Mining activities generate a large volume of materials and waste that must be stored properly in waste rock dumps called landfills or dumps and tailings deposits called tailings dams. These mining waste usually contains sulfides which, in contact with water and the atmosphere, begin complex processes of physical, chemical and biological transformations, ultimately causing the generation of acid mine drainage.

To cope with this issue, in our Environmental Geochemical Division, we have developed several studies for the design of mine water treatment plants. In general, these plants, whether conventional or HDS (High-Density Sludge), operate at a pH ranging from 9 to 11, and their main process is neutralization and precipitation, to which are usually added other devices of secondary treatment such as ozone, reverse osmosis, ionic exchange, and nano and ultrafiltration, among others. In both cases, generated sludge is stored in the tailings dam, reducing tailings storage capacity.

In recent years, the Peruvian environmental legislation has become more demanding, mainly in terms of reference values such as Maximum Permissible Limits (MPL) for effluents generated in mining operations, and Environmental Quality Standards (EQS) for water. In addition, the population requires, in the first place, the development of sustainable mining projects with lower water consumption, and in second place the inclusion of methods that allow exploiting mining waste solids or liquids as second generation resources with potential for development and recovery to obtain products with economic value.

In order to achieve the usage of mining waste and to reduce the discharges to the environment, we have developed acid water treatment systems that allow recovering byproducts that can provide an added economic value, called “Phased Treatment”. This method reduces mine water treatment costs, extends the life of the waste storage facilities, and reduces the discharge of solid and liquid waste to the environment.

For acid water treatment systems sizing, it is essential to have a good geochemical characterization of the effluent, covering from field monitoring using mobile equipment to perform in situ flow measurements, pH,
dissolved oxygen, conductivity, temperature, turbidity, acidity, alkalinity, Fe2, Fe3 and Fe total, to water testing for analysis of total and dissolved concentrations of chemicals. The hydro geochemical characterization must include the total acidity of the mine effluents for the design of the treatment plant, taking into account the protonic acidity due to free hydrogen ions (H+) plus the metallic acidity in the water; mainly due to contents of Fe, Al and Mn. These are considered acid generator elements because they can generate H+ through oxidation and hydrolysis, per the following reactions:

\[
\begin{align*}
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \frac{3}{2}\text{H}_2\text{O} & \rightarrow \text{FeOOH} + 2\text{H}^+ & \text{Eq. 1} \\
\text{Fe}^{3+} + 2\text{H}_2\text{O} & \rightarrow \text{FeOOH} + 3\text{H}^+ & \text{Eq. 2} \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ & \text{Eq. 3} \\
\text{Mn}^{2+} + \frac{1}{2}\text{O}_2 + 3\text{H}_2\text{O} & \rightarrow \text{MnOOH} + 2\text{H}^+ & \text{Eq. 4}
\end{align*}
\]

An important variable in the design of a treatment plant is the consumption of reactive materials required to reach the pH ranges in which each element to be removed from the water forms its solid phase. For this purpose, experimental tests of neutralization and precipitation in the laboratory are carried out, which are then adjusted together with pilot testing in the field. This rate of experimental consumption in conjunction with the hydraulic and geochemical characteristics helps determining the size of the treatment.

The dose of consumption of reactive material obtained, also determines the sequence of operation, treatment times and the volume of sludge to be generated during the treatment.

**Neutralization tests with the recovery of by-products.**

Below, we present experimental results for the design of a phased acid water treatment plant in three stages, with the aim of obtaining usable by-products that provide economic value. The following table shows the pH and major metal load of a mine drainage, from which were conducted phased neutralization tests, to obtain three by-products with high content of Fe, Al and Zn.

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Mg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
</tr>
<tr>
<td>2.9</td>
<td>180</td>
<td>90</td>
<td>95</td>
<td>70</td>
<td>5</td>
<td>1200</td>
</tr>
</tbody>
</table>

Total Concentrations

Figures 1 and 2 represent the consumption curves of lime and the evolution of redox potential during the neutralization process (Eh,pH curve). The areas of hydrolysis or buffering in the curve of consumption of lime (equivalent acidity), are clearly indicated by the pH and the slope changes of the curve, from which can also be deduced the amount of lime required to remove Fe, Al and Zn from the water in the form of solid phases.

![Figure 1. Evolution of the Eh in a step-by-step sequential essay](image)

![Figure 2. Consumption of lime and pH ranges of areas of hydrolysis.](image)
If Fe and Al sludges are not removed in the first stages of the treatment process, their formed solid phases will re-dissolve and go back into the water at a pH greater than the mobilization range of these elements (4 and 5.5, respectively), therefore requiring the addition of more alkaline material (lime) in order to make them form solid phases again (pH 9) to remove them from the water. This would cause not only an increase of the lime consumption by the process, but the addition of other agents called flocculants, coagulants and others that help the formation of solid phases would also be needed. These additions increase the amount of equipment needed in the treatment plant, making the treatment process of acid mine water more expensive.

**CONCLUSIONS**

Characterization of acid mine water by acidity helps exploring the possibilities of recovering by-products with economic value and choosing the most suitable and efficient treatment system, because besides the protonic acidity, it includes the mineral acidity, which is an aspect that is generally overlooked in the typical characterization methods.

The sizing of the acid water treatment system based on acidity content and conducted in stages allows obtaining a better usage of the resources by requiring lower amounts of lime in the neutralization process, and in addition, allowing the recovery of metals from the generated sludges. This makes the treatment of acid water cheaper, more efficient, and allows for better environmental control.

The sludges obtained by the treatment of mine water through this three-stage system, could have the following usages: the sludge with Fe content (M-1) could be used as ceramic pigment; the sludge with aluminum (M-2) could be used in the mine’s blasting works, improving the explosives; and the sludge with high Zn content (M-3) could be processed to obtain a zinc concentrate.

By applying step-by-step sequential treatment systems to acid waters, sludges with similar and well-defined characteristics are obtained, with chances of metal recovery from these.

Water from the treatment process can be discharged to a receiving body, prior quality control, without causing an environmental impact or alteration. The sludges that have no recovery potential will be stored in suitable tanks or will be sent to the tailings storage facility.