

**HYDROGEOCHEMICAL STUDY OF THE GROUNDWATER AROUND THE ABANDONED
KETTARA MINE SITE, MOROCCO**

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ABSTRACT

Acid mine drainage (AMD) remains one of the major environmental problems for the mining industry particularly for many abandoned mine sites. The production of AMD as is commonly known can significantly affect the surrounding groundwater and surface water of the mine site. With the objective to investigate the impact of the AMD produced at the abandoned Kettara mine site (Morocco), groundwater sampling campaign was performed at this site. The sampled waters were analyzed to determine the hydrogeochemical composition, and then results were analyzed using different studied methods such as multivariate statistical analysis and geochemical modeling techniques.

Investigation results show that the hydrochemistry of sampled waters is characterized by the relatively significant enrichment of Ca^{2+} , Mg^{2+} and SO_4^{2-} . The typical mine waters belong to the $(\text{Ca}^{2+} + \text{Mg}^{2+})\text{-SO}_4^{2-}$ type. Seasonal variations in major ion concentrations were partly attributed to dissolution/precipitation processes. The saturation index (SI) calculation of the representative dissolved minerals in waters show that groundwater samples are undersaturated with respect to most potential sulphated secondary minerals.

KEYWORDS

Kettara abandoned mine, Acid mine drainage, Hydrochemistry, Groundwater, Contamination

INTRODUCTION

Acid Mine Drainage (AMD; also called ARD for Acid Rock Drainage) from mine wastes is one of the most challenging environmental problems currently facing the mining industry. Mining operations produce large amounts of waste such as waste rock and tailings that must be properly managed to protect the environment. In this regard, more attention is required when these wastes contain sulphidic minerals such as pyrite and pyrrhotite. The oxidation of sulphides exposed to atmospheric conditions tends to acidify waters which are then more prone to mobilise metals contained in the rock; these two phenomena generate an acidic leachate called AMD (e.g., Ritcey, 1989; SRK, 1989; Aubertin et al., 2002).

When mine wastes have the potential to produce AMD, waste management and mine site rehabilitation should be performed to inhibit the AMD generation; effluents produced should also be managed properly to meet existing regulations on water quality (see Maqsoud et al., 2012). If not managed properly, such as the case of the Kettara mine site, AMD production occurs and can affect the surrounding mine site area.

In arid or semi-arid climatic conditions, where the precipitations and surface runoff are limited, the groundwater resources are highly affected. For this reason, this study is performed to evaluate the groundwater quality around the Kettara abandoned mine site and to examine the potential effects of AMD production in the groundwater contamination.

This paper provides a conceptual assessment in order to better understand the dominant hydro-geochemical processes controlling spatial variation in chemical composition of the groundwater. The

hydro-geochemical processes governing water quality were determined by examining the groundwater types based on major ion data and principal components analysis (PCA).

MATERIALS AND METHODS

The Study Area

Kettara Mine

The abandoned Kettara pyrrhotite ore mine is located approximately 30 km north–north–west of Marrakech city in the core of the central Jebilet Mountains (see Figure 1 for location). The mining village of Kettara and the mining infrastructure are located downstream from the tailings pond area (Figure 1b). According to the latest statistics (2004), the population of Kettara is approximately 2,000. The climate is classified as semi-arid with a mean annual rainfall of approximately 250 mm. Rainfall can occur over short periods and with high intensity. The annual potential evaporation typically exceeds 2,500 mm.

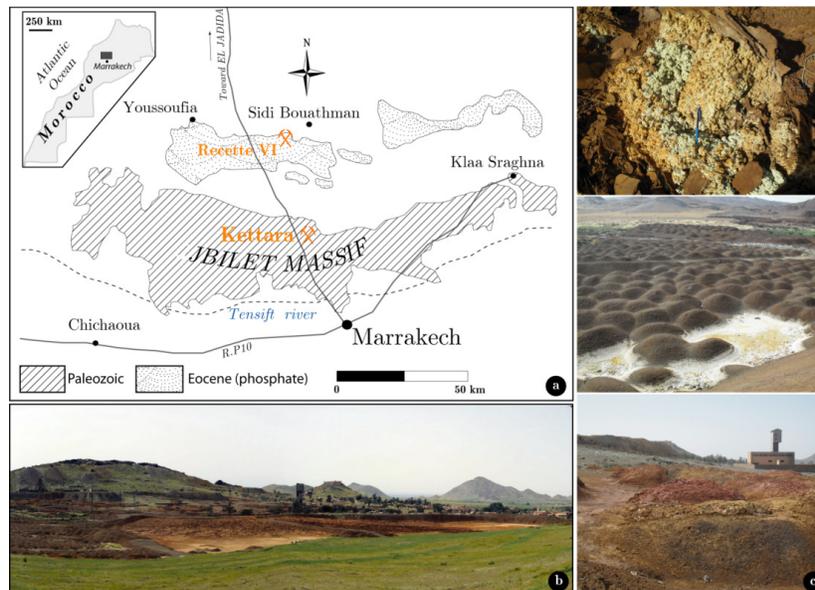


Figure 1 – The study area: (a) Location, (b) a panoramic view, and (c) photos illustrating the presence of secondary minerals

From 1964–1981, the mine produced more than 5.2 million metric tonnes of pyrrhotite concentrate containing an average of 29 % wt sulphide. The Pyrrhotite extraction generated tailings with a wide range of particle size distribution. Although ore reserves were still abundant, the mine was closed in June 1982 due to difficulties encountered during pyrrhotite concentrate production.

Based on the grain-size distribution (see Bossé et al., in press), tailings materials can be divided into two classes: a) coarse tailings (fine gravel) deposited on the 15 m high dyke and in 1 m high tailings piles; b) fine tailings (silt) deposited in the tailings pond. The Kettara wastes contain 1.6–14.5 wt% sulphur, mainly as sulphide minerals (e.g., pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite; Hakkou et al., 2008). The large particle size and the high hydraulic permeability of tailings allow oxygen transport and water percolation; consequently, the pollution potential of the coarse tailings in Kettara is much greater than that of the fine tailings.

Because Kettara mine tailings were abandoned for many years without any rehabilitation, significant amounts of AMD were produced and tailings piles and pond will continue to release AMD for a

long time. Also, several secondary minerals have been observed at the surface of the mine site and additional precipitates occur in other forms, such as ‘blooms’ or efflorescent salts. The presence of these minerals in large quantities shows that AMD generation is still very active at Kettara mine site.

Geological and hydrogeological setting

The central Jebilet metapelites (Sarhlef schists) outcrop a few kilometres north of Marrakech in a wide area corresponding to the central unit of the Hercynian Jebilet massif. The Sarhlef schists are derived from Middle to Upper Visean shales deposited in an anoxic platform and are affected by a very-low-to low-grade metamorphism contemporaneous with a post-Visean shortening. Deformation and metamorphic gradients are observed towards the major shear zones, and there are numerous intrusions present in the unit (Huvelin, 1977). Sulphide deposits in the studied area are generally located close to the intrusions. These ore bodies are organized into subvertical lineaments concurrently with the regional schistosity.

The Kettara sulphide deposit is a typical example of a metamorphosed deposit hosted by Visean volcano-sedimentary formations. The tectonic and microtectonic structures observed in the neighborhoods of the principal surface of the tailings correspond to strike-slip faults with quartzo-carbonated seams and micro-fractures with quartzitic seams, and schistosity, which affects all of the black shale formation (Lghoul et al., 2012).

In the central Jebilet, Sarhlef shales and Bamega granite are the two major aquifers in the area. The sheet of water in these formations is relatively shallow. The aquifer is characterized by a low permeability where the transmissivity is about of $9 \times 10^{-4} \text{ m}^2/\text{s}$ and the storage coefficient about 5×10^{-2} (El Mandour, 1990).

The piezometric map, which was built with more than 15 measurement points (Figure 2), shows that the water table is located at an average depth of 18 m. The depth of the water table can be explained by an overexploitation of groundwater by agricultural activities. Analysis of the map also shows that the direction of the groundwater flow is generally from north-east to south-west.

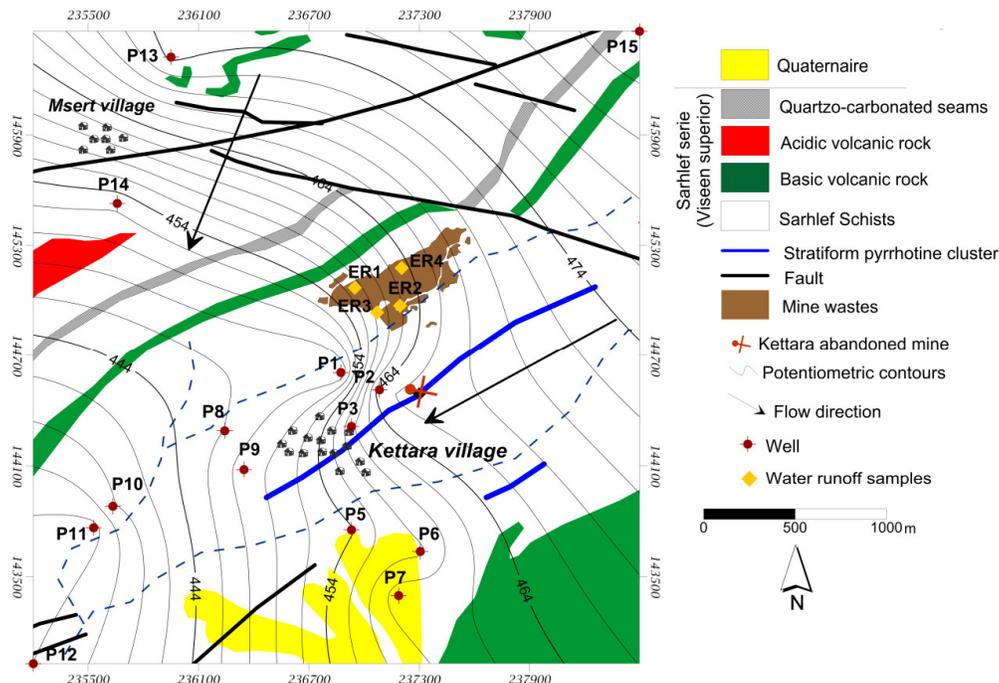


Figure 2 – Geological and hydrogeological map of study area

Sampling and analytical procedure

The physico-chemical water quality was determined for surface water and groundwater collected during a campaign performed in March 2011. A total of 15 groundwater samples were collected from various wells located in the study area. All the samples were collected in clean polyethylene bottles and were transported to the laboratory in iceboxes. The samples were stored at 4 °C before chemical analyses. Samples for Si, Sr, Cr and F elemental analyses were collected separately and were acidified with ultrapure nitric acid (pH < 2).

Water analysis (Table 1), including sampling and preservation, were carried out according to the standard ISO methods and to the analytical procedures recommended by the French Association for Normalization (AFNOR, 1997). Analyses were performed on the water samples after filtration using 0.45 µm acetate cellulose membranes. The parameters including SO_2^{-4} , Cl^- , Na^{2+} , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^{-3} , Al^{3+} , Si^{2+} and Cr^{2+} were determined according to the methods described in Table 1.

Table 1 – Methods used to determine the physicochemical quality of groundwater

Element	Analysis method
Cl^-	Norm AFNOR NFT 90-014
HCO_3^-	Norm AFNOR NFT 90-036
SO_4^{2-}	Norm NFT 90-040
Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Al^{3+} , Si^{2+} , Sr^{2+} , Cr^{2+}	Atomic absorption and ICP-AES

ICP-AES analyses were conducted by the Chemistry Laboratory of Materials and Environment. Temperature, electrical conductivity (EC) and pH of water were measured at the same time with the water level measurements.

Statistical analysis

To determine the impact of different sources of pollution on groundwater and surface water, a PCA was performed, which is a technique of statistical analysis, dealing with at least two variables. Graphs are built from the matrix of the correlations, and the PCA describes, diagrammatically, the relationship between the various variables and the chosen factors. These graphs are planned in a circle of radius 1. The greater the correlation of the variable (-1 or +1) to a factor, the more the variable is correlated to this factor. The position of variables is thus determined by their correlation with the factors. The closer together two variables are, the greater their correlation. This method was adopted in numerous hydrogeochemical studies (Bakalowicz, 1979; Blavoux & Mudry, 1985; Lasne, 1992; Maqsoud, 2007). Its efficiency is superior to the other methods such as Collins, Stiff, Schoeller and Piper diagrams (Güler et al., 2002).

To validate the classification of different groups given by the PCA, a descending hierarchical classification was performed associated with the PCA in order to build homogeneous groups. The results of this classification allowed to determine four groups of wells. The PCA was performed using the statistical software XLSTAT 2010 version © Addinosof.

Geochemical modeling

Water chemistry was interpreted with the assistance of the equilibrium chemical-speciation/mass-transfer model Chess (Van der Lee, 1998). The degree of saturation is expressed as the SI. The SI corresponds to the difference of logarithms of ion activity product and solubility constant. Chess was used to calculate the saturation indices for discrete minerals that may be controlling the concentrations of dissolved species in the waters.

INVESTIGATION RESULTS

Runoff water chemistry

This work presents the hydrochemical characteristics of AMD in Kettara mine wastes. The samples were collected at four major locations (Figure 2) where ER1 and ER4 correspond to the water runoff from the fine tailings pond and ER2 and ER3 correspond to the surface water runoff from the coarse tailings piles (Ouakibi et al., in press). The water-sampling surveys used in the current analysis were carried out in March 2011.

Low-pH conditions promote the dissolution of many metal-bearing solids and metals desorption from solid surfaces. Thus, the release of major ions is strongly associated with low pH. Increases in pH can lead to pronounced decrease in the concentrations of dissolved metals released from mine wastes.

Collected samples show a high sulphate content (14,200 mg/L) that can explain the observed gypsum around ponds after evaporation events (Denimal et al., 2002). The variation in chemistry between the different water types based on metal content is shown in Ficklin diagram (Plumlee et al., 1992) (Figure 3). The surface water runoff from the four sampling points is categorized mostly as High-acid Extreme-metal, High-acid High-metal and Acid High-metal.

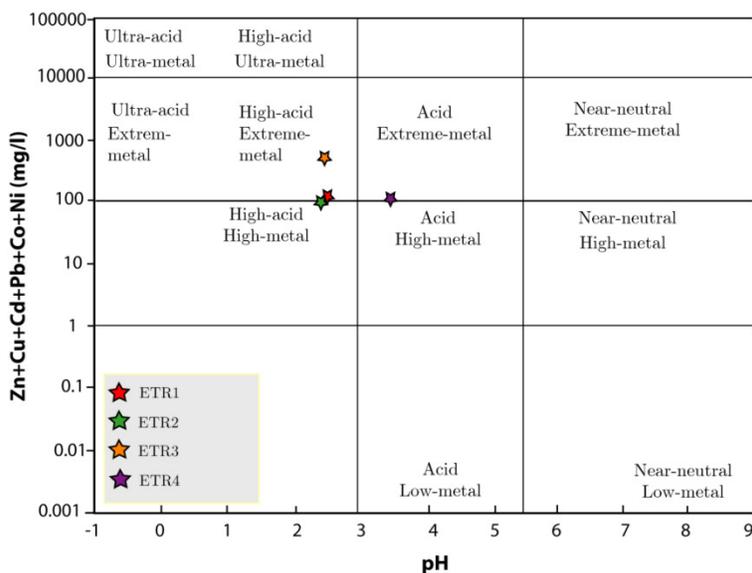


Figure 3 – Presentation of various Runoff samples in Ficklin diagram

Based on these characterizations and the case where there is infiltration of runoff water, groundwater could be contaminated. For this reason, groundwater samples were analyzed and the results are presented below.

Groundwater chemistry

Correlation analyses were carried out for major ions and results are presented in Table 2. This table shows that EC is correlated positively to HCO_3^- , SO_4^{2-} , Mg^{2+} , Ca^{2+} and $\text{Na}^+\text{SO}_4^{2-}$ are correlated positively to Ca^{2+} and Mg^{2+} . However, HCO_3^- are correlated positively with EC, Ca^{2+} , Mg^{2+} ; Mg^{2+} is correlated positively to EC, HCO_3^- , SO_4^{2-} , Ca^{2+} and negatively to pH; Na^+ is only correlated to EC and the Si^- did not present any correlation with the other parameters.

Table 2 – Correlation among measured parameters for wet seasons

	EC	pH	HCO ₃	SO ₄	Cl	Mg	Ca	Na	Si
EC	1								
Ph	-0,528	1							
HCO ₃	0,728	-0,834	1						
SO ₄	0,693	-0,477	0,543	1					
Cl	-0,006	0,007	0,029	0,369	1				
Mg	0,963	-0,571	0,772	0,968	0,021	1			
Ca	0,931	-0,583	0,693	0,946	0,057	0,958	1		
Na	0,608	-0,035	0,311	0,507	-0,088	0,446	0,307	1	
Si	-0,062	-0,084	-0,080	0,492	0,028	-0,010	0,008	-0,161	1

PCA was applied to determine the impact of AMD on groundwater. For this PCA, the calculation was limited to three factors; the total percentage of the variance expressed by these three factors is about 79.34 % (see Table 3). The factor F1, which express 53.62 % of the variance, is correlated positively to EC, HCO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺ and negatively to the pH. These ions characterize carbonate minerals. The factor F1 is also correlated to the SO₄, which participates to the biogeochemical cycle and in the case of higher concentrations it can be related to sulphide minerals. The factor F1 opposes most dissolved mineral to the pH: when the mineral concentration increases the pH decreases. These conditions are mainly observed in the context of the AMD contamination. Consequently, the factor F1 can be considered as an indicator of the AMD contamination.

The factor F2 (14.45 %) is correlated positively to Na⁺ and negatively to Si (see Table 3). The Na⁺ and the Si are completely separated and indicate their different origin (see Table 2 for correlation). The sodium can have atmospheric (rainfall), or anthropological (salting of roads) origins or can occur from dissolution of silicate mineral (clay). In our case, the Na⁺ is weakly correlated to Cl⁻, excluding the atmospheric and the anthropological origins. Consequently, the Factor 2 can be considered as an indicator of silicate mineral dissolution. Finally, the Factor 3 (11.27 %) is only correlated positively to the Cl⁻ and cannot be interpreted.

Table 3 – Correlation between variables and Factors F1, F2 and F3

	F1	F2	F3
EC	0.952	0.207	0.058
pH	-0.710	0.303	0.355
HCO ₃	0.854	-0.038	-0.165
SO ₄	0.803	-0.288	0.172
Cl	0.054	-0.457	0.838
Ca	0.943	-0.056	0.044
Mg	0.974	0.047	0.035
Na	0.448	0.683	0.165
Si	-0.014	-0.634	-0.307

In the spatial representation, it seems that that the factor F1 opposes water with high concentration of HCO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺ and lower pH, to water with low concentration of these minerals and high pH. The projection of individuals on the plane F1–F2 (see Figure 4) allows identification of four distinct groups of samples. The samples of Group 1 (P1, P8 and P9) are typical in terms of their higher EC (Table 2) resulting from the higher concentrations of salts such as Cl, Na⁺, Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻. Group 2 is composed of samples P2, P3, P10, P11 and P15. This group contains the water samples with higher concentrations of HCO₃⁻. Group 3 composed of P5, P6 and P7 indicates samples with lower EC values (Table 2) and lower levels of pollution. This could be attributed to the location of these three wells upstream of all pollution sources. Group 4 contains wells P12 and P14 with moderate mineralization, which is a characteristic of water samples with intermediate EC.

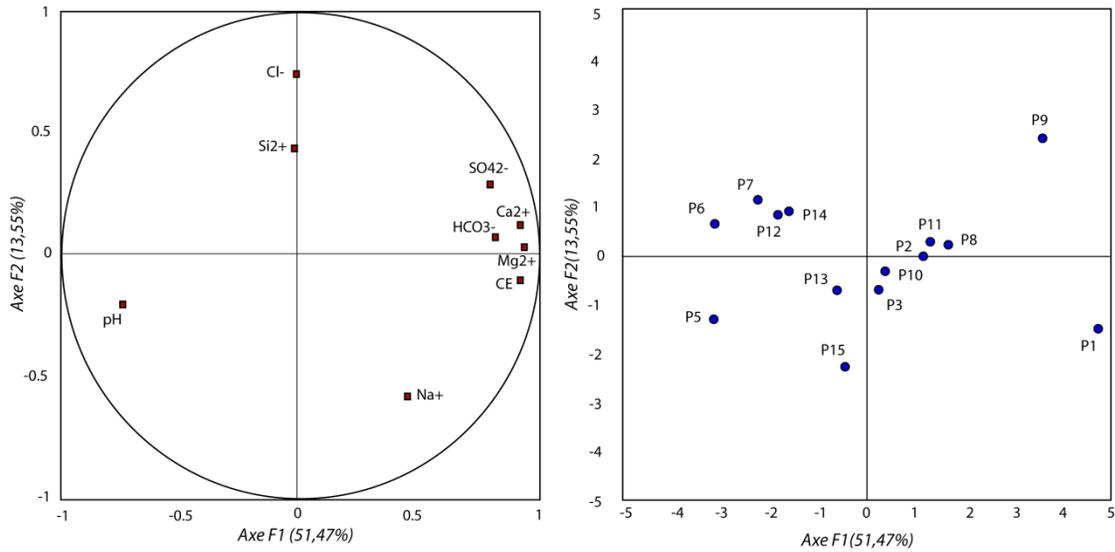


Figure 4 – Principal component analysis for groundwater (wet season): In the left projection of variables on the plane F1–F2; and in the right projection of individuals on the plane F1–F2

The major ion composition of these samples was dominated by sulphates (with higher calcium content than the other samples) and they had similar level of mineralization (Figure 5). The group 1 has the highest concentration and it corresponds to the most mineralized group. This group is located near the mine wastes and their mineralization can be attributed to the AMD contamination.

Box plots (Figure 6) show the distribution of concentration of the major elements. In general, median SO_4^{2-} , Ca^{2+} and Mg^{2+} concentrations were high in samples with relatively high EC.

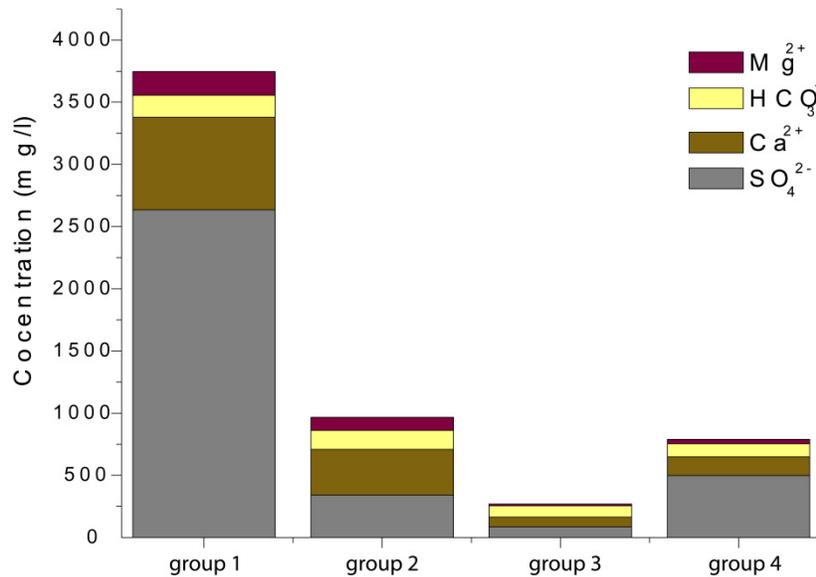


Figure 5 – Dendrogram showing classification of major ions concentration into the four groups

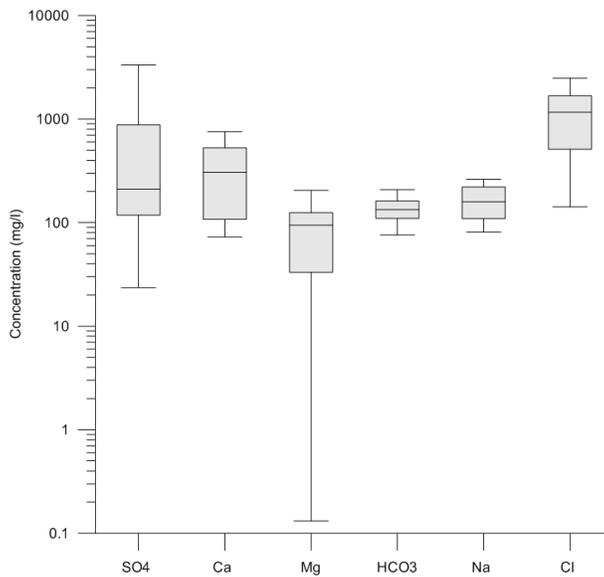


Figure 6 – Boxplots showing the distribution of major compositions in groundwater samples

The general concentration profiles observed from upstream to downstream are presented in Figure 7, which shows that the concentrations of major ions are higher at the source, close to the mine wastes (upstream), and generally decrease downstream. Run-off from the mine (ER3) has led to enrichment in sulphate ions. The spatial distribution of sulphate contents shows the impact of AMD on the water quality of the aquifer. Thus, one can observe that sulphate concentration decreases from 2,600 mg/L upstream to 200 mg/L downstream. This decrease can be attributed to the natural attenuation by water dilution.

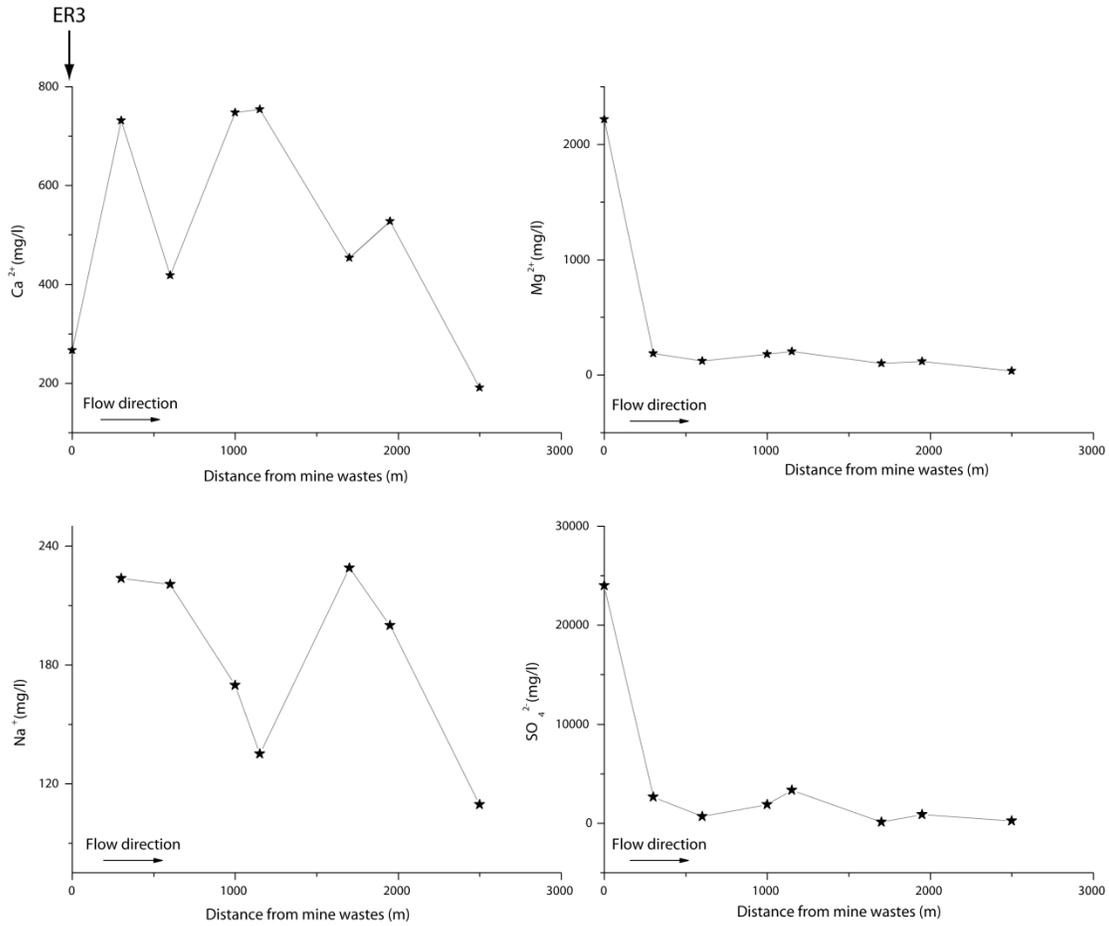


Figure 7 – Concentration versus downstream distance of selected majors ions

The SIs of various minerals are plotted against the sum of Ca^{2+} , SO_4^{2-} and HCO_3^- for the four groups in Figures 8 and 9. The obtained SI shows that groundwater is undersaturated with respect to most potential sulphated and carbonated secondary minerals. This suggests that the groundwater has short residence time and the natural equilibrium with these minerals is not reached (Bhattacharya et al., 2012). Thus, the increase in Ca^{2+} and Mg^{2+} and SO_4^{2-} concentrations may be a result of the dissolution of calcite, dolomite and gypsum.

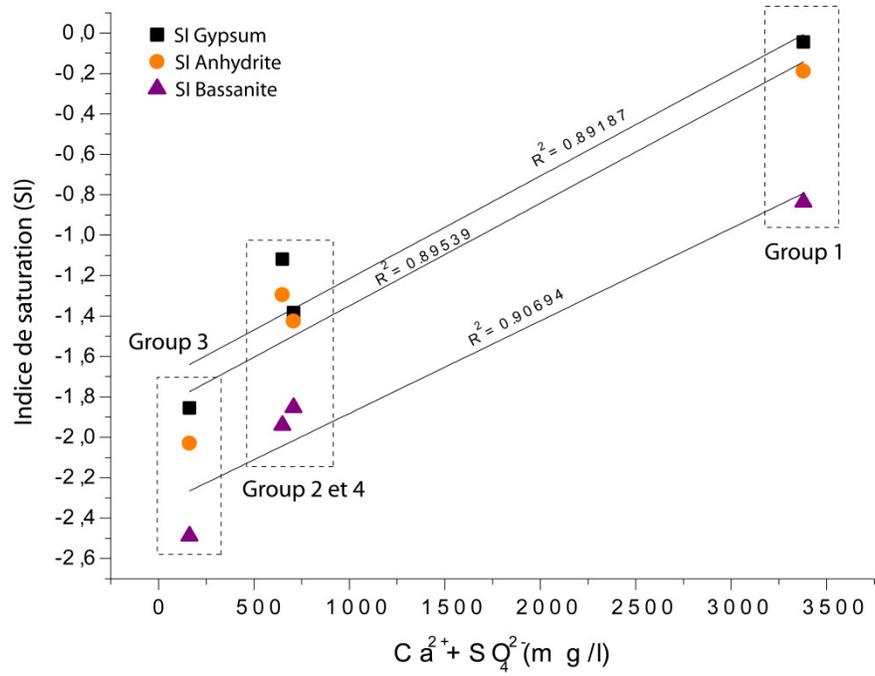


Figure 8 – Saturation indices of main sulphate minerals

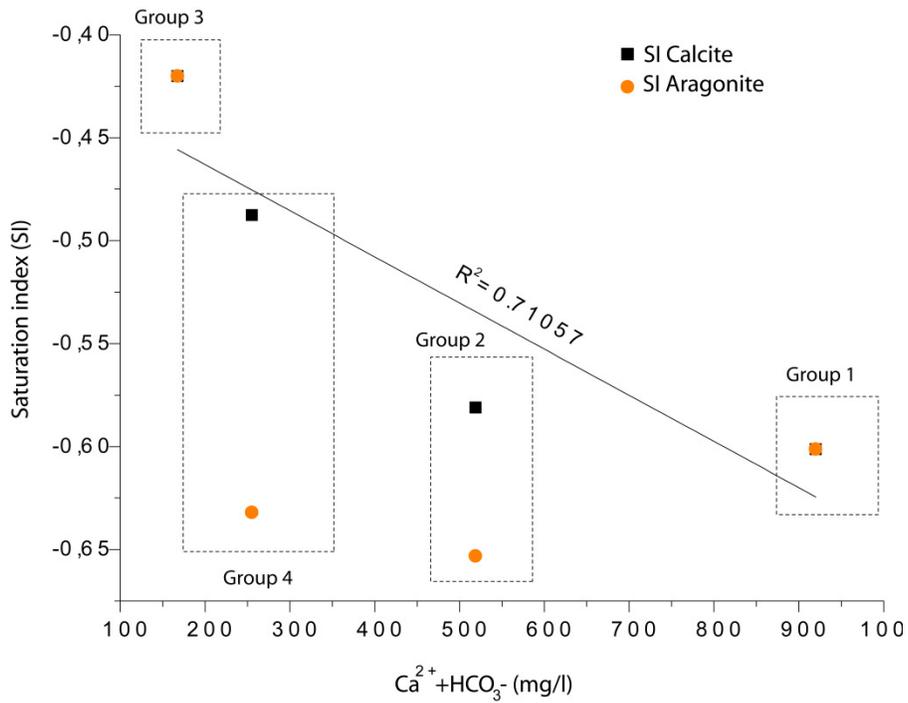


Figure 9 – Saturation indices of calcite and aragonite

CONCLUSIONS

This study was performed with the main objective to characterize the impact of the production of AMD on the quality of the surface and groundwater around the mine site. Results indicate that dissolution of gypsum and anhydrite could be responsible for the deterioration of groundwater in the study area. That may explain the high concentration of sulphates in the groundwater. Based on sulphates concentration, well water can be considered as non-potable (higher than 250 mg/L) and can affect the health of populations.

The results of the study will help to identify pollutants from the abandoned mine drainage and assess the degree of pollution along the stream pathways. They can also be used to prepare a treatment program for polluted water and prevent the streams from further pollution in the future, and investigate the environmental impact.

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