

**The Pennsylvania State University**  
**Center for Critical Minerals**

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**Secondary Cobalt and Manganese Resources in  
Pennsylvania: Quantities, Linkage with Mine  
Reclamation, and Preliminary Flowsheet Evaluation  
for the U.S. Domestic Lithium-Ion Battery Supply  
Chain**

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**PREPARED FOR**

**LEONARDO TECHNOLOGIES, INC. (LTI) OF BANNOCK, OH**

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## Executive Summary

The Commonwealth of Pennsylvania has a long history of mining and metallurgical activities that date back to the Industrial Revolution. This has resulted in legacy environmental justice issues (Interagency Working Group on Coal and Power Plant Communities and Economic Revitalization, 2021) and environmental degradation that has yet to be remediated. Further, as coal markets have waned due to energy transitions, the region has been left with a lack of economic opportunities. According to the most recent data from the Appalachian Regional Commission (2021), there are 133 economically distressed areas in the Commonwealth of Pennsylvania, characterized by low median family incomes and elevated poverty rates. The loss of mining jobs has contributed significantly to the situation.

This report presents potential opportunities for the domestic U.S. production of cobalt and manganese, two battery metals in the Electric Vehicle supply chain, from secondary materials left by past industrial activities in the Commonwealth. The recovery and sale of cobalt and manganese from these materials can provide economic opportunities in distressed areas of Pennsylvania, and revenues, when integrated with reclamation of mines and industrial sites hosting the materials, help cover reclamation costs. In addition to remediating environmental degradation, these activities can foster economic revitalization in the communities, and development of the U.S. domestic electric vehicle supply chain, through the production of battery raw materials from these resources.

Cobalt and manganese are both included on the U.S. Department of the Interior's critical mineral list, and the U.S. is heavily reliant on imports for its requirements for both. Cobalt is used in key applications with national security implications, such as aircraft engines, magnets, marine propulsion systems, missile guidance systems, radar, and sensors, and demand is forecast to grow due to its use in batteries for electric vehicles. Manganese has a long history of battery applications including for electric vehicles. Work toward finding U.S. domestic resources for battery metals, especially cobalt, is responsive to numerous U.S. Federal policy drivers including "Building Resilient Supply Chains, Revitalizing American Manufacturing, and Fostering Broad-Based Growth", a recent report (100 Day Supply Chain Report) from the White House, submitted in response to Executive Order 14017, issued during February, 2021.

It is hoped that these results can assist in attracting investment in regional production facilities in the electric vehicle supply chain, helping to build resilience into the economies of these energy transition-impacted communities.

Specification findings include:

1. The preliminary estimate is that coal refuse in Pennsylvania contains approximately 52,000 metric tons of cobalt. This tonnage is similar to the entire U.S. cobalt reserves presented in the 100 Day Supply Chain Report. Over a half million metric tons of

manganese are contained in these accumulations. Significant manganese is also contained in the Palmerton dump left by a large zinc smelting operation,

2. The preliminary estimate is that 60 metric tons of cobalt and over 5,500 metric tons of manganese are being discharged with acid mine drainage into the Commonwealth's waterways every year. Recovery of these elements could provide domestically-sourced materials for the lithium-ion battery industry in the U.S.
3. The sale of cobalt and manganese commodities, recovered from these materials, could help offset the costs of mine reclamation and stream restoration in Pennsylvania, which has the majority of the funding needs in seven key categories in the OSMRE abandoned mine land inventory.
4. Results of initial process development have been presented, for the integration of cobalt and manganese from secondary materials, into the lithium-ion battery supply chain. The "plug-in" point would be downstream of the critical gap- "materials purification and refinement." Preliminary laboratory results have shown that (1) a pyrite concentrate can be produced from coal refuse that is suitable as fuel for a sulfation roasting process, and (2) the selective precipitation process can produce a relatively high grade manganese concentrate, in which cobalt is also enriched. This could ultimately result in sustainable and flexible steps in the battery supply chain, replacing the conventional steps (raw materials and material purification and refinement) with a U.S. domestic alternative that is compatible with secondary materials.

The 60-70% increase in total world cobalt demand for use in batteries, driven by expansion of electric vehicle use, can be expected to further increase demand for cobalt products (IEA, 2021). This report has reviewed byproducts of the mining and metallurgical industries in Pennsylvania as potential sources of cobalt for meeting the needs of U.S. industry. Pennsylvania led the nation in cobalt mine production from 1941 to 1950 and from 1960 to 1971. This was accomplished by Bethlehem Steel which recovered cobalt-rich pyrite concentrates from tailings produced at their iron ore mine operations in Pennsylvania. Elevated cobalt levels have been found in previous exploration work by the Department of Energy's Office of Fossil Energy and Carbon Management, as well as by characterization work by the U.S. Geological Survey involving acid mine drainage. These results have been used in conjunction with data on tonnages of mining and metallurgical byproducts in Pennsylvania to develop preliminary estimates of cobalt and manganese contained in these byproducts.

The recovery of critical mineral commodities from materials left at the sites of old mining and metallurgical industrial activities can also help offset the costs of reclaiming these sites and restoring the land to productive use. This has been demonstrated by the independent power industry in Pennsylvania, which, through recovery of fuel from abandoned mine properties, has reclaimed over 200 million metric tons of old coal refuse deposits, restored over 1,200 miles of



degraded streams, and reclaimed over 7,200 acres of abandoned mine lands in Pennsylvania, at no cost to the taxpayer. The needs for environmental reclamation in Pennsylvania continue. A recent examination of funding needs for seven categories of hazards at abandoned mine lands under the Office of Surface Mining, Reclamation and Enforcement (OSMRE) Abandoned Mine Land (AML) Program showed a composite funding requirement of over \$6 billion, with Pennsylvania accounting for the majority of the need (57%). The sustainable integration of mine land reclamation with critical mineral recovery could result in additional business activities that could fund reclamation of these sites out of revenues, in this case from the sale of recovered critical mineral commodities. This is especially important as reductions in coal production in the U.S. have resulted in reductions in the tax revenues that fund the AML Program.

Critical mineral production integrated with mine land reclamation can help to anchor new businesses in this part of the Northern Appalachian Region, which hosts economically distressed areas. Regional cobalt and manganese resources could attract sustainable manufacturing associated with the electric vehicle battery supply chain and build resilience into the regional economy. Preliminary results presented in this report suggest that the potential cobalt and manganese resources could be significant in the Commonwealth.

## 1. Introduction

### 1.1. Cobalt and Manganese: U.S. Perspective

Cobalt in the U.S. is used for the production of superalloys for gas turbines, for carbides used in cutting and wear-resistant applications, and in other uses in the metallic and chemical sectors (U.S. Geological Survey, 2021). Cobalt is also used worldwide in the production of cathodes for lithium-ion batteries, and U.S. import-dependence for cobalt products, along with forecast increases in demand for batteries for electric vehicle applications, can create opportunities for U.S.-sourced cobalt products.

In 2018, the U.S. Department of the Interior released its list of critical minerals, in response to White House Executive Order 13817 (U.S. Department of the Interior, 2018). The use of cobalt in aircraft engines, magnets, marine propulsion systems, missile guidance systems, radar, and sensors contribute to its importance with respect to the U.S. military and civilian industries (Slack et al., 2017).

The 60-70% increase in total world cobalt demand for use in batteries, driven by expansion of electric vehicle use can be expected to further increase demand for cobalt products (IEA, 2021). This can also drive demand increases for manganese.

Cobalt and manganese commodities have existing markets in the U.S., and the U.S. is import-dependent for both types of materials. Table 1 presents key data regarding U.S. consumption, import-reliance, reserves, and requirements for the electrification of 20% of the U.S. light duty vehicle fleet. Recent U.S. import-reliance for both cobalt and manganese has been significant. U.S. mine production of cobalt in 2019 was 500 metric tons (Shedd, 2021), and that figure for manganese was zero (Schnebele, 2021). The total U.S. reserves for cobalt would be exhausted in less than 4 years at recent apparent consumption levels. U.S. reserves for manganese are significantly higher, although they are characterized by very low grades and potentially high extraction costs.

Results to be discussed in this report will identify additional potential resources for both cobalt and manganese in byproducts of mining and metallurgy in Pennsylvania (here called “secondary materials”). The use of these materials could significantly expand the availability of U.S.-produced cobalt and manganese feedstocks for lithium-ion battery production. Production of these materials from mining and metallurgical byproducts can help cover the costs of reclaiming sites damaged by past industrial activities in Pennsylvania. In addition to driving environmental restoration, the production of these materials in Pennsylvania can help anchor downstream stops in the supply chain entirely within the U.S., with attendant national security and balance of trade benefits.

**Table 1: Key U.S. Cobalt and Manganese Statistics**

Commodity	U.S. Apparent Consumption, 2019, Metric Tons	U.S. Net Import-Reliance, 2019, Metric Tons	Needed to Electrify 20% of the U.S. Light Duty Vehicle Fleet, Metric Tons	U.S. Reserves, Metric Tons
Cobalt	12,500 <sup>†</sup>	78%	31,820	55,000
Manganese	780,000 <sup>††</sup>	100%	29,660	230,000,000

Data Sources: Shedd (2021), Schnebele (2021), The White House (2021)

<sup>†</sup>Defined as secondary production + imports – exports + adjustments for Government and industry stock changes for refined cobalt (Shedd, 2021)

<sup>††</sup>Defined as imports – exports + adjustments for Government and industry stock changes (Schnebele, 2021)

## 1.2. Review of Previous Findings

A previous report (Rozelle et al., 2020) discussed numerous market and policy drivers regarding cobalt use in the U.S. up to 2020. The byproduct nature of cobalt production was discussed, along with ore grades and production flowsheets.

Pennsylvania led the nation in cobalt mine production from 1941 to 1950 and from 1960 to 1971. This was accomplished by Bethlehem Steel which recovered cobalt-rich pyrite concentrates from tailings produced at their iron ore mine operations in Pennsylvania. These recovered cobalt concentrates were then processed in Maryland and Delaware for the production of cobalt products.

Elevated cobalt grades have been found in the Pennsylvania coal measures as well as in sludges produced by the treatment of acid mine drainage (AMD), some of which compare favorably with commercial cobalt ores.

The findings from that report warranted suggestions for further work, which are addressed in this report. They include:

- An inventory of past metal mine operations in Pennsylvania, expanded to include a large smelter - discussed in Section 2.
- Development of an estimated cobalt resource in acid mine drainage, expanded to include coal preparation refuse and one deposit of smelter byproducts (Section 3).
- Initial process development for production of salable cobalt and manganese commodities from currently produced AMD sludges, expanded to include material recovered from coal preparation refuse, along with preliminary laboratory test results, designed to “plug-in” downstream of the critical gap in the lithium-ion battery supply chain - discussed in Section 4.

- Literature survey of cobalt and manganese in sedimentary rock - refer to Appendix 1.

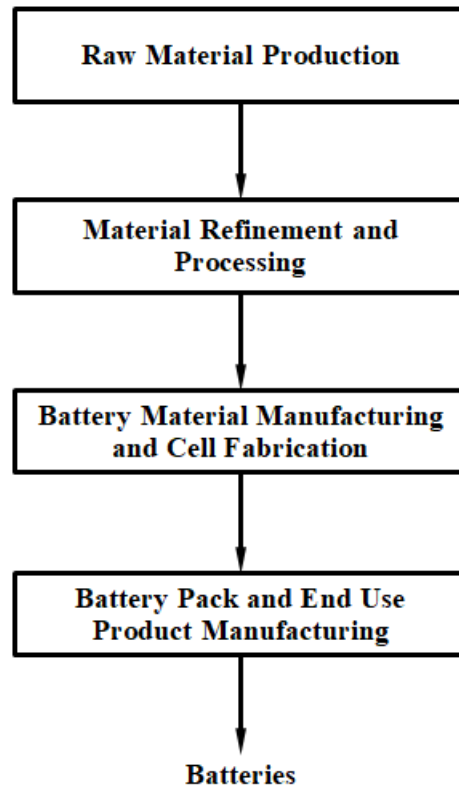
### 1.3. The Lithium-Ion Battery Supply Chain

U.S. supply chain vulnerabilities with respect to lithium-ion batteries have been identified in multiple Executive Branch reports, including:

- The Defense Industrial Capabilities Report to Congress (Department of Defense, 2021).
- 100 Day Supply Chain Report “Building Resilient Supply Chains, Revitalizing American Manufacturing, and Fostering Broad-Based Growth” (The White House, 2021).

The supply chain, as presented in the 100 Day Supply Chain Report, appears in Figure 1. The supply chain as discussed in that report mentions five steps, from raw material production through recycling. Figure 1 shows the four steps required to produce batteries.

**Figure 1: The Lithium-Ion Battery Supply Chain**



A discussion of the supply chain condensed from the 100 Day Supply Chain Report follows.

## **Raw Materials Production**

This involves production of raw battery materials (cobalt, graphite, lithium, manganese and nickel) from rock and aqueous deposits, along with upgrading the quality (grade) of the materials through the processing using mineral processing or extractive metallurgy techniques, or combinations of both. Concentrates that are produced as such are enriched in the target mineral commodity but not necessarily suitable for direct use in downstream “Battery Material Manufacturing and Cell Fabrication” operations. The products of this step are referred to in the 100 Day Supply Chain Report (the White House, 2021) as “raw [battery] produced materials in their base form”. That report states that “Almost all production of raw materials for lithium-ion batteries, apart from some lithium extraction and refinement, occurs abroad today.”

## **Materials Purification and Refinement**

In this step the commodities (raw battery materials) from the previous step (“in their base state”) are rendered in chemical forms of suitable purity for the next step (“Processed Material Manufacturing”). The 100 Day Supply Chain Report notes that “The United States currently has virtually no domestic processing capacity, so the limited raw materials produced today are primarily shipped overseas for processing”, and as feedstocks for the next step, “Battery Material and Cell Manufacturing” products from this step are referred to as “processed elements”.

It bears mention that in addition to natural graphite, synthetic graphite is produced in the U.S., and that growth in the lithium-ion battery market has been forecast to drive demand growth for both natural and synthetic graphite (Shaw, 2018, Woodworth, 2018).

## **Battery Processed Material and Cell Manufacturing**

Processed elements from the previous step are combined in this step, which also includes cathode and anode powder production, electrolyte mixing, separator production, binder and conductive additive production, and electrode and cell manufacturing. The Defense Industrial Capabilities Report to Congress (Department of Defense, 2021) has noted that “Most domestic lithium ion cell packagers rely on foreign suppliers. Rapid expansion of the electronic vehicle market is likely to exacerbate these risks, especially if designs deviate significantly from military requirements, foreign markets drive adoption, or foreign competitors lead the way in manufacturing infrastructure investment.”

## **Battery Pack and End Use Product Manufacturing**

This step involves assembling of manufactured cells from the previous step into final battery pack assemblies and integration into the end products (The White House, 2021).

This report is focused on secondary resources involving mining and metallurgical byproducts in Pennsylvania. The contained cobalt and manganese in these materials will need to be converted into forms that can “plug-in” to the existing supply chain as presented in this Section.

Two steps in the supply chain have been noted as being of concern (The White House, 2021):

- Raw Materials Production: “Almost all production of raw materials for lithium-ion batteries, apart from some lithium extraction and refinement, occurs abroad today.”
- Materials Purification and Refinement: “The United States currently has virtually no domestic processing capacity, so the limited raw materials produced today are primarily shipped overseas for processing.”

The second step has also been labeled as a “critical gap” by the 100 Day Supply Chain Report. The subsequent discussion here will include both observations on potential cobalt and manganese resources in Pennsylvania, and process options to produce products (“refined” cobalt and manganese compounds) from these resources that can “plug-in” to the Li-ion battery supply chain downstream of the Materials Purification and Refinement step. As such, constraints associated with both domestic raw materials production, and the production of refined products in the U.S., would be addressed.

This report focuses on the lithium-ion battery supply chain, which requires roughly 15 kilograms of cobalt for EV battery cathodes per vehicle (e.g., Watari et al., 2019). In addition to recovering cobalt from unconventional or secondary sources, low- to no-cobalt cathode technologies are emerging to address the drastic rise in demand. Performance is maintained in low-cobalt battery cathodes by substituting in more nickel or manganese. Manganese present in secondary materials in Pennsylvania is also discussed here. The recovery of manganese from these materials can provide U.S. domestically-sourced feedstocks of that element for the battery industry, as well.

## 1.4 Environmental Considerations

### 1.4.1. Secondary Cobalt Resources in Pennsylvania

Rozelle et al. (2020) discussed the significance of metal mine tailings in Pennsylvania, with respect to U.S. cobalt production. Significant U.S. cobalt production resulted from the recovery of sulfide minerals from tailings produced at the Cornwall Iron Ore Mine in Cornwall, Pennsylvania. Cobalt found in the production from the Grace Iron Ore Mine was also discussed. In addition to mine (concentrator) tailings, the many extractive metallurgy operations in Pennsylvania have produced significant tonnages of byproducts such as slags and other pyrometallurgy residues. An example will be presented here that resulted from decades of zinc smelting in the Commonwealth.

That work also presented elevated contents of both cobalt and manganese found in acid mine drainage treatment sludges. Given that elevated cobalt contents have been found through DOE sampling and analysis work in the Pennsylvania coal measures, coal refuse has been added for examination of its potential to supply cobalt and manganese for the U.S. domestic lithium-ion battery supply chain.

All of these are byproducts of past mining and metallurgical activities.

The secondary materials discussed are:

- Coal refuse
- Metallurgical byproducts
- Sludges produced from systems treating acid mine drainage (AMD)

#### 1.4.2. Secondary Resources and Scope of Reclamation Needs in Pennsylvania

The cobalt- and manganese-bearing materials that are the subject of this report are all associated with significant environmental degradation due to past industrial activity in the Commonwealth.

Metal mine tailings and coal refuse are resultant from past mineral processing activities. AMD either contributes to significant degradation of stream water quality, or, where treated, results in solid byproducts (sludges) requiring disposal. Restoration of land bearing the solid materials can require their re-handling and placement in forms and locations compliant with current environmental standards. These activities contribute significantly to the reclamation costs. However, recovery of salable materials can be integrated with these reclamation activities, offsetting reclamation costs and, in some cases, inducing positive earnings for reclamation activities. Examples of the latter include coal refuse recovery operations that have produced fuel for independent power producers in the Northern Appalachian Region, which results in reclamation at no cost to the taxpayer. As of 2019, these activities had resulted in the removal of over 204 million metric tons of coal refuse dumps, the restoration of over 1,200 miles of degraded streams, and the reclamation of over 7,200 acres of abandoned mine lands, supporting 3,000 full-time equivalent jobs and resulting in \$615 million in annual economic benefit (Econsult Solutions, Inc., 2019).

The sustainable recovery of critical mineral commodities from materials on abandoned mine lands can also help fund reclamation, while producing feedstocks required for items such as lithium-ion batteries and magnets.

The Surface Mining Control and Reclamation Act of 1977 (SMCRA) provided for both the regulation of surface coal mining and reclamation requirements, as well as establishing a fee on coal production that the Federal Government uses to fund the reclamation of abandoned mine properties (The Pennsylvania Department of Environmental Protection, 2019).

Fees that fund reclamation under the Office of Surface Mining (OSMRE) Abandoned Mine Land (AML) program are charged per ton of coal production. The AML Program has produced significant environmental improvements, with the reclamation of degraded lands that had previously contributed to degraded water and air, public safety hazards, and diminished economic opportunities. However, as coal production in the U.S. is forecast to decrease, fees collected for the AML Program will show an attendant reduction, while there are significant remaining reclamation needs, notably within the Commonwealth of Pennsylvania.

The reclamation needs within the AML Program are grouped by priority based on hazards, higher priority categories include Dangerous Highwalls, Dangerous Impoundments, Dangerous Piles or Embankments, Polluted Water, Human Consumption, Polluted Water, Agricultural or Industrial, Underground Mine Fires, and Spoil Areas (The Pennsylvania Department of Environmental Protection, 2021). Table 2 lists the reclamation funding requirements for these hazards by state in the AML inventory, as of February, 2021.

**Table 2: AML Funding Requirements by State, for Dangerous Highwalls, Impoundments, Piles or Banks, Polluted Water, Underground Mine Fire, and Spoil Area Categories, Data from the OSMRE Abandoned Mine Land Inventory System (Office of Surface Mining, 2021)**

States	Funding Requirements	Per Cent of Total
Pennsylvania	\$3,788,117,843	57.1%
West Virginia	\$1,077,112,903	16.2%
Kansas	\$634,361,600	9.6%
Ohio	\$213,721,025	3.2%
Montana	\$150,916,413	2.3%
Alabama	\$144,886,514	2.2%
Indiana	\$141,113,909	2.1%
Oklahoma	\$80,908,755	1.2%
Illinois	\$66,029,529	1.0%
Kentucky	\$59,056,378	0.9%
Other States	\$273,481,557	4.1%
Total	\$6,629,706,426	100.0%

While this report also discusses metal mine and smelter byproducts, with separate reclamation needs, the scope of the problem for coal properties alone in Pennsylvania is substantial, and Pennsylvania accounts for the majority of the reclamation needs for these categories nationwide.

Much of the reclamation work required to restore the degradation under the hazard types in Table 2 will require re-handling and excavation of materials on the sites, and application of AMD treatment technologies to remediate water quality issues. ***Integration of the recovery of cobalt and manganese products, with reclamation activities, presents a significant opportunity for private funding of reclamation activities, simultaneously with development of new sustainable U.S. domestic production facilities in the lithium-ion battery supply chain. This***



*opportunity has led to the preliminary laboratory and flowsheet design work to be reported here.*

Significantly, Table 2 shows that the majority of the reclamation needs for these categories (57%) are in Pennsylvania, and Pennsylvania and West Virginia together account for more than 70% of the U.S. total.

## 2. Inventories of Secondary Materials

### 2.1. Overview

Exploration work conducted under this project includes both development of inventories of available secondary resources and sampling and analyses of rock and byproduct samples from the coal measures in Pennsylvania. The latter has been done to provide samples for preliminary metallurgical test work.

Inventories of coal preparation refuse, AMD, and metal mine and smelting byproducts have been developed for this project through the collection of published information from Penn State, the Pennsylvania Geological Survey (PSGS), the United States Geological Survey (USGS), the United States Environmental Protection Agency (USEPA), and other sources. Examples of these materials where elevated concentrations of cobalt and manganese have been found were reported previously (Rozelle et al., 2020). Work that will be reported here has developed preliminary tonnage estimates for these elements in Pennsylvania coal refuse, rates of discharge of cobalt and manganese with acid mine drainage in the Commonwealth, and an estimate of manganese contained in an example smelter byproduct dump in Carbon County.

### 2.2. Geologic Considerations Regarding the Pennsylvania Coal Measures

Cobalt concentrations in Pennsylvania coal measures (coal underclay, coal seam, roof rocks) may have been derived from a multitude of sources. Appendix 1 describes the range of cobalt metallogenic models that could apply to Pennsylvania coal measures. Trace element enrichment (i.e. cobalt) within the Appalachian plateau are strongly heterogenous as only select sedimentary units contain anomalously high trace element concentrations (Bank et al., 2016; Rozelle et al., 2019; Hower et al., 2020). This heterogenous nature suggests that localized secondary enrichment has occurred where trace element concentrations were elevated following deposition. Mechanisms for secondary enrichment for coal measures, specifically within the Northern Appalachian basin, include laterization, hydrothermal alteration (open-system), and in-situ leaching (closed system) (e.g., Bolger and Weitz, 1952, Bank et al., 2016; Hower et al., 2020). Combined geochemical and geophysical evidence point to laterization as the primary means for secondary enrichment.

Laterites are residual sedimentary rocks (or paleosols) that are the product of weathering of the underlying parent rocks (Marsh and Anderson, 2011). For more details about laterites, see Appendix 1. In general, laterites primarily form in tropical climates where the potential for intense chemical weathering is optimal. Elements such as Ca, Mg, K, and Na are leached from

the system, whereas elements such as Fe, Al, Co, and REE crystallize or are incorporated into secondary phases as goethite, hematite, and clay minerals (Verplanck, 2017). The crystalline core of the Appalachian orogen (southeastern source) and Canadian Shield (northwestern source) contains numerous cobalt-bearing mineral deposits that could have provided source material for the Pennsylvanian-age sediments. Paleomagnetic and paleontological evidence (e.g., Scotese, 1999 and references therein) suggests that the Northern Appalachian Basin was positioned near the equator during the time that the Pennsylvania coal basins were deposited. Proximity to these tropical latitudes led to intense weathering, leaching of fluid mobile elements, enrichment of immobile elements (e.g., Ti, Zr, REE), and development of the Pennsylvanian age laterite deposits.

### 2.3. Coal Refuse

As has been noted previously (Rozelle et al., 2018), the use of mechanical coal preparation in Pennsylvania dates back to the early 1870's, and this has led to significant accumulations of coal preparation refuse in the Commonwealth. Technology developments in both the use of coal and preparation technologies have led to the reworking of old refuse dumps for production of coal as well as other materials such as lightweight aggregates, simultaneously with the generation of new refuse from mining operations. More recently the development of the independent power industry in the Commonwealth has led to significant reclamation of both refuse dumps and associated land, integrated with power generation based on the use of the circulating fluidized bed boiler (see Section 1.4.2. of this report).

In 1975, a report on the subject to the National Science Foundation (National Research Council, 1975) noted the presence of 3,000-5,000 coal refuse accumulations in the Eastern U.S. coal fields, aggregating a cumulative 3 billion short tons. Nationwide tonnage estimates, such as this, are somewhat dated, suggesting the usefulness of up-to-date inventories of these accumulations.

Coal refuse includes the rejects of mechanical coal preparation, which falls into two categories: The first is coarse refuse, typically conveyed out of the preparation plant as a solid. The second is tailings, which are composed of much finer solids and are frequently pumped in an aqueous suspension into an impoundment. According to the National Science Foundation report, the fine material (here called tailings) comprised about 10% of the total refuse generated.

Published data on tonnages and locations of refuse deposits are not abundant. With respect to Pennsylvania, those developed for the anthracite fields are the most detailed, having been done by the U.S. Bureau of Mines (McCartney and Whaite, 1969), and Penn State (Peters et al., 1968). The former inventoried all production-related waste including coarse- and fine refuse, as well as mine refuse such as tunnel rock that was removed and stored on the surface. The latter work includes tonnages for preparation refuse at specific mine sites as of the time of publication.

The McCartney and Whaite (1969) work found that there were 910 million cubic yards of anthracite waste on the surface in 1969. A variety of bulk density figures for preparation refuse

are available in the literature. A figure of one short ton per cubic yard, derived from the National Science Foundation Report (1975) will be used here, along with the pre-1970 figure of 910 million short tons of waste in the Anthracite Region. As such the assumed tonnage was 830 million metric tons as of 1970.

Less is known about the tonnage of refuse accumulations in the Pennsylvania bituminous coal field. However, annual refuse generation was reported from the 1940's through 1975 by the U.S. Bureau of Mines Minerals Yearbooks (1945-1975). The cumulative total from these reports is 334 million metric tons.

The total coal refuse material as of 1975 in Pennsylvania is estimated as 1.16 billion metric tons. This figure does not include preparation refuse in either the anthracite fields or the bituminous field produced since 1975. The latter will be significant. Uncertainties with respect to the bulk densities of the material in the anthracite fields are also a concern. However, this is a high-level estimate and further work will be required to address these items.

As mentioned in Section 1.4.2, 204 million metric tons of refuse dumps have been reclaimed by the independent power industry in the Commonwealth since 1986. As such, the remaining material for the purposes of contained cobalt and manganese estimates is 956 million metric tons.

#### 2.4. Metal Mine and Smelting Byproducts

While this project was originally to “build an inventory of metal mine dumps in Pennsylvania associated with commercial ore deposits”, the Commonwealth has hosted significant smelting operations involving both ferrous- and non-ferrous metal production. Previous analytical work has established (as will be summarized here) that significant amounts of manganese are currently contained in these accumulations in Pennsylvania., other commodities on the Critical Mineral list such as indium have also been found in this class of byproduct. An example byproduct dump from smelting operations has also been included in this report.

Metal-rich geologic occurrences, prospects, and historic and contemporary metal mines in Pennsylvania were catalogued by Penn State and published by the PSGS in 1970 (Rose, 1970). A list of metal mines and occurrences associated with early Mesozoic basins in the Eastern U.S. was published by the USGS in 1992 (Robinson, Jr. and Sears, 1992).

The work by Rose divided the locations by production class (mineral locality, prospect, producing mine), and divided the producing mines by value of the mine production. This was calculated based on total cumulative production from each operation and the value of that production at 1970 metal process. Where that value was less than \$1,000,000, the operation was considered “low production”, where the value exceeded \$1,000,000, it was classified as high production. There are also 23 deposit types covered in the Rose work, largely grouped by age (Pre-Cambrian, Paleozoic and Triassic).

Based on these sources and additional work by the PSGS (Hickok, 1939), an inventory of metal mines in the Commonwealth appears in Appendix 2. According to the inventory there were a total of 81 metal mines (both high and low production) in Pennsylvania. A total of 16 mines were in the “high production” category. The geographic distribution of these operations, within the Commonwealth, is shown in Figure 2, which also includes Palmerton zinc smelter of the New Jersey Zinc Company and its successors. That operation produced a significant volume of smelter byproducts.

Of the “High” Production category, mineral processing operations at Gap, Cornwall and Grace mines have been discussed in Rozelle et al., (2020). The Friedensville operation mentioned in Appendix 2 was a significant producer of zinc ore in Lehigh County, in a district with production of this type dating back to the mid-19<sup>th</sup> Century (Childs, 1957), and production from the operation ran from 1958 to 1984 (Rose, 1970, Socolow, 1984). When it closed, it was the last producing metal mine in the Commonwealth.

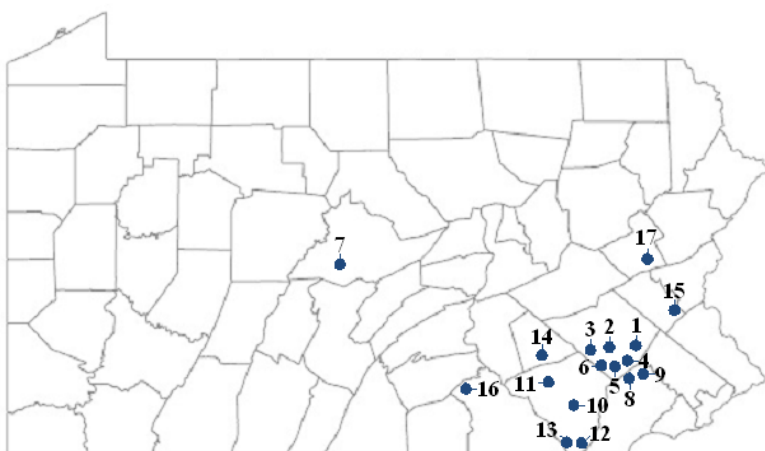
The Friedensville mine was developed and operated by the New Jersey Zinc Company, at that operation ore was concentrated through flotation, and the concentrate was shipped to the company’s Palmerton Smelter in nearby Carbon County. The Palmerton smelter bears mention here as it left a large accumulation of smelter byproducts that constitute a significant potential resource of critical mineral commodities, including manganese.

The Palmerton Smelter operated from 1898 through the 1980’s, producing slab zinc and zinc oxide from ores produced by the company in New Jersey, at Friedensville, and other sources (New Jersey Zinc Company, 1987). The smelter also produced byproduct cadmium metal, lead sulfate, spiegeleisen (ferromanganese) and sulfuric acid (EPA, 1979). Through decades of smelting operations, the Palmerton facility produced 25 million metric tons of pyrometallurgical byproducts, including byproduct solids from vertical retort- and waelz kiln smelting processes. The collection of residues at the site is collectively known as the “cinder bank”. The selected remedy under the Superfund Record of Decision (EPA, 1988) involved leaving the material at the site, and cost was cited when ruling out reprocessing of the material. However, the potential for sites of this type to furnish critical minerals feedstocks can argue for reconsideration, if reprocessing of the material can be done in a fashion that would comply with all environmental regulations. Benefits would include:

- Permanent removal of environmentally objectionable materials left at the site
- New economic opportunities in the impacted community
- Expansion of the supply of U.S.-sourced raw materials in the supply chain

The materials at the Palmerton site were produced by non-ferrous smelting operations. In addition to primary smelting operations, other byproducts have been produced by secondary smelting operations in the Commonwealth, notably involving lead and copper recycling. A survey of slags and other pyrometallurgical byproducts, where they have remained at the smelter sites or been stored elsewhere in the Commonwealth, may find additional opportunities for the recovery of critical mineral commodities.

**Figure 2: Locations of High Production Metal Mines in Pennsylvania (Including the Palmerton Zinc Smelter)**



- |                                |  |
|--------------------------------|--|
| 1. Boyertown Mines (Iron)      | 10. Gap Mine (Nickel)                  |
| 2. Fritz Island Mine (Iron)    | 11. Bamford Mine (Zinc)                |
| 3. Wheatfield Mine (Iron)      | 12. Wood Mine (Chromium)               |
| 4. Jones & Kinney Mines (Iron) | 13. Red Pit Mine & Vicinity (Chromium) |
| 5. Grace Mine (Iron)           | 14. Cornwall Mine (Iron)               |
| 6. Bylers Mine (Iron)          | 15. Friedensville Mine (Zinc)          |
| 7. Scotia Mines (Iron)         | 16. Dillsburg Mines (Iron)             |
| 8. Warwick Mine (Iron)         | 17. Palmerton Smelter (Zinc)           |
| 9. French Creek Mines (Iron)   |  |

## 2.5. Acid Mine Drainage

AMD is the result of the interactions involving pyrite, oxygen and water in rock that has been exposed by mining operations. Changes in the water characteristics, notably a reduction in pH, lead to the leaching of elements from the minerals in the strata that are exposed to the water. The resultant water has dissolved concentrations of elements such as aluminum, and typically high acidity levels, that render it toxic to aquatic life, and Pennsylvania has 5,500 miles of streams that have been degraded by this type of pollution (The Pennsylvania Department of Environmental Protection, 2021).

Dissolved elements that are on the Critical Mineral list can be found in elevated concentrations in AMD. A lack of comprehensive inventories of AMD discharges and flow rates, as well as variations in flow rates with respect to season (Vass et al., 2019), is a constraint to quantification of critical mineral resources in AMD. However, methodologies have been presented for high-level estimation of overall AMD production rates, and ultimately quantification of the production rate of rare earth elements in AMD (Stewart et al., 2017, Vass et al., 2019).

Stewart et al. (2017) developed a methodology based on coal basinal areal extent, ground water recharge rate, and a fraction of the areal extent that has been mined. As noted in the work of Vass et al. (2019), this could lead to an overestimation. However, the Vass et al. work did not present their estimation methodology. Additionally, of importance to Pennsylvania, it is unclear how much of the anthracite fields in the Commonwealth were included in either of those works. In the case of the Pennsylvania anthracite fields, most of the area lies in the Susquehanna River Basin and while significant portions of the Eastern Middle anthracite field are outside that area, the largest discharge from that field, the Jeddo Tunnel, discharges in the Susquehanna watershed.

The Susquehanna River Basin has published a quantification of discharges (Susquehanna River Basin, 2011). That work aggregates 664 ft<sup>3</sup>/s (18,800 l/s) from 320 discharges. Portions of the Southern anthracite field that discharge in the Schuylkill- and Lehigh River Basins are not included in this estimate.

The methodology of Stewart et al. (2017) will be used here to estimate the composite AMD discharge from the Pennsylvania bituminous coal field, using 14,200 square miles (36,800 km<sup>2</sup>) as the areal extent of the field (Reese and Sisler, 1928), and a recharge rate of 7.8 l/s used by Stewart et al., and the assumption that 20% of the areal extent is subject to infiltration and AMD production. The result is 57,000 l/s of aggregate discharges in the bituminous coal field in Pennsylvania, which will be the value used here.

### **3. Resource Estimates and Methodologies**

#### **3.1. Cobalt and Manganese in Coal Refuse**

In Section 2 a review of the available information was used to develop a figure of 956,000,000 metric tons of coal refuse on the ground, which includes both coal preparation refuse and, in the case of the anthracite fields, mine rock.

Refuse dumps include both above ground accumulations and tailings impoundments. These materials have been rejected through the coal preparation processes, and the dumps vary widely on composition by coal field, operation, and within the same dump. In some cases the refuse originated with a single seam coal production operation. In others, especially in the anthracite fields, the material was produced from multiple seam mines and is derived from multiple horizons.

A high-level estimate of the cobalt and manganese contained in these dumps can be developed using the tonnage estimate and analyses of the cobalt and manganese grades found in the NETL database (NETL, 2016), a technique somewhat similar to using mine water analyses and discharge rates to calculate total discharges as seen in the preceding discussion regarding acid mine drainage. Table 3 shows the maximum, minimum and average cobalt and manganese grades for the rock and refuse samples in the database.

**Table 3: Number of Sites, Ranges, and Average Cobalt and Manganese Concentrations for Rock and Preparation Refuse in Pennsylvania**

Material	Analyses	Maximum, ppm*		Minimum, ppm*		Average ppm*	
		Co	Mn	Co	Mn	Co	Mn
Rock	221	1,210	17,239	1.08	3.91	37.6	806
Refuse	7	83.9	944	31.8	181	57.0	615

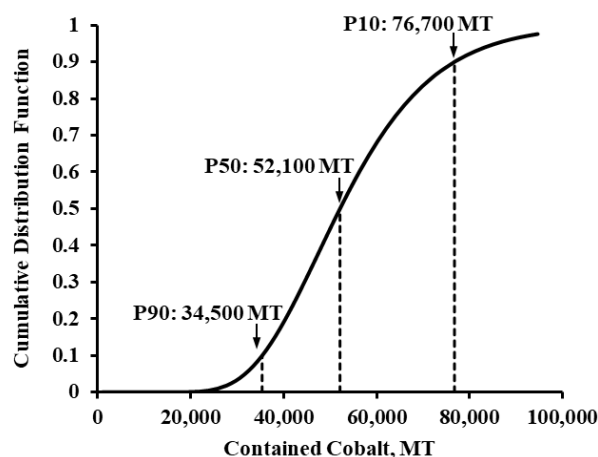
Data from NETL EDX (2016)

\*Dry Basis

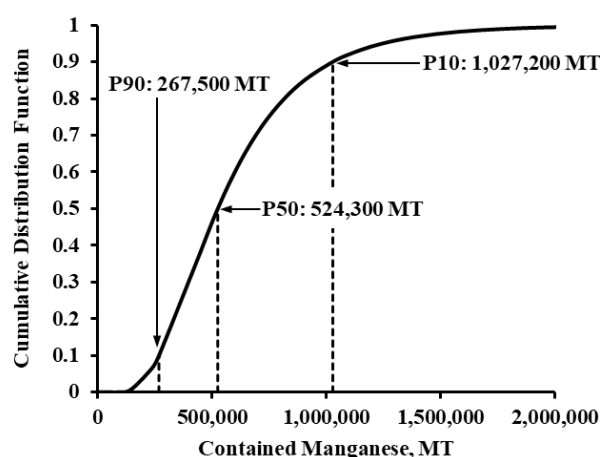
Average and standard deviation values of the natural logarithms of the refuse analyses were used with the Excel LOGNORM.DIST function to develop cumulative grade distributions for both cobalt and manganese. These grades were multiplied by the total tonnage estimate (956,000,000 MT) to produce the cumulative distribution curves, for contained cobalt and manganese, shown in Figure 3a-b. The contained tonnage values for cobalt (Figure 3a) and manganese (Figure 3b) were used to develop uncertainty ranges for contained tonnages of cobalt and manganese, through development of probability values (probabilities of contained tonnages exceeding a given value). The P90 is the low estimate, corresponding to a cumulative distribution function value of 0.1. The P10 is the high estimate, corresponding to a cumulative distribution function value of 0.9. The P50 value corresponds to the calculated contained tonnages at a cumulative distribution function value of 50%.

It bears mention that the P50 contained cobalt value (52,100 metric tons) is close to the entire U.S. cobalt reserves as noted in the 100 Day Supply Chain Report (55,000 metric tons). It is likely that a similar set of calculations involving refuse dumps in other states would indicate an aggregate potential resource, across all states, that is significantly higher than the 55,000 metric ton reserve noted in the 100 Day Supply Chain Report.

**Figure 3a-b: Calculated Cumulative Distributions and Uncertainty Ranges for Contained Cobalt and Manganese in Pennsylvania Coal Refuse**



**Figure 3a**



**Figure 3b**

The P50 contained manganese value is over a half million metric tons. By comparison, the apparent U.S. consumption of manganese in 2019 was estimated at 780,000 metric tons (Schnebele, 2021).

While the average cobalt concentration of the refuse samples is approximately three times higher than the average cobalt concentration of the crust (Rudnick and Gao, 2003), at these cobalt grades economics would dictate that recovery of a cobalt concentrate as a byproduct of the recovery of other materials from refuse reprocessing. Other products that have been recovered from coal refuse are summarized in Rozelle et al., (2018), and the concept of multi-product operations can improve the economic prospects of the concept. Additionally, further exploration of cobalt concentrations in refuse dumps could reveal deposits with higher cobalt grades.

Ultimately, given the heterogeneity of coal refuse, the suitability of individual dumps for recovery of salable materials should be considered on a case by case basis, involving significant sampling and assaying of the materials in an individual deposit. A focus on materials at a single site could be used to develop both a set of sampling and analysis procedures and economic evaluations that could potentially be replicated at other sites.

Industry in Pennsylvania has demonstrated that when there is a market for materials found in refuse dumps, jobs are created and environmental restoration of degraded mine lands takes place on a significant scale, funded by the market for the recovered commodities. The concept of recovering critical mineral commodities from refuse dumps can further extend this type of result and accelerate the restoration of lands occupied by the dumps to productive use.



### 3.2. Metal Mine and Smelting Byproducts: The Example of Palmerton

The Palmerton smelter produced a cinder dump with approximately 25 million metric tons of material. The ores processed in the smelter contained, in addition to zinc, sufficient contents of other elements to produce cadmium, lead, and manganese products. Significantly, there was also a plant for the production of indium on site prior to the closure of the smelter (New Jersey Zinc Company, 1987). While indium is not among the battery metals found in the 100 Day Supply Chain Report, it is one of the critical mineral commodities mentioned in the semiconductor supply chain section of that document.

The cinder bank at Palmerton was subjected to a sampling and analysis program in the 1980's. Limited research on extraction of salable materials from the bank continued to that decade as well, and the U.S. Bureau of Mines indicated that the bank, according to New Jersey Zinc (1987) was "one of the largest deposits of manganese in the United States".

Waelz kiln residue from the smelter, in the 1980's, was typically 10% manganese, that from the vertical retort process was 0.9% Mn, and from the oxide plant, 3% (New Jersey Zinc Company, 1987). Spiegeleisen was produced at the plant from some of the residues, and the estimate of the manganese content of the material at the site is 1%. That calculated figure, along with the measured contents of other metals, is shown in Table 4. Cobalt analyses were not included in that work, however, any further research oriented toward reprocessing of this type of material for metals recovery should include cobalt assays for evaluation of byproduct recovery.

**Table 4: Estimates of Contained Metals in the Palmerton Cinder Bank**

Metal	Zinc	Copper	Lead	Manganese <sup>†</sup>	Indium
Metric Tons	680,000	81,000	91,000	250,000	545

Data from New Jersey Zinc Company (1987)

<sup>†</sup>Estimate Based on Deposit Tonnage and Manganese Grade

### 3.3. Cobalt and Manganese Discharge Rates with Acid Mine Drainage

As seen in Section 2 of this report, a total of 75,800 l/s is assumed as the total AMD discharge rate resultant from coal production operation in Pennsylvania, including 18,800 l/s from the anthracite fields and 57,000 l/s from the bituminous field. As has been done previously for a similar estimation involving rare earth elements (Stewart et al., 2017), the data sets from Cravotta III (2008) and Cravotta III and Brady (2015) were used. These data sets include flow rates and analyses from 45 sites in the anthracite fields and 137 in the bituminous field, the latter including six where the effluent was tested twice. Data used from the 2015 work involved only the "inflow" (pre-treatment) flow rates and analyses. Table 5 shows the ranges of dissolved cobalt and manganese concentrations for the data sets, grouped by anthracite and bituminous fields.

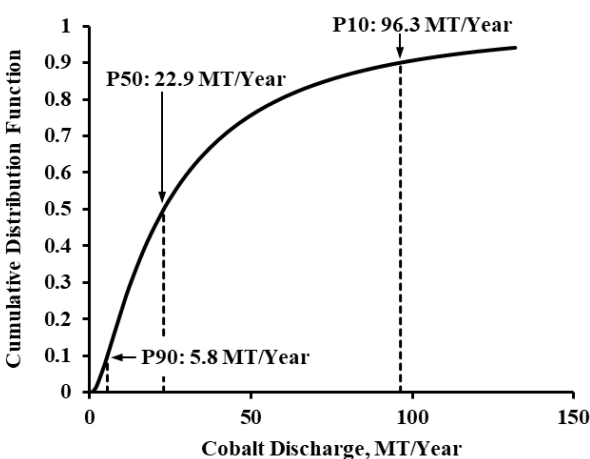
**Table 5: Number of Sites, Ranges, and Average Cobalt and Manganese Concentrations for AMD Sites in Pennsylvania**

Field(s)	Sites	Maximum, $\mu\text{g/l}$		Minimum, $\mu\text{g/l}$	
		Co	Mn	Co	Mn
Anthracite	45	770	19,000	0.43	19
Bituminous	137	5,180	136,000	0.124	19

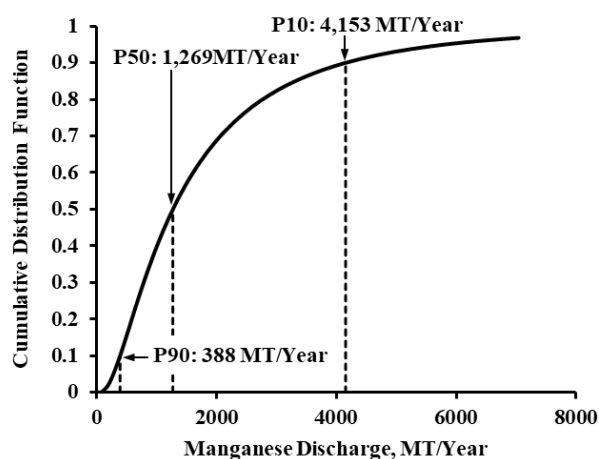
Data from Cravotta III (2008) and Cravotta III and Brady (2015)

The data sets from these papers include dissolved cobalt and manganese concentrations, as well as flow rates, for the discharges analyzed. The natural logarithms of these concentrations were used, along with discharge flow rates, to develop weighted (according to flow rate) averages and standard deviations for the data sets, and these values were used to develop cumulative distribution functions for cobalt and manganese concentrations, using the Excel technique discussed in Section 3.1. Four sets of distributions (cobalt and manganese in the anthracite and bituminous coal fields) were then used, along with the total discharge rates for each field, to develop cumulative distribution functions and uncertainty ranges for the total discharges of cobalt and manganese for each field. The probability values P90, P50 and P10 correspond to cumulative distribution function values of 0.1, 0.5 and 0.9, respectively. The P50 values will be used here as preliminary estimates. The results are shown in Figures 4a-b and 5a-b.

**Figure 4a-b: Calculated Cumulative Distributions and Uncertainty Ranges for Cobalt and Manganese Discharge Rates with AMD in the Pennsylvania Anthracite Fields**



**Figure 4a**



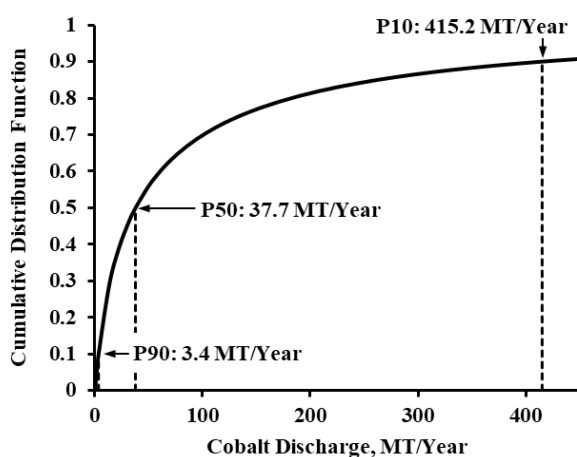
**Figure 4b**

The total cobalt discharge estimate (P50) is 60 MTPY. By comparison, the 100 Day Supply Chain Report (The White House, 2021) states that 31,820 MT of cobalt is required to electrify

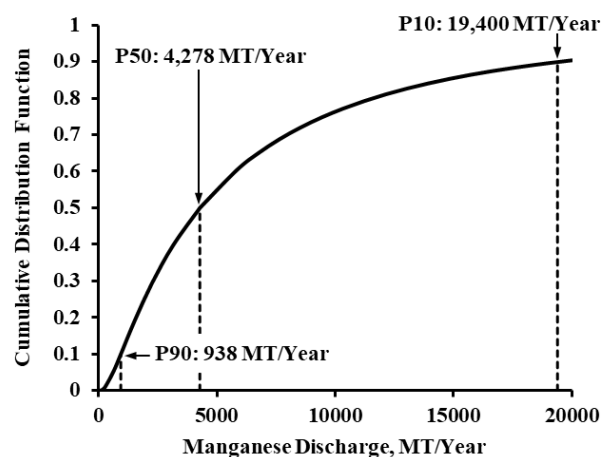
20% of the U.S. light-duty vehicle fleet. As such, the tonnage of cobalt recovered from AMD in Pennsylvania could all be absorbed into the projected market associated with EV batteries.

The manganese discharge estimate with AMD (P50) in Pennsylvania is over 5,500 MTPY. This is significant with respect to the 29,660 MT of manganese required to electrify 20% of the light-duty vehicle fleet (The White House, 2021).

**Figure 5a-b: Calculated Cumulative Distributions and Uncertainty Ranges for Cobalt and Manganese Discharge Rates with AMD in the Pennsylvania Bituminous Field**



**Figure 5a**



**Figure 5b**

The ranges for cobalt and manganese concentrations in AMD suggest that large volumes of water would need to be processed to recover compounds containing these elements. However, sludges from conventional AMD treatment systems can have cobalt grades exceeding 1,000 ppm and manganese grades exceeding 1 wt% (Rozelle, 2021). The volume of a high-grade sludge is significantly smaller than AMD per unit of contained cobalt, and the scope of a cobalt and manganese recovery system can be minimized through integration of a recovery system with a conventional AMD treatment and using the sludge as feedstock, as opposed to attempting to directly recover it from the AMD. That is the design philosophy used in the Preliminary Flowsheet Design Sections of this report.

As stated in the 100 Day Supply Chain Report, there is a dearth of U.S. capacity for producing refined products, i.e. the Material Purification and Refining step in the supply chain (The White House, 2021). As cobalt and manganese recovery from AMD would result in raw (base form) products that are water-soluble (i.e. not ore mineral forms or metal), integration of their recovery from AMD with the production of battery-grade feedstocks would combined the Raw Material and Material Purification and Refining steps in the supply chain. Noting that the concept would be combined with AMD treatment and remediation of streams degraded by past industrial

activity, this would be responsive to two of the recommendations in the 100 Day Supply Chain Report:

- Support cobalt recovery from recycled and unconventional sources
- Identify opportunities for supporting sustainable production and refining of cobalt

This would also establish a domestic supply of refined manganese products for the battery industry. Simultaneous production of both refined cobalt and manganese compounds could improve the economics of a production system, due to increased revenues, as compared to those derived from the recovery of a single commodity. The potential market for sludges recovered from AMD treatment system could offset the costs of construction and operation of these systems, and could provide an incentive to construct more, effecting improvements in the water quality of streams that have been degraded by past mining activities.

## **4. Preliminary Flowsheet Design: Mineral Processing and Extractive Metallurgy Test Work**

### **4.1 “Plug-In” Points in the U.S. Domestic Supply Chain and Intermediate Product Requirements**

The types of secondary materials examined in this work fall into two categories. The first involves minerals that have been discarded from coal preparation or other mineral concentration processes, such as those found in coal refuse. These materials will be referred to as “mineral products”. The second is acid mine drainage treatment sludge, which is material that was originally leached from minerals in coal-bearing strata, and was precipitated from solution. This will be referred to as “AMD sludge”. The latter type of material can be assumed to be significantly more water-soluble than the former.

As discussed in Section 1.3. of this report, the first two steps in the Li-ion battery supply chain are of concern:

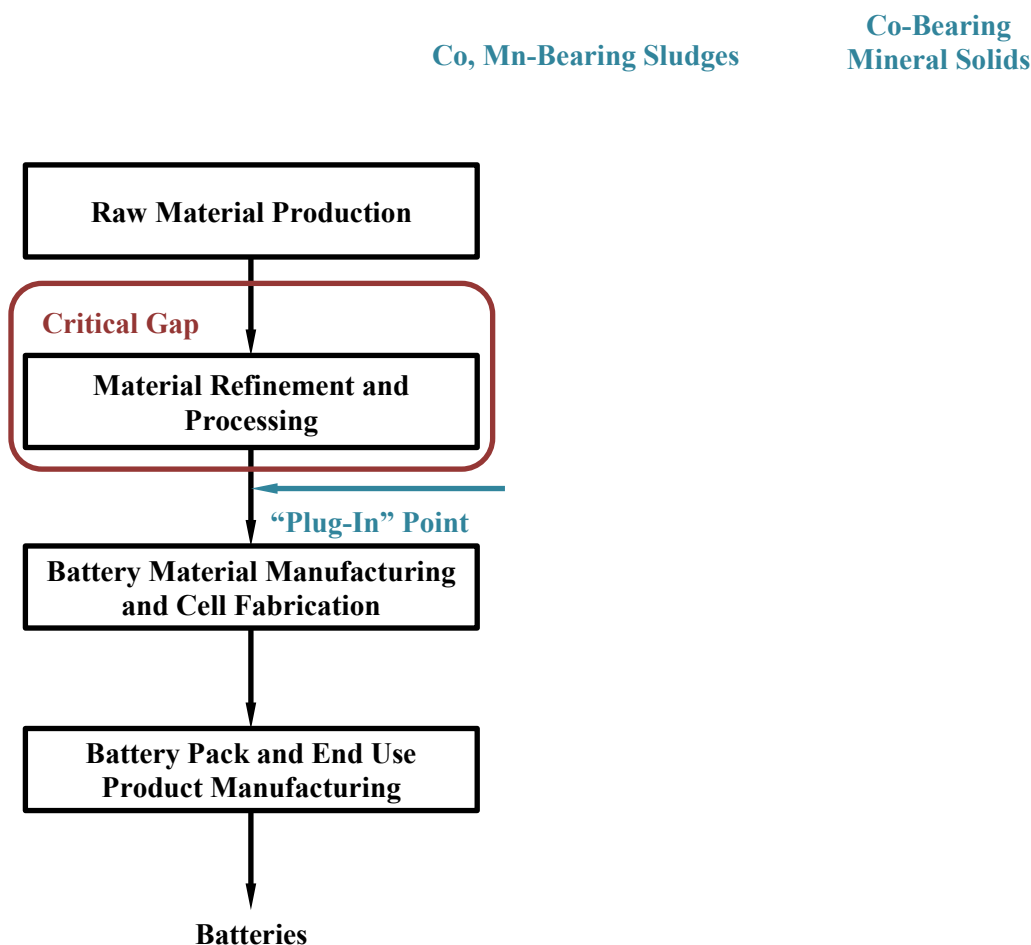
- Raw Materials Production
- Materials Purification and Refinement

The second of these steps is the critical gap, and the transformation of the two types of material into a form that can be “plugged-in” to the supply chain downstream of this gap is the objective of the flowsheet design and laboratory work to be discussed here. The “plug-in” point is shown in Figure 6.

A review of techniques available for the production of metal salts used in the production of Li-ion battery cathode materials appears in Ma et al. (2020). That work cites cobalt sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , 20.2% minimum Co) and manganese sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 31.8% minimum Mn) as the most common commercial cobalt and manganese products used in the production of cathode materials. The flowsheet development in this report will begin with the two classes of materials listed above and end with a low-grade hydrometallurgical concentrate product that

would be further processed to battery grade cobalt- and manganese sulfate products. The Ma et al. work discussed processes for the production of these high-purity salts from recycled battery (acid) leach solutions, and addition of the flowsheet developed here could ultimately result in sustainable and flexible steps in the battery supply chain, replacing the conventional steps (raw materials and material purification and refinement) with a U.S. domestic alternative that is compatible with secondary materials.

**Figure 6: “Plug-In” Point for Cobalt and Manganese Recovered from Secondary Materials**



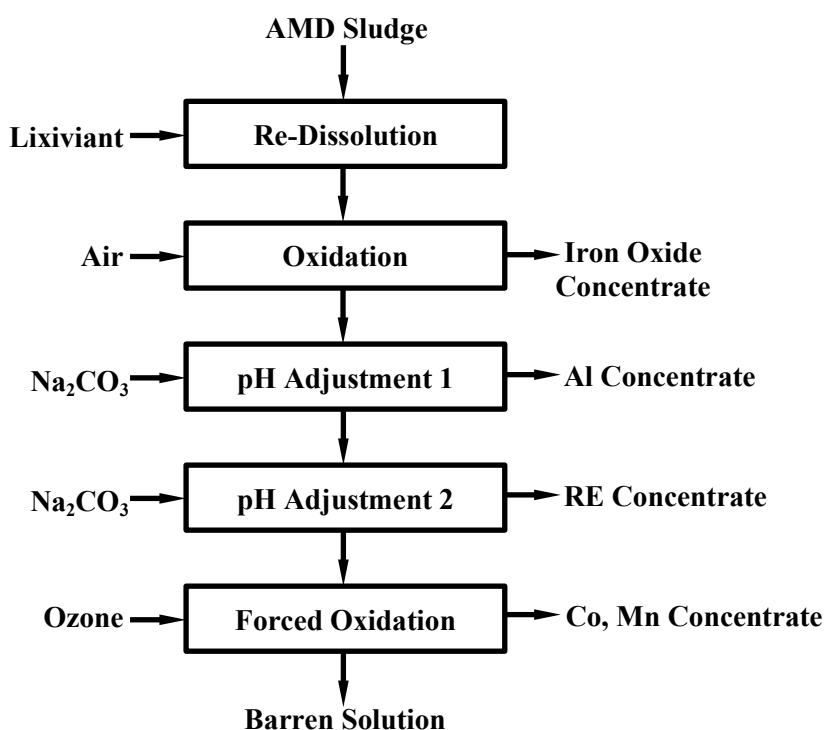
#### 4.1.1. Cobalt- and Manganese-Bearing Sludges

The acid mine drainage sludges and mineral products are expected to have differing process requirements in order to produce the concentrates that could be used for production of the battery-grade salts. The approach taken here is first to develop a system to process AMD sludges (Hassas et al., 2020, Hassas et al., 2021), which have been leached from their original mineral forms and precipitated, and then to add a capability to produce a cobalt-bearing leach solution from the mineral products derived from coal refuse. In effect, the AMD processing system would

“plug-in” to the supply chain and the system for extracting cobalt from the mineral products would “plug-in” to the AMD process.

Figure 7 shows the first portion of the flowsheet, re-dissolving the AMD sludge with sulfuric acid and using a selective precipitation process to produce multiple concentrates (iron-rich, rare earth-rich and cobalt/manganese-rich). The re-dissolution step and the selective precipitation steps are integrated with the supply chain in Figure 8. This process is an adaptation of a selective precipitation system previously reported by Hassas et al. (2020, 2021) for AMD, and involves multiple steps with oxidation or pH adjustment of the solution. Four precipitates are produced sequentially: iron-rich, aluminum-rich, rare earths-rich and the fourth, using ozone for oxidation, is rich in cobalt and manganese. Research on the use of ozone for separate removal of iron and manganese from mine water dates back to 1974 (Rozelle and Swain, 1974). Preliminary laboratory results for this process applied for multi-product recovery will be reported here.

**Figure 7: The Selective Precipitation Process**

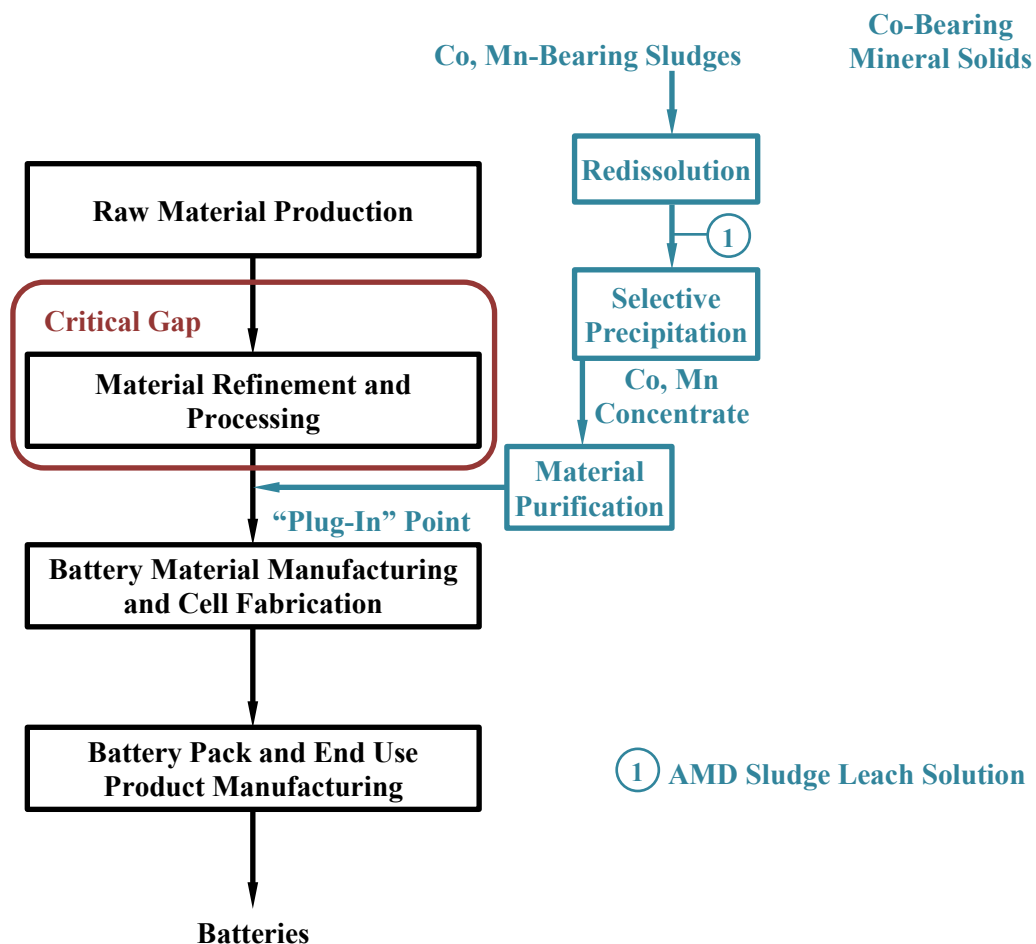


The products from this step would then be sent to a purification step, possibly along the lines of those discussed in Ma et al. (2020). This added system would “plug-in” downstream of the Material Refinement and Processing step.

Some AMD sludges from Pennsylvania, have also been found to have significant values of contained rare earth elements (Rozelle et al., 2019). The system shown in Figure 8 includes

recovery of a rare earth concentrate. Sale of this product would improve process economics, and provide an additional domestically-sourced critical mineral commodity.

**Figure 8: The Addition of Cobalt and Manganese Recovery from AMD Sludge**



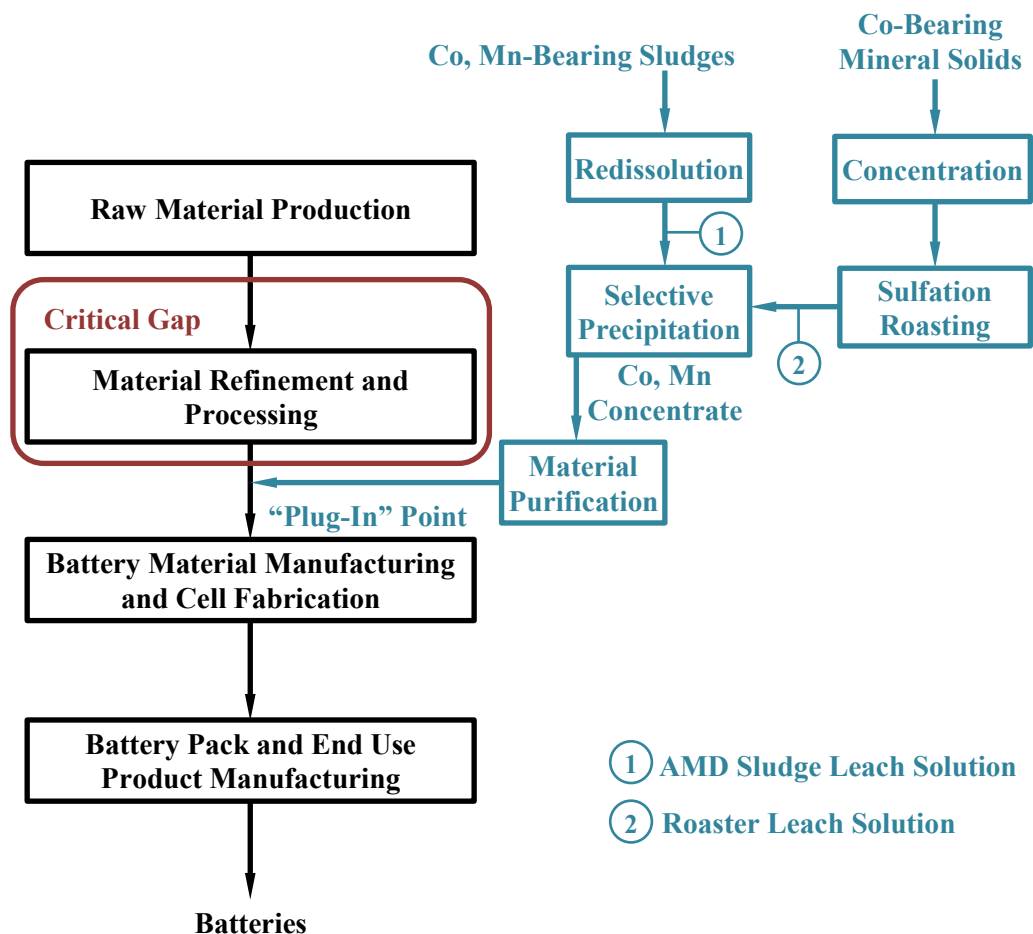
#### 4.1.2. Cobalt-Bearing Mineral Solids from Coal Refuse

The cobalt-bearing mineral products would be produced from coal refuse, and the requirement is that the extraction should produce a cobalt-bearing leach solution that can be fed to the selective precipitation step, shown in Figure 7, for the production of low-grade concentrates. The mineral form of the cobalt is yet to be gleaned, and pending further information under that topic the system used for integrating mineral product processing is a combination of concentration through mineral processing with fluid bed sulfation roasting, which has been used commercially to produce cobalt from Pennsylvania metal mine tailings (Rozelle et al., 2020). This would apply to cobalt present in the material in sulfide minerals. This addition, as seen in Figure 9, “plugs-in” to the selective precipitation step for the AMD sludge processing system.

As mentioned, sulfation roasting has been used to process cobalt-bearing mineral concentrates from Pennsylvania in the past. Sulfation roasting has several advantages, including the ability to process low-grade concentrates. The energy for the process is supplied by the combustion of sulfur present in pyrites, with the sulfur-bearing products of combustion removed from the process offgas and recovered as sulfuric acid. The roasting of cobalt-bearing pyrite concentrates results in an iron oxide-rich stream of roaster products, which have been commercially integrated into blast furnace ironmaking (Rozelle et al., 2020). Advantages inherent in the process include:

- Sustainable low carbon operation, the “fuel” for the process is sulfur, sulfuric acid is co-produced that can be used for hydrometallurgical applications
- The roaster solids may be useful as feedstock for the steel industry
- Multiple byproducts can add revenue to the process and improve economics

**Figure 9: The Addition of Cobalt Recovery from Mineral Products**



The process for extraction of cobalt from the mineral product type of material also includes a concentration step ahead of the roaster. In the case of past operation of this type of system, the



feed cobalt grade, required by the roaster, would be ~1% cobalt, the grade of a pyrite concentrate used in past sulfation roasting operation in the U.S. (Scharf and Dominguez, 1956).

Physical concentration of the mineral product materials will be required to produce the feed for the roasting step, both for the cobalt concentrate and the sulfur required for the roasting process.

#### 4.2. Mineral Processing Test Results

While more work is required regarding the nature of the cobalt minerals in coal refuse, preliminary mineral processing tests have been focused on the potential to concentrate and recover pyrite from these materials. Pyrite is required for the process, and maximizing the iron and sulfur contents can help minimize the contribution of gangue elements to the solution produced when the roaster solids are leached.

Preliminary studies have been conducted using a laboratory concentrating table to concentrate pyrite from coal refuse. The tests were conducted using a Deister laboratory concentrating table, measuring the iron and sulfur contents of the products using an Olympus Vanta hand held X-Ray fluorimeter.

Hand-picked high-pyrite content materials were selected from coal refuse for the test work. For the results presented here, the material was crushed and sized at -1.160 mm, +0.212 mm. Three products were collected from the table (lights, middlings and heavies). Figure 10 shows the material balance results from the test (feed parameters were reconstituted from the product material balance). The heavy product was over half the yield, with 33.1% Fe and 29.4% S. These results are lower than the 41.2% Fe, 48.9% S material fed to the roaster at Bethlehem Steel (Scharf and Dominguez, 1956), and further concentration of the coal refuse materials, or adjustment of the table parameters would be required to produce the pyrite grade cited in that work. However, these preliminary results suggest that a table separation could be suitable for pyrite production from coal refuse in Pennsylvania.

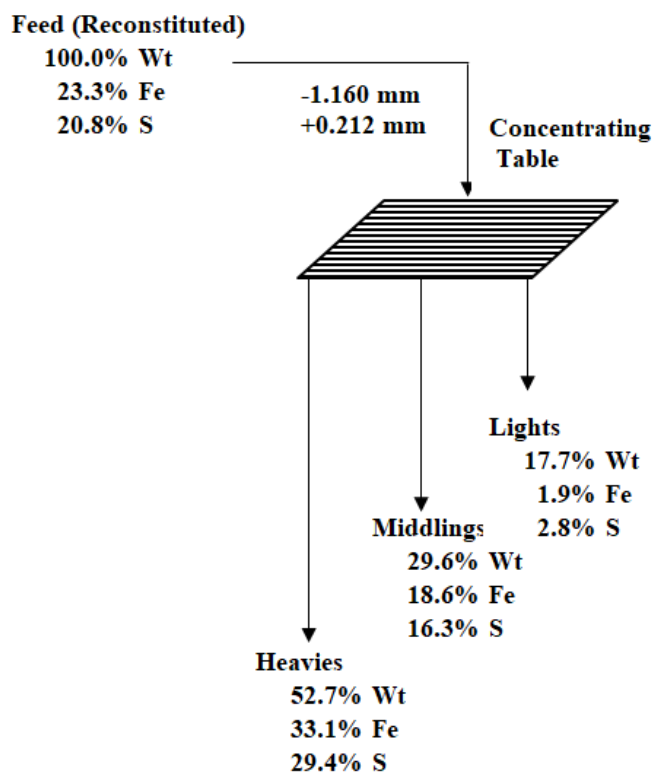
An example image of the recovered pyrite appears in Figure 11.

#### 4.3. Extractive Metallurgy Test Results

The selective precipitation process shown in Figure 7 can concentrate species in the feed solution into multiple solid products. Experimental work on a leach solution, produced from a central Pennsylvania AMD sludge material, is shown in Figure 12. These results are part of a preliminary set of tests to examine the effect of process conditions on recoveries and grades of the species of interest (Fe, Al, REEs, Co and Mn), for process optimization. These parameters have yet to be optimized, but preliminary testing suggests that (1) the first step efficiently removed most of the iron, (2) most of the rare earth content reports to the solids produced in the third step, and (3) the forced oxidation step (using ozone) produces a significant manganese grade, also containing 7,000 ppm cobalt.

Work is ongoing regarding the application of the sequential precipitation technology for leach solutions (produced from both the re-dissolution of AMD sludge and roaster solids leaching). The goal of process condition optimization is the maximization of grades and recoveries for the target species in each step.

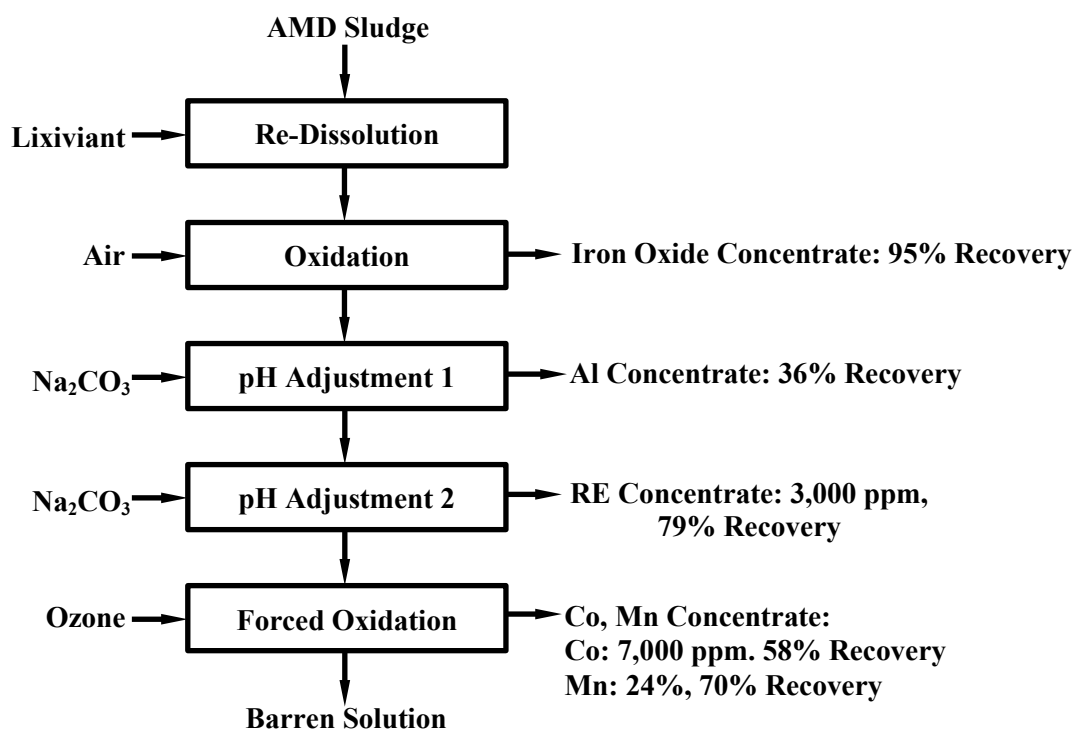
**Figure 10: Concentrating Table Test Results for High-Sulfur Content Coal Refuse**



**Figure 11: Example Pyrite Concentrate from Table Tests**



**Figure 12: Preliminary Test Results, Selective Precipitation Process Applied to Cobalt and Manganese-Bearing Leach Solution**



## 5. Summary of Results

### 5.1. Resources and Potential Production

The production of batteries for electric vehicle applications in the U.S. can require significant tonnages of cobalt and manganese, as shown earlier in Table 1. There are other markets for cobalt in the U.S., and apparent consumption in 2019 was 12,500 metric tons (Shedd, 2021). Given that the U.S. cobalt reserves in the U.S. total 55,000 metric tons, identification of new cobalt resources in the U.S. that could lead to commercial production, could lead to an easing of U.S. import-dependence.

Secondary materials in Pennsylvania have accounted for the majority of U.S. mine production of cobalt in the past. This report has presented preliminary findings toward that end. A previous report (Rozelle et al., 2020) noted that elevated cobalt contents in one of these secondary materials, acid mine drainage sludge, is linked to elevated manganese contents. Manganese is also a battery metal, and has been examined here.

The results of a literature survey and geologic discussion are presented in Appendix 1, including a discussion of possible similarities between some cobalt enrichments in the Pennsylvania coal

measures and cobalt laterite deposits. This may provide useful information for further exploration and metallurgical test work.

Findings of this report are:

1. The preliminary estimate is that coal refuse in Pennsylvania contains approximately 52,000 metric tons of cobalt. This tonnage is similar to the entire U.S. cobalt reserves presented in the 100 Day Supply Chain Report. Over a half million metric tons of manganese are contained in these accumulations. Significant manganese is also contained in the Palmerton dump left by a large zinc smelting operation.
2. The preliminary estimate is that 60 metric tons of cobalt and over 5,500 metric tons of manganese are being discharged with acid mine drainage into the Commonwealth's waterways every year. Recovery of these elements could provide domestically-sourced materials for the lithium-ion battery industry in the U.S.
3. The sale of cobalt and manganese commodities, recovered from these materials, could help offset the costs of mine reclamation and stream restoration in Pennsylvania, which has the majority of the funding needs in seven key categories in the OSMRE abandoned mine land inventory.
4. Results of initial process development have been presented, for the integration of cobalt and manganese from secondary materials, into the lithium-ion battery supply chain. The "plug-in" point would be downstream of the critical gap- "materials purification and refinement, replacing the critical gap with a flexible process. Preliminary laboratory results have shown that (1) a pyrite concentrate can be produced from coal refuse that is suitable as fuel for a sulfation roasting process, and (2) the selective precipitation process can produce a relatively high grade manganese concentrate, in which cobalt is also enriched.

## 5.2. Suggestions for Further Work

Improving the knowledge base of cobalt and manganese resources in Pennsylvania could identify near-term opportunities for production operations. This would require working with industry to identify opportunities such as materials with the highest cobalt grades and process options to recover cobalt and manganese from them.

Specific suggestions toward that end are as follows:

1. An in-depth examination of the coal refuse resource in the bituminous coal field of Pennsylvania that has been produced since 1975. This will likely add significantly to the tonnage estimate.

2. A reconnaissance of individual refuse dumps in Pennsylvania, followed by a detailed evaluation of the critical mineral content of an example accumulation that has indicated an elevated cobalt content.
3. Detailed mineral processing test work on coal refuse materials with elevated cobalt contents.
4. Fundamental work on the nature of cobalt presence in these secondary materials, which can fill knowledge gaps and support process development research.
5. Possible resource data have been presented for one accumulation of smelter byproducts. The Commonwealth has a long history of both ferrous and non-ferrous pyrometallurgy operations. A reconnaissance and inventory of all past operations could result in the identification of additional resources.

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## Appendix 1

### Geological Considerations Associated with Secondary Cobalt and Manganese Resources in Pennsylvania

#### *Cobalt Geochemistry and Minerals*

Cobalt has two main oxidation states ( $2^+$  and  $3^+$ ). The ionic radius of cobalt is 0.72 angstroms (Å) for  $\text{Co}^{2+}$  and 0.63 Å for  $\text{Co}^{3+}$ , both of which are similar to the ionic radii of  $\text{Mg}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}$ , allowing substitution for these elements by cobalt in many minerals.

Estimates of the crustal abundance of cobalt within the Earth's bulk continental crust vary between 15-30 ppm (29 ppm Co, on average), similar to other transition metals such as copper, zinc, and nickel (Roberts and Gunn, 2014).

Pure cobalt is not found in nature, but, because of its chalcophile and siderophile properties, it preferentially bonds with iron, nickel, copper, and sulfur. The mineralogy of cobalt deposits is diverse and includes both primary and secondary phases (Table A1-1). In primary deposits, most cobalt is recovered from sulfide minerals. Secondary cobalt-rich phases, which form during surficial weathering, occur as sulfate minerals. Although there are several important cobalt-rich sulfide minerals (linnaeite, siegenite, carrollite, and cobaltite), most recovered cobalt occurs substituted within sulfide minerals (e.g., arsenopyrite, pyrrhotite, pyrite, or pentlandite) (Donaldson and Beyersmann, 2010).

**Table A1-1: Common Cobalt-Bearing Minerals**

<b><u>Sulfides</u></b>		Pyrite	$(\text{Fe},\text{Co})\text{S}_2$
Carrollite	$\text{Cu}(\text{Co},\text{Ni})_2\text{S}_3$	Pyrrhotite	$(\text{Fe},\text{Co})_{1-x}\text{S}$
Pentlandite	$(\text{Fe},\text{Ni},\text{Co})_9\text{S}_8$	<b><u>Secondary</u></b>	
Linnaeite	$\text{Co}_3\text{S}_4$	Erythrite	$\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
Siegenite	$(\text{Co},\text{Ni})_3\text{S}_4$	Heterogenite	$\text{CoO}(\text{OH})$
<b><u>Arsenides</u></b>		Asbolane	$(\text{Ni},\text{Co})_{2-x}\text{Mn}(\text{O},\text{OH}) \cdot n\text{H}_2\text{O}$
Skutterudite	$(\text{Co},\text{Fe},\text{Ni})\text{As}_{2-3}$	Heazlewoodite	$(\text{Ni},\text{Co})_3\text{S}_2$
Safflorite	$(\text{Co},\text{Fe})\text{As}_2$	<b><u>Oxyhydroxides</u></b>	
<b><u>Sulfarsenides</u></b>		Goethite	$\text{Fe}^{3+}\text{O}(\text{OH})$
Cobaltite	$\text{CoAsS}$	Limonite	$\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$
Glaucodot	$(\text{Co},\text{Fe})\text{AsS}$	Lithiophorite	$\text{AlMnO}_2(\text{OH})_2$

## ***Cobalt Metallogenic Deposits***

### Stratiform Sediment-Hosted Cu-Co Deposits

Most of the world's cobalt is produced as a byproduct of copper mining in sediment-hosted Cu-Co deposits that form strata-bound and commonly stratiform zones within siliciclastic or carbonate strata (Hitzman et al., 2005). Globally, these deposits contain chalcopyrite, pyrite, carrollite, plus minor amounts of bornite and chalcocite. Sediment-hosted copper deposits are stratabound in that they are restricted to a narrow range of layers within a sedimentary sequence but do not necessarily follow sedimentary bedding (Cox et al., 2003). They form after the host sediment is deposited and often prior to lithification.

The consensus opinion for genesis is that metalliferous saline hydrothermal fluids were introduced at low to moderate temperatures during diagenesis and the early stages of deformation and metamorphism (e.g., Zientek et al., 2013). Cox et al. (2003) stated that for a sediment-hosted copper deposit to form, four conditions are required:

1. There must be an oxidized source rock that must be hematite stable and contain ferromagnesian minerals or mafic rock fragments from which copper can be leached.
2. There must be a brine source to mobilize copper. Evaporites are commonly the source of the brine.
3. There must be a source of reduced fluids to precipitate copper (and other metals) and form a deposit. The reduced fluid can be derived from organic-rich shales and carbonate rocks, pockets of hydrocarbons in the host rock, or sedimentary fluids in equilibrium with pyrite.
4. There must be favorable conditions for fluid mixing (e.g., high permeability and fluid pressure).

If any of these conditions are not met, a deposit will not form. Cobalt is common in many stratiform sediment-hosted Cu deposits where it is found as a substitute in chalcopyrite, pyrite, galena, and sphalerite. The presence of cobalt in some deposits and not in others suggests that the sedimentary exhalative process may be important (Brown, 1984).

### Ni-Co Laterite Deposits

Laterites are red regolith's that develop in humid tropical climates during the weathering of ultramafic bedrock (high Fe and Mg content and <45 weight percent SiO<sub>2</sub>). Ore zones range in thickness from about 10 m to as much as 40 m, and generally contain >1 wt% Ni and <0.15 wt% Co. Ni-Co laterites are supergene deposits of Ni ± Co formed from the pervasive chemical and mechanical weathering of ultramafic rocks (Marsh and Anderson, 2011). The formation of secondary concentrations of Ni ± Co requires an ultramafic protolith or source rock that is primarily enriched in metals. Extreme weathering removes all elements except the least soluble ones from the protolith.

From top to bottom, Ni-Co laterite deposits are composed of overburden, limonite, saprolite, and weathered ultramafic source rocks. Limonite, which is an iron ore, tends to contain the highest concentrations of cobalt, where saprolite (chemically weathered rock) yields the higher nickel grades. Major ore constituents include nickeliferous serpentine, nickel- or cobalt-bearing clays, erythrite, heterogenite, absolonite, heazlewoodite, and orthohydroxide minerals (goethite, limonite, and lithiophorite).

#### Black Shale hosted Ni-Cu-Zn-Co Deposits

Black shales are well known for containing elevated contents of many metals of economic interest, including: Cu, Mo, Ni, Zn, Co, Mn, Cd, Ag, Au, Se, Cr, V, U, and PGE's (e.g., Desborough and Poole, 1983; Coveney, 2003). Metals concentrated in black shales may reside in pyrite, organic matter, aluminosilicate minerals (e.g., illite), and locally in sphalerite and chalcopyrite. Metalliferous black shales exhibit a wide range of physical and chemical characteristics in which they show diversity in their depositional and geologic histories, carbon and carbonate content, and ore formation. However, unifying characteristics of metalliferous black shales are their fine-grained character, enhanced metal content (enriched in any given metal by a factor of 2), dark color, and an inferred association with organic matter (Huyck, 1990).

The continuous influx of metal-bearing fluids results in the deposition of relatively large concentrations of metalliferous minerals. Organic matter hosted within the shales creates a reducing environment allowing soluble metal sulfates and noble metals to precipitate (Meyers et al., 1992; and references therein). Further enrichment of cobalt could be produced by hydrothermal leaching, mobilization, and concentration into sulfide minerals during deformation and regional metamorphism.

#### Iron Oxide (Cu-Au -Ag-U-REE-Co-Ni) Systems

Iron oxide systems deposits are defined primarily on their bulk composition instead of physical (i.e., tectonic) characteristics. Iron-oxide-copper-gold (IOCG) deposits contain some of the world's largest known resources of Cu, U, REE, and Au, and are attractive exploration targets due to their large size, relatively simple metallurgy, and local endowment of critical metals (Hitzman, 2000; Williams et al., 2005; Groves et al., 2010). The geologic diversity of these systems has contributed to multiple genetic hypotheses: (1) magmatic-hydrothermal, (2) terrestrial hydrothermal wherein key fluids are basinal or surficial nonmagnetic brines circulated by igneous or crustal heat, (3) metamorphic-hydrothermal wherein fluids derived from distinctive crustal sources by metamorphic devolatilization, or (4) magmatic where ore-forming fluids are a fluid-bearing iron oxide melt (Barton, 2014). They tend to be structurally or stratigraphically controlled, associated with voluminous Na-Ca-K metasomatism, and lack well-defined tectonic and igneous controls.

The Missouri iron metallogenic province within the St. Francois Mountains terrane of southeast Missouri hosts deposits of iron-oxide  $\pm$  apatite  $\pm$  rare earth element, iron oxide-copper-gold, and

iron-rich sedimentary deposits (Day et al., 2016). The Missouri iron metallogenic province was an important source for iron ore production in the past and continues to be prospective for undiscovered Fe, Cu, Co, Au, and REE resources. Small quantities (~ 2000 Mt) of manganese and manganese iron ore were mined as early as 1881. In addition to the Missouri iron metallogenic province, there are several low-Ti iron oxide deposits exposed within the orogenic core of the Appalachians. Cobalt concentrations of these deposits range from 13 - 47 ppm with ores that yield ~90 ppm Co (Matt et al., 2017). Cobaltiferous sulfides from IOCG deposits may have provided sulfur-bearing mineral detritus into the Appalachian basin.

#### Mississippi Valley-Type Zn-Pb (-Co-Ni) Sulfide Deposits

Mississippi Valley-Type (MVT) deposits account for 24 percent of the global resources for Pb and Zn in sediment- and volcanic-hosted deposits (Leach et al., 2010). MVT ores consist mainly of sphalerite, galena, and generally lesser amounts of iron sulfides. The most important characteristic of MVT ore deposits is that they are epigenetic deposits hosted mainly by dolostone and limestone in platform carbonate sequences and usually located at flanks of basins, orogenic forelands, and foreland fold and thrust belts inboard of the clastic rock-dominated passive margin sequence (Leach and Sangser, 1993; Leach et al., 2005). Mineralization characteristically involves the migration of low-temperature, high saline brines and the subsequent precipitation of ore and gangue minerals as open-space fillings in paleokarst structures or as replacement zones in carbonate rocks. They occur in large districts and have no spatial or temporal association to igneous rocks, which distinguishes them from skarn or other intrusive rock-related Pb-Zn ores. Abundant evidence has shown that the ore fluids were derived mainly from evaporated seawater and were driven within platform carbonates by large-scale tectonic events.

MVT deposits are found throughout the world, but the largest occur within the continental interior of North America. The southeast Missouri Co-Cu-Pb-Zn district is the world's largest lead producer and a significant producer of by-product Zn, Cu, Co, Ag, and Cd. Siegenite is the source of cobalt which develops rims on early cavity-filling chalcopyrite and sphalerite (Hagni, 2008). Chalcopyrite concentrates produced from the Old Lead Belt typically contain 28 weight percent Cu and form 0.5 – 1.5 weight percent each of Ni and Co (Clifford and Higley, 1978).

#### Magmatic Ni-Cu-(Co-PGE) Sulfide deposits

Large resources of cobalt are contained in Ni-Cu-(Co-PGE) sulfide deposits hosted in mafic and ultramafic igneous rocks (e.g., Naldrett, 2004; Eckstrand and Hulbert, 2007). Ore deposits are comprised of semi-massive to massive sulfides that occur within or near basal zones of layered intrusive complexes, in discordant magmatic conduits, and with ultramafic intrusions and lava flows. Mineralization consists of disseminated to massive concentrations of iron-copper-nickel-PGE-enriched sulfide mineral concentrations in zones that can be tens to hundreds of meters thick (Zientek, 2012). Nickel is the principal metal commodity, and it is accompanied by



subequal proportions of copper in most deposits. Cobalt residing in cobaltiferous pentlandite, and to lesser extent in linnaeite, is recovered as a by-product.

Mineralizing processes involve magmatic segregation of sulfides and, in some deposits, hydrothermal mobilization into post-magmatic structures. Sulfide mineralization is found adjacent to or along strike with the country rocks that are enriched in sulfur-bearing, iron-bearing, and (or) carbonate minerals. The mineralization can be laterally persistent, commonly extending the length of the intrusion, but generally tapers to hundreds of meters in thickness. Sulfide abundance is typically about 3 to 5 volume percent.

#### Fe-Cu-Co Skarn and Replacement deposits

Pluton-related skarn and replacement deposits form by the introduction of hydrothermal fluids into chemically reactive rocks, mainly carbonate (limestone and dolomite), and by metasomatic processes that introduce metals and other components into the precursor strata (Slack et al., 2017). These deposits occur proximal or distal to intrusive bodies and contain a diverse suite of metals (e.g., Megaw, 1998; Meinert et al., 2005). Sulfide minerals may include pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena, together with abundant magnetite in some deposits.

The Cornwall and Morgantown (Grace Mine) Fe-Cu-Co deposits of southeastern Pennsylvania are two of only a few cobaltiferous skarn deposits in the world (Lapham and Gray, 1973). Pyrite in the deposit was unusually rich in Co, which was recovered as a by-product.

#### Volcanogenic Cu (-Zn-Co-Ag-Au) Massive Sulfide Deposits

Volcanogenic massive sulfide (VMS) deposits occur in marine volcanic and volcano-sedimentary belts and are mined principally for Cu, Zn, Pb, Ag, and Au (Galley et al., 2007; Shanks and Thurston, 2012). These deposits form at or near the seafloor where circulating metalliferous hydrothermal fluids driven by magmatic heat are quenched by mixing with seawater or porewaters in near-seafloor lithologies. VMS deposits develop within mid-ocean ridges and mature back-arc basins, sediment-covered rifts and ridges, intraoceanic/continental margin arcs and associated back arc rifts.

Ore deposits occur as massive sulfide lenses that vary widely in shape and size and may be pod- or sheet-like. VMS deposits range in size from small pods of less than a ton (which are commonly scattered through prospective terrains) to supergiant accumulations such as Rio Tinto (Spain) which yields 1.5 billion Mt (Shanks and Thurston, 2012). Major sulfide minerals are pyrite, pyrrhotite, chalcopyrite, and sphalerite with some deposits containing appreciable amounts of galena, tetrahedrite, and gold. Most VMS deposits lack elevated Co contents (<0.1 weight percent), but several have high grades especially deposits hosted predominantly by ultramafic or mafic volcanic rocks.

Over 70 major (>1 million Mt) strata-bound and stratiform VMS deposits occur in the fragmented Appalachian-Caledonian orogen. These deposits developed in ophiolites formed either at a major ocean spreading axis or within back- or interarc-basins as well as intraplate oceanic plateaus or seamounts (Stephens et al., 1984). In the central Appalachians, Fe-Cu-Co-Zn-Ni mineralization of the Sykesville district (Maryland) occurs in a narrow 16 km long belt. Mineralization occurs within a banded iron-formation and consists dominantly of magnetite, chalcopyrite, siegenite, sphalerite, and pyrite with lesser amounts of hematite and bornite (Candela et al., 1989). Four abandoned mines in the Sykesville district lie along the contact between serpentinized ultramafic rocks and metasediments. Cobalt is hosted within siegenite and carrollite with concentrations up to 32 and 3 weight percent respectively. Ores recovered from Springfield mine yield Co concentrations up to 0.2 weight percent (Candela et al., 1989).

### ***Manganese Geochemistry and Mineralogy***

Manganese is the 12th most abundant element in the Earth's crust with average crustal rocks containing about 0.1 percent manganese. It is a potentially mobile element and occurs in three oxidation states in nature ( $2^+$ ,  $3^+$ , and  $4^+$ ). The solubility and mobility of Mn in solution is strongly dependent on the pH and oxidation potential (Eh) of the manganese-bearing solution. In general, manganese solubility is highest in more acidic conditions (lower pH) and less oxidizing (lower Eh) conditions in which dissolved Mn exists primarily in the most soluble  $2^+$  oxidation state (Cannon et al., 2017).

Table A1-2 lists common manganese minerals. Most manganese ore formed at ambient conditions on the Earth's surface, both subaerial and submarine. The most common manganese minerals within ore deposits are manganese oxides and carbonates, with manganese carbonates being the most voluminous Mn minerals.

### ***Manganese Metallogenic Deposits***

#### **Manganese Deposits in Marine Sedimentary Rocks**

Extensive layers of Mn-rich sedimentary rocks formed on ancient seabeds and have since been part of continents through tectonic uplift and continental accretion. There are two primary types of sedimentary manganese deposits distinguished based on the nature of rocks with which they are interlayered: (1) Mn-rich sediments that occur independent of iron and (2) Mn-rich sediments interlayered with iron-rich strata. The difference between the two is the degree of oxygen depletion in ocean waters that varies from anoxic or suboxic (in which the solubility of both manganese and iron are enhanced), to euxinic and sulfidic (in which manganese solubility is enhanced but iron solubility is depressed). Low-iron deposits are thought to have formed in shallow marine settings adjacent to stratified oceans that contained a low oxygen deepwater mass. In such water masses, dissolved hydrogen sulfide causes iron to be precipitated as sulfide minerals in black shale and leaves very low concentrations of dissolved iron in the seawater (Cannon et al., 2018). Mn-rich sedimentary deposits interlayered with iron-rich strata commonly

occur in banded iron formations (BIF) that are found worldwide in Precambrian sequences. The main characteristic of these deposits is the interlayering of iron- and manganese-rich layers, which indicate that the deposit formed from an ocean in which both iron and manganese were enriched, but the two metals were differentiated from each other at the site of deposition, perhaps by subtle changes in oxidation state or acidity of the ocean water (Cannon et al., 2018).

**Table A1-2: Common Manganese-Bearing Minerals**

<b>Oxides and Hydroxides</b>		Lithiophorite	$\text{LiAl}_2(\text{Mn}^{4+}, \text{Mn}^{3+})_6(\text{OH})_6$
Pyrolusite	$\text{MnO}_2$	Romanechite	$\text{Ba}_{0.66}(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10} \cdot 1.34\text{H}_2\text{O}$
Ramsdellite	$\text{MnO}_2$	Todorokite	$(\text{Ca}, \text{Na}, \text{K})_x(\text{Mn}^{4+}, \text{Mn}^{3+})_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$
Nsutite	$\text{Mn}(\text{O}, \text{OH})_2$	Bimessite	$(\text{Na}, \text{Ca})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$
Cryptomelane	$\text{K}_x(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$	Vemadite	$\text{MnO}_2 \cdot n\text{H}_2\text{O}$
Manjiroite	$\text{Na}_x(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$	Psilomelane	$\text{Ba}(\text{Mn}^{2+})(\text{Mn}^{4+})_8\text{O}_{16}(\text{OH}_4)$
Coronadite	$\text{Pb}_x(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$	<b>Silicates</b>	
Hollandite	$\text{Ba}_x(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$	Neotocite	$(\text{Mn}, \text{Fe})\text{SiO}_3 \cdot \text{H}_2\text{O}$
Bixbyite	$\text{Mn}_2\text{O}_3$	Bementite	$(\text{Mn}, \text{Mg}, \text{Fe})_6\text{Si}_4(\text{O}, \text{OH})_{18}$
Braunite	$\text{Mn}^{2+}\text{Mn}^{3+}_6(\text{SiO}_4)_8$	Rhodonite	$\text{MnSiO}_3$
Manganosite	$\text{MnO}$	Tephroite	$\text{Mn}_2\text{SiO}_4$
Jacobsite	$\text{MnFe}_2\text{O}_4$	Spessartine	$\text{Mn}^{2+}_3\text{Al}_2(\text{SiO}_4)_3$
Manganite	$\text{MnOOH}$	<b>Carbonates</b>	
Groutite	$\text{MnOOH}$	Rhodochrosite	$\text{MnCO}_3$
Fetknechtite	$\text{MnOOH}$	Kutnahorite	$\text{Ca}(\text{MnMgFe})(\text{CO}_3)_2$
Pyrochroite	$\text{Mn}(\text{OH})_2$	<b>Sulfides</b>	
Chalcophanite	$\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$	Alabandite	$\text{MnS}$

### Supergene Enrichment Deposits

Many of the currently mined manganese deposits that formed in the oceans were enriched by secondary surface processes. Supergene deposits form where chemical reactions taking place within tens of meters of the surface redistributing manganese at a local scale and leach out nonmanganese components further enriching the ore. Supergene deposits are most abundant in areas of low tectonic activity and develop the highest grades in tropical regions where humid conditions and abundant vegetation form deep tropical soils (Cannon et al., 2017). The generation of humic acids by decomposition of abundant organic matter results in the dissolution of manganese-bearing minerals and transportation of manganese downward in the soil profile. It is then re-precipitated where soil water encounters less acidic conditions. This same acidic soil solution dissolves and removes other components as well, resulting in a residual enrichment of

manganese minerals (Verentsov, 1996). Supergene Mn deposits tend to have developed most frequently in areas of low topographic relief, commonly on plateaus, where slow erosion allows time for these ore-forming processes to take place.

### ***The Pennsylvania Coal Measures***

#### Eastern and Western Pennsylvania Sedimentary Provenance

The depositional history of Pennsylvanian age (323-299 Ma) sediments in Pennsylvania is complex, consisting of repeated deep erosion, influxes of high-energy clastic sediments, and sea-level changes. Sedimentation in the Appalachian foreland basin was primarily driven by the Alleghanian orogeny. The Alleghanian orogeny is the last major Appalachian orogen mountain building event that occurred across central and western Pennsylvania (e.g., Hatcher et al., 1989). This event is thought to have occurred over as many as five pulses of deformation from the Mississippian to the Permian, as a result of the collision of the African continent (Gondwana) with the North American continent (Laurentia).

Pulsed uplift of the Appalachian orogenic highland during the Alleghanian orogeny shed enormous amounts of igneous, metamorphic, and recycled sedimentary and metasedimentary detritus northward and westward creating a vast thick wedge of sediments that tapered from southeast to northwest. The sediment wedge contains large amounts of granitoid conglomerates and coarse-grained quartz sands that form the basal sediment units beneath and above coal layers across Pennsylvania (Wood et al., 1969; 1986; Edmunds et al., 1999).

Contrast to the southeast-northwest transverse drainage, south to southwest-directed longitudinal (orogen-parallel) drainage characterized the distal parts of the basin in the Early Pennsylvanian (Archer and Greb, 1995, Grimm et al., 2013). Sediments deposited within the distal epicontinental shelf in central and western Pennsylvania were derived primarily from southeastern Appalachian orogenic highlands and Precambrian cratonic sources to the north. U-Pb geochronology of detrital zircons suggest that the westward drainage system fed the northern part of the longitudinal system, with little contribution from the northern craton (Thomas et al., 2017).

The crystalline core of the Appalachian orogen contains numerous mineral deposits that could have provided source material for the Pennsylvanian sediments. Pre- to Syn-Carboniferous ore deposits in areas of New Jersey, southeastern Pennsylvania, and Maryland, consist primarily of various forms of Ni-Cu-Co sulfide, chromite and Zn-Fe oxide deposits with cobalt ore occurrences concentrated within Ni-Cu-Co sulfide deposits. Sulfide and chromite ore are hosted within mafic to ultramafic rock (Fe- and Mg-rich igneous rocks that contain <55 weight percent SiO<sub>2</sub>) and deep marine sediments. Zn- and Fe-oxide ore deposits are hosted within marble and minor felsic intrusive rocks. Uplift and erosion of ore-bearing rocks within the core of the Appalachian orogen appears to be a primary cause for the enrichment of cobalt and manganese within Pennsylvanian age sediments.

In the Eastern Middle Anthracite field of eastern Pennsylvania, sedimentary rocks contain schist and gneiss conglomerate cobble clasts and lithic fragments combined with common metamorphic minerals (e.g., garnet, kyanite, sillimanite, and staurolite) indicating a metamorphic source region. The most apparent source of metamorphic detritus is the neighboring Appalachian orogen hinterland which was actively being uplifted during this time period (e.g., Hatcher et al., 1989). However, in western Pennsylvania, multiple lines of evidence suggest a northern cratonic source contribution for sediments in addition to an Appalachian orogen source terrain (e.g., Robinson and Prove, 1995).

Schatzel and Stewart (2012), developed model Nd ages from neodymium isotopic compositions of coals and shales associated with the Lower Kittanning coal bed, to determine the source of the sediments. Depleted mantle model ages range from 1.35 – 4.18 Ga with the majority falling within 1.35 – 2.40 Ga. These results suggest that a significant portion of the Lower Kittanning sediments were derived from a source older than the roughly 0.3 – 0.5 Ga orogenic magmatic rocks of the Appalachian orogeny, and that sediments were derived from the Canadian Shield as well as from the Appalachian orogen.

#### Regional and Local Metamorphism of the Pennsylvania Coal Measures

Although there were at least three, and possibly more, major orogenic pulses responsible for the formation of the Appalachian orogen, only the final one—the Alleghenian Orogeny—appears to have had any real effect on the coal-bearing rocks of the Valley and Ridge Province in Pennsylvania. The Allegheny Orogeny was the most significant mountain-building development in the present geologic structure of the Valley and Ridge Province of central and eastern Pennsylvania (including the Anthracite Fields).

The coal beds were deposited during the Pennsylvanian Period approximately 315 million years ago. At the type section of the Pottsville Group strata located on Sharp Mountain at Pottsville, Pennsylvania, the Mammoth coal seam and associated strata have been uplifted from horizontal to a nearly vertical structural orientation (Hughes and others, 2011).

Intense orogenic activity in the Valley and Ridge Province during the Permian Period resulted in substantial increase in rank of the anthracite coals due to metamorphism as compared to time-equivalent coal beds in the Appalachian Plateau Province of the bituminous region. The Anthracite Fields are largely preserved within the synclinal basins which are essentially surrounded by sandstone/conglomerate ridges that are more resistant to erosion than the coal and associated finer-grained sedimentary rocks (Hughes and others, 2011).

Coalification models require that anthracite probably formed at temperatures between 200 and 250°C (390 and 480°F) at a burial depth of five miles. This great overthrust block of the Alleghenian orogenic pulses may have forced warm, deep-seated crustal rocks rooted south of the Great Valley to over-thrust to the north, become highly folded, heating the underlying rocks to create anomalous local metamorphic conditions in the Anthracite region. All traces of the

rocks that made up this hypothetical over-thrust orogenic body of rocks have since been eroded away (Levine, 1986).

It is noteworthy that the same crustal conditions of metamorphism did not occur in western Pennsylvania, hence, the mineralogy of the underclays in Pennsylvania is different. Therefore, the mineralogical changes observed in the Anthracite Fields are a result of some combination of regional and local metamorphism and local environment(s) of deposition. Mineralogical indicators of regional metamorphism include the occurrence of ammonium illite and pyrophyllite in the anthracite underclays in the Anthracite Fields (Carpenter, 1986).

Reported higher temperatures (250 - 450°C) and mineral assemblages observed in anthracite underclays suggest hydrothermal alteration to account for the presence of a mineral assemblage including pyrophyllite, phlogopite, chlorite, and possibly microcline (Carpenter, 1986; Daniels et al., 1990). The metamorphism of the underclays is consistent with the rank of the coal, although changes in the underclays are more subtle than the metamorphic-induced changes of the coal. The chemistry and structure of the coal change drastically from the bituminous to the anthracite rank, the changes in the underclays are less distinct, but they are detectable and serve as an indicator of the degree of metamorphism (Carpenter, 1986).

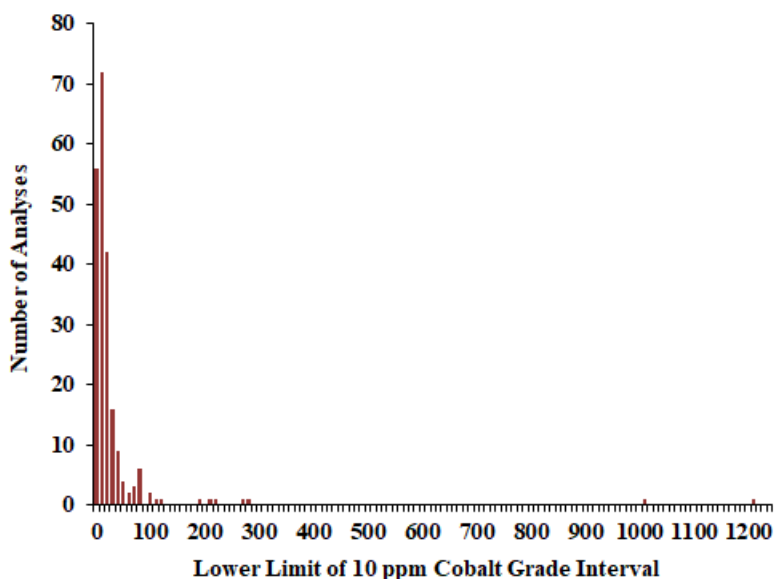
#### Mechanism for Cobalt and Manganese Metallogenesis in the Coal Measures

Against this backdrop of metamorphic terrane is a complex metallogenic history for cobalt and manganese that may have been formed as both primary and secondary deposits. Principal terrestrial deposits include primary magmatic Ni-Cu(-Co-PGE) sulfides, primary and secondary stratiform-hosted Cu-Co sulfides and oxides, and secondary Ni-Co laterites. In recent years there has been heightened interest in the trace element resources hosted within coal-bearing basins. Measurements of coal, surrounding coal measures (i.e., heavy-mineral sandstones and underclay), and coal ash, contain localized high concentrations of noble metals and rare metals (REE, Zr, Hf, Ga, Ge, Sc, Se, Y) (Franus et al., 2015; Qin et al., 2015; Dai et al., 2018; Chelgani and Hower, 2018). Due to the strong association of cobalt with nickel, which is much more prevalent in the Earth's mantle and core, cobalt enrichments are typically not associated with clastic sedimentary basins.

Elevated cobalt contents have, however, been found in the Pennsylvania coal measures. Previous work by the Department of Energy has involved sampling and analysis of rocks associated with coal beds in the Commonwealth. Cobalt grades found in 221 samples from the anthracite and bituminous fields appear in Figure A1-1. Data were obtained from the National Energy Technology Laboratory web site (NETL, 2016). The analyses (221 total) have been grouped into 10 ppm (dry basis) increments from 0 to 1,250 ppm cobalt, presenting the number of analyses in each increment. The data demonstrate that while most of the analyses are less than 100 ppm, some exceed 200 ppm and range up to in excess of 1,200 ppm.

Further understanding of the mechanism by which these accumulations occurred, along with the resultant mineral forms, could assist in predicting their locations in the coal measures.

**Figure A1-1: Distribution of Cobalt Grades Among Analyses for the Pennsylvania Coal Measures**



### Possible Provenance and Development of Nickel-Cobalt Anomalies in Pennsylvania Coal Measures

Today's highly explored laterites account for almost 20% of nickel-cobalt metal production worldwide. As stated previously, laterites are residual sedimentary rocks, or soils, that are the product of weathering of the underlying parent rocks. One theory for the origin of underclay in the Appalachian Basin has suggested that the development of colloidal material was the result of lateritic weathering (Bolger and Weitz, 1952). This interpretation was supported by geochemical analyses of the Lower Kittanning where Th/K and Ti/Al ratios suggest leaching of highly to slightly fluid mobile elements (K and to some extent Al) due to intense weathering (Banks et al., 2016).

Paleomagnetic and paleontological evidence (e.g., Scotese, 1999 and references there in) suggest that the northern Appalachian Basin lied in proximity of the equator during Pennsylvanian time. Lying at these tropical latitudes led to intense weathering, leaching of fluid mobile elements, enrichment of immobile elements (e.g., Ti, Zr, REE), and development of the Pennsylvanian age laterite deposits. Weathering of mafic- to ultramafic-rich rock fragments and minerals hosted within the sediments most likely led to the localized Ni-Co enrichment. Remnant oceanic mafic to ultramafic parent rocks within the core of the Appalachian orogen and Canadian shield are the most probable source of nickel- and cobalt-bearing sedimentary detritus that composes sedimentary rocks of eastern and western Pennsylvania roughly 300 million years ago.

Sediments derived from northwestern and southeastern source areas must have become very deeply weathered to the point where nickel- and cobalt-bearing laterites were formed on the alluvial plains downstream and away from the uplifted areas. Nickel and cobalt liberated from the source rock was transported and deposited in basins within the massive sedimentary wedge of advancing sediments that tapers away from the Appalachian orogeny and across Pennsylvania. Further examination of the Pennsylvania coal measures using the laterite model may yield useful information toward finding the highest cobalt concentrations of these rocks.

#### Summary of Geologic Considerations

Of the types of secondary materials that are the subject of the work reported here, all are byproducts of mining activities in Pennsylvania, where metal mining operations, notably in the Fe-Cu-Co skarn and Cu-Ni volcanic massive sulfide deposit types are hosted. In the case of the Pennsylvania coal measures, anomalous elevated cobalt contents have been found in excess of 1,000 ppm.

***Source rocks for the coal measures included the Appalachian orogen and those in the vicinity of the Canadian Shield. Both have hosted commercially mined metal deposits, and both of which are likely sources of cobalt and manganese minerals in the Pennsylvania coal measures. The relative contribution of each source is location-dependent, with the Appalachian orogeny the source of the rocks in the anthracite fields, and the Canadian Shield contributing more sediment to the western bituminous coal measures.***



## Appendix 2: List of Pennsylvania Metal Mines and Occurrences

Deposit types listed in the Table A2-1 are as follows, along with host rock groups (Rose, 1970), are:

- Cornwall-type magnetite copper deposits (Triassic Host Rock Group), including production of iron ore and byproduct cobalt at the Cornwall and Grace Operations (Rozelle et al., 2020)
- Brown Ore, also called “bog ore”, mined in Centre County
- Nickel and copper sulfides in mafic to ultramafic (Pre-Cambrian and Piedmont Host Rock Group), an example of which is the Gap nickel operations that produced byproduct cobalt (Rozelle et al., 2020)
- Appalachian-type Zn-Pb deposits in Cambro-Ordovician limestone (Paleozoic Host Rock Group)
- Cr with minor Ni, Cu and Fe, associated with ultramafic rocks (Pre-Cambrian and Piedmont Host Rock Group)
- Native Cu and Cu sulfides in Metabasalt (Pre-Cambrian and Piedmont Host Rock Group)
- Sandstone-type Cu-U, U, and Cu deposits (Paleozoic Host Rock Group)
- Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Triassic Host Rock Group)
- Cu in Triassic sediments adjacent to diabase, and related deposits (Triassic Host Rock Group)
- Zn-Pb Sulfides in Helderberg-Tonoloway Limestones (Paleozoic Host Rock Group)
- Cu, Au and other elements in Triassic diabase (Triassic Host Rock Group)

The operations in the table have produced iron, copper, lead, zinc, chromium and nickel, as well as byproducts such as cobalt.

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup>**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Berks	Boyertown	Fe (Cu)	Cornwall-type magnetite copper deposits	High
Berks	Fritz Island mine	Fe, Cu, Pb, Zn, Sb	Cornwall-type magnetite copper deposits	High
Berks	Wheatfield mine	Fe (Cu)	Cornwall-type magnetite copper deposits	High
Berks	Jones & Kinney mines	Fe, Cu, Pb, Zn, W	Cornwall-type magnetite copper deposits	High
Berks	Grace mine	Fe, Cu, Zn, Pb	Cornwall-type magnetite copper deposits	High
Berks	Bylers mine	Fe	Cornwall-type magnetite copper deposits	High
Centre	Scotia	Fe	“Brown Ore” (Hickok, 1939)	High
Chester	Warwick mine	Fe, Cu	Cornwall-type magnetite copper deposits	High
Chester	French Creek mines	Fe, Cu, Zn, Co	Cornwall-type magnetite copper deposits	High
Lancaster	Gap Nickel mine	Ni, Cu, Co, Au, As	Ni and Cu sulfides with mafic and ultramafic rocks	High
Lancaster	Bamford mine	Zn, Pb, Ag, Cu, As, Sb	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	High
Lancaster	Wood mine	Cr, Ni, Cu	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	High
Lancaster	Red pit & vicinity	Cr, Ni	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	High
Lebanon	Cornwall mine	Fe, Cu, Co, Ni	Cornwall-type magnetite copper deposits	High

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Lehigh	Friedensville	Zn, Cd, Cu	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	High
York	Dillsburg	Fe, Cu	Cornwall-type magnetite copper deposits	High
Adams	Eagle Metallic Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Adams	Bingham Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Adams	Reed Hill Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Adams	Russell Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Adams	Snively Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Berks	Fegley Mine	Fe	Cornwall-type magnetite copper deposits	Low
Berks	Gilbert Shaft	Fe	Cornwall-type magnetite copper deposits	Low
Berks	Brower	Fe	Cornwall-type magnetite copper deposits	Low
Berks	Esterly mine	Fe	Cornwall-type magnetite copper deposits	Low
Berks	Raudenbush mine	Fe	Cornwall-type magnetite copper deposits	Low
Berks	Ruth mine	Fe	Cornwall-type magnetite copper deposits	Low

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

County	Mine	Metal(s)	Deposit Type	Production
Blair	Birmingham	Pb, Zn, Ba	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Blair	Culp	Pb, Zn	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Blair	Scalp Level	Pb, Zn	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Bradford	Carpenter mine	Cu, U	Sandstone-type Cu-U, U, and Cu deposits	Low
Bradford	Near New Albany	Cu (U)	Sandstone-type Cu-U, U, and Cu deposits	Low
Bradford	Near New Albany	Cu	Sandstone-type Cu-U, U, and Cu deposits	Low
Bucks	New Galena mine	Pb, Zn, Cu, Ag	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low
Bucks	Solebury mine	Cu	Cu in Triassic sediments adjacent to diabase, and related deposits	Low
Bucks	Buckmanville mine	Cu, Ba	Cu in Triassic sediments adjacent to diabase, and related deposits	Low
Carbon	Mt. Pisgah	U	Sandstone-type Cu-U, U, and Cu deposits	Low
Chester	Hopewell mine	Fe, Zn, Cu	Cornwall-type magnetite copper deposits	Low
Chester	Leighton mine	Fe	Cornwall-type magnetite copper deposits	Low
Chester	Steels mine	Fe	Cornwall-type magnetite copper deposits	Low

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Chester	Southeast of Hopewell	Fe	Cornwall-type magnetite copper deposits	Low
Chester	Morris Copper mine	Cu	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low
Chester	Charlestown mine	Pb	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low
Chester	Montgomery mine	Pb, Zn, Ag	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low
Chester	Wheatley, Phoenix, Brookdale and Chester Co. mines	Pb, Zn, Cu, minor Au, Ni, Sb, As, Cd, Mo, V, Co, W	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low
Chester	Bailey's mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	Webb farm	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	White Barrens area	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	Pine Grove mines	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	Smith-Hilaman's mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	Scott-Engine mines	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Chester	Kirk mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Chester	Hillside mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Columbia	Alamedia and Webb mines	Pb, Zn	Zn-Pb Sulfides in Helderberg-Tonolaway Limestones	Low
Dauphin	Hummelstown	Fe	Cornwall-type magnetite copper deposits	Low
Delaware	Moro Phillips mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Delaware	Hibbard's placer	Cr	Placer Deposit	Low
Delaware	Fairlamb's placer	Cr	Placer Deposit	Low
Delaware	Black Horse mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Franklin	Virgin Mine	Cu	Native Cu and Cu sulfides in Metabasalt (Lake Superior type)	Low
Lancaster	E. Petersburg	Zn	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Lancaster	Herr's mine	Zn	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Lancaster	Pequea mine	Pb, Ag, Zn, Mo, Cu, Cr	Appalachian-type Zn-Pb deposits in Cambro-Ordovician Limestone	Low
Lancaster	Brown's mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Lancaster	Carter mine	Cr, Ni	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Lancaster	Newbold mine	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Lancaster	Cedar Hill quarry-Tyson Reynolds mine	Cr, Cu, Zn, Ni	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Lancaster	Line pit	Cr	Cr with minor Ni, Cu and Fe, associated with ultramafic rocks	Low
Lebanon	Rexmont Reservoir	Fe	Cornwall-type magnetite copper deposits	Low
Lebanon	Doner mine	Fe	Cornwall-type magnetite copper deposits	Low Production
Lebanon	Carper mine	Fe	Cornwall-type magnetite copper deposits	Low Production
Montgomery	Young's mine	Cu, Au	Cu in Triassic sediments adjacent to diabase, and related deposits	Low Production
Montgomery	Penna. Copper Mine	Cu	Cu in Triassic sediments adjacent to diabase, and related deposits	Low Production
Montgomery	Old Perkiomen mine	Cu	Cu in Triassic sediments adjacent to diabase, and related deposits	Low Production
Montgomery	Perkiomen mine	Cu, Pb, Zn, Ag, Mo, Cd, As	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low Production
Montgomery	Ecton mine	Cu, Pb, Zn, Ni, Mo, As	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low Production

**Table A2-1: Metal Mines in Pennsylvania<sup>†</sup> (Continued)**

<b>County</b>	<b>Mine</b>	<b>Metal(s)</b>	<b>Deposit Type</b>	<b>Production</b>
Montgomery	Wetherill mine	Cu, Pb, Zn	Zn-Pb-Cu in quartz veins cutting Triassic and Precambrian rocks (Phoenixville type)	Low Production
Northampton	Leithsville	Cu	Cu in Triassic sediments distant from diabase	Low Production
Northumberland	Doughty mine	Pb, Zn, Cu	Zn-Pb Sulfides in Helderberg-Tonolaway Limestones	Low Production
York	Bender and vicinity	Cu, Zn	Cu, Au and other elements in Triassic diabase	Low Production
York	Grantham	Fe	Cornwall-type magnetite copper deposits	Low Production

<sup>†</sup>Data from Rose (1970), Robinson Jr. and Sears (1992), and Hickok IV (1939).