Electrochemical Metals Production Breakout

What is the origin of the major energy losses associated with electrochemical metal extraction, and what opportunities are available to mitigate losses and/or recover heat?

Losses

- The Cold wall in Hall-Héroult cell design adds to thermal inefficiencies
- Ohmic losses for electrolyte and losses due to use of multipolar cells
- Lorentz waves in the cell due to similar densities of liquid aluminum and electrolyte
- Large anode-to-cathode space needed while maintaining a 950°C system temperature with Liquid Al

Past work and challenges

- Using $AlCl_3$ feedstock yields purity problems (such as water)
- Inert anodes has been examined for years and more energy is required when using them (1 volt higher to form oxygen rather than carbon monoxide)
- Drain wetted cathode can not be integrated with the current Halls-Héroult process

Opportunities

- Different chemistries such as the use of aluminum hydroxide (for Aluminum)
- Side wall heat recuperation or side wall materials like a grade of silicon carbide
- Substitute for cryolite-based electrolyte
- Hybrid approach – Best of both thermochemical and electrochemical processes

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CHANGING WHAT'S POSSIBLE

Are there transformative routes to more efficient light metal (Al, Mg, Ti) extraction via electrochemistry, and have novel electrolytes been developed or are any under development that enable, high efficiency, reduced emissions, and/or heat recuperation? At what point in the process should heat be extracted for recuperation?

<u>Transformative opportunities to improve efficiency</u>

•Eliminate the number of steps when processing ore to metal and do so continuously

•Ionic liquids with higher charge transfer resistance at lower temperature (for Mg)

•Multivalent ion conductors at sub1000°C temperature is an opportunity to improve efficiency by not having all process energy supplied by electricity (hybrid)

•New chemistries for Lower operating temperature electrolytes that makes powder (referring to Ti)

What are the major technical barriers and risks to implementing these routes, and what technologies are available today to enable success that may not have been available twenty years ago?

Risks and Barriers

- Unknown results about Alumina’s solubility in ionic liquids
- First principle calculations for new materials may not be accurate estimates
- Metal fog and metal dissolution that creates electronic conductivity of electrolyte is a loss, (for aluminum it does not short between anode and cathode)
- Metal dissolution is a more significant problem with Titanium
- Challenges for small plants:
    - The need to buy the rectifier set
    - and a big cell volume is required to keep sidewalls cold
- Small scale economics work better for recycling plants outside of major scrap generating cities

Enabling technologies available

- Improvements in current density: heat loss comes from ohmic losses, drive for a smaller footprint.
- Ion-conducting membranes are a lot better today
- Better power electronics today

Heat Recuperation and Power Generation Breakout

What are the major barriers to waste heat recuperation in light metal (Al, Mg, Ti) extraction processes (electrochemical or thermochemical), and what transformative heat recuperation strategies can potentially overcome the barriers to waste heat capture in metal extraction processing?

- Utilization of captial – LCOE lower than off-peak power cost assuming demand for electricity. Can this happen?
    - Deployment logistics – integration into existing, specific plants/systems
    - T range: 350-400 deg C (sidewalls)
    - Catalyst for gas clean-up to lower Temperature?
    - Is there a material or coating at 1000 deg C that HF will not attack? Something besides HF will allow ceramics
- Ideal, green-field system
    - Capture at highest possible Temperature
    - Exhaust gases not corrosive and particulate free
    - Containment with integrated heat removal (molten salts/glass for storage for CSP)
    - Can this handle intermittency? Hybrid system?
    - Co-located and integrated with power generation facility
- Good engineering design can’t be forgotten. Systems level innovation?

What power generation cycles are feasible using waste heat capture from metal extraction processes, and are any of these economically viable?

- scCO2 cycles: cheaper because of smaller footprints
- MHD generator (NASA concept design for Temperature > 2000°C
  - Metal is working fluid. How do you get metal to flow?
  - Look at DOE Nuclear?
- Thermoelectrics? What Temperature?
  - Combined with heat engine to increase efficiency: 50% efficiency
  - Advantage: packaging, low maintenance, filling heat mismatches
  - Still need to extract heat? Second HX?
  - Durability because of exotic material
- SOFC could take advantage of high Temperature
- Metal Rankine cycles for high Temperature operations
- Organic Rankine cycles for calciner operations

For what temperature range should heat recuperation technologies be developed for metal extraction processes? What are the challenges and risks of operating at these temperatures? What are high Temperature strategies?

- Retrofits: a lot of low Temperature.
- Greenfields: Adaptable because of systems integration opportunities.
- Electrolytic process for Mg? Recovering Heat of vap at 1100°C. What will you do with it? Lots of opportunities.
- Titanium: new technologies all over map
  - 65% of energy in distillation.
  - New processes don't have that.
- Carbothermic: >2000°C – big energy recovery opportunities
  - Material issues – reactor operates reliably for long periods of time
- Does solar have energy density? Concentrate it.
  - Works better for Zn (not Al)
- Ceramics?
- Materials technologies need to be enhanced with heat transfer technologies
- New heat engine based on piston structure, low speed with high efficiency using air as working fluid?
  - Lower cost for small or medium power generation integrated with metal extraction.
  - Combined with TE
- Steam of scCO2 turbines as small as gas turbines? Efficiency sacrifices
- A lot of heat at low T for existing processes
- Low T process with with 1A/cm2?
  - Balance capital intensity and operating cost? Room Temperature, but made of plastic – huge process, but very cheap materials and operating
  - What is physical limit?

Can efficient retrofit heat recuperation solutions be developed for existing smelters?

- Metal furnace heat recovery?
- Make the wall of pot a heat exchanger. Low Pressure, high heat exchange device.
- Gases: won't replace blower, need high efficiency, low Pressure Heat exchanger that isn't huge or expensive.
- High Temperature separate type heat pipes
    - heat pipes >1000kW, separate heat use from heat source. Transfer heat over long distance. Completely sealed corrosive gases from condenser.
    - Highly flexible
    - Enables power generation
- Al smelters: >70% below 100 °C.
- Do we care about low grade heat?
    - Near commercial technologies are challenged by capital limitations
    - High T HF removal system?
    - T are low to prevent HF from escaping
        - 1 unit process gas for 20 units air. A sealed pot that wasn't opened would lead to higher T.
- What about liquid metal? Metal tapped in a batch mode.
    - Ideally, metal flows from pot to casting.
- Heat exchanger materials that can make them cheaper, reliable and robust?
    - Conductive polymers?
    - Working fluids to increase thermal effectiveness
        - Not nanofluids
        - Molten salts/glasses are high T. What about low T?
    - Microchannels have a problem with clogging and have high manufacturing cost
    - Automotive technologies with advanced surfaces. This environment is more aggressive.

Recycling and Other Innovative Metals Production Concepts Breakout

What are the major technical barriers to efficient and quality recycling of light metals (Al, Mg, Ti), and are there transformative solutions to enable efficient and high quality recycling?

- Need to have high throughput because it is low value, so scaling down is a capex issue
- Transportation cost of KY to LA is 3x more expensive then LA to Beijing
- US and EU are stuck with stringent regulations while in the east these don't exist so we export
- US markets are targeting high end products
- Customers care about cost so specs are based on chemistry, not performance.
- No closed business case to recycle on site by end users.

How can alloyed metals be identified, separated, and recycled to meet ASTM specifications for aerospace or ground vehicle applications?

- Removing iron content out of the Al rich scrap (TWITCH)
- Genetic tagging by rare earth doping in trace amounts
- Also differentiate scrap by using XRD, eddy current or LIBS technologies
- Improve flue gas heat losses in the melting process to improve the overall thermal efficiency
- Being able to sort a molten stream of various metal components

Why is a large fraction of U.S. scrap metal shipped overseas, and what technical innovations are required to enable U.S. scrap processing to be more competitive? Would heat recovery during the recycling process give a technological edge?

•Developing countries have a demand for a 90%+ recycling rate, USA is 30-40%.
•In developing countries standards are not stringent even the automotive industry are not using very specified products.
•Current scrap melters have a maximum efficiency of 30% efficient

Can urban mining provide a recyclable product to meet ASTM specifications?

- Primary production mind state needs to change: When making end parts from primary metal, the alloys should be recycling friendly
- Re-harvesting premium scrap by end users

Renewable Metals Production Breakout

Are there efficient renewable energy routes to light metal (Al, Mg, Ti) extraction, such as, a) solar thermochemical, b) hybrid solar thermochemical/electrochemical, c) wind/carbothermal or hydrothermal, and others?

- Use solar for process heat, minimize electrical usage and improve kinetics (1800 K is a good target)
  - Volatilization becomes a challenge near 1800 K and above
  - 1800 K might not be an absolute upper limit (e.g. graphite)
- Solar may fit in well with batch/semi-batch processes due to diurnal cycle (or wind)
  - Al is already kind of a batch process due to anode replacement
- add carbon to aid with reduction
- Use molten salts at lower temps (<1000 deg C, <800 deg C) to provide longer solar-driven batches
  - this relaxes material constraints
  - work at elevated temperatures to permit solar heat input into ΔH
- Use all photons (may not have to split spectrum): Use solar IR to heat up processes, use PV to drive electrical processes
- Use UV to do photochemistry, e.g. partial reduction (modeled on $TiCl_2$, $AgCl_2$ photodissociation)
- Mg is the easiest, bring concentrated sunlight to the electrochemical processes

Which routes make best use of available energy sources, and does using multiple renewable energy sources provide an advantage over using a single source (i.e. solar and wind or biomass and solar)?

- Tailor renewable sources where there is a need (CSP for thermal, wind/PV for electrical)
    - Al production now uses electricity and thermal – substitute renewables for each element
- Hybridization of solar with fossil during no/low sun periods (at night)
- Wind/carbothermal may not be directly applicable here (little need to site together)
    -but could use cheap electricity from remote wind power for electrical power
- Biomass conversion is at best 6.5% efficient, best value is to burn it for heat
    - Other ways of capturing solar are far more efficient
    - Use waste biomass from other processes (might only be niche size)
- Valuable to make a carbon-based anode from biomass?
- Risk is increased when you combine multiple technologies together
    -Best way to innovate is by combining proven technologies

Are any of these renewable energy metal extraction solutions cost competitive in the long term?
In the near term, is there a path to market with any of these renewable energy routes?

-If one takes into account the hidden costs of carbon dioxide/climate change mitigation, then renewable implementations can be competitive

- policy has to help drive cost reduction
- Need full life cycle analyses on all conventional processes (and potential approaches) for carbon footprint, energy costs, take everything into account

- look at $ per output not solar efficiency per output

- High cost of collecting photons means efficiency is a good measure of cost
- even great thermochemistries can suffer from high cost of concentrating optics (avoid optics by developing one sun photochemistry)
- heat from solar (now) ends up being more expense than from natural gas

- Delocalized character of solar aids in recycled materials processing (as a first market)

- Solar is present everywhere as are recycled metals

- Need industry/academic cooperation to try out novel ideas
- investments in new processes are very large, will be difficult for established companies to switch

What are the major technical barriers and risks to implementing these routes?

- Cost of heliostats (<$100/m2 target), optics OR make process more (very) efficient
- Balance of plant
- greater understanding of electrolyte needed
    - Greater fundamental understanding about Mg electrolysis is needed (electrochemical reaction at electrode, resistance losses in electrolyte)
- reduce overpotentials to enable the use of solar heat
- compatibility of real starting materials with electrochemistry (feedstock impurities)
- alloy separations/product purification (in carbothermal routes)
- higher thermal efficiency, reducing losses
    - Novel modes of heat recovery
- handling of nanoparticles
- noble metal usage, expense of electrocatalyst
- practical engineering challenges (interface between light/reactor, process design)
- electrode materials (esp anode at higher temperatures, oxygen stability)
- running electrochemistry at 1200-1800 K / materials stability
- how do we speed up mass transfer rates?
    - process intensification reduce resistances to mass transfer

Thermochemical Metals Production Breakout

Are there transformative carbothermic routes to more efficient light metal (Al, Mg, Ti) extraction via thermochemistry, and can methane be used effectively as a feedstock?

Transformative paths

- Radiation heat transfer instead of mass conduction for heating is transformative especially for small scale and smaller residence times
- Nitride (through Ammonia) to displace carbides, easy to change back to Alumina too

Methane reducing agent

- Cracking of Methane forms carbon black which is not a good reducing agent, but could be used as a feeder gas
- Hydrogen can cause further quenching problems in reactor volume

Is hydrogen based metal reforming a viable path to low emissions thermochemical metal extraction, and do the thermodynamics of hydrothermic light metal (Al, Mg, Ti) reforming compare favorably to carbothermic reforming?

Hydrogen used in thermal reduction

- Hydrogen can be used as a reducing agent to form TiH4 which enables fixing of the grain size and intra-structure but different equipment/technology is required
- Pure thermal processes with Hydrogen will not work but combining hydrogen and electrochemistry (such as surface reduction) is possible

Can heat recuperation be integrated with any of these transformative routes, and at what point in the process should the heat be extracted?

<u>Recuperation</u>

- Game breaking potential could be redox cycles that are driven by waste heat
  - This may require new tools for screening, testing and further expertise in UFT (CPU), redox cycles and reaction kinetics
- Heat recuperation ties in better with carbothermal process rather than electrowinning as radiant heat capture is less limited in the system
- Optical properties, optimizing transport problem by using techniques like Iron doping
- Bayer process – Bring equipment closer together to capture waste heat by preventing major dissipation

<u>Limitations</u>

- Dopants reduce with temperature
- Heat transfers very quickly in large open volumes
- Challenge with using nanostructures is if the temperature rises too high their behavior alters significantly.

What are the major technical barriers and risks to implementing the transformative routes, and what technologies are available today to enable success that may not have been available twenty years ago?

Risk

- Use cheap electricity during night and figure out how to avoid using peak power
- Full Life Cycle (sustainability) analysis of replacing one material with another from ore to end products needs to be done, example Ti used instead of steel for lightweighting.
- Economics of smaller scale modular systems for these metals are unknown

Enabling Technologies available

- CSP at over 1000°C
- More integrated Brayton cycle systems available today
- More sophisticated Power Electronics

Are there promising approaches from past research efforts that were not adopted but may find success today?

- Titanium produced as a co product of rare earth metals.
  - Either US rare earth production needs to step up significantly or conventional ore reserves like (rutile and illmenite) need to deplete in order for the economics to be justified.