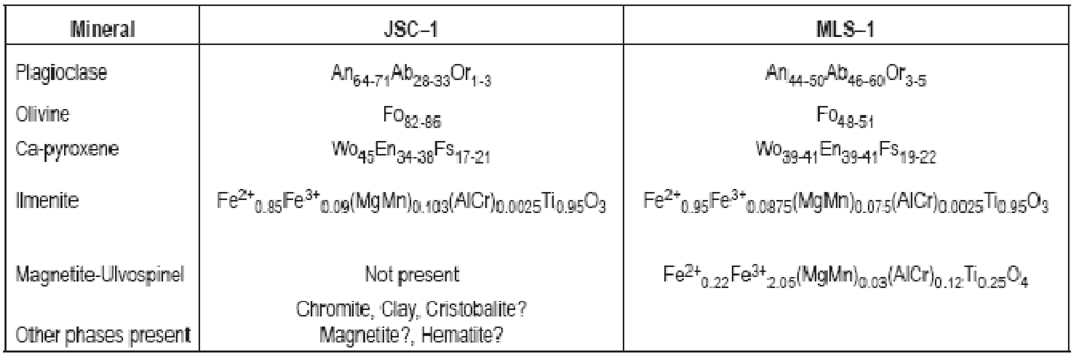


FIGURE 2- 5: Mineralogical composition of Lunar dust

As reported elsewhere **(i.e. Sibille et al. 2005, Heiken et al., 1993)** silicates, are the main costituents of lunar bulk soil as reported in the following **Table 2-10.**

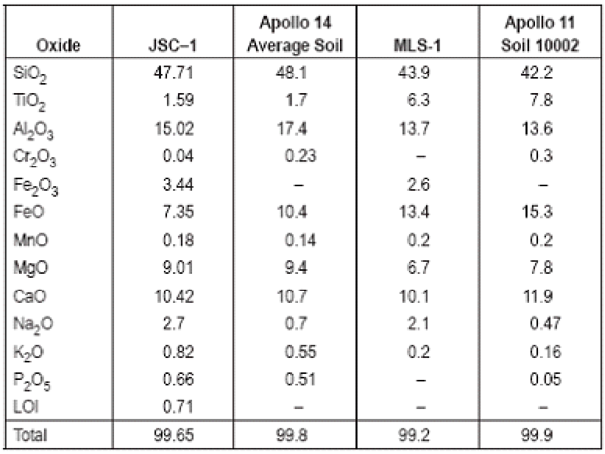
TABLE 2- 10: Mineralogic Composition Of Lunar Regolith



Mineral	JSC–1	MLS–1
Plagioclase	$An_{64-71}Ab_{28-33}Or_{1-3}$	$An_{44-50}Ab_{46-60}Or_{3-5}$
Olivine	Fo_{82-86}	Fo_{48-51}
Ca-pyroxene	$Wo_{45}En_{34-38}Fs_{17-21}$	$Wo_{39-41}En_{39-41}Fs_{19-22}$
Ilmenite	$Fe^{2+}{}_{0.85}Fe^{3+}{}_{0.09}(MgMn)_{0.103}(AlCr)_{0.0025}Ti_{0.95}O_3$	$Fe^{2+}{}_{0.95}Fe^{3+}{}_{0.0875}(MgMn)_{0.075}(AlCr)_{0.0025}Ti_{0.95}O_3$
Magnetite-Ulvospinel	Not present	$Fe^{2+}{}_{0.22}Fe^{3+}{}_{2.05}(MgMn)_{0.03}(AlCr)_{0.12}Ti_{0.25}O_4$
Other phases present	Chromite, Clay, Cristobalite? Magnetite?, Hematite?	

Thecomposition in terms of oxide minerals, instead, with reference to the Apollo samples is reported in the following **Table 2-11 (Sibille et al., 2005)**.

TABLE2- 5: Oxide minerals composition of lunar regolith



Oxide	JSC–1	Apollo 14 Average Soil	MLS-1	Apollo 11 Soil 10002
SiO_2	47.71	48.1	43.9	42.2
TiO_2	1.59	1.7	6.3	7.8
Al_2O_3	15.02	17.4	13.7	13.6
Cr_2O_3	0.04	0.23	–	0.3
Fe_2O_3	3.44	–	2.6	–
FeO	7.35	10.4	13.4	15.3
MnO	0.18	0.14	0.2	0.2
MgO	9.01	9.4	6.7	7.8
CaO	10.42	10.7	10.1	11.9
Na_2O	2.7	0.7	2.1	0.47
K_2O	0.82	0.55	0.2	0.16
P_2O_5	0.66	0.51	–	0.05
LOI	0.71	–	–	–
Total	99.65	99.8	99.2	99.9

As it will be discussed deeply in what follows the use of these resources to make possibile the human presence in Space was addressed by many authors **(Guter et al., 1963, Heiken et al., 1976, Waldron et al., 1982, Hepp et al., 1991, Simonsen et al., 1992, Sanders et al., 2000)**. Due to the difficulties to recover original lunar regolith, lot of simulants have been developped and used to lead experiments in a easier and cheaper way.

2.3.1.1 LUNAR SOIL SIMULANTS

A Lunar regolith simulant is a terrestrial material synthesized in order to approximate the chemical, mechanical, and engineering properties of, and the mineralogy and particle size distributions of, lunar regolith. Lunar regolith simulants are used by researchers who wish to research the materials handling, excavation, transportation, and uses of lunar regolith. Samples of actual lunar regolith are too scarce, and too small, for such research

2.3.1.1.1 MLS-1

MLS-1 (Minnesota Lunar Simulant 1) is a lunar simulant that was developed at the University of Minnesota. The basaltic rock used in this simulant was mined from a quarry in Duluth, Minnesota. It contains plagioclase, olivine, pyroxene and ilmenite as some of its major minerals. The minerals and grain sizes resemble the chemistry of the Apollo 11 mare material (specifically soil sample 10084).

2.3.1.1.2 JSC-1

JSC-1 (Johnson Space Center Number One) is a lunar regolith simulant that was developed in 1994 under the auspices of NASA and the Johnson Space Center. Its developers intended it to approximate the lunar soil of the maria. Unlike MLS-1, it simulates a soil that is poor in titanium. It is a basaltic ash with a high glass content.

2.3.1.1.3 JSC-1A

In 2005, NASA contracted with Orbital Technologies Corporation (ORBITEC) for a second batch of simulant in three grades:

- JSC-1AF, fine, 27 micron average size
- JSC-1A, a reproduction of JSC 1, less than 1 mm size
- JSC-1AC, coarse, a distribution of sizes < 5 mm

2.3.1.1.4 FJS-1

FJS-1 (Fuji Japanese Simulant 1) was developed in Japan from Mount Fuji area basalts. The grain size and mineralogy of these basalts simulate well the samples from the Apollo 14 mission.

2.3.1.1.5 FJS-2

FJS-2 is similar to FJS-1 however olivine was added to change the composition slightly. FJS-2 is a better Apollo 14 simulant than FJS-1.

2.3.1.1.6 FJS-3

FJS-3 is composed of the root simulant, FJS-1, with added olivine and ilmenite. FJS-3 is a good simulant for Apollo 11 samples.

2.3.2 ISRU and ISFR lunar applications

2.3.2.1 *OXYGEN PRODUCTION*

It is well known that the oxygen represents one of the most critical factor for the human survival in space environment, being it used as a life consumables and as a propellant. Its production in space, indeed has been addressed in recentdecades and over twenty different chemical and physical processes have been proposed for the production of oxygen from Lunar materials **(Kesterke et al., 1970, Lindstrom et al., 1979, Williams et al., 1985, Linne et al., 1989, Shadman et al., 1989, Ramohalli et al., 1990, Lynch et al., 1989, Colson et al., 1990, Taylor et al., 1990, Sullivan et al., 1990, Senior et al., 1991, Briggs and Sacco, 1988, Allen et al., 1992, Massieon et al., 1992, Altemberg et al., 1992, Hepp et al., 1992, Koelle et al., 1992, Burt et al., 1992, Taylor et al., 1992, Knudsen et al., 1992, Rosemberg et al., 1992, Gibson et al., 1994, Khetpal et al., 2003, Sherwood et al., 1992, Christiansen et al., 1988, Allen et al., 1994, Dalton and Hohmann, 1972, Gibson and Knudsen, 1985; Gibson et al., 1990, Stump et al., 1989, Weissbart et al., 1969; Reedy 1992; Lawton et al., 1986; Bent et al., 1987, Volk and Stotler, 1970; William and Mullins 1983; Williams 1985; Briggs and Sacco, 1988; Gibson and Knudsen, 1988, Mc Gannon et al., 1964; Volk and Stotler et al., 1970, Ness et al., 1990,Vaniman and Heiken, 1990, Allen et al., 1992, Allen et al., 1994, Dalton and Hohmann 1972; Gibson and Knudsen, 1985, Briggs and Sacco, 1988, Lewis et al., 1988, Shadman et al., 1991, Christiansen et al., 1988, Burt et al., 1988, Steurer and Nerad 1983, Senior et al., 1991, Cutler et al., 1984, Binder et al., 1990, Bhogeswara et al., 1979, Balasubramaniam et al., 2009, Waldron et al., 1989, Semkow and Sammells, 1987, Waldron and Criswell, 1979 Waldron and Criswell, 1982, Sullivan et al., 1990, Lavagna et al., 2007, Kaneko et al., 1993)**. Rocket propellant from water ice has also been proposed for the moon, mainly from ice that has been found at the poles. The likely difficulties include working at extremely low temperatures and simply digging the material. Most schemes electrolyse the water and form hydrogen and oxygen, liquify and cryogenically store them, which requires large amounts of equipment and power to achieve.

It is possible to classify the processes for oxygen production upon the manner in which the reactants are processed. The potential processes for Lunar oxygen production then fall into the following categories:

- solid/gas interaction
- pyrolysis
- silicate oxide melt
- aqueous solution
- coproduct recovery

In the next pages a classification of the most important process with a brief explaination as reported by **Taylor et al. (1992)**. Economical analisis, cost and benefits related to the production of Oxygen from Lunar materials have been performed **(Sherwood et al., 1992)**.

In gas-solid processes, lunar minerals are reacted with gases in order to produce oxygen. The most important processes that will be detailed in next paragragraphes are here reported.

- Ilmenite Reduction with Hydrogen
- Ilmenite Reduction with C/CO
- Ilmenite Reduction with Methane
- Glass Reduction with Hydrogen
- Reduction with Hydrogen Sulfide
- Extraction with Fluorine
- Carbochlorination
- Chlorine Plasma Reduction

The feedstock involved in this kind of processes consists on ilmenite $FeTiO_3$ or Lunar regolith as detailed in what follows.

Pyrolysis relies on the application of heat to a feedstock in order to induce a chemical change. This consists usually on a partial decomposition of metal oxides associated with vaporisation and/or ionisation of the material. Such a process generally requires high temperatures, in the range of 2000 to 10,000 °C, generated by a plasma torch, microwaves technology or a solar furnace. The most studied processes based upon this kind of interaction between heat and bulk are reported below:

- Vapour Pyrolysis
- Ion Plasma Pyrolysis
- Plasma Reduction of Ilmenite

In silicate/oxide melt processes bulk rock and soil with their silicate and oxide minerals are reacted upon in the molten state to produce oxygen. This can be achieved by electrolysis or pyrochemical techniques. Fluoride flux can be added to the silicate melt to lower the melting temperature and to increase the efficiency of the electrolysis process, other schemes involve the addition of various reducing agents to break down the molten components. The most common melting processes aimed to produce Lunar Oxygen are the following:

- Molten Silicate Electrolysis
- Fluxed Molten Silicate Electrolysis
- Caustic Dissolution and Electrolysis
- Carbothermal Reduction
- Magma Partial Oxidation
- Li or Na Reduction Ilmenite

According with the acqueous solution techniques bulk regolith or separated minerals can be dissolved in strong acids to create metal salts and water, that can be electrolysed to produce oxygen. The processes of dissolution that, by far, have as a core of process the use of HF acid and of H_2SO_4 acid .

In what follows an essential description of each process will be given, in order to clarify the strategy, the advantages and the drawbacks of each process.

2.3.2.2 SOLID/GAS INTERACTION PROCESSES

2.3.2.2.1 ILMENITE REDUCTION WITH HYDROGEN

The reduction of Ilmenite by hydrogen involves the following chemical reaction

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A conceptual design for fluid bed ilmenite reduction is detailed in **Figure 2-6** consistying of a fluidised bed, with the hydrogen flowing upwards and the solid flowing downwards.

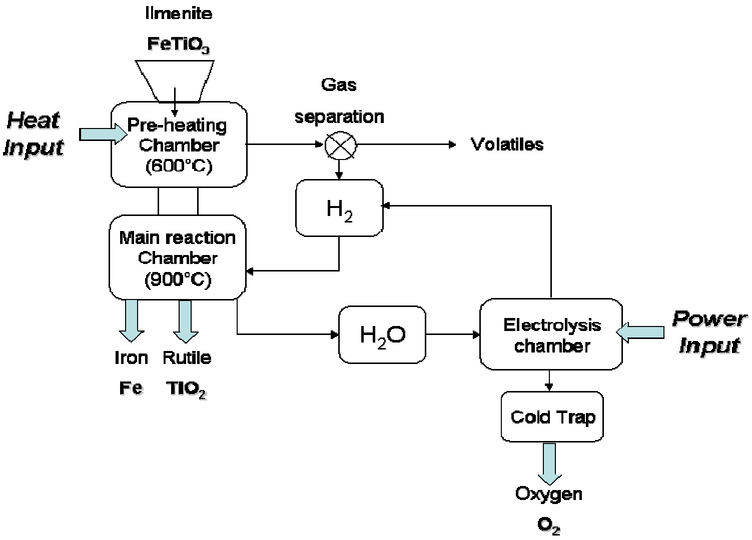


FIGURE 2-6: Flow Diagram For The Production Of Oxygen By Hydrogen Reduction Of Ilmenite

Cold Ilmenite fed from a hopper at reactor chamber pressure top bed through a wer feeder, where is heated by hot recycled hydrogen. In this manner the Hydrogen cools sufficiently for the blower to perform reliably. The unused hydrogen and newly produced water vapour are then channelled into the solid state ceramic electrolyser which operates at the same temperature as the main reactor to avoid the need for cooling the water product and re-heating the hydrogen. Oxygen is removed for liquefaction and storage and the Hydrogen returned to the top bed. Spent solids over flow into the bottom chamber where they exchange heat with the returning hydrogen. In order to obtain a suitable reaction rates and acceptable conversion efficiency are needed reaction temperatures between 700 and 1000 °C. The bulk of regolith needs to be beneficiated exploiting the electrostatic separation technology in order to create a rich-ilmenite feedstock. The Ilmenite, then, needs to be heated until a temperature of 900°C. The water produced is then electrolized into H_2 and O_2 and the hydrogen is recycled. The concept behind this process is simple, and ilmenite is abundant in many mare rocks and soils. Carbotek, Inc. has patented an ilmenite, hydrogen-reduction technique involving a fluidized-bed for the production of LLOX. Although the chemistry of this process is not complicated, lunar ilmenite commonly contains chemical impurities, whose effects upon the kinetics of ilmenite reduction with hydrogen, or any other gas, remains an unknown.

The chemical reaction for this process is endothermic (heat is adsorbed) thus heat must be added to drive the reaction towards completion. Reaction temperatures of 900°C or higher are needed in order to obtain acceptable rates and conversion efficiencies **(Christiansen et al., 1988, Allen et al., 1994)** The water that is produced is separated by electrolysis into hydrogen and oxygen, and the hydrogen is recycled.

A fluidized bed reactor has been proposed for the reduction step **(Dalton and Hohmann, 1972, Gibson and Knudsen, 1985; Gibson et al., 1990)**. According to this early concept, a beneficiation step separates the small fraction of ilmenite from the rest of the soil even if later research demonstrated that this separation of ilmenite could not be so usefu, because of the glass phase also contains a significant amount of extratable oxygen. A system of storage hoppers then feeds the ilmenite into the top three-stage fluidized-bed reactor chamber. As the ilmenite flows from the first to the second level, it is heated to about 1000 °C. Hydrogen gas flows up through the bed and reacts with the ilmenite to form water vapour into hydrogen and oxygen. The oxygen is liquefied and stored, and the hydrogen flows back into the bottom of the rector. A solid setting tamk removes the reactor residuals from the bottom of the reactor. **(Stump et al., 1989)**. If the electrolysis phase is carried out at the same temperature as the reduction reaction, an energy saving would be achieved. Sustantial progress has been made in developing the electrolytic cells that could carry out this high temperature electrolysis **(Weissbart et al., 1969; Reedy 1992; Lawton et al., 1986; Bent et al., 1987)**. The chemistry of this process is fairly simple, and it has been demonstrated in the laboratory **(Volk and Stotler, 1970; William and Mullins 1983; Williams 1985; Briggs and Sacco, 1988; Gibson and Knudsen, 1988)**. The reactions are known to work, and further refinement will reduce plant mass and energy requirements and oxygen production and hydrogen recovery are simultaneous events. This decreases complexity, which increase reliability. Many Earth analogues exist for this kind of process **(Mc Gannon et al., 1964; Volk and Stotler et al., 1970)**. As long as the reaction temperature remains below the melting point of the Ilmenite fed, reactor materials problems are minimal. It also appear that some aspects of the fluidized bed process will work better on the Moon that the Earth. For example, the low lunar gravity allows wider particle size distribution in the fluidized bed **(Ness et al., 1990)**. This means that less materials needs to be removed at the high and at the low ends of the size distribution before the feedstock enters the reactor, when compared to equivalent terrestrial processes. A disadvantage of a process that requires hot hydrogen is that the gas will be difficult to retain. Hydrogen is a very small molecule and it is also quite reactive. Another issue with ilmenite reduction process is that only ilmenite is utilized. Although early estimates suggested that as much as 14% percent of the lunar mare regolith was ilmenite, more recent calculations show that the actual portion of separable ilmenite cristals is closer to 2 percent **(Vaniman and Heiken, 1990)**. If this is the case, then 475 tonnes of mare soil would have to be mined in order to obtain 9.5 tonnes of ilmenite, to subsequently obtain one tonne of oxygen. An alternative method would be to collect and crush rocks and boulders of high-titanum basalt **(Vaniman and Heiken, 1990)**. The problem in that case would be to separate basalt boulders from regolith breccia boulders, and that technique has not yet been tested. A process that was able to use unbeneficiated soil and could consume all of the ilmenite within this feed would have an advantage in mining rates; and **Allen et al. (1992, 1994)** have now shown that hydrogen reduction has approximately the same efficiency on unbeneficiated lunar mare soil as it does on beneficiated ilmenite. Another problem is that the kinetics for hydrogen-reduction reaction are very slow. It takes about an hour at temperature of 1000 °C, to remove approximately 70 percent of the available oxygen **(Dalton and Hohmann 1972; Gibson and Knudsen, 1985)**. It seems that by raising the temperature of 1073 °C the rated is sped up to 0,25 hours for equal conversion **(Briggs and Sacco, 1988)**. However, caution is advised when comparing the results of one of experiment with the result obtained from a different worker in a different laboratory. At 1000°C approximately 10.5 percent of the available hydrogen is converted to water during each pass and at 1200° about 19 percent of the hydrogen is converted **(Gibson and Knudsen, 1985)**. The energy cost of this process has been calculated at 5000 calories per gram of oxygen produced **(Lewis et al., 1988). Shadman et al. (1991)**investigates the kinetics and the mechanism of reduction of synthetic ilmenite by hydrogen in the temperature range of 807-1014 °C by experimenatlly and by mathematical point of view. At temperatures below 876 °C, the temporal profiles of conversion have a sigmoidal shape and indicate the presence of three different stages (induction, acceleration, and deceleration) during the reduction reaction while the profiles at 876,945, and 1014 °C do not have these three stages. The results indicate that the TiO_2 can be reduced to lower oxides of titanium at temperatures higher than 876 °C e this aspect is directly related to the energy required by the process.

2.3.2.2.2 ILMENITE REDUCTION WITH C/CO

The idea of using CO as the reducing gas to process ilmenite is based upon the same general scheme as with the use of hydrogen as the reductant, described in the previous paragraphe.The reactions involved in this process are similar to that for the fluidized bed scheme discussed above.

$$FeTiO_3 + CO \rightarrow Fe + TiO_2 + CO_2$$

$$CO_2 \rightarrow CO + \frac{1}{2}O_2$$

The product from this reduction process is $C0_2$ which must be "cracked" to liberate oxygen. Thisis a very endothermic reaction which will consume significant energy. In addition, many of the same advantages and disadvantages mentioned in the hydrogen section above are equally applicable here.

As said previously the solar-wind implanted carbon in the soil (20-30 ppm), particularly in ilmenite; with the roasting of the soil for the liberation of hydrogen and helium, this carbon also will be released and could be recovered. The ilmenite feedstock, with its solar-wind implanted particles, will also contribute carbon, as well as hydrogen, to the overall process. Thus, it may be possible to make up consumption losses of the reactant from indigenous sources, but the presence of solar-wind hydrogen (hundreds of ppm) from the ilmenite may complicate the overall process into one involving methane as well.

Zhao and Shadman (1991) have studied the kinetics of the CO reduction of ilmenite. They have demonstrated that the rate of reduction of ilmenite by CO is slower than that with H_2, as expected.

However, for a given temperature, the difference is less than an order of magnitude.

In another variant of the ilmenite-reduction process **(Chang 1959)** suggested that either H_2 or CO or a combination of both could be used as a reducing gas.

2.3.2.2.3 ILMENITE REDUCTION WITH METHANE

The reduction of ilmenite by methane has been proposed by **Friedlander (1985)**. Equations which represent this reduction reaction can be written as:

$$FeTiO_3 + CH_4 \rightarrow Fe + TiO_2 + CO + 2H_2$$

$$2CO + 6H_2 \rightarrow 2CH_4 + 2H_2O$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Acquiring a feedstock which is ilmenite-rich will necessitate a high-Ti mare ore-a site-specific requirement. Considerable beneficiation of a mare basalt or soil will be necessary. In addition, the presence of the sulphide mineral troilite (FeS), commonly associated with ilmenite in mare rocks and soils, may represent a problem in this process, as well as for most other processes discussed below. It can lead to the generation of corrosive H_2S and will necessitate a process step for removal of either the troilite from the feedstock or H_2S from the products. Of course, there are several methods by which troilite, with its sulfur component, can be removed from the feedstock, but this additional step in the beneficiation scheme is a complication which will be an economic consideration. In general, the simplicity of the beneficiationprocess is of major importance for the lunar production facility. Indeed, the mining and beneficiation processes may prove to be the key discriminator among competing oxygen production processes.

2.3.2.2.4 GLASS REDUCTION WITH HYDROGEN

Lunar glass, particularly from mare regions, can contain FeO contents up to 20 wt%. It has been demonstrated **(McKay et al., 1991)** that this FeO component of the glass can be readily reduced by hydrogen to yield elemental Fe^O (native Fe) and water. Thermodynamically, the glass is considerablymore unstable than the silicate minerals from which it formed; hence, the rapid kinetics of reduction. The water so produced can be easily hydrolyzed or otherwise electrolyzed to yield oxygen and recyclable hydrogen.

$$FeO_{(glass)} + H_2 \rightarrow Fe^0 + H_2O$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Glass is an abundant constituent of the lunar regolith. The lunar soil contains considerable glass, mostly as the result of melting produced by meteorite and micrometeorite impacts but also from volcanic activity. The impact glass usually welds together rock and mineral fragments into aggregates called agglutinates that frequently constitute over 50 vol% of a given mature soil. In addition, there are entire regions of the Moon which have blankets (1-4 m deep) of volcanic glass as pyroclastic deposits.

Although this scheme for oxygen production is a relatively recent development, it is not too soon to consider its feasibility. It may be possible to utilize a fluidized bed reaction vessel, similar to that proposed for the reduction of ilmenite with hydrogen. Considerations of the possible feedstocks would depend upon the actual engineering of the process.

Indeed, considering a more general process in which a generic metal is made reacting with hydrogen, as reported in the following equation,

$MO(glass) + H_2 \rightarrow M + H_2O$

this process keep to be valid, even if is easier to break the FeO bond than any other bond in lunar chemistry.

Measurements were made of the amount of iron reduction and the sample weight loss versus temperature, time and hydrogen flow rate. The highest percentage of oxygen was released at 1100°C. At higher temperatures, less oxygen was releasedbecause the sample began to melt, which lowed its permeability to the hot hydrogen gas. **Allen et al. (1994)** showed that iron oxide blebs were produced on lunar simulant glass grains by passing hot hydrogen gas over the grains in a closed system. Some tests were run on Apollo 11 glass samples which have been reduced with hydrogen at 1000-1100 °C. The glass were partially to fully devitrified during this process, so the kinetics of glass reduction were partially controlled by the reduction of ilmenite and pyroxene.

Lunar glass is a viable source of oxygen when heated: **Allen et al. (1994)** tested also the reduction of of a lunar basalt sample from the Apollo 17 collection. The reaction was rapid, with rapid evolution of water occurring within minutes after the introduction of hydrogen. The reduction of Minnesota Lunar Simulant (MLS-1) basalt by hydrogen at 1100°C was not quite as rapid as with the actual lunar samples. In this case about 90 percent of the weight loss occurred in the first ten minutes.

2.3.2.2.5 REDUCTION WITH HYDROGEN SULFIDE

Dalton and Hohman (1972) proposed to reduce unbeneficiated lunar soil with hydrogen sulfide gas. In particular, the oxides of Fe, Ca and Mg are proposed to be reduced as shown below; this includes the recovery of sulfur, the electrolysis of the water, and cyclical production of reductant hydrogen sulphide, according to the following theoretical reactions:

$$MO + H_2S \rightarrow MS + H_2O \ (M = Fe, Ca, Mg)$$

$$MS + heat \rightarrow M + S$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

$$H_2 + S \rightarrow H_2S$$

Although this process appears simplistic from a theoretical perspective, it is far more complicated. It is the silicate minerals in the lunar rocks and soils that contain all of the Ca and Mg and most of the Fe. And these silicates are not easily broken down by hydrogen sulfide- i.e., the kinetics are complicated and slow, even at 1000°C. It would be difficult to handle soil at and above such high temperatures since the agglutinate (glass) component will readily sinter, thereby decreasing porosity and permeability. At higher temperatures, necessary for reasonable process yields, the soil will melt. In addition, because of the toxic nature of hydrogen sulfide, it would be necessary to purify the oxygen extensively, if it were to be used for life-support purposes. Of course, the problem of purification of the oxygen is applicable to most oxygen generation processes, particularly since troilite, the sulphide mineral, is ubiquitous in all mare rocks and soils, as well as present in many highland sources, albeit at much lower contents.

2.3.2.2.6 EXTRACTION WITH FLUORINE

Fluorine gas, F_2, is highly reactive and can be utilized to liberate metal from all oxides, thereby creating metal fluorides **(Christiansen et al., 1988)**. The proposed feedstocks can be either anorthite or ilmenite in a two-stage fluidized bed reactor **(Burt 1988)**. Using anorthite, the reaction which occurs in the first stage is:

$$CaAl_2Si_2 + 2F_2 \rightarrow CaF_2 + AlSiO_4F_2 + SiO_2 + O_2(g)$$

Additional fluorine is fed into the bottom of the second stage:

$$CaF_2 + AlSiO_4F_2 + SiO_2 + 6F_2 \rightarrow CaAlF_5 + AlF_3 + 2SiF_4(g) + 3O_2(g)$$

The product gas is passed through a bed of NaF which effectively scrubs out the SiF_4 gas, but the resultant Na_2SiF_6 must be treated with Na to recover the NaF and produce Si. The $CaAlF_5$ and AlF_3 are treated with Na to yield CaF_2, NaF and A1 metal. Additional steps are required to recover reactantsand release additional oxygen. Totally, 8 steps are required, using several separate reactors, and each with its own operating conditions.

Unlike the reduction processes discussed above (e.g., H_2, CO), the extraction with fluorine liberates oxygen directly without the need for a thermochemical reduction to split off the oxygen from the reductant (e.g., H_20, $C0_2$). Instead, the SiF_4 gas must be totally scrubbed out, and the oxygen must be depoisoned for human consumption. The feedstock requirements will require considerable beneficiation of the rocks/soils from the highlands (anorthite concentrate) or high-Ti mare (ilmenite).

The overall process of extraction with fluorine is complicated, involving many steps and several reactors. The process implications would seem impractical: complete recovery of fluorine would seem unlikely, and the corrosive nature of fluorine will require special inert materials,necessitating a large Earth supply involvement. Considerable technology development is required, and process mass and energy requirements are not known for comparative purposes. Lastly, the considerable danger of working with fluorine or metal fluoride gases is a major safety consideration.

2.3.2.2.7 CARBOCHLORINATION

The carbochlorination process involves using a CO-Cl_2 gas mixture or Cl_2 in the presence of solid carbon to react with anorthite and/or ilmenite **(Christiansen et al., 1988)**. A fluidized-bed reactor operating at770°C was proposed to react:

$$CaAl_2Si_2O_8 + 8C(s) + 8Cl_2 \rightarrow CaCl_2 + 2AlCl_3(g) + 2SiCl_4(g) + 8CO$$

$$FeTiO_3(s) + C(s) + \frac{3}{2}Cl_2(g) \rightarrow FeCl_3(g) + TiO_2(s) + CO(g)$$

Several staged condensation, hydrolysis, and electrolysis steps would be necessary to separate gaseous components $AlCl_3$, $SiCl_4$, $FeCl_3$, Cl_2 and CO, and to recover reactants and oxygen. Chlorine gas at temperatures of 1000°C normally only reacts with oxides, such as ilmenite. In order to facilitate effectivereaction with the silicate minerals, it is necessary to have carbon present.

Carbon acts as a reducing agent, forming CO, while the Cl_2 oxidizes the metal, forming a volatile chloride. In this manner, a new surface is continually exposed for reaction **(Lynch 1989)**.

There are a large number of processing steps involved in this overall scheme; such complexities add problems with regards to system reliability, efficiency of reactant recovery,'etc. Chlorine is a hazardous gas to work with. The efficient recovery of carbon and chlorine reactants is unlikely, even using a largenumber of processing steps with large mass and energy requirements. On the positive side, this process would seem to be capable of using bulk lunar soil, either mare or highlands.

2.3.2.2.8 CHLORINE PLASMA REDUCTION

Lynch (1989) has suggested the use of a "cold" plasma reactor to create a chlorine plasma. Calculations and preliminary experiments suggestthat in such a plasma, stable metal oxides (e.g., $FeTi0_3$, ilmenite) can undergo chlorination and yield oxygen as a by-product. The term "cold" plasma is misleading in that the plasma is only relatively cooler than a normal plasma, indeed, temperatures of up to 2000°C are encountered. The term "cold" indicates a significant difference between the molecular temperature and the kinetic temperatures of the electrons in the molecule, which can be thousands of degrees hotter than the overall temperature of the molecule. The extremely reactive nature of the cold plasma is a function of these temperature differences between the electrons and the overall molecule. It is the presence of broken bonds, partially filled orbitals, and unbalanced charges that makes these molecules so highly reactive. The basic process can be described with the following reaction:

$$Cl_2 + MO \rightarrow MCl_2 + \frac{1}{2}O_2$$

After the oxygen has been released from the metal oxide, it is necessary to remove the chlorine from the metal chloride. This can be accomplished by electrolysis. Experimentation is currently in progress **(Lynch 1989)**. The kinetics of chlorination are being examined as a function of temperature, chlorine content in the gas, total pressure, power levels, and plasma density.

2.3.2.3 PYROLYSIS PROCESSES

2.3.2.3.1 VAPOUR PYROLYSIS

With vapor pyrolysis, high temperatures (2200 to 2700°C) are utilized to vaporize the feedstock and transform oxygen-bearing compounds into monoxides and oxygen **(Steurer and Nerad 1983)**. After vaporization, the gas is rapidly cooled, so that everything except the oxygen is condensed back into a liquid or solid. This condensation step is critical because it must be accomplished before the metal species can recombine with the oxygen. Long-term fouling of condenser surfaces will lower process efficiency. **Senior et al. (1991)** has demonstrated the feasibility of the pyrolysis portion of this process using a solar furnace and anorthite and ilmenite. However, unbeneficiated regolith can also be used as feedstock. The direct use of solar energy is a key benefit to this process.

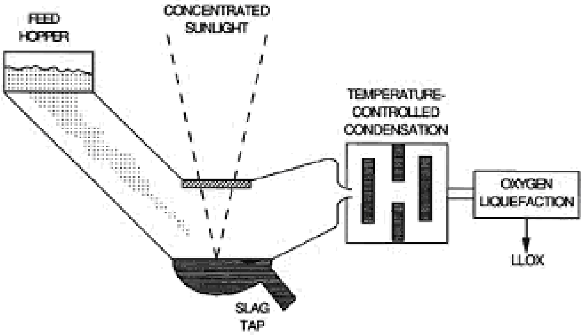


FIGURE 2- 7: Schematic Diagram For The Production Of Oxygen By Water Pyrolisis

This process is characterized by its total reliance on space resources, namely "hard" vacuum and solar energy, thereby eliminating the need for consumables from Earth **(Steurer and Nerad 1983)**. Vacuum reduction and distillation of metals are well-known terrestrial processes. The condensation step in this process is in need of considerable study, although vacuum coating technology should be applicable here.

2.3.2.3.2 ION PLASMA PYROLYSIS

At temperatures of 7000 to 10,OOO°C, oxide dissociation products are ionized **(Steurer and Nerad 1983)**. At 7700°C, over 90% of the metallic dissociation products (Fe, Ti, Al, Mg) and 25% of the Si are ionized. However, only 1% of the oxygen is ionized. The highly ionized metals are extracted from the vapor by electrostatic or electromagnetic fields, whereas neutral oxygen flows downstream for collection. In theory, this has the advantage of higher oxygen yields than the vapor reduction process. The condenser problem will be significant because considerable quantities of non-ionized metals and non-ionized Si must be removed. Unlike the vapor phase reduction process where a solar furnace is possible, this scheme with temperatures approaching 10,OOO°C will be extremely energy intensive. Considerable problems with containment materials are to be expected.

2.3.2.3.3 PLASMA REDUCTION OF ILMENITE

The important chemistry occurring in the plasma is the production of radicals. The formation of hydrogen radicals from diatomic hydrogen can be represented by

$$H_2(g) + microwaves \rightarrow 2H(g)$$

These hydrogen radicals have a much greater chemical reactivity than diatomic hydrogen and enhance the rates and yields of the reduction reactions, provided that the radicals do not recombine.

The production of hydrogen radicals in plasma has two effects on the reduction of oxides. Firstly, the temperature required for a spontaneous reduction is significantly lowered. Oxide reduction is generally favoured in the presence of Hydrogen, while direct reduction with H_2 is not favoured at low process temperatures. A lower temperature will decrease energy requirements and possibly increase the reliability and ease of operation of the process equipment. Secondly, the enhanced kinetics offered by the presence of hydrogen radicals in the plasma suggests that unbeneficiated regolith may be useable for oxygen production.

2.3.2.4 <u>SILICATE/OXIDE MELT PROCESSES</u>

2.3.2.4.1 MOLTEN SILICATE ELECTROLYSIS

In its conceptually simple form, electrolysis entails immersing two electrodes in a vat of molten silicate and imposing a current between the electrodes. Oxygen is derived at the anode and metal (mostly Fe and Si) at the cathode. No moving parts or reagents are needed, and the one-step process takes place in a single reaction pot. A design for a molten silicate electrolysis cell by **McCullough and Mariz (1990)** is shown in **Figure 2-8**, where the anodes are at the upper portion of the furnace and the cathodes are at the bottom. Ascan be seen, this cell is designed for a continuous mode of operation, rather than by batch mode.

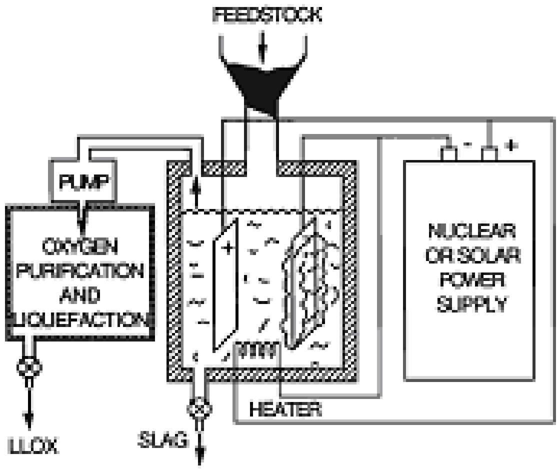


FIGURE 2- 8: Schematic Diagram Of Electrolysis Of Molten Silicate

The energy requirements of the electrolysis process depend both on the composition of the silicate melt and the design of the electrolysis cell. The fraction of the current that goes towards producing oxygen (0_{2eff})depends primarily on the concentrations of FeO in the melt **(Haskin et al. 1992)**. The presence of FeO substantially increases the energy required to produce oxygen because Fe^{2+} may be oxidized by anode products to Fe^{3+} thatis,FeO decreases the 0_{2eff}. Efficient oxygen production appears to require that the melt be less than about 5 wt% FeO. Conductivities in melts of interest for silicate melt electrolysis range over more than 2 orders of magnitude, with conductivities being lowest (<0.2 $cm^{-1}ohm^{-1}$) at low temperature in melts rich in $Si0_2$ and Al_20_3 and highest (>2 $cm^{-1}ohm^{-1}$) at high temperature in melts rich in MgO, CaO, and FeO.

Effects of compositional parameters on the energy required to produce a given amount of oxygen by electrolysis of silicate melt are complex but known to a first approximation. In general, the energy required increases with increasing concentrations of SiO_2, $A1_20_3$, and FeO in the melt. The energy required decreases as the size of the electrolysis cell increases (increasing electrode surface area) and as the distance between electrodes is decreased. Additional compositional constraints are placed on the steady-state melt by the need to maintain container and electrode materials in equilibrium. Composition can be controlled through variations in the feedstock composition, rate of feedstock flow-through, and electrode potential.

The number of process steps and equipment is low. Oxygen is liberated directly with no need for further refinement (versus H_20 or $C0_2$ products which require reduction).

There are no major mass penalties to be supplied from Earth because there is no need for reactants, while electrodes's life is still an unknown. The production of iron may be possible, albeit impure.

Because of limited industrial experience with high-temperature silicate melts, the actual design of a working electrolysis cell is less well determined than the physical-chemical properties of the melts. However, substantial study of hightemperature refractory materials in silicate melts is needed before appropriate container and electrode specifications can be chosen.

2.3.2.4.2 FLUXED MOLTEN SILICATE ELECTROLYSIS

The employment of a flux, such as a fluoride melt, to dissolve the silicate feedstock can alleviate some of the difficulties of high-temperature corrosion experienced by the simple molten silicate process. Operating temperatures are decreased and electrolyte conductance is increased, versus molten silicate electrolysis without flux. Lower specific energy consumption can be projected.

Initially, the fluxed molten silicate process was aimed at recovery of Si and Al and was only secondarily concerned with oxygen **(Keller 1986,1998)**. This process used Al as a reactant, in addition to fluoride flux. An early concept of the process is depicted in **Figure. 2-9**.

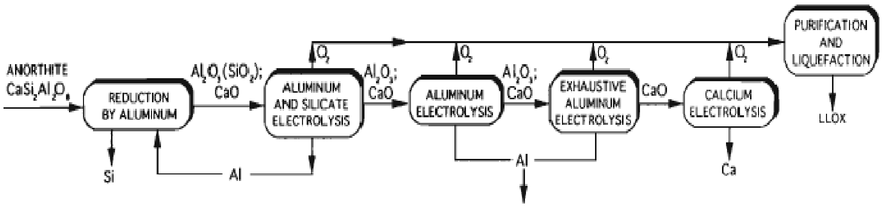


FIGURE 2- 9: Flow Diagram For Llox Production By Electrolysis Of Fluxed Molten Silicate

Anorthite, $CaA1_2Si_20_8$, is dissolved in a molten mixture of fluorides at about 1000° C. Aluminum is added to the melt and reduces the silica to Si, according to the following equation:

$$3CaAl_2Si_2O_8 + 8Al \rightarrow 6Si + 3CaO + 7Al_2O_3$$

When all of the available silica has been reduced to Si, the Si is recovered from a hyper-eutectic Si-Al alloy by cooling the alloy melt to 700°C and filtering the solid Si formed. The electrolyte which now contains alumina and calcium oxide is pumped into an electrolysis cell where the oxides are reduced. Electrolysis results in the formation of oxygen at the anode and Al and Ca at the cathode. Auxiliary process steps are conceived to beneficiate the ore, to separate pure Si, to recover electrolyte components, and to purify the off-gases.

Most of the advantages mentioned under the molten silicate electrolysis process are equally applicable here. However, the fluxed-melt process, in practice, may have lower energy requirements and lesser corrosion problems, both of which are mainly due to lower reactor temperatures. Importantly, oxygen is recovered directly at the anode and the process can be expanded to produce valuable metals.

There is a need for additional research in order to quantify yields and optimize operating conditions, including an efficient way to recycle electrolyte components back into the system. It would appear that the simple fluxed molten silicate process, versus the one using the addition of Al, will be the scheme to be researched more thoroughly in the future.

2.3.2.4.3 CAUSTIC DISSOLUTION AND ELECTROLYSIS

In this process molten NaOH at 400°C is used to dissolve minerals from bulk lunar soil **(Dalton and Hohman 1972)**. This caustic molten solution is then electrolyzed to yield oxygen at the anode and sodium at the cathode. The sodium then reduces the oxides in solution, producing metals and Na_2O. This process can be made continuous if the mixed caustic and solid products are withdrawn from near the cathode of the reactor, and another unit is used to separate and recycle the caustic agent (NaOH) to the pre-electrolysis solution tank.

Except for magnesium and calcium oxides, reduction of the other oxides appears possible, thus resulting in a high oxygen yield. With considerable development of several additional steps, it may be possible to separate the mixed metal product into its constituent metals. The recovery of the caustic reagent from reactor residual solids may require centrifuges and dryers. It is anticipated that the mass penalties from caustic loss will be substantial.But, it is possible that caustic loss can be supplemented with indigenous sodium present in the mineral plagioclase. Considerable research would be required for this process, particularly the electrode stability and the long-term performance of the electrolyzer cell. Using KOH as an alternative flux for this process, as proposed by **Cutler (1984)**, would face most of the same problems

In addition, a variation of this caustic solution process has been proposed by **Binder (1990)**: as shown in **Figure 2-10**the proposed scheme consists on several steps involving fractional condensation, flotation and filtration, evaporation, hydration, electrolysis, etc. This complicated palnt design is proposed to becapable to separate all of the metals and oxygen from the lunar regolith.

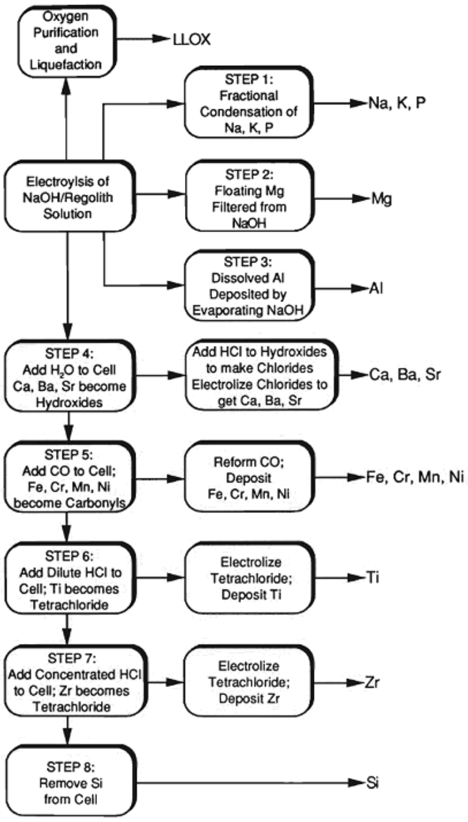


FIGURE 2- 10: Flow Diagram For Caustic Dissolution And Electrolysis With The Production Of Metals And Llox

The complex, multi-step nature of these schemes, coupled with the hazardous nature of the NaOH, is a distinct disadvantage which may make this overall process impractical.

2.3.2.4.4 CARBOTHERMAL REDUCTION

Schemes for the production of oxygen using molten reactant and involving carbon in some form are called carbothermal processes. These combine chemistry from steel-making and from coal-gas forming with electrolysis or thermolysis of water. Although these processes operate best on melts of simple oxide minerals, like ilmenite ($FeTi0_3$), it may be possible for the carbothermal reduction of melts of anorthite ($CaA1_2Si_20_8$), but at extremely high temperatures (2000° C; **Bhogeswara et al., 1979**).

The reduction of molten silicates and oxide phases by carbon in various forms (i.e., C, CH_4, CO) was the subject of the pioneering work of **Rosenberg (1985)** and **Rosenberg et al. (1966)**. Experiments were performed on the reduction of molten silicates by methane at about 1600°C according to thefollowing process chemistry:

$$\begin{aligned}&Mg_2SiO_4(l)+2CH_4\rightarrow 2MgO+Si+4H_2+2CO\\&CO+3H_2\rightarrow CH_4+H_2O\\&H_2O\rightarrow H_2+{}^1\!/_2O_2\end{aligned}$$

The feedstock mineral considered above is olivine, but other phases such as pyroxene [$Ca(Mg,Fe)Si_2O_6$] should work equally well. In other words, it may well be possible to utilize unbeneficiated soil. The second reaction demonstrates the hydrogenation of the carbon monoxide, using a nickel catalyst, to recover the reactant methane and water. And the water can be electrolyzed to release oxygen. Carbon or carbon monoxide, in place of methane, can also be used as the reductant. In fact, with methane, it seems that the CH_4 actually cokes to $C + 2H_2$, and the carbon is the reductant, according to the following equations:

$$\begin{aligned}&CH_4\rightarrow C+2H_2\\&Mg_2SiO_4+2C\rightarrow 2MgO+Si+2CO\end{aligned}$$

There is the possibility that some SiC may form in this process, thereby tying up carbon and placing a penalty on reactant recovery.This process depicted in **Figure 2-11**has been also analyzed by **Balasubramaniam et al. (2009)** with modelling purposes.

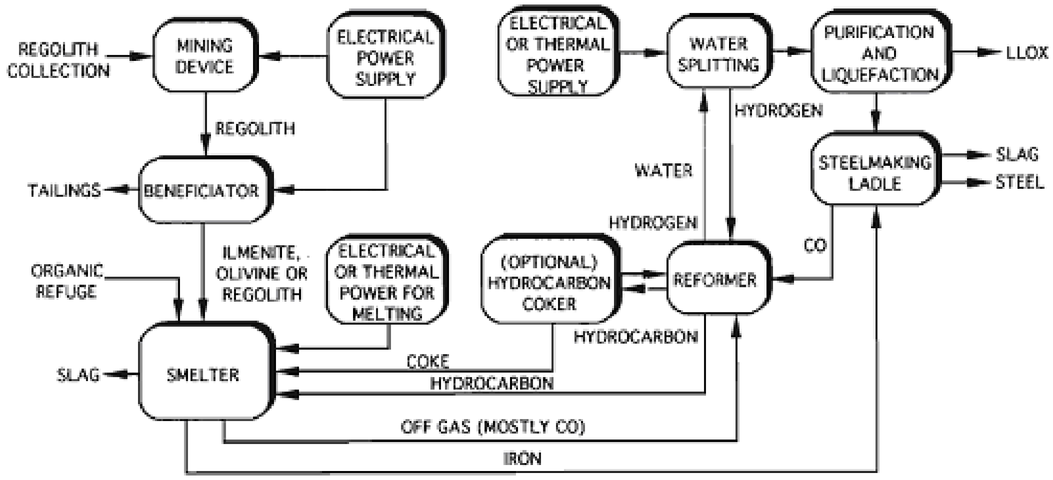


FIGURE 2- 11: Flow Diagram For The Production Of Llox By Carbothermal Reduction

Cutler and Krag (1985) have proposed an oxygen and iron production scheme using coke (devolatilized carbon) to reduce molten ilmenite: the process includes 3 major steps: ilmenite smelting, irondecarburization, and hydrocarbon reforming. The product water is electrolyzed to yield oxygen and recyclable hydrogen. Ilmenite is melted (1400°C) in the smelting step and reacts endothermically with the carbonaceous materials to form iron by the following reactions:

$$
\begin{aligned}
&FeTiO_3 + C(s) \rightarrow Fe(l) + CO(g) + TiO_2(s) \\
&CO + 3H_2 \rightarrow CH_4 + H_2O \\
&H_2O \rightarrow H_2 + \tfrac{1}{2}O_2
\end{aligned}
$$

Approximately 10% anorthite is added as a flux to form a slag with a melting point below iron. Effectively, the ilmenite (90%) + flux (10% anorthite) + carbon-bearing solids form FeC, + CO + $Ti0_2$. The carbon-bearing Fe is decarburized by controlled addition of oxygen to form CO. The CO is reacted with hydrogen to form water and methane. The hydrocarbon is cracked to yield carbon and hydrogen, and the water is electrolyzed to yield oxygen and hydrogen, which is recycled. The several steps in this process have been well established in the steel industry, but operate under rather extreme conditions.

In this process silica and ferrous oxide, originally present in the feedstock in olivine and pyroxene, as well as in ilmenite, are reduced.

The high temperatures (about 1600°C) needed for the reactor and several of the steps will require considerable energy input. The high temperatures and the corrosive nature of the melt will also take a toll on reactor linings. The reductant makeup from Earth may be considerable, estimated at 5 to 20% of the carbon. However, indigenous solar-wind implanted carbon in lunar soil (average = 20 ppm) could offset some of this supply. In addition, although steel is a necessary by-product, steel making is a batch process, at least on Earth. Therefore, the automation for a continuous process will be difficult.

2.3.2.4.5 MAGMA PARTIAL OXIDATION

Waldron (1989) has presented a five-step process which starts with an Fe-rich mare basalt rock or soil. The principle is to extract the FeO from the rock by first getting it all into a magnetic phase which can be separated from the remainder of the rock components. In order to accomplish this, the rock and/or soil is melted in the presence of 1 atmosphere of oxygen. After controlled cooling to promote crystallization, the solid is pulverized, and the mineral magnetite (Fe_3O_4) is extracted magnetically. This is dissolved inan "aqueous mineral acid" which is then electrolyzed to recover Fe and O_2. Although this scheme would seem to be straightforward, no experiments have been performed to determine the feasibility of such a process. Indeed, the beneficiation of the solidified silicate melt to release the magnetite might be difficult if the oxide is fine-grained and/or closely intergrown with silicate phases, both likely possibilities.

2.3.2.4.6 LI OR NA REDUCTION ILMENITE

Semkow and Sammells (1987) proposed an indirect electrochemical reduction of lunar oxides using lithium (or sodium) to reduce oxides to metal and Li_2O. Either bulk lunar soil or mineral separates, including ilmenite, could be utilized. A temperature of 727°C was proposed for ilmenite. Lithium will reduce FeO, TiO_2 and SiO_2, but not Al_2O_3, CaO or

MgO. The reaction product would consist of metals, the unreduced oxides, and Li_20. A sublimation step conducted at 700°C would separate the Li_20, which would then undergo a reduction step in an electrolytic cell at about 900°C, requiring LiF and LiCl as fluxing, thereby lowering viscosity and resistivity. The liquid Li would thereby be recovered at the cathode with the evolution of oxygen at the anode. This process can utilize any bulk regolith; thereby, the location of the plant would be versatile, i.e., non-site specific. Theoretically, the yield of oxygen by this process would be high, because lunar regolith typically contains about 45 wt% of O_2. On the negative side, the complete recovery of Li_2O from the Li reduction reactor's solid product will be difficult, if not impossible, and require substantial sublimation at vacuums of about 0.02 torr. The electrolytic cell, to be run at 900°C, would need further research in order to evaluate cell corrosion, general degradation of materials (particularly the anode and cathode), flux loss, and effects of long-term operation. The mass penalty for Li, LiF and LiCl makeup supply from Earth may be large.

2.3.2.5 ACQUEOUS SOLUTIONS PROCESSES

2.3.2.5.1 HF ACID DISSOLUTION

Waldron and Criswell (1979,1982) described a hydrofluoric acid-leach process, wherein lunar regolith is dissolved to create metal fluorides and water. Several batch-mode, acid-leach reactors would produce steam and SiF_4 and precipitate the metal fluorides. Fluorine and HF are recovered from the metal fluorides in a complex procedure with multiple unit operations involving high-temperature hydrolysis (>1000°C), electrolysis, ion exchange, distillation, centrifuges and drying steps. Plant location for this process would not be site-specific, because any feedstock can be used. Calculations suggest that 586 tonnes of plant mass will be required to produce 1000 tonnes of oxygen per year. This is high in comparison to some of the processes reviewed above. Unfortunately, the disadvantages to ,this HF acid dissolution and electrolysis process are many **(Christiansen et al.**

1988). The acid-leach reactors are operated in batch mode, making automation difficult, if not impossible, and some reactant HF is lost, and fresh HF must be added during each new batch set-up. The large number of separate steps in the process require many small pieces of equipment. This will require greater design, development and evaluation costs than processes with fewer but larger unit operations.

2.3.2.5.2 H_2SO_4 ACID DISSOLUTION

Sullivan et al. (1990) has recently proposed a sulfuric acid dissolution process to digest an ilmenite feedstock, according to the reaction:

$$FeTiO_3 + H_2SO_4 \rightarrow FeSO_4 + H_2O + TiO_2$$

The resultant slurry is filtered to remove any unreacted solids (e.g., silicates), and the clean solution is passed through an electrolysis cell wherein oxygen and iron are separated by the reaction:

$$FeSO_4 + H_2O \rightarrow H_2SO_4 + Fe + \frac{1}{2}O_2$$

Elements of this process are based on well-known commercial practices and procedures; but these industrial processes are aimed at recovering Fe and TiO_2, not oxygen.

More recently these processes have been analyzed in terms of feasibility for future missions and modified to improuve the efficiency of processes. For instance **Lavagna et al. (2007)** demonstrated that the the process less sensitive with respect to the input material (lunar regolith) is the Carbothermal reduction of Piroxene, whose reaction are similar to those reported in the previous pages and reported here for sake of simplicity. The first step is the reduction of minerals (Anorthite, Olivine, Pyroxene)

$$CaAl_2Si_2O_8 + CH_4 \rightarrow 2Si + 8H_2 + 4CO + CaO + Al_2O_3$$
$$Mg_2SiO_4 + 2CH_4 \rightarrow 2MgO + Si + 4H_2 + 2CO$$
$$MgSiO_3 + 2CH_4 \rightarrow MgO + Si + 4H_2 + 2CO$$

The second step is the oxydation of carbon monoxyde by hydrogen:

$$4CO + 12H_2 \rightarrow 4CH_4 + 4H_2O$$

And finally the electrolysis of water

$$4H_2O \rightarrow 4H_2 + 2O_2$$

With respect to this last chemical reaction, that is involved in lot of processes, **Kaneko et al. (1993)** investigated the behavior of water electrolysis in microgravity and under a normal gravity. The results suggested that the process of the water electrolysis under the microgravity condition is controlled by the mass transfer of water to the electrode surface, though the process under the normal gravity condition is controlled by the electrode reaction. This could be an important issue to be taken into accountin the design of space electrolyzers.

2.3.3 Beneficiation and mining of lunar soil

As it has been discussed, in lot of these processes are involved specific minerals, in particolar way ilmenite. The constraints and the requirements of various activity on the Moon have been analyzed by **Satish et al. (2005)**, with particular reference of drilling, blasting, excavation, comminution and beneficiation. Specifically, in recent literature lot of methods have been proposed in order to enrich lunar regolith in this oxyde mineral **(Ruiz et al., 1982, Dela'o et al., 1990, Taylor et al., 1990, Oder et al., 1990, Ruiz et al., 1990, Taylor et al., 1992, Agosto et al., 1992, Mckay et al., 1992)** utilizing both electrostatic and magnetic technologies. In addition also the problem of mining lunar soil has been adressed in last decades **(Carrier et al., 1979, Detweller et al., 1990, Zuppera et al., 1991, Chamberlain et**

al., 1991, Paterson et al., 1992, Hall et al., 1992, Siekmeier et al., 1992, Gertsch et al., 1992, Bence et al., 1992).One of the most relevant scientific contribution in this field has been proposed by **Landis (2007)**, that described some methods to refine lunar regolith to obtain silicon, titanium, metals, calcium, magnesium and glass. **Xeng et al. (2009)** analyzed with deep detail the excavation force that will be encountered on the Luna surface.

2.3.4 Solar Power on the Moon

It has long been suggested that solar cells could be produced from the materials present on the lunar surface. In its original form, known as the solar power satellite, the proposal was intended as an alternate power source for Earth. Solar cells would be shipped to Earth orbit and assembled, the power being transmitted to Earth via microwave beams. Despite much work on the cost of such a venture, the uncertainty lay in the cost and complexity of fabrication procedures on the lunar surface. Solar power cells are likely to be primary method of obtaining electrical power on the Moon. Electrical power can be used directly for many operations, and can be the power source for converting the output water of fuel cellsback into hydrogen and oxygen. A solar cell (also referred to as a photovoltaic cell) is a device that converts photons from the Sun (solar radiation) into electricity. When they first became available, they were used in solar-powered calculators and other low-powerapplications. As their efficiency improved, they began to be used in remote areas where electrical power from transmission lines (the grid) is unavailable. Because photovoltaic systems are modular, their electrical power output can be engineered for almost any application: for instance large arrays of photovoltaic cells are also used to power spacecraft. Solar cells are a type of semiconducting device and the common photovoltaic structure consists on semiconductor material into which a diode, or p-n junction. **Freundlich et al. (2005)** have been proposed a method of fabricate power system utilizing lunar resources exploiting the ultra vacuum level on the lunar surface and the presence of some materials from which thin film solar cells could be made by direct evaporation. This experimental activity consisted on the heating of JSC (as a simulant): when the regolith reaches 1300°C it starts soften. The resulting melt was very viscous and evolved in gas bubbles. By 1600°C the regolith has completely melted and the viscousity low. The sample has been then cooled: the temperature falls quickly (1-2 minutes to around 300°C). The resistivity of the melted regolith glass substrates was found to exceed 10^6 Ωcm.This material could be viewed as a substrate on which by evaporation it is possibile to produce a thin film of solar cell. Specifically, small parabolic collectors generate the 1300°C – 1500°C needed for the solar cell fabrication to focus the concentrated solar energy onto the regolith for melting onto specially designed evaporation ovens for silicon and metal deposition.

While silicon is the most common mayterial used for this kind of applications, the use of Ilmenite as a semiconductor layer has been recently addressed. It is worth noting that in order to modify the conductivity, small amounts of impurities are introduced into the cristal lattice: this is called "doping". In the following **Table 2-11** a comparison among ilmenite parameters with respect to most known semiconductors is reported.

TABLE 2-11: Properties of various semiconductors

	Ilmenite	Silicon	Silicon carbide	Gallium Arsenide
Resistivity	1.11 Ωm	0.23 Ωm	0.1 Ωm	0.004 Ωm
Band gap	2.54 eV	1.12 eV	2.9 eV	1.43 eV
Melting point	1683 K	1385 K	3070 K	1784 K
p-type semiconductor	Pure Ilmenite	On doping	On doping	On doping
n-type semiconductor	In solution with α-Fe_2O_3	On doping	On doping	On doping

For their important applications solar cells have been deeply analized in recent years **(Igniatiev et al., 1991, Glaser et al., 1992, Woodcock et al., 1992). Glaser et al. (1992)**investigated the eletrical needs considering different mission scenarios. In addition **Ignatiev et al. (2000)** investigated the possibility to generate power on the Moon using solar (photovoltaic) systems. Being the lunar environment a vacuum with pressures generally in the 1 x 10^{-10}torr range, such conditions provide an ideal environment for direct vacuum deposition of thin film solar cells using the waste silicon, iron, and TiO_2 available from the lunar regolith processing meant to extract oxygen. **Woodcook et al. (1992)** proposed an integrated solution among the main system of enegy production in Space –nuclear, solar and chemical.

2.3.5 Construction Materials

The utilization of lunar resources to produce novel materials exploitable for the production of physical assets have been proposed in last decades **(Criswell et al., 1978, Ehricke et al., 1976, Waldron et al., 1981, Ozdemir et al., 1990, Ramohalli et al., 1992, Sherwood et al., 1992, Desai et al., 1992, Fabes et al., 1992, Leong et al., 1992). Waldron et al. (1981)** proposed an electrochemical refining process for the separation and recovery of principal and trace elements from reduced metallic particles found in lunar soils. **Desai et al. (1992)** developed a versatile engineering materials production from locally available materials in space. Specifically, it has been proposed the development of the technologies for manufacture structural and construction materials on the Moon, utilizing local lunar soil (regolith), without the use of water. **Leon et al. (1992)** proposed a process for producing useful ceramics materials from lunar resources using the by products of lunar oxygen production processes analizing also the effect of particle’s size on the material strenght.

The development of innovative technologies in the framework of the ISFR (In-Situ Fabrication and Repair) and ISRU (In-Situ Resources Utilization) concepts is relevant for facilitating and time extending future human exploration on the Moon, Mars, near Earth asteroids, etc.**(Bassler et al., 2006; Hammond et al., 2006; Howell et al.,**

2008). In this regard, several studies have been recently addressed with the final aim to obtain suitable structures for protection against cosmic rays, solar wind and meteoroids, making use of available *in-situ* Lunar resources **(Allen et al., 1994; Toutanji et al., 2005; Tucker et al., 2006; Martirosyan and Luss, 2006; Faierson et al., 2010a; Faierson et al., 2010b; Corrias et al., 2010, Corrias et al., 2010, White et al., 2011)**.

For instance, a process where regolith Lunar simulant was sintered at 1100°C by radiant and microwave heating was proposed **(Allen et al., 1994).** Lunar regolith was also utilized for fabricating a thermo-plastic material **(Toutanji et al., 2005)** and fiberglass for reinforcing Lunar concrete **(Tucker et al., 2006)**. Other experiments related to the production and the utilization of lunar resources toi produce and utilize lunar concrete have been proposed **(Matzumoto et al., 1992, Ishikawa et al., 1992, Agosto et al., 1992, Carley et al., 1992)**. This processes are related to the fact that lot of minerals in the bulk are not present as a single oxide but as a mineralogic specie. One of the main mineral present as a single oxide is lime (CaO). Specifically, **Agosto et al. (1992)** proposed the enrichment of the lime content to levels like those of Portland cement.

The other investigated methods are mainly based on the exploitation of combustion synthesis-type reactions for the fabrication of ceramic composites using Lunar regolith in the starting mixture **(Martirosyan and Luss, 2006; Faierson et al., 2010a; Faierson et al., 2010b; Cao et al., 2011; Corrias et al., 2011; White et al., 2011)**. For instance, the exothermic chemical reaction:

$$x(Ti + 2B) + (1-x)JSC\text{-}1 \rightarrow x(TiB_2) + (1-x)JSC\text{-}1,$$

that displays a SHS behavior when $x>0.25$, was proposed as a possible method for the preparation of Lunar bricks using JSC-1 Lunar regolith simulant **(Martirosyan and Luss, 2006).** On the other hand, the direct aluminothermic reduction of Lunar regolith was found to produce, after a relatively long preheating stage (7-15 min), a ceramic composite material, mainly consisting of Al_2O_3, Si, $CaAl_4O_7$ and $MgAl_2O_4$. **(Faierson et al., 2010a; Faierson et al., 2010b).** Along these lines, taking advantage of the presence of significant amounts of iron oxides in Martian soil, the highly exothermic, i.e. $(-\Delta H_r^o)$ = 851.444 kJ/mol of Al_2O_3 **(Barin, 1989)**, self-propagating aluminothermic reduction of hematite:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

could be exploited in the framework of the ISRU principle. This statement holds also true when considering the reduction of ilmenite ($FeTiO_3$), whose presence is up to 20 wt.% on the Moon, by aluminum **(Schrunk et al., 2008)**.

Following **Faierson et al. (2010a, 2010b)** work,the use of Mg as reducing agent to be reacted with JSC lunar regolith was recently preferred to Al, because of the correspondingly higher adiabatic temperature **(White et al., 2011)**.

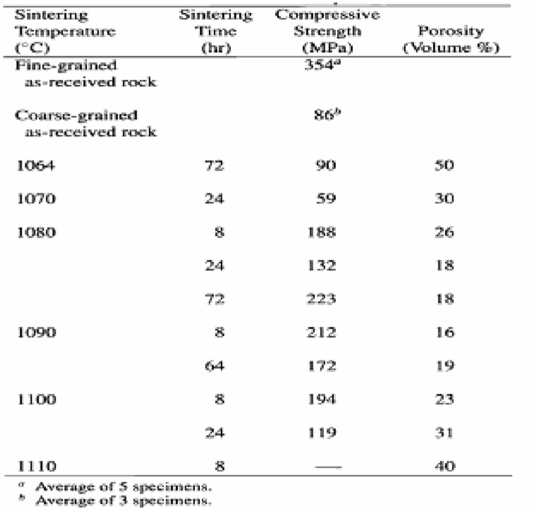
More recently, a novel recently patented process based on the occurrence of Self-propagating High temperature Synthesis (SHS) reactions potentially exploitable for the in-situ fabrication of construction materials in Lunar and Martian environments has been proposed **(Corrias et. al., 2010)**. Specifically, the SHS process involves thermite reactions type between Lunar or Martian regolith simulants and aluminum as reducing agent. To overcome the fact that the original content of ilmenite ($FeTiO_3$) and ferric oxide (Fe_2O_3) on Moon and Mars soils, respectively, is not enough to make the SHS process possible, suitable amounts of these species have to be added to the starting mixtures.

The dependence of the most important processing parameters, particularly the composition of the starting mixture, evacuation level, and gravity conditions, on SHS process behaviour and product characteristics is specifically examined for the case of Lunar regolith. All the obtained findings allows us to conclude that the optimized results obtained under terrestrial conditions are valid for in-situ applications in Lunar environment. In particular, parabolic flight experiments evidenced that neither SHS process dynamics nor product characteristics are significantly influenced in both Lunar and Martian systems when passing from Earth to low gravity conditions. Finally, the complete scheme involving all stages required for the fabrication of physical assets to be used as protection against solar rays, solar wind and meteoroids, etc., is reported.

2.3.5.1 SYNTHERING EXPERIENCES

Synthering is a term applied to an elevated temperature heat treatment of a porous material in which the particles form strong bonds with a concurrent reduction in the volume of pore space. Therefore, in order for synthering to occur, a mechanism for material transport must be present. The two dominant transport mechanisms that occur in ceramic powders are diffusion and viscous flow, although other mechanisms may also be present; in particular, vapour transport may be relatively important in a vacuum synthering condition (which would exist on the lunar surface). On the basis of the transport mechanisms, synthering can be categorized as either solid-state synthering or liquid-phase (viscous) synthering. In this report we will examine each synthering mechanism in turn and show that liquid-phase or viscous synthering is the technique most useful for lunar basalt materials.Solid-state synthering involves material transport by diffusion. Rapid diffusion rates are achieved by heating the compacted powder to a sufficiently high temperature (typically greater than half of the melting temperature) so that the initial bridges or necks which exist between particles grow as a result of mass transport to these regions. The mass transport can take place by the movement of atoms or vacncies along a surface or grain boundary or through the bulk of the material. The driving force for this process results from the fact that the powder particles are in contact with one another in the compacted body but a significant amount of pore space exists between the particles (typically 25 to 60 volume percent porosity). At high temperatures, when sufficient atom mobility is present, atom diffuse to the initial particle contacts or bridges to eliminate the solid/vapour interfaces that exist within the compact, replace these interfaces with lower energy solid/solid interfaces. As atom diffusion (or other transport mechanisms) permit the particles to be bonded together, the pore space originally present shrinks and may be eliminated if synthering is carried out for sufficiently long times. In 1995 **Pletka** proposed an experimentation with Lunar Regolith simulant: powder was hydrostatically pressed into rods measuring 100 mm in length and 10 mm in diameter using a pressure of 345 MPa. The rods were then synthered under an argon (inert) atmosphere. Synthering times ranged from 8 to 72 hours and the temperatures were varied 1000 to 1110°C. The following **Table 2-12** summarizes the experimental conditions in the synthering experiments.

TABLE 2- 12: Experimental conditions in synthering experience



Sintering Temperature (°C)	Sintering Time (hr)	Compressive Strength (MPa)	Porosity (Volume %)
Fine-grained as-received rock		354[a]	
Coarse-grained as-received rock		86[b]	
1064	72	90	50
1070	24	59	30
1080	8	188	26
	24	132	18
	72	223	18
1090	8	212	16
	64	172	19
1100	8	194	23
	24	119	31
1110	8	—	40

[a] Average of 5 specimens.
[b] Average of 3 specimens.

In addition, as reported by **Allen (1998)**, Lunar Regolith can be synthered also with the application of high temperature for a shorter time.

The following **Table 2-13** summarize their results:

TABLE 2-13: Experimental parameters in synthering experience

Parameter	Radiant Heating-1	Radiant Heating-2
Material	MLS-1 Basalt	Glass rich JSC-1
Brick size [cm]	7.9 x 5.5 x 3.6	13.1 x 5.6 x 4.6
Temperature [°C]	1100	1100
Time [h]	2	2.5

As it apparent the energy requirement for synthering processes is not low because of the high temperatures to be reached and the long time necessary for the process.

2.3.6 Other processes on the Moon

Other processes related to the the extraction of volatile materials implanted by the solar wind in the lunar soil have been proposed **(Carter et al., 1985, Ganguly et al., 1989, Gamguly et al., 1990, Lewis et al., 1990, Wittenberg et al., 1992)**. **Carter et al. (1985)** performed the theoretical evaluation of the lunar regolith fines as a primary source of hydrogen. This analysis revealed that a minimum order of magnitude increase in hydrogen content is possible in beneficiated fines because both particle size and particle shape play a significant role in the relationship of volume percent of surface coating to grain size. Indeed, the lunar regolith fines meet the basic requirement for beneficiation because a major portion (minimum two-thirds) of the hydrogen occurs in the less than 20-micron-size fraction, a relatively small part of the fines. Beneficiation should be accomplished by a combination of vibratory screening followed by cyclone and/or possibly electrostatic separation. **Lewis et al. (1990)** investigated about a processes for the coproduction of metals from extra-terrestrial materials in conjunction with plausible schemes for oxygen extraction continue. **Wittenberg et al. (1992)** described a process to perform the in situ heating of the lunar regolith in order to release the solar wind gases.

Lot of these processes are more related to the extraction of Helium to be utilized to fed nuclear plants **(Swindle et al., 1990, Swindle et al., 1992, Crab et al., 1992, Li et al., 1992, Kulcinski et al., 1992,**

Missali et al., 1993). Swindle et al. (1990) have proposed that lunar He-3 could be used as a fuel for terrestrial nuclear fusion reactors. Thie analysis demonstrated that the available amount of Helimu 3^+ is sufficient for early reactors, at least, but that the mining problems, while not necessarily insurmountable, are critical. **Li et al. (1992)** have considered several techniques for mining and processing the regolith on the lunar surface. These techniques have been proposed and evaluated based primarily on the following criteria: (1) mining operations should be relatively simple; (2) procedures of mineral processing should be few and relatively easy; (3) transferring tonnages of regolith on the Moon should be minimized; (4) operations outside the lunar base should be readily automated; (5) all equipment should be maintainable; and (6) economic benefit should be sufficient for commercial exploitation. Finally other processes to recreate an artifical atmosphere heve been proposed during the years **(Mignon et al., 1992, Burns et al., 1992, Easterwood et al., 1992, Macelroy et al., 1994). Mignon et al. (1992)** outlined the importance of synergy and linkages between bioregenerative life support systems and the materials produced by in-situ materials. By means of these technologies it was possibile to produce a broad spectrum of byproducts such as oxygen, hydrogen, processed soil material, ceramics, refractory, and other materials. **Easterwood et al. (1992)** analyzed an integrated life support system based on food production, waste management and utilization, and product synthesis. Inputs include an atmosphere, water, plants, biodegradable substrates, and manufacutured materials such as fiberglass containment vessels from lunar resources. Outputs include purification of air and water, food, and hydrogen (H_2) generated from methane (CH_4).

2.4 ISRU and ISFR processes on Mars

2.4.1 Mars: Main physical features and exploitable resources

As said also previously numerous spacecraft, including orbiters, landers, and rovers, have been sent to Mars by the Soviet Union, the United States, Europe, and Japan to study the planet's surface, climate, and geography. The main results of this investigation are reported in this paragraph. Mars and Earth are the two planets in the Solar System which are the most alike in climatical aspects. They are both terrestrial i.e. they consist of rock and metal, and the gravity on the surface of Mars is 0.38g compared Earth ($g = 9.81ms^{-2}$). Mars rotates at approximately the same rate as Earth (a Martian day called ‘sol’ is 24.66 Earth hours), and its orbit around the Sun takes 669 sols, which is a little less than two Earth years. The obliquity of the two planets (the inclination of the rotational axis to the ecliptica) However, the eccentricity of Mars' orbit is greater than that of Earth, which results in a greater dierence between the maximum solar insolation on the northern and southern hemisphere. The feature of Martian topography is striking, northern plains trampled by lava flows disparity with the southern highlands, bumpy and cratered by ancient impacts. The surface of Mars as seen from Earth, is divided into two kinds of areas, with differing albedo. The paler plains covered with dust and sand rich in reddish iron oxides were once thought of as Martian 'continents' and given names like Arabia Terra (land of Arabia) or Amazonis Planitia (Amazonian plain).The dark features were thought to be seas, hence their names Mare Erythraeum, Mare Sirenum and Aurorae Sinus. The largest dark feature seen from Earth is Syrtis Major.Mars has polar ice caps that contain frozen water and carbon dioxide that vary with the Martian seasons - the carbon dioxide ice sublimates in summer, revealing a surface of layered rocks, and forms again in winter. An extinct shield volcano, Olympus Mons (Mount Olympus), is at 27 km the highest mountain in the solar system. It is in a vast upland region called Tharsis, containing several large volcanos.

The atmosphere of Mars is comparatively thin and the air pressure on the surface is only 750 Pascal, about 0.75 percent of the average on Earth. Though, the scale height of the atmosphere is about 11 km, fairly higher than Earth's 6 km.

The constituents of the martian atmosphere include 95 percent carbon dioxide, 3 percent nitrogen, 1.6 percent argon, and traces of oxygen and water.

In the following **Table 2-14** the macroscopic martian environment characteristics are summarized.

TABLE 2- 14: Main Martian environment characteristics

Parameter	**Value**
Gravity acceleration	1/3 g
Pressure value	6-10 torr
Atmosphere	CO_2 (95,3% v/v)
Temperature	150-240 K
Solar constant	607 W/m^2

In addition, methane was apparently discovered in the atmosphere by Earth-based telescopes in 2003, and perhaps confirmed in March 2004 by the Mars Express Orbiter, present measurements state an average methane concentration of about 11±4 ppb. The thin atmosphere cannot embrace heat and is the cause of the lower temperatures on Mars. The presence of methane on Mars would be very fascinating, since as an unstable gas it indicates that there must be a source of the gas on the planet.Volcanic activity, comet impacts and the existence of life in the form of microorganisms such as methanogens are among possible however as yet unconfirmed sources.

The methane appears to occur in patches, which suggests that it is being hastily broken down before it has time to become uniformly distributed in the atmosphere.

In the winter months when the poles are in continual darkness, the surface gets so cold that as much as 25% of the entire atmosphere condenses out into meters thick slabs of CO_2 ice. When the poles are again exposed to sunlight the CO_2 ice sublimates, creating massive winds that sweep off the poles as fast as 250 mph. These continuing actions transfer large amounts of dust and water vapor giving rise to Earth-like frost and large cirrus clouds. Mars is mainly composed of basalt and andesite rock on its surface, covered in many places by meters or more of a dust as fine as talcum powder. Mars Global Surveyor spacecraft observations says that the magnetic fields on Mars exposed that parts of the planet's crust has been magnetized in alternating bands, usually measuring 100 miles wide by 600 miles long (160 km by 1000 km), in a similar pattern to those found on the ocean floors of Earth. In 1999 one fascinating theory, published saying that these bands could be evidence of the past operation of plate tectonics on Mars, although this has yet to be confirmed. New findingssupport this theory, and seem to indicate an early era of tectonic activity similar to that found on Earth due to sea-floor spreading. If true, the processes involved may have helped to sustain an Earth-like atmosphere by transporting carbon rich rocks to the surface, while the presence of a magnetic field would have helped to protect the planet from cosmic radiation.Phobos and Deimos are the two moons of Mars and their orbits are seen from above Mars' North Pole. Both Phobos and Deimos are tidally locked with Mars, always pointing the same face towards it. Since Phobos orbits around Mars faster than the planet itself rotates, tidal forces are slowly but steadily decreasing its orbital radius. At some point in the future Phobos will be broken up by gravitational forces. Deimos, on the other hand, is distant enough that its orbit is being gradually boosted instead. Both satellites were discovered in 1877 by Asaph Hall, and are named after the characters Phobos (panic/fear) and Deimos (terror/dread). As seen from Mars, Phobos has an angular diameter of between 8' (rising) and 12' (overhead), while Deimos has an angular diameter of about 2'. The Sun's angular diameter, by contrast, is about 21'.

Martian soil, as reported by many authors **(Bell et al., 1999, Hepp et al., 1991, Barlow et al., 1991, Marshall et al., 1999, Clark et al., 1992)** is mainly composed by stable silicate minerals as reported in **Table 2-15**.

TABLE 2- 65: Martian Soil composition

Mineral	Formula	Percentage
Halite	NaCl	1,02
-	MgSiO4	8,22
Maghemite	Fe2O3-gFe2O3	6,32
Montronillonite	(Na,Ca)0,3 (Al,Mg)2Si4O10 nH2O	34,11
Nontronite	Na0,3Fe+++2(Si,Al)4O10 (OH)2 nH2O	34,38
Saponite	(Ca,Na)0,3(Mg,Fe)3(Si,Al)4O10(OH)2 nH2O	15,82
Residual	-	14,18

2.4.1.1 MARTIAN SOIL SIMULANTS

Up to now, no Martian regolith has been returned to Earth, making it necessary to find an Earth-based materialanalogue which mimics the mechanical, chemical and physical properties of these soils that were determinedduring previous Mars missions. Indeed, for reseach purposes it have been developed some simulant to the regolith of Mars for support of scientific research, engineering studies, and education.

2.4.1.2 JET PROPULSION LABORATORIES (JSC) SIMULANTS

The JSC Mars-1A simulant provided by the Kennedy Space Center is a palagonite tephra collected from the slopes of the Pu’u Nene cinder cone on the Island of Hawaii. Palagonitic tephra from this cone has been repeatedly cited as a close spectral analog to the bright regions of Mars. The chemical composition is compared to that of a typical Mars surface sample analyzed at the Viking lander 1 site.

2.4.1.3 MOJAVE MARTIAN REGOLITH SIMULANT

The Jet Propulsion Lab have identified and characterized another basaltic Mars simulant. The source rock for the simulant is a basalt mined from the Tertiary Tropico Group in the western Mojave Desert. The Mojave Mars Simulant (MMS) was chosen for its inert hygroscopic characteristics, its availability in a variety of forms, and its physical and chemical characteristics. The MMS dust and MMS sand are produced by mechanically crushing basaltic boulders. This is a process that more closely resembles the weathering/comminution processes on Mars where impact events and aerodynamic interactions provide comminution in the (relative) absence of water and organics.

2.4.2 ISRU and ISFR martian applications

It is well known that to make possible the future human missions on Mars it is necessary to develop and optimize innovative technologies related both to the exploitment of natural resources and to the optimal management of biological products. For its reletive similarity to the Earth lot of authors have hypotisized the human colonisation of Mars, with the presence of outposts **(Kaloupis et al., 1992, Barker et al., 1998, Finn et al., 2000)** and the design of lander and vehicles useful for future space missions **(Linne et al., 1991, Zuppero et al., 1991, Colvin et al., 1991, Dowler et al., 1991, Pelaccio et al., 1992, Bowles et al., 1992, Abrego et al., 1993, Norman et al., 1993, Borowsky et al., 1998, Rice et al., 1999). Kaloupis et al. (1992)** analyzed the opportunity of using indigenous Space Materials to make Mars exploration mission scenarios more affordable by reducing the initial mass necessary in Low Earth Orbit (LEO). **Colvin et al. (1991)** focused on oxygen production using resources indigenous to Mars.

Specifically , a bank of solid zirconia electrolytic cells that will electrochemically separate oxygen from a high temperature stream of carbon dioxide is at the center of the oxygen production system. **Pelaccio et al. (1992)** identified and characterized promising chemical propulsion system designs which use two or more of the following propellant combinations: LOX/H_2, LOX/CH_4, and LOX/CO. The engine systems examined emphasized the usage of common subsystem/component hardware where possible. In support of this study, numerous mission scenarios were characterized that used various combinations of Earth, lunar, and Mars propellants to establish engine system requirements to assess the promising engine system design concept examined, and to determine overall exploration leverage of such systems compared to state-of-the-art cryogenic (LOX/H_2) propulsion systems. **Borowsky et al. (1998)** discussed the use of nuclear thermal rocket (NTR) as a leading propulsion options for future human missions to Mars because of its high specific impulse capability and its attractive engine thrust-to-weight ratio.

The technologies involved in the space exploration of Mars are related to the totale recycle of liquid and solid wastes produced by the crew, to the production of water and food, to the production of power from renewable energy sources (as solar radiation) and to the captation and utilization of carbon dioxide that as discussed previously is the main constituent of martian atmosphere. In this framework the technologies already discussed with reference to ISS prolonged stay of astronauts and MELISSA project have given lot of useful information about minimum requirementsand constraints tht guarantee the sussistance and operativity of the crew in extraterrestrial contests. Various authors have investigated the martian in-situ resources with the perspective of utilizing them in the colonization of Mars **(Conrad et al., 1964, Mayer et al., 1984, Ramohalli et al., 1987, Stocker et al., 1989, Ramohalli et al., 1991, Stancati et al., 1991, Cordell et al., 1988, Mayer et al., 1989, Cordell et al., 1991, Evans et al., 1992, Sadeh et al., 1992, Mancinelly et al., 1992, Cooper et al., 1997, Sanders**

et al., 1998). In addition –in a analogous way of the lunar applications- lot of international meetings have been organized in order to promote the international collaboration in this topic **(Smernoff et al., 1989, Wykes et al., 1992, Bruckner et al., 1993, Gross et al., 1999, Goodrich et al., 2001, Rice et al., 2003).** In this chapter the more significant and investigated processes related to the exploitment of martian resources to produce life consumables products and structural elements will be discussed.

2.4.3 Oxygen and water production by carbon dioxide

The most known process to produce oxygen from martian atmosphere is the RWGS (Reverse Water Gas Shift) process. Roughly speaking this process requires as a input hydrogen brought from the Earth and carbon dioxide from martian dioxide from martian amtosphere and givs as outputs oxygen and water. Specifically the whole process consists on two main steps. In the fisrt step hydrogen is oxydized by carbon dioxide –Sabatier Reactor- according to the following reaction

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

In which methane and water are produced. While the methane is stored as a propellant, water is electrolyzed to produce hydrogen and oxygen, as stated by the following reaction:

$$2H_2O -> 2H_2 + O_2$$

The oxygen produced is stored to be utilized as life consumable product or as a propellant and the hydrogewn is recycled to fed the first reaction. Anyway it is apparent that a continous hydrogen supply from Earth must be taken into account as a certain percentage of hydrogen in each cycle is used to form methane. This process has been analyzed for several decades by lot of authors that have been also proposed some modifications, in order to satisfy particular constrains. These modifications, anyway, are not sustantial but mainly related to split by-products in differewnt ways **(Frisbee et al., 1987, Carnevale et al., 1988, Ramohalli et al., 1987, Shridhar et al., 1992,Salerno et al., 1993, Acosta et al., 1994, Shridhar et al., 1999, Wegeng et al., 2000, Finn et al., 2000, Dale et al., 2003).** While the process seems simple in principle lot of difficulties have to be taken in to account in building a breadboard on the martian surface. Hydrogen storage seems to be difficult because of the low boiling point at low pressure environment and this leads to the necessity of the requirements of too much CO_2 too quickly, as reported by **Mueller et al. (1996)**. The production of oxygen runs best at a pressure of one atmosphere and at a temperature of 573 K so a compressor for carbon dioxide is needed. **(Naumov et al., 1979)** Another difficulty is related to the low efficiency of single vacuum pump. Indeed, carbon dioxide at 1 bar obtained froman atmosphere at 7 mbar requires –by isentropic compression- about 380 kJ per kg of CO_2. The isentropic compression –ideal case- is formalized by an adiabatic transformation in the following form:

$$PV^{\gamma} = cost$$

and

$$W = -\Delta U = nC_v(T_1 - T_2) = \frac{1}{\gamma - 1}(P_1V_1 - P_2V_2) = \frac{nRT_1}{\gamma - 1}\left[1 - \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}\right]$$

Taking into account a temperature range of 150 and 273 K and considering the molar weight of CO_2 (44.01 g/mol) the adiabatic compression requires an energy amount in the range of 200 and 364 kJ/kgCO_2, as confirmed by **Linn et al. (1999)**. In addition mechanical single stage vacuum pumps for 140:1 compression ratio are tipically characterized by low efficiency (about 7%), thus the enrtgy demand is about 5207 kJ/kgCO_2. On a basis of this large amount of energy different technologies to pressurize the carbon dioxide have been proposed. **Hu et al. (2007)** have proposed a catalytic microchannel reactor for in situ propellant production for Mars exploration, with particular reference with catalist development. **Holladay et al. (2006)** have designed and realized a pilot plant in order to better understand the feasibility of the RWGS plant. The results obtained appearedvery promising: the RWGS plant using Ru/CeO-ZrO_2 was found to be robust over a wide range of conditions and showed and deactivation during testing. Finally the mission scenarios that involve this kind of technologies have been proposed during last decades: for instance **Sridhrar et al. (1995)** have proposed a mars sample return mission in which oxygen for return propellant would be produced using martian atmosphere. As already stated all these technologies are integrated and developped with different purposes as reported by **Tikhomirov et al. (2006)** that studied approaches to design biological life support systems for Mars mission, taking advantage also by a microalgae reactor.

The compression of martian atmosphere through temperature swing absorption **(Rapp et al., 1997)** has been proposed. In the latter one it is foreseen a nightly cycle of absorption and a dayly cycle of absorption, obtaining the pressure gain by the temperature effect on the equilibrium law.

2.4.4 Propellant production on Mars

A significant evaluation of the technologies related to the use of carbon dioxide in ISRU/ISFR view was proposed by **Ash et al. (1978)** that demonstrated that a system that utilizes atmospheric carbon dioxide and soil moisture to produce liquid methane-oxygen propellant requires a lander mass which is less than half the mass of the ascent vehicle. In addition to carbon dioxide these authors exploited the presence of water on Mars, already inequivocally demonstrated by probes. As already discussed, indeed, the water is available on the Martian surface and in its atmosphere, even if the the quantity of water in a saturated atmosphere is only in the order of $1*10^{-4}$ kg of water per kg of atmosphere. Soil moisture content varies from nominally 100% incertain region (north pole, for instance) to less than 1% in the upper few cwntimeters of soil around Viking Landers. The propellant chosen in that analysis to refuel the lander was methane-oxygen, Even if liquid hydrogen-oxygen propellant is superior in terms of performances, but the 20 K boiling point of hydrogen (at one atmosphere) requires substantial cryogenic refrigeration. The cooiling power required for hydrogen liquefaction and storage could be high enough to lower the plant efficiency and the needed plant results in an eccessive system mass requirements. A variety of fuels can be examined from different combinations of carbon dioxide and water in terms of propulsive performance, liquefaction energy and storage characteristics. Figure of merit of more representative propellant candidates are listed in **Table 2-16** (**Ash et al., 1978**).

TABLE2 16: cryogenic and propulsive characteristics of some propellants (Ash et al., 1978, modified)

	Liquefaction Temperature [K]	Liquefaction Energy [kJ/kg]	Oxidizer/Fuel ratio [-]	Combined average density [kg/m^3]	Specific impulse [kN/s/kg]
Constituent					
Oxidizer					
O_2	90.2	310	-	-	-
Fuel					
H_2	20.4	5900	5.0	324	4.18
CO	81.6	390	0.5	887	2.54
CH_4	111.4	460	3.4	812	3.35

Although some details related to the values reported in the previous **Table 2-16** are repoted in **Ash et al., (1978)**, it is important to outline that methane propellant was selected as the primary propellant candidate because it requires simple chemical processes and modest liquefaction work, while simultaneously producing a relative high performance propellant. Anyway, **Shafirovich et al. (1993)** evaluated the possibility of using magnesium and carbon dioxide for extraterrestrial missions on Mars.

2.4.5 Energy production on Mars

The energy production on Mars is mainly related to tecnologies as

- Nuclear plant
- Fuel cells
- Photovoltaic plants

So far one of the most significant simulation about this kind of technology has been developed by **Kerslake et al. (2003)** that proposed one plant that integrated photovoltaic panels and fuels cells. Specifically the plant proposed consists on photovoltaic plant, a DSCU (Direct Current Switching unit), a regenerative fuel cell based on H_2/O_2, a proton exchanger membrane, an elòectrolyzer, a DDCU (dc-to-dc convertr unit), and an output unit. Specifically, The design is dominated by the 5000-m^2-class PV array that is deployed orthoginally as four tent structures. Each tent structure is approximately 5-m on a side and 100-m long and The PV array is divided into 8 independent electrical sections, each comprising one side of a tent structure. Array strings contain a sufficient number of seriesconnected cells to provide 600 volts maximum power voltage at end-of-life. By means of these materials and apparatuses it has been estimated that it is possibile to produce 120 kW during the martian day (sol) and 50 kW during the night.

2.4.6 Carbon Dioxide: a key resource

As said previously the carbon dioxide is one of the most useful and available resources resource on Mars. In this framework, the opportunities and prospects in the chemical recycling of carbon dioxide to fuels,as a complementary technology to carbon sequestration and storage are tremendously important. It is remarked that therequisites for this objective are the minimization-as much as possible-of the hydrogen consumption, the production of end-products that can be easily stored and transported, and the utilization of renewableenergy sources

The processes already proposed include

- Reverse water–gas shift (already discussed in this work)
- Hydrogenation to hydrocarbons, alcohols, dimethyl ether and formic acid,
- Reaction withhydrocarbons to syngas,
- Photo- and electrochemical/catalytic conversion, and
- Thermochemicalconversion
- Use of micro algae.

As stated by **Centi et al. (2011)** and references therein, in general, there are four main approaches to convert CO_2

1.To use high-energy starting materials such as hydrogen,unsaturated compounds, small-membered ring compounds, and organometallics.

2.To choose oxidized low-energy synthetic targets such as organiccarbonates.

3.To shift the equilibrium to the product side by removing a particular compound.

4. To supply physical energy such as light or electricity.

All thes approaches are under investigation both for Space applications and for terrestrail ones, being the carbon dioxide one of the main causes of greenhouse effect.In this perspective, the production of photosynteic oxygen and edible biomass using martian CO_2 has been recently addressed **(Cao et al., 2010)**. The process takes advantage of two parts, the biological section and the chemico-physical one, both of them powered by solar panels.The chemico-physical section consists mainly of microwave systems, adsorber units and appropriate kind of chemical reactors.

In the microwave systems water from the soil bulk is extracted in form of vapour. The condensed vapour is then sent to an electrolizer to produce hydrogen and oxygen. Adsorber units are used to pressurize and separate the carbon dioxide from the Martain atmosphere. Carbon dioxide is sent to an electrolizer to produce CO and CO_2, that can be used as a propellants, and Ar and N_2 (also present in the Martian atmosphere) are used to produce gaseous ammonia. The latter one is then sent with the oxygen inside of a suitable reactor where appropriate pressure and temperature conditions are set to promote the reaction between these two gases. During these process, known as Ostwald process the HNO_3 is produced. Finally the latter one is made reacted with HNO3 to produce NH_4NO_3 that is generally used as a fertilizer.

In the biological section a suitable algae strain –transported from the Earth- grows in an appropriate acqueous medium.

The latter one takes advantage of the water extracted from soil (as in the biological section) and of the NH_4NO_3 produced in the chemico-physical section. In addition the micro and micro nutrients are extracted from soil by means of an appropriate leaching solutions and the HNO_3 produced in the chemico-physical section is also fed to this solution. Finally the CO_2 purified by adsorber units is fed by appropriate pumps to this medium, giving the algae a suitable carbon source and promoting the mixing of all of these elements. The solar radiation is used both to accomplish the photosynthetic activity and to maintain the medium at a suitable temperature to avoids limitating effects. The oxygen produced during the photosynthetic activity, sepated by a degaser, is stored end used as replenishment elements for ECLSS systems. Finally the metabolic wastes, algae biomass extracted from the reactor, appropriate organic acids transported from the Earth and fertilizers are fed to the cultivation area to promote vegetable food production.

On a basis of mass balances and data reported in scientific literature, in addition to the experimental activity leaded with reference a specific steps of the patent, as the photobioreactor the products flows reported in this table can be estimated. Analogously, on a basis of data related of existing plant and our calculation can be estimated a payload of about 80 tons.

2.4.7 Agricolture on Mars

Mars is the second target of our manned space flight next to theMoon, and possibly the most distant extraterrestrial body to which wecould travel, land and explore within the next half century. A Mars mission mustinclude at least 1.5 years for round trip travel, and a restricted opening ofthe launch window, both for forward and return flights once every twoyears.Agriculture can be broadly defined as a human activity that produces and supplies organisms and their products to us for sustaining our life and for assisting with the development of human society. The agricultural organisms are various, including crops,In addition to producing foods, the function of biological andecological systems. As well, Martian agriculture must revitalize air andwater, in addition to supplying ordinary agricultural products like foods, fibers and timber. Recycled use of materials is a major function of agriculture on Mars. As reported by **Wada et al. (2009)** Martian agriculture is also characterized by limited species in the ecosystem, contained inside a small dome constructed on either the surface or subsurface of Mars. The selection of a dwelling site is an important early step in the initiation of humanhabitation on Mars. Criteria used in the selection of habitation sites on Earth could be applied to the Martian case, with certain modifications. Humans usually dwell in sunny places whereboth a watering spot and a shelter are within easy distance. This means that detailed topographic maps of Mars are very helpful for selecting the dwelling site. If the regolith at theselected site is sandy loam or loamy sand in texture and its sedimentation thickness is about 1 meter, the emigrants are fortuitous, because other textures of regolith or thinner sediment of regolith are considered unsuitable for agriculture, as discussed below.Unfortunately,information about the regolith is still fragmentary, and somewhat contradictory in certain parts. We shall explore Mars to map and collect comprehensive data on the regolith, which is required to design space agriculture and select the habitation site.

The regolith on Mars is widely covered by hematite. This indicates that ferruginousminerals such as olivine, pyroxene and hornblende have been weathered to release ferrousiron, which is oxidized by mechanisms not yet fully understood. In addition, the presence of $CaSO_4$ and jarosite indicates that even Ca^-, Na^-, and K^-rich minerals such as feldspars have been weathered. However, the common presence of olivine indicates that the degree of the weathering is generally low. Furthermore, the presence of jarosite would mean the regolith is acidic, because jarosite is formed and kept intact under acidic conditions. While on the contrary, the presence of $MgCO_3$ or $CaCO_3$ would mean the regolith is somewhat alkaline.

In any case, the following stepwise efforts are necessary in order to form Martian soil:

Desalinization: Martian regolith usually contains water-soluble salts. If theirconcentration is so high as to harm most organisms except for halo-tolerant or halophilous organisms, desalinization (removal of the water-soluble salts) is imperative. Desalinization can be achieved by leaching the salt-affected regolith with non-saline water. The leaching water enriched with the salts (e.g. NaCl, $NaSO_4$, $CaCl_2$, $CaSO_4$) can be used to strengthen regolith bricks for use in the construction of space habitation.

Neutralization: The pH of the regolith may vary from place to place. pH should be very low in places dominated by jarosite and should be high in places dominated by $NaHCO_3$ orNa_2CO_3. However, in most places, pH may be somewhat high where $CaCO_3$ or $MgCO_3$ isfound. Common plants are damaged by soil with too low or too high pH. Accordingly, we must prepare methods of neutralization for both too acidic and too alkaline regolith. The application of calcareous algae rich in $CaCO_3$, or fine regolith rich in olivine, is effective for increasing the pH of acid regolith. For alkaline regolith, the application of peat moss with low pH may solve the problem.

Improvement of physical properties: From a soil chemist's standpoint, the sediment offine textured regolith is considered to be favorable for agriculture, because its cation exchange capability (CEC), mineral nutrient content, and ability to retain organic matter are expected to be high. However, from a soil physicist's standpoint, fine textured sediment is problematic because of poor aeration and poor drainage, which result in O_2-deficiency for plant roots and microorganisms living in the sediment, and the difficulty in desalinizationby leaching, respectively. When water is added to the sediment of fine textured regolith, a largeportion of the pores in the sediment are liable to be completely filled with water by capillary force (capillary water) working against gravity. Accordingly, loamy textured soils have been considered to be desirable for common upland crops in terrestrial agriculture. This suggests that a sandy loam or loamy sand texture of Martian regolith is desirable for Martian agriculture under low gravity. However, the aeration and drainage of soil is controlled not only by texture but also by a mode of aggregation of soil particles. For instance, drainage of terrestrial soils with sandy loam or loamy sand texture is often poor.

Nutrients: Most of the plant nutrients, except N and P, are expected to be available onMars, because they may take forms accessible to plant roots after they are released fromminerals by weathering. N is not a component of any minerals and accordingly is utterlyabsent in the regolith. Application of some N fertilizer (NH_3, NO_3^-, urea, excreta of animals)or cultivation of some green manure crop plants capable of N-fixation is inevitable. However,the N-fixation is not active if the amount of available P is far short of the demand of the greenmanure crop plants.

P is actually contained in the minerals of the Martian regolith, and may be released byweathering in a similar way as other nutrients. However, the released P is considered to beunavailable for plant roots, due to its strong adsorption (P-fixation) on $CaSO_4$, $CaCO_3$ andiron oxides. Thus, P fertilizers should be applied by three appropriate measures to avoid thisP-fixation. The first is to apply P fertilizers mixed with peat moss **(Kawakami et al., 2007)**.

The second is the removal of $CaSO_4$ by leaching if the main P-adsorbent is this substance.

The third is the adjustment of pH at about neutral where P-adsorption with both $CaCO_3$ andiron oxides is most suppressed if these two substances are dominant P-adsorbents.

Organic matter: Organic matter contributes to many important functions of the soil, two of which may be essential in forming desirable Martian soil. One function is to form and maintain aggregates of suitable sizes in the fine regolith. The other is to store nutrients (bioelements), especially N. The nutrients stored in organic matter are released when the organic matter is microbiologically decomposed. Therefore, accumulation of organic matter containing N in the regolith is imperative to establish space agriculture. This can be achieved by applying compost and excreta of animals.

Microorganisms: Microorganisms inhabiting the soil are responsible for the most of the functions of the soil, such as decomposition of various organic waste, release of nutrients stored in the organic matter, nitrification, denitrification and N-fixation. To endow the regolith with these functions, the Martian regolith should be inoculated with desired microorganisms. For this purpose, it is promising to use peat moss, which contains the desired microorganisms. The processes going on during the first stage of agriculture on mars are summarized in **Figure 2-12**.

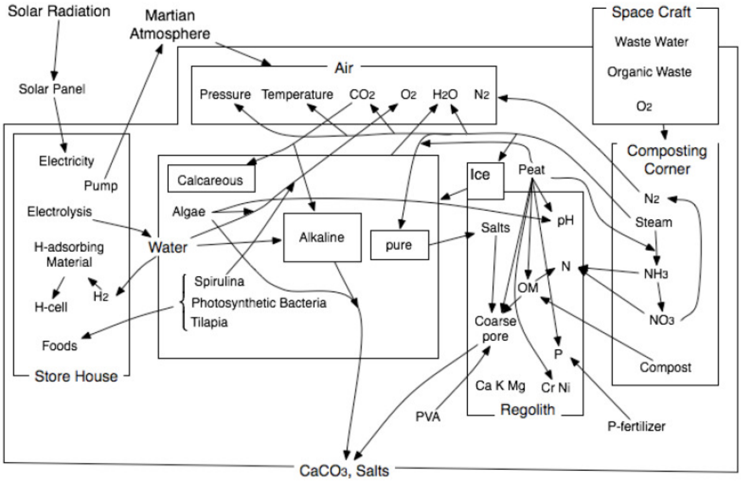


FIGURE 2- 12: Agricolture on mars

When the goal of the first stage is almost attained, the second stage of space agriculture should be started. The main objectives in the second stage are to establish a sustainable agriculture that can continuously supply to the emigrants clean air and water, as well as foods, fiber and timber, mainly by recycling substances. Then, most of the tasks in the first stage should continue to work tokeep the conditions inside the domes favorable for recycling substances, as reported by **(Katayama et al. 2007)** and depicted in **Figure 2-13**.

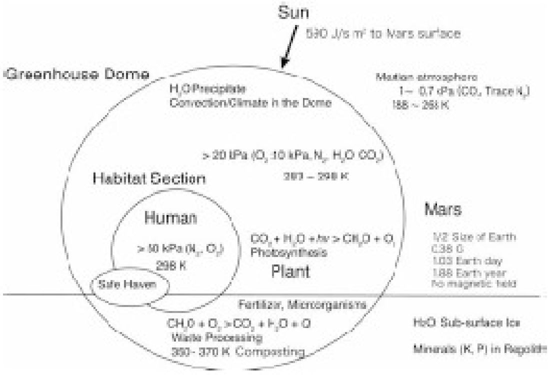


FIGURE 2- 13: Scheme of pressurized martian greenhouse for space agricolture (kanazawa et al., 2008)

Cereals and potato are promising candidates for the carbohydrate source in spaceagriculture. Among various cereals, rice is most favorable, because the yield of rice is higher than that of other cereals. In addition, potato is expected to be cultivable on Martian soil, because thecultivation of potato originated in Inca, on cold infertile soils in the high plateaus of theAndean Mountains. Finally, sweet potato is another promising high-yielding crop plant, which can grow in infertile soil. Unfortunately, sweet potato has low cold resistance and storability.However, its cold resistance could be increased by breeding or genetic engineering, and it can be changed into storable foods by several simple processing methods.

2.4.8 Materials production on Mars

Moore et al. (2005) reviewed the applications of SHS to fabricate and repair a wide range of materials and components as structural components, sterilization technologies of Mars Materials, production of ceramics for acoustic damping of Rocket Engines and space joining.

SHS reactions are commonly recognized as highly exothermic interactions between particulate materials characterized by their ability of self-sustain themselves in the form of a reaction (combustion) wave upon ignition **(Varma et al., 1998, Cincotti et al., 2003)**. The temperature of the combustion wave can be very high (as high as 2500 ^{0}C) and the rate of wave propagation can be relatively rapid (as high as 25 cm s^{-1}). This type of reactions provide an attractive, energy-efficient approach to the synthesis of simple and complex materials including solid solution, composite materials and metastable phases.

Reactions between particulate materials in a self-propagating mode present an attractive alternative to conventional methods of materials preparation for a variety of reasons:

a) the simplicity of the process and its relatively low energy requirement

b) the high purity of products obtained by this method

c) the possibility of obtaining complex or metastable phases

d) the possibility of simultaneous formation and densification of the desired materials

e) the possibility of performing the reaction under the desired gas atmosphere or under vacuum

f) the possibility of limiting/avoiding the gas expulsion from the reacting system

As for this latter aspect, it should be noted that gases that may undergo expulsion from the reacting system may be related to the gasification of specific reactant impurities and/or to gases entrapped in the reacting mixture during its preparation. The presence of such gases can be limited/avoided by following specific preparation procedures of the reactants which might require fully vacuum operation.For these reasons the application of SHS reactions in Space exploration contest has been analized also recently for its simplicity **(Sytschev et al., 2009)**.

Moore et al. (2005) have proposed several SHS systems useful to fabricate and repair components in the space environment and to utilize the planetary mineral resources for fabrication and repair of components.The advantage of SHS for both ISFR and ISRU is that can be used to synthesize, repair and join a wide range of advanced materials, fully dense or with controlled porosity, in low vacuum and low and microgravity environments.

2.4.8.1 PRODUCTION OF GLASS-CERAMIC MATERIALS

Composites with a glass matrix were first produced using the SHS technique. For example a composite with a CaO-Al_2O_3-SiO_2-BaO matrix can be produced by the following SHS reaction

$$\mathrm{Ti+B_2O_3+Al+}\alpha\mathrm{CaO+}\beta\mathrm{SiO_2}+\gamma\mathrm{BaO}\rightarrow\mathrm{TiB_2+(\alpha CaO\times Al_2O_3\times\beta SiO_2\times\gamma BaO)_{matrix}}$$

The composition of the products is determined by the reaction stoichiometry coefficients α, β, γ. A typical combustion temperature for this reaction was around 2000°C, and the matrix is fully molten during the reaction.

2.4.8.2 STERILIZATION OF MARS MATERIALS

In the field of space exloration, one of the biggest risk is represented by the contamination of terrestrial species by extraterrestrial ones. In order to avoid it, a specific sterilization system has been proposed. Specifically one pound of Mars minerals should be kept inside an aluminium canister to be heated to 500°C for at least 0.5 to 10 seconds. A modified version of the previous SHS reaction permitted the fulfilment of the NASA requirement above.

2.4.8.3 POROUS CERAMICS FOR ACOUSTIC DAMPING FOR ROCKET ENGINES

The goal of this investigation is to use SHS technology to manufacture ceramic-based acoustic liners capable of withstanding temperatures up to 2000°C. Two SHS reaction systems have been used for this application:

- the foamed ceramic of Al_2O3-B_4C produced by the following SHS system

$$2B_2O_3 + 4Al + C \rightarrow B_4C + 2Al_2O_3$$

- the SHS reaction system based on the reaction below

$$3TiO_2 + 3B_2O_3 + 10Al \rightarrow 3TiB_2 + 5Al_2O_3$$

These two SHS systems were engineered to produce the required acoustic damping materials of 21% B_4C-79% Al_2O_3 with a range of porosities from 66-76% from reaction system. The transmission loss varied from 29 dB to 50 dB, representing a significant reduction in the noise levels.

2.4.8.4 WELDING AND JOINING

A promising system for the SHS joint system is based on NiAl components, according to the following equation:

$$Ni + Al + xAl_2O_3 \rightarrow NiAl - xAl_2O_3$$

The welding has shown a typical microstructure across the NiAl-Joint ($NiAlxAl_2O_3$)-NiAl interface. Welding and joining for Space applications involving SHS techniques both in low gravity environments and in terrestrial ones have been deeply analyzed in the literature.

2.4.8.5 DRUG DELIVERY SYSTEMS FOR ASTRONAUTS

Astronauts engaged in long-term space exploration missions will need some substantial medical support for the bone loss phenomena that occur in microgravity. In addition, the concept of delivering medicines through the blood system orally has been proven to be a problem in microgravity conditions.

The required drugs/medicines would be infiltrated into the porous scaffold that may implanted into a convenient muscle and released in a controlled manner into the astronaut's blood system. One of these system that has been evaluted for this purpose is the following one:

$$3CaO+P2O5 \rightarrow Ca_3(PO_4)_2$$

This porous calcium phosphate-based drug delivery system has been synthesized with a specific pore size that ranges between 200-500 µm and is comparable to that in human bones.Along these lines an important aspect to be taken into account in this sector is the role played by the gravity in self-propagating high-temperature synthesis reactions as reported –among the others- by **Locci et al. (2006)**. In fact, combustion synthesis and related structure formation mechanisms involve several stages including melting of reactants and products, spreading of the melt, droplets coalescence, diffusion and convection, buoyancy of solid particles, and solidification of liquid products, most of which are affected by gravity.

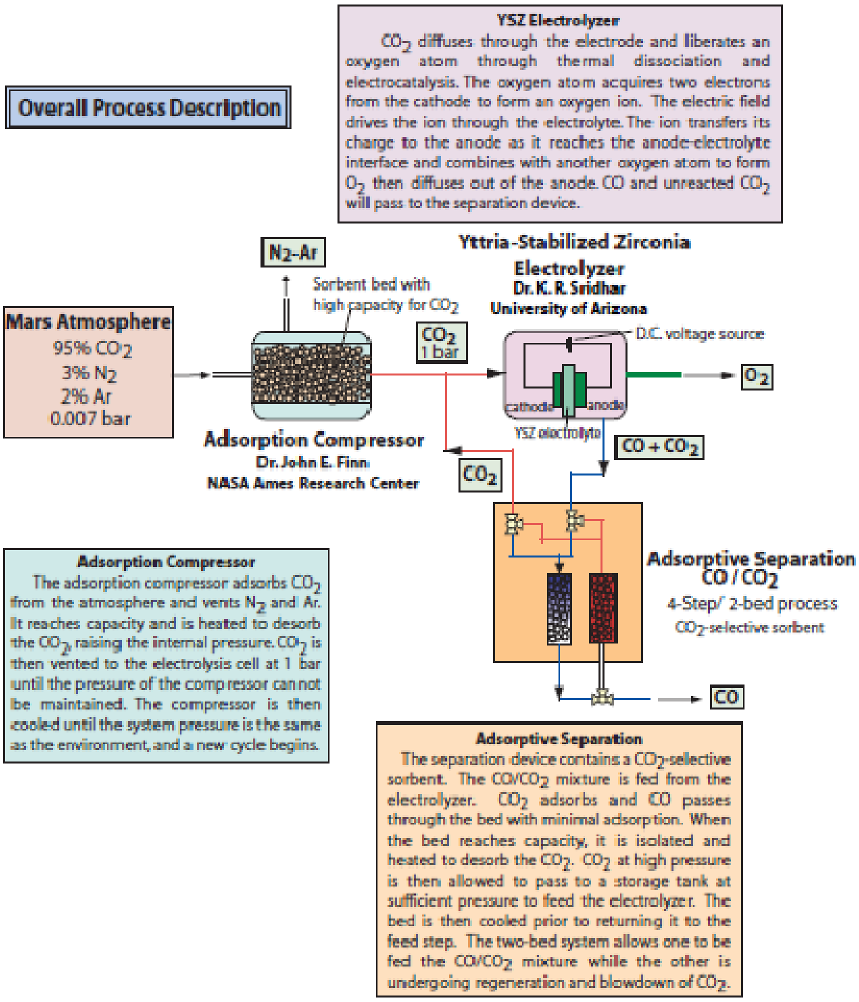
It is found that natural convection within the gas phase has a negligible effect in comparison to radiation on heat loss from the external surface of the reacting pellet to the surroundings. This finding, in addition to the fact that the rate of heat released by chemical reaction is found to be insensitive to g-level, indicates that gravity is not expected to substantially affect combustion temperature, which is in agreement with experimentalevidence.

Viceversa, it is seen that even small sample porosity variations due to pellet expansion are expected to play an important role by influencing heat transfer (that is, apparent thermal conductivity) inside the reaction zone. This aspect justifies the relatively slower combustion front and earlier quenching extinction when reaction is performed under reduced gravity conditions. Moreover, free convection taking place in the molten phase during combustion synthesis process is expected to represent a reasonable justification of the general experimental evidence that under terrestrial conditions combustion front velocity is relatively higher for the case of ignition from the bottom, with respect to the case of ignition from the top.

In addition, coalescence of product solid particles may be considered responsible for the relatively coarser microstructure typically observed under terrestrial conditions, as compared to that obtained under low-gravity, while microsegregation is likely to contribute to homogeneity.

More recently also methods for the steel production by harvesting materials onMars have been proposed. **Stoker et al., (2003)** proposed refining metallic iron out of Martian iron oxides, first by concentrating the iron oxides with anacid leeching, followed by hydrogen reduction.

More recently **Landis (2009)** have proposed other processes based on the fact that on Mars the carbon dioxide atmosphere and absence of liquid water allows nickel–iron meteorites to avoid oxidization,and their on remains in reduced form for long periods, potentially for millions of years. One of the most feasible process, for the low temperaturtes involves, is the Carbonil process. According to this process it is possibile to use carbon monoxide. This gas could be easily manufactured from the Martian atmosphere for instance using the process proposed by **Walton et al. (2004), Sridhar et al. (2005), Mulloth et al. (1998)**.



YSZ Electrolyzer

CO_2 diffuses through the electrode and liberates an oxygen atom through thermal dissociation and electrocatalysis. The oxygen atom acquires two electrons from the cathode to form an oxygen ion. The electric field drives the ion through the electrolyte. The ion transfers its charge to the anode as it reaches the anode-electrolyte interface and combines with another oxygen atom to form O_2 then diffuses out of the anode. CO and unreacted CO_2 will pass to the separation device.

Adsorption Compressor

The adsorption compressor adsorbs CO_2 from the atmosphere and vents N_2 and Ar. It reaches capacity and is heated to desorb the CO_2, raising the internal pressure. CO_2 is then vented to the electrolysis cell at 1 bar until the pressure of the compressor can not be maintained. The compressor is then cooled until the system pressure is the same as the environment, and a new cycle begins.

Adsorptive Separation

The separation device contains a CO_2-selective sorbent. The CO/CO_2 mixture is fed from the electrolyzer. CO_2 adsorbs and CO passes through the bed with minimal adsorption. When the bed reaches capacity, it is isolated and heated to desorb the CO_2. CO_2 at high pressure is then allowed to pass to a storage tank at sufficient pressure to feed the electrolyzer. The bed is then cooled prior to returning it to the feed step. The two-bed system allows one to be fed the CO/CO_2 mixture while the other is undergoing regeneration and blowdown of CO_2.

FIGURE 2- 14: OVERALL PROCESS DESCRIPTION

According to the proposed process an adsorption compressor adsorbs CO_2 from the atmosphere and compresses it to a pressure of 1 bar. The CO_2 is then passed to a solid oxide electrolysis cell . This electrolysis cell makes use of yttria-stabilized zirconia to produce oxygen from the compressed planetary CO_2 and will then reject CO and unreacted CO_2 in a separate stream. Carbon monoxide can be used to transport the metals in the form of volatile iron-and nickel-carbonyl. Nickel carbonyl is gaseous at temperatures above 40 ◦C; iron carbonyl gaseous above103◦C. Distillation can then separate the iron and nickel, allowing the composition to be modified as desired.This is a process used in mining. The reactions are

$$Ni + 4CO \rightarrow Ni(CO)_4$$

$$Fe + 5CO \rightarrow Fe(CO)_5$$

If desired,objects can be directly manufactured by chemical vapor deposition, a process in which the metal is deposited directly on the object being manufactured.

2.4.9 Integrated life support system on Mars

All the results acquired in the MELISSA project (and already discussed in previuos chapters) have been transposed and integrated in the design of useful technologies to allow outposts for future martian missions. Frequently, indeed, plants proposed are designed as an integration of agriculture systems, pressurized environment systems, and propellant production. More recently it has been proposed and patented a process for the production of fertilizers, water, oxygen, and vegetable food from Martian atmosphere and soil in cooperation with the already discussed ECLSS techniques **(Cao et al., 2010).**This process takes advantage of two parts, the biological section and the chemico-physical one, both of them powered by solar panels.The chemico-physical section consists mainly of microwave systems, adsorber units and appropriate kind of chemical reactors.

In the microwave systems water from the soil bulk is extracted in form of vapour. The condensed vapour is then sent to an electrolizer to produce hydrogen and oxygen.

Adsorber units are used to pressurize and separate the carbon dioxide from the Martain atmosphere. Carbon dioxide is sent to an electrolizer to produce CO and CO_2, that can be used as a propellants, and Ar and N_2 (also present in the Martian atmosphere) are used to produce gaseous ammonia. The latter one is then sent with the oxygen inside of a suitable reactor where appropriate pressure and temperature conditions are set to promote the reaction between these two gases. During these process, known as Ostwald process the HNO_3 is produced. Finally the latter one is made reacted with HNO_3 to produce NH_4NO_3 that is generally used as a fertilizer.

In the biological section a suitable algae strain –transported from the Earth- grows in an appropriate acqueous medium.

The latter one takes advantage of the water extracted from soil (as in the biological section) and of the NH_4NO_3 produced in the chemico-physical section. In addition the micro and micro nutrients are extracted from soil by means of an appropriate leaching solutions and the HNO_3 produced in the chemico-physical section is also fed to this solution. Finally the CO_2 purified by adsorber units is fed by appropriate pumps to this medium, giving the algae a suitable carbon source and promoting the mixing of all of these elements. The solar radiation is used both to accomplish the photosynthetic activity and to maintain the medium at a suitable temperature to avoids limitating effects.

The oxygen produced during the photosynthetic activity, sepated by a degaser, is stored end used as replenishment elements for ECLSS systems. Finally the metabolic wastes, algae biomass extracted from the reactor, appropriate organic acids transported from the Earth and fertilizers are fed to the cultivation area to promote vegetable food production.

3 Self-propagating High-temperature Reactions for the Fabrication of Lunar and Martian Physical Assets

The development of a new process potentially useful for future manned Lunar and/or Martian space missions in the framework of the so-called ISRU (In-Situ Resource Utilization) and ISFR (In-Situ Fabrication and Repair) concepts is described and discussed in this work. This process involves the fabrication of physical assets by Self-propagating High temperature Synthesis (SHS) for construction applications in Lunar and Martian environments starting from different Lunar or Martian regolith simulants and aluminum, as reducing agent. In addition, although Moon and Mars already contain ilmenite ($FeTiO_3$) and iron oxides, respectively, the latter ones are also added to the initial mixtures to promote suitable SHS reactions. A complete scheme for the fabrication of physical assets to be used as protection against solar rays, solar wind and meteoroids, where all required stages are indicated, is finally proposed in the framework of a recently filed patent.

3.1 Introduction

According to very recent news from the USA administration, future human space exploration scenarios are consistent with the following perspectives: utilization of ISS (International Space Station) until 2020 and beyond, assembly of post ISS infrastructures, long-cruise stages to get to other destinations, human activities on near a planetary body surface (Moon, near Earth asteroids, Mars and its moons).

Specifically, NASA has anticipated that the establishment of a space base will necessitate the development of innovative technologies in the framework of the ISFR (In-Situ Fabrication and Repair) and ISRU (In-Situ Resources Utilization) paradigms **(Bassler et al., 2006, Hammond et al., 2006, Howell et al., 2008, Sanders et al., 2010, Moore et al., 2010)**. In particular, the utilization of in-situ resources will result in a strong reduction of transport costs and a significant increase of the efficiency of the corresponding operations. Due to their differences from the Earth, several challenges will be encountered in the Moon, near Earth asteroids, Mars and its moons environment. For example, it will be necessary to create specific protection against cosmic rays, solar wind and meteoroids which impact the planetary body surface in a far greater quantities than experienced in Earth. Along these lines, the development of processes with the final goal to obtain suitable protection structures has been recently addressed in several studies **(Allen et al., 1994, Toutanji et al., 2005, Tucker et al., 2006, Martirosyan et al., 2006, Faierson et al., 2010a).**

In particular, **Allen et al. (1994)** have investigated sintering of regolith Lunar simulant using radiant and microwave heating at temperature of 1100°C. The use of Lunar regolith for obtaining a thermo-plastic material **(Toutanji et al., 2005)** and fiberglass for reinforcing Lunar concrete have been also proposed **(Tucker et al., 2006)**. More recently, it wasshown that a reaction between a Lunar regolith simulant and aluminum powder exhibits a thermite type behavior **(Faierson et al., 2010a)**. In the latter investigation, a mixture of 67 wt % regolith simulant and 33 wt% Al was reacted under standard Earth atmosphere to producea ceramic composite material where the major chemical species identified were Si, Al_2O_3, $CaAl_4O_7$ and $MgAl_2O_4$.

In this context, self-propagating high temperature synthesis (SHS) reactions, that are characterized by the fact that, once ignited by an external source, are able to self-sustain in the form of a combustion wave through the reacting mixture without requiring additional energy **(Munir et al., 1989)**, could provide a useful contribution. The SHS method has received worldwide attention for its simplicity, short reaction time, easy to build equipment, low energy requirements, and the possibility of obtaining a variety of advanced materials, such as ceramics, intermetallics, composites, solid solutions, functionally graded materials, and so on **(Munir et al., 1989, Cincotti et al., 2003)**. The SHS method was also utilized by **Martirosyan and Luss**

(2006)for the preparation of ceramic composites to be potentially used for "Lunar bricks" starting from a mixture consisting of Lunar soil simulant (JSC-1), titanium and boron according to the exothermic chemical reaction $x(Ti + 2B) + (1-x)JSC\text{-}1 \rightarrow x(TiB_2) + (1-x)JSC\text{-}1$. Specifically, it was found that the condition to be verified for making the process self-sustaining is $x>0.25$.

Along these lines, it should be noted that several thermite reactions, where a metallic or non metallic oxide are exothermically reduced by a metal to form more stable products **(Wang et al., 1993)**, display a SHS character. For instance, the aluminothermic reduction of hematite (Fe_2O_3), i.e. $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$, is the most representative self-propagating thermite reaction due to its extremely high exothermic character, i.e. $(-\Delta H_r^o)$ = 851.444 kJ/mol of Al_2O_3 **(Barin et al., 1989)**. The latter one could be then exploited in the framework of the ISRU principle, taking advantage of the presence of significant amounts of iron oxides in Martian regolith. Analogous considerations can be made regarding the presence up to 20 wt.% of ilmenite ($FeTiO_3$) on Moon soil **(Schrunk et al., 2008)**. In this case, it should be noted for instance that the reduction of $FeTiO_3$ by SHS was recently addressed in the literature according to the following reactions: $FeTiO_3 + 3Mg \rightarrow 3MgO + TiFe$ **(Wu et al., 2006)** and $FeTiO_3 + 7Al + 3C \rightarrow 3Al_2O_3 + TiC + Fe_3Al$ **(Zou et al., 2007)**.

In the present work, a process consisting of first blending Lunar or Martian regolith simulants with suitable amounts of additive ($FeTiO_3$ or Fe_2O_3, respectively) to simulate the enrichment of the corresponding soils in these species, and Al, as reducing agent, is proposed. In particular, the relative amounts of each component required to guarantee, upon ignition, the self–propagating conditions in the resulting mixtures and obtaining products to be used as construction material in Lunar or Martian environment, will be identified. Regarding the experimental conditions to be adopted during SHS experiments, it is important to note that low pressure atmospheres and microgravity environment are encountered, although at different levels, either on

Moon or Mars. A complete scheme for the fabrication of physical assets to create protection against solar rays, solar wind and meteoroids, where the SHS reactions above represent the core of the entire process, is finally proposed in this work.

3.2 Experimental section

The chemical composition, as provided by the corresponding vendors or recent literature **(Peters et al., 2008)**, of JSC Lunar regolith, JSC Martian regolith, and Mojave Martian regolith simulants used in the present investigation, heretoafter also indicated as R_L, R_M, and R_{Moj}, respectively, are reported in **Table 3-1**in terms of oxides wt%.

TABLE 3-1: Chemical composition (oxide wt%) of JSC-1A Lunar Mare, JSC Mars-1A Martian and Mojave Martian Regolith simulants.

Major element composition[a]	**R_L**	**R_M**	**R_{Moj}**
Silicon Dioxide (SiO_2)	46 - 49	34.5 - 44	49.4
Titanium Dioxide (TiO_2)	1 - 2	3 - 4	1.09
Aluminum Oxide (Al_2O_3)	14.5 - 15.5	18.5 - 23.5	17.10
Ferric Oxide (Fe_2O_3)	3 - 4	9 - 12	10.87
Iron Oxide (FeO)	7 - 7.5	2.5 - 3.5	-
Magnesium Oxide (MgO)	8.5 - 9.5	2.5 - 3.5	6.08
Calcium Oxide (CaO)	10 - 11	5 - 6	10.45
Sodium Oxide (Na_2O)	2.5 - 3	2 - 2.5	3.28
Potassium Oxide (K_2O)	0.75 - 0.85	0.5 - 0.6	0.48
Manganese Oxide (MnO)	0.15 - 0.20	0.2 - 0.3	0.17
Chromium III Oxide (Cr_2O_3)	0.02 - 0.06	-	0.05
Diphosphorus Pentoxide (P_2O_5)	0.6 - 0.7	0.7 - 0.9	0.17
Sulfur Trioxide (SO_3)	-	-	0.10
Loss on ignition LOI	-	-	(3.39)

aThe normal convention for data presentation uses oxide formulae from an assumed oxidation state for each element (with the exception of Fe) and oxygen is calculated by stoichiometry.

It is important to notice that these are representations of the corresponding chemical compositions while actual phases or minerals in the simulants are reported in **Tables 3-2, 3-3** and**3-4**, respectively. It is seen that, plagioclase, Ca-rich pyroxene, olivine and ilmenite minerals are, along with other minor phases, the main constituents of JSC simulant **(Sibille et al., 2005)**. Analogously, JSC and Mojave Martian regoliths consist primarily of plagioclase feldspar, pyroxene, iron oxides (magnetite, hematite), ilmenite and olivine **(Peters et al., 2008, Sibille et al., 2005, Allen et al., 2006).**

TABLE 3-2: Main mineral species identified in JSC lunar mare simulant **(Sibille et al., 2005)**[b]

Mineral group	Chemical species and related formulae
Ilmenite	($FeTiO_3$)
Plagioclase	Anorthite ($CaAl_2Si_2O_8$)
	Albite ($NaAlSi_3O_8$)
	Orthoclase ($KAlSi_3O_8$)
Olivine	Fosterite (Mg_2SiO_4)
Ca-Piroxene	Wollastonite ($CaSiO_3$)

[b]Chromite ($FeCr_2O_4$), cristobalite (SiO_2), magnetite (Fe_3O_4) and hematite (Fe_2O_3) are also likely present as minor phases

TABLE 3-3: Main mineral species identified in JSC martian simulant **(Allen et al., 2006)**

Mineral group	Chemical species and related formulae
Fe(Ti)-oxides	Ti-magnetite ($Fe(Fe,Ti)_2O_4$)
Plagioclase feldspar	Anorthite ($CaAl_2Si_2O_8$)
Olivine	Fayalite (Fe_2SiO_4)
	Fosterite (Mg_2SiO_4)
Ca-Piroxene	Enstanite ($MgSiO_3$-$(Mg,Fe)SiO_3$)
	Wollastonite ($CaSiO_3$)
	Ferrosilite ($FeSiO_3$)

TABLE 3-4: Main mineral species identified in Mojave martian simulant **(Peters et al., 2008)**[c]

Mineral group	Chemical species and related formulae
Fe-oxides	Magnetite ($FeO{\cdot}Fe_2O_3$)
	Hematite (Fe_2O_3)
Ilmenite	($FeTiO_3$)
Plagioclase feldspar	Anorthite ($CaAl_2Si_2O_8$)
Fe-Olivine	(Fe_2SiO_4)
Ca-Piroxene	($Ca\ (Cr,Al,Fe)(Si,Al)_2O_6$)

[c] Manganite ($MnO(OH)$), barite ($BaSO_4$), and apatite ($Ca_5(PO_4)_3[F, OH, Cl]$) are also likely present as minor phases

All regolith simulants were preliminarily sieved and the resulting – 45μm fractions were used for the experiments. Moreover, to remove water from moisture and hydrated minerals, both Martian regolith simulants were also desiccated at 700 °C for 2 h. The latter experimental conditions were chosen after performing thermogravimetric analysis (TGA) of both materials from room temperature to 900 °C using a NETZSCH STA 409PCSimultaneous DTA-TGA Instrument. The obtained results will be shown in the "Results and discussion" section.

The mixtures to be reacted by SHS have been prepared by adding and blending Al, ilmenite or hematite (Fe_2O_3) to regolith simulants. A summary of the mixtures taken into account in the present investigation are reported in **Table 3-5.** Specifically, the Al/$FeTiO_3$ molar ratio is maintained equal to 2 or 3 in systems S1_R_L# and S2_R_L#, respectively, while the amount of Lunar regolith in the mixture is gradually increased. On the other hand, the two mixtures indicated as S3_R_M#_R_{Moj}# in **Table3-5** contain Martian regolith simulant. Specifically, while the content of Al, Fe_2O_3 and the total amount of regolith (45.2 wt.%) is maintained the same in both mixtures, R_{Moj} is the only simulant used in the first case while it is combined with R_M in the second one.

TABLE 3-5: Summary of the mixtures investigated.

Mixture ID	$FeTiO_3$ (wt %)	Fe_2O_3 (wt %)	Al (wt%)	R_L (wt %)	R_M (wt %)	R_{Moj} (wt %)	Self-propagation
S1_R_L0	73.77	-	26.23	-	-	-	Yes
S1_R_L10	66.39	-	23.61	10	-	-	Yes
S1_R_L20	59.02	-	20.98	20	-	-	Yes
S1_R_L25	55.32	-	19.68	25	-	-	No
S2_R_L0	65.21	-	34.79	-	-	-	Yes
S2_R_L10	58.69	-	31.31	10	-	-	Yes
S2_R_L20	52.17	-	27.83	20	-	-	Yes
S2_R_L30	45.65	-	24.35	30	-	-	Yes
S2_R_L35	42.39	-	22.61	35	-	-	No
S3_R_M0_R_{Moj}45	-	38.81	15.99	-	-	45.2	Yes
S3_R_M13_R_{Moj}32	-	38.81	15.99	-	13.6	31.6	Yes

After blending, each mixture was compacted using an uniaxial press to provide a series of cylindrical pellets (11 mm diameter and 25 mm height) to be reacted. A schematic representation of a single SHS reactor and the corresponding ancillary devices is reported in **Figure 3-1**.

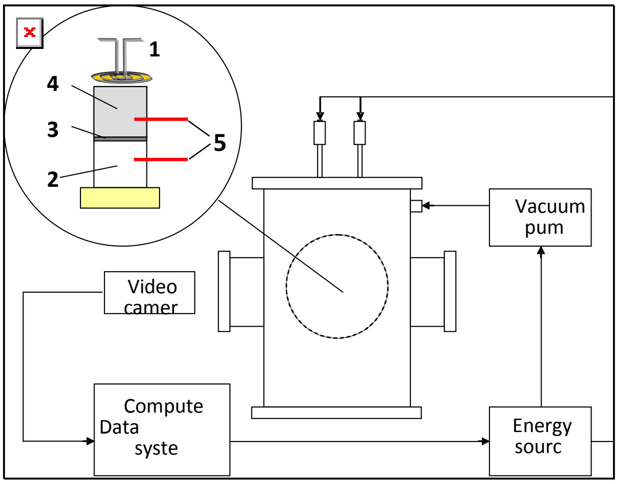


FIGURE 3-1: Schematic representation of the experiment set-up used for SHS experiments: (1) ignition source, (2) starting mixture, (3) reaction front, (4) final products, (5) thermocouples.

The experimental set up used in the present investigation consisted of a battery of reaction chambers, a power supply (Legrand safety isolating transformer, mod. 642310, primary 230-400V, secondary 12-24V, power 1000 VA) which provides the energy required for reaction ignition, a video camera (Imaging Source CMOS color camera, model DFK 21AUC03, using Pentax lenses, model B1218A) and a computer system connected to a data acquisition board (cDAQ-9174 equipped with NI 9481 high voltage relay module, NI 9213-16ch-24bit thermocouple module and NI 9239-4ch-24bit analog input module, National Instruments) and supported by a software package (LabVIEW, National Instruments). The temperature during reaction evolution was measured using two thermocouples (W-Re, 0.13 mm diameter, Omega Engineering Inc.), 8-10 mm distant each other, embedded in the pellet as indicated in Figure 1. The reaction chambers were evacuated to about 20 mbar. The combustion front was generated at one sample end by using of a heated tungsten coil (R.D. Mathis Company, USA), which was immediately turned off as soon as the reaction was initiated. Then, the reaction self-propagates until reaches the opposite end of the sample.

The obtained SHSed products were characterized in terms of chemical composition and microstructure by X-ray diffraction (XRD) analysis (Philips PW 1830 diffractometer using CuKα Ni-filtered radiation). Compressive strength tests on SHSed samples were carried out using a METRO COM (mod. 100 MI) press equipped with a 10 kN load cell (METIOR CVS).

3.3 Results and discussion

Preliminary tests conducted using as received Martian regoliths evidenced that, due to the excessive presence of water inside the original hygroscopic materials, particularly in the R_M type, a significant gas expulsion occurred during SHS which lead to the incomplete reaction and/or pellet disintegration. In addition, it was recently observed that the strong hygroscopic tendency of JSC Martian regolith make results reproducibility difficult**(Peters et al., 2008)**. To overcome such problem, moisture and chemically adsorbed water had to be preliminarily removed. The experimental conditions required were identified on the basis of TGA tests results reported in **Figure 3-2**,where the mass change of the regolith samples heated up to 900 °C as described in the "Experimental section" is shown. It is clearly seen that the weight of JSC Mars-1A simulant decreases significantly (~40%) while this phenomenon takes place only at a minor level (~5%) when processing R_{Moj} material. Consequently, 700 °C was the temperature level chosen for pretreating both Martian simulants before using them in the starting mixtures to be reacted by SHS.

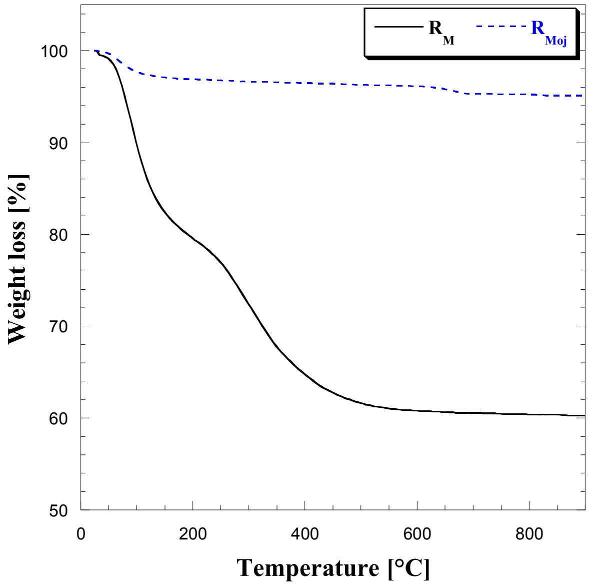


FIGURE 3-2: Weight change of R_M and R_{Moj}samples during TGA up to 900 °C.

Among the mixtures investigated in this work, those ones which displayed a self–propagating character are indicated in **Table 3-5**. Specifically, as far as the Lunar systems are concerned, the SHS reaction goes to completion if the regolith content is below 25 or 35 wt. % in the systems S1_R_L# or S2_R_L#, respectively.

An example of the sequence of the SHS process including thethree main stages involved, i.e. ignition, front propagation, and product cooling, is reported in **Figure 3-3** for the case of the S2_R_L30 system.

It is seen that, once ignited (0.1 s), the reaction self-propagates completely through the entire pellets in about 10 seconds. Thus, the average value of combustion front velocity for this system is about 2.5 mm/s. Subsequently, the sample is allowed to cool down to room temperature.

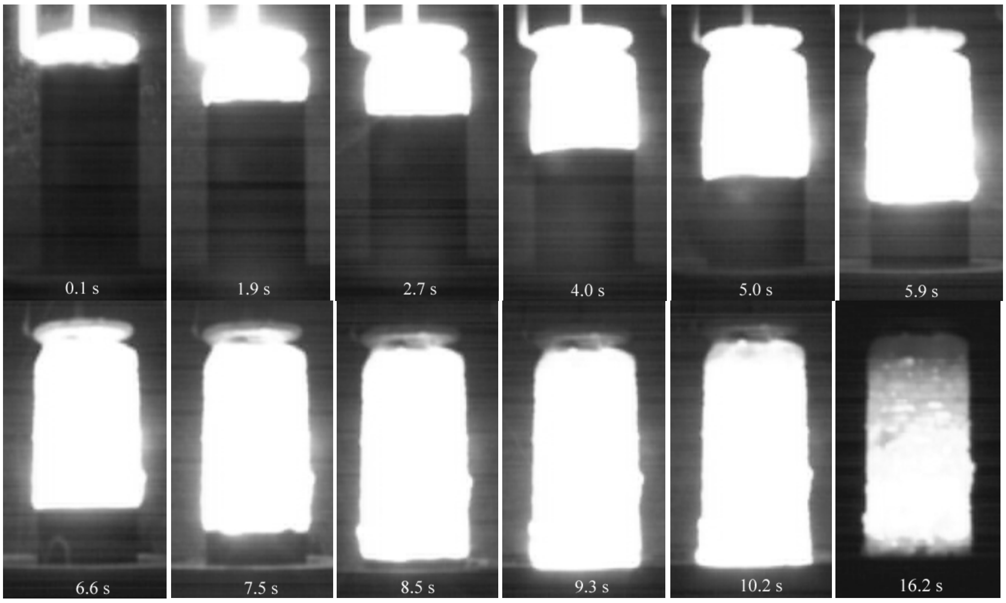


FIGURE 3-3: Video output showing the SHS process evolution for the case of the S2_R$_L$30 system.

Typical temperature profiles recorded during the process by two thermocouples embedded in the reacting sample is reported in **Figure 3-4** for the same system.

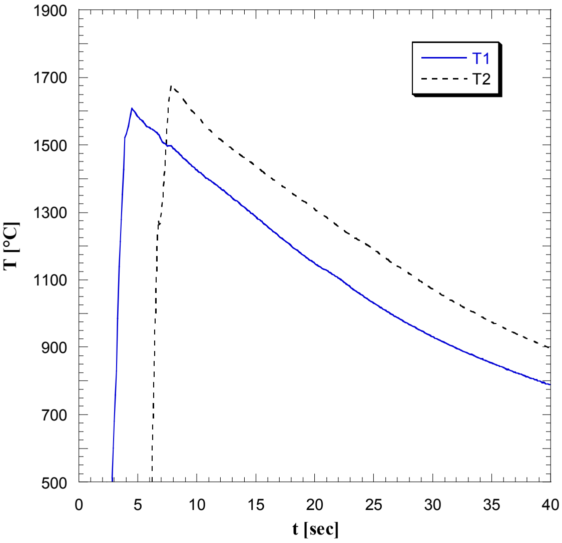


FIGURE 3-4: Temperature profiles recorded during the SHS process for the case of the S2_R$_L$30 system.

FIGURE 3-5: Image of the final sample obtained after the SHS reaction of one of the mixtures (system $S2\_R_L30$) containing lunar regolith simulant.

It is apparent that the temperature suddenly increases when the reacting front approaches to the position where the thermocouples are placed, thus reaching its maximum value in the range 1610-1700 °C. From these profiles was also possible to estimate the average velocity of the propagating front that is, for the $S2\_R_L30$ system, in the range of 2.2-2.5 mm/s, i.e. consistently with the result obtained from video output displayed in **Figure 3-3**. In general, all SHS reactions investigated were observed to propagate completely in less than 25 seconds and maximum temperature values measured during reaction evolution were typically in the 1500-2000 K range.

An example of SHSed product is shown in **Figure 3-5** for the $S2\_R_L30$ system. It is seen that the sample maintained at the end of the process approximately its original cylindrical shape which is an important issue in view of the obtainment of structural component with selected dimensional characteristics.

Let us now examine the composition of the obtained SHSed samples. No traces of initial reactants are detected in final products by XRD analysis. This statement is confirmed by the XRD patterns shown in **Figure 3-6(a)-3-6(b)** relative to systems containing Lunar ($S2\_R_L30$) and Martian ($S3\_R_M13\_R_{Moj}32$) regolith simulants, respectively. For the sake of simplicity, peaks reflection corresponding to the crystalline phases present in Lunar and Martian soil simulants are indicated in cumulative manner and labeled as R_L, R_M and R_{Moj}, respectively, in **Figure 3-6(a)-3-6(b)**. It is seen that Al_2O_3 and Fe are the crystalline phases formed in both situations as a consequence of the aluminothermic reaction. Magnesium spinel, calcium aluminates, namely grossite ($CaAl_4O_7$) and hibonite ($CaAl_{12}O_{19}$), and titanium are additionally found by XRD when processing Lunar systems. Other minor or non-crystalline products are also possibly present.

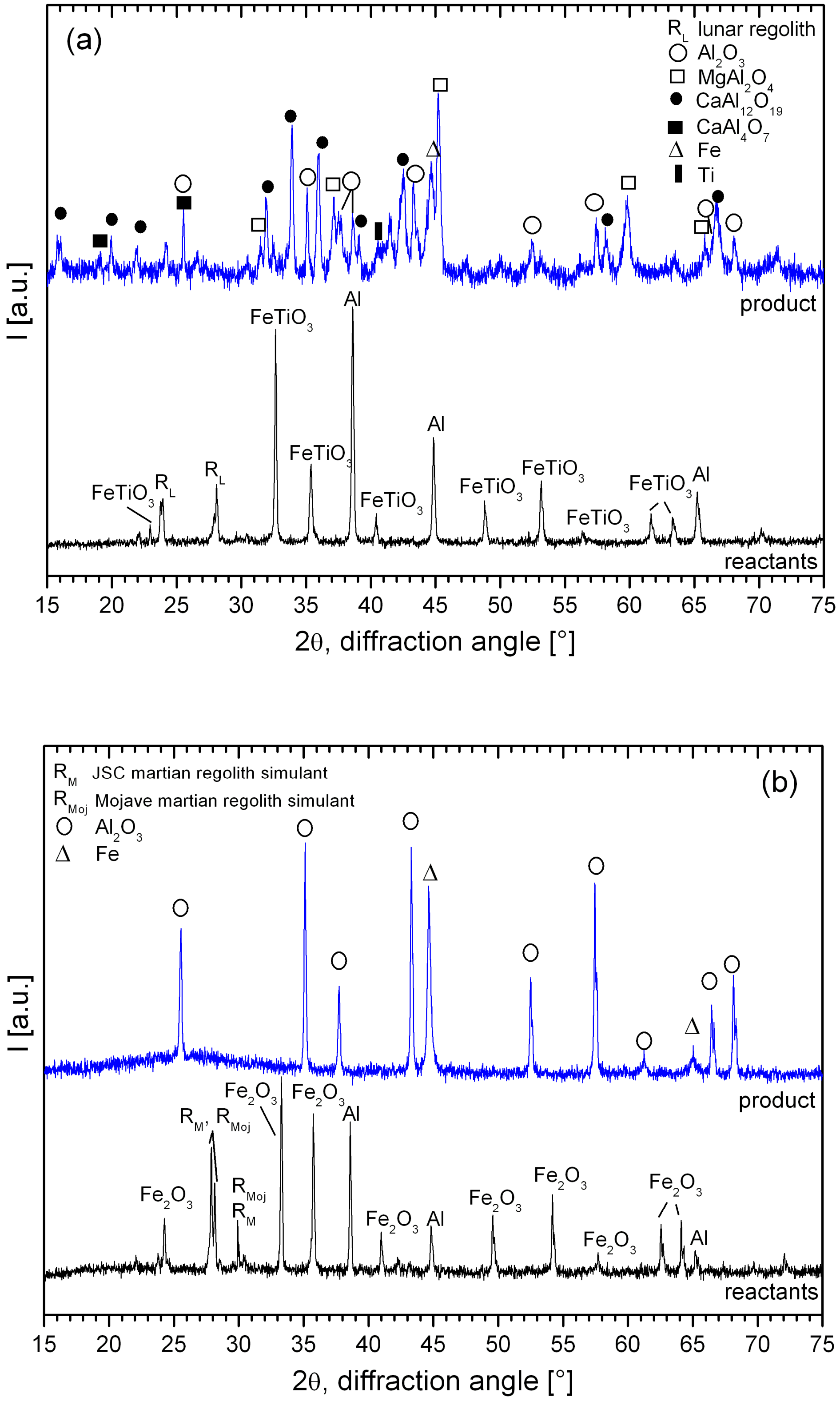


FIGURE 3-6: XRD spectra of original reactants and corresponding products obtained after the SHS reaction of mixtures containing (a) Lunar (system S2_R_L30) and (b) Martian (S3_R_M13_R_{Moj}32) regolith simulants.

The majority of the obtained crystalline phases corresponds to those recently found by **Faierson et al. (2010 a)**in the product resulting from the geothermite reaction of Lunar regolith simulant with 33 wt%Al. It should be noted that no ilmenite was added to the regolith in this investigation. Correspondingly, the process was unable to self-propagate upon ignition, while very long heating times, i.e. 7-15 min, were needed to activate the reaction in the starting mixture. Based on the results obtained in the present work, it is clear that, in order to promote the SHS reaction, the starting mixtures containing Lunar or Martian regolith have to be preliminarily enriched with one of their main constituent phases, namely ilmenite or ferric oxide, respectively, before being reacted with Al.To this aim, various enrichment technologies, based on well known principles as electrostatic and magnetic separation, have been developed **(Agosto et al., 1985 and Quinn et al., 2009)**.Along these lines, as far as Lunar regolith is concerned, it should be noted that the foreseen step where the lunar soil is *in-situ* enriched in ilmenite may lead to a significant decreasing of the amount of Al required by the process, i.e. about 21 wt.% for the S1_R_L25 system, as compared to that (33 wt.%) utilized by **Faierson et al. (2010 a).**

The effect of Al content in the mixture on the corresponding SHS behaviour (cf. **Table 3-5**) is discussed in what follows. It is found that the main phases detected in the end product relative to the base system (S1_R_L0) are Al_2O_3, Fe, and Ti. Other minor phases, i.e. $Al_3Ti_{0.75}Fe_{0.25}$, etc., are also found as secondary products. This behaviour is in agreement with the occurrence of the reaction $FeTiO_3 + 2Al \rightarrow Al_2O_3 + Ti + Fe$. The high exothermicity of the latter one, i.e. ($-\Delta H_r^o$) = 440.157 kJ/mol of Al_2O_3 **(Barin et al., 1989)**, justifies the self-propagating behaviour exhibited by this system (cf. **Table 3-5**). Moreover, as R_L is added to the mixture, relatively low stable oxides, including ilmenite, present in the simulant are also correspondingly reduced, although other minerals behave like diluents, thus gradually decreasing the exothermic character of the reacting system. This feature is consistent to the inability of the reaction to self-propagate if the R_L content is above a certain threshold, i.e. 20 wt.% as far as the S1_R_L# is concerned. It is also seen in **Table 3-5** that when additional Al is used, i.e. S2_R_L# samples as compared to S1_R_L# ones, the limit of R_L content above which the process does not display a self-sustaining behavior is correspondingly increased to 30 wt.%. Consequently, the aluminothermic reduction of a higher amount of the oxides originally present in Lunar regolith correspondingly occurs.

Preliminary results from mechanical characterization of the obtained SHSed samples are quite promising. Indeed, the average compressive strength for S1_R_L20 and S2_R_L30 systems are 27.2 ± 3.6 and 25.8 ± 3.6MPa, respectively. These values are significantly higher as compared to those ones, in the range of 10-18 MPa, reported in the literature for products obtained by the geothermite-based process mentioned previously **(Faierson et al., 2010 a).** These differences could be likely ascribed to the beneficial addition of ilmenite to the original regolith that increases reaction exothermicity, thus improving sintering phenomena in processing powders and, consequently, material strength.

All the results described and discussed above relate to experiments performed under terrestrial (1g) conditions. Nevertheless, products obtained under microgravity (~10^{-2} g) environment during a recent parabolic flight campaign are characterized by very similar compositions. This is an important issue for validating results obtained at 1g for Lunar and Martian applications in the framework of ISRU and ISFR concepts. In this regard, the related complete proposed process recently filed as Italian patent **(Cao et al., 2010)**, is depicted in **Figure 3-7**.

Briefly, it consists first in the electric power production through a combination of photovoltaic (PV) arrays and fuel cells (FC) **(Kerslake et al., 2000, Ignatiev et al., 2004)**. The produced electric power allows then the excavation of Lunar or Martian regolith using suitable tools**(Wilkinson et al., 2007, Caruso et al., 2008)**. Lunar and

Martian regolith are consequently enriched with ilmenite or hematite by means of electrostatic or magnetic techniques, respectively **(Agosto et al., 1985, Quinn et al., 2009)**. The so-enriched minerals are mixed with suitable amounts of Al powder to obtain mixtures which undergo SHS reactions upon ignition. The obtained physical assets can be suitably mounted to obtain the desired structures. Further details are reported elsewhere**(Cao et al., 2010)**.

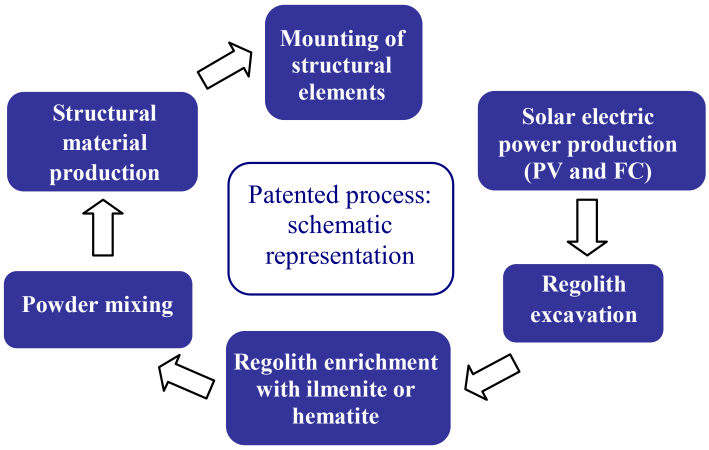


FIGURE 3-7: Schematic representation of the patented process **(Cao et al., 2010)**.

3.4 Conclusions

A new process based on the occurrence of SHS reactions for obtaining composite ceramics to be used as construction materials according to the ISRU and ISFR principles is described and discussed in this work. Specifically, powder mixtures made of Lunar or Martian regolith simulants, aluminum, as reducing agent, ilmenite (Moon) or ferric oxide (Mars), as additives, are reacted by SHS under vacuum conditions. The relative amounts of regolith, aluminum and additive to guarantee, upon ignition, the self–propagating conditions in the resulting mixtures are identified. The obtained products mainly consist of Al_2O_3, Fe and, for the case of Lunar regolith, Ti, Ca- and Mg-aluminates. Compressive strength measurements provided average values of 27.2 ± 3.6 and 25.8 ± 3.6 MPa, for the S1_R_L20 and S2_R_L30 systems, respectively. These values are significantly higher in comparison to those (10-18 MPa) reported in the literature relatively to products obtained from the direct thermite reactions between Lunar regolith simulant and Al. It should be noted that, while in this study $FeTiO_3$ or Fe_2O_3 were added to promote the self-sustaining character in the original mixtures, an enrichment stage of these two species already present in Lunar and Martian regoliths, respectively, is foreseen for a practical utilization of this process. This and other auxiliary technical operations are taken into account in the recently patented process for the fabrication by SHS of physical assets for construction applications in Lunar and Martian environments.

4 Optimization of the Self-propagating High-temperature Process for the Fabrication in-situ of Lunar Construction Materials

One of the steps of a recently patented process based on the occurrence of the highly exothermic self-propagating thermite reduction of ilmenite ($FeTiO_3$) for the *in-situ* fabrication of composite ceramics in Lunar environment is systematically investigated. Because its relatively lower volatility, Al is preferred to Mg as reducing agent. Mixtures with the Al/$FeTiO_3$ molar ratio higher than 0.9 exhibit a self-propagating (SHS) behavior while, as the amount of the reducing metal in the mixture is increased, the reactive process proceeded faster and the combustion temperatures become higher as a consequence of the increased system exothermicity. Correspondingly, the amount of regolith to be combined to $FeTiO_3$ and Al reactants in the framework of ISRU (In-Situ Resource Utilization) principle could be gradually augmented thus allowing us the identification of the optimal mixture composition. The obtained product, consisting of a complex mixture of various Al-, Ti-, Mg-, and Ca-oxides along with metallic and intermetallic phases, is characterized by good compressive strength properties (25.8-27.2 MPa) that make it promising as construction material. Parabolic flight experiments evidenced that neither SHS process dynamics nor product characteristics are significantly influenced when passing from Earth to low gravity conditions. All the obtained findings allows us to conclude that the optimized results obtained under terrestrial conditions are valid for *in-situ* applications in Lunar environment, with the only exception for the slight overpressure required for controlling the occurrence of Al vaporization during SHS.

4.1 Introduction

It is well recognised that human exploration on the Moon, Mars and near Earth asteroids, etc., could be strongly facilitated and significantly time extended by the possibility of "In-Situ Fabrication and Repair" (ISRU) infrastructures and equipments for satisfying the needs encountered during Space Mission**(Bassler et al., 2006, Hammond et al., 2006, Howell et al., 2008).** Moreover, to overcome the obvious difficulties and costs related to the transportation of the required material from the Earth, the so-called "In-Situ Fabrication and Repair" (ISFR) term is often used in combination with the ISRU concept.

In this context, several technologies have been proposed in the last two decades by groups of scientists and engineers with the aim of developing suitable constructions to be placed on the Moon for the protection against cosmic rays, solar wind, meteoroids, etc., making use of available in-situ Lunar resources **(Allen et al., 1994, Toutanji et al., 2005, Tucker et al., 2006, Martirosyan et al., 2006,Faierson et al., 2010a and b, Corrias et al., 2011, White et al., 2011)**. Most of the proposed methods **(Martirosyan et al., 2006,Faierson et al., 2010a and b, Corrias et al., 2011, White et al., 2011)**are based on the occurrence of combustion synthesis-type reactions for the fabrication of ceramic-based products using Lunar regolith. For instance, the preparation of Lunar bricks was investigated starting from a mixture of JSC-1 Lunar regolith simulant, Ti and B, according to the exothermic chemical reaction $x(Ti + 2B) + (1-x)JSC\text{-}1 \rightarrow x(TiB_2) + (1-x)JSC\text{-}1$, that displays a self-propagating high temperature synthesis (SHS) behavior when $x>0.25$**(Martirosyan et al., 2006)**. Another recently proposed route is represented by the direct aluminothermic reduction of Lunar regolith simulant for producing ceramic composite materials**(Faierson et al., 2010a and b)**. Apparently, this system does not display the classical SHS behavior, i.e. local and very rapid ignition to generate a self-propagating combustion front **(Munir et al., 1989, Varma et al., 1998)**, since a relatively long preheating step (7-15 min) was needed to activate the thermite reaction in the starting mixture.

On the other hand, the SHS conditions can be satisfied as reported in a recently proposed and patented process **(Corrias et al., 2011, Cao et al., 2011)** based on the occurrence of a self-sustaining combustion synthesis reaction in a mixture obtained after blending JSC Lunar regolith with suitable amounts of ilmenite ($FeTiO_3$), to simulate the enrichment of the soils in this species, and Al, as reducing agent. This process takes advantage of the strongly exothermic character of the aluminothermic reduction of ilmenite ($FeTiO_3$), whose presence is up to 20 wt.% on Moon soil **(Schrunk et al., 2008)**, being the latter one an important aspect in the framework of the ISRU principle. In this context, it should be noted that the reduction of $FeTiO_3$ by SHS was for instance addressed in the literature according to the following reactions: $FeTiO_3 + 3Mg \rightarrow 3MgO + TiFe$ **(Wu et al., 2006)** and $FeTiO_3 + 7Al + 3C \rightarrow 3Al_2O_3 + TiC + Fe_3Al$ **(Zou et al., 2007)**.

A similar approach was adopted by **White et al. (2011)**where the use of magnesium as reducing agent was considered preferable, in comparison with aluminium, on the basis of the higher adiabatic temperature and the consequently enhanced SHS character.

The versatility of the SHS technology for ISRU and ISFR applications was emphasized in a paper review**(Moore et al., 2005)**, where the possible exploitation of this synthesis method for the fabrication of structural components, acoustic damping and in-space sterilization of materials coming from Mars was specifically addressed.

In the framework of the self-propagating metallo-thermic reduction of Lunar regolith enriched in iron-titanate, the choice of the reducing agent, along with the influence of the most important processing parameters such as composition of the starting mixture, gas pressure level, and gravity conditions, is examined in a systematic manner in the present work. The motivation for this study is the optimization of the SHS process for evaluating its possible utilization under the atmospheric and gravity conditions encountered on the Moon, that are quite different from the Earth.

4.2 Experimental Materials and Methods

4.2.1 General issues

The JSC lunar regolith simulant utilized in this work was provided by Orbital Technologies Corporation (Madison, WI, USA).

The XRD analysis of the as received simulant is reported in **Figure 4-1**. Plagioclase, specifically anorthite ($CaAl_2Si_2O_8$), Ca-rich pyroxene, in particular wollastonite ($CaSiO_3$), and olivine, namely fosterite (Mg_2SiO_4), are the main phases detected in the resulting, rather complex, pattern. Ilmenite minerals and other minor phases are also generally present among regolith constituents**(Shrunk et al., 2008)**.

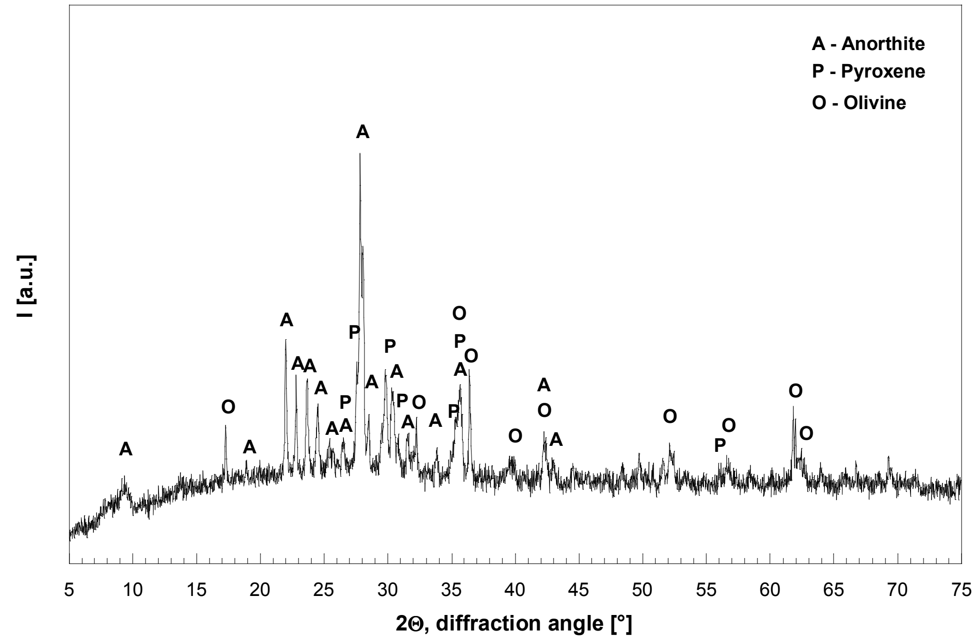


FIGURE 4-1: XRD analysis of the as-received Lunar regolith.

Lunar regolith was first sieved to produce a –45μm powder fraction and then blended in suitable proportions with Al (Alfa Aesar, -325 mesh, 99,5% purity) and $FeTiO_3$ (Alfa Aesar, -100 mesh, 99,8%+ purity) powders to obtain the mixtures to be reacted by SHS under either terrestrial or low-gravity conditions. The general reaction stoichiometry is the following:

$FeTiO_3 + xAl + y(wt.\%)\ R_L \rightarrow$ Products (1) where, x was varied in the range 0.9-3, while y was increased from 0 to the maximum allowable weight percentage, depending on the corresponding x value, able to guarantee the SHS character in the resulting reacting system. To distinguish mixtures composition, along with the corresponding experimental conditions adopted during SHS, the various systems will be indicated as S_x#_R_L#_P#_#g, where x# is the Al/$FeTiO_3$ molar ratio, R_L# represents the weight percentage (y) of lunar regolith in the mixture, P# is the gas pressure level (Torr) inside the reaction chamber, and #g indicates if the experiment is performed under terrestrial conditions (1g) or during parabolic flights (0g).

Each mixture was compacted using an uniaxial press to obtain a series of pellets with cylindrical (11 mm diameter and 25 mm height) or parallelepiped (14 mm x 17 mm x 33 mm) shape.

The apparatus shown in **Figure 4-2a-4-2b** has been specifically designed to perform SHS reactions on the ground and onboard of the Airbus 300 during the 53rd ESA Parabolic Flights Campaign held in Bordeaux (France) last October 2010. The equipment (cf. **Figure 4-2a**) consists of two reaction chambers, each of them containing six holders, a power supply (Legrand safety isolating transformer, mod. 642310, primary 230-400V, secondary 12-24V, power 1000 VA) required for reaction ignition and a vacuum pump.

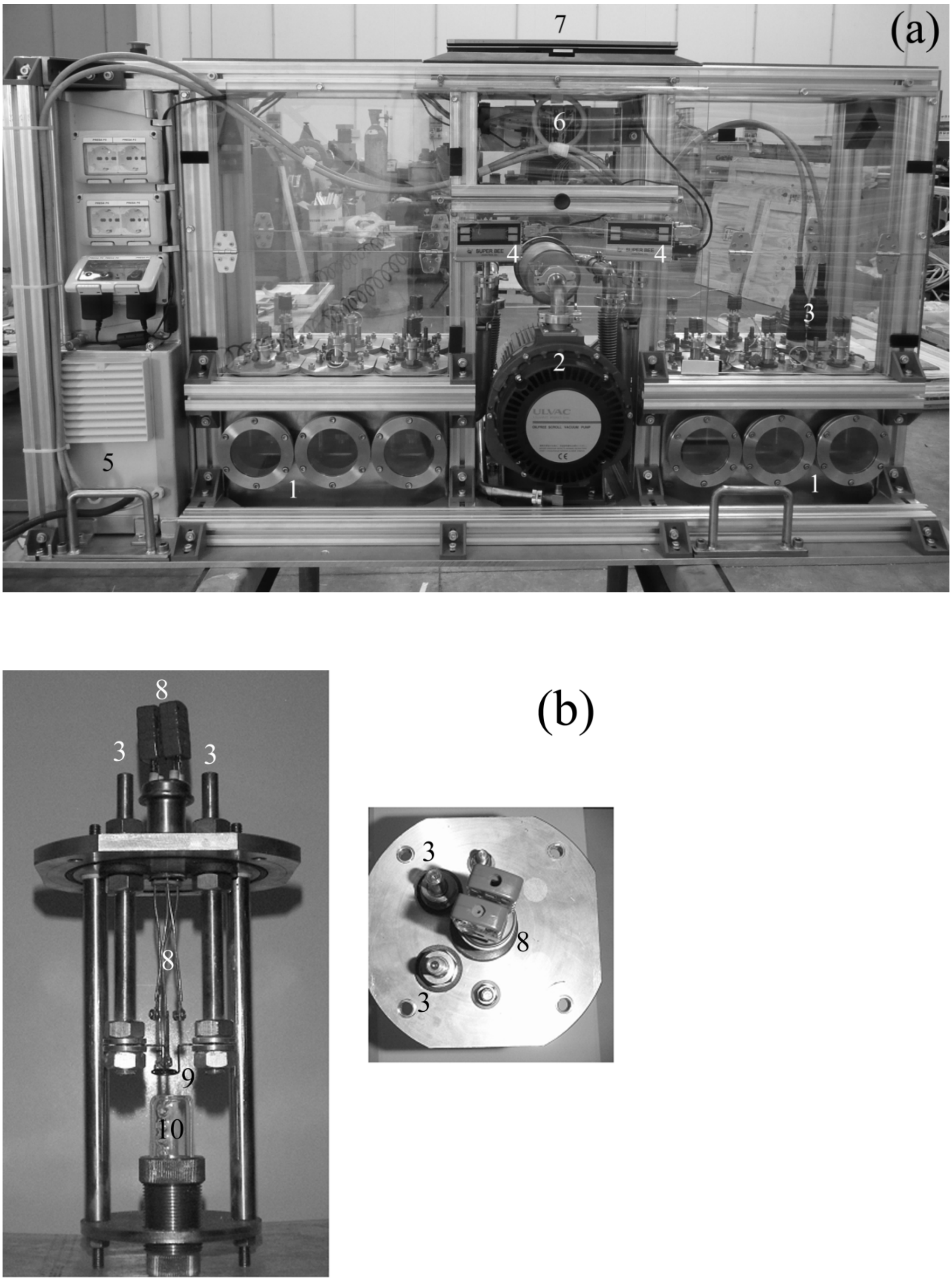


FIGURE 4-2: Complete (a) and individual holder (b) views of the apparatus used for SHS experiments performed on the ground and during parabolic flights: (1) reaction chambers, (2) vacuum pump, (3) electrodes, (4) vacuum sensors, (5) power supply, (6) data acquisition system, (7) notebook, (8) thermocouples and related feedthroughs, (9) heating filament, (10) quartz container.

Each individual holder (cf. **Figure 4-2b**) is equipped with a tungsten coil (R.D. Mathis Company, USA) that was electrically heated when connected, through the corresponding electrodes, to the power supply. Temperature during reaction evolution was measured using two thermocouples (W-Re, 0.13 mm diameter, Omega Engineering Inc.) connected to the related feedthroughs placed on the top of the holder (cf. **Figure 4-2b**). During terrestrial experiments, a two-colour pyrometer Ircon Mirage OR 15-990 (Ircon, USA) was also used for measuring temperature-time profiles in the sample surface during SHS evolution. The process was monitored through a video camera (Imaging Source CMOS color camera, model DFK 21AUC03, using Pentax lenses, model B1218A) and a computer (notebook) system connected to a data acquisition board (cDAQ-9174 equipped with NI 9481 high voltage relay module, NI 9213-16ch-24bit thermocouple module and NI 9239-4ch-24bit analog input module, National Instruments) and supported by a software package (LabVIEW, National Instruments).

The desired pressure level, in the range of 3-760 Torr, was monitored through appropriate vacuum sensors (cf. **Figure 4-2a**).

For systems displaying an SHS character, the combustion front generated at the top of the pellet using the heated tungsten filament propagates spontaneously through the mixture until it reaches the opposite end of the sample.

Theoretical densities of selected optimized systems were determined on fully dense specimens produced by consolidating via spark plasma sintering the powders obtained after crashing SHSed products.

The chemical composition and microstructure of the obtained reacted samples was determined by X-ray diffraction (XRD) analysis (Philips PW 1830 diffractometer using CuKα Ni-filtered radiation). End products microstructure was examined by Scanning Electron Microscopy (SEM) using a Hitachi S4000 microscope. Compressive strength tests on SHSed samples were carried out on cylindrical specimens using a METRO COM (mod. 100 MI) press equipped with a 10 kN load cell (METIOR CVS).

4.2.2 Parabolic flight experiments

The reduced gravity environment was obtained inside a special airbus (Airbus A300) through series of parabolic manoeuvres. Specifically, the aircraft starts from a steady normal horizontal flight, and then it takes a 1.8 g load factor nosing up to 45° and climbing to 7500 m. Then the engine thrust is reduced to the minimum required to compensate air-drag. At this point, the aircraft follows a free-fall ballistic trajectory during which weightlessness is achieved. This phase lasts for about 25 s and the peak of the parabola is reached at about 9000 m. At the end of the low gravity period, i.e. again at 7500 m, a symmetrical pull-out phase is executed to bring the aircraft to its steady horizontal flight in about 20 s.

A normal mission lasts about 2 h and consists of 30 parabolas. During each parabola, gravity is lower than $2\ 10^{-2}$ g. Typically, ignition of the SHS reaction was performed at the injection phase (the entry of zero g phase).

The entire SHS apparatus shown in **Figure 4-2** was mounted on an aluminum plate provided of suitable holes to permit its fixation to the airbus rails. As indicated in **Figure 4-2b**, a quartz container was used to sustain, during low gravity experiments, the pellet in a stable position.

4.3 Results and discussion

4.3.1 Selection of the reducing agent

A thermodynamic calculation of the adiabatic temperature was conducted recently for mixtures where Aluminum or Magnesium are considered as possible reducing agents to be directly reacted with JSC lunar regolith **(White et al., 2011).** Based on the relatively higher adiabatic temperature predicted for Mg-based mixtures, the latter ones were preferred, in comparison with the analogous Al-based systems, for being reacted by SHS.

However, the low pressure level characterizing lunar atmosphere plays an important role in the identification of the most suitable reducing metal to be utilized. Indeed, the high temperature achieved during the SHS process can lead, unless sufficiently high pressure condition are guaranteed, to excessive gas expulsion during the fabrication process if high volatile reactants are used. The direct consequences of this fact are significant reactants/products loss, sample weight decrease, increasing in product porosity, possibility of the interruption of combustion front propagation, difficulties in process control, etc.

In this regard, the effect of pressure on the boiling temperatures of Mg and Al is shown in **Figure 4-3**.

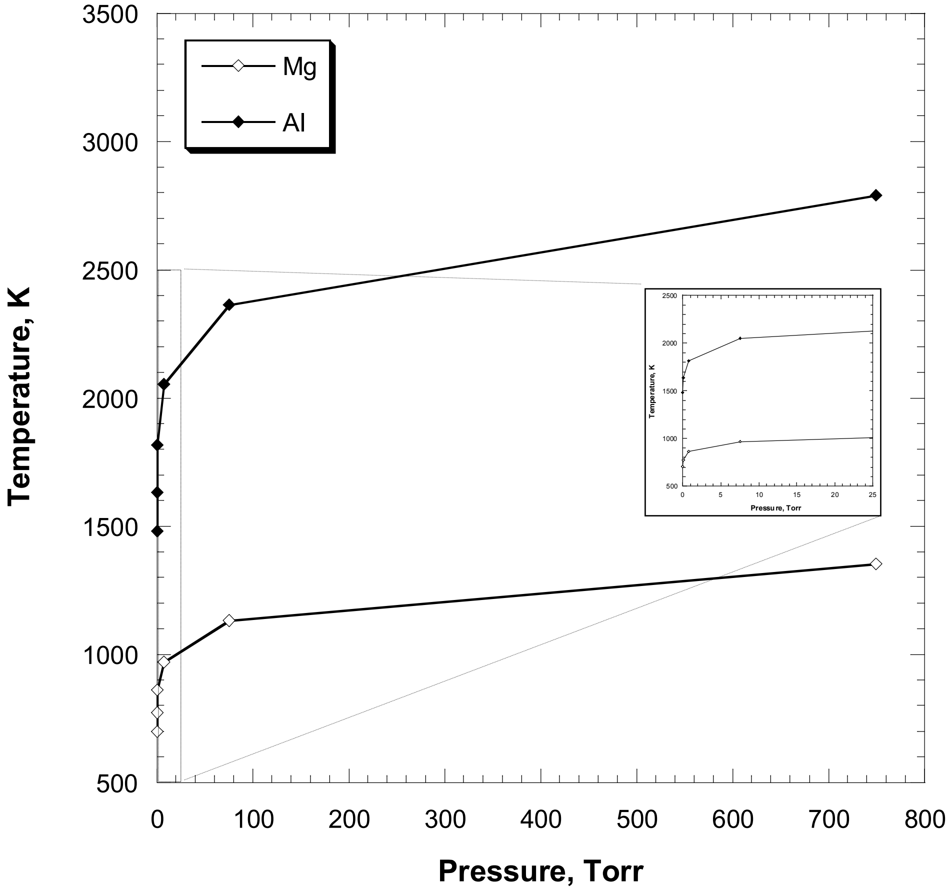


FIGURE 4-3: Dependence of boiling temperature on pressure for metal aluminum and magnesium

On the basis of the reported data, it is clearly seen that Mg is much more volatile and, under the temperature conditions encountered during SHS process evolution, the possible negative phenomena described above may play a relevant role. This prediction was experimentally confirmed in our study when the SHS process was carried out at relatively low pressures (25 Torr) using Mg as reducing agents. In fact, a significant amount of gases was liberated during the SHS process and the resulting product changed significantly his shape and increased his porosity. Moreover, when the pressure level was further decreased, these features lead to pellet disintegration.

Consistently with the relatively lower vapor pressure of Al, these undesired phenomena resulted significantly mitigated when reacting Al-based mixtures. Nevertheless, as shown in section 4.3.4 where the experimental results related to the influence of pressure will be reported and discussed, care should be taken also in this case when operating at very low pressure levels.

Based on the considerations above, Al was chosen as reducing metal in our investigation. In this regard, it should be noted that aluminum could be extracted from Lunar minerals containing this element or otherwise recovered from some components or portions of vehicles previously utilized for space missions and available on the Moon **(White et al., 2011)**.

4.3.2 Effect of the Al/$FeTiO_3$ molar ratio

If no regolith was added to the mixtures, all the systems based on reaction (1) exhibited a self-propagating behavior only if $x \geq 0.9$. Moreover, as shown in **Figure 4-4**, when the Al/$FeTiO_3$ content is augmented, both the average velocity of the combustion front (v_f) and the maximum combustion temperature (T_c) correspondingly increased. This is an indication, at least in the compositional range investigated in this work, of the progressively enhanced exothermic character of reaction (1) with increasing amounts of Al in the system.

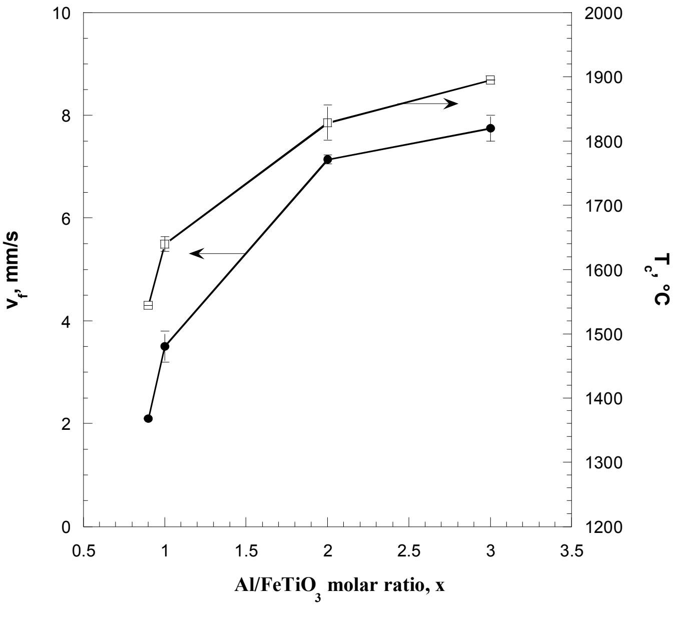


FIGURE 4-4: Average front velocity and combustion temperatures as a function of the (Al/$FeTiO_3$) molar ratio in the starting mixture (y=0 in Reaction (1)).

The compositions of the resulting products are summarized in **Figure 4-5**.

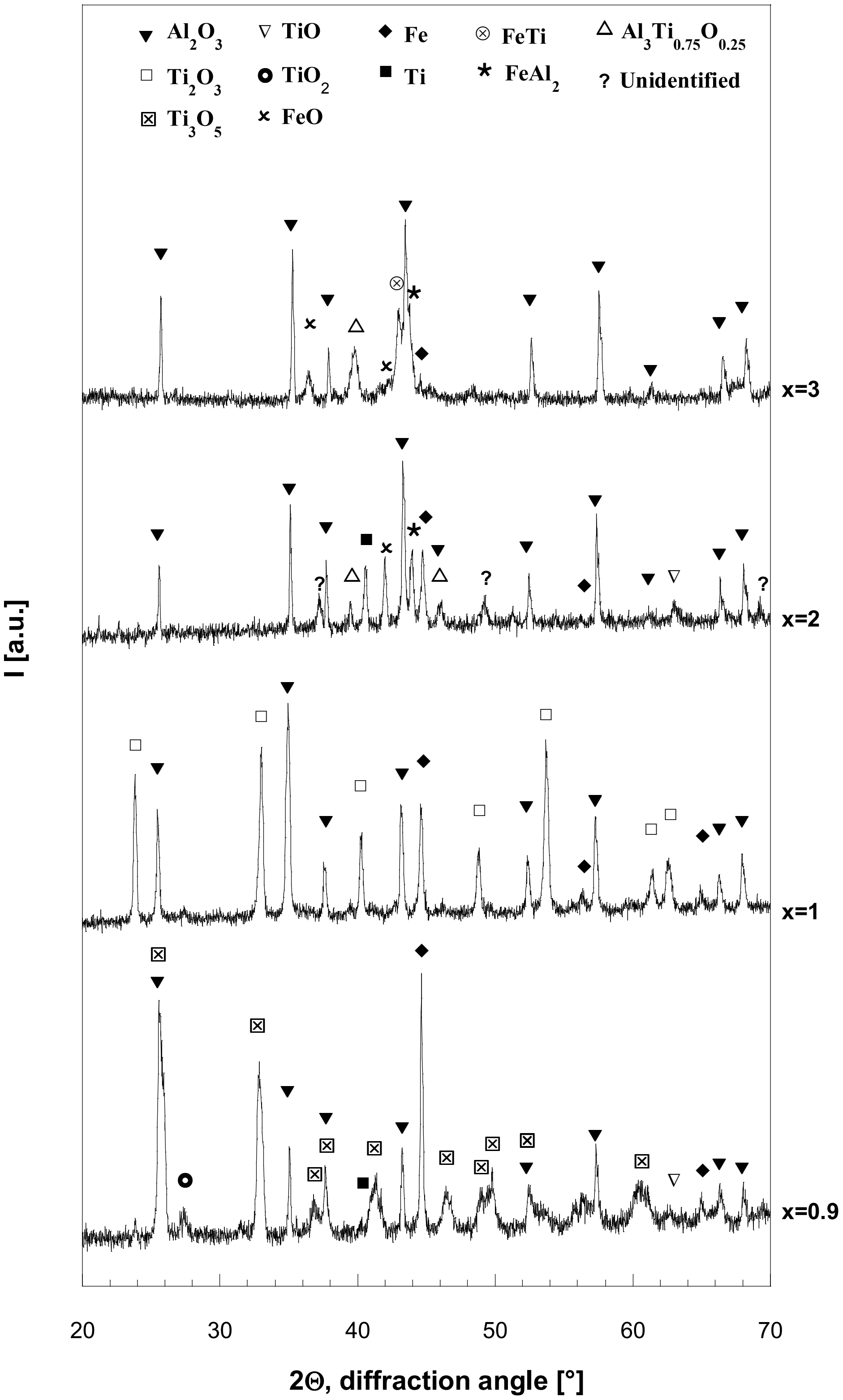


FIGURE 4-5: XRD patterns of SHSed products obtained using different x values (y=0 in Reaction (1)).

Although product composition depends on the system under consideration, all the reported XRD spectra indicate that the SHS process leads to ceramic-metal composites with no traces of initial reactants.

Each system will be analyzed separately in what follows, with the aim of identifying the possible global reaction describing the corresponding chemical transformation occurring during the SHS process.

For instance, the formation of the main phases, i.e. Al_2O_3, Fe, and Ti_3O_5, detected by XRD in the final product obtained when using the lowest Al/$FeTiO_3$ ratio (x=0.9), is consistent with the occurrence of the following reaction:

$FeTiO_3 + 0.9Al \rightarrow 0.45Al_2O_3 + Fe + 0.33Ti_3O_5$ (2).

The exothermicity of the latter one, i.e. $(-\Delta H_r^o)$ = 330.044 kJ/mol of $FeTiO_3$**(Barin et al., 1989)**, justifies the self-propagating behaviour exhibited by this system.

It should be noted that the secondary species TiO_2 and Ti, also found as minor phases in the SHSed product, are not accounted for in the previous reaction.

When the x value was increased to 1, a relatively less oxidized Ti oxide, namely Ti_2O_3, was formed instead of the Ti_3O_5 phase observed at x=0.9. Moreover, no secondary species were detected in the end-product. These outcomes provide an indication of the higher reducing environment produced by the additional Al. Accordingly, the chemical transformation possibly taking place in this case can be described through the following global reaction:

$FeTiO_3 + Al \rightarrow 0.5Al_2O_3 + Fe + 0.5Ti_2O_3$ (3).

The enhanced self-propagating character displayed by the latter one as compared to system (2) **(cf. Figure 4-4)** is consistent to the corresponding higher enthalpy of reaction (3), i.e. $(-\Delta H_r^o)$ = 362.753 kJ/mol of $FeTiO_3$**(Barin et al., 1989).**

Analogously, according to the XRD pattern of the SHSed product shown in **Figure 4-5**, the base reaction involved when the Al/$FeTiO_3$ molar ratio is raised to 2 is the following:

$FeTiO_3 + 2Al \rightarrow Al_2O_3 + Ti + Fe$ (4)

The increase in front velocity and combustion temperature as compared to the systems with lower x values (cf. **Figure 4-4**) is justified also in this case by the relatively higher exothermicity ($-\Delta H_r^o$ = 440.157 kJ/mol of $FeTiO_3$**) (Barin et al., 1989)**. It should be noted that, as shown in **Figure 4-5**, the additional presence of some partially reduced species, particularly FeO, in the end-product, can be associated to the fact that Al not only acts as reducing agent but also reacts with elemental iron to form $FeAl_2$, also detected by XRD. Thus, the main chemical transformations taking place during SHS for the system with x=2 can be summarized as follows:

$FeTiO_3 + 2Al \rightarrow (1-x)Al_2O_3 + Ti + (1-4x)\ Fe + 3xFeO + xFeAl_2$ (5)

Nevertheless , other minor species, including some unidentified phases, are not accounted for in this reaction.

The principal new outcome observed as the $Al/FeTiO_3$ ratio was augmented to 3 is the appearance of the FeTi phase at the expenses of elemental Fe and Ti, that tend to disappear from the XRD pattern. In addition, Al_2O_3 remains the main phase detected by XRD while $Al_3Ti_{0.75}O_{0.25}$ and $FeAl_2$ contents increase. Regarding the presence of FeO in the final product, the considerations made previously when examining the case of x=2 are still valid in this case.

The SEM microstructure of a reaction product synthesized under terrestrial conditions when setting x=2 and y=0 in reaction (1) is shown in **Figure 4-6**.

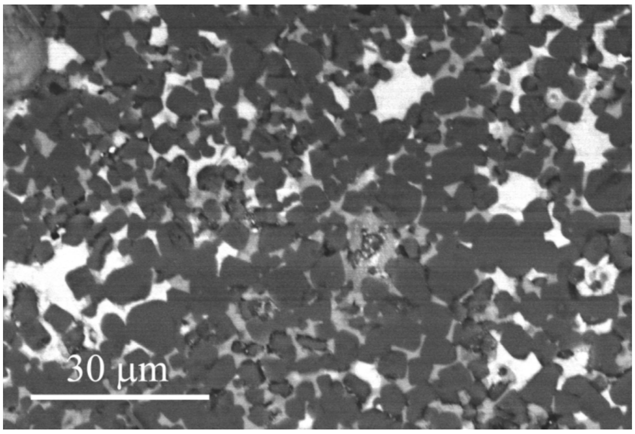


FIGURE 4-6: SEM microstructure of the S_x2_R$_L$0_P25_1g SHSed end-product.

According to the corresponding XRD pattern (cf. **Figure 4-5**), the obtained composite material consists of Al_2O_3 grains (dark phase) surrounded by a multiphase metal matrix of Ti, Fe and intermetallic alloys.

4.3.3 Effect of the regolith content

The addition of lunar regolith in the initial mixtures (y>0 in reaction (1)) strongly affects SHS process dynamics of the corresponding reacting systems. The influence of regolith content on the measured average front velocity and combustion temperature is plotted in **Figure 4-7** for the different (Al/FeTiO3) molar ratios investigated. It is clearly observed that both these parameters decrease as the y value is augmented.

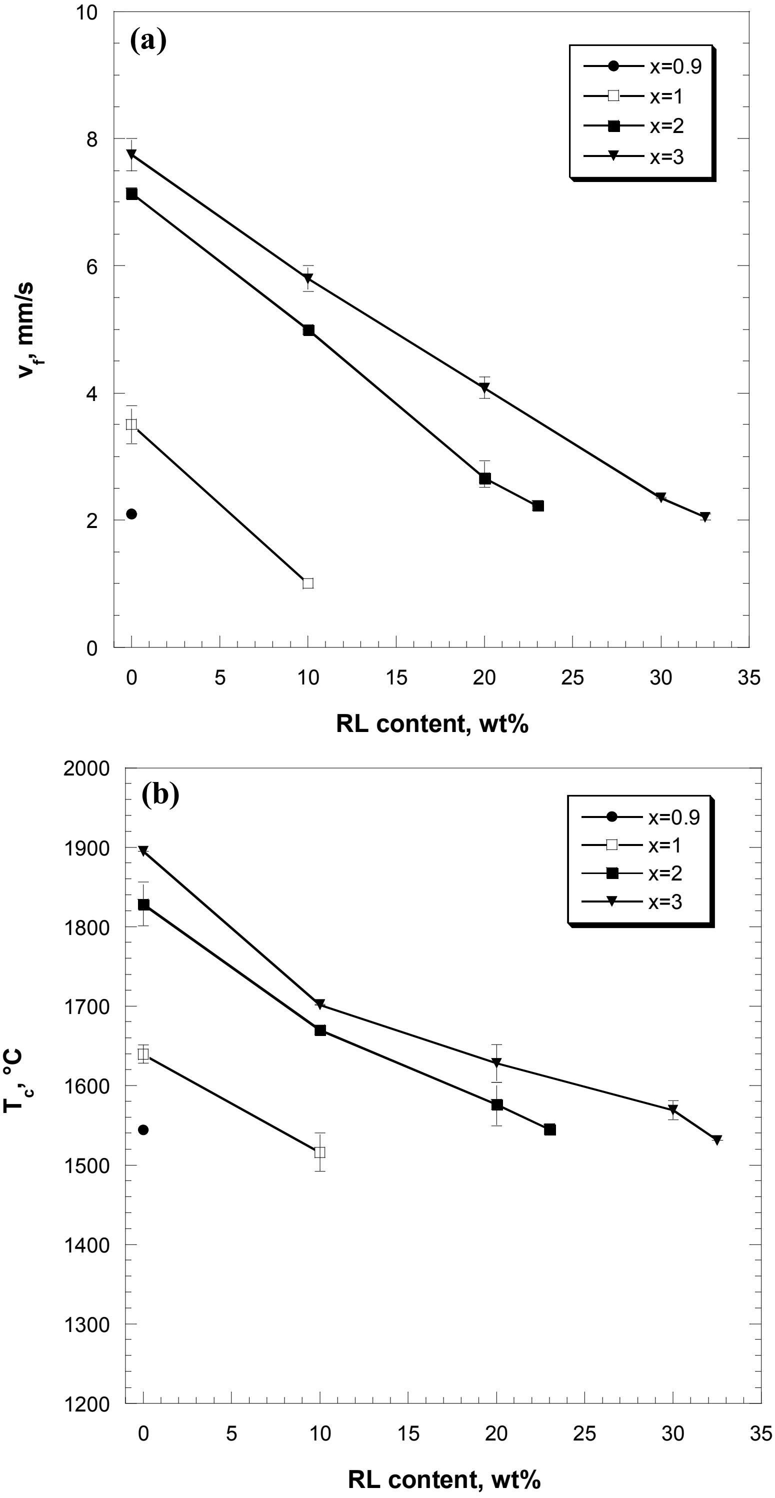


FIGURE 4-7: Average front velocity (a) and combustion temperature (b) for the different (Al/FeTiO$_3$) molar ratios investigated as a function of the Lunar regolith content in the starting mixtures.

Moreover, a threshold (y$_c$) related to the amount of regolith that can be added to the mixture to maintain the self-propagating behaviour is identified. Specifically, above y$_c$, whose value depends on that of x, the corresponding systems cease to react by SHS. It is also possible to observe from **Figure 4-7** that the minimum allowable values of front velocity and combustion temperature for guaranteeing the SHS character in the reacting systems are in the ranges 1-2 mm/s and 1500-1550 °C, respectively. In particular, the latter condition is perfectly consistent to the range of 1800-2000 K that is the empirical requirement for the adiabatic temperature generally reported in the SHS literature for self-sustaining systems **(Munir et al., 1989, Varma et al. 1998)**.The composition of the mixtures able to react by SHS and corresponding to the maximum amount of simulant regolith used, that represents the optimal condition in the framework of the ISRU concept, is reported in **Figure 4-8** as a function of the (Al/$FeTiO_3$) molar ratio.

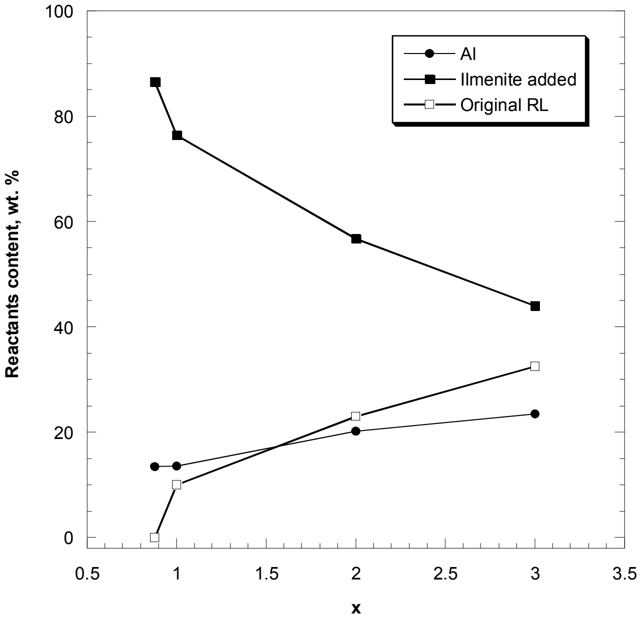


FIGURE 4-8: Composition of the optimal reacting mixtures as a function the (Al/$FeTiO_3$) molar ratio used in reaction (1).

It is clearly seen that, if the amount of regolith in the mixture is increased the weight percentage of Al has to be correspondingly augmented for guaranteeing the self-propagating character of the reacting system.Based on these results and considering the percentage of ilmenite present on Moon soil **(Schrunk et al., 2008)**, it is possible to estimate the total amount of $FeTiO_3$, as the sum of the fraction originally present in the Lunar regolith and that additionally provided from the external, as required for obtaining the optimal SHS systems. Moreover, according to the considerations reported in a recent paper **(Corrias et al., 2011)**, the sum of these two contributions "simulates" the amount of $FeTiO_3$ in a "modified" Lunar soil, obtained after an enrichment treatment for suitably increasing ilmenite content is applied. Thus, the resulting enriched soil could be directly reacted by SHS with Al. Consequently, as reported in **Figure 4-9,** it is possible to determine the dependence of the minimum amount of Al required for making the reactive process self-sustaining as a function of the ilmenite content in the enriched regolith. Regarding this aspect, its should be noted that although $FeTiO_3$ amount in certain Lunar basaltic sites could be even higher than 20 wt.% **(Schrunk et al., 2008)**, our calculations are based on the assumption that the original content of $FeTiO_3$ in the regolith is in the range 7-15 wt.%, as obtained from a recent NASA report relatively to Lunar Mare rock types **Sibille et al. (2005)**.

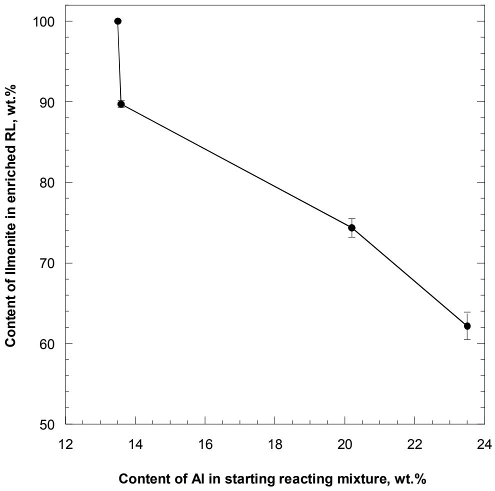


FIGURE 4-9: Dependence of the minimum amount of Al required to make the reactive process self-sustaining as a function of the total ilmenite ($FeTiO_3$) content in the enriched regolith.

Figure 4-9 indicates that the minimum amount of reducing agent required for sustaining the SHS aluminothermic process is about 13 wt.% and corresponds to x=0.9 and y=0 in reaction (1). On the other hand, when the maximum amount of Al investigated in this work is added to the mixture, i.e. about 23.5 wt.% (corresponding to x=3), the enrichment stage has to produce a regolith with approximately 61 wt.% of $FeTiO_3$. Thus, depending upon the relative lack of Al available on Moon soil or energy to be spent for the enrichment treatment, different regolith/Al mixtures can be identified for the fabrication of Lunar construction material by SHS.

An example of end-product in the parallelepiped configuration, which could be considered as a possible “Lunar brick” prototype, is shown in **Figure 4-10** for the case of S_x3_R_L32.5_P25_1g system.

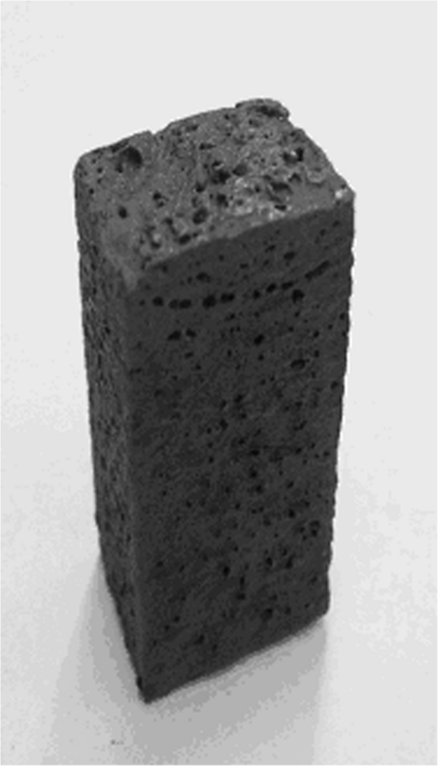


FIGURE 4-10: Image of the final sample obtained by self-propagating reactive process for the case of parallelepiped configuration (S_x3_R_L32.5_P25_1g system).

An important issue in view of the obtainment of structural component with selected dimensional characteristics is represented by the fact that the original specimen shape is maintained during the course of the reaction process. This holds also true when considering cylindrical pellets.

Figure 4-11 shows the composition of the products obtained using the the different optimal (x, y) combinations identified in the present work (**cf. Figure 4-8**).

Analogously to the systems reacted when no regolith was present in the mixture, the starting reagents are also in this case completely converted in multiphase products. Nevertheless, as the Al/$FeTiO_3$ molar ratio is augmented and the maximum amount of regolith allowable for guaranteeing the SHS behaviour in the resulting system is correspondingly increased, a variety of additional phases have been detected by XRD (cf. **Figure 4-11)**.

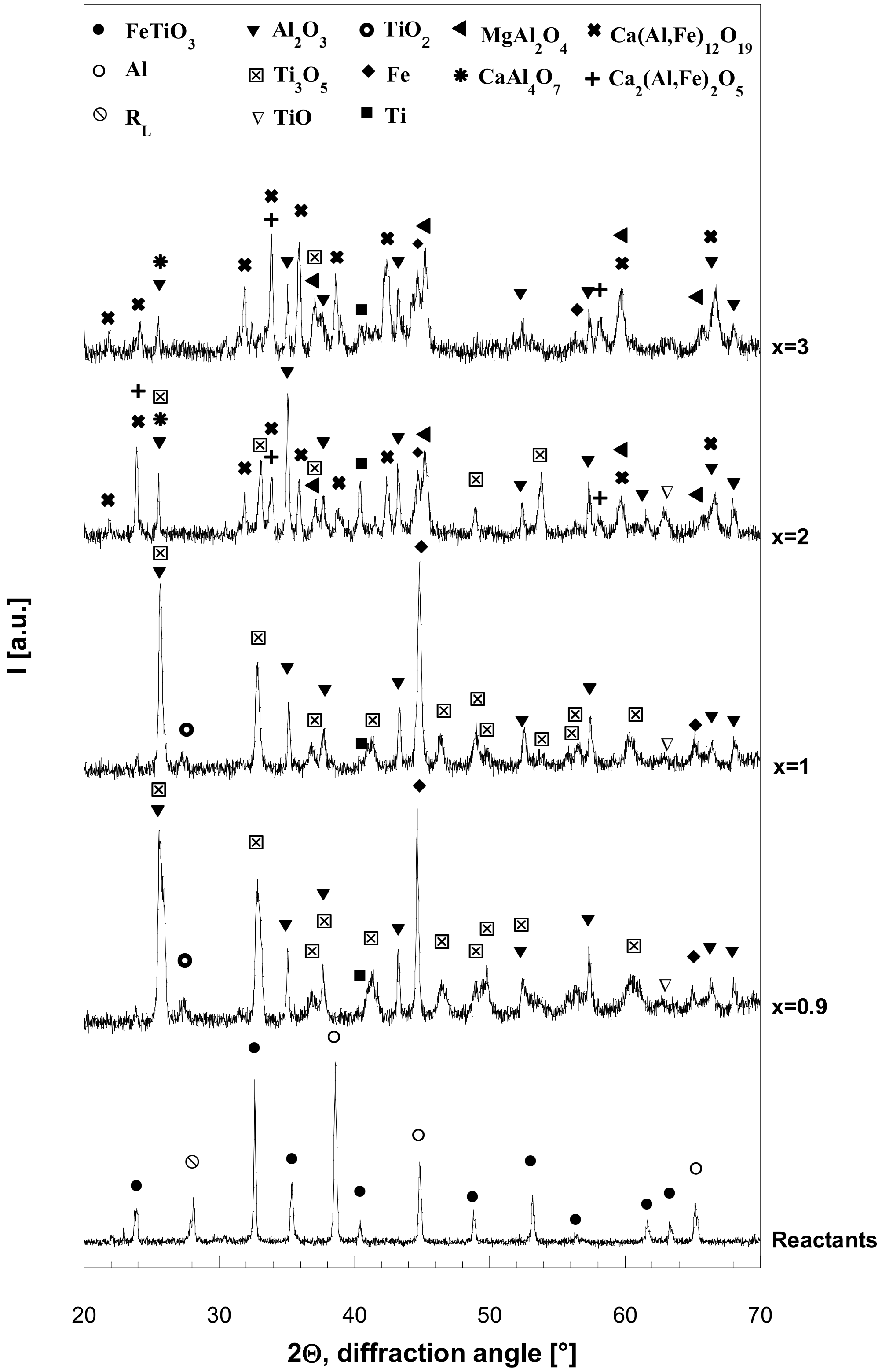


FIGURE 4-11: XRD patterns of reactants (x=3, R_L=32.5 wt.%) and SHSed products obtained under the optimal conditions when using different x values.

Specifically, as compared to the base case corresponding to the system with x=0.9 and y=0, product composition changes only slightly when adding 10 wt.% of regolith to the starting mixture (x=1), being Al_2O_3, Fe, Ti_3O_5, Ti and TiO_2 still the only phases identified in the end product by XRD. On the other hand, when x≥2 and the amount of simulant that is possible to process is correspondingly augmented, the situation varies significantly. Several mixed oxides, namely magnesium spinel ($MgAl_2O_4$) and various calcium aluminates ($Ca(Al,Fe)_{12}O_{19}$, $Ca_2(Al,Fe)_2O_5$ and $CaAl_4O_7$) are produced during SHS in these circumstances. Other minor or non-crystalline phases, particularly silicates, are also likely formed. The presence of all these species is the result of the chemical interaction of Al with the main constituents initially present in Lunar simulant regolith, i.e. $FeTiO_3$, $CaAl_2Si_2O_8$, $CaSiO_3$, and Mg_2SiO_4.

It should be noted that the composition above is also qualitatively similar to that recently reported by **Faierson et al. (2010a)**relatively to end-products formed when Lunar regolith simulant was directly reacted with Al (33 wt.% in the mixture). In this case, the reaction was conducted under the so-called volume combustion regime, i.e. after a slowly heating stage (7-15 min) until the mixture achieved the ignition temperature.

An example of SEM micrograph related to a product obtained from starting mixtures containing lunar regolith is shown in **Figure 4-12** relatively to the S_x2_R_L30_P25_1g system. As compared to the case described in **Figure 4-6**, the several phases originally present in Lunar regolith lead to the formation of ceramic-metal composites characterized by a relatively complex microstructure. Specifically, the presence of peculiar filament-like structures is well evidenced, particularly inside sample pores (cf. **Figure 4-12b**).

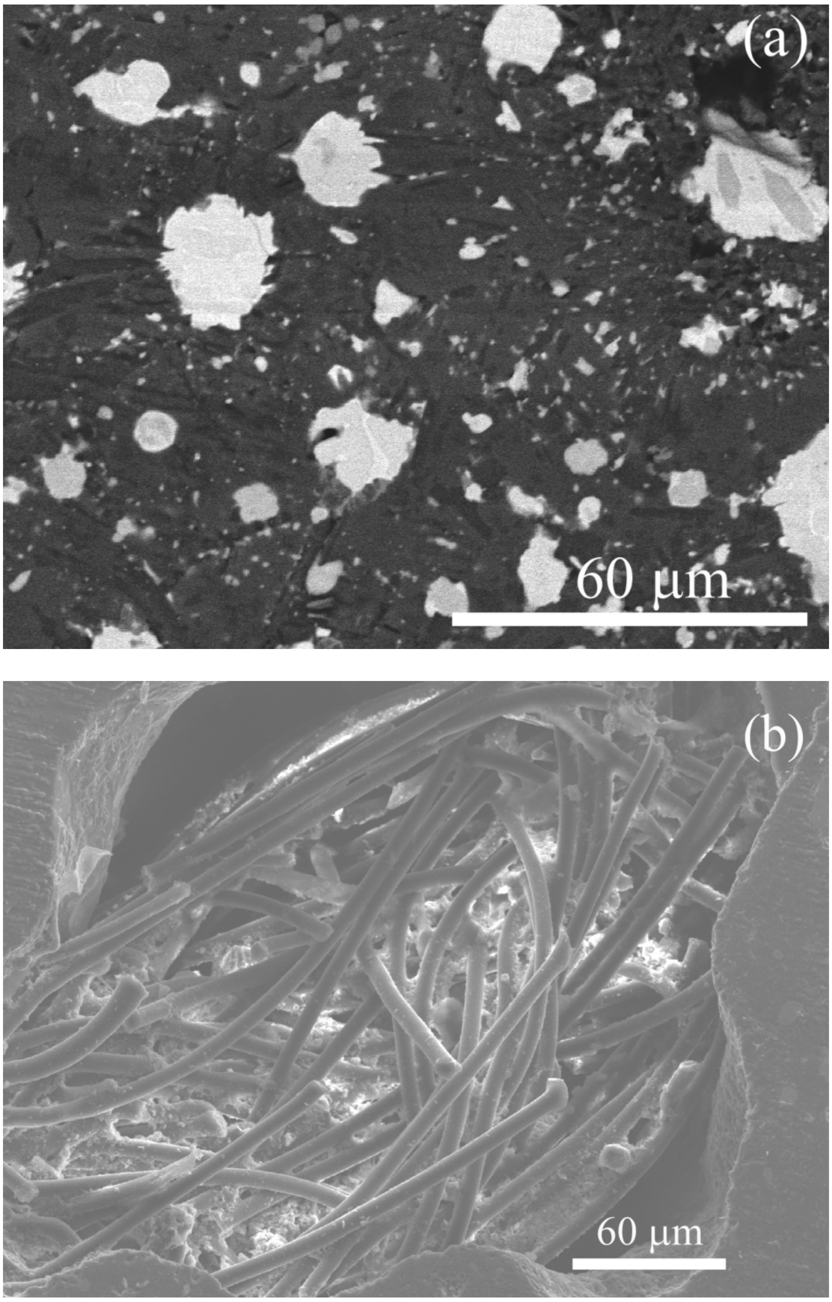


FIGURE 4-12: SEM microstructures of (a) the S_x2_$\mathrm{R_L}$30_P25_1g SHSed end-product: (a) general view of the bulk region; (b) peculiar whisker-type phase inside a sample pore.

Their formation can be likely associated to the occurrence of a vapor-liquid reaction mechanism as a consequence of the Al vaporization taking place during SHS evolution. Unfortunately, EDS analysis did not provided any reliable information regarding the composition of this phase, as we could find them isolated only inside the pores.

Nevertheless, being most likely Al involved in their formation, they presumably consist of Al-based oxides.

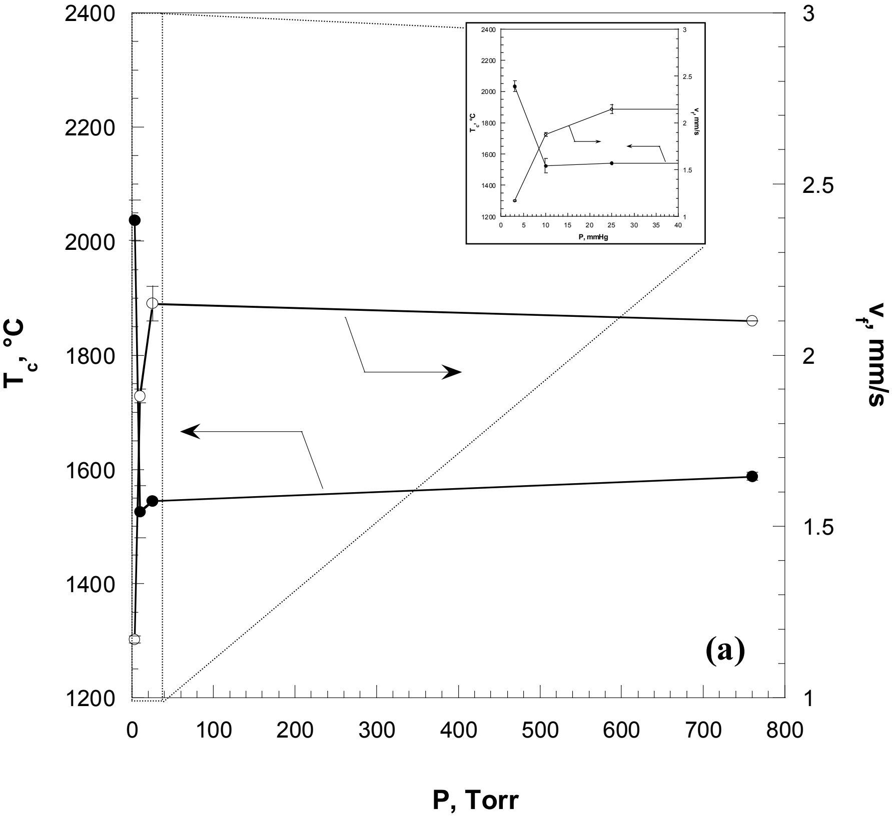
The presence of whiskers having diameters as small as about 25 nm and probablycomposed by Al nitrides and oxides was observed by Fayerson and Logan **(Faierson et al., 2010 a, Faierson et al. 2010b)** when performing, under standard (air) conditions, the direct geothermite reaction of Lunar regolith with Al. However, no whiskers were found in this study when the reaction was conducted in a vacuum environment (about 0.6 Torr).

The characterization from the compressive strength point of view of the end-product synthesized in the present investigation was conducted on cylindrical S_x2_RL20_P25_1g and S_x3_RL30_P25_1g samples and provided average values of 27.2 ± 3.6 and 25.8 ± 3.6 MPa, respectively. These values are significantly higher in comparison to the best results reported in the literature, i.e. about 18 MPa, relatively to products obtained from the direct aluminothermic reaction of Lunar regolith stimulant **(Faierson et al., 2010 a, Faierson et al. 2010b)**. The observed improvement could be likely due by the increase in reaction exothermicity due to the relatively higher content of ilmenite in the mixture used in the present work. Indeed, such reaction conditions are beneficial for enhancing sintering phenomena during SHS and, consequently, increasing the strength of the resulting material.

4.3.4 Effect of the pressure level

All the results reported and discussed in previous sections referred to SHS experiments performed when the evacuation level inside the reaction chamber was 25 Torr. However, since the atmosphere pressure on the Moon is extremely low, i.e. about 10^{-12} Torr **(Schrunk et al. 2008)**, while, as discussed in section 3.1, the SHS process behavior and related product characteristics can be negatively affected under such condition, the influence of this parameter is systematically investigated in this work.

The average front velocity and combustion temperature as a function of the gas pressure inside the SHS chamber is reported in **Figures 4-13a-4-13b**, for the cases of x=0.9 and 2, respectively. Only slight differences in wave velocity and combustion temperature are manifested when decreasing the pressure from 1 atm (Argon environment) down to 25 Torr. Nevertheless, the situation completely changed when the pressure was further decreased to 3 Torr. Correspondingly, as observed in **Figures 4-13a-4-13b** (see also the related insets), the combustion temperature increases while front velocity decreases. Analogous results are obtained when different Al/FeTiO$_3$ molar ratios were considered.



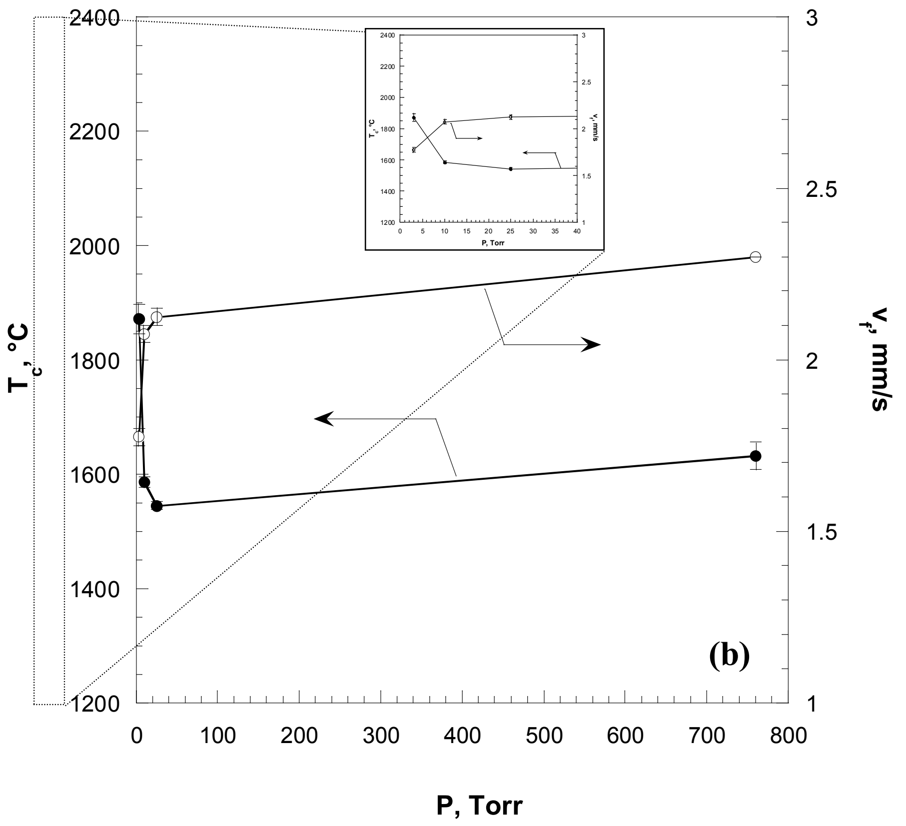


FIGURE 4-13: Effect of pressure on combustion temperature and front velocity during self-propagating high-temperature process for the cases of ($Al/FeTiO_3$) molar ratios equal to 0.9 (a) and 2 (b).

These outcomes can be strictly associated to the corresponding weight loss displayed by samples during the SHS process, as evidenced in **Figures 4-14a-4-14b** where the behavior of reacting systems with x=0.9 and 2, respectively, is shown.

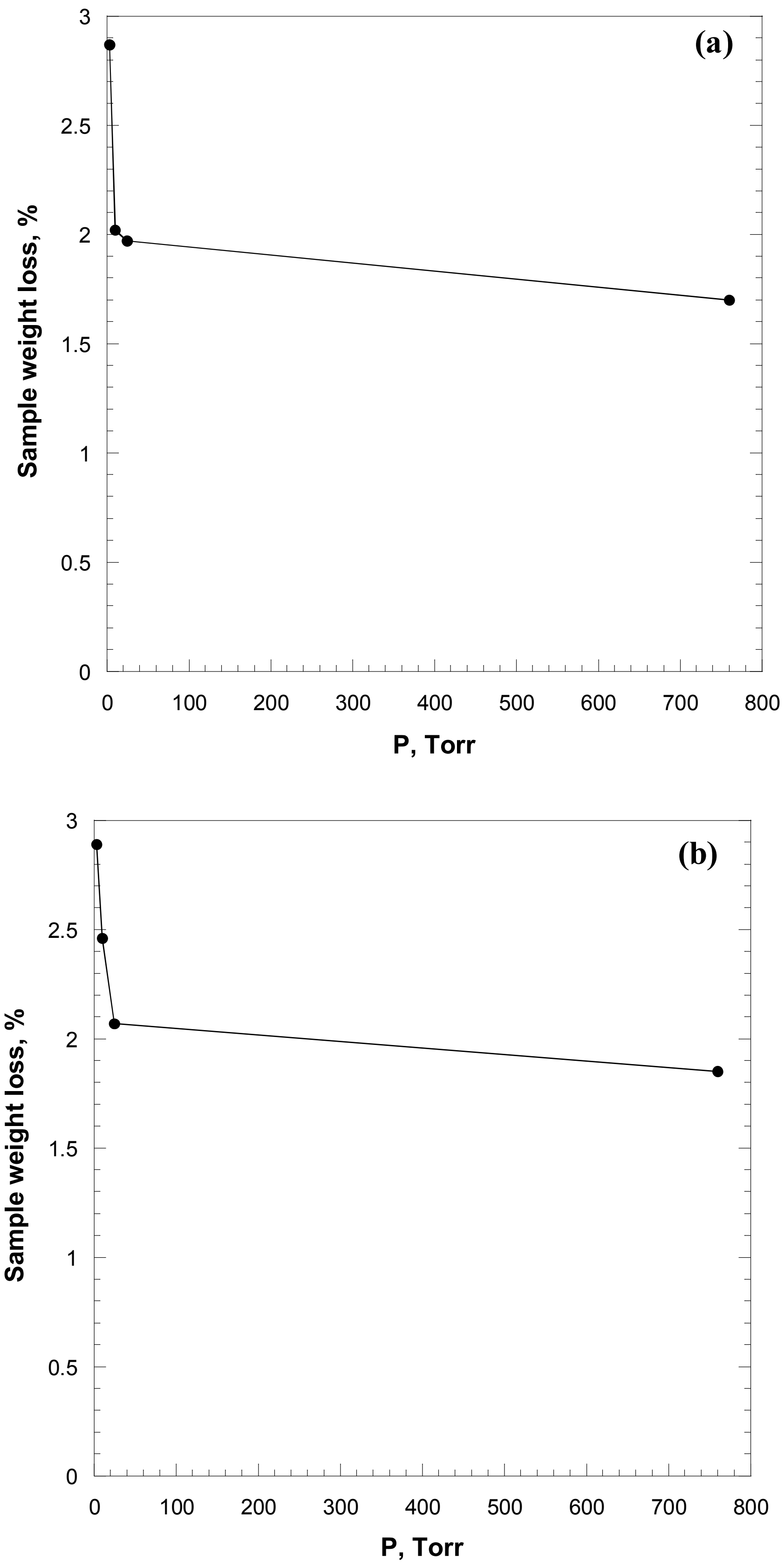


FIGURE 4-14: Effect of vacuum level on weight loss in samples obtained by self-propagating high-temperature process for the cases of ($Al/FeTiO_3$) molar ratios equal to 0.9 (a) and 2 (b).

The possible reason for the observed behavior relates to the fact that, on the basis of the consideration made in section 3.1, as pressure level is decreased, a relatively larger amount of vapour Al is expected to be developed (cf. **Figure 4-3**). Consequently, part of reactants are progressively expulsed during reaction evolution, thus causing the observed decreasing in sample weight. If the process is conducted at very low pressure, this situation could become critical to lead sample disintegration.

As far as the behavior displayed by wave velocity is concerned, it is likely that the formation of significant amounts of gases may hinder heat transfer inside the reacting pellets that have to be, on the other hand, satisfied for guaranteeing the progress of the SHS process. Thus, the fact that propagation of the reaction front is lowered find a possible justification. Nevertheless, the corresponding behavior displayed by the measured combustion temperature may be associated to the more reactive character of Al when in vapour state, that corresponds to the situation encountered if the aluminothermic based process is performed under lower pressure conditions.

Based on the consideration above, it is possible to assess that if the fabrication process based on SHS reactions proposed in this work is performed under the pressure conditions typically present on lunar environment, the features discussed previously may play an important role. On the other hand, if the process is conducted above a certain pressure threshold (few Torr), no inconvenience will be encountered.

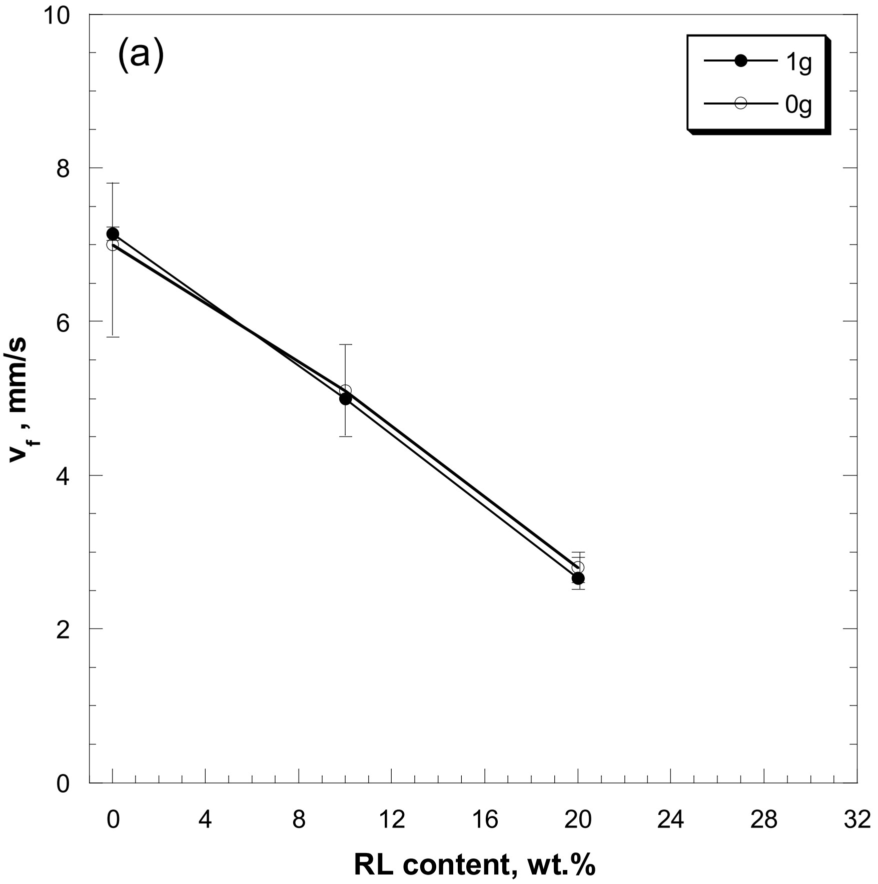
It should be noted that, no remarkable differences in product composition was found within the range of pressure level investigated in the present work.

4.3.5 Effect of gravity

Due to the low gravity conditions present on the Moon, i.e. about 1,622 m/s^2**(Schrunk et al., 2008)**, another important parameter to be investigated in view of the possible exploitation *in-situ* of the fabrication process considered in this work is the gravity level under which the self-propagating reaction (1) is conducted.

To evaluate possible differences in process dynamics and/or end-product characteristics as compared to the analogous related to terrestrial (1g) conditions, SHS experiments have been also performed in a microgravity (~10^{-2} g) environment during a recent parabolic flight campaign, while maintaining the pressure inside the chamber equal to 25 Torr. Specifically, low-gravity tests have been carried out on lunar regolith-based systems with x=2 or 3 and R_L content in the range 0-30 wt.%.

The average velocity of the reaction front measured under the two gravitational conditions above are compared in **Figures 4-15(a)-4-15(b)** for the cases of x equal to 2 and 3, respectively. The sample height was set to 25 mm in order to guarantee that, according to the measured reaction front velocity values (> 2 mm/s), the SHS process duration falls entirely within the time interval of about 20 *s* where the 2 10^{-2} g condition is established during each parabola.



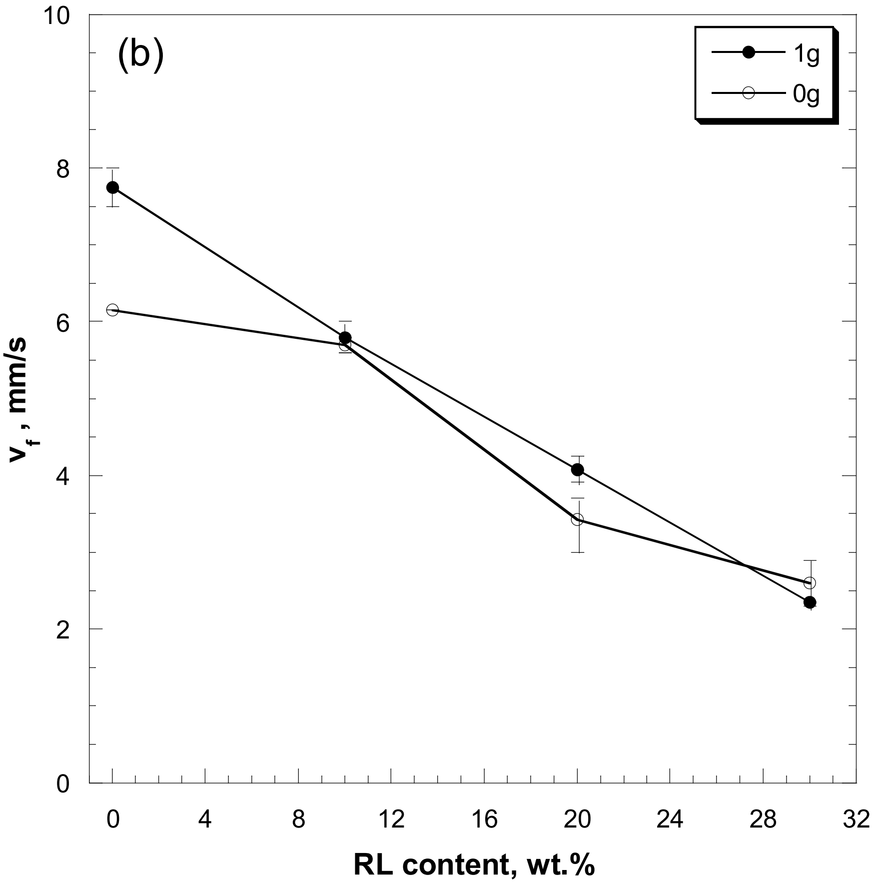


FIGURE 4-15: Effect of gravity level on the average velocity of the self-propagating combustion front for the cases of ($Al/FeTiO_3$) molar ratios equal to 2 (a) and 3 (b).

No significant differences are displayed when comparing the two situations, except for the case of x=3 and y=0, where the reaction front was observed to propagate relatively slower under microgravity conditions. A similar finding was reported in the literature when investigating the self-propagating combustion synthesis of TiB_2-Ti aluminides based composites under terrestrial and low-gravity conditions **(Locci et al., 2006)**.

The only discrepancy observed when x=3 and y=0 can be somehow related to the larger formation of molten/gaseous phases taking place when processing relatively higher exothermic systems, since, under such circumstances, gravity could mainly affect the process. In any case, this effect tends to vanish when processing the mixtures with compositions similar to the optimal ones identified in the framework of the proposed fabrication process (cf. **Figure 4-7**). Moreover, it should be noted that, since gravity level on the Moon is even higher than that encountered during the 20 s parabolic flight interval, the observed slight differences are expected to be further reduced in Lunar environment.

These considerations hold also true when the comparison is extended to combustion temperature, although some problems arose with thermocouple measurements, particularly during parabolic flights experiments, whose signals were disturbed when the more exothermic systems are reacted.

Analogous outcomes come also from the compositional point of view and weight loss. In fact, the same phases with similar content were found when characterizing products obtained either under terrestrial or microgravity conditions.

Figure 4-16 shows the micrograph related to the SHSed product obtained under low-gravity conditionswhen setting x=2 and y=0 in reaction (1).A microstructure very similar to that related to the analogous product resulting when performing the reaction under terrestrial conditions (cf. **Figure 4-6**) is obtained.

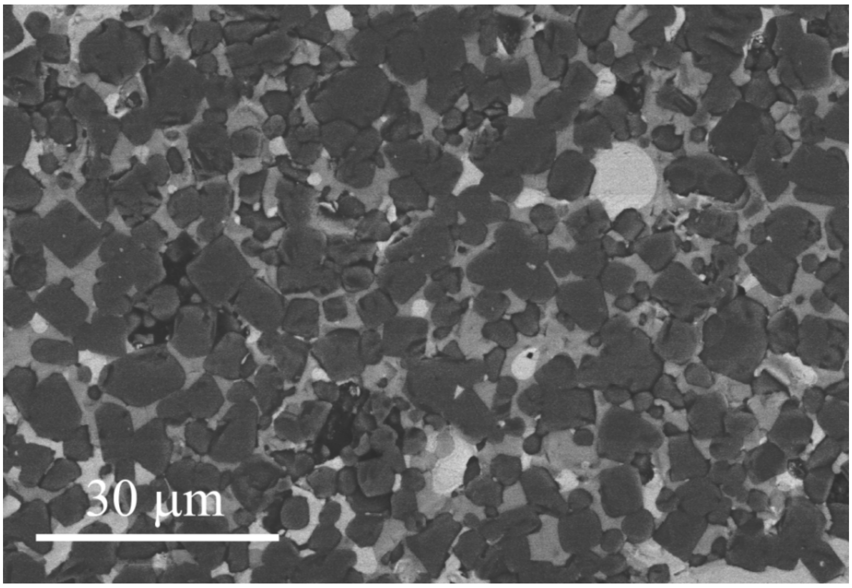


FIGURE 4-16: SEM microstructure of the S_x2_R_L0_P25_0g SHSed end-products.

This holds also true when the comparison is extended to systems involving Lunar regolith in the starting mixture.

On the basis of the considerations previously made, the effect of gravity plays a marginal role for the SHS systems taken into account in this work, in particular when processing the relatively low exothermic mixtures, which are, on the other hand, the most interesting from the ISRU point of view.

4.3.6 Concluding remarks

The recently patented process based on the exploitation of the self-propagating thermite-type reduction of ilmenite for ISRU and ISFR applications in Lunar environment is systematically investigated in this work. Specifically, the dependence of the most important processing parameters, particularly the composition of the starting mixture, evacuation level, and gravity conditions, on SHS process behaviour and product characteristics is examined.

Regarding the characteristics of the mixture to be reacted, an important role is played by the choice of the reducing agent, namely magnesium or aluminum. Although, as pointed out in a recent paper **(White et al., 2011)**, mixtures containing magnesium display, as compared to those involving aluminum as reductant, a relatively higher self-propagating character because their superior adiabatic temperature, it is shown in this work that the extremely high volatility of the first metal makes the process very difficult to control and the resulting products tend to disintegrate during SHS evolution even at relatively mild evacuation levels. Consequently, the self-propagating aluminothermic reduction of ilmenite was considered as the base SHS reaction of the fabrication process taken into account in this work.

Since, according to the proposed fabrication process, Lunar regolith has to be preliminarily enriched in ilmenite before being reacted with Al, another relevant aspect relates to the identification of the optimal mixture composition able to guarantee the self-propagating behavior in the resulting system while reducing the expenses for the enrichment treatment.

In this regard, it is observed that mixtures with the Al/$FeTiO_3$ molar ratio less than 0.9 do not exhibit a SHS behavior and, when this threshold value is set, no additional simulant is allowed to be added to the mixture for maintaining the self-propagating character. However, as the amount the reducing metal in the mixture is gradually increased, the SHS process proceeded faster and the measured combustion temperatures become higher as a consequence of the increased system exothermicity. Correspondingly, in the framework of ISRU applications, the amount of regolith to be combined to $FeTiO_3$ and Al reactants could be gradually augmented thus allowing us to identify the optimal mixture composition at the various Al/$FeTiO_3$ molar ratios. Specifically, the minimum amount of Al required by the system for self-propgating increases from 13.5 wt.%, for the case of regolith consisting of pure ilmenite, to 23.5 wt.%, needed when the starting mixture contained 32.5 wt.% of simulant. In particular, the latter condition simulates a reacting system consisting of Al with an enriched Lunar soil containing about 62 wt.% of ilmenite. It should be noted that the introduction of the enrichment step leads to a significant decrease in the amount of Al needed by the process as compared to that (33 wt.%) utilized by **Faierson et al. (2010a).**

Regarding end-product composition, Al_2O_3, Fe, and Ti along with, depending upon the Al/$FeTiO_3$ ratio considered, various Ti oxides, are formed in absence of regolith in the initial mixture. The occurrence of possible global reactions is postulated for justifying the formation of these phases.

On the other hand, a very complex composite ceramic-metal material also consisting of, besides the species mentioned above, additional mixed oxides, such as $MgAl_2O_4$, $Ca(Al,Fe)_{12}O_{19}$, $Ca_2(Al,Fe)_2O_5$ and $CaAl_4O_7$, were produced by SHS when Lunar regolith was present in the starting mixture.

Compressive strength is in the range of 25.8-27.2 MPa, thus showing a significant improvement from this point of view as compared to materials produced from the direct thermite reaction of Al with Lunar regolith simulant (10-18 MPa). This outcome is likely associated to the most favorable reaction conditions encountered in our study due to the presence of a superior ilmenite percentage in the initial mixture. Indeed, the corresponding increase in the exothermicity of the reacting system promotes the interaction among reactant particles towards the obtainment of strongly sintered materials.

As far as the effect of vacuum conditions present inside the combustion chamber are concerned, it is found that the SHS process dynamics and product characteristics change only slightly when the pressure level is decreased from 760 down to about 10 Torr. However, the consequences of the enhanced Al vaporization during the process, i.e. sample weight loss, temperature increase and front velocity decrease, becomes significant when further evacuating the system. Thus, in view of the possible exploitation of this fabrication process on the Moon, the synthesis reaction should be conducted in a closed environment at a slight overpressure (few Torr) as compared to that (10^{-12} Torr) present on Lunar soil.

Finally, the results obtained during parabolic flight experiments performed to verify the possible effects caused by the change in gravity when passing from Earth to Moon conditions reveal that neither SHS process dynamics nor product characteristics are correspondingly influenced in relevant manner.

All the outcomes reported and discussed in this work allows us to assess that the optimized results obtained under terrestrial conditions are still valid for *in-situ* applications in Lunar environment.

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