MSFC-2204

Marshall Space Flight Center

Ceramics for Molten Materials Transfer

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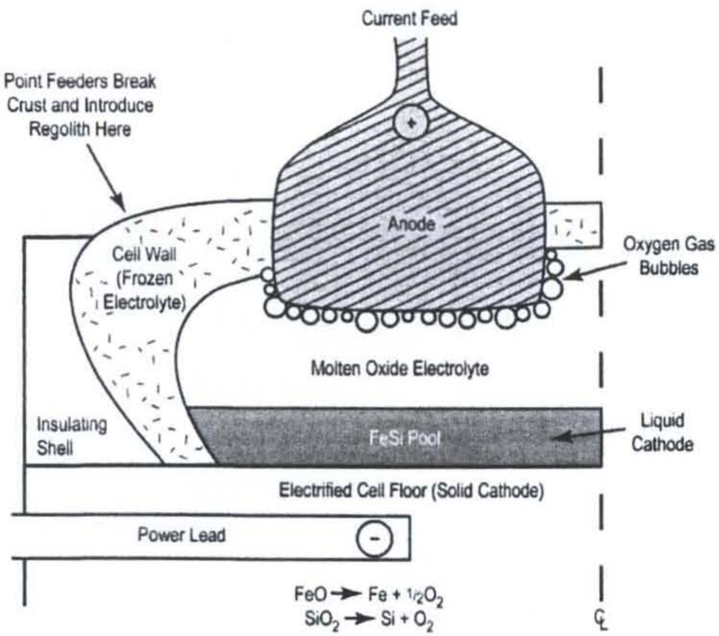
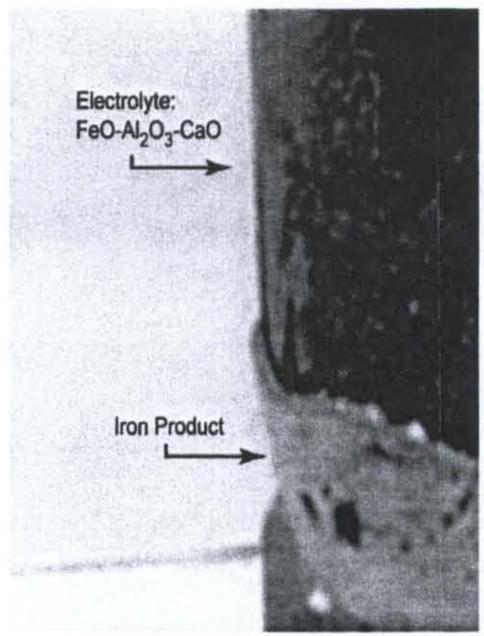
Outline

- Introduction
- Electrowinning cell feeding
- Material removal from the electrowinning cell
  - Removal of gasses
  - Removal of solids
  - Removal of liquids

High Temperature Metal Oxide Electrolytic Cell

- **Liquid oxide bath from regolith**
- **Inert Anode**
- **Conductive Cathode in contact with liquid metal**
- **Selective extraction of elements**
- **Oxygen production**





Products

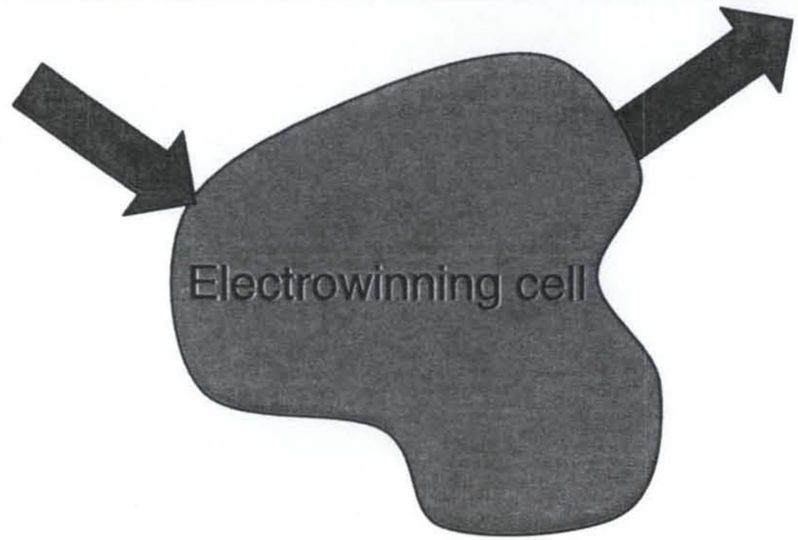
Element	Potential
Fe	-0.44
Si	-0.90
Al	-1.67
Mg	-2.35
Ca	-2.84

Electrolysis is one method to selectively extract metals and silicon

(Donald Sadoway, Massachusetts Institute of Technology, 2004)

Introduction

Gas: inert gas
Solid: charging materials



Gas: oxygen, others?
Liquid: electrolyte, metal
Solid: metal

Working hypothesis:

Anticipated processes and characteristics

Process	Products	Temperature	Process duration
High temp. (HTEW)	Molten metal & alloys, molten oxides, gases	>1400°C	4 - 24hrs
Low temp. (LTEW)	Solid metal & alloys, molten mix of fluorides, chlorides & oxides	~1000°C	?

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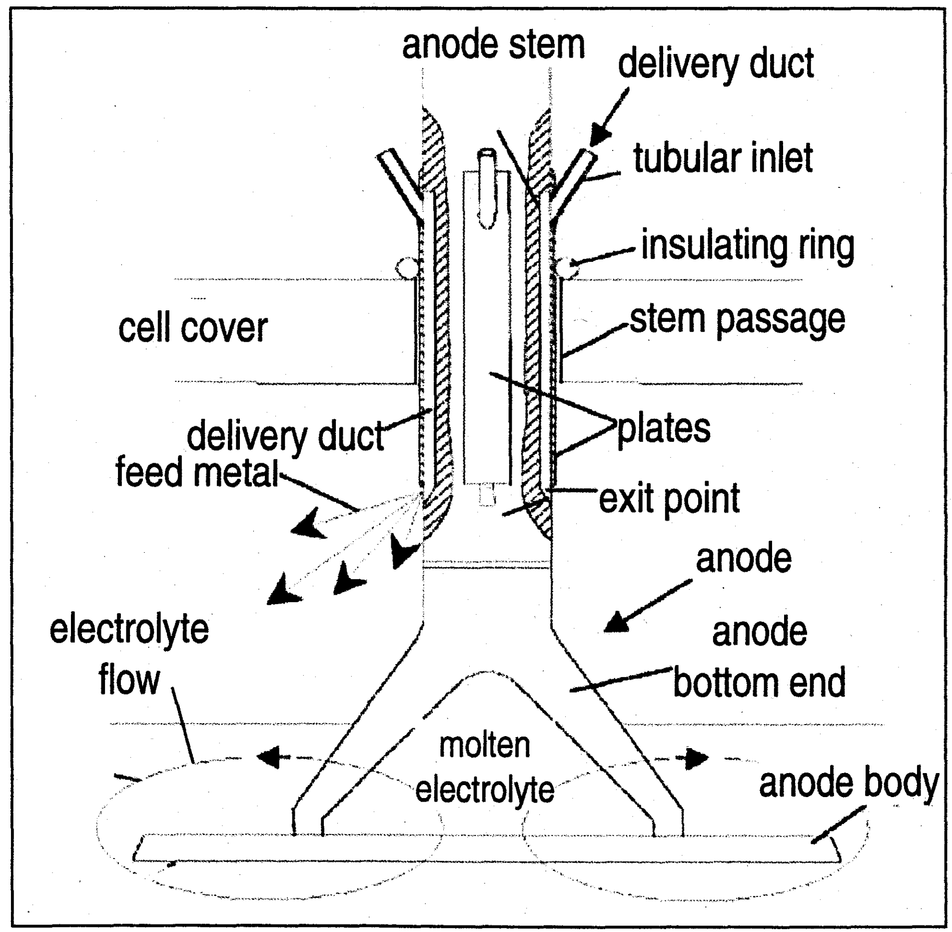
Electrowinning Cell Feeding

Feed device for metal compound

- Description of technology
  - delivery duct delivers metal compound to circulating electrolyte, enhancing dissolution
  - metal compound can be delivered above or under the surface of the electrolyte
- History – 2006 patent
- Application of technology – electrowinning processes with metal-based anodes below 940 °C
- Limitations for application to lunar missions – none apparent

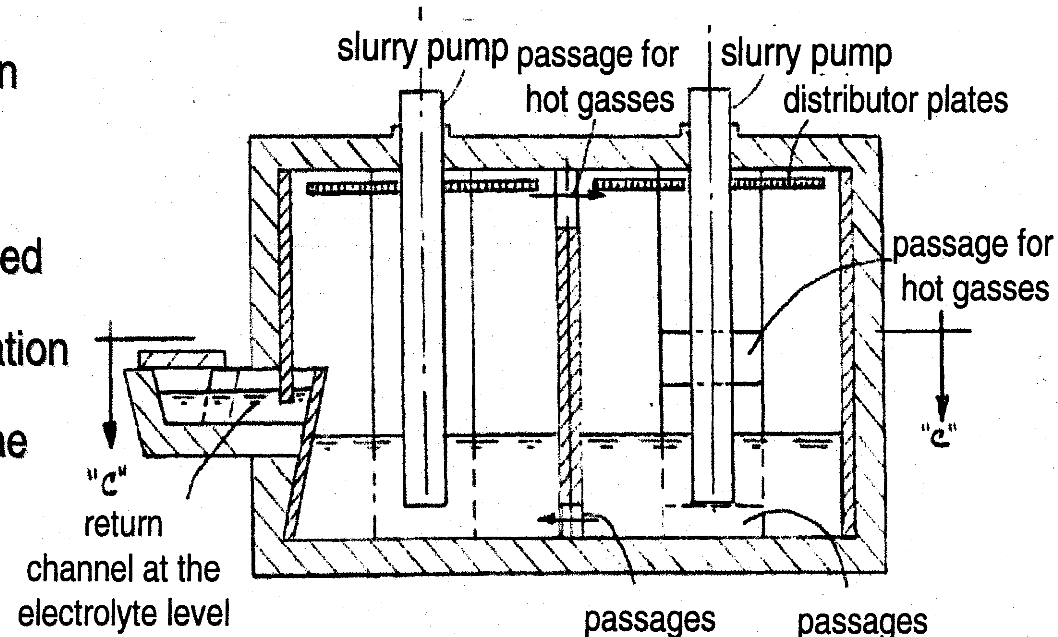


Berclaz G., De Nora V., Electrolytic cell with improved feed device, *World Intellectual Property Org. Patent*, WO 2006/129267 A2 (2006)

Electrowinning Cell Feeding

Feed device for hygroscopic metal compounds

- Description of technology
  - allows the use of hydrated or oxygen containing feed-stock for cells that require freedom from oxygen containing compounds
  - furnace adjacent to cell (see fig.) used to melt and chlorinate feed-stock
  - pumps used to maintain melt circulation in furnace
  - melt pumped through channels to the electrolytic cell; excess electrolyte returned to furnace
- History – 2001 patent
- Application of technology – described for production of Li and Mg
- Limitations for application to lunar missions – irrelevant unless the lunar environment contains free water or oxygen



Furnace for melting solid or hydrated metal compounds

Siviloti O., Method and apparatus for feeding electrolytic cells, *Canadian Patent*, CA 2,340,528 (2001)

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Removal of Gasses

Oxygen removal from containers

- Description of technology
  - flooding of the environment with nitrogen or argon gas
  - oxygen residual ~ 1%
- History – described in patent by Maget et al.
- Application of technology – used in the pharmaceutical industry
- Limitations for application to lunar missions
  - large capital expenditure
  - requires large quantities of nitrogen or argon

- Description of technology
  - limitation of free volume in the cell
  - evolved oxygen pressure use for self-removal
- History – to design
- Application of technology – none known
- Limitations for application to lunar missions – none apparent

Removal of Gasses

Gas Extraction from Closed Cells

- Description of technology
  - removal of gasses particularly oxygen from closed containers
  - apparatus senses the oxygen

FIG. 1 is a schematic side elevation view, partially in section, showing the principal components of the electrochemical oxygen extractor.

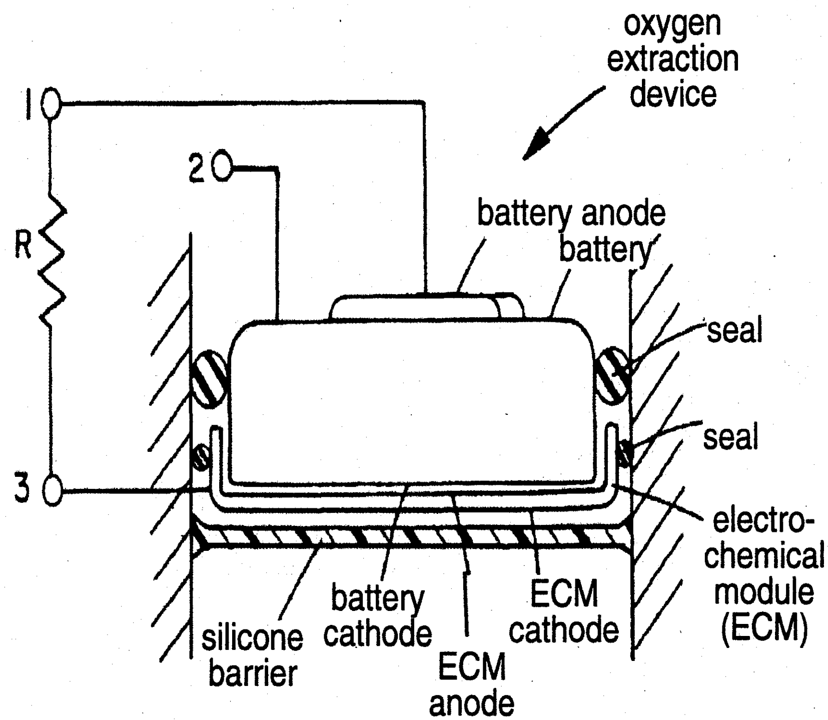
FIG. 2*a* illustrates the configuration for a prior art zinc-air battery operated with oxygen from air, where the air is supplied simultaneously to the battery and the electrochemical cell.

FIG. 2*b* illustrates the configuration of the present invention for a zinc-air battery extracting oxygen from a container, wherein the oxygen flows solely toward the air intake port of the zinc-air battery.

FIG. 3*a* is a schematic diagram showing the electrochemical oxygen extractor in a closed system configuration.

FIG. 3*b* is an equivalent diagram showing the electrochemical oxygen extractor in an open system configuration.

missions
  - some infrequent maintenance may be required
  - need appropriate sensors for high temperature processes

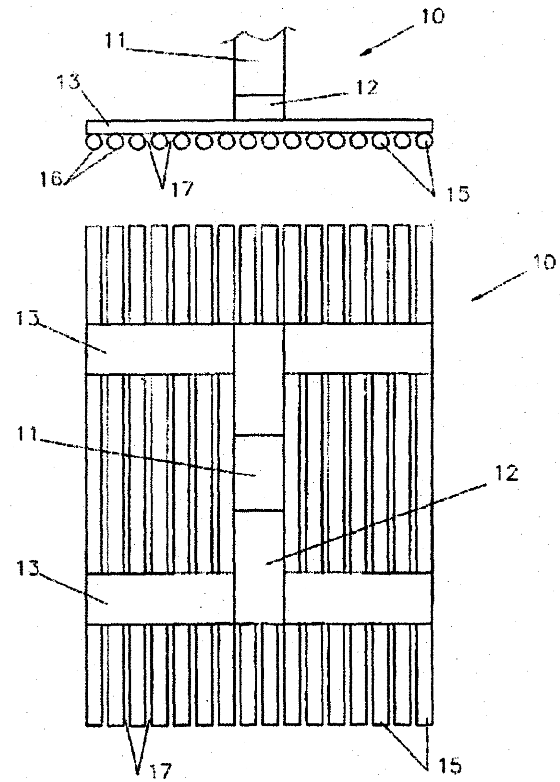


Electrochemical oxygen extractor

Maget H.J.R, Rosati R.J., Gas extraction from closed containers, *U.S. Patent 6,171,368 B1* (2001)

Removal of Gasses

- Description of technology
  - Metal based anode with electrically conductive structure parallel to the cathode
  - Parallel electrically active anode members (see fig.) on which oxygen is evolved during electrolysis
  - Electrolyte is circulated through the gaps driven by the escape of the oxygen
- History – 2003 patent
- Application of technology – described for aluminum electrowinning cell
- Limitations for application to lunar missions – none apparent



Oxygen Extracting Anodes

De Nora, V., Moltech, S.A., Aluminum Electrowinning Cells with Oxygen-Evolving Anodes, *U.S. Patent 6,540,887 B2* (2003)

Material Removal from the Electrowinning Cell

Removal methods for solids and liquids

- removal of solids
  - freezing of the electrolytic cell and removal of solids
  - removal of solid metal sheet from the liquid electrolyte
- removal of liquids
  - molten liquid pumping systems
  - gravity separation systems
  - pressurized removal systems

Removal of Solids

Freezing of the Electrolytic Cell and Removal of Solids

- Description of technology
  - used in experiments of electrowinning of molten titanium from titanium dioxide
  - at the end of each run the cell temperature was reduced below 1600°C, the anode was lifted above the electrolyte surface and the system cooled to room temperature
  - once cooled, the contents of the cell were removed
  - internal dimensions of the cell: diameter-80 mm, height -120 mm.
- Application of technology – High and low temperature electrowinning
- Limitations for application to lunar missions
  - Potential use for an initial lander mission to return sample to earth and analyze them

Removal of Solids

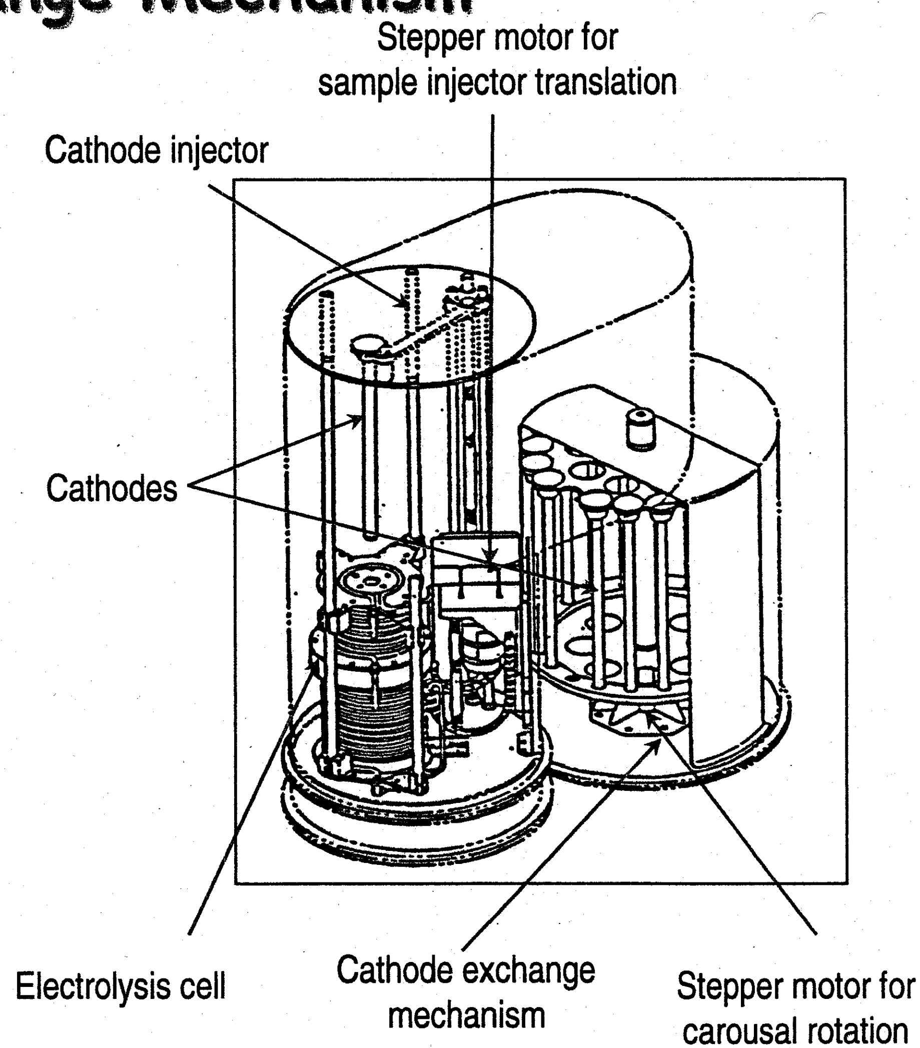
Removal of Solid Metal Sheet from the Liquid Electrolyte

- Description of technology – 2 steps:
  - remove cathode from electrolysis cell after specified time (thickness of metal deposit)
  - remove solid metal sheet from cathode
- Limitations for application to lunar missions - cathode removal
  - for an initial lander mission - cathode returned to earth for analysis of metal deposit
  - for a pilot plant where metal deposit is used on lunar surface
    - to minimize crew intervention use an automated cathode exchange mechanism (see next slide)
    - metal deposit stripped from cathode using a patented stripping mechanism (see subsequent slide)
    - cathode exchange mechanism and the cathode stripping mechanism needs to be coupled
  - may require some crew intervention working with hot electrode to exchange electrodes and moving electrodes from the electrolysis cell to a stripping chamber unless they are coupled

Removal of Solids

Cathode Exchange Mechanism

- Description of technology
  - o cathode carousel is computer driven and can be commanded to place a specific cathode at the engagement position
  - o cathode injection arm can rotate about vertical axis and translate in vertical direction
  - o injector arm rotates to cathode engagement position and translates down to engage an electrode
  - o after engagement it translates up with electrode and rotates to electrode insertion position
  - o it then translates down to insert electrode into electrolysis cell
  - o reverse motions are applicable to eject the electrode from the cell and place it back on the carousel
  - o electrical connections for electrolysis is on injector arm - each electrode does not need a separate electrical connection



Removal of Solids

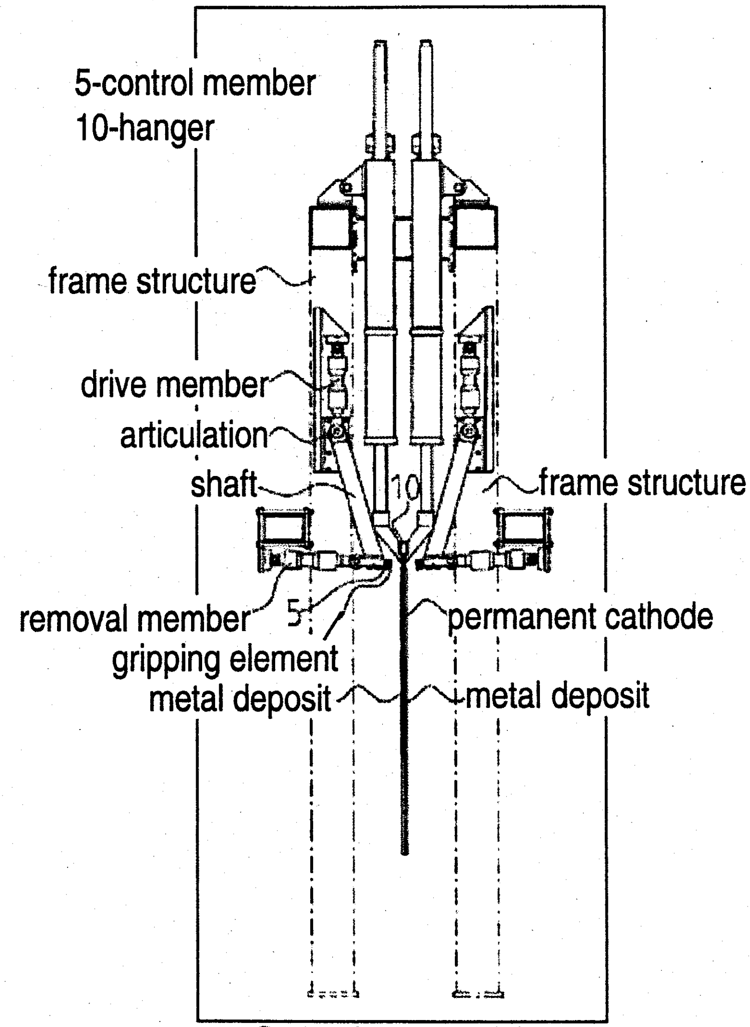
Cathode Exchange Mechanism

- History
  - The sample exchange mechanism has been successfully flown on the shuttle as part of the Crystal Growth Furnace (CGF) and Advanced Automated Directional Solidification Furnace (AADSF)
  - CGF could accommodate 6 samples and AADSF could accommodate 3 samples
  - Total weight of sample exchange mechanism was approximately 15 lbs
  - Weight of each sample assembly is approximately 4 lbs

Removal of Solids

Stripping Mechanism 1

- Description of technology
  - in modern production plants for Cu, Ni or Zn the cathode is usually made of a different metal than the metal to be produce
  - metal to be produced is removed in plate-like sheets (typically over 5 mm thick) from surface of permanent cathodes
  - permanent cathodes are continuously circulated between the electrolytic tanks and removal station
  - interval between removals is typically from one to seven days.
- History – 2003 patent



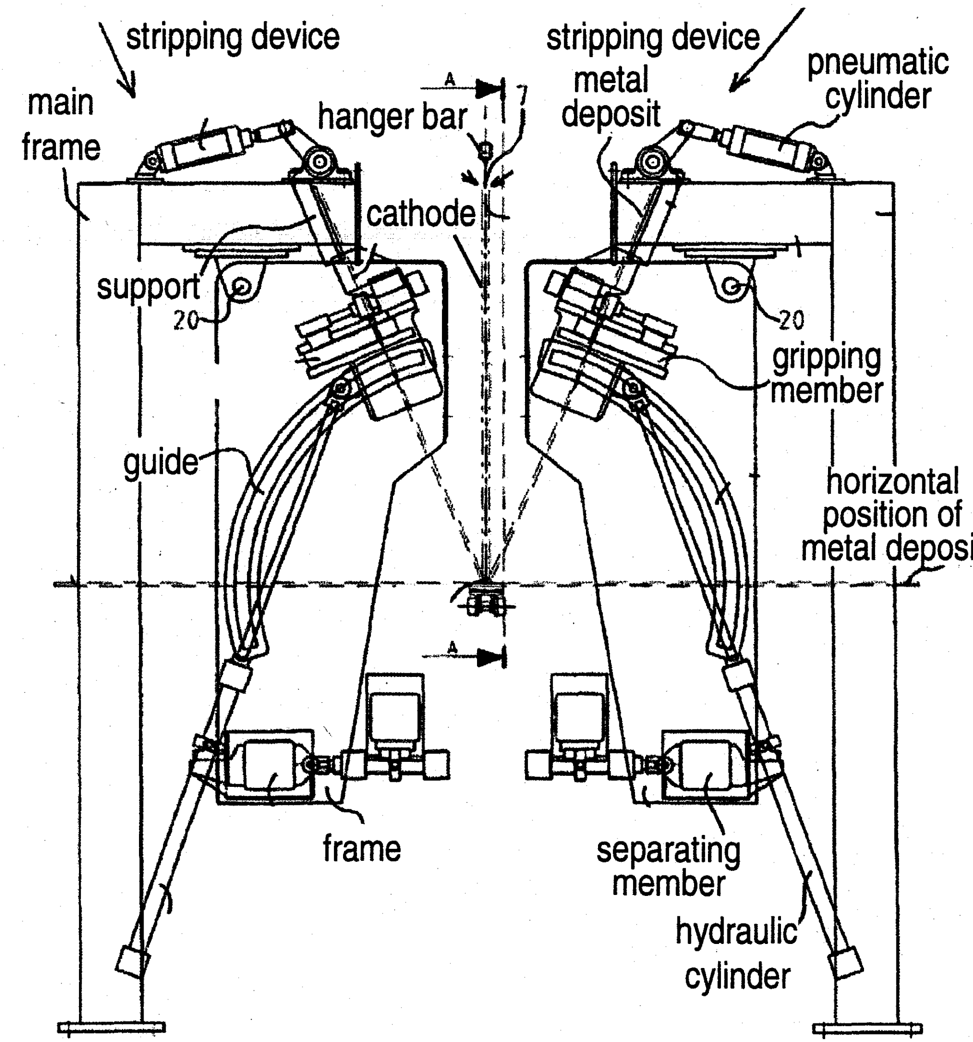
Stripping machine

Martilla T., U.S. Patent 6,635,159 B1 (2003)

Removal of Solids

Stripping Mechanism 2

- Description of technology
  - metal to be produced is removed in plate-like sheets (typically over 5 mm thick) from surface of permanent cathodes
  - grooves are produced in the metal plates to facilitate breaking and removal
- History – 2003 patent



Eriksson O. et al., Device for separating metal deposit from cathode, *U.S. Patent 6,632,331 B1* (2003)

Removal of Liquids

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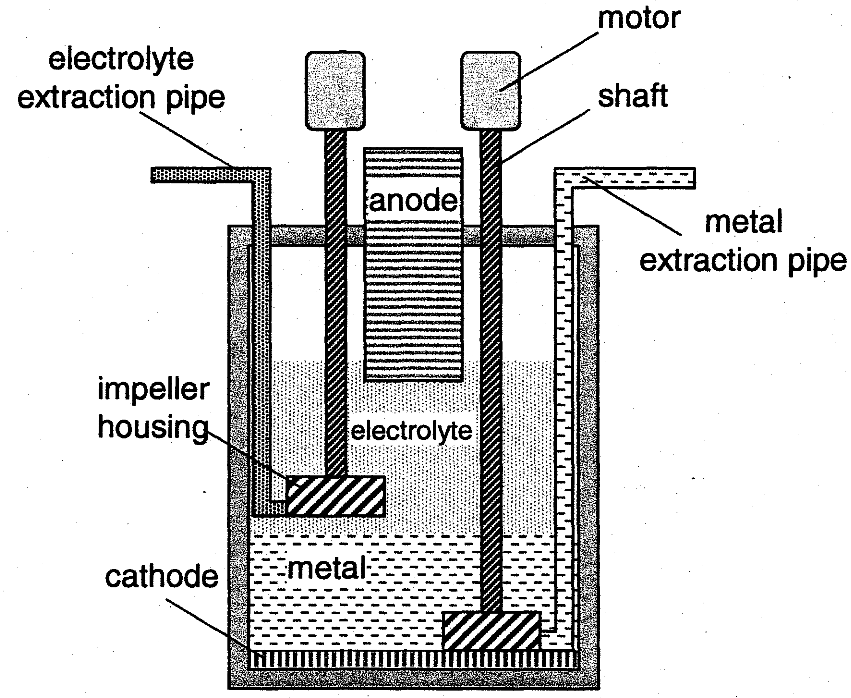
Molten Liquid Pumping Systems

- Description of technology
  - o pump pushes liquid reactants upward and out of the cell
  - o submerged intake allows separation of two different fluids by adjusting device height
  - o advantages: large volume transfer per unit time, less superheat required
  - o types of pumping systems
    - ➢ positive-displacement pressure pump
    - ➢ centrifugal pump
    - ➢ electromagnetic pump



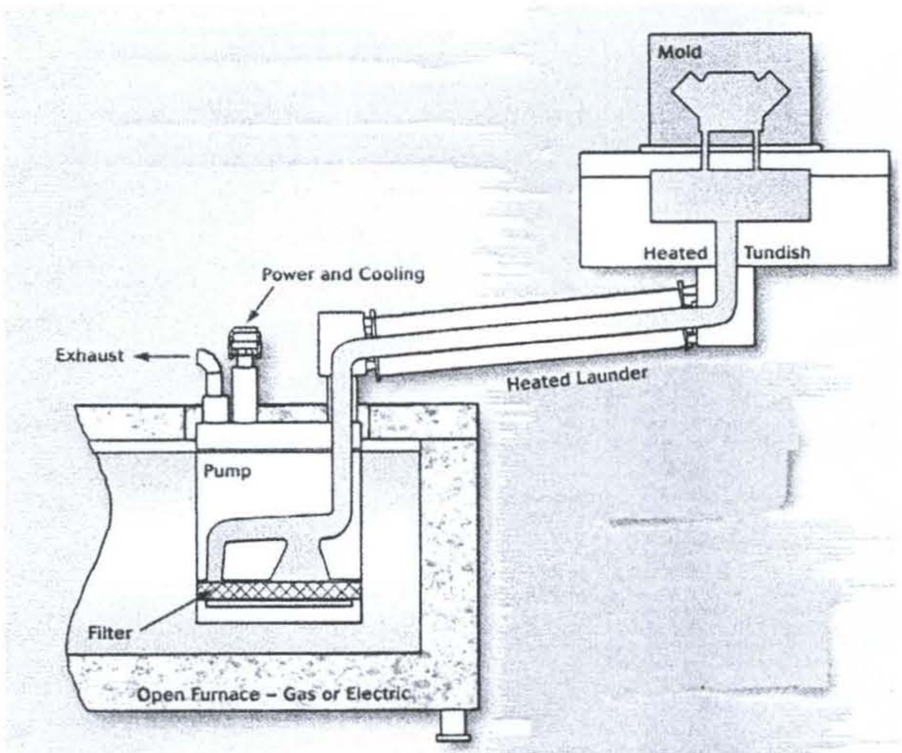
Arrangement for two centrifugal pumps for transfer of electrolyte and molten metal

Neff D.V., in *ASM Handbook Vol. 15 Casting*, D.M. Stefanescu ed., ASM International (1992) p486

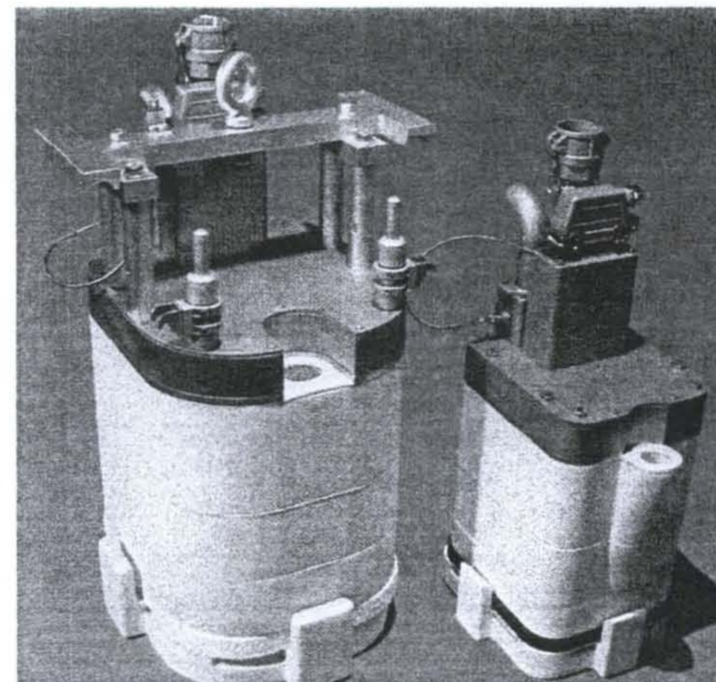
Removal of Liquids

Molten Liquid Pumping Systems

-electromagnetic pumps-



Arrangement for electromagnetic pump used in casting



Industrial electromagnetic pumps

(CMI Novacast Inc.)

Removal of Liquids

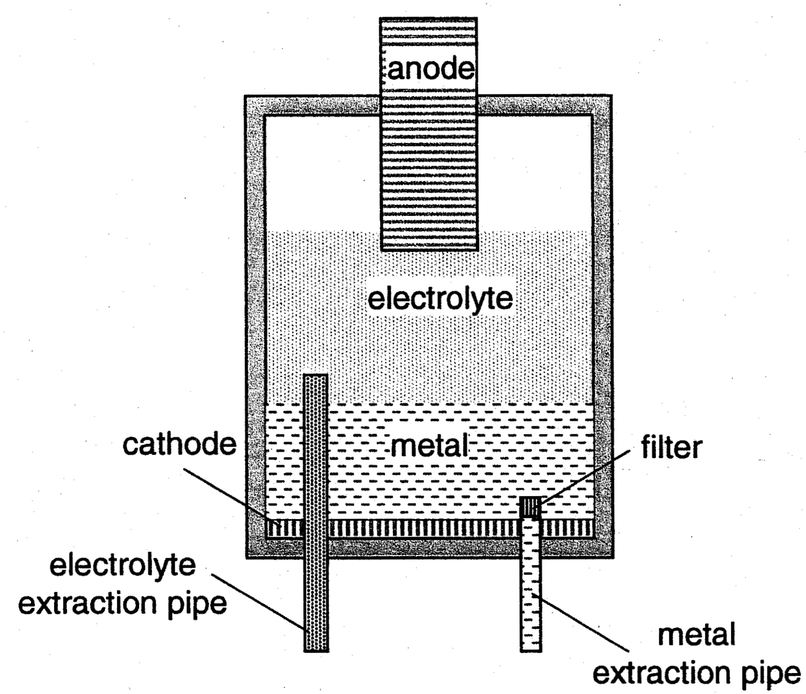
Molten Liquid Pumping Systems

- Technology application, scale and results
  - commonly used with Al, Mg, Zn and Pb molten alloys
  - size scaling is not a problem; *e.g*, one foundry has poured a 9,000 kg casting using a transfer pump
  - temperature scaling: centrifugal pump used to pump 72,600 kg molten Cu for 55 min
- Application of technology – high temperature electrowinning
- Limitations for application to lunar missions
  - for mechanical pumps - spare parts to be procured from earth
  - electromagnetic pumps have no moving parts but only good for metals

Removal of Liquids

Gravity Separation Systems

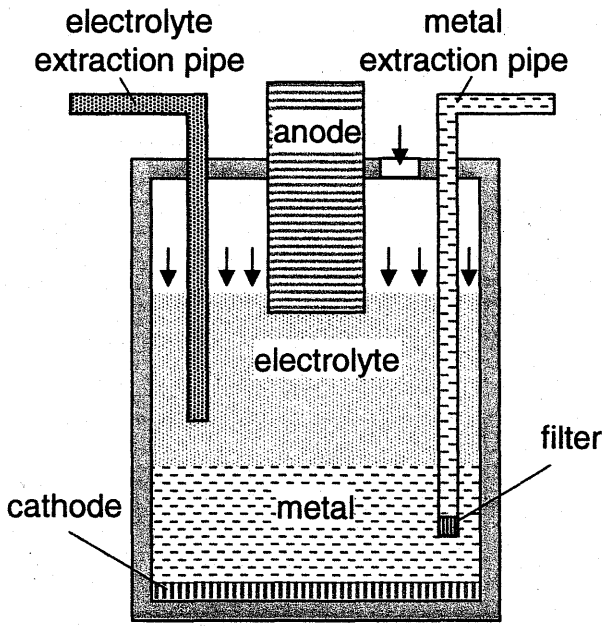
- Description of technology
  - o pipes submerged in the reactants at levels appropriate for the two products
  - o removal of materials controlled by plugging the extraction pipes, or by translating the pipes vertically above the surface of the electrolyte
  - o acts as a level control mechanism
  - o filters could be used on metal extraction pipe to insure complete separation from electrolyte or oxide inclusions
- History - technology will be specially design for the current project
- Limitations for application to lunar missions
  - o high viscosity of materials and low lunar gravity



Removal of Liquids

Pressurized Removal Systems

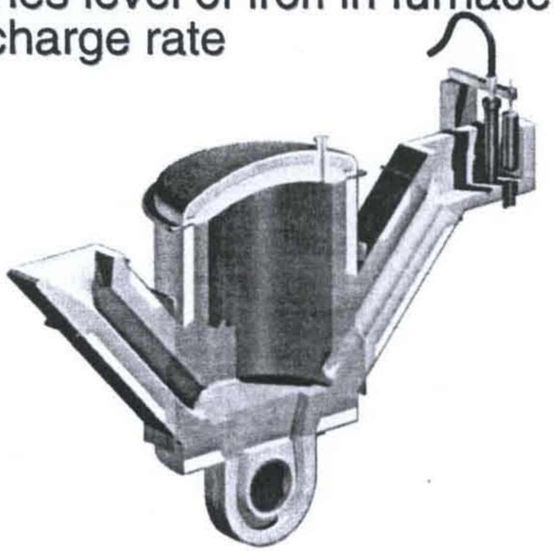
- Description of technology
  - pressure is applied on top of the liquids in the cell to remove electrolyte and molten metal
  - pressure can be exercised either by the residual oxygen that is produced in the electrolytic cell, or by an inert gas to be pumped form outside
- History – used for medium and large scale (tons/hr) molten metal transfer in foundries (see next slide)
- Limitations for application to lunar missions
  - availability of a pressurizing gas (residual oxygen for production cells or external inert gas for small demonstration cells)

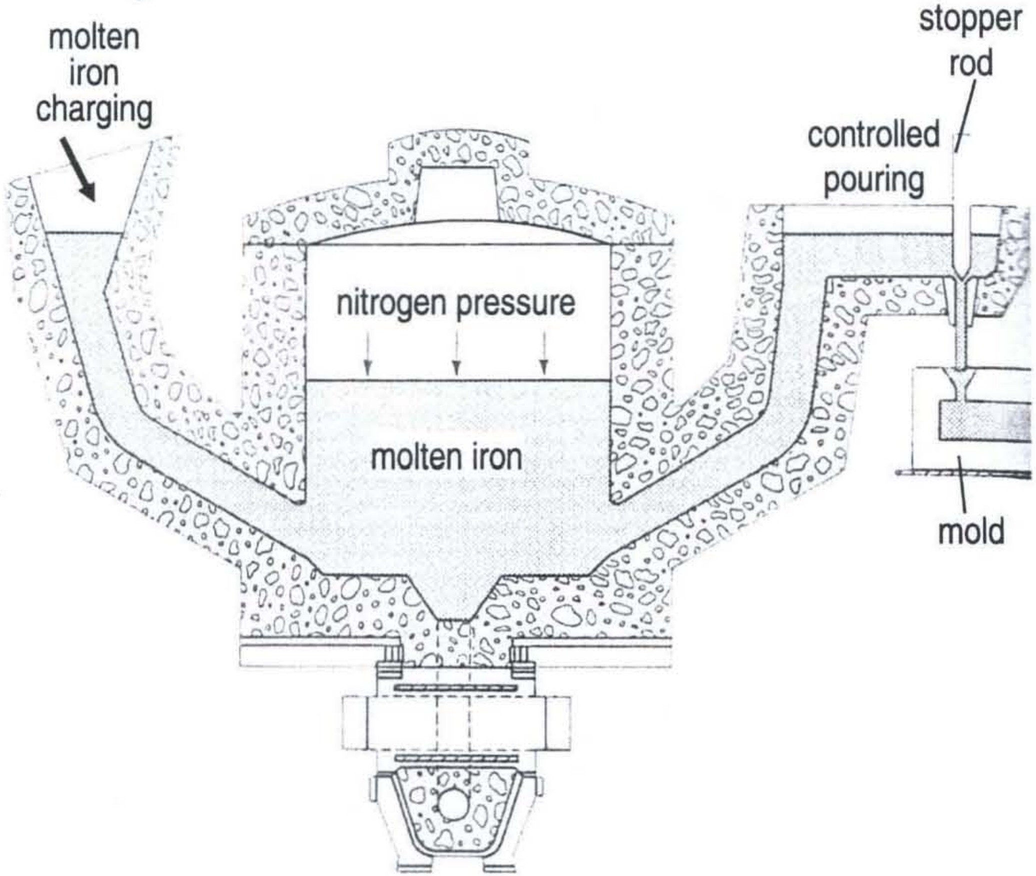


Removal of Liquids

Pressurized Removal System for Cast Iron

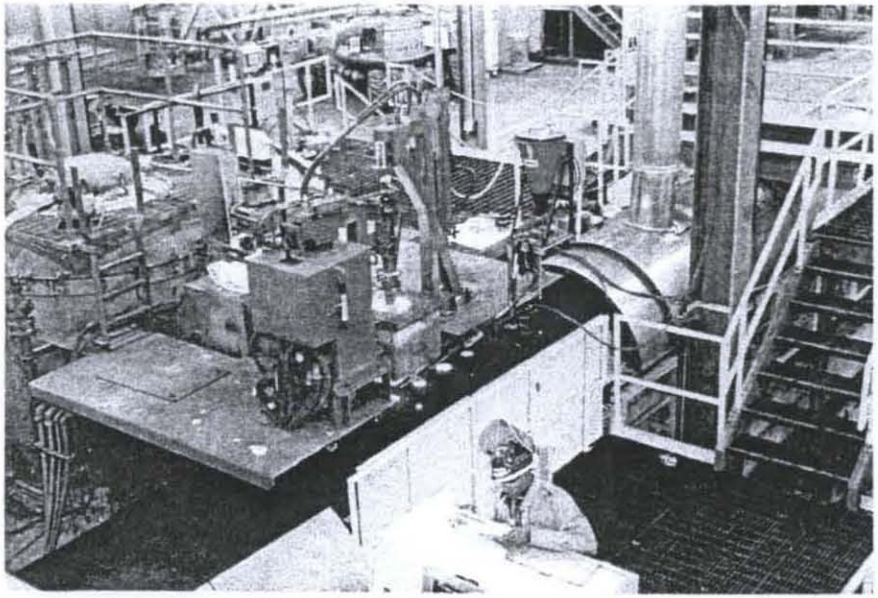
- operating temp. ~1450°C
- can operate for 24 hrs before stopping for stopper rod maintenance
- industrial records show operation times before relining of 10 to 24 months
- no technical size limitation
- pressure above molten iron establishes level of iron in furnace and discharge rate



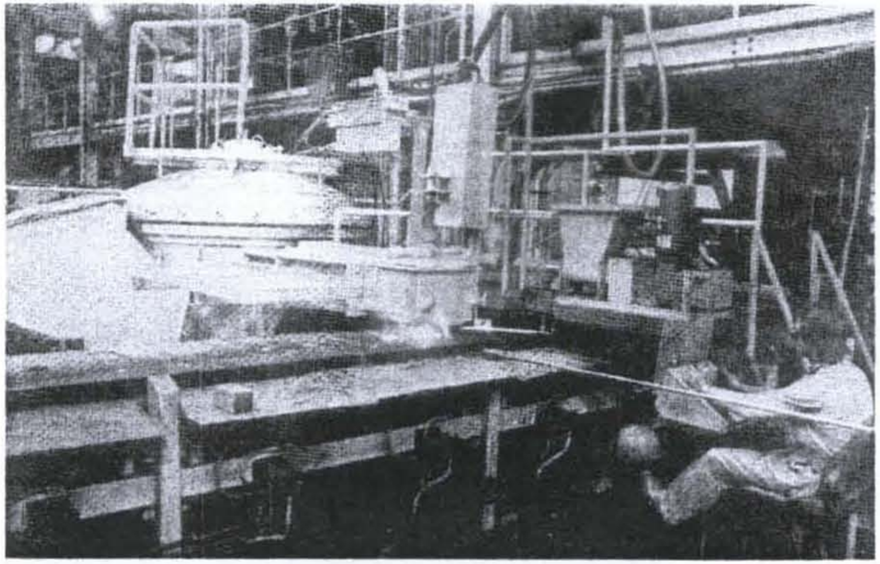


Removal of Liquids

Pressurized Removal Systems for Cast Iron

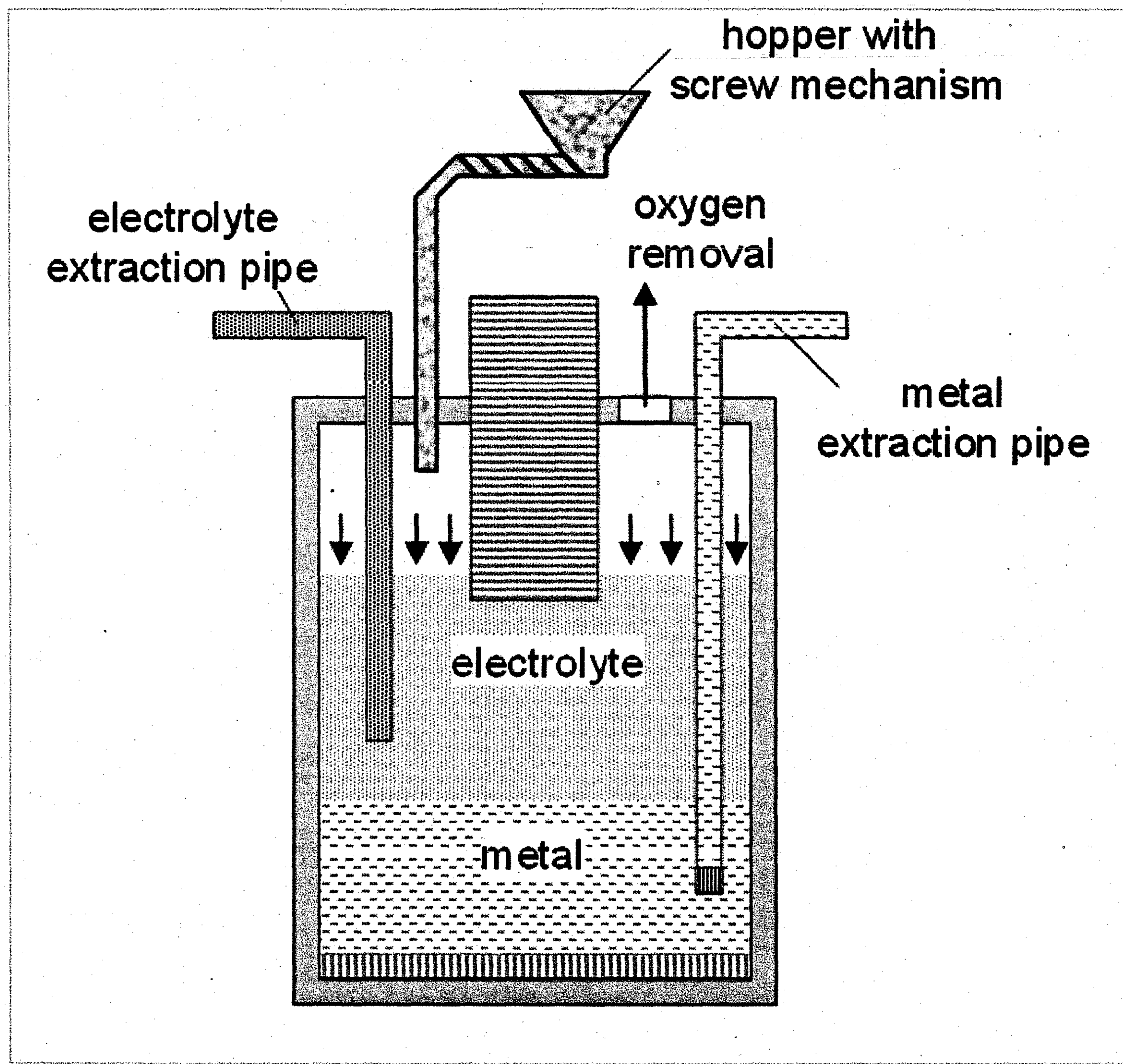


25,000 lb pressure-pour furnace for cast iron



7,500 lb pressure-pour furnace for cast iron
(Waupaca foundry, WI)

Schematic Representation of the Demonstration Unit for Molten Materials Transfer and Handling from an Electrowinning cell.



CONCLUSIONS

The paper reviews the main issues associated with molten materials transfer and handling on the lunar surface during the operation of a high temperature electrowinning cell used to produce oxygen, with molten iron and silicon as byproducts.

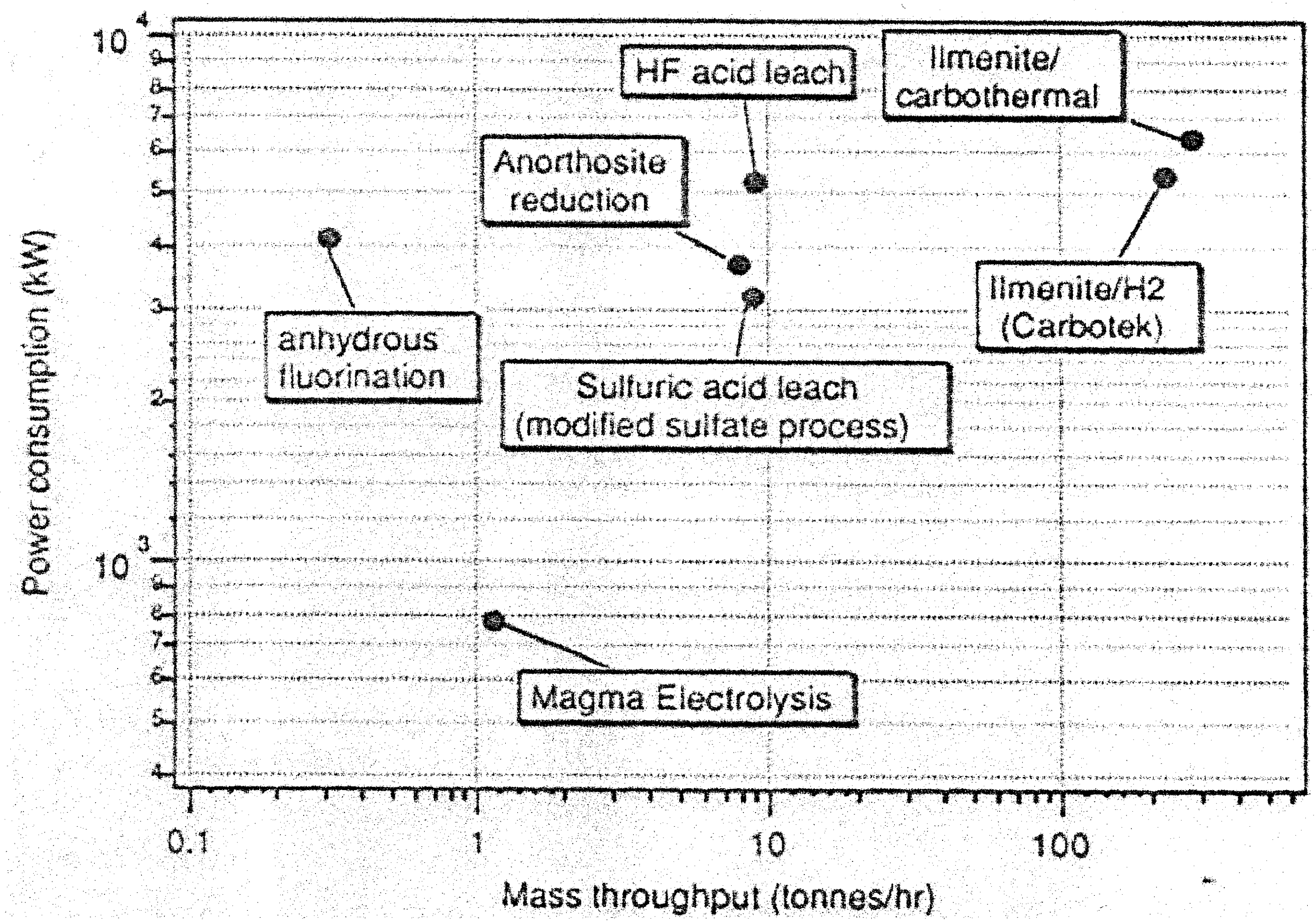
A combination of existing technologies and purposely designed technologies show promise for lunar exploitation.

An important limitation that requires extensive investigation is the performance of refractory currently used for the purpose of molten metal containment and transfer in the lunar environment associated with electrolytic cells.

The principles of a laboratory scale unit at a scale equivalent to the production of 1 metric ton of oxygen per year are introduced. This implies a mass of molten materials to be transferred consistent with the equivalent of 1kg regolith/hr processed.

Back Up Slides

Production of O_2 from Lunar Regolith (1 kT O_2/yr basis)



(From L.W. Mason, in Space 92, p.1139, ASCE (1992))

Engineering with Lunar Elements

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Lunar Elements Only						Material Class	Lunar Elements Plus ~ 5% or Less Earth Imports				
High Capacity				Limited Capacity			High Capacity				Limited Capacity
Al	Mg	Fe	Ti	Cr	Ni	Structural Metals	Al	Mg	Fe	Ti	Cr
Wrgt EC 1060 1100 3003 5005 5050 5052 5056 5083 5086 5154 5357 6063 6101 6151 Cast A13 43 214 220 356 360 Al Mag 35	AM10 0 M1A A3A	1020 1095 1340 5140 A24 2 X70 9260 501	99.2 99 Ti- 8Mn 4-4 Al/M n	S Steel 410 430 Nichrom e	Z-Ni Permalloy Permendu r 200 201 211 212 Inconel 600 702 721 722		7075 7178 MA67 MA87	ZK60 AZ80A	404 2 434 0 864 0 6B	6-4 Al/V 5-2.5 Al/Sn 7-4 Al/Mo 6-2-4-2 Al/Sn/ Zr/Mo	SS 440C 446

Waldin and Criswell

Engineering with Lunar Elements 2

Al_2O_3 in Al, Mg Fe, Glass in Mg, Ti_5Si_3 in Ti	Al_2O_3 in Ni SiO_2 in Ni	Reinforced metals		
Cast Basalt Dark Glass Foamed Glass		Structural non metals		
Al_2O_3, CaO, MgO, TiO_2, SiO_2, Spinels, Mixed ceramics, "S" fiber, Ti_5Si_3	Cr_2O_3, K_2TiO_3	Thermal materials, refractorys, insulation, fibers		
		Electric / magnetic Materials		
Fe, Al, Mg	Ni-Cr	Conductors		
Kanthal A-1		Restistance alloys		
Si	AlP, FeS_2, NiO, CoO	Semiconductors		
Same as thermal except Ti_5Si_3) + titnates		Dieletrics / ins.		
Fe, Si—steels (M15, M5-8) Fe_3O_4, $MgFe_2O_4$, sendust	Permalloy Permendur Cr)3	Magnetics		
Fe_3O_4, TiO		Electrodes		
Same as refractorys except CaO + garnets		Abrasives		SiC(30%) TiC(20%)
O_2, O_3	SO_2, SO#, CrO_3	Fluid / Volatiles, Cryogenic ambient mp < 500 CNaH	H_2O (11%), H_2O_2 (6%), H_2SO_4, H_2SO_3, H_3PO_4	H_2S(6%), H_3P(9%) NaOH

Waldin and Criswell