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NRRI REPORT OF INVESTIGATION

OPPORTUNITIES OFFERED BY EMERGING HYDROMETALLURGICAL TECHNOLOGIES

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Date: August 2022
Report Number: NRRI/RI-2022/10

Funding:

Funding for this project was provided by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR)

ENVIRONMENT
AND NATURAL RESOURCES
TRUST FUND

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Recommended Citation:

Rao, S., Mlinar, M., Hudak, G., Kangas, K., and Peterson, D. 2022. Opportunities offered by emerging hydrometallurgical technologies: Report to the Legislative-Citizen Commission on Minnesota Resources. Natural Resources Research Institute, University of Minnesota Duluth, Report of Investigations NRRI/RI-2022/10. 170 p.

Keywords: hydrometallurgy, critical metals, battery metals, carbon mineralization, mercury capture, waste resources, recycling, climate technology

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Abstract

Minnesota has abundant mineral resources, including deposits of iron, iron manganese, copper-nickel-cobalt-platinum group elements, titanium-vanadium, copper-zinc, gold with and without silver, sand, and aggregate. Commercial and industrial byproducts such as mine tailings, industrial residues, and waste electrical and electronic equipment also contain valuable mineral resources.

To address significant environmental impact concerns associated with mining, collection and processing of these materials, new processing technology approaches with reduced water and energy consumption and minimal environmental footprints are needed to support production of value-added products. Emerging hydrometallurgical processing technologies offer promising opportunities. Hydrometallurgy techniques have a range of applications from extraction of high-value products from mineral and recycled materials to water remediation to generating secondary products for carbon sequestration.

To evaluate the technical, economic, and environmental resiliency of emerging hydrometallurgical innovations, the Minnesota Legislative-Citizen's Commission on Minnesota Resources (LCCMR) provided funding to the Natural Resources Research Institute (NRRI) to evaluate how to best support the development of emerging hydrometallurgical technologies in the state.

To support this effort, NRRI evaluated:

1) A summary of perceived current and future hydrometallurgical needs of stakeholders based on a "voice of customer" (VOC) survey.
2) A discussion of how to apply hydrometallurgical capabilities to Minnesota-specific mineral and waste resources to maximize long-term economic, environmental, and social benefits and resilience.
3) A vision developed to advance Minnesota's research capabilities in mineral characterization, mineral processing, extraction, and refining via hydrometallurgy that will lead to more efficient and effective utilization of Minnesota minerals and waste resources in the future.

This research digs deeper into emerging applications of hydrometallurgical techniques in the production of value-added materials from a range of primary and secondary resources. The report also explores how application of these techniques to regional resources could potentially foster a more diversified minerals economy in Minnesota, develop treatment technologies to protect water resources, utilize regional resources for carbon mineralization, and supply materials required to build clean energy technologies.

Acknowledgements

The work highlighted in this project was made possible by a grant from the Legislative-Citizen Commission on Minnesota Resources (LCCMR) under M.L. 2019, First Special Session, Chapter. 4, Article. 2, Section. 2, Subdivision. 3 (r)). The authors thank Dr. Rolf Weberg for his thoughtful guidance as well as his unwavering support and encouragement throughout the life of the project. The authors also extend special thanks to Dr. Pat Schoff, Mr. Glenn Barr, Dr. Joyashish Thakurta, Ms. Anda Bellamy, Ms. June Breneman, and participants of the Voice of Customer Survey who gave their valuable time to carefully read the manuscript and provide us with feedback. The authors wish to thank the NRRI finance and administrative team for their financial, technical, and administrative assistance in managing the project.

Executive Summary

What will Minnesota's minerals economy look like in 2050? What is the role of emerging hydrometallurgical technologies that will enable sustainable use of mineral and waste resources in Minnesota?

The Legislative-Citizen Commission on Minnesota Resources (LCCMR) commissioned this study to identify and evaluate emerging hydrometallurgical technologies with applications for processing Minnesota mineral and waste resources while reducing water and energy use in an effort to minimize the industry's environmental footprint.

This NRRI study, "Opportunities Offered by Emerging Hydrometallurgical Technologies," offers one possible vision for the development of the minerals economy. It also highlights major issues and trends that will shape global, national, regional, and state agendas up to 2050 and provides a framework to support the actions required.

Hydrometallurgy is a branch of extractive metallurgy that relies on manipulating solution chemistry for the dissolution, concentration, and purification of metals or metal compounds from ores, concentrates, tailings, wastewater and various recycled and residual wastes. Techniques that complement hydrometallurgy include mineral characterization, mineral processing, wastewater treatment, pyrometallurgy, vapor metallurgy, and electrometallurgy.

The primary applications for hydrometallurgical techniques include:

- Production of critical metals from primary mineral resources;
- Production of materials used in the construction of renewable energy technologies like rechargeable batteries, energy storage, solar panels, and wind turbines; and
- Extraction of metals from secondary resources like mine tailings, urban waste, metallurgical waste, manufacturing scrap, and various industrial residues that contain critical metals.

Other emerging applications of hydrometallurgical techniques include:

- Removal of metallic and non-metallic contaminants from wastewater to protect land and water resources; and
- Production of secondary materials for climate change mitigation via carbon mineralization.

This report includes:

- *An assessment of Minnesota's mineral and waste resources* that have the highest potential for hydrometallurgical processing. Key resources include:
    - Copper-nickel-platinum group element (Cu-Ni-PGE) resources of Duluth Complex.
    - Nickel-copper-platinum group element (Ni-Cu-PGE) resources present in the Tamarack Intrusive Complex.
    - Titanium-iron vanadium deposits that occur in oxide ultramafic intrusions (OUIs) along the western margin of Minnesota's Duluth Complex.
    - Copper-zinc deposits and gold-silver deposits associated with greenstone belts.
    - Iron-manganese (Fe-Mn) deposits that occur in the Cuyuna District of east-central Minnesota.
    - Aggregate and byproduct resources that occur across the state that may contain recoverable quantities of critical metals.
    - Incinerator ash from Minnesota's coal-burning power plants and waste-to-energy facilities, which can contain a variety of critical metals.

    - Electronic waste (e.g., e-waste or waste electrical and electronic equipment), which can contain a variety of critical metals.

- *A review of challenges* encountered by stakeholders during the commercial development of mineral and waste resources using hydrometallurgical technologies. Key challenges include:
    - Lack of research supporting the development of advanced processing techniques requiring less water and energy and reducing environmental footprints.
    - Lack of R&D support to advance the production of value-added products via hydrometallurgy from regional resources.
    - Absence of a regional laboratory to support the timely completion of economic and environmental impact assessments of emerging hydrometallurgical technologies.
    - Lack of diversification of research facilities supporting diversification of minerals economy in the state of Minnesota.
    - Lack of research to minimize mercury discharge from future industries to mercury-impaired waters.

- *A summary of emerging hydrometallurgical innovations* that may resolve various challenges identified in the stakeholder engagement survey. These include:
    - Establishing a regional laboratory that advances the development of hydrometallurgical techniques with lower water and energy requirements and reduced environmental footprints.
    - Innovations that advance the production of value-added materials from regional resources;
    - Research and development that supports the production of secondary materials to support Minnesota’s climate mitigation strategies.
    - Innovations that promote regional production of critical metals from Minnesota resources.
    - A regional laboratory that provides data to support timely completion of environmental impact assessments of emerging innovations.
    - Research supporting the development of water remediation strategies to reduce mercury discharge from hydrometallurgical processing facilities.

- *A list of research priorities* that support deployment of emerging hydrometallurgical technologies specifically for battery material production, critical minerals extraction, waste rock assessment, treatment technologies for heavy metal removal, and carbon sequestration. Key priorities include:
    - Define viable hydrometallurgical technologies to produce high-value materials from Minnesota’s mineral and waste resources;
    - Explore the potential applications for hydrometallurgical techniques to understand the environmental impact of waste rocks and tailings via accelerated aging; and
    - Understand the potential applications of hydrometallurgical techniques to create secondary products that could potentially allow CO_2 sequestration.
    - Explore hydrometallurgical technologies to reduce mercury concentration from potential process waste to below 0.77 ng/L (the Fond du Lac Band standard).

- *Identifying bench-scale and semi-pilot laboratory tools* that will allow the State of Minnesota to conduct successful research for advancing the technological readiness level of emerging hydrometallurgical technologies. At a minimum, the following bench-scale and semi-pilot equipment and tools are necessary:
    - Advanced mineral processing tools like fine grinding, gravity separators, and flotation cells that allow beneficiation of mineral and waste resources.
    - Metal dissolution and CO_2 sequestration tools like continuous stirred tank reactors and pressurized autoclave reactors.
    - Solution purification and contaminant removal tools that allow separation and purification of leach liquors using solvent extraction, ion exchange, and adsorption techniques.
    - Metal recovery tools to produce high-purity metal compounds using precipitation and electrowinning.
    - Waste rock characterization tools to help investigate leachate quality and dissolved metal flux from potential oxidation of waste rock, mine tailings, and/or electronic waste.
    - Column chromatography and column reactors for research on mercury and other heavy metal removal from potential mine discharges using novel sorbents.
    - The capital estimates for bench-top and semi-pilot laboratory prototypes range from $600,000 to $1.2 million. The personal, installation, and collaboration costs range from $300,000 to $400,000.

TABLE OF CONTENTS

List of Tables

List of Figures

Summary of Grant

The University of Minnesota-Duluth Natural Resources Research Institute (UMD NRRI) was awarded a grant (M.L. 2019, First Special Session, Chapter. 4, Article. 2, Section. 2, Subdivision. 3 (r)) by the Legislative-Citizen Commission on Minnesota Resources (LCCMR) to identify and evaluate emerging hydrometallurgical technologies with applications for processing Minnesota mineral and waste resources.

Summary of Intent

The summarized intent for the grant is noted below.

- Identify and prioritize hydrometallurgical techniques that offer unique capabilities to:
    - extract high-value metal products from Minnesota mineral resources and mineral-based waste materials at high purity and reduced energy consumption with closed-loop water cycling systems;
    - allow collection of metallic byproducts for an enhanced economic and environmental benefit to Minnesota; and
    - enable a circular economy approach for metallic resources and waste streams.
- Engage industry and engineering collaborators across the state of Minnesota to identify and evaluate the relevance of current and emerging hydrometallurgical technologies.
- Establish a benchmark of current North American hydrometallurgical processing research capabilities and applicability to Minnesota resources.
- Provide a foundation for the concept and design development for a unique hydrometallurgical research facility at the NRRI Coleraine Laboratory.

Report Layout

Brief descriptions of sections of this report are listed below.

- Part I: Brief introduction to hydrometallurgy
    - The report starts with a brief introduction to hydrometallurgy and the relevant unit processes. The section also provides a brief comparison of the hydrometallurgical process and the conventional (and complementary) pyrometallurgical smelting process. A visualization of potential applications of hydrometallurgical processes to Minnesota resources is also presented.
- Part II: List of regional resources amenable to hydrometallurgical technologies
    - This section lists regional mineral and waste resources that have the potential to be upgraded to high value-added products using hydrometallurgical processes.
- Part III: Opportunities and challenges for hydrometallurgical technology development
    - This part summarizes the key opportunities for hydrometallurgical process development in the state of Minnesota. It also summarizes the critical needs, wants, and expectations of stakeholders as gathered via the “Voice of Customer” survey. The section also highlights key challenges faced by stakeholders during the commercial development of resources using hydrometallurgical processes.
- Part IV: Emerging hydrometallurgical technologies
    - A brief overview of emerging technologies in the areas of battery material production, critical metal extraction, carbon mineralization, and heavy metal capture are highlighted. The section also reviews emerging hydrometallurgical techniques that enable the production of value-added materials using less energy and water, and with a reduced environmental footprint.

- Part V: Strategic fit of emerging technologies to the NRRI mission
    - This section describes how emerging technologies identified in Part IV align with the NRRI mission and how these emerging technologies are relevant to creating the minerals economy of the future in Minnesota.
- Part VI: Research priorities for NRRI
    - This section lists the top research priorities that relate to the development, demonstration, and commercialization of emerging hydrometallurgical technologies in the state of Minnesota. Emphasis is given to creating solutions that use Minnesota's mineral and waste resources in a manner consistent with the United Nations' definition of "sustainability."
- Part VII: Conceptual design of a hydrometallurgical research laboratory
    - This section provides a list of bench scale equipment necessary to support the research priorities identified in section VI.
- Part VIII: Benchmarking North American hydrometallurgical research facilities
    - This section lists the research capabilities of leading hydrometallurgical research laboratories in North America.
- Part IX: Skill sets required to sustain hydrometallurgical research laboratories
    - This part of the report lists the skill sets and qualifications required to manage and sustain a hydrometallurgical research laboratory in Minnesota.
- Part X: Collaborators and potential funding opportunities
    - Potential research collaborators and funding agencies are highlighted.
- Part XI: Summary and recommendations
    - This section summarizes the key research priorities to advance the technology readiness level of emerging hydrometallurgical technologies. The section also lists the key research equipment and skill sets that are necessary to onboard and sustain hydrometallurgical research programs at NRRI.
- Appendix A: Hydrometallurgical research equipment
    - A list of key laboratory equipment required to develop and demonstrate emerging hydrometallurgical technologies are highlighted in this section.
- Appendix B: Emerging hydrometallurgical technologies
    - A detailed description of emerging hydrometallurgical technologies and their commercial advancements are listed in this section. The report identifies potential opportunities to apply these techniques to regional resources.
- Appendix C: Commercial hydrometallurgical operations in North America
    - This section lists commercial North American operations that practice hydrometallurgical techniques to process copper, nickel, PGE, titanium, and manganese ores and concentrates. The section also lists facilities that use pyrometallurgical and electrometallurgical techniques in conjunction with hydrometallurgy.
- Appendix D: Mineral resources of Minnesota
    - This section summarizes the regional mineral resources that are most suitable for hydrometallurgical processing.
- Appendix E: Waste resources of Minnesota
    - A detailed description of regional waste resources that are most suitable for hydrometallurgical processing are summarized in this section.

- Appendix F: Case study on hydrometallurgical process development at Long Harbor
    - This section reports on R&D work conducted by Vale to support the development, demonstration, and commercialization of hydrometallurgical processing of nickel-copper-cobalt concentrates at Long Harbor, Newfoundland.
- Appendix G: Application of biohydrometallurgical technologies
    - This section reviews biological leaching processes practiced in base metal and precious metal extraction, and highlights opportunities to use biomass in metal recovery applications.
- Appendix H: Application of hydrometallurgy to mine wastewater treatment
    - This section reviews hydrometallurgical processes used to remove metal and other inorganic contaminants from mine wastewater.
- Appendix I: Historical hydrometallurgical investigations conducted by NRRI
    - Hydrometallurgical research work conducted by NRRI on various mineral resources is highlighted in this section.

(Note: Where available, hyperlinks are provided.)

Part 1: Brief Introduction to Hydrometallurgy

Metallurgy is the science and art of extracting metals from their ores, refining them, and preparing them for use (Schuhmann, 1952). Hydrometallurgy is a subdivision of extractive metallurgy that is reliant upon aqueous chemistry for the dissolution, concentration, and purification of metals or metal compounds from ores, concentrates, and various recycled or residual materials (Habashi, 1993).

Some unique advantages offered by hydrometallurgical techniques are described below.

- With the gradual depletion of ore grades of base metals, precious metals, and critical metals, it is becoming increasingly challenging to process lean and complex ores via conventional mineral processing and pyrometallurgical techniques. Hydrometallurgical techniques, on the other hand, were developed to extract metals from lean, complex, and low-grade ores.
- Conventional pyrometallurgical processes such as roasting and smelting produce undesirable gaseous emissions, making them increasingly difficult to permit. Unlike pyrometallurgical processes, hydrometallurgical methods eliminate the emissions of sulfur dioxide while treating sulfide concentrates. However, acid mist from electrowinning tank houses and undesirable emissions from the solvent extraction circuit and CO_2 emissions from limestone acid neutralization pose environmental, health, and safety concerns.
- Hydrometallurgical techniques can produce high-purity metal or metal compounds in a variety of forms such as powders, nodules, and coherent surface deposits.
- The waste liquors from hydrometallurgical processes can be regenerated and reused in metal extraction and purification stages.

Figure 1 presents a hypothetical overview of potential applications of hydrometallurgical techniques to Minnesota’s mineral and waste resources. Figure 2 illustrates the roles that hydrometallurgical techniques could potentially play in delivering the United Nations sustainable development goals (UN SDG).

Hydrometallurgical processes have grown in importance over the past few decades and assume a leading role in metals processing, but there are some significant challenges that are presented such as (Habashi, 1993):

- Hydrometallurgical processes produce large volumes of waste effluents. Disposal and reuse of such wastes poses environmental challenges.
- Reaction rates of hydrometallurgical processes are relatively slower compared to pyrometallurgical processes. Hence, throughput rates of hydrometallurgical plants are lower as compared to smelters.
- Hydrometallurgical plants require special materials of construction due to the corrosive nature of some reagents.
- In some instances, the higher cost of reagents and capital costs could potentially render the hydrometallurgical processes economically and environmentally unviable unless offset by factors like byproducts sale and recycling of reagents.

A detailed comparison between hydrometallurgical and the traditional pyrometallurgical processes is shown in Table 1.

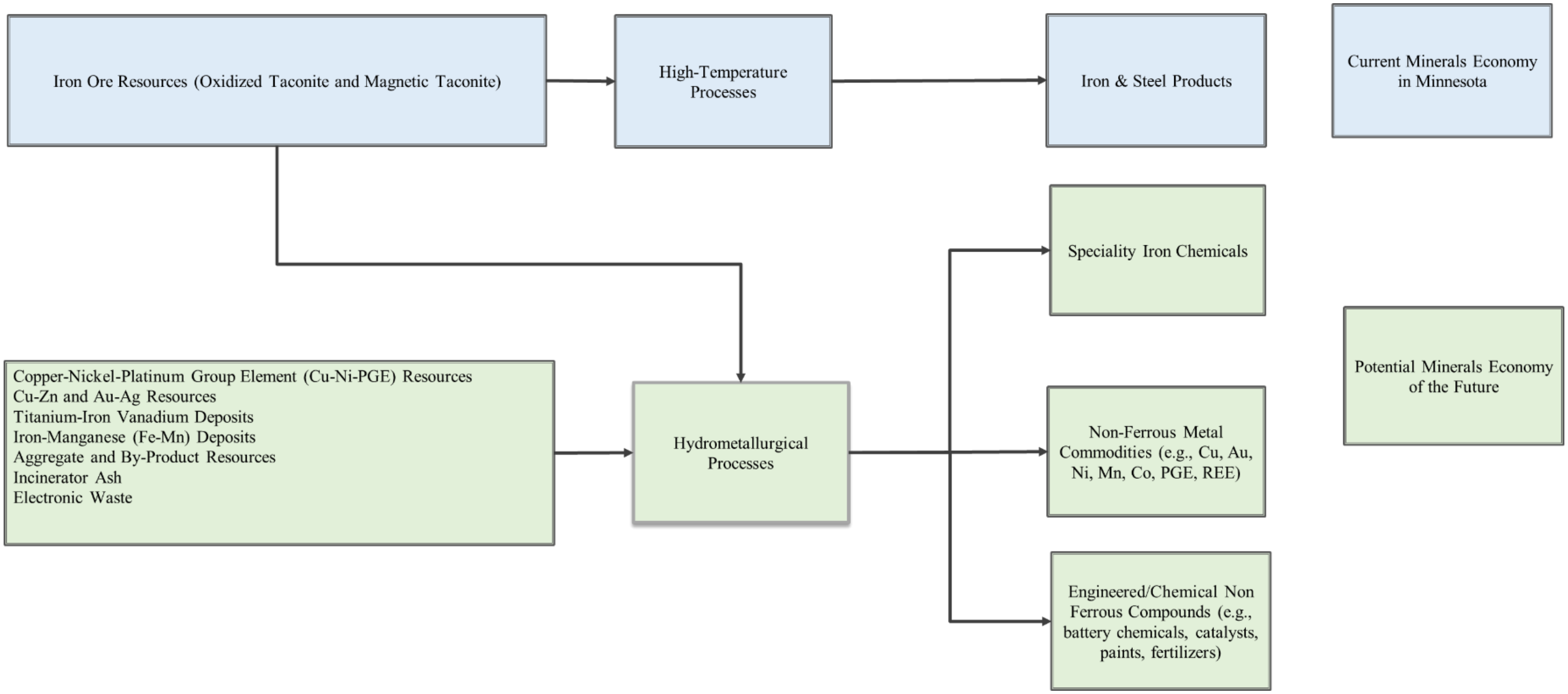

Figure 1. Potential applications for hydrometallurgical technologies to Minnesota resources.

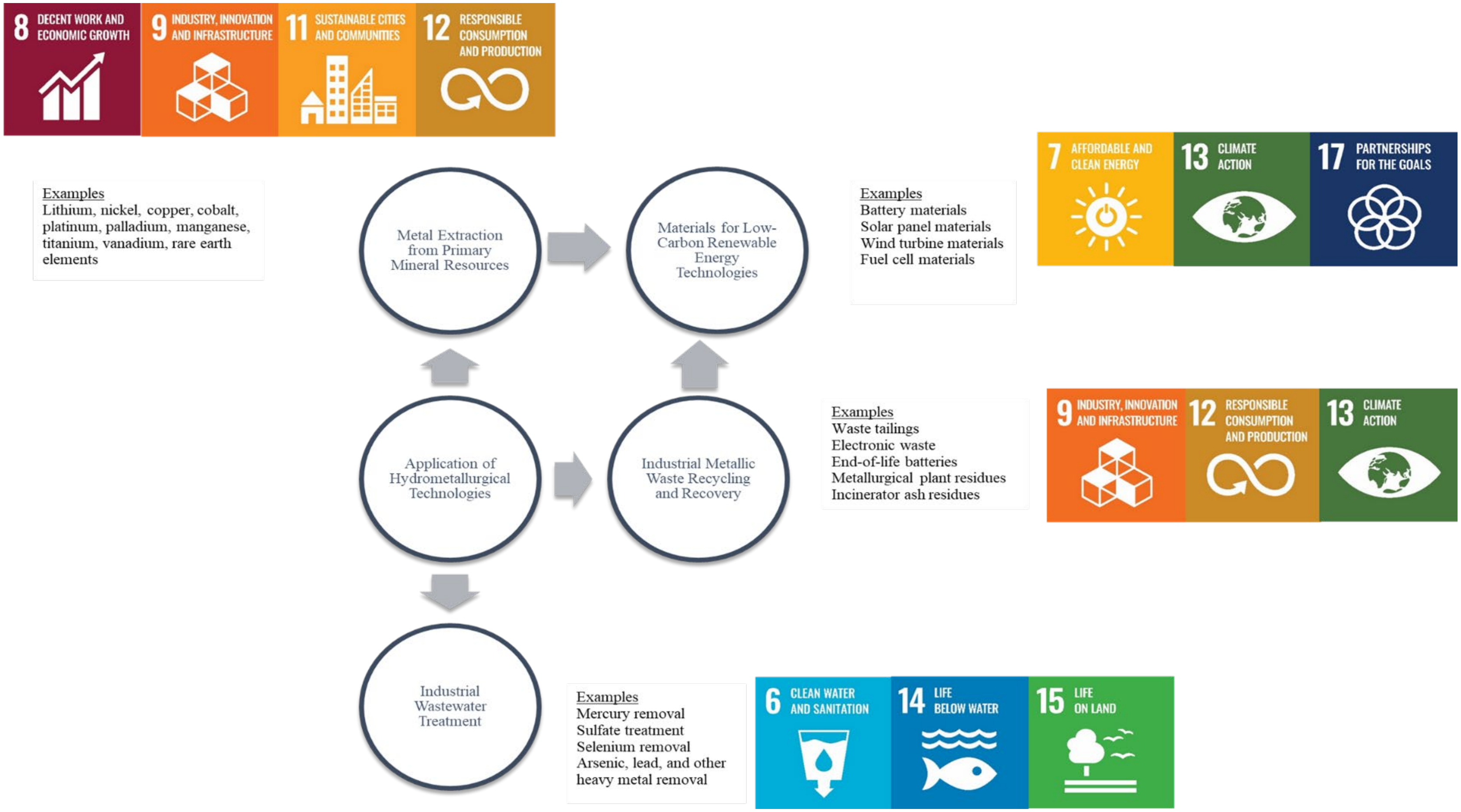

Figure 2. Role of hydrometallurgy in sustainable development.

Table 1. Comparison between hydrometallurgical and pyrometallurgical technologies (adopted from Anderson, 2014).

Metric	Category	Pyrometallurgy	Hydrometallurgy
Treatment of low-grade ores	Process	Less economical to process low-grade ores due to consumption of large amounts of energy to melt and separate gangue minerals	Suitable for treating a wide variety of low-grade ores
Reaction Kinetics	Process	Reaction rates are higher, as higher temperatures promote faster kinetics	Significantly slower compared to pyrometallurgical processes
Materials handling	Process Equipment	Requires vessels capable of handling molten metals, slags, and waste gas	Requires vessels capable of handling corrosive reagents
Economies of Scale	Economics	Suitable for large economies of scale, which requires large capital investment	Hydrometallurgical techniques are suitable for smaller scale operation. Requires lower capital investment compared to new pyrometallurgical smelters
Treatment of Secondary resources (Urban Waste)	Waste Reduction	Not suitable to treat urban wastes on a standalone basis. Requires a final hydrometallurgical or electrometallurgical process to upgrade the smelter products	Suitable to produce high-value-added products from secondary metal resources
Environmental consideration	Social License	Requires special emission control systems to capture waste gas and dust generated from processes	Requires safe handling and treatment of waste effluents
Treatment of sulfide ores	Process	Generates large volumes of SO_2 that must be captured and converted to sulfuric acid	Eliminates generation of sulfur dioxide. Technology aids in recovery of sulfur in elemental form
Solid residues	Waste Reduction	Process residues such as dusts, slags, and others may contain valuable metals that require further processing	Solid residues from hydrometallurgical processes requires washing, neutralization, and related treatment before discarding it to tailings storage facility
Toxic gasses	Environmental Impact	Generates toxic gasses that require specialty emission treatment and control systems to protect the ambient air quality	Toxic fumes are generated in relatively small quantities in the reactors

General Hydrometallurgical Processes

Metallic elements found in mineral concentrates, waste tailings, and industrial wastes can be transformed into high-purity materials by a series of hydrometallurgical processes like metal extraction, solution purification, and metal recovery. The following section provides a brief description of major hydrometallurgical unit operations like leaching, solvent extraction, ion exchange, carbon adsorption, precipitation, and electrowinning processes. The processing flowsheet and operating conditions for each of these processes are unique to the target metal under investigation (Habashi, 1993). The commonly practiced hydrometallurgical unit processes and unit operations for metal extraction are shown in Table 2, and a typical sequence of operation for a hydrometallurgical operation is shown in Figure 3.

Leaching

Leaching is carried out to dissolve the whole, or some part, of the feed material containing various metallic minerals. The selectivity of dissolution of an element depends on the nature of the reagent, while the kinetics of the reaction depends on factors such as temperature, pressure, concentration of the reagent, pulp density, residence time, and degree of aeration of the leaching reagent. Other than water, leaching agents commonly used are categorized into following areas: acids, bases, aqueous salt solutions (Habashi, 1993). The selection of appropriate leaching agents depends on following criteria:

- Solubility: the mineral or metal of interest should have large and rapid solubility in the leaching reagent.
- Selectivity: An ideal reagent will extract only desired constituents present in the material.
- Regeneration: Ability to regenerate reagents for reuse in the leaching step minimizes reagent consumption.
- Materials of construction: Highly corrosive leaching agents require specialty alloys such as stainless steel, titanium, or Hastalloy for safe handling.
- Cost: Reagents should be economical and readily available.

Pregnant leach solutions contain dissolved metal or metallic compounds that require further processing. In most cases, this involves chemical separation in which dissolved metals are concentrated, purified, or removed. A range of methods are employed and comprise processes such as solvent extraction, ion exchange, adsorption, membrane filtration, and precipitation.

Solvent Extraction

Solvent extraction (or commonly known as liquid-liquid extraction) is a process in which dissolved metal or metal ion species are extracted from the aqueous phase by contacting it with an organic solvent. The process is based on the immiscible nature of the solvent in which metal or metal ion complex would dissolve completely to form organometallic complex, while the other unwanted ions remain in the aqueous phase. During the process, the organic solvent and the aqueous phases are intimately mixed and subsequently allowed to disengage via settling. Subsequent to separation of two liquids, the metal species are transferred back to the aqueous phase in a concentrated and purified form by adjusting the solution conditions to reduce the metal solubility in the organic phase via a process called stripping (Free, 2013; Habashi, 1993).

Ion Exchange

In the ion exchange process, the resin is made to absorb a suitable ion of the desired metal ion or complex through an ion-exchange reaction. The absorbed ion is then stripped into solution by employing a process called elution. The stripping solution is called eluant, and the solution into which the ions have been stripped is known as eluate (Free, 2013).

Ion exchange gained significance during the World War II Manhattan Project when it was industrially adopted to recover uranium from leach liquors. The major commercial applications of ion exchange include base metals (copper, cobalt, and nickel), gold, and uranium extraction. Other areas where ion exchange has found a niche include rare earth metal extraction, PGM recovery, and lithium extraction from brines (Habashi, 1993).

Adsorption

Adsorption on activated carbon is predominantly used for concentrating gold and silver from cyanide leach solutions. Activated carbon is typically made using coconut shells, but other materials like peach pits, nut shells, sugar, wood, and coal are also used. Adsorption is typically carried out in countercurrent columns or tanks filled with activated carbon. When adsorption is complete, the pulp is screened to separate the activated carbon, and then the metal ion complex is stripped from carbon using a caustic cyanide solution at higher temperature. The stripped solution is subjected to metal recovery process to recover the metal. Subsequently, the activated carbon is subjected to regeneration by thermal activation to remove organic contaminants and subjected to acid wash to remove inorganic constituents like carbonates (Free, 2013).

Precipitation

Precipitation is used to purify or concentrate pregnant leach solutions by removing specific impurities by adjusting the pH of the solution. The differences in solubilities of metals as a function pH facilitates separation of species (Free, 2013).

Electrowinning

In electrowinning, the dissolved metal is recovered from the solution using electrolysis. The metal is recovered by applying a potential to drive electrochemical reactions. An external electricity source supplies the potential and current. The dissolved metal is reduced, and deposits at the cathode and other ions or molecules are oxidized at the anode, which is made from inert insoluble conductor. The electrodes are typically placed in an electrolyte- or ion-conducting medium with sufficiently high conductivity. Metals that are primarily produced via electrowinning include copper, nickel, cobalt, zinc, aluminum, lithium, titanium, indium, tantalum, niobium, hafnium, zirconium, molybdenum, vanadium, beryllium, chromium, cadmium.

Table 2. General unit operations and unit processes in hydrometallurgy (adapted from Habashi, 1993).

Unit Process	Unit Operations	Purpose
Extraction	• In situ leaching • Heap/Dump leaching • Agitation leaching • Pressure leaching • Bioleaching	Selective dissolution of metals from feed material using a solvent
Purification/Concentration	• Precipitation • Ion Exchange • Solvent Extraction • Adsorption • Membrane filtration	Concentration or purification of leach solutions before metal recovery
Recovery	• Electrowinning • Cementation • Electrorefining	Recovery of pure metals or metal compounds from concentrated solutions

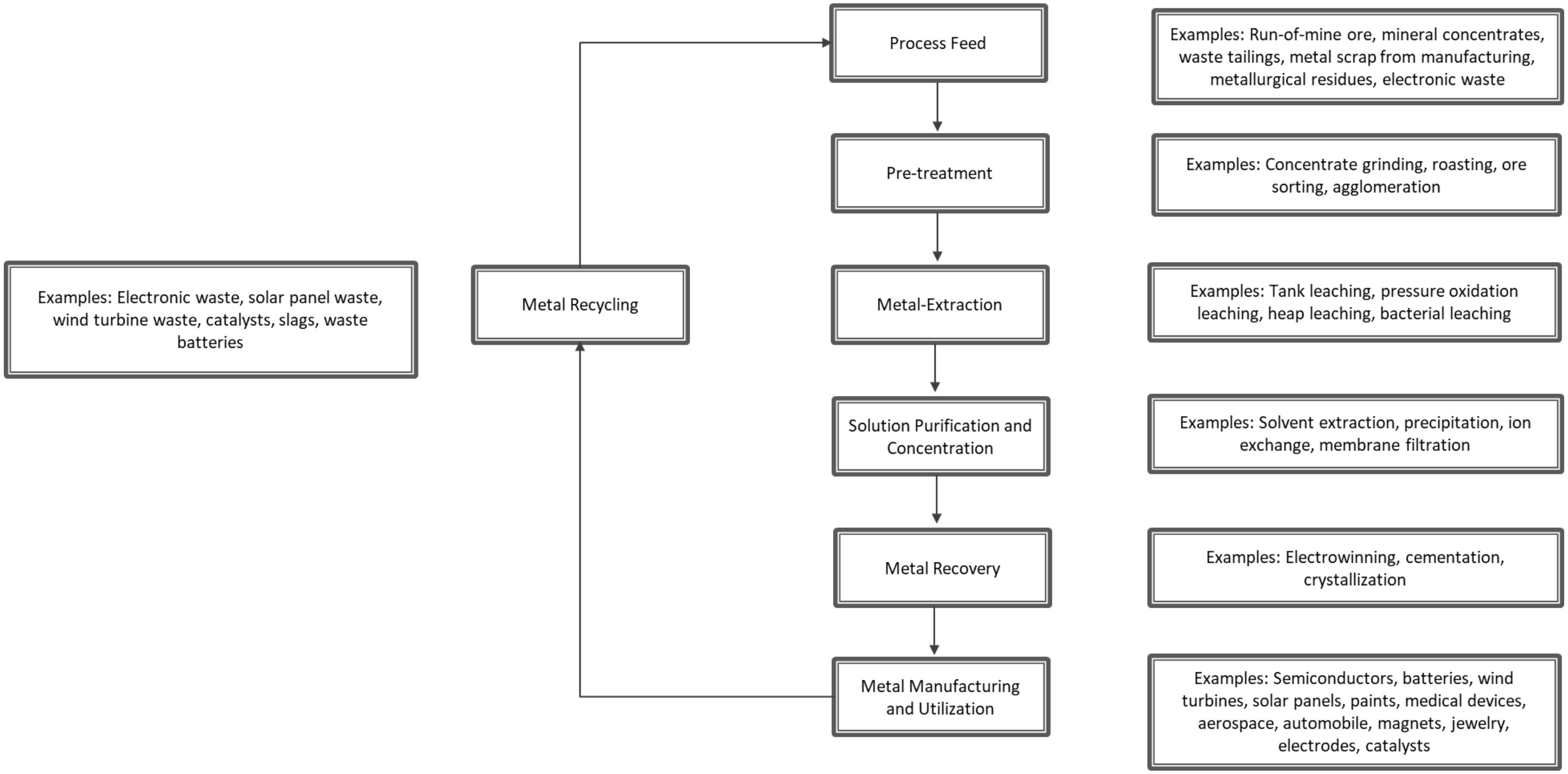

Figure 3. Typical process flowsheet for a hydrometallurgical process (adapted from Free, 2013).

Emergence of Hydrometallurgical Innovations in the United States

While early roots of hydrometallurgy are shrouded in history, the modern day growth in the importance of hydrometallurgical innovations originates from the discovery of transuranium elements for the Manhattan Project at the University of Chicago Metallurgical Laboratory (Met Lab). Early notable hydrometallurgical inventions stem from the works of Nobel Laureate Dr. Glenn T. Seaborg at the Met Lab, where he led a team that was responsible for devising a hydrometallurgical process for the separation, concentration, and isolation of plutonium from spent fuel using a bismuth-phosphate precipitation process. (U.S. Department of Energy- Office of History and Heritage Resources, 2005). This process was later scaled up by a billion fold by DuPont Corporation at the U.S. Atomic Energy Commission's production plant in Hanford, WA (Seaborg, 1965). Other significant hydrometallurgical inventions from the Manhattan Project related to rare earth element and uranium extraction, which is contemplated as the starting point of the present great interest in the use of ion exchange and solvent extraction methods for inorganic and radiochemical separations (Anderson, 2014). Another significant breakthrough that resulted in the far-flung adoption of hydrometallurgical processes beyond the nuclear industry was attributed to the invention of selective solvent extractants by Minnesota-based General Mills Chemical Company. Pioneering work of National Academy of Engineering inductee Joe E. House (then head of General Mills Chemicals' Minerals Industry Division) in the 1960s sparked a fundamental shift in the way the worldwide copper industry operates today. House and a team of chemists at the General Mills developed an extractant – trademarked LIX – capable of extracting copper from a solution while leaving behind other metals dissolved in the same solution (National Academy of Engineering, 1998). As a direct result of this work, copper mineralization that was previously classified as waste is now mined and economically processed. In 2017, solvent extraction and electrowinning accounted for more than 50% of U.S. copper production and more than 20% of copper production worldwide (USGS, 2017). Since these early discoveries, hydrometallurgical techniques have been applied extensively not only for the separation and extraction of non-ferrous metals, but also in water purification, wastewater treatment, and environmental remediation (Free, 2013). Today, hydrometallurgical processes are widely used in the synthesis of battery materials, photovoltaic materials, automotive catalysts, fertilizers, electro optic materials, medical device substrates, etc. (Free, 2013).

Early Drivers for the Adoption of Hydrometallurgical Techniques

Enactment of Clean Air Act

Prior to widespread industrial adoption of hydrometallurgical technologies in the U.S., high-temperature smelting and refining technologies were the prominent method of producing non-ferrous metals like copper, molybdenum, lead, and zinc. Prior to the enactment of the Clean Air Act, these smelters were the major sources of sulfur dioxide, metal fumes, nitrogen oxide, and carbon monoxide in North America (Free, 2013). Uncontrolled smelting practices also emitted hazardous air pollutants like lead, arsenic, mercury, zinc, cadmium, beryllium, antimony, and selenium into the ambient air (Free, 2013). Because smelting and refining processes require high temperatures to reduce the mineral concentrates into pure metal and to refine metals and alloys (for example, iron melts at 1536 °C, copper melts at 1083 °C, and aluminum melts at 660 °C), many other metals and metal compounds volatilize into the waste gas streams (for example, boiling points of mercury, cadmium, zinc, arsenic, and selenium are 357 °C, 765 °C, 906 °C, 613 °C, and 685 °C respectively). As atmosphere around smelters became more noxious, SO_2 emissions came under severe scrutiny as a significant contributor to air pollution and acid rain. The Clean Air Act amendments of 1977 established national ambient air quality standards (NAAQS) for emissions of air pollutants including SO_2 that endangered public health and welfare (Free, 2013). The enactment of the Clean Air Act mandated smelters to install pollution control equipment to reduce sulfur dioxide emissions. To meet these standards, most smelter operations in North America installed gas cleaning and acid plants to demonstrate compliance with emission limits set by the Clean Air Act (Parameswaran, et al., 2018). However, gas cleaning and acid plants required a relatively high (at least 4 percent) SO_2 concentration in the off-gas for economical operation and compliance with pollution limitations. Waste gases with weaker SO_2 concentrations, such as those from the older reverberatory furnaces, were not suitable for conversion of SO_2 into sulfuric acid. The transition from reverberatory furnace to the modern flash and electric arc furnaces led to the production of strong sulfur dioxide concentrations in off-gas that were amenable for conversion to sulfuric acid, thus paving a way for smelters to eliminate a larger percentage of the sulfur dioxide emissions (Parameswaran, et al., 2018). An example of this modern advancement is the smelter constructed by Rio Tinto on the shores of the Great Salt Lake in Utah, which is designed to capture in excess of 99.9% of the sulfur that enters in the feed (Metso Outotec , 2017).

Although the transition from reverberatory to modern furnaces and emission control technologies brought social, environmental, and improved operational benefits, it also cost the domestic copper industry enormous capital expenses, which led to closure of significant domestic smelting capacity. For instance, U.S. primary and secondary copper smelter production drastically reduced from a 1981 level of nearly 1.4 million tonnes to about 0.5 million tonnes in 2015 (U.S. Congress, Office of Technology Assessment, 1990; USGS, 2017).

Besides shutting down inefficient smelters with old-fashioned reverb furnaces, the copper industry was forced to consider radically different technologies to comply with stringent regulations. The responses of the copper industry to the Clean Air Act were twofold. The first was to turn to oxide minerals, which contained no sulfur, and that route led to the development of solvent extraction and electrowinning processes. The second was to subject sulfide minerals to processes like bio-hydrometallurgy and pressure hydrometallurgy that turned the sulfur present in the ore into elemental sulfur or gypsum instead of gaseous SO_2. By 2017, 52% of the refined copper production in the U.S was produced via solvent-extraction and electrowinning technologies (USGS, 2017).

Declining Ore Grade and Increased Ore Complexity

The ore grades of base metal ores like copper and nickel have been gradually declining around the world. For example, in the early 1900s the average copper ore grade processed in the United States was 2%, but by the end of the 20th century ore grade had declined to 0.5% and has diminished to less than 0.5% today (Izatt, et al., 2014). The industry’s response to this decline was three-pronged. First, declining ore grades led to greater use of hydrometallurgical processes, which have greater tolerance for impurities compared to smelting technology. For instance, copper in the low-grade dumps was unrecoverable by the conventional smelting process and hence discarded as waste (Brierley, 2014), but copper could be extracted from low-grade oxide ores and some sulfidic ores through leaching, solvent extraction, and electrowinning technologies (SX-EW). Second, the copper ores that contained low levels of iron were better suited for hydrometallurgical processing, but copper ores that contained higher levels of iron were commonly processed using the pyrometallurgical route because the iron enabled them to be concentrated quite easily while utilizing the heat generated from the exothermic reaction resulting from oxidation of iron and sulfide minerals. Lastly, companies that aimed at producing a concentrate for sale to a smelter (in order to minimize capital costs, operating costs, and permitting requirements) could not produce a concentrate of sufficient grade to carry the transport costs at an acceptable recovery. In this case, potential hydromet routes were deemed less capital intensive than smelting.

Ability to produce high purity-value added products

Hydrometallurgical processes gained prominence because of their ability to produce high-purity finished products for the nuclear industry. During the Manhattan project, high-purity rare, refractory, and nuclear metals like uranium, plutonium, zirconium, hafnium, thorium, and beryllium were extensively generated using hydrometallurgical processes (Anderson, 2014). Today, hydrometallurgy is applied to extract a wide variety of pure metals (e.g., Al, Mg, Mn, Co, Pt, Pd, Ag, Au, Ni, Cu, REE, Li, In, Zn), powders, or compounds from a variety of feedstock including run-of-mine ores, concentrates, waste dumps, mine wastewater, matte, metallurgical waste, and urban waste products (Anderson, 2014).

Energy, Water and Carbon Footprint

As orebodies of metallic minerals become increasingly dilute and complex, extraction of metals from these leaner ore bodies and resulting process streams require increased energy consumption and associated greenhouse gas emissions. The increased energy consumed derives primarily from the need in the mining and mineral processing stages to move and treat additional material to produce the same amount of final product (Izatt, et al., 2014). A further consequence of the increased energy requirement is increased greenhouse gas emissions arising from the consumption of fossil-derived energy. Paralleling this increased energy and greenhouse gas emissions is an increased requirement for water to treat the additional gangue materials. The mining and processing of metals utilize about 7% of total world energy and 0.03% of total world water (Izatt, et al., 2014). Therefore, it is of paramount importance that any new technologies proposed to treat such low grade resources have improved metal extraction efficiencies coupled with lower energy, water, and environmental footprint. To validate the benefits of such emerging technologies, they must be compared to current lifecycle performance benchmarks for energy, water, and greenhouse gas emissions intensity, which will indicate the likely scope for reducing the environmental footprint. In light of increasing challenges, sustainable hydrometallurgical technologies will likely be those that can recover metals with higher energy and water efficiency and superior yield and purity while simultaneously recovering multiple metals from the same stream (Izatt, et al., 2014).

Waste Solids Management and Mine Drainage

Mining lean deposits with declining ore grades produces higher amounts of mine waste (tailings plus waste rock) and increased consumption of energy, water, and chemicals. It is estimated that 6.4×10^9 metric tons of ore is extracted annually from the Earth (2004), of which > 90% is discarded as mine and mill wastes (Izatt, et al., 2014).

When hydrometallurgical processes are employed to process lean ores, the process residues and waste solutions may require appropriate treatment before discharging to the surrounding environment. While waste generated by pyrometallurgical processes is relatively stable for ambient storage, solid residues and bleed aqueous solutions from hydrometallurgical processes are generally not stable because of the presence of soluble metal species. Hence, disposal in tailings may be hazardous because of the danger of contaminating surface waters in the event of tailings dam failure (Government of British Columbia, 2014). The occurrence of sulfide minerals such as pyrrhotite, pyrite, and chalcopyrite in tailings also presents environmental challenges. Under appropriate conditions these minerals may react with oxygen and water to produce sulfuric acid, which can solubilize other minerals and release metal ions like arsenic, antimony, bismuth, lead, zinc, mercury, etc. into the solution (AMIRA International, 2002). Moreover, processing low grade ore bodies tends to be water intensive, but improved liquid-solid separation methods that facilitate reuse of water may reduce consumption of freshwater in mining operations.

Iron control in Hydrometallurgy

Iron is the fourth most abundant material present in Earth's crust. Iron occurs in the crystal structure of over 600 minerals. Iron is present in non-ferrous ores as ore minerals, gangue minerals, and solid solution minerals. In ore minerals of major nonferrous metals (Cu, Ni, Co, PGM, Mn, and Ti), iron is present as an essential constituent of a mineral used as a source of another metal. Examples include ilmenite and titanomagnetite for titanium; chalcopyrite and bornite for copper; pentlandite and nickeliferous limonite for nickel; and rhodonite and rhodochrosite for manganese. In gangue minerals, iron is an essential constituent of a mineral that is undesirable in the ore. Examples include pyrrhotite and pyrites, which are common gangue minerals present in base metal ores. Moreover, iron oxides, iron silicates, and iron carbonates are abundantly present as gangue minerals in many oxidized non-ferrous ores. Finally, in solid solution minerals, iron substitutes an essential element either in ore or gangue minerals. Examples include sphalerite and cobaltite (Monhemius, 2016).

During hydrometallurgical processing of major non-ferrous ore minerals, iron presents the following challenges and opportunities:

- The Pourbaix diagram for the Fe-H_2O system indicates that iron in the ferrous oxidation state is soluble in highly acidic to mildly alkaline pH conditions, whereas ferric iron is soluble only in acidic solutions ($pH < 3$) and oxidizing conditions ($Eh > 0.77$ V). Therefore, while subjecting non-ferrous ore minerals to leaching, iron present in the ore mineral is readily soluble in the leach solution along with other metals of interest. As a result, iron removal from the solution becomes an essential prerequisite before solution purification and metal recovery steps (Monhemius, 2016).

- The narrow solubility range of ferric iron in the Pourbaix diagram indicates that iron can be separated from the solution by oxidizing it to the ferric state followed by increasing the pH of the solution to greater than three. This causes the iron to precipitate as ferric hydroxide, which is relatively insoluble under specific pH and electrochemical potentials (Monhemius, 2016). Unlike fayalite, disposing of ferric hydroxide precipitates from hydrometallurgical processes in ways that satisfy regulatory standards is of paramount importance to both existing and developing hydrometallurgical technologies.

- In smelting processes used for the production of non-ferrous metals, iron present in the smelter feed ends up in the slags as fayalite, ferrous silicate (Fe_2SiO_4), together with many other deleterious impurity elements. Fayalite is chemically and environmentally inert material posing minimal risk to the local surroundings (Monhemius, 2016).

- Monhemius (2016) illustrates the huge scale of iron waste generated by hydrometallurgical processing of copper and zinc sulfide concentrates, estimating that a typical copper concentrate consists of 30% Fe and 25% Cu, compared with a typical zinc concentrate with around 10% Fe and more than 50% Zn. Thus, a ton of electrowon copper produced via hydrometallurgical means would necessitate the disposal of around six times as much iron as that arising from the production of a ton of electrolytic zinc.

- Monhemius (2016) comments that it is not cost effective to use hydroxide precipitation to remove more than about 1 to 2 g/l of ferric iron from process solutions. This is primarily because iron hydroxide precipitates have a tendency to form gelatinous compounds with large surface area that are difficult to filter and often trap valuable elements in their crystal structure.

Sulfur Management in Hydrometallurgy

Historically, high-temperature processing of sulfide concentrates of Cu, Zn, and Pb release sulfur dioxide into the ambient atmosphere. Following the introduction of the Clean Air Act, sulfur dioxide emissions were sequestered and converted into sulfuric acid. The development of hydrometallurgical processes in the 1960s facilitated the production of elemental sulfur instead of sulfur dioxide or sulfuric acid. In hydrometallurgical processes, sulfide minerals under oxidizing conditions in acid media dissociate into elemental sulfur, while the metallic element solubilizes into the solution (Habashi, 1996). Elemental sulfur in hydrometallurgical residues represents both a disposal challenge and a byproduct recovery opportunity. Sulfur and related sulfur compounds in waste tailings could potentially generate acid and cause pH changes in surface water bodies if sufficient neutralizing minerals are absent. Therefore, recovery of sulfur from the residue not only mitigates the volume and reactivity of the residues but also presents opportunities in byproduct sale (Conard, 1992). With stakeholders increasingly aware and pro-active about the residue and tailings generated from hydrometallurgical facilities, emerging technologies should invariably evolve to meet the challenges of waste management. For leach residues with significant amounts of elemental sulfur, known processes such as flotation and hot filtration are preferred technologies for byproduct recovery.

Waste Effluent Management

As mining operations evolve from processing high-grade ores to low-grade sulfidic mineral resources, the volume of surface material mined, water consumption, and the wide range of contaminants that appear in wastewater increases exponentially. To meet the strict regulatory limits of contaminants in mine discharge, the industry is challenged to investigate and develop cost-effective technologies to reclaim, reuse, and recycle mine wastewater prior to discharge.

Part II: List of Regional Resources Amenable to Hydrometallurgical Technologies

In this section, mineral and waste resources potentially amenable to hydrometallurgical processing have been identified. Hydrometallurgical techniques can potentially facilitate: 1) production of value-added materials used in renewable energy technologies like rechargeable batteries, solar panels, fuel cells, and wind turbines; 2) production of critical metals from mineral and waste resources; 3) remediation of inactive or closed processing facilities to protect land and water resources; and 4) production of secondary products for CO_2 sequestration via carbon mineralization. Brief descriptions of these resource categories are presented here, and detailed descriptions are shown in Appendix B.

- NI 43-101 compliant mineral resource estimates for many of the Duluth Complex contact-type Cu-Ni-PGE magmatic sulfide deposits total 9.57 billion metric tons with average grades of 0.406% Cu, 0.126% Ni, and 0.326 g/t Pt-Pd-Au. Major deposits include Birch Lake, Maturi, Mesaba, NorthMet, Serpentine, and Spruce Road (Polymet Mining, 2019; Duluth Metals Corp, 2014; Teck Resource, 2019).

- The mineral resource estimate for the Tamarack Intrusive Complex conduit-type Ni-Cu-PGE sulfide deposit in east-central Minnesota is 11.09 million metric tons with average grades of 0.8% Cu, 0.1393% Ni, and 0.223 g/t Pt-Pd-Au (Talon Metals, 2021).

- Minnesota's OUI-associated Ti-Fe-V deposits include: 1) Longnose, with a NI 43-101 indicated resource of 58.1 million tons averaging 16.6% TiO_2 (inferred 65.3 million tons averaging 16.4% TiO_2) based on 27 drill holes and using a cutoff grade of 8% TiO_2; 2) Titac, with a NI 43-101 inferred resource of 45.1 million tons averaging 14% TiO_2 based on 32 drill holes and using a cutoff grade of 8% TiO_2 ; and 3) Water Hen, with a crudely estimated 62 million tons averaging 14% TiO_2, based on 37 drill holes (Minnesota Minerals Coordinating Committee, 2016).

- The iron formations and associated ore deposits of the Cuyuna iron range in east-central Minnesota contain appreciable quantities of manganese (Schulz, et al., 2017). Lewis (1951) estimated that 455 million metric tons of manganiferrous iron formation containing 2 to 10 percent manganese were available to open-pit mining to a depth of 45 meters. Beltrame et al., (1981) estimated a minimum of 170 million metric tons of manganiferrous rock with an average grade of 10.46 weight percent manganese. The manganese estimates are not as reliable because data used to make these estimates were prepared for different reasons at different times, using different databases and methodologies.

- Minnesota produces a wide variety of aggregates and byproducts (Minnesota DNR, 2022). The lithogeochemistry of these materials is currently being compiled so that analysis for potential resources amenable to hydrometallurgical processing can be evaluated.

- In Minnesota, eight waste-to-energy (WTE) facilities generate electricity by combusting mixed municipal solid waste (MMSW) and refuse-derived fuel (RDF). Incinerator ash from these facilities typically contains metals like arsenic, cadmium, chromium, lead, mercury, selenium, nickel, copper, tin, silver, barium, boron, and zinc (Michaels & Krishnan, 2018).

- Coal combustion residuals (CCR) generated from coal-fueled heat and power plants typically contain metals such as antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury nickel, selenium, silver, and thallium (Environmental Protection Agency, 2015).

- Electronic waste, referred to as e-waste or waste electrical and electronic equipment (WEEE), contains critical metals like cobalt, lithium, rare earth elements, gallium, germanium, tantalum, tungsten, platinum, and palladium. In Minnesota, approximately 199.4 million pounds of household electronic waste was collected for recycling between 2013 and 2018 (Minnesota Pollution Control Agency, 2021).

Part III: Opportunities and Challenges for Hydrometallurgical Technology Development

Summary of Intent

NRRI conducted a "Voice of Customer" (VOC) survey involving 20 external participants. The purpose of this stakeholder engagement was to:

- better understand the current and future needs of Minnesota's minerals industries;
- understand current hydrometallurgical technologies and plant practices;
- inform research strategies and prioritize technology development; and
- assess NRRI's value proposition hypotheses:
    - *Hydrometallurgical processes will play an important role in the treatment of the state's base, precious, and critical mineral resources and waste resources.*
    - *NRRI's hydrometallurgical R&D capabilities will enhance the competitiveness of the minerals industry, diversify the state's minerals industry, and address environmental issues related to mineral extraction.*

The VOC survey was accomplished through interviews with a broad range of stakeholders around the country. These included current or prospective mineral/metal producers, metal recyclers, hydrometallurgical R&D labs, engineering and technology providers, consultants, academia and educators, regulators, and federal agencies.

Stakeholder Engagement via Voice of Customer Survey

The following section summarizes the critical needs, wants, and expectations of stakeholders as gathered via the VOC survey.

- Value-added products: Many prospective miners envision shipping mineral concentrates to international markets for further refining. However, due to rising transportation and toll smelting and refining costs, some miners believe that international shipping is not sustainable. Additionally, prospective miners noted difficulties in producing smelter-grade concentrates via flotation technologies from some of the resources in the Duluth Complex. To overcome these challenges, some prospective miners plan to employ hydrometallurgical techniques to produce value-added products from nickel and PGE concentrates. Others are evaluating the feasibility of producing battery-grade materials from high-grade Ni-Cu-PGE mineralization (e.g., Tamarack deposit, Aitkin County).

- Protecting water resources and mitigating mine drainage impacts: Regulatory agencies noted that any research to produce byproducts and/or reduce potential pollutants from mine wastewater could help with both real and perceived impacts of mining. Prospective miners mentioned that some of their current efforts to understand and mitigate mine drainage challenges include evaluation of desulfurization techniques, dry stacking of waste tailings, and removal of selenium from mine wastewater.

- Critical minerals research: Several participants noted the current United States dependency on imports for domestic consumption of critical metals as indicated in the USGS Mineral Commodity Summaries[1]. The USGS noted the need for a coordinated, long-term program to maximize the nation's understanding of subsurface critical mineral resources and potential recovery of critical metals from historical metal mining waste, and in 2019, initiated the Earth Mapping Resources Initiative Program (Earth MRI). The USGS stated that such efforts would

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[1] See USGS Mineral Commodity Summaries

enhance the understanding of domestic resources of critical minerals, energy resources, groundwater resources, and geologic hazards. The USGS also stressed the need for partnerships with academia to determine the feasibility of extracting byproduct mineral commodities, such as critical minerals, from mine tailings and subsurface critical mineral resources[2].

- Diversification of minerals economy: Some respondents indicated that diversification of the minerals sector economy in Minnesota would lessen the negative impact of iron mining downturns. While discussing innovative solutions to diversify the minerals sector economy, participants indicated that hydrometallurgical techniques would facilitate the production of value-added products from Minnesota's mineral resources and enhance the royalty value of minerals owned by the State (e.g., School Trust Fund, University Trust Fund). A few participants believe that public concerns related to social acceptance of hydrometallurgical techniques could potentially be alleviated by making current and future research data readily accessible to the public.
- Need for advanced processing and environmental characterization laboratory:
    - Due to the lack of advanced research and development (R&D) facilities in Minnesota, stakeholders, including prospective miners, school trusts, and mineral rights holders, rely on international laboratories to support their geometallurgical, advanced processing, and environmental testing programs. The COVID-19 pandemic and closure of international borders resulted in lengthy delays to complete scientific studies.
    - Participants noted that hydrometallurgical processes are widely used in the extraction of base metals, precious metals, and critical metals. However, barriers to adoption of hydrometallurgical processes in Minnesota do not arise from its technological risks, but rather from the inherent risks of water pollution occurring from mining activities. Participants acknowledged that predicting and managing the occurrence of mine drainage to minimize risks to human and environmental health is one of the key challenges facing the mining industry. For this reason, each mineral deposit is assessed on its own merits to ensure that waste is managed appropriately as part of a mine material characterization program. Participants noted that the tools needed to estimate the magnitude of the risk are not readily available in Minnesota.
    - Prospective miners noted that bench- and pilot-scale testing is required throughout the development of a mineral deposit to minimize risk that emerging technologies can bring. Moreover, embedding these tests into the design phase ensures that risks are identified early, allowing stakeholders to make well-informed decisions, and if needed, to adopt technologies to meet statutory requirements.
- Alternatives to hydrometallurgical techniques: Participants noted there has been a steady decline in smelter production in the United States since the 1980s. The reasons cited for smelter production decline include: 1) the need to install expensive emission control technologies to meet the stringent emission standards in the United States; and 2) the steady decline in ore-grade in the United States. To meet stringent emission standards, smelters demand a higher-grade concentrate (e.g., Cu, Ni grade) and have a low tolerance for impurities such as arsenic, selenium, mercury, cadmium, bismuth, antimony, lead, zinc, fluorine, etc. As a result, smelters are not widely used to process low-grade ores. In contrast, participants noted that low-

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[2] See USGS critical mineral recovery

temperature processes like hydrometallurgical techniques have a high tolerance for impurities present in low-grade ores.

- Reuse and recycling of critical metals: The U.S. Department of Energy's Advanced Manufacturing Office (AMO) states that its research focuses on four areas: 1) diversifying supplies: 2) developing substitutes; 3) driving reuse and recycling; and 4) crosscutting research. AMO officials noted that there is a growing need to eliminate and reduce reliance on rare-earth metals and other materials critical to the success of clean energy technologies. Additionally, AMO asserts that a domestic supply chain would reduce the U.S dependence on foreign sources for critical metals. To support these efforts, AMO funds the Critical Materials Institute (CMI), whose research focuses on recycling rare earth materials, battery materials (lithium, cobalt, manganese, and graphite), indium, and gallium.
- Timeline associated with environmental review and permitting process: Minnesota's lengthy timeline to complete environmental review and permitting processes compared to other states or nations was a common concern cited by stakeholders. Many participants noted that, while Minnesota's review process is intended to identify and address environmental issues, the process can be stalled or delayed over issues that lack regulatory clarity, and this often results in extensive review or even litigation, either of which can significantly increase the time required to complete permitting in Minnesota.

Additional Needs of Stakeholders

In addition to identifying stakeholder needs via structured interviews, NRRI identified broader societal needs via an ethnographic study. The insights from this study are summarized below.

- Mercury impaired waters: The Final Environmental Impact Statement (FEIS) for the NorthMet Project states that the project would deposit 164 pounds of mercury in the hydrometallurgical residue facility (HRF) each year. The report states that over the course of the proposed 20-year mine life, the operation would deposit up to 3,280 pounds of mercury in the HRF along with other metals like arsenic, manganese, copper, cobalt, and lead (Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015). The Fond du Lac Band of Lake Superior Chippewa is concerned about the impacts of HRF waste release on wetland, drinking water supplies, wild rice, fisheries, and public health downstream in any direction of the proposed mining project in the event of a tailings dam failure at the proposed NorthMet's HRF waste facility (Fond du Lac Band of Lake Superior Chippewa v. Thiede, Calkins, Polymet Mining Inc, 2020). Moreover, the FEIS points out that the wastewater treatment facility at the proposed NorthMet project would be designed to meet water quality based effluent limits that are protective of the Great Lakes Initiative (GLI) chronic wildlife standard of 1.3 ng/L mercury, but this limit exceed the Fond du Lac Band's human health chronic standard of 0.77 ng/L (Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015). Furthermore, the existing water quality data collected by the MPCA near the NorthMet project indicate that mercury values consistently exceed Class 2B water quality standards in many of the lakes and rivers in the NorthMet Project Proposed Action area. Because of this, the Fond du Lac Band is concerned that any new or expanded discharges to the St. Louis River upstream may adversely affect mercury bioaccumulation in fish in the St. Louis River. Mercury bioaccumulation is a particular concern to tribal authorities, as many tribes rely on fish for subsistence and cultural practices. Under the Clean Water Act (section 401) or Clean Air Act (section 301 (d)), Anishinaabe Tribes can enact water or air quality standards for the reservation when discharges upstream or upwind of a reservation have the potential to exceed those standards (U.S. Environmental Protection

Agency, 2021). Since the enactment of section 301(d) of the Clean Water Act, in-stream mercury concentrations in the St. Louis River have been exceeding the Fond du Lac Band’s human health chronic standard (Fong, 2022).

- Climate change: There is a growing emphasis on limiting global warming to 1.5 °C by 2050 as called for in the Paris Agreement. Many governments and international climate panels have proposed agendas to achieve net-zero carbon dioxide emissions by 2050 as well. However, numerous industries, including the chemicals, cement, and metal industries, cannot readily avoid carbon emissions. To minimize carbon emissions from such carbon-intensive industries, it is essential to deploy some form of carbon capture and storage (CCS) (United States Department of State and the United States Executive Office of the President, 2021). Mafic and ultramafic rocks like basalts, gabbros, peridotites, and their metamorphosed equivalents (greenstones) have mineral assemblages with the potential to sequester carbon dioxide (CO_2). Recent studies presented by Mineralogic (Diedrich, 2022) at the 2022 Minnesota Minerals & the Green Economy Forum reveal that the geology of the Duluth Complex and Tamarack complex is particularly amenable to carbon mineralization. However, studies by Santos et al. (2015) note that during carbon mineralization, olivine minerals – present in mafic and ultramafic rocks – convert the silicates (mainly forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4)) into carbonates and silica. This reaction is exothermic and is, thus, thermodynamically favored. The reaction mechanism contains three main steps: the dissolution of CO_2 in the aqueous solution to form carbonic acid; the dissolution of magnesium in the aqueous solution, and the precipitation of magnesium carbonate. However, Santos et al. note that dissolution of alkaline earth elements is the rate-limiting step, and as a result, the primary challenges in scaling mineral carbonization techniques are related to improving the dissolution kinetics of alkaline earth elements from silicates using a wide range of additives and varying operating conditions such as temperature, pressure, CO_2 concentration, solid to liquid ratio, and particle size. Minnesota has significant amounts of these rock types, and further research to characterize their potential and applicability for carbon sequestration is necessary. The hydrometallurgical research tools identified in this research will help gather data related to:
    - impact of temperature, humidity, particle size, and surface area of the olivine mineral on mineral dissolution;
    - impact of pH, temperature and availability of cations, such as magnesium (Mg) and calcium (Ca) on the rate of carbonate mineral precipitation; and
    - develop maps of mafic and ultramafic rocks that include their mineral content and estimates of their potential rates of CO_2 uptake through carbon mineralization.
- Electrification powered by renewables: To reduce carbon footprints, stakeholders across a range of industries have been making strides to substitute electricity for fossil fuels. Accelerated adoption of renewable energy sources, battery storage systems, electric vehicles, and electrification of heating are predicted to increase the demand for nonferrous metals like copper, nickel, manganese, cobalt, vanadium, platinum group elements, rare earth elements, lithium, and aluminum (Deloitte, 2021). However, the mining industry faces several challenges to meet this increasing demand, including but not limited to: 1) supply chain disruption brought on by the COVID-19 pandemic and geopolitical crises; 2) social expectation on ethical sourcing of metals from conflict-affected areas; 3) the steady decline in discovery rates for new ore bodies via mineral exploration; and 4) declining ore grades that are simultaneously associated with increases in waste generation, energy and water consumptions, and carbon emissions brought on by more extensive processing. To overcome these challenges, there is a strong demand for

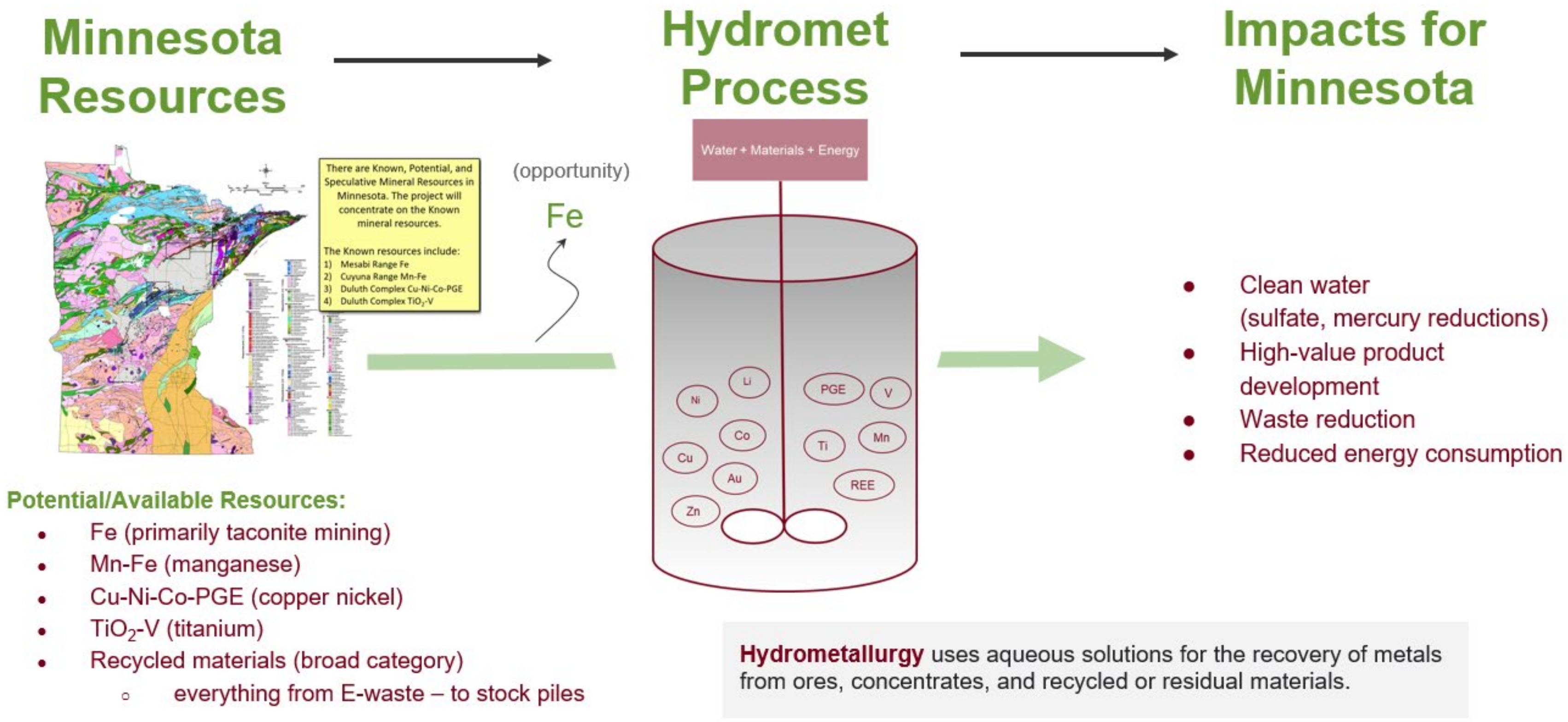
technologies that can improve both water and energy efficiencies, minimize waste generation and pollution, and improve recycling rates of critical metals, as well as produce value-added materials to support a carbon-neutral economy.

Part IV: Emerging Hydrometallurgical Technologies

One of the primary objectives of this research was to identify current and emerging hydrometallurgical technologies with applications for processing Minnesota mineral and waste resources. Based on inputs from stakeholders, NRRI focused on gathering more information on emerging technologies that could potentially:

1. Diversify the state’s minerals economy;
2. Enable conversion of waste to value opportunities;
3. Assess carbon mineralization potential of local geological formations and waste resources; and
4. Advance technology readiness levels of emerging hydrometallurgical technologies that help protect our water resources, create new jobs, and enhance the competitiveness of the state's minerals economy.

The following sections focus on emerging technologies that have been demonstrated at lab and pilot scale elsewhere and have or have not been demonstrated using Minnesota’s mineral and waste resources. (Note: the list is not exhaustive.) Hydrometallurgical technologies that are commercially practiced in the United States and rest of the world are listed in Appendix C. Note that the report does not delve into conventional hydrometallurgical technologies with limited evidence of previous application to Minnesota mineral resources. Figures 4 and 5 summarize NRRI’s research focus in hydrometallurgy and technologies with applications for processing Minnesota’s mineral and waste resources.



Minnesota Resources

There are Known, Potential, and Speculative Mineral Resources in Minnesota. The project will concentrate on the Known mineral resources.

The Known resources include:

1) Mesabi Range Fe
2) Cuyuna Range Mn-Fe
3) Duluth Complex Cu-Ni-Co-PGE
4) Duluth Complex TiO_2-V

(opportunity)

Fe

Potential/Available Resources:

- Fe (primarily taconite mining)
- Mn-Fe (manganese)
- Cu-Ni-Co-PGE (copper nickel)
- TiO_2-V (titanium)
- Recycled materials (broad category)
    - everything from E-waste – to stock piles

Hydromet Process

Water + Materials + Energy

Hydrometallurgy uses aqueous solutions for the recovery of metals from ores, concentrates, and recycled or residual materials.

Impacts for Minnesota

- Clean water (sulfate, mercury reductions)
- High-value product development
- Waste reduction
- Reduced energy consumption

Figure 4. NRRI's vision for application of hydrometallurgical technologies to Minnesota resources.

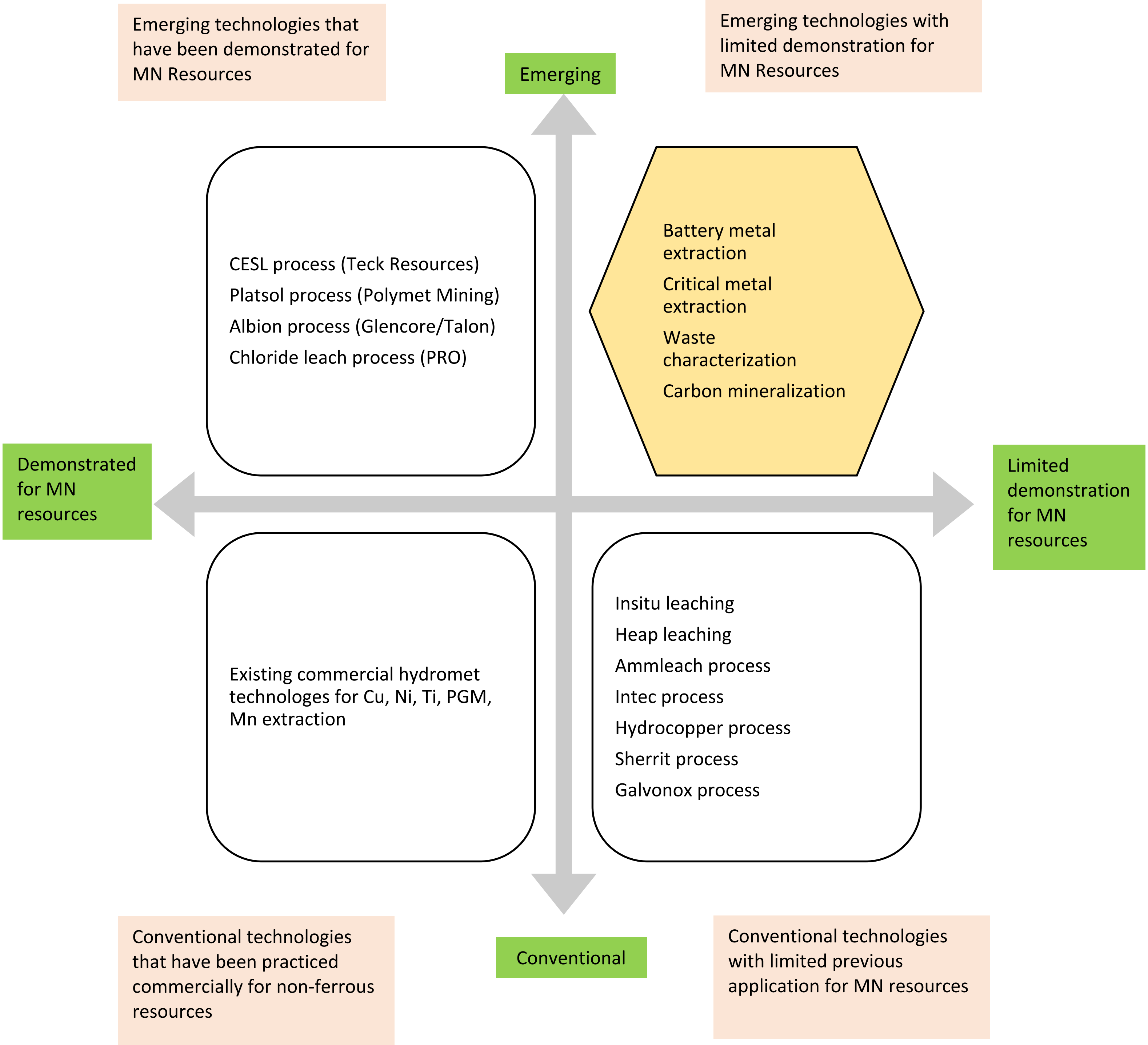


Figure 5. Hydrometallurgical technology categories and their relevance to Minnesota resources.

Emerging technologies with limited demonstration to Minnesota resources

The technologies in this category have been demonstrated at lab- and pilot-scale elsewhere but have not been applied to Minnesota's mineral and waste resources. As such, the relevance of these technologies to Minnesota's mineral and waste resources includes significant research and development opportunities. The technologies in this category have been sub-categorized into four groups based on their end-use application: 1) battery metals for energy storage technologies; 2) critical metal extraction technologies; 3) carbon mineralization technologies; and 4) heavy metal capturing technologies.

In some cases, hydrometallurgical technologies support the production of feedstocks or secondary materials for these emerging technologies. In other instances, the hydrometallurgical technologies enable the production of value-added material from mineral- and waste resources. An attempt has been made to identify potential applications of these technologies to Minnesota specific resources. Table 3 summarizes the feedstock requirements for these technologies and detailed descriptions of each can be found in Appendix B. A few notable examples of emerging technologies are:

- Hydro-to-Cathode™ technology converts mixed streams of waste lithium-ion batteries into various nickel manganese cobalt (NMC)-based cathode active materials, resulting in 50% reduction in cost and 93% reduction in emissions compared to the production of virgin cathodes from newly mined material (Ascend Elements, 2021).
- 100% of industrialized iron-based cathode manufacturing is currently located in China, threatening the long-term scalability of electrification in the United States. Mitra Chem, a Silicon Valley startup, aims to boost the production of iron-based cathodes for electric vehicles and stationary storage in the United States (Mitra Chem Technologies, 2021).
- The One Pot Process enables the production of cathode materials directly from nickel, manganese, and cobalt metal powders, thus eliminating the need for metal sulfate salts as a starting feedstock material. As a result, the process eliminates sulfate waste, generation of wastewater, and added shipping costs (Nano One Materials Corp., 2021a, 2021b, 2021c).
- Iron Salt Technology is designed for storage of renewable energy from wind and sun. The iron-based electrolyte is non-flammable and is mostly pure water. The low cost and abundant availability of iron-based storage media offers a potential to shape the future of energy storage beyond lithium (VoltStorage GmbH, 2021).
- Our Next Energy (ONE), a Michigan-based startup, has designed a battery pack that can extend the driving range of an electric vehicle to 750 miles on a single charge. The higher energy density of manganese-based cathodes translates into longer range, while the lithium iron phosphate cathode chemistry reduces costs and eliminates fire risks by eliminating the use of more expensive nickel and cobalt chemistry (Our Next Energy, 2021).
- Phoenix Tailings, a University of Connecticut-affiliated startup, is working to build a solution to extract critical metals from legacy tailings ponds (Small Business Innovation Research (SBIR), 2020; Severance, 2020).
- Redwood Materials, a Nevada-based startup, is creating a circular supply chain for batteries and helping partners across the electric vehicle and clean energy industries by providing pathways, processes, and technologies to recycle and remanufacture lithium-ion batteries (Redwood Materials, 2021).

- Nth Cycle, a Boston-based startup that has developed an electro-extraction technology to extract critical metals from batteries, e-waste, low-grade ore, and mine tailings (Nth Cycle, 2021).
- Heirloom Carbon is a San Francisco-based startup that aims to enhance carbon mineralization to help minerals absorb CO_2 from the ambient air in days, rather than years. Heirloom Carbon Technologies asserts it can obtain carbon removal for $50 a ton and aims to remove one billion tons by 2035 (Temple, 2021).
- Tusaar Corp has developed a biocarbon sorbent for removal of lead, mercury, uranium, and other toxic metals from water and the environment (Tusaar Corp, 2022).
- Claros Technologies, a University of Minnesota startup, has developed a ''Clarosorb Hg" sorbent that captures toxins like mercury and PFAS. The sorbent finds application in a variety of industries, including industrial water treatment, watershed management, and air pollution control (Claros Technologies, 2022).
- Blue Planet Systems, a Silicon Valley-based start-up, has developed a geomimetic mineralization technology, which uses CO_2 from any source and at any concentration as a feedstock to create carbon-negative aggregate. Blue Planet’s process uses carbon dioxide exactly as it comes out of the power plant without having to purify it (an energy and capital-intensive process) and turns it into calcium carbonate, essentially artificial limestone (Pultarova, 2019).

Table 3. Summary of emerging technologies and their potential applications to Minnesota resources (United Nations, 2022).

Technology Group	Emerging Technology	Technology Function	Feedstock Requirements	Emerging Applications of Hydrometallurgy to Minnesota-Centric Resources
Battery Materials for Energy Storage Technologies	One Pot Process	Production of higher performance cathode materials	Pure metallic powders (e.g., Co, Mn, Ni); lithium carbonate	Hydromet may allow production of high-purity nickel, cobalt, manganese metal powders from Cu-Ni-Co-PGM, Mn-Fe, Ti-V or waste batteries.
	Battery Grade Nickel Sulfate	Production of raw materials for battery manufacturing	Nickel sulfide concentrate	Hydromet may allow production of battery-grade nickel sulfate powders from Cu-Ni-Co-PGM or waste battery resources.
	Battery Grade Manganese Sulfate	Production of raw materials for battery manufacturing	Manganese oxide or carbonate ores	Hydromet may allow production of battery-grade manganese sulfate powders from Mn-Fe resources
	Direct Nickel Process	Production of mixed hydroxide precipitate for the EV battery industry	Nickel laterite ores	Hydromet may allow production of hydroxide precipitate from potential olivine-rich Ni/Co resources.
	Hydro-to-Cathode Technology	Transforms old batteries into advanced battery materials	E-waste (Li-ion batteries)	Transform old batteries into advanced battery materials using hydrometallurgical techniques
	Li-cycle Spoke & Hub Technology	Process for recovery of critical materials from all types of lithium-ion batteries	E-waste (Li-ion batteries)	Li-Cycle's hydromet technology may allow production of lithium carbonate, nickel sulfate, cobalt sulfate, and manganese carbonate from waste batteries
	Iron Salt Technology & Vanadium Redox Flow Technology	Long duration battery for ensuring grid scale base load	Vanadium-based liquid electrolyte	Hydromet may allow production of vanadium- and iron-based compounds from Ti-Fe-V resources

Technology Group	Emerging Technology	Technology Function	Feedstock Requirements	Emerging Applications of Hydrometallurgy to Minnesota-Centric Resources
		capability of wind and solar parks	and iron-based electrolyte	
	Iron-Based Cathode by Mitra Chem Technologies	Production of iron-based cathodes for the electric vehicle and energy storage market	Battery grade iron compounds (e.g., iron sulfate, iron oxide, etc.)	Hydromet may allow production of iron compounds suitable for Lithium-iron-phosphate (LFP) applications
Critical Metal Extraction Technologies	Electro-Extraction Technology by Nth Cycle	Recover critical minerals from separated e-waste, low-grade ore, and mine tailings	Critical minerals from e-waste, low-grade ore, and mine tailings	Nth Cycle's electro-extraction process enables production of critical metals such as Ni, Co, Cr, Mn, Ti, Cu, and PGM
	Re-mining technology by Phoenix Tailings	Recovery of critical raw materials used in: cell phones, automobiles, aerospace and more from old legacy tailings	Mine tailings	Phoenix Tailings hydromet-based technology may allow production of iron compounds, titanium, alumina, and rare earth elements
	Catalytic leaching technology by Jetti Resources	Extract copper from low-grade primary sulfides such as chalcopyrite	Copper concentrate	Jetti's process may allow recovery copper from Cu-Ni-Co-PGM resources at atmospheric temperature and pressure
Mineral Carbonization	Carbfix	Provides a natural and permanent solution to store CO_2	Geological formations containing mafic and ultramafic rocks	Evaluate the in-situ CO_2 sequestration potential of various rock formations in Minnesota

Technology Group	Emerging Technology	Technology Function	Feedstock Requirements	Emerging Applications of Hydrometallurgy to Minnesota-Centric Resources
	Carbin Minerals	Enables mines to become massive carbon sinks while producing the metals needed to drive the clean energy transition	Mine tailings	Evaluate the in-situ CO_2 sequestration potential of various rock formations in Minnesota
	UBC's CO_2 mineralization and concurrent metal extraction	CO_2 sequestration and critical metal extraction	Ca-Mg rich mafic & ultramafic rocks containing Ni-Co & PGMs	UBC's process may allow simultaneous CO_2 sequestration (ex-situ) as well as Ni-Co-PGM extraction from Cu-Ni-Co-PGM resources
Heavy Metal Capturing Technologies	Sulfur Based Sorbents	Adsorption of mercury from water	Mine drain containing mercury	Sulfur-based sorbents may allow mercury capture from potential discharges to mercury-impaired waters
	Tusaar Corp' Biocarbon Sorbent	Adsorption of mercury and other heavy metals from water		Biocarbon-based sorbents may allow mercury capture from potential discharges to mercury-impaired waters
	Zero Valent Iron (ZVI) Technology	Removal of selenium from water	Waste tailings and rocks capable of releasing selenium and other heavy metals	Apply zero-valent-iron to potentially capture selenium and other heavy metals from industrial discharges
	Advanced Biological Metals (ABMet) Technology	Removal of selenium from water		Biological remediation techniques may allow capture of selenium and other heavy metals from potential discharges

Technology Group	Emerging Technology	Technology Function	Feedstock Requirements	Emerging Applications of Hydrometallurgy to Minnesota-Centric Resources
	Saturated Rock Fill (SRF) Technology	Removal of selenium from water		Apply SRF technology to prevent oxidative dissolution of pyrite that leads to release of Se and nitrate ions into water

Part V: Strategic Fit of Emerging Technologies to NRRI Core Competencies

NRRI is an applied research organization whose mission is to deliver integrated research solutions that value our resources, environment, and economy for a sustainable and resilient future. NRRI's research informs decisions on natural resource utilization and drives economic opportunities for the State of Minnesota and beyond. The economy of the future will be defined by the natural resource nexus of water, energy and materials within the sustainable development nexus of the environment, economy and society.

Several challenges were noted from the VOC stakeholder engagement survey, including:

- Timeliness of environmental review and permitting process
- Need for advanced processing and environmental characterization laboratory
- Need for value-added products
- Complementary techniques to hydrometallurgical techniques
- Diversification of minerals economy
- Protecting water resources and mitigating mine drainage
- Reuse and recycling of critical metals
- Mercury impaired waters
- Climate change
- Minerals required to support clean energy technologies

Table 4 describes the alignment of NRRI's mission and core competencies with stakeholder needs and Figure 6 plots those needs against NRRI's core competencies. Permitting timelines for new development projects is a concern for stakeholders, but because NRRI is not a regulatory agency, this topic is outside the scope of work for NRRI. However, NRRI could potentially supply experimental data to support the environmental impact assessments of emerging hydrometallurgical technologies. Similarly, the safety of tailings storage facilities is a concern for stakeholders; NRRI's current research competencies do not focus on geotechnical stability of tailings dams.

Based on surveys, five key stakeholder needs aligned with NRRI's core competencies. These were: 1) feasibility of battery metal extraction for renewable energy storage systems from Minnesota's mineral and waste resources; 2) defining beneficiation characteristics for regional critical mineral resources; 3) potential mine drainage assessment from potential waste resources via accelerated aging; 4) characterization of mineral formations and waste tailings for permanent sequestration of CO_2; and 5) mercury removal treatment technologies.

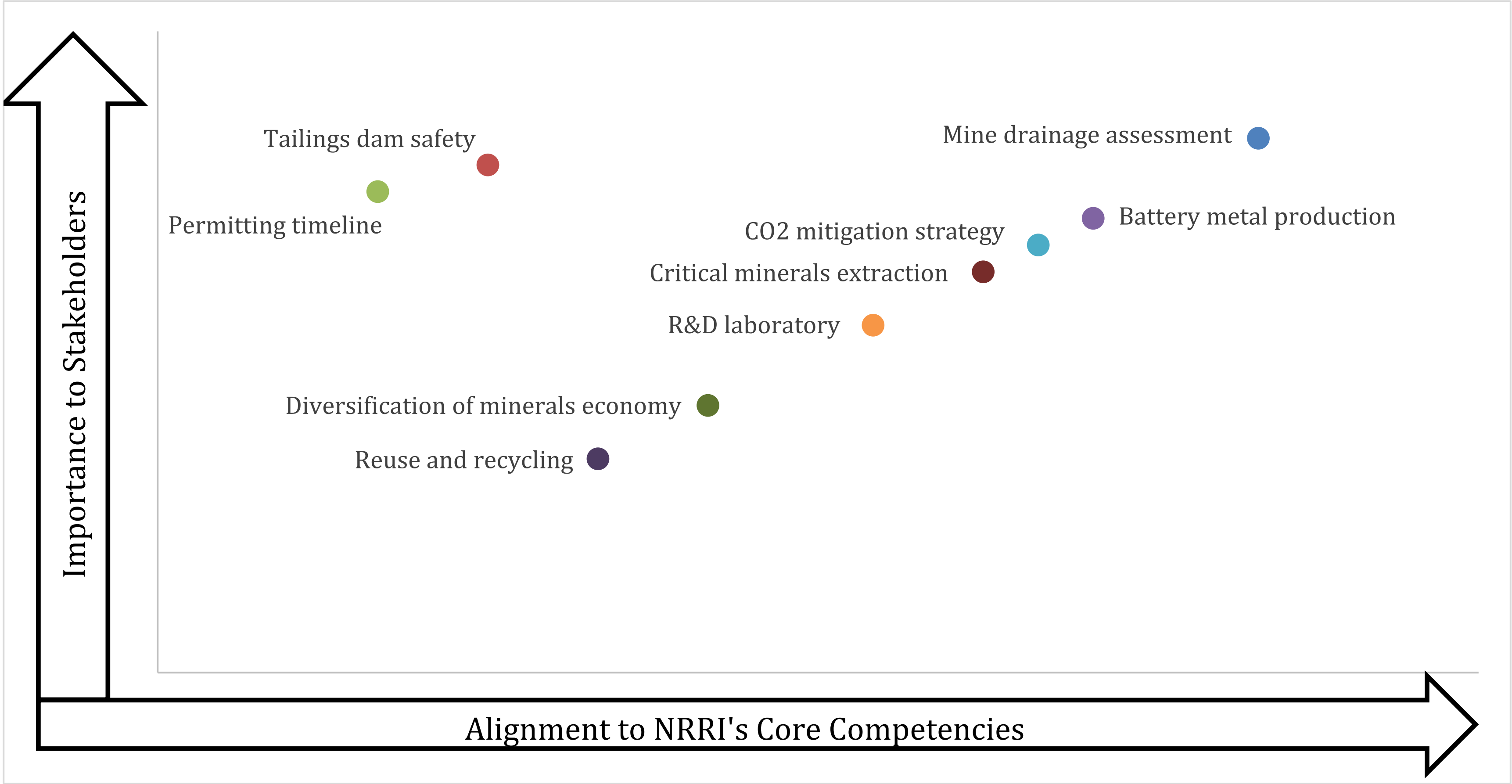


Figure 6. Relevance of stakeholder issues to NRRI's core competencies.

Table 4. Alignment of stakeholder needs to NRRI's core competencies.

Stakeholder Needs	Emerging New Technologies	NRRI Mission Alignment	Research Relevance to Minnesota
Battery metal extraction and long-duration energy storage technologies	1. One Pot Process (Nano One) 2. Iron Salt Technology & Vanadium Redox Flow Technology (Volt Storage) 3. Direct Nickel Process (Altilium Group, 2021) 4. Catalytic leaching technology (Jetti resources) 5. Hydro-to-Cathode Technology (Ascend Elements) 6. Iron-Based Cathode (Mitra Chem Technologies)	1. Implement new processes and introduce new products derived from Minnesota ores and waste resources 2. Energy and storage siting in Minnesota 3. Diversify Minnesota's mineral portfolio 4. Maximize the value of mined materials while minimizing the risk	1. Implement new processes and introduce battery materials from Minnesota's copper, nickel, iron, manganese, titanium and vanadium resources 2. Support the development and commercialization of mineral projects by collaborating with other public and private entities to create a climate where private investment is encouraged and new technology and process innovation is supported
Critical metal extraction technologies	1. Phoenix Tailings-Re-mining technology 2. Lilac Solutions Ion-Exchange Technology 3. Nth Cycle Electro-Extraction Technology 4. Li-Cycle Spoke & Hub Hydrometallurgical Technology	1. Resource conservation and innovative utilization 2. Identify, quantify, and characterize mineral-based secondary products 3. Pursue value-added product development and technology opportunities	1. Implement new processes and introduce high-value-added materials from Minnesota's e-waste, low-grade ores, and mine tailings 2. Encourage deployment of new technologies in rural Minnesota that add value to Minnesota's minerals
Heavy-metal-capturing technologies	1. Sulfur-based sorbents 2. Nano selenium sponges (Claros Technologies) 3. Biocarbon sorbent (Tusaar Corp) 4. Zero Valent Iron (ZVI) 5. Advanced Biological Metals (ABMet) 6. Saturated Rock Fill (SRF)	1. Promotes water quality and equity 2. Remediation strategies to improve degraded ecosystems 3. Allows management of water resources in a sustainable way that allows for efficient use of the resources by humans and wildlife	1. Supports First Nations and Indigenous heritage protection 2. Helps future industries to gain social license to operate with Indigenous communities 3. Facilitates delisting of 27% of the total inventory of mercury-impaired waters in Minnesota (Minnesota Pollution Control Agency, 2022) 4. Helps achieve Fond du Lac Band's human health chronic standard of

Stakeholder Needs	Emerging New Technologies	NRRI Mission Alignment	Research Relevance to Minnesota
			0.77 ng/L mercury from potential mine/municipal discharges (Fong, 2022) 5. Helps demonstrate new control technologies for containing and treating acid mine drainage that can be associated with mining
Mineral carbonization technologies	1. Carbfix Technology 2. Carbin Minerals 3. Direct Air Capture via Enhanced Weathering (DACEW)	1. Promotes decarbonization strategies 2. Carbon capture and storage siting in Minnesota 3. Utilizes Minnesota's inventory of carbon-reactive minerals to capture CO_2 4. Support for demonstration projects of new technical developments that show good promise for enhancing the competitiveness of Minnesota mines	1. Understand the spatial distribution of Mesoproterozoic Duluth Complex rocks (OUIs) and how that relates to CO_2 storage 2. Characterize the carbon storage capacity of waste mineral resources in Minnesota via ex-situ carbon mineralization 3. Understand challenges specific to scaling carbon mineralization technologies in Minnesota 4. Evaluate the chemistry and carbon reactivity of different rock types, the porosity and permeability of the potential reservoir, and its pressure and temperature state during CO_2 injection and mineralization 5. Evaluation of the potential effect of geochemical contamination from in-situ carbon mineralization 6. Evaluate the impact of carbon mineralization on terrestrial, coastal, and Lacustrine environments

Part VI: Research Priorities for NRRI

Based on the VOC survey, funding availability for each opportunity, and alignment with NRRI core competencies, five key research opportunities were identified. The proposed research emphasizes creating solutions to help utilize Minnesota's mineral- and waste resources in a manner consistent with the United Nations' definition of "sustainability" (United Nations, 2022).

- Defining Beneficiation Technologies for the Production of Battery-Grade Materials from Minnesota's Mineral and Waste Resources
  In Minnesota, Cu-Ni±PGE and Ni-Cu±PGE mineralization is associated with the Duluth Complex and the Tamarack Intrusive Complex, respectively. Historical recovery studies have investigated three different processing routes for nickel extraction from these resources, including:
  1) flotation concentration that produces smelter grade nickel concentrates;
  2) hydrometallurgical processing that includes pressure oxidation leaching (PLATSOL™ and CESL) to process nickel concentrates into upgraded nickel-cobalt hydroxide products; and
  3) hydrometallurgical processing that includes atmospheric oxidative leaching (ALBION Process™ and Mixed-Chloride Technology) to solubilize nickel from nickel concentrates. These leaching and related impurity removal techniques are not optimized for battery-grade nickel production, and instead result in intermediate nickel products. With accelerated adoption of electric vehicles (EVs), Deloitte forecasts a 10-to-20-fold increase in demand for battery-grade nickel by 2030, which could potentially intensify if nickel becomes a critical catalyst in the hydrogen economy (Deloitte, 2021). Further research is necessary to upgrade regional mineral and waste resources to battery-grade products like nickel sulfate (see Table 8 for product specification), high-purity manganese sulfate monohydrate, and lithium titanium oxide. NRRI may explore emerging hydrometallurgical technologies that allow production of battery grade metals required for the production of cathode active materials from regional virgin ores, intermediate mixed hydroxide precipitates (MHP), and waste scrap materials, while understanding the impacts on water consumption, waste generation, and production costs. Appendix A shows how analytical tools like ICP-MS and research process equipment like Armfield Reactors, Applikon Dependable Instruments Benchtop Reactor, and Büchi AG miniPilot Reactor can be used in these research efforts.

- Waste Rock Characterization Via Accelerated Aging
  Historically, humidity cell tests are used to: 1) simulate geochemical weathering (natural oxidation) processes; 2) determine the rate of acid generation and variation over time in leachate water quality; 3) provide a preliminary assessment of acid rock drainage (ARD) control options; and 4) evaluate potential solid materials generated by the weathering process (ASTM International, 2018). Humidity cell tests often last from weeks to years and typically require data collection on a seven-day cycle; as a result, they usually involve significant time and expense. Moreover, determination of acid drainage potential from a humidity cell test is often inconclusive due to failure to deplete neutralization potential to levels at which acid generation becomes measurable (U.S. Environmental Protection Agency (EPA), 1994). NRRI may consider conducting experiments utilizing a pressurized reactor to evaluate accelerated aging, which may allow collection of relevant humidity cell data over a shorter period.

- Mapping Domestic Critical Mineral Resources and Defining Beneficiation Technologies
  Minnesota contains a variety of critical minerals resources including cobalt, manganese, platinum group elements, titanium, and vanadium. Current NRRI research associated with the US Geological Survey Earth Mapping Resources Initiative program (Earth MRI) will improve our understanding of critical mineral resource potential within the state (United States Geological

Survey, 2021). NRRI has identified advanced processing tools that may be suitable for critical mineral processing within Minnesota, including the Magotteaux Mill, Attritor Mill, Computerized Laboratory Flotation Cell, Ore Sorting, Reflux Classifier, which will help assess the beneficiation characteristics of critical mineral resources, and the Parr Bench-Top Autoclave Reactor, Armfield Reactors, Applikon Dependable Instruments Benchtop Reactor, and Büchi AG miniPilot Reactor, which will support investigations that assess amenability of ore samples to hydrometallurgical processing.

- Characterization of Mineral Formations and Waste Tailings for Permanent Sequestration of CO_2
  The Intergovernmental Panel on Climate Change (IPCC) suggests removing large volumes of CO_2 from the atmosphere to achieve the climate goals in the Paris Agreement (United States Department of State and the United States Executive Office of the President, 2021). One approach for atmospheric CO_2 removal is carbon mineralization, in which certain rock types containing calcium, magnesium or other elements bind with CO_2 to form carbonate minerals. Examples of rock types that contain calcium or other elements that bind CO_2 include ultramafic or mafic igneous rocks (Sandalow, et al., 2021), such as peridotite, gabbro, basalt, and their metamorphosed equivalents (greenstones), which are found throughout Minnesota and contain minerals such as olivine, pyroxene, plagioclase, zeolites, etc. However, a deeper understanding of the carbon mineralization process is required to practice at large scale (U.S. Department of State, 2021) and hydrometallurgy will play a key role in generating secondary products used in carbon mineralization process. In conjunction to CO_2 sequestration, hydrometallurgical processes may enable the extraction of energy-relevant minerals like nickel, cobalt, manganese, and vanadium from mafic and ultramafic rock (Wicks, 2022). Appendix A shows how process research tools like Applikon Dependable Instruments Benchtop Reactor, Büchi AG miniPilot Reactor, and Parr bench-top autoclave reactors support carbon mineralization and critical mineral extraction research.

- Explore Treatment Technologies to Reduce Mercury Concentration to 0.77 ng/L (the Fond du Lac Band standard)
  In-stream mercury concentrations in the St. Louis River, measured by the Fond du Lac Band, have been below the Great Lakes Initiative (GLC) Chronic Wildlife Standard of 1.3 ng/L but exceed the Fond du Lac Band's human health chronic standard of 0.77 ng/L. For this reason, the Fond du Lac Band is concerned about any new or expanded discharges to the St. Louis River upstream of the Fond du Lac Indian Reservation that could adversely affect mercury bioaccumulation in fish. Bioaccumulation of mercury in aquatic organisms is a concern to tribal authorities, as many tribes rely on fish for subsistence and cultural practices. NRRI will review the existing scientific literature for treatment technologies capable of achieving a mercury concentration of 0.77 ng/L from industrial waste discharges.

Part VII: Conceptual Design of a Hydrometallurgical Research Laboratory

Summary of Intent

The purpose of the conceptual design is to provide a foundational understanding of key laboratory tools required to support the development of emerging hydrometallurgical technologies with applications to Minnesota mineral and waste resources. As discussed in the previous section, bench-scale testing is a prerequisite to a pilot-scale program; therefore, the current effort is to devise a strategy to identify bench-scale and semi-pilot simulators to support and sustain a hydrometallurgical research facility. Because each pilot plant operation has distinct objectives, feedstocks, unit operations, scale, lifespan, operational conditions, and materials of construction, there is no “one size fits all” pilot or demonstration solution. Therefore, NRRI will focus on conducting research on bench-scale and semi-pilot scale, which requires significantly less capital expense and fewer permitting requirements.

In the event a need arises for a hydrometallurgical pilot or demonstration plant to support the development and commercialization of novel technologies, NRRI may collaborate with engineering companies or commercial laboratories (example labs are listed in Tables 7 and 8).

Hydrometallurgical Process Development

Metallurgical studies are necessary during all stages of mineral resource development beyond exploration and discovery. They provide the basis and justification for process and equipment design as well as for waste handling systems, resource estimation, environmental impacts, reclamation strategies, permitting requirements, marketability of products, and economic evaluation of proposed projects. Metallurgical studies can be carried out from bench- and pilot-scales through demonstration plants, and while progression from bench- to demonstration-scale increases complexity, timelines, and expense, it also reduces the risk associated with commercial development (McNulty, 2002). A brief overview of these testing scales and their objectives are given below.

Bench-Scale Testing

Bench-scale tests are carried out on representative samples of the anticipated feed in beakers, flasks, and small-scale simulators like batch flotation cells, leaching tanks, autoclaves, etc. These tests are carried out under well-defined chemical and physical conditions to provide reliable information about underlying principles. Ideally, bench-scale tests will determine the probable process flowsheet, physical and chemical operating conditions, anticipated product quality, and material balance for the design of the pilot plant (McNulty, 2002).

Pilot-Scale Testing

Pilot tests are performed on larger samples (few hundred kilograms to a ton) in small-scale prototypes operating intermittently or continuously, with the primary goal of confirming the results of bench-scale observations. Additional objectives could include: 1) a study of the impacts of recycled streams on final product quality; 2) production of large samples for further treatment like smelting or byproduct recovery; 3) determining the marketability of products to potential customers; 4) training plant operators; 5) generating information needed for regulators; and 6) proof of concept to help obtain financing. Pilot-scale confirmation of bench-scale results enables well-informed selection of processing unit operations, equipment size, materials of construction, and general arrangement for commercial plant layouts (McNulty, 2002).

Demonstration Plants

Demonstration plants are fully integrated collections of semi-commercial unit operations that can be used to operate successive unit processes. Feed rates for demonstration-scale plants range from a few kilograms to several tons per hour, and their primary purpose is to reduce risk of project development for novel technologies through the identification of process risks that are typically not observed in pilot plants or in short-duration campaigns (McNulty, 2002).

Laboratory Prototypes and Simulators

The following section identifies laboratory equipment needed to address stakeholder needs identified in the VOC survey, including extracting critical metals and battery grade materials from mineral and waste resources, assessing the potential for carbon mineralization, and investigating impacts of waste rocks and other waste resources on water quality, including mine water remediation.

Battery Metal Production, Critical Metal Extraction, and Carbon Mineralization

- Advanced mineral processing tools for beneficiation of ores from Cu-Ni-Co-PGE and Ti-V deposits, Fe and Mn-Fe deposits, and aggregate and byproduct resources like mine tailings, industrial residues, and electronic waste.
- Metal dissolution and CO_2 sequestration tools to evaluate amenability of samples for conventional or novel leaching technologies and carbon mineralization potential of CO_2 reactive minerals and rocks.
- Solution purification tools to allow separation and purification of leach liquors using solvent extraction, ion exchange, adsorption techniques.
- Metal recovery tools to produce high-purity metal compounds using precipitation and electrowinning techniques.

Waste Rock Characterization

- Pressurized batch reactors for accelerated aging to investigate leachate quality and dissolved metal flux from potential oxidation of waste rock, electronic waste, and/or mine tailings.

Mine Water Remediation

- Column chromatography and column leach reactors to capture mercury and other heavy metals using novel sorbents.

Hydrometallurgical Research Equipment

Table 5 lists strategic equipment identified in the VOC survey and categorized based on scale, process, function, and application. Table 6 provides a high-level budgetary capital estimates for some of the critical laboratory equipment. Note the cost does not include building, installation, and commissioning costs.

Table 5. Laboratory equipment required to support a hydrometallurgical research facility.

Laboratory Equipment	Scale	Category	Function	Potential Application
FRITSCH Mortar Grinder PULVERISETTE 2	Lab	Milling	Used for wet and dry grinding, mixing, and homogenization. The mill allows cryogenic grinding at lab-scale.	Suitable for grinding hard, medium-hard, soft, brittle, fibrous and abrasive materials prior to leaching
Magotteaux Mill™	Lab	Milling	Simulate the pulp chemical conditions of the plant grinding mill in the laboratory	Investigate the impact of grinding chemistry on extraction processes such as flotation and leaching
Union Process Attritor Mill (vertical ball mill)	Lab	Milling	Lab scale wet or dry grinding	Allows grinding under inert atmospheres, operates at controlled temperatures, overcomes product contamination, and allows estimation of precise grinding energy consumption
Laboratory Hydrocyclone Rig	Mini-pilot	Classifier	Particle classification	Prepare ground slurries for downstream metallurgical processes like flotation and leaching
Mozley Superpanner	Bench	Gravity Separator	Separates mineral grains of close specific gravity at a laboratory scale	Allows gravity separation of ilmenite, manganese iron ores, PGE minerals, and CO_2 reactive rocks
FLSmidth Reflux Classifier	Mini-pilot	Gravity Separator	Separates fine particles based on a difference in density or particle size	Investigate amenability of ilmenite ores, manganese iron ores, PGE minerals, CO_2 reactive rocks to gravity separation
Magotteaux Float Cell™	Bench	Flotation Separator	Bottom-driven float cell that allows continuous pulp chemistry monitoring	Investigate amenability of ilmenite ores, manganese iron ores, PGE minerals, CO_2 reactive rocks to flotation separation

Laboratory Equipment	Scale	Category	Function	Potential Application
LAARMANN Computerized Laboratory Flotation Cell (fully computerized)	Bench	Flotation Separator	Digitally controlled flotation cell ideally suited in duplicating plant processes and operations	Cells and impellers are designed to handle corrosive flotation conditions
Glencore L150 Laboratory Jameson Cell	Mini-pilot	Flotation Separator	Enables ultrafine particle flotation	Suitable for sulfide, non-sulfide and industrial minerals flotation
TOMRA Ore Sorting	Mini-pilot	Sorter	Sensors separate valuable mineral ores from waste rocks based on their color, atomic density, transparency or conductivity	Sensor-based ore sorting systems allows dry material separation of various ores and industrial waste materials
Bottle Roller	Bench	Leach Reactor	Simulate atmospheric leaching at lab scale	Investigate amenability of ilmenite, manganese iron ores, Cu-Ni-PGE minerals, CO_2 reactive rocks to atmospheric leaching
Armfield Reactors (fully computerized)	Bench	Leach and Precipitation Reactor	Simulates continuous stirred tank reactor, tubular reactor, batch reactor, laminar flow reactor, and plug flow reactor in lab-scale	Investigate the effect of varying the temperature, mixing speed, feed rate, etc. on reaction rate; allows determination of the residence time using tracer techniques; allows evaluation of empirical rate expressions from experimental data

Laboratory Equipment	Scale	Category	Function	Potential Application
Applikon Dependable Instruments Benchtop Reactor	Bench	Leach and Precipitation Reactor	Simulation of atmospheric leaching (mixed chloride, Albion, bacterial leaching process) and metal precipitation on a bench scale	Suitable for producing leach liquors from ilmenite ores, manganese iron ores, Cu-Ni-PGE minerals, and CO_2 reactive rocks for downstream metal extraction processes; suitable to study precipitation of metals from leach liquors
Chem Glass Jacketed Lab Reactor	Mini-pilot	Leach and Precipitation Reactor	Allows chemical process development, scale-up, process simulation and kilo-scale production	Suitable to produce large batches of leach liquors; allows simulation of precipitation and crystallization processes
Parr Bench-Top Autoclave Reactor	Bench	Pressure Reactor	Simulation of pressure oxidative leaching processes such as Platsol and CESL in lab scale	Investigate amenability of ilmenite ores, manganese iron ores, Cu-Ni-PGE minerals, CO_2 reactive rocks to pressure oxidative leaching
Column Leach Reactor	Mini-pilot	Plug Flow Leach Reactor	Simulation of bacterial heap leaching; simulation of sorbent adsorption	The reactor is suitable to study bacterial leaching of Cu-Ni-PGE minerals. Also, suitable to screen sorbents for contaminant extraction from wastewater
Bench Scale Leach Pilot Plant	Bench	Leaching Reactor	Simulation of atmospheric leaching on a continuous bench and mini-pilot mode	Suitable for low-volume low-flow continuous integrated bench and min-pilot plant extraction of metals via leaching
Parr Multiple Pressure Reactor System	Bench	Pressure Reactor	Simulation of accelerated aging at high temperature, high pressure, and with various gas compositions	Suitable to evaluate leachate quality from accelerated aging of waste rocks

Laboratory Equipment	Scale	Category	Function	Potential Application
Filter Press	Bench	Solid-Liquid Separator	Separate insoluble solids from leach liquors	Allows to separate leach liquors from solid residues for solvent extraction, ion exchange, and precipitation experiments
Thermo Scientific Benchtop Orbital Shakers Eppendorf ThermoMixer Gerhardt Thermoshake Incubator Shaker Burrell Scientific Variable Speed Wrist Action® Shaker	Bench	Liquid-Liquid Separator	Screen various organic extractants. determine reaction time, temperature, extractant concentration, salt concentration, pH, determine the number of stages and optimal aqueous-to-organic phase ratio of extraction, scrubbing and stripping based on McCabe-Thiele diagrams	Allows development of a solvent extraction process to selectively separate targeted metals ions from leach liquors
Rousselet Robatel Mixer Settler	Bench	Liquid-Liquid Separator	Simulation of solvent extraction on a continuous counter current mode	Examine the possibility of scaling up the solvent extraction process and/or producing larger volumes of purified metal solution
Bench Scale Electrowinning Pilot Plant	Bench	Electrochemical Reactor	Simulate electrowinning on a bench scale	Allows electrowinning copper, cobalt, nickel, gold, chromium, zinc and other metals
Column Chromatography	Bench	Ion Exchange/ Adsorption	Simulate ion exchange and adsorption processes in a lab scale	Allows the design of a metal-separation process using ion-exchange resins and various other adsorbents, which are mostly suitable for the selective extraction of various diluted streams and solutions

Table 6. Summary of budgetary estimate required to support hydrometallurgical research.

Component	Budgetary Estimate (as of June 2022)
Laboratory and Semi-Pilot and Analytical Equipment	$600,000 to $1.2 million
Installation and Facilities Support	$100,000-$200,000
Personnel	$200,000 to $300,000

Part VIII: Benchmarking North American Hydrometallurgical Research Facilities

This section summarizes the capabilities of some of the leading research laboratories in North America. Table 7 shows a list of some of the North American laboratories with hydrometallurgical capabilities. Table 8 summarizes a list of key research and analytical equipment of these institutions. (Note: The list is not exhaustive and does not cover some of the commercial laboratories).

Table 7. A comprehensive list of institutes and laboratories with hydrometallurgical research capabilities in North America.

Laboratory Name	Type	Location
ALS Global	Commercial	BC, Canada
COREM	Commercial	Quebec City, Canada
Hazen Research, Inc.	Commercial	Golden, Colorado
Kemetco Research Inc.	Commercial	BC, Canada
Kingston Process Metallurgy Inc.	Commercial	Ontario, Canada
Metals U.S/Intellimet	Commercial	Montana, USA
McClelland Laboratories	Commercial	Nevada, USA
Met-Solve Laboratories Inc. (Sepro-Laboratories)	Commercial	BC, Canada
Process Research ORTECH (PRO)	Commercial	Ontario, Canada
SGS Lakefield	Commercial	Ontario, Canada
Saskatchewan Research Council	State-owned	Saskatchewan, Canada
XPS Expert Process Solutions	Commercial	Ontario, Canada
Ames National Laboratory	Federal	Iowa, USA
Argonne National Laboratory	Federal	Illinois, USA
Idaho National Laboratory	Federal	Idaho, USA
Oak Ridge National Laboratory	Federal	Tennessee, USA
Colorado School of Mines	University	Colorado, USA
McGill University	University	Montreal, Canada
Missouri University of Science And Technology	University	Missouri, USA
Montana Technological University	University	Montana, USA
Penn State University	University	Pennsylvania, USA
Queens' University	University	Ontario, Canada
University of Alaska	University	Alaska, USA
University of British Columbia	University	BC, Canada
University of Kentucky	University	Kentucky, USA
University of Nevada Reno	University	Nevada, USA
University of Toronto	University	Toronto, Canada
University of Utah	University	Utah, USA
Virginia Tech	University	Virginia, USA
Worchester Polytechnic Institute	University	New York, USA

Table 8. Comparison of research capabilities of leading North American research institutes.

Laboratory Facility	Research Capabilities	Analytical Capabilities
Hazen Research, Inc., Colorado, USA	Atmospheric and Pressure Leaching, Pressure Oxidation, Crystallization, Precipitation Solvent Extraction, Ion Exchange, Electrochemistry, Solid/Liquid Separation, Rheometry/Viscometry, Roasting, Calcining, Fluid-Bed Reactors, Rotary Kilns, Induction Furnaces, Multiple-Hearth Furnace	X-ray diffraction (XRD), QEMSCAN, Electron microprobe analysis, High-resolution SEM and microanalysis, ICP–OES, ICP–MS, XRF, Flame, Cold Vapor, and Hydride AA, LECO, Wet Chemistry Methods, Ion Chromatography, Fuels Analysis
Colorado School of Mines, Colorado, USA	Leaching Systems, Precipitation Systems Sol Gel Processing, Molten Salt Electrorefining, Molten Salt Electrowinning, Molten Salt Heat Treatment Baths, High Temperature Melting Furnace, Vacuum Furnace (2200 °C)	Extrel ELQ - 400 Triple Quadruple Mass Spectrometer, Extrel ELQ - 400 LC/MS Triple Quadruple Mass Spectrometer, Perkin Elmer Q-Mass 910 GC/MS Systems, JEOL M Station High Resolution Mass Spectrometer, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Infrared Spectroscopy (FTIR), UV-Vis Spectroscopy Fluorescence Spectroscopy, Leco Interstitial Analyzers, Scanning and transmission electron microscopy (SEM/TEM/STEM), energy dispersive spectroscopy of X-rays (EDS), electron backscatter diffraction (EBSD), focused ion beam (FIB), X-ray diffraction (XRD), atomic force microscopy (AFM), and laser/Raman confocal microscopy.
Montana Technological University, Montana, USA	Leach Reactors, Solvent Extraction/Ion Exchange, Electrometallurgy, Crystallization, Gaseous Precipitation, Cementation	LEO Scanning Electron Microscope (SEM) w/ Energy Dispersive X-ray Spectroscopy (EDS), Automated Mineralogy using Mineral Liberation Analysis (MLA), TESCAN MIRA 3 - Field Emission Scanning Electron Microscope (FE-SEM), Cathodoluminescence (CL), Energy Dispersive X-ray Spectroscopy (EDS), Wavelength Dispersive X-ray Spectroscopy (WDS), Electron Backscatter Diffraction (EBSD), Automated mineralogy with TIMA-X Rigaku Ultima IV X-ray Diffractometer w/ thermal stage up to 1500 °C, Bruker S2 X-ray Fluorescence Spectrometer, Thermo Electron Duo View iCAP 6500 ICP-OES,

Laboratory Facility	Research Capabilities	Analytical Capabilities
University of Alaska, Mineral Industry Research Laboratory (MIRL), Alaska, USA	Laboratory leaching, precipitation and solvent extraction equipment	ICP/DCP, AA, XRD XRF, Electron Microprobe Analyzer (EPMA), and electron microscopes
University of Toronto, Ontario, Canada	Parr Instrument Autoclaves (2-L size); Glass Leaching Reactors (6 reactors); Auto lab Potentiostat/Galvanostat PGSTAT101 with NOVA software, Faraday Cage and RDE accessories; Bottle roll test set up for cyanidation; pH, ORP, DO and ion analyzers and controllers	Agilent Technologies Microwave Plasma Atomic Emission Spectrometry (MP-AES 4200) multi-element analyzer; Two Atomic Absorption Spectroscopy Machines; 916 Ti-Touch Titrator with silver electrode for Free Cyanide titration; STA 449 F3 Jupiter – Simultaneous Thermal Analyzer TGA DSC from Netzsch; Thermo Scientific Genesys 10S UV-Vis; ELTRA CS2000 Carbon and Sulfur Determinator; OXFORD Instruments X-Supreme X-ray fluorescence (XRF) machine, Laser Particle Size Analyzer
McGill University, Montreal, Canada	Study of the associated solution chemistry (complexation, solubilities and activities both via experimentation and chemical modeling), determination of precipitation/crystallization kinetics in batch and/or continuous reactor set-ups, or electrochemical deposition	SEM, TEM, XRD, FTIR, Raman, BET, TGA XPS; Perkin Elmer Atomic Absorption Spectrometer 311. Highly sensitive instrument (ppm level); Varian AA 240 FS Atomic Absorption Spectrometer; Horiba Laser Scattering Particle Size Analyzer; Philips PW 1710 Powder X-Ray Diffractometer; Bruker D8 Discovery X-Ray Diffractometer; X-Ray Photoelectron Spectroscopy (XPS): Thermo Scientific K-Alpha.
Kingston Process Metallurgy Inc., Ontario, Canada	Molybdenum disilicide tube furnaces (1700 °C), SiC tube furnaces (1400 °C), Resistance element furnaces (1200 °C), Induction furnace (10 kW), Mini-kiln and rotary furnaces, Fluid bed reactors (batch or continuous, as well as two stage), Controlled atmosphere molten salt electrolysis, Potentiostat for electrochemical studies, Denver flotation cell, Bench scale autoclaves, In-line HCl and Cl2, Gas scrubber facility	ICP-OES. Atomic absorption spectroscopy (AA), Custom large scale (<10 g) thermogravimetric analyzer (TGA), Variety of magnetic separators, Infrared spectroscopy/gas chromatography, Portable 300 AMU mass spectrometer, Surface profilometers, Optical microscopy/image analysis, Scanning electron microscopy, Custom differential thermal analysis (TDA), Karl-Fisher water analysis

Laboratory Facility	Research Capabilities	Analytical Capabilities
Kemetco Research, British Columbia, Canada	Leaching studies, Heap leach studies, Pressure oxidation, Roasting/reductive roasting, Bioleaching Solid-liquid separation, Precipitation and dissolution studies, Solvent extraction, Ion exchange, NF, RO, UF studies, Electrowinning	Total metals (ICP), Gold and silver, Mercury analysis, Iron speciation, Nitrogen speciation, Phosphorus speciation, Liquid chlorine analysis, Chloride, chlorate Bromine, bromide, Fluoride Iodine, Sulfur and thiosalts speciation, Cyanide speciation, TRS gas analysis, Xanthate analysis, Alkalinity, acidity, Oxidizer classification, Resin and fatty acids, Comprehensive water/wastewater characterization
Process Research ORTECH, Ontario, Canada	Pilot continuous atmospheric leaching system; Bench scale titanium and pilot scale stainless steel autoclaves for high pressure leaching with capacity of up to 50 gallons; Solvent extraction system consisting of mixer settlers; pulse column and fixed bed and continuous ion exchange systems; Lab and pilot scale liquid/solid separation equipped with thickeners and filters; Electrowinning cells for product recovery	ThermoScientific ICAP 6000 Series ICP Spectrometer; Perkin Elmer Instruments AAnalyst 100 Atomic Absorbance Spectrometer; ThermoScientific Niton FXL FM-XRF Analyzer; ELTRA CS 2000 Carbon Sulfur Determinator
Saskatchewan Research Council (SRC), Saskatchewan, Canada	Acid-roasting, Caustic cracking, Leaching, Solvent extraction, Fractional precipitation, Effluent treatment	Electron microprobe, X-ray fluorescence (XRF), ICP-OES and ICP-MS Analysis

Part IX: Skill Sets Required to Sustain Hydrometallurgical Research

The following skill sets are essential to develop and execute a hydrometallurgical research program at NRRI.

Aqueous Research Chemist/Metallurgist

This position generally requires:

- Background experience in hydrometallurgy, mineral processing, and wastewater treatment processes including flowsheet, development, bench-scale test work and pilot plant programs
- Advanced understanding of metallurgical engineering fundamentals, including heat transfer, mass transfer, fluid mechanics, chemical kinetics, thermodynamic analysis, mass and energy balance, unit operation design
- Experience in designing and developing novel chemistries and extractive metallurgical approaches in aqueous or solvent-based systems
- Experience designing and performing experiments to evaluate the feasibility and performance of new chemistries and separation technologies, including but not limited to, leaching, solid-liquid separation, water treatment and reclamation, filtration, ion exchange resins
- Experience developing and running thermodynamic and kinetic calculations and models
- The abilities to analyze experimental data and communicate results to the R&D team
- The ability to develop and implement chemical processes at the lab scale and support knowledge transfer to process engineers for system scale-up

Research Technician

This position generally requires:

- A basic understanding of laboratory instrumentation
- The ability to perform hydrometallurgical and advanced mineral processing sampling duties and test work procedures such as flotation, comminution, sizing, leaching, precipitation, solvent extraction, column chromatography and filtration
- Skills to prepare working stock, calibration, and reagent solutions as directed
- The ability to ensure research equipment functionality and provide assurance of calibration of the instruments
- The skills to operate general hydrometallurgical laboratory equipment
- Experience and abilities to perform routine maintenance on existing research instruments
- Skills to coordinate and execute test work as instructed by research metallurgists
- The ability to maintain accurate records of experiments, reagents, amounts of charges, and observations during experiments
- Skills for obtaining, preparing, and submitting samples for assay
- Knowledge and use of chemical handling and safe laboratory practices with the ability to adhere to SHE policies

Analytical Chemist

This position generally requires:

- A proficient knowledge of laboratory and quality systems
- An understanding of and the ability to apply basic analytical chemistry principles
- Skills necessary to develop and validate analytical methods, Standard Operating Procedures (SOPs) and other operating, safety, and quality documents for method development, transfer, and validation studies
- The ability to analyze data, run statistical analysis, and present findings to both technical and non-technical audiences
- The ability to perform routine operation, maintenance, calibration of analytical instruments
- Skills necessary to prepare standards and reagents as required and documents work appropriately
- Skills necessary to prepare samples for analysis
- The ability to perform sample analysis and interpret analysis data obtained from a variety of samples via ICP MS, ICP OES, AAS, IC, and XRF methods
- Skills necessary to perform analytical work related to quality assurance and sample analysis during test campaigns

Part X: Collaborators and Potential Funding Opportunities

NRRI's hydrometallurgical research seeks to develop relationship and collaboration with all parties involved in the minerals economy:

- Regional Partners: Iron Range Resources & Rehabilitation (IRRRB), Minnesota Geological Survey (MGS), Minnesota Pollution Control Agency (MPCA), Minnesota Department of Natural Resources (MNDNR), Minnesota Department of Transportation (MNDOT)
- NRRI seeks to develop relationship with Minnesota Native American/First Nations communities: Bois Forte Band of Chippewa, Fond Du Lac Reservation, Grand Portage Band of Lake Superior Chippewa, Leech Lake Band of Ojibwe, Lower Sioux Indian Community, Mille Lacs Band of Ojibwe, Prairie Island Indian Community, Red Lake Band of Chippewa Indians, Shakopee Mdewakanton Sioux (Dakota) Community, Upper Sioux Community, and White Earth Reservation.
- Federal Partners: U.S. Department of Interior's Bureau of Indian Affairs (BIA), Minnesota Chippewa Tribal Agencies, United States Forest Service (USFS), Bureau of Land Management (BLM), National Science Foundation (NSF), United States Geological Survey (USGS), U.S. Environmental Protection Agency (U.S. EPA), U.S. Department of Energy (U.S. DOE), U.S Army Corps of Engineers (USACE), US Department of Defense (U.S. DOD), Small Business Innovation Research (SBIR), Small Research Technology Transfer (STTR)
- Private Entities: Mineral Resource Companies, Battery Manufacturers, Climate Tech Companies, Energy Companies, Engineering/Environmental Consulting Firms
- Venture Capitalist Firms: SOSV, Lower Carbon Capital, Andreessen Horowitz, Prelude Ventures, Khosla Ventures, Total Energies, Energy Impact Partners, High-Tech Gründerfonds, Battery, Mercia, New Venture Associates, Wellington, General Catalyst, Kleiner Perkins, Alumni Ventures, Union Square Ventures, Clean Energy Ventures, Grey Croft, GV, Mayfield, Accel, Founders Fund, Imagine H2O
- Private Foundations: The Wells Fargo Foundation, The McKnight Foundation, The Saint Paul Foundation, The Minneapolis Foundation, Otto Bremer Trust, United Health Foundation, Medtronic Communities Foundation, The Bush Foundation, U.S. Bancorp Foundation, General Mills Foundation, Fred C. and Katherine B. Andersen Foundation, Minnesota Community Foundation, 3M Foundation, Northwest Area Foundation, The Hormel Foundation, The Blandin Foundation, Carl and Eloise Pohlad Family Foundation, Target Foundation, Central Minnesota Community Foundation, Best Buy Foundation, Curtis L. Carlson Family Foundation, Land O'Lakes Foundation, F. R. Bigelow Foundation, The Cargill Foundation, The Xcel Energy Foundation, Andreas Foundation, The St. Paul Travelers Foundation, Ecolab Foundation, Northland Foundation, Patrick and Aimee Butler Family Foundation, CHS Foundation, RBC Foundation, George Family Foundation, I.A. O'Shaughnessy Foundation, Blue Cross and Blue Shield of Minnesota Foundation, Initiative Foundation, J.A. Wedum Foundation, Grantham Foundation.

Part XI: Summary and Recommendations

The commercial development of new mineral and waste resources requires mineral exploration, mineral characterization, mineral processing development, feasibility analysis, environmental impact assessments and regulatory permits to proceed. Some regional mineral deposits and waste resources listed in this report are complex and relatively low grade, and conventional smelting and refining technologies (high-temperature processes) are most likely not feasible to convert these resources into high-value products required for the clean energy technologies. To address significant environmental impact concerns associated with mining, collection and processing of these materials, new processing technology approaches with reduced water and energy consumption and minimal environmental footprints are needed to support production of value-added products. Emerging hydrometallurgical processing technologies offer promising opportunities.

This report provides a summary of the following:

1. Minnesota's mineral and waste resources that have the highest potential for hydrometallurgical processing.
2. Challenges anticipated by stakeholders during the commercial development of mineral and waste resources using hydrometallurgical technologies.
3. Emerging hydrometallurgical innovations that may resolve various challenges identified by means of the stakeholder engagement survey.
4. Research priorities that support development of emerging hydrometallurgical technologies for Minnesota's mineral and waste resources.
5. Bench-scale and semi-pilot laboratory tools that will allow NRRI to initiate research for advancing technological readiness level of emerging hydrometallurgical technologies.

1. Minnesota Resources Amenable to Hydrometallurgical Processing

Minnesota possesses a variety of mineral and waste resources that could be efficiently and safely extracted and processed using hydrometallurgical technologies. These include:

- Copper-nickel-platinum group element (Cu-Ni-PGE) resources of northeastern Minnesota's ~1.1-billion-year-old Duluth Complex,
- Nickel-copper-platinum group element (Ni-Cu-PGE) resources in satellite Mid-Continent Rift-related intrusive rocks such as those in the Tamarack Intrusive Complex,
- The ~1.1-billion-year-old titanium-iron vanadium deposits in oxide ultramafic intrusions (OUIs) along the western margin of Minnesota's Duluth Complex,
- Copper-zinc deposits and gold-silver deposits associated with Minnesota's ~2.7-billion-year-old greenstone belts,
- Iron-manganese (Fe-Mn) deposits in the Cuyuna District of east-central Minnesota,
- Aggregate and byproduct resources that occur across the state and which may contain recoverable quantities of critical metals,
- Incinerator ash from Minnesota's coal-burning power plants and waste-to-energy facilities which can contain a variety of critical metals, and
- Electronic waste (e.g., e-waste or waste electrical and electronic equipment), which can contain a variety of critical metals.

2. Challenges and Opportunities Anticipated During Resource Development

The study summarizes the challenges and constraints anticipated by various stakeholders during the commercial development of these resources as gathered through a VOC survey and ethnographic study.

- Domestic supply of critical metals: The United States is increasingly reliant on foreign imports for its domestic consumption of critical metals (Department of Interior, 2018). Advanced hydrometallurgical technologies are necessary to determine the feasibility of extracting critical minerals from domestic mine tailings, in-ground critical mineral resources, and recycled materials such as e-waste.
- Diversification of minerals economy: Fluctuating demand and price for iron and steel products causes frequent shutdowns to Minnesota iron ore mines, resulting in job losses and more frequent negotiation of taconite royalties with the State. Advanced hydrometallurgical processing facilities are necessary to support a diversified minerals economy and lessen the negative impact of downturns in the iron and steel industry.
- Impact of water quality: Predicting and managing water quality degradation from mining to minimize risks to human and environmental health is a key challenge facing the minerals industry. Advanced waste characterization tools may enhance the knowledge on potential environmental impacts of some of the less explored mineral and waste resources.
- Mercury impairment: Bioaccumulation of mercury in aquatic organisms is a concern to tribal authorities, as many tribes rely on fish for subsistence and cultural practices. Tribal authorities are concerned that existing impairments will make the cumulative effects of mercury from new or expanded mine discharges greater. Technologies that help to meet the Fond du Lac Band’s human health chronic mercury standard of 0.77 ng/L will assist the future industries to maintain social license to operate.
- Absence of local research laboratories: Current and prospective private and public mineral rights-holders and academic researchers rely on international laboratories to support their geometallurgical, advanced processing, and environmental testing and research programs, resulting in lengthy delays to complete the environmental impact assessments and process development programs.
- Reliance on foreign smelters for processing: Rising transportation, toll smelting, and refining costs negatively impact economic viability of local companies that may rely on international smelters for further processing of mineral concentrates. Research to evaluate the feasibility of producing value-added products regionally may help create domestic supply chain for critical metals, high value return to the state, and increase in jobs.
- Technology constraints: To meet stringent quality standards, conventional metallurgical smelters and refineries demand a high-quality concentrate with low impurity levels. However, historical studies have demonstrated technical difficulties to produce smelter grade concentrates from Minnesota’s ore copper, nickel, PGE, ilmenite, and manganese resources. For instance, the challenge with regional Cu-Ni-PGM concentrates has been to separate the Cu and the Ni into concentrates that have acceptable payabilities with acceptable recoveries.

3. Emerging Opportunities

This research describes emerging areas that might benefit from application of hydrometallurgical technologies including:

1) Battery metal extraction from in-situ mineral and waste resources,
2) Critical metal extraction from waste tailings, low-grade ores, and urban wastes,
3) Mercury and heavy metal capture from metallurgical waste streams, and
4) Production of secondary products used in CO_2 storage via carbon mineralization.

4. Key Research Priorities

To support the development and commercialization of emerging technologies listed above, the following research and development priorities have been identified via the VOC survey:

- Define viable hydrometallurgical technologies to produce high-value materials from Minnesota's mineral and waste resources;
- Explore the potential applications for hydrometallurgical techniques to understand the environmental impact of waste rocks and tailings via accelerated aging; and
- Understand the potential applications of hydrometallurgical techniques to create secondary products that could potentially allow CO_2 sequestration.
- Explore hydrometallurgical technologies to reduce mercury concentration from potential process waste to below 0.77 ng/L (the Fond du Lac Band standard).

Conceptual Design of a Hydrometallurgical Research Facility

This research has identified capital required to support a laboratory and semi-pilot facility focused on developing emerging hydrometallurgical techniques for Minnesota's mineral and waste resources. The key components supporting this research include:

- Research tools required to support proof of concept studies, product development, flowsheet development, process optimization, and equipment scale-up strategies;
- Research tools that allow bench-scale metal extraction studies from a wide variety of resources including but not limited to minerals, waste tailings, metallurgical waste, metallurgical residues, urban waste, incinerator ash, electronic waste, etc.;
- Research equipment to characterize solid mine waste and liquid effluent from hydrometallurgical processes;
- Simulation and modeling tools that estimates emissions, water, material, and energy requirements for emerging hydrometallurgical processes;
- Skillsets and technical competencies that are required to conduct and manage hydrometallurgical research programs; and
- Funding opportunities, research collaborators, and potential private and public partnerships to support the research program at NRRI.
- The capital estimates for bench-top and semi-pilot laboratory prototypes range from $600,000 to $1.2 million. The personal, installation, and collaboration costs range from $300,000 to $400,000.

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APPENDICES

Appendices Table of Contents

List of Figures

List of Tables

Appendix A: Hydrometallurgical Research Equipment

Appendix A presents a descriptive list of research equipment that is necessary or useful in developing processes and is arranged by different hydromet process subcategories.

A.1. Hydrometallurgy Laboratory Equipment

The hydrometallurgy laboratory will house metal extraction, mine wastewater treatment, waste characterization, and carbon mineralization equipment. The following equipment list is not exhaustive, but it highlights strategically important tools that are necessary to meet the research needs of stakeholders.

A.1.1. Atmospheric Leaching, Precipitation, and Crystallization Reactors

Bottle roller: Bottle roll tests are the industry standard for assessing the metal recovery possible by atmospheric leaching and provide information on expected recovery rates, reagent costs, and required addition rates. They also provide an indication of the results from the pilot plant and commercial scale leach circuit. These tests can deliver the following data: recovery of metals, leach kinetic data, and plots for all metals tracked and acid consumption with leach time data and curves.

Armfield reactors: This benchtop unit can simulate five different reactor types: continuous stirred reactor, tubular reactor, batch reactor, laminar flow reactor, and plug flow reactor. This unit is a fully computer controlled unit supplied with a hot water re-circulator used to control the temperature of the reactions, glass feed vessels for the reactants, two peristaltic pumps to pump the reagents to the reactors, computer software for data logging, sensors, and instrumentation.

Applikon Dependable Instruments benchtop reactor: This jacketed reactor system is used in academic, government, and industrial laboratories for process development in laboratory scale. The system is equipped with a glass reactor, gas flow controllers and rotameters, spargers, condensers, sensors, controllers, valves, and tubing. The reactors are available in 2, 3, 5, 7, 15, and 20L (0.5gal to 5gal) total volume. The system is equipped with a controller that provides programmable control and optimization of system parameters such as dissolved oxygen concentration, pH level, RedOx potential, temperature, turbidity, and stirring speed. The software that accompanies the system enables process data acquisition and storage.

Büchi AG miniPilot reactor: The Büchi miniPilot reactor is an ideal tool for hydrometallurgical process development, process simulation and kilo-scale production. The system is supplied with interchangeable reactors of 5, 10, and 15 liters including interchangeable stirrers, sampling devices, pH probes, process monitoring, and control. The explosion-proof design and inert materials allow safe processing of solvents and acids in a completely sealed reaction vessel. With permissible operating range for pressure between -1.0 (full vacuum) to +1.0 bar and temperature between -60 °C to +200 °C, the system is suitable for simulation of atmospheric leaching at low, medium, and high-temperatures.

Column leach reactor: A column reactor is chiefly used to 1) simulate biological heap leaching of metallic ore samples, 2) determine the oxidation rate, sulfate production, and metal release from waste rocks or tailings, and 3) study filtration or adsorption behavior of various sorbents or filter media. The leaching column is made of PVC and stainless steel. It has a stainless steel solution tank with a sampling point, valves, and a variable speed pump to control the flow rate of reagents through the column. A 10-mesh stainless steel screen covers the drain plate at the bottom of the column to prevent fine-grained material from plugging the recirculation pump. A peristaltic pump is used to re-circulate the leach solution.

Bench scale leach pilot plant: This setup is ideal to simulate an atmospheric leaching process for the continuous production of leach solution to support downstream metal recovery processes. The setup includes 1) feed preparation tank with tank cover, baffles, and overhead agitator, 2) variable speed slurry feed pump, 3) four cascading leach vessels with covers, baffles, and overhead agitators, 4) immersion heaters with temperature controllers, 5) reagent delivery burettes, Teflon stopcocks incorporating needle metering valves, 6) reagent feed tank with metering pump, and 7) discharge tanks with tank covers.

A.1.2. High-Pressure Leaching and Mineral Carbonization Reactors

Parr bench-top autoclave reactors: These bench-top autoclaves are ideal tools to conduct oxidative leaching and mineral carbonization studies of mineral ore samples. Parr offers a number of different reactors in a variety of sizes and with different mountings for operating pressures to 5000 psi (345 bar) and temperatures to 500 °C. The system is also supplied with a wide range of accessories for feeding of liquids or solids or gas into the reactor. Parr controllers offer PID control with auto tune, ramp and soak programming, separate heating and cooling control loops, stirrer motor speed control, full or half power heater option, lockout relay and reset for over temperature protection, expansion modules for tachometer, pressure, and high temperature alarm.

A.1.3. Mine Rock Characterization via Accelerated Aging

Parr multiple reactor system: Historically, humidity cell tests are used to: 1) simulate the geochemical weathering (natural oxidation) processes, usually at an accelerated rate, 2) determine the rate of acid generation and variation over time in leachate water quality, and 3) provide a preliminary assessment of acid rock drainage (ARD) control options. However, a humidity cell test is typically run for ten weeks and follows a seven-day cycle. As a result, tests might require a long time for completion with correspondingly high costs. Moreover, confirmation of acid rock drainage potential from the humidity cell is often inconclusive due to the time required to deplete neutralization potential to levels at which acid generation becomes measurable. To accelerate the aging by several orders of magnitude, a multiple pressure reactor system is proposed by NRRI. The pressure reactor system uses a combination of pressure, temperature, and oxidizing gasses to accelerate the acid generation and sulfate oxidation. This accelerated approach may provide an assessment of leachate quality and dissolved metal flux that could be expected from waste rocks or mine tailings. The proposed multiple pressure reactor system uses a combination of sixteen standard autoclaves with heaters, valves, pressure gages and rupture disc assemblies and two 4871 Process Controllers with sixteen 4875 Power Controllers. It allows the user to run multiple reactions simultaneously, applying the principles of high-throughput experimentation. Individual variables that can be controlled are gas mixtures, liquids, catalysts or other solids, stirring speed, temperature, pressure, and time.

A.1.4. Advanced Solution Purification Equipment

Liquid-liquid separation consists of transferring metal ions contained in feed solution into an immiscible solvent. The solvent that is enriched in metal ions is called extract, while solution deprived of metal ions is referred to as raffinate. The following section describes tools used in developing solvent extraction processes in lab and bench-scale.

Laboratory Solvent Extraction Equipment

Orbital shakers, centrifuge mixers, variable wrist action shakers, incubator shakers, etc., support lab-scale investigations focusing on selectively separating targeted metal ions from leach solutions via solvent extraction processes. These tools are used in screening organic extractants to selectively extract a targeted metal ion from solution. Additionally, they help in determining reaction time, temperature, extractant concentration, pH, number of stages, and optimal aqueous-to-organic phase ratio of extraction, scrubbing, and stripping based on McCabe-Thiele diagrams.

Rousselet Robatel mixer settler: While lab-scale mixers allow flow sheet design to determine the number of stages and optimal aqueous-to-organic phase ratio of extraction, scrubbing, and stripping steps, Rousselet Robatel mixer-settlers help to evaluate the possibility of scaling up the process and/or producing larger volumes of purified metal solution in a continuous counter current mode. A lab-scale mixer-settler consists of a mixing chamber where an agitator brings the feed solution in intimate contact with organic solvent. A subsequent settling chamber allows static decantation of the two phases, whereas the coalescence plates facilitate the separation of emulsions into light and heavy fractions. The two fractions then pass to subsequent purification stages by overflowing through the light phase and heavy phase weirs.

Bench Scale Solvent Extraction Pilot Plant: The MAEB bench-scale mini-pilot unit is suitable for flowsheet evaluation, pilot plant operation, and small-scale production. Mixer-settlers can be arranged into multiple stages to simulate extraction, scrubbing, and stripping stages. Each active mixer volume is 0.12 liter, and the settler volume is 0.48 liter with a loading surface area of 0,006 m^2. Recommended maximum total flow (organic + aqueous + recycle) is 10 l/h at normal settling velocity. The mixer-settler units are available in polymethyl methacrylate (PMMA) or polyvinylidene fluoride (PVDF) plastics, with the former allowing visual inspection of operation while the latter resists corrosive attacks and is suited for work in the temperature range up to 80° C.

A.1.5. Bench Scale Electrowinning Pilot Plant

This bench-scale electrowinning unit is suitable for pilot plant operation and small-scale production. The process is suitable to recover copper, nickel, gold, cobalt, and other metals from purified solutions obtained from the solvent extraction process. The cathodes used in the cells can be manufactured from various metals including 316L stainless steel and titanium, whereas anodes can be made from lead-calcium-tin (Pb-Ca-Sn) and Lead-silver (Pb-Ag) alloys.

A.1.6. Solid-Liquid Separation Equipment

1. Benchtop filter press: A plate filter press allows separation of solids from liquids. By allowing separation of leach liquor from undissolved solids, the filter press allows the generation of leach solutions for downstream metal recovery processes like precipitation, solvent extraction, ion exchange, and adsorption. Additional applications include cake recovery, low solids recovery from precipitation, or clarification processes.

2. Laboratory candle filter: The candle filter allows lab-scale solid liquid separation of products from bench-scale leaching, precipitation, and crystallization processes.

A.1.7. Column chromatography

3. Lab-scale chromatography helps to screen ion-exchange resins and adsorbents for selective separation of metals from various diluted streams.

A.1.8. Analytical Tools

4. ICP-MS: Inductively coupled plasma mass spectrometry (ICP-MS) is an elemental analysis technology capable of detecting most of the periodic table of elements at milligram to

nanogram levels per liter – making ICP MS a preferred choice over ICP OES and AAS for performing trace element analysis.

5. QEMSCAN: QEMSCAN is an acronym for Quantitative Evaluation of Materials by Scanning Electron Microscopy. It utilizes Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) to create an image of a sample based on chemical composition. These images can be processed to provide information about the chemical and mineral composition of the sample, as well as the textures, mineral abundances, mineral associations, grain sizes, liberation characteristics, surface exposures, etc.

A.1.9. Process Modeling, Simulation and Statistical Analysis Tool

HSC Chemistry 10: This software toolkit allows thermochemical and mineral processing calculations that are useful during process research and development as well as for estimating process efficiencies, yields, and environmental footprints. The salient features of this tool include:

- HSC provides the heat of the reactions, the equilibrium constant at any temperature and number of species. The calculated heat of reaction is the amount of heat that will be absorbed or released in the reaction and the equilibrium constant predicts the direction of the reaction.
- HSC helps to carry out heat balance calculations, thus allowing estimating the energy requirements and the cost of the process, as well as the operation preconditions.
- HSC is capable of calculating the environmental impact of a reactor, section, or total plant developed in the HSC Sim module.
- HSC helps to draw phase stability diagrams, which show the stability (predominance) areas of condensed phases in a ternary system as a function of temperature or in isothermal conditions with the remaining constraints on the other axis. These diagrams are very useful when a fast estimation of the prevailing phases is needed.
- HSC helps to generate Eh-pH diagrams that illustrate the stabilities of ionic and non-ionic species in water solutions. This knowledge is critical to understanding problems of corrosion, dissolution, leaching and selective precipitation.
- HSC’s mass balance module helps to estimate the performance of a process, detect bottlenecks in the circuit, and to create models of the processing stages.

METSIM®: This software is a general-purpose process simulation system designed to assist the engineer in performing mass and energy balances of complex processes.

Stat-Ease Design-Expert Software: This software provides tools to design an ideal experiment on a process, screen for vital factors and components, characterize interactions, and help visualize the response surface from all angles with rotatable 3D plots.

A.2. Advanced Mineral Processing

A.2.1. Sample Preparation Equipment

The following section lists sample preparation and comminution equipment necessary to compliment the hydrometallurgical testing.

Laboratory oven: a forced-air convection oven provides controlled heat to dry drill core samples, run of mine ores, bulk ore samples, comminution, and beneficiation test samples.

Splitters: Sample splitters and reducers ensure the test sample has materials with particle sizes in representative portions to original or bulk material.

Sieves and sieve shaker: ISO 565, 3310-1 allows determination of particle size distribution of test samples.

Screen trays and screen shakers: The screen trays have areas much larger than round test sieves and allow particle size determinations on large samples of ores and coarse materials from 4" (101 mm) to 14 mesh (1.4 mm) sizes.

Laboratory crushing: Laboratory jaw crusher, cone crusher, and rolls crusher enable particle size reduction of test samples from 4" to 14 mesh (1.4 mm).

Traditional laboratory grinding equipment: Batch-type laboratory ball mill and rod mill helps in preparation of test samples for laboratory beneficiation tests. Typical functions include grinding the ore samples to achieve mineral liberation.

A.2.2. Advanced Laboratory Grinding Equipment

Magotteaux mill: This laboratory mill is designed to simulate the physical (particle size distribution) and chemical conditions (Eh, pH, temperature, dissolved oxygen, etc.) of the plant grinding mill. The mill runs at variable speed with temperature control and continuous chemistry monitoring, thus allowing the study of the impact of grinding media and the resulting grinding chemistry on downstream beneficiation processes, including froth flotation and leaching.

M4 IsaMill: This fine grinding mill produces steep particle size distribution without needing internal screens or closed circuit hydrocyclones, which are favorable in flotation and leaching processes. The pilot scale unit determines power requirements while investigating media consumption and downstream processing performance on real plant streams.

Attritor mill: In this laboratory stirred ball mill, the material to be ground is placed in a stationary tank with the grinding media, which are agitated by a shaft with arms rotating at high speed. Working at 10 times faster than conventional laboratory ball mills, the Attritor mill allows wet or dry grinding, introduction of inert atmospheres, operation at controlled temperatures, varying grinding speed, product contamination, changing media size and type, while obtaining precise energy consumption information.

6. Classification

Laboratory hydrocyclone rig: This rig enables closed circuit grinding, finer particle separation and enrichment, desliming, and thickening of mineral samples. These rigs are ideal to obtain cut sizes from 1000 µm down to 3-4 µm.

A.2.3. Advanced Beneficiation Equipment

Mozley superpanner: This laboratory unit is suitable to evaluate the amenability of ore samples to gravity separation. The sample requirements are small (few 100g), making it possible to use this technique when insufficient material is available for larger scale tests such as spiral testing.

Reflux classifier: This technology is emerging as the industry standard for fine gravity separation. It consists of a lower fluidized bed section and an upper section of parallel inclined channels. This combination provides both a gravity separation and deslime of the feed.

Magotteaux float cell: This laboratory flotation machine comes with a bottom-driven agitator that allows operators to uniformly remove froth from the entire surface of the cell, thus minimizing operator errors while maximizing test reproducibility. The equipment also allows continuous monitoring of pulp chemistry throughout the test as the probes remain in the pulp.

LAARMANN computerized laboratory flotation cell: This laboratory flotation machine allows digital control of cell level, agitator speed, airflow rate, and automatic froth remover. The technology uses stainless steel, acrylic, polyurethane, and PTFE coating as materials of construction, thus making it suitable for hot slurry and corrosive applications.

Ore sorting: By continuously measuring color, atomic density, or conductivity of test samples, sorters selectively separate the valuable mineral ores from waste rocks using a pulse of pressurized air directed with precision by an amplified mechanical, hydraulic, or pneumatic process. By eliminating waste rocks at the early stages of processing, sensors not only minimize the consumption of energy, water, and reagents, but also reduce the carbon footprint of the extraction process.

L150 laboratory Jameson Cell: By utilizing fine bubbles and intense mixing between air and bubbles, Jameson cells maximize bubble particle attachment to maximize concentrate recovery while upgrading concentrate grade through its integrated wash water system. This allows the Jameson Cell to achieve flotation targets in a single stage that would normally require several stages with conventional cells, thus reducing the footprint of the installation. The laboratory cell is appropriate for testing on small batches of samples (between 20-40 kg) or for small-scale continuous operation (~390L/hour).

Appendix B: Emerging Hydrometallurgical Technologies

Appendix B lists emerging technologies and provides a section on relevance to Minnesota.

B.1. Battery Metal Extraction Processes

B.1.1. One-Pot Process

Nickel sulfate is the preferred feedstock for conventional battery cathode manufacturing (Campagnol, et al., 2017) but this process presents several disadvantages (Tesla, 2020). Nickel ore is mined, crushed, concentrated, and upgraded to nickel matte using a pyrometallurgical smelting process. Subsequent hydrometallurgical processes consisting of leaching, solvent extraction, precipitation, and electrowinning techniques convert the nickel matte into nickel metal, which is crystallized to produce nickel sulfate (Talon Metals Corp, 2021). This process consumes large amounts of water and chemicals, while generating large amounts of wastewater and byproducts. To overcome these issues, Nano One Materials, a Vancouver based start-up has developed a “one-pot process” for the production of cathode materials directly from metal powders (Figure 7). The technology combines feedstock conversion, precursor formation, and lithiation and coating steps into one reaction. Benefits include: 1) by using metal powders instead of metal sulfate compounds, the process eliminates the generation of sulfur and wastewater streams; 2) because nickel metal powder weighs one-fifth the weight of nickel sulfate, the process eliminates the shipment of water and sulfur, thereby reducing the transportation costs; 3) the process also eliminates the need for costly and energy-intensive crystallization steps, which is traditionally used in conversion of metal powders to metal sulfates or hydroxides; and 4) by eliminating the generation of sulfate based byproducts and wastewaters, the process eliminates the environmental cost of handling waste stream of water and sulfate (Figure 7; Nano One Materials Corp., 2021). Tesla’s Battery Day presentation hints at using a similar process as one-pot process to manufacture cathodes for their electric vehicle battery pack (Tesla, 2020).

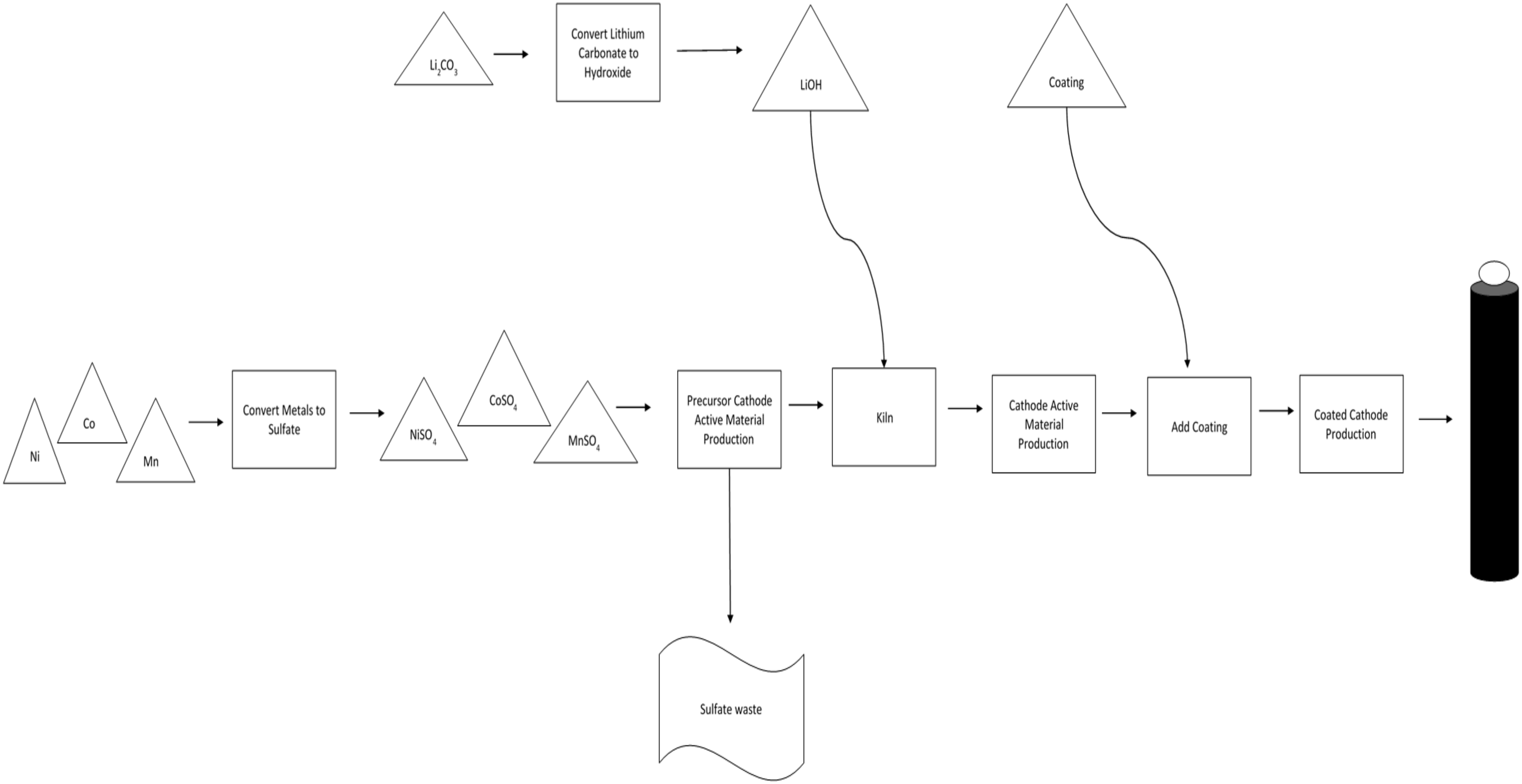
Potential Applications to Minnesota Resources

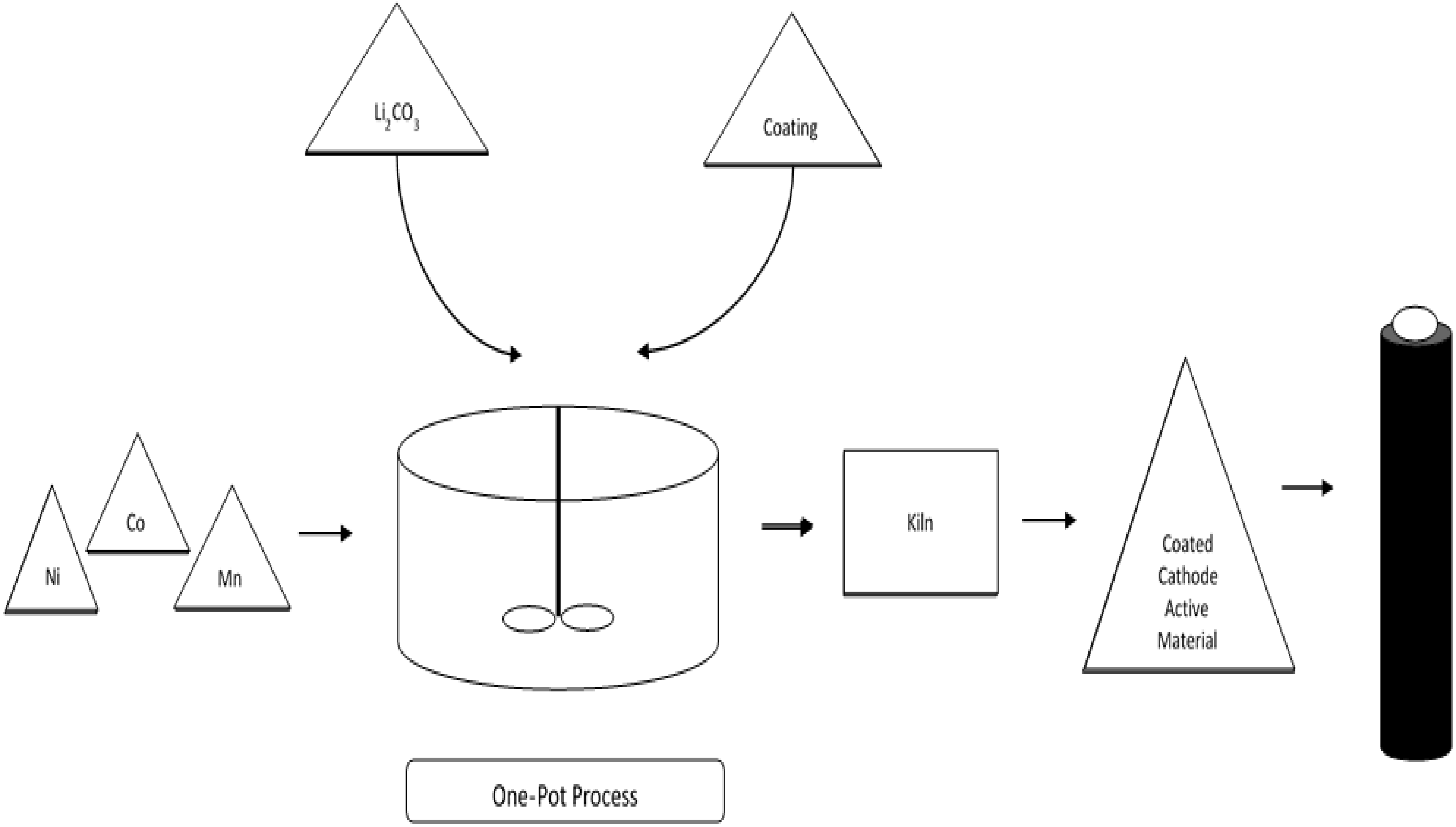
The possibility of using One-Pot process technology to produce cathode active materials using Minnesota’s nickel resources requires further technical evaluation. Prospective mining business models rely on international smelters to process their nickel sulfide concentrate, which could lead to loss of revenues to the State of Minnesota. However, stakeholders interested in adopting the “mine-to-cathode” approach could benefit by integrating “one-pot process” into their hydrometallurgical complex. The potential benefits of this approach include:

- Allows conversion of class 1 nickel products to cathode active materials
- Offers an alternative to pyrometallurgical processes (e.g., smelting and refining), which require large capital investments, making it difficult for new players to enter the market
- Supports the diversification of the product portfolio from State’s nickel resources
- Enhances the royalty value of minerals owned by the State

Figure 7. Comparison of traditional cathode process vs. Nano One® One-Pot Process for cathode manufacturing (adapted from Nano One Materials Corp, 2021).

Traditional cathode manufacturing from metal sulfate




Li_2CO_3
Coating
Co
Ni
Mn
Kiln
Coated Cathode Active Material
One-Pot Process

B.1.2. Battery Grade Nickel Sulfate Production

Nickel sulfate is a primary raw material for the production of lithium nickel cobalt manganese (NCM) and lithium cobalt aluminum oxide (NCA) batteries (Future Battery Industries Cooperative Research Centre, 2020). Battery manufacturers desire tight control over the impurities present in the nickel sulfate, which is critical for maintaining chemical stability and performance of batteries. In addition, uniform and fine crystals with zero-level moisture content and dust contamination are required. Several compositions of nickel sulfate used in battery manufacturing are shown in Table 9.

Table 9. Product specification for battery grade nickel sulfate

Element	Australia	Europe	China
Ni (%)	22	22	22
Co (ppm)	40-120	2-10	10-30
Cu (ppm)	1-9	1-2	1-1
Al (ppm)	1	1	10
As (ppm)	1-2	1	2
Ca (ppm)	1-2	1	5-7
Cd (ppm)	1	1-2	1-10
Cr (ppm)	1	1	3
Fe (ppm)	1-6	1-2	2-10
K (ppm)	1	1	-
Mg (ppm)	1-4	1	20
Mn (ppm)	1	1	-
Na (ppm)	1-5	5	30
P (ppm)	1	2	-
Pb (ppm)	1	1-2	5-10
Si (ppm)	1-2	5	10
Zn (ppm)	1-5	1-2	1-10

Nickel sulfate can be produced using a variety of intermediate nickel products like nickel matte, mixed sulfate precipitate (MSP) and mixed hydroxide precipitate (MHP) or via Class 1 nickel products such as high-purity nickel metal powders or briquettes (Future Battery Industries Cooperative Research Centre, 2020). An example of a hydrometallurgical process used in the production of battery-grade nickel sulfate directly from nickel sulfide concentrate is shown in Figure 8. The process consists of pressure oxidative leaching of nickel sulfide concentrate followed by a solvent extraction process to separate cobalt and copper ions from the pregnant leach solutions. These ions are further stripped from the organic phase and precipitated as mixed sulfide products. The raffinate from the cobalt and copper solvent extraction process passes through an additional solvent extraction stage to separate nickel ions. Subsequent stripping of the organic phase results in a nickel rich aqueous solution. Finally, a crystallization process is used to precipitate nickel sulfate powders from this aqueous phase.

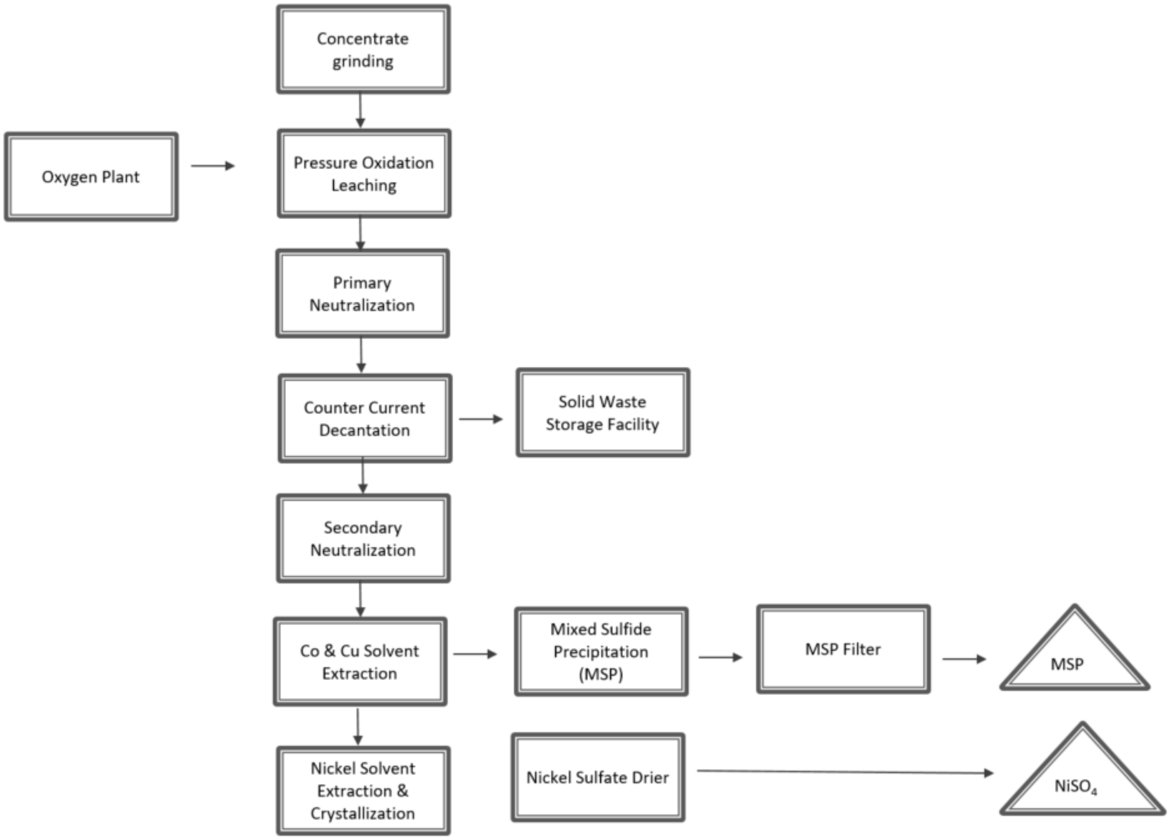


Figure 8. Hydrometallurgical flowsheet for the production of battery grade nickel products (adapted from Future Battery Industries Cooperative Research Centre, 2020).

In Minnesota, Talon Metals has recently completed a flowsheet design (Figure 9) to produce nickel sulfates directly from the Tamarack nickel sulfide concentrates (Talon Metals Corp, 2021), which is similar to the one described above. Figure 10 shows the traditional hybrid pyrometallurgical and hydrometallurgical flowsheet that is used to produce nickel sulfate from nickel mineral concentrates.

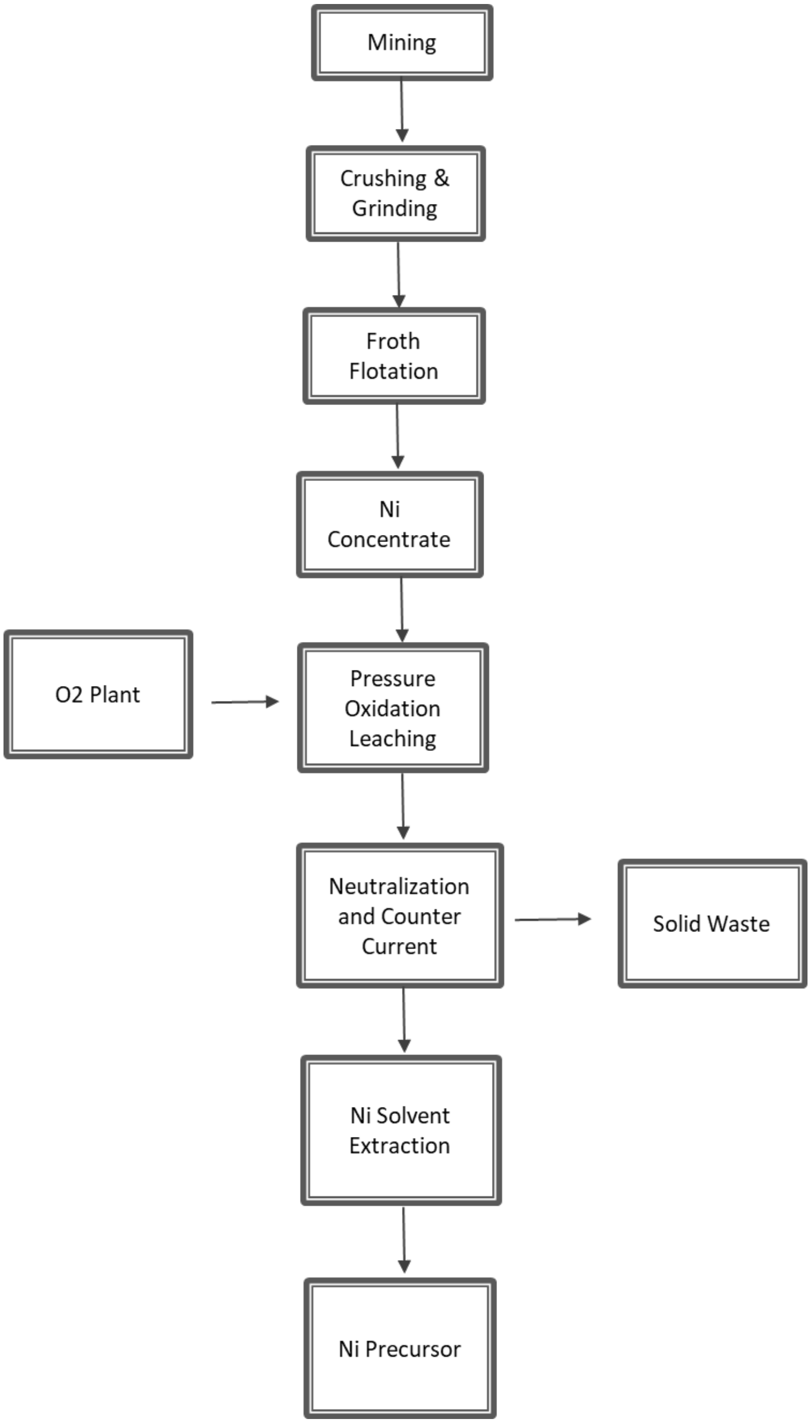


Figure 9. Hydrometallurgical flowsheet proposed for Tamarack deposit (adapted from Talon Metals Corp, 2021).

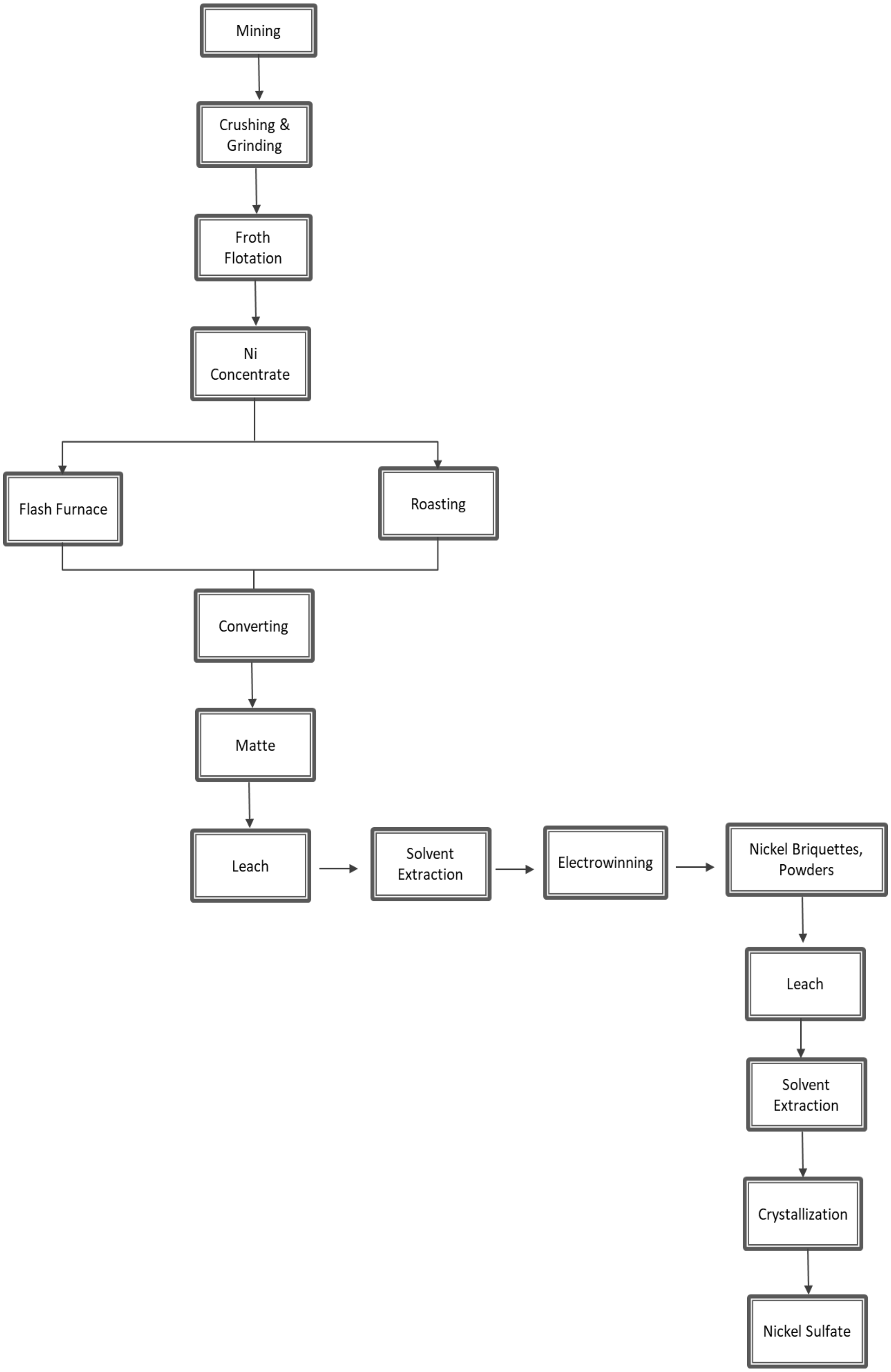


Figure 10. Traditional hybrid pyrometallurgical and hydrometallurgical flowsheet used in production of nickel sulfate(adapted from Talon Metals Corp, 2021).

Potential Applications to Minnesota Resources

Historical nickel recovery methods from Cu-Ni ± PGE mineralization in Minnesota have followed three different processing routes. These include:

- Conventional processing comprising a flotation concentrator that produced smelter grade nickel concentrates
- A hydrometallurgical process that included a pressure oxidation leaching (PLATSOL™ and CESL) to process nickel concentrates into upgraded nickel-cobalt hydroxide
- A hydrometallurgical process that included an atmospheric oxidative leaching (ALBION Process™ and Mixed-Chloride Technology) to solubilize nickel from nickel concentrates.

Each of these routes is limited to producing intermediate nickel products like mixed hydroxide precipitate and are not optimized for producing battery-grade nickel products. As nickel sulfate is the preferred feedstock of battery manufacturers, further technical evaluation should focus on developing environmentally benign methods to produce nickel sulfate directly from local nickel concentrates. The potential benefits of this approach include:

- Offers an alternative to pyrometallurgical processes (e.g., smelting and refining), which require large capital investment, thus making it difficult for new players to enter the market,
- Supports the diversification of the product portfolio from State's nickel resources, and
- Enhances the royalty value of minerals owned by the State.

B.1.3. Battery Grade Manganese Sulfate Production

High-purity manganese sulfate monohydrate (HPMSM) is used as a precursor material for lithium nickel cobalt manganese (NCM) and lithium manganese oxide (LMO) batteries. Battery-grade HPMSM must contain a minimum of 31.8% Mn by weight. Alkali and alkaline cations negatively affect high-temperature morphology and cycling performance of Li-ion batteries. An impurity of concern is the element selenium. Due to safety issues surrounding the toxicity of hydrogen-selenide, battery manufacturers limit the selenium concentration to 3 ppm (Future Battery Industries Cooperative Research Centre, 2020). A typical composition of HPMSM is shown in Table 10.

Table 10. Product specification for battery grade manganese sulfate (adapted from Future Battery Industries Cooperative Research Centre, 2020).

Element	Specification
Mn (%)	31.8
Pb (ppm)	10
As (ppm)	10
Cd (ppm)	10
Ca (ppm)	50
Mg (ppm)	50
Na (ppm)	50
Fe (ppm)	10
Zn (ppm)	10
Cu (ppm)	10

A hydrometallurgical processing flow sheet used in the production of HPMSM or high-purity electrolytic manganese metal (HPEMM) from manganese oxide ores is shown Figure 11. The process is currently practiced commercially at the Manganese Metal Company in South Africa (Manganese Metal Company (Pty) Ltd, 2022). HPMSM can be directly produced using oxide or carbonate ores of manganese. A reductive leaching or calcination step is necessary for oxide ores. This step lowers the oxidation state of manganese to Mn^{2+}, which is amenable to acid dissolution. Subsequent steps include iron oxide precipitation and solution purification steps. The flowsheet is capable of producing HPEMM or HPMSM depending on the marketing demand (Manganese Metal Company (Pty) Ltd, 2022).

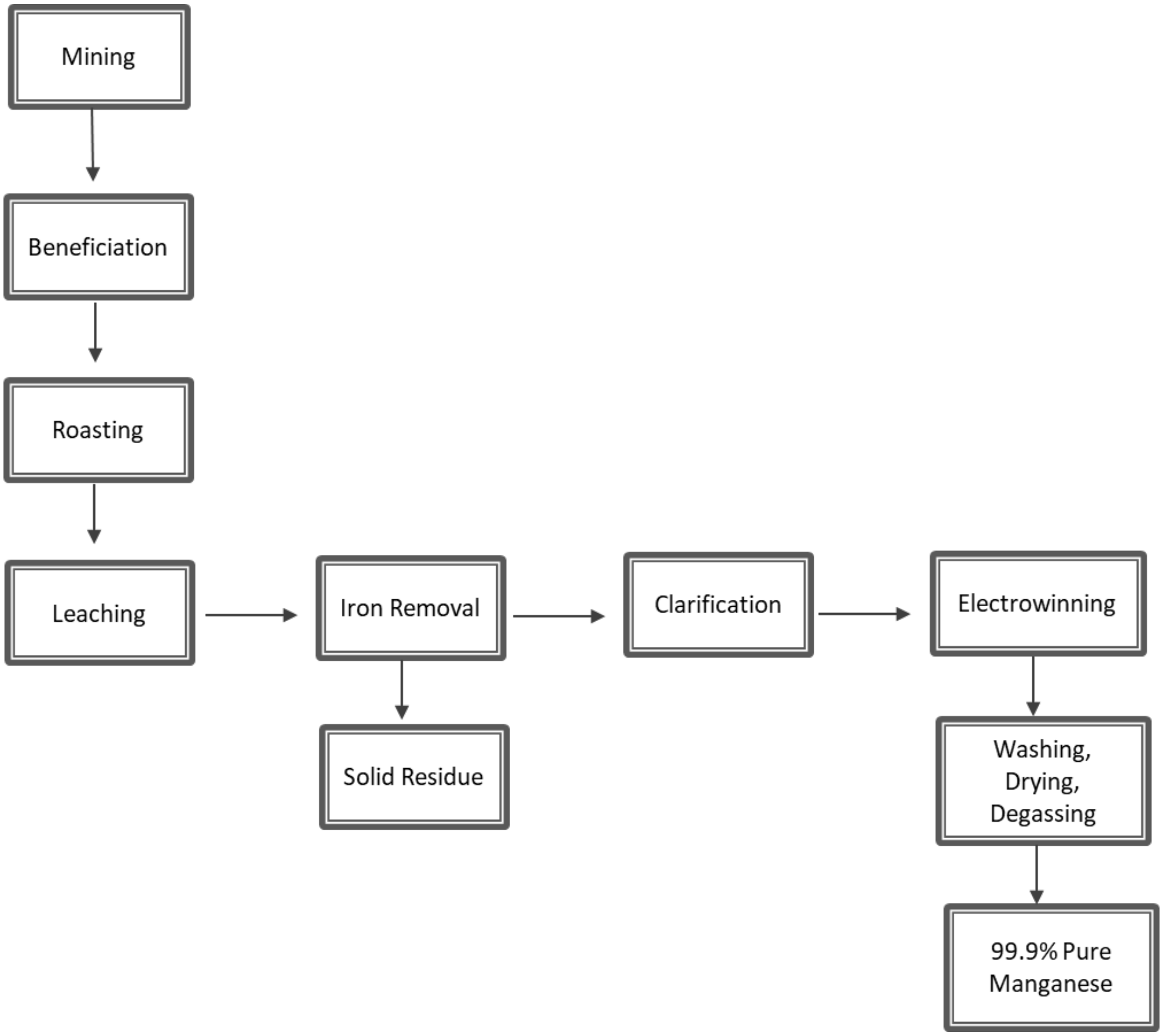


Figure 11. Hydrometallurgical flowsheet used in the production of high-purity electrolytic manganese metal (adapted from Manganese Metal Company (Pty) Ltd, 2022).

Potential Applications to Minnesota Resources

The pursuit of higher battery energy density and the use of costly raw materials such as cobalt have pushed the battery industry to select cathodes with lower cobalt content. Manganese sulfate is therefore used to replace part of the cobalt content in NCM batteries to reduce manufacturing costs (Li, et al., 2020). Historical laboratory studies on manganese ores from the Emily Manganese Deposit have demonstrated the feasibility of producing electrolytic manganese metal and electrolytic manganese dioxide (Cooperative Mineral Resources, 2020). Because manganese sulfate monohydrate (HPMSM) is a preferred feedstock of lithium-ion battery manufacturers, future research could focus on evaluating the feasibility of producing HPMSM directly from the manganese oxide deposits from the Cuyuna District of central Minnesota.

B.1.4. Direct Nickel Process (DNi-Process)

Altilium, a British-based startup, is commercializing an alternative to the conventional high-pressure acid leaching (HPAL) process (Figure 12). Their technology allows for the extraction of nickel from laterite ores at atmospheric pressure and at low temperature. The process is capable of generating mixed hydroxide precipitates (MHP), which is the preferred feed material for nickel sulfate manufacturers. The process also allows for the recycling of 95% of the nitric acid used to extract the metals. Furthermore, the process produces a nitrogen-rich inert residue that can be dry stacked and returned to the mine to encourage the growth of local flora. The flowsheet is capable of generating other byproducts such as hematite, magnesium oxide, aluminum hydroxide, and scandium oxide (Robinson, et al., 2017; Altilium Group Ltd, 2021).

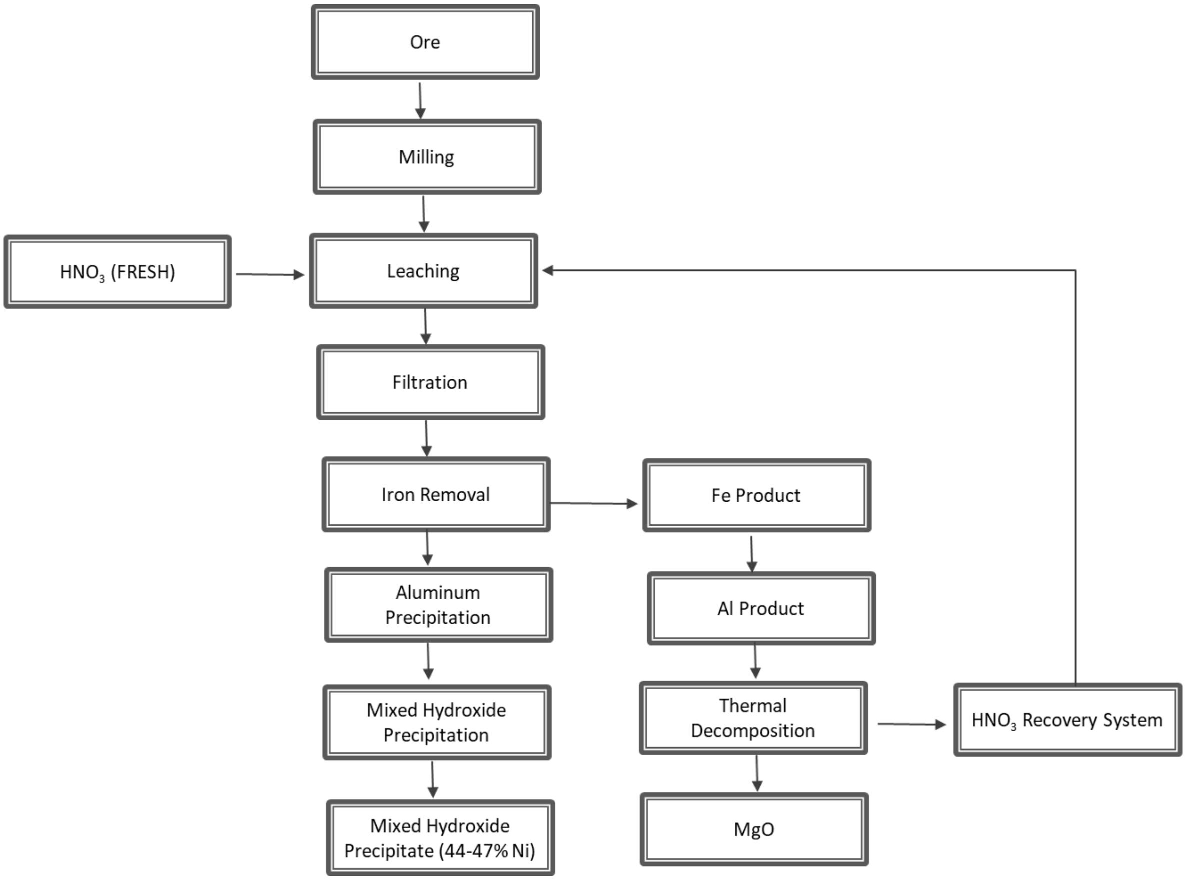


Figure 12. Process flowsheet for Direct Nickel Process (adapted from Altilium Group Ltd, 2021).

Potential Applications to Minnesota Resources

Historical metallurgical test work on Duluth Complex Cu-Ni-PGE mineralization has shown low nickel and cobalt recoveries from non-sulfide minerals (Polymet Mining Inc., 2007). The laboratory studies indicate a loss of about 25-35% of nickel while concentrating sulfides. The unrecoverable nickel occurs as magnesium-iron-nickel silicate that is tied up in the mineral olivine. Mineralogical studies on the NorthMet deposit indicate that approximately 25-35% of the rock is composed of olivine, which contains an average of about 0.1% Ni (Polymet Mining Inc., 2007). Future research could focus on using the Direct Nickel process to recover nickel and cobalt that is tied up in the mineral olivine. The benefits of this approach include:

- Allows the conversion of nickel in olivine-rich tailings to battery-grade materials,
- Potential recoveries of nickel and cobalt offers additional revenue streams, and
- Provides a method to recover metals from waste tailings.

B.1.5. Hydro-to-Cathode Technology

Founded in 2015 as a spinout from the lab of Prof. Yan Wang at Worcester Polytechnic Institute (WPI), Hydro-to-Cathode technology converts mixed streams of lithium-ion batteries, regardless of their chemistry, into various nickel manganese cobalt (NMC)-based cathode active materials (Sa, et al., 2016). Instead of extracting and separating the metals out individually like conventional hydrometallurgical technologies and then reintegrating into battery materials, Hydro-to-Cathode goes directly from the leaching and dissolution processes into battery material production, thereby avoiding the individual extraction of the reclaimed metals (Zou, et al., 2013; Zheng, et al., 2018) and enabling direct use of these materials in making new batteries. Massachusetts-based Ascend Elements plans to scale-up the technology by 2023. Ascend Elements states that the technology enables 35% reduction in cost, 32% reduction in emissions, and 13% reduction in energy consumption to produce NMC active materials compared to the production of virgin cathodes (Ascend Elements, 2021).

Potential Applications to Minnesota Resources

This technology offers a possibility of recovering cathode active materials from the end-of-life batteries collected from various sources in Minnesota.

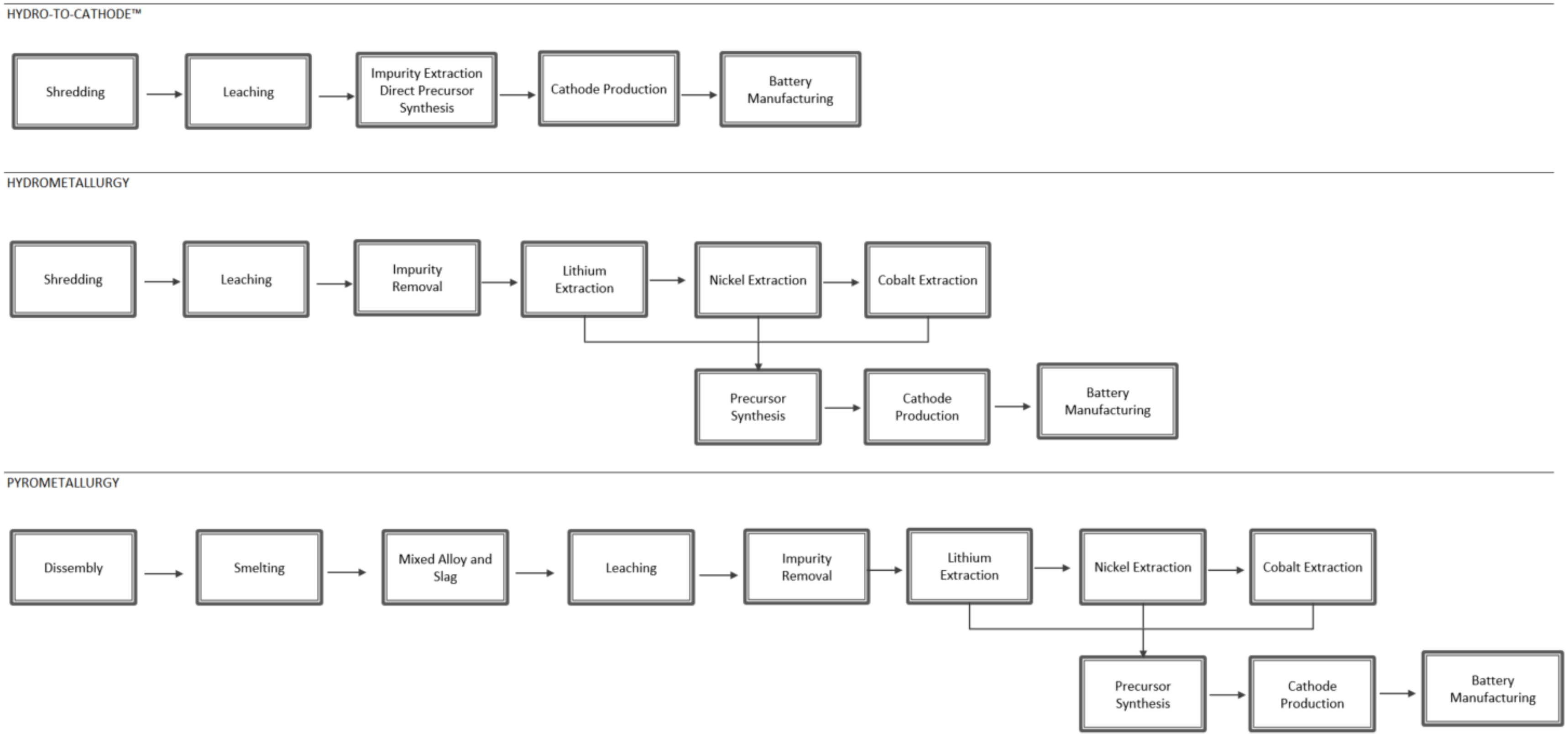


Figure 13. Flowsheets comparing Hydro-to-Cathode™ with traditional hydrometallurgical and pyrometallurgical treatment of end-of-life batteries (adapted from Ascend Elements, 2021).

B.1.6. Li-Cycle

Li-Cycle is a Canadian based startup that has developed a proprietary "Spoke and Hub" recycling technology to process battery manufacturing scrap and end-of-life batteries (Li-Cycle, 2021). The process flowsheet (Figure 14) employs a shredding process, which converts the used battery into a black mass containing lithium, cobalt, nickel, and other metals. This black mass is further processed using a proprietary hydrometallurgical process that transforms it into various battery grade materials.

Potential Applications to Minnesota Resources

This technology offers a possibility of recovering cathode precursors from the end-of-life batteries collected from various sources in Minnesota.

B.1.7. Iron Salt Technology and Vanadium Redox Flow Technology

VoltStorage, a Munich-based startup, is a provider of smart solar storage systems based on Iron Salt Technology (and Vanadium Redox Flow Technology), which is designed to make renewable energy available 24/7. The advantages of an iron (or vanadium) electrolyte consist largely in using pure water with the device, which makes it non-flammable in the event of extreme environmental conditions or malfunctions. In addition, iron can be **100%** recycled, and is available in large quantities in Minnesota, and worldwide. The vanadium used in the storage medium is a byproduct of iron production (VoltStorage GmbH, 2021).

B.1.8. Mitra Chem Technologies -Lithium Iron Phosphate Batteries

Today, 100% of industrialized iron-based cathode manufacturing capacity is in China. Mitra Chem, a Silicon Valley startup, aims to boost the North American battery supply chain by producing an iron-based cathode for the Western mass-market EV industry. Mitra Chem states that its iron-based cathode moves away from the use of elements such as nickel and cobalt due to price volatility and known supply-chain ethics issues. Mitra Chem also asserts that its approach can shorten the lab-to-production timeline by >90% by allowing the invention of new battery chemistries (Palihapitiya, 2021; Alamalhodaei, 2021). Mitra Chem is currently building a R&D facility in Mountain View, California, with the aim of producing pre-pilot iron-based cathodes by mid-2022 (Mitra Chem Technologies, 2021).

Potential Applications to Minnesota Resources

Hydrometallurgical processes offer a possibility of producing iron and vanadium compounds that are suitable for energy storage systems. Future research efforts could focus on evaluating the feasibility of producing such compounds from Minnesota’s Cu-Ni-Co-PGE, Fe-Ti-V deposits, and Fe and Mn-Fe deposits.

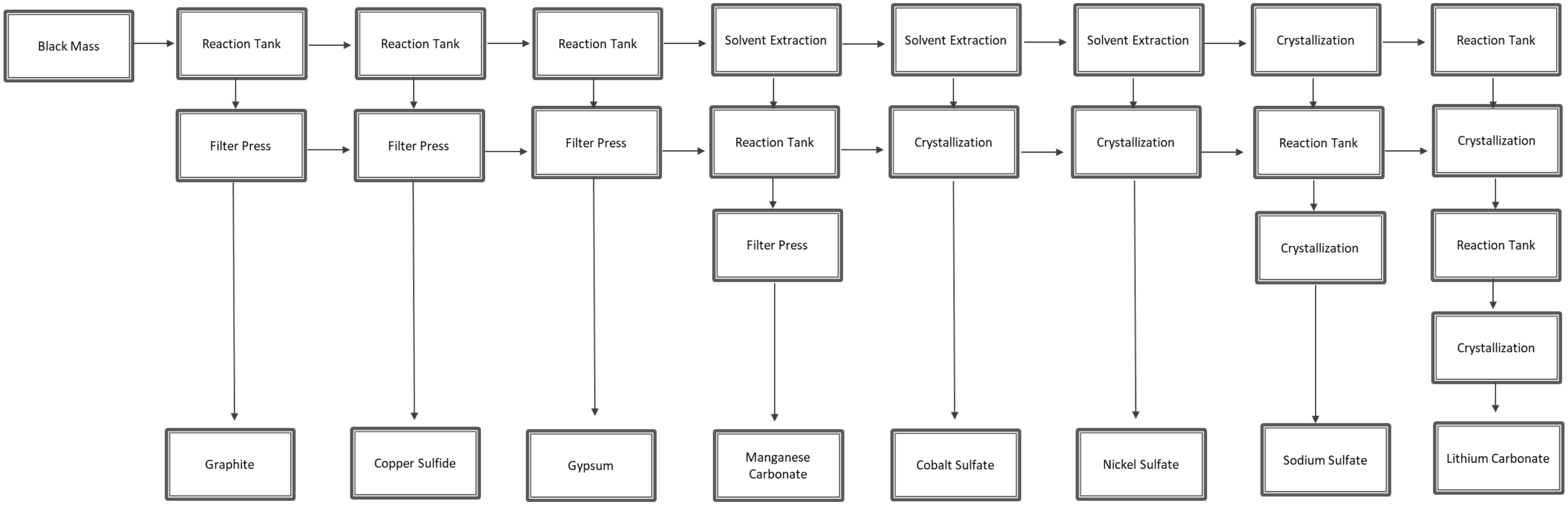


Figure 14. Hydrometallurgical process used by Li-Cycle for the treatment of end-of-life batteries (adapted from Li-Cycle, 2021).

B.2. Critical Metal Extraction from Low-Grade Ores and Waste Tailings

B.2.1. Lilac Solutions

Lilac Solutions, a startup in Oakland, California, has developed a new ion exchange technology to extract lithium from brines without the need for evaporation ponds (Lilac Solutions, 2021). In the Lilac Solutions process, proprietary beads are loaded into columns, brine flows through the columns, and the beads absorb lithium. Hydrochloric acid is used to flush out the lithium, yielding lithium chloride. Further processing converts lithium chloride into lithium carbonate or lithium hydroxide, which is sold to battery manufacturers.

Potential Applications to Minnesota Resources

This technology could potentially facilitate the recovery of lithium from end-of-life batteries in Minnesota.

B.2.2. Jetti Resources

Jetti Resources, in partnership with the University of British Columbia, has developed a catalytic technology that allows leaching of copper from low-grade primary sulfides at atmospheric temperature and pressure (Figure 15). The catalyst (thiourea – an organosulfur compound having a thiocarbonyl functional group) negates the detrimental passivation layer that usually forms on chalcopyrite during oxidative heap leaching. Ferric ions, which are responsible for the breakdown of chalcopyrite, also promote its passivation by enabling the formation of copper deficient iron-sulfur layers (Dixon, et al., 2019). UBC researchers postulate that the proprietary catalyst facilitates the disruption of sulfur metal bond of the mineral, allowing copper extraction to take place while regulating the effects of the ferric ions that contribute to the passivation layer (Dixon, et al., 2019). Currently, the low-grade copper ores may not be economical for bioleaching methods and are often disposed of as waste. The catalytic technology integrates with existing heap leaching methods and downstream processing operations to extract copper from primary sulfides (Rebolledo, et al., 2019).

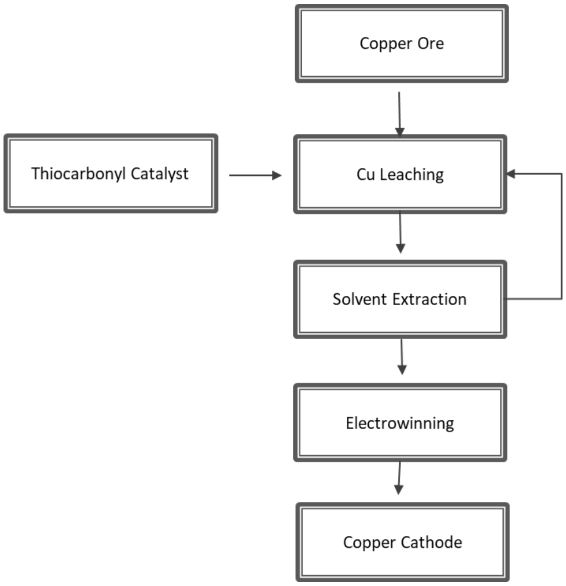


Figure 15. Process flowsheet for Jetti Process (adapted from Dixon, et al., 2019).

Potential Applications to Minnesota Resources

Historical recovery attempts have focused on producing smelter-grade copper concentrates from Minnesota's Cu-Ni-Co-PGE mineralization (Black, et al., 2018; Mayhew, et al., 2009; Talon Metals Corp, 2021). Some stakeholders believe that the shipment of concentrates to international markets is not sustainable due to fluctuating demand and supply for copper metal. Therefore, further technical evaluation is necessary to determine the feasibility of using the Jetti Process for the recovery of copper metal. The benefits of such an approach include:

- Offers a potential alternative route to smelting and pressure oxidative leaching process, which requires large capital investment, thus making it difficult for new players to enter the market,
- Allows the production of copper metal in the state of Minnesota, and thereby
- Enhancing the royalty value of minerals owned by the State.

B.2.3 Phoenix Tailings

Phoenix Tailings is a University of Connecticut-affiliated startup that is working to build a solution that could not only clean up legacy tailings ponds but could also turn the waste materials they hold into valuable, usable products (Small Business Innovation Research (SBIR), 2020; Severance, 2020).

Potential Applications to Minnesota Resources

Due to the proprietary nature of the above technology, a detailed description of this process is not publicly available. Phoenix Tailings website indicates that their re-mining technology is capable of recovering rare earth elements like cerium, lanthanum, neodymium, samarium, and scandium from waste tailings.

B.2.4. Nth Cycle

Nth Cycle is a Boston-based startup that has developed an electro-extraction technology that extracts critical metals from batteries, e-waste, low-grade ore, and mine tailings so they can be reused to make new clean energy products (Nth Cycle, 2021).

Potential Applications to Minnesota Resources

Due to the proprietary nature of the above technology, a detailed description of this process is not publicly available. Nth Cycle's website indicates that their electro-extraction technology is capable of recovering critical metals from batteries, e-waste, low-grade ore, and mine tailings.

B.3. Carbon Mineralization Technologies

B.3.1. Carbfix

Carbfix is an Icelandic startup that has developed a technology that attempts to permanently sequester CO_2 in underground geological formations. The technology dissolves CO_2 in water and then injects the solution into the ground, where it interacts with reactive rocks (basalt) to form mineral carbonates.

These efforts culminate a decade of lab and field research that explored various aspects of water-rock-CO_2 interaction. The research used laboratory and pilot scale pressure reactors to study the impact of mineralogy, water chemistry, time, temperature, pressure, and pH on 1) dissolution rates of CO_2 into aqueous phase, 2) release rates of cations from CO_2 reactive rocks, 3) precipitation of carbonate minerals, and 4) co-precipitation of other minerals. The data from these studies were used for reaction path modeling studies to predict the basalt-CO_2-water interaction prior to the field pilot study and to characterize prospective geological formations suitable for CO_2 injection (Snæbjörnsdóttir, et al., 2020).

Potential Applications to Minnesota Resources

To support federal government endeavors to define conditions under which mineral carbonation processes could remove 10 $GtCO_2$ per year by 2050, NRRI could conduct geological resource assessment and characterization of mafic and ultramafic rocks in Minnesota. This will require mapping of local geologic resources and detailed spatial, mineralogical, lithogeochemical, and mineral chemical characterization to assess their potential for large-scale in-situ carbon mineralization like the Carbfix Project.

B.4. Mercury and Selenium Removal Technologies

B.4.1. Sulfur based sorbents

Professor Justin Chalker at the Flinders University, Australia has synthesized a low-cost mercury-capturing polymer synthesized entirely from waste material (Worthington, et al., 2017). The research at Chalker's Lab demonstrated the effectiveness of sorbents in capturing common forms of mercury pollution, including liquid mercury metal, mercury vapor, and inorganic mercury and organomercury compounds. Further, the research indicates that neither the polymer nor the mercury-bound polymer is toxic to human cells. Research is currently underway to develop applications for in situ remediation of mine tailings, soil, and agricultural wastewater (Worthington, et al., 2017).

B.4.2. Tusaar Corp

The University of Colorado has developed a biosorbent to remove lead, mercury, uranium, and other toxic metals from water and the environment (Carlson, et al., 2020). Tusaar Corp has licensed the technology from University of Colorado. The U.S. National Science Foundation and the U.S. Department of Energy (Tusaar Corp, 2022) funded the research.

B.4.3 Zero Valent Iron (ZVI) technology

ZVI reduces selenium oxyanions to elemental selenium. Ferrous cations can also reduce selenate to selenite and subsequently remove selenite by adsorption to iron hydroxides (Regenesis, 2022).

B.4.4. Advanced Biological Metals (ABMet) technology

This technology uses special strains of common nonpathogenic microbes that facilitate the precipitation of soluble selenium into elemental selenium. ABMet systems find applications in jurisdictions that require low effluent selenium concentrations by current or future regulations (Suez Water Technologies and Solutions, 2022).

B.4.5. Saturated Rock Fill (SRF) Technology

Enviromin, Inc. in cooperation with Center for Biofilm Engineering (CBE) at the Montana State University and Teck Resources Limited has developed the Saturated Rock Fill for in-situ reduction of selenium from mine drainage. Waste rocks from certain mineral resources can release toxic concentrations of selenium into water upon exposure to air and water. The technology utilizes a biological reduction of oxidized selenium (Se (VI)) to less mobile (Se (0)) forms within the mine waste rock (Kirk, et al., 2017).

B.4.6. Membrion Technologies

Membrion Technologies is a Seattle-based startup that has developed a ceramic ion exchange membrane for removing salt and heavy metals from wastewater. While membrane fouling and poor chemical durability are among the limitations of traditional polymer membrane on the market today, Membrion's ceramic membranes resist fouling, have no lower pH limit, and can handle harsh oxidizers present in many wastewaters (University of Washington, 2021).

Potential Applications to Minnesota Resources

The Fond du Lac Band is concerned that existing mercury impairments will make the cumulative effects of mercury from new or expanded discharges greater (Fong, 2022). Therefore, the Band is proposing that future discharges to impaired waters must meet the Fond du Lac Band's human health chronic mercury standard of 0.77 ng/L (Fong, 2022). Future research programs could evaluate feasibility of using mercury-capturing sorbents to lower the mercury concentrations from potential discharges.

B.5. Demonstrated Hydrometallurgical Technologies for Regional Mineral Resources

The technologies in this category have been demonstrated at bench and/or pilot scale for various mineral resources in Minnesota. Examples of these technologies include CESL, PLATSOL™, Albion Process™, and Mixed Hydrochloride processes. Following is a brief description of each of these technologies.

B.5.1. Cominco Engineering Services Limited (CESL)

CESL has developed a hydrometallurgical process for treating copper and nickel sulfide concentrates, including bulk concentrates from Teck Resources Mesaba Cu-Ni Project, located approximately 5 miles south of Babbitt, MN. The deposit contains a geologic resource in excess of 1 billion metric tons grading approximately 0.43% Cu and 0.09% Ni with minor Co and PGM values (Mayhew, et al., 2009). Figure 16 shows the proposed flowsheet for the Mesaba CESL Refinery. Table 11 shows the product quality of mixed hydroxide precipitate that was produced using the proposed flowsheet.

The CESL Process is composed of the following steps (Mayhew, et al., 2009):

- Light regrinding of the concentrate is necessary to increase the surface area of the particles, which improves the leaching kinetics in an autoclave.
- The leaching process is composed of two stages: 1) The first stage involves oxidation of sulfide concentrates at medium temperatures (150° C) and elevated pressure (200 psi) in the presence of chloride ions (12 g/L). The sulfide minerals are oxidized in the autoclave to form basic metal sulfate, hematite, and elemental sulfur. The chloride ion is added to accelerate the leach kinetics and minimizes the sulfur oxidation to sulfate, thereby allowing for economic recovery of metals from a bulk concentrate. The autoclave discharge is then thickened and filtered. The filtrate is recycled back to the autoclave, while the filter cake residue is sent to an atmospheric leach reactor; 2) In the second stage, an atmospheric leach, the filter cake residue is dissolved under mild acid conditions at atmospheric temperature and pressure.
- The pregnant leach solution from the atmospheric leach step is sent to the copper solvent extraction circuit for selective copper recovery using an organic mixture of 40% v/v extractant (LIX 973N®) and 60% v/v kerosene diluent (conosol 170E).
- The pregnant electrolyte from the solvent extraction process is sent to a conventional electrowinning circuit to produce Grade A copper cathode (99.999% Cu).
- The raffinate from copper solvent extraction process is fed to the nickel recovery circuit.
- The nickel recovery circuit consists of three steps: 1) iron and aluminum removal step via two step precipitation, 2) zinc, copper, and cadmium are precipitated as sulfides using H_2S gas, and 3) nickel/cobalt precipitation with the addition of calcined magnesia.

- Key metallurgical results from the Mesaba pilot campaign are as follows:
    - copper extraction was 95%
    - nickel extraction was 95%
    - cobalt extraction was 97%
    - sulfide oxidation was 6.9%
- The chemical composition of mixed hydroxide precipitate is shown in Table 11.

Table 11. Mixed hydroxide precipitate generated from the Mesaba pilot campaign (adapted from Mayhew, et al., 2009).

Ni (%)	**Co (%)**	**Mg (%)**	**Ca (%)**	**Cu (%)**	**Fe (%)**	**Mn (%)**	**Zn (%)**
46.0	2.0	0.8	0.6	0.02	0.1	0.68	0.02

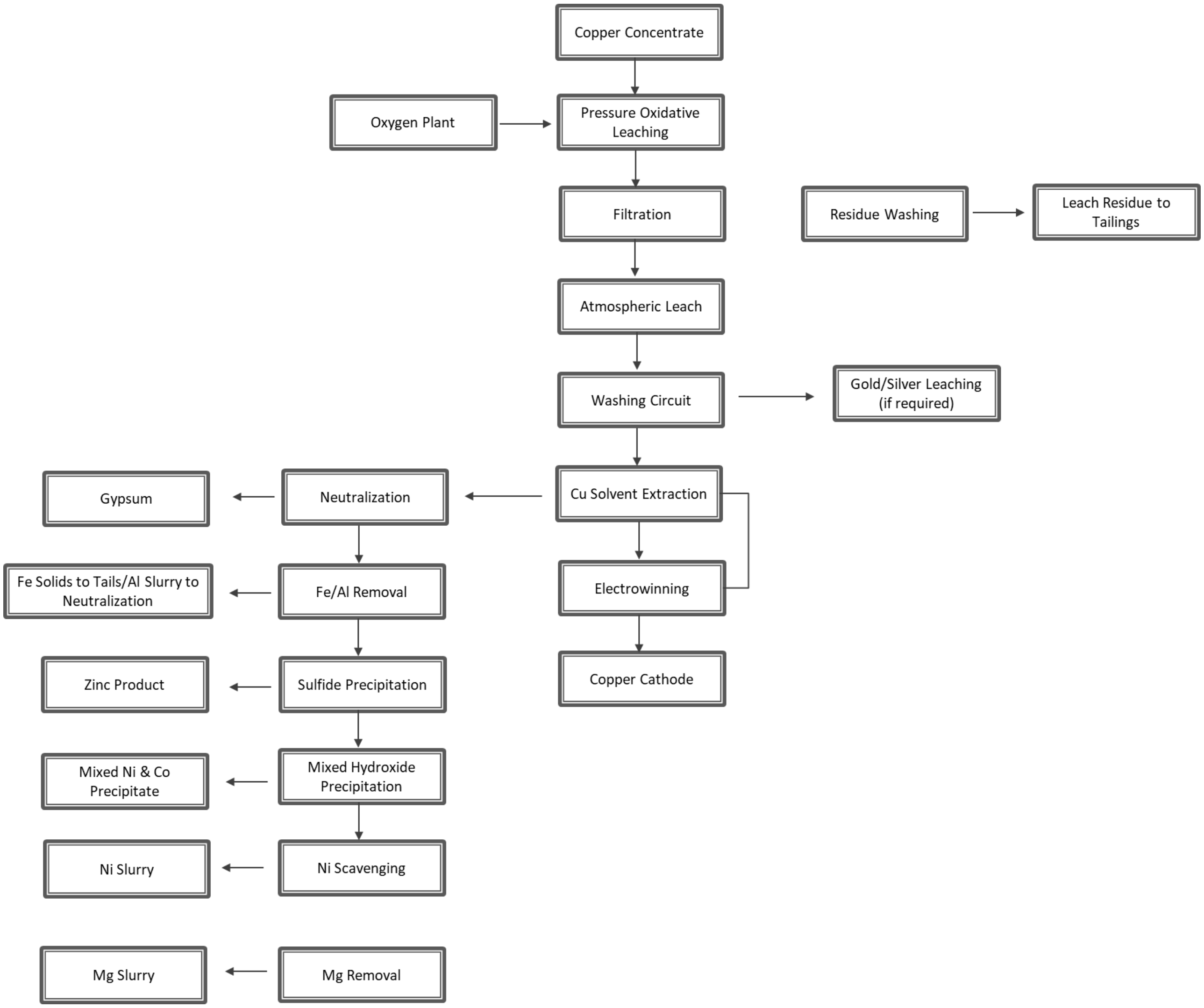


Figure 16. CESL hydrometallurgical flowsheet developed for the Mesaba deposit (Source: adapted from Mayhew, et al., 2009).

B.5.2. PLATSOL™

The PLATSOL™ process was developed to process polymetallic sulfide concentrate containing copper, nickel, cobalt, platinum, palladium, gold, and silver (Black, et al., 2018). Polymet Mining Inc. intends to use the PLATSOL™ process to treat flotation concentrates from the NorthMet deposit (Black, et al., 2018). The total proven and probable mineral reserves for the NorthMet Deposit are estimated to be 254.669 million tons at an equivalent copper grade of 0.586% (Black et al., 2018). The majority of the metals of interest are concentrated in chalcopyrite, cubanite, pentlandite, and pyrrhotite. Platinum, palladium, and gold are found in bismuthides, tellurides, and alloys (Black, et al., 2018). Figure 17 shows a flowsheet for the PLATSOL™ process for the proposed NorthMet Project. The PLATSOL™ process is composed of the following steps (Black, et al., 2018):

- The process uses chloride-assisted total pressure oxidation to extract base- and precious metals into the autoclave (pressurized vessel operated at high temperature) solution. The process is completed at high oxygen over pressure (110 psi) and high temperatures (225° C) with additions of 5–20 g/L NaCl to promote PGM minerals dissolution. Under the above conditions, base metals (Cu, Ni) and precious metals (gold (Au), platinum (Pt), and palladium (Pd)) are co-dissolved in a single step. The autoclave oxidation process converts sulfide minerals into metal sulfates, and iron minerals primarily into hematite, while the precious metals are converted to chloro-complexes. The leach residue consists of iron precipitates, unreacted gangue (non-ore minerals), and minor amounts of residual base and precious metal minerals.
- After the autoclave leaching, the solids are separated from the leach solution and washed. The leftover residues are then sent to waste disposal while the leach solution advances to metal recovery.
- The recovery of Au, Pt, and Pd from the autoclave solution is accomplished by precipitation with CuS. The CuS is less noble compared to Au, PdS, and PtS; hence, the PGMs in solution precipitate in exchange for Cu going into solution.
- In the subsequent step, PGM filtrate is mixed with copper sulfide concentrate resulting in an enriching copper grade.
- Residual soluble copper present in the depleted liquor from the copper enrichment stage is precipitated with NaHS.
- The Cu-NaHS filtrate streams are then subjected to a Fe/Al removal stage. In this stage, Fe/Al is precipitated by adding lime and oxygen. As this occurs, iron is oxidized from the ferrous to the ferric state with oxygen or air with limestone addition for neutralization and pH control.
- The filtrate from the Fe/Al stage is treated with magnesia (MgO) to precipitate mixed cobalt and nickel hydroxide.
- The filtrate from the first mixed hydroxide precipitation stage is treated with hydrated lime to further recover additional nickel and cobalt precipitates.
- Finally, to control the build-up of magnesium in solution, a magnesium removal step (with lime) is introduced into the circuit. Magnesium sulfate reacts with lime to form magnesium hydroxide and gypsum.

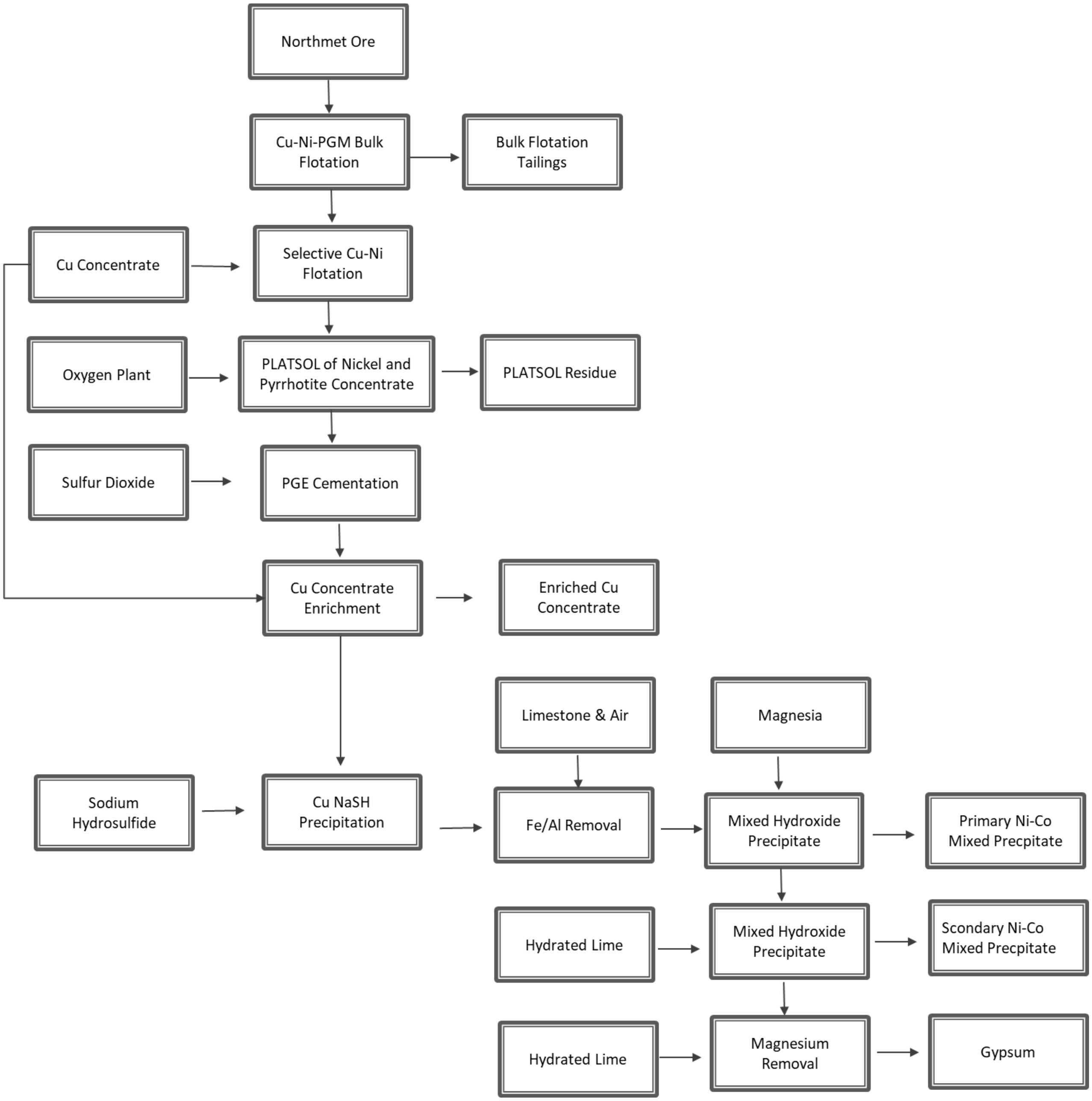


Figure 17. PLATSOL™ hydrometallurgical flowsheet developed for the NorthMet Project (adapted from Black, et al., 2018).

B.5.3. Albion Process™

The Albion Process™ was developed by Glencore to treat refractory precious metal and base metal concentrates that are unsuitable for toll smelting (Glencore Technology, 2020). The process employs ultrafine grinding of concentrates in an IsaMill™ prior to an atmospheric leaching process. Fine grinding increases the surface area and prevents the passivation of minerals during leaching reactions. Passivation generally occurs by precipitation of iron oxides and/or elemental sulfur on the mineral surface. These precipitates prevent the access of oxidants to the mineral surface, thereby preventing the dissolution reactions. The finely ground concentrate is then fed to a stainless steel reactor fitted with HyperSparge™ supersonic oxygen injectors to maximize oxygen mass transfer and facilitate the oxidation reactions. The process runs at atmospheric pressure and temperature and under mildly acidic conditions. The leach liquor is then directed to metal recovery circuits that use conventional technologies to produce the desired saleable products (Glencore Technology, 2020). Figure 18 shows a simplified flowsheet for the Albion Process™.

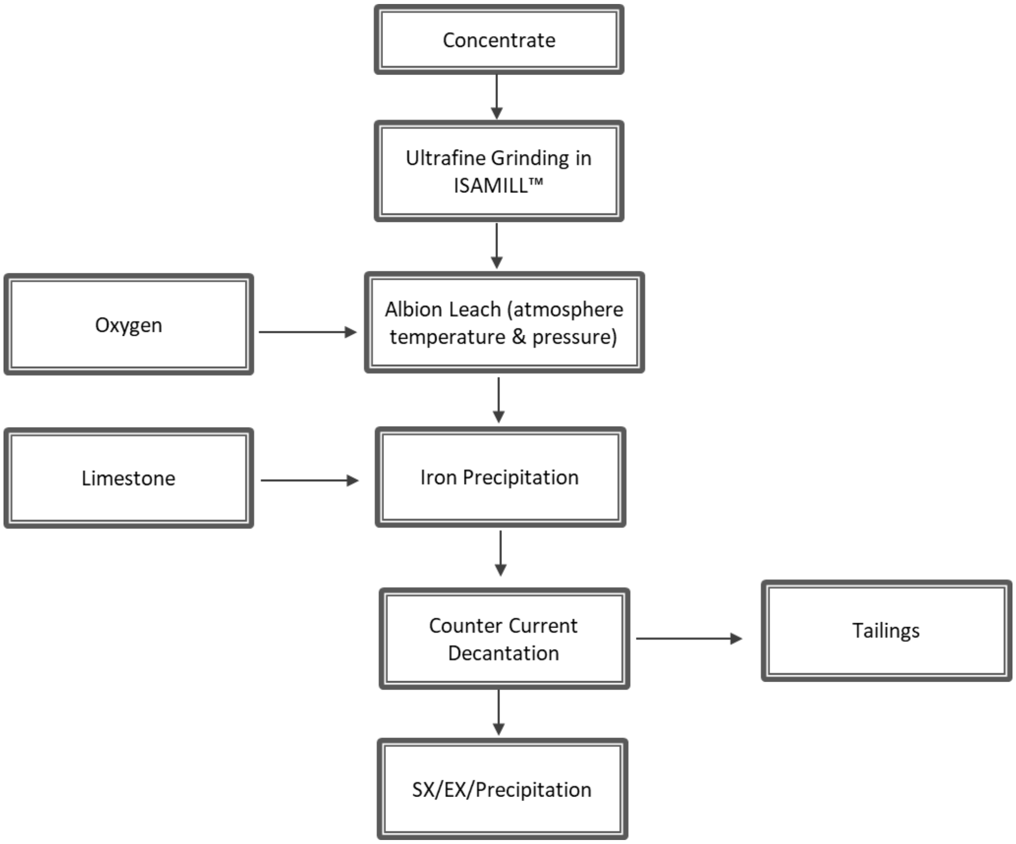


Figure 18. General schematic for the Albion Process™ (Source: adapted from Glencore Technology, 2020).

Table 12 compares the three hydrometallurgical extraction methods that have been demonstrated for Minnesota's mineral resources.

Table 12. Comparison of CESL, PLATSOL™, and Albion Process™.

Process	Lixiviant	P80 grind size, µm	Leaching temperature °C	Pressure (psi)	Unique feature	Sulfur product	Leaching time, hours	Maturity Stage as of June 2022	Reference
CESL	Sulfate + Chloride	15-40	150	200	10-15 g/L Cl^-	Sulfur	1-2	Final feasibility	(Mayhew, et al., 2009)
PLATSOL™	Sulfate + Chloride	15	<220	110	5-20 g/L Cl^-	Sulfate	1-2	Final feasibility	(Black, et al., 2018)
Albion Process™	Sulfate	10-15	85-90	Atmosphere	O_2 injected at 450–550 m/s	Sulfur	22	Commercial	(Glencore Technology, 2020)

Appendix C: Existing Hydrometallurgical Technologies

Appendix C provides a brief summary of existing hydrometallurgical technologies that are industrially practiced to extract copper, nickel, cobalt, gold, platinum group elements, titanium dioxide, manganese, lead, and zinc.

C.1. Commercial Plant Operations in North America

In addition to identifying key research facilities, the study identified key industrial facilities where hydrometallurgical techniques are commercially practiced for the extraction of non-ferrous metals like copper, nickel, cobalt, gold, platinum group elements, titanium dioxide, manganese, lead, and zinc. Figure 19 shows the location of these metallurgical complexes and Table 13 provides a comprehensive list of commercial operations in North America.

In some instances, hydrometallurgical techniques are exclusively used for the extraction of metals. Examples include Freeport McMoran's Morenci facility in Arizona (Figure 20), Vale's Long Harbor facility in Newfoundland (Figure 21), and Terrafame's Sotkamo facility in Finland (Figure 22). In other instances, they are used to upgrade the pyrometallurgical smelter and converter products. Examples include Glencore's Nikkelverk facility in Norway (Figure 23), Sibanye-Stillwater's facilities in Rustenburg, South Africa (Figure 24) and Stillwater, Montana (Figure 27), and Rio Tinto Iron and Titanium's QIT facility in Quebec, Canada (Figure 25).

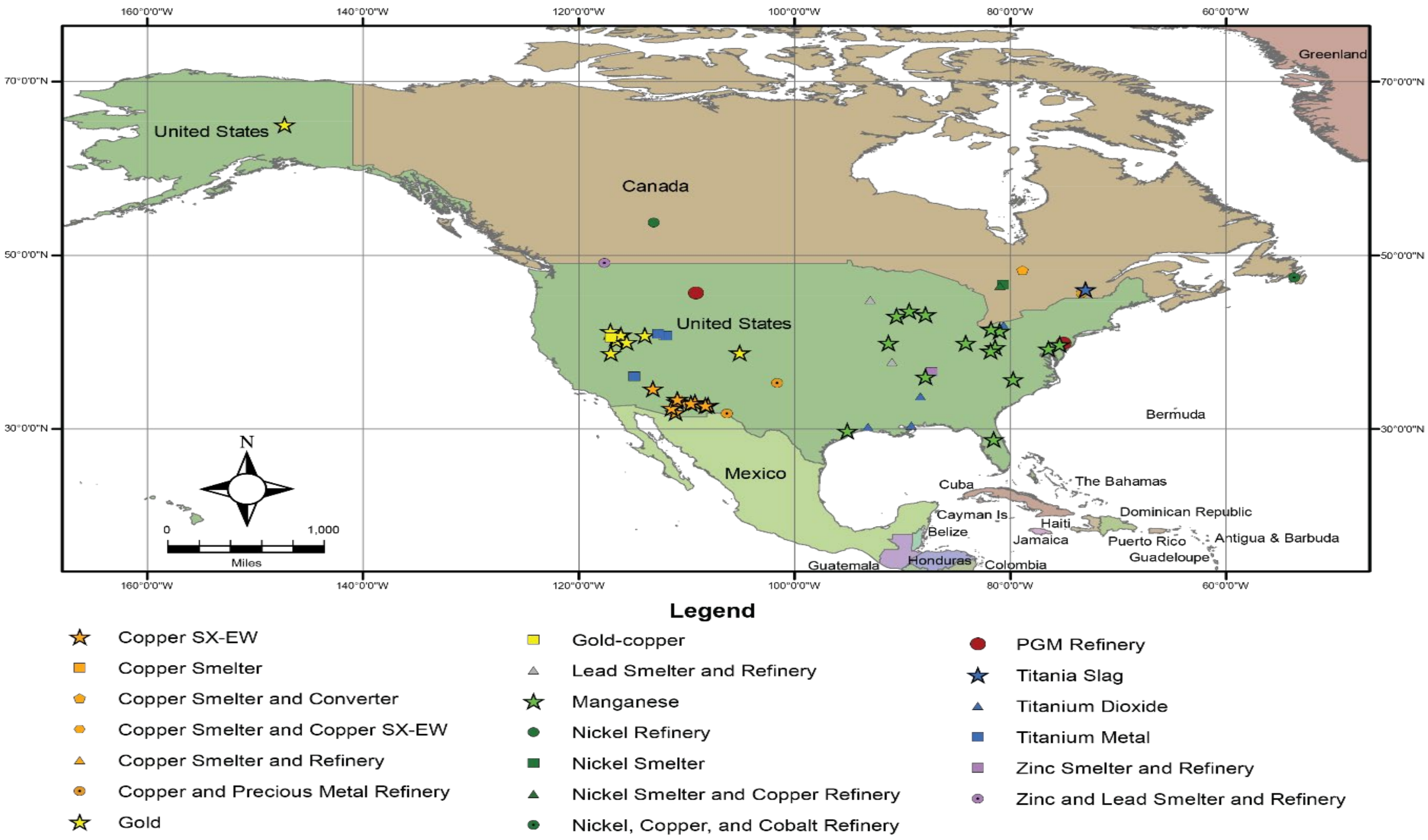


Figure 19. A map of commercial non-ferrous metallurgical operations in North America.

Table 13. A list of non-ferrous metallurgical extraction facilities in North America.

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
Stillwater Sibanye	Stillwater, MT	PGM Refinery	PGM concentrate, nickel sulfate, copper cathode	EAF smelting, Kaldo converter	Nickel atmospheric leach, nickel sulfate crystallization, copper-PGM pressure leach, copper electrowinning, selenium/tellurium precipitation.
Johnson Matthey	West Deptford, NJ	PGM Refinery	Gold, iridium, platinum, palladium, rhenium, rhodium, ruthenium, silver	Reverberatory furnace	HCl/Cl_2 pressure leaching, solvent extraction, precipitation, reduction using hydrazine
Freeport McMoran	Morenci, AZ	Copper SX-EW	Copper cathode, molybdenum concentrate	Smelting ceased in 1984	MT Pressure concentrate leaching and ROM bio heap leaching-SX-EW
	Baghdad, AZ	Copper SX-EW	Copper cathode, molybdenum concentrate	Not used	HT Pressure concentrate leaching and ROM heap leaching-SX-EW
	Sierrita, AZ	Copper SX-EW	Copper cathode, molybdenum, rhenium	Molybdenum roasters	Heap leaching-SX-EW
	Miami, AZ	Copper Smelter and Copper SX-EW	Copper cathode, precious metals	IsaSmelt™ technology (primary furnace) and ELKEM electric furnace (secondary); four Hoboken style converters	Heap leaching-SX-EW
	Safford, AZ	Copper SX-EW	Copper cathode	Not used	Heap leaching-SX-EW

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
	Chino, NM	Copper SX-EW	Copper cathode, molybdenum	Smelter ceased in 2005	Heap leaching-SX-EW
	Tyrone, NM	Copper SX-EW	Copper cathode	Not used	Heap leaching-SX-EW
	El Paso, TX	Copper and Precious Metal Refinery	Copper cathode, silver, gold, PGE, tellurium, selenium	Not used	Electrorefining, copper pressure leach, ferric chloride leach of silver, HCl leach of gold/PGE, solvent extraction of silver and gold,
Rio Tinto Kennecott	Magna, UT	Copper Smelter and Refinery	Copper cathode, gold, silver, molybdenum oxide, rhenium, selenium, tellurium	Smelting (The smelter at Kennecott captures 99.9 percent of the sulfur in the feed, making it one of the cleanest in the world)	Electrorefining (99.999 percent pure copper); rhenium via ion exchange; chlorination process to recover gold, silver, lead, and selenium.
ASARCO	Hayden, AZ	Copper Smelter	Copper cathode, sulfuric acid	Smelting/converting (oxygen flash smelting furnace, Anode Furnace)	-
	Ray, AZ	Copper SX-EW	Copper	Not used	Heap leaching-SX-EW
	Silver Bell, AZ	Copper SX-EW	Copper	Not used	Heap leaching-SX-EW
	Amarillo Copper Refinery, TX	Copper and Precious Metal Refinery	Copper, silver, gold, platinum, palladium, antimony, nickel sulfide, selenium, and tellurium	Not used	Electrorefining, Hydrometallurgy to recover precious metals

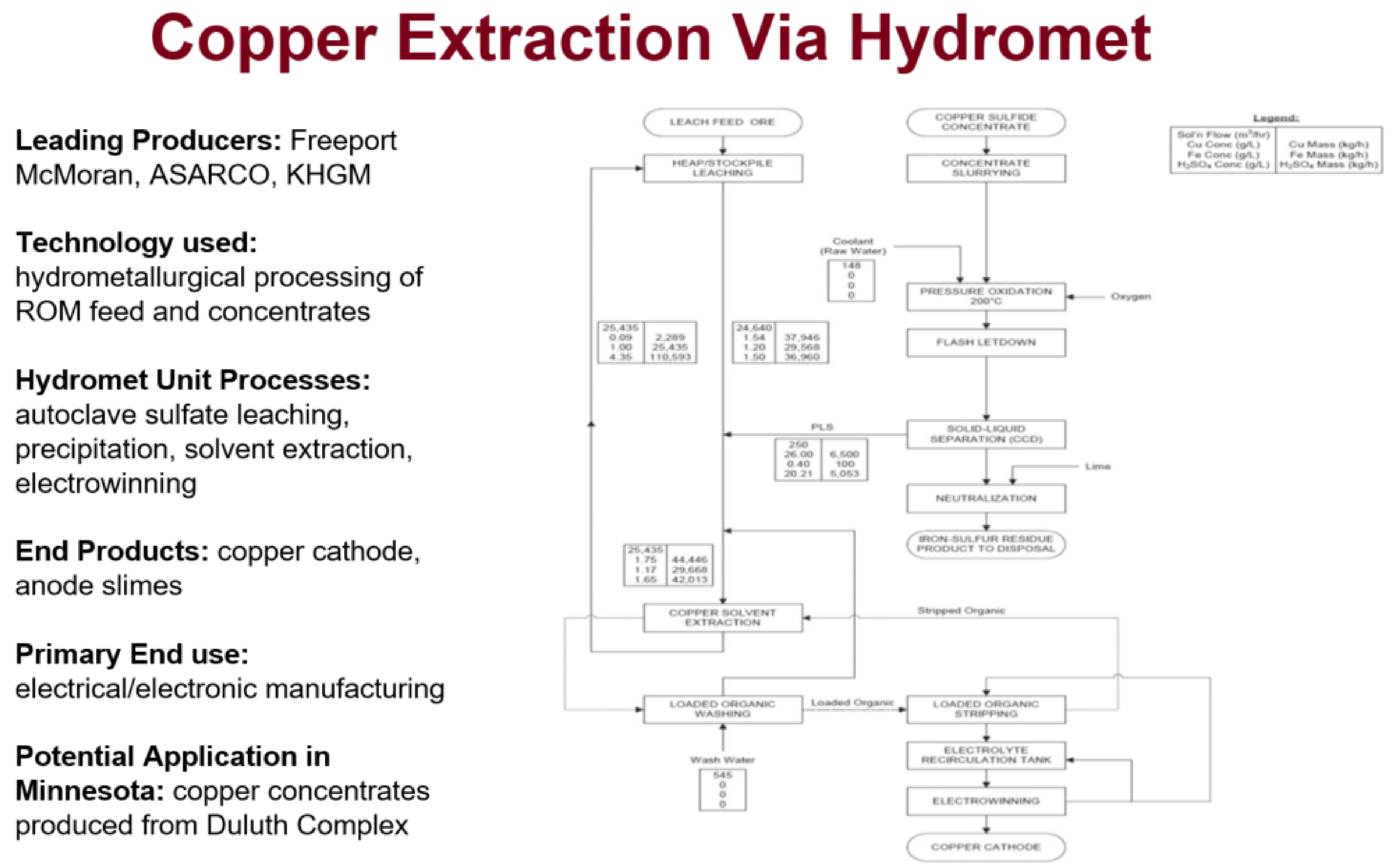
Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
KHGM	Carlota Mine, AZ	Copper SX-EW	Copper cathode	Not used	Heap leaching, SX-EW
Hecla Mining	Fire Creek, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Cyanide leaching, Carbon in Leach, Merrill Crowe Precipitation
Newmont Corporation	Cripple Creek & Victor, CO, USA	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap leaching-EW
	Cortez, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap Leaching, Cyanide leaching, Carbon in Leach, Electrowinning
	Carlin, NV	Gold	Gold dore	Smelting and Roasting	Heap Leaching, Autoclaves, Cyanide leaching, Carbon in Leach, Electrowinning
	Turquoise Ridge, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap Leaching, Autoclaves, Cyanide leaching, Carbon in Leach, Electrowinning
	Phoenix, NV	Gold-copper	Gold dore, copper	Smelting gold bearing conc. from hydromet circuit	gold from cyanide leaching; a copper from heap leach pad and a solvent extraction electrowinning (“SX/EW”) plant
	Long Canyon, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap leaching
Kinross Gold	Fort Knox, AK	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Run-of-mine valley-fill cyanide heap leaching, agitated cyanide leaching, and a carbon-in pulp (CIP) circuit;, EW
	Round Mountain, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap leach, Carbon in Column, EW

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
	Bald Mountain, NV	Gold	Gold dore	Smelting gold bearing conc. from hydromet circuit	Heap leach, EW
Glencore	Sudbury Integrated Nickel Operations (Sudbury INO), ON	Nickel Smelter	nickel, copper and cobalt in matte, sulfuric acid	Roaster, electric arc furnace smelting, converter	Flotation to recover copper from slag
	Horne Copper Smelter, Rouyn-Noranda, Quebec	Copper Smelter and Converter	Copper anodes, sulfuric acid	Smelter, converter, anode furnace	Flotation to recover copper from slag
	Canadian Copper Refinery, Quebec	Copper and Precious Metal Refinery	Copper cathodes, gold, silver and other specialty metals and chemicals, including selenium, tellurium dioxide, nickel sulfate and a concentrate of platinum group metals	Not used	Electrorefining copper, anode slimes treated via hydrometallurgy to recover PGMs, nickel sulfate, selenium, tellurium dioxide, gold, and silver
Vale	Long Harbor, Nova Scotia	Nickel, Copper, and Cobalt Refinery	Nickel, copper, cobalt	Not used	Pressure oxidation leaching, copper solvent extraction, cobalt solvent extraction, copper & cobalt & nickel electrowinning

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
	Copper Cliff Nickel Refinery, Sudbury	Nickel Smelter and Copper Refinery	Nickel, nickel oxide, copper, anode slimes from electrorefining copper, carbonyl residue	Bulk smelting, Nickel refining (carbonyl process), Ni Matte Roasting to NiO	Electrorefining Copper
Sherritt International Corp.	Fort Saskatchewan, Saskatchewan	Nickel Refinery	High purity nickel and cobalt powder and briquettes	Sintering nickel and cobalt products	High-pressure ammoniacal leaching; high pressure hydrogen reduction; precipitation
Teck Resources	Trail, British Columbia	Zinc and Lead Smelter and Refinery	Refined zinc and lead, germanium, indium, and cadmium	Roasting, melting/casting of Zn; flash smelting of Pb; slag-fuming furnace;	Pressure leaching plant, cementation, electrowinning, vacuum distillation, oxide leaching
Honeywell Electronic Materials	SLC, UT	Titanium Metal	Titanium metal sponge	Refining (electrode vacuum arc furnace)	Hunter process (sodium reduction)
Allegheny Technologies Inc.	Rowley, UT	Titanium Metal	Titanium metal sponge	Refining (electrode vacuum arc furnace)	Kroll process (Magnesium reduction)
Titanium Metals Corp. (TIMET)	Henderson, NV	Titanium Metal	Titanium metal sponge	Refining (electrode vacuum arc furnace)	Kroll process (Magnesium reduction)
Chemours	DeLisle, MS;	Titanium Dioxide	TiO_2 pigment	Chlorination process, fractional distillation	Not used
	New Johnsonville, TN	Titanium Dioxide	TiO_2 pigment	Chlorination process, fractional distillation	Not used

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
Tronox	Hamilton, MS	Titanium Dioxide	TiO_2 pigment	Chlorination process, fractional distillation	Not used
INEOS	Ashtabula, OH	Titanium Dioxide	TiO_2 pigment	Chlorination process, fractional distillation	Not used
Venator Corp	Lake Charles, LA	Titanium Dioxide	TiO_2 pigment	Chlorination process, fractional distillation	Not used
Rio Tinto Iron and Titanium	Sorel-Tracy, QC	Titania Slag	Upgraded TiO_2 slag, high purity pig iron, iron powders	EAF smelting, roasters	High pressure/autoclave-HCl leaching
Nyrstar	Clarksville, TN	Zinc Smelter and Refinery	Special high grade (SHG) zinc, zinc alloys and sulfuric acid, germanium concentrate, leach products, zinc sulfate, copper sulfate, cadmium metal	Roasting and casting	Atmospheric sulfate leaching, precipitation, electrowinning
Doe Run	Viburnum, MO	Lead Smelter and Refinery	Refined lead	Blast furnace smelting and casting	Stable fluoboric acid leaching, electrowinning
Gopher Resource	Eagan, MN	Lead Smelter and Refinery	Recycled pure lead, antimonial and calcium lead alloys	Blast furnace smelting and casting	Not used
	Baltimore, MD	Manganese			Proprietary technologies

Company Name	Location	Type of Plant	Products	Pyrometallurgy	Hydrometallurgy/Electrometallurgy
Prince International Corporation (Vibrantz Technologies)	Houston, TX	Manganese	Manganese chemicals (EMD, MnO, $MnCl_2$, $MnSO_4$, $Mn(NO_3)_2$, $MnCO_3$), Iron oxides	Proprietary technologies	
	Mount Dora, FL	Manganese			
	New Johnsonville, TN	Manganese			
	New Castle, DE	Manganese			
	Quincy, IL	Manganese			
	Milwaukee, WI	Manganese			
Energizer Holdings, Inc.	Asheboro, NC	Manganese	Batteries using many technologies including lithium, alkaline, carbon zinc, nickel metal hydride, zinc air, and silver oxide	Proprietary technologies	Proprietary technologies
	Garrettsville, OH	Manganese			
	Westlake, OH	Manganese			
	Marietta, OH	Manganese			
	Dayton, OH	Manganese			
	Fennimore, WI	Manganese			
	Portage, WI	Manganese			
Felman Production, LLC	Letart, WV	Manganese	Ferro silicomanganese, Ferromanganese	Submerged arc furnaces	Not used



Copper Extraction Via Hydromet

Leading Producers: Freeport McMoran, ASARCO, KHGM

Technology used:
hydrometallurgical processing of ROM feed and concentrates

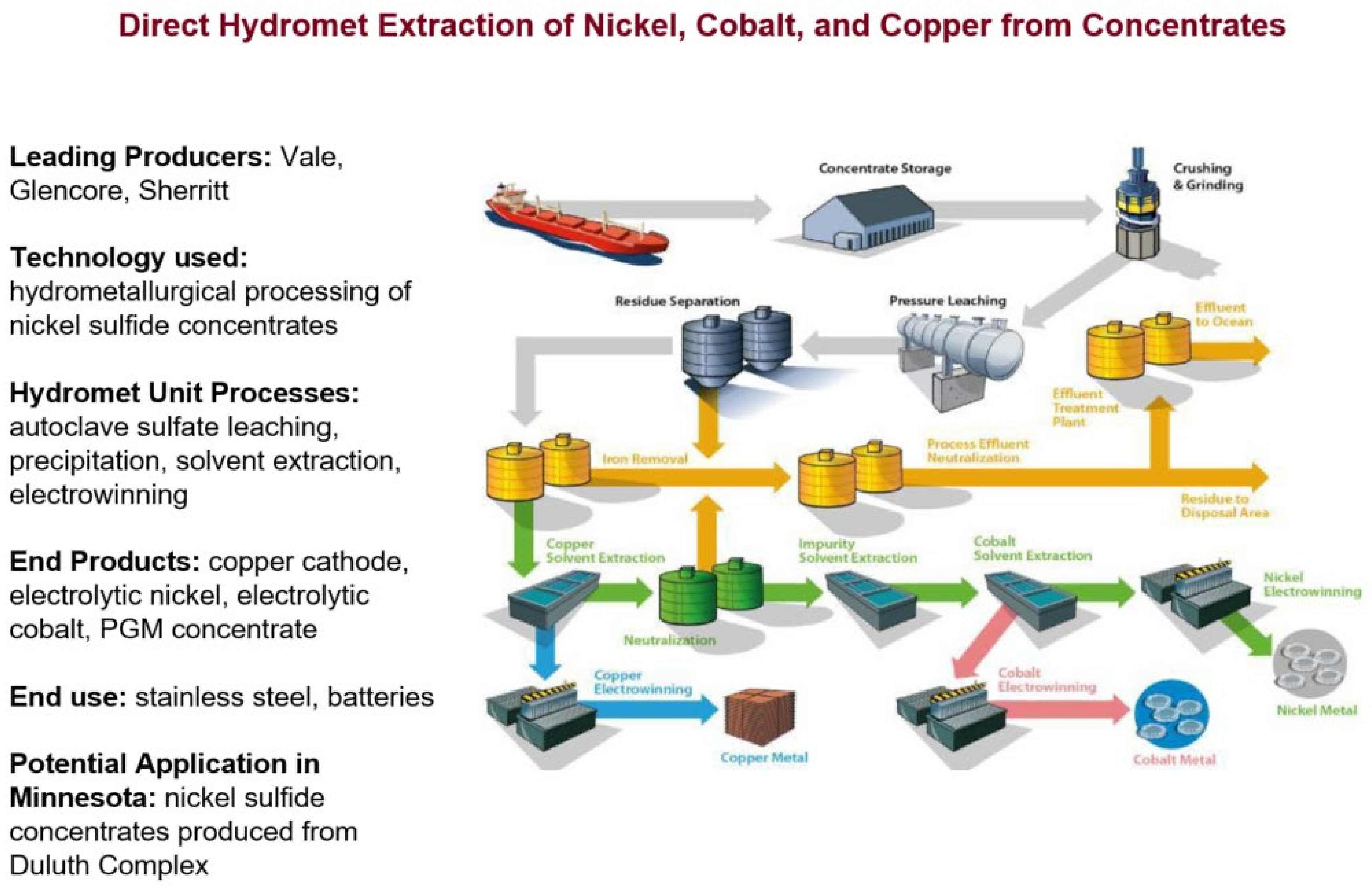
Hydromet Unit Processes:
autoclave sulfate leaching, precipitation, solvent extraction, electrowinning

End Products: copper cathode, anode slimes

Primary End use:
electrical/electronic manufacturing

Potential Application in Minnesota: copper concentrates produced from Duluth Complex

Figure 20. Medium-temperature pressure oxidation process practiced at Freeport McMoran's Morenci facility, AZ, USA (Source: Green, et al., 2018).



Direct Hydromet Extraction of Nickel, Cobalt, and Copper from Concentrates

Leading Producers: Vale, Glencore, Sherritt

Technology used: hydrometallurgical processing of nickel sulfide concentrates

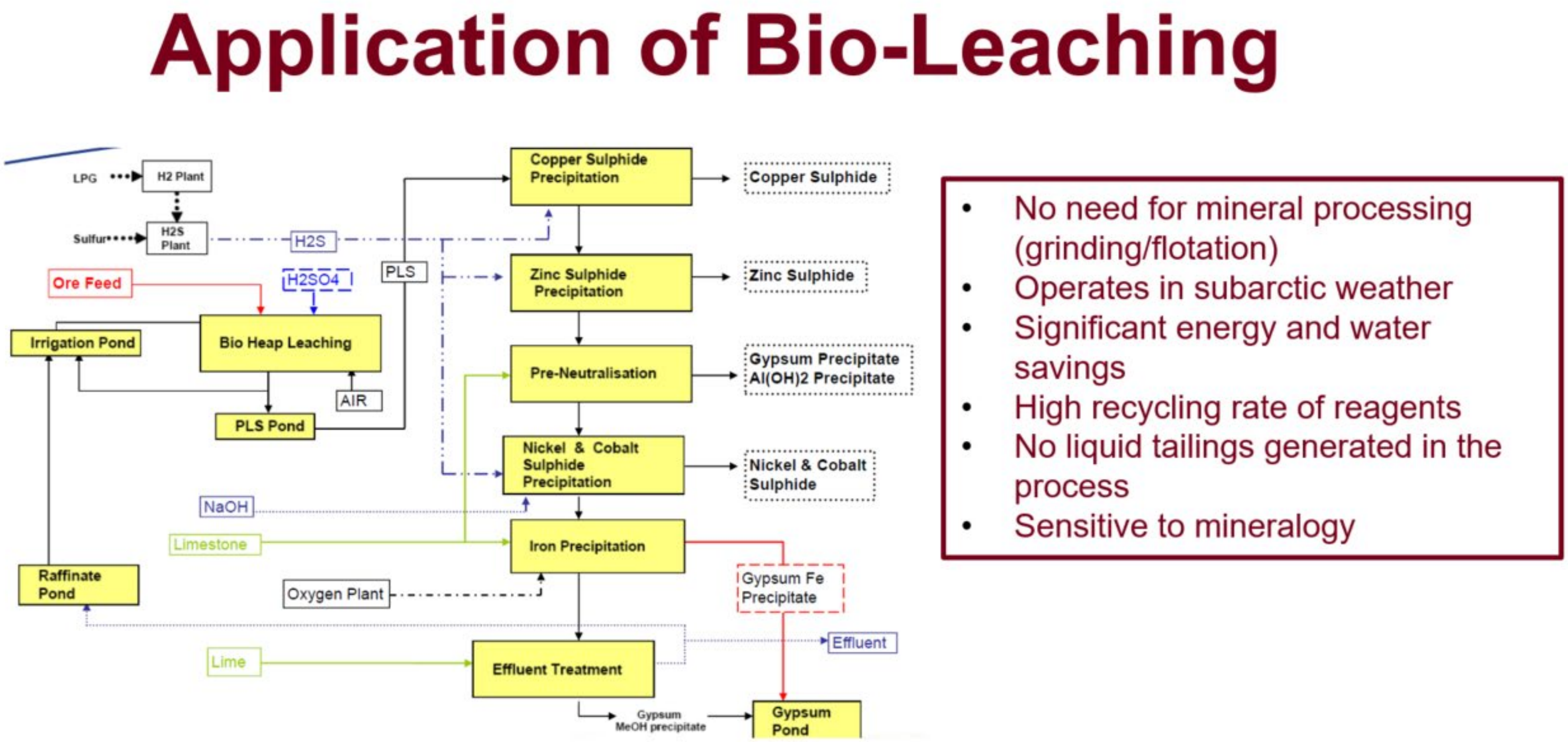
Hydromet Unit Processes: autoclave sulfate leaching, precipitation, solvent extraction, electrowinning

End Products: copper cathode, electrolytic nickel, electrolytic cobalt, PGM concentrate

End use: stainless steel, batteries

Potential Application in Minnesota: nickel sulfide concentrates produced from Duluth Complex

Figure 21. Pressure oxidation leaching process practiced at Voisey's Bay Long Harbor facility (Source: Wheaton Precious Metal, 2018).



Application of Bio-Leaching

- No need for mineral processing (grinding/flotation)
- Operates in subarctic weather
- Significant energy and water savings
- High recycling rate of reagents
- No liquid tailings generated in the process
- Sensitive to mineralogy

Figure 22. Biological leaching process practices at Terrafame in Sotkamo, Finland (Source: Pitkäjärvi, 2011).

Nickel and Cobalt Extraction from Matte using Hydromet

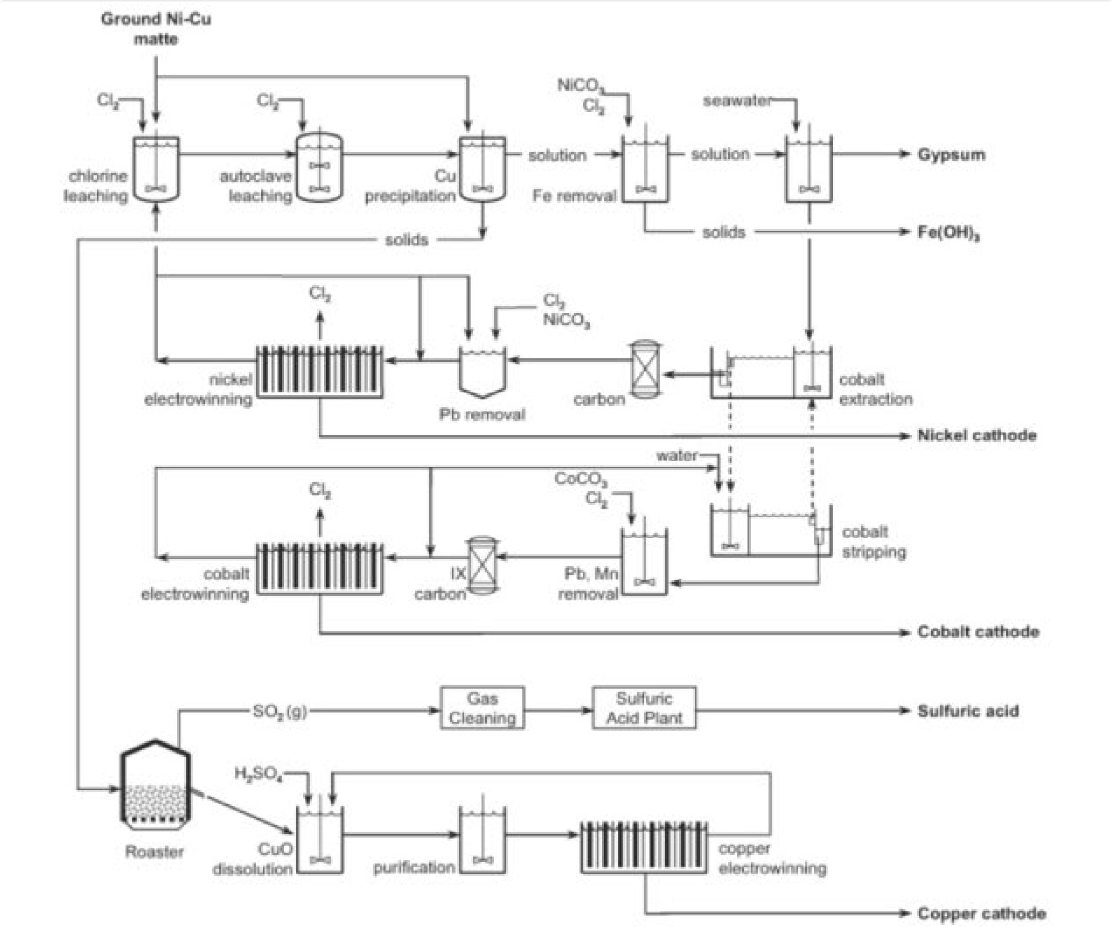


Figure 23. Chloride-based autoclave pressure leaching practiced at Glencore's Nikkelverk, Kristiansand in Norway (Source: Crundwell, et al., 2011).

PGM Refining Via Hydromet

Leading Producers: Johnson Matthey, Sibanye Stillwater

Technology used: hydrometallurgical processing of PGM sulfide concentrates/catalysts

Hydromet Unit Processes: chloride leach, solvent extraction, precipitation via H2 reduction

End Products: Gold, iridium, platinum, palladium, rhenium, rhodium, ruthenium, silver

Primary End use: catalysts, jewelry

Potential Application in Minnesota: PGM sulfide concentrates produced from Duluth Complex

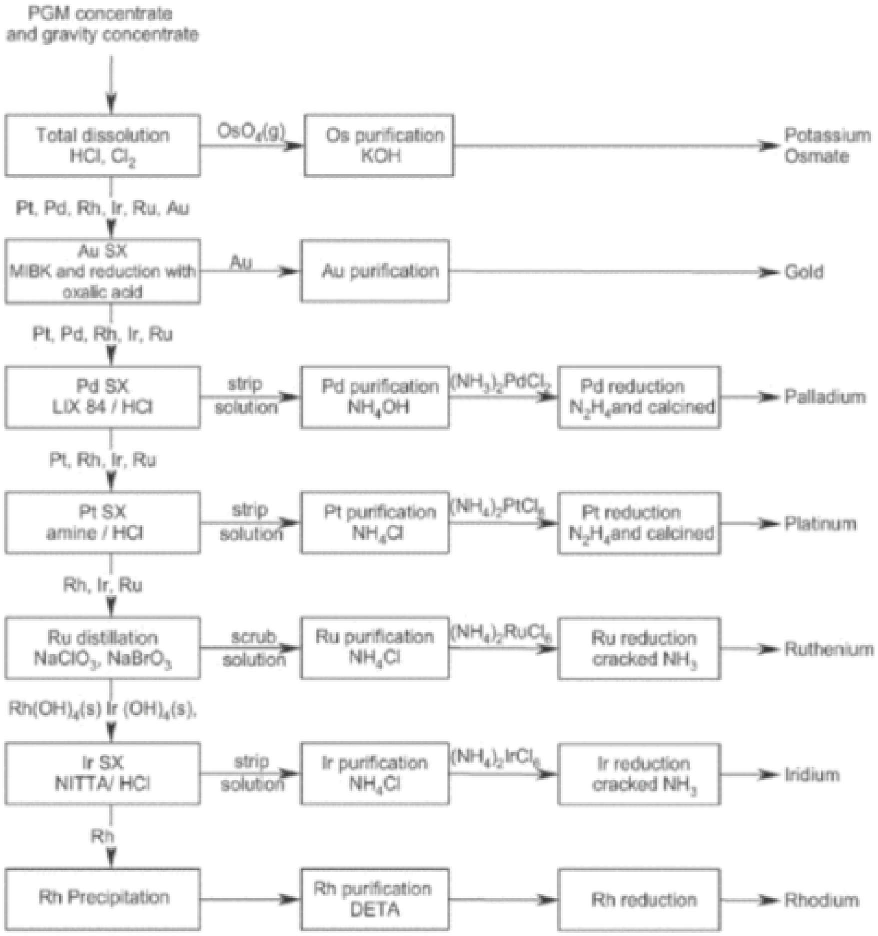
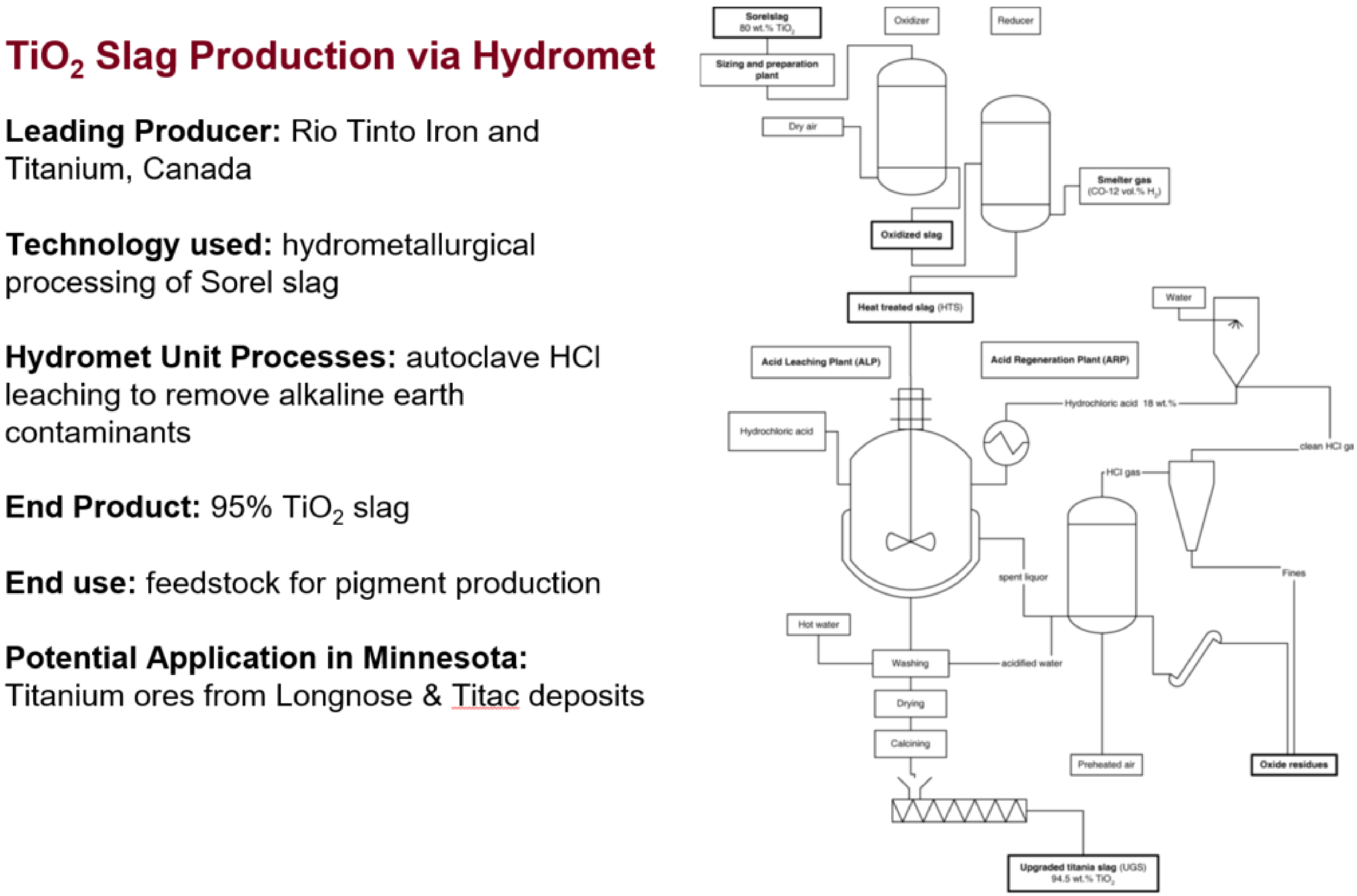


Figure 24. Hydrometallurgical flowsheet used in the extraction of platinum group elements at Rustenburg, South Africa (Source: Crundwell, et al., 2011).



TiO_2 Slag Production via Hydromet

Leading Producer: Rio Tinto Iron and Titanium, Canada

Technology used: hydrometallurgical processing of Sorel slag

Hydromet Unit Processes: autoclave HCl leaching to remove alkaline earth contaminants

End Product: 95% TiO_2 slag

End use: feedstock for pigment production

Potential Application in Minnesota: Titanium ores from Longnose & Titac deposits

Figure 25. Hydrometallurgical process used in the production of high-purity titanium dioxide slag in Quebec, Canada (Source: Guéguin & Cardarelli, 2007).

Manganese Extraction via Hydromet

Leading Producer: China (95% of global output). 3 sites in the USA

Technology used: hydrometallurgical process developed by US Bureau of Mines

Hydromet Unit Processes: sulfate leaching, precipitation, electrolysis

End Product: Electrolytic Manganese Metal (EMM)

Primary End uses: batteries, steelmaking, aluminum alloys

Potential Application in Minnesota: Cuyuna Range Manganese Ores

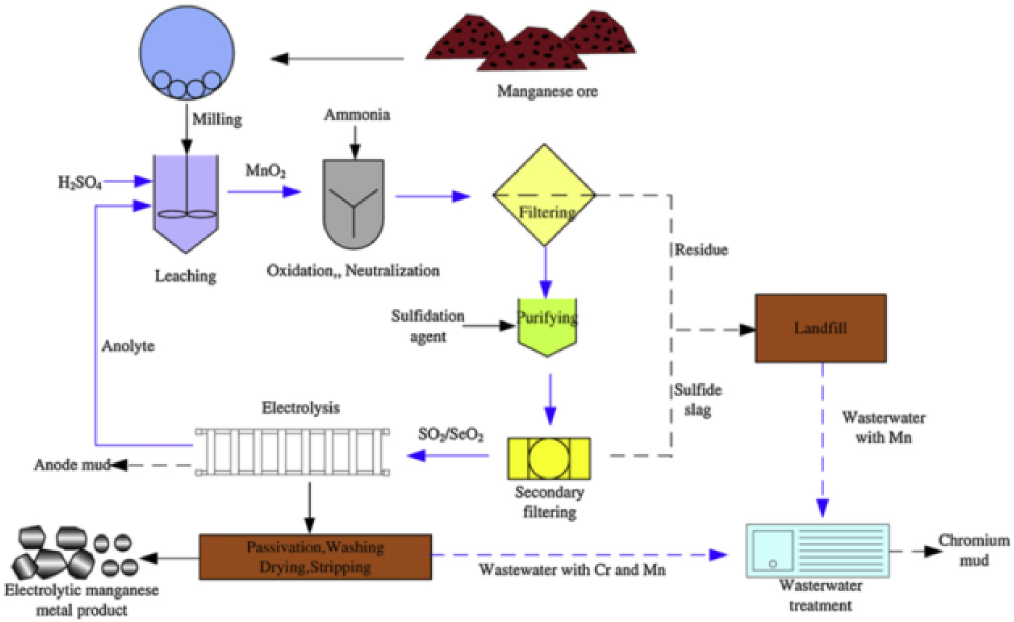


Figure 26. Hydrometallurgical process flowsheet used in the production of electrolytic manganese metal in China (Source: Duan, et al., 2011).

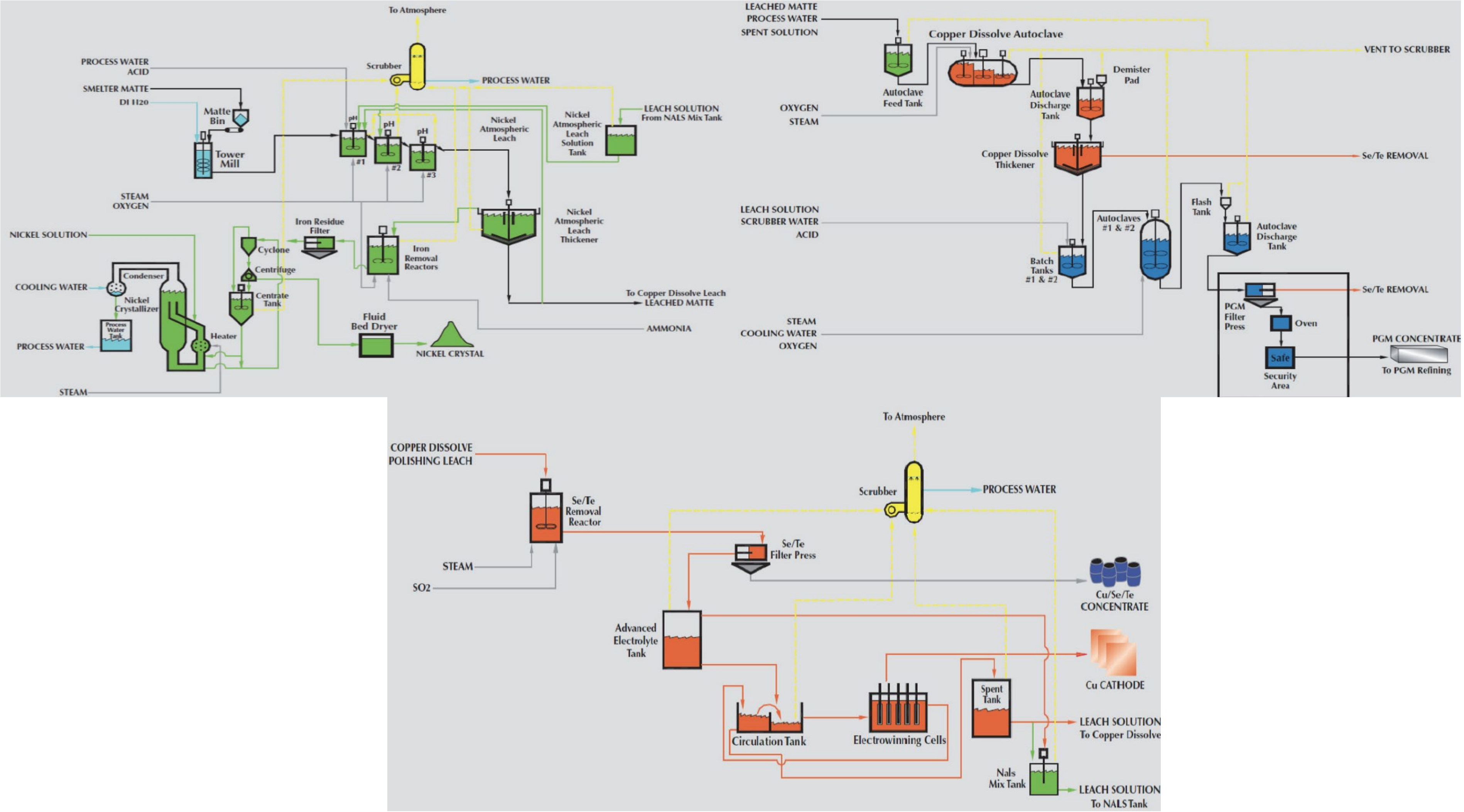


Figure 27. Hydrometallurgical flowsheet practiced at Sibanye Stillwater Complex in Montana, USA (Source: Sibanye-Stillwater, 2018).

Appendix D: Mineral Resources of Minnesota

Appendix D provides a brief and generalized descriptions of mineral and waste resource of Minnesota.

D.1. Mineral Resources of Minnesota

Three general mineral resources categories that have potential hydrometallurgical applications have been identified for this project. These categories include: 1) non-ferrous resources, which include Cu-Ni-Co-PGE and Ti-V deposits, 2) ferrous resources, which include Fe and Mn-Fe deposits, and 3) aggregate and byproduct resources. Brief and generalized descriptions of these resource categories are presented in the following section of this report.

D.1.1. Non-ferrous Resources

The non-ferrous mineral resources consist of mafic magmatic mineral systems outlined in recent USGS publications (Schulz, et al., 2017 and Hofstra and Kreiner, 2020), including: 1) Contact-type Ni-Cu-PGE sulfide deposits, 2) Conduit-type Ni-Cu-PGE sulfide deposits, and 3) Iron-Titanium oxide (Fe-Ti-V-P) deposits (Figure 28).

D.1.1.1. Contact-type Cu-Ni-Co-PGE sulfide deposits

Contact-type Cu-Ni-PGE magmatic sulfide deposits (Zientek, 2012) of the midcontinent of North America are exemplified by the large, mainly disseminated sulfide deposits that occur along the basal contact of the Duluth Complex where magmas intruded and incorporated footwall Paleoproterozoic Animikie Group metasedimentary rocks and Archean granitoids. Major deposits include Birch Lake, Maturi, Mesaba, NorthMet, Serpentine, and Spruce Road (Figure 29). Disseminated and local massive sulfide mineralization of the Duluth Complex was historically estimated to contain about 4.4 billion metric tons of ore with average grades of 0.66% Cu and 0.2% Ni at a 0.5% Cu cut-off (Listerud and Meinike, 1977). Recent exploration and project development has led to upgraded mineral resource estimates for many of these deposits (Table 14), resulting in a combined upgraded estimate of 9.57 billion metric tons with average grades of 0.406% Cu, 0.126% Ni, and 0.326 g/t Pt-Pd-Au.

The Duluth Complex contact-type deposits typically contain interstitial disseminated sulfide minerals (pyrrhotite, chalcopyrite, cubanite, and pentlandite) at trace-to-10% of the mineralized rock by volume by visual estimate (Miller, et al., 2002). Mineralization can be extremely erratic in spatial extent and ore grades within basal units of the intrusions (Miller, et al., 2002). Thériault, et al. (2000) described mineralization in the basal section of the Partridge River intrusion as consisting of three distinct parts: 1) Cu-rich, PGE-poor disseminated sulfides, 2) Cu-rich, PGE-rich disseminated sulfides, and 3) semi-massive to massive sulfides. They interpreted these variations as resulting from systematic variations in magma inputs and flow regimes and accompanying sulfur contamination. Disseminated mineralization was a product of dispersed sulfides unable to coalesce because of disruption by multiple episodes of magma pulses along the basal contact (Miller, et al., 2002). Where mineralization is more consistently stratabound, such as in parts of the Maturi deposit in the South Kawishiwi intrusion, channelized magma flow was a likely organizing influence that also increased the metal content of transported sulfides (Peterson and Albers, 2007). Rare pyrrhotite-rich massive sulfide concentrations are spatially related to nearby sulfide-rich footwall rocks and/or fold structures (Hauck, et al., 1997). The Local Boy massive sulfide ore zone in the Babbitt deposit, Partridge River intrusion, has 5 to 25% Cu, 11 ppm Pd, and 8 ppm Pt, which are the highest PGE values reported for the Duluth Complex (Miller, et al., 2002).

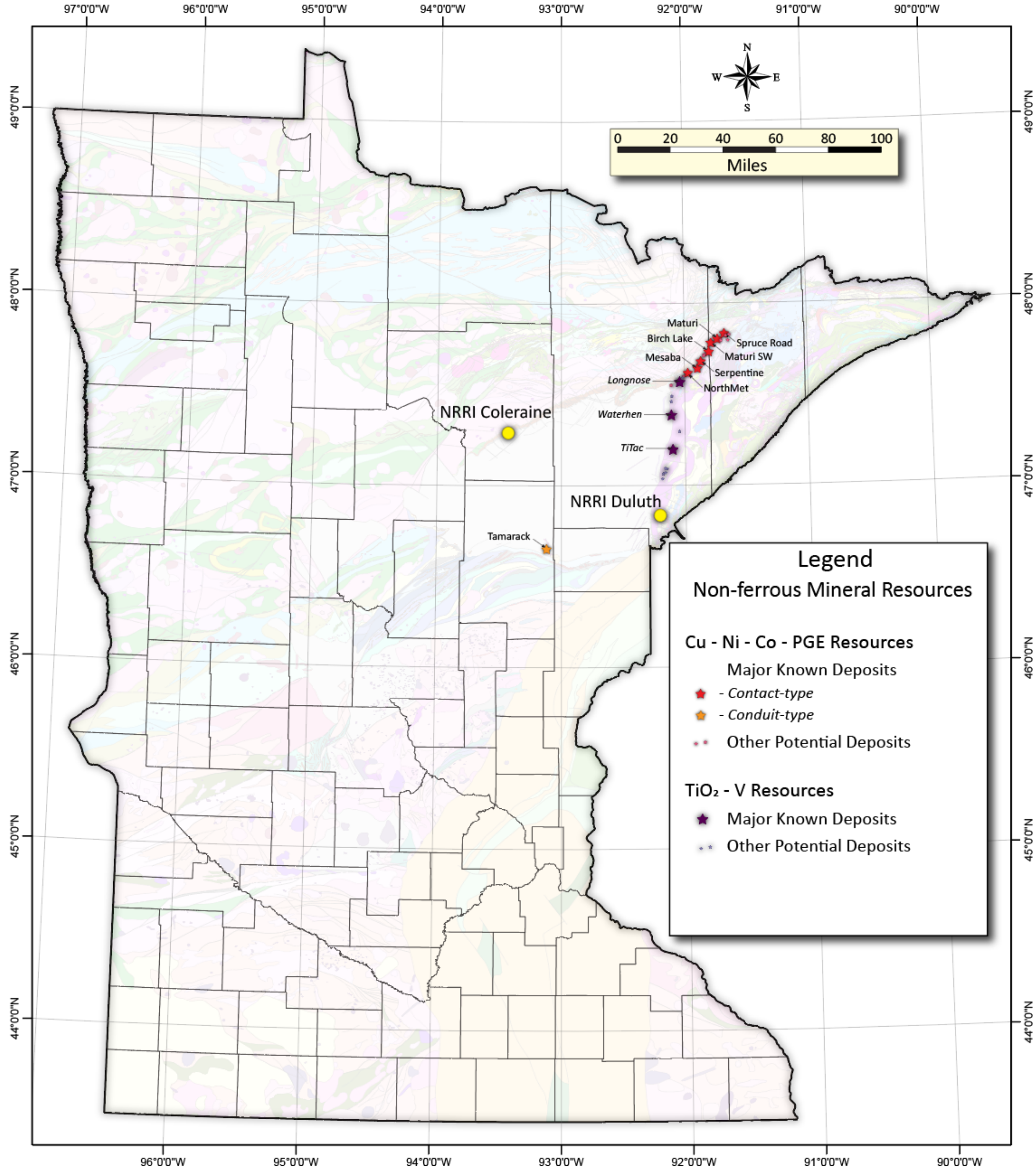


Figure 28. Location map of identified non-ferrous mineral resources in Minnesota.

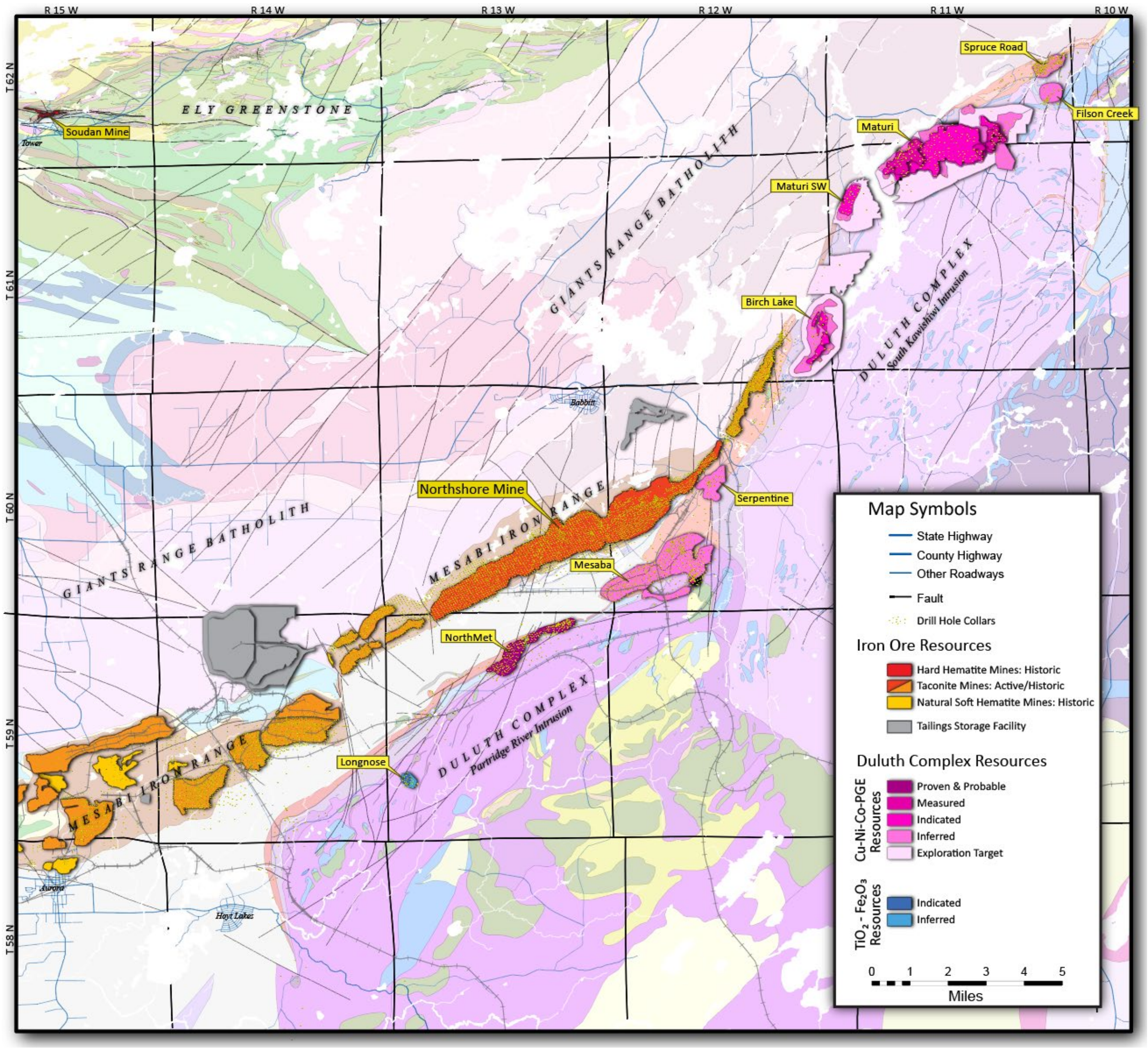


Figure 29. Bedrock geology and mineral resource location map of the contact-type deposits of the Duluth Complex and adjacent areas.

Table 14. Ni 43-101 compliant grade-tonnage estimates of mafic magmatic sulfide deposits associated with the Mid-Continent Rift.

STATUS	DEPOSIT	YEAR	TYPE	CATEGORY	TONNES	Cu %	Ni %	Co %	Pt g/t	Pd g/t	Au g/t	Ag g/t	Reference
CURRENTLY ACTIVE PROJECTS	NorthMet	2019	Contact	Proven	173,495,000	0.288	0.083	0.0074	0.075	0.270	0.039	1.050	PolyMet Mining 2019
	NorthMet	2019	Contact	Probable	116,904,000	0.288	0.081	0.0074	0.073	0.256	0.037	1.080	
	NorthMet	2019	Contact	Measured	351,500,000	0.240	0.073	0.0071	0.064	0.222	0.033	0.880	
	NorthMet	2019	Contact	Indicated	443,700,000	0.230	0.069	0.0068	0.061	0.207	0.030	0.870	
	NorthMet	2019	Contact	Inferred	457,700,000	0.236	0.067	0.0056	0.062	0.214	0.031	0.087	
	NorthMet	2019	Contact	Combined	1,543,299,000	0.245	0.072	0.0066	0.064	0.223	0.033	0.676	
	Maturi	2013	Contact	Measured	267,891,654	0.630	0.200	0.0100	0.148	0.345	0.084	2.116	Duluth Metals Corp, 2014
	Maturi	2013	Contact	Indicated	702,342,426	0.580	0.190	0.0100	0.160	0.360	0.071	2.116	
	Maturi	2013	Contact	Inferred	509,837,824	0.510	0.170	0.0100	0.138	0.317	0.047	2.056	
	Maturi	2013	Contact	Geologic	394,625,362	0.465	0.165	0.0100	0.120	0.290	0.070	2.056	
	Maturi	2013	Contact	Geologic	500,000,000	0.480	0.170	0.0100	0.080	0.185	0.048	2.000	
	Maturi	2013	Contact	Geologic	889,041,046	0.430	0.150	0.0100	0.065	0.157	0.041	2.000	
	Maturi	2013	Contact	Combined	3,263,738,313	0.503	0.171	0.0100	0.113	0.261	0.057	2.050	
	Mesaba	2018	Contact	Measured	244,100,000	0.470	0.110	0.0090	0.040	0.120	0.030	1.200	Teck, 2019
	Mesaba	2018	Contact	Indicated	1,334,100,000	0.420	0.100	0.0070	0.030	0.090	0.030	1.000	
	Mesaba	2018	Contact	Inferred	1,462,000,000	0.350	0.090	0.0060	0.040	0.130	0.030	0.700	
	Mesaba	2018	Contact	Combined	3,040,200,000	0.390	0.096	0.0067	0.036	0.112	0.030	0.872	
	Tamarack	2020	Conduit	Indicated	3,926,000	1.020	1.910	0.0500	0.410	0.260	0.200	0.000	Talon Metals, 2021
	Tamarack	2020	Conduit	Inferred	7,163,000	0.680	1.110	0.0300	0.260	0.160	0.140	0.000	
	Tamarack	2020	Conduit	Combined	11,089,000	0.800	1.393	0.0371	0.313	0.195	0.161	0.000	
CURRENTLY INACTIVE PROJECTS	Maturi SW	2013	Contact	Indicated	93,440,028	0.480	0.170	0.0100	0.080	0.185	0.048	2.000	Duluth Metals Corp, 2014
	Maturi SW	2013	Contact	Inferred	29,029,912	0.430	0.150	0.0100	0.065	0.157	0.041	2.000	
	Maturi SW	2013	Contact	Combined	122,469,940	0.468	0.165	0.0100	0.076	0.178	0.046	2.000	
	Birch Lake	2013	Contact	Indicated	90,446,319	0.520	0.160	0.0100	0.233	0.511	0.114	2.000	
	Birch Lake	2013	Contact	Inferred	216,998,590	0.460	0.150	0.0100	0.180	0.370	0.087	2.000	
	Birch Lake	2013	Contact	Geologic	302,999,703	0.410	0.135	0.0100	0.135	0.275	0.065	2.000	
	Birch Lake	2013	Contact	Combined	610,444,612	0.444	0.144	0.0100	0.166	0.344	0.080	2.000	
	Spruce Road	2013	Contact	Inferred	435,448,676	0.430	0.160	0.0100	0.100	0.200	0.050	2.000	
	Serpentine	2011	Contact	Inferred	445,524,000	0.260	0.090	0.0172	0.026	0.064	0.024	1.000	
	Filson Deeps	2011	Contact	Inferred	33,600,000	0.510	0.170	no data	0.420	0.840	0.160	no data	
	Hanna Showing	2011	Contact	Inferred	330,000	0.920	0.320	no data	0.350	0.810	0.230	no data	
	Wetlegs	1970's	Contact	Inferred	54,000,000	0.268	0.078	0.0067	0.080	0.280	0.040	1.000	
	Wyman Creek	1970's	Contact	Inferred	11,800,000	0.30	0.180	0.0067	0.080	0.280	0.040	1.000	
				Totals	*9,571,943,540*	*0.406*	*0.126*	*0.0087*	*0.080*	*0.202*	*0.044*	*1.382*	

A critical component for development of contact-type sulfide deposits was the addition of country rock sulfur to mid-continent rift system mafic melts (see Ripley, 1981; Ripley and Al-Jassar, 1987; Arcuri, et al., 1998; Thériault, et al., 2000). Deposits in the Partridge River intrusion are clustered where pulses of metal-bearing mafic magma interacted with and incorporated footwall sulfur-bearing country rock (Ripley, 2013). A detailed study by Queffurus and Barnes (2014) suggest that sulfur contamination for a number of deposits resulted from *in situ* sulfide dissolution of sulfur-rich xenoliths of a pyrrhotite-bearing unit in the footwall Virginia Formation.

D.1.1.2. Conduit-type Ni-Cu-PGE sulfide deposits

Conduit-type Ni-Cu-PGE sulfide deposits are defined as magmatic sulfide mineralization restricted to small- to medium-sized mafic and/or ultramafic irregularly shaped tube-like intrusions or dikes that served as pathways for flow-through of picritic and/or Mg-rich basaltic magmas (Schulz, et al., 2014). These important sulfide deposits are unique in that they typically contain more metal and sulfur than could be derived from a magma volume equal to the limited volume of the small intrusions that host deposits. This implies that these deposits were products of a greater volume of magma than the current volume of the host intrusion. Thus, conduit-type sulfide deposits are the product of a large volume of magma that moved through open conduit systems, enriching an immiscible sulfide liquid with metals such as Ni, Cu, and PGE. Rocks that make up host intrusions generally do not represent primary magmas, but are accumulations of olivine, pyroxene, and immiscible sulfide liquid. Host rocks for Mid-Continent Rift conduit-type sulfide deposits with Ni>Cu are products of high MgO magmas that erupted only during the Plateau Stage of rift development (Nicholson, et al., 1997).

The best documented conduit-type sulfide deposits within the Mid-Continent Rift include the Eagle deposit in northern Michigan (the only operating primary nickel mine in the US since production began in 2014), the Tamarack deposit in east-central Minnesota, and the Current Lake deposit in northern Ontario. The ultramafic Tamarack Intrusive Complex (see Figure 29 for location and Table 14 for grade-tonnage data), with a minimum intrusion age of 1105.6±1.2 Ma (Goldner, 2011), is made up of several distinct intrusive bodies, including an ovoid-shaped Bowl Intrusion of oxide gabbro and two sulfide mineralized intrusive dike-like peridotite bodies that give the complex a tadpole shape (Taranovic, et al., 2015) (Figure 30). Mineralization at Tamarack consists of disseminated to net textured to massive pyrrhotite, pentlandite, chalcopyrite, and minor cubanite (Taranovic, et al., 2015).

Conduit-type sulfide deposits need country rock sulfur additions to magma to achieve sulfur saturation and formation of an immiscible sulfide liquid. Sulfur isotope data from the Eagle deposit (Ding, et al., 2012) and the Tamarack deposit (Taranovic, et al., 2018) are consistent with sulfur additions to ultramafic magmas from Paleoproterozoic metasedimentary country rocks and Archean basement rocks.

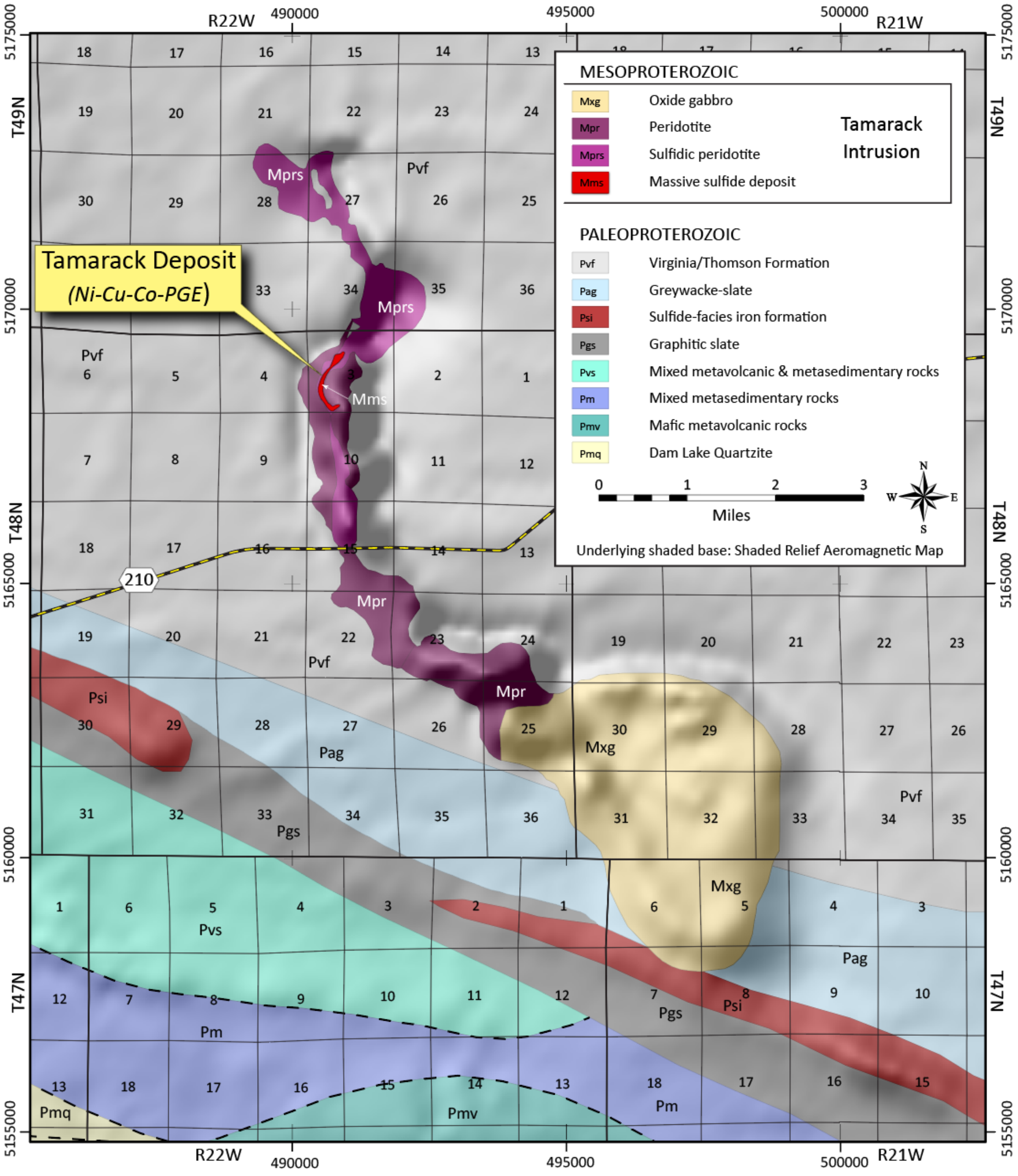


Figure 30. Bedrock geologic map of the Tamarack Ni-Cu-Co-PGE conduit-type sulfide deposit.

D.1.2. Ti-V Resources of the Duluth Complex

Small titanium-iron±vanadium oxide-rich, plug-like, discordant intrusions along the southern basal section of the Duluth Complex are called Oxide-Ultramafic Intrusions, or OUIs. Rock types carrying the Ti-Fe±V oxide mineralization in OUIs include dunite, peridotite, and pyroxenite, typically with more than 10% semi-massive to massive oxide zones (Severson and Hauck, 1990). Deposits, including the major OUIs Longnose, TiTac, and Water Hen, can also carry minor Cu sulfide mineralization. Several OUIs are in faults or are close to fault zones, typically with nearby large inclusions of Biwabik Iron-formation (Hauck, et al., 1997). Such relationships suggested to Severson (1995) that there was a genetic connection between OUI Ti-Fe±V mineralization and inclusions of iron-formation, and further speculation that OUIs may have initially formed at depth and were injected upward along fault zones (Severson, 1995); alternately OUIs may have formed from a differentiated iron-rich melt that drained down into ultramafic cumulates along fault zones.

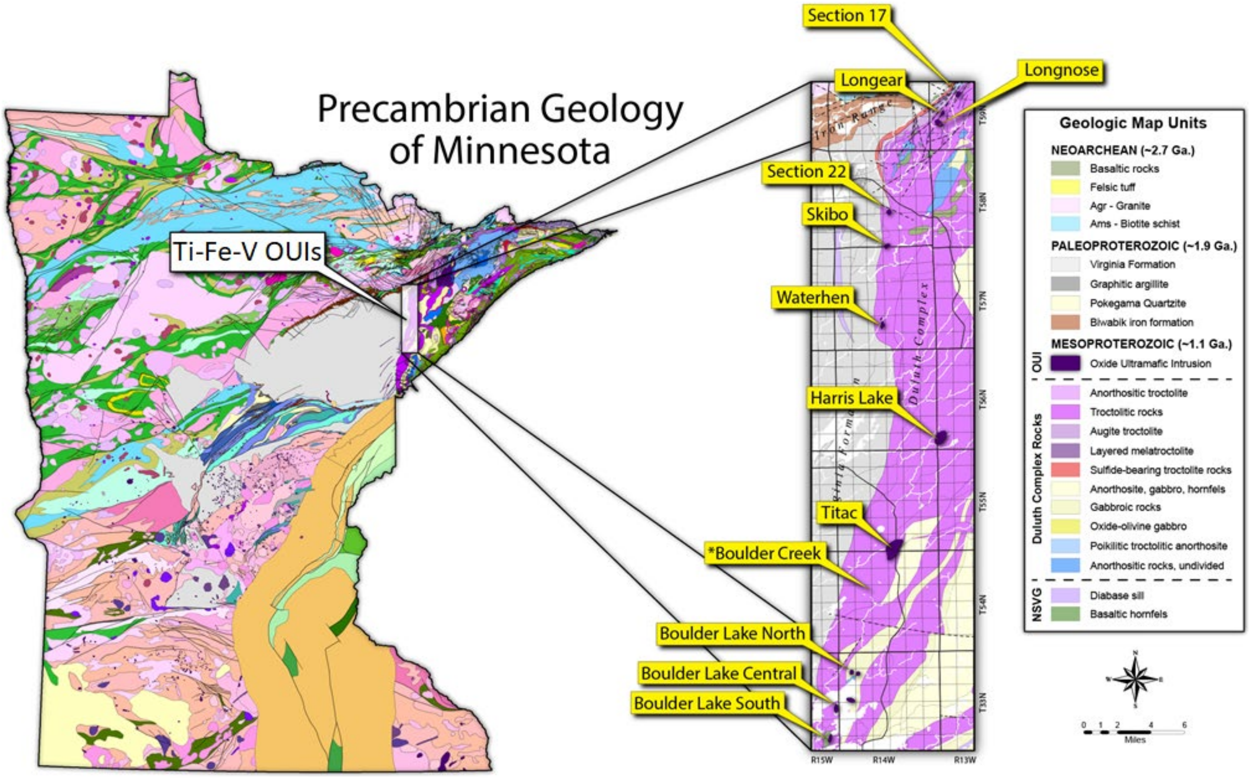


Figure 31. Bedrock geologic and location map of Ti-Fe-V resources associated with cross-cutting oxide-ultramafic intrusions of the western Duluth Complex.

Identified OUI-associated Ti-Fe-V deposits include the: 1) Longnose deposit, with a NI43-101 indicated resource of 58.1 million tons averaging 16.6% TiO_2 (inferred 65.3 million tons averaging 16.4% TiO_2) based on 27 drill holes and using a cutoff grade of 8% TiO_2, 2) Titac deposit, with a NI43-101 inferred resource of 45.1 million tons averaging 14% TiO_2 based on 32 drill holes and using a cutoff grade of 8% TiO_2, and 3) Water Hen deposit, with a crudely estimated 62 million tons averaging 14% TiO_2, based on 37 drill holes.

D.1.3. Ferrous Resources

Non-ferrous mineral resources consist of several categories of marine chemocline mineral systems outlined in recent USGS publications (Schulz, et al., 2017; Hofstra and Kreiner, 2020) including the Superior-iron deposits of the Mesabi Iron Range and iron-manganese deposits in the Cuyuna Iron Range (Figure 32).

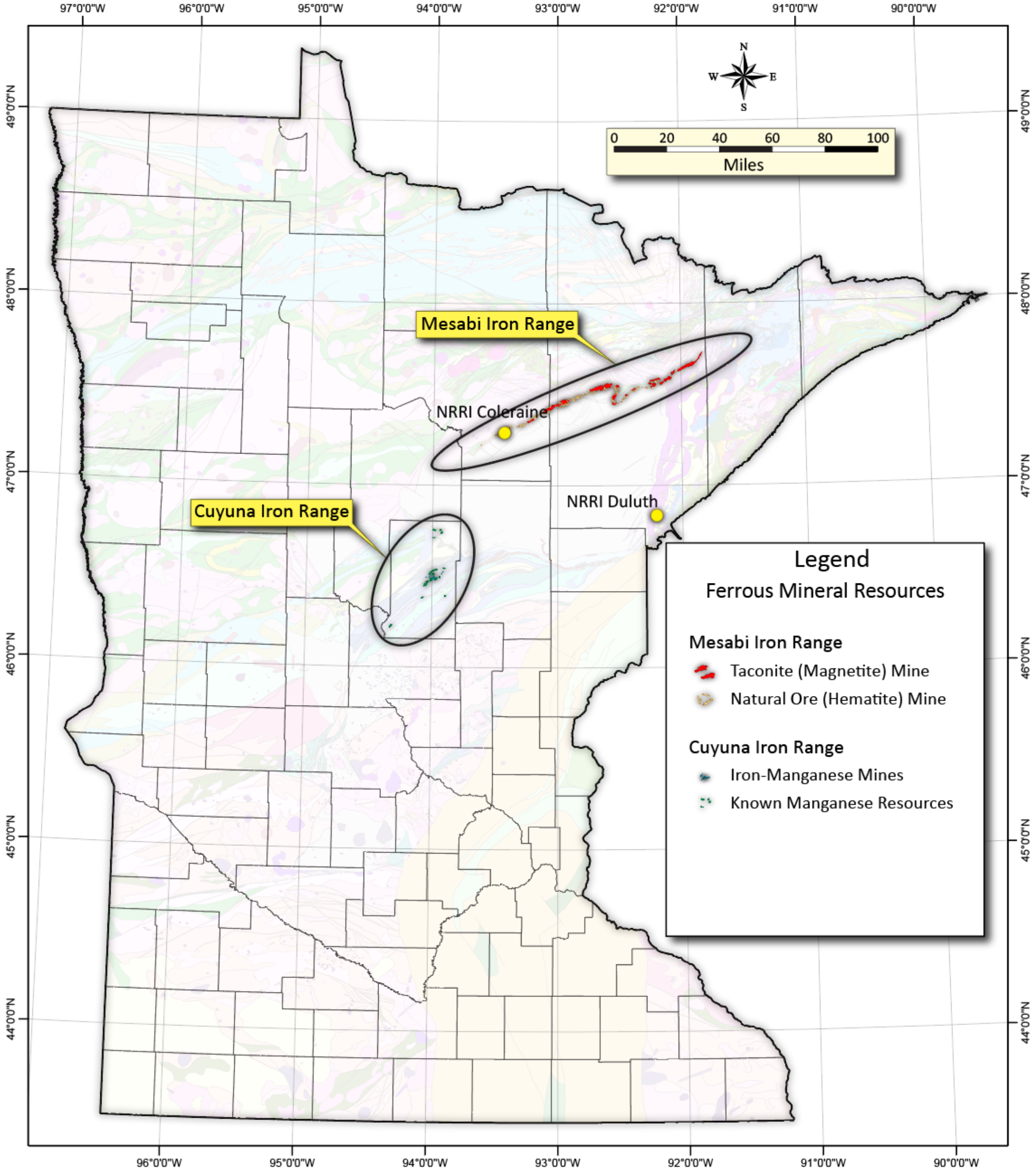


Figure 32. Location map of identified ferrous mineral resources in Minnesota.

D.1.3.1. Superior Type Iron Resources of the Mesabi Iron Range

Minnesota's Superior type iron formations are exemplified by the Biwabik Iron Formation along the length of the Mesabi Iron Range (Figure 33), located primarily in St. Louis and Itasca counties. The Mesabi Iron Range is 120 miles long, averages one to two miles wide, and is comprised of rocks of the Paleoproterozoic Animikie Group, which consists of three conformable major formations: Pokegama Formation at the base, Biwabik Iron Formation in the middle, and the overlying Virginia Formation. These three formations display gentle dips to the southeast at an angle of 3-15 degrees.

The Biwabik Iron Formation is subdivided into four informal members referred to as (from bottom to top): Lower Cherty, Lower Slaty, Upper Cherty, and Upper Slaty (Wolff, 1917), each of which are typically characterized by a granular (sand-sized) texture and thick-bedding (beds ≥ several inches thick). The slaty members are typically fine-grained (mud-sized) and thin-bedded (≤1 cm thick beds). Cherty members are largely composed of chert and iron oxides (with zones rich in iron silicate), while the slaty members are composed of iron silicates and iron carbonates with local chert beds. Both cherty and slaty iron-formation types are interlayered at all scales, but one type typically predominates in each of the four informal members, and they are so-named for this dominance Severson, et al. (2009).

The Biwabik Iron Formation is around 175-300 feet thick in the extreme eastern end of the Mesabi Iron Range at Dunka Pit, 730-780 feet thick in the central Mesabi Iron Range/Virginia Horn area near Eveleth, around 500 feet thick in the western Mesabi Iron Range near Coleraine, and eventually exhibits a "nebulous ending about 15 miles southwest of Grand Rapids" (Marsden, et al., 1968) on the extreme western end of the Mesabi Iron Range.

Leached and iron enriched direct ores (or natural ores) in the Mesabi Iron Range have been depleted and current mining focuses on taconite, a hard, non-oxidized ore typically containing 30-35% iron and 40-50% SiO_2 (Morey, 1992) that is mined and processed using magnetic separation methods. Maps of currently active taconite mining operations on the Mesabi Iron Range are presented in Figure 33 and compiled grade/tonnage ore reserve calculations for these operations are given in Table 15.

Table 15. Reported grade/tonnage of active taconite operations.

MINE NAME	**YEAR	CATEGORY	TONNES	*FE %
Northshore	2019	Proven & Probable	829,096,800	24.3
United Taconite	2019	Proven & Probable	817,920,250	22.3
Hibbing Taconite	2019	Proven & Probable	123,856,495	19.7
Minorca	2018	Proven & Probable	101,000,000	23.5
Minntac	2019	Proven & Probable	420,644,700	?
Keetac	2019	Proven & Probable	373,906,400	?

* Reported as recoverable magnetic Fe %

** Data compiled from company annual reports

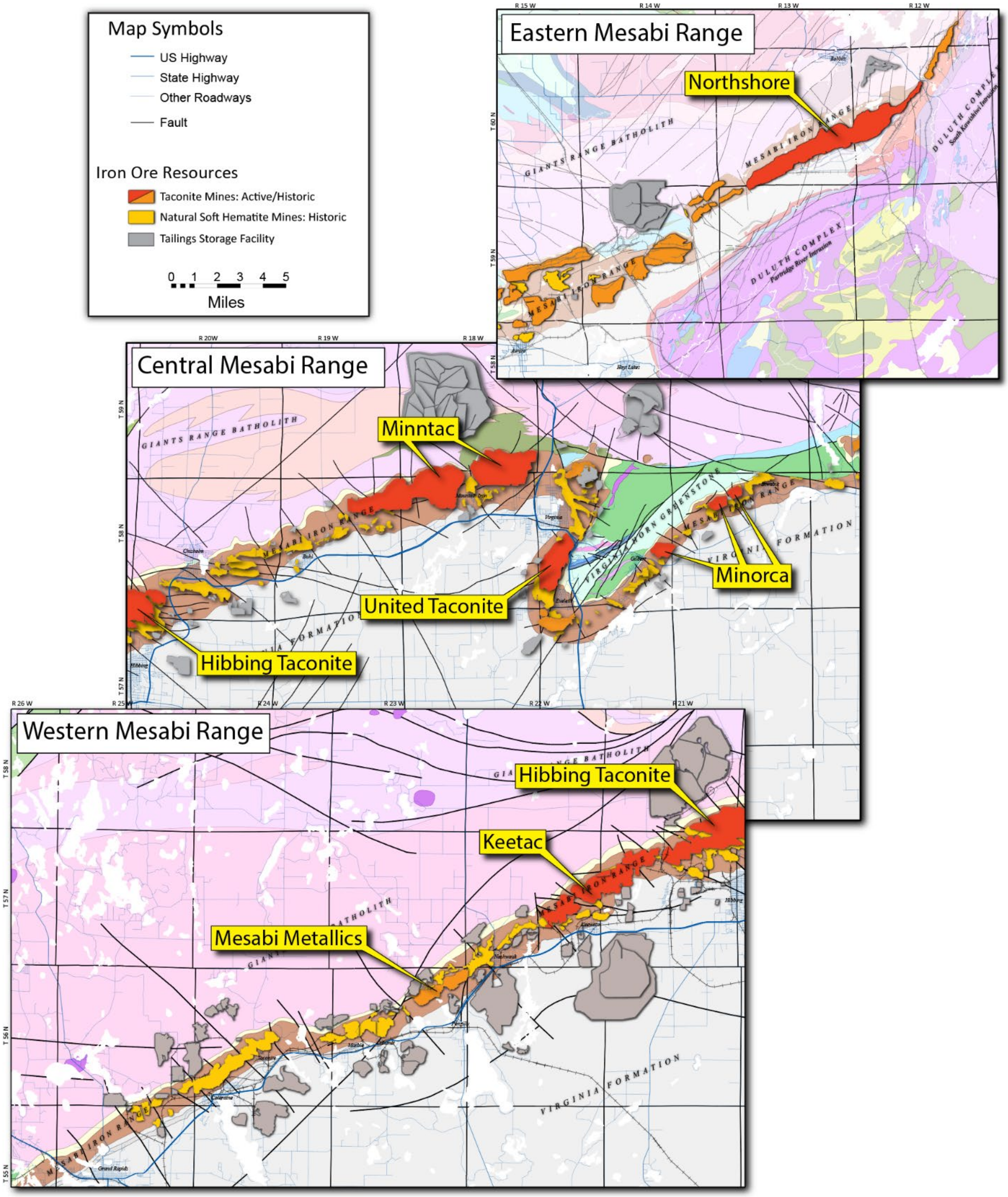


Figure 33. Bedrock geology and iron mining features of the Mesabi Iron Range.

D.1.3.2. Mn-(Fe) Resources of the Cuyuna Iron Range

Since their discovery in 1904, it has been recognized that the iron-formations and associated ore deposits of the Cuyuna iron range in east-central Minnesota contained appreciable quantities of manganese which was extracted as ferromanganese ore from several mines on the North range from 1911 to 1984. The presence of this manganese resource sets the Cuyuna range apart from other iron-mining districts of the Lake Superior region.

The Cuyuna iron range is about 160 km southwest of Duluth in Aitkin, Cass, Crow Wing, and Morrison Counties (Figure 34). It is part of an Early Proterozoic geologic terrane that occupies much of east-central Minnesota. The Cuyuna iron range is traditionally divided into the Emily, North range, and South range districts. The Emily district extends from the Mississippi River northward through Crow Wing County and into southern Cass County, and comprises about 1165 square kilometers. Although extensive exploratory drilling has been conducted in the Emily district, mining never commenced.

The North range, a much smaller area about 19 km long and 8 km wide, is near the cities of Crosby and Ironton in Crow Wing County and was the principal site of mining activity (Figure 34), which largely ceased by 1970. The South range, where only a few underground mines were operated in the 1910s and 1920s, comprises an area of northeast-trending, generally parallel belts of iron-formation extending from near Randall in Morrison County northeast for about 100 km. In addition to the three named districts, numerous linear magnetic anomalies occur east of the range proper, and may indicate other poorly defined beds of iron-formation.

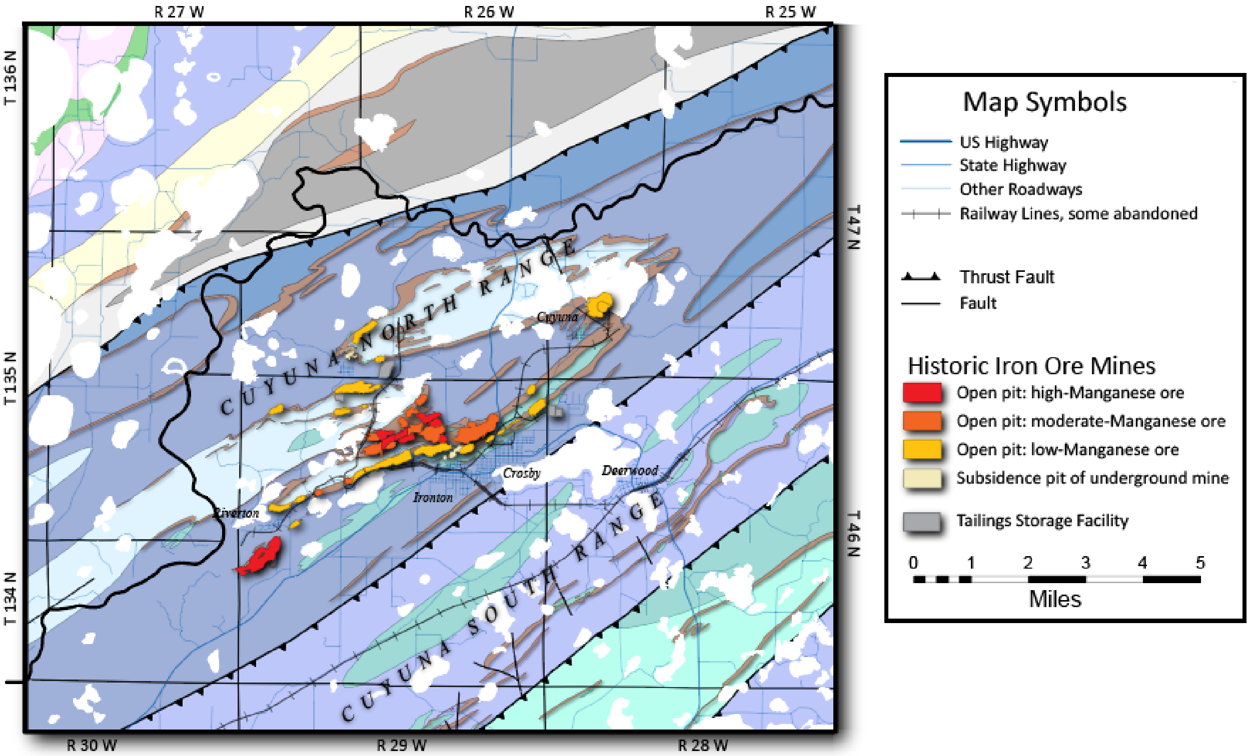


Figure 34. Bedrock geology and open pit Fe-Mn mine map of the North Range of the Cuyuna Iron Range.

Three major insights regarding the geology of the Cuyuna range have emerged from the geologic mapping and associated studies of Southwick, et al., (1988) which utilized geophysical and drilling data. First, there is clear evidence that iron sedimentation occurred at several different times and under varying geological conditions, which invalidates the stratigraphic premises of Morey (1978). Major iron-formations are associated stratigraphically with volcanic rocks in the South range, with black shale and argillite in the North range, and with shallow-water deposits of sandstone and siltstone in the Emily district.

Second, the iron-rich strata of the Emily district are correlative with the Biwabik Iron Formation of the Mesabi Range, as inferred by Marsden (1972) and Morey (1978). However, they and the other sedimentary rocks of the well-known Animikie Group occur above a major deformed unconformity that cuts across previously deformed, somewhat older sedimentary and volcanic rocks of the North range. There, a prominent iron-rich unit named the Trommald Formation and several other units beneath the unconformity form part of a locally twice-deformed sequence. Therefore, the rocks of the North range and the Emily district cannot be correlative, but are separate stratigraphic entities. Because the stratigraphic succession of folded sedimentary rocks on the North range comprises a distinct stratigraphic entity, Southwick, et al. (1988) referred to it informally as the North Range group with the understanding that a formal name may be justified at a later time. As defined by Schmidt (1963), the stratigraphic sequence in the North range consists of a quartz-rich lower unit named the Mahnomen Formation, a middle iron- and locally manganese-rich sequence assigned to the Trommald Formation, and an upper greywacke shale interval called the Rabbit Lake Formation.

Third, Southwick, et al. (1988) recognized several geophysically defined structural discontinuities in the southern part of the Cuyuna iron range, within and southeast of the South range. These discontinuities are marked by demonstrable contrasts in metamorphic grade, by differing structural styles, and by different lithic components. One of the most pronounced of these, the Serpent Lake structural discontinuity, passes along the south edge of the North range. This discontinuity is interpreted as a tectonic boundary, probably involving major thrust faults between slices of folded rocks. Thus, it seems fairly certain that the iron-rich strata of the South range are not correlative with either the Trommald Formation of the North range or the iron-rich strata of the Emily district.

The fact that iron-formation occurs within three different stratigraphic and structural contexts in the Cuyuna iron range is of considerable importance to the ultimate development of the manganese resource. Because we now recognize that the Emily district, the North range, and the South range are separate entities, we can no longer develop regional syntheses that extrapolate mineralogical and structural attributes from one entity to another.

Several attempts have been made over the last 70 years to estimate the size of the manganese resources of the Cuyuna iron range. For example, Lewis (1951) estimated that 455 million metric tons of manganiferous iron-formation containing 2 to 10 percent manganese were available to open-pit mining to a depth of 45 meters. Dorr, et al., (1973) used that estimate to establish that the Cuyuna range contains approximately 46 percent of known manganese resources in the United States. US Steel geologist Richard Strong (1959) estimated iron and manganese resources from several well-drilled deposits in the Emily District, and Beltrame, et al. (1981) estimated a minimum of 170 million metric tons of manganiferous rock with an average grade of 10.46 weight percent manganese. All of these grade/tonnage estimates (Lewis, 1951; Strong, 1959; Beltrame, et al., 1981) should be considered with a certain amount of skepticism for at least two reasons. First, the manganese data were, for the most part, byproducts of data that were acquired originally by various mining companies as they explored for iron. Second, the various estimates were prepared for different reasons at different times, using different data bases and methodologies. Therefore, the results are neither comparable, nor do they necessarily reflect the actual resource. Table 16 lists manganese resource grade and tonnages for properties studied by Strong (1959) and Beltrame, et al. (1981) and their locations are presented in Figure 35.

Despite their problematic nature, the estimates of Lewis (1951) and Beltrame, et al. (1981) do show that the Cuyuna range contains a large, but low-grade resource. This large size, combined with the fact that the manganese deposits are located in an established mining district, makes the Cuyuna range an ideal place to study geological and technological factors needed to evaluate this and other sedimentary manganese deposits in the United States. Especially important are studies of the geologic habit of the manganese and the controls on its distribution and subsequent concentration into deposits of minable size.

Table 16. Manganese grade and tonnage estimates from reports by Strong (1959) and Beltrame, et al. (1981).

MAP ID	PROPERTY	AREA	TYPE	YEAR	TONNES	MN %	MN lbs	SOURCE
1	West Ruth Lake Deposit	Emily District	Measured	1959	24,012,200	15.28	8,088,891,898	DNR 136-25-00, File #1, Item #5
4	Lake Mary Deposit	Emily District	Measured	1959	8,536,562	8.30	1,561,700,137	DNR 136-25-00, File #1, Item #5
2	East Ruth Lake Deposit	Emily District	Measured	1959	4,874,300	7.65	821,956,313	DNR 136-25-00, File #1, Item #5
3	Emily-Shawnut Reserve	Emily District	Measured	1981	833,709	10.56	194,006,830	MGS Report of Investigations 24
5	Zeno Reserve	North Range	Measured	1981	1,284,211	12.81	362,676,390	MGS Report of Investigations 24
28	Pontiac Mine	North Range	Measured	1981	883,351	16.81	327,418,704	MGS Report of Investigations 24
6	Gloria Mine	North Range	Measured	1981	559,711	12.59	155,354,314	MGS Report of Investigations 24
12	Sagamore Mine	North Range	Measured	1981	641,491	8.79	124,279,088	MGS Report of Investigations 24
7	Huntington Mine	North Range	Measured	1981	866,032	3.59	68,479,191	MGS Report of Investigations 24
	Minnesota Land and Colonization Reserve	North Range	Indicated	1981	298,099	10.14	66,639,577	MGS Report of Investigations 24
	Martin Mine	North Range	Measured	1981	460,879	6.52	66,265,395	MGS Report of Investigations 24
	Milford Mine	North Range	Measured	1981	272,226	9.68	58,094,992	MGS Report of Investigations 24
	Kona Reserve	North Range	Indicated	1981	261,770	9.07	52,343,277	MGS Report of Investigations 24
	Merritt No. 1 Mine	North Range	Measured	1981	129,200	15.10	43,000,065	MGS Report of Investigations 24
	Alstead Mine	North Range	Measured	1981	119,216	13.23	34,771,874	MGS Report of Investigations 24
	Preston Reserve	North Range	Indicated	1981	232,418	4.47	22,880,709	MGS Report of Investigations 24
	Manuel Mine	North Range	Measured	1981	205,190	5.04	22,784,115	MGS Report of Investigations 24
	Carlson-Nelson Mine	North Range	Measured	1981	302,046	3.32	22,107,769	MGS Report of Investigations 24
	West Airport Mine	North Range	Measured	1981	237,077	3.50	18,311,205	MGS Report of Investigations 24
	Hillcrest Mine, North	North Range	Measured	1981	60,224	12.97	17,220,404	MGS Report of Investigations 24
	Algoma Mine	North Range	Measured	1981	57,836	12.87	16,410,074	MGS Report of Investigations 24
	Arko Mine	North Range	Measured	1981	46,738	14.38	14,820,953	MGS Report of Investigations 24
	Ferro Mine	North Range	Measured	1981	26,309	23.17	13,438,912	MGS Report of Investigations 24
	Syracuse Reserve	North Range	Measured	1981	47,005	12.68	13,140,051	MGS Report of Investigations 24
	Northland Mine	North Range	Measured	1981	64,858	8.86	12,668,669	MGS Report of Investigations 24
	Hunter Reserve	North Range	Measured	1981	71,851	7.84	12,418,886	MGS Report of Investigations 24
	Mangan No. 2	North Range	Measured	1981	135,326	3.46	10,317,782	MGS Report of Investigations 24
	Aune Reserve	North Range	Measured	1981	90,530	4.66	9,300,626	MGS Report of Investigations 24
	Rowe Mine	North Range	Measured	1981	51,121	6.06	6,830,395	MGS Report of Investigations 24
	Sisters Mine	North Range	Indicated	1981	14,631	19.70	6,354,392	MGS Report of Investigations 24
	Armor No. 2 Mine	North Range	Measured	1981	164,803	1.39	5,050,259	MGS Report of Investigations 24
	Ironton Mine	North Range	Measured	1981	45,019	4.34	4,307,441	MGS Report of Investigations 24
	Joan No. 1 and Mallen Mines	North Range	Measured	1981	5,806	21.03	2,691,845	MGS Report of Investigations 24
	Hennen Reserve	North Range	Measured	1981	22,866	3.99	2,011,393	MGS Report of Investigations 24
	Mallen Mine	North Range	Measured	1981	64,204	1.41	1,995,790	MGS Report of Investigations 24
	South Yawkey Mine	North Range	Measured	1981	3,963	3.59	313,655	MGS Report of Investigations 24
	Wearne Mine	North Range	Measured	1981	1,348	1.67	49,630	MGS Report of Investigations 24
70	Omaha Mine	South Range	Measured	1981	1,507,189	3.14	104,335,269	MGS Report of Investigations 24
	Clearwater Lake Reserve, X-43	South Range	Measured	1981	581,549	3.61	46,234,409	MGS Report of Investigations 24
	Willcuts Reserve	South Range	Measured	1981	232,767	1.45	7,440,861	MGS Report of Investigations 24

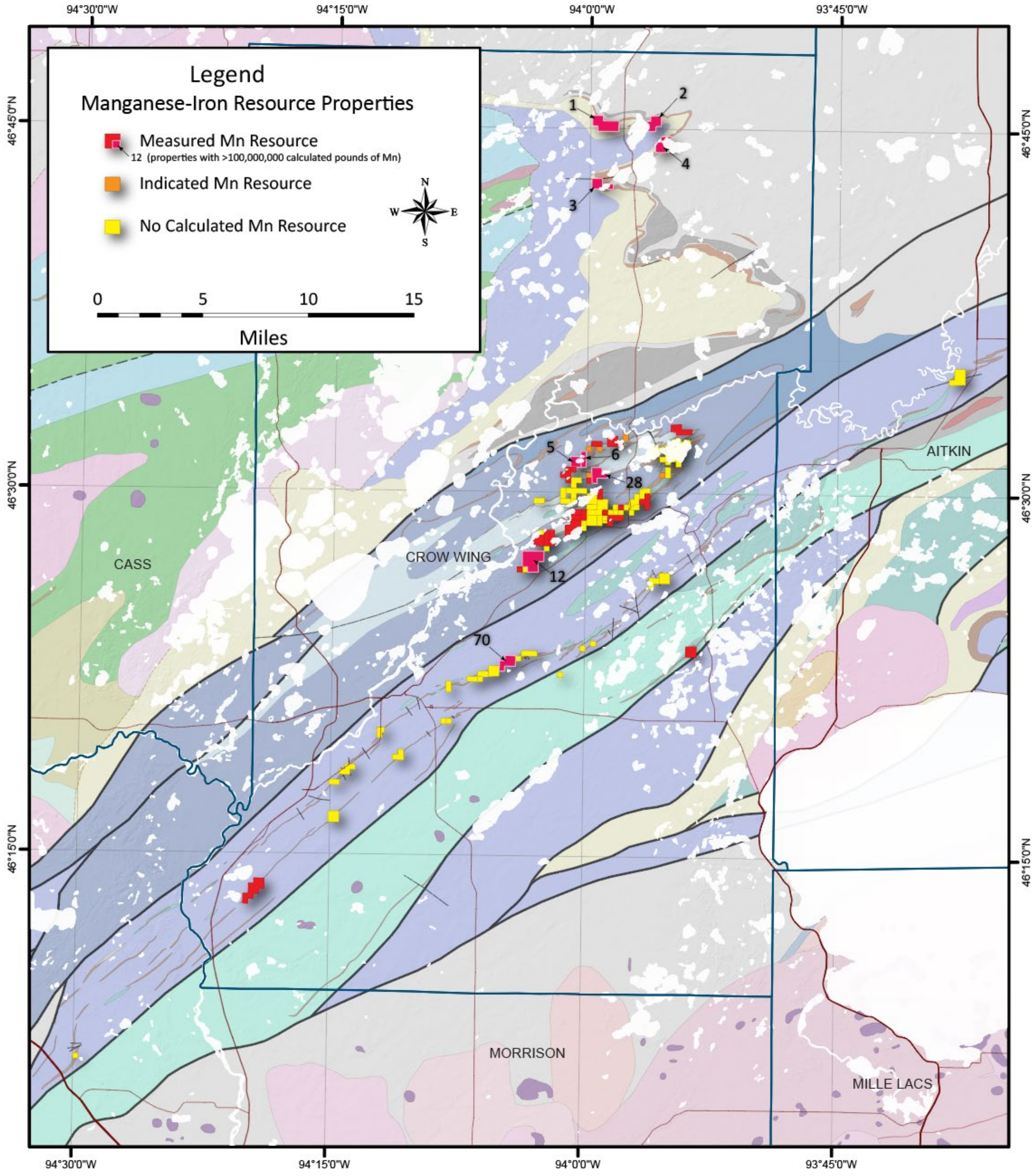


Figure 35. Bedrock geology and location map of properties outlined in reports by Strong (1959) and Beltrame, et al. (1981) that includes manganese grade-tonnage estimates. Labeled parcels correlate with the MAP ID column in Table 16 and are those with an estimated resource greater than 100,000,000 pounds of manganese metal.

D.2. Aggregate and Byproduct Resources

D.2.1.Byproducts

Aggregate resources are mined throughout the state (Figure 36) and have been described in a variety of references (Austin, 1972; Davidson, 1972; Miller, et al., 2002; Jirsa and Boerboom, 2003; Oreskovich, et al., 2004; Zanko, et al., 2003; Boerboom, et al., 2005; Severson, et al., 2009; Zanko, et al., 2010). In addition, the Minnesota Department of Transportation provides an aggregate sources database with gravel pit and rock quarry aggregate information.

Minnesota produces a wide variety of aggregates and byproducts (Table 17). Locally, the mining of carbonate rocks in southeastern Minnesota produces fine-grained carbonate products used as agricultural lime, and coarse fines which are used in other applications. Pond fines are commonly produced in and around the Twin Cities metropolitan area and are also produced locally out-state. Quarry stone (dimension stone) resources are mined throughout the state and vary from coarse-grained mafic plutonic rocks associated in the Duluth Complex (NE Minnesota), to felsic plutonic rocks and granitic gneisses in central Minnesota, to dolomitic quarry stone in south central and southeastern Minnesota. Miscellaneous resources occur locally throughout the state, and include baghouse dust, boulders, drilling dust, filter cake, foundry sand, over-sized rocks, process wastes, sandstone rubble, and tower sand. The lithogeochemistry of these materials is currently being compiled so that analysis for potential resources amenable to hydro-metallurgical processing can be evaluated.

Table 17. Summary of aggregate and byproduct resources in Minnesota. Data compiled from Zanko, et al., (2003), Oreskovich, et al. (2004), and the Minnesota Department of Transportation Aggregate Source Information System (ASIS).

MATERIAL TYPE	NUMBER OF LOCATIONS	MINNESOTA REGIONS
Aggregate Resources	8151	Throughout MN
Ag-Lime	48	Southeastern MN
Coarse Fines	11	Southeastern MN, North-Central MN
Pond Fines	22	Southern MN, Northeastern MN (Mesabi Range)
Quarry Stone	14	Southern MN, Central MN, Northeastern MN
Taconite Tailings	5	Northeastern MN (Mesabi Range)
Other	9	Throughout MN

Iron mining byproducts, such as course tailings, are produced along the Mesabi Iron Range (Figure 36) (Zanko, et al., 2003; Zanko, et al., 2010). Zanko, et al. 2003 conducted detailed lithogeochemical analyses of tailings from the EVTAC (United Taconite), Hibtac, Minntac, Minorca and Northshore processing facilities and reported rare earth element concentrations normalized to the bulk earth (Hickey et al., 1986) and North American shale (Gromet, 1984) standards (Figures 37 and 38). Relative to the “Bulk Earth Standard” (Hickey, et al., 1986), coarse taconite tailings appear to be moderately enriched in cesium (40-~160 times), slightly enriched (>1 - ~20 times) in rubidium, thorium, niobium (with the exception of Hibtac and Northshore), lanthanum, cerium, strontium, neodymium, samarium yttrium and ytterbium, and depleted (<1 times) in zirconium (with the exception of Minntac and EVTAC (United Taconite). Relative to the North American Shale Composite composition (Gromet, et al. 1984), coarse tailings consistently have enrichment factors less than ~20x for all rare earth elements. These enrichment factors are significantly below enrichment factors normally present in rocks that are processed for rare earth elements.

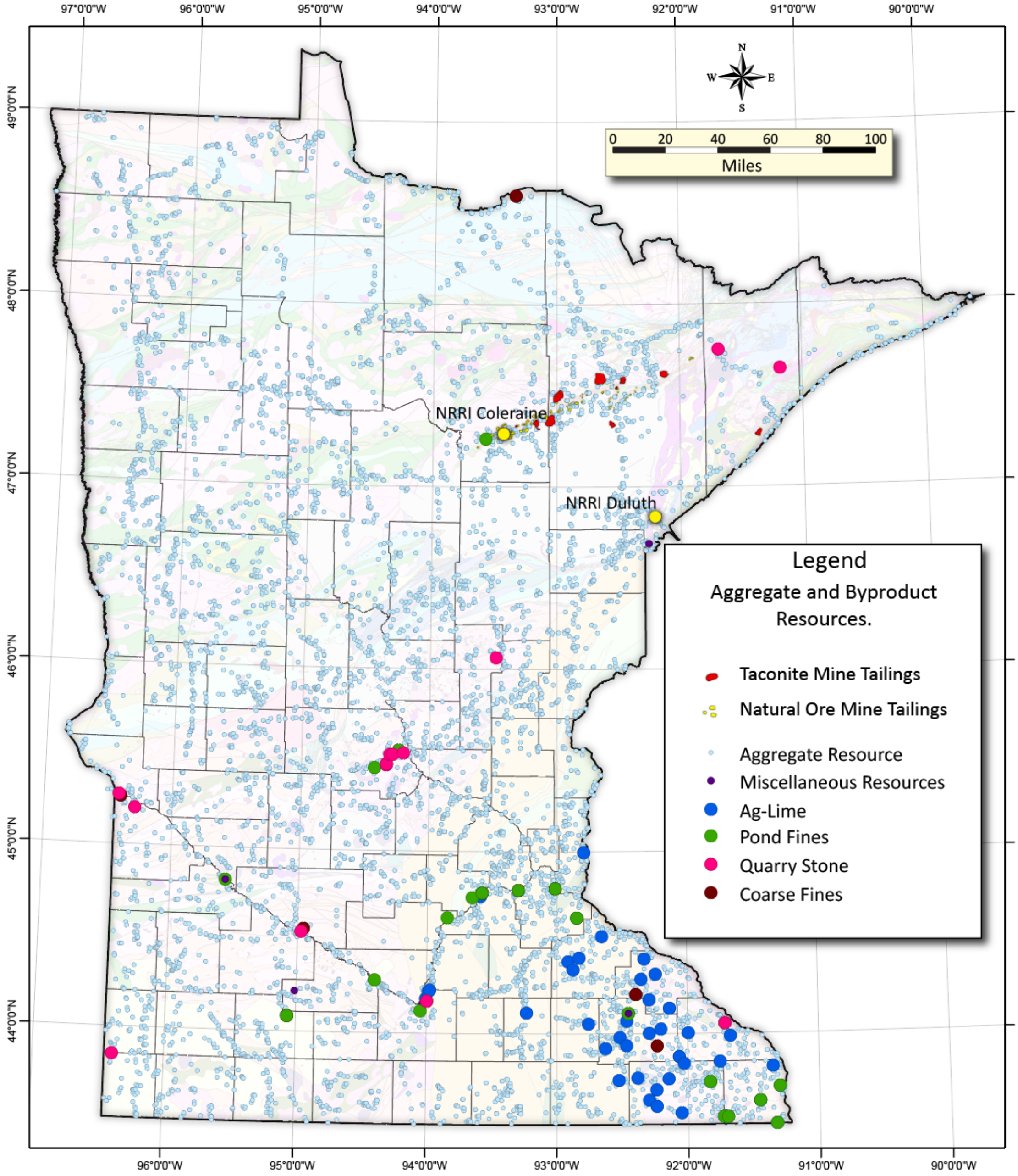


Figure 36. Distribution of aggregate and byproduct resources within Minnesota. Geographical locations derived from Oreskovich, et al. (2004) and the Minnesota Department of Transportation Aggregate Source Information System.

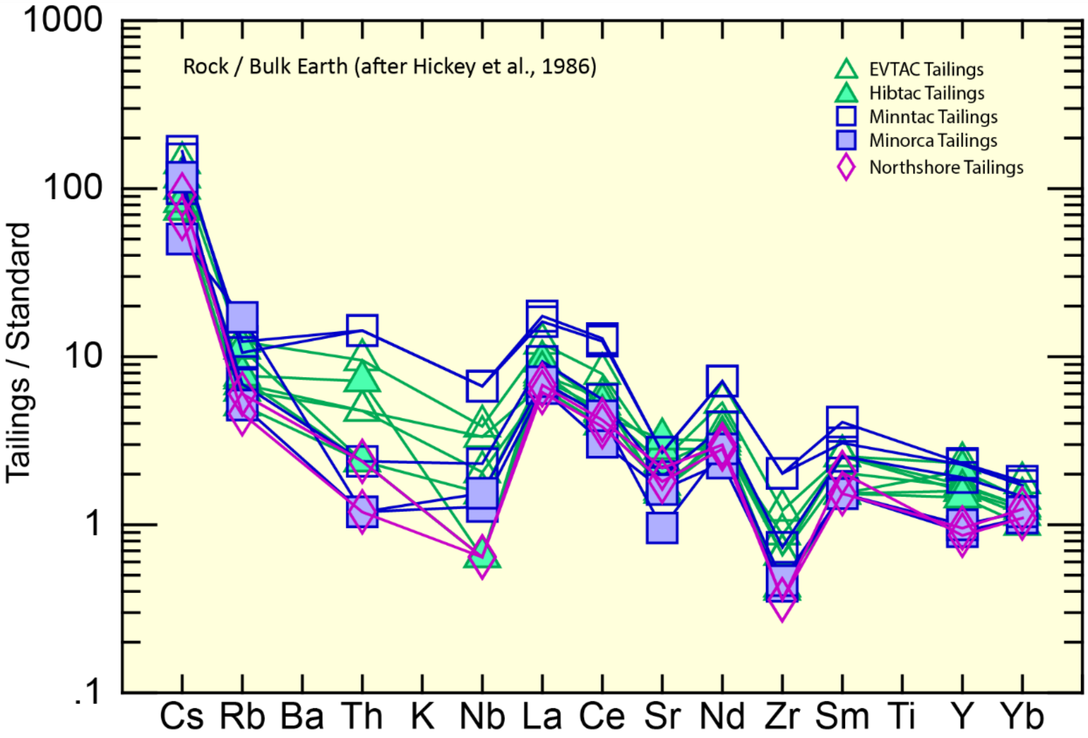


Figure 37. Comparison of tailings compositions (Zanko, et al., 2003) relative to a bulk earth composition (Hickey, et al., 1986).

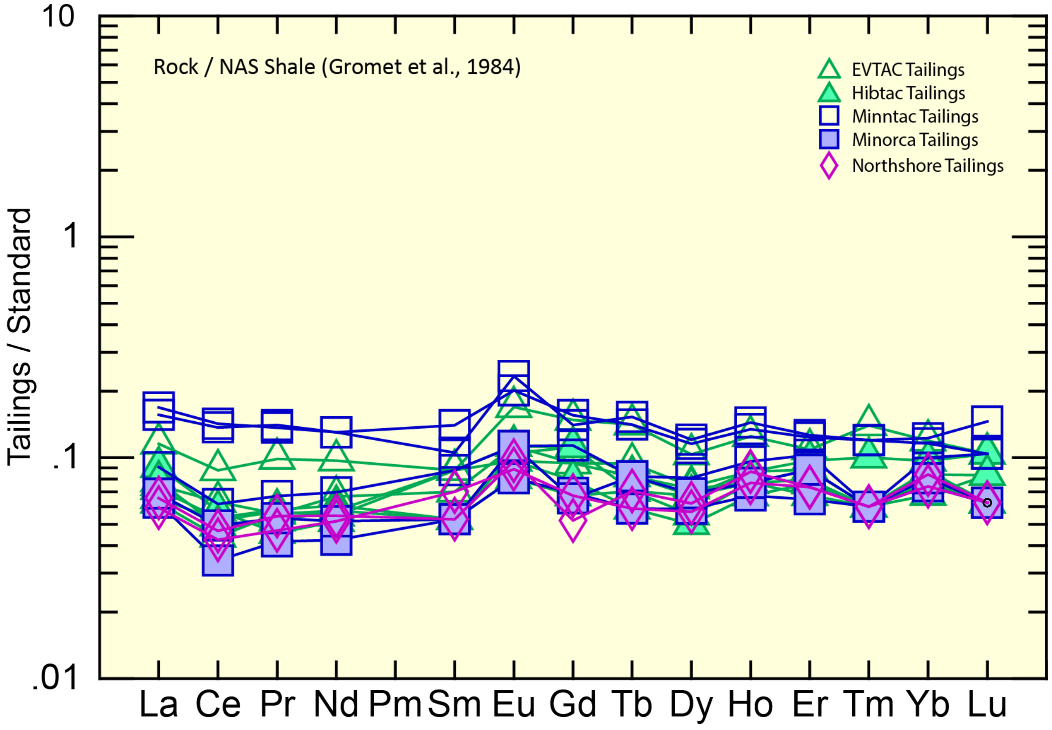


Figure 38. Comparison of tailings compositions (Zanko, et al., 2003) relative to the North American Shale Standard (Gromet, et al., 1984).

Our current understanding of the materials that comprise aggregate and byproduct resources within the state suggests that most will not be high priority targets for hydrometallurgical processing for major or trace elements (including critical mineral resources). Compilation of lithogeochemical analyses from selected rock units utilized for dimension stone is currently being undertaken. Granitoid dimension stones from east-central Minnesota are believed to be similar in age to the Wolf River Batholith in Wisconsin, which has elevated rare earth element concentrations relative to other granitoid rock bodies in the upper Midwest. Evaluation of the lithogeochemistry of the Minnesota granitoid rocks may provide additional information regarding whether waste products from dimension stone mining may be amendable for hydrometallurgical processing to produce trace metals and/or rare earth elements.

Appendix E: Waste Resources of Minnesota

Appendix E presents some of the waste resources that may contain critical metals.

E.1. Waste Resources in Minnesota

E.1.1. Waste-to-Energy Facilities in Minnesota

Waste-to-energy (WTE) facilities burn mixed municipal solid waste (MMSW) and refuse-derived fuel (RDF) in combustors to generate steam that is used to produce electricity. In Minnesota, there are eight WTE facilities: Great River Energy-Elk River Station in Elk River, Hennepin Energy Resource Co. (HERC) in Minneapolis, Olmsted Waste-To-Energy Facility in Rochester, Perham Resource Recovery Facility in Perham, Polk County Solid Waste Resource Recovery Plant in Fosston, Pope/Douglas Solid Waste Management in Alexandria, Xcel Energy – Red Wing Steam Plant in Red Wing, and Xcel Energy – Wilmarth Plant in Mankato (Michaels & Krishnan, 2018). Although Minnesota's solid waste hierarchy prioritizes waste-to-energy over landfilling, critics of this technology are concerned about possible air pollution and disposal of ash resulting from the combustion of mixed municipal solid waste and refuse-derived fuel.

E.1.2. Coal Combustion Residuals

Coal combustion residuals (CCR) are generated from the combustion of coal while generating steam to produce electricity by electric utilities and independent power producers. CCR includes fly ash, bottom ash, boiler slag, and flue gas desulfurization materials. CCR can be sent off-site for disposal or beneficial use or disposed in on-site landfills or surface impoundments. A potential list of CCR generating facilities in Minnesota are shown in Table 18 below.

Table 18. Summary of coal combustion residual generating facilities in Minnesota.

Plant	Operator	County
Black Dog Power Station	Xcel Energy	Dakota
Clay Boswell Power Station	Minnesota Power Inc.	Itasca
Fox Lake Generating Station	Alliant Energy	Martin
NSP-M Minnesota Valley Plant	Xcel Energy	Granite Falls
Riverside Power Station (NSP)	Xcel Energy	Hennepin
Sherburne County Power Station	Xcel Energy	Sherburne
Syl Laskin	Minnesota Power Inc.	St. Louis
Allen S. King	Xcel Energy	Washington
High Bridge	Xcel Energy	Ramsey
Taconite Harbor Energy Center	Minnesota Power Inc.	Cook
Silver Bay Power Co.	Cleveland Cliffs Inc.	Lake
Hoot Lake	Otter Tail Power Co.	Otter Tail
Austin Northeast	City of Austin	Mower
Hibbing	Hibbing Public Utilities Commission	St. Louis
Silver Lake	Rochester Public Utilities	Olmsted
Virginia	City of Virginia	St. Louis
Willmar	Willmar Municipal Utilities	Kandiyohi

E.1.3. Waste Electrical and Electronic Equipment (WEEE)

According to the Minnesota Pollution Control Agency, *electronic waste, or e-waste, includes any tool, equipment, or appliance containing a printed circuit board or a cathode ray tube (CRT). E-waste includes computers and peripherals, such as keyboards, monitors, and mice. It also includes many common business items like telephones, cameras, scanners, manufacturing control equipment, and medical devices* (Minnesota Pollution Control Agency, 2011). In Minnesota, approximately 199.4 million pounds of household electronic waste was collected for recycling between 2013 and 2018 (Minnesota Pollution Control Agency, 2018).

Minnesota's electronics recycling legislation was signed into law in May 2007 (Minnesota Electronics Recycling Act (115A.1310). In Minnesota, the Minnesota Pollution Control Agency (MPCA) regulates E-wastes under the Hazardous Waste Rules. E-waste is classified as hazardous because of its potential to release toxic heavy metals, such as lead, cadmium, and mercury, into the environment if not managed and disposed of properly. The law formally identifies many stakeholders and details specific responsibilities and requirements for each, including registration and annual reporting on their activities. Stakeholders affected by the Minnesota Electronics Recycling Act must be registered with the MPCA. By law, organizations that are not registered cannot collect or recycle covered electronic devices (CED).

Stakeholders involved in e-waste recycling are shown below:

Manufacturers
A manufacturer makes video display devices for sale under its own brand, or has others make products under its brand.

Collectors
A collector is “a public or private entity that receives covered electronic devices from households and arranges for the delivery of the devices to a recycler.”

Recyclers
Recyclers accept “covered electronic devices” from households or collectors of these devices in Minnesota. Recyclers dismantle the devices for further processing or process the devices into raw materials for use in new products.

A map of Minnesota manufacturers, collectors, and recyclers can be found in Figure 39.

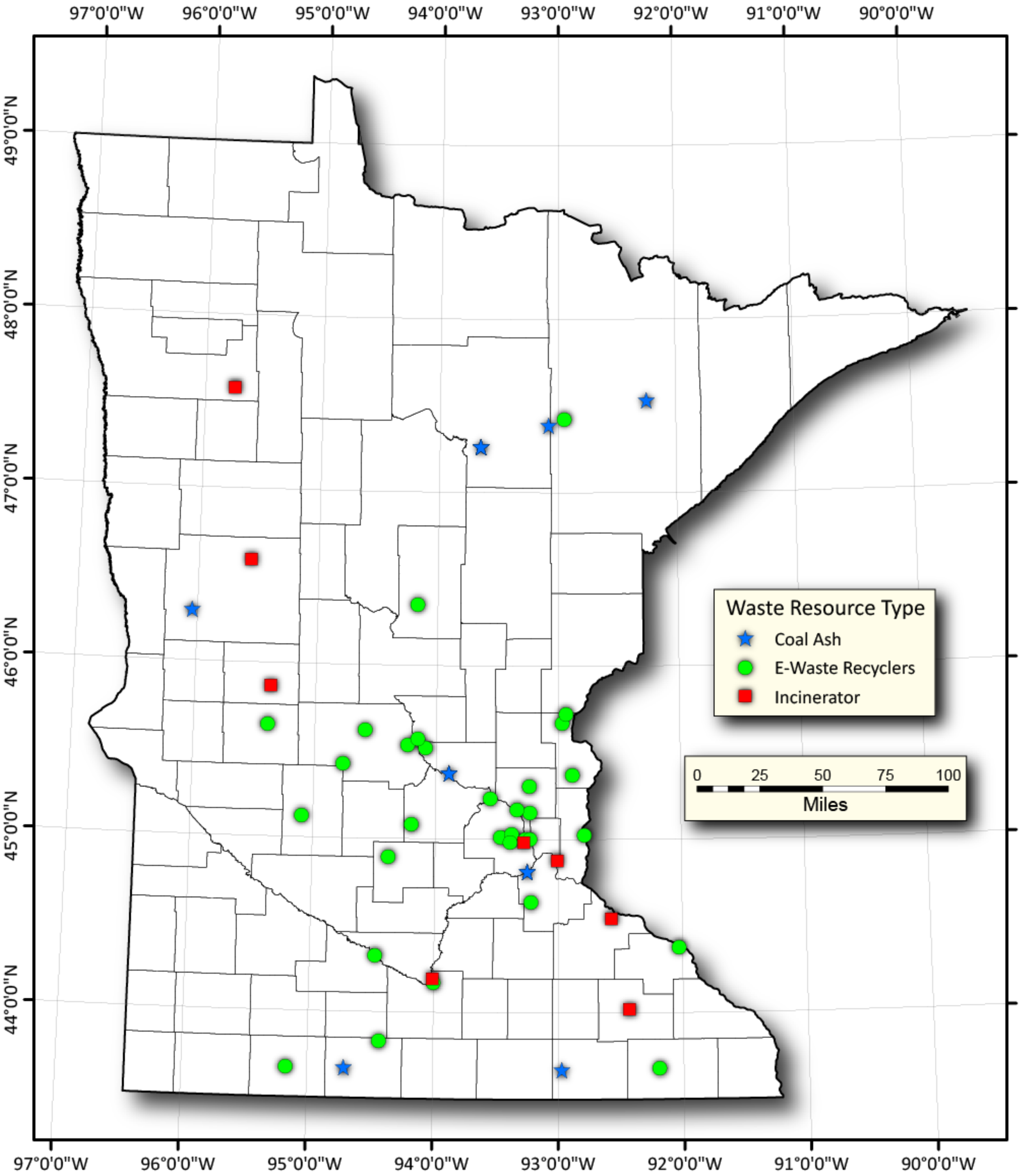


Figure 39. Map of waste-to-energy, e-waste recycling, and coal-fired power plants in Minnesota.

Appendix F: Short Case Study on Vale’s Long Harbour Hydrometallurgical Processing Plant

Appendix F illustrates the application development of hydrometallurgical technologies at Vale’s Long Harbor facility.

F.1. Introduction

A relatively recent example of a hydrometallurgical facility operating in an environment similar to Minnesota's is Vale Inco's Voisey's Bay and Long Harbour Processing Plant (LHPP) which are located in Labrador and Newfoundland, Canada, respectively. This is of interest for the current "LCCMR Develop Emerging Hydrometallurgy Technologies" project for many reasons. First, the material that is fed to the LHPP is a nickel sulfide concentrate produced from Voisey's Bay Mine located in Labrador. Nickel sulfide is most commonly used as feed to smelters instead of a hydrometallurgical processing plant, but in this case, Vale developed a novel hydrometallurgical process to produce high-purity nickel, cobalt, and copper products. There were economic, political/legal, and technological forces at play that ultimately led Vale to develop a hydrometallurgical process rather than a traditional smelting process for this project. This case study is a brief review of this project and serves as a source of information for review and to extract lessons learned.

F.2. Nickel Sulfide Ores

Approximately half of the world's primary nickel production is from nickel sulfide ores like pentlandite, which has the chemical formula $(Ni, Fe)_9S_8$, and contains approximately 36% Ni, 30% Fe, and 33% S by weight. Other sulfide minerals often associated with pentlandite are pyrrhotite (Fe_8S_9) and chalcopyrite ($CuFeS_2$), with additional accessory ore minerals containing varying degrees of copper, cobalt, silver, gold, and platinum-group elements (Crundwell, et al., 2011).

F.2.1. Typical Processing of a Nickel Sulfide Ore

An example process flowsheet for processing of nickel sulfide ore can be seen in Figure 40. As illustrated, nickel sulfide ore is commonly crushed and ground to a size that achieves liberation (in this example, less than 50 microns), followed by a bulk sulfide flotation process. The bulk sulfide contains both nickel and copper sulfides, and therefore often undergoes a differential flotation process in which the copper is separated into a separate stream and sent to a copper smelter. The remaining nickel concentrate stream is then sent to either a flash smelting or electric furnace melting step to produce a molten sulfide matte product, which is subjected to a Peirce-Smith converting process to reduce the iron content. The product, a molten low-iron sulfide matte, is then used as a feedstock to produce the nickel and other byproducts via hydrometallurgical and/or pyrometallurgical techniques (Crundwell, et al., 2011).

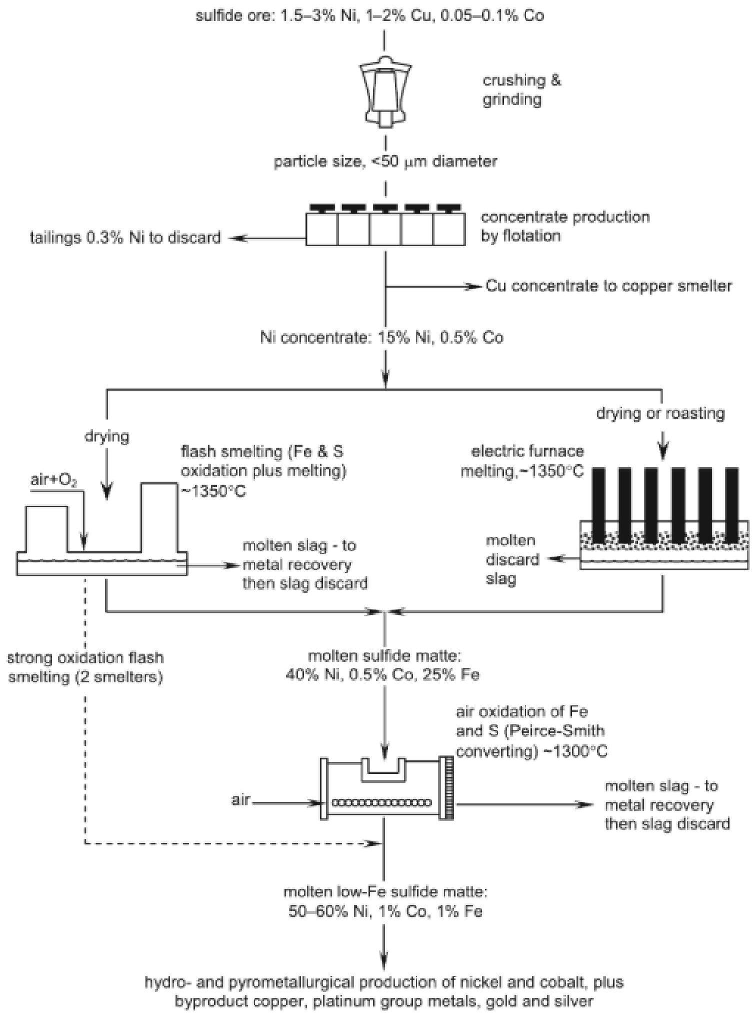


Figure 40. Main process steps for extracting nickel and cobalt from sulfide ores (Source: Crundwell, et al., 2011).

F.2.2. Smelting vs. Hydrometallurgical Processing of Nickel Concentrate

It is possible to use concentrate as the raw feed for a hydrometallurgical process; however, historically this has been found to be more difficult for recovery of both the precious metals and base metals. Therefore, it is more common to use smelting first, due to its ability to remove gangue, sulfur, and iron from the concentrate, followed by further processing using pyrometallurgical and/or hydrometallurgical process (Crundwell, et al., 2011).

F.3. Voisey's Bay Mill

F.3.1. Deposit

The Voisey's Bay nickel deposit was discovered in 1993 by Archean Inc., and through continued exploration, it has been estimated to contain 141 million tons at 1.6% nickel (Anon., 2020b). According to Wells, et al. (2007):

> *"The deposit is a 600 m long by 350 meter wide by 110 meter deep zone of massive sulfides with a feeder zone of troctolite-gabbro below, which contains disseminated sulfides. The deposit was covered by about 20 meters of quaternary overburden which was scraped off to reveal the ore. The total reserve in the Ovoid was 32 million tonnes at an average grade of 2.99%, Ni, 1.73% Cu and 0.15% Co. The massive sulfide ore consists mainly of a hexagonal pyrrhotite with blocky pentlandite, chalcopyrite, cubanite and magnetite…the only liberation concern is in the chalcopyrite which has fine pentlandite disseminated in many particles…this intergrowth makes production of copper concentrate with low nickel assay challenging and requires fine grinding of the copper rougher concentrate."*

F.3.2. Process

In 1995-1998 and 2001, Vale Inco, a subsidiary of Vale, conducted various bench- and pilot-scale comminution and beneficiation test programs with disseminated sulfide ores. In 2001, market conditions dictated that a higher-grade nickel sulfide concentrate be produced than originally planned to reduce the cost of concentrate transportation and smelting (Wells, et al., 2007). This material would also ultimately be the feed for a new processing plant within the Labrador province according to agreements between Vale and the Labrador and Newfoundland governments, as described in the following sections.

Through various iterations of bench-scale studies and three pilot-scale testing programs, a flowsheet was developed to produce a >20% Ni concentrate from a feed blend of 75% massive sulfide and 25% disseminated sulfide (Wells, et al., 2007). Mineral processing included various stages of milling and sulfide flotation to produce three products: a nickel sulfide concentrate, a copper sulfide concentrate, and a middlings concentrate that was ultimately added to the nickel sulfide concentrate stream. The chemical reagent suite included lime for pH adjustment, Dowfroth 250 as a frother, and Flex 31 (a blend of SIPX and auxiliary surfactant) as a collector (Wells, et al., 2007). The final flowsheet that was used at the Voisey's Bay mill can be seen in Figure 41.

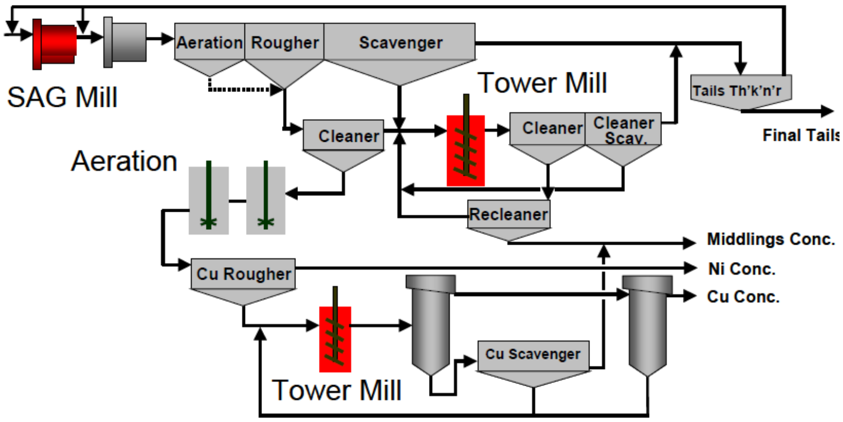


Figure 41. Voisey's Bay mill flow sheet design circa 2005 (Wells, et al., 2007).

Open pit mining started in 2005 and currently hosts approximately 500 people who support the mining and milling operations. It was announced in 2018 that Vale would be extending the life of the mine by at least 15 years by constructing an underground mine (Anon., 2020b). Transportation of the nickel sulfide concentrate is currently conducted via large bulk carrier ships from Voisey's Bay to their final destinations, including smelters or the Long Harbour Processing Plant (LHPP). The first nickel concentrate was shipped from Voisey's Bay to the LHPP in May 2015 (Campbell, 2015).

F.3.3. Decision for Hydrometallurgical Processing

Through various negotiations between Vale and the government of Newfoundland and Labrador, it was agreed that the nickel sulfide concentrate would be shipped to Sudbury, Ontario, and Thompson, Manitoba, smelting facilities until 2011; afterwards, Vale had to construct a new processing facility in southeastern Newfoundland to create jobs within the province (Anon., 2020a,b). This agreement also limited the amount of nickel concentrate that could be exported outside the Province, as well as replace all nickel concentrate they export (Vale, 2012).

Using hydrometallurgical processing would allow for discrete nickel, copper, and cobalt products to be produced at the hydrometallurgical plant. This hydrometallurgical process was also thought to be "more efficient and sustainable way to process concentrate than the more traditional methods of smelting and refining" (Roberts, 2014). Other advantages of hydrometallurgy include no SO_2 emission, improved nickel and cobalt recovery, and reducing the energy requirements for producing the final nickel product (Chapman & Zacharewych, 2018; Vale, 2012).

F.4. Long Harbour Processing Plant

F.4.1. Process

The Long Harbour Processing Plant (LHPP) uses ground nickel concentrate to produce final nickel, cobalt, and copper products. The process involves a chlorine pre-leach, a pressure-leaching autoclave, a solid-liquid separation, a series of solvent extraction for recovering each element independently, and electrowinning to produce the final products (Crundwell, et al., 2011).

According to Chapman & Zacharewych (2018):

> *"The purpose of the Impurity Solvent extraction circuit is to remove impurities such as Cu, Mn, Ca, Pb, Fe and Zn from the pregnant leach solution prior to cobalt solvent extraction. The purpose of this cobalt solvent extraction circuit is to separate cobalt from nickel contained in the pregnant leach solution. In the copper solvent extraction circuit, copper is stripped by spent electrolyte and sent to Copper Electrowinning.*
>
> *The nickel electrowinning circuit produces both finished nickel rounds and concentrate leaching lixiviant. Nickel metal is produced by electrowinning where the nickel deposited at the cathode, and oxygen, chlorine, and acid are all generated at the anode. The anode products are used for concentrate leaching in both the pre-leach and pressure oxidative leach circuits. The feedstock to the Ni electrowinning circuit is purified rich nickel solution from Cobalt Solvent Extraction. The cobalt electrowinning circuit produces finished cobalt. Cobalt metal is produced by electrowinning, with the cobalt deposited on mandrels as rounds while oxygen and acid are generated at the Pb anodes. The feedstock to the Co electrowinning circuit is strong cobalt solution from the Co solution purification circuits. Cobalt anolyte is returned to the Co SX circuit as strip solution. The purpose of the copper electrowinning circuit is to recover copper as an electrowon cathode product from a purified copper solution generated in copper solvent extraction and return an acidic spent copper electrolyte back to copper solvent extraction for use as the strip solution.*

> *The waste from the nickel electrowinning process is recycled back to the pre-leaching and autoclave steps in the process, and the organics used in solvent extraction are also recycled. The major discharge streams are the neutralized solid residue and the impurity bleed stream in the purification circuit.”*

F.4.2. Plant Construction and Commissioning

This process was piloted at a demonstration plant in country of Argentina and provinces of Newfoundland, and Labrador, between 2004-2008 (Anon., 2020a). The total cost of the research was estimated at over $200M CAD over six years, from approximately 2002-2008 (Campbell, 2015; Vale, 2020). Due to the use of chlorine gas in the process, anti-corrosive materials were needed throughout the operation, which likely resulted in high capital costs. This also means there are significant environmental, health, and safety concerns with this process (Cheng & Urbani, 2005).

Long Harbour Processing Plant (LHPP) construction was completed in 2009 at a cost of $2-2.5B (Anon., 2020b; Roberts, 2014). The plant was designed to produce 50 thousand tons per annum nickel, with associated cobalt and copper products. After many delays and cost over-runs, the LHPP was constructed and production began in July 2014, with final costs estimated at greater than $4.25B (Campbell, 2015; Roberts, 2014). Commissioning and early production was completed with nickel matte material from Indonesia, with the first small load of concentrate from Voisey’s Bay in May of 2015 (Campbell, 2015).

Appendix G: Biohydrometallurgical Technologies

Appendix G reviews the application of biohydrometallurgical process in the areas of metal extraction and minewater remediation.

G.1. Review of Biohydrometallurgy

Biohydrometallurgical technologies that are applied to recover metals from polymetallic ores, waste tailings, and remediation of toxic wastes are briefly reviewed, as well as advancements in water and solid mine waste bioreclamation, metals biosorption, and wetland treatment of acid mine drainage. The review specifically focuses on biohydrometallurgical technologies that have been demonstrated at pilot scale or implemented at commercial scale.

Biological processes (also referred as bioleaching, biohydrometallurgy, or biomining) encompasses the overlapping areas of microbiology, biochemistry, genetic engineering, and extractive metallurgy. These processes, which employ deliberate use of microorganisms to recover metals, have been commercially utilized since 1950s (Brierley, 2014). Today biological processes are commercially practiced for extraction of nickel, zinc, cobalt, silver, and uranium (Brierley, 2016), and biohydrometallurgical processes account for around 20% of the world's mined copper and 3% of mined gold production (Brierley, 2016). Additionally, biological processes are utilized for removal of heavy metals from industrial, mining, and agricultural waste runoffs.

G.2. Commercial Applications of Biohydrometallurgy in Mining Sulfidic Ores

G.2.1. Bioleaching-Heap Reactors

According to Brierley (2014), 23 copper heap bioleaching plants have been constructed since 1980, and 16 are currently in operation. The first known industrial patent for a biohydrometallurgical process was issued in 1954 to Kennecott Copper Corporation, which used a bio-heap-leach process at a copper dump leach operation. The patent claimed the use of thermophilic microbes for oxidation of ferrous sulfate to ferric sulfate, which acts as a lixiviant for the oxidation of sulfide minerals. The patent also recognized the need for aeration to promote the bio-oxidation of the ferrous sulfate. Advancements in heap stacking, forced aeration systems, and a variety of inoculation technologies have expanded the use of bioleaching processes at relatively large scales (Free, 2014).

The Talvivaara mine located in subarctic eastern Finland utilizes bioleaching for recovery of nickel, zinc, cobalt, and copper from low-grade polymetallic sulfide minerals (black schist deposit). The leaching is done in heaps with an acidic solution containing a complex consortium of microorganisms of mesophilic and thermophilic archaea. The internal temperatures in the heap range from 10-90° C with heat generated by rapid oxidation of pyrrhotite in the ore, which supports the growth of the extreme thermophiles. After subsequent oxidation of pyrite, pentlandite, and sphalerite, the ore is subjected to secondary bioleaching to recover cobalt, which is locked in the chalcopyrite matrix. Copper, nickel, cobalt, and zinc are recovered from pregnant liquor solution using hydrogen sulfide and pH control (Brierley, 2016).

Table 19 lists selected examples of bio-heap leaching plants processing copper ores (Brierley, 2014).

Table 19. List of bio-heap leaching plants (Source: Brierley J., 2014).

Plant Name	Country	Operator	Annual Cathode Copper Production, tons
Morenci	USA	Freeport McMoran	380,000
Nifty Copper	Australia	Metals X	16,000
Cerro Colorado	Chile	BHP	115,000
Ivan-Zar	Chile	Compania Minera Milpro	12,000
Punta Del Cobre	Chile	Sociedad Punta del Cobre	8,000
Quebrada Blanca	Chile	Teck Resources	75,000
Andacollo Cobre	Chile	Teck Resources	21,000
Cerro Verde	Peru	Freeport McMoran	54,200
Zaldivar	Chile	Barrick Gold	150,000
Los Bronces	Chile	AngloAmerican	50,000
Lomas Bayas	Chile	Glencore	60,000
Escondida	Chile	BHP	180,000

G.2.2. Bioleaching-Stirred Tank Reactors

The continuous stirred-tank reactor for biological processing of sulfide concentrates was pioneered by Gencor Process Research (now BHP Process Research) South Africa for the recovery of gold from sulfidic-refractory gold ores. The first commercial bioxidation plant was built by Goldfields in 1986 at the Fairview Mine in South Africa. The process has been commercially used for more than 30 years, and is currently used in several locations throughout the world (see Table 20). The largest bioxidation operation is located in Uzbekistan, which processes around 2000 tons per day of sulfidic refractory gold flotation concentrate (Free, 2014). Since its inception in 1986, bioxidation technology has also been expanded for bioleaching cobalt from pyritic tailings.

The bioxidation process operates at a temperature range of 40 to 45°C and at a pH range of 1.2 to 1.6 at dissolved oxygen level of more than 2 ppm. The reactors are aerated to provide both oxygen and carbon dioxide to assist the bacterial oxidation. The total residence time varies from 4 to 6 days. In some instances, additional nutrients are added to optimize the process. The process uses a range of bacteria: *Thiobacillus ferroxidans*, *Thiobacillus thiooxidans*, and *Leptospirillum ferroxidans* (Free, 2014). A list of current operating mines using bioxidation plants with continuous stirred reactors is shown in Table 20 (Brierley, 2014).

Table 20. List of continuous stirred tank bioreactor plants (Source: Brierley J., 2014)

Mine	Country	Concentrate treated per day, tons
Fairview	South Africa	62
Wiluna	Australia	158
Ashanti	Ghana	960
Fosterville	Australia	211
Suzdai	Kazakhstan	520
Bogoso	Ghana	820
Kokpatas	Uzbekistan	2,138
Olimpiada	Russia	8,220

G.3. Application of Bioleaching to Non-sulfide Ores (Manganese ores)

In the 1990s, the U.S. Bureau of Mines investigated bioheapleaching as a means of recovering manganese from low-grade manganese ores from the Three Kids Mine in Arizona (Noble, et al., 1993). Leaching experiments were carried out in columns using indigenous heterophilic microorganisms and sugarcane molasses as the nutrient source. Manganese extractions of more than 90% were achieved in 12 weeks of bioleaching column tests. The Bureau also investigated two methods to recover manganese from the bioleach pregnant leach solution: 1) adsorption onto weak cation exchange resin, followed by stripping and precipitation techniques; and 2) direct precipitation of the manganese as $MnCO_3$ using ammonium carbonate. Both methods removed 95% of solubilized manganese as carbonate salt. The study concluded that these low-cost technologies enhanced the potential for future commercialization of a biological process for extracting manganese from low-grade domestic ores (Noble et. al., 1993).

G.4. Applications in Bioremediation in the Minerals Industry

Biological treatment of mine wastewaters is attractive because microorganisms are:

- Capable of reducing dissolved species in solution to form compounds which are amenable to conventional solid-liquid separation,
- Capable of oxidizing species into compounds that are readily adsorbed or complexed for removal purposes,
- Capable of providing adsorption sites that facilitate removal of toxic species, and
- Capable of altering the toxicity of certain species (Free, 2014).

Examples of commercial applications of biotechnology to mine site wastewater treatment and reclamation are presented below.

G.4.1. Sulfate Removal

The most widely used applications of microorganisms in mine water treatment use sulfate reducing bacteria to reduce sulfate to sulfide and elemental sulfur. The resulting hydrogen sulfide can react with metal cations to produce metal sulfide precipitates that can be removed using conventional solid-liquid separation technologies.

G.4.2. Biosorption of Metals from Wastewater

Biosorption is the property of microbial biomass to bind metals to charged functional groups such as amino, imino, carboxylic, sulfonic, phosphonic, carbonyl, ether, alcohol, oxime, phenolic, thiether, thiophenolic, and substituted phosphine. In most instances, the biomass is immobilized on organic polymers (such as polyethyleneimine, glutaraldehyde, carrageenan, and alginate) or inorganic polymers such as silica gel or polysulfone beads (Free, 2014). Typical requirements for biomass are good mechanical integrity, high particle porosity or surface area, hydrophilicity, low interference from other species, ease of handling and regenerability (Conard, 1992). Biosorption is used to sequester heavy metals from industrial effluents and for recovering critical metals from processing solutions (Marshall & Ikhu-Omoregbe, 2012). Adsorption capabilities of various biomass types is shown in Table 21 below (Free, 2014).

Table 20. Biosorption capabilities of killed biomass (after Free, 2014).

Biomass Type	Metal	Uptake (mg/g)
Freshwater alga	Silver	86-94
Brown seaweed	Cadmium	215
Brown seaweed	Cobalt	100
Bacillus biomass	Chromium	118
Bacillus subtilis	Copper	152
Rhizopus arrhizus	Mercury	54
Fucus vesiculosus	Nickel	40
Bacillus subtilis	Lead	601
Freshwater alga	Palladium	436
Streptomyces longwoodensis	Uranium	440

G.5. Application of Biohydrometallurgy to Minnesota's Mineral Resources

Biohydrometallurgy is widely applied to commercially extract metals like copper, nickel, gold, cobalt, and others from low-grade ores. The attractiveness of using biohydrometallurgical techniques is that they are technologically simple, involve relatively minor capital and operating expenses, and are capable of producing environmentally acceptable effluent that are suitable for disposal on conventional tailings dams (Du Plessis et. al, 2007; Peterson & Dixon, 2007; Domic, 2007).

Potential research and development opportunities for bio-hydrometallurgy include:

- Identification of novel strains of bioleaching microorganisms that are specific to minerals: pyrrhotite, cubanite, bornite, chalcopyrite, pentlandite, manganite, pyrolusite, ilmenite, and titanomagnetite.
- Scaling up technologies for the production of genetically modified bioleaching microorganisms.
- Carrying out bioleaching amenability tests and pilot scale validation tests using different low-grade sulfide and oxide ores present in Minnesota.

G.5.1 Development of Engineered Biosorbent from Minnesota Biomass

The traditional techniques for the recovery of metals from processing solutions or waste effluents include precipitation, solvent extraction, adsorption, ion exchange, and membrane processes. Such processes have several economical and technical constraints. The precipitation processes have limited applications where stringent regulatory limits have to be achieved. Ion-exchange and membrane processes are relatively effective; however, they require expensive ion-exchange resins (adsorbent materials), and membrane processes generate waste brines that requires complex residual management practices (Free, 2014). There is a need to develop a cost-effective alternative for removal of metals from solutions as well as for removal of metals from industrial mining (e.g., selanate, selenite, arsenate, arsenite etc.), and agricultural activities.

Biomass is abundantly available in Minnesota, however, current knowledge on the application of Minnesota’s biomass resources for biosorption is limited. NRRI should explore opportunities to utilize Minnesota’s forest resources in order to design suitable biosorbents for specific metal binding abilities. Research efforts should focus on understanding the mechanism of metal adsorption by microorganisms as a means to engineer a biosorbent with increased metal adsorption capacity and improved kinetics for metal recovery.

Appendix H: Application of Hydrometallurgy to Mine Wastewater Treatment

Appendix H reviews the application development of hydrometallurgical processes in mine wastewater treatment.

Application of Hydrometallurgy to Mine Wastewater Treatment

Any mining activity that exposes mined materials to air and water has the potential to generate leachate with increased solute concentrations, which can significantly impact water quality during operations and after closure and influence the industry's social license to operate. This report points out some areas where the field of hydrometallurgy will be able to contribute to protecting the water quality and meet stricter discharge regulations that have lower permissible contaminant levels.

H.1. Importance

As mining operations evolve from high-grade to low-grade resources, the volumes of mined surface material and water consumption increases exponentially, along with a wide range of contaminants that appear in wastewater. The strict regulatory limits on mine discharge contaminants present a challenge to the industry to investigate and develop cost-effective technologies to reclaim, reuse, and recycle mine wastewater.

The goal of water treatment technologies include:

- To re-use water in processing plants
- To protect equipment from corrosion or fouling by scaling
- To recover valuable and hazardous metals
- To achieve contaminants levels required by statutory organizations

H.2. Existing Mine Wastewater Treatment Technologies

Over the past few decades, a wide variety of treatment technologies for the removal of residual constituents in mine effluents have been studied, developed, and applied. Key considerations for selecting the most suitable water treatment method are water chemistry, flow rate, treatment targets, and solid-liquid residue management. Proven treatment technologies classified by the type of unit operation or process, or by the principal constituent removal function performed are listed in Table 22.

Table 21. List of commercially practiced wastewater treatment technologies at mine sites.

Technology Category	Typical Applications	Purpose	Examples
Neutralization	Acid mine drainage	Removal of excess acidity or alkalinity	Acid Neutralizing Chemicals- Calcium hydroxide (lime), sodium carbonate (soda ash), sodium hydroxide (caustic soda); Alkali Neutralizing Chemicals- Carbonic acid, sulfuric acid, hydrochloric acid
Chemical Precipitation	Saleable metals precipitation, heavy metals removal from effluent	Removal of metallic and non-metallic components	Precipitation of metal sulfides Precipitation of metal hydroxides Precipitation of metal carbonates. Precipitation of sulfates/phosphorus
Adsorption	Removal of arsenic, cadmium and selenium	Removal of heavy metals.	Adsorption of selenite or cadmium hydroxides Arsenic sequestration Phosphorus adsorption on iron hydroxides
Ion Exchange	Removal of potentially toxic inorganic compounds or ions	Deionization of water; removal of metals contaminants from waste waters	Removal of nitrogen and phosphorus Removal of heavy metals Removal of total dissolved solids Cyanide recovery
Membrane Processes (Reverse Osmosis, Ultrafiltration, Microfiltration, Nano-filtration, Electrodialysis)	Removal of both major iron salts and metals/metalloids to low levels; Recover and reuse process water	Desalination	TSS & turbidity removal Hardness removal/wastewater softening Sulfate/nitrate removal Heavy metals removal
Biological treatment	Acid mine drainage, bioremediation, bio sorption	Removal of sulfate and heavy metals	Nitrogen removal Selenite and Selenate removal Sulfate removal Arsenic sequestration

H.3. Case Study 1: Water Treatment Plant at Eagle Mine LLC, Michigan

Case study 1 illustrates the water treatment plant at the Eagle Mine in Michigan that is treating mine wastewater to meet the regulatory limitations. The discharge water quality is set by permit No. MI0058649 issued by the Michigan Department of Environmental Quality (MDEQ) authorization to discharge under NPDES. The wastewater treatment stages consist of: metals precipitation/sedimentation, filtration, reverse osmosis, microfiltration, ion exchange, and evaporation/crystallization (State of Michigan Department of Environmental Quality, 2015). The ion exchange regenerant and RO concentrate liquid wastes are sent to the evaporator and crystallizer system and converted to solids that are disposed of off-site as non-hazardous solid waste. The water treatment process generates a filter press waste stream consisting of dewatered solids from the clarification treatment process that is primarily comprised of calcium and magnesium, and a crystallizer waste stream, which is essentially sodium chloride (Eagle Mine, LLC, 2017).

H.4. Case Study 2: Proposed Wastewater Treatment Plant at the NorthMet Project

Polymet Mining, Inc. (Polymet) is proposing to develop the NorthMet copper nickel-platinum group elements (PGE) mine and associated processing facilities in northeastern Minnesota. A pilot study conducted by Polymet evaluated the following water treatment technologies:

- Greensand filtration for iron, manganese, and total suspended solids removal,
- Reverse osmosis for sulfate and dissolved solids removal,
- VSEP for RO concentrate volume reduction,
- Chemical addition for permeate stabilization, and
- Chemical precipitation of the reject concentrate for removal of metals and sulfate

Table 23 presents the target wastewater treatment facility (WWTF) effluent concentrations for the different mine phases. Pilot testing of a WWTF with RO demonstrated that all of the target closure effluent concentrations could be achieved with the planned WWTF design (Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015).

Pilot testing suggested construction of a Plant Site WWTP that uses reverse osmosis or similar membrane separation technology to treat any water that cannot be recycled prior to environmental discharge. This unit would be designed to achieve an effluent sulfate concentration that meets the 10 mg/L sulfate standard for waters used for the production of wild rice. A second Mine Site WWTF would use chemical precipitation and filtration to treat affected mine water as well as the reject concentrate from the Plant Site WWTP. After the reclamation stage the Mine Site WWTF would be converted to RO (or an equivalent treatment technology) to provide water treatment during post-closure maintenance. For RO operation, a distillation process would reduce the concentrate to a moist solid that would be disposed of offsite (Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015). Applicable surface water quality evaluation criteria are listed by use classification in Table 24.

Table 22. Wastewater treatment facility preliminary water quality targets (Source: Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015).

	Targets			
	Operations	**Reclamation**	**Closure and Post-Closure Maintenance**	**Basis**
Metals (µg/L)				
Aluminum	125	125	125	M.R., part 7050.0222 Class 2B (chronic standard)
Antimony	31	31	31	M.R., part 7050.0222 Class 2B (chronic standard)
Arsenic	10	10	4	Federal Standard (pMCLs)
Barium	2,000	2,000	2,000	Minn. Groundwater (HRL, HBV5, or RAA)
Beryllium	4	4	4	Federal Standard (pMCLs)
Boron	500	500	500	M.R., part 7050.0224 Class 4A (chronic standard)
Cadmium	5.1	4.2	2.5	M.R., part 7052.0100 Class 2B (chronic standard)
Chromium III	86	86	86	M.R., part 7052.0100 Class 2B (chronic standard)
Cobalt	5	5	5	M.R., part 7050.0222 Class 2B (chronic standard)
Copper	20	17	9.3	M.R., part 7052.0100 Class 2B (chronic standard)
Iron	300	300	300	Federal Standard (sMCLs)
Lead	10.2	7.7	3.2	M.R., part 7050.0222 Class 2B (chronic standard)
Manganese	50	50	50	Federal Standard (sMCLs)
Nickel	113	94	52	M.R., part 7052.0100 Class 2B (chronic standard)
Selenium	5	5	5	M.R., part 7052.0100 Class 2B (chronic standard)
Silver	1	1	1	M.R., part 7050.0222 Class 2B (chronic standard)

	Targets			Basis
	Operations	Reclamation	Closure and Post-Closure Maintenance	
Metals (µg/L)				
Thallium	0.56	0.56	0.56	M.R., part 7050.0222 Class 2B (chronic standard)
Zinc	260	216	120	M.R., part 7050.0222 Class 2B (chronic standard)
General Parameters (mg/L)				
Chloride	230	230	230	M.R., part 7050.0222 Class 2B (chronic standard)
Fluoride	2	2	2	Federal Standard (sMCLs)
Hardness	250	200	100	Hardness PWQT chosen to establish PWQTs for metals with a hardness based standard
Sodium	60% of cations	60% of cations	60% of cations	M.R., part 7050.0224 Class 4A (chronic standard)
Sulfate	250	150	9	Operations: Federal Standard (sMCLs) Long-term closure: M.R., part 7050.0224 Class 4A

Table 23. Surface water quality evaluation criteria applicable to different classes of surface water (Source: Minnesota Department of Natural Resources, United States Army Corps of Engineers, United States Forest Service, 2015).

Parameter	Units	Class 1B pMCL	Class 1B sMCL	Class 2A	Class 2Bd	Class 2B	Class 3B	Class 3C	Class 4A	Class 4B	Class 5	Class 6
General												
Alkalinity	mg/L	--	--	--	--	--	--	--	--	--	--	--
Calcium	mg/L	--	--	--	--	--	--	--	--	--	--	--
Chloride	mg/L	--	250	230	230	230	100	250	--	--	--	--
Fluoride	mg/L	4	2	--	--	--	--	--	--	--	--	--
Hardness	mg/L	--	--	--	--	--	250	500	--	--	--	--
Magnesium	mg/L	--	--	--	--	--	--	--	--	--	--	--
pH	s.u.	--	6.5–8.5	6.5–8.5	6.5–9.0	6.5–9.0	6.0–9.0	6.0–9.0	6.0–8.5	6.0–9.0	6.0–9.0	--
Potassium	mg/L	--	--	--	--	--	--	--	--	--	--	--
Sodium	mg/L	--	--	--	--	--	--	--	--	--	--	--
Sulfate	mg/L	--	250	--	--	--	--	--	10	--	--	--
TDS	mg/L	--	500	--	--	--	--	--	700	--	--	--
Metals Total		--	--	--	--	--	--	--	--	--	--	--
Aluminum	µg/L	--	50–200	87	125	125	--	--	--	--	--	--
Antimony	µg/L	6	--	5.5	5.5	31	--	--	--	--	--	--
Arsenic	µg/L	10	--	2	2	53	--	--	--	--	--	--
Barium	µg/L	2,000	--	--	--	--	--	--	--	--	--	--
Beryllium	µg/L	4.0	--	--	--	--	--	--	--	--	--	--
Boron	µg/L	--	--	--	--	--	--	--	500	--	--	--
Cadmium	µg/L	5	--	2.5	2.5	2.5	--	--	--	--	--	--
Chromium (III)	µg/L	100	--	86	86	86	--	--	--	--	--	--
Cobalt	µg/L	--	--	2.8	2.8	5.0	--	--	--	--	--	--
Copper	µg/L	--	1,000	9.3	9.3	9.3	--	--	--	--	--	--
Iron	µg/L	--	300	--	--	--	--	--	--	--	--	--
Lead	µg/L	--	--	3.2	3.2	3.2	--	--	--	--	--	--
Manganese	µg/L	--	50	--	--	--	--	--	--	--	--	--
Mercury	ng/L	2,000	--	1.3	1.3	1.3	--	--	--	--	--	--
Nickel	µg/L	--	--	52	52	52	--	--	--	--	--	--
Selenium	µg/L	50	--	--	--	--	--	--	--	--	--	--
Silver	µg/L	--	100	0.12	1.0	1.0	--	--	--	--	--	--
Thallium	µg/L	2	--	0.28	0.28	0.56	--	--	--	--	--	--
Vanadium	µg/L	--	--	--	--	--	--	--	--	--	--	--
Zinc	µg/L	--	5,000	120	120	120	--	--	--	--	--	--

Appendix I: List of High Value Products

Appendix I provides a tentative list of key products in each of the value chains that could be potentially produced from regional resources.

Regional Resource/Value Chain	Raw Material Feedstock	Bulk Commodities	Engineered Product	Chemical compound
Titanium -Oxide Bearing Ultramafic Intrusions	Ilmenite concentrate/pellet	TiO_2 slag, Titanium sponge metal	TiO_2 pigment, Mn-Li-Ti battery material (Li-Ti oxide anode), titanium alloys	Titanium iodide, barium titanate, strontium titanate, titanium tetrachloride, alkyl/butyl titanate, titanium oxide chloride, potassium titanate, titanium disulfide, titanium hydride, titanium carbide, titanium nitride
Vanadium-Titanomagnetite - Oxide Bearing Ultramafic Intrusions	Titano-magnetite concentrate	Vanadium slag/vanadium metal/ferrovanadium	Vanadium pentoxide, vanadium flow battery chemicals	vanadium trioxide, vanadates, vanadyl sulfate, vanadium halides, vanadium carbides, organic vanadium compounds, vanadium nitrides, vanadium hydrides, vanadium silicides,
Manganese ores - Cuyuna Iron Range	Manganese slag/concentrate	Ferromanganese, silicomanganese	Electrolytic manganese metal (EMM), Electrolytic manganese dioxide (EMD), Chemical Manganese Dioxide (CMD)	MnO, Mn_2O_3, Mn_3O_4, Manganese acetate, manganese borate, manganese carbonate, manganese chloride, manganese nitrate, manganese phosphates, manganese sulfate, potassium manganates
Copper- disseminated sulfide deposit Duluth Complex	Copper sulfide concentrate/matte	Electrolytic copper metal	Copper alloys (brass, bronze, gun metals, beryllium copper, copper nickel alloys).	Copper sulfate, Copper acetates, Cuprous oxide, Cupric oxide (black copper oxide), Cupric chloride, Copper oxychloride, Cuprous chloride, Cupric nitrate, Copper cyanide, Copper soaps, Copper naphthenate
Nickel-disseminated sulfide deposit Duluth Complex	Nickel sulfide concentrate/matte/mixed hydroxide precipitate	Electrolytic nickel metal	Nickel alloys (stainless steel, superalloys)	Nickel oxyhydroxide, Lithium nickel manganese cobalt oxide, Lithium nickel cobalt aluminium, nickel sulfate, Nickel chloride, nickel sulfamate, nickel oxide, nickel hydroxycarbonate, nickel nitrate, nickel diacetate, nickel hydroxide, nickel sulfide, nickel subsulfide

Regional Resource/Value Chain	Raw Material Feedstock	Bulk Commodities	Engineered Product	Chemical compound
Cobalt-disseminated sulfide deposit Duluth Complex	Cobalt sulfide concentrate/matte/ mixed hydroxide precipitate	Electrolytic cobalt metal	lithium cobalt oxide, nickel-manganese-cobalt, nickel-cobalt-aluminum battery materials	Cobalt(II) acetate, Cobalt(II) acetate tetrahydrate, Cobalt(II)carbonate, Cobalt carbonyl, Cobalt(II) chloride, Cobalt(II)hydroxide, Cobalt(II)naphthenate, Cobalt(II) nitrate, Cobalt(II,III) oxide, Cobalt(II) sulfate
PGM-disseminated sulfide deposit Duluth Complex	PGM sulfide concentrate/matte	Platinum, Palladium	Iridium, rhenium, rhodium, ruthenium	ammonium chloroiridate, chloroirdic acid, iridium acetate, iridium trichloride ammonium tetrachloropalladate, palladium chloride, palladium nitrate, tetrammine palladium hydrogen carbon, tetrammine palladium nitrate, ammonium tetrachloroplatinate, ashby catalyst, chloroplatinic acid crystal,dihydrogen dinitrosulphatoplatinum, hexahydroxyplatinic acid, karstedt catalysts, platinum nitrate, perrhenic rhenium acid, ROPAC, rhodium acetate dimer/trimer
Gold-disseminated sulfide deposit Duluth Complex	Gold sulfide concentrate	Gold dore, pure gold	Gold Alloys	ammonium tetrachloroaurate, gold chloride, gold bromide, potassium chloroaurate, sodium chloroaurate,

Appendix J: List of Historical Hydrometallurgical Studies at NRRI

Appendix J provides a list of past publicly funded hydrometallurgical studies at NRRI.

1. Metallurgical testing of copper-nickel bearing material from the Duluth gabbro progress summary (CMRL/TR-98-17).
2. Metallurgical testing of copper-nickel bearing material from the Duluth gabbro (NRRI/TR-98/29).
3. Characterization of residue from the pressure oxidation leaching of bulk copper-nickel sulfides from the Duluth gabbro (NRRI/TR-99/41).
4. Extraction of copper from chalcopyrite concentrates without sulfuric acid generation via chlorination - ii. Selective oxidation of chlorinated products (NRRI/TR-99/42).
5. Extraction metallurgy of copper from chalcopyrite concentrates
6. Without sulfuric acid generation via chlorination - iii. Integration of gaseous chlorination and selective oxidation (NRRI/TR-99/43).
7. Extraction of copper from chalcopyrite concentrates without sulfuric acid generation via chlorination - i. Gaseous chlorination of sulfide concentrates (NRRI/TR-2000/57).
8. Low temperature gaseous chlorination for sulfur oxide free extraction of copper from chalcopyrite concentrates (NRRI/TR-2002/06).
9. Pilot-scale demonstration of ilmenite processing technology (NRRI/TR-2017/25).
10. Continuous pilot-scale demonstration of ilmenite processing technology (NRRI/TR-2021/19).
11. Bench-scale evaluation of hydrometallurgical processing to recover vanadium from Minnesota titanium resources (NRRI/TR-2021/24)

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