Acid Drainage Treatment Using Phyllite Rock in an Underground Mine

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ABSTRACT

Tizapa mine is located in the State of Mexico, Mexico, the ore deposit is volcanogenic and its mineralization consists of Fe, Zn, Pb, Cu and As sulfides and Ag sulfosalts. Pyrite is the most abundant sulfide mineral and is found in massive and disseminated form. The host rock is schist and graphitic phyllite, their composition is mainly quartz, plagioclase, chlorite and muscovite; but the phyllite also has abundant calcite as filling fissures. Presence of water in the underground mine generates acid mine drainage (AMD) in old working areas. Water source was evaluated by testing soil infiltration, permeability and fracturing of the rock. AMD pH varies from 2.4 to 3.4; it has high conductivity and soluble concentrations of Fe, Al, Cu, Cd, Mn, Zn and sulfates. The flow varies from 0.7 L/s to 1.7 L/s and the presence of water is mainly associated to an upper aquifer. AMD drains down a ramp and it is directed to an active treatment plant inside the mine. Treatment involves raising the pH using sodium carbonate to a 5.5 value. Phyllite associated with calcite allows proposing a passive treatment system alternative to control the AMD. The objective of this work is to develop a passive system using phyllite rock to neutralize the AMD within the mine to replace the current active treatment plant. Stirring batch tests were conducted to raise the pH to values between 6.2 and 6.6. Removal of 100% (Fe, Al, and Cu), 19-40% (Cd), 0-32% (Mn) and 4-36% (Zn) was achieved. Currently, the research is focused on the design of an open canal system with phyllite to install it in different parts of the mine and force the AD to flow through it.

Keywords: Acid mine drainage, passive treatment, phyllite rock, underground mine

INTRODUCTION

Acid mine drainage (AMD) is a natural phenomenon that occurs in mining working areas or waste deposits where sulphide minerals have been exposed to environmental conditions of weathering (Lottermoser, 2007). There has been much research on the development of treatment methods for the control of AMD, mainly into so-called passive treatments (López et al., 2002; Johnson et al., 2005). Some of the main passive treatment methods have been applied to AMD such as limestone canal systems (Alcolea et al., 2012) or permeable reactive barriers (Macías et al., 2012). These applications have been made to treat acid drainage generated in waste deposits, or acid drainage which comes from mining works and receives treatment outside of the mine. However, little research has been done on controlling acid drainage inside mines which are still in operation and where this may have further effects on the aquifers. The poor quality water in abandoned mining areas is partly associated with the generation of acid drainage from mining works (Younger et al., 2002; Wolkersdorfer, 2008). Tizapa mine is located in the State of Mexico, Mexico (Figure 1). The ore is a volcano-sedimentary deposit of massive Zn-Pb-Cu with Ag and Au values sulphide mineral (Coremi, 1996; Alfonso et al., 2011). Mineralization consists mainly of pyrite, sphalerite, chalcopyrite, arsenopyrite, pyrrhotite and freibergita. In old working areas located nearest to the surface, AMD is being generated by the presence of water, coming primarily from shallow aquifers and surface infiltration from rainwater. Inside the mine AMD is drained by canals leading to a treatment plant where it is then neutralized by a solution of sodium carbonate. The neutralized water is used for mineral processing.

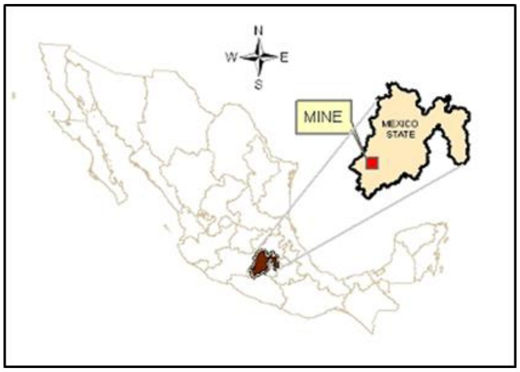


Figure 1 Mine location

Stratigraphy of the area consists of metamorphic rocks from the Triassic-Jurassic: phyllites and gneisses; above these, it is a set of metavolcanic rocks consisting of phyllites and schists of chlorite and sericite. Over the metamorphic rocks, lies a group of Cretaceous rocks: limestone and clastic rocks. Finally Quaternaries conglomerates and basalts cover the volcano-sedimentary sequence (Alfonso et al., 2011). The host rock associated to the ore deposit is chlorite and sericite schist at the base and graphitic phyllite at the top (Figure 2). Phyllite rock has abundant content of calcite mineral ($CaCO_3$), which allows considering its usefulness in a treatment system to neutralize the AMD. Also, near the mine there is a small outcrop of limestone which can be used for treatment too.

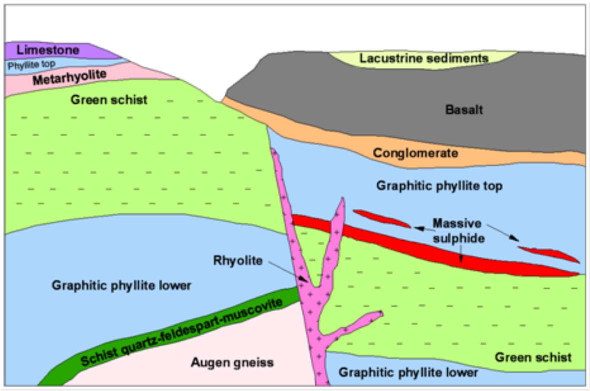


Figure 2 Mine stratigraphy and rocks associated to ore deposit

The aim of this work is to develop a passive treatment system using the phyllite rock, which could be installed inside the mine to control the AMD. Currently, work is carried out at laboratory level and conditions inside the mine are under study for the system installation.

METHODOLOGY

Identification and measurement of the AMD

Walks through the mine were performed to identify the AMD generating sites. The pH at each of these AMD generating sites was measured and located on the mine maps. The AMD flow rate was estimated by using the volumetric gauging method at each of the generating sites. The measurements were made three times, each one at different seasons of the year; the first one in May (end of low water season), the second one in July (in the middle of rainy season) and the third one in September (end of rainy season).

Water source

To determine from where the mine water is coming, analysis of the available information on rainfall (registered by a mine's weather station) and aquifers located in the area (information generated by the Water National Commission of Mexico) were conducted. Three infiltration tests were performed on the soil at the mine's surface, and the watershed runoff rate where the mine is located was determined. Furthermore, permeability tests were conducted on samples of three different rock types recovered by drilling cores: phyllite, shale and tuff. Finally, an analysis of the rock's fracturing, in places where acidic water is generated, was made.

AMD and rock characterization

Four mine's AMD samples were taken and analyzed to obtain the pH, electrical conductivity, and the concentration of major ions and trace elements. Trace elements were determined by Optical Emission Spectrometry with Inductively Coupled Plasma (ICP-EOS) on a Perkin Elmer instrument; and major ions by ion chromatography using an 883 Basic IC plus Metrohm chromatograph.

Three phyllite rock samples were taken inside the mine and a limestone sample was taken from an outcrop located outside the mine. The mineralogical composition of the rocks was determined by optical microscopy (parallel light and polarized light) and X-ray diffraction on a Shimadzu Lab X XRD-6000 equipment. The metal concentration was obtained by XRF on a Siemens SRS 3000 instrument. An analysis by scanning electron microscopy coupled with x-ray spectrometry by dispersive energy (SEM-EDS) was carried out.

Batch tests in flasks

Preliminary laboratory tests were made in batches; phyllite rock with acid drainage was stirred in 250 mL flasks at 200 rpm. During the first stage, the parameters evaluated were, the rock's grain size (2, 2.36 and 3.35 mm), the stirring time (18, 24 and 36 hours) and rock/AMD ratio (1/5, 1/10 to 1/20). With these tests, the schist's ability to neutralize acidity was determined. In the second stage, batch testing continued to determine the minimum time required to achieve a neutral pH; for this stage only rocks with a grain size of 3.35 mm was used, but the rock/AMD ratios remained (1/5, 1/10 and 1/20). The stirring was stopped every five minutes to measure the pH; tests were stopped when a pH value between 5 and 6 was achieved. The solutions obtained after neutralization were analyzed by ICP-EOS.

In a third stage, two step stirring tests were conducted. In the first step the AMD was stirred with phyllite rock until a pH value of 5 was reached, and in the second step the resulting solution was stirred with limestone to raise the pH above 7. The final solutions obtained were analyzed to determine the concentration of trace elements and major ions. Residual sediments obtained in both steps were analyzed by scanning electron microscopy coupled with x-ray spectrometry by dispersive energy (SEM-EDS) on a Hitachi Tabletop TM-1000

Filled cells testing

Currently, tests are carried out using an acrylic cell filled with the phyllite rock, through which the AMD flow passes. The cell can hold 3.5 L and 5 kg of rock with a size between 4.75 and 12.5 mm (Figure 3). The aim of these tests is to evaluate the retention time needed to raise the pH; therefore, the flow rate passing through the cell varies (2.5 to 12.5 ml/s).

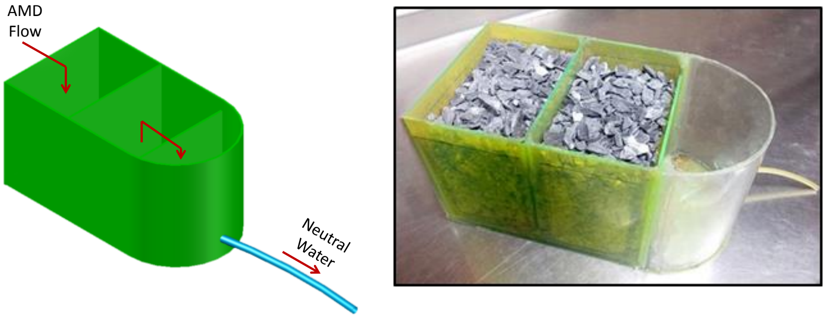


Figure 3 Testing in rock filled cell (currently in development)

The results are positive so far; however, are not reported in this paper because they are not yet considered conclusive. After these tests, the next step will be to upscale the system in order to perform a pilot test inside the mine.

RESULTS AND DISCUSSION

AMD generation

Eleven sites where AMD is generated were located within the mine, all of these connected to old mining works located between levels 1226 and 1040 m.a.s.l., and corresponding to the mine zone nearest to the surface. Measured pH varies from 2.4 to 4.6. All AMD runoff is driven by canals to the principal ramp where it is lead to the treatment plant.

The measured flow of AMD in May was 0.73 L/s, in July was 0.95 L/s, and in September was 1.74 L/s. Neutral water runoff was also found inside the mine and flows obtained were 2.05 L/s in May, 2.27 L/s in July and 1.8 L/s in September.

Water source

Infiltration tests on soils show that infiltration rates are slow to moderate (0.078 to 2.07 cm/h). Furthermore, measured permeability in the rock samples is very low; the average value is between 4.8 E-10 cm/s and 5.09 E-06 cm/s.

In order to determine rainwater infiltration volume in the study area, the average rainfall data recorded at the mine's meteorological station was used, and for the runoff coefficient the Mexican regulations methodology (SEMARNAT, 2002) was used. Furthermore, the subwatershed area was measured in the zone where AMD is generated. It was determined that the water runoff coefficient is 0.184 and, considering that subwatershed area is 0.151 km^2, it was estimated that rainwater infiltration volume is 0.031 Mm^3/year.

The maximum value of water running inside the mine, measured in September 3.54 L/s (AMD plus neutral water), was considered as a constant throughout the year, giving an estimation of 0.112 Mm^3 of water running inside the mine pear year. Comparing this value with the calculated stormwater infiltration value of 0.031 Mm^3/year, the rainwater represents only 27.7% of the total water in the mine.

In Zacazonapan town (4 km away from the mine) it is reported that the Temascaltepec aquifer is 1 to 2 meters deep and has a 1368 m.a.s.l. elevation (Conagua, 2008). This aquifer provides water to the stream "El Ahogado" which runs next to the mine at an elevation of 1226 m.a.s.l., and so, it is interpreted that the aquifer water flows over the old mining works which generate AMD.

Structural analysis of the rock where AMD is generated shows a high degree of natural fracturing at 1052, 1100 and 1200 m.a.s.l. elevations in two preferred directions: NW-SE and NE-SW.

From the information presented above it has been concluded that rainwater contribution to the water running through the mine is minimal, due the low permeability of soil and rock. From the information available about the aquifer, it is estimated that it runs close to surface level and above the mining works. Due the high fracturing level, water from the aquifer and rainwater flow through the fractures to the mining works thus generating AMD.

AMD and rock characterization

The pH values and electrical conductivity are shown in Table 1. The pH values obtained confirm the acidity of water and the high electrical conductivity is largely due the ions in solution and salts dissolved in water.

Table 1 Trace elements concentration in AMD

Sample	pH	EC (mS)	Al	Cd	Cu	Fe	Mn	Si	Zn
			mg/L						
DA 6	2.44	11.31	41	6	12	563	41	35	483
DA 6 - A	2.53	8.02	36	5	12	527	37	32	471
Pileta	2.9	4.72	9	2	2	178	26	17	363
DA 8	3.38	1.87	<LD	0.2	<LD	0.3	4	8	77

LD (mg/L): Al (0.08), Cu (0.12)

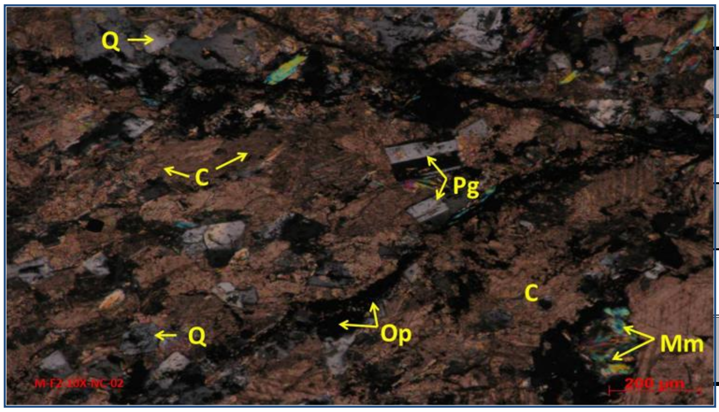
Significant concentrations of Al, Cd, Cu, Fe, Mn, Si and Zn were found (Table 1). Other elements, As, Cr, Mo, Sb, Se, Ti, Tl and V, were analyzed and are in concentrations below the detection limit.

Major concentrations of ions (Table 2) are high for Na, K, Ca and Mg cations due to the dissolution of silicate minerals present in the rocks which began to dissolve after the carbonates were consumed. A high concentration of sulphates indicates the chemical oxidation process of sulphides and is directly related to water soluble iron. Presence of chlorides is related to chlorite content in the schist rock.

Table 2 Major ion concentrations in AMD

Sample	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
	ppm					
DA 6	228	21	438	1,759	92	18,732
DA 6 - A	197	4	369	1,674	82	16,555
Pileta	354	19	310	1,601	176	10,118
DA 8	114	14	252	380	35	2,896

Petrographic analysis showed that there is abundant calcite in the phyllite rock (Figure 4); however, the presence of plagioclase mineral is also interesting, since it is reported in literature that this could be used to neutralize AMD (Romero et al., 2007).



Op	Opaque minerals
Mm	Muscovite mica
C	Calcite
Pg	Plagioclase
Q	Quartz

Figure 4 Photomicrograph of phyllite rock 10 X magnification

XRD confirms that phyllite has high calcite content and abundant presence of plagioclase and micas. The mineralogy suggests that phyllite has potential to neutralize AMD. Limestone was also analyzed and dominance of calcite and quartz was observed; to a lesser extent, intermediate plagioclase and phyllosilicates (chlorite and mica) are also present.

Batch tests in flasks

In the first stage of the tests, pH values of 5.35 (3.35 mm, 18 hours, 1/20) to 7.36 (2 mm, 36 hours, 1/5) were achieved. The neutralization process is enhanced with smaller particle sizes, lower rock/AMD ratio, and increased stirring time. Figure 5 shows only the pH increase using 3.35 mm particle size; as larger particle sizes will be needed when moving forward in the research.

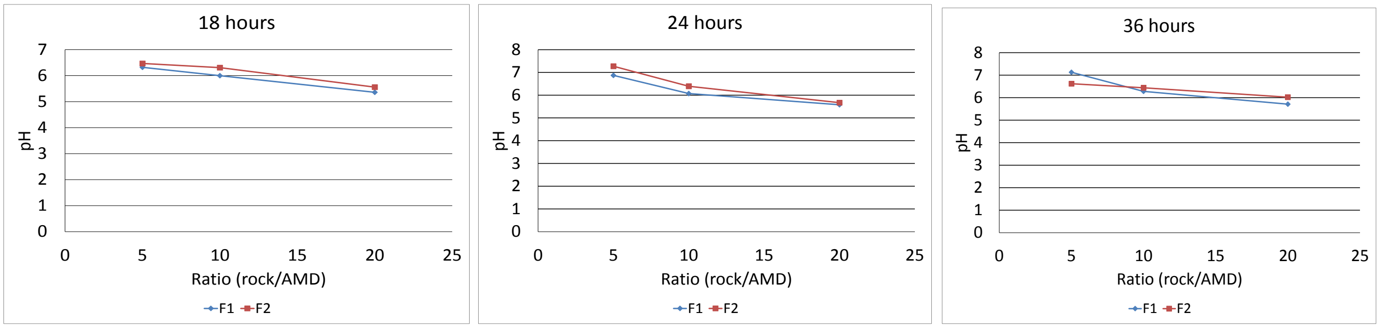


Figure 5 pH values reached in stirring tests with particle size of 3.35 mm

In the second stage of tests, the highest stirring time was necessary for the 1/20 ratio test, as 180 minutes were needed to reach a maximum pH value of 4.7. With the 1/5 ratio test, a minimum stirring time of 30 minutes was enough to reach a pH value of 5.55 (Figure 6).

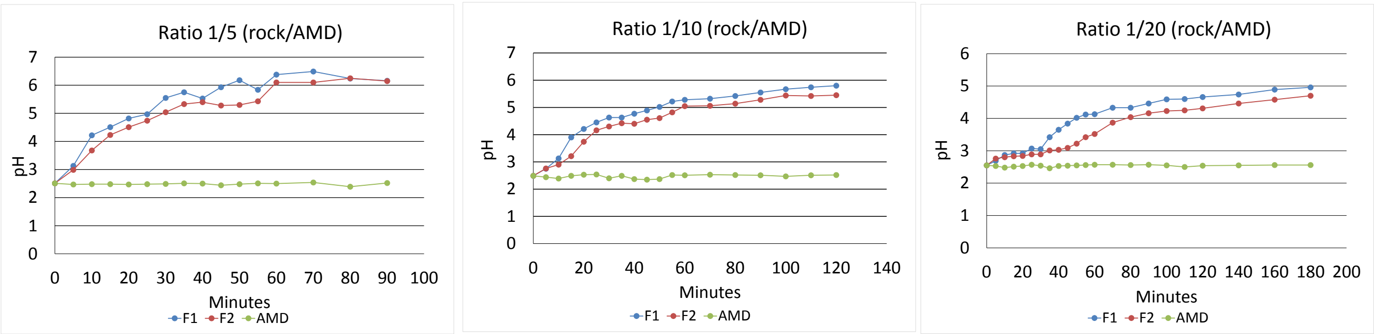


Figure 6 Minimum stirring times to achieve neutral pH values

Table 3 shows trace element concentrations in the solutions after neutralization; samples B-20, B-10 and B-5 correspond to acid drainage without treatment. A direct relationship between pH reached and rock/ AMD ratio is observed. The highest pH value was obtained with a 1/5 ratio. It is noted that with a 1/10 ratio, total removal of Fe, Al and Cu is achieved at a pH value of 4.97 (F1-10). Cd and Zn concentration decreases from pH values above 6.55 (F2-5), achieving at this value an 18% removal for Cd and 20% for Zn. In contrast, Mn remains practically at the same level, because this element requires pH values above 8 to precipitate (Luan, et al., 2012; Silva, et al., 2012.). Si removal is also high, between 65 to 76% with a 1/5 ratio.

Table 3 Trace element concentrations in neutralized solutions (second stage)

Sample	pH	EC (mS)	Al	Cd	Cu	Fe	Mn	Si	Zn
			mg/L						
B - 20	2.53	8.21	21	2	2	128	2	23	294
F1 - 20	4.39	7.62	1	2	1	<LD	3	20	295
F2 - 20	3.88	7.49	4	2	1	1	3	23	300
B - 10	2.49	8.02	19	2	2	116	2	21	293
F1 - 10	4.97	7.34	<LD	2	<LD	<LD	2	12	269
F2 - 10	4.73	7.38	<LD	3	0.1	2	4	22	319
B - 5	2.62	7.6	20	2	2	112	2	22	309
F1 - 5	6.57	6.96	<LD	2	<LD	<LD	3	5	217
F2 - 5	6.55	6.81	<LD	2	<LD	<LD	3	8	247

LD (mg/L): Al (0.08), Cu (0.12), Fe (0.01)

In the third stage, stirring was done in two steps, the first with phyllite rock and the second with limestone. Sample B corresponds to untreated AMD. Table 4 shows that pH values between 5.0 and 6.67 were reached with phyllite rock in the first step, and between 7.33 and 7.64 were reached in the second step with limestone rock. In the first step, 100% of Al, Cu and Fe was removed; and between 9 and 41% of Cd, 45 and 74% of Si, 2 and 12% of Zn and 0 and 32% of Mn, were removed. In the second step, almost 100 % removal of Cd was achieved, as well as a removal from 82 to 92% of Si, 95 to 99% of Zn and 89 to 97% of Mn.

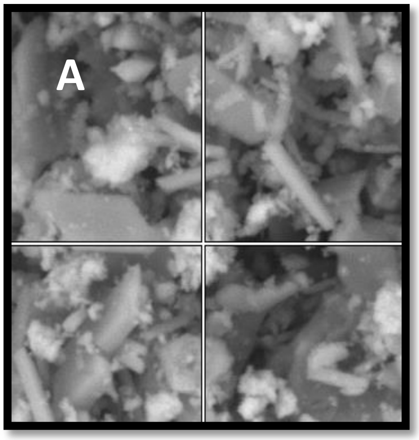
Table 4 Trace elements concentration in neutralized solutions of 1st and 2nd steps (third stage)

Sample	pH		Al		Cd		Cu		Fe		Mn		Si		Zn	
			mg/L													
	1a	2a	1a	2a	1a	2a	1a	2a	1a	2a	1a	2a	1a	2a	1a	2a
B	2.74	2.82	19	18	2	2	2	2	112	102	23	22	24	23	320	309
F1	6.64	7.26	<LD	<LD	1.3	0.1	<LD	<LD	<LD	<LD	16	2	6	2	205	14
F2	5.00	7.33	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	20	1	10	2	259	1
F2-d	6.67	7.64	<LD	<LD	2	<LD	<LD	<LD	<LD	<LD	26	2	13	3	311	2

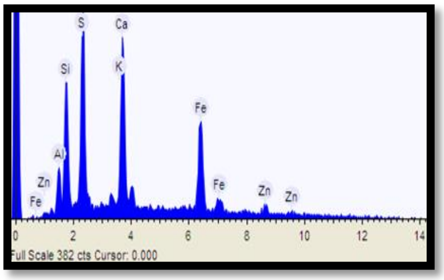
LD (mg/L): Al (0.08), Cd 80.02), Cu (0.12), Fe (0.01), Mn (0.007), Si (0.008) y Zn (0.007)

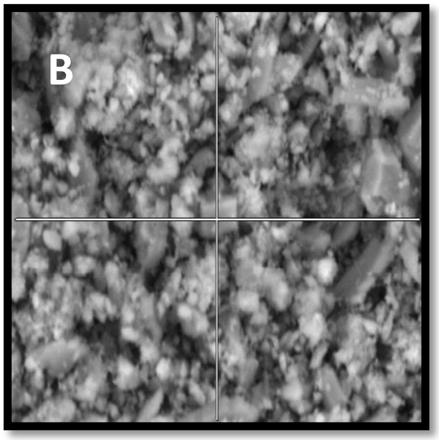
Concentration of Al, Fe, Zn and Mn in the phyllite rock, determined by XRF, were of 7.28%, 2.95%, 0.02% and 0.05%, respectively; in the after neutralization phyllite sediment photomicrographs (Figure 7 – A), it is observed an increase in the concentration of Fe (40.5%) and Zn (2.7%). The limestone rock has in its composition 3.69% of Al, 2.09% of Fe, 0.01% of Zn and 0.14% of Mn; the after neutralization limestone sediment photomicrographs (Figure 7 – B), also show an increase on Fe (2.5%), Zn (16.8%) and Mn (1.1%) concentrations. These results indicate that Fe, Zn and Mn are been retained in the rock's sediments after the neutralization of AMD.

At this stage it was determined that it is appropriate to use phyllite rock to increase pH to values between 5 and 6, and precipitate Al, Cu and Fe; then use limestone to raise pH above 7 and remove the largest portion of Cd, Mn and Zn.



F1-S		
%		
Al	Fe	Zn
4.0	40.5	2.7





F1C-S			
%			
Al	Fe	Mn	Zn
2.1	2.5	1.1	16.8

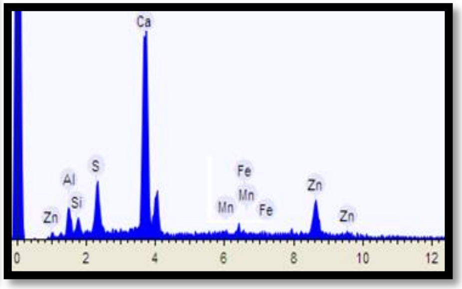


Figure 7 Photomicrographs obtained by SEM-EDS of phyllite (A) and limestone (B) sediments after neutralization.

CONCLUSIONS

The AMD inside the mine is generated in the old mining works, close to the surface level, due to the contact of exposed sulphide minerals with the water of a shallow aquifer and the rainwater flowing through fractured rock. It is possible to lead AMD through canals to the principal works of the mine for a subsequent treatment. The phyllite rock associated with the ore deposit is useful in neutralizing the AMD due to its high content of calcite. Laboratory tests results show that it is possible to achieve pH values between 6 and 7 with phyllite rock. The phyllite allows removal of 100% of Al, Fe and Cu at pH values between 5 and 6. Using limestone, available on an outcrop near the mine, it is possible to raise pH above 7 achieving removal of 100% of Cd, 95% of Zn and 89% of Mn. It is advisable to continue the tests with rock packed cells and then design a system that can be scaled to install it inside the mine.

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