

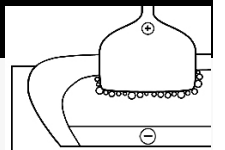
Advances and Innovations in the Extraction of Aluminum, Magnesium, Lithium, and Titanium

Donald R. Sadoway

Department of Materials Science & Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

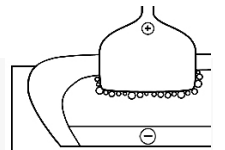
Outline of the lecture

- ⇒ where do metals come from?
- ⇒ needs of the current technology
- ⇒ radical innovation



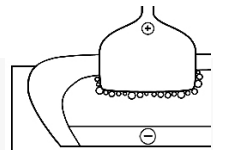
Selected Properties of Structural Metals

	Fe	Al	Mg
m.p. (°C)	1535	660	650
b.p. (°C)	2860	2518	1093
ρ (g/cm ³)	7.87	2.70	1.74
E (GPa)	211	71	45
E/ρ	27	26	26



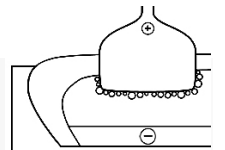
Selected Properties of Structural Metals

	Fe	Al	Mg	Ti
m.p. (°C)	1535	660	650	1675
b.p. (°C)	2860	2518	1093	3260
ρ (g/cm ³)	7.87	2.70	1.74	4.51
E (GPa)	211	71	45	116
E / ρ	27	26	26	26



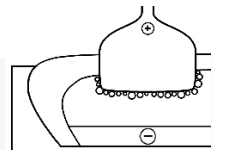
Selected Properties of Structural Metals

	Fe	Al	Mg	Ti	Li
m.p. (°C)	1535	660	650	1675	181
b.p. (°C)	2860	2518	1093	3260	1342
ρ (g/cm ³)	7.87	2.70	1.74	4.51	0.53
E (GPa)	211	71	45	116	4.9
E / ρ	27	26	26	26	9.2



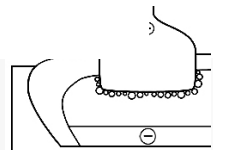
Selected Properties of Structural Metals

	Fe	Al	Mg	Ti	Be
m.p. (°C)	1535	660	650	1675	1287
b.p. (°C)	2860	2518	1093	3260	2469
ρ (g/cm ³)	7.87	2.70	1.74	4.51	1.85
E (GPa)	211	71	45	116	287
E / ρ	27	26	26	26	155



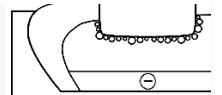
Selected Properties of Structural Metals

	Fe	Al	Mg
capacity (10 ⁶ tpy)	800	25	0.60
price (\$/kg)	0.40	1.85	3.40
sales (10 ⁹ \$)	320	46	2.0
abundance (%)	4.1	8.2	2.3
(rank)	4	3	7
$-\Delta_f G_{M_xO_y}$ (kJ/mol O ₂)	503	1055	1138
(kJ/g M)	6.7	29	23



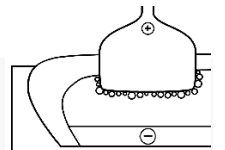
Selected Properties of Structural Metals

	Fe	Al	Mg	Ti	Li
capacity (10^6 tpy)	800	25	0.60	0.10	625*
price (\$/kg)	0.40	1.85	3.40	10	80
sales (10^9 \$)	320	46	2.0	1.0	0.05
abundance (%)	5.0	8.2	2.1	0.66	0.0017
(rank)	4	3	8	9	22
$-\Delta_f G_{M_xO_y}$ (kJ/mol O_2)	503	1055	1138	889	1122
(kJ/g M)	6.7	29	23	19	40




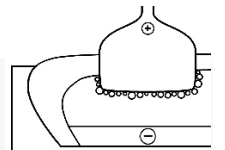
Major Aluminum Producing Countries

	nameplate capacity (10^3 tpy)
U.S.A.	4200
China	3900
Russia	3400
Canada	2800
Australia	1900
Brazil	1300
Norway	1100

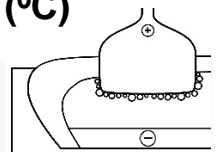
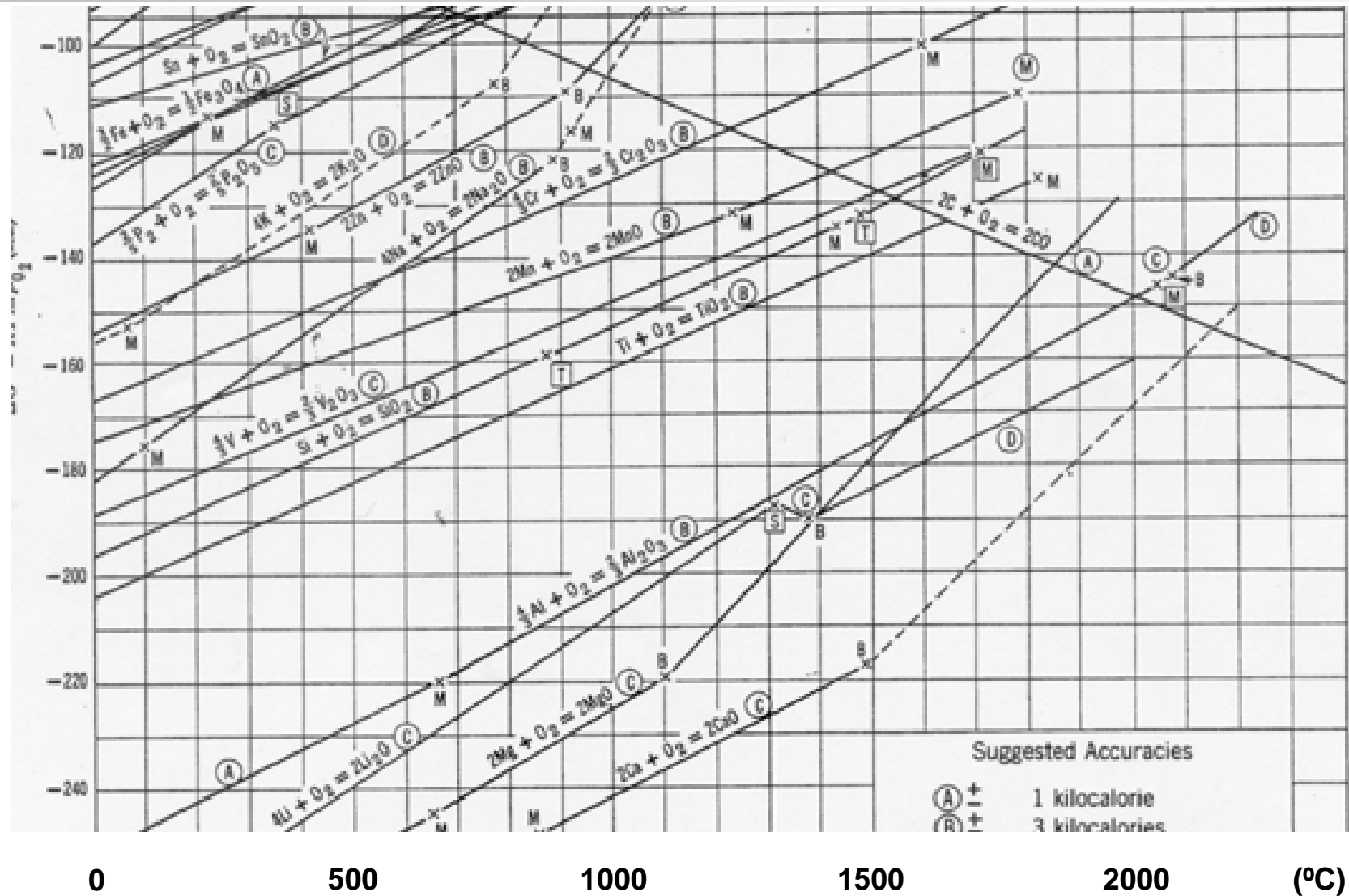


Where do metals come from?

- ⇒ occur naturally as compounds
- ⇒ beneficiated  high-purity feed
- ⇒ reducing agents: H, C, M, e⁻
- ⇒ options for alumina reduction?



Where do metals come from?



Hall-Héroult electrolysis

electrolyte: $\text{Na}_3\text{AlF}_6 - \text{AlF}_3 - \text{CaF}_2$

feed: Al_2O_3

temperature: 970°C

anode: carbon

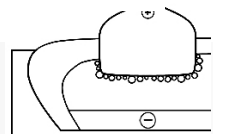
anodic reaction: $3 \text{O}^{2-} + 1.5 \text{C} \rightarrow 1.5 \text{CO}_2 + 6 \text{e}^-$

cathode: carbon

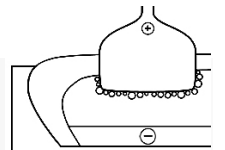
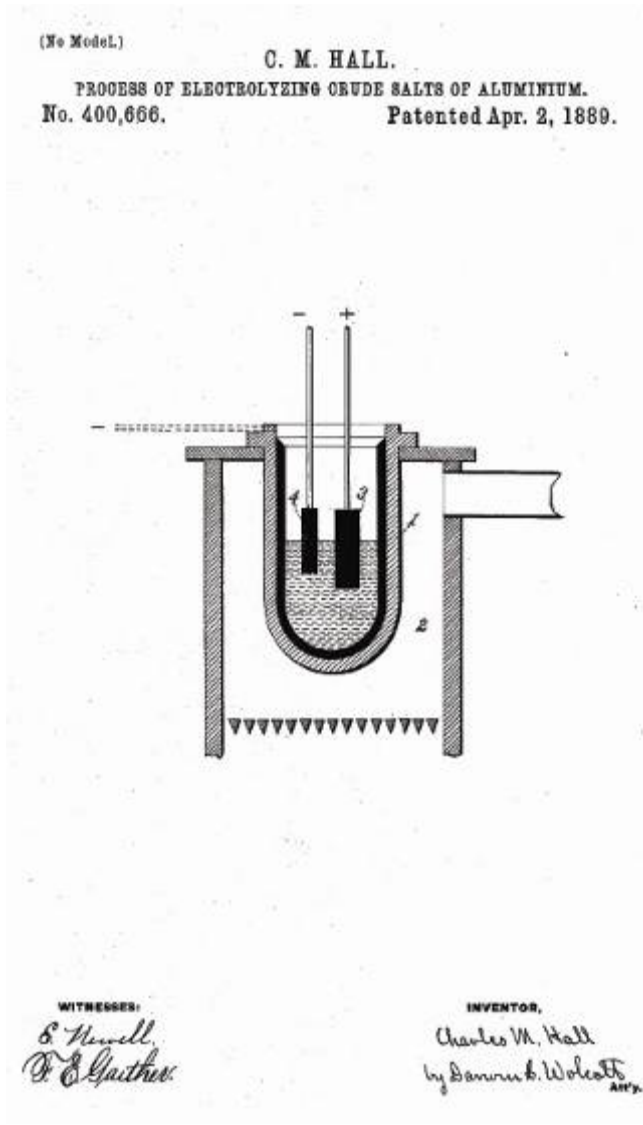
cathodic reaction: $2 \text{Al}^{3+} + 6 \text{e}^- \rightarrow 2 \text{Al}$

overall reaction: $\text{Al}_2\text{O}_3 + 1.5 \text{C} \rightarrow 2 \text{Al} + 1.5 \text{CO}_2$

standard potential: $E^\circ = 1.2 \text{ V}$



Where it all began



Where it all began

UNITED STATES PATENT OFFICE.

CHARLES M. HALL, OF OBERLIN, OHIO.

PROCESS OF ELECTROLYZING CRUDE SALTS OF ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 400,666, dated April 9, 1889.

Application filed August 17, 1886. Serial No. 232,910. (No specimens.)

To all whom it may concern:

Be it known that I, CHARLES M. HALL, a citizen of the United States, residing at Oberlin, in the county of Lorain and State of Ohio, have invented or discovered certain new and useful Improvements in the Manufacture of Aluminium by Electrolysis of its Fused Salts, of which Improvements the following is a specification.

In applications filed July 6, 1886, and February 2, 1887, and serially numbered 207,601 and 226,206, respectively, I have described and claimed processes for the reduction of aluminium by dissolving alumina in a bath formed of a fused fluoride salt of aluminium and then separating the aluminium by an electric current. In the process described in application, Serial No. 207,601, I employed a bath formed of the fluorides of sodium and aluminium, (represented by the formula $\text{Na}_2\text{Al}_2\text{F}_6$) with or without the addition of the fluoride of lithium, and in the process described in application, Serial No. 226,206 I employed a bath formed of the fluorides of potassium and aluminium, (represented by the formula $\text{K}_2\text{Al}_2\text{F}_6$) with or without the addition of the fluoride of lithium. The salts forming either of the above-mentioned baths are placed in a suitable vessel, preferably one formed of metal and lined with carbon, and then subjected to sufficient heat to fuse them and form a homogeneous bath. Electrodes formed of carbon or any suitable metal and connected to opposite poles of a dynamo-electric machine are then placed in the bath, or the containing vessel may be employed as the negative electrode. The alumina is now added to the bath, and being dissolved aluminium is reduced at the negative electrode, and being fused by the heat of the bath sinks to the bottom of the vessel, the oxygen being liberated at the positive pole.

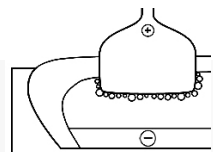
By the above-described processes I have been able to obtain good results, but have found that during a continuous use of either of the above baths for a considerable time a black compound is formed which clogs the bath, thereby increasing the resistance thereof, and to the extent of such increased resistance decreasing the amount of aluminium produced. The formation of the black

compound, which occurs sooner in the bath composed of the fluorides of sodium and aluminium than in that composed of the fluorides of potassium and aluminium, necessitates a comparatively frequent renewal of the bath.

The object of the invention described herein is to provide a bath wherein the objections heretofore mentioned do not obtain, and which can be used continuously without changes or renewal, except to supply loss occurring from evaporation.

In the accompanying drawings forming a part of this specification is shown a construction of apparatus applicable for carrying out my improved process.

In the practice of the present invention I form an electrolyte or bath of the fluorides of calcium, sodium, and aluminium, the fluorides of calcium and sodium being obtained in the form of fluor-spar and cryolite, respectively, and the fluoride of aluminium being obtained by saturating hydrated alumina ($\text{Al}_2\text{H}_2\text{O}_3$) with hydrofluoric acid. The compound resulting from the mixture of the above-mentioned fluorides, which is represented approximately by the formula $\text{Na}_2\text{Al}_2\text{F}_6 + \text{CaAl}_2\text{F}_6$, is placed in a suitable vessel, 1, preferably formed of metal and lined with pure carbon, for the purpose of preventing the admixture of any foreign material with the bath or with the aluminium when reduced. The vessel 1 is placed in a furnace, 2, and subjected to sufficient heat to fuse the materials placed therein. Two electrodes, 3 and 4, of any suitable material, preferably carbon, when pure aluminium is desired, and connected to the positive and negative poles of any suitable generator of electricity, preferably a dynamo-electric machine, are placed in the fused bath; or, if desired, the carbon-lined vessel may be employed as the negative electrode, as represented in dotted lines. Alumina in the form of bauxite, anhydrous oxide of aluminium, or any other suitable form of alumina, preferably the pure anhydrous oxide Al_2O_3 , artificially prepared, is then placed in the bath, and, being dissolved thereby, aluminium is reduced by the action of electric current at the negative electrode and being fused by the heat of the bath sinks down to the bottom of the vessel, the bath being of a less specific gravity than the aluminium.



Where it all began

400,866

This difference in specific gravity is an important feature of my process, as the superincumbent bath serves to protect the aluminium from oxidation. The oxygen of the alumina is liberated by the action of the electric current at the positive electrode, and, when the latter is formed of carbon, combines therewith and escapes in the form of carbonic oxide (CO) or carbonic acid (CO₂).

As the aluminium is reduced, more alumina is added, so that the bath may be maintained in a saturated condition with the fused alumina. The addition of more alumina than can be dissolved at one time is not detrimental, provided the bath is not chilled, as such excess will sink to the bottom and be taken up by the bath, as required.

The proportions of the materials employed in forming the bath or electrolyte are approximately as follows: Fluoride of calcium, two hundred and thirty-four parts; cryolite, the double fluoride (Na₃Al₂F₁₂) four hundred and twenty-one parts, and fluoride of aluminium, eight hundred and forty-five parts, by weight. These proportions can, however, be widely varied without materially changing the efficiency of the bath. During the reduction of the aluminium the positive electrode, when formed of carbon, is slowly consumed and must be renewed from time to time; but the bath or electrolyte remains unchanged for a long time. In time, however, a partial clogging occurs, which, however, does not render the bath wholly ineffective, but does necessitate an increase in the electro-motive force of the reducing-current, the resistance of the bath being increased in proportion to the degree to which the bath becomes clogged, thereby increasing the cost of reduction. In order to entirely prevent any clogging of the bath, I add approximately three or four per cent. (more or less) of calcium chloride to the bath or electrolyte hereinbefore described. As the addition of the calcium chloride pre-

vents, as stated, any clogging or increase of resistance in the bath, it can be used continuously without renewals or any additions, except such as may be needed to replace loss by evaporation, and without increasing the electro-motive force of the reducing-current; and, further, the addition of the calcium chloride enables each atom of carbon of the positive electrode to take up two atoms of oxygen, forming carbonic acid, (CO₂) thereby reducing the amount of carbon consumed in proportion to the amount of aluminium produced. The calcium chloride being quite volatile is subject to loss faster than the rest of the bath, and must be renewed occasionally on this account.

In reducing aluminium, as above described, I prefer to employ an electric current of about six volts electro-motive force; but the electro-motive force can be varied within large limits.

I claim herein as my invention—

1. As an improvement in the art of manufacturing aluminium, the method herein described, which consists in fusing a combination of the fluoride of aluminium, the fluoride of calcium, and the fluoride of sodium, adding alumina to the bath so formed, and then passing a current of electricity through the fused mass, substantially as set forth.

2. As an improvement in the art of manufacturing aluminium, the method herein described, which consists in fusing a combination of the fluoride of aluminium, the fluoride of calcium, the fluoride of sodium, and the chloride of calcium, adding alumina to the bath so formed, and then passing a current of electricity through the fused mass, substantially as set forth.

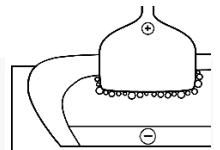
In testimony whereof I have hereunto set my hand.

CHARLES M. HALL.

Witnesses:

W. B. CORWIN,

DARWIN S. WOLCOTT.

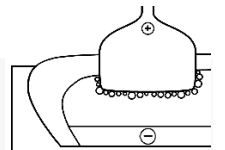


needs of current technology

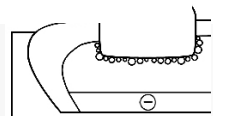
drivers:

⇒ **cost**

⇒ **environmental compliance**

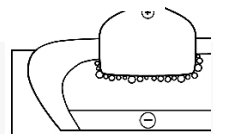


environmental drivers



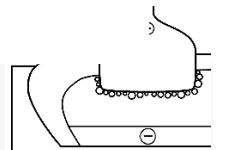
Prospective changes: a wish list

- ⇒ new electrode materials –
inert anodes & wettable cathodes
- ⇒ new electrolyte chemistries –
“low-ratio” bath
- ⇒ lower energy consumption
- ⇒ reduced emissions
- ⇒ 1000 kA cell: economy of scale?



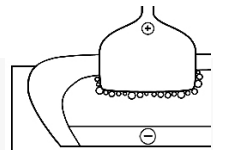
Properties of an inert anode

- * physically stable at service temperature
- * resistant to attack by fluoride electrolyte
- * resistant to attack by pure oxygen
- * electrochemically stable
- * electronically conductive
- * resistant to thermal shock
- * mechanically robust
- * easy to deploy (electrical connection to bus, startup, power interruptions, ...)
- * affordable



The Materials Menu

- * **ceramics**
- * **cermets**
- * **metals**
- * **coatings**



Ceramic Anodes

☺ advantages

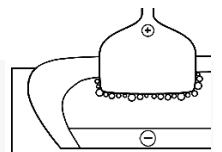
- * fully oxidized \therefore stable with hot O_2

☹ concerns

- * electronic conductivity
- * solubility in cryolite
- * thermal shock resistance
- * mechanical stability
- * operational challenges

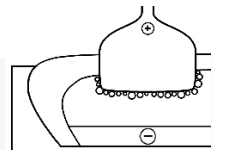
☹ examples

- * SnO_2
- * ferrites, spinels, perovskites



The Materials Menu

- * ceramics
- * **cermets**
- * metals
- * coatings



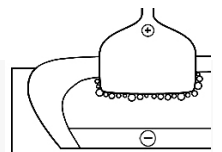
Cermet Anodes (ceramic/metallic composites)

☺ advantages

- * combine features of ceramics and metals, i.e., chemical inertness + high electronic conductivity

☹ concerns

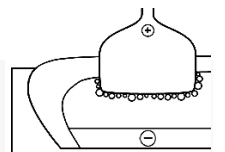
- * phase boundaries
- * solubility in cryolite
- * thermal shock resistance
- * mechanical stability
- * manufacturing net shapes
- * operational challenges



Cermet Anodes (ceramic/metallic composites)

☹ examples

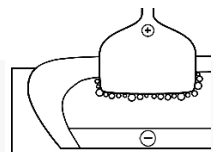
- * metal dispersion in a ceramic matrix,
e.g., copper, nickel, silver in a
nickel ferrite matrix, NiFe_2O_4
- ♦ ceramic provides bulk,
offers chemical stability
- ♦ metal confers conductivity & toughness



Metal Anodes (ceramic/metallic composites)

☺ advantages

- * combine features of ceramics and metals,
i.e., chemical inertness +
high electronic conductivity
- * high electronic conductivity
(more uniform current distribution)
- * thermal shock resistance
- * mechanically robust
- * easy to fabricate & deploy
- * self-repairing in service



Metal Anodes (ceramic/metallic composites)

☹ concerns

* stability of surface film

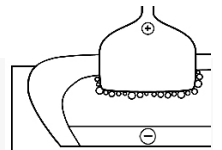
☺ example

* thin oxide film on surface of metal alloy,
e.g., Al_2O_3 on Cu – Al (90:10 by mass)

♦ alloy provides bulk,

confers high electrical conductivity

♦ surface film protects alloy from chemical
destruction by reaction with Hall bath
and oxygen



Metal Anodes

85% Cu

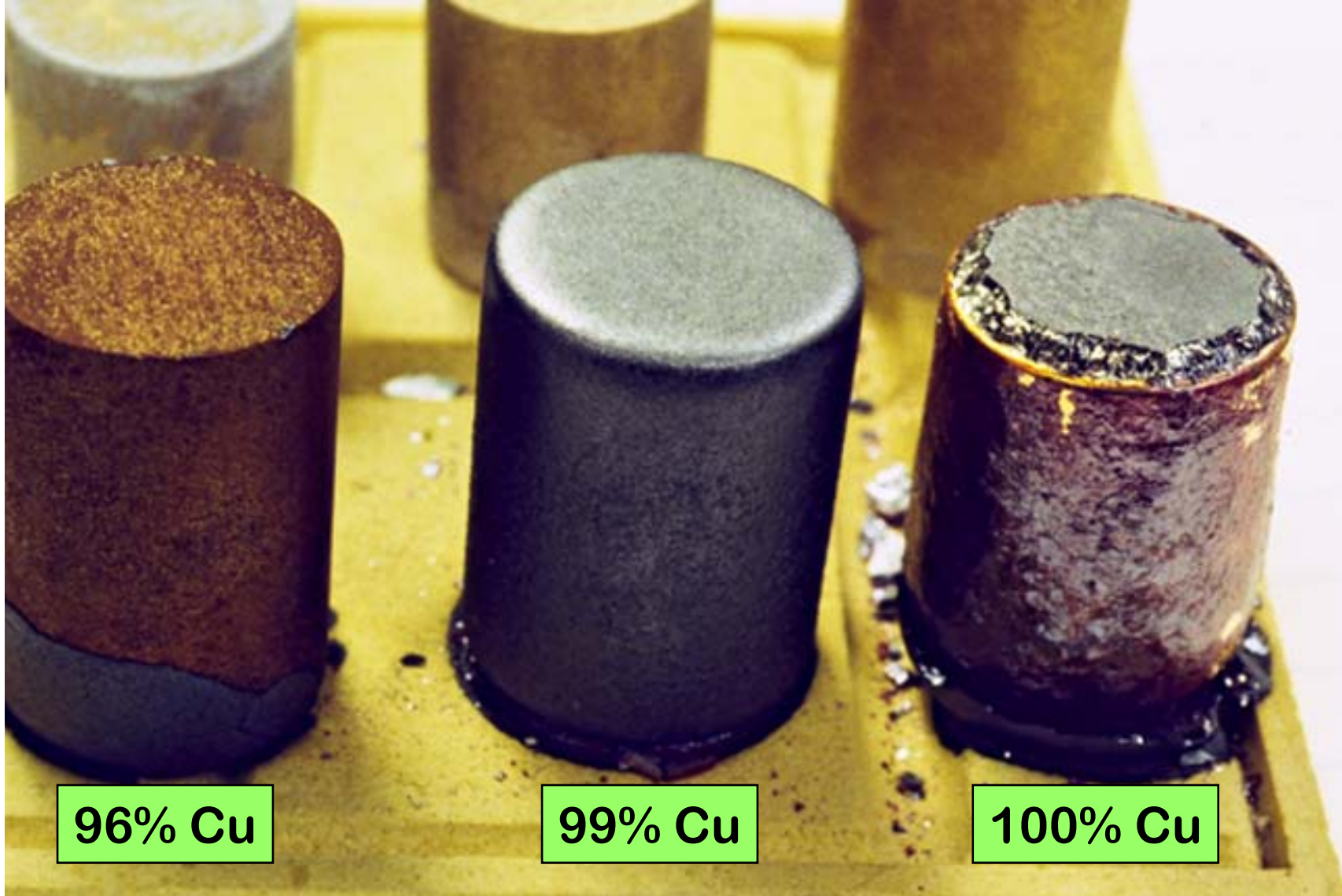
ceram

90% Cu

allic c

93% Cu

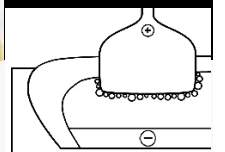
sites)



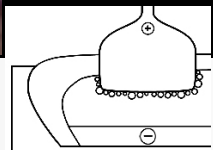
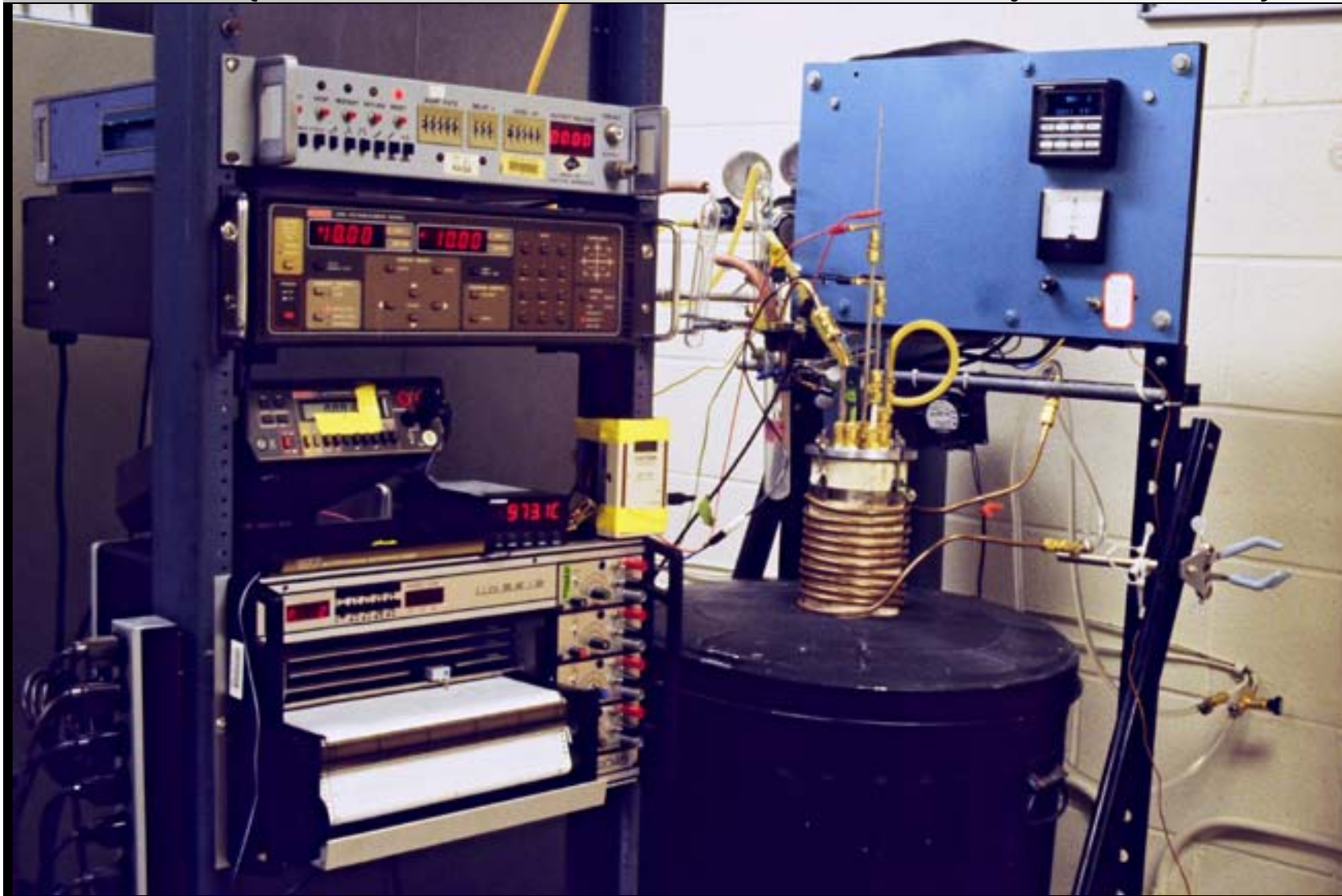
96% Cu

99% Cu

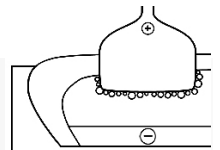
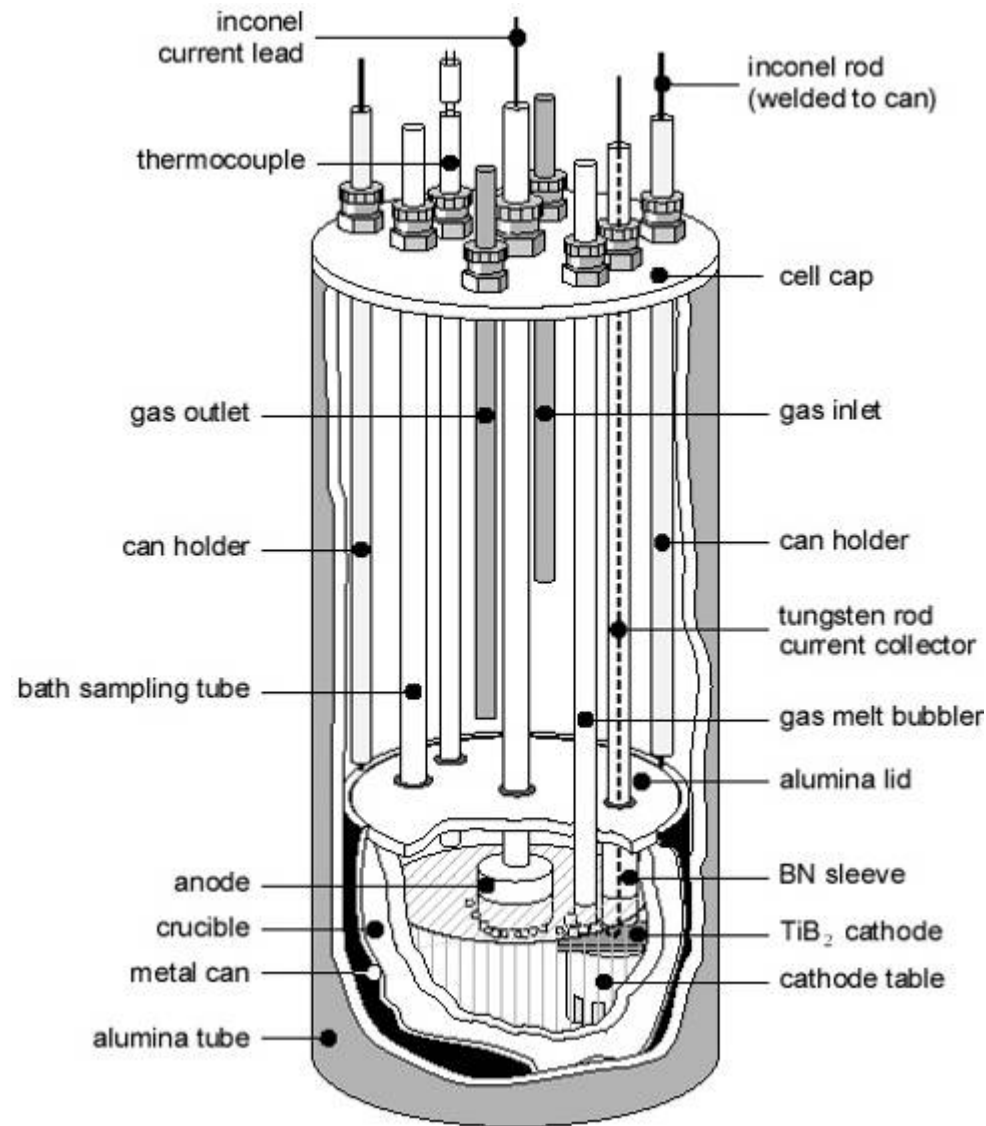
100% Cu



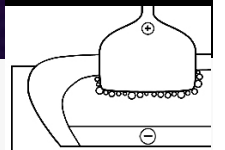
Metal Anodes (ceramic/metallic composites)



Metal Anodes (ceramic/metallic composites)

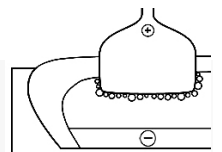


Metal Anodes (ceramic/metallic composites)



attributes of dynamic surface film: reaction layer

- * reaction layer is self repairing,
i.e., self forming in service
- * nca is dynamically stable in service:
chemistry, electrochemistry, adhesion, ...
- * designed to thrive in Hall cell environment
- * reduced contact resistance of connections
- * superior conductivity ratio, κ_{th}/κ_{el}



these reaction layers are not coatings

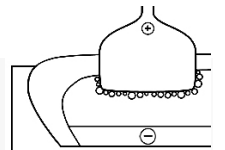
there are only two kinds of coatings:

- * made imperfect

- * become imperfect in service

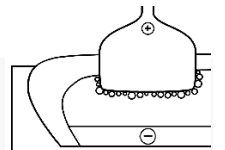
∴ only a self repairing coating is acceptable

☞ reaction layer



status report: taking the pulse

- * what are the prospects for delivery of the inert anode?
 - ☞ “Prediction is very difficult, especially about the future.”
- Niels Bohr

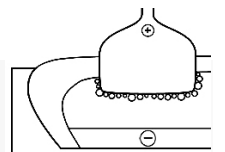


Radical innovation

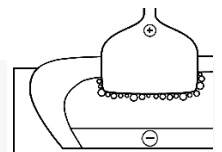
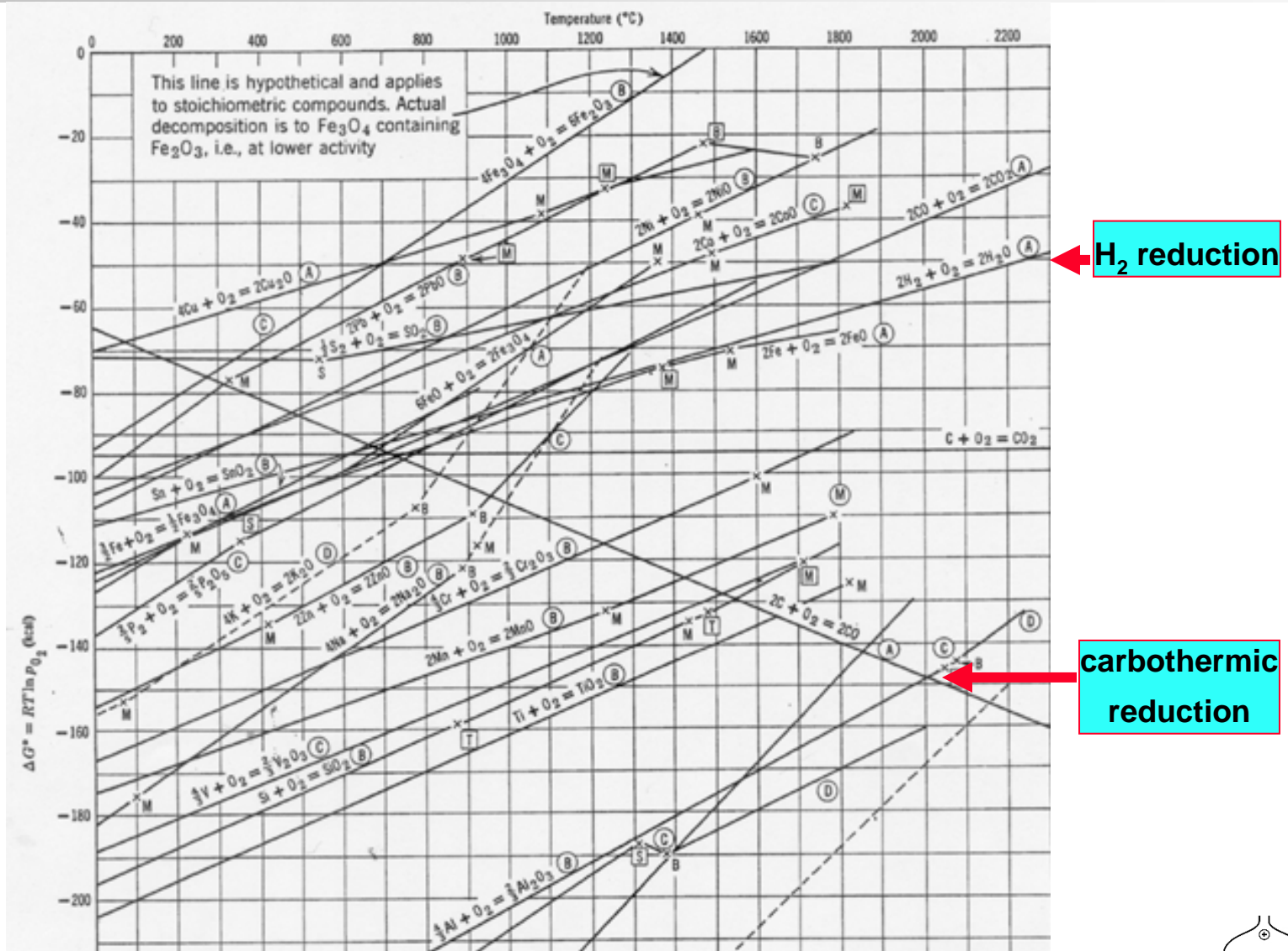
- ⇒ remember the menu of reducing agents
- ⇒ assume that alumina is the feed

assessment options:

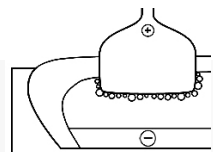
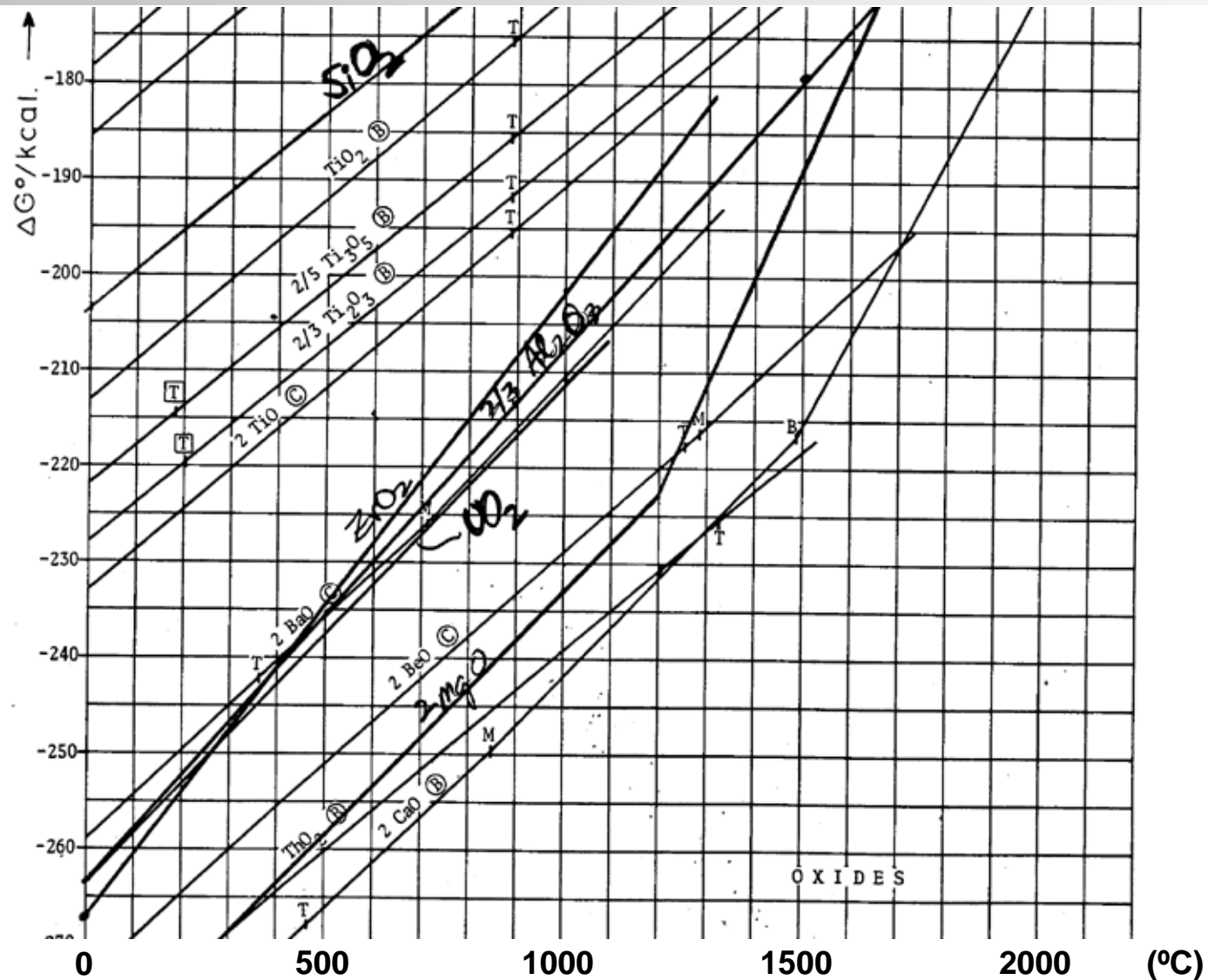
- ① laboratory curiosity (not scalable)
- ② technical success (economic failure)
- ③ disruptive technology (new era 💣)



Ellingham diagram: oxides



Ellingham diagram: oxides



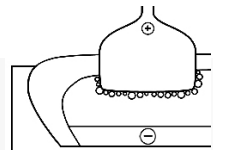
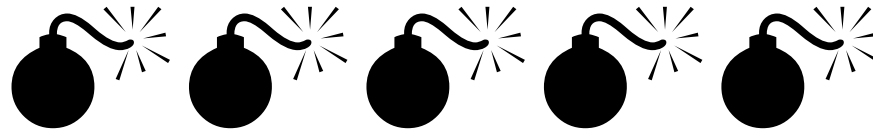
Radical innovation

carbothermic

metallothermic

electrochemical

plasma

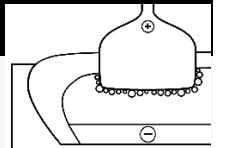


Government response

ALUMINUM INDUSTRY TECHNOLOGY ROADMAP

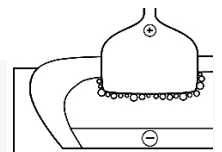
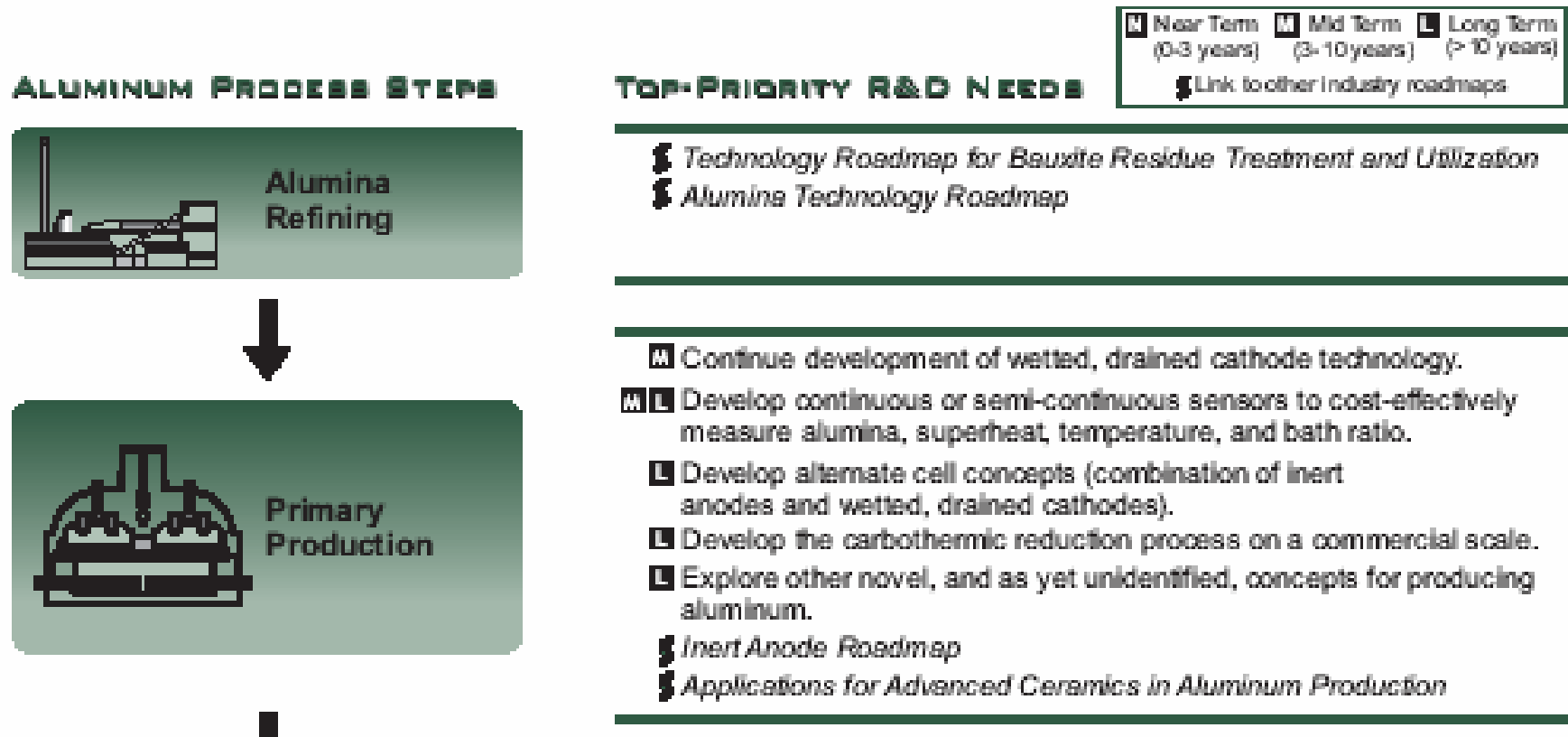


FEBRUARY 2003



Government response

Exhibit 1-2. Top-Priority R&D Needs for Major Aluminum Process Steps



Government response

Exhibit 2-2. Technical Barriers: Primary Production (priorities in bold)

ELECTROLYTIC REDUCTION PROCESSES

- Lack of mathematical models to predict the performance of cell design concepts
- Lack of robust bath chemistry (constrained by cryolite-based electrolyte)
- Incomplete knowledge of how to raise thermal efficiency of reduction without negatively impacting the process
- Lack of economical method to retrofit older cells (including buswork)
- Lack of economical technique to remove impurities from alumina in dry scrubbers
- High cost of reduction equipment
- Large gap between theoretical and actual energy efficiency, and high associated power costs

ALTERNATIVE REDUCTION PROCESSES

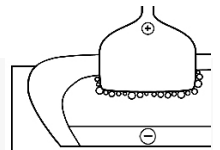
- Lack of feasible, economical electrolyte compositions that would require lower voltage without compromising product quality
- Lack of systems approach to developing overall alternative processes
- Difficulties maximizing use of chemical versus electrical energy in alternative processes

ENABLING TECHNOLOGIES

- Inadequate process tools, sensors, and controls for reduction cells
 - inability to measure cell variables (other than resistance) in real time
 - lack of non-contact sensors
- Lack of cost-effective metal-purification technologies
- Inadequate process optimization models
- Lack of materials (cathode, anode, and sensor tubes) that can withstand exposure to molten aluminum and cryolite

INSTITUTIONAL BARRIERS

- Government role in research is unclear; collaboration between government, academia, and industry is not optimized; limited cross-institutional communication
- Low researcher awareness of the state of the technology and of previous and ongoing research
- Lack of regulatory cooperation (e.g., spent potliner)



Government response

Exhibit 2-3: R&D Needed: Primary Production

N: Near Term (< 3 years) M: Mid Term (3-10 years) L: Long Term (> 10 years)

ELECTROLYTIC REDUCTION PROCESSES

Priority Level R&D Need

TOP

Develop alternative cell concepts (including materials development). (L)
• combination of inert anode/wetted, drained cathode
• systems approach for designing dimensionally stable cells

TOP

Continue development of wetted, drained cathode (including materials development). (M)

HIGH

Improve and decrease cost of alumina purification technologies. (M-L)

HIGH

Develop technology to run production cells for extended periods of time without an anode effect (minimize anode effects per pot day). (N)

HIGH

Achieve more robust bath chemistry. (L/ongoing)

HIGH

Examine alternative carbon sources; learn to cope with new anode materials (high sulfur, ash). (Ongoing)

HIGH

Develop advanced refractories for the cell. (Ongoing)

HIGH

Develop a cell capable of performing effectively with power modulations (e.g., off-peak power).

MEDIUM

Continue development of inert anodes (including materials development). (M-L)

MEDIUM

Refine method to extract impurities from alumina used in dry scrubbers. (N)

MEDIUM

Develop cost-effective, low-resistance, external conductors and connections for both the anode and cathode. (M-L)

MEDIUM

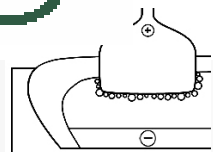
Develop extended-life pot lining (> 5,000-day life). (L)

MEDIUM

Improve waste heat recovery (from exit gases and from the cathode). (L)

MEDIUM

Perfect the continuous, pre-bake anode. (M)

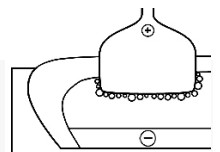


Government response

ALTERNATIVE REDUCTION PROCESSES

Priority Level R&D Need

- TOP** Develop the carbothermic reduction process on a commercial scale. (L)
- TOP** Develop novel, and as yet undefined, concepts for producing primary aluminum. (L)
- HIGH** Develop solid-oxide, fuel cell-type anode with sodium sulfide electrolyte. (L)
- HIGH** Explore electrolytic production of solid aluminum. (L)
- MEDIUM** Explore chloride reduction for liquid aluminum. (L)

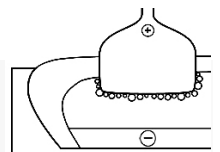


Government response

ALTERNATIVE REDUCTION PROCESSES

Priority Level R&D Need

- TOP** Develop the carbothermic reduction process on a commercial scale. (L)
- TOP** Develop novel, and as yet undefined, concepts for producing primary aluminum. (L)
- HIGH** Develop solid-oxide, fuel cell-type anode with sodium sulfide electrolyte. (L)
- HIGH** Explore electrolytic production of solid aluminum. (L)
- MEDIUM** Explore chloride reduction for liquid aluminum. (L)



Government response

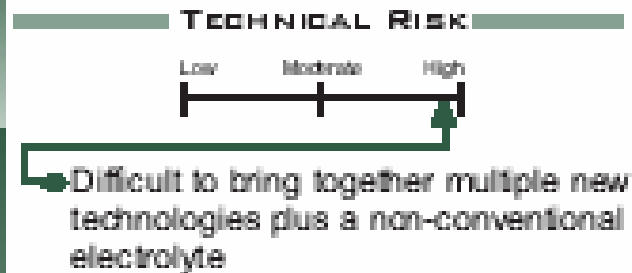
R&D PRIORITY

Develop alternative cell concepts
(combination of inert anodes and
wetted, drained cathodes)

KEY TECHNICAL ELEMENTS

- ◆ Identify or develop materials that fulfill performance requirements, including:
 - longevity
 - manufacturability
 - solubility
 - conductivity
 - thermal shock resistance
- ◆ Revise cell geometry to optimize process.
- ◆ Resolve materials engineering issues created by electric connections.
- ◆ Address scale-up complexities (e.g., 10,000 amps).
- ◆ Develop models (magnetohydrodynamic, process, thermoelectric, etc.) applicable to the new cell (current models are inappropriate).

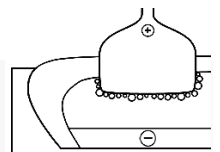
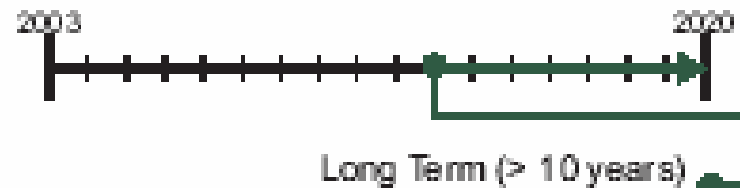
RISK



PAYOFFS

- ↓ Capital Cost ↓ Footprint
- ↓ Emissions (eliminate CO₂, PFCs, SO_x, NO_x, polycyclic aromatic hydrocarbons from process via materials selection)

TIME FRAME



Government response

R&D PRIORITY

Develop the carbothermic reduction process on a commercial scale

KEY TECHNICAL ELEMENTS

- ◆ Conduct scale-up activities on current processes.
- ◆ Develop metal purification techniques (when starting with a metal with unconventional impurities).

RISK

TECHNICAL RISK

Low Moderate High

◆ High technical risk

PAYOFFS

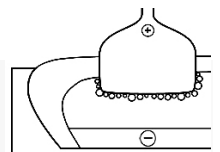
- ◆ Energy consumption (large savings, but on-site carbon emissions will increase)
- ◆ Capital and operating costs
- ◆ Environmental footprint

TIME FRAME

2003

2020

Long Term (> 10 years)



Government response

R&D PRIORITY

Explore other novel, and as yet undefined, concepts for producing aluminum

KEY TECHNICAL ELEMENTS

- ◆ Conduct fundamental research to identify novel concepts.
- ◆ Demonstrate promising concepts at bench scale.

RISK

TECHNICAL RISK

Low Moderate High



◆ High technical risk associated with new concepts

PAYOFFS

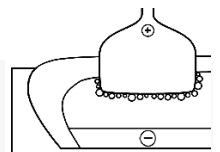
Not well defined, but must be significant to be justified

TIME FRAME

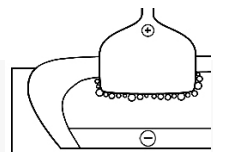
2003

2020

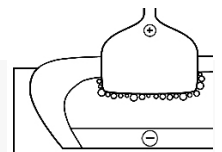
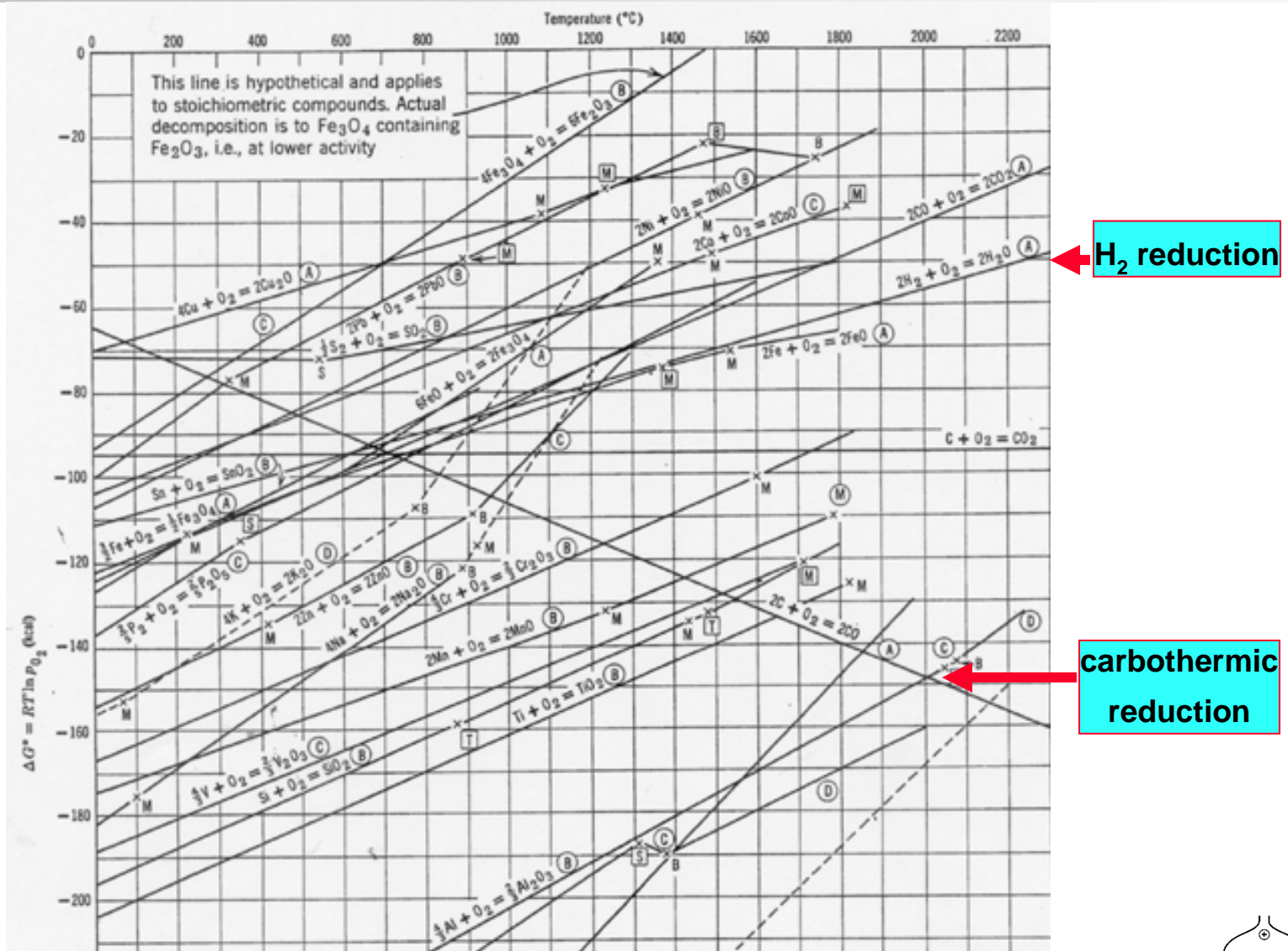
Long Term (> 10 years)



carbothermic reduction of alumina



Ellingham diagram: oxides



carbothermic reduction of alumina

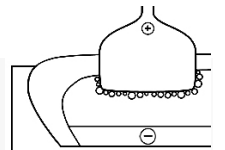


☺ attractiveness:

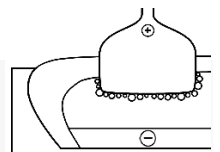
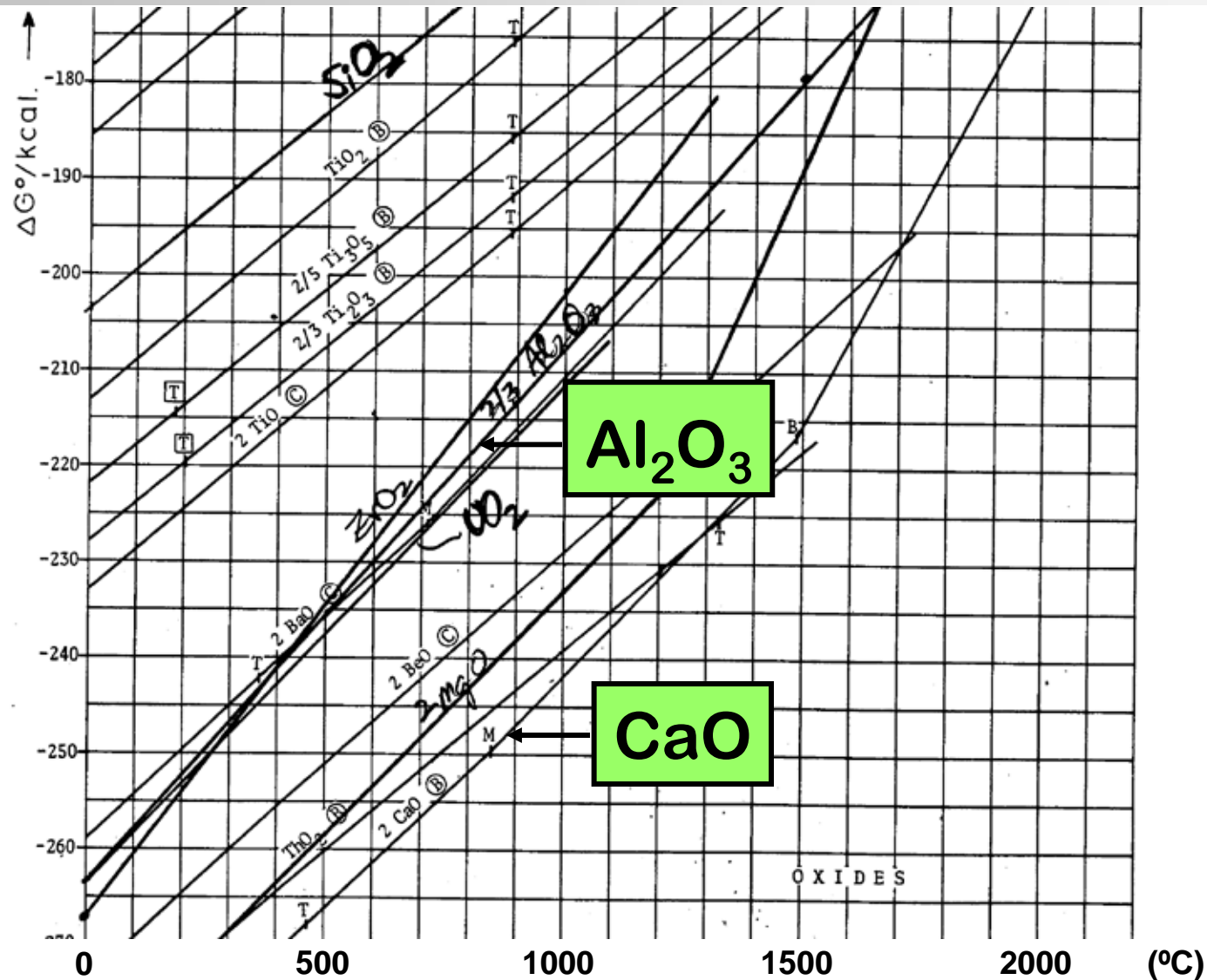
- ⇒ lower energy consumption
- ⇒ improved economy of scale

☹ technical issues:

- ⇒ materials of construction
- ⇒ temperature
- ⇒ back reaction (losses & impurities)



electrolytic-calciothermic reduction



electrolytic-calciothermic reduction

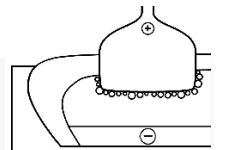
electrolyte: $\text{CaO} - \text{CaCl}_2$

cathode: $3 \text{Ca}^{2+} + 6 \text{e}^- \Rightarrow 3 \text{Ca}$

$3 \text{Ca} + \text{Al}_2\text{O}_3 \Rightarrow 3 \text{CaO} + 2 \text{Al}$

anode: $3 \text{O}^{2-} + 1.5 \text{C} \Rightarrow 1.5 \text{CO}_2 + 6 \text{e}^-$

$3 \text{O}^{2-} \Rightarrow 1.5 \text{O}_2 + 6 \text{e}^-$ (preferably)



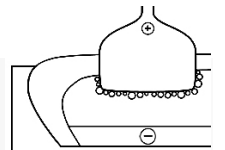
electrolytic-calciothermic reduction

☺ attractiveness:

- ⇒ improved economy of scale
- ⇒ lower energy consumption

☹ technical issues:

- ⇒ materials of construction
- ⇒ CHCs  inert anode



metallothermic reduction

conventional wisdom:

⇒ strictly a *chemical* reaction

⇒ rate limited by mass transfer

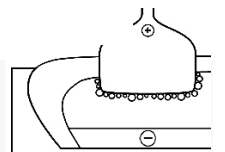
our hypothesis:

⇒ *not* strictly a *chemical* reaction

⇒ electron transfer is involved

☞ metallothermic redⁿ is an
electronically mediated reaction

(EMR)



metallothermic reduction

J. Mater. Res., Vol. 13, No. 12, Dec 1998 © 1998 Materials Research Society

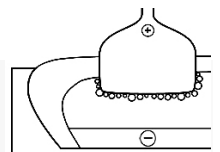
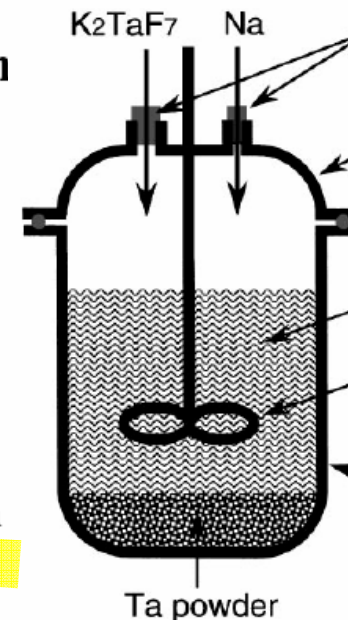
Metallothermic reduction as an electronically mediated reaction

Toru H. Okabe^{a)} and Donald R. Sadoway

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

(Received 9 December 1997; accepted 15 April 1998)

The commonly held view that metallothermic reduction is strictly a chemical reaction and that the process is rate limited by mass transfer has been found to be incomplete. In a study of the production of tantalum powder by the reaction of K_2TaF_7 with sodium, it has been shown that there are two dominant kinetic pathways, both involving electron transfer. Furthermore, the overall rate of reaction is limited by electron transport between the reactants. This indicates that metallothermic reduction is an "electronically mediated reaction" (EMR). Experiments found that the location of the tantalum deposit and its morphology are governed by the reaction pathway.



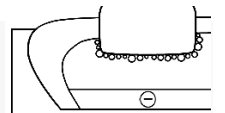
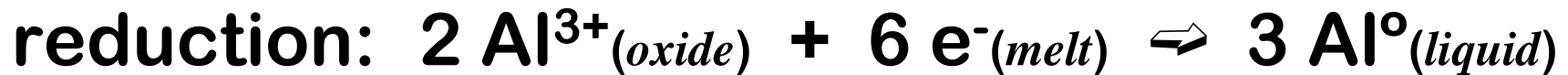
metallothermic reduction



from an EMR perspective:

reaction medium or “melt”: $\text{CaO} - \text{CaCl}_2$

which is a mixed conductor (e^- & M^{n+})



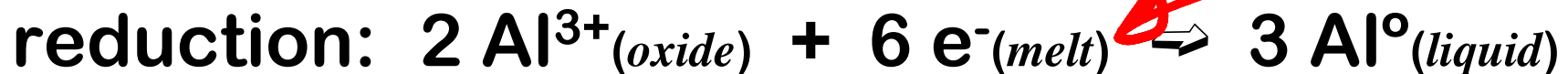
metallothermic reduction



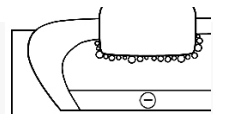
from an EMR perspective:

reaction medium or “melt”: $\text{CaO} - \text{CaCl}_2$

which is a mixed conductor (e^- & M^{n+})



☞ very fast kinetics 😊



molten oxide electrolysis

electrolyte: MgO - CaO - BaO - La₂O₃

feed: Al₂O₃

temperature: 1800°C

anode: ???

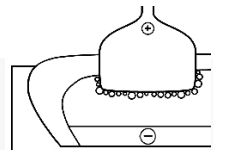
anodic reaction: $3 \text{O}^{2-} \rightarrow 1.5 \text{O}_2 + 6 \text{e}^-$

cathode: ???

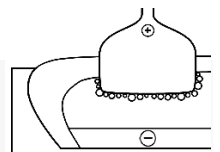
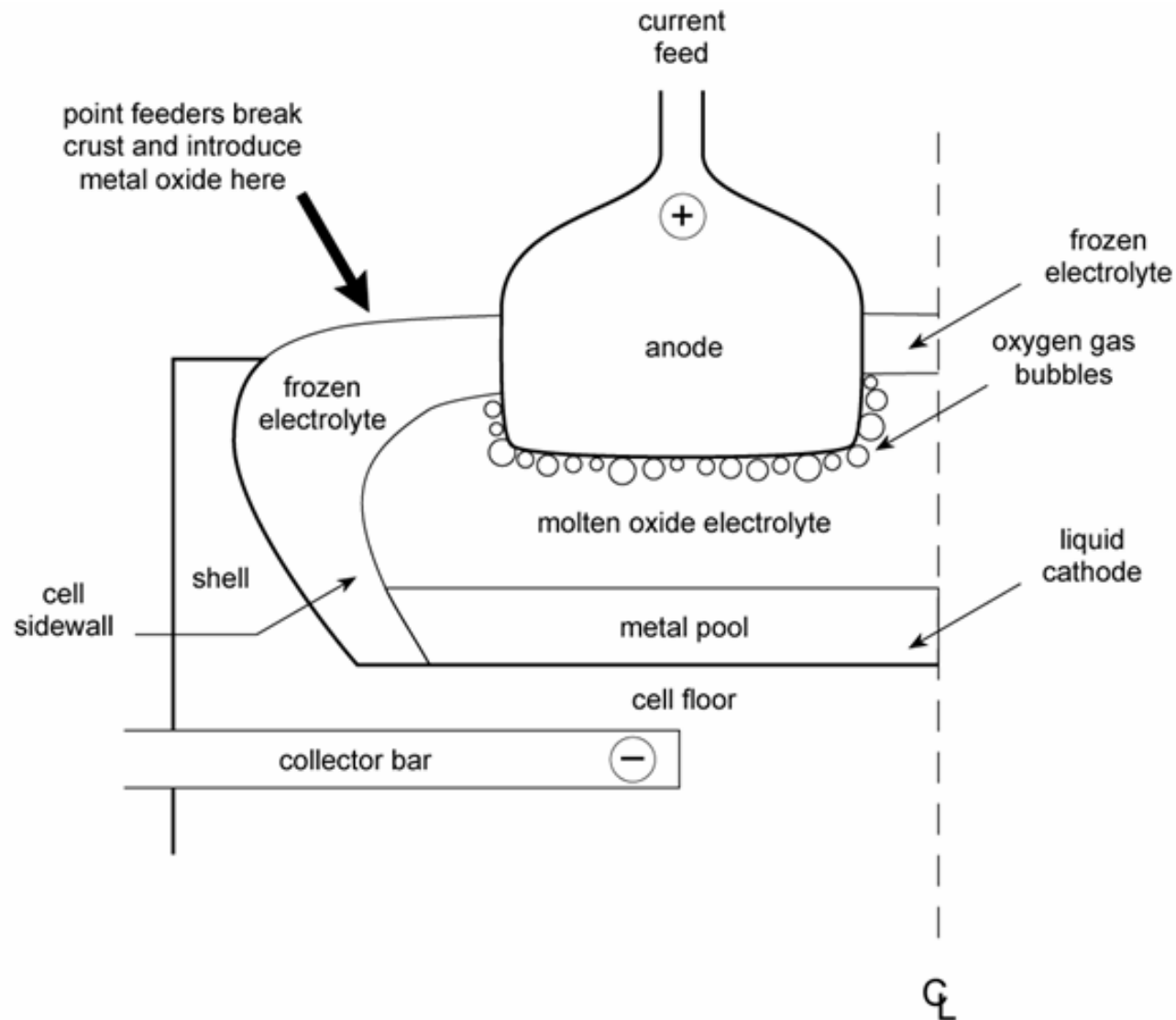
cathodic reaction: $2 \text{Al}^{3+} + 6 \text{e}^- \rightarrow 2 \text{Al}$

overall reaction: $\text{Al}_2\text{O}_3 \rightarrow 2 \text{Al} + 1.5 \text{O}_2$

standard potential: $E^\circ = 1.74 \text{ V}$



schematic of prototype cell



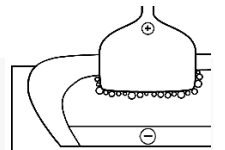
molten oxide electrolysis

☺ attractiveness:

- ⇒ improved economy of scale
- ⇒ environmentally sound

☹ technical issues:

- ⇒ materials, materials, materials



molten oxide electrolysis

UNITED STATES PATENT OFFICE.

ROBERT H. AIKEN, OF WINTHROP HARBOR, ILLINOIS.

PROCESS OF MAKING IRON FROM THE ORE.

No. 816,142.

Specification of Letters Patent.

Patented March 27, 1906.

Application filed June 1, 1903. Serial No. 159,609.

To all whom it may concern:

Be it known that I, ROBERT H. AIKEN, a citizen of the United States, residing at Winthrop Harbor, in the county of Lake and State of Illinois, have invented certain new and useful Improvements in Processes of Making Iron from the Ore, of which the following is a specification.

This invention relates to producing iron from the ordinary oxid ores by first dissolving the oxid in a molten bath or slag and then decomposing the dissolved oxid and depositing the metal as iron by the action of an electric current.

I have found that under proper conditions iron oxid is readily dissolved in molten silicate of one or more of the metals not less electropositive than iron and that when so dissolved it is readily deposited by a moderate current of electricity. Excellent results are obtained by gradually feeding preferably pulverized Fe_2O_3 or Fe_3O_4 into a molten bath of FeOSiO_2 and maintaining a direct electric current through the mass. The addition of CaO , MgO or other oxid acting similarly lowers the fusing-point of the bath, aids solution, insures an advantageous basic character for the bath, and is therefore desirable though not indispensable. As much as twenty per cent. of Fe_2O_3 can be dissolved in basic silicate of proper constitution. The apparatus employed may be without novelty, the anode being preferably carbon or the like, the deposited metal serving as the cathode, and the comminuted material being stirred into the bath as the operation proceeds. The voltage is kept at the proper point during the operation—that is, it is made high enough to overcome the resistance of the bath and decompose the iron oxid held in solution—but not high enough to separate to any material extent the silicon or other more electropositive metals entering into the combination of the silicate. The temperature of the bath is maintained by supplying a current of the proper number of amperes per unit area for this purpose.

It is to be observed that this process is continuous and that the furnace may be very large, the latter point being important in that it permits economy in the matter of current,

If during the continuance of the current the supply of oxid be such that there is a deficiency in the bath, the electrically-low oxid of the silicate will be decomposed, provided, of course, that the voltage of the current be sufficiently high to decompose such oxid; but on the introduction of a plentiful supply of iron oxid the silicate will seize upon enough to make good the former loss. It is then quite possible to modify the process by supplying oxid at such a rate that the deposited metal will be taken from the silicate of iron already in the furnace in part, if not entirely, and perhaps with an acid silicate it may be practically possible to so far modify the process that there shall be absolutely no solution of the iron oxid in the silicate bath. In other words, it is possible to carry the process to the point where practically no iron remains in the silicate-bath provided that the bath contains other suitable bases, as before suggested. Such a course of procedure would not give a continuous process obviously. However, when the bath always contains a considerable amount of dissolved iron oxid and the electrolysis is practically a continuous process, the proportion of oxid contained at any given time may vary from a much smaller amount to about twenty per cent. of the silicate.

What I claim is—

1. The method of making iron from iron oxids which consists in dissolving the oxid in a molten silicate of one or more metals not less electropositive than iron, and passing through the solution a continuous current adapted to decompose said oxid.

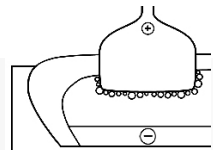
2. The method of making iron from iron oxids which consists in forming a bath of molten silicate of one or more metals not less electropositive than iron, gradually feeding into said molten bath the oxid to be operated upon, and maintaining a direct electric current through the mass.

In testimony whereof I have signed my name to this specification in presence of two witnesses.

ROBERT H. AIKEN.

Witnesses:

J. JEROME LIGHTFOOT,
WALLACE GREENE.



molten oxide electrolysis

UNITED STATES PATENT OFFICE.

ROBERT H. AIKEN, OF WINTHROP HARBOR, ILLINOIS.

PROCESS OF MAKING IRON FROM THE ORE.

No. 816,142.

Specification of Letters Patent.

Patented March 27, 1906.

Application filed June 1, 1903. Serial No. 159,609.

To all whom it may concern:

Be it known that I, ROBERT H. AIKEN, a citizen of the United States, residing at Winthrop Harbor, in the county of Lake and State of Illinois, have invented certain new and useful Improvements in Processes of Making Iron from the Ore, of which the following is a specification.

This invention relates to producing iron from the ordinary oxid ores by first dissolving the oxid in a molten bath or slag and then decomposing the dissolved oxid and depositing the metal as iron by the action of an electric current.

I have found that under proper conditions iron oxid is readily dissolved in molten silicate of one or more of the metals not less electropositive than iron and that when so dissolved it is readily deposited by a moderate current of electricity. Excellent results are obtained by gradually feeding preferably pulverized Fe_2O_3 or Fe_3O_4 into a molten bath of FeOSiO_2 and maintaining a direct electric current through the mass. The addition of CaO , MgO or other oxid acting similarly lowers the fusing-point of the bath, aids solution, insures an advantageous basic character for the bath, and is therefore desirable though not indispensable. As much as twenty per cent. of Fe_2O_3 can be dissolved in basic silicate of proper constitution. The apparatus employed may be without novelty, the anode being preferably carbon or the like, the deposited metal serving as the cathode, and the comminuted material being stirred into the bath as the operation proceeds. The voltage is kept at the proper point during the operation—that is, it is made high enough to overcome the resistance of the bath and decompose the iron oxid held in solution—but not high enough to separate to any material extent the silicon or other more electropositive metals entering into the combination of the silicate. The temperature of the bath is maintained by supplying a current of the proper number of amperes per unit area for this purpose.

It is to be observed that this process is continuous and that the furnace may be very large, the latter point being important in that it permits economy in the matter of current,

If during the continuance of the current the supply of oxid be such that there is a deficiency in the bath, the electrically-low oxid of the silicate will be decomposed, provided, of course, that the voltage of the current be sufficiently high to decompose such oxid; but on the introduction of a plentiful supply of iron oxid the silicate will seize upon enough to make good the former loss. It is then quite possible to modify the process by supplying oxid at such a rate that the deposited metal will be taken from the silicate of iron already in the furnace in part, if not entirely, and perhaps with an acid silicate it may be practically possible to so far modify the process that there shall be absolutely no solution of the iron oxid in the silicate bath. In other words, it is possible to carry the process to the point where practically no iron remains in the silicate-bath provided that the bath contains other suitable bases, as before suggested. Such a course of procedure would not give a continuous process obviously. However, when the bath always contains a considerable amount of dissolved iron oxid and the electrolysis is practically a continuous process, the proportion of oxid contained at any given time may vary from a much smaller amount to about twenty per cent. of the silicate.

What I claim is—

1. The method of making iron from iron oxids which consists in dissolving the oxid in a molten silicate of one or more metals not less electropositive than iron, and passing through the solution a continuous current adapted to decompose said oxid.

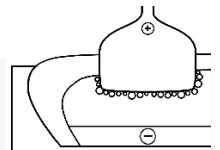
2. The method of making iron from iron oxids which consists in forming a bath of molten silicate of one or more metals not less electropositive than iron, gradually feeding into said molten bath the oxid to be operated upon, and maintaining a direct electric current through the mass.

In testimony whereof I have signed my name to this specification in presence of two witnesses.

ROBERT H. AIKEN.

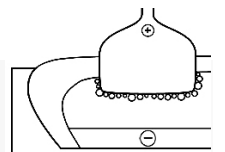
Witnesses:

J. JEROME LIGHTFOOT,
WALLACE GREENE.



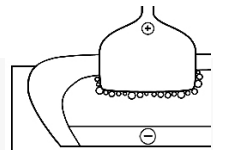
database is incomplete

- ❑ physical chemistry of electrolytes
- ❑ materials science of electrodes



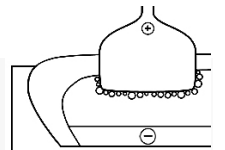
feasibility assessment:

- electrical conductivity measurements
- transference number measurements
- modeling electrical properties
- applicability to iron production



conductivity measurements

- inventing two new techniques for aggressive melts at high temperatures:
 - ① moveable coaxial cylinders
 - ② 4-point crucible



moveable coaxial cylinders

United States Patent [19]
Sadoway et al.

[11] **Patent Number:** **5,489,849**
 [45] **Date of Patent:** **Feb. 6, 1996**

[54] **HIGH ACCURACY CALIBRATION-FREE ELECTRICAL PARAMETER MEASUREMENTS USING DIFFERENTIAL MEASUREMENT WITH RESPECT TO IMMERSION DEPTH**

[75] Inventors: **Donald R. Sadoway**, Belmont; **Kevin G. Rhoads**, Andover; **Naomi A. Fried**, Cambridge; **Susan L. Schiefelbein**, Boston, all of Mass.

[73] Assignee: **Massachusetts Institute of Technology**, Cambridge, Mass.

[21] Appl. No.: **212,478**

[22] Filed: **Mar. 14, 1994**

[51] Int. Cl.⁶ **G01N 27/02**

[52] U.S. Cl. **324/447; 324/449; 204/406; 205/81**

[58] **Field of Search** **324/444, 446, 324/447, 448, 449, 720, 691; 204/406; 205/81-83**

[56] **References Cited**

Jones, Grinnell, et al., "The Measurement of the Conductance of Electrolytes. III. The Design of Cells," *Journal of the American Chemical Society*, pp. 411-419, (Feb. 1931).
 Bard, A. J., et al., *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, pp. 316-369. Date unavailable.

Macdonald, J. R., et al., *Impedance Spectroscopy—Emphasizing Solid Materials and Systems*, John Wiley & Sons, pp. 1-29. Date unavailable.

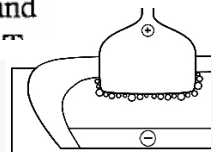
Thomas, J. L., "Precision Resistors and Their Measurements," National Bureau of Standards Circular 470, Issued Oct. 8, 1948.

(List continued on next page.)

Primary Examiner—Kenneth A. Wieder
Assistant Examiner—Christopher M. Tobin
Attorney, Agent, or Firm—Hamilton, Brook, Smith & Reynolds

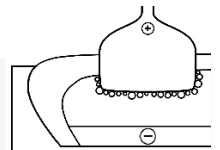
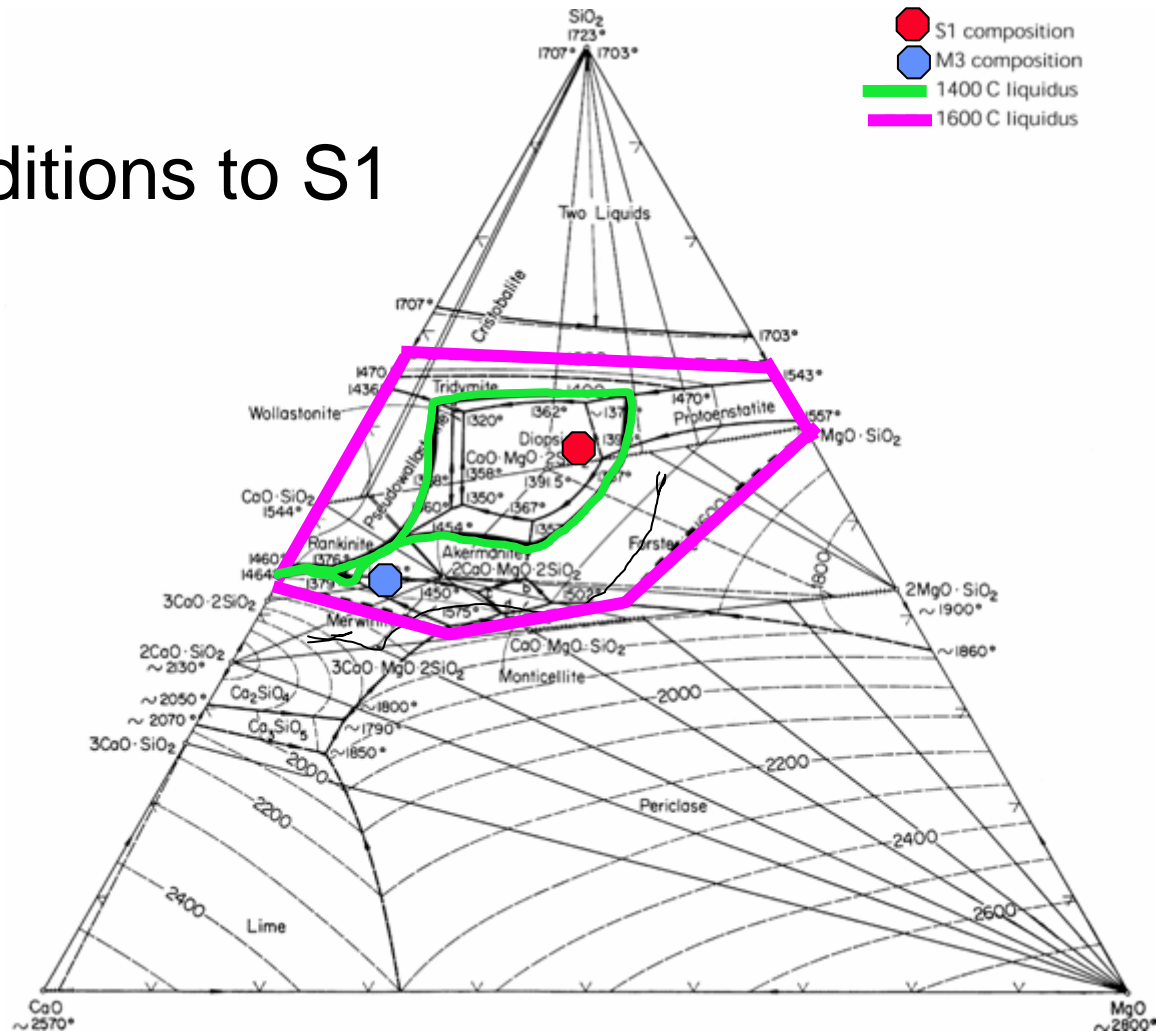
[57] **ABSTRACT**

An apparatus and method for measuring electrical parameters of a medium such as electrical conductivity and dielectric constant between a pair of electrodes are disclosed. The medium can be a liquid, gas, powder, etc., and

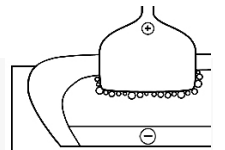
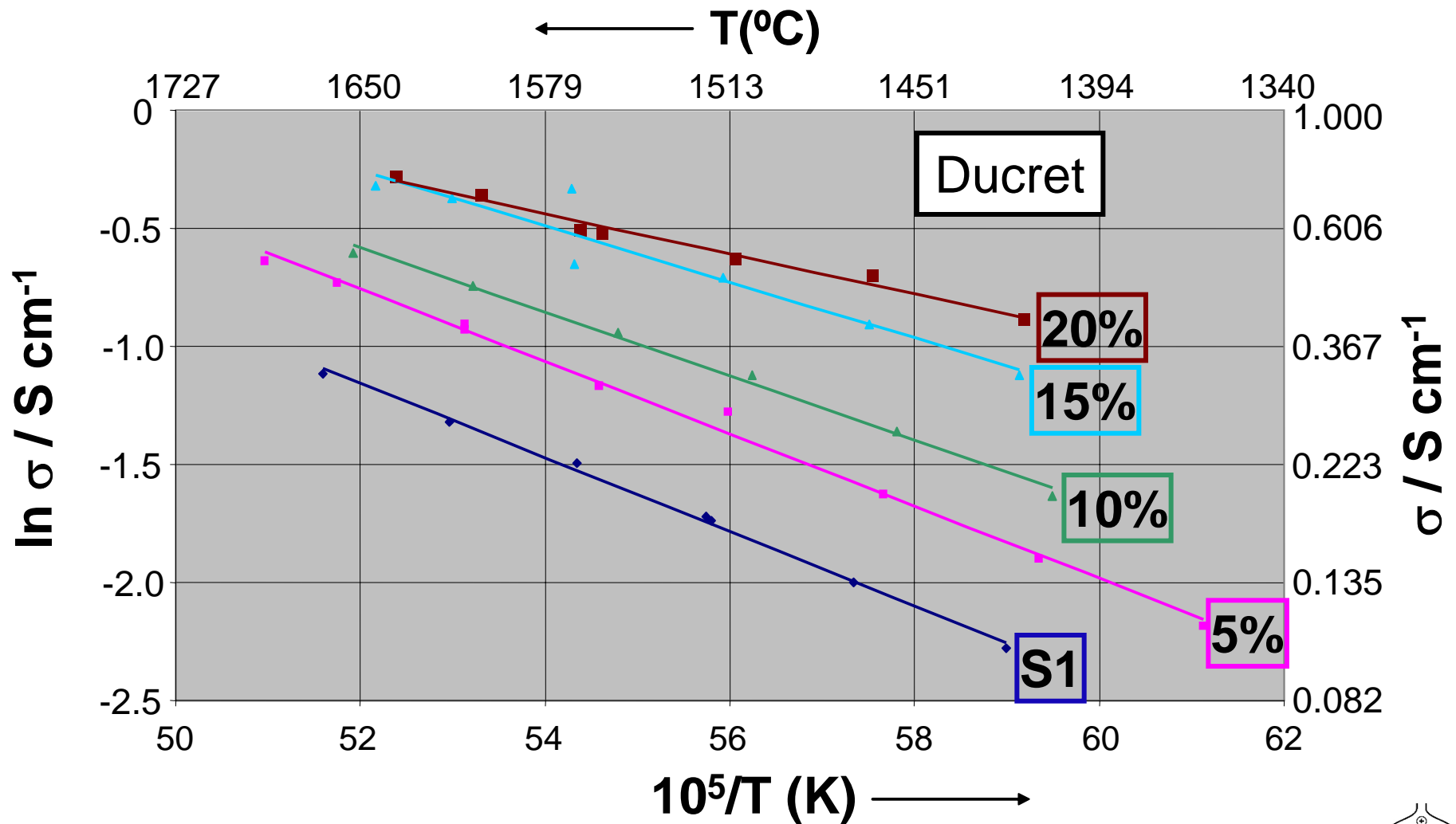


solvent compositions

FeO additions to S1



effect of FeO addition: $\sigma = \sigma(T, c)$

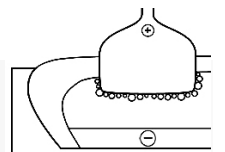


electrowinning experiments

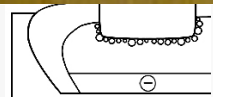
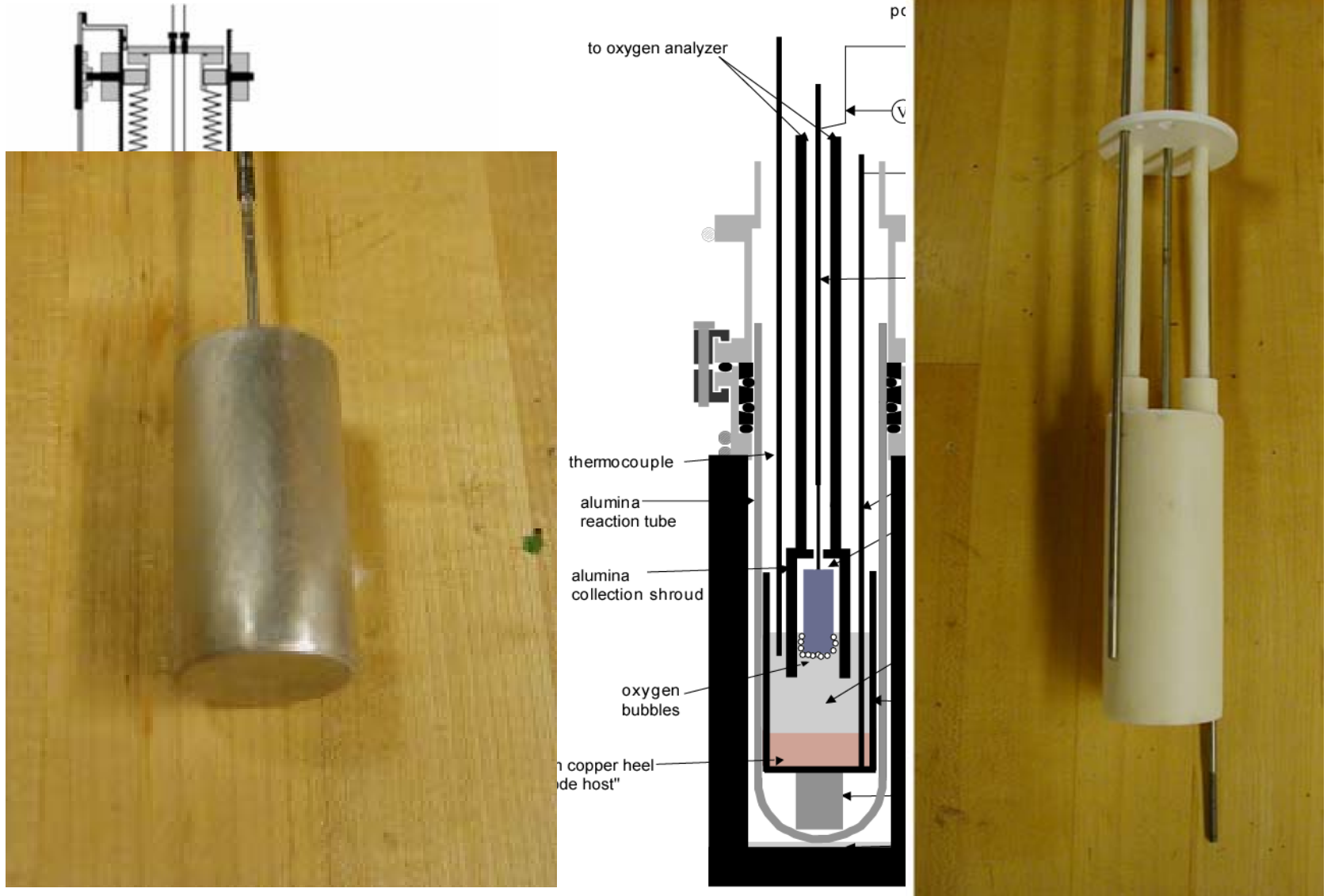
□ galvanostatic electrolysis at 1450°C

(-) $\text{Cu}_{(l)}$ | $\text{FeO} - \text{MgO} - \text{CaO} - \text{SiO}_2$ | Pt (+)

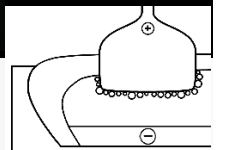
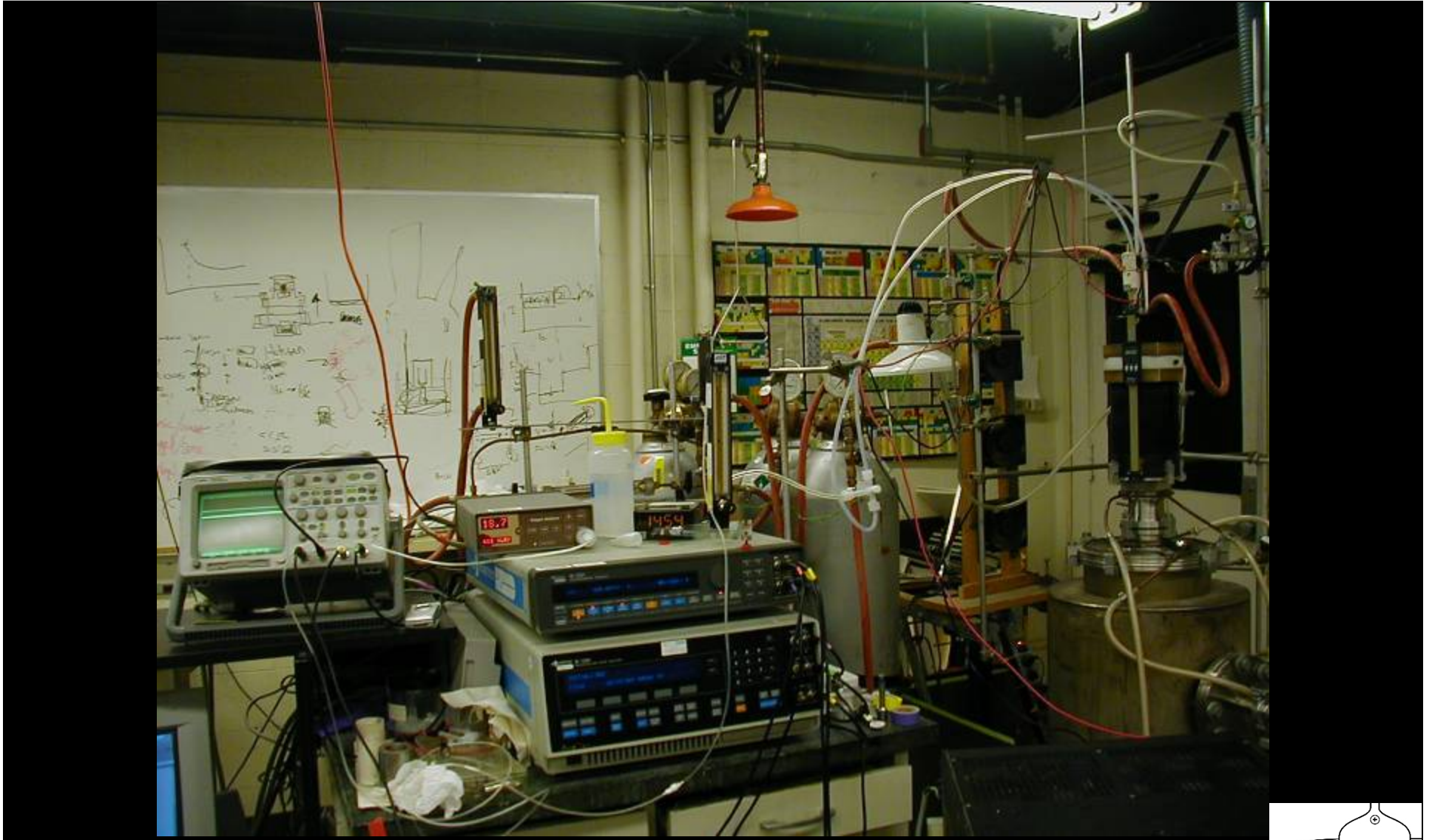
□ electrolytic generation of iron metal and oxygen gas confirmed



laboratory-scale electrolysis cell

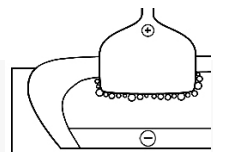


laboratory-scale electrolysis cell

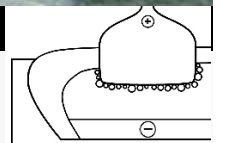


observations

- **electrolysis products**
 - ✓ anode : **oxygen**
 - ✓ cathode : **iron**
- **Faradaic efficiency (anodic)**
 - ☐ measured value 39%
 - ☐ theoretical limit 85% (t_e)



observations



applicability to lunar oxygen generation

daily oxygen requirement = 2.75 kg

Faradaic efficiency = 85% (based on t_{ionic})

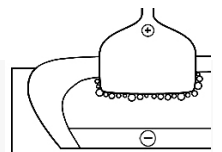
current = 452 A

cell voltage = 2 V ($2.5 \times \Delta H_{\text{FeO}}$)

power supply = 904 W

current density = 5 A cm⁻²

electrode area = 90 cm²



plasma processing

2 approaches:

⇒ thermochemical

⇒ electrolytic

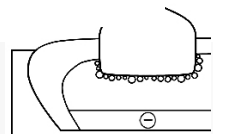
😊 attractiveness:

⇒ avoids certain materials problems

⇒ environmentally sound

😞 technical issues:

⇒ poor energy efficiency

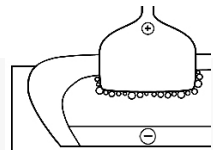


So, what have we learned today?



“I’ve learned a lot in sixty-three years. But, unfortunately, almost all of it is about aluminum.”

© 1977 The New Yorker Magazine, Inc.



magnesium chloride electrolysis

electrolyte: NaCl - KCl - CaCl₂

feed: MgCl₂

temperature: 740°C

anode: carbon

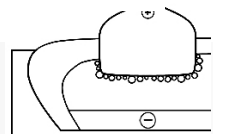
anodic reaction: $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$

cathode: mild steel

cathodic reaction: $\text{Mg}^{2+} + 2 \text{e}^- \rightarrow \text{Mg}$

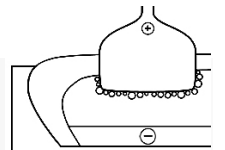
overall reaction: $\text{MgCl}_2 \rightarrow \text{Mg}_{(l)} + \text{Cl}_2$

standard potential: $E^\circ = 2.5 \text{ V}$



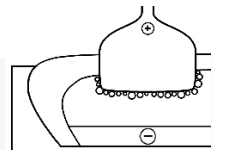
challenges and opportunities

- * new electrode materials (inert):
 - ⇒ reduce C loss in Dow cell
 - ⇒ enable longer-lived bipolar cell
- * new route to anhydrous MgCl_2
- * new electrolyte chemistries
- * lower energy consumption
- * reduced emissions
- * higher space/time yield

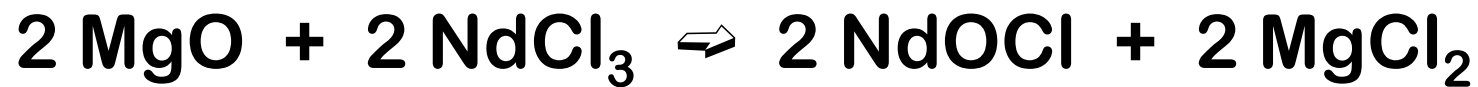


paradigm shifts

- * electrolysis of MgO from a melt of NdCl_3
- * carbothermic reduction to metal
- * electrolytic-calciothermic redn
- * electrolysis of MgO from an oxide melt



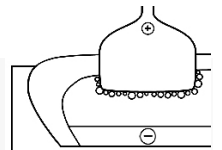
electrolysis of MgO from a melt of NdCl₃



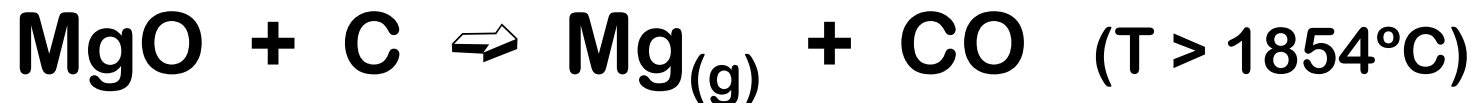
electrolyte: 65% MgCl₂ - 10% NdCl₃ - 25% NdOCl



-R.A. Sharma, General Motors

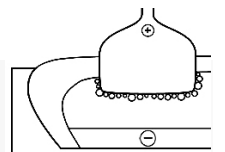


carbothermic reduction



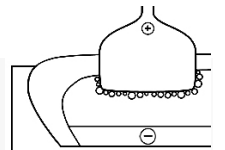
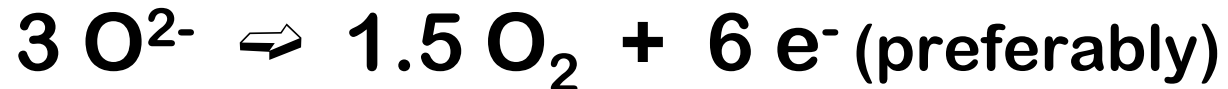
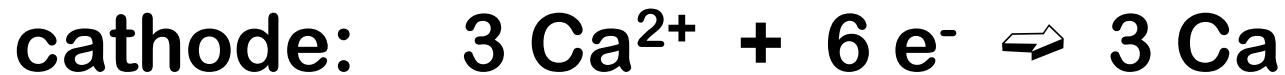
☹ separation of Mg and CO, both gases 🖱

☹ alloy Mg into solvent melt ?



electrolytic-calciothermic reduction

electrolyte: CaO - CaCl₂



molten oxide electrolysis

electrolyte: $\text{CaO} - \text{La}_2\text{O}_3$

feed: MgO

temperature: 1900°C

anode: ???

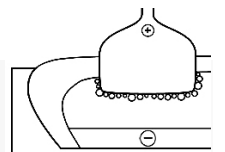
anodic reaction: $\frac{1}{2} \text{O}^{2-} \rightarrow \text{O}_2 + 2 e^-$

cathode: ???

cathodic reaction: $\text{Mg}^{2+} + 2 e^- \rightarrow \text{Mg}_{(g)}$

overall reaction: $\text{MgO} \rightarrow \text{Mg}_{(g)} + \frac{1}{2} \text{O}_2$

standard potential: $E^\circ = 1.47 \text{ V}$



lithium chloride electrolysis

electrolyte: LiCl - KCl eutectic

feed: LiCl

temperature: 400 - 460°C

anode: carbon

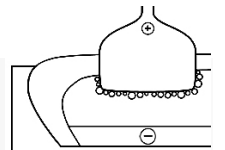
anode reaction: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{e}^-$

cathode: mild steel

cathode reaction: $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}_{(l)}$

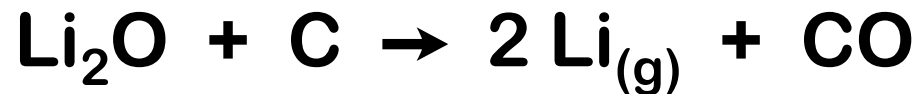
overall cell reaction: $\underline{\text{LiCl}} \rightarrow \text{Li}_{(l)} + \frac{1}{2} \text{Cl}_2$

standard potential: $E^\circ = 3.6 \text{ V at } 427^\circ\text{C}$

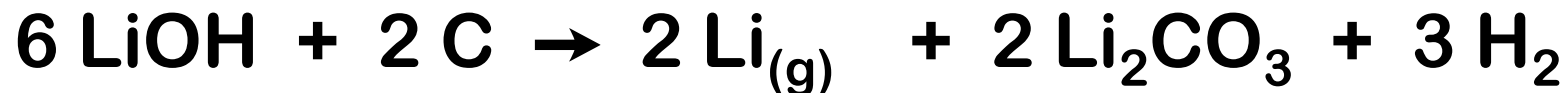


carbothermic reduction

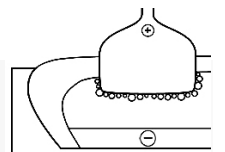
(lithia feed, carbon reductant)



(LiOH feed, carbon reductant)

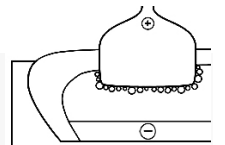
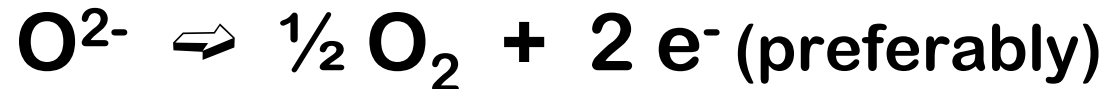
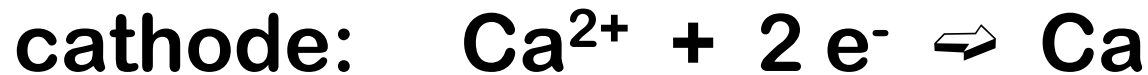


(LiOH feed, iron carbide reductant)



electrolytic-calciothermic reduction

electrolyte: CaO - CaCl₂

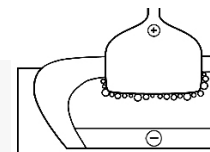


metallothermic reduction

oxide feed:



hydroxide feed:



molten oxide electrolysis

electrolyte: $\text{CaO} - \text{MgO} - \text{SiO}_2 - \text{Al}_2\text{O}_3$

feed: Li_2O

temperature: 1400°C

anode: ???

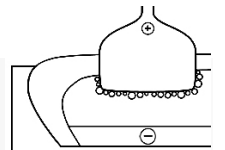
anodic reaction: $\frac{1}{2} \text{O}^{2-} \rightarrow \text{O}_2 + 2 e^-$

cathode: ???

cathodic reaction: $2 \text{Li}^+ + 2 e^- \rightarrow 2 \text{Li}_{(g)}$

overall reaction: $2 \text{Li}_2\text{O} \rightarrow 2 \text{Li}_{(g)} + \frac{1}{2} \text{O}_2$

standard potential: $E^\circ = 1.9 \text{ V}$



molten oxide electrolysis

electrolyte: $\text{CaO} - \text{MgO} - \text{BaO} - \text{Al}_2\text{O}_3$

feed: TiO_2

temperature: 1700°C

anode: ???

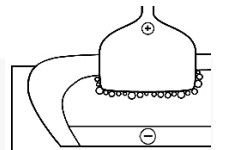
anodic reaction: $2 \text{O}^{2-} \rightarrow \text{O}_2 + 4 \text{e}^-$

cathode: ???


cathodic reaction: $\text{Ti}^{4+} + 4 \text{e}^- \rightarrow \text{Ti}_{(\ell)}$

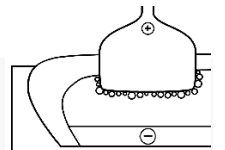
overall reaction: $\text{TiO}_2 \rightarrow \text{Ti}_{(\ell)} + \text{O}_2$

standard potential: $E^\circ = 1.53 \text{ V}$



... in summary

- lithium and titanium prices out of line
 - ☞ situation ripe for innovation:
 - new chemistry 
 - fewer unit operations



... in summary

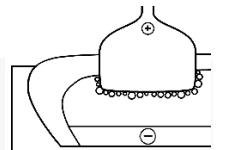
⇒ lithium and titanium prices out of line

☞ situation ripe for innovation:

- new chemistry 

- fewer unit operations

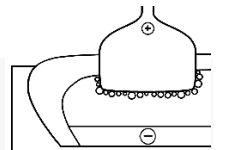
↪ JAPAN!



... in summary

- ⇒ lithium and titanium prices out of line
 - ☞ situation ripe for innovation:
 - new chemistry 🌍
 - fewer unit operations
- ⇒ shift away from $C + Cl_2$
 - ∴ thermochemistry ☹️ ⇒
 - electrochemistry 😊
- ⇒ sustainable metallurgy requires paradigm shifts 💣

☞ *major role for research in molten salts!*



Acknowledgments



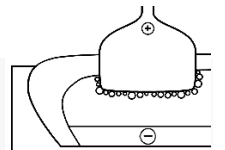
National **A**eronautics
& **S**pace **A**dministration



National **S**cience **F**oundation



Department **o**f **E**nergy



acknowledgments



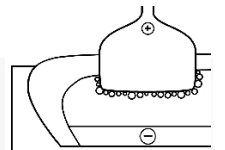
Environmental **P**rotection **A**gency



The Aluminum Association, Inc.



Electric **P**ower **R**esearch **I**nstitute



Towards sustainability through better technology

