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Critical Minerals and Acid Mine Drainage in Black Hawk Mine Waste, Grant County, New Mexico

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ABSTRACT

There are more than 15,000 abandoned mine features in New Mexico. A considerable number of these mines have not been cataloged or assessed for prioritized reclamation efforts. These mine wastes can be examined as a resource of critical minerals. Many of legacy mine waste deposits have undiscovered commodities and critical minerals, due to low recovery processes during past production. In this project, Black Hawk mine wastes in Grant County, New Mexico are examined by thorough mineralogical and geochemical characterization. This project seeks to characterize and estimate the critical minerals in mine wastes of Black Hawk mine, and determine the acid generating potential of mine waste. Identifying and producing critical minerals in New Mexico may directly benefit the U.S economy and national security.

INTRODUCTION

Critical minerals are nonfuel minerals that are essential to the economical and national well-being of a country whose sources are vulnerable to disruption. Examples of this include the production of renewable energy, electronics, agricultural production, and common household items (McLemore, 2020). Critical mineral resources in New Mexico must be recognized before government authorities withdraw land from mineral entry, or make other decisions regarding land use. Moreover, identification of these minerals may directly enhance the overall economic well-being of the United States. Figure 1 illustrates the critical minerals known to occur in New Mexico. Advancements in mining and processing technologies, as well as improved analytical techniques, have made it more feasible to extract critical minerals from waste materials. The U.S. Department of Defense, Department of the Interior, and Department of Energy established a preliminary list of critical minerals in 2019 and revised that list in 2022 (Fig. 1). Currently, 53 minerals are listed as critical for the United States. Copper is not considered a critical mineral by the USGS because the nation currently produces enough copper for domestic use. Copper is also imported from countries with which there are secure trade agreements, so the current supply of copper for domestic use is not in jeopardy. Recently, the DOE has noted copper as a critical mineral. Uranium was listed as a critical mineral in 2019 because of its use in Navy nuclear reactors. However, because uranium is used as a fuel, it was removed from the list in 2022. The critical minerals list is reviewed by the government agencies every 2 to 3 years (McLemore and Gysi, 2023).

Mine wastes are important potential resources of critical minerals, particularly because in the original mine production, base and precious metals and not the critical minerals were produced. Consequently, mine wastes would

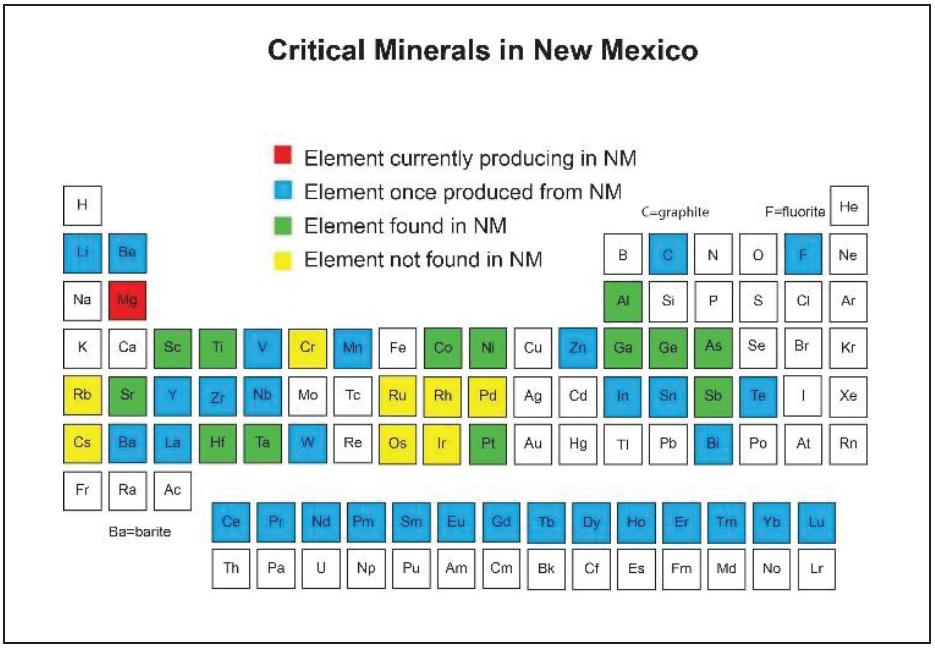

Figure 1. Periodic table showing critical minerals in New Mexico, as revised in 2022 (McLemore and Gysi, 2023)

contain any critical minerals in addition to those minerals that are present in the deposit. Therefore, these mine wastes could be as a potential resource of critical minerals.

Acid drainage, also known as acid rock drainage (ARD) or acid mine drainage (AMD), occurs in mine waste rock, tailings, and structures like pits and underground workings. pH levels in mine waste can influence the mobility, and availability of critical minerals. Some critical minerals could dissolve or leach more readily in acidic or alkaline conditions (EPA, 1993). For instance, certain rare earth elements (REEs) and metals like aluminum and iron are more soluble in acidic environments. Therefore, understanding the pH levels in mine waste is crucial for assessing the potential release, and migration of critical minerals (Plante et al., 2012; Shu et al., 2001). Paste pH is a straightforward static test that determines whether stored acidity is present in mine waste samples (Lapakko 2002, European Commission 2009), which is used in this study. New Mexico has more than 15,000 abandoned mine that need re-evaluation of the critical mineral potential. There is a need to classify these waste dumps to understand their chemical composition, mineralogy, and to evaluate their potential critical minerals value.

Black Hawk mine in Grant County, New Mexico has produced silver from 1881 to 1960. This study aims to characterize and estimate the critical minerals found in the Black Hawk Mine wastes. In addition, this study will determine the potential of acid mine drainage from the Black Hawk mine wastes.

STUDY AREA

The Black Hawk district (also known as Bullard's Peak district), west of Silver City is an example of a 5-element arsenide vein mineral system (Figure 2). Known critical minerals in the district include Co, Ni, As, REE, Bi, W, Te, fluorite and Zn. Mining began in the district in 1881 with the discovery of the unusual silver-nickel-cobalt deposit at the Alhambra mine (Gillerman and Whitebread, 1953).

Subsequent prospecting soon discovered additional deposits. In 1920, pitchblende (uraninite) was recognized in mine dumps in the area, and in 1949 the area became of interest as a possible source of U, Ni, and Co. Types of additional deposits found in the Black Hawk mining district include: Laramide veins, W placer deposits, REE-bearing episyenites and pegmatites. Total metal production from 1881–1960 is estimated at 3,000 lbs Cu, 1,000 oz Au, 1,286,000 oz Ag, and 4,000 lbs Pb (McLemore et al., 1996). In addition, 10,542 short tons of (2.7–71 % WO_3) tungsten ore (Richter and Lawrence, 1983; Dale and McKinney, 1959) and 615 short tons of fluorspar ore have been produced from the district (Williams, 1966; McAnulty, 1978).

Four mineral assemblages are reported at the Black Hawk mine: 1) silver-argentite-uraninite-niccoliterammelsbergite, 2) silver-rammelsbergite-gersdorffitenickel

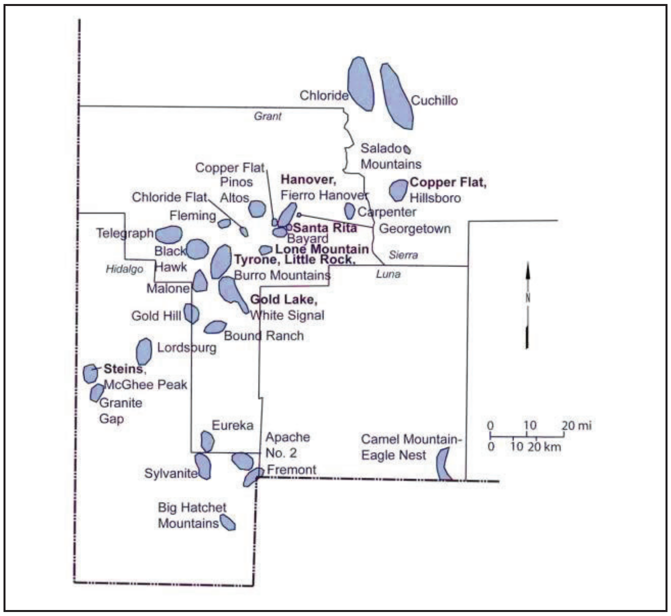

Figure 2. Southwestern New Mexico districts with Laramide mineral deposits, polymetallic veins, and plutons (McLemore, 2008)

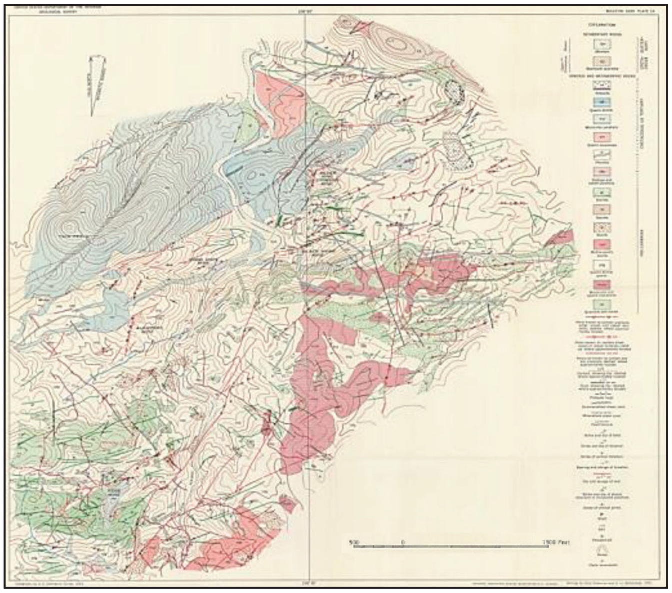

Figure 3. Geologic map of the Black Hawk mining district, Grant County, New Mexico. From (Gillerman & Whitebread, 1953)

skutterudite, 3) chalcopyrite-tennantite-galenasphalerite, and 4) acanthite-jalpaite-pearceite-covellite (Von Bargen, 1979, 1993). Pitchblende is found with minor pyrite, chalcopyrite, galena, manganocalcite, and various nickel and cobalt sulfarsenides and arsenides (Gillerman, 1964; Von Bargen, 1979, 1993).

Precambrian quartz diorite gneiss, which intrudes quartzite, schist, monzonite, and quartz monzonite, is the most widespread rock in the district (Figure 3). The mineral deposits contain silver, nickel, cobalt, and uranium minerals. The minerals, which include native silver, argentite, niccolite, millerite, skutterudite, nickel skutterudite, pitchblende, and sphalerite, are in a carbonate gangue. These rocks are cut by many igneous rocks of pre-Cambrian and younger age, the most common of which is monzonite porphyry of probable Late Cretaceous or early Tertiary age (Gillerman & Whitebread, 1953).

This district contains Ni, Co, Bi, As, and Ag along with some local elements such as U, Zn, Cu, and Pb. Many of these elements are critical minerals. Hillebrand (1889) presented a chemical study of a combination of nickelskutterudite and silver. According to von Bargen (1993), the ore solutions are higher in sulfur and uranium, much lower in bismuth and antimony content, and had a relatively high nickel-to-cobalt ratio in Black Hawk district. In this area, gersdorffite (NiAsS) is frequently found as a thin layer. The earliest nickel arsenide to form is nickeline (NiAs), which is frequently covered with gersdorffite or rammelsbergite. Under polarized light, nickeline is highly anisotropic mineral exhibits a color shift from light pink to darker. $NiAs_{x-3}$, or nickel-skutterudite, is one of the main deposits of nickel arsenide. Early mineralogists found it very challenging to analyze this material chemically due to the combinations of replacement minerals, gangue, and silver. Of all the arsenides, it contains the most cobalt, iron, and sulfur. It also crystallizes into dodecahedral crystals up to 2 cm in size.

MATERIALS AND METHODS

Sampling and Sample Preparation

See McLemore and Owen (2024) for sampling procedures. Figure 4 is shows the Black Hawk mine waste sampling locations (Fig. 4). Some general precautions in sampling include the following. All equipment has been cleaned to prevent cross-contamination of the sample. Sampling tools (buckets, sampling bags, shovels, trowels, and sieves) constructed of materials suitable for environmental sampling (typically stainless steel, plastic, or aluminum). Devices plated with chrome or other materials are not useful as they can introduce contaminants to the samples. All equipment used for sampling had been rinsed with deionized water and air-dried prior to use. Sample collector wore disposable gloves while sieving to avoid contamination.

Geochemical Analyses

Geochemical data are a critical part of geologic mapping and for evaluation for critical mineral resources central to the mission of Earth MRI. Geochemical analyses of

Figure 4. Black Hawk mine waste composite sample locations

samples collected for this study were determined by ALS Laboratories and the USGS laboratory. Samples were submitted to the laboratory when sample preparation occurred. Duplicate samples and standards were analyzed and uncertainty of analyses is generally <5%. Chemical plots were created using ioGAS-64 (ioGAS™ - REFLEX (reflexnow.com). Chemical analyses will be released in future reports.

Petrography and Mineralogy

Mineralogy of selected samples was determined by visual and X-ray diffraction (XRD). XRD analysis was performed on either whole rock or mineral separates performed on a PANalytical X- Pert PRO® diffractometer at the NMBGMR XRD Diffraction Laboratory. Analyses were conducted using 45 kV X-ray beam tension and 40 mA Xray beam current. XRD scans were identified using X'Pert HighScore Plus® software, which identifies intensity peaks and matches patterns to a Powder Diffraction File database. XRD data will be available in the final report.

Paste pH and Fizz Test

A sample is typically considered acid generating if the pH is less than 4 (Borden, 2001). In order to determine the pH of the pore water produced by the dissolution of secondary mineral phases on the surfaces of oxidized rock particles, paste tests are used to assess the geochemical behavior of mine waste materials subject to weathering in the field (Figure 5). Results are recorded in Table 1.

Also, fizz test was performed to find out how much hydrochloric acid (HCl) needs to be added to a 2 g sample in order to digest carbonate (and other neutralizing minerals) and then determine the amount of NP (Figure 6). Results are recorded in Table 1.

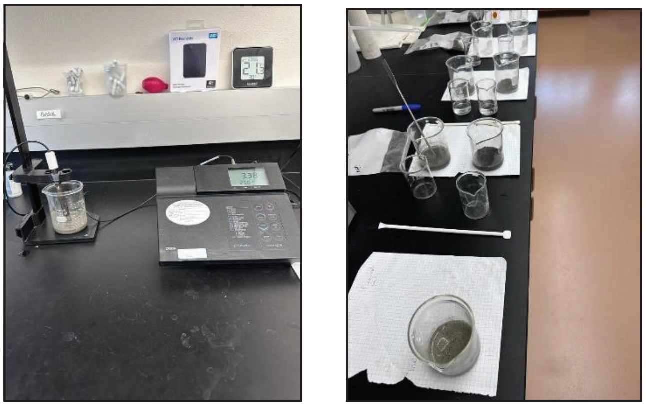

Figure 5. Paste pH test on sieved samples

Figure 6. Fizz test on Black Hawk mine waste sample. The photo is illustrating that after adding HCl, sample started to fizz

RESULTS AND DISCUSSION

Critical Minerals in Mine Waste

Overall, 17 samples were collected and separated as fines and coarse. Figures 7–10 show some of the whole rock geochemical data of samples from Black Hawk mine wastes. Figure 7 shows a positive strong correlation (0.94) between copper and arsenic.

Tellurium (Te) and tantalum (Ta) are critical minerals and Figure 8 shows correlation of 0.75 between Te and Ta. Te is by-product of other deposit types (porphyry copper deposits).

Based on ioGAS correlation matrix and whole rock geochemistry results, Figure 9 shows a positive and strong correlation (0.94) between Cadmium (Cd) and Zinc (Zn).

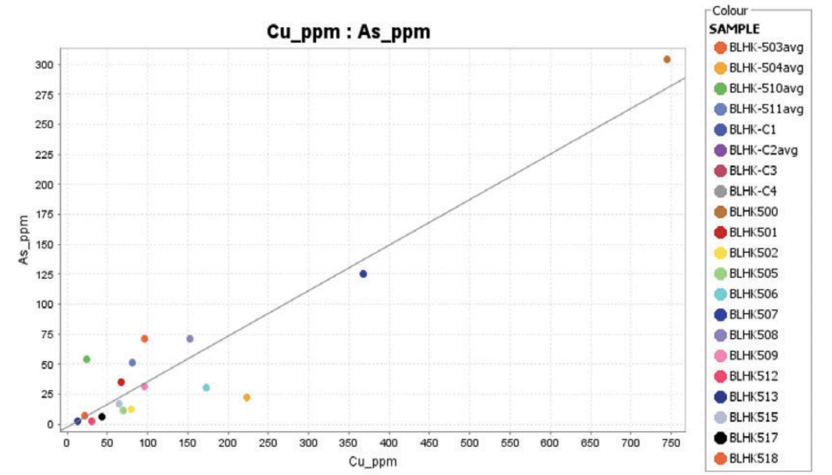

Figure 7. Whole rock geochemical data from Black Hawk mine waste, showing As concentration (ppm) versus Cu concentration (ppm).

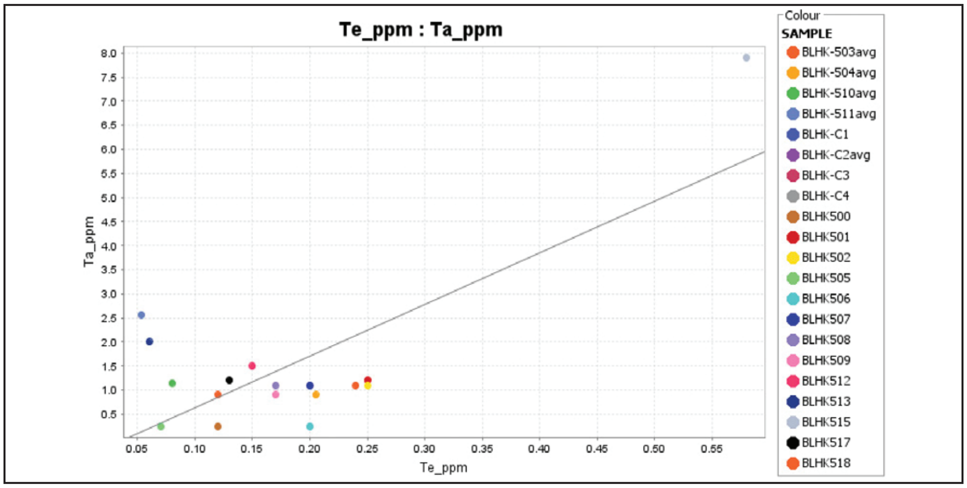

Figure 8. Whole rock geochemical data from Black Hawk mine waste, showing Ta concentration (ppm) versus Te concentration (ppm)

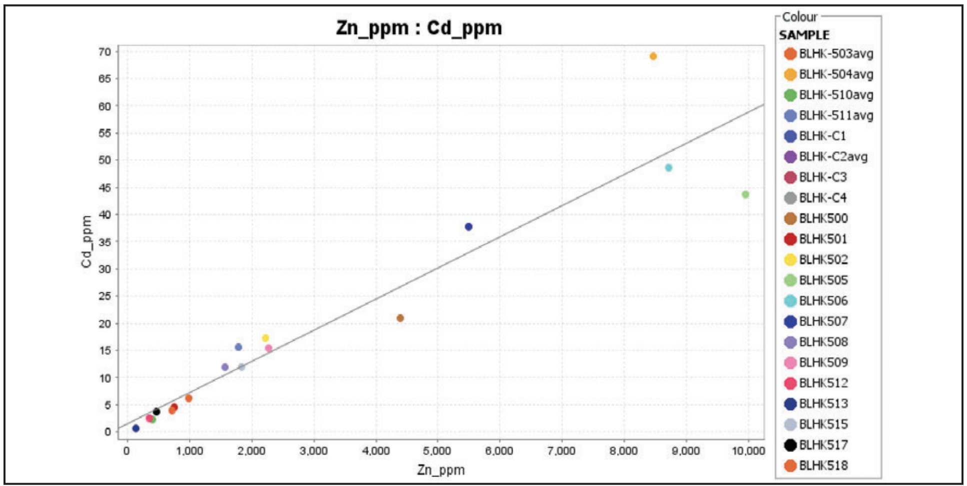

Figure 9. Whole rock geochemical data from Black Hawk mine waste, showing Cd concentration (ppm) versus Zn concentration (ppm)

Paste pH Tests and Net Acid Generation Graph

The Black Hawk mine waste samples exhibit consistent geochemical behavior. The paste pH test showed that paste samples have pH ranges between 5.23 to 8.47 (Table 1).

Static tests are geochemical analyses to predict the potential of a waste sample to produce acid. The generation of acid in sulfidic wastes can be determined by Acid Base Accounting (ABA) and Net Acid Generation (NAG) tests. To enable waste sorting, the NAGpH value is typically plotted against the Neutralization Potential Ratio (NPR) value.

Acid Base Accounting refers to the numerical data used to predict acid generation. The three components of the ABA are: (1) determination of acid production; (2) determination of acid consumption; and (3) calculation of net acid production or consumption using the data from (1) and (2). The Acid Potential (AP) is measured by analyzing the sample for its sulfur content. The Neutralization Potential (NP) is determined by analyzing the acidity consumption of a sample in acid (HCl or H_2SO_4). Net Neutralization Potential (NNP) gives the waste's capacity to neutralize any acid generated and is the difference between the Acid Potential and the Neutralization Potential. The ratio NP/AP, known as the Neutralization Potential Ratio (NPR) (Lottermoser, 2010).

Table 1. Black Hawk mine wastes paste pH recorded and fizz test results.

Sample ID	Wt. of Sample (g)	Fizz Test (Y/N)	pH	Ave. pH
BLHK501	25.011	No	5.76	5.78
	25.007		5.80	
BLHK503	25.011	No	5.23	5.235
	25.004		5.24	
BLHK507	25.012	Yes	7.56	7.85
	25.016		8.14	
BLHK508	25.010	Yes	7.71	7.635
	25.015		7.56	
BLHK510	25.018	No	8.12	8.195
	25.006		8.27	
BLHK512	25.001	No	6.93	6.955
	25.010		6.98	
BLHK517	25.002	No	6.82	6.91
	25.014		7.00	
BLHK542	25.060	Yes	8.27	8.37
	25.070		8.47	
BLHK549	25.040	No	7.21	7.355
	25.020		7.50	

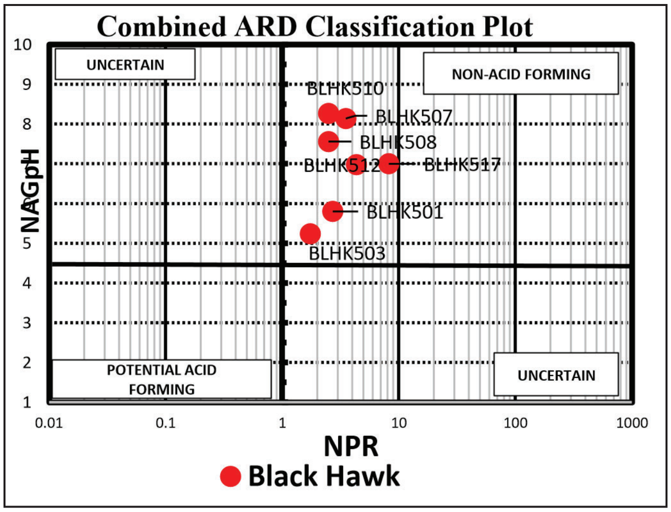

Figure 10. Acid Rock Dranaige (ARD) graph of Black Hawk mine waste samples

$$AP\ (\text{kg }CaCO_3/\text{tonnes}) = \text{wt.\% }S \times 31.25$$
$$NP\ (\text{total }C) = \text{wt.\% }C \times 83.3 \text{ x } C$$
$$NNP = NP - AP,\ NPR = NP/AP$$

Figure 10 shows is combined ARD classification plot and is illustrating that the Black Hawk mine wastes samples fall in the non-acid forming quadrants (Fig. 10).

PRELIMINARY CONCLUSION

The main objective of this study was to evaluate the critical minerals in Black Hawk mine wastes. The presence of these critical minerals in the waste material could be of economic interest. The recognition of critical minerals is seen as crucial for enhancing the overall economic wellbeing of the United States. Determination of acid generating potential in the area suggests that Black Hawk mine wastes are in non-acid forming quarter.

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