Treatment of high total dissolved solids and acidity in Cerro de Pasco mining wastewater, Peru

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Abstract The current wastewater treatment plant at the Cerro de Pasco mine in Peru is a low density sludge process and treats 630 m^3/h with an influent pH of 2.5 and elevated metals concentrations. The project goals include increasing capacity to 1,375 m^3/h, meeting new mine discharge regulations, and reducing unit operating costs. Technologies considered included high density sludge (HDS), sulfide treatment for recovery of copper, and neutralization with limestone. The sulfide and limestone processes are projected to reduce annual chemical costs by 15 % and 20 %, respectively.

Keywords HDS, Limestone, Sulfide, Mine Peru

Introduction

The Vulcan SAC-owned Cerro de Pasco mine produces lead, zinc and silver and is located in Chaupimarca district, Cerro province, about 295 km from Lima at an altitude of 4,300 m. The current wastewater treatment plant at the mine is a low density sludge lime neutralization plant that treats approximately 630 m^3/h of influent water with a pH of 2.5 and elevated metals concentrations. The mine will need to increase the capacity of the plant to 1,375 m^3/h to treat all acidic water at the site in order to comply with recent mine discharge regulations. There are end-of-pipe discharge requirements (LMP) for some parameters. The current annual lime cost is projected to increase five-fold due to the plant expansion. The future influent water has a pH of 2.0, 16.2 g/L of acidity as $CaCO_3$, and a TDS concentration of 19 g/L. The influent acidity includes 15.7 g/L of metal acidity. The current plant treats water from 5 sources; the future plant will treat higher flows from the current sources as well as two additional sources. The contaminants of concern (COCs) are those parameters that exceed the LMPs: As, Cd, Cu, Fe, Pb, Zn.

Treatment alternatives evaluation

A treatment alternatives evaluation was conducted in order to select a treatment technology that would meet treatment goals and reduce lime costs. Neutralization methods considered included low density sludge (LDS), high density sludge (HDS), and neutralization with limestone. Given the high influent copper concentrations, metal recovery options were also considered including sulfide treatment, ion exchange, and solvent extraction and elec-

	Existing plant	Future plant
Flow rate, m^3/hr	630	1,375
Quicklime (CaO) dose, g/L	10.9	11.1
Quicklime (CaO) consumption, tonne/yr	49,080	121,740

Table 1 *Estimated lime costs for existing LDS plant and future LDS plant*

trowinning. Sulfide treatment allows recovery of copper from the mine water as a marketable copper sulfide, generating revenue through copper concentrate sales to offset costs. The sulfide process is used in conjunction with a neutralization process (*e.g.* HDS) to treat for other metals and acidity.

A summary of the treatment alternatives is provided in Attachment 1. In Attachment 1, Table 1A, the existing LDS plant is considered the base case and cost difference with other neutralization methods are provided. Switching to HDS is estimated to save 23 % and switching to limestone/lime neutralization is estimated to save 20 % of the annual chemical cost. In Attachment 1, Table 1B, metal recovery alternatives are presented. The sulfide process is projected to reduce annual operation costs by 15 %. Ion exchange, which is predicted to result in 18 % savings, was not retained because the technology has not been demonstrated at full scale for copper recovery on a similar water matrix. Based on this evaluation, HDS, limestone pretreatment, and sulfide pretreatment were chosen to carry forward for bench testing.

Bench testing methods

The bench testing objective is to provide indications of treatment performance and design parameters and form a basis for the development of full-scale design criteria and operating conditions. The bench testing was comprised primarily of jar testing that can be used to quickly and easily evaluate contaminant removal over a range of treatment conditions with relatively small quantities of water. Lab grade hydrated lime ($Ca(OH)_2$) was used for all lime titrations and added as a 30 % by weight slurry. Lab grade limestone ($CaCO_3$) was used for all limestone titrations and added as a 20 % by weight slurry.

The seven water sources were mixed according to predicted flow contributions from each source; this will be referred to as the total blend. The second blend used only the Source 2 and 6 waters; this is referred to as the copper recovery blend. This was the blend evaluated for the possibility of copper recovery using sulfide. Six lime titrations (T1 – T6) were performed on the total blend to determine the optimum pH for metals removal. Five additional lime titrations (O1 – O5) were performed with aeration by inserting a coiled air diffuser wand into the bottom of the beaker. The goal was to see how aeration with similar lime dosing affected the end pH and metals removal. Six limestone titrations (LS1 – LS6) were performed on the total blend. Once a limestone dose was selected, two-stage neutralization was evaluated (R1 – R6). Limestone was added at a set dose of 10 g/L to six different samples and allowed to react, and then lime doses between 1 and 6 g/L were added, with no solids separation step in between the two stages.

The goal of the copper recovery blend titration tests was to evaluate the pretreatment conditions which are necessary to produce a marketable sulfide product in subsequent tests using sulfide reagent, sodium hydrosulfide (NaSH). The copper recovery blend contained high levels of iron, arsenic and other metals which needed to be removed in order to maximize the value of the copper sulfide product. Titration testing was performed using the copper recovery blend water in nine jar tests. The objective of this testing was to determine the pH that would maximize arsenic removal while minimizing copper loss, and to produce pretreated copper solution for subsequent testing.

HDS recycle testing, which involves successive batch HDS neutralization cycles, was performed to provide a comparison between HDS and conventional lime treatment on settling, filtration, and effluent quality. Tests were performed using the total blend water.

Results

Lime titrations

It was found that a pH of 8.1 at a lime dose of 10 g/L resulted in metal concentrations that me*et al.* l discharge requirements. A theoretical dose, based on metals removal, was calculated at 10.1 g/L. The actual required dose was equal to the theoretical, which indicates high lime utilization. This was the lowest pH that met *al.* l treatment targets, and is within the range of the current plant, which operates at a pH of around 8 using a lime dose of between 5 and 10 g/L, depending on the time of year. The titration curve is shown in Fig. 1. Informal testing showed that the titration curve hit a plateau (buffering zone) at roughly pH 8, between a lime dose of 9 and 10 g/L.

The samples which were provided supplemental air had a higher final pH than the samples which were simply mechanically mixed (“non-aerated”), with the same lime dose as shown in Fig. 1. The reaction time was with supplemental aeration was reduced to roughly an hour.

The analytical results for both the “aerated” and “non-aerated” samples are presented in Attachment 2. The lime dose, final pH after the 3 hour reaction time, and aeration are indicated in the field results section of the Attachment 2. Analytical samples for pH, dissolved metals, and sulfate were submitted to an outside laboratory on samples T-3 through T-6, and O-1 through O-5. T-1 and T-2 did not have a high enough pH value to warrant analytical sampling, as it was thought the metals removal would not be high enough at such a low pH. T-5 and T-6 both meet *al.* l the treatment targets; however, T-5 has a lower lime dose, so it was chosen as the optimum treatment condition for subsequent testing. Metal concentrations in T-3 and T-4 were several orders of magnitude greater than in T-5 and T-6. O-1 and O-2 exhibited unexpectedly low metal removal rates. However, because their final pH is far greater than is considered representative for the treatment plant, these samples were not carried forward for further discussion. Metals removal in samples O-3, O-4, and O-5 was fairly similar for both the aerated and non-aerated samples at the same general pH, although there were a few minor differences. Manganese removal was higher with aeration; this would be an expected result for manganese.

Limestone titrations

The selected dose was determined to be 10 g/L which results in a pH of 5.8. A theoretical dose, based on metals removal, was calculated at 10.3 g/L. The actual required dose was equal to

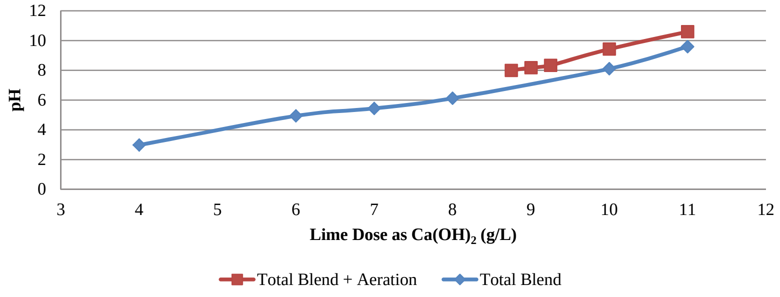

Fig. 1 *Lime titration of total blend with and without aeration*

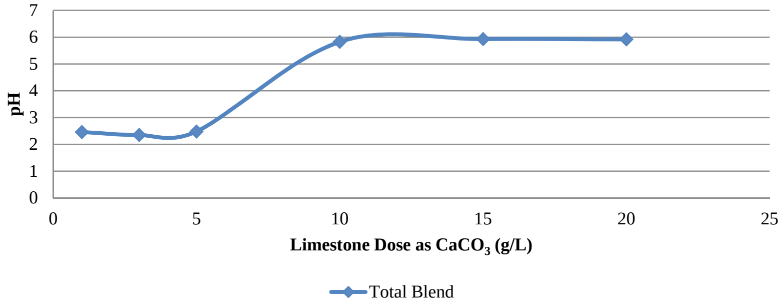

Fig. 2 *Limestone titration of total blend*

the theoretical, which indicates high limestone utilization. There was a steep inflection point between pH 2.48 and 5.83, corresponding to lime doses of 5 g/L and 10 g/L, respectively. This pH range is where iron begins to precipitate, resulting in the rapid change in pH. The pH stops increasing after 10 g/L; it appears that the maximum possible pH through limestone addition is around 5.8. Fig. 2 shows the titration curve for the total blend with limestone addition.

Much lower lime doses were required if limestone was used for pre-neutralization; 10 g/L limestone and 3 g/L lime reached the same pH of around 8.1 as 10 g/L of lime only. This method also results in a lower reaction time. The limestone stage reached a pH within 0.3 of the final pH within 30 minutes. It was allowed to react for two hours to confirm the final pH, but this could be shortened considerably. The reaction time for the lime stage then ranged between 30 and 60 minutes as opposed to upwards of three hours without the limestone pre-neutralization. The reason for this is believed to be related to the carbon dioxide formed by limestone when it reacts with acid. The bubbles formed when the limestone reacts may be generating enough shear force to break up the gypsum particles before they can completely coat any unreacted limestone. The bubbles also create a lower bulk fluid viscosity, which can assist with mixing.

Copper recovery blend

There were a number of challenges encountered while conducting the titration testing on the copper recovery blend: high lime demand, high solids generation, and difficulty in selectively removing iron and arsenic without also removing copper. A theoretical dose, based on metals removal, was calculated at 119 g/L for the high strength, high copper solutions. A large dose of lime, 75 g/L, was required to neutralize the copper recovery blend to a pH of 4.66. The solids generation was commensurately high, and the solids produced a viscous slurry that was difficult to mix. The solids produced in the procedure were low density and settled poorly. After two hours settling time, there was no free liquid on the top of the solids, indicating that the solids were too thick to consolidate. The samples were filtered in an outside laboratory before analysis. Only the two samples that had a pH of less than 4 produced visible free water (decant). The solids produced in these tests were unusual because two different solid morphologies were observed: a red, less viscous material, and a thick, black material. The black material could be removed from the slurry using a strainer. At the pH range tested, significant copper removal occurred. The highest residual copper in a sample was 12 mg/L which is a 99.4 % removal from a starting point of 1,966 mg/L of copper. Three other samples had residual copper values of less than 1 mg/L. The low levels of copper remaining after pretreatment were unexpected, and further optimization work on the pretreatment process is required before the metal recovery step can be demonstrated to produce a marketable, clean copper sulfide product. For example, a lower pH should be tested in future, or more process alternatives may be tested to demonstrate economic metal recovery options.

High density sludge recycle testing

The large amount of solids generated in the later recycles resulted in the sample only undergoing hindered settling wherein liquid moves up through the spaces between particles, and the solids settle as a unit, maintaining their relative position to other particles. A clear solid-liquid interface develops as the particles settle. Compression settling occurs when the solids have reached a concentration where further settling can only take place through compression of the structure. The weight of the particles and the supernatant causes compression. Unhindered settling occurs when the solids particles drop out of solution at different rates. Heavier particles settle first, while lighter particles take more time to settle out. This can be observed as clear decant on top, leading into a cloudy layer in which particles are still settling, and finally into the sludge layer, where particles have settled and are beginning to compact. Several tests were conducted to experiment with unhindered settling. A small amount of sludge was diluted with additional decant water, and more polymer was added and the mixture allowed to settle. The sludge settled more quickly, but the clarity of the overflow was compromised as expected. Overall more pin floc was seen in the decant with unhindered settling. However, the projected clarifier underflow concentration is not significantly affected by the dilution. Attachment 3 shows the interface height over time for select recycle batches. It can be seen that the interface height increased at first while the amount of solids generated was increasing, then began to decrease as the solids began to compact and densify. Most compression during each recycle had occurred by 50 minutes into the settling test, although 60 minutes of settling time was allowed for maximum compaction. Some samples were left overnight. Once compression had begun to occur, even the extended settling time did not result in a lower interface height. The HDS evaluation was performed to 13 recycles in an effort to confirm underflow densification.

Total suspended solids (TSS) values for the underflow are shown in Attachment 4. The underflow shows a rising trend with recycle number in thirteen consecutive batch recycle tests. The maximum density was approximately 21 %, though higher density can be expected in continuous pilot or full scale trials. Analytical results from Recycle #10 decant are provided in Attachment 5. The recycles were run in a pH range of 8.0 – 8.5, recycle #10 reached a pH of 8.4. Metals removal remained high, similar to the removal rates seen in the initial lime titration. Both sulfate and manganese removal showed significant improvement over the single pass titrations run at a similar pH. Since the recycle tests resulted in more efficient sulfate and manganese removal for a given pH setpoint compared to simple titrations, then by the same token, the same sulfate and manganese removal can be expected at a lower pH with recycle compared to simple titrations.

Discussion

Most operating facilities treating acid rock drainage do not use limestone as a neutralizing agent, but limestone is commonly used to neutralize high strength acidic wastes such as autoclave barren solutions. Some of the advantages to using limestone instead of lime are: lower material costs, denser sludge, and lower sludge volumes. Typical disadvantages include the inability to raise the pH above 5.0-7.0, low utilization efficiencies due to armoring, and longer reaction times (EPA 1983, Hammarstroma *et al.* 2003). The practical limit of pH 5–7 is due to declining reaction kinetics. In order to achieve higher neutralization pH, a two-stage neutralization is typically used, with lime being added to a second reactor following the limestone reactor. Based on bench results for the Cerro de Pasco mine wastewater, the chemical cost savings of utilizing limestone and lime are 20 % if limestone is ½ the cost of lime on a weight basis. If limestone is less expensive relative to lime, the cost savings increase. Depending on local availability, in some cases limestone may be quarried and milled at a substantial savings for high acidity wastewaters. Limestone-lime combination treatment can reportedly produce less and denser sludge than lime alone (EPA 1974). The EPA reported that the volume of sludge produced in limestone-lime treatment is roughly one-third the volume versus hydrated lime alone. The solids content can also be up to five times higher. Testing results indicated that limestone also produced a shorter reaction time than lime. Under bench test conditions using batch reactors, a reaction time of three hours was required to reach a stable pH with lime. In two stage tests the limestone reached its final pH of about 5.8 in thirty minutes, and the additional lime reaction time was thirty minutes, resulting in a combined reaction time of one hour. It is possible that the carbon dioxide generated by the limestone reaction helped to improve mixing in the reactor and in preventing the formation of gypsum around unreacted lime. Based on research done on scale formation, gypsum preferentially precipitates onto the surface of bubbles (Amjad 1988). As the gypsum precipitates onto the carbon dioxide bubbles, it is prevented from forming on the surface of the lime or limestone particles, thereby decreasing reaction time of both the limestone and lime addition. Finally, the use of limestone has been discouraged for low strength wastewaters with higher starting pH due to armoring with metal hydroxides with waters that contain more than 50 mg/L of acidity or 5 mg/L of iron (Skousen *et al.* 1995).

Conclusion

The Cerro de Pasco mine wastewater is notable for its elevated acidity and TDS. Conventional lime treatment processes, such as LDS and HDS, are effective in achieving the treatment goals but require high annual chemical costs. Alternate neutralization methods using limestone or copper recovery through sulfide precipitation are two potential ways to decrease or offset operating costs. A copper recovery approach is believed to have potential application at the site, in that copper supplied may be sold to offset treatment costs. However, difficulty in separating arsenic to produce a marketable copper sulfide concentrate, and high sludge generation rates represent barriers to implementation of the technology. Limestone as a pre-neutralization step may offer benefits, including a net reduction in reagent cost and a reduction reagent armoring at low pH, resulting in better reaction rates.

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Electronic attachements can be found at:
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