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Contribution of Electricity to Materials Processing: Historical and Current Perspectives

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Corresponding Author:	Antoine Allanore, Ph.D. MIT Cambridge, MA UNITED STATES
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First Author:	Antoine Allanore, Ph.D.
First Author Secondary Information:	
Order of Authors:	Antoine Allanore, Ph.D.
Order of Authors Secondary Information:	
Abstract:	<p>Most major materials extraction processes are more than 100 years old, developed at a time of limited awareness of their environmental impact and the issue of resources limitations. In this context, it is proposed to look back at materials processes progress in parallel with the history of electric power generation. This overview reveals that electricity became a key energy vector for chemical and materials processing in less than a century. The role of electricity in the production of the highest tonnage metals, i.e. aluminium and steel proved to be crucial, leading to higher productivity and lower energy consumption for both metals. Finally, a review of the recent developments in electrolytic steel shows that new electricity-based processes are possible, offering the opportunity for a symbiosis between future carbon-free power generation and materials processing.</p>

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4 Contribution of Electricity to Materials Processing:
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6 Historical and Current Perspectives

7 Antoine Allanore

8 Department of Materials Science & Engineering

9
10 Massachusetts Institute of Technology,

11 77 Massachusetts Avenue, #13-5066

12
13 Cambridge, MA, 02139

14
15 allanore@mit.edu,

16
17 Phone: +1 617 452 2758

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20 **Abstract**

21 Most major materials extraction processes are more than 100 years old, developed at a time of limited awareness of
22 their environmental impact and the issue of resources limitations. In this context, it is proposed to look back at
23 materials processes progress in parallel with the history of electric power generation. This overview reveals that
24 electricity became a key energy vector for chemical and materials processing in less than a century. The role of
25 electricity in the production of the highest tonnage metals, i.e. aluminium and steel proved to be crucial, leading to
26 higher productivity and lower energy consumption for both metals. Finally, a review of the recent developments in
27 electrolytic steel shows that new electricity-based processes are possible, offering the opportunity for a symbiosis
28 between future carbon-free power generation and materials processing.
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35 *1. The availability of electricity: a timeline*

36 The impact of electricity on the level of technological development achieved by mankind is hard to
37 summarize. The upper part of Figure 1 presents the timeline in the mastering of electricity and reveals that electric
38 power became available quantitatively and reliably only at the beginning of the 19th century, thanks to a first key
39 invention: the battery by A. Volta in 1799. Several decades elapsed before the second key discovery: a device that
40 was able to reliably convert mechanical power to electricity, invented by M. Faraday in the form of a disk generator
41 in 1831. The battery and the disk were both immediately adopted by scientists in their laboratory as a source of
42 electricity. The successful demonstration of the electromagnetic conversion method led to numerous developments,
43 and in particular to the invention of the dynamo for high power application by C. Wheatstone and W. Siemens
44 simultaneously in 1867. The next key step in this timeline are the invention and construction of the first dam for
45 electric power generation, which occurred presumably close to Niagara Falls (Schoelkopf Power Station No. 1,
46 1881). One year after, the first coal-fired power station was built and operated in New York City (Edison's Pearl St
47 station, 1882).
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55 A century of inventions and developments passed before mankind was able to reliably generate large
56 quantity of electricity, an achievement considered as one of the pillars of the 2nd industrial «revolution».
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6 2. *Adoption of electricity: the role of chemists*

7 As illustrated in the center of part of the timeline in Figure 1 ‘philosophers’ of the early 19th century were
8 well ahead of their time and immediately embraced this new form of energy as a mean to isolate elements and
9 investigate their physical properties.

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11 As early as 1807, the potential difference at the terminal of a battery was identified by chemists as a
12 powerful tool for the investigation of the ‘true elements of bodies’. It indeed allowed the experimentalists to expose
13 any chemical media to a finite and controllable difference of chemical potential. Helped by the availability at the
14 Royal Society of the world largest battery, H. Davy became a chemist of standing and isolated alkaline and alkaline
15 earth elements thanks to electrolysis [1]. The isolation of these reactive elements was a first in chemistry and helped
16 in less than two decades to separate other elements thanks to metallothermic reaction, e.g. beryllium («glucinium»
17 by reduction of its chloride salts with electrolytic potassium [2,3]). Less than two decades after Volta’s invention,
18 electricity was also identified as a mean to provide heat and obtain temperatures hardly achievable with previous
19 laboratory techniques: J. G. Children melted metallic iridium and osmium in 1813 using a battery as electricity
20 source [4]. It is also thanks to electricity that H. Moissan - who isolated fluorine thanks to electrolysis in 1886 [5] -
21 was able to reach temperatures in excess of 3000°C in his electric furnace that relied solely on arc-generated
22 radiative heat [6]. It is with this tool that he investigated diamond synthesis and the melting point of refractory
23 oxides.

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25 The use of a continuous source of electricity and the principle of electrolysis was also adopted by chemists
26 to produce essential gases in significant quantities and in pure form: hydrogen [7], oxygen [7] or ozone¹. Some of
27 these processes or products nowadays are interestingly advocated as a solution to mitigate mankind’s impact on the
28 environment. The remarkable efficiency of electrolysis for separation has continued to be appraised by chemists in
29 the 20th century, for example after the discovery of deuterium for the forthcoming production of heavy-water [8].
30 The production of chlorinated compounds by electrolysis² was also an early discovery and scaled up at the pace of
31 industrial electricity deployment [9]. The chlor-alkali production ultimately became one of the most important
32 process in the chemicals industry³, consuming around 3% of the electricity in USA. It is in this industry that
33 electrochemical experts see the last technical breakthrough of key importance for energy and the environment: the
34 dimensionally stable anode (DSA®) for chlorine evolution invented by H. DeBeer and industrialized by the V. & O.
35 DeNora in the 1970’s [11]. From a materials perspective, it is fair to stress that the technological progress and the
36 sustainability of these electrochemical processes relied intensively on the application of materials science which
37 provides a link to the section below.

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52 ¹ Ozone was identified as the «odor of electricity» because of its production during thunderstorm. Its first isolation
53 by electrolysis is due to C. F. Schönbein, *Ber. Verh. Nat. Ges. Basel*, 1838-40, 4, 58, from a lecture on March 13,
54 1839, see Mordecai B. Rubin, Technion-Israel Institute of Technology, The History of ozone. The Schönbein
55 Period, 1839-1868, *Bull. Hist. Chem.*, vol. 26, Number 1 (2001)

56 ² Chlorine as an element was isolated and identified by L.J. Gay-Lussac in 1809 without assistance of electricity

57 ³ The author cannot refrain from quoting Clifford A. Hampel, a chemical engineer :‘The chlorine industry,[...],
58 produces the two greatest tonnage products of the electrochemical industry [...] This statement neglects the
59 production of steel made in electrical furnaces’, *The Encyclopedia of Electrochemistry*, (1964), R. K. Krieger
60 Publishing Company, Huntington, NY, p172, see [10]

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6 *3. Contribution of electricity to metal processing*

7 The timeline in Figure 1 also shows that many philosophers at the time of Alessandro Volta were not only
8 chemists, but also metallurgists. In 1805, three decades before Faraday's laws on electrolysis, L. Brugnatelli
9 demonstrated the principle of electrodeposition of gold using Volta's battery [12]. In 1808, H. Davy demonstrated
10 the use of an arc to melt and join metal thus giving birth to fusion welding techniques. These early successes
11 initiated an intimate relationship between electricity and metallurgy at both low and high temperatures.
12

13 In less than 70 years, the field application of electrolytic methods in aqueous-based electrolyte was
14 broadened and investigated for the extraction or manufacturing of most common metallic elements (33 out of 70)
15 e.g., for plating, refining or forming [13]. Industrial electrolysis at low temperature is nowadays a key process for
16 primary and secondary metal extraction, and enables the large-scale availability of some of the most important
17 metals.
18

19 Electrolytic techniques for metal separation at high-temperatures in molten salts were also applied early as
20 pioneered by H. Davy in 1807 [1]. The corresponding industrial processes were designed and operated less than a
21 century later, for sodium (from sodium hydroxide by Castner in 1891 [14] and later sodium chloride electrolysis by
22 Downs [15]), magnesium (chloride electrolysis principle by Faraday in 1833 [16]), lithium (commercial production
23 started in 1923 from chlorides) or rare-earth elements (in chlorides or fluorides [17,18]). One metal, isolated before
24 the advent of electrolysis, has lead to one of the most fascinating business and technological adventure of the 20th
25 century: aluminium. Considered as a precious metal before the invention of molten cryolite electrolysis
26 simultaneously by C.M. Hall [19] and P. Héroult [20] in 1886, aluminium has become a commodity in less than 25
27 years.
28

29 The use of electricity for high temperature metal extraction or refining in electric furnaces was also
30 promptly adopted, with a very sound physical understanding of the thermodynamics attributes of electricity [21].
31 The invention of the direct arc-heating furnace is credited to W. Siemens [22] as early as 1878. At that time, an arc
32 was created between an electrode and the material to be processed. The combination of direct arc and resistance
33 heating was patented in 1887 and operated in France (La Praz) to melt steel for the first time by the very same P.
34 Héroult in 1900 [23, 24]. In this specific case the arc was generated between two electrodes through a resistive
35 media - a slag - in contact with the material of interest. After several decades of domination by the Héroult type of
36 furnace, and after its important transition from AC to DC operation, direct arc heating furnaces for smelting
37 operation became commercially available to process oxide materials and are used today for the extraction of a wide
38 range of products, from ferro-alloys to platinum group elements [25].
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40 *4. Benefits of materials processing with electricity*

41 The use of electricity in metal production provides unique process attributes: low capital cost, high purity
42 of the metal product, easy process control, flexible production capacity... These key features shall not mask another
43 asset of the industrial application of electricity: using electricity helps to reduce the energy consumption and
44 improve productivity.
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4 In the context of the promotion of sustainable materials processing techniques, it is of interest to recall the trend in
5 the energy intensity⁴ for aluminium production (Hall-Héroult electrolytic process (HH)) along with the increase in
6 the corresponding reactor productivity (Figure 2). These data are praised by the aluminium sector and are worth
7 sharing with the whole materials community: the use of electricity led simultaneously to a rapid and drastic
8 reduction of the specific energy consumption and a considerable increase in the cell capacity (productivity per
9 square meter of cathode). For comparison, the time variation of the energy consumption for primary steel production
10 (ironmaking, Blast-Furnace based (BF)) and steel electric remelting (Electric Arc Furnace (EAF) based) is presented
11 in Figure 2 revealing a similar rate of improvement during the same period, though limited to an energetic efficiency
12 factor slightly higher than 2 for BF, while aluminium is close to 1.5.

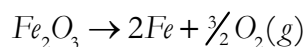
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18 The less favorable efficiency for ironmaking may be due to the reliance on a gas-solid reduction reaction
19 which require numerous pre- and post- operations (coke oven, sintering, basic oxygen furnace respectively),
20 ultimately leading to temperature discontinuities and energy losses along the various steps [2]. One has to emphasize
21 that these numerous steps have been developed on purpose to guarantee the impressive productivity of the blast-
22 furnace. As a matter of fact some ironmaking integrated plants are operating today close to what is considered an
23 optimal level of energy consumption, although radically different techniques are under development to allow further
24 reduction in energy intensity and GHG emissions. Interestingly, in the USA and some other countries, a significant
25 reduction in energy consumption and CO₂ emissions for steelmaking occurred at the end of the 20th century (Figure
26 3), coinciding with a more intensive use of the electric arc furnace. This demonstrates that using electricity for
27 steelmaking is a modern reality and actually provides benefits.

34 35 *5. The ironmaking dilemma*

36 The ironmaking issue is a key challenge both from the society and engineering standpoints. The immediate
37 availability of carbon sources, initially as charcoal, has tied the iron smelting operation to carbon around 4000 years
38 ago [26]. This successful relationship is a gift to mankind: both carbon and iron oxide are abundant, the Gibbs
39 energy of formation of iron oxide is low - it is relatively easy to reduce iron oxide to metal -, carbon provides unique
40 mechanical properties to iron and finally the amount of heat generated during the combustion of carbon is sufficient
41 to guarantee the production of molten metal. Without any attempts to criticize the technological and scientific
42 developments that shaped the existing steel industry processing it is of interest to review the fundamental nature of
43 iron extraction.

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48 Adopting a holistic approach - backed-up by thermodynamics -, one can depict the extraction of iron from
49 the oxide as a separation process, an operation which in principle does not require the use of another chemical. To
50 be efficient, this step requires careful monitoring of the amount of chemical energy, equivalent to work in
51 thermodynamic terms [30]. This is needed to separate the oxygen anions from the metal (reaction 1).

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56 ⁴ The energy index is defined here as the ratio of the actual specific energy consumption (Best Available Technique)
57 to the thermodynamic minimum for the oxide separation into its constitutive elements (metal and oxygen) in the
58 case of primary extraction, and minimum heat needed to melt the metal in the case of the EAF. This is a fair
59 comparison for production of primary aluminium and steel since both processes rely on the use of carbon as reactant
60 and ultimately produce CO₂.



Simultaneously a definite amount of heat is needed to sustain the reaction and obtain the metal in the liquid form.

A *carbonated chemical* (carbon, or more accurately CO) was used in the early age of mankind to provide the work needed to conduct the separation, but its reaction with the iron oxide is difficult to master on large scale. An advanced reactor to operate this reaction has therefore been developed i.e. the blast-furnace (BF).

As noticed in the schematic of current ironmaking flow-sheet (Figure 4), a number of reactors have been added to the BF to produce virgin steel at high tonnage today. Indeed, to cope with the gas/solid reaction principle and provide high enough productivity, ancillary steps have ingeniously been designed to prepare the compounds needed for the reduction (lime, sintering/pelletizing and coke plant). Because the reduction temperature is achieved by combustion, oxygen is used in the blast, requiring nitrogen separation for better efficiency. At that stage, the reactants, fluxes and fuels are ready to be introduced in the BF. These preparations are required to achieve the simultaneous control of the three most important chemical engineering phenomena in the reduction step: 1) the gases, solids, and liquids pattern; 2) the advancement of the reaction and 3) the heat-balance. Despite these astonishing engineering developments, and because of the large affinity of carbon for iron, the level of the former element in the product out of the blast-furnace («pig iron») is far too high for most applications. A decarbonization step (basic oxygen furnace or converter) is therefore added in which oxygen is used to eliminate the excess of carbon reductant initially introduced. It is only after these processing steps that steel of acceptable carbon content is obtained, and secondary metallurgists can operate.

We therefore see that the *chemical approach* for steel production in a single high capacity reactor requires large capital investments in both the BF and its ancillary reactors and is likely to pose some challenges in reducing further the energy consumption [32]. Furthermore, one of the key consequences in the dependency on carbonated compounds is the nature of the gases ultimately emitted, CO and CO₂. In the early 21st century, it is established that the most advanced integrated steel mills have a greenhouse gases intensity of around 1.8 tCO₂-t_{HotRolledCoil}⁻¹ [31].

From the society perspective, the low price-point of steel - less than 0.6 \$.kg⁻¹ - and its world annual consumption - 1.5 billion tonnes -, make its sustainability issue of key importance: steel currently ranks number 1 materials in terms of Greenhouse Gases impact in most developed countries. This reality has been acknowledged as early as 1990's by steelmakers and metallurgists [32,33], and ultimately lead to the bold and pioneer decision of the steel industry to investigate new methods for steel-production, all across the globe and with various approaches and targets⁵. Some of these approaches, interestingly, consider taking further advantage of electricity for steelmaking thus bridging the existing technological gap between iron and the other metals.

6. Challenges in existing electrochemical techniques for metal extraction

The picture presented above that describes the efficiency and importance of electricity-based materials processing does not imply the absence of technical challenges in electrochemical technologies.

⁵ For example Ulcos (www.ulcos.org) in Europe in 2004, AISI CO₂ Breakthrough (<http://www.steel.org>) in North America in 2005, Course 50 (http://www.jisf.or.jp/course50/outline/index_en.html) in Japan in 2008

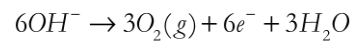
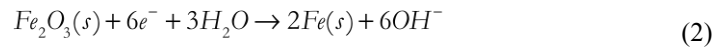
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4 Metal extraction by aqueous electrochemistry suffers many limitations for high throughput and low specific
5 energy consumption. The low current density - typically less than $0.05 \text{ A} \cdot \text{cm}^{-2}$, the limited cell height, the large inter-
6 electrode distances, the presence of a physical separator between the electrodes, or the limited deposit thickness due
7 to dendritic growth are individually or collectively responsible for these limitations.
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10 High current densities are obtained in molten salts but in processes that produce solid metal lead to
11 dendritic or powder deposits. This product form requires significant additional energy downstream for rinsing and
12 salts recovery, as well as numerous pre or post-processing steps (powder handling, compaction, re-melting). The
13 batch-mode of operation of these processes clearly limits their field of application. One of the key issue for the
14 sustainability of molten-salts electroextraction processes is the absence of satisfactory inert anode materials, i.e.
15 which could replace consumable carbon electrode and sustains oxygen evolution. This «ultimate materials»
16 challenge [34], despite some pioneering efforts, remains current in particular for fluoride-based electrolyte.
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22 7. Openings: direct oxide processing at low and high temperature by electrolysis

23 Innovative approaches therefore seem requested to adapt electrolytic techniques for tonnage production of
24 metals. Two paths have recently been proposed and demonstrated for iron, at low and high temperature. These
25 techniques are not limited to this element by any means, but they do point the way with respect to such high tonnage
26 - low cost metal.
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30 At low temperature (100°C), the electrolysis of iron oxides particles in suspension was patented in 1918
31 [35]. It consists in the electrolysis of iron oxide particles (hematite typically) in a concentrated aqueous alkaline
32 electrolyte ($\text{pH}=15$, 100°C). The particles are suspended at relatively high concentration and are subjected to
33 electrolysis following reaction (2) on the cathode and (3) on the anode:
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40 (3)

41 It is only recently that an insight into the cathode reaction mechanism has been provided, revealing a topochemical
42 electroreduction mechanism of an oxide slab [36] operative in absence of bulk solid-state diffusion. This
43 mechanism, involving reaction of particles directly in contact with the cathode without dissolution of iron ions in the
44 bulk electrolyte [37] prevents loss of efficiency through ion valence shifting between the cathode and the anode.
45 The mechanism justifies the high selectivity of the process (selectivity higher than 90%), the high current densities -
46 up to $1.5 \text{ A} \cdot \text{cm}^{-2}$ [38], and the advanced energetic efficiency (higher than 80%). This last feature is partly inherited
47 from the high conductivity of the sodium hydroxide electrolyte, the absence of a separator, and the availability of
48 high efficiency oxygen evolving anodes for such electrolyte. This unusual electrolysis configuration, which involves
49 suspension handling and particle-metal surface interactions [39] has been operated in various cell designs (plates,
50 cylinders [40]) and lead to the development of large scale innovative reactor design for iron production, which
51 produces plates up to 3kg and 5 mm thickness (Figure 5).
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4 The commercial version of the process is envisioned with a vertical stacking of the cells to reduce the foot print of
5 the extraction process. Meanwhile, the energy consumption has reached values ($2600\text{kWh.t}_{\text{Fe}}^{-1}$) already close to the
6 thermodynamic minimum, providing another example of the sole ability of electrical technique to lead to the rapid
7 development of processes with high energetic efficiency.
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10 At high temperature, the concept of Molten Oxide Electrolysis (MOE) championed by Prof. D. Sadoway
11 [41] has been developed for a suite of metals, including iron. The key idea is to operate in a molten oxide electrolyte
12 - a slag in pyrometallurgist language - in a configuration very similar to the Hall-Héroult cell. The operating
13 temperature of 1600°C allows the direct production of liquid metal in a semi-continuous manner and the presence of
14 an oxide melt enables the building of a frozen side-wall. This reduces the capital-costs of such high-temperature
15 reactors. The demonstration of simultaneous iron production and oxygen generation at the bench scale has been
16 published recently [34, 42]. Efforts have been conducted to find an anode material that sustains the corrosive oxide
17 environment [43] and the oxygen evolution at such temperature. The foreseen current density (above 2A.cm^{-2}), the
18 absence of carbon in the reactor, and the low capital costs are among the key assets of this technology and explain
19 the continued interest and support of this technique by steel producers worldwide. The process operates in an
20 optimized energetic set-up, i.e. it is the synthesis of an electrolytic process (for the ability to provide exactly the
21 amount of work needed to decompose the oxide) and the electric arc furnace⁶. The corresponding minimum energy
22 consumption for MOE-steel is then $2600\text{kWh.t}_{\text{liquid Fe}}^{-1}$ which, taking into account typical heat-losses in advanced
23 high-temperature electrolysis cells (40%), translates to around $3600\text{kWh.t}_{\text{liquid Fe}}^{-1}$. In such conditions, as presented
24 in Figure 6, CO_2 mitigation for steelmaking could be achieved as early as 2013 for example using a natural gas
25 combined cycle power plant. Thus carbon-free sources of electricity can ultimately provide GHG-free steelmaking
26 thanks to electrolysis.
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36 Both approaches have key common features: 1) iron ore particles are directly reduced with the
37 corresponding ability to process fines or ultrafines ore, 2) perfectly controlled energetic conditions are determined
38 solely by the electrolyte composition and the cell design and 3) metal of unique metallurgical composition is
39 produced. It is important to realize that MOE provides the advantage of directly producing molten iron at high
40 throughput in a continuous manner, making it ideally designed for tonnage metal production such as steelmaking.
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45 Conclusion

46 Electricity in materials processing has a key role that started with its mastering by mankind at significant
47 scale. For the extraction of metals in particular, it is noticeable that the process efficiency and productivity have
48 been significantly improved at a high pace, leading to a reduction of the corresponding energy consumption as
49 illustrated for aluminium. Electricity has also become a key energy vector in steelmaking and thanks to new
50 concepts in electrochemistry, one may foresee its usage for primary iron production as well. Recent results indeed
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56 ⁶ Though an electric arc furnace uses the principle of an «arc», or a plasma - high voltage and low current. This is in
57 striking difference with the thermodynamic requirements for metal extraction where the energy input is ideally in
58 the form of work (definite cell voltage close to the thermodynamic minimum) and the productivity has to be as high
59 as possible (high current).] (to provide heat in an efficient manner), taking advantage of the thermodynamic
60 principle of equivalence of work and heat at high temperature
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suggest that significant mitigation of the GHG impact of ironmaking is possible with ‘electrolytic steel’, in particular in the context of a decarbonization of power generation or the creation of a CO₂ emissions trading system.

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4 **List of Figures**
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7 **Figure 1.** *Selective timeline of development in electricity generation (top), application of electricity for isolation of*
8 *elements (bottom, 'I'), demonstration of process principles (bottom, 'P') and industrial applications (bottom, 'A').*
9 *Sources are cited in the text.*
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13 **Figure 2.** *Chronological variation of the specific energy efficiency index (ratio between the actual specific energy*
14 *consumption and the thermodynamic minimum, 6.6, 3.5 and 22.9 MJ/t for primary iron (BF), iron remelting (EAF)*
15 *and aluminium (HH) respectively ([26], AISI and [31]), line and symbols on the left axis) and the reactor*
16 *productivity index (ratio based on the 1990 value, provided by [27] and [30], histogram on the right axis).*
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20 **Figure 3.** *Chronological variation of the share of the electric arc furnace route (square) and the specific energy*
21 *consumption for steel production (ratio between the actual specific energy consumption and the value in 1990,*
22 *circles) in the United States [AISI and Iron and Steel Technology].*
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26 **Figure 4.** *Simplified flow-sheet of an integrated steel plant for production of virgin steel based on iron ore reduction*
27 *by coal in a blast-furnace reactor.*
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31 **Figure 5.** *Deposits obtained by alkaline electrolysis of iron oxide particles in suspension, in a rotating cylinder (a,*
32 *scale bar 2cm, deposit of 1.5kg and 5mm thickness) or parallel plates configuration (b, scale bar 10cm, deposit of*
33 *3.5kg and 5 mm thickness).*
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37 **Figure 6.** *CO₂ mitigation by electrolytic route (4000 kWh.t_{Fe}⁻¹) depending on the power generation source*
38 *(in parenthesis, GHG content in gCO₂.kWh⁻¹)*
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Figure 1

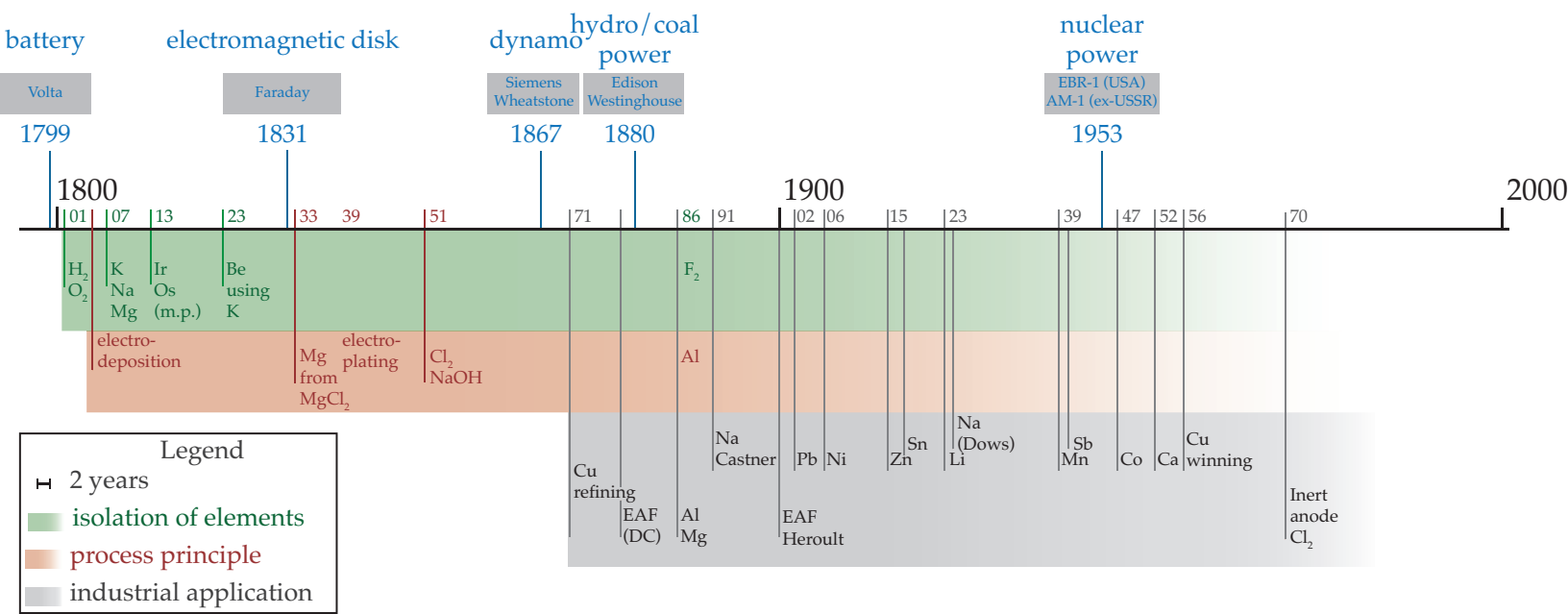


Figure 2

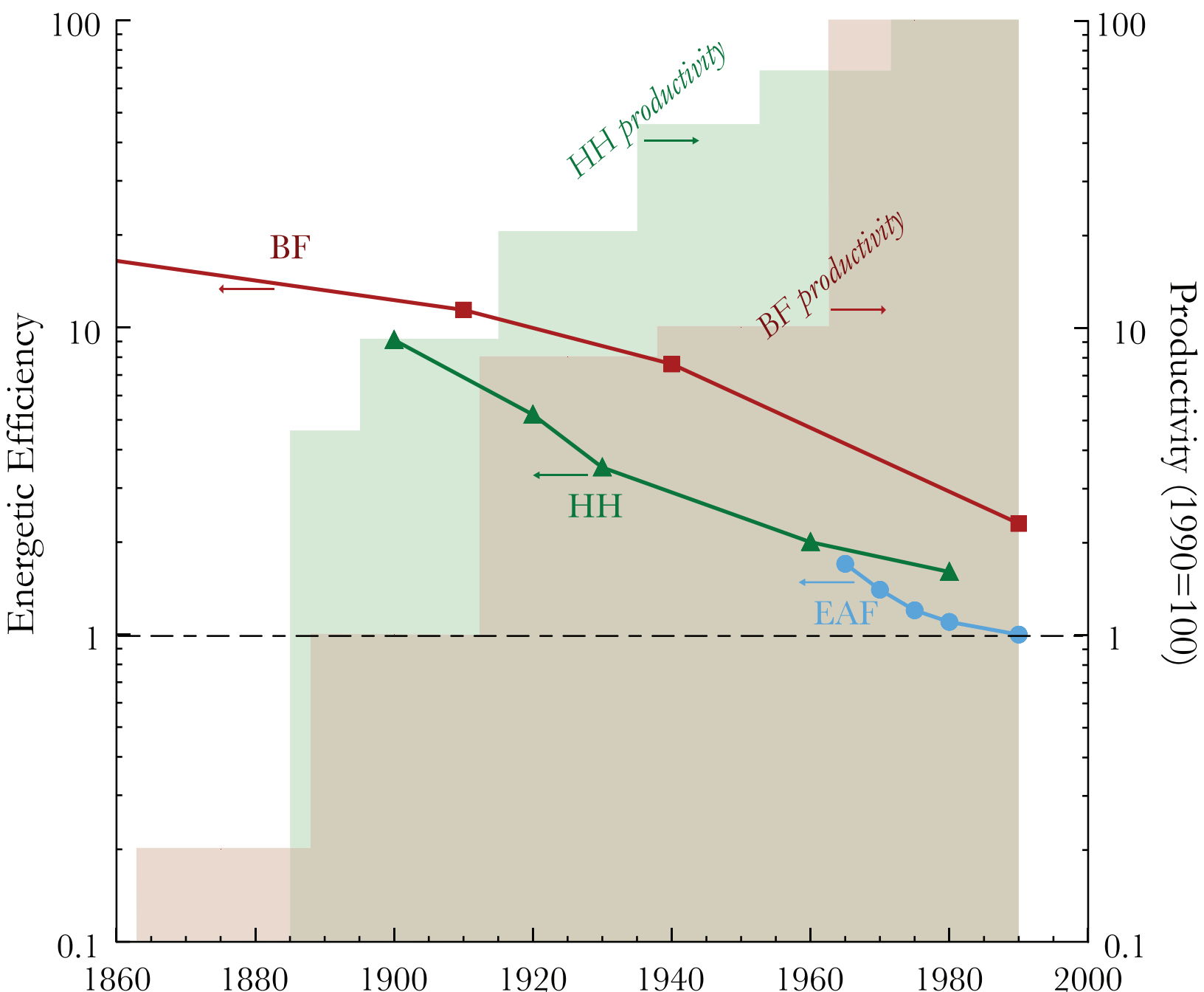


Figure 3

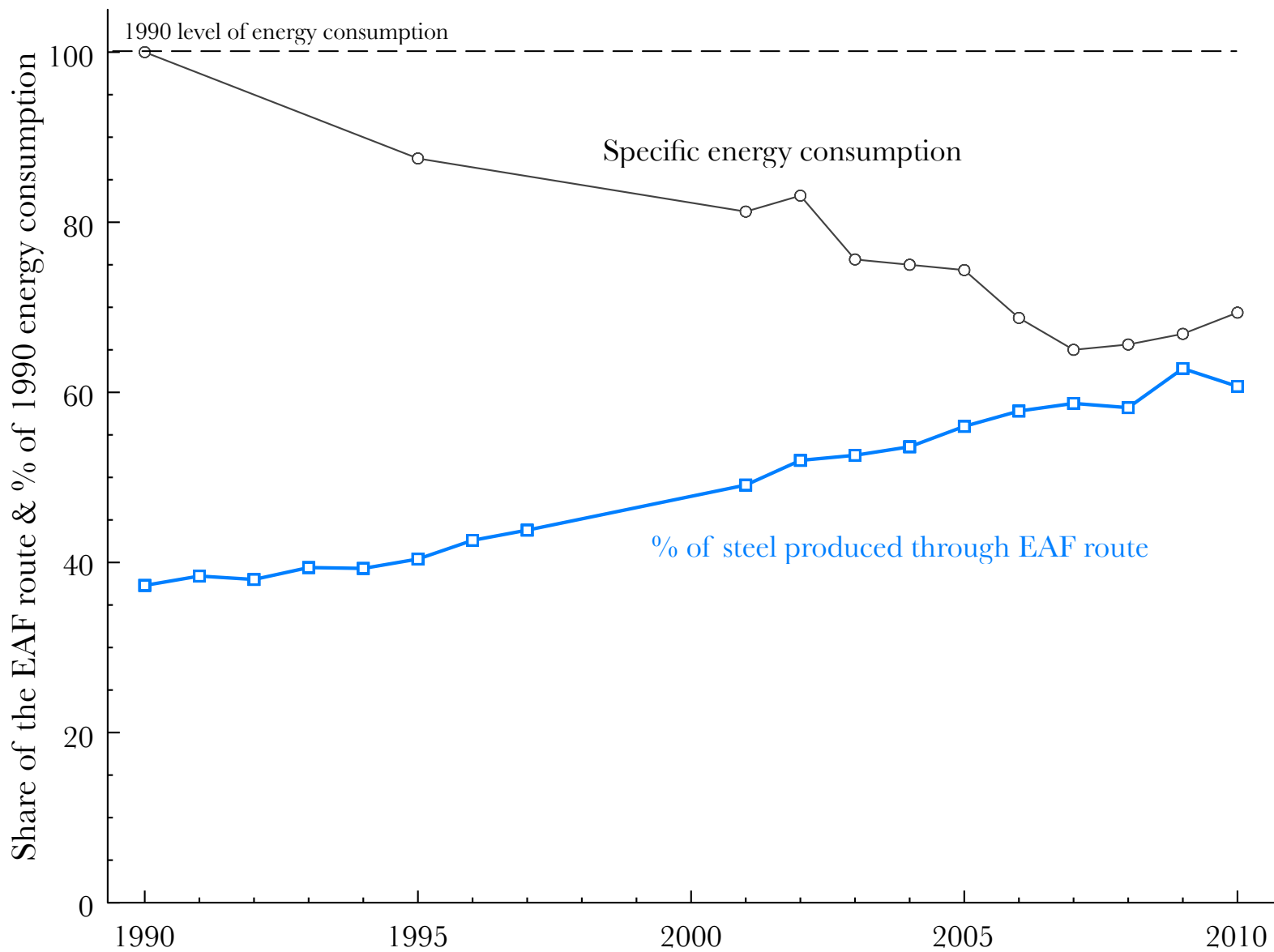


Figure 4

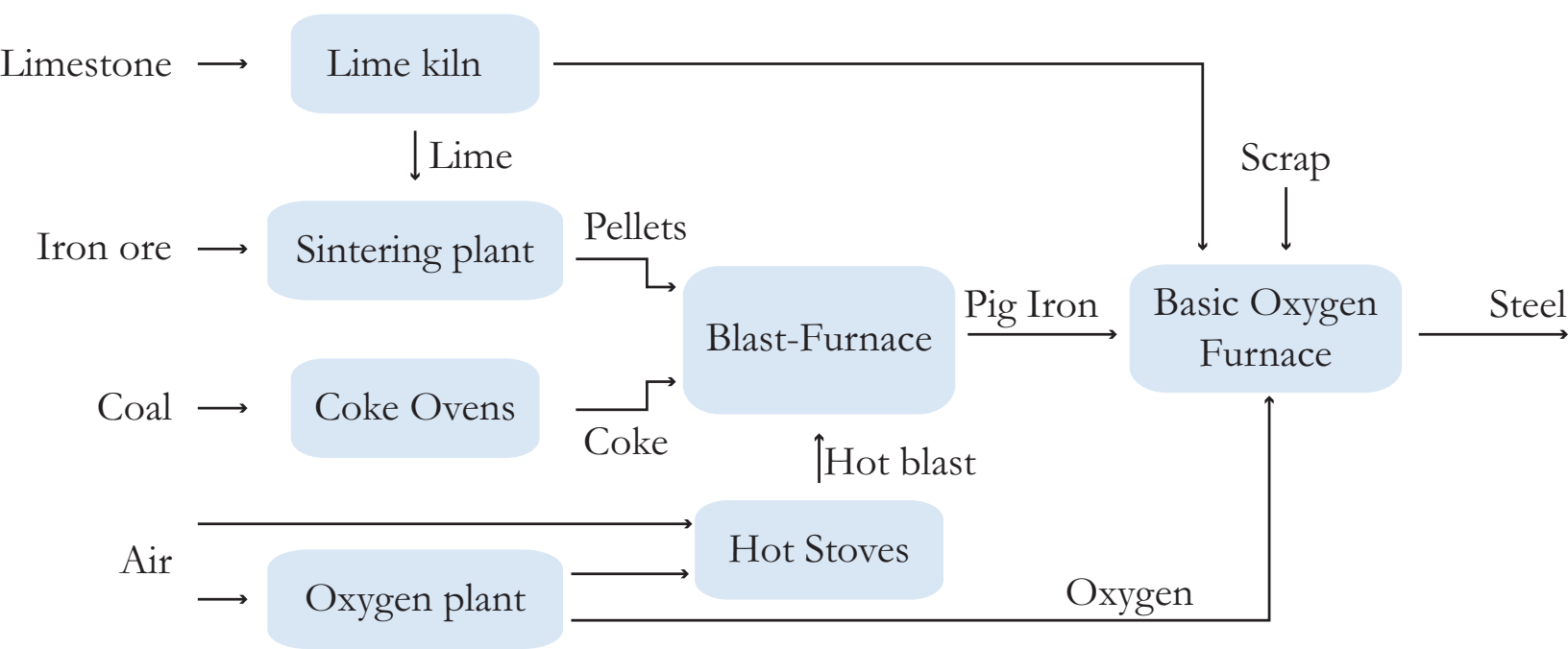
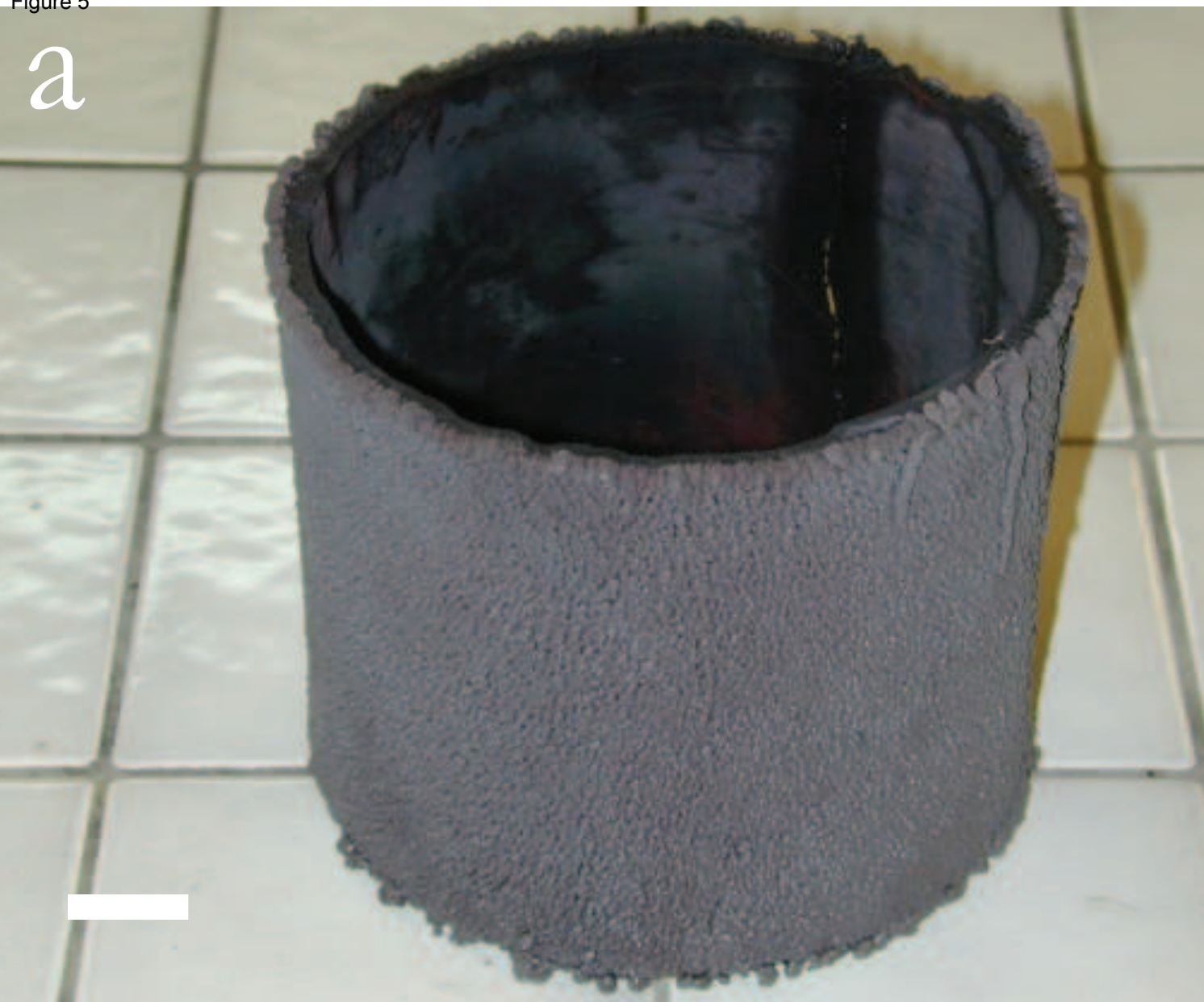


Figure 5

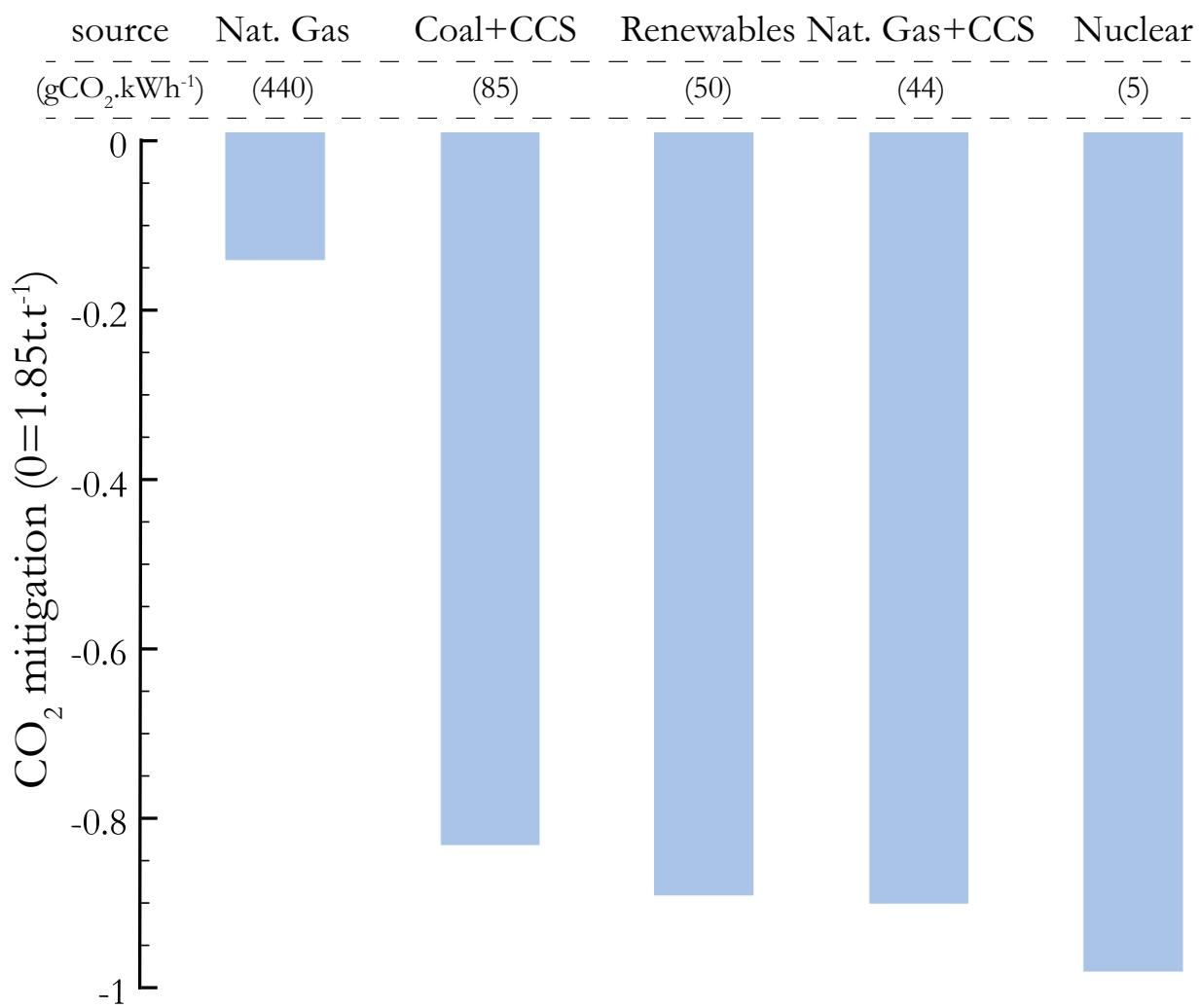
a



b



Figure 6



Dr. Antoine Allanore is the co-recipient of Vittorio De Nora Prize from TMS in 2012, commemorating the centennial anniversary of the birth of Vittorio De Nora. This award recognizes outstanding materials science research and development leading to the reduction of environmental impacts, particularly greenhouse gas emissions. The prize comes with an invitation to present a lecture at the TMS Annual Meeting. In 2012, Dr. Allanore has been appointed the Thomas B. King Professor of Metallurgy at the Massachusetts Institute of Technology (Cambridge, MA), in the Department of Materials Science and Engineering.

Dr. Allanore earned a chemical engineering degree from the Ecole Nationale Supérieure des Industries Chimiques de Nancy. He also obtained his M.Sc and Ph.D in chemical engineering from the Institut National Polytechnique de Lorraine. Prior joining MIT as a post-doctoral researcher in 2010 alongside Prof. Sadoway, he worked as a research engineer at ArcelorMittal R&D on the development of new electrolytic processes for primary steel production. In 2011, Dr. Allanore was a TMS Extraction and Processing Division Young Leader Professional Development Award winner.