

OVERVIEW OF METHODS FOR EXTRATERRESTRIAL MATERIALS PROCESSING

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Abstract

A brief survey of processing systems suitable for conversion of lunar soil fractions to refined industrial feedstocks are given. Description of a "baseline" process using hydrochemical or metallurgical separation of compounds of major and minor elements using HF acid leaching as the initial step is presented. Rough engineering parameters including power and heat rejection requirements, potential loss of earth supplied reagents during recycling, and mass: output ratios of equipment, reagent inventory, and associated power and radiator facilities are described. Minimal practical scales for such systems and manpower requirements are discussed.

INTRODUCTION

The high costs and engineering difficulties associated with transporting appreciable mass from the earth's surface to earth orbit or deep space have prompted a number of prior studies on the feasibility and techniques applicable to the use of extraterrestrial materials and in particular lunar materials to supply feedstocks for a variety of industrial activities¹. The evolution of space activities can be expected to lead to a progressive increase in the scale of engineering projects with quasipermanent or permanent manned stations in orbit and/or the lunar surface. The benefit:cost ratio of such activity will in large measure depend on the ability to reduce the materials or mass fraction of capital and expendable requirements which must be lifted from earth.

A lunar materials industry, in common with its counterpart on earth, may anticipate commercial use of both native mineral products (raw or beneficiated) and processed or refined materials (metals, oxides, etc.) for various applications, with price/performance criteria determining use patterns. Modified natural products obtained by controlled additions of refined materials may also constitute an important class of materials with a cost intermediate between natural and refined materials.

The input compositional limitations of a lunar materials industry will be constrained by the distribution and composition of various lunar soils and rocks and their respective mineral or amorphous (glassy) fractions. For natural products, the output compositional limitations will be determined by the efficiency of various physical beneficiation methods such as magnetic, electrostatic or thermal separation, while for refined products, the output compounds will depend on the specific chemical transformations incorporated in the processing or refining cycles adopted.

Materials processing in space

A study is underway at the Lunar and Planetary Institute (Houston) concerning both the processing

of lunar materials and space manufacturing, in which we consider the following questions:

- What resources can be mined and recovered from the moon?
- What ranges of industrial feedstock can be provided from lunar materials?
- What specific schemes can be identified for physical and chemical processing of lunar materials?
- Can a bootstrap operation be established?

Table I shows the composition of the two major constituents of the mare and highlands regions of the moon². Meteoritic bombardment has tended to homogenize the distribution of minerals in these two regions to great depths. There are no aqueous processes operating on the moon to concentrate minerals or elements. Thus we expect to work with the dust and surface rocks of the moon, rather than look for deep veins of minerals. It is evident that the chemical/metallurgical industry in space will be substantially different from that on earth, due to scarcity of key elements such as H, C, Na, Cl, etc.

Table II shows elements that are potentially recoverable from the moon. (The designations "major," "minor," and "trace" are ours.) The light trace-elements are mostly due to solar wind bombardment of the lunar surface. Alpha radiation, due to radioactive decay, is responsible for some helium, while impacts of carbonaceous meteorites are responsible for some of the carbon that is present.

(Native products)

Natural mineral products may be obtained from either raw or beneficiated lunar soils or rocks. Native lunar soils may be sintered or fused to obtain a variety of ceramic, cast basalt, and dark-glass products.

Using physical beneficiation methods, one may anticipate recovering specific mineral fractions of pyroxenes, plagioclase, olivine or ilmenite of compositions shown in Table I with admixtures of up to 10% or higher of residual mineral or glassy material. In addition, magnetic separation of lunar soils can be expected to yield from 0.1 to 0.5 wt % of free iron admixed with some nickel-iron alloy. This probably represents the simplest method of obtaining structural metals.

Trace minerals such as spinels, troilite (FeS) and various glasses may also be recoverable by physical methods, while thermal desorption of fine soil particles may permit recovery of light trace elements.

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(Refined products)

The major elements can be recovered using hydrochemical, pyrochemical, electrochemical or physical processes. This can be performed in orbit or on the moon. The chemical plant would also have to be responsible for the recycling of nonlunar materials. The minor elements could either be co-recovered from the major-element processing or be obtained by separate means. In the latter case, the processing could only be performed on the moon, as it would be uneconomical to ship large quantities of soil into space solely for the purpose of obtaining minor constituents. An exception may be possible for those elements such as Cr, P and S which tend to concentrate in trace mineral fractions if the latter can be efficiently concentrated.

While the overall abundances of many of the trace elements on the moon do not greatly differ from those on earth, the absence of known concentrated deposits (ore bodies) of such elements makes prospects for their efficient recovery rather dim. Of course, one may still bring critical materials from the earth in modest amounts. Also, note that the major lunar elements constitute the preponderant mass of mineral elements used in earth industry (excepting air, water and fuels).

Table III shows a list of useful products, with examples of what could be made at a space manufacturing-facility, primarily from lunar materials. Although not listed, water would be made from oxygen obtained from lunar materials and hydrogen brought from earth. (Hydrogen is also a trace element on the moon, but even though its weight abundance may typically range between 50-100 ppm, its atomic abundance may be 1% that of silicon. If extractable, this hydrogen could be used to produce the water needed to replace that lost in process recycling - since no recycling process is 100% efficient.)

The structural metals listed in Table III (Al, Fe, Mg, and Ti) will have to be alloyed in order to develop useful mechanical properties. Table II shows that several elements (e.g., Si, Cr, Mn) used in forming commercial alloys of the structural metals are potentially recoverable from the moon. In addition, there is "neutral" iron on the moon that also contains nickel and some cobalt, which could possibly be recovered. Finally, if enough carbon were recoverable from the trace amounts present on the moon (or brought from earth, or possibly obtained from a carbonaceous asteroid), and small amounts of other key alloying elements were imported from earth, one could produce many ferrous and non-ferrous alloys that are commonly used today.

In the case of steels, the more important alloying elements not readily available on the moon are C, Ni, Mo, W, V, and Nb (Cb). The physical properties of several commercial alloys containing these elements are generally similar to alloys in which such elements are absent but which instead contain lunar-indigenous elements. (The properties compared included tensile strength, yield strength, hardness, and elongation.) Therefore, for use as structural metals in space, it is possible to produce alloys possessing a broad range of properties (as commonly required on

earth) by alloying with carbon, lunar-indigenous elements, and/or minor amounts of lunar-deficient elements (LDE).

Several commercial aluminum alloys can be made from lunar-indigenous materials. However, higher strengths, approaching those of the strongest aluminum alloys made on earth, can only be obtained by alloying with small amounts of lunar-deficient elements, particularly Zn.

Only a few commercial alloys of magnesium and titanium can be formed solely from elements recoverable from the moon; but here again, as in the cases of steel and aluminum, significant improvements in properties can be obtained by alloying with minor amounts of lunar-deficient elements. The strongest magnesium alloys will require such lunar-deficient elements as Zn, while the strongest titanium alloys will need Mo.

It is evident that the structural metals to be manufactured in space will consist of alloys that are already in use, are well-characterized, and can furnish almost any desired property currently available. Nonmetallic materials similarly may be made solely from lunar sources, or modified with additions of lunar-deficient elements.

Produce-mix options depend on the type of raw material used and the nature and quantities of finished products required for specific applications. Table IV shows ranges of materials outputs available by varying the mineral input and process conditions. Figure 1 illustrates ratios of specific element to total metal equivalents and silica:oxygen equivalents for representative lunar minerals. The moon contains large quantities of a variety of minerals, so that the type of industry that might be attempted in space can be chosen after examining the various options available, rather than its being limited by any specific method or process for converting lunar material.

In building a large space manufacturing-facility via bootstrap operations:

1. Some materials almost certainly would have to be brought from earth.
2. The extent of additional structures that could be processed and manufactured in space from lunar materials would depend more critically on fabrication limitations than materials availability.
3. Versatility and properties would demand substantial use of steels, rather than aluminum or magnesium, as structural and magnetic metals and in tooling and manufacturing equipment.
4. Reprocessing and recycling carbon to form baked carbon and graphite products would be difficult in space. If possible, substitutes for such products would be highly desirable.

CHEMICAL PLANT DESIGN

Process constraints

A successful orbital (or lunar surface) materials processing plant must operate with several constraints which rarely concern industrial plants operating on earth. These include:

1. Lack of virtually inexhaustible supplies of air and water.
2. Lack of unlimited heat sinks offered by (1).
3. Lack of plentiful fuel supplies: coal, oil, electric, gas, etc.
4. Lack of expendable oxidizing and reducing agents.
5. Lack of expendable acids and bases (except CaO).
6. Lack of key chemicals: ammonia, salt, chlorine, caustic, soda ash, carbon dioxide, sulfuric and phosphoric acids, carbon and graphite and organics.
7. Lack of ordinary solvents.
8. Lack of unlimited inertia in foundations or equipment (except on lunar surface).
9. Lack of support vendors.

Some factors that must be considered in designing a chemical plant in space are shown in Table V. A chemical plant for extraterrestrial materials processing may be expected to use equipment very similar to that employed in earth-based plants. Because of the importance of minimal mass of items to be shipped from earth, most apparatus will be constructed of materials of high specific strength (strength/weight ratio), perhaps using thin linings of corrosion-resistant materials (e.g., even gold).

Equipment must be compatible with the process constraints mentioned earlier, and with the special space environmental factors encountered during transport, assembly and operation. These include an unlimited vacuum sink, an adjustable level of artificial gravity (except on the lunar surface), provision for radiative dissipation of process heat loads, and recycling of lunar-deficient elements used as reagents, solvents or catalysts.

In space, the most practical source of energy is the sun. Solar cell arrays or large solar mirrors (with aluminized surfaces) would be used to concentrate the sunlight and supply electrical and thermal energy to the space manufacturing-facility.

Several different processes for extracting the major elements of lunar soil have been proposed. These have included reagentless processes such as direct electrolysis of raw or beneficiated lunar soils (molten silicates), and magnetic recovery of neutral iron; anhydrous high-temperature processes such as carbo- and silico-thermic reduction and carbochlorination, and lower-temperature hydrochemical processes such as acidic and basic leaching. (A discussion of some specific processes will appear later.)

Any needed reagents that contain lunar-deficient elements (LDE) must be removed with high efficiency from the output streams of the processing plant and recirculated or regenerated, with

efficiencies approaching or exceeding 99%. This is necessary to avoid the necessity of massive earth-lift.

The requirement of high recycle efficiency for LDE has a corollary in that the plant's products must include only the chemical elements present in the feedstock. Since the only nonmetallic elements present in significant quantities from various lunar raw materials are silicon and oxygen, the output streams must necessarily be limited to elements, alloys, silicides, and simple and complex oxides.

The selection of a specific process must await the establishment of criteria for process evaluation, and the formulation of figures of merit to allow comparative "ratings" of alternative systems. Much of the information necessary to evaluate these processes sufficiently to permit rational selection must be obtained by further literature searches and experimental investigations.

Of course, the prime consideration in evaluating space processing and manufacturing systems must center on the cost of producing items in orbital locations vs. the cost of earth-based manufacture and launch into orbit. In such comparisons, it is essential that functional substitutions be considered, since some items such as organics, fiber-reinforced resins, beryllium products, copper, silver, refractory and precious metals, plus materials having appreciable water content, would be difficult to produce from lunar materials. Fortunately, acceptable substitutes exist for any of those substances that would be needed in substantial amounts.

Since the principal motivation for considering orbital or lunar industrialization is to lower earth-launch costs (> \$100/kg) for massive space projects, it is essential that the mass of capital equipment, expendables, reagent inventory and support facilities initially lifted from earth be far exceeded by the annual output mass of such operations. Analysis to date of the materials-processing portion of such operations shows that this requirement is readily met.

The overriding importance of minimal mass makes it imperative that input materials and reagents move expeditiously through the sequence of processing steps without substantial delays and that certain features should probably be avoided or minimized, if possible, including:

1. Steps that require long completion times.
2. Steps in which the input material is present in low concentration.
3. Mass transport of volatiles at very low pressures.
4. Phase separations from viscous suspensions.
5. Reactions with low conversion per pass.
6. Reactions involving handling or storage of large volumes of gas.
7. Reactions involving large transfers of heat, using fluid/vapor heat exchangers without phase change.

8. Processes that reject large amounts of process heat at low temperatures (below 200-300°C).

9. Processes for which suitable structural materials do not offer reasonable service lives.

Other criteria for process evaluation include reliability, manpower requirements, potential hazards to onsite personnel, adaptability in processing scrap materials, and ease of repair in case of malfunction. Corrosion of parts that can only be replaced from earth supply is naturally far more serious than corrosion of lunar-derived parts.

The original cost of chemical process equipment is expected to be dwarfed by orbital lift costs in almost all cases and thus would be of minor importance. If replacement items for many of these units could be fabricated from lunar materials, this would reduce costs in expansion or replacement operations.

Space environmental factors

(Vacuum)

The vacuum-sink availability for space processing facilities may be useful for several types of operations. The most generally useful would be the ability to employ refractories and structural materials that are normally sensitive to oxidation, at higher temperatures than would otherwise be possible (except inside vacuum furnaces). Thus, ordinary steels could be used for retorts in metals reductions; and such materials as titanium and refractory metals, carbon and carbides, boron nitride and other non-oxide refractories could be used for structural and insulation purposes without danger of excessive oxidation. This should permit improved multilayer radiation-shield insulations for extremely-high-temperature processes (although sublimation may limit the utility of such systems for certain applications).

On the other hand, the use of space vacuum in separation techniques may have very limited application, since the escape of volatiles, particularly water vapor, could rarely be tolerated.

Notwithstanding the availability of vacuum, most of the processing facilities should probably be located in a large container that has an atmosphere and temperature compatible with human activity. This would permit easier inspection, maintenance and operation.

(Gravity)

The reduced gravitational attraction at lunar-based plants — or the adjustable centrifugal forces for simulated gravity in orbital plants — will allow some mass savings in support structures for process equipment. It seems likely that most of the chemical unit-operations would not operate satisfactorily under conditions of weightlessness, since all mass-transfer operations, except for introduction of pure gases into a vessel, would be unnecessarily complicated by absence of a gravitational effect. Fixed-volume storage tanks or reactors for solids, liquids or slurries would be difficult to load or unload, and such operations

as filtration, distillation, countercurrent extraction or flow, and so on, would be rendered difficult if not impossible.

The most likely uses for weightless processing would be for heating corrosive reaction masses by radiation or induction, using gas-jet or electromagnetic repulsion to prevent contact with the walls of a chamber.

Most elements of an orbital processing system that are relatively safe could likely be located in a large (but possibly segmented) pressure vessel slowly rotated to provide artificial gravity.

(Heat sink)

The unavailability of massive, external, air or water heat-sinks makes management of process waste-heat especially important. All major heat-rejection loads will ultimately have to be transferred to space radiators. In addition, the poor heat-transfer characteristics of vapor heat-exchange devices make such elements heavy and thus undesirable. Generally, to raise or lower the temperature of a gas stream it will be preferable to adiabatically compress or expand the gas, rather than use wall- or tube-type heat exchangers. Similarly, in distillation operations it will be advantageous to use the heat of condensation to drive the boiler, after heat-pumping it up to a suitable temperature by adiabatic compression. The mass penalty for additional pumping power will usually be far lower than for other alternatives in the disposition or transfer of process heat.

Unavoidable low- or medium-temperature heat loads, such as from electrolytic cells, may require heat pumping to higher temperatures to avoid excessive space-radiator masses. A simplified analysis indicates that below some temperature — determined by mass/power ratios of space power systems and mass/area ratios of space radiators — it becomes desirable to heat-pump all heat-rejection loads to such baseline temperatures. Similarly, refrigeration equipment for liquefaction of cryogenics should have heat-rejection temperatures at the same baseline level. Preliminary engineering studies show that minimal heat-rejection temperatures are in the 500 to 600 K range.

Recycling requirements

Most earthbound processing plants have a single principal product (or a few coproducts), whose mass-transformation rate is often substantially exceeded by the conversion rates of the reagents, solvents, air and water flows associated with the operations.

Lunar or orbital plants will generally have to recover, reclaim and recycle normally expendable reagents and solvents, due to the general lack of volatiles (except oxygen) available from lunar sources. The problem is more acute than it first seems, because the rate of cyclic transport of water, steam or various reagents may in some cases amount to 10 to 100 times the rate of lunar "ore" passing through the process. Yet the tolerable loss or attrition in these mass loops must be held *in total* to a small fraction of the production rate

of useful products, since an earth-mass lift requirement for reagent replacement approaching that of plant output obviously could not be cost effective.

While recycling operations may require chemical conversions, such as the separation or splitting of salts to yield acids and alkalis, it is simpler to consider recycling on an elemental basis. Thus, for most systems studied to date, only a very few elements must be monitored closely. As an example, for the HF acid-leach process, only H, F, Na and possibly N must be recycled with high efficiency. Even here, usable amounts of Na and H may be recoverable from the lunar raw material.

Recycling losses will probably be more prevalent when lunar-deficient elements are incorporated in solid phases of negligible vapor pressure. This may create difficulties in the use of processes involving reagents at high temperatures — such as slags or liquid-metal phases that may "lock in" lunar-deficient elements.

Reagent and equipment mass

For solution processes, the mass of the solvent system will generally exceed the mass of lunar input material in a specific vessel (except where solutions of over 50% by weight are practical). A more typical level may be about 5 to 10% by weight of solute. Further, not all of the solute may be transferred per pass during the various separation or extraction steps, so the ratio of solvent to "active solute" mass is normally much greater than unity.

Fortunately, for aqueous solutions, most of the solvent mass need not be transported from the earth, since the oxygen content, which represents 88.8% of the mass of water, is derivable from lunar materials. Even the hydrogen content may be extracted in sufficient quantities to largely (or entirely) replace that lost in the residual moisture content of products.

Now, let us consider the relative magnitude of equipment and reagent mass for the various units needed for a chemical processing plant. Specifically, one would like to know whether the process vessels, tanks, pipes, etc., weigh more or less than their contents. Analysis shows that, for most cases of equipment that contain 10% or more material in condensed phases, the contents may be expected to far outweigh the container (where the latter is constructed of high-specific-strength materials with minimal safe wall-thickness). Conversely, for gases, the container will invariably outweigh the contents. Furthermore, in the case of gases, the ratio of container to content mass is practically independent of pressure.

This finding reiterates the undesirability of processes that require storage or handling of large volumes of gas. In addition, for processes operating primarily in condensed phases, the mass of the processing operation, apart from power and radiator facilities, will probably be dominated by the masses of reagents involved. These masses, in turn, will depend on reaction and process times for the individual steps.

The engineering characterization of any proposed process may be identified by parameters as shown in Table VI. The sizing (volume) of equipment for any segment may be expressed as:

$$V = \frac{\dot{Q}_i \ell}{\rho_i v_i} = \frac{\dot{Q}}{\rho_i} t'$$

where \dot{Q}_i is the mass flowrate of component i (kg/s), ℓ is a characteristic length (meters) of flowpath in the apparatus, ρ_i is the partial density of component i (kg/m³), v_i is a characteristic velocity of the i th component (m/s), and t' is the process time (s).

Each process step is characterized by an equivalent time (h), representing the time required for the passage of sufficient input material to equal the weights of gross or net contents or container for the step in question.

Summation of the appropriate equivalent times therefore yields the total time required for the passage of sufficient input raw-material to equal the gross or net reagent masses, or the structural masses, for the processing system. Additional equivalent times may be derived to account for masses required for mechanical and thermal power sources; for distribution equipment, motors, pumps, compressors; for heat-transfer equipment, space-radiator facilities; and for other necessary support functions. A summary of the equivalent times for a specific process are developed in a later section.

Unit operations

(Materials handling)

Except for storage, these operations are not expected to require substantial masses. Most material can pass through a materials-handling step with velocities of 0.01 to 1 m/s or even higher, so such units would rarely have to handle more than a few minutes' throughput of the operation. Fine grinding using a ball mill or equivalent is somewhat slower, but it is not expected to be necessary for processing of lunar soils. Entrainment of liquids or dust in gas flows may become a problem in lunar gravity or low artificial gravity, but inertial gas or hydrocyclones or other devices may be used to suppress carryover.

(Phase separation)

The actual physical separation of different phases is usually limited by pressure or inertial considerations, such as foaming or entrainment in distillation columns, or sedimentation velocities in centrifugal filters or in centrifuges, although the material process-time may be limited by heat-transfer rates, growth rates of crystallites or precipitates, etc.

Because of the recycle nature of the various materials flow-loops, it may be preferable to shorten process times (even at the expense of recycling larger-than-normal fractions of intermediate flowstreams) to reduce the masses of intermediate stages. However, at the exit stages of the plant, it is important to limit the loss of reagents, especially those containing lunar-deficient elements, so it is necessary to attempt to carry those steps nearly to completion.

As an illustration of the basic problem that might be common to any process that uses water as an intermediate rinse or reagent, we may discuss drying of nonmetallic output streams. Most finely divided metallic oxide or silica solids have an adsorbed or chemisorbed water content that can be removed by application of heat, time and pressure differentials. For many cases in which industrial drying of solids is practiced, the observed drying rate or rate of weight loss is initially nearly constant, but below a certain moisture content, the rate drops and often becomes nearly proportional to the "excess residual water content" or content in excess of the equilibrium level corresponding to the local temperature and pressure³. For such a dependence, drying would continue at a progressively slower rate for an infinitely long time and never reach constant weight. For a practical process, the operation must be terminated at some reasonable time or residual moisture content. One can derive an optimum drying time or moisture content in terms of the minimized total mass of drying equipment and replacement mass to supply hydrogen for water lost. Using typical operating parameters, the optimum residual moisture content may be expected to fall below 0.1%, but one can tolerate mass losses of 5-10 times that level.

Since the same mathematical dependence often occurs for chemical reactions approaching equilibrium, the preceding technique may be employed to calculate optimum process times and convergence (toward equilibrium) for chemical reactors.

(Heating and refrigeration)

Process-heat requirements may be satisfied by primary electrical or solar thermal sources, or indirectly by using steam or other working fluids, or by exchange with other process flowstreams. If processes are to use solar thermal energy, one may anticipate a substantial mass reduction for equivalent power levels. For example, mass reductions by factors of 30 or more may be possible by substituting solar-thermal for solar-electric power.

The coupling of thermal energy into powdered solids is often troublesome, and can rarely be done efficiently by radiation. One would normally prefer to heat such material by exchange with recirculating gases that are heated in an adjacent unit (by solar-furnace, electric-arc, resistance or induction sources). In certain cases, it may be possible to heat the powdered solids by high-frequency dielectric energy, or perhaps by using microwave energy.

(Heat transfer)

In heat exchange in which gas flow in one or both streams plays a part, one would like to operate at very high velocities or Reynold's numbers since the heat transfer coefficients in turbulent flow are roughly proportional to the 0.8 power of velocity or Reynold's number⁴. Heat transfer involving fluids in boiling or condensing flow are much higher than when no phase change is involved, so when liquids must be heated it is advantageous to operate under conditions of solution pressure and heater temperature to produce nucleate boiling at the interface when vapor pressures permit such operating modes.

Refrigeration or cooling operations may be required for process steps or for collecting, separating and storing noncondensable gases. Oxygen storage and hydrogen storage will probably represent the largest power and equipment requirements. Liquefaction of these gases would greatly reduce masses of the storage vessels required to handle them. By subcooling down to the triple point or lower, even further weight reductions are possible⁵.

(Reaction)

The design of reactors is usually dictated by the heat-balance requirements (endothermic or exothermic) and whether internal or external heating or cooling are required. Internally heated or cooled systems would usually be designed in large tubular, cylindrical or spherical vessels, while external heat transfer would usually require a large surface area and at least one short dimension (about 0.2 to 0.5 m). Electrolytic cells usually require a low anode-cathode separation (about 0.1 m or less) to avoid excessive power losses, but the cell may contain multiple anodes and cathodes and thus attain considerable minimum dimensions. However, it is heat-rejection requirements that usually limit the size of electrolytic cells.

SPECIFIC PROCESSES

Previous studies of extraterrestrial materials processing have generated proposed processes ranging from reagentless electrolysis to various high and low temperature thermochemical or electrochemical separations. We have reexamined these systems based on the selection criteria discussed earlier and briefly review their principal features and problems in this section. In addition, we present a description of two hydrochemical processes involving basic or acidic leaching of lunar ore. The latter system which we designate the HF acid leach process seems to offer the best prospects for efficient processing of lunar materials and we have designated it as our "baseline" process for more extended analysis and engineering studies to develop models for space industrialization.

Electrolysis of molten silicates

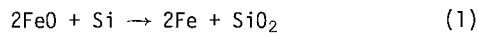
Limited investigations of direct electrolysis of molten silicates of compositions similar to lunar basalts have been performed⁶. The high melting-points and viscosities of molten silicates have created problems and prompted studies of various fluxing additions to the melt. This modification, of course, negates the "reagentless" advantage of the direct electrolysis route and requires consideration of extraction and recycling of fluxing reagents.

The chief objections (or problems awaiting solution) are the corrosion or durability of anodes used for oxygen recovery, and the purification and separation of cathodic reduction products (which are likely to consist of iron-aluminum-silicon alloys plus minor amounts of additional impurities).

Carbothermic/silicothermic reduction

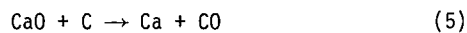
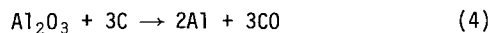
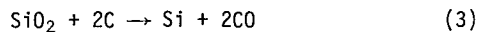
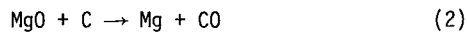
One of the first serious attempts to define a process option was performed by Phinney *et al.*⁷,

at the 1976 NASA-Ames Summer Study, in which silicothermic and carbothermic reduction of bulk lunar soil was discussed. After crushing the raw material, and magnetically separating the ferrous from the nonferrous fractions, reduction could commence. Silicon will reduce iron at 1,300°C, as shown by Eq. (1):



The products can be separated by centrifugation.

The iron-free silicates would be reduced by carbon at 2,300°C, as shown by Eq. (2-5):



By this process, it would be expected that aluminum and silicon would form a melt, while the other reduced metals, including the major impurities Ti, Mn and Cr, would be removed as vapors. However, this reaction scheme is much more complicated. At 2,300°C, condensed compounds, such as SiO, Al₄C₃, and Al₄O₄C are present, along with gases such as Al₂O, SiO, Al, and Si.

The pressures of Al₂O and Al are so high that liquid aluminum cannot be formed at normal operating pressures. Perhaps the greatest defect of the carbothermic reduction process is that although the winning of aluminum on earth via such a process was envisaged as early as the 1940s⁸, no plant for producing aluminum by this method has proved practical.

Carbo-chlorination process

At the 1977 NASA-Ames Summer Study, Rao *et al.*⁹ decided quite early that carbothermic reduction would probably be impractical for space processing. They opted for carbo-chlorination of lunar anorthite, CaAl₂Si₂O₈, and lunar ilmenite, FeTiO₃, which could be beneficiated from lunar soil¹⁰. The desired products are aluminum, iron, silicon (or silica), and titanium.

During our subsequent study at the Lunar and Planetary Institute, it became obvious that carbo-chlorination would create a major plant-size problem. The recycling of chlorine and carbon would require facilities much larger than the basic processing plant. One of the major advantages of carbo-chlorination is that it would require only a minimum of hydrometallurgical operations. Water would be needed, however, for hydrolysis, chlorine regeneration and possibly as a coolant for the system. In order to minimize the size of the heat-rejection radiators, large amounts of heat energy would have to be raised (heat pumped) to about 280°C, to achieve a mass efficient system.

These results led us to believe that processes that rejected less heat at low temperatures and made use of hydrometallurgical operations would tend to be more useful options for space processing.

NaOH basic-leach process

A review of the literature¹¹⁻¹⁴ indicates that anorthite can be decomposed with NaOH in an autoclave; and subsequent treatment of those products with more base can eventually yield alumina and calcium silicate — the latter could be used to make glass or could be hydrolyzed to yield lime and silica. For both basic and acidic leaching, sodium present in lunar soil can probably make up for any sodium lost during recycling. In this process, calcium impurities in the recycled NaOH would not present a problem, inasmuch as base, and not pure NaOH, is needed.

HF acid-leach process

This process uses low-temperature hydrochemical (hydrometallurgical) steps to separate the silica content of the lunar raw material from the other metallic oxides by conversion to fluorides and fluosilicates. This is followed by vaporization of the silica as SiF₄, and separation of the calcium and the structural metals (Al, Fe, Mg, Ti) by a variety of solution, precipitation, ion exchange, or electrolytic steps. Generalized process equations are given in Table VII. Iron may easily be recovered from solutions by electro-winning, but the remaining metals, except Mg, are preferably recovered by sodium reduction of the corresponding fluorides, fluosilicates or fluo-aluminates. Magnesium may be made by silicon reduction of MgO.

Sodium for the reduction of the metals and silicon can be conveniently obtained by a slight modification of the Castner cell, which at one time was the major commercial device for producing sodium. The Castner cell uses the electrolysis of molten NaOH to produce Na, O₂ and H₂. For lunar operations, the hydrogen is an undesirable byproduct, which can be largely eliminated by using a diaphragm cell and vacuum-drying the anolyte to remove the water formed by discharge of OH⁻ ions.

Metal oxides and silica are obtained, where desired, by hydrolysis of the corresponding fluorides or fluosilicates with steam (or with NH₃, if desired, for SiO₂) or by ion exchange (or permeation) methods. Detailed analyses of the options available for these separations remain to be completed.

A flowsheet for the HF acid-leach process is shown in Fig. 2.

Of the processes studied to date, the HF acid-leach one appears to have the best potential for minimal operating mass, ease of element separations to high purity, flexibility, and favorable energy and heat-rejection requirements.

A number of details and options remain to be investigated. Many of these specific process steps can be fully defined by straightforward experiments. If any readers are interested in undertaking some of these experiments (many are relatively simple), the authors of this article would be pleased to hear from them.

Separation of the fluoro compounds of the metallic elements by solubilities of fluorides or fluosilicates as a function of pH and F:Si ratio — with or without additional ion-exchange or

electrolytic steps — will require extended literature searches and laboratory investigations. Pyrolytic and hydrolytic behavior of fluorides, fluosilicates and fluotitanates will also require additional research.

Despite these informational gaps, nearly all of the proposed operating steps have been studied on a laboratory scale, and about 75% of the steps have been conducted on a pilot or commercial scale under equivalent or comparable conditions.

(Thermochemistry)

The heat transfer requirements of the HF acid leach process may be derived from existing thermochemical data for the compounds present in the process equations. These may be used to prepare the ΔH vs T map shown in Fig. 3. In this figure the enthalpy changes involved in water transfer — distillation and condensation — have been omitted. The electrolysis heat load represents only the ohmic heat loss of the process step.

The total input power requirement is projected to total 4100 KWH/metric ton. For the plant sizing analysis, this was increased to 7130 KWH/metric ton to allow for various losses.

(Plant sizing)

The techniques of plant sizing and mass estimation developed in the preceding discussion were applied to the HF acid leach process. The results are shown in Table VIII. By summing the equivalent times for containers, net masses of lunar deficient elements and extra inventory and equipment, one obtains a total equivalent time of 81 hrs. If one uses gross instead of net reagent mass, the total becomes 155 hrs. In either event, the plant should be able to process more lunar ore than its total mass each week, or on an annual basis it could supply more than 50 times the earth lift mass of the plant.

(Reagent replacement mass)

The principal lunar deficient elements used in the HF acid leach process are H, F, Na and optionally N. (Sodium is probably not a serious consideration since it is a minor lunar element and frequently occurs at levels exceeding 2.5% of the total metallic equivalents in feldspar fractions from mare soils.) These recycling elements will occur principally as chemically or physically combined water or hydroxyl ion (H) or fluoride ion (F) and as ammonia or ammonium ion (N).

The hydrogen and nitrogen content of vacuum dried, calcined refractory oxides or other compounds can be reduced to almost any desired level given sufficient time and temperature at low pressure although mass efficient operation may not be served by drying to less than 0.1% as discussed earlier. If we assume a conservative residual content of 0.5% H₂O and 0.1% NH₃ for the non-metallic output streams and zero for these impurities in metal outputs, the ratios of reagent replacement mass:input mass for H and N may be expected to fall in the ranges $3.7 - 7.4 \times 10^{-4}$ and $4.1 - 8.2 \times 10^{-4}$ depend on amount of reduced products. The moisture content or dew point of oxygen can be held to insignificant levels.

The residual fluorine level will occur principally as residue from steam hydrolysis of refractory fluorides, and cannot be baked out in a practical manner. Analytical studies¹⁵ suggest that the fluorine content of pyrohydrolyzed fluorides can be reduced to 0.25 to 0.5% without undue extension of the process. Vacuum cycling may possibly lead to lower residual levels. We may anticipate F replacement mass:input mass ratios in the range of $1 - 2 \times 10^{-3}$ and possibly lower with improved vacuum desorption.

Total reagent replacement mass:input mass can probably be held below one part in 300 with further improvements likely. At this rate, the reagent replacement mass requirement would equal the initial net plant mass in 3 to 6 years. It may be noted that replacement mass need not be supplied in elemental, toxic or hazardous forms.

(Minimum scaling)

There is no fundamental reason why the chemical processing facility could not be reduced down to laboratory bench scale. Table VIII indicates a total process time of less than 36 hrs. The longest process time other than electrolysis is 3 hrs. for which the corresponding units would contain 3 kg of lunar ore at an average throughput of 1 kg/hr or 7.13 metric tons/year with an 81% duty cycle. At a very small scale, the mass:throughput and power:throughput ratios may be expected to increase — perhaps by as much as a factor of two.

The concept of bootstrap growth of processing capacity can increase the annual output mass:net plant mass ratio by an amount limited by the reagent requirements for lunar deficient elements. For the HF acid leach process, the LDE net reagent mass represents 28% of the net plant mass, so the annual output:net plant mass ratio could be nearly quadrupled by expanding equipment capacity using lunar materials. Even greater increases may result from process revisions or modifications of operating cycles which can reduce the equivalent times required for LDE reagents.

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High-titanium basalts				
Modal abundance (Vol.%)	Pyroxene	Olivine	Plagioclase	Opagues (mostly ilmenite)
	42.60%	0-10%	15-33%	10-34%
Component (Wt.%)				
SiO ₂	44.1-53.8	29.2-38.6	46.9-53.3	< 1.0
Al ₂ O ₃	0.6- 6.0	-	28.9-34.5	0 - 2.0
TiO ₂	0.7- 6.0	-	-	52.1-74.0
Cr ₂ O ₃	0 - 0.7	0.1- 0.2	-	0.4- 2.2
FeO	8.1-45.8	25.4-28.8	0.3- 1.4	14.9-45.7
MnO	0 - 0.7	0.2- 0.3	-	< 1.0
MgO	1.7-22.8	33.5-36.5	0 - 0.3	0.7- 8.6
CaO	3.7-20.7	0.2- 0.3	14.3-18.6	< 1.0
Na ₂ O	0 - 0.2	-	0.7- 2.7	-
K ₂ O	-	-	0 - 0.4	-
Low Titanium basalts				
Modal abundance (Vol.%)	42-60%	0-36%	17-33%	1-11%
Component (Wt.%)				
SiO ₂	41.2-54.0	33.5-38.1	44.4-48.2	< 1.0
Al ₂ O ₃	0.6-11.9	-	32.0-35.2	0.1- 1.2
TiO ₂	0.2- 3.0	-	-	50.7-53.9
Cr ₂ O ₃	0 - 1.5	0.3- 0.7	-	0.2- 0.8
FeO	13.1-45.5	21.1-47.2	0.4- 2.6	44.1-46.8
MnO	0 - 0.6	0.1- 0.4	-	0.3- 0.5
MgO	0.3-26.3	18.5-39.2	0.1- 1.2	0.1- 2.3
CaO	2.0-16.9	0 - 0.3	16.9-19.2	< 1.0
Na ₂ O	0 - 0.1	-	0.4- 1.3	-
K ₂ O	-	-	0 - 0.3	-
Highlands rocks				
Modal abundance (Vol.%)	5-35%	0-35%	45-95%	0-5%
Component (Wt.%)				
SiO ₂	51.10-55.4	37.70-39.9	44.00-48.0	0 - 0.1
Al ₂ O ₃	1.00- 2.5	0 - 0.1	32.00-36.0	0.80-65.0
TiO ₂	0.45- 1.3	0 - 0.1	0.02- 0.03	0.40-53.0
Cr ₂ O ₃	0.30- 0.7	0 - 0.1	0 - 0.02	0.40- 4.0
FeO	8.20-24.0	13.40-27.3	0.18- 0.34	11.60-36.0
MgO	16.70-30.9	33.40-45.5	0 - 0.18	7.70-20.0
CaO	1.90-16.7	0.20- 0.3	19.00-20.0	0 - 0.6
Na ₂ O	-	-	0.20- 0.6	-
K ₂ O	-	-	0.03- 0.15	-

Table I (LEFT)

Ranges of chemical compositions for the major minerals

Table II Potential availability of lunar elements

Major elements ≥ 1% lunar
O, Si, Al, Ca, Fe, Mg, Ti

Minor elements 0.1 - 1%
Cr, Mn, Na, K, S, P

Trace elements < 0.1%
H, He, C, N plus all others

(Beneficiation may permit concentrating some trace elements into minor or higher range.)

Table III Useful products derivable primarily from lunar sources

STRUCTURAL MATERIALS	
Metals	Steels, aluminum, magnesium, titanium and alloys
Reinforced Metals	Metals above reinforced with silica, steel, alumina or titanium silicide
Glasses	Calcium, magnesium, aluminum, or titanium silicates, fused silica, foamed glasses
Ceramics	Alumina, magnesia, silica, complex oxides, fused basalts
Hydraulic Cements	(Need water)
THERMAL AND SPECIALTY MATERIALS	
Refractory and Hard Materials	Ceramics above plus chromia, titania, titanium silicides
Abrasives	Alumina, garnets, silicon carbide, titanium carbide (limited by C)
Insulation	Ceramics above plus fiberglass, fibrous or powdered ceramics
ELECTRICAL MATERIALS	
Conductors	Aluminum, magnesium, iron, resistance alloys (FeCrAl), silicon
Electrodes	Fe ₃ O ₄ , TiO, graphite (limited by C)
Magnetic Materials	Iron alloys, magnetic ceramics (ferrites, magnetoplumbites)
Electrical Insulation	See glasses, ceramics and thermal insulation
FIBROUS MATERIALS	
	Glass, silica, synthetic mineral wool
	For apparel, paper, filters, etc.
PLASTICS AND ELASTOMERS	
	Silicone resins (limited by C)
SEALANTS, ADHESIVES AND COATINGS	
	Soluble silicates
	Anodized coatings
	On aluminum, magnesium, titanium
	Electroplating
	Chromium, etc.
	Sputtered or vacuum deposited coatings

Table III (cont'd.)

LUBRICANTS, HEAT TRANSFER FLUIDS	
	Sulfides, graphite (limited by C)
	SO ₂ , He
INDUSTRIAL CHEMICALS	
	Detergents, cleansers, solvents, acids, bases
	H ₂ SO ₄ , H ₃ PO ₄ , CaO, NaOH
BIOSUPPORT	
	Oxygen (breathing), 16/18 of water by mass
	SiO ₂ - soil component (including trace nutrients)
	Bioelements O,Ca,C,Fe,Mg,K,P,N,Na,H others

Table IV Product-mix options

Metal/silica ratio		
Equivalents	1:1	Olivine, anorthite, orthosilicates
	0.5:1	Pyroxene, metasilicates
	0:1	Silica
	1:0	Ilmenite, spinel, troilite, etc.
		Neutral iron
Aluminum/iron ratio		
Negative correlation		
Approximate range 5:1 to 1:4 (whole soils)		
Nonstructural-/structural-metal ratio		
Ca:Al	Plagioclase:	~ 1:2
Ca:(Mg+Fe)	Pyroxenes:	1:1 to 0.1:1
	Ilmenite:	0:1
Light-metal/iron ratio		
(Al+Mg):Fe	Similar to Al:Fe	
Silicon/silica ratio		
Reduction requirements		
Demand conditioned on use of photovoltaic systems		
Metal/metal-oxide ratio		
Reduction requirements		
Depends on demand for metals vs. refractories and pigments		
Oxygen/metal ratio		
Depending on ratio of oxygen to the structural metal (and silicon) demand. Oxygen may appear as an unneeded byproduct, or iron and other reductants may be surplus materials		
Reinforced/normal-metal ratio		
Demand dependent on suitability of reinforced metals to replace a variable portion of reinforced resins in structures		

Table V Chemical plant design

-
- Selection of process options
- Special space environmental factors
- Gravity (natural or artificial)
 - Vacuum
 - Heat rejection
 - Recycling of nonlunar-indigenous materials
- Description of unit operations
- Materials handling
 - Phase separations
 - Heat exchange
 - Reactors
 - Energy requirements
 - Heat-rejection requirements
- Sizing factors
- Kinetics limited
 - Heat-transfer limited
 - Momentum limited
-

Table VI Engineering design parameters

Equipment	Capacity	Typical stream velocity, V_f (or characteristic velocity)	Process time	Other
Motors, pumps, compressors (except vacuum)	$\frac{10^3 \text{ kW}}{\text{m}^3}$	10 to 100 m/s	1 s	$\frac{1 \text{ kg}}{\text{kW}}$ or $\frac{\text{t}}{\text{MW}}$
Distillation columns	mass flowrate 1-5 kg/m ² s	1 to 3 m/s (vapor) (entrainment limited)	5-10 s	length: 0.4 - 0.6 m/plate
Sedimentation centrifuges	volumetric flowrate	settling velocity (10 μm particles) 10^{-5} m/s x g typical velocity: 10^{-2} m/s @ 1,000 g	0.5-2 min	power 50-100 $\frac{\text{kW}}{\text{m}^2}$
Rotary kilns	Loading density 0.05 - 0.2 t/m ³	3 to 10 m/h (axial) (0.0033 - 0.0083 m/s)	2-10 hr	rotary power 0.1 - 0.2 $\frac{\text{kW}}{\text{m}^3}$
Ion-exchange columns	0.5-3 equiv. $\frac{\text{kg}(\text{resin})}{\text{kg}(\text{resin})}$	0.2 to 0.5 m/min (0.0033 - 0.0028 m/s)	5-15 min	
Aqueous-systems heat transfer				
Nucleate boiling	15-240 kW/m ²			$h = 2-16$ kW/m ² K $\Delta T = 10-20\text{K}$
Condensation (inside tubes)	30-1,000 kW/m ²	30 to 150 m/s (vapor)		$h = 3-50$ kW/m ² K $\Delta T = 10-20\text{K}$
Electrolytic cells	$i = 10^3 - 10^4$	ion-migration velocity $10^{-7} - 10^{-5}$ m/s	10-50 h	

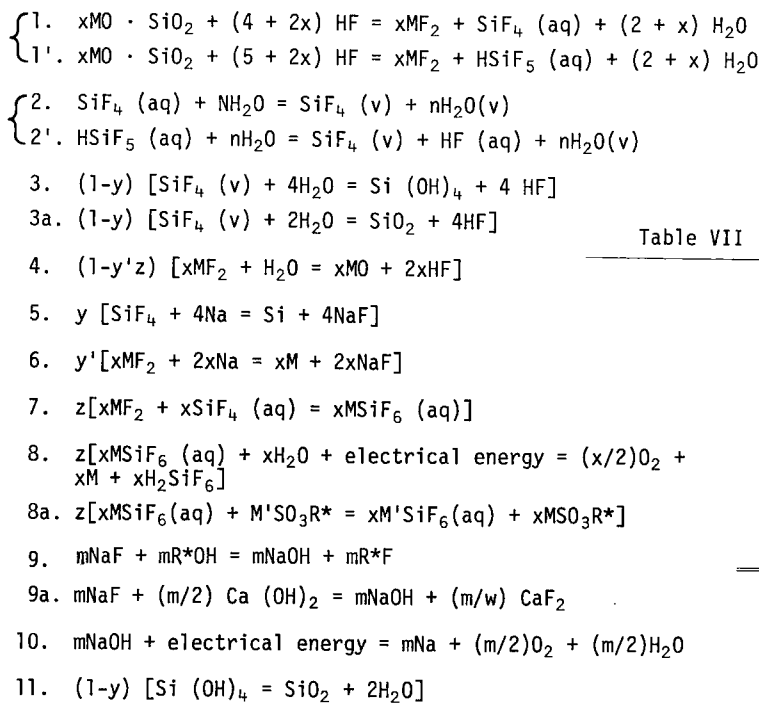


Table VII HF acid leach process equations

R* = ion-exchange
 m = 4y + 2xy'

Table VIII Equipment and reagent masses - process and equivalent times

Step	t	R _m	r _m	R' _m	h ₁ =tR _m	h ₂ =tr _m	h ₃ =tR' _m
	Process Time(hr)	Contents Equiv. input	Mass Ratios Container Equiv. input	Net contents(LDE) Equiv. input	Equivalent Times* (hr) Container	Content	Net(LDE)contents
Acid Leach	.5	.2	.48	7.95	11.1	.24	3.97
Sedim.centrifuge/ Distill	.0167	22.2	28.8	7.95	.371	.48	.133
Hydrolyze	.5	44.9	.96	14.7	22.5	.48	7.36
Sedim. Centrif.	.0167	44.9	42.6	14.7	.75	.71	.207
Distill/ Condense	.00278	7.06	86.4	2.14	.0196	.24	.006
Distill(1/2)	.00278	22.5	86.4	7.36	.0625	.24	.020
Hydrolyze/dry	3.0	3.0	.55	.728	9.0	1.66	2.18
Distill	.00278	7.63	86.4	1.36	.021	.24	.004
Electrolysis	27.5	1.45	.173	.036	40.05	4.75	1.0
Metals reduction	3.0	1.76	.48	.7	5.28	1.43	2.1
Regeneration(est).	.5	5.0	.48	.7	2.5	.24	.35
Misc.	.5	1.0	.4	1.0	.5	.2	.5
Subtotal	35.54				92.15	10.91	17.83
EXTRA MASS		(metric tons @ 4.21 ton/hr input)			equiv. time (hr)		
Reagent Inventory			20			4.7	
Compressors			10			2.4	
Heat Exchangers			10			2.4	
Pipes, Valves			5			1.2	
Electrical			6			1.4	
Structural & misc.			25			5.94	
Radiators (20 MW)			24			5.7	
Elec. Power (30 MW)			120			28.5	
Subtotal			220			52.24	

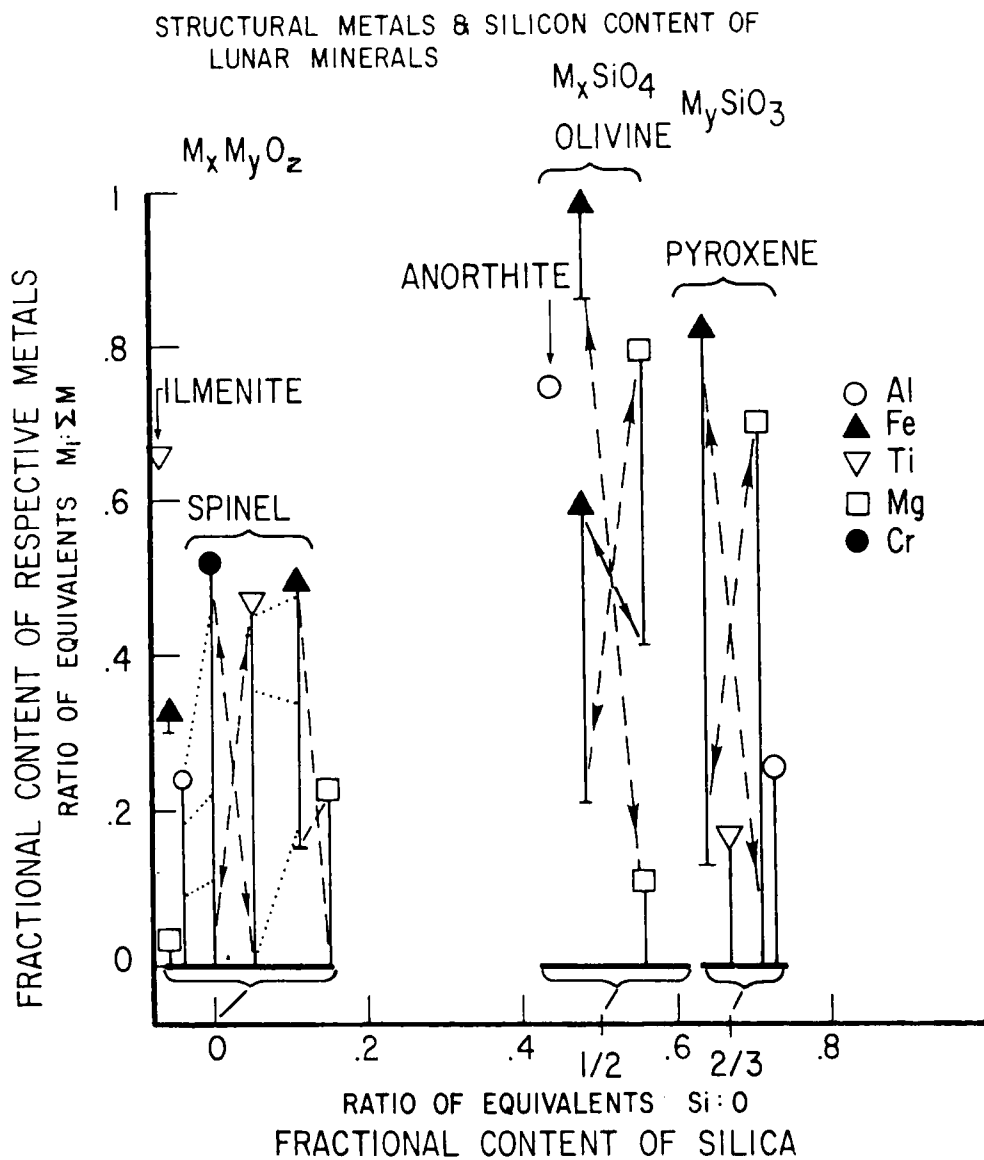
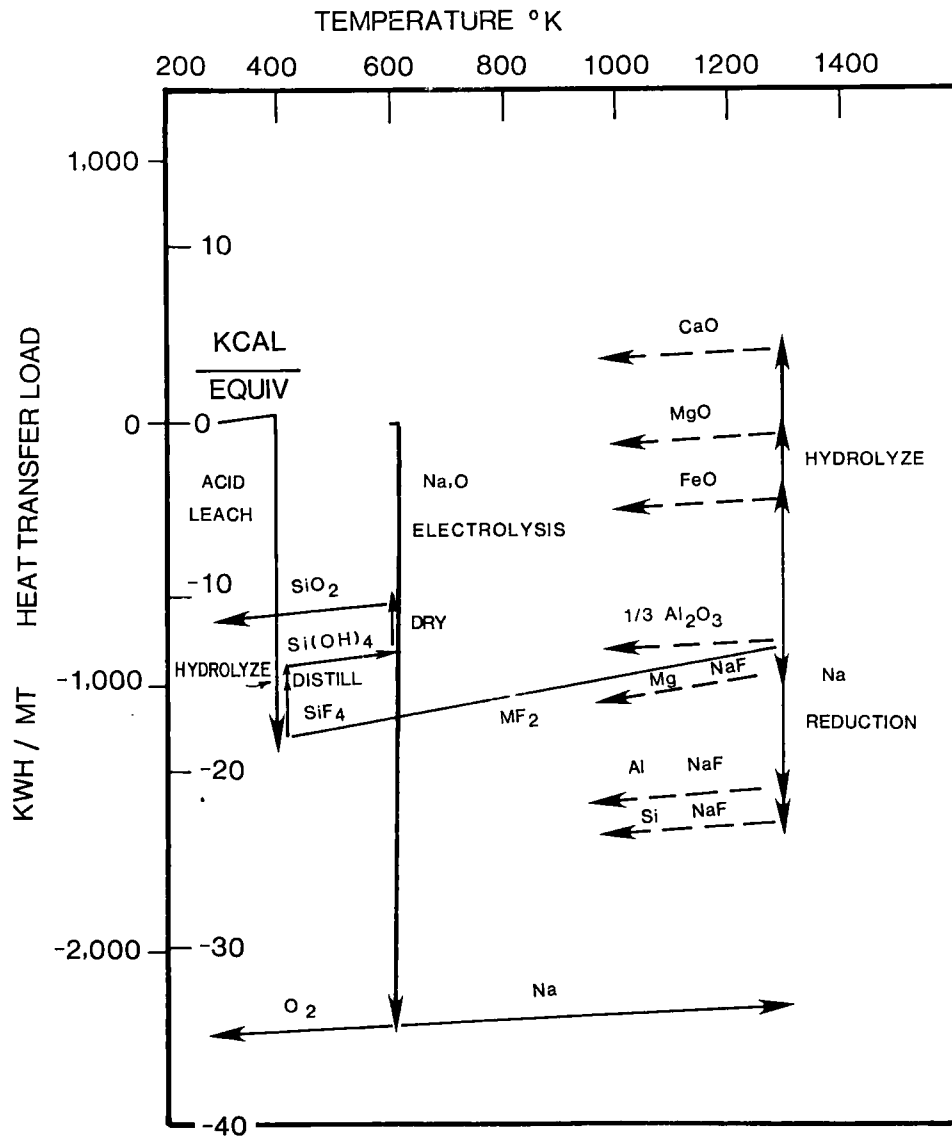


Figure 1.



TEMPERATURE/HEAT LOAD DIAGRAM FOR HF ACID LEACH PROCESS

Figure 3