

# 1.0 Introduction

This document contains the work plan for the Emerald Isle Mine Preliminary Assessment and Site Investigation (PA/SI). The work plan outlines all work to be completed for the project according to the project scope.

## 2.0 Project Scope

The scope for the project is outlined below:

### 1.0 - Work Plan

- 1.1 - Appendix A: Sampling Analysis Plan

- 1.2 - Appendix B: Health and Safety Plan

### 2.0 - Field Investigation

### 3.0 - Analysis

- 3.1 - Dry and Sieve Samples

- 3.2 - X-Ray Fluorescence Analysis

- 3.3 - Acid Digestion of Soil and Sample Prep

- 3.4 - ICP-MS or FAAS Analysis

- 3.5 - Correlation of ICP/FAA or XRF/FAA

### 4.0 - Risk Assessment

- 4.1 - Human Health Risk Assessment

- 4.2 - Ecological Risk Assessment

### 5.0 - Project Impacts

### 6.0 - Project Management

Following this scope ensures that the critical path of work is achieved by dates set in the schedule.

## 3.0 Site Background

Emerald Isle Mine is a former copper mine located in the Northwest region of Arizona at 35°21'43.98" N 114°11'32.84" W in Mohave County. The mine is about 20 miles northwest of Kingman and four miles south of Chloride, at an elevation of about 3680 feet. This information is shown in Figure 3.1 and 3.2:

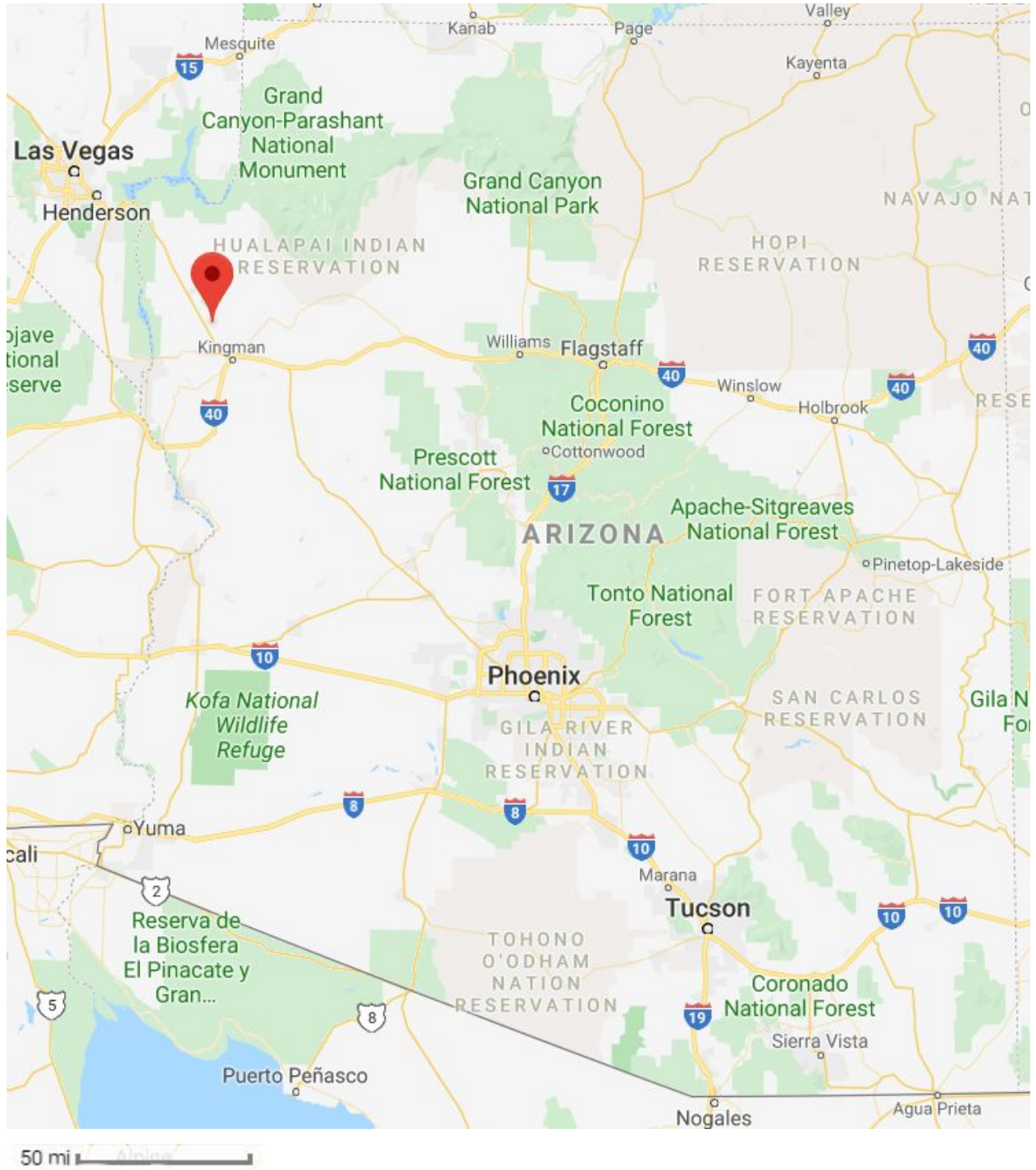


Figure 3.1: Vicinity Map for Emerald Isle Mine



*Figure 3.2: Emerald Isle Mine Location*

As seen in the figures, the mine is located just east of Arizona Highway 93. The mine is abandoned as of the early 2000's, when the last test drilling occurred. The mine is approximately 440 acres and includes a small open pit mine, a Solvent Extraction/Electrowinning (SX/EW) plant shown in Figure 3.4, a leach pad for heap leaching, a pad with tailings from a previous operation, three small low-grade stockpiles, and some various mine infrastructure (buildings, office trailer, equipment). The locations of these items are shown in figure 3.3. Mining operations began in 1917 and continued at various times until 1943. From 1944 to 1948, about 55,000 tons of copper were reported to have been recovered. The El Paso Natural Gas Company and Arimetco, Inc. were the primary operators from mid-20th century until the mid 1970s. All of the blasting and leaching from the open pit was carried out in the 1970's by El Paso. TSC Enterprises Inc. purchased the property from El Paso in 1980, but the property remained inactive until 1987, when Arimetco Inc. purchased the property and resumed copper production. In 2004, Suite Genevieve Resources Ltd. drilled and extracted core samples for total copper in addition to soluble copper and zinc; since that time, the mine has remained unoperated [1].



Figure 3.3: Emerald Isle Site Features



Figure 3.4: Abandoned Electrowinning Equipment (photo credit - Sydney Adamonis)

The mine was left in decrepit condition with barrels of aromatic oxime and a few buildings on the site. There is a building which can be assumed to be the SX/EW building along with two large tanks that must have been used to hold chemicals during production, this can be seen in Figure 3.5 [2]. The building still contains the electrowinning tubs used to plate pure copper. The open pit has clearly not been operated in years considering the amount of brush and dirt, from storm events that has washed into it. The leaching lixiviant pits are in similar condition except for a few newer looking pumps and piping, which can be seen in Figure 3.6. The lining underneath the lixiviant pits is fraying at the surface and it can be assumed that it is also weathering underneath the remaining chemical. The majority of structures on the site are rusted through, including fuel tanks, drill frames and housings, and large amounts of scrap metal. The heap leach pile still has pipes running into it and along its sides, but it is unclear when these were last operated. The leach pile rises about 20 feet above the lixiviant pond and contains nearly all of the tailings from the last operation. Other tailings on the site are in large piles that are fairly distinguishable from native soil. A small arroyo runs through the middle of the site and contains a bed made of fine sediment deposits from storm events.



*Figure 3.5: Basin and Old Emerald Isle Mining Equipment (photo credit - Sydney Adamonis)*



*Figure 3.6: Pregnant Leachate Pond (photo credit - Sydney Adamonis)*

Overall, the site's dry climate and low annual rainfall make the condition of the site fairly stable. Since the last activity at the mine was in 2004, little has changed since mining operations halted.

### 3.1 BLM Investigation

The Bureau of Land Management Abandoned Mine Lands Program (ALM) has expressed interest in investigating the Emerald Isle Mine for possible risk to nearby communities, recreational users of the site, and the environment surrounding the site. SPNG will be performing a preliminary assessment and site investigation to determine the human and environmental risk which will aid in determining further steps for the site. The work being done is an essential step in the CERCLA process for finding superfund sites.

## 4.0 Investigative Approach

This section contains the approach that SPNG will be using to complete the site investigation. The site investigation and all sampling is critical to performing an accurate risk assessment. The Sampling Analysis Plan (SAP) located in Appendix A describes in detail the sampling and analysis process, with all methods and procedures.

# Appendix A

## 1.0 Sampling Analysis Plan

This document includes a detailed sampling plan with mapped surface and soil sampling schema to execute in the field. The SAP will also include all aspects of sample processing and lab analysis.

### 1.1 Sampling Preparation

With the Emerald Isle being \_\_ acres, discrete sampling

#### 1.1.1 Quality Assurance/Quality Control

For analysis quality assurance, there will be nine replicates of each soil sample in XRF analysis. Additionally, a small suite of samples will undergo secondary analysis by either flame atomic absorption spectrophotometry (FAAS) or inductively coupled mass spectrometry (ICP-MS) in replicates of three. Results of these methods for select elements will be compared against the initial XRF results to deem their accuracy. The analytical methods mentioned above are a higher resolution of true concentrations. I have worked extensively with both of these instruments and am familiar with the theory. I have referenced EPA methods for soil digestion required in both the FAAS and ICP-MS analysis as well as methods for the instrumental analysis on both instruments. I am experienced in using them, but they will act as my reference at any point of confusion [10] [11] [12].

Quality control will be done with extensive math checks in the result processing and final reporting of elements in mg/kg or ppm. This is the standard presentation of elemental concentrations in soil and sediments. All team members will be involved in the result processing to ensure quality control of presented results.

### 1.2 Sampling Procedures

#### 1.2.1 Standard Soil Sampling

Soil sampling techniques are fairly uniform for all contaminant analysis. This topic was thoroughly discussed in courses CENE 282 and CENE 332. There are many options for field

sampling of soil and it is dependent on factors like: planned analysis, materials available, funds, site accessibility and intended application of results.

Bias is a very important consideration to account for both before and while sampling. This source of systematic error creates systems like grid sampling, random spot sampling and other methods that remove bias from sampling [3]. In many soil remediation projects where analysis of soil is needed, grids will be made using uniform scaling and each portion will have a single sample taken. If the number of samples able to be analyzed is lower, a grid with number assignments for each quadrangle can be used with a random number generator to collect unbiased samples. If bias is allowed and well documented, it can be beneficial to collect hotspot samples based off of decisions based in the field. This process of hotspot choosing is helpful to obtain a theoretical upper bound of expected concentrations. Similarly, background samples must be chosen close to the area where no expected contamination is present. The more numbers and alternative background sites, the better for QA/QC methods. Another significant consideration is whether or not depth sampling is required. This means anything under the top 3” of topsoil.

### 1.2.2 Composite Sampling Techniques

Composite sampling of soil is a technique used to increase the area represented in results without increasing the number of samples. This in turn, saves on cost and analysis time. In this method, many samples from deemed homogeneous units are combined and mixed to create one single sample [7]. Bias is important to incorporate in composite sampling to avoid from taking for instance, 3 samples in the grid from background areas and two from a heap leach pile. Lastly, an ultimate benefit of this sampling method in mine analysis is that analytes of interest will not react with one another when mixed [7].

### 1.2.3 Decision Unit formation

If composite sampling is to be used and the site is of substantial area, decision units (DU) can be used to segment the site into areas of alternative focus. This is beneficial when a site may be well over 100 acres or so and have sites of expected concentrations. For example, a heap leach pad area could be a decision unit while another would be all areas that contained the metallic acid solution and maybe a third for general processing areas on-site. Site research and history should be heavily scrutinized before even considering DU categorization. Even a preliminary site visit can be conducted to familiarize and help generate ideas for DU boundaries. This method is published by the US EPA in their guide for “Strategic Sampling Approaches” [8].



## 1.3 XRF Analysis

X-ray fluorescence will be used in the analysis in this project. This method uses x-ray radiation to excite atoms and they release photons. The photon absorption and emission wavelengths are the detected identifier of the elements. This is similar to spectrophotometry in the fact that elements are characterized by the wavelength in nanometers of their emitted photon wave pattern [9]. XRF analysis is very simple because it does not require media alteration or really any sample prep. All samples will undergo XRF elemental analysis as it is the primary method of measurement following US-EPA method 6200. A benefit of this method is the possibility of in-situ testing any area the team deems testable to aid in DU formation and sampling scheme.

## 1.4 ICP-MS/FAA Subset Verification

### 1.4.1 Acid Digestion

Two methods provided by the EPA can be used for soil digestion. They are for partial or full digests. Partial digests account for only surface leaching of sediment while a full digest breaks up the silicate matrices and puts all soil material into solution. A decision will be made on which digestion method will be used once samples are returned to NAU and analyzed for overall soil class and organic content.

In the partial digest method US EPA 3051, 10mL of concentrated Nitric Acid (60-70%) is added to a digestion vessel containing between 0.1-0.5g of soil and heated in a microwave digester. The digested solution must then be filtered and diluted to the desired concentration for analysis. In FAA and ICP-MS analysis, 2% nitric acid solution is used as the dilution matrix. Additionally in the 2% nitric for ICP-MS will be a uniform concentration of an internal standard [1].

In the full digestion, method 3052 by the EPA, 9mL of concentrated nitric acid (68-70%) is added to a digestion vessel containing between 0.1-0.5g of soil and heated in a microwave digester. Once cooled, vessels are re-opened and added 3mL of concentrated Hydrofluoric acid (HF) and undergo another microwave digestion period. The HF acid must then be neutralized with Boric acid at a ratio of 0.45g/mL of HF added and placed in the digester one more time. Samples can then be filtered and diluted for analysis.

In both digestion techniques, at least one reagent blank (no soil) should be made and carried through all steps of analysis to determine method and instrumental detection limits. This can be done by taking the average signal of blanks and adding three times the standard deviation.

### 1.4.2 FAA Analysis

For the elemental analysis of Emerald Isle mine samples, Flame atomic absorption spectroscopy (FAAS) will be used for higher concentrated contaminants determined in prior XRF analysis. FAAS works on the principle of light absorption by pure elements. This instrument is often

restricted to analyzing single elements at a time and is constricted to a small range of entry concentrations. Hollow cathode lamps commonly composed of the analyte of interest are stimulated by electrical current and emit light through a narrow emission port. This light travels through a flame that is simultaneously burning a carrier gas, oxidant and nebulized samples of diluted soil digest. Light is then passed through a wavelength selector set to the value of the analyte programmed into the existing instrument software. The detection is based on absorbance which is calculated by Beer's law (equation below) and essentially the difference in light emitted by the initial lamp and that transmitted through the sample rich flame.

<https://www.edinst.com/blog/the-beer-lambert-law/>

$$A = \epsilon cl$$

<i>A</i>	Absorbance	
$\epsilon$	Molar absorption coefficient	M <sup>-1</sup> cm <sup>-1</sup>
<i>c</i>	Molar concentration	M
<i>l</i>	optical path length	cm

The instrument to be used for sample analysis is

1.4.3 ICP-MS Analysis

1.4.4 Contaminants of Concern Determination

## Appendix B: Health and Safety Plan (HASP)

### 1.0 Health and Safety Plan (HASP)

The Health and Safety Plan will address considerations for the health and safety of team members through the duration of the project. This includes training certifications, hazards associated with the project, and on site safety measures.

## 2.0 Health and Safety Training

Various training certifications were completed in order to begin work on this project. Those trainings are detailed below.

### 2.1 EH&S Field Safety Training

The EH&S Field Safety Training is required through Northern Arizona University to complete work in the field. The training covers general safety procedures for all field work outside of NAU's campus. This training ensures that team members will act and perform duties safely while in the field on sampling trips.

### 2.2 BioRAFT Chemical Hygiene Training

The BioRAFT chemical hygiene training is required through Northern Arizona University to complete any and all lab work. The training covers general lab safety procedures, personal protective equipment, chemical handling, and waste disposal procedures. This training ensures that team members will complete lab work in a safe manner and avoid possible incidents with dangerous chemicals used in the analysis phase.

## 3.0 Hazard Assessment

This section details the possible hazards associated with all work completed on this project.

### 3.1 Physical Hazards

The physical hazards associated with this project begin with the sampling trip on January 24th-26th. With any field work, physical hazard is expected to be present in the travel to and from the site. For this reason, all drivers will be certified through NAU's Van Safety training program through Fleet Services. This will ensure safety when traveling to and from the site. Upon reaching the site, physical hazards include falling hazards, tripping hazards, sharp objects, rough terrain, and dust exposure. For these reasons, team members should demonstrate caution when navigating the site. A buddy system will be created to keep track of team members when working on different areas of the site. Personal protective equipment (PPE) will also be worn to ensure protection from common physical hazards. PPE will be discussed further in section 4.1. The weather will be moderate, expected to be around 55 degrees. Weather is not expected to be a concern, but jackets should be brought in case of rain.

## 3.2 Chemical Hazards

Chemical hazards begin on the sampling trip when collecting samples. The preliminary site visit did not indicate any prominent chemical hazards on site; regardless, caution is advised when taking samples to ensure that dust inhalation is minimized. There are also areas on site with solvent extraction acids still present. These areas present both a physical and chemical hazard and should be treated with caution. If skin or eyes come into contact with the acid, the area should be flushed with water. If any acid is ingested, medical attention should be called right away.

Upon returning to the lab, chemical hazards will increase substantially due to the procedures for analysis. SDS sheets will be used for each chemical in the lab to determine the hazard associated with it. The acid digestion step of analysis has the most chemical hazard associated with it. Nitric acid and hydrofluoric acid will be used to digest samples, making it imperative to maintain safe lab practices. Lab PPE will also be worn at all times in the lab to ensure the safety of team members.

## 4.0 Safety Measures

This section will detail the safety measures that will be taken on site during the sampling trip and in the lab during analysis..

### 4.1 Personal Protective Equipment

On site, personal protective equipment includes boots, pants, gloves, and dust masks to keep sensitive areas from being exposed to any possible contaminants. This also serves to prevent contamination of the samples.

Once in the lab, gloves, lab coats, goggles, and closed toed shoes will be worn at all times. This will maintain safety in the lab and reduce risk of contact with dangerous chemicals. In addition, fume hoods will be used to complete acid digestion of samples.

### 4.2 Decontamination

Decontamination will be completed between taking each sample on site and also after leaving the site. Each sample has a unique elemental composition which must be conserved when moving to a new sample location. This is done by decontaminating the sampling equipment between samples and using a new pair of disposable gloves at each sample location. Decontamination of sampling equipment is done by thoroughly washing off the trowel or auger.

After sampling is completed, personal equipment like boots and clothing items should be washed thoroughly to ensure that any contaminated soil is not carried back to campus or the hotel. This will reduce exposure to any possible contaminants of concern at the site. Because of the low level of expected contamination at the site, this step will mainly be an extra factor of safety.

### 4.3 Emergency Response Procedures

During the sampling trip, all injuries will be reported to the supervisor. Should the injury be of serious concern, emergency services will be contacted and the team member will be transported there by ambulance or by a team member. The travel time from Kingman Regional Medical Center is about 23 minutes. In case of emergencies, Kingman Regional Medical Center can be reached at:

3269 Stockton Hill Rd., Kingman, AZ  
(928) 757-2101 or by dialing 911

In lab work, all accidents and injuries will be reported to lab supervisors. Should there be a significant spill or accident in the lab, dial the NAU emergency contact numbers listed below:

Chemical Spill or Accident

Environmental Health & Safety: Jim Biddle, 928-220-1728

Michael Kelly: 928-308-6507

Garett Hall: 928-607-3059

After hours: call NAUPD 3-3000

All emergency procedures are also outlined in the NAU Field Safety Checklist.

### 5.0 Waste Disposal Procedures

During the sampling trip, waste will be accrued from sampling as well as from group members. The waste from the site is able to be disposed of in the landfill, so all waste will be disposed of in garbage bags on site.

In the lab, any acids used during the acid digest portion of the lab shall be disposed of in waste containers with appropriate labels. Any waste from the drying and sieving portion of the lab shall be disposed of in buckets set aside by the CENE soils lab management.

## References

- [9] *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*, Method 6200, February 2007.
- [10] US EPA, *Flame Atomic Absorption Spectrophotometry*, Method 7000B, February 2007.
- [11] US EPA, *Inductively Coupled Plasma- Mass Spectrometry*, Method 6020A, January 1998.
- [1] US EPA, *Microwave Assisted Digestion of Sediments, Sludges, Soils and Oils*, Method 3051, February 2007.
- [2] US EPA, *Microwave Assisted Digestion of Siliceous and Organically Based Matrices*, Method 3051, December 1996.