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Mining Environmental Liability and Its in Situ Treatment with Calcium Oxide for Zinc Removal

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Abstract: Mining environmental liabilities have negative effects on human health, the ecosystem and property. This study was conducted at the Cercapuquio Mining Environmental Liability (MEL) in the district of Chongos Alto. The wastewater analysis was conducted at Universidad Continental and data were obtained on metal content and hydrogen potential. This investigation revealed that the Cercapuquio MEL wastewater had a higher concentration of zinc, 9,916 mg/L, and the pH level was 7.53 (alkaline), which is why this effluent exceeds the maximum permissible limit of the annual average. A neutralizing reagent was also prepared by recycling eggshells, calcined at 1000 °C for 40 min, obtaining quicklime with 61.30% calcium oxide (CaO). For wastewater treatment, the quicklime obtained in neutralizing solution was used, which, when applied to the effluent, had the effect of lowering the zinc concentration from 9.916 mg/L to 0.051 mg/L and the pH from 7.53 to 10.36. The average zinc removal achieved in the effluent is 96%.

Keywords: calcium oxide, eggshell, environmental liabilities and wastewater.

1 Introduction

Peru has a long mining tradition dating back to pre-Inca times. During the XX century, exploration works have been intensified throughout the country, especially in the Andes, which has allowed the opening of new mining deposits. Several of them are still in operation, while the others, for reasons of profitability, have been abandoned [1]. However, at present, Peruvian mining has many challenges to face, such as: guaranteeing the community a sustainable mine closure and avoiding the generation of Mining Environmental Liabilities (MEL), some private companies have taken possession of the MELs to give them an effective solution, because they constitute a problematic outcome for Peruvians [2].

Peru has implemented a law to manage MELs. Law N° 28271 of 2004, establishes criteria that regulates the identification of MELs for their remediation both in the affected areas and in their surroundings, that is, to mitigate their negative impacts on property, ecosystem and human health. MELs are those effluents, emissions, construction debris and waste produced by mining operations, which are currently abandoned or inactive, are also registered in the inventory of the Ministry of Energy and Mines (MINEM) [3] The main problem for the remediation of MELs is not being able to identify those responsible for the Ex Mining Units (EMU), which is why the State is responsible for their remediation [3]. Soil contamination is a damage caused by the abandonment of a MEL, as these works have generated a clear impact effect, as is the case of the abandonment of mining waste [4]. When abandoned, heavy metals tend to concentrate in plants and organic tissues [5]. The concentrations of heavy metals found constitute an alarm on the ecosystem, due to their possible bioavailability in certain environmental circumstances and at the same time impair water quality [6].

Entrepreneurs in industries with sufficient capital are not interested in installing effective treatment techniques due to weak governmental control and poor enforcement of environmental regulations. The environment can be harmed by heavy metal pollution. They remain for a long time in solution in soil and water and do not decompose like other organic pollutants. Heavy metal contaminants are all soluble at low pH, so toxicity problems are greater in the environment. In the removal of heavy metals from effluents, several types of treatments are used, which are divided into physical, chemical and biological methods. In relation to other procedures, chemical for the treatment of waste from the mining industry, adsorption is the most widely used procedure due to its ease and versatility of design, as well as its performance. The most common adsorbents, such as activated carbon, silica gel, applied aluminum oxide and ion exchange resins, have high performance [7]. This research was carried out with the objective of recycling eggshells to obtain calcium oxide and determine its effectiveness for the neutralization of zinc in wastewater.

2 Methods and Materials

2.1. Study Area

The research study was carried out in the Mining Environmental Liability (MEL) Ex Mining Unit (EMU) Cercapuquio, located in the district of Chongos Alto, province of Chupaca, department of Junin (See Fig. 1); at an altitude of 4327 m.a.s.l. and UTM 454934.074E 8626061.783N. This MEL is registered in the inventory of the Ministry of Energy and Mines (MINEM) 2021 with the following code 010319603; 010347794[8].

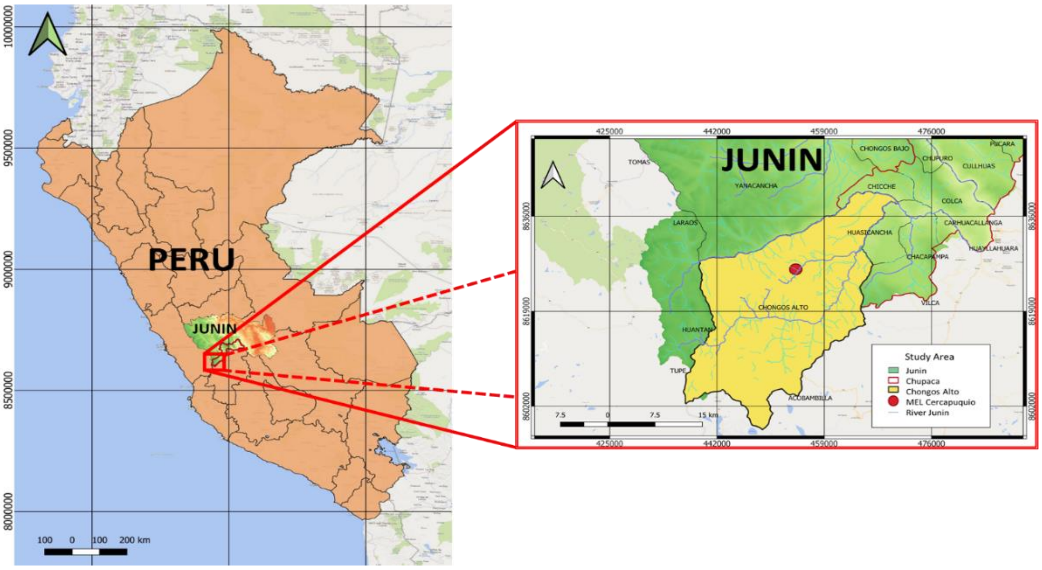

Fig. 1. Geographic location of the Cercapuquio MEL.

2.2. Sampling Method

A monitoring chain of custody was used, we chose an important point of the tailings dam of the Cercapuquio MEL to determine the study of the metal content and the pH level of the wastewater; we extracted the sample with a sterilized 1000 ml container and then added 20 drops of nitric acid to capture the metals. The analysis study was carried out in a private laboratory. In Table 1 we specify the test methodology used by the laboratory to determine the metal content and pH.

Table 1. Standards applied in the analysis of heavy metals and pH.

Assay	Reference Method	Description
Arsenic	SMEWW-APHA-AWWA-WEF Part 3500-As B, 23nd Ed.2017	As, Atomic Absorption Spectrometric Method.
Copper	SMEWW-APHA-AWWA-WEF Part 3500-Cu B, 23nd Ed.2017	Cu, Atomic Absorption Spectrometric Method.
Zinc	SMEWW-APHA-AWWA-WEF Part 3500-Zn B, 23nd Ed.2017	Zn, Atomic Absorption Spectrometric Method.
Iron	SMEWW-APHA-AWWA-WEF Part 3500-Fe B, 23nd Ed.2017	Fe, Atomic Absorption Spectrometric Method.
Lead	SMEWW-APHA-AWWA-WEF Part 5210-Pb B, 23nd Ed.2017	Pb, Atomic Absorption Spectrometric Method.
pH	SMEWW-APHA-AWWA-WEF Part 4500 - H+ B, 23nd Ed.2017	pH Value. Electrometric Method.

The results obtained from the laboratory show in Table 2 that the wastewater from the Cercapuquio MEL has a higher presence of zinc, 9.916 mg/L and low iron content, 0.218 mg/L, and the pH level is 7.53, which indicates alkalinity. With the sampling method used, no other heavy metals were detected.

Table 2. Results of heavy metals and pH.

Assay	Result	Unit
Arsenic	<0.001	mg/L
Copper	<0.001	mg/L
Zinc	9.916	mg/L
Iron	0.218	mg/L
Lead	<0.001	mg/L
pH	7.53	pH unit

2.3. Maximum Allowable Limit

In Table 3 specifies the parameters of the Maximum Permissible Limit (MPL) that effluents from mining activities must have, the concentration of chemical elements at the annual average is 1.2 mg/L of zinc and 1.6 mg/L of iron. If the effluent exceeds the heavy metal concentration limits, it can be harmful to human health and the environment. According to the regulations of Supreme Decree N. 010-2010-MINAM, the established parameters must be met [9].

Table 3. Maximum Allowable Limit.

Parameters	Unit of measurement	Annual Average
Zinc	mg/L	1.2
Potential Hydrogen (pH)	pH unit	6.0 to 9.0

3 Laboratory Analysis

3.1. Preparation of Quicklime

For the in situ treatment of the PAM Cercapuquio effluent, we required a reagent that could trap or remove zinc; we decided to prepare calcium oxide (CaO) also known commercially as quicklime (CaO). We chose to obtain quicklime by calcining eggshells. Eggshells are mainly composed of calcium carbonate (CaCO3), which, when calcined, transforms its chemical composition and becomes CaO. In Table 4 describes the procedure we performed in the Continental University laboratory.

Table 4. Preparation of quicklime.

Standards	Process	Formula
Specific Research Method	We recycled 300 g of eggshell, proceeded to clean it by removing as much testicular membrane as possible and left it to dry for 8 hours. In the laboratory of the Continental University, we used equipment and materials to carry out the calcination process. In a mortar we started grinding the eggshell and then we poured it into two 125g crucibles, the obtained weight of the eggshell was 220 g.	$CaCO_3$
Law of Conservation of Mass	We introduced the two crucibles in the muffle at room temperature, we waited for it to reach 1000 °C and let 40 minutes elapse, we turned off the muffle and let it cool at room temperature, after 4 hours the muffle had a temperature of 300 °C, we removed the two crucibles and put it in the Schreiber desiccator to accelerate the cooling. Finally we sprayed it with the mortar and filled it in a zipper bag eliminating as much air as possible to avoid humidity. The product was weighed on an analytical balance and 116g of quicklime were obtained.	$CaCO_3 + \Delta$ = CaO + CO2

The purity of quicklime was sent to a private laboratory for analysis; the result obtained is 61.3% calcium oxide and the remaining is inert material. That is to say that in 116 gr. of quicklime, the CaO purity is 71.1 g.

3.2. Calcium Oxide Effect

In Table 5 describes the application of calcium oxide in the wastewater of the Cercapuquio MEL, it is expected that the calcium oxide reagent can remove zinc.

4 Statistical Analysis

The wastewater samples were collected at the Cercapuquio MEL, this study focused on the removal of zinc from different tests with quicklime; statistical results were obtained synthesized by bar and scatter plots, Ms Excel software was used. They were also tested by analysis of variance (ANOVA) by the F value, the critical value of F and a confidence level of 95%.

Table 5. Application of calcium oxide in wastewater.

Standards	Process	Formula
Specific Research Method	We performed the experiment in 4 containers by pouring 1L, 3L, 5L and 10L of waste water into each container. For the reagent, we dissolve 15 g of calcium oxide in 100 ml of drinking water. With a syringe we extracted 1 ml of the reagent and applied it in 1 L of wastewater, after 15 min. we observed that the zinc was sedimenting, but the water still had low turbidity. Then we filtered with qualitative filter paper in one bottle. For the other bottles, 1 ml of reagent was applied for each 1 L, that is, for 3 L we applied 3 ml of the reagent and so on for 5 L and 10 L of wastewater.	Removal % = $\frac{Ci - Cf}{Ci} * 100$ Where: Ci: Initial concentration Cf: Final concentration
D. S. N° 010-2010-MINAM.	After the procedure, we measured the pH of each container with a potentiometer, giving alkaline results.	pH = −log [H+]

5 Results

Table 6 shows 4 tests that we performed with CaO, the dose of 0.613 g of CaO per 1L of wastewater was applied, the initial zinc concentrate is 9.916 mg/L, in the 1L test, zinc decreased to 0.051 mg/L, 3L test decreased to 0.375 mg/L, 5L test decreased to 0.425 mg/L and in the 10L test it decreased to 0.742 mg/L. CaO proved to be efficient in the reduction of zinc concentrate with an average efficiency of 96%.

Table 6. Results of zinc removal.

Assays (L)	Initial zinc content (mg/L)	g. of CaO/L of wastewater	Final zinc content (mg/L)	Efficiency (%)	pH initial	pH final
1	9.916	0.613	0.051	99.49	7.53	10.36
3		1.839	0.375	96.22		9.84
5		3.065	0.425	95.71		9.23
10		6.130	0.742	92.52		8.82

The results of the tests in 1L, 3L, 5L and 10L, the zinc content is reduced to less than 1.2 mg/L allowed and it is observed that the zinc has decreased when CaO is applied to an average of 0.4 mg/L. (See Fig. 2).

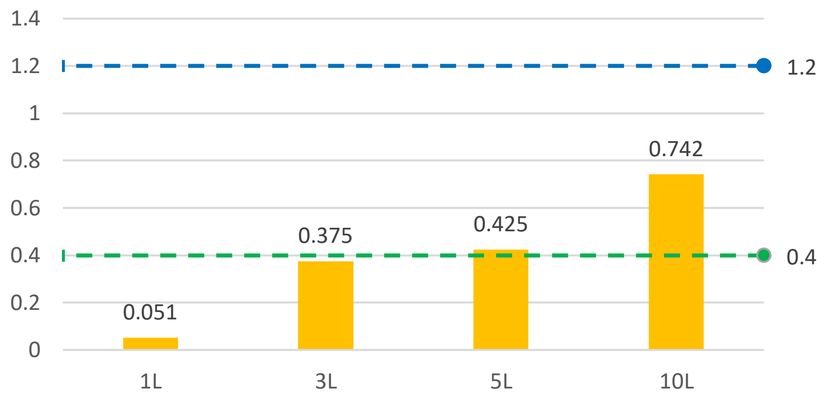

Fig. 2. The final zinc content complies with the maximum permitted limit.

The alkalinity increases slightly when the volume of wastewater is lower, as can be seen in the difference between the 1L and 10L tests. The average hydrogen potential of the tests is 9.56 pH, being remarkable the difference with the initial pH 7.53. (See Fig. 3).

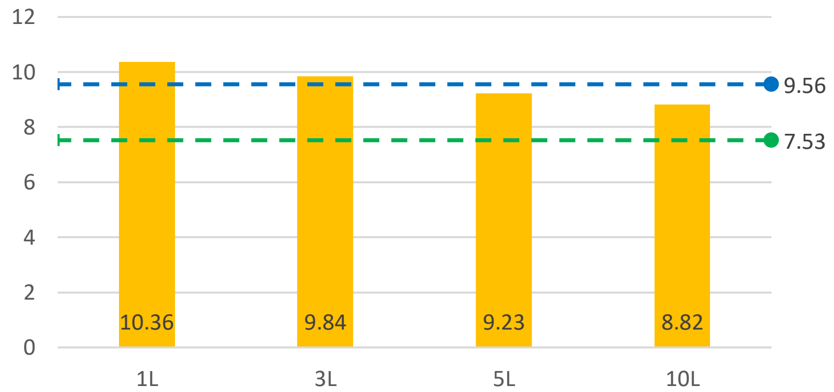

Fig. 3. Hydrogen potential of the assays.

The determined dose decreases its zinc removal efficiency each time the volume of wastewater increases. The effect of pH on zinc removal efficiency, i.e., the highest removal efficiency is 99.49% in the 1L wastewater test and the pH increases its alkalinity from 7.53 to 10.36, while the removal efficiency in the 10L wastewater test is 92.52% and the pH increases its alkalinity from 7.53 to 8.82. (See Fig. 4).

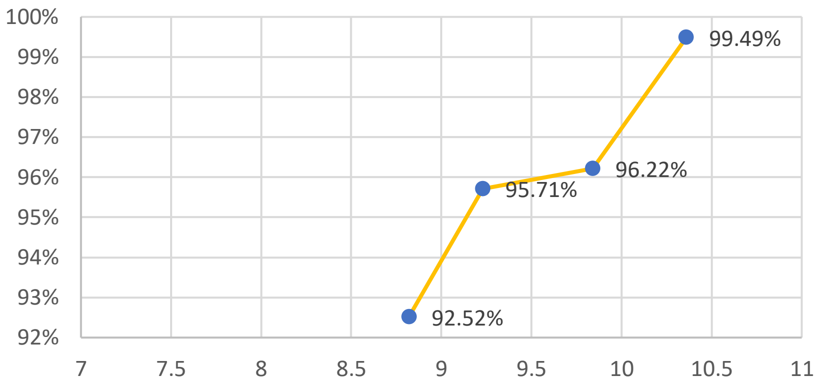

Fig. 4. Effect of pH on zinc removal efficiency.

5.1. Analysis of Variance

The statistical analysis in Table 7 shows that the total sum of squares is 41.2757558, a degree of freedom of 15 observations was determined. For the row (wastewater) F is greater than the critical value, meaning that the H0 that there is a difference between the amounts of wastewater is rejected, and for the column (CaO dose) F is less than the critical value, meaning that the H0 that there is no difference between the CaO doses is accepted.

Table 7. Analysis of variance of two wastewater factors.

Origin of variations	*Sum of squares*	*Degrees of freedom*	*Mean of squares*	*F*	*Probability*	*Critical value for F*
Files	18.2733013	3	6.09110042	4.68315981	0.030968955	3.862548358
Columns	11.2967033	3	3.76556775	2.89516743	0.094356241	3.862548358
Error	11.7057513	9	1.30063903			
Total	41.2757558	15				

H_{oFA}: μR1 = μR2 = μR3 = μR4

H_{iFA}: At least one of the wastewater quantities is different.

6 Discussion of the Results

Water contamination by metal ions causes different effects on the environment and human health. Therefore, eggshell adsorption is proposed as a simple and low-cost procedure to remove these pollutants from wastewater [10]. Eggshell as waste was efficiently used as a neutralizer for effluent treatment. Eggshell powder efficiently removed heavy metal ions from wastewater and its removal efficiency reached 99% [11]. According to the results of zinc adsorption, it is shown that the metallic content reduced in the 4 wastewater tests, after applying CaO or quicklime, this means that it reduced 96%=0.396 mg/L of the metallic content when CaO was applied. Since it complies with the maximum permissible limit of zinc 1.2 mg/L [9]. The MEL wastewater has an alkaline pH of 7.53, and it is also affected when CaO is applied to it, this is observed in Fig. 3 the pH variation in the 1L, 3L, 5L and 10L tests and the average pH tends to reach 9.56.

7 Conclusion

With the results presented in this research, it was demonstrated that calcium carbonate calcination is an efficient and sustainable method to reduce the concentration of zinc in an effluent. Eggshell was used, applying a calcination process to obtain calcium oxide. The calcium oxide was used for a zinc removal treatment, a dose of 0.613 mg/L was applied to reduce the zinc concentration in the effluent. The results obtained were very positive as zinc was removed with an average efficiency of 96%. By analyzing these results, we conclude that eggshell is an effective element to apply to effluents with high zinc concentration.

References

1. Chappuis, M.: Remediación y activación de pasivos ambientales mineros (PAM) en el Perú. (2019)
2. Rodríguez, C., Julca, D.: Gestión del cierre de minas Estudio técnico-legal sobre el alcance de la legislación peruana. (2020)
3. Catillo, L., Satalaya, C., Paredes, Ú., Encalada, M., Zamora, J., Cuadros, M.: Pasivos ambientales mineros en el Perú: Resultados de la auditoría de desempeño sobre gobernanza para el manejo integral de los PAM. Documento de Política en Control Gubernamental. Contraloría General de la República. (2021)
4. Somgohano, R.E.: Evaluación de la fitoxicidad en suelos contaminados por metales pesados en pasivos ambientales minero-metalúrgicos, (2013)
5. Gobierno de la Rioja: Salud y metales pesados - Medio ambiente - Portal del Gobierno de La Rioja, https://www.larioja.org/medio-ambiente/es/calidad-aire-cambio-climatico/calidad-aire/red-biomonitarizacion-metales-pesados-rioja/salud-metales-pesados
6. Aguirre, S.E., Piraneque, N.V., Linero-Cueto, J.: Heavy metals concentration and physical-chemical water quality of the Ciénaga Grande de Santa Marta. Rev. U.D.C.A Actual. Divulg. Cient. 24, (2021). https://doi.org/10.31910/rudca.v24.n1.2021.1313
7. Stadelman, William J.; Cotterill, O.J.: Eggs and egg products. John Wiley and Sons: New York, NY, USA (2000)
8. Ministerio de Energía y Minas - R.M. Nº 200-2021-MINEM/DM - Minería, http://www.minem.gob.pe/_legislacionM.php?idSector=1&idLegislacion=13423
9. Ministerio del Ambiente: Decreto Supremo N° 010-2010-MINAM | Ministerio del Ambiente, https://www.minam.gob.pe/disposiciones/decreto-supremo-n-010-2010-minam/
10. Zonato, R. de O., Estevam, B.R., Perez, I.D., Aparecida dos Santos Ribeiro, V., Boina, R.F.: Eggshell as an adsorbent for removing dyes and metallic ions in aqueous solutions. Clean. Chem. Eng. 2, 100023 (2022). https://doi.org/10.1016/J.CLCE.2022.100023
11. Hassan, E.S.R.E., Rostom, M., Farghaly, F.E., Abdel Khalek, M.A.: Bio-sorption for tannery effluent treatment using eggshell wastes; kinetics, isotherm and thermodynamic study. Egypt. J. Pet. 29, 273–278 (2020). https://doi.org/10.1016/j.ejpe.2020.10.002