

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

**Final Report on**

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**Availability and Estimate of Resources of Cobalt in  
Pennsylvania**

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**PREPARED FOR**

LEONARDO TECHNOLOGIES, INC. (LTI) OF BANNOCK, OH  
(UNDER THE US DEPARTMENT OF ENERGY'S (DOE) AGREEMENT NUMBER DE- FE0022594)

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## Executive Summary

Cobalt is a critical mineral as defined by the U.S. Department of the Interior in response to Executive Order 13817 (2017). Cobalt metal is used in superalloys required in the hot gas path of stationary gas turbines and jet engines, as well as in samarium cobalt magnets, the domestic production capability of which was found to be essential to the National Defense under Presidential Determination 2019-20. Cobalt compounds are used in lithium-ion batteries, as are manganese compounds. The Defense Industrial Base Report, in response to Executive Order 13806 (2017), expressed concerns regarding the U.S. supply chains for rechargeable batteries. The U.S. is import-reliant for cobalt.

Cobalt production of Pennsylvania's geologic resources dates back to the 1870's. From 1941 to 1951, and again from 1959 to 1971, the Pennsylvania iron ore operations of Bethlehem Steel constituted the largest production in the U.S. of cobalt concentrates. Today, Pennsylvania is producing acid mine drainage treatment sludges, and the literature suggests that some of these, notably in the Anthracite Region, have significant contents of both cobalt and manganese.

Data presented in this report suggest that there is significant cobalt potential in unconventional resources such as metal mine byproducts and acid mine drainage treatment sludges. A cobalt- and manganese-bearing zone has been found in the coal measures of the Pennsylvania with a cobalt grade roughly equivalent to commercial ores.

Opportunities exist to re-establish cobalt production in Pennsylvania. However, knowledge gaps must be filled in order to de-risk these types of activities before they can attract the required private investment.

A first step toward filling these knowledge gaps will be a set of activities designed to build bases for private investment. These are as follows:

1. Build an inventory of metal mine dumps in Pennsylvania.
2. Develop an estimate of the potential AMD resource (cobalt and manganese), building on existing discharge information, and adding cobalt and manganese assays for water samples (where no treatment system is used) and sludge samples where treatment is in place. Given the current information, this would begin with the Pennsylvania Anthracite Region.
3. Begin process development for production of salable cobalt and manganese commodities from currently produced AMD sludges. This would be followed by process development for selective precipitation of critical mineral commodities, which could be applied to new AMD treatment systems.
4. Restart exploration activities in the Pennsylvania, focused on high cobalt- and manganese content zones in the coal measures, also including coal preparation byproducts.

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## 1. Introduction

In May, 2018, the U.S. Department of the Interior released a list of minerals “Deemed Critical to U.S. National Security and the Economy” (U.S. Department of the Interior, 2018). Included on that list is cobalt, which is used in the production of batteries and the superalloys required for hot gas path components in both stationary gas turbines (for power generation) and jet engines (Defense Logistics Agency, 2020).

In 2005, worldwide cobalt consumption by end use included batteries (23%), superalloys (21%), catalysts (11%), and hard materials (11%), with hardfacing and other alloys, and magnets included among the applications accounting for the balance of global demand (Kapusta, 2006). Since then, cobalt demand has grown significantly, largely driven by its application in batteries and as of 2017, battery applications accounted for over half of global cobalt consumption. Cobalt demand for batteries alone, by 2027, could be double the total cobalt market in 2017 (Anonymous, 2018), with the total 2027 market exceeding 310,000 metric tons per year (MTPY).

In 2019, U.S. net import reliance for cobalt materials was 78%. China was the world’s leading producer of refined cobalt, based mostly on feedstocks imported from the Democratic Republic of Congo (Shedd, 2020). China was also the largest cobalt consumer, its rechargeable battery industry accounting for 80% of the country’s cobalt consumption.

Cobalt applications include use in lithium-ion, nickel-cadmium, and nickel metal hydride batteries Slack et al., 2017). Lithium-ion batteries are of note, as the 2018 Defense Industrial Base Report (U.S. Department of Defense, 2018) noted that:

*“Asian markets dominate the rechargeable battery industry. Domestic rechargeable battery producers cannot compete in production volume and labor availability and cost. Most domestic lithium ion cell packagers rely on foreign commercial lithium ion cell suppliers from countries such as South Korea, China, and Taiwan. Cell availability for military battery packaging is a risk across the board for rechargeable batteries as commercial cell manufacturers, often foreign-owned, are unwilling to divert production from their commercial customers to U.S. military battery manufacturers.”*

In addition to its use in superalloys and batteries, cobalt is also used in magnetic applications involving marine propulsion systems, missile guidance systems, and radar, and the U.S. import-dependence for cobalt (China as the leading source) has been noted elsewhere (Slack et al., 2017).

## 2. Background

Cobalt technology evolution has resulted in its current applications in jet engines, magnets and rechargeable batteries. Products that use cobalt are used in the defense sector, and activities that can support U.S. domestic cobalt production are responsive to several Federal policy drivers.

### 2.1. Overview of Technology Drivers and the Cobalt Market

The use of cobalt as a colorizing additive for glass and other ceramic products dates back over 4,000 years (Bilbrey, 1962, Shedd et al., 2017). The name “cobalt” derives from the 16<sup>th</sup> Century term “*kobold*”,

which referred to malicious gnomes that frequented mines in Saxony, also used to refer to sulfide ores that were difficult to smelt. These materials could, however, be processed with potash and silica to produce a blue glass (Carderelli, 2018).

Cobalt metal was first produced by the Swede Georg Brandt in 1735, but the colorizing agent application remained to dominant market for cobalt prior to World War I. During the two and a half decades that preceding World War I, however, there was a significant amount of research dedicated to the use of nickel in alloys, notably for defense applications (Rozelle et al., 2019). In the U.S., Elwood Haynes had followed work on nickel alloy development with examination of cobalt alloys also containing chromium, molybdenum and tungsten (Haynes, 1913). Turbo-supercharger buckets were first produced from a cobalt-based alloy in 1941 (Bilbrey, 1962), and the subsequent introduction of the jet engine led to a continuous evolution of superalloys designed for the harsh environments found in both jet engines and gas turbines used for stationary power generation. It bears mention that the results of Haynes' research were commercialized through Haynes International, which continues to produce nickel- and cobalt-based alloys.

Magnet applications for cobalt date back to the introduction of the Alnico magnet in the 1930's (Bilbrey, 1962). More recently, the roots of the samarium cobalt permanent magnets date back to the 1960's, and work at the U.S. Air Force Materials Research Laboratory (Lewis and Jimenez-Villacorta, 2013). More recently, while the U.S. has a significant import-dependence for cobalt, Presidential Determination 2019-20, of July 22, 2019, found that "the domestic production of Samarium Cobalt Rare Earth Permanent Magnets is essential to the national defense" (Presidential Determination Pursuant to Section 303 of the Defense Production Act).

Both recent and forecast growth in cobalt demand are driven by the rechargeable battery market. The potential for cobalt use in this application was reported by the Goodenough Laboratory in the United Kingdom in the early 1980's (Mizushima et al., 1981), where transition metal lithium oxides ( $\text{LiMO}_2$ ) were being investigated for battery applications. Included among these was a material with an  $\text{LiCoO}_2$  composition, prepared from lithium carbonate and cobalt carbonate. This material was used in the lithium-ion batteries introduced by Sony Corporation in 1991 (Blomgren, 2017). Significantly, manganese is also currently used in cathodes for Li-ion batteries (Blomgran, 2017), and the potential for manganese recovery with cobalt production, from Pennsylvania resources, will be discussed in a subsequent section of this report.

Application for cobalt products are included in the defense, medical products, transportation systems, and energy supply chains in the U.S. Key end uses include jet engines, magnets (notably found in electric motors) and cathodes found in batteries. Superalloy production requires cobalt metal, while growth in global cobalt demand is expected to be driven by the cobalt chemical (sulfate or oxide) needs of the Li-ion battery industry (Anonymous, 2017). Production of SmCo magnet alloy can require cobalt metal (direct melting of alloy components or electrolysis using a cobalt anode), as well as cobalt compounds where co-reduction of alloying agent compounds is used (Krishnamurthy and Gupta, 2016). As such, the end use application will determine the form of cobalt required of a production operation and, hence, the type of processing equipment required to service a given cobalt application.

## 2.2. U.S. Policy Drivers Related to Cobalt

In 2015, non-fuel minerals used by major industries that added \$2.5 Trillion to the U.S. economy, but there were significant U.S. import-dependencies for numerous mineral commodities, including cobalt (U.S. Geological Survey, 2016).

In 2017, two Executive Orders were issued by the White House. The first, Executive Order 13806, resulted in the Defense Industrial Base Report (U.S. Department of Defense, 2018). That report noted U.S. supply chain concerns involving both magnets and rechargeable batteries. The second of these was Executive Order 13817, which resulted in the list of Critical Minerals released in 2018 by the U.S. Department of Interior (U.S. Department of Interior, 2018). Cobalt is among the commodities on the list. Executive Order 13817 also directed the Secretary of Commerce, in coordination with heads of selected executive branch agencies and offices, to submit a report, ““A Federal Strategy to Ensure Secure and Reliable Supplies of Critical Minerals”, which was released in 2019 (U.S. Department of Commerce, 2019). Among the actions recommended by that report was 1.3:

*“Complete technical and economic feasibility studies of the production of critical minerals and related manufactured materials from secondary and unconventional sources (including coal-based resources, mine tailings, smelter slag, waste streams, end-of-life products, and seawater deposits). (DOE, DOC (NOAA), DOD, DOI [United States Geological Survey (USGS)], and EPA; 1-2 years)”*

It bears mention that the U.S. Department of Energy is identified as the lead agency for this action.

On July 22, 2019, a Presidential Determination (No. 2019-20) was issued by the White House, finding that under section 303 of the Defense Production Act of 1950, “the domestic production capability for Samarium Cobalt Rare Earth Permanent Magnets is essential to the national defense”, and that “Without Presidential action under section 303 of the Act, United States industry cannot reasonably be expected to provide the production capability for Samarium Cobalt Rare Earth Permanent Magnets adequately and in a timely manner.”

In summary, work toward the production of cobalt products from domestically sourced resources is directly responsive to:

- Concerns regarding the battery and magnet supply chains noted in the Defense Industrial Base Report.
- The identified need for technical and economic feasibility studies for the production of a critical mineral (cobalt) and its related manufactured materials from secondary and unconventional sources, as noted in the Department of Commerce 2019 Report.
- The finding in Presidential Determination No. 2019–20 of July 22, 2019, that the domestic production capability for Samarium Cobalt Rare Earth Permanent Magnets is essential to the national defense.



### 3. A Discussion of Commercial Cobalt Minerals

#### 3.1. The Byproduct Nature of Cobalt Production

Nearly all of the global mine production of cobalt is as a byproduct of the production of other metal commodities (Slack, 2017). Primary products where cobalt is a byproduct include copper, such as the case of production in Congo, nickel from sulfide and laterite deposits, and platinum group metal production. The last of these includes the case of relative small production in the U.S., platinum group metal production (Slack, 2017).

Modest amounts of cobalt have also been recovered from the processing of lead and zinc ores in the U.S., as discussed elsewhere (Vhay, 1979).

A set of chemical formulae for the cobalt-bearing minerals to be discussed here appears in Table 1.

**Table 1: Cobalt-Bearing Minerals of Interest**

Mineral	Formula	Reference
Asbolite	$(\text{CoNi})_{0.2}\text{MnO}_2 \cdot 4\text{H}_2\text{O}$	Peek et al., 2009
Carrollite	$\text{CuCo}_2\text{S}_4$	Peek et al., 2009
Cobaltiferous Pyrite	$(\text{FeCo})\text{S}_2$	Peek et al., 2009
Cobaltite	$\text{CoAsS}$	Slack et al., 2017
Linnaeite	$(\text{CoCuNiFe})_3\text{S}_4$	Peek et al., 2009
Pentlandite	$(\text{FeNiCo})_9\text{S}_8$	Peek et al., 2009

#### 3.2. Copper Byproducts

The majority of the global cobalt mine output is produced from sediment-hosted Cu-Co deposits, and those of the Central African Copperbelt (Congo and Zambia) have the most contained cobalt (Shedd et al., 2017). In 2019, Congo (Kinshasa) accounted for over 70% of world mine production of cobalt (Shedd, 2020). The cobalt-bearing minerals of interest are sulfides, including linnaeite and carrollite (Peek et al., 2009).

#### 3.3. Nickel Byproducts

Magmatic Ni-Cu sulfide deposits are significant nickel producers, with the ores also including lesser concentrations of copper. Operations involved with deposits may also produce cobalt and platinum group elements (PGEs) as byproducts. Notable among these deposits, as byproduct cobalt producers, are the Sudbury District in Ontario and the Noril'sk Region in Russia (Slack et al., 2017). Cobalt production from these deposits is also derived from sulfide minerals: pentlandite and cobaltiferous pyrite (Peek et al., 2009).

Laterite deposits are significant producers of nickel, notably from Australia, New Caledonia, and Cuba. Cobalt is present in an oxide mineral, asbolite (Peek et al., 2009).

In 2019, the combined mine production of cobalt from Australia, Canada, Cuba, New Caledonia, and Russia was approximately 14% of the world cobalt total.

Lancaster County, Pa. also is home to a sulfide deposit (Vhay, 1979) that has produced both nickel- and copper ores. In the early 1860's Joseph Wharton acquired the property at Gap, Pa. primarily for nickel production, and co-produced both cobalt and copper compounds (Yates, 1977). Wharton's operation supplied both nickel and cobalt to the U.S. market from 1860 to 1893 (Vhay, 1979).

### **3.4. Platinum Group Metal Byproducts**

Sulfide ore mining operations in some cases produce PGE-enriched concentrates, the PGE concentrations occurring in PGE mineral grains, as well as through PGE substitution in pentlandite. Operations in both South Africa and Russia produce PGEs, also including cobalt, nickel and copper as byproducts (Grundwell et al., 2011). Small amounts of byproduct cobalt have been produced at the Stillwater PGE smelter in Montana (Slack et al., 2017).

In this type of operation, cobalt is enriched in flotation concentrate, and further enriched in the converter matte (Grundwell, 2011), the latter being an operation that selectively removes iron and sulfur (Rozelle et al., 2019).

### **3.5. Iron Ore Byproducts**

Magnetite skarn deposits in Pennsylvania were worked by Bethlehem Steel for iron ore production during the 20<sup>th</sup> Century, at the Cornwall and Grace operations (Robinson, Jr., 1988). In addition to iron ore (beneficiated magnetite), byproduct cobalt was produced from these operations, and the Cornwall mine also produced gold and silver (Lapham and Gray, 1973). The byproduct metals, occurring in sulfide minerals (Robinson, Jr., 1988), were recovered from iron ore beneficiation tailings. Sulfide recovery from these tailings will be discussed in a subsequent Section. Cobalt-bearing sulfide concentrates were roasted and leached for cobalt recovery, also to be discussed subsequently.

These operations produced byproduct cobalt from 1941 to 1971, during 1941-1950 and from 1960 to 1971, Bethlehem Steel at these operations was the largest U.S. domestic producer of mined cobalt, as was Pennsylvania (U.S. Bureau of Mines, 1942-1972).

### **3.6. Stand-Alone Cobalt Production Operations**

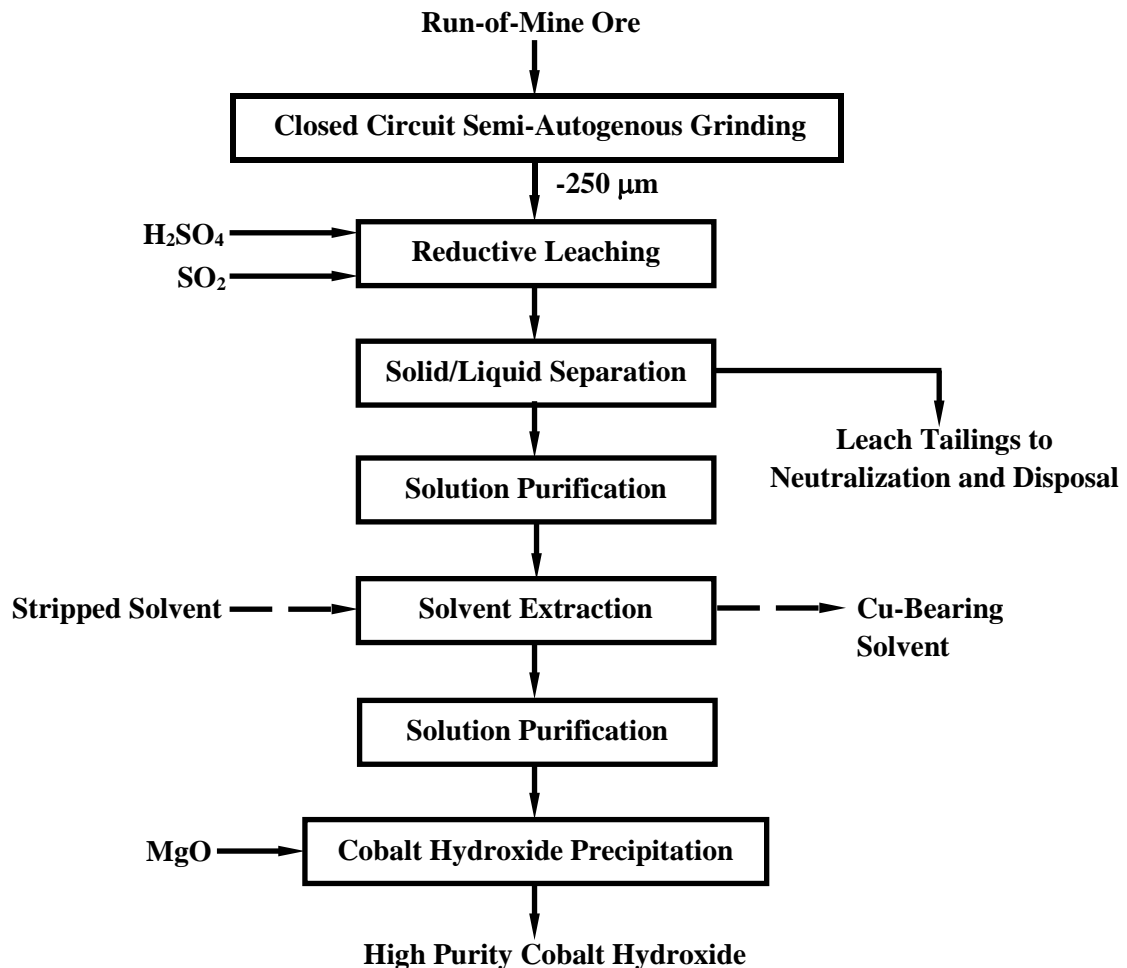
Cobalt has been produced as the primary product from a metasedimentary resource in Idaho (the Blackbird District). The cobalt bearing minerals have been identified as cobaltite and cobaltiferous pyrites (Nash et al., 1988). The Howe Sound Mining Company began exploration of the property in 1942 (Reed and Herdlick, 1947), was contracted by the Federal Government to supply cobalt in 1951 (Bilbrey, Jr., 1962), and the operations were idled when that contract concluded in 1959 (Bilbrey and McDougal, 1960).

It bears mention that, between 1951 and 1959, Bethlehem Steel was displaced by the Howe Sound subsidiary Calera Mining as the largest cobalt producer in the U.S.

#### 4. Overview of Cobalt Process Technology

As discussed in Section 2, the production of cobalt for markets associated with key policy drivers can require the production of either cobalt metal or cobalt compounds. Feedstocks largely derive from sulfide minerals, and either arsenide (cobaltite) or oxide ores associated with laterite nickel deposits, such as asbolite. As most cobalt production is derived from the production of other metals, these minerals have been transformed into byproducts of pyrometallurgical or hydrometallurgical processes, now serving as feedstocks for cobalt production.

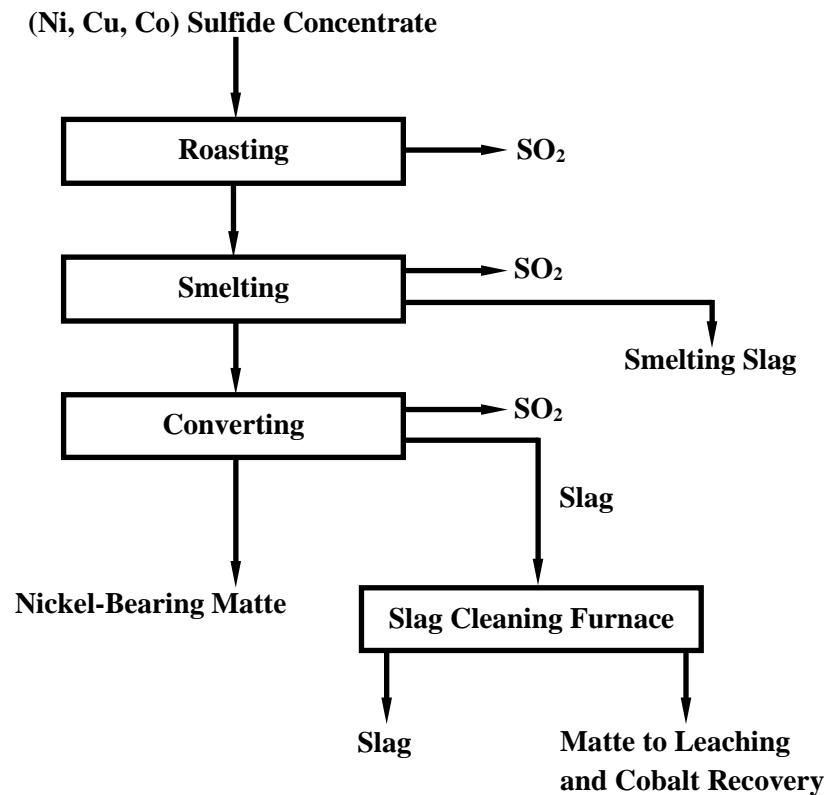
Production of cobalt from African ores currently dominates the global market, and an example flowsheet is shown in Figure 1. The process involves leaching of ground ore in sulfuric acid with sulfur dioxide added to the process. Following purification of the leach solution, solvent extraction removes copper from the solution. Following additional purification of the aqueous phase, magnesium oxide is added to produce a high-purity cobalt hydroxide product (Grundwell et al., 2011).



**Figure 1: Example Flowsheet for the Recovery of Byproduct Cobalt from African Copper Ore, from Grundwell et al., 2011.**

Cobalt recovery from nickel sulfide ores is driven by the process used for nickel production, and this typically involved successive pyrometallurgy steps where a nickel sulfide matte is produced and purified through removal of iron, sulfur, and other gangue elements.

An example flowsheet is shown in Figure 2, where a pentlandite physical concentrate is roasted, smelted, and converted to produce the nickel-bearing matte. The first step removes sulfur and oxidizes iron species. The second removes sulfur and iron, the latter being removed in a silicate slag through the addition of a siliceous flux, and the last step, converting, further reduces the iron and sulfur contents (Boldt, 1967).

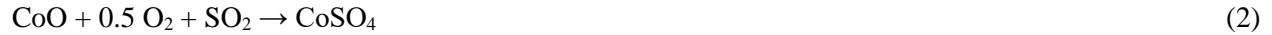


**Figure 2: Nickel Sulfide Smelter Flowsheet with Cobalt Recovery, from Grundwell et al., 2011.**

The converting step separates iron and sulfur from the matte through partitioning to other phases (slag and gas, respectively). Conditions required to achieve this involve those that promote oxidation of iron from the sulfide matte, while maintaining nickel as a sulfide. The free energies of iron, nickel, and cobalt sulfides under converter conditions are shown in Figure 3. Over the range of conditions required to maintain iron oxide and nickel sulfide as the stable species, cobalt may be present as either sulfide or oxide. As such, cobalt may partition between the converter matte and slag phases to a lesser extent compared with nickel or iron (Grundwell et al., 2011). Process options for cobalt recovery from leach solutions, derived from sulfide ore processing, include electrowinning and hydrogen reduction (Grundwell et al., 2011).

Fluid bed sulfation roasting has been applied to cobalt bearing pyrite concentrates, as will be discussed with respect to Pennsylvania's cobalt resources. Sulfation roasting involves the conversion of a metal

sulfide to a soluble metal sulfate, with exothermic sulfide oxidation supplying both process energy and the gaseous sulfur dioxide required for sulfate formation. Reactions involving cobalt are as follows:



Laterite ores may be smelted to produce ferronickel or a nickel matte, the latter involving sulfur addition to the process. Where ferronickel is produced, contained cobalt in the product is not considered to be of economic value to the users (Grundwell et al., 2011). Where a nickel sulfide matte is produced, further hydrometallurgical processing can recover high-purity cobalt (Grundwell, 2011). Processing of limonitic laterite ores typically involves hot sulfuric acid leaching, and cobalt can be recovered from the purified leach solutions through hydrogen reduction or electrowinning (Grundwell et al., 2011).

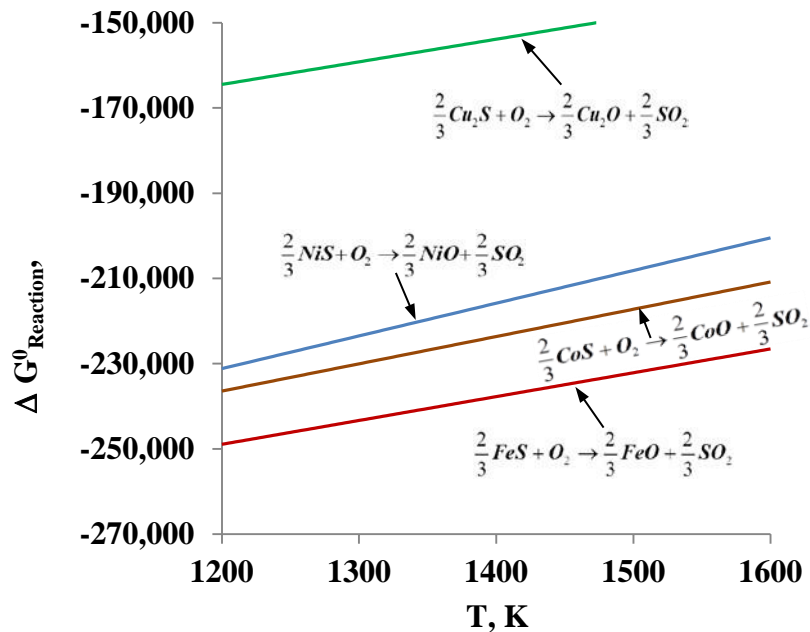


Figure 3: Free Energies of Reaction for the Oxidation of Selected Sulfides, from Rozelle et al., 2019.

Cobalt can also be recovered from byproduct nickel-bearing leach solutions produced at operations where platinum group metals are the primary products (Grundwell et al., 2011).

## 5. Cobalt in Pennsylvania

### 5.1. Nickel Ore Byproducts

Nickel was discovered in potentially economic quantities in the Gap, Pennsylvania in the early 1850's, in an area that had been mined for copper production (Yates, 1977). Intermittent attempts were made to produce nickel from this property, in Lancaster County, prior to the acquisition of its controlling interest by Joseph Wharton in 1863. This acquisition included an associated refining facility built in Camden,

New Jersey (Yates, 1977). Initially selling matte to European refiners, Wharton commenced both process and product research and development activities, and marketing of nickel metal products that included displays at international exhibitions such as those at Vienna (1873), Philadelphia (1876), and Paris (1878). This research and marketing effort contributed to the longer term viability of the Gap operations. The Gap sulfide ore also contains elevated concentrations of cobalt, and cobalt oxides was also produced by Wharton's company until 1899 (Vhay, 1979), while the Gap mining operations closed in 1894 (Matousek and Chadwick, 2005).

The physical concentration system at Gap used a hand sorting and jig process to produce concentrate, and smelting operations used roasting and smelting for the hand-sorted larger size fractions, while the finer jig product was fed directly to the smelting step, which produced a matte for shipment to the refinery in New Jersey. Slag samples at Gap have assayed at 200-300 ppm cobalt (Matousek and Chadwick, 2005).

## **5.2. Iron Ore Byproducts**

As mentioned, the largest source of cobalt production in the U.S. during 1941-1950 and 1960-1971 was the set of Bethlehem Steel iron ore operations in Pennsylvania. This production came from the Cornwall and Grace mines, with a combined cumulative production of 150 million tons from magnetite skarn deposits (Robinson, 1988).

Iron ore production at Cornwall, in Lebanon County, began in 1942 and continued for 230 years (Anonymous, 1972). In addition to iron ore, the operation produced byproduct cobalt, silver and gold. Iron ore was first produced at the Grace mine, in Berks County, in 1958 (Sims, 1968), and production continued until 1977 (Anonymous, 1977).

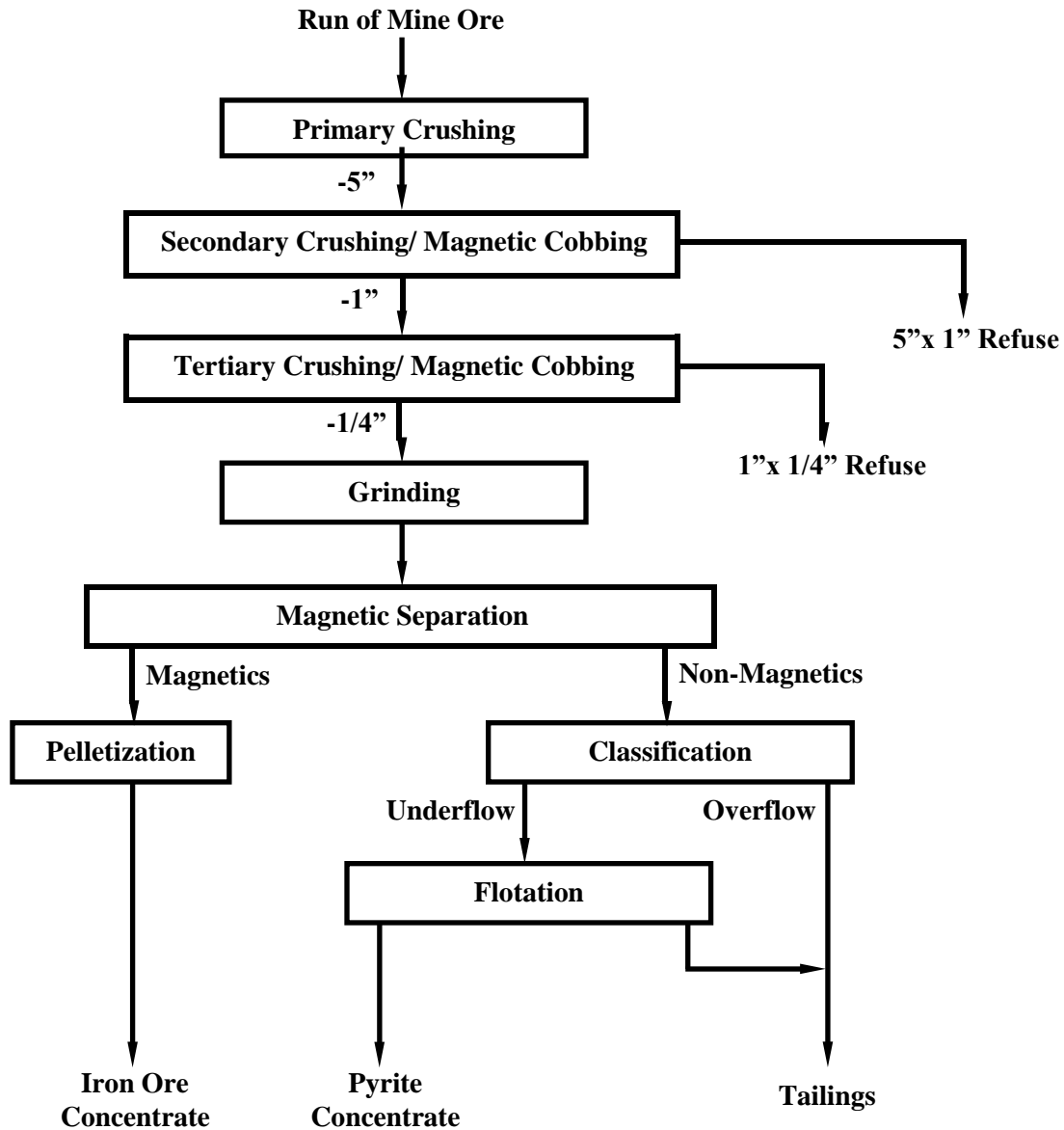
Magnetic separation was used at both the Cornwall and Grace operations for the concentration to produce the beneficiated magnetite product (Moyer and Schumacher, 1966, Cochran, 1969). Magnetic separation tailings included pyrites, which were recovered by flotation as seen in Figure 4.

Pyrite concentrates were processed for cobalt recovery at the Pyrites Company facility in Wilmington, Delaware (Davis, 1942). The process used for cobalt recovery is presented in Figure 5. The pyrite concentrate was first roasted, followed by high temperature chloridizing prior to a water leach. Following solution purification, a cobalt product was precipitated and calcined. The calcined product was either sent to cobalt oxide production or fed to a kiln with charcoal for reduction to cobalt metal (Anonymous, 1951).

By the early 1950's, Bethlehem Steel's mill at Sparrows Point Maryland was its largest, and pickling operations there required significant quantities of sulfuric acid. The company built a sulfuric acid plant at the mill, and sulfuric acid production operations commenced in 1953. The sulfur dioxide feed to the acid plant was generated by a pyrite-fed fluid bed roasting system, shown in Figure 6. The system included three 18 ft diameter fluid bed reactors, cyclones for removal of solids from the offgas which then was routed to the acid plant. Solids feed involved addition of water to the pyrite materials, to make up a slurry that was pumped to the reactors. Where the pyrites were those produced as byproduct at Bethlehem's Pennsylvania ore operations, the reactor temperatures were maintained at a lower temperature (873 K) with some sacrifice in sulfur conversion to sulfur dioxide. Other (non cobalt-bearing) pyrites were also used at the plant for SO<sub>2</sub> production, and a higher reactor temperature (1073 K) was used to maximize sulfur conversion to sulfur dioxide (Scharf and Dominguez, 1956).

The roasted solids resultant from the fluid bed roasting process at Sparrows point contained over 1% cobalt, and could be water leached for cobalt recovery without the need for the chloridizing step seen in Figure 5, (Scharf and Dominguez, 1956). The destination of the roasted solids was the Pyrites Company in Wilmington, for production of cobalt products including metal (Davis and Buck, 1957).

Domestic production of the cobalt-bearing pyrite concentrates ceased at the end of 1971 (Corrick, 1973), although Bethlehem Steel’s iron ore production continued from the magnetite deposits after this date.



**Figure 4: Grace Mine Concentrator Flowsheet, from Cochran (1969)**

Cumulative production of iron ore from the Grace and Cornwall operations has been approximately 150 million tons. Published material balance data for the concentrators at those operations yield a tailings production rate of 35% of the concentrator feed for the Cornwall operation (from Shale, 1953), and 34%

for the Grace Operation (from Cochran, 1968). Given the amount of ore that was produced in each case, tailings production for the operations was in the millions of tons. Both operations were equipped to produce a pyrite fraction (i.e. recover cobalt). However, closure of the pyrite roasting system at Sparrows point occurred prior to the closure of, notably, the Grace operation. The concentrator there was capable of producing 900,000 tons per year of tailings, and recovery of cobalt could provide an economic incentive should any environmental cleanup of the tailings from that operation.

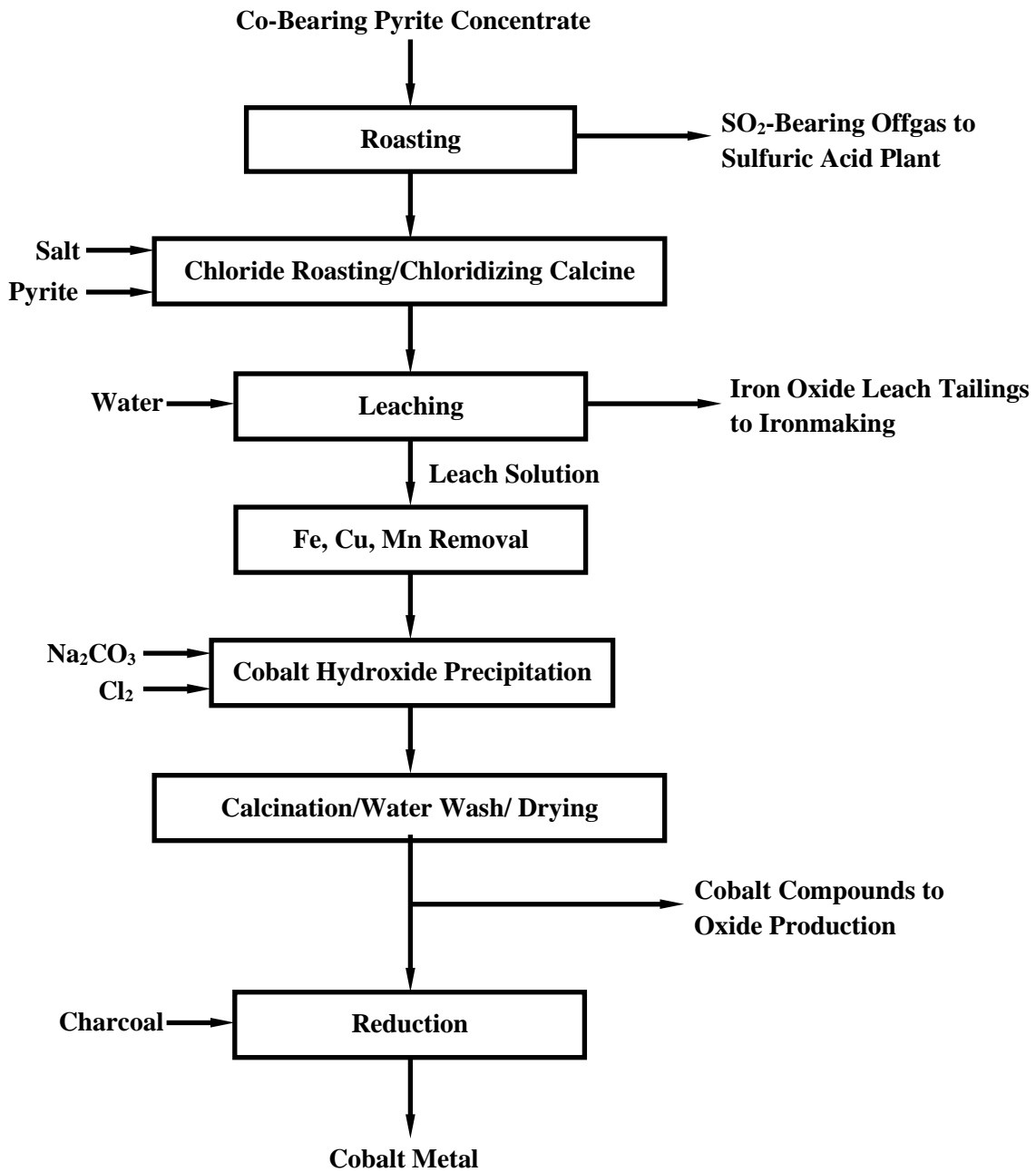
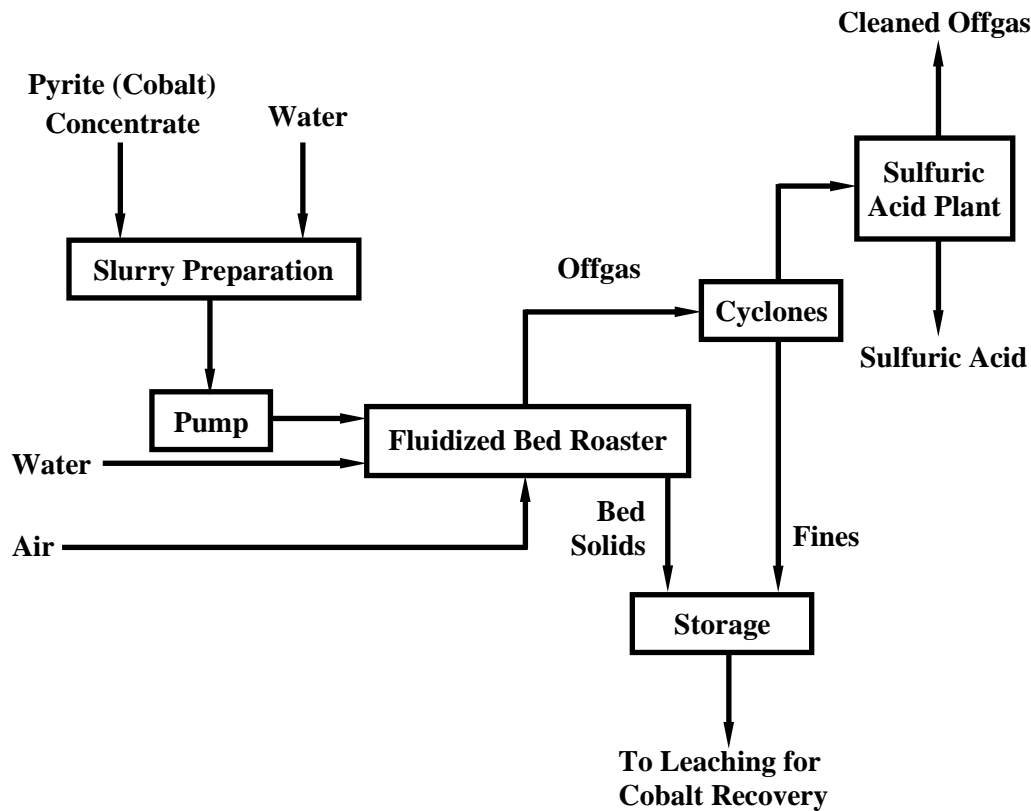


Figure 5: Flowsheet for Cobalt Recovery from Pyrite Concentrate, The Pyrites Company, Wilmington, Delaware, from Anonymous, 1951.



### 5.3. Coal Byproducts- Acid Mine Drainage Sludges

Acid mine drainage (AMD) from abandoned mine properties, in 2004, had degraded over 3,000 miles of streams in the Commonwealth of Pennsylvania. One loss due to this environmental damage was that due to the fact that these streams could not support recreational fishing. The cost of remediation of acid mine drainage and reclamation of abandoned mine lands, in Pennsylvania, was estimated to be between \$5 billion and \$15 billion in 2002 (Cravotta, 2008).

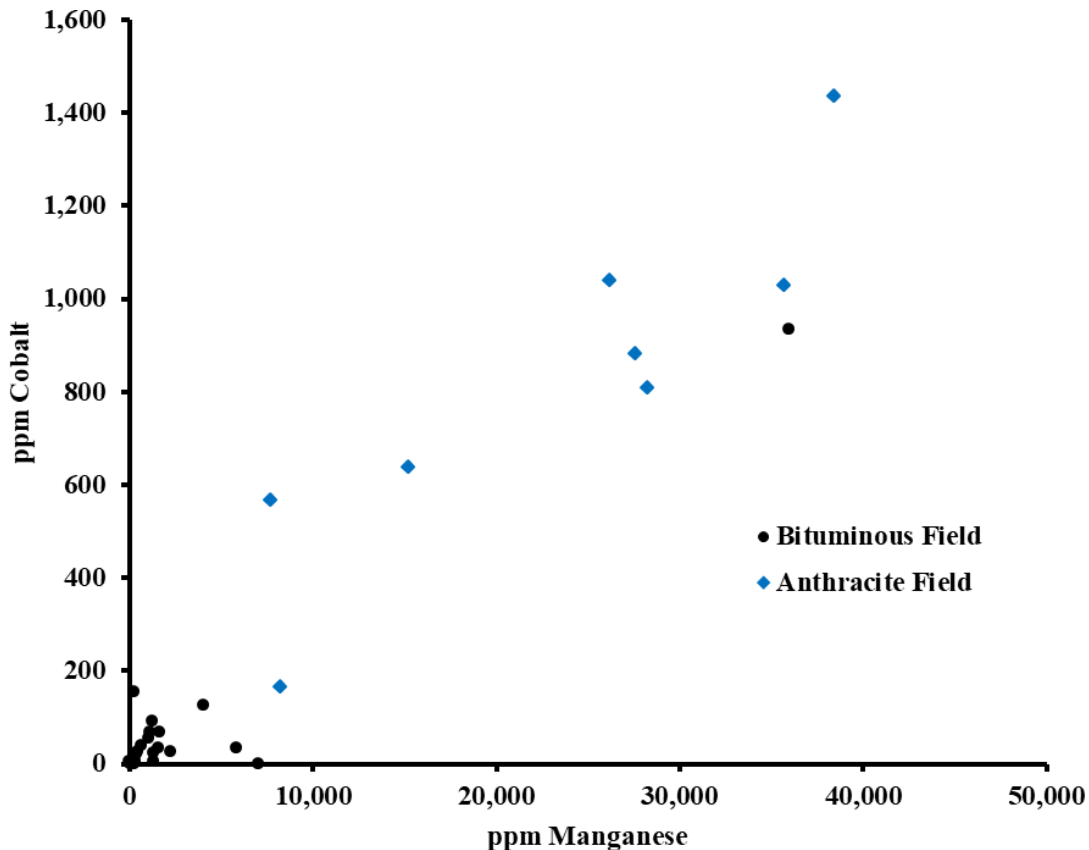


**Figure 6: Fluidized Bed Roasting for Cobalt Recovery at the Bethlehem Steel Sparrows Point Mill, from Scharf and Dominguez, 1956.**

The passage of water through the coal measures can result in the oxidation of sulfides in the rock and the result is the production of sulfuric acid and dissolved iron (Stauffer and Lovell, 1968). The reduced pH of the water in contact with the rock can essentially result in a hydrometallurgical extraction of many species into solution, including those that are considered critical mineral commodities.

Two elements found in AMD that have received significant attention in the literature, dating back over five decades, are cobalt and manganese. These two elements, as seen in Section 2.1, are used in rechargeable batteries. AMD neutralization processes create sludges consisting of elements that have precipitated through the pH change. Where solid manganese oxide phases are present in the precipitate, cobalt has been found to preferentially sorb on them.

Figure 7 presents manganese and cobalt contents for thirty five AMD sludge analyses, from three literature sources. A broad correlation is evident, and notably where manganese contents exceed 1 wt%, cobalt contents exceed 600 ppm. It also bears mention that the majority of the high manganese and cobalt content sludges were produced from AMD in the Pennsylvania anthracite field. However, Penn State has more recently found AMD sludges from the bituminous coal field in Pennsylvania with cobalt grades in the 1,200 to 1,800 ppm range.



**Figure 7: Correlation of Cobalt and Manganese Contents, Northern Appalachian AMD Sludges, Data from Sibrell et al., 2010, Kairies et al, 2005, and Cravotta, 2007.**

As will be discussed subsequently, some of the cobalt contents seen in Figure 7 approach the ore grades of deposits that are commercial cobalt producers worldwide. Additionally, manganese contents for these materials are substantial, and including manganese recovery with cobalt production could substantially improve the economic viability of the overall process.

The sludge analyses found in Figure 7 represent sludges from existing AMD treatment systems. For the treatment of currently untreated discharges, there are opportunities for process design that could further improve the grades of recovered solids. As an example, work from the 1970's examined the removal of manganese separately from iron (Rozelle and Swain, 1974). This could result in a recovered precipitate with a considerably higher critical mineral ore grade.

It also bears mention that, while some sludges have significant ore grades when considered as cobalt and manganese resources, these species can be expected to be largely precipitated from solution. As such, leaching from a mineral concentrate, an expensive extractive metallurgy requirement, is not required. This can significantly improve the economics associated with cobalt and manganese production from these materials. Given the scope and cost challenges associated with the restoration of streams that have been degraded by acid mine drainage in Pennsylvania, the sale of cobalt and manganese concentrates generated from AMD treatment systems could also significantly improve the economics associated with the installation of new treatment facilities. As is the case with reclamation of iron ore tailings, this could provide both domestic critical mineral resources and co-current environmental restoration activities.

#### **5.4. Coal Byproducts- Cobalt in the Coal Measures**

Following erosion, most cobalt is thought to reach areas of sedimentation in solution, where it is deposited mainly with clay materials or iron or manganese oxides. Normal shales exhibit cobalt contents in the 8 ppm range, in black shales cobalt content ranges from 5 to 50 ppm, and in carbonaceous shales the cobalt content is around 14 ppm (Vhay, 1977). Data are available for the cobalt contents of both coal and associated rock, and these contents are typically low. With respect to coal itself, a search of the U.S. Geological Survey database (Pennsylvania anthracite and bituminous fields) yielded no samples with grades of over 500 ppm cobalt.

However, higher cobalt contents can be found in iron-rich sediments, up to 300 ppm (Vhay, 1977). Iron-rich zones are found in the coal measures in Pennsylvania, and have been sources of commercial iron ore production (McGuire, 2012).

While the coal measures in Pennsylvania have been shown to produce AMD sludges with elevated cobalt contents, the rocks themselves have been the subject of little exploration. An exception has been the Office of Fossil Energy/National Energy Technology Laboratory sampling and analysis program that took place from 2014 to 2016. Results of the work included both manganese and cobalt assays. One result from that work was the analysis of a sample from the Pennsylvania anthracite field, the highest assay found in the NETL EDX database. That sample, N-213, analyzed at 1,140 ppm (dry basis) cobalt and 16,238 ppm (dry basis) manganese. This material, as will be presented, compares favorably with the ore grades of commercial cobalt deposits, and, like AMD sludges from the anthracite region, also contains significant amounts of manganese.

Given the elevated cobalt levels found in some AMD treatment sludges, finding elevated cobalt concentrations in the Pennsylvania coal measures is not unexpected. Initial results from the Office of Fossil Energy National Energy Technology Laboratory exploration program can provide an initial basis for further exploration along these lines.

## **6. Summary**

### **6.1. Pennsylvania Opportunities Compared with Commercial Ores**

Pennsylvania has been a significant source of cobalt with respect to U.S. domestic production, leading the nation from 1941 to 1951 and from 1959 to 1971. Cobalt concentrates have been produced from nickel-bearing sulfide ores and as pyrite concentrates that were byproducts of iron ore (magnetite) production.

**Table 2: Example Cobalt Ore Grades for Worldwide Commercial Deposits and Resources in Pennsylvania**

Location	Type <sup>†</sup>	Cobalt Grade, PPM	Reference
Congo	1	600-11,200	Slack et al. (2017)
Russia	2	100-1,000	Slack et al. (2017)
Russia	3	140-2,300	Slack et al. (2017)
Australia	1	500-1,200	Slack et al. (2017)
Australia	2	270-800	Slack et al. (2017)
Australia	3	140-2,000	Slack et al. (2017)
Philippines	2	600-1,160	Slack et al. (2017)
Cuba	2	1,000-1,800	Slack et al. (2017)
Madagascar	2	910-1,040	Slack et al. (2017)
Papua New Guinea	2	600-1,000	Slack et al. (2017)
Canada	3	100-900	Slack et al. (2017)
Pennsylvania Coal Measures	4	1,140	FE-NETL (NETL EDX Database)
Pennsylvania (Iron Ore)	5a	200	Sims (1968)
Pennsylvania (Sulfide Concentrate)	5b	6,800	Sims (1968)
Pennsylvania (AMD Sludge)	6a	1,030-1,485	Sibrell et al. (2010)
Pennsylvania (AMD Precipitate)	6b	2,500	Burgos et al. (2012)

<sup>†</sup>Ore Types:

1. Stratiform sediment-hosted Cu-Co deposit
2. Ni-Co laterite
3. Magmatic Ni-Cu (-Co-PGE) sulfide
4. Underclay
5. Commercially produced magnetite deposit, 5a is ore and 5b is a pyrite concentrate recovered at the Bethlehem Steel Grace Mine.
6. Acid mine drainage sludge, 6a covers precipitates at field AMD treatment sites, 6b was produced in the laboratory from mine water.

The legacy of mine production in Pennsylvania, involving both metal- and coal production, offers opportunities for re-establishment of domestic cobalt production in the Commonwealth. Several of these opportunities can also result in environmental restoration, involving reclamation of metal mine tailings dumps and installation of AMD treatment systems that can eliminate sources of acid pollution, while recovering both cobalt and manganese.

This White Paper has discussed metal mine byproducts, acid mine drainage sludges, and a prospect in the Pennsylvania coal measures as potential cobalt resources in Pennsylvania. Table 2 presents a list of ore grades found in commercial cobalt deposits worldwide, in comparison with cobalt grades found in the Pennsylvania materials discussed here.

With respect to ore grade, the Pennsylvania products presented in Table 2 compare favorably with the commercial deposits. The exception is the (run of mine) iron ore, the pyrite concentrate produced from the ore, however, was in the range of the best commercial ore grades found in the table.

While most of the cobalt production from the commercial deposits is byproduct in nature, the Pennsylvania resources also offer multiple product opportunities. The sludges that contain elevated cobalt contents also have high manganese contents. Both are considered to be critical minerals. Cobalt-bearing pyrite concentrates that were produced at the Bethlehem Steel operations also produced other commodities such as gold and silver. Reclaiming tailings from those operations could also offer multiple product opportunities.

## **6.2. Suggestions for Further Work**

Results that have been presented here suggest significant opportunities to develop U.S. domestic cobalt production from Pennsylvania mineral resources. Some of these also offer co-production of manganese.

These results suggest that private capital could be attracted to the development of commercial production activities. An additional benefit to this would be that, notably in the case of AMD remediation, this private investment would also result in significant restoration of past environmental damage from mining activities. However, knowledge gaps must be filled in order to de-risk these types of activities before they can attract the required investment.

A first step toward filling these knowledge gaps will be a set of activities designed to build bases for private investment. These are as follows:

1. Build an inventory of metal mine dumps in Pennsylvania that operated in sulfide ores and the magnetite skarn deposits that were worked by Bethlehem Steel. While achieving smaller production, other mines operated in those deposits (Robinson and Sears, 1992), and any mine dumps, while smaller, could offer both reclamation and cobalt production opportunities.
2. Develop an estimate of the potential AMD resource (cobalt and manganese), building on existing discharge information, and adding cobalt and manganese assays for water samples (where no treatment system is used) and sludge samples where treatment is in place. Given the current information, this would begin with the Pennsylvania Anthracite Region which covers 480 square miles and is well characterized with respect to acidic discharges.
3. Begin process development for production of salable cobalt and manganese commodities from currently produced AMD sludges. This would be followed by process development for selective

precipitation of critical mineral commodities, which could be applied to new AMD treatment systems, an example of which was discussed in Rozelle and Swain (1974).

4. Restart exploration activities in the Pennsylvania, focused on high cobalt- and manganese content zones in the coal measures, also including coal preparation byproducts.

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