Treatment of copper mine tailings using a slurry approach: a case study
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Abstract

A small copper concentrator produced approximately 100,000 cubic yards of tailings. A nearby residential area expressed serious reservations about these tailings and as a result, the mining company plans to move the tailings using a slurry approach to a place where a copper smelter is located. These copper tailings have trace concentrations of Fe, As, Mn, Hg, Zn, Se, and Cd. The iron oxides and sulfides cause acid generation and contaminate the surface and ground water. The objective of this study is to design and demonstrate the recovery and transport of mine tailings in a slurry; recover as much of the valuable metals as feasible; treat the tailings to a pH of 7.0 or higher; and design a system to recover the water from the slurry for reuse in the transport and treatment system. Various treatment techniques available for mine tailing remediation were analyzed and hydro-metallurgical approach combined with the use of ferrate was chosen. All aspects of the recovery system were designed to meet the Federal and the State of New Mexico’s codes. Process economic studies were carried out to determine the final project cost. An Environment Safety & Health (ES&H) plan was developed to protect mine workers and to monitor the impact of the remediation process on the surrounding environment. In addition, a community action plan was also developed to provide information about the remediation project to the local community.

1 Introduction

A mining company had a small copper concentrator on its property that has been removed. This concentrator produced approximately 100,000 cubic
yards of tailings. It is required to move these tailings to a new impoundment using a slurry approach which has to be completed in 24 months. A nearby residential area expressed concern over the possible future impact to their water supply due to the presence of the old tailings. The objectives are to recover and transport the mine tailings in a slurry to a new impoundment, recover as much of the valuable metals as feasible, treat the tailings to a pH of 7.0 - 9.0 and design a system to recover the water from the slurry for reuse in the transport and treatment of the system.

2 Technology Alternatives and Selection

Technology Alternatives

Technologies available in the scientific literature to deal with copper ores (since the concentration of copper in those tailings is within ore classification) fall into three distinct categories:

- **Flotation-Pyro-Metallurgical**: The copper is separated from the gang material using froth flotation, collected and dewatered using filtration and subsequently sent to a smelting operation.

- **Hydro-Metallurgical**: Copper ores are leached using sulfuric acid (or other agents) and the pregnant leach solution is sent to a Solvent Extraction - Electro - Winning (SXEW) circuit or cementation.

- **Biological Treatment**: Bacterial action is used to transfer the copper from the solid matrix to a solution which subsequently is sent to SXEW or cementation.

Technology Selection

The use of the hydro-metallurgical approach combined with the use of ferrate was chosen over the other two approaches. In preliminary laboratory results, it was found that synergism in leaching copper can be attained by combining ferrate with acid leaching which lead to synergistic factors as high as 2. Further tests are to be carried out in the future to confirm this and to optimize the ferrate to acid ratio which will maximize the copper yield. An additional benefit of the Ferrate-Leaching (will be referred to as FL) approach is that the ferrate oxidizes the sulfates almost instantaneously. This in turn, reduces the volume of process equipment required for the planned throughput.
Environmental Engineering and Management

The pyro-metallurgical approach was not chosen due to problems which include the recovery of SO$_2$ and environmental controls. Furthermore, the biological treatment minimally requires 48 hours to attain the leaching level which can be reached within minutes using the FL approach. One more advantage of using the FL approach is that other metals present in the tailings may be recovered by subsequent SXEW, this is discussed in more detail in the “Recovery of Metals” section.

3 Process Design

Tailings Recovery and Preparation for Transport

Prior to transportation the tailings must be recovered for all valuable metals, as per all environmental and process guidelines. One important requirement is that the dust stirred up during tailing excavation be minimized. The dust can be easily minimized by keeping the tailings damp during excavation. A water tanker will be used for this purpose. Included in the preparation of the site for tailings removal is an adequate drainage system and a holding pond. The drainage system will allow an excess water to flow into the holding pond. The water in the holding pond can be emptied periodically for use in the slurry system. The holding pond will also prevent any acid runoff into the local water supply during tailings recovery.

The tailings will be slurried by pushing them into the concrete slurry mixing tank. This will be done using a scraper/bulldozer. The slurry tank will be located in close proximity to the existing tailings pile to minimize distance traveled. Using a time constraint of a 330 day year with 24 hour days, approximately 12.6 cubic yards of tailings must be excavated each hour. An average dry tailings weight of 2,350 lb/yd$^3$ (1.4 g/cm$^3$) was assumed. This corresponds to approximately 29,700 lb of tailings being mixed with water per hour of operation. Another requirement was that the tailings be mixed into a slurry for transport to the new site. It was decided that a slurry consisting of 10% tailings and 90% water be used. This mixture allows for viscous flow of the slurry. The slurry is to be mixed in a large continuously stirred tank. For this task, two concrete vessels, each with a one hour residence time, and a corresponding volume of 20,000 ft$^3$ are used, with the second serving as an emergency back-up. The two hour residence time of the mixing tanks gives adequate mixing time (refer to process flow diagram, Figure 1).
Slurry Transport and Water Recovery Systems

Once the tailings have been mixed in a slurry, they must be transported to the new impoundment. The slurry transport system consists of two pumps, two pipelines and a water recovery unit. The slurry is first pumped into the pipeline which leads to the limited impoundment. Two inline pumps with a total head of 67 ft lb/L are needed. The pipeline is approximately ½ mile long with an inside diameter of 10 inches. The liquid holdup is approximately 1371 ft³. This corresponds to a residence time of about 17 minutes, and a flow rate of 2.5 ft/s. This flow rate should prevent any solids settling in the pipeline. A hydrocyclone system is used to separate the water from the tailings.

To determine the size of the hydrocyclone needed, it was assumed as average of 30% sand, 50% silt and 20% clay was an approximate analysis of the tailings. The United States Department of Agriculture (USDA) particle size standards are also assumed. With sand 2 to 0.05 mm, silt 0.05 to 0.002 mm and clay less than 0.002 mm. The optimum particle diameter to remove with the hydrocyclone was found to be 0.0152 mm which corresponds to a flow rate of 20,420 lb of tailings and 76,400 lb of water. The hydrocyclone would have a pressure drop of 35 psi and a diameter of 1.75 ft. This stream is then pumped into the lined impoundment. Removing any additional water is not economically feasible.

The slurry from the hydrocyclone underflow is pumped into a lined impoundment, where it was allowed to settle. Water is pumped off the top. It is assumed that 20% of the water entering is lost due to evaporation. More details on the impoundment design can be found in the section entitled "Discharge of Treated Tailings/Impoundment Design". A flow of 214,000 lb/hr of water can be recovered using this system. This water is then pumped into the second pipeline. Two pipeline pumps are used with a total head of 455 ft lb/L. After exiting the second pipeline the water then enters a water holding tank. The water is combined with new tailings and the entire process is repeated.

Treatment of Tailings

Once the tailings have been mixed into a slurry, the first step is to adjust pH of the resulting slurry. Optimum use of ferrate requires that it be allowed to react with the tailings at a pH of 8.0 or above. While the tailings are pumped from the slurry chamber, caustic is added at the section of the
pump. A pH meter samples the pipe contents for pH and a process control loop is used to adjust caustic rate addition.

The use of ferrate oxidation has been chosen in part because the reaction of ferrate with substrates present in the tailing material takes place fast. The reaction of ferrate with sulfide has been studied (Johnson) as follows:

\[
\text{Sulfide: } 5 \text{H}_2\text{O} + 2 \text{FeO}_4^{2-} + 3 \text{HS}^- \rightarrow 2 \text{Fe}^{3+} + 3 \text{S} + 13 \text{OH}^- \quad (1)
\]

The reactions involved the tailings material are believed to proceed as:

\[
\begin{align*}
\text{Pyrite: } & \quad \text{FeS}_2 + \text{FeO}_4^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + 2 \text{S} + 8 \text{OH}^- \quad (2) \\
\text{Covellite: } & \quad 3 \text{CuS} + 2 \text{FeO}_4^{2-} + 8 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + 2 \text{Fe}^{3+} + 3 \text{S} + 16 \text{OH}^- \quad (3) \\
\text{Chalcocite: } & \quad 3 \text{Cu}_2\text{S} + 4 \text{FeO}_4^{2-} + 16 \text{H}_2\text{O} \rightarrow 6 \text{Cu}^{2+} + 4 \text{Fe}^{3+} + 3 \text{S} + 32 \text{OH}^- \quad (4) \\
\text{Chalcopyrite: } & \quad 3 \text{CuFeS}_2 + 5 \text{FeO}_4^{2-} + 20 \text{H}_2\text{O} \rightarrow 3 \text{Cu}^{2+} + 8 \text{Fe}^{3+} + 6 \text{S} + 40 \text{OH}^- \quad (5)
\end{align*}
\]

where the ferrate reacts with the sulfides to produce iron(III), elemental sulfur and copper hydroxides. One major advantage of using ferrate is that, as reported by Johnson it provides a mechanism for "self removal". If a suitable reductant is not available, ferrate will react with water to form iron(III) and molecular oxygen.

\[
\text{Water: } 2 \text{FeO}_4^{2-} + 9 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + 3 \text{O}_2 + 10 \text{OH}^- \quad (6)
\]

Thus excess ferrate added to the system will not damage the process stream.

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Figure 1: Process Flow Diagram
Once the tailings reach a pH of 8.0, potassium ferrate ($k_2FeO_4$) is combined with the tailings in a reactor. The tailings and ferrate react and flow into a second reactor. The purpose of the second tank is to allow gases generated in the reaction to escape and to insure that the reactants are well mixed.

Once the sulfides have been oxidized, sulfuric acid is added to solubilize the copper present in the tailings as oxide precipitates. The result of the reactions is copper sulfate as shown in the reaction (7).

$$\text{Copper: } Cu(OH)_2 + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + 2H_2O \quad (7)$$

Once the copper is in solution it can be recovered from the process. The details of the copper recovery are discussed in the following section. The steps in the treatment of the tailings can be found in Figure 1.

**Recovery of Metals**

The solvent extraction phase is composed of two stages, the extraction stage and the stripping stage. In the extraction stage, the pregrent leach liquor (acidic) is contacted with an organic extractant (LEX) which is selective for copper. The extraction mechanism of copper is believed to proceed as a complex mechanism whereby copper is chelated. This reaction can be represented by the simplified general reaction (Noyes$^{2,3}$).

$$Cu^{2+}(aq) + RH \rightarrow R_2Cu + 2H^+(aq) \quad (8)$$

where RH is an organic compound and RH and $R_2Cu$ are not soluble in the aqueous solution. In the stripping stage, reaction (8) is forced to go in the reverse direction by contacting the extract phase with a strong acid solution. This step will transfer the copper into this acid solution in a concentration that can be used directly for electro-winning.

At this time, the only metal to be recovered will be copper. Other precious metals are found in the stream. However, the recovery of these metals must be investigated. The cost of recovery, additional process equipment and generation of additional waste streams must be weighed against the advantages of recovery. At this time, the design does not include the recovery of other metals.

**Discharge of Treated Tailings / Impoundment Design**

Once the copper has been extracted from the solution, pH is adjusted to 8.0 by adding necessary quantities of lime. This results in precipitation of many of the metals in the process stream. Due to the use of ferrate, the iron
precipitates as iron(III) and sulfur as elemental sulfur. The resultant precipitates do not include pyrite. Therefore, the tailings will not generate acid over the long term.

Separation is done using a hydrocyclone. The hydrocyclone separates the tailings into two streams, coarse tailings containing mostly solids and the fine tailings containing mostly water. The tailings are then deposited in a lined impoundment. The tailings impoundment is designed with the uppermost safety in mind. There are two main elements that compose a tailings impoundment, the confining embankment (tailings dam) and the impoundment of deposited material (4). Since there is no existing pit or valley that can be used for the embankment, the confining embankment will be constructed using the tailings material.

High density polyethylene (HDPE) lines will be used to deliver the tailings to the impoundment since they resist wear from the solids in the tailings. The lines are also resistant to chemical corrosivity.

A main element for safety of the impoundment is the confining embankment. The embankment will be constructed using tailings material in the structural zone. The tailings dam should be designed by an engineer with extensive knowledge and experience in embankment design. Tailings material is separated by use of a hydrocyclone into course material and fine material. The coarse material or hydrocyclone underflow is used to construct the embankment. The fine material or hydrocyclone overflow is deposited into the impoundment.

Diversion of natural surface water is accomplished by construction of channels around the impoundment. It is important not only to ensure that there is no contamination of the surrounding environment, but also to ensure the integrity of the structure. A barge pump is used to provide a decant system. This was chosen over other decanting methods, such as a tower or chute, because it is safer and more flexible. The increased safety and flexibility is because the pump is accessible and can be moved as the profile changes over the life of the impoundment.

Contamination of the surrounding area can be caused by seepage of the liquid from the impoundment into the ground water or surface water, or by dispersion of the solids. This is avoided by installing a protective liner at the base of the impoundment before deposition begins and capping the impoundment when deposition is complete. The lining is made of an
impermeable material. The capping is also made of an impermeable layer. Once the impoundment has been capped, a layer of soil and grass will be placed upon the cap. A grass that is native to New Mexico will be planted. This will not only help prevent erosion of the surface, but it will also have a positive visual impact for the surrounding area. The decant system in the impoundment allows further separation of the water from the solids. All of the water reclaimed using these two methods is reused for the transport/treatment at the beginning of the process.

Sampling of Soil and Groundwater

Analysis will be conducted to determine if contaminants from the unlined impoundment have migrated into the surrounding soil and/or groundwater. Monitoring wells will be installed at strategic locations downstream from the impoundment. In addition, various soil samples will be drawn at locations surrounding the impoundment. X-ray fluorescence will be used to determine if there are any metal contaminants. An advantage to this method is that large areas can be sampled quickly. If contaminants are detected in either the soil or the groundwater, a complete remediation process will be designed and implemented.

4 Bench-Scale

Design

The bench-scale process has been designed to model the process that will take place on the full-scale level; therefore, the steps in the bench-scale process are the same as the steps for the full-scale. First, the tailings will be mixed with water to form a slurry in a vessel. Second, the slurry will be adjusted to a pH of 8.0. Then the ferrate will be added. Once the ferrate has been properly mixed and allowed to react, sulfuric acid will be added. At this time, all of the copper will be in solution. An extraction will be performed to separate the copper from the stream. The remainder of the stream will be adjusted to a pH of 8.0. The resultant precipitant will be separated from the water.

Results

Laboratory experiments on the bench-scale level have shown promising results. An experiment was conducted to compare the amount of copper
recover using sulfuric acid alone, ferrate alone, and a combination of ferrate and sulfuric acid. The solutions were analyzed using an atomic absorption spectrophotometer for the amount of copper in solution. As expected, when ferrate was used alone there was no copper in solution. This is because at a pH of 8.0 the copper is insoluble as copper hydroxide. When the solution containing both ferrate and copper was analyzed, the concentration of copper was shown to be significantly higher than the concentration of copper when only acid was used. This indicates that the ferrate is oxidizing the copper present. It is believed that all of the copper present in the tailings is solubilized, however, the initial concentration of copper in the tailings was not known. Further studies could be done to indicate what percentage of total copper is solubilized using K$_2$FeO$_4$ and H$_2$SO$_4$.

5 Assessments

Economics

The total project cost is estimated as approximately $8,000,000. The total capital investment of the project is approximately $1,800,000 and was estimated using a Lang factor (Peters$^5$). The operating costs are approximately $6,000,000 per year of operation (Peters$^{5,6,7}$). The operating costs were calculated by taking into account annual earnings of approximately $6,000,000 per year from the sale of copper. The price of copper was estimated at $0.79/lb (Peters$^{5,6,7}$). The price of ferrate is currently approximately $1.00/lb. However, it was assumed that the cost will decrease as ferrate is procured in large quantities.

Impact on Community

The process has been designed to minimize the impact to the community from process start to completion. During the process, the amount of water used is kept to the minimum allowable level. Water used is recycled in the process. While tailings are being recovered into the slurry, the dust levels are kept to a minimum. The process has been designed to require a minimum amount of heavy machinery to reduce the impact of noise levels. Since the process has been designed to be a “closed-loop” system, the community should not be impacted by any process waste streams. Public involvement and ownership of the project is the best way to not only guard...
against interference, but assure assistance in accomplishing the cleanup task.

6 Conclusions

The process described provides for the recovery and transport of the mine tailings, design of the slurry system, the recovery of the metals present in the tailings, the recovery of water for reuse and the treatment of tailings for final disposition in a lined, copper impoundment. Estimated cost is about $8,000,000 to be completed within a time frame of 24 months. Impact on the community has been minimized with meeting all regulatory requirements.

References


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