Electrolytic extraction of a metal from its metal compound: estimates of optimal energy requirements and their consequences.

by

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Abstract. To ensure the sustainability of a world whose growing population demands more materials, products, and energy, we must closely examine the sustainability of the industries that supply them. Metal-making industries encounter an opportunity space at the extraction stage of a metal life cycle when aiming at making a significant impact in energy efficiency and carbon emission mitigation.

We first develop a thermodynamic model that establishes the technical criteria for the most efficient operation of an electrolytic cell for a variety of metals. Second, we explore the rigidity of the operating boundary conditions and their impact on energy consumption. We then proceed to examine the energy and carbon impact of a hypothetical electrolytic ferrochromium operation in the United States. This case study demonstrates that the thermodynamic model can serve as a reference framework through which diverse stakeholders can compare the environmental impact of existing and innovative metal extraction processes in order to make informed decisions about environmental regulation, investments, subsidies, and mineral resource management.
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2. Goals and Scope

As a technology and policy student I saw the extraction of metals as an interesting physics problem as well as one with relevant implications. Here I found a truly interdisciplinary intersection, where I needed to equally scrutinize the environmental and economic implications as well as at the underlying science of extracting metals.

As anyone involved in the metal-making business will know, each existing metal extraction process has been developed within a diverse of boundary conditions, such as ore availability, demand patterns, and the reactivity of the metal. There are numerous technological and geo-political challenges. Though we will not make any broad generalizations, we present industry and decision makers with challenges related to technological innovation within an indispensable part of many nations’ economies.

Existing economic, industrial, and political paradigms govern the way we make metal and distribute it throughout the world. These paradigms persist in many forms. For example, there are rules that rigidly distinguish between what is considered economically viable ore and just mineral-containing soil. Such rules have important implications when accounting for a country’s stocks and reserves of metals and minerals, which in turn impact the way extraction operations are planned and executed. Similarly, extractive industries worldwide face differing environmental standards of operation, which affect operation and even capital costs. These regulatory and industrial practices have come together through dozens of decades in order to provide metallurgical products demanded at the time. But what of the future? Will the same products be demanded, or will we have to revise these paradigms? We submit that many of these paradigms can and should be challenged, even for some metals whose demand is not expected to change much. And though here we address mostly the extraction stage in the lifetime of a metal product, decisions made at this stage often define other boundary conditions of the upstream and downstream supply chain. We find interesting science in the process of making metal. In addition, we can ask questions about what it would mean for an industry to reorganize itself.

In particular, we are interested in the environmental implications of doing so. Considering “the environment” is a considerably large problem including anthropogenic air, land, and water emissions that affect or entirely interrupt these resources’ natural cycles. We will
hereafter treat environmental impact and the air emissions related to metal-making activities as synonymous. Within air emissions, we focus on carbon emissions. We chose this subset of environmental concerns as they are increasingly relevant in climate change conversations.

There is convincing evidence that climate change is largely related to anthropogenic greenhouse gas emissions [1]. These emissions are the consequence of many economic activities, which have increased dramatically in scale and intensity since the Industrial Revolution. Metal-making activities contribute to the atmospheric concentration of greenhouse gases. And though there is evidence that we have gotten more efficient at making metal over the years [2], the carbon mitigation needed cannot be accomplished by technology alone. Indeed, there are networks of stakeholders at every stage of a metal’s life cycle that influence the deployment factors of a technology, such as efficiency and scale. Here we propose that government is a key actor in providing “policies that are consistent with increasing levels of public commitment and political resolve” [3] to solve the threats posed by the increasing concentration of greenhouse gases in our atmosphere.

In the scope of metal making activities and their contribution to greenhouse gas emissions, we propose that the active role of government can be a catalytic agent by providing the legal and economic frameworks that support certain extractive industries while adhering to carbon mitigation goals. On a domestic level, there are various legal and policy tools available through which nations can incentivize businesses to use best available technologies and change consumption habits while maintaining a healthy economy. The success of such measures is highly dependent on the patterns of supply and demand of the industry, as well as the sociopolitical infrastructure of said nations. For example, despite the technological progress and cost-reduction that renewable energy technologies have undergone, it is often only through government initiatives that companies and laboratories are able to secure funding for research, development, and deployment. This modest [4] investment reflects some of the deep-seated economic and technological barriers that stand in the way of more efficient and carbon-lean electricity generation.

Though government is a powerful tool through which to enact many of these changes, there also needs to be a serious commitment from industry stakeholders. It is widely known that producers of metal in some countries often outsource their production activities to countries with
more lenient environmental codes, while total CO₂ emissions are on the rise. Similar leniency in occupational health and safety, as well as other cost and logistic operations, indirectly incentivize environmentally risky operations.

Thus, this thesis intersects topics such as industrial sustainability, mineral resource management, energy efficiency in metal extraction, and thermodynamic modeling, among others. In summary, the main questions we set forth to answer are:

- What would the energetic model of the electrolytic extraction of a metal from its metal compound from a macroscopic thermodynamic perspective look like?
  - What are the inputs/outputs?
- How realistic is this model?
- What are the key physical, chemical, and/or engineering parameters that most influence the efficiency of this process?
- Once energy consumption has been calculated, what are the implications of implementing this technology?
  - For example, what is a hypothetical carbon impact of producing a specific metal electrolytically in the United States?
  - Which metals would benefit most from a carbon lean processing route?
  - What are the geopolitical, technological, or economic challenges to widespread implementation?

Each of these goals is different in purpose, scope, and topic. Thus different analytical methods apply for each.

3. Motivation and background

Which technologies will most advance energy efficiency and carbon mitigation goals? How can we better implement innovation into dynamic and stagnant industries? What current political/economic infrastructures need to be inspected to achieve sustainability goals when different stakeholders with competing interests are involved? These are all important questions that need to be answered for a variety of economic pursuits. In this document we will focus on
the extractive metallurgical industry. We seek to explore the possibility of implementation of carbon-free electrolytic extraction of metals as a new industrial paradigm.

The importance of metals is undeniable. They are a fundamental medium for the transfer of art, technology, and wealth. For thousands of years, their properties have been harnessed to drive economic, technological, and social change. Today, metal making activities make up a considerable amount of many nations’ economies. In the U.S., primary metal production amounted to US$200 billion 2007 [5].

And though the value of a specific metal may fluctuate over time, the global consumption of metals is projected to rise, as is its environmental impact. The steel industry produced 1,582 million tonnes of product in 2013 [6], and its primary production is projected to nearly double by 2030 [7]. Global steel production activities are quoted to be responsible for 4-5% of carbon emissions alone [8]. Such prospects exert an alarming amount of pressure on natural resources to supply our needs, as the supply chain of metals is an energy-intensive one.

In 2013, the International Energy Agency quoted metal-making activities to be responsible for 22% of global energy use (Fig.1) [9]. In fact, the same report illustrates that over the past twenty years, total energy consumption for metal making activities has followed an upward trend1.

---

1 Despite this overall upward trend, over time primary metal production has also become more efficient in a per-ton basis (MJ/t metal)
2 The ratios in Fig.5, however, do no account for varying ore purity among these metals. For example, copper is on average three times more concentrated in the soil than nickel, but the average copper ore grade is 0.6% Cu while the average nickel ore grade is 1.3% Ni. These variations have important ramifications in the cost and energy
There is an urgent global need to enhance energy efficiency and curb carbon emissions. A significant amount of carbon abatement goals could be met by way of employing alternative technologies in carbon-heavy industries. Participants in the materials extraction industry sometimes hesitate to switch to best available technologies due to market insecurities, costs, or even misguided government subsidies. Industries often do not internalize environmental and social costs into operation costs, while governments sustain economic paradigms that rely on money rather than on energy intensiveness as a measure of exchange [10].

There are many scientific, economic, and political misconceptions and disagreements that delay cohesive action. For example, high-energy consumption is often affiliated with high-output economies in many economic analyses, whereas disengaging energy consumption from economic growth would challenge existing paradigms in order to alter the current fossil fuel-dependent techno-economic infrastructure.

In the realm of metal-making paradigms, the production of metal is often regarded as a perfected art, and in some ways, it is. Metal making societies have had hundreds of years to fine tune these processes to use abundant natural resources and labor. But the byproducts of their operations have increasingly come under scrutiny due to potential negative environmental impacts. Indeed, their process emissions as well as the energy needed to provide the electricity for these processes contributes to CO₂ emissions that reach the gigaton scale (Fig.2) [11]. Thus, many stakeholders in the industry are faced with engineering, economic, and political challenges posed by this important industry for a sustainable future.
First, let’s consider the engineering challenges. A metal’s life cycle is described by the stages of manufacturing or processing it undergoes. These are typically mining, extraction and refining, manufacturing and further processing, use, and waste management. This processing chain is represented in Fig. 3. The extraction stage, in orange, is the focal point of this work.

Figure 2: (left vertical axis) Cumulative energy demand of different metals in 2008; aluminum has been scaled down by a factor of three and iron by a factor of 10. (right vertical axis) Global carbon dioxide emissions associated with the production of each metal; iron has been scaled down by a factor of 4. Source: Nuss and Eckelman, 2014.

![Figure 3: Stages of a typical life cycle of a metal. The main bond-break step to extract metal from a compound occurs at the "Smelting & Refining" stage. In this graphic, the inputs are electricity and heat, which are reflective of extraction inputs for producing some metals such as iron, aluminum, and zinc. However, other metallurgical processes exist, such as hydrometallurgy, which employ liquid solutions for component separation. Source: UNEP International Resource Panel report: Environmental Risks and Challenges of Anthropogenic Metals Flows and Cycles.](image-url)
The extraction of metals is a bond-breaking endeavor. Existing extraction process routes involve chemical and thermal energy to leach, float, reduce, concentrate, and separate metal compounds and obtain pure metal or metal alloys with minimum impurities. Because most metals exist in the form of stable metal compounds in the earth’s crust, extracting these metals – breaking the chemical bond to separate the metal – constitutes the greatest energy requirement in its life cycle (see Fig. 4). With the exception of the pyrometallurgical extraction of copper, the extraction stage accounts for 60-80% of the embodied energy for primary production of base metals (lead, zinc, copper) in MJ/kg of metal [11].

![Figure 4: Global energy consumption for the production of different metals, divided into two stages of their life cycle: mining and mineral processing, and extraction/refining. Source: Norgate and Jahanshahi, 2011.](image)

In addition, there is a significant opportunity space to improve energy efficiency of extraction methods. Fig. 5 illustrates that various extraction processes spend one order of magnitude more energy than the heat of formation of their corresponding metal compounds ($\Delta H^\circ$)².

²The ratios in Fig. 5, however, do not account for varying ore purity among these metals. For example, copper is on average three times more concentrated in the soil than nickel, but the average copper ore grade is 0.6% Cu while the average nickel ore grade is 1.3% Ni. These variations have important ramifications in the cost and energy expenditure of extraction since the ore concentrates will also be different. For the moment, we will not address these issues.
The primary extraction of a metal will vary according to the ore grade and the end product desired, among other variables. Fig. 6 illustrates an example, which is the process flow sheet for the production of steel from an iron ore.
The main bond-breaking step is highlighted in blue in Fig. 6. The blast furnace processing route produces over 70% of world steel supply, and it uses about 11.6 GJ per tonne of steel [13]. The flow sheet below illustrates the electrolytic extraction of aluminum, which uses about 221 GJ per tonne of aluminum to produce aluminum from aluminum oxide through the Hall-Heroult process [14].

Figure 6: Process flow sheet for the production of steel, with the main bond-breaking step highlighted in cyan and some of the environmentally hazardous waste streams highlighted in red.
Many metal extraction processes resemble that of the steel-making flow sheet in length and multiplicity of steps. In addition, they sometimes require hazardous leachants that generate considerable amounts of waste streams. There are arguably many evolutionary improvements to existing extraction processes; in what conditions could we propose the following, for a variety of metals?

Here, we explore the disruptive potential of electrolytic extractive processes as an alternative to existing processes. First, we analyze the thermo-energetic performance of such a process for a variety of metals. In our analysis, we find that this extractive approach offers

---

3 In this thesis, we omit the role of impurities in the metal oxide feedstock and metal.
promise in terms of energy usage for a variety of metals. By delving further, we find the fundamental optimization parameters needed to achieve enhanced energy efficiency.

We then include economic and political challenges to implement this technology, which could be a powerful alternative to current extractive options from a carbon-emission perspective. Metal production activities account for nearly a third of global industrial CO$_2$ emissions, totaling 2.6 metric gigatons of CO$_2$ in 2004 alone [15]. By proposing a hypothetical scenario that brings together the electrolytic technology along with the relevant geographic and economic considerations, we gain insight about how realistic and beneficial it would be to implement this technology.

There is ample space for public policies to incentivize the implementation of new technologies. Accelerating the deployment of next-generation extractive technologies and/or processing routes could help mitigate the supply risks that often threaten the development of energy-harvesting and energy-efficient technologies due to stagnant industries with limited capacity or volatile production parameters. This is particularly important for metals with unique physical and chemical properties, such as the rare earth and other strategic metals. The supply chains for these materials could benefit from electrolytic extraction, which with the right engineering design – such as inert anodes, customized electrolytes, and a clean energy supply – could be part of sustainable industrial systems which forego CO$_2$ emissions and hazardous waste streams.

4. Introduction – electrowinning a metal from its feedstock

The study of electrochemical reactions is a tradition that dates back many decades and has proven fruitful for an extremely diverse set of fields. In bringing the first energy-producing device, Alessandro Volta helped usher in the era of electricity and its diversely useful applications. The principles of electrochemistry have been applied to solve problems in materials science, biological systems, as well as energy storage and conversion. The field’s versatility has proved fascinating for fundamental science as well as engineering approaches. Indeed, “…electrochemical science transfers readily into technology, i.e. is an effective agent for this
often difficult process.” [16], and “with respect to energy and raw material efficiency, electrochemistry offers unique possibilities which in very few cases have been realized to a satisfactory extent.” [17]

But the most relevant use of electrochemistry for our purpose is its use to convert inorganic matter into metals. We herein focus exclusively on the extraction stage of the production of a metal, i.e. obtaining pure metal from a pure metal compound (such as a metal oxide or a metal sulfide). In reality, metals are extracted from ores with a specific

As seen in Table 1, only certain metals are extracted electrolytically currently. However, the electrolytic production of metal is not a new idea; the earliest reduction of zinc, tin, and antimony dates to the eighteenth century. But perhaps the most well-known success story in this field began in 1866 when Charles Hall and Paul Hérout independently and simultaneously developed the technology that would remove aluminum from its precious metal status in a short period of time. This technology lowered the barrier to access aluminum to find useful applications in many industries.

Table 1: Global annual production of different metals by electrolysis. Source: Allanore, 2007.

<table>
<thead>
<tr>
<th>Metal</th>
<th>T / °C</th>
<th>Annual Production / Mt/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>Zinc</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>0.3</td>
</tr>
<tr>
<td>Aluminum</td>
<td>960</td>
<td>48</td>
</tr>
<tr>
<td>Magnesium</td>
<td>750</td>
<td>0.6</td>
</tr>
<tr>
<td>Lithium</td>
<td>450</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The principle of electrolysis is to drive a non-spontaneous and often endothermic chemical reaction by way of an electric potential between two electrodes in a reaction cell (reactor). Michael Faraday first discovered the fundamental chemistry behind the phenomenon in 1889, and it has since become a useful practice in the extraction of different materials, such as hydrogen production by splitting water molecules. Here we are interested in the electrolytic production of metal, wherein metal is separated from its constituent compound and is deposited on to the cathode. A variety of techniques exist to accomplish this, and each has been tailored to fit the feedstock available and the product demanded by the market.
4.1 Existing electrolytic operations

There exists a diverse set of electrometallurgical operations worldwide. We will focus on the extraction of a metal by electrolysis, or the *electrowinning* of a metal. The extraction of metal through electrolysis has been accomplished for a couple different metals. Each has production parameters suited to the metal’s melting temperature, feedstock composition, reactivity, and many other boundary conditions. Table 1 illustrates the variety and scales of existing electrolytic extraction operations worldwide.

Most notably, all of the world’s aluminum production today, which amounts to over 50 million tonnes annually [18], is produced electrolytically. Aluminum oxide (identified as “primary alumina” and “enriched alumina” in Fig. 9) is dissolved in a cryolite (Na₃AlF₆) bath and subsequently electrolyzed at 960°C. The molten aluminum is continuously removed (tapped) from the electrolytic cell.

![Figure 9: Schematic of the material and energy balance of a Hall-Heroult Cell. Directly from Gusberti et al., 2009.](image)

But this process not only uses electricity as an energy input. The electrolytic cell uses a consumable carbon anode which combusts with oxygen at the operating temperature. The combustion, being an exothermic reaction, releases both heat and chemical energy, which are...
used as inputs for the reduction of aluminum. This contributes significantly to anthropogenic contributions of carbon emissions annually.

\[ 2Al_2O_3(s) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g) \]

In addition, more than half of the world’s electricity that goes into primary aluminum production comes from coal generators, and over the years the increasing world production capacity is increasingly being supplied by coal-fired electricity [19].

At the forefront of candidate for future production of metals by electrolysis are titanium and iron. The physical properties of titanium have made it a highly sought after metal; though due to the difficulty of its extraction and processing, it is costly. About 120,000 tonnes of titanium are produced annually, of which more than 90% is made through the Kroll process. For decades the search for electrochemical alternatives to the existing process have been sought, and only recently there has been some progress in the effort to produce electrolytic titanium at small scales [20].

The value of iron is indisputable; however, it is produced by pyrometallurgical methods that emit large amounts of greenhouse gases. For these reasons, the electrolytic extraction of iron is an extremely valuable alternate process route that has recently been proven at the lab scale [21]. This progress is particularly valuable since it produces oxygen gas as well as metallic iron simultaneously.

Thus, there is an opportunity space for a variety of extraction processes in terms of improving energy efficiency and mitigating environmental impacts. This is true for both existing pyrometallurgical and electrolytic extraction processes. However, this work focuses on electrolytic extraction as an alternative to existing processes that do not already use it.

4.2 Carbon-free electrolysis as an alternate extractive route?

Though the earth’s crust harbors metals as oxide and sulfide ores due to the abundance and reactivity of both oxygen and sulfur in our planet, this work focuses on a variety of metal compounds (MₓYᵧ) as the primary feedstock. In addition, we focus on carbon-free electrolysis, whereby the use of inert electrodes only yields metal at the cathode and oxygen or sulfur gas at
the anode. When such a process is feasible, then how much energy is needed? What is the consequent carbon impact? What would be benefits of realizing it?

By first deriving the formulas describing the basic thermodynamic principles, we gain insight into the key parameters that govern the efficiency and energy intensiveness of the process. The thermo-energetic balance of the process provides an estimate of the minimum energy requirement for the electrolytic extraction of a metal. Given available technology, we next assess realistic inefficiencies and reevaluate the results.

At the core of our analysis is the specific energy consumption to extract metal electrolytically, which is expressed in terms of kilowatt-hours per tonne of metal.

\[
\text{specific energy consumption} = \frac{kWh}{\text{tonne of metal}}
\]

This metric is the energy intensiveness of extraction per unit of output. With some unit conversion, it is equivalent to Joules needed to produce one tonne of metal.

4.3 The promise of electricity for industry

There are further advantages of producing metal electrolytically. Many of these are not quantifiable, but they are worth mentioning. Among the most notable is its reliance on electricity as its main energy input. Apart from making progress in the energy efficiency and reducing direct process emissions, metal producers can further reduce their carbon footprint by using “green” sources of energy. Here the potential of electricity as a green energy vector should not be understated. Though currently many countries rely heavily on reliable sources of energy to produce electricity – namely hydrocarbons – there is great promise in the development of renewable sources of energy. There are many different ways to harvest energy from renewables, but they often do not operate at sufficiently large scales. In addition, each source of renewable energy has geospatial (biofuels, wind, solar), economic (solar), or technological limitations. Market uncertainties and deep-seated business practices, coupled with intermittency and cost considerations, often prevent renewable energy technologies from reaching full market potential [23].
Even for countries that heavily depend on coal as a source of energy (such as the U.S.), the dissemination of efficient base load coal plants could contribute to carbon mitigation goals. Domestic electricity suppliers could in turn have higher returns on investments, increase output, increase market competitiveness, encourage job growth, lower vulnerability to energy supply chain interruptions, and reduce dependence on foreign energy supplies. There is a huge potential in electrifying the materials extraction process, as it may allow for more streamlined manufacturing processes, tight control of energy inputs, as well as little energy loss due to transmission and input. Our knowledge about how to generate, transport, store, and use electricity is expanding rapidly, as well as our ability to harness renewable sources of energy. Already in 2004, about 19% of global energy use was carried as electricity [24]. Allanore offers a fascinating parallel between the rise of electrified systems, innovation in electricity generation, and the way making metal has evolved in the past two centuries, which has more increasingly become reliant on electricity [25]. In other words, “electricity is the future.”

4.4 Government and innovation in the extractive industry context

Government can be (and has been) an active participant in the acceleration of innovation in extractive industries. This role is related to the efficient management of mineral resources, which is closely tied to other important socioeconomic goals. On one hand, public policy can be a powerful ally for industry and domestic economic growth by enabling investment, research, and development. On the other hand, it can advance environmental strategies. This is often a delicate balance but one that can be achieved. Such concepts are often described as sustainable development and/or industrial ecology in the context of metal making economies, in which government plays an important role.

But the initiatives that public policy makers can take can widely. Each extractive industry is subject to different market forces and regulatory boundaries, and deploying innovation to achieve sustainable goals needs to be defined carefully within these. Therefore, our approach is to present case studies for specific metals which could benefit from electrolytic extraction. Through these case studies, the relevance of this processing route can be seen more concretely.

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4 Quoted from Professor Gerbrand Ceder during the Spring 2013 class titled, “Materials Science and Engineering of Clean Energy” at the Massachusetts Institute of Technology.
5. Methods of analysis

5.1 The electrolytic cell – theoretical framework

Here, we develop a macroscopic model of an ideal electrolytic process for a metal compound. First, we assume that the electrolytic process takes place in a reactor (or electrolytic cell). In this reactor, there is a steady state input of a certain metal compound ($M_x Y_z$) where the metal ($M$) is separated from its electronegative element, which becomes a divalent gas ($Y_2$).

The process pictured above is typically endothermic and non-spontaneous$^5$ – that is, energy is required to drive the reaction

$$M_x Y_z \rightarrow xM + \frac{z}{2} Y_2$$

[1]

The reaction is assumed to occur in an isothermal reactor and is performed by providing the electrolytic cell with an electric potential difference called $U_{cell}$. The resulting flow of charge in the schematic below provides the entirety of the energy needed to drive this process.

---

$^5$ Note that at sufficiently high temperatures (what is a “high temperature” depends on which metal compound), this reaction becomes spontaneous.
We derived $U_{cell}$ by dissecting the physics of the chemical phenomena taking place inside the cell (see Appendix B for detailed derivation). We submit that $U_{cell}$ can be conceptually split in two processes. One is that of breaking the chemical bonds that hold the metal compound $(M_iY_j)$ together. The other is that of maintaining the heat balance throughout the process, which includes warming the metal compound from room temperature to a target temperature, providing heat energy for reaction [1] to occur, and removing the products from the reactor. This can be expressed as

$$U_{cell} = U_{chem} + U_{ohm}$$

where $U_{cell}$ is the total cell voltage, $U_{chem}$ is the potential difference dedicated to separating the metal compound into $M$ and $Y$, and $U_{ohm}$ is the potential difference dedicated to maintaining a steady state heat balance. In addition, each of these potential differences can be analyzed by the physical phenomena that govern them (see Appendix B for complete derivation):

$$U_{chem} = \frac{-1}{e_{FM}} \Delta_r G_T^o$$

where

$$\Delta_r G_T^o = xG_{M,T}^o + \frac{z}{2} G_{Y, T}^o - G_{M_xY_z, T}^o$$

where $G_{i,T}^o$ is the molar Gibbs free energy of species $i$ at the target temperature $T$ (in Joules per mole of the species), $e_{FM}$ is the number of electrons exchanged to form the metal from its compound its compound, and $F$ is Faraday’s constant (96,485.3415 Coulombs per mole of electrons).

$$U_{ohm} = \frac{1}{e_{FM}} \left[ T_0 C_{M_xY_z, T_0}^P - xT C_{M, T}^P - \frac{zT}{2} C_{Y, T}^P - \Delta_w H_{T_0 \to T}^o - T (xS_{M,T}^o + \frac{z}{2} S_{Y, T}^o - S_{M_xY_z, T}^o) \right]$$
where \( C_{iT}^p \) is the molar heat capacity of species \( i \) at temperature \( T \) (in Joules per mole per Kelvin), \( \Delta_w H_{i_0 \rightarrow T} \) is the change in enthalpy of heating the metal compound from temperature \( T_0 \) to temperature \( T \) (in Joules per mole of metal compound), \( S_{dT}^i \) is the entropy of species \( i \) at temperature \( T \) (in Joules per mole per Kelvin), and \( T \) is the target temperature (in Kelvin). Combining these, and normalizing per one mole of metal,

\[
U_{\text{cell}} = \frac{1}{eF} \left[ \sum_i C_{iT}^p - \frac{eF}{2x} \right] + \sum_i S_{dT}^i - G_{MT} - G_{MY} + \frac{1}{x} \sum_i G_{MY} \right] \tag{5}
\]

These equations yield the minimum required voltage needed to extract metal. It is important to note that this electric potential between the electrodes is the fundamental driving force of the Faradaic processes happening inside the cell. The potential difference is obtained by introducing an anode and a cathode, where the ionic species exchange electrons at the surfaces (Fig. 12).

**Figure 12:** Schematic of the electrolytic reactor – the electric potential is driven by an outside emf. The anode is the positively charged, and the cathode is the negatively charged electrode.

More explicitly, the cathodic and anodic reactions are as follows

\[
M^{(e\bar{M})} + e_M^{\bar{M}} \rightarrow M \text{ (cathode)} \tag{6}
\]

\[
\frac{z}{x} Y^{e-} \rightarrow \frac{1}{2x} Y_2 + e_M^{\bar{M}} \text{ (anode)} \tag{7}
\]

\( e_M^{\bar{M}} \) is the number of electrons exchanged to make the metal from its compound per mole of metal, which can be calculated from the valency \( e \) of the electronegative element \( Y \):

\[
e_M^{\bar{M}} = \frac{ze}{x} \tag{8}
\]
At the cathode, the addition of electrons will change \( M \) from an ion into pure metal. At the anode, \( Y \) becomes oxygen, sulfur, or chlorine gas. The exchanged electrons in the presence of an electric potential will result in a total current \( I_{\text{total}} \). The continuous electron exchange inside the cell and electron flow outside the cell, and the resulting products being released at each electrode, follow Faraday’s first law of electrolysis:

\[
n'_{M} = \frac{I_{\text{Faradaic}}}{e_{M}F} \left[ \text{mol metal} \right] \quad [8]
\]

where \( n'_{M} \) represents the moles of metal being deposited per second due to \( I_{\text{Faradaic}} \), \( e_{M} \) is the number of exchanged electrons per mole of the metallic species, and \( F \) is Faraday’s constant. Note that the metal-producing current (Faradaic current) and the amount of metal produced are proportional to each other.

From a different perspective, the external flow of a current in the presence of an electric potential in a closed circuit simulates a simple circuit with an emf and resistor in series (see Fig. 12). Such a circuit follows the power equation

\[
P = U_{\text{cell}}I_{\text{total}} \quad [Watts] \quad [9]
\]

using equations [8] and [9] and some unit conversion, this becomes the specific energy expenditure requirement to produce metal in kilowatt-hours per tonne of metal.

\[
E_{M} = \frac{U_{\text{cell}}e_{M}F}{3.6m_{M}} \left[ \frac{kWh}{\text{tonne metal}} \right] \quad [10]
\]

\( m_{M} \) is the molar mass of the metal in grams per mole, \( e_{M} \) is the number of exchanged electrons per mole of the metallic species, and \( F \) is Faraday’s constant.

The MATLAB numerical computing environment was used to analytically calculate these equations. The thermodynamic data for each metal, metal compound, or element involved in the calculations was obtained from the commercial thermodynamic database FactSage. For a detailed description of the code built for this model, see Appendix D.

5.2 Methods for determining the efficiencies of electricity-driven processes

The electrowinning model described above is a mass and energy balance that is idealized by assuming the process to be adiabatic. In keeping with the physical realities of our proposed
energy estimate, two different efficiencies are now incorporated into the analysis to relax the adiabatic constraint. Each of these is associated with the two fundamental processes taking place: 1) the heating of the metal compound inside the reactor, which includes maintaining a steady state heat balance; and 2) the decomposition of the metal compound.

“Efficiency” is a concept that is often misunderstood, misrepresented, or dismissed. It is important to understand the mechanisms by which processes operate at sub-optimal levels, whether it is by natural irreversibilities (second law of thermodynamics) or engineering design. Here we present an in-depth analysis of the sources of inefficiencies as well as their estimates, which can be achieved with simple assumptions within an order of magnitude.

An engineering standard for energy efficiency is the thermal efficiency as defined by Carnot,

\[ \eta = 1 - \frac{T_1}{T_2} \]  \hspace{1cm} [11]

where, given the system/process boundaries, \( T_1 \) is the temperature of the “cold” portion of the system and \( T_2 \) is the temperature of the “hot” portion. This formulation implies that a greater temperature difference between the two yields a more efficient a process. In our case, the “hot” temperature is the electrolytic cell, which continually uses electricity to generate the necessary heat to warm up the metal compound and drive the decomposition reaction. The “cold” temperature is that of the reactor’s surroundings.

From a practical standpoint, inefficiencies are apparent when a process needs more energy than the theoretical minimum. This “extra energy” manifests itself as a bulk number and it is sometimes difficult to discern its causes. Energy efficiency is typically expressed as a percentage that compares the input energy to the losses associated with the process.

\[ \text{practical efficiency} (\mu) = 1 - \frac{\text{energy lost}}{\text{input energy}} \]  \hspace{1cm} [12]

Thus,

\[ E_{\text{real}} = \frac{E_{\text{min}}}{\mu} \]  \hspace{1cm} [13]
where $E_{real}$ is the actual energy needed to run a process and $E_{min}$ is the minimum energy of the process.

5.2.1 Assessing heat efficiency
Heat inefficiencies are associated with practical heat losses due to natural radiation/convection/conduction as well as hot gases escaping the reactor. They are therefore highly dependent on the operating temperature. A survey of electricity-based metallurgical processes at different temperatures was conducted in order to quantify this temperature dependence and assess a realistic energy expenditure. Such processes are the ones that use electricity to warm up, smelt, or process a metal. The survey included high temperature processes (2,000°C) as well as lower temperature processes (80°C). A regression is obtained from the survey and applied to the electrolytic model, therefore accounting for whatever material or design limitations are available to thermally insulate this process. We denote this heat efficiency as alpha ($\alpha$).

\[
\text{practical heat efficiency (}\alpha\text{)} = 1 - \frac{\text{heat energy lost}}{\text{heat input energy}}
\]

The methods described in section 5.1 were obtained assuming a perfectly adiabatic and perfectly selective process. The first condition can be relaxed by using $U_{ohm}$, the heat balance necessary for steady state operation. To assess practical heat losses of the modeled electrolytic process for each temperature, any heat losses ($a$) correspond to this heat term.

\[
U_{ohm} = \frac{1}{\alpha e_{MF}} \left[ T_0 - C_{P,T_0} - T C_{P,T} - \frac{zT}{2x} C_{P,T} - \frac{1}{x} \Delta w H^0_{T_0} - T (S_{M,T} + \frac{z}{2x} S_{Y,T}) - \frac{1}{x} S_{M,T} \right] [14]
\]

So that $U_{cell}$ is now

\[
U_{cell} = \frac{1}{\alpha e_{MF}} \left[ T_0 - C_{P,T_0} - T C_{P,T} - \frac{zT}{2x} C_{P,T} - \frac{1}{x} \Delta w H^0_{T_0} - T (S_{M,T} + \frac{z}{2x} S_{Y,T}) - \frac{1}{x} S_{M,T} \right] [15]
\]

5.2.2 Assessing Faradaic efficiency
It is more difficult to evaluate the inefficiencies associated with the decomposition of the metal compound. A Faradaic efficiency, or current efficiency, is often expressed as

\[
\beta = \frac{i_{\text{Faradaic}}}{i_{\text{total}}} \quad [16]
\]
where $\beta$ denotes the overall current efficiency, $I_{total}$ is the total current in the system, and $I_{Faradaic}$ is the portion of the total current which contributes to metal-making. $I_{Faradaic}$ represents the selectivity of the current for the desired product out of the reactor. $\beta$ could be assessed as a bulk inefficiency to the specific energy requirement:

$$E_M = \frac{U_{cell} e M}{3.6 \beta m_M} \left[ \frac{kWh}{tonne \text{ metal}} \right]$$

Rather than assessing $\beta$ as a bulk calculation in equation [18], we are interested in carefully analyzing the physical phenomena that can cause Faradic inefficiencies, such as:

- The re-combination of metallic species to form the metallic compound,
- The partial reduction of the metallic species to intermediate valencies, and
- The electronic conductivity of the supporting media.

![Figure 13: (left) schematic of a perfectly efficient electrolytic process, wherein all of the current is Faradaic (i.e. metal-making) current. (right) schematic of an inefficient Faradaic process, wherein some of the current is Faradaic (i.e. metal-making) current and some of the current is spent in other processes: either electronic conduction, reoxidation, OR partial reduction.](image-url)
Each of these phenomena can be expressed as a resulting $I_{\text{inefficiency}}$, or a portion of the total current that is not useful. The following is a study of the sources of Faradic inefficiencies for the case of the electrolytic extraction of iron ($Fe$) from iron oxide ($Fe_2O_3$) at 1600°C, but the methods can be transposed to other metals.

*Re-oxidation of metallic species*: once the metal has been deposited at the cathode, it can re-oxidize inside the cell by recombination. The metallic species could migrate and exchange electrons as in the following reaction

$$2M \rightarrow 2M^{2+} + 4e^-$$ \hspace{1cm} [19]

while the divalent gas exchanges electrons

$$Y_2 + 4e^- \rightarrow 2Y^{2-}$$ \hspace{1cm} [20]

This is accounted for as an inefficiency since the thermal and chemical energy to reduce the metal has been spent, but it reverses to become a metal compound. If/when this re-oxidation phenomenon occurs, energy is released inside the electrolysis cell. This energy is the heat of the reaction, or enthalpy of reoxidation ($\Delta_r H_{\text{reoxidation}}$):

$$\Delta_r H_{\text{reoxidation}, 1600^\circ C} = -494,484 \text{ joules/mole Fe}$$ \hspace{1cm} [21]

Such energy is released into the system purely as heat, and will contribute positively to the heat balance.

*Partial reduction of metallic species*: some metals can exhibit mixed valency. For example, the following can occur in the case of iron

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$ \hspace{1cm} [22]

The partial reduction of a species must be accompanied by a corresponding oxidation reaction, such as
\[
\begin{align*}
Fe^{2+} &\rightarrow Fe^{3+} + e^- \quad [23] \\
O^{2-} &\rightarrow \frac{1}{2} O_2(g) + 2e^- \quad [24]
\end{align*}
\]

We consider the reaction
\[
Fe_3O_4(l) \rightarrow 3FeO(l) + \frac{1}{2} O_2(g) \quad [25]
\]
and submit that this reaction occurs as an isothermal process. Note that here we have used magnetite, \(Fe_3O_4\), because it is the iron oxide compound containing \(Fe^{3+}\) thermodynamically stable at the temperature of interest, \(\sim 1600^\circ C\) in equilibrium with \(O_2\).

The occurrence of such partial reduction alters the energy balance in two ways. Firstly, it lowers the chemical energy requirement to pass the current. For the case of the partial reduction of iron oxide, the chemical energy is equal to
\[
-\Delta_r G_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2} = 42,278 \frac{\text{Joules}}{\text{mol Fe}} \quad [26]
\]

Secondly, this reduction has an effect on the heat balance. The heat generated by this reaction can be calculated by the change in entropy:
\[
T\Delta_r S_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2} = -87,094 \frac{\text{Joules}}{\text{mol Fe}} \quad [27]
\]

Electronic conduction: at the core of Faraday’s law of electrolysis is the premise that ion mobility permits the electron exchange at the reactive interfaces (anode and cathode) so that an electronic current may flow outside of the cell in the circuit. However, for some electrolytes, some electrons may escape from the anode to the cathode and travel through as though encountering a dielectric. Such electronic conductivity can contribute to the overall heat balance of the process.

The effects of these inefficiencies on the energy balance of the thermodynamic model were calculated one at a time, assuming mutual exclusivity. That is, if a Faradaic inefficiency were to be present, only one of the three phenomena would be the cause. Thus the effects of each can be studied in the initial ideal model.
5.3 Methods for case studies

Next we move beyond the technical analysis of extracting metal. In terms of environmental impact, our foremost priority is to examine potential carbon impacts. We proceed to hypothesize a scenario wherein an electrolysis plant is commissioned to produce metal from a pure oxide. In doing so, we consider the different aspects of carrying out such an operation in a specific location. First, we take the energy requirement result from the electrolytic model for this specific metal and use this as the main energy input to produce this metal. Since we focus on carbon-free electrolysis (oxygen gas as the only by product), the local electricity-generation portfolio becomes the main source of carbon emissions.

The results of this analysis is heavily dependent on the geographical location of the hypothetical plant, as well as which metal is being produced. We therefore have conducted a case study that examines the potential carbon impact of producing ferrochromium in the United States. This analysis is in Section 7 of this document, where methods, results, and discussion are presented together. An additional case study for the electrolytic production of rare earth metals from rare earth oxides is presented in Section 8.

5.4 Assumptions

This macroscopic model assumes a steady-state process of molten metal production; that is, there is a stoichiometric mass and energy balance of the inputs \((M_xY_z)\) and outputs \((xM & zY)\). Any kinetic effects that might practically limit our process are ignored. The model also assumes no energy recovery from products, such as recovery from the off gas as heat.

It is also worth looking at an existing electrolytic process to review some of the more subtle assumptions of the model. The total voltage of a typical Hall-Heroult cell, for example, is “spent” in various processes involving kinetics, heat balance, as well as the process of electrolytically decomposing the aluminum oxide into aluminum and other gases (Fig.14).

In the model presented here, there are only two ways in which the total voltage is spent. This assumption is justified once noting that in the Hall-Heroult cell, the majority is dedicated to the “bath” and “decomposition” portions of the process, which corresponds to our \(U_{ohm}\) and \(U_{chem}\) respectively.
\[ U_{cell} = U_{chem} + U_{ohm} = U_{decomposition} + U_{bath} = U_{total} \]  

6. Results

Here we present the results of the macroscopic model that describes the electrowinning of a metal from its metal compound, and the inefficiency calculations, along with their impact on the energy requirement for electrowinning.

6.1 The efficient extraction of a metal from its compound

Fig. 15 illustrates the result of the macroscopic model described above: a temperature-dependent estimate of \( U_{cell} \) for the extraction of iron (\( Fe \)) from iron oxide (\( Fe_2O_3 \)) in the temperature range 298K to 3,298K. These results assume perfect heat and Faradaic efficiency (\( \alpha, \beta=1 \)). The voltage required to separate iron from its oxide increases to maintain the desired temperature in steady state. There is an abrupt jump in this energy expenditure as well as \( U_{cell} \) at 1811 K, which is indicative of a phase change (the melting of iron). To extract liquid iron at 1600°C, 2.2V must be applied to the electrolytic reactor. This corresponds to a minimum specific energy consumption of 3,163 kWh per tonne of iron.
To analyze the energetics of the electrolytic cell, the individual components of $U_{cell}$ must be examined with changing temperature. Figure 16 illustrates the temperature dependence of $U_{chem}$ relative to $U_{cell}$.
6.2 Results for the thermal efficiencies of electricity-driven processes

Table 2 shows the processes and corresponding operating temperatures that were accounted for in the survey of industrial-scale electricity-driven processes.

Table 2: List of the existing electricity-driven processes that were surveyed for practical heat inefficiencies, organized by increasing temperature.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Process</th>
<th>$\alpha$ (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>$\text{H}_2\text{O}$ electrolysis</td>
<td>25</td>
<td>Das and Nath., 2007</td>
</tr>
<tr>
<td>973</td>
<td>$\text{MgCl}_2$ electrolysis</td>
<td>68</td>
<td>Amundsen et al., 2012</td>
</tr>
<tr>
<td>1233</td>
<td>$\text{Al}_2\text{O}_3$ electrolysis</td>
<td>64</td>
<td>Gusberti, 2009</td>
</tr>
<tr>
<td>2068</td>
<td>Induction furnace</td>
<td>68</td>
<td>Peaslee et al., 2000</td>
</tr>
<tr>
<td>3073</td>
<td>FeCr EAF</td>
<td>80</td>
<td>Biermann et al., 2012</td>
</tr>
</tbody>
</table>

The practical heat efficiency of each of these processes is illustrated in Fig. 17. This practical heat efficiency can be described with the logarithmic fit:

\[
\alpha = 26.064 \ln(T) - 125
\]

[25]

Figure 17: Results of the heat efficiency survey and the Carnot efficiency calculations.
6.3 A realistic estimate of the extraction of a metal from its compound – heat inefficiencies

Fig. 18 represents the specific energy expenditure of extracting iron from iron oxide when the heat efficiencies presented in Fig. 18 are taken into account ($\alpha \neq 1$).

![Figure 18: Results of the thermodynamic model expressing perfect thermal efficiency ($\alpha = 1$, blue line) and a realistic reassessment of that result with the results of the practical heat efficiency results ($\alpha \neq 1$, black line).](image)

For the extraction of $(Fe)$ from iron oxide $(Fe_2O_3)$ at 1873 K, the heat efficiency is about 70% (30% of the heat energy input is lost to the environment). Thus the energy requirement becomes 4,118 kWh/t Fe, which is about 955 kWh/t Fe more than for the perfectly efficient case. This result is the energy expenditure of a hypothetical electrolytic reactor that operates within existing technological thermal limits (heat efficiencies) for the industrial use of electricity for metal extraction at high temperatures.

6.4 A realistic estimate of the extraction of a metal from its compound – Faradaic inefficiencies

Fig. 19 illustrates the Faradaic inefficiency results for the electrolytic extraction of iron from iron oxide. The operating temperature is 1,873 K, which corresponds to $U_{cell}=2.2V$, $U_{ohm}=1.60V$, and
$U_{chem}=0.60V$ in the perfectly efficient case ($\beta = 1$). The detailed calculations of the energy balance of each phenomenon are shown in Appendix C. Four results are shown: the effect of the electronic conductivity on the energy balance (orange), the effect of the reoxidation phenomenon on the energy balance (teal), the effect of the partial reduction phenomenon on the energy balance (blue), and the effect of accounting for the Faradaic inefficiency as just a bulk calculation on the specific energy requirement (magenta).

![Figure 19: Results of the Faradaic inefficiency calculations.](image)

### 7. Discussion

This section will discuss the macroscopic model that describes the electrowinning of a metal from its metal compound and the inefficiency calculations (and their impact on the energy requirement for electrowinning).

#### 7.1 Discussion of the thermodynamic model

Fig. 15 illustrates the results from the macroscopic model for the electrolytic extraction of a metal from a pure metal oxide, in the case of perfect efficiency. In the case of the extraction of iron from iron oxide, the results are within reasonable agreement of a similar model in previous
work [25]. This calculation was performed for the extraction of other metals from their respective metal compounds, such as: chromium from chromium oxide, aluminum from aluminum oxide, magnesium from magnesium chloride, neodymium from neodymium oxide, lanthanum from lanthanum oxide, copper from copper sulfide, and zinc from zinc oxide. The results for all of these were similar to those illustrated in Fig. 18: the specific energy expenditure increases with increasing temperature continuously until a phase transformation causes abrupt increases (the figures of the results for each metal are presented in Appendix D). In the case of aluminum, magnesium, and zinc, which currently are extracted through electrolysis, the results are within reasonable agreement of reference data.

Table 3: Comparison of results for the specific energy consumption from thermodynamic model to reported data.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal compound</th>
<th>Model results$^a$ / kWh/t metal</th>
<th>Reference$^b$ / kWh/t metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>ZnO</td>
<td>1,537-2,114</td>
<td>3,250-3,380$^c$</td>
</tr>
<tr>
<td>Mg</td>
<td>MgCl$_2$</td>
<td>9,886-12,955</td>
<td>10-20,000$^d$</td>
</tr>
<tr>
<td>Al</td>
<td>Al$_2$O$_3$</td>
<td>9,781-11,913</td>
<td>9,260$^e$</td>
</tr>
</tbody>
</table>

$^a$ The lower limit in the range shown corresponds to $a=1$; the upper limit to $a\neq1$

$^b$ For Zn and Mg, the references are reported industrial data; for Al, the reference is a thermodynamic calculation similar to the one in this work.

$^c$ Zabaleta, 2011

$^d$ Frank et al, 2012 (Ullmann Encyclopedia of Industrial Chemistry).

$^e$ Jarrett, 1981

For the electrowinning of zinc from zinc oxide, the results of the model are 40-50% off the reported industrial data. The thermodynamic model does not account for kinetic considerations, which play a vital role in low temperature processes. Such considerations are negligible at higher temperatures, making the thermodynamic approach of the model yield more accurate results.

In Fig. 16, the teal line, which represents $U_{chem}/U_{cell}$, illustrates that increasing temperatures allow the system to access different thermodynamic conditions, where heat rather than chemical energy dominates the energetics of the process. The chemical energy contribution falls quickly with increasing temperature. Using this observation, we can focus on $U_{ohm}$ to optimize this electrolytic process. For an electrolytic cell,
\[ U_{ohm} = \frac{ig}{\kappa} \]  

where \( j \) is current density between the anode and cathode, \( g \) is the anode-cathode distance, and \( \kappa \) is the conductivity of the medium between the anode and cathode. We find that this latter parameter is key to optimizing such a process (for details, see Appendix A).

The heat and Faradaic efficiencies are important parameters for the thermal and mass balance of the electrolytic cell. Certainly, the efficiency of heating the material (contingent upon the subsequent heat losses due to cell design) will heavily impact the heat balance of the inputs and outputs. In agreement with Carnot efficiency, higher temperatures yield higher practical heat efficiency.

The nature of the Faradaic inefficiency will determine its impact on the energy balance. As can be seen in Fig. 19, using equation [18] to assess an overall Faradaic inefficiency as a “global” \( \beta \) parameter can lead to over-estimating or under-estimating the specific energy requirement. With increasing Faradaic inefficiency, the inaccuracy of this approach becomes larger.

Rather, using the methods outlined in section 5.2.2, a more complex story develops:

- In the case of electronic conduction and partial reduction, \( E_{Fe} \) increases constantly with decreasing Faradaic efficiency; however, it does not increase by as much as by \( E_{Fe}/\beta \) (over-estimation).
- \( E_{Fe}/\beta \) is instead an under-estimation of the effect of reoxidation on the overall energy balance.

8. **Ferrochromium: a strategic metal that could benefit from electrolytic extraction**

8.1 **Introduction**

In 2013, the U.S. was one of the top five producers of stainless steel in the world. It produced 87 million tonnes of stainless steel that same year, which accounted for approximately 331 million
tonnes of CO₂ emissions while consuming approximately 3.2×10¹¹ mega Joules of energy [26]. To achieve these scales the U.S. relied heavily on imported materials to make stainless steel. One such group of materials is ferrochromium alloys, which make up at least 10.5% of stainless steel by weight [27]. Currently the U.S. does not produce any ferrochromium. In 2012, 500,000 tonnes of ferrochromium, valued at US$691,000,000, were imported, and over 90% of this material was used for stainless steel production [28].

In light of these facts, we present an analysis of the now obsolete American ferrochromium producing industry. Our analysis includes a historical account of its disappearance as well as its potential in the scope of mitigating global carbon emissions. Both perspectives evaluate the technological, economic, and regulatory boundaries of this industry, which is similar to other capital-intensive manufacturing industries. Such diverse tools are useful when examining the central tensions brought about by an industry that adds significant value to developing and developed economies yet is subject to ambivalence from the public and private sector. This case study offers insight into the role of innovation, competing stakeholder views, and public policy in an industrial landscape.

Chromium-containing materials are very valuable, and their supply chain provides an interesting case study. The earliest stages of ferrochromium production are physically concentrated while its end uses are ubiquitous and global. Primary ferrochromium is obtained exclusively from chromite ore. The chromite ore is the spinel (Fe,Mg)O(Cr,Fe,Al)₂O₃; depending on its chromium oxide content (Cr₂O₃ content), iron to chromium ratio (Fe:Cr ratio), and aluminum content, it is categorized into three categories: refractory grade chromite ore, metallurgical grade chromite ore, and chemical grade chromite ore. We are interested in metallurgical grade ore, which contains 39-54 wt.% Cr₂O₃ and is found in a handful of places on earth. In decreasing order, the following countries currently produce all the global supply of chromite ore: South Africa, India, Kazakhstan, Finland, Zimbabwe, Brazil, Iran, and Turkey. South Africa supplies nearly half of the world’s total chromite ore per year [29]. Over 70% of chromite ore stays in its country of origin to be transformed into ferrochrome [30], which poses a supply risk of this material to the U.S.

It is worth noting that the terms “resource” and “reserve” mean different things. According to the USGS,
Resource — A concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth’s crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible.

Reserve — That part of the resource which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials; thus, terms such as “extractable reserves” and “recoverable reserves” are redundant and are not a part of this classification system [31].

These definitions make chromium stocks dynamic quantities. Such dynamism is sensitive to technological changes, particularly in geological surveying and extraction processes (though also partly sensitive to changing paradigms and standards of mineral economics). Thus, a country’s stocks and values of mineral resource and reserve bases can change over time. This point is of particular importance to the present investigation, which presents a disruptive innovation in extractive technology that could change what is considered as economically extractable ore.

Chromium is most often found in ferrochromium alloys that vary in chromium content. These alloys usually contain a 50-70% concentration of chromium and are in turn used in various steel products. The main categories of ferrochrome alloys are:

- High Carbon FeCr (>60% Cr, 4-6%C)
- Charge FeCr (50-60% Cr, 6-8%C)
- Medium Carbon FeCr (56-70% Cr, 1-4% C)
- Low Carbon FeCr (56-70% Cr, 0.015-1%C)

In the present case study we will not differentiate between these different types of ferrochromium. Currently, stainless steel production accounts for more than 90% of ferrochromium use [32]. Stainless steels are also classified by the differing chromium, nickel, molybdenum, iron, and carbon content; most stainless steels contain between 10-27% chromium. As ferroalloys are most often classified by their chromium and carbon content, the original composition of the ore (most notable the Fe:Cr ratio) is very important to determine its value. For example, chromium-heavy ore might yield a more valuable ferrochromium product, but
extracting such an alloy faces some extraction difficulties. The high chromium content requires a higher operational temperatures (which in turn requires considering the high vapor pressure of chromium at high temperatures), and iron is reduced more easily. Such considerations will determine the downstream operations and its ultimate market value.

8.2 Existing operations for ferrochromium production.

Ferrochromium alloys are produced by electric arc smelting. It is performed in different configurations, namely the shape of the furnace, charge (raw material) capacity, AC/DC electricity input, and the number/type of electrodes. Depending on the charge, the electric arc will either be submerged, open to the air, or shielded. An electric arc forms at the tips of the electrodes and travels through the highly resistive charge in order to generate heat to reach operating temperatures of up to 2,800°C. For the most part, electric arc furnaces (EAFs) are used for ferrochromium production. EAFs use electricity, coal, and coke as the primary energy inputs to reduce the chromite ore (inserted as both lumpy ore and fine concentrate) into ferrochromium. An EAF will have one or more graphite electrodes that use 50-120 MW of electricity. The coal and coke combust and provide heat and chemical energy for the following simplified reactions:

\[ Cr_2O_3 + 3C(s) \rightarrow 2Cr + 3CO(g) \]
\[ FeO + C \rightarrow Fe + CO(g) \]
\[ Fe + Cr \rightarrow FeCr \]

Producing ferrochromium by EAF leads to a significant amount of indirect and direct carbon emissions. Coke and coal usage accounts for about 60% of process (direct) greenhouse gas (GHG) emissions [33]. Direct carbon emissions are quantifiable through a survey of ferrochromium operations worldwide, and have been estimated to be 1.6 tCO₂/t FeCr. By contrast, indirect carbon emissions can vary substantially depending on the location of the EAF. The main source of indirect carbon emissions is at the electricity-generating step of the process; therefore, an EAF located where electricity is generated using renewable or carbon-lean resources has a cleaner emission profile due to its electricity-intensiveness (anywhere from 2,900 to 4,100 kWh of electricity are required to make a ton of ferrochromium currently [34]). Typically, the cost of producing ferrochromium is associated with the cost of chromite ore (30%), electricity costs (30%), costs of reducing agents (20%), and other (20%) [35].
It is important to note that the heavy dependence on electricity makes the current ferrochrome production route at least partially comparable to the proposed electrolytic route. The close relationship between ferrochromium and the often-evolving electricity markets also makes this an interesting case study. Indeed, despite South Africa’s advantageous position in terms of chromite reserves and resources, the recent uncertainty of supply and volatile prices of electricity have forced the local industry to adapt by exporting substantial amounts of ore and producing ferrochromium abroad. This example is illustrative of the importance of geographically driven production decisions for mineral resources.

8.3 FeCr production in the U.S. – a historical perspective

The deployment of the electric arc furnace in the late 1800s enabled the United States to produce domestic ferrochromium from domestic and imported chromite ore\textsuperscript{6}. Worldwide, ferrochromium production operations were closely tied to their customers – that is, their production depended on the local demand for steel. But over the course of the 20\textsuperscript{th} century, these operations have depended less on the downstream supply chain. Instead, they have become more cost effective by moving closer to chromite ore deposits. Therefore, the U.S., a major steel producer but a minor chromite ore producer, has seen a decline production of ferrochromium over the last fifty years (see Fig.21). In general, ferroalloy production in the Western world declined steeply after 1989 due to major shifts in the economic, political, and industrial landscape worldwide. In 1997 the U.S. ferrochromium industry reported a production volume of 60,700 tonnes (MT) of product out of a maximum production capacity of about 80,000 MT, with just two active producers in the country: Er hemat (formerly Elkem metals) and Macalloy Corporations [35]. After 1997, smaller quantities of FeCr were produced, making production capacities un-reportable in order to protect proprietary company information. The 2009 U.S. recession had a strong impact on the industry, and thereafter all ferrochromium production in the U.S. halted [36, 37, 38].

\textsuperscript{6} The first high-carbon ferrochromium made in the U.S. was produced in 1897, according to the International Chromium Development Association.
Government stocks of chromium-containing metal have declined from a peak of 2,270,000 MT in 1964 to 107,000 MT in 2012, but consumption of ferrochromium has hovered at around 250,000 MT per year since 1964. Fig. 22 illustrates ferrochromium has thus been increasingly imported into the U.S. to meet demand from steel producers [39].
Ferrochromium operations in the U.S. ultimately halted due to both global market forces and domestic environmental policies. On one hand, the developing world successfully leveraged its raw mineral resource and manufacturing capital to dominate the supply and demand of both chromite ore and ferroalloy products. Particularly after the 1980s, the U.S. could not compete with rapidly increasing production capacities of ferrochromium from chromite ore-producing countries.

At this time, the countries that would become world leaders in chromite ore production—such as South Africa and Kazakhstan—went through important social and political transformations. The dissolution of the former Soviet Union allowed Kazakhstan to gain independence. Many in the country and around the world leveraged the push for privatization of many industries to capitalize on the rich Kazakhstani mineral resources [40]. By 1993, South Africa had already become a principal supplier of chromite ore in the world market. Though still experiencing some economic and political uncertainties, the official end of Apartheid in South Africa resulted in increased foreign investment for the exploration and development of chromium-containing resources (among many other mineral resources). During this time, for these countries “mineral exports were vital to foreign exchange earnings, and governments clearly saw the advantages of expanding both the variety and quantity of such exports for funding internal development. [41]” Coupled with the vertical integration of the ferrochromium industry, such suppliers displaced the less geologically auspicious Western world.

The National Defense Stockpile, created to address mineral and material shortages critical to national security issues, fueled much of the ferrochromium production prior to the fall of the Soviet Union. The fall of the Soviet Union and relative peacetime brought a decreased sense of urgency to have chromium-containing materials in the public sector. Thus, in the 1990s and throughout the 2000’s Congress has authorized the disposal of stocks of these materials and cut funds for the contracts that allowed companies like MacAlloy Corporation and Elkem metals to maintain ferrochromium operations and expand production volume [42].

Simultaneously, increasingly stringent environmental codes took a toll on these operations. Concerns over particulate and hexavalent chromium emissions into local air and water streams forced the MacAlloy operations in South Carolina to shut down in 1998.
Ferrochromium production appears to have continued at the turn of the century, presumably by using the existing production capacity at the Eramet Marietta (formerly Elkem Metals), Ohio plant. But even their low production volumes were under the scrutiny of local communities concerned with violations of environmental codes [43].

The shutdown of this industry is an example of the barriers and inflexibility posed by incumbent market participants in a capital-intensive sector in the presence of evolving markets and regulatory codes. The electric arc furnace was developed and deployed as a processing route that exploited the mature resources and knowledge of the nineteenth century. This technology remained the only standard (except evolutionary innovations and adaptations) throughout the course of the next century. Such capital and operational rigidity could not adapt to rapidly changing labor markets, supply shocks, and regulatory landscapes.

It is important to develop extractive and processing routes that simultaneously acknowledge environmental impact and adapt to changing operational conditions to meet the demand of the material. The paradigm of sustainable materials extraction usually meets both criteria. To propose a sustainable ferrochromium production landscape, we must eliminate carbon reliance both as an input and as a source of electricity generation. As a carbon-lean (and potentially carbon-free) metal production technique, the electrolytic method central to this thesis is particularly promising. We thus examine the CO₂ impact of such a proposition as well as the policy framework that would facilitate such an operation.

8.4 Could we propose a clean FeCr production landscape in the U.S.?

There are economic and political advantages to producing ferrochromium domestically. From an economic perspective, vertically integrating ferrochrome production to viable chromite sources in the U.S. could open a channel of income and job growth where electricity is abundant and low-cost. From a political perspective, the U.S. has expressed interest in increasing production and stocks of chromium-containing materials. In fact, in 1987 the U.S. officially declared chromium-containing metals of strategic importance for structural materials as well as military applications.

However, the U.S. has only heavily invested in mining domestic chromite in times of war [44]. The U.S. relies in imports of chromium-containing minerals and metals from South Africa,
Kazakhstan, and China. Political and diplomatic tensions could jeopardize the U.S.'s access to valuable ferrochromium supply. The U.S. Geological Survey (USGS) and the U.S. Bureau of Mines (USBM) has undertaken a series of explorative studies to better assess the stocks and possible sources of domestic chromium. Domestic chromite deposits have been identified in many states – West Virginia, Washington, Tennessee, South Carolina, Wyoming, Ohio, New York, Minnesota, Kentucky, Iowa, California, and Oregon. But the feasibility of an extractive operation depends on its remoteness, how the ore can be extracted, and the ore composition.

An in-depth geological survey of the viability of these ores is out of the scope of this thesis. However, we can estimate how much of the chromium resources in the U.S. could be available for the electrolytic extraction based on the exploratory reports of select deposits undertaken by the USBM, as well as the Mineral Commodity Summaries from the USGS. Much of this knowledge was acquired during wartime, when the U.S. sought to increase its stocks of chromium-containing materials, and formed strategic partnerships with industry.

In 2012 the USGS reported 620,000 tonnes of domestic chromite ore, normalized to 45 wt.% \( \text{Cr}_2\text{O}_3 \) content [45]. Chromite ore containing 45 wt.% \( \text{Cr}_2\text{O}_3 \) is today's standard of economic viability. This standard, however, dismisses lower-grade chromite ore that could be recovered with innovative extractive resources. In addition, the Bureau of Mines has conducted successful research to produce chromite ore concentrate suitable for metallurgical use from low-grade domestic chromite ore [46].

Of the many exploration projects in the U.S. which have identified such resources, we will focus on the results of the 1982 USBM report. It concluded that the U.S. is home to 4.6 million tonnes of demonstrated chromite ore of varying grades, which could produce 5.4 million tonnes of ferrochrome via EAF [47]. However, investment in these resource would only be possible if the price of ferrochromium exceeded US$770/tonne in 1981 dollars, which is equivalent to US$2,000/tonne in 2014 dollars. As of November 2014, the spot price of ferrochromium was US$2,280/tonne [48], with strong demand in future prospects.

Within this report, we consider the potential of extracting ferrochromium via electrolysis from a select Midwestern and Western deposits, which are located near low-cost electricity generated with carbon-lean portfolios. These include deposits in Oregon, Montana, and Alaska, as illustrated in Table 3.
Table 4: Estimates of U.S. chromite deposits, with a focus on the Mid- and Western U.S.

<table>
<thead>
<tr>
<th>State</th>
<th>Deposit</th>
<th>Ore grade / %Cr₂O₃</th>
<th>Demonstrated chromite ore reserve / MT</th>
<th>Cr₂O₃ / MT</th>
<th>Potential FeCr / MT²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska</td>
<td>Claim Point</td>
<td>17.8</td>
<td>267,000</td>
<td>47,600</td>
<td>55,878</td>
</tr>
<tr>
<td>Alaska</td>
<td>Red Bluff Bay</td>
<td>12.0</td>
<td>30,000</td>
<td>3,600</td>
<td>4,226</td>
</tr>
<tr>
<td>Montana¹</td>
<td>Gish Mine</td>
<td>15.0</td>
<td>500,000</td>
<td>75,000</td>
<td>88,043</td>
</tr>
<tr>
<td>Oregon</td>
<td>SW OR Beach Sands</td>
<td>5.6</td>
<td>10,827,000</td>
<td>604,100</td>
<td>709,161</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>730,300</td>
</tr>
</tbody>
</table>

¹ The information from the important Ben Bow and Mouat deposits in Montana was withheld in this report. Chrome Corp. of America reported 14.6 million tons of chromite ore of 26% Cr₂O₃ grade in Montana in 1994 [48].
² Data in this column assumes that 1 MT Cr₂O₃ yields 1.17 MT of ferrochromium.

By the standards of the USBM in 1982, the U.S. could make over eight hundred thousand tonnes of ferrochromium, which today are worth about US$2 billion. And though some mineral accounting standards have changed since 1982, much of the work in this area is yet to be done. Indeed, “...the prospects for the level of activity in U.S. mining depend on the political and economic climate in which the industry operates to a far greater extent than on the availability of mineral deposits --many of them as yet unidentified.” [49]

8.5 CO₂ impact of past FeCr production in the U.S.

Now we will estimate the CO₂ impact of past ferrochromium operations via EAF, and compare them to the hypothetical CO₂ emissions of ferrochromium production by electrolysis. In order to achieve the former goal, we will use the following inventory data:

- **Electricity requirement.** Specific electricity requirement for the EAF route is 3,500 kWh/t FeCr (average between the minimum 2,800 kWh/t and maximum 4,100 kWh/t FeCr).

- **CO₂ emissions.** The current EAF route for ferrochromium production has indirect and direct CO₂ emissions.
  - Direct process emissions originate from coke and limestone use, and amount to approximately 1.6 tCO₂/t FeCr [50].
Indirect process emissions depend on the electricity-generation portfolio of the location of the EAF in each state.

- **Production quantity and locations.** The last reported production of ferrochromium was 60,700 gross weight tonnes in 1997 [51]. This production volume occurred in two places in the U.S.: Marietta, Ohio, and Charleston, South Carolina.

Fig. 23 illustrates the electricity generation portfolios of these two states in 1998. In Ohio, the average electricity carbon footprint was $9 \times 10^{-4}$ short tons of CO$_2$ per kWh of electricity generated in the late 1990s [52]. Ohio relied (and still today relies) heavily on coal-powered electricity. South Carolina, by contrast, uses nuclear and coal generated electricity, making its carbon intensity $4 \times 10^{-4}$ short tons of CO$_2$ per kWh of electricity generated in the late 1990s [53].

Table 4 illustrates the calculated carbon impact of the Ohio and South Carolina ferrochromium operations for the year 1997. Though the capacity of the Eramet site is estimated to be greater than that of MacAlloy, the ferrochromium produced in Ohio may have been more CO$_2$-intensive than the ferrochromium produced in South Carolina, both in bulk CO$_2$ emissions and in tons of CO$_2$ emitted per ton of ferrochromium produced.

In 1997, over two hundred thousand tonnes of CO$_2$ emitted in the U.S. were related to ferrochromium production (Table 4). By comparison, South African ferrochromium producers emitted two and a half million tonnes of CO$_2$ in the same year [54]. As such, the U.S. CO$_2$ emissions significantly contributed to world emissions for this industry.
Table 5: Estimates of CO₂ emissions stemming from ferrochromium production in the U.S. in 1997.

<table>
<thead>
<tr>
<th>1997 Production of FeCr in U.S.</th>
<th>Eramet - Marietta, OH</th>
<th>Macalloy - Charleston, S.C.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed cap. / ktpy</td>
<td>30.0</td>
<td>60.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Production volume / ktpy</td>
<td>27.1</td>
<td>33.6</td>
<td>60.7</td>
</tr>
<tr>
<td>Direct CO₂ / tCO₂/t FeCr</td>
<td>1.6</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td>Indirect CO₂/ tCO₂/t FeCr</td>
<td>3.15</td>
<td>1.38</td>
<td>-</td>
</tr>
<tr>
<td>Estimated CO₂ emissions</td>
<td>4.75</td>
<td>2.98</td>
<td>3.77</td>
</tr>
<tr>
<td>/ tCO₂/tFeCr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estimated CO₂ emissions</td>
<td>128,805</td>
<td>100,227</td>
<td>229,033</td>
</tr>
<tr>
<td>/ tCO₂ in 1997</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With time, industries can become “cleaner,” i.e., less carbon-emission intensive. Table 5 illustrates this concept: assuming the Eramet Marietta operations had sustained the production volume of the 1990s, the CO₂ emissions today would have decreased both in gross tonnage and in a per-ton of ferrochromium basis. This may be because of less coal reliance in the Ohio electricity generation portfolio, or because coal plants have become cleaner.
Table 6: Estimated CO₂ emissions stemming from ferrochromium production in 2009.

<table>
<thead>
<tr>
<th>2009 Projected Production of FeCr in U.S. a</th>
<th>Eramet - Marietta, OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed cap. / ktpy</td>
<td>20.0 b</td>
</tr>
<tr>
<td>Production volume / ktpy</td>
<td>14.0 b</td>
</tr>
<tr>
<td>Direct CO₂ / tCO₂ / t FeCr</td>
<td>1.6 c</td>
</tr>
<tr>
<td>Indirect CO₂ / tCO₂ / t FeCr</td>
<td>2.94 d</td>
</tr>
<tr>
<td>Estimated CO₂ emissions / tCO₂ / tFeCr</td>
<td>4.54</td>
</tr>
<tr>
<td>CO₂ emissions / tCO₂ in 2013</td>
<td>63,532</td>
</tr>
</tbody>
</table>

a MacAlloy Corp in South Carolina no longer existed in 2009.
c Assuming 70% of total capacity
ethnic Using the U.S. Energy Information Agency’s reported CO₂ footprint for electricity generation in the state of Ohio.

8.6 Proposed FeCr production by electrolysis in the U.S.

Now we will compare the results of 7.1.4 to the potential CO₂ emissions of ferrochromium production by electrolysis. The chromite ore is composed of both iron and chromium oxides, so the energy requirement of extracting a ferrochromium alloy can be calculated by using the weight percentage of each metal, assuming a certain alloy composition. At 1600°C, the model constructed in this thesis results in a minimum specific energy requirement of 3,875 kWh per ton of iron from iron oxide and 4,165 kWh per ton of chromium from chromium oxide for the perfectly efficient case. The numbers are 4,118 kWh/t Fe and 5,171 kWh/t Cr when heat inefficiency is accounted for (Table 6). For our purpose, we will use the latter numbers to make more realistic calculations; therefore, we will assume that 4,866 kWh are needed to produce one tonne of ferrochromium, assuming a 71-29 Cr-Fe composition of the final product. This estimate also ignores the energy needed to melt and separate impurities in the chromite and in the final ferrochromium alloy.
Table 7: Estimated minimum energy requirement to produce electrolytic ferrochromium, alpha, beta = 1.

<table>
<thead>
<tr>
<th>Energy Requirement / kWh/t product</th>
<th>Chromite Composition / %</th>
<th>Estimated Energy Requirement / kWh/t FeCr</th>
<th>Product Composition / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr from pure Cr₂O₃</td>
<td>Fe from pure Fe₃O₄</td>
<td>Cr₂O₃</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Cr from Fe Cr₂O₃</td>
<td>Cr from Cr₂O₃</td>
<td>Cr₂O₃</td>
<td>Cr from Fe Cr₂O₃</td>
</tr>
<tr>
<td>α=1</td>
<td>4,165</td>
<td>3,163</td>
<td>45</td>
</tr>
<tr>
<td>α≠1</td>
<td>5,171</td>
<td>4,118</td>
<td>45</td>
</tr>
</tbody>
</table>

We emphasize the value of the chromite deposits in Midwestern and Northwestern United States, which have access to cheap and relatively “clean” electricity generation portfolios. Oregon is a leading state in carbon-lean electricity generation, with roughly 70% of its total electricity generated using the hydroelectric route. As a comparison, the Montana electricity generation portfolio is a combination of coal and renewable sources (Fig. 23).

Figure 23: Electricity generation portfolios for Oregon and Montana in 2014.
The average carbon footprint of electricity in generation in Oregon is 0.18 kg CO$_2$/kWh, while it is 0.66 kg CO$_2$/kWh in Montana [55]. However, a more striking comparison is the CO$_2$-intensity of the electricity sector in the U.S. versus that of South Africa (Fig. 24). The U.S. emits roughly half of the CO$_2$ of electricity producers in South Africa [56].

![Figure 24: Comparison of the CO$_2$ intensity of the U.S. and South Africa. Source: The Eskom Factor Report, 2011.](image)

Table 7 lists the CO$_2$ impact of producing ferrochromium by EAF in Ohio, Montana, and South Africa. Even by producing ferrochromium via the EAF, Montana and Oregon would have a smaller carbon footprint than the footprint made by EAFs in existing locations.
Table 8: Estimates of the CO₂ impact of producing ferrochromium by EAF in South Africa and in different states in the U.S.

<table>
<thead>
<tr>
<th></th>
<th>Energy / kWh/t FeCr</th>
<th>Direct Emissions / tCO₂/tFeCr</th>
<th>Indirect Emissions / tCO₂/tFeCr</th>
<th>Total Emissions / tCO₂/tFeCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAF FeCr in South Africa</td>
<td>3,500</td>
<td>1.6</td>
<td>3.22</td>
<td>4.82</td>
</tr>
<tr>
<td>EAF FeCr in Ohio</td>
<td>3,500</td>
<td>1.6</td>
<td>2.94</td>
<td>4.54</td>
</tr>
<tr>
<td>EAF FeCr in Montana</td>
<td>3,500</td>
<td>1.6</td>
<td>2.01</td>
<td>3.61</td>
</tr>
<tr>
<td>EAF FeCr in Oregon</td>
<td>3,500</td>
<td>1.6</td>
<td>0.42</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Table 8 contrasts the carbon intensity of the EAF route and the electrolytic route with the same geographical variation. Producing ferrochromium electrolytically in Montana, which relies heavily on coal-generated electricity, has a smaller carbon footprint than the EAF processing routes in the locations that have produced ferrochromium in the past. Producing ferrochromium electrolytically in Oregon would have a carbon footprint that is smaller by an order of magnitude.

Table 9: Comparison of CO₂ emissions between the EAF and electrolytic process routes.

<table>
<thead>
<tr>
<th></th>
<th>Energy / kWh/t FeCr</th>
<th>Direct Emissions / tCO₂/tFeCr</th>
<th>Indirect Emissions / tCO₂/tFeCr</th>
<th>Total Emissions / tCO₂/tFeCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAF FeCr in S.A.</td>
<td>3,500</td>
<td>1.6</td>
<td>3.22</td>
<td>4.82</td>
</tr>
<tr>
<td>EAF FeCr in Ohio</td>
<td>3,500</td>
<td>1.6</td>
<td>2.94</td>
<td>4.54</td>
</tr>
<tr>
<td>Electrolytic FeCr in Montana</td>
<td>4,866</td>
<td>0</td>
<td>2.80</td>
<td>2.80</td>
</tr>
<tr>
<td>Electrolytic FeCr in Oregon</td>
<td>4,866</td>
<td>0</td>
<td>0.59</td>
<td>0.59</td>
</tr>
</tbody>
</table>

8.7 The role of political and economic infrastructures on the innovation landscape for extractive industries – a domestic and international perspective

The electrolytic extraction of ferrochromium from chromite ore in the United States will not occur spontaneously. As an innovative processing route in the ferrochromium industry
requiring heavy infrastructural costs, government can incentivize such efforts to facilitate innovation.

This is not a new role for the American government. Indeed, government agencies led much of the exploratory work to determine the economic viability of the identified chromite resources in the mid-to-late 20th century. The success of the American ferrochromium producing industry pivoted on the availability of government contracts at the time, which increasingly leveraged the government stockpile of chromite ore to supply domestic demand for ferrochromium.

There is also opportunity for international collaboration. Historically, ferrochromium operations have moved closer to sources of chromite ore, which in general translates into mining and smelting operations in developing countries such as South Africa. This might have been a cost-competitive strategy during a time when these countries exploited their abundant resources, such as coal to generate electricity, but there are policies set in motion currently that could justify different strategies. Industry in South Africa, for example, is coming under increasing pressure to alter existing operations to meet policy standards, which emphasize energy efficiency and a reduced environmental impact. Indeed,

“South Africans were confronted by average power-price increases of 25 percent in each of the past six years to help [the primary electricity provider] finance about 500 billion rand of spending through 2017 to overcome an electricity shortage.” [59]

Prices are expected to rise by 8-13% annually, which is higher than the inflation rate [60]. Several blackouts have also prompted Eskom, South Africa’s publicly owned electricity provider, to entreat industrial electricity users to cut consumption during peak demand hours by 10% [61]. The South African government is also seeking to implement policy measures to improve energy security and price stability. Some of these include ambitious renewable-energy centered energy strategies to cut carbon emissions in the coming years.

These outlooks pose significant challenges to South African ferrochromium producers, who for the past forty years have benefitted from government policies – tax rebates low-interest
loans, subsidies, etc. [62] – to build capacity with the electric arc furnace and reliably cheap
coal-generated electricity. These past support systems are incongruous with the short to medium-
term outlook and could translate into price spikes of chromium-containing materials in a world
that already depends heavily on these valuable South African exports. With respect to the fast-
paced development of South African chromite deposits, it has been noted that “the sustainability
of (recent) economic growth over the long-term is highly questionable.” [63]

Private and public entities in countries such as the U.S. and South Africa could make
strategic investments to order to mitigate medium to long-term ferrochromium supply risks. The
U.S. should build ferrochromium producing capacity, keeping in mind the current and upcoming
environmental regulations. Here, the electrolytic production route is a promising one in terms of
energy efficiency and low carbon emissions for a valuable material stream. Doing so will in part
protect the U.S. against ferrochromium supply while building a sustainable industrial ecology
that can serve as an example for other industries.

The U.S. has as its disposal chromite ore in government/private stockpiles, which could
be used as a short-term source of ore feed. Part of the chromite material could be imported from
the major chromite ore producers (see above). In parallel, the U.S. can continue to explore its
domestic or neighboring chromite resources. The Fraser Institute Survey of Mining Companies
frequently ranks countries by the Policy Potential Index (PPI) and the Current Mineral Potential
(CMP). The PPI rates a jurisdiction’s mineral resource “attractiveness” according to its
regulatory and legal landscape. It includes environmental regulation, uncertainty in policy
enforcement, and trade barriers, among other metrics. It ranges from 0-100, 100 being the
highest score achievable. The CMP is a measure of the capacity for exploration in a jurisdiction
based on the identified mineral resources and the regulations related to exploration, and it ranges
from 0 to 1, 1 being the highest score. Both indices are gleaned from surveys distributed to
multiple mining companies. Both indices, though by no means comprehensive or entirely
objective, are metrics used to assess the merit of investment regarding mineral resources for
multiple jurisdictions all around the world.

7 The most notable neighboring resource, Canada’s “Ring of Fire” deposits in Ontario, could be a valuable
source of chromite ore should the U.S. decide not to produce it domestically. The Big Daddy Deposit in
the Canadian Ring of Fire is still under scrutiny to determine the economic viability of its chromite, but so
far an estimated 16.3 million tonnes of a 40.66% Cr₂O₃ grade have been identified [51].
Based on these indices, U.S. mineral resource development is not an unfavorable investment today. The 2012-2013 Fraser report assigned a PPI of over 45 to multiple states in the U.S., many of which are located in the Western and Northwestern U.S. In the 2008-2013 time period, all of the thirteen states (except California) improved their PPI rating. The median PPI for the U.S. as a whole for 2012-2013 was 61.9, and the average was 65.9. South Africa, on the other hand, received an overall PPI of 35, down from 44.5 in the previous year. The U.S. median and average CMP was 0.46 and 0.50 respectively, while the overall South African CMP was 0.28 [50].

Given this knowledge, both countries stand to benefit from an arrangement that would leverage their individual advantages in order to create a cleaner and more stable supply of ferrochromium to the world market. While South Africa has extensive mineral resources, upcoming regulatory and pricing frameworks could threaten the prosperity of ferrochromium producers in the country. On the other hand, the U.S. could engage the generous opportunity space provided by innovative technologies – such as an electrolytic processing route – that harness cheap and relatively clean electricity to revive the dormant ferrochromium industry.

9. Further advantages of producing metals by electrolysis

Though it’s difficult to some advantages of electrolysis as an alternative extraction route, some are worth noting. Most notable are:

- More streamlined processing, with possible process automation and simplification, as well as flexibility depending on the inputs available and outputs desired.
- Different labor market (other welfare gains), tight control (“turning a knob” control), more organized energy utilization,
- Utilizing available ore that was previously uneconomical to mine (e.g. lower grade ore),
- Added value of high-purity product: prediction of carbon content is difficult at best, but in comparison to the product from other metallothermic or carbo-thermic processes, the carbon content could be reduced by an order of magnitude.
- Offsetting the cost of electricity by cleaning up the operations
10. Conclusion

As a central medium for economic and technological exchange, the metal-making industry can make significant contributions to sustainability goals in terms of energy efficiency and carbon emission mitigation at the extraction stage alone.

We propose the development of carbon-free electrolysis as a novel and necessary metal extraction paradigm. This is labeled as a paradigm because it involves strategic deployment that considers not only careful choice of reactor design (inter-electrode gap, supporting electrolyte, etc.) but also a fitting geo-political landscape for a specific metal. This thesis traces many of these considerations, which span scientific, engineering, and regulatory considerations.

In specific, it may be useful to recall the main questions we set forth to answer:

- Can we model the electrolytic extraction of a metal from its metal compound using a macroscopic thermodynamic model?
- If so, is our estimate realistic?
  - How do we make this estimate as realistic as possible?
- What are the key physical, chemical, and/or engineering parameters that most heavily influence the efficiency of this process?
- Once efficiency is “mastered,” what are the wider implications of implementing this technology?
  - For example, what is a hypothetical carbon impact of producing ferrochromium electrolytically in the United States?

Firstly, the macroscopic mass/energy balance presented achieved a realistic estimate of the energy consumption needed to extract metal electrolytically. This was achieved without taking into account ore impurities or kinetic limitations. Despite this, the model describes the technical criteria for a practical efficient operation of an electrolytic metal extraction process. This simple model can be a powerful tool with which to inform policymakers regarding emerging extraction technologies. The formulation of this model for electrolytic extraction is based on basic thermodynamic principles, which are applicable to a wide variety of metal compounds. Therefore, its results can serve as a standard of reference for policy makers and industry
stakeholders seeking to evaluate innovation in extractive metallurgy in the future. Innovative extractive methods can be compared existing methods as well as to the one proposed here, which is purely electricity-driven.

Within the analysis of the model – including its formulation, efficiency assessment, and optimization – we reach some important conclusions. The electrical conductivity $\kappa$ is a powerful parameter with which to optimize the energy consumption of the electrolytic isolation of a metal from a metal compound (See Appendix A). It provides a handle to control the ohmic voltage drop present in the electrolytic cell, which is the dominant energy term in the overall energetic balance. Thus by altering the conductivity of the medium between then anode and cathode one can closely monitor the total energy density of the process.

The heat and Faradic efficiencies are also key in determining the energy balance. They may act as additive losses or can compensate each other through different accounting methods. These three parameters can be favorably manipulated by someone interested in making metal by custom-making an electrolyte which will have the “right” combination of electronic conductivity, ionic mobility, etc. to most efficiently control the efficient extraction if the metal at the specific target temperature in a steady state.

In addition, the model gave us insight into the energetic evolution of the system with respect to temperature. We find that at higher temperatures, the heat drives the energetics of the process. In addition to this, favorable thermodynamics allow for high practical process efficiency at higher temperatures, particularly to make liquid metal.

The results of model provided an interesting perspective to propose the novel extraction of various strategic metals. Firstly, it presents a promising opportunity to revive a dormant ferrochromium industry in the U.S., which for decades was central to the health of the American industrial economy. Ferrochromium production by electric arc smelting in the U.S. was phased out due to environmental regulation and the global economic forces. But similar conditions are exerting considerable amounts of pressure in many developing countries, which are currently the leading ferrochromium producers. The electrolytic extraction of ferrochromium modeled here is estimated to have a specific energy requirement within the range of the specific energy requirement by electric arc smelting. Thus the electrolytic extraction of ferrochromium from (domestic or foreign) chromite could forego some of the cost and uncertainty of retro-fitting $20^{th}$-
century technology with the industrial infrastructure of the future, which relies mainly on electricity and has the opportunity of becoming CO₂-free.

For another group of strategic metals, the rare earths, the results of the model were also interesting and unexpected. The specific energy expenditures for the extraction of a single rare earth metal from a pure oxide is remarkably low due to their high molar mass and density (see Appendix D). Realizing such an electro-winning process would very significantly alter the footprint that current rare earth extraction processes exert on environmental and political dynamics.

References


[13] Industrial Efficiency Technology Database, by the Institute for Industrial Productivity http://ietd.iipnetwork.org/content/blast-furnace-system


http://www.worldstainless.org/Files/issf/non-image-files/PDF/ISSF_Stainless_steel_and_co2.pdf

[28] Ibid.


[31] Ibid.


[56] Ibid.


[58] Ibid.


Appendix A

Optimization of an electrolytic process

An electrolytic reactor will face some physical and engineering challenges (tapping of reactor, refractory choice, slag, etc.). Such challenges will usually be metal or process-specific, and will not be addressed here. Instead, with the purpose of process optimization, we can look at the analytic expression of the electrolytic process in order to dissect which parameters, if any, can be fine-tuned in order to create the optimum conditions.

It is useful to consider the physical and chemical parameters that govern the electrolytic process. The energy expenditure is driven by \( U_{\text{cell}} \), or the total potential applied to the electrolytic cell. In equations [4] and [5] \( U_{\text{chem}} \) is the minimum thermodynamic energy \( \Delta G \), which is fixed by the bond in the metal compound. On the other hand, \( U_{\text{ohm}} \) can be optimized.

![Graph showing the relationship between energy terms and temperature](image)

\[ U_{\text{cell}} = U_{\text{chem}} + U_{\text{ohm}} \]

As seen in Fig. 25, \( U_{\text{ohm}} \) becomes the dominant energy term with increasing temperature. In an electrolytic cell,

\[ U_{\text{ohm}} = \frac{j\alpha}{\kappa} \]  

Where \( j \) is the current density between the anode and cathode (in amperes per square centimeter), \( g \) is the inter-electrode gap (in centimeters), and \( \kappa \) is the conductivity of the inter-electrode
medium. Therefore, by altering \( j/g/K \) one can alter \( U_{\text{ohm}} \) and ultimately the optimal, minimum energy requirement.

Efforts to control the current density \( j \) often stall. There are limited amounts of materials that can carry high current densities in a stable manner. Thus, optimization of this parameter becomes a material engineering problem. The inter-electrode gap \( g \) is a physical parameter that can be optimized with relative straightforwardness, though it is limited by some practical realities such as the efficient removal of the gas phase.

Thus, \( k \) remains as the governing physical parameter that determines the heat balance. Optimizing this parameter translates into optimizing the entire electrolytic process, and this can be done through a thoughtful choice of the electrolytic medium. The chemical composition of the electrolyte will determine its charge-transfer characteristics.

Using [A1], we can:

- Fix \( j \) and \( g \)
- Use the results of the thermodynamic model; namely, the minimum \( U_{\text{ohm}} \) (no Faradaic or heat losses) at the ideal operating temperature
- Obtain a first-order estimate of what the "ideal" electrolyte would be for each process.

Table 9 is a more detailed description of the calculation parameters, and compares these results with those of existing electrolytic operations.

---

**Table 10:** Calculation of ideal electrolyte conductivity for existing electrolytic processes. The last two columns indicate industrial practices.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Operating Temp. / K</th>
<th>( U_{\text{ohm}} / \text{V} )</th>
<th>( j / \text{A/cm}^2 )</th>
<th>( g / \text{cm} )</th>
<th>Calculated ( \kappa / \text{S/cm} )</th>
<th>Industrial supporting electrolyte</th>
<th>Industrial conductivity ( \kappa / \text{S/cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>313</td>
<td>1.65</td>
<td>0.085&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5-8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.3-0.4</td>
<td>ZnSO&lt;sub&gt;4&lt;/sub&gt;-H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mg</td>
<td>973</td>
<td>2.52</td>
<td>0.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8-12&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.5-3.8</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;-KCl-CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Al</td>
<td>1233</td>
<td>2.37</td>
<td>1.3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>4.5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.5</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-Na&lt;sub&gt;3&lt;/sub&gt;AlF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>2.1-2.7&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Günter, 2012 (*Ullmann Encyclopedia of Industrial Chemistry*).
<sup>b</sup>Copham and Fray, 1990.
<sup>c</sup>Amundsen et al, 2012 (*Ullmann Encyclopedia of Industrial Chemistry*).
<sup>d</sup>Frank et al, 2012 (*Ullmann Encyclopedia of Industrial Chemistry*).
<sup>e</sup>Hives et al, 1993.
It is worth noting that the energetic model does not take into account kinetic effects of these electrochemical reactions. Kinetic effects are particularly prominent for the case zinc electrowinning from zinc oxide at 313K, as the metal product is deposited as a solid. Despite this assumption, the results of the model for zinc electrowinning are remarkably close to the reported conductivity of the industrial electrolyte used for this process. Kinetic effects become less relevant at higher temperatures, making the model results more representative of the industrial reality.

By comparing the results from columns six and eight in Table 9, we can conclude that the industrial electrolytic processes listed do not operate at maximum heat efficiency, likely due to a lack of optimization of the supporting electrolyte. In the interest of extracting liquid metal from a metal oxide or a metal chloride (rows two and three of Table 10), these results indicate that a total conductivity in the order of magnitude of 2-4 S/cm is needed for the ideal electrolyte (depending on the operating conditions). In addition, for the purpose of transporting metal ions to produce liquid metal, the candidate electrolyte should be in a liquid or molten state. Such boundary conditions call for the use of molten oxides and molten salts as the supporting media. These material systems involve complex transport phenomena – both ionic and electronic – that are influenced by temperature, ionic species present, and other physical parameters.

Understanding the degree of electronic and ionic conduction of a candidate electrolyte is of central importance to anyone seeking to optimize the supporting electrolyte for a metal electrowinning process. Knowing the conductivity of the electrolyte for electrolytic extraction is an important step in designing a process that can run at a steady state by obtaining the optimal heat balance. This can be done for different metals (even rare earths), each of which will demand a set of optimal conditions at a certain temperature.

Firstly, someone interested in extracting metal will calculate the minimum voltage needed for such a process. Then they must determine the ohmic (heat) contribution needed to maintain steady state operation (i.e., $U_{ohm}$). From $U_{ohm}$ (as well as a knowledge of the design parameters $j$ and $g$), the contender will know what conductivity the electrolyte needs to have to meet the operation requirements. With this information the contender can move forward by designing the “right” electrolyte by adjusting its composition.
Appendix B

Here we present a formal derivation of eqns. [3] and [4]. With the purpose of deriving these equations, which use thermodynamic variables to describe the process of warming up and decomposing the metal compound, we take a parallel approach. The first perspective is that of a chemical engineer: a mass and energy balance must occur in the electrolytic cell.

In our endeavor, all the metal compounds being studied – oxides, sulfides, and chlorides – are assumed pure and decompose into metal and a divalent gas $Y_2$. That is,

$$M_xY_z \rightarrow xM + \frac{z}{2}Y_2 \text{ (g)} \tag{B1}$$

$Y_2$ is either pure oxygen gas $O_2$, pure sulfur gas $S_2$, or pure chlorine gas $Cl_2$. $M$ & $Y_2$ exit the cell at target temperature $T$, while $M_xY_z$ enters the reactor at room temperature $T_0$.

$$E \text{ [Joules/second]} = \dot{n}_{\text{inputs}}C_{\text{input},T_{\text{input}}}T_{\text{input}} - \dot{n}_{\text{outputs}}C_{\text{outputs},T_{\text{output}}}T_{\text{output}} - \dot{n}_{\text{input}}\Delta_w H_{T_0,T} - \dot{n}_{\text{reaction}}\Delta_r H_{T_{\text{reaction}}} \tag{B2}$$

Where $\dot{n}_i$ is the number of moles of input/output per second and $C_{\text{input/output},T_{\text{input/output}}}$ is the standard state molar heat capacity of the input/output (in Joules per mole per Kelvin) at its corresponding temperature $T_{\text{input/output}}$ (in Kelvin). It is important to note that the inputs come in at an initial temperature ($T_0$) and are warmed up to a target temperature ($T$). That is,

$$T_{\text{input}} = T_0$$
$$T_{\text{outputs}} = T$$

The reactant (input) is then decomposed into the products (outputs) in [B1] at constant temperature $T$.

$$T_{\text{reaction}} = T = T_{\text{outputs}}$$

In addition, $\Delta$ signifies an exact variation in a thermodynamic variable. The symbol $\Delta_r$ represents an exact change in a thermodynamic variable due to a chemical reaction (in this case, the decomposition of the metal compound) at the constant target temperature of the reactor $T$. 

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$\Delta w$ is the change of that thermodynamic variable due to warming up from $T_0$ to $T$. In other words,

$$\Delta_r H^0_T = H^0_{products,T} - H^0_{reactants,T}$$  \[B3\]

$$\Delta_w H^0_{T_0\rightarrow T} = H^0_{reactants,T} - H^0_{reactants,T_0}$$  \[B4\]

and $\dot{n}_M$ is the moles of metal produced per second. Due to the stoichiometry of \[B1\],

$$\frac{\dot{n}_{MxYz}}{x} = \dot{n}_M = \frac{z}{2x} \dot{n}_{Yz}$$  \[B5\]

assuming no accumulation of feed or products inside of the reactor. $\dot{n}_M$ is calculated through Faraday’s first law of electrolysis

$$\dot{n}_M = \frac{I_{Faradaic}}{e_M F} \left[ \text{mol/sec} \right]$$  \[B6\]

where $I_{Faradaic}$ represents the Faradaic current in the reactor (in amperes), $e_M$ is the number of electrons transferred to the metal ion at the cathode, and $F$ is Faraday’s constant. $e_M$ can be calculated by using

$$e_M = \frac{z \epsilon}{x}$$  \[B7\]

where $\epsilon$ is the valency of $Y$. Normalizing all quantities to correspond with one mole of metal, \[B2\] becomes the mass and energy balance

$$\dot{E} = \frac{I_{Faradaic}}{e_M F} \left[ \frac{T_0}{x} C_{MxYz,T_0} - T C_{p,M,T} - \frac{zT}{2x} C_{p,Yz,T} - \frac{1}{x} \Delta_w H^0_{T_0\rightarrow T} - H^0_{M,T} - \frac{z}{2x} H^0_{Yz,T} + \frac{1}{x} H^0_{MxYz,T} \right]$$  \[B8\]

A parallel perspective is that of the electrical engineer. The electrical engineer treats the electrolytic cell as a circuit, which dissipates power

$$P = U_{cell} I_{total} \left[ \text{Watts} \right]$$  \[B9\]

Where $I_{total}$ is the total current flowing in the circuit in amperes, and $U_{cell}$ is the total voltage applied to the electrolytic cell. We submit that $U_{cell}$ is “spent” on two very different physical phenomena inside the cell. One is decomposing the compound into the outputs $M$ and $Yz$. The other is heating the inputs to the target temperature and providing heat energy needed to drive \[B1\]. In other words,
\[ U_{\text{cell}} = U_{\text{chem}} + U_{\text{ohm}} \]  \[ \text{[B10]} \]

where \( U_{\text{chem}} \) is the minimum chemical energy needed to separate the metal compound into the products

\[ U_{\text{chem}} = -\frac{\Delta_r G_T^*}{e_MF} = \frac{-\left(\Delta_r H_T^* - T \Delta_r S_T^*\right)}{e_MF} \]  \[ \text{[B11]} \]

where \( \Delta_r G_T^* \) is

\[ \Delta_r G_T^* = G_{M,T}^* + \frac{z}{2} G_{Y_T,T}^* - \frac{1}{x} G_{M_x Y_e,T}^* \]  \[ \text{[B12]} \]

\( G_T^{products/reactants} \) are the isothermal Gibbs free energy of the products or reactants (in Joules per mole). Also,

\[ \Delta_r S_T^* = S_T^{products,T} - S_T^{reactants,T} \]  \[ \text{[B13]} \]

\( S_T^{products/reactants} \) represent the isothermal entropy of the products or reactants (in Joules per mole per Kelvin) at the target temperature \( T \) (in Kelvin). Thus,

\[ P = (U_{\text{ohm}} - \frac{\Delta_r H_T^* - T \Delta_r S_T^*}{e_MF})I_{\text{total}} \]  \[ \text{[B14]} \]

Combining the electrical engineer’s and the chemical engineer’s perspectives ([B7] and [B13]),

\[ I_{\text{Faradaic}} \left( \frac{T_0}{e_MF} \right) \left[\frac{\Delta_r H_T^* - T \Delta_r S_T^*}{e_MF}\right]I_{\text{total}} \]  \[ \text{[B15]} \]

And assuming that \( I_{\text{total}} = I_{\text{Faradaic}} \),

\[ U_{\text{ohm}} = \frac{1}{e_MF} \left[ T_0 \frac{C_M^P}{x C_{M_x Y_e,T_0} - T C_{M,T}^P - \frac{T_0}{2x} C_{Y_T,T}^P - \frac{1}{x} \Delta_w H_{T_0,T}^* - T \Delta_r S_T^*} \right] \]  \[ \text{[B16]} \]

And expanding \( \Delta_r S_T^* \),

\[ U_{\text{ohm}} = \frac{1}{e_MF} \left[ T_0 \frac{C_M^P}{x C_{M_x Y_e,T_0} - T C_{M,T}^P - \frac{T_0}{2x} C_{Y_T,T}^P - \frac{1}{x} \Delta_w H_{T_0,T}^* - T \left( S_{M,T}^* + \frac{z}{2x} S_{Y_T,T}^* - \frac{1}{x} S_{M_x Y_e,T}^* \right) \right] \]  \[ \text{[B17]} \]

So that \( U_{\text{cell}} \) is

\[ U_{\text{cell}} = \frac{1}{e_MF} \left[ T_0 \frac{C_M^P}{x C_{M_x Y_e,T_0} - T C_{M,T}^P - \frac{T_0}{2x} C_{Y_T,T}^P - \frac{1}{x} \Delta_w H_{T_0,T}^* - T \left( S_{M,T}^* + \frac{z}{2x} S_{Y_T,T}^* - \frac{1}{x} S_{M_x Y_e,T}^* \right) - \frac{z}{2} G_{Y_T,T}^* + \frac{1}{x} G_{M_x Y_e,T}^* \right] \]  \[ \text{[B18]} \]
The signs of each term in this equation are consistent with the physical reality of the mass flow in the cell. The thermodynamic terms of the inputs (reactants, which enter the electrolytic cell) carry a positive sign, while the outputs (products, which exit the cell) and the endothermic process of warming the metal compound from room temperature to target temperature carry a negative sign.

Finally, $U_{cell}$ is used to obtain the specific energy expenditure:

$$P_M = \frac{U_{cell}M_F}{3.6m_M} \text{ kWh/tonne metal}$$  \hspace{1cm} [B19]

where $e_M$ is the number of electrons transferred to the metal ion at the cathode, $F$ is Faraday’s constant, and $m_M$ is the mass of the metal in grams per mole.

**Appendix C**

It is worth noting that to obtain [B18], we assumed that the total current in the system corresponds exactly to the metal-making (Faradic) current (see Fig.13).

$$I_{total} = I_{Faradaic}$$  \hspace{1cm} [C1]

This is useful as a first order estimate – that is, it allowed us to set a minimum energy requirement that assumes perfect current efficiency.

However, there are physical limitations to this efficiency in practice. As mentioned in the methods section, and particularly for high temperature processes (such as those involving molten salts), there could be Faradic inefficiencies in the form of electronic conduction, partial reduction of metal species, and re-oxidation (re-sulfurization, re-chlorination) of metal species. This can be expressed as additional currents:

$$I_{total} = I_{Faradaic} + I_{inefficiency} = I_{Faradaic} + I_{reoxidation} + I_{partial\ reduction} + I_{e^-\ conduction}$$  \hspace{1cm} [C2]
Figure 13: (left) schematic of a perfectly efficient electrolytic process, wherein all of the current is Faradaic (i.e. metal-making) current. (right) schematic of an inefficient Faradaic process, wherein some of the current is Faradaic (i.e. metal-making) current and some of the current is spent in other processes.

These introduce energetic flows into our system, which may contribute to or diminish the energetic requirement described in [B18]. When present, these additional energetic flows force us to reexamine our equations from [B15] onward. $I_{\text{total}}$ can no longer be treated as one variable that can be evenly distributed into the terms of

$$U_{\text{cell}} = U_{\text{chem}} + U_{\text{ohm}}$$  \hspace{1cm} [C3]$$

Rather, each “current” in [C2] must be coupled to the $U_i$ that corresponds to the physical process. Consider

$$P = U_{\text{cell}} I_{\text{total}} \text{ [Watts]}$$  \hspace{1cm} [C4]$$

$$P = U_{\text{cell}} (I_M + I_{\text{inefficiency}})$$  \hspace{1cm} [C5]$$

$$P = (U_{\text{chem}} + U_{\text{ohm}})(I_M + I_{\text{inefficiency}})$$  \hspace{1cm} [C6]$$

$$P = U_{\text{chem}}(I_M + I_{\text{inefficiency}}) + U_{\text{ohm}}(I_M + I_{\text{inefficiency}})$$  \hspace{1cm} [C7]$$
In the case of reoxidation:

\[ P = U_{\text{chem}} I_M + U_{\text{chem, reoxidation}} + U_{\text{ohm}} I_M + U_{\text{ohm, reoxidation}} \]

which reduces to

\[ P = U_{\text{chem}} I_M + U_{\text{ohm}} (I_M + I_{\text{reoxidation}}) \]

In the case of electronic conduction:

\[ P = U_{\text{chem}} I_M + U_{\text{chem, e-conduction}} + U_{\text{ohm}} I_M + U_{\text{ohm, e-conduction}} \]

which reduces to

\[ P = U_{\text{chem}} I_M + U_{\text{ohm}} (I_M + I_{\text{e-conduction}}) \]

And in the case of partial reduction:

\[ P = U_{\text{chem}} (I_M + I_{\text{partial reduction}}) + U_{\text{ohm}} (I_M + I_{\text{partial reduction}}) \]

Each of these phenomena contribute to the energy balance uniquely depending on the metal and metal compound, as well as the operating temperature. The following is a study of the sources of Faradic inefficiencies for the case of the electrolytic extraction of iron \((Fe)\) from iron oxide \((Fe_2O_3)\) at 1600°C, but the methods can be transposed to other metals.

**Re-oxidation of metallic species**: once the metal has been deposited at the cathode, it can re-oxidize inside the cell by recombination. The metallic species could migrate and exchange electrons as in the following reaction

\[ M \rightarrow M^{5+} + 4e^- \]

while the divalent gas exchanges electrons

\[ Y_2 + 4e^- \rightarrow 2Y^{2-} \]

This is accounted for as an inefficiency since the thermal and chemical energy to reduce the metal has been spent, but it reverses to become a metal compound. If/when this re-oxidation phenomenon occurs, energy is released inside the electrolysis cell. This energy is the heat of the reaction, or enthalpy of reoxidation \((\Delta_r H_{\text{reoxidation}})\):
\[ \Delta_r H_{\text{reoxidation, 1600}^\circ C} = -494,484 \text{ joules/mol Fe} \]  

Such energy is released into the system purely as heat, and will contribute positively to the heat balance.

**Partial reduction of metallic species:** Some metals can exhibit mixed valency. For example, the following can occur in the case of iron

\[ Fe^{3+} + e^- \rightarrow Fe^{2+} \]  

The partial reduction of a species must be accompanied by a corresponding oxidation reaction, such as

\[ Fe^{2+} \rightarrow Fe^{3+} + e^- \]  

\[ O^{2-} \rightarrow \frac{1}{2} O_2(g) + 2e^- \]  

We consider the reaction

\[ Fe_3O_4(l) \rightarrow 3FeO(l) + \frac{1}{2} O_2(g) \]  

and submit that this reaction occurs as an isothermal process. Note that here we have used magnetite, \( Fe_3O_4 \), because it is the iron oxide compound containing \( Fe^{3+} \) thermodynamically stable at the temperature of interest, \( \sim 1600^\circ C \) in equilibrium with \( O_2 \).

The occurrence of such partial reduction alters the energy balance in two ways. Firstly, it lowers the chemical energy requirement to pass the current. For the case of the partial reduction of iron oxide, the chemical energy is equal to

\[ -\Delta_r G_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2} = 42,278 \text{ joules/mol Fe} \]  

Secondly, this reduction has an effect on the heat balance. The heat generated by this reaction can be calculated by the change in entropy:

\[ T\Delta_r S_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2} = -87,094 \text{ joules/mol Fe} \]  

**Electronic conduction:** at the core of Faraday’s law of electrolysis is the premise that ion mobility permits the electron exchange at the reactive interfaces (anode and cathode) so that an
electronic current may flow outside of the cell in the circuit. However, for some electrolytes, some electrons may escape from the anode to the cathode and travel through as though encountering a dielectric. Such electronic conductivity can contribute to the overall heat balance of the process.

The effects of these inefficiencies on the energy balance of the thermodynamic model were calculated one at a time, assuming mutual exclusivity. That is, if a Faradaic inefficiency were to be present, only one of the three phenomena would be the cause. The results are below.

**Results**

Table 10 illustrates the Faradaic inefficiency accounting for the case of the electrolytic extraction of iron from iron oxide. The operating temperature is 1,873K, which corresponds to $U_{cell} = 2.2V$, $U_{ohm} = 1.6V$, and $U_{chem} = 0.60V$. The columns are arranged in decreasing Faradaic efficiency.

Table 11: Faradaic and inefficiency current accounting for the range $\beta = 60\text{-}100\%$

| For Fe from Fe$_2$O$_3$ at 1873K, $U_{ohm} = 1.6V$, $U_{chem} = 0.6 V$ |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | 100% $\beta$   | 90% $\beta$    | 80% $\beta$    | 70% $\beta$    | 60% $\beta$    |
| $I_{\text{total}}/kAh/t Fe$    | 1,439           | 1,583           | 1,727           | 1,871           | 2,015           |
| $I_{\text{Faradaic}}/kAh/t Fe$ | 1,439           | 1,439           | 1,439           | 1,439           | 1,439           |
| $I_{\text{Inefficiency}}/kAh/t Fe$ | 0               | 144             | 288             | 432             | 576             |

Tables 11-13 list the results of the energy balance in the case that all of the Faradaic inefficiency stems from reoxidation phenomena.

Table 12: Inefficiency current accounting for the case of reoxidation phenomena.

| For Fe from Fe$_2$O$_3$ at 1873K, $U_{ohm} = 1.6V$, $U_{chem} = 0.6 V$ |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                 | 100% $\beta$   | 90% $\beta$    | 80% $\beta$    | 70% $\beta$    | 60% $\beta$    |
| $I_{\text{total}}/kAh/t Fe$    | 1,439           | 1,583           | 1,727           | 1,871           | 2,015           |
| $I_{\text{Faradaic}}/kAh/t Fe$ | 1,439           | 1,439           | 1,439           | 1,439           | 1,439           |
| $I_{\text{Reoxidation}}/kAh/t Fe$ | 0               | 144             | 288             | 432             | 576             |
| mol Fe reoxidized               | 0               | 0.10            | 0.20            | 0.30            | 0.40            |
| $\Delta_c H_{\text{Reoxidation,1600K}}/J$ | 0               | -49,426         | -98,852         | -148,279        | -197,705        |
Table 13: Effect of reoxidation phenomena on heat balance

<table>
<thead>
<tr>
<th></th>
<th>100% β</th>
<th>90% β</th>
<th>80% β</th>
<th>70% β</th>
<th>60% β</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{total}$/kAh/t Fe</td>
<td>1,439</td>
<td>1,583</td>
<td>1,727</td>
<td>1,871</td>
<td>2,015</td>
</tr>
<tr>
<td>$I_{Faradaic}$/kAh/t Fe</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
</tr>
<tr>
<td>$I_{reoxidation}$/kAh/t Fe</td>
<td>0.0</td>
<td>143.9</td>
<td>287.8</td>
<td>431.7</td>
<td>575.6</td>
</tr>
<tr>
<td>mol Fe reoxidized</td>
<td>0</td>
<td>0.10</td>
<td>0.20</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>$\Delta H_{reoxidation, 1600°C}$/J</td>
<td>0</td>
<td>-49,426</td>
<td>-98,852</td>
<td>-148,279</td>
<td>-197,705</td>
</tr>
<tr>
<td>$U_{ohm}$/V</td>
<td>1.60</td>
<td>1.77</td>
<td>1.94</td>
<td>2.11</td>
<td>2.28</td>
</tr>
<tr>
<td>Change in $U_{ohm}$/V</td>
<td>0.00</td>
<td>0.17</td>
<td>0.34</td>
<td>0.51</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 14: Effect of reoxidation phenomena on overall energy balance.

<table>
<thead>
<tr>
<th></th>
<th>100% β</th>
<th>90% β</th>
<th>80% β</th>
<th>70% β</th>
<th>60% β</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P = U_{chem} I_{Faradaic} + U_{chem} I_{PR} + U_{ohm} I_{Faradaic} + U_{ohm} I_{PR}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U_{ohm} I_{Faradaic}$</td>
<td>2,301</td>
<td>2,547</td>
<td>2,792</td>
<td>3,038</td>
<td>3,284</td>
</tr>
<tr>
<td>$U_{ohm} I_{reoxidation}$</td>
<td>0</td>
<td>255</td>
<td>558</td>
<td>911</td>
<td>1,314</td>
</tr>
<tr>
<td>$U_{chem} I_{Faradaic}$</td>
<td>860</td>
<td>860</td>
<td>860</td>
<td>860</td>
<td>860</td>
</tr>
<tr>
<td>$U_{chem} I_{reoxidation}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{Fe}$</td>
<td>3,161</td>
<td>3,661</td>
<td>4,211</td>
<td>4,810</td>
<td>5,457</td>
</tr>
<tr>
<td>$E_{Fe}/\beta$</td>
<td>3,161</td>
<td>3,512</td>
<td>3,951</td>
<td>4,516</td>
<td>5,268</td>
</tr>
</tbody>
</table>
Tables 14-17 list the results of the energy balance in the case that all of the Faradaic inefficiency stems from partial reduction (PR).

Table 15: Inefficiency current accounting for the case of partial reduction phenomenon.

| For Fe from Fe₂O₃ at 1873K, $U_{ohm} = 1.6V$, $U_{chem} = 0.6V$ |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
|                                 | 100% β | 90% β | 80% β | 70% β | 60% β |
| $I_{\text{tot}} / kAh/t Fe$    | 1,439 | 1,583 | 1,727 | 1,871 | 2,015 |
| $I_{\text{Faradaic}} / kAh/t Fe$ | 1,439 | 1,439 | 1,439 | 1,439 | 1,439 |
| $I_{PR} / kAh/t Fe$           | 0.0    | 143.9 | 287.8 | 431.7 | 575.6 |
| mol Fe Partially Reduced      | 0      | 0.10  | 0.20  | 0.30  | 0.40 |
| $T\Delta_r S_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2} / J$ | 0     | -8,706 | -17,411 | -26,117 | -34,822 |
| $-\Delta_r G_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2} / J$ | 0     | -4,226 | -8,452 | -12,678 | -16,904 |

Partial Reduction (PR): effect on chemical energy balance ($U_{chem}$)

<table>
<thead>
<tr>
<th></th>
<th>100% β</th>
<th>90% β</th>
<th>80% β</th>
<th>70% β</th>
<th>60% β</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{tot}} / kAh/t Fe$</td>
<td>1,439</td>
<td>1,583</td>
<td>1,727</td>
<td>1,871</td>
<td>2,015</td>
</tr>
<tr>
<td>$I_{\text{Faradaic}} / kAh/t Fe$</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
</tr>
<tr>
<td>$I_{PR} / kAh/t Fe$</td>
<td>0.0</td>
<td>143.9</td>
<td>287.8</td>
<td>431.7</td>
<td>575.6</td>
</tr>
<tr>
<td>mol Fe PR</td>
<td>0</td>
<td>0.10</td>
<td>0.20</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>$-\Delta_r G_{Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2} / J$</td>
<td>0</td>
<td>-4,226</td>
<td>-8,452</td>
<td>-12,678</td>
<td>-16,904</td>
</tr>
<tr>
<td>Chemical energy balance / J</td>
<td>-172,370</td>
<td>-168,145</td>
<td>-163,919</td>
<td>-159,693</td>
<td>-155,467</td>
</tr>
<tr>
<td>$U_{chem} / V$</td>
<td>0.60</td>
<td>0.58</td>
<td>0.57</td>
<td>0.55</td>
<td>0.54</td>
</tr>
<tr>
<td>Change in $U_{chem} / V$</td>
<td>0.00</td>
<td>-0.02</td>
<td>-0.03</td>
<td>-0.05</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Table 16: Effect of partial reduction phenomenon on the chemical energy balance ($U_{chem}$).
Table 17: Effect of partial reduction phenomenon on heat energy balance ($U_{ohm}$)

<table>
<thead>
<tr>
<th>Partial Reduction (PR): effect on heat balance ($U_{ohm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
</tr>
<tr>
<td>$I_{total}$ / kAh/t Fe</td>
</tr>
<tr>
<td>$I_{Faradaic}$ / kAh/t Fe</td>
</tr>
<tr>
<td>$I_{PR}$ / kAh/t Fe</td>
</tr>
<tr>
<td>mol Fe $PR$</td>
</tr>
<tr>
<td>$dH(PR)$ / J</td>
</tr>
<tr>
<td>$U_{ohm}$ / V</td>
</tr>
<tr>
<td>Change in $U_{ohm}$ / V</td>
</tr>
</tbody>
</table>

Table 18: Effect of partial reduction phenomenon on the overall energy balance.

<table>
<thead>
<tr>
<th>all in kWh/t Fe</th>
<th>$P=U_{chem Faradaic} + U_{chem PR} + U_{ohm Faradaic} + U_{ohm PR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$100% \beta$</td>
<td>$90% \beta$</td>
</tr>
<tr>
<td>$U_{ohm Faradaic}$</td>
<td>2,301</td>
</tr>
<tr>
<td>$U_{ohm PR}$</td>
<td>0</td>
</tr>
<tr>
<td>$U_{chem Faradaic}$</td>
<td>860</td>
</tr>
<tr>
<td>$U_{chem PR}$</td>
<td>0</td>
</tr>
<tr>
<td>$E_{Fe}$</td>
<td>3,161</td>
</tr>
<tr>
<td>$E_{Fe}$ / $\beta$</td>
<td>3,161</td>
</tr>
</tbody>
</table>
Table 18-19 lists the results of the energy balance in the case that all of the Faradaic inefficiency stems from electronic conduction.

Table 19: Inefficiency current accounting for the case of electronic conduction phenomenon.

<table>
<thead>
<tr>
<th></th>
<th>100% β</th>
<th>90% β</th>
<th>80% β</th>
<th>70% β</th>
<th>60% β</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{total}$ / kAh/Fe</td>
<td>1,439</td>
<td>1,583</td>
<td>1,727</td>
<td>1,871</td>
<td>2,015</td>
</tr>
<tr>
<td>$I_{Faradaic}$ / kAh/Fe</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
<td>1,439</td>
</tr>
<tr>
<td>$I_e$ / kAh/Fe</td>
<td>0</td>
<td>144</td>
<td>288</td>
<td>432</td>
<td>576</td>
</tr>
</tbody>
</table>

Table 20: Effect of electronic conduction phenomenon on the overall energy balance.

<table>
<thead>
<tr>
<th></th>
<th>100% β</th>
<th>90% β</th>
<th>80% β</th>
<th>70% β</th>
<th>60% β</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{ohm, Faradaic}$</td>
<td>2,301</td>
<td>2,301</td>
<td>2,301</td>
<td>2,301</td>
<td>2,301</td>
</tr>
<tr>
<td>$U_{ohm, e}$</td>
<td>0</td>
<td>230</td>
<td>460</td>
<td>690</td>
<td>920</td>
</tr>
<tr>
<td>$U_{chem, Faradaic}$</td>
<td>860</td>
<td>860</td>
<td>860</td>
<td>860</td>
<td>860</td>
</tr>
<tr>
<td>$U_{chem, e}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_{Fe}$</td>
<td>3,161</td>
<td>3,391</td>
<td>3,621</td>
<td>3,851</td>
<td>4,081</td>
</tr>
<tr>
<td>$\frac{E_{Fe}}{\beta}$</td>
<td>3,161</td>
<td>3,512</td>
<td>3,951</td>
<td>4,516</td>
<td>5,268</td>
</tr>
</tbody>
</table>
Appendix D

Additional results from the macroscopic model.

For Figures 26-32, the left vertical axis represents the specific energy needed per ton of aluminum metal, and the right vertical axis represents the overall cell voltage needed for the electrolytic extraction of aluminum. The blue line illustrates the calculations for $\alpha=1$, and the black line illustrates the calculations for the case of $\alpha\neq1$. Both calculations assume $\beta=1$ for simplicity.

Figure 26: Energy requirements for the extraction of aluminum from aluminum oxide ($Al_2O_3$).

Figure 27: Energy requirements for the extraction of chromium from chromium oxide ($Cr_2O_3$).
Figure 38: Energy requirements for the extraction of copper from copper sulfide (Cu₂S).

Figure 29: Energy requirements for the extraction of lanthanum from lanthanum oxide (La₂O₃).

Figure 30: Energy requirements for the extraction of magnesium from magnesium chloride (MgCl₂).

Figure 31: Energy requirements for the extraction of neodymium from neodymium oxide (Nd₂O₃).
Appendix E

The main requirement to execute the equations above was a program that could analytically execute equations as well as retrieve the necessary thermodynamic data to do so.

The thermodynamic data such as the molar Gibbs free energy, entropy, and enthalpy were obtained from FactSage, a software that can provide raw thermodynamic data as well as perform calculations such as equilibrated reactions, phase diagrams, and other thermodynamic calculations. We used FactSage's "View Data" module to obtain the temperature-dependent enthalpies, entropies, and Gibbs free energies in 1-Kelvin increments. The output was a text file that contained five column vectors, and each column contained the values of each thermodynamic variable. These text files were manually compiled into one excel file and dedicated one excel sheet to each of the metals, metal compounds, and gases.

All thermodynamic variables in the equations are temperature-dependent. We therefore created an iterative loop in MATLAB these variables were picked up by the code after indexing the temperatures at which these thermodynamic variables were needed in "ThermoData.xlsx". Once indexed, the values were used as inputs into the equations. The loop went through one
iteration for every metal of interest (i.e., it executed the equations to obtain the energy requirement for the extraction of iron from iron oxide, aluminum from aluminum oxide, chromium from chromium oxide, magnesium from magnesium chloride, copper from copper sulfide, zinc from zinc oxide, neodymium from neodymium oxide, and lanthanum from lanthanum oxide). The temperature dependent equations for each metal were executed for the temperature range 298 K (room temperature) to 3298 K. The outputs were organized into vectors and subsequently written into an excel file for ease of access and analysis. The rest of this appendix is the MATLAB code itself, which is titled “Umin.mat”. Note that the text that follows the “%” symbol are comments, which were included to help guide the reader through the logic of the operations. Figure 33 presents a schematic representation of the following MATLAB code.
Start

Define: constants, variables, metals of interest, temperature range

Inputs: read .xlsx file with thermodynamic data, construct internal matrix with these data

Thermodynamic calculations: iterative loop for each metal of interest

Match metal with corresponding metal compound, gas

Retrieve H, S, and G of the metal compound, metal, and gas from internal matrix

Calculate $U_{\text{chem}}, U_{\text{chem}}, U_{\text{opt}},$ and $E_{\text{m}}$ by using $H, S, G$ retrieved for every temperature from $T_i = 298K$ to $T = 3298K$

Store values of $U_{\text{chem}}, U_{\text{chem}}, U_{\text{opt}},$ and $E_{\text{m}}$ for metal $i$

Outputs: Graphs and tables of $U_{\text{chem}}(T), U_{\text{chem}}(T), U_{\text{chem}}(T),$ and $E_{\text{m}}(T)$

Figure 33: Schematic of MATLAB algorithm.
clear all;
b =1; %electrical efficiency
F = 96485.3415; %Faraday constant
Metals= {'Fe','Al','Mg','Cu','Zn','Nd','Eu','La','Cr','K'}; %the metals we are interested in
N={ 'Fe','Fe2O3','O2',2,3,3;
    'Al','Al2O3','O2',2,3,3;
    'Mg','MgCl2','Cl2',1,2,2;
    'Cu','Cu2S','S2',1,2,1;
    'Zn','ZnO','O2',1,1,2;
    'Nd','Nd2O3','O2',2,3,3;
    'Eu','Eu2O3','O2',2,3,3;
    'La','La2O3','O2',2,3,3;
    'Cr','Cr2O3','O2',2,3,3;
    'K','K2O','O2',2,1,1}; %This N vector groups the metal compounds with their respective metal and gas products as well as the subscripts x and z in the metal compound with formula MxYz
MP = {'Fe',55.85;'Al',26.98;
    'Mg',21.31;'Cu',63.546;
    'Zn',65.38;'Nd',144.24;
    'Eu',151.96;'La',138.91;
    'Cr',51.99;'K',39.0983}; %this vector pairs atomic mass with its corresponding metal of interest
IT = 298; %initial temperature in Kelvin
Tf= 3298; %final temperature in Kelvin
ndata = importdata('ThermoData.xlsx'); %this imports the entire excel data into the MATLAB workspace
for i = 1:1:length(Metals)%this loop "picks" which metal it is going to execute calculations with
    clear MetalData%clear data from previous loops
clear OxideData

clear GasData

Metal = Metals(1,i); %indicates which metal it is working with according to the iteration in the loop

    ind = find(ismember(N(:,1),Metal(1))); %indicates which metal compound (oxide, chloride, sulfide) it is working with according to the iteration in the loop

Comp = N(ind,2); %indicates which metal compound (oxide, chloride, sulfide) it is working with according to the iteration in the loop

Gas = N(ind,3); %indicates which gas it is working with (oxygen, sulfur, chlorine) according to the iteration in the loop

    x = N{ind,4}; %subscript of metal compound - metal
z = N{ind,5}; %subscript of metal compound - oxygen/sulfur/chlorine

    n = N{ind,6}; %number of electrons exchanged per mol. Metal.

MetalData = getfield(ndata,Metal{:}); %grabs the thermodynamic data specific to the metal in the loop

CompData = getfield(ndata,Comp{:}); %grabs the thermodynamic data specific to the metal compound in the loop

GasData = getfield(ndata,Gas{:}); %grabs the thermodynamic data specific to the gas in the loop

S1_index = find(MetalData(:,1) >= IT & MetalData(:,1) <= Tf); %index the row in the data where temperature is target temperature

S2_index = find(MetalData(:,1) == IT); %find the row where temperature is room temperature

Tvec = MetalData(S1_index,1); %Temperature vector, a single column vector with temperature from 298 to 3298 K in 1 K increments

    a=1;%(26.064*log(Tvec) - 125.73)/100;%heat efficiency, alpha

U1 = zeros(1,length(Tvec)); %empty vector that will store Ohmic potential (Uohm) for each metal

U2 = U1; %empty vector that will store Chemical potential (Uchem) for each metal

CPComp = CompData(S1_index,2); %heat capacity of metal compound at target temperature

H2Comp = CompData(S1_index,3); %heat content of metal compound at target temperature

H1Comp = CompData(S2_index,3); %heat content of metal compound at room temperature
CPMetal = MetalData(Sl_index,2); %heat capacity of metal at target temperature

CPGas = GasData(Sl_index,2); %heat capacity of gas at target temp

H2Gas = GasData(Sl_index,3); %heat content of gas at target temp

G2Comp = CompData(Sl_index,4); %Gibbs free energy of metal compound at target temperature

G2Metal = MetalData(Sl_index,4); %Gibbs free energy of metal at target temperature

G2Gas = GasData(Sl_index,4); %Gibbs energy of gas at target temperature

S2Comp = CompData(Sl_index,5); %entropy of metal compound at target temperature

S2Metal = MetalData(Sl_index,5); %entropy of metal at target temperature

S2Gas = GasData(Sl_index,5); %entropy of gas at target temperature

[U1(Sl_index), U2(Sl_index)] =
Umet(Tvec,a,F,n,x,z,S2Comp,S2Metal,S2Gas,G2Comp,G2Metal,G2Gas,CPGas,CPComp,CPMetal,H1Comp,H2Comp);

%The above function executes the thermodynamic equations derived in Appendix B.

U3 = U1 + U2; %U1 = Uohm; U2 = Uchem; U3 = Ucell.

U4 = (U2./U1); %U4 is a ratio that illustrates whether the chemical or heat energy is the dominant term at the target temperature

eval(['U1' Metal{1} ' = U1;']); %evaluates and saves Uchem, Uohm, Ucell, and Uratio for each metal

eval(['U2' Metal{1} ' = U2;']);

eval(['U3' Metal{1} ' = U3;']);

eval(['U4' Metal{1} ' = U4;']);

ind=find(ismember(MP(:,1),Metal)); %index to single out the atomic mass needed to proceed with calculations according to the metal in the loop

Mp = cell2mat(MP(ind,2)); %defines the atomic mass

[E] = Energy(U3,F,b,n,Mp); %this function calculates the specific energy of making the metal
I = E./U3;

eval(['E' 'Metal{1}' ' = E;' ]); %evaluates and saves the specific energy requirement for each metal

eval(['I' 'Metal{1}' ' = I;' ]); 

end

UMET.M

function [Uohmmet,Uworkmet] = Umet(Tvec,a,F,n,x,z,S2Comp,S2Metal,S2Gas,G2Comp,G2Metal,G2Gas,CPGas,CPComp,CPMetal,HiComp,H2Comp)

    Uohmmet = (-1)*((Tvec).*(1./(n*a.*F)).*((1/x)*CPComp - (z/(2*x))*CPGas - CPMetal - (S2Metal + (z/(2*x))*S2Gas) - (1/x)*S2Comp)) - ((1./(x*n*a.*F)).*(H2Comp-H1Comp));

    Uworkmet = (1/(n*F)).*(G2Metal+(z/(2*x))*G2Gas-(1/x)*G2Comp));

End

ENERGY.M

function [E] = Energy(U3,F,b,n,Mp)

%note: the original energy calculation is in Joules per second. Here we
%convert it into a kWh/t metal metric, where E(kWh) = E(J)/360,000

    E = (n*U3.*F)./(3.6*b*Mp);

end