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Treatment of mining acidic leachates with indigenous limestone, Zimapan Mexico

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HIGHLIGHTS

- Suitability of native limestones for an acid mine drainage passive treatment system was evaluated.
- Rock dissolution was studied by kinetic batch experiments of H^+ decrease in a Fe-rich acid media.
- The limestone with the highest kinetic constant removed more than 98% As from leachates.
- Chamosite, identified by XRD may participate in the removal of Al, SiO_2 and a fraction of Fe.
- IR and SEM-EDS showed that As removal was mainly from co-precipitation with Fe-hydroxides.

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ABSTRACT

An experimental study to evaluate the potential of using indigenous limestones in a passive system to treat acid mine drainage, at a mining zone of Mexico was carried out. Chemical and mineralogical characteristics of four types of native rocks (KIT1, KIT2, KSS, QZ) showed distinct $CaCO_3$ contents. Synthetic aqueous leachates from an old tailings impoundment had a pH of 2.18, 34 mg/L As, 705 mg/L Fe_{total}, and 3975 mg/L SO_4^{2-}. To evaluate dissolution behavior of rocks, kinetic batch experiments with an acid Fe-rich solution were performed. Decaying kinetic constants adjusting H^+ concentration to a first order exponential process were: KIT1 (k = 2.89), KIT2 (k = 0.89) and KSS (k = 0.47). Infrared spectrum and XRD of precipitates showed schwertmannite formation. To determine As and heavy metals (Fe, Cd, Zn, Al) removal from the synthetic leachates, batch experiments using KIT1 were developed. Arsenic decreased from 34.00 mg/L to 0.04 mg/L, Fe and Al were totally removed, and concentrations of Zn and Cd decreased 88% and 91% respectively. Analyses by IR and SEM-EDS indicate that co-precipitation with Fe-Hydroxides formed upon leachate interaction with limestone is the main As removal process. Chamosite, identified by XRD may participate in the removal of Al, SiO_2 and a fraction of Fe.

1. Introduction

Ore benefit gives important economic profits worldwide. Nevertheless, ore extraction and processing also produce hazardous wastes such as tailings. Frequently, these wastes contain sulfides like pyrite (FeS_2), pyrrothite ($Fe_{1-x}S$), galena (PbS), sphalerite (ZnS), and arsenopyrite (FeAsS) [1,2]. Weathering oxidizes sulfides producing acid mine drainage (AMD) solutions characterized by high concentrations of metals, sulfates and an acid pH [1]. In Zimapán, México, mining has been an important economic activity since the XVI century [3]. This activity has produced about seven tailing piles which are located at the town outskirts [4]. The potential environmental effect of tailings has promoted the development of diverse studies on the residues, soils and waters. Romero et al. [2] characterized the mineralogy and geochemistry of some of the tailing piles. They identified secondary phases like gypsum ($CaSO_4{\cdot}2H_2O$), K-jarosite ($KFe_3(SO_4)_2(OH)_6$), beudantite ($PbFe_3(AsO_4)(SO_4)(OH)_6$), and goethite ($\alpha$-FeOOH), formed by sulfides alteration, and measured up to 897.5 mg/L Fe, 48.86 mg/L As, 400 mg/L Zn and 3625 mg/L SO_4 in aqueous extractions. Méndez and Armienta [4] studied the geochemical fractionation of As in some tailings, among them the called Compañía Minera Zimapán (CMZ), one of the oldest deposits. High available As concentration (435 mg/kg) and leachates with an acid pH (3.0), were determined. AMD produced in the rainy season from these tailings flows over the pile and reaches the Tolimán River [5]. This process has also been linked with As contamination of nearby shallow wells used by dwellers for irrigation [6]. Observed environmental effects

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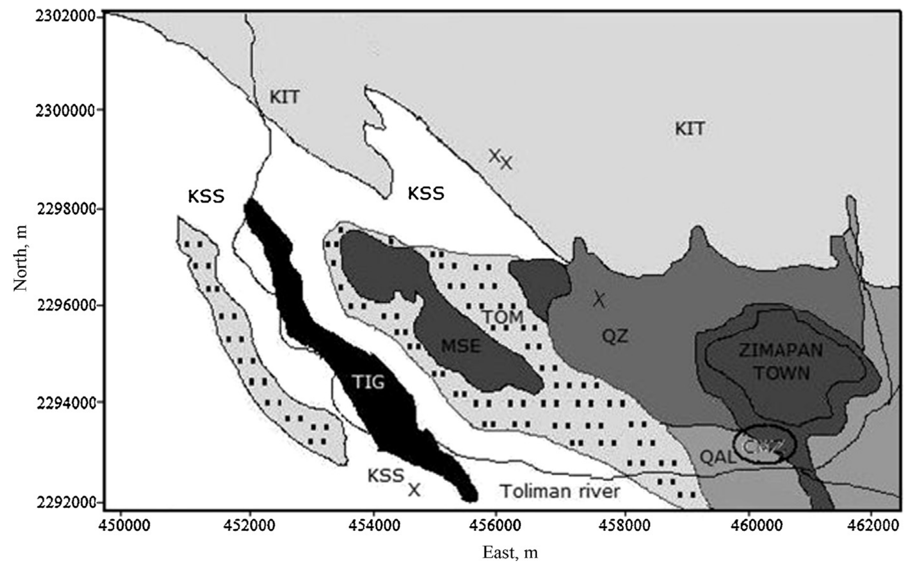

Fig. 1. Geological map of Zimapán (UTM coordinates). KIT (Tamaulipas Formation), TOM (Morro Formation), Tig (Intrusive igneous rocks), MSE (Las Espinas Formation), KSS (Soyatal Formation), QZ (Zimapan Fanglomerate), QAL (Quaternary Alluvium). CMZ represents the studied tailings impoundment, X corresponds to sampling sites.

evidence the need to develop mitigation alternatives to decrease the tailings impact. Passive treatment systems (PTS) are one method used to treat AMD. These systems allow the flow of water while improving its quality [7]. Cravotta III [8] described a PTS as crushed limestone that is placed in a buried bed to intercept AMD. These systems have been evaluated at laboratory scale using batch and column experiments [9–11], and at field scale at several locations [8,12,13]. PTS have been proven adequate to increase pH and remove Cu, Zn, Pb and Cd [9,11]. Limestones, which have been used as fillings of PTS are abundant at Zimapán. Using of these rocks is a cheap option since expenses to buy and transport raw material are minimized. Besides, since these systems do not require constant supervision, they are a potential option to use at Zimapán. Additionally, remediation technologies of mining zones are an emerging field in México; hence, the effectiveness of such methods requires detailed studies.

Upon interaction with AMD, limestone dissolves and pH increases [8] (Eqs. (1)–(3)):

$$CaCO_{3(s)} + H_{(ac)}{}^{+} \leftrightarrow Ca_{(ac)}{}^{2+} + HCO_{3(ac)}{}^{-} \tag{1}$$

$$CaCO_{3(s)} + H_2CO_3{}^{0} \leftrightarrow Ca_{(ac)}{}^{2+} + 2HCO_{3(ac)}{}^{-} \tag{2}$$

$$CaCO_{3(s)} + H_2O \leftrightarrow Ca_{(ac)}{}^{2+} + HCO_{3(ac)}{}^{-} + OH_{(ac)}{}^{-} \tag{3}$$

As pH rises, presence of Fe and Al in the acid solution promotes formation of Fe and Al hydroxides ((Eqs. (4) and (5)) [10]. These hydroxides may retain metals and As oxyanions (as $HAsO_4{}^{2-}$, $H_2AsO_4{}^{-}$) by sorption processes [14]. However, metal oxyhydroxides formation has opposite effects since they also cover the limestone surface decreasing its reactivity [11,12]:

$$Fe_{(ac)}{}^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H_{(ac)}{}^{+} \tag{4}$$

$$Al_{(ac)}{}^{3+} + 3H_2O \leftrightarrow Al(OH)_{3(s)} + 3H_{(ac)}{}^{+} \tag{5}$$

In view of these opposite effects, the limestone to be used in a PTS must be evaluated to assess a long life time and a high removal of contaminants. Effectiveness of PTS depends mainly on the specific limestone mineralogy, AMD composition, and environmental conditions. In spite of the importance of these factors to improve PTS performance, few studies have been focused on evaluating natural geologic materials outcropping in a specific mining zone to build the PTS. In fact, the traditional procedure to evaluate limestone to treat AMD is by following the kinetic rocks dissolution behavior based on the determination of Ca and/or alkalinity [8,15]. This study was developed with the aim of identifying the best indigenous limestone from four types of rocks outcropping in Zimapán, Mexico to be used in a PTS to efficiently treat AMD produced from CMZ. Two experiments were done to reach this goal. In the first one, a novel approach to determine the effectiveness of each indigenous limestone to treat ADM was applied by monitoring the decay of H^+ ions in an acid solution containing high Fe(III) and SO_4. In the second one, the capacity of the rock with the highest kinetic constant to remove arsenic and metals from acid synthetic leachates in batch experiments was evaluated. Removal mechanisms of species present in the leachates were proposed based on mineralogical analyses (XRD, SEM–EDS, FTIR-ATR), and by using thermodynamic data to calculate saturation indices to predict possible formation of mineral phases. A global reaction considering initial and final concentrations was used to calculate Ca and alkalinity produced by the rock–leachate interaction process by minimizing the cation–anion difference. Results will also be used as a basis to built column experiments to better simulate a limestone-based PTS.

2. Methods

2.1. Site description

Zimapán, is located west of Hidalgo State, Central México at 20°44′ N latitude and 99°23′W longitude and 1780 m a.s.l. It is a semi-arid zone with a rainfall range from 400 mm to 1100 mm and a population of 38,516 in habitants reported in 2010 [16]. Geological framework is constituted by various Formations, among them (Fig. 1): the Lower Cretaceous Tamaulipas Formation formed by limestones (KIT), the Upper Createaceous Soyatal Formation formed by shales alternating with marls and limestones (KSS), the Las Espinas Formation from the Tertiary constituted by volcanic rocks (MSE), the El Morro Group from the Tertiary formed by semi angular limestone marls and volcanic clasts (TOM), the Quaternary Zimapán Fanglomerate formed by limestone fragments from the Lower Cretaceous cemented by caliche (QZ). Intrusive quartz-monzonitic rocks varying from diorite to granodiorite are also present in the area (TIG) [17]. Zimapán is an important location of ore deposits, mainly replacement bodies and skarns. Main minerals are: pyrite, pyrrhotite, sphalerite, galena,