U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

Electrochemical Machining to Eliminate SCCP Coolants in Manufacturing

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AGENDA

- Short Chain Chlorinated Paraffin
  - What are they?
  - What are they used for?
  - Environmental Hazards
  - Alternatives
- Electrochemical Machining
- Electrowinning

CHLORINATED PARAFFINS – WHAT ARE THEY?

Short Chain Chlorinated Paraffin (SCCP)

- Chlorinated Paraffins or alkanes are widely used for industrial applications
  - Approximately 200 commercial products
  - Long term use of ~40 years.
  - Chlorinated alkanes are capable of mixing with many organic solvents
- Paraffin chain lengths ranging from 10-38 carbon atoms.
  - Synthesized by the reaction of chlorine gas with n-alkanes; the result is chlorinated paraffin and HCl.
  - Complex substances due to the varying degrees of chlorination with 10-38 chain lengths
  - Short Chain range from 10-13
- Produced world wide
  - Major domestic producers: OxyChem and Dover Chemicals

CHLORINATED PARAFFINS – WHAT ARE THEY USED FOR?

Short Chain Chlorinated Paraffin uses

- Plasticizers in paints, sealants and adhesives,
- PVC flame retardant
- Lubricants for car engines, electric generators and wind power facilities, and for drilling in oil and gas exploration, petroleum refinery to produce diesel oil;
- Secondary plasticizers in flexible polyvinyl chloride (PVC) manufacturing
- Metal processing
  - Lubrication and coolant of metal working operations
  - Used in extreme pressure and high temperature operations
    - Elevated temperatures release HCL to form a thin metal chloride film
    - Reduces friction and adiabatic heat

CHLORINATED PARAFFINS – ENVIRONMENTAL HAZARDS

Short Chain Chlorinated Paraffin Hazards

- SCCPS are bio-accumulative
  - Increased duration and probability for exposure and chronic toxicity
  - Release of low concentrations can be hazardous
  - Toxic to aquatic organisms
- Release in the environment can occur in all stages of SCCP lifecycle.
  - Misting and vaporization of force coolant emulsions have resulted in human exposure and long distance transportation through airborne routes.
- Potential carcinogen to humans
  - Short-chain (C12), 58% is classified as a carcinogen
- SCCPS have been found in air, sediment, groundwater and wastewater.
  - Found in aquatic species, marine mammals, birds, and humans.
  - Found in Artic food sources
- Stockholm Convention on Persistent Organic Pollutants global ban of SCCPs in 2017

CHLORINATED PARAFFINS – ALTERNATIVES

Short Chain Chlorinated Paraffin

- Boring and broaching operations of difficult to machine materials require significant heat management to achieve high quality cutting
  - Oil based emulsions without SCCPS may not achieve the required lubricity
    - Resulting in tool and part damage
  - Conventional machining requires coolant and lubrication
- Alternative processes
  - Cryogenic Cooling
    - Practical for milling applications
    - More environmentally friendly than other hydrocarbon based coolants
    - Limited deployment
  - Non-contact machining processes
    - No heat generation during process
    - Accurate replacement of conventional processing

ECM TECHNOLOGY

Electrochemical Machining (ECM)

- A non-conventional machining method that uses controlled metal removal by anodic dissolution in an electrolyte cell.
- Considered a reverse plating operation

Advantages

- ECM is well suited for difficult to machine materials such as aerospace materials and high strength steels
  - Especially for complex shape tight tolerance components
- Material hardness, toughness, strength, etc… does not influence the performance of ECM
- Non-Contact method eliminates residual stresses from the machining process
- Low cost tooling
- High accuracy machining with high quality surface finish

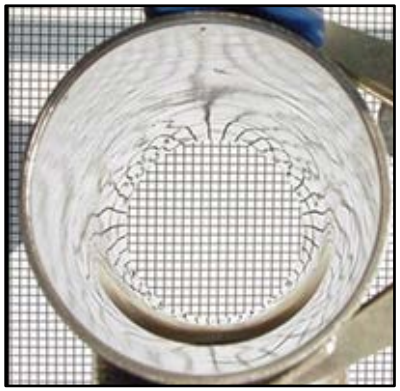
Limitations

- The process will generate a non-toxic sludge that will need to be disposed.
- Small amounts of hydrogen will need to be managed.
- Most electrolytes employ salt which require careful attention to prevent corrosion

ECM TECHNOLOGY

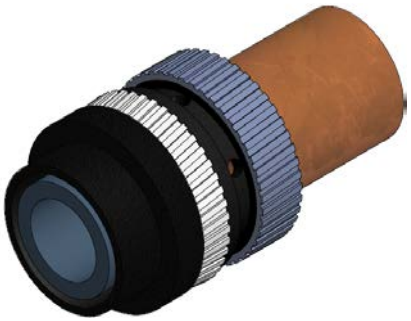
ECM production

- GE has two facilities with ECM production lines
  - GE Rutland has 7 ECM machines for Inconel and Titanium machining
    - 20,000 turbine blades produced annually
- Ford, Swagelok, Boeing, ATK and Rolls Royce use ECM for production components.
- Kennametal/Extrude Hone
  - ECM die sinking machine
  - Small component production
- GKN
  - 70 plus machines
  - Splines on Inconel tubes for oil and gas industry

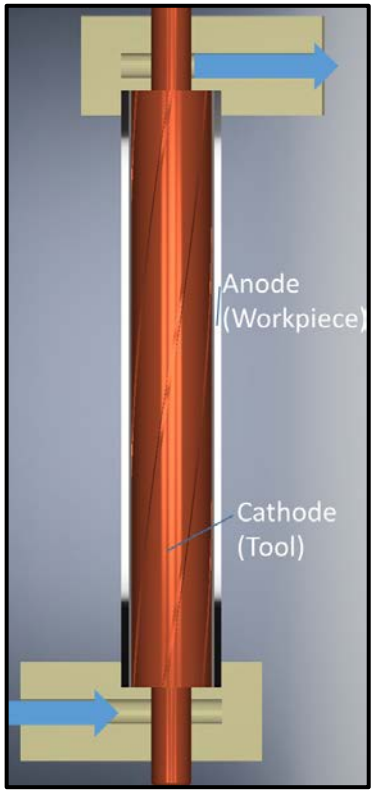


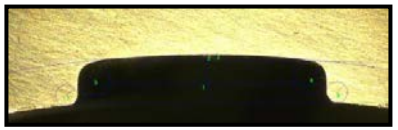
ECM TECHNOLOGY - DEFENSE

- Navy and Air Force development late 1970's
  - Plunge Cathode developed for 5" Navy Gun rifling
    - Small cathode better current density
    - Moderately complex design
    - Requires tool/tube rotation
    - Better electrolyte flow for long tube lengths



  - Stationary Cathode developed for medium caliber rifling
    - Straightforward design
    - High current requirements
    - Problematic electrolyte flow for long tubes
    - Currently in production





ECM TECHNOLOGY - DEFENSE

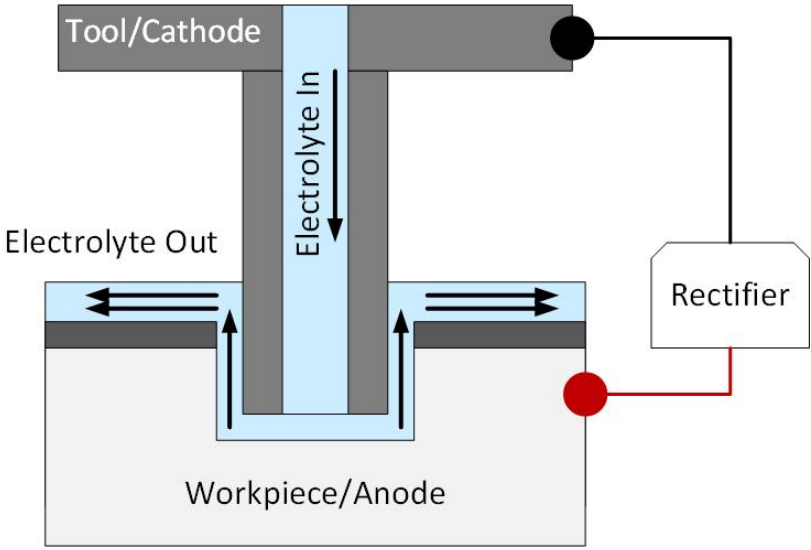
ECM Defense Applications

- Deburring and part cleaning
- Additive Manufacturing
  - Surface smoothing
  - Complex machining
- Small and large diameter boring
  - Guided boring for accurate centerline
  - Cooling channels
- Turbine Blade Manufacturing
  - Rotary and fixed wing aircraft
- Difficult to machine materials
  - Tungsten
  - Uranium
  - Magnesium
  - Penetrators

ECM TECHNOLOGY – HOW DOES IT WORK?

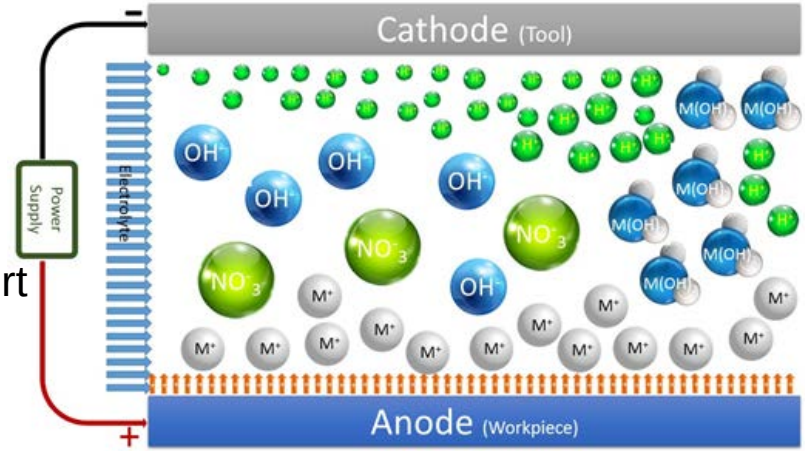
Electrochemical Machining

- An electrolyte flows between the electrode gap while a high current at low voltage is passed between the gap resulting in a redox reaction on the electrode surfaces.
- Metal ions are removed from the surface effectively machining the surface to the desired shape.



Waveform

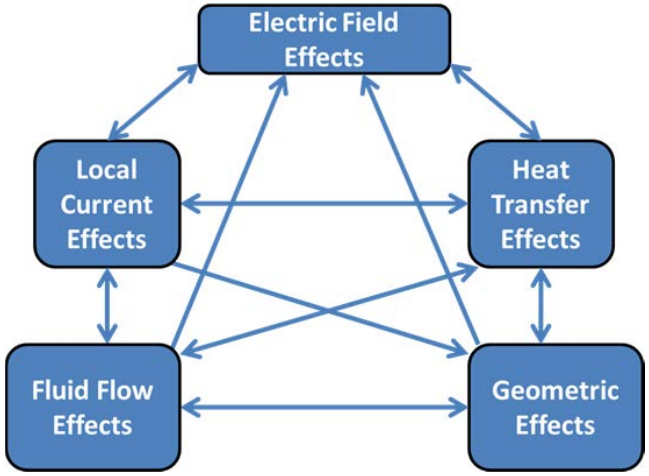
- Direct Current
  - Non - passivating metals
- Pulse/Pulse Reversing
  - Ideal for passivating metals
  - Focus current distribution with short pulses
  - Surface Leveling



ECM TECHNOLOGY – HOW DOES IT WORK?

Electrochemical Machining (ECM)

- Metal is removed by electrolyte flow
- Typical ECM use constitutes a non-hazardous waste stream
  - Sludge is formed via a reaction with the metallic ions and hydroxides in the bulk solution.
  - Private ECM industry utilizes third party sources for waste processing.
  - Sludge is filtered and pressed.
    - Solids disposed in a landfill.
- Sludge contains 80% water, 14% salt and 6% metal hydroxides
- Army SBIR developed a recycling ECM process (RECM)
  - Faraday Technology Inc. adapted Electrowinning to recovery metals from ECM electrolyte
  - Demonstrated under ESTCP project



ECM Reactions

Anode/Work piece

$$2M^0 \rightarrow 2M^{2+} + 4e^-$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Cathode/Tool

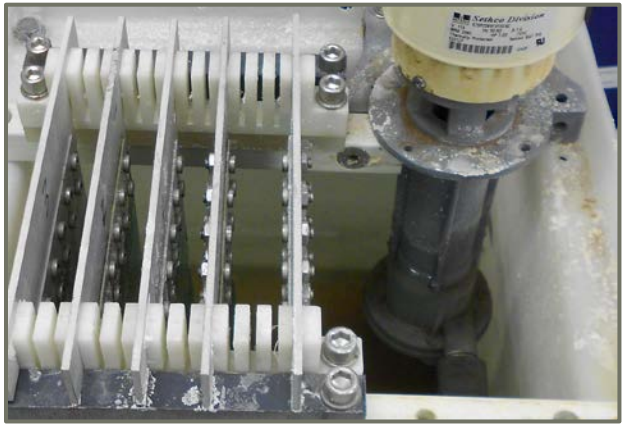
$$H_2O + e^- \rightarrow 1/2H_2 + OH^-$$

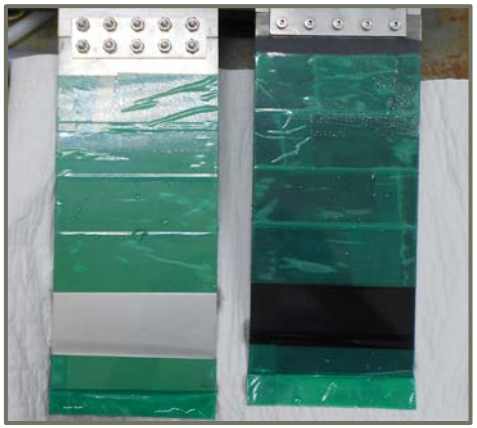
$$M^0 + H_2O \rightarrow 1/2H_2 + M(OH)$$

ELECTROWINNING

Electrowinning for Waste Recovery

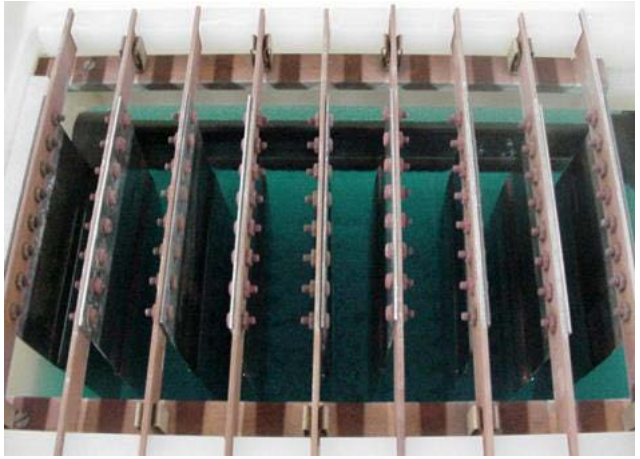
- Electrowinning is an electrolytic process used to recover metals
  - Typically used for recovery of metal from electroplating rinse waters.
  - Cell contains rectifier, pumping and electrode plates
  - Operation continuously – 24 hours a day
- Traditional EW uses a direct current applied to the stream
  - Metal ions move toward the negatively charge cathode and deposit on the plate surface.
  - Metal is either used for other applications or recycled as scrap metal
  - Traditionally used for valuable metal
    - copper, silver, gold and zinc



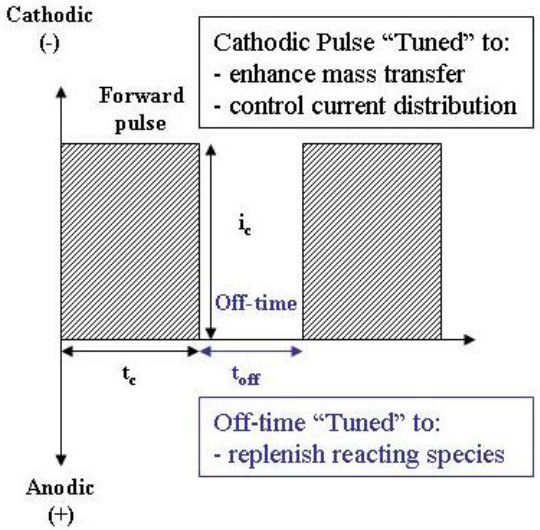


ELECTROWINNING

Electrowinning for Electrochemical machining removes metals by plating the metal ions to a substrate.



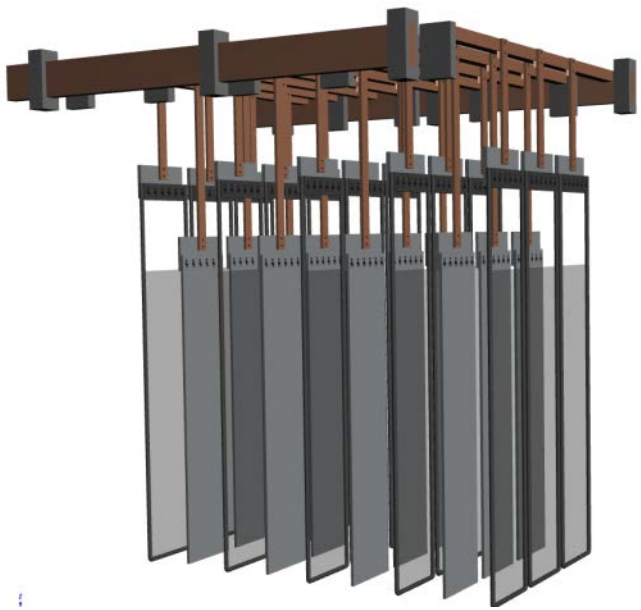
- Eliminates the formation of metallic hydroxides and sludge formation.
- The electrolyte is purified by removing the ions added by the electrochemical machining process.
- Pulsed waveforms are used to enhance traditional DC electrowinning.
  - Control mass transport, thickness and deposit uniformity
  - Low adhesion for easy removal.

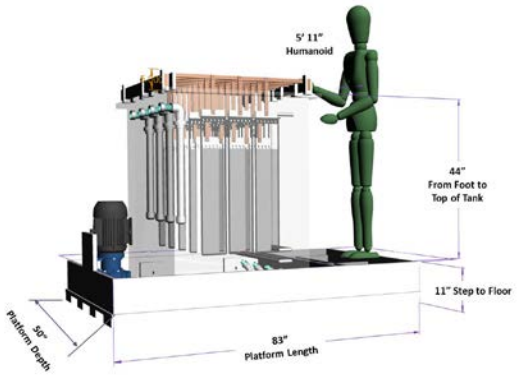


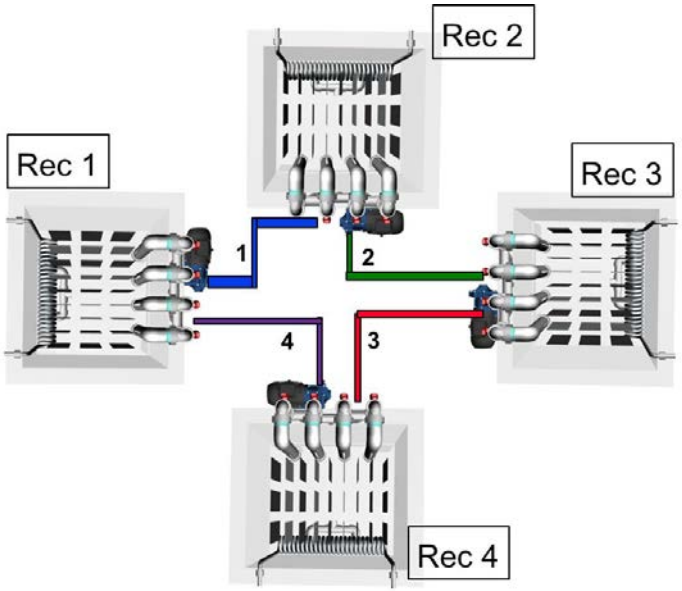
ELECTROWINNING

Electrowinning System

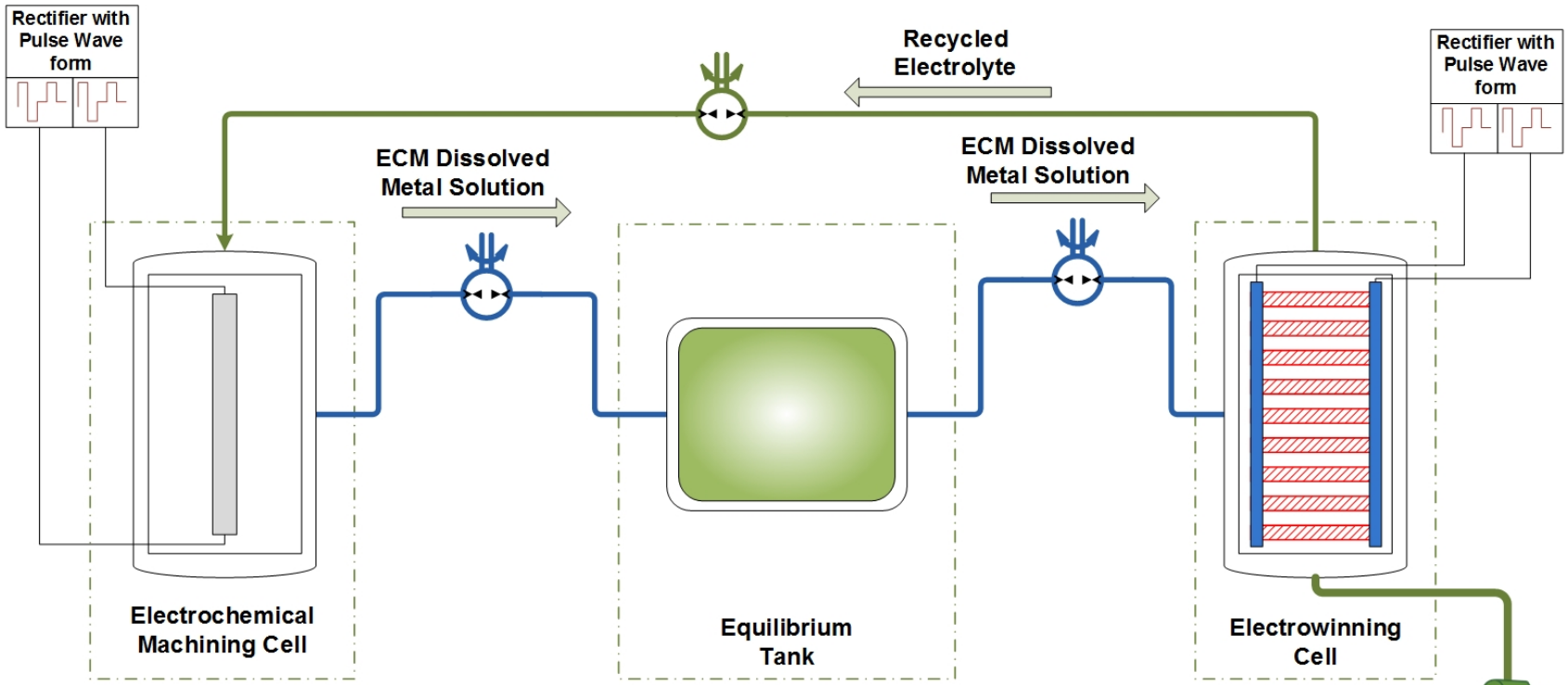
- Electrolyte must be compatible for ECM and EW
  - Iron – Ammonia Sulfate
  - Copper – Sodium-Ammonium Nitrate
- Modular System
  - Plates can be added and removed to tune system to ECM metal removal rate
  - Multiple units can be daisy chained together to increase capacity
  - Batch processing and feed through configurations







ELECTROWINNING



Anode/Work piece

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$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Cathode/Tool

$$4H^+ + 4e^- \rightarrow 2H_2$$

Cathode

$$2M^{2+} + 4e^- \Rightarrow 2M^0$$

Anode

$$4H^+ + 4e^- \Rightarrow 2H_2$$

$$2H_2O \Rightarrow O_2 + 4H^+ + 4e^-$$

SUMMARY

- SCCP pose a serious hazard to the environment
  - Future intent is to ban these chemicals globally
- Alternative machining methods are available
  - ECM does not use any hydrocarbon based lubricants
    - SCCP coolants are eliminated
  - Electrowinning offers a recyclable and sustainable manufacturing process
    - Environmentally friendly
    - Meet Army's Net Zero Initiative

Questions?