

Origin of neutral mine water in flooded underground mines: an appraisal using geochemical and hydrogeological methodologies

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Abstract

Mine water pollution management needs an understanding of its origin and temporal changes. The study of the processes that control mine water quality usually comprises hydrochemical and mineralogical analysis of the site. However, in flooded underground mines access to the mineral phase is very difficult. In this paper, the evolution of the drainage quality of an underground sulfide mine with a neutral pH has been studied. The basic information consists of chemical analyses, drainage flow data, and water level data within the mine collected in a six years period since mine drainage started. The study is done using 3 techniques: (1) geochemical equilibrium modeling, (2) mass balance (hydrochemistry and drainage flow relationship), and (3) the relationship between water level and hydrochemistry. The geochemical modeling indicates that throughout the six-year period, the water is saturated with calcite, and the P_{CO_2} of the system is constant and greater than the atmospheric P_{CO_2} . During the first 10 months water was saturated with respect to gypsum and later undersaturated. The mass balances suggest that acidity produced by pyrite oxidation is neutralized by dissolution of calcite and ankerite, and CO_2 degassing; but neutralization mechanisms have temporal variations. Mass balances show that the ratio between Fe precipitated inside the mine, and Fe released by pyrite oxidation increases with time. The relation between mine water level and water quality indicates that during maximum water level events the relative proportion of dissolved Zn was greater, suggesting a mechanism of efflorescent salt dissolution. The overall interpretation indicates the importance of kinetic processes that affect pyrite oxidation, the dissolution of carbonates and, possibly the aging of iron hydroxides.

1 Introduction

Natural waters affected by mine activities have a wide range of chemical characteristics (Schmiermund and Drozd 1997; Banks et al. 1997). Acid mine drainage (AMD) has received great attention from scientific and applied research due to its environmental impact. When mine and mine-waste drainage has neutral pH, with a high concentration of sulfate and dissolved metals, the term neutral (or alkaline) mine drainage is applied (Scharer et al. 2000). Neutral mine drainage (NMD) has received less attention than AMD, but NMD can have environmental adverse effects caused mainly by precipitation of dissolved Fe and Zn. The NMD origin has been studied at several mine environments: open mine-pits (Shevenell et al. 1999), tailings ponds (Al et al. 2002), waste rock-dumps (Benvenuti et al. 2000), mine connected rivers (Webb and Sasowsky 1994), underground mine adits (Balistrieri et al. 1999; Younger 2000), and limestone drains (Cravotta III and Trahan 1999). There exist as well experimental laboratory studies about the NMD formation (Nicholson et al. 1990; Jurjoveck et al. 2002).

Usually, the main processes that cause NMD are pyrite oxidation and carbonate dissolution; but mine drainage waters are the result of several reactions between water, minerals and air (Nordstrom and Alpers 1999). These reactions can involve, among others:

- oxidation of pyrite and other sulfide
- dissolution of host rock minerals (carbonate and silicate)
- precipitation and dissolution of iron hydroxide and hydroxysulfate
- coprecipitation and adsorption of dissolved metals
- precipitation and dissolution of iron-sulfates
- gypsum precipitation and dissolution
- CO₂ degassing

The study of the processes that control mine water quality usually comprises water quality analysis, (chemistry and environmental isotopes), the mineralogical study of the site, gas phase study, and geochemical modeling. At waste rock dumps, open pits or within tailings impoundments, where mineral phase sampling and inspection is relatively easy, the mineralogical study is possible. However, when mine water is generated at deep underground mines, sampling of the mineral phases is more difficult and the principal tools to study mine water origin are water chemistry analysis and geochemical modeling (Alpers and Nordstrom 1999; Perry 2001).

Mine drainage quality usually has temporal changes that are observed both at natural sites and in laboratory tests. These changes can be related with changes in mineral availability within sulfide ores or in the host rocks, and with hydrologic changes. Mineral availability can be related to mineral depletion, surface coatings or with kinetic processes. The processes that produce changes in the chemical quality of mine waters need to be understood, to decide the remedial actions necessary to allviate any environmental impact..

The objective of the study is to use hydrologic and hydrochemistry data collated from mine in Northern Spain (Troya) to research geochemical processes that cannot be directly observed or accessed. Specific objectives of the study are the reactions that neutralize the acidity produced by pyrite oxidation, the origin of dissolved iron in neutral mine water, and the causes of quality changes observed after the mine closure.

2 The Troya mine

Troya is an underground Pb-Zn mine located in Northern Spain (Fig. 1). The 5m thick orebody is stratiform, and consists mainly of pyrite, marcasite, sphalerite, galena and chalcopyrite; the gangue minerals include barite, quartz, siderite, and ankerite; and the mineralization is hosted by limestones at the bottom and marls at the top (Fernández Martínez and Velasco 1999). The orebody was discovered in 1973, and the mining company began extracting the ore in 1986. The mine was closed in 1993 due to a roof collapse. The original deposit contained $3.5 \cdot 10^6$ t grading 13.1 % Zn , 1.0 % Pb and 27.6 % Fe, and during exploitation $2.2 \cdot 10^6$ t were extracted. Mining was carried using the bord and pillar. The mine has two accesses, the north and the south declines with the north decline the lowest topographically at 335 mAOD.

The limestones underlying the orebody constitute a karstic aquifer that had to be drained in order to exploit the mine. In 1982 the original piezometric level was located around 435 mAOD. with the aquifer drained by a spring. From 1982 to 1993 several wells located inside the mine pumped water at an average flow of 54 L/s, the spring dried up and the piezometric level dropped down to 190 m a.s.l. When the pumping ceased the piezometric level began to rise, and in March, 1995, when the piezometric level reached around 335 m a.s.l. the water started flowing out from the north decline. At present, the mine is partially flooded with a flooded volume of $0.38 \cdot 10^6$ m³, and considering the mean annual discharge (37 L/s), the calculated mean time residence of water in the mine void is about 120 days.

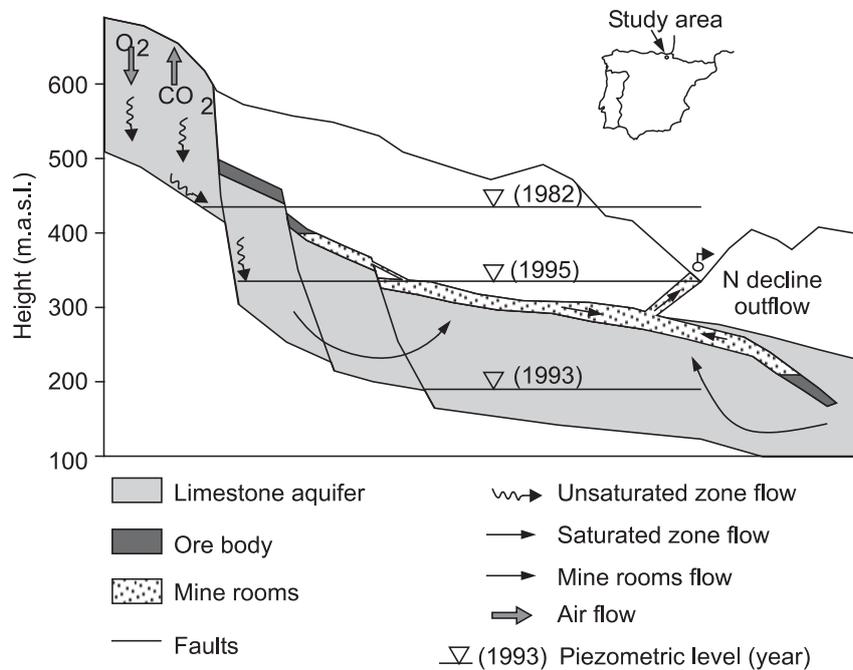


Fig. 1. Site location and hydrogeological cross-section of the Troya mine. Ore-body and mine room thickness is exaggerated, usually they are 5 m thick.

The water flowing from the north decline in 1995 had a neutral pH, but high Fe and Zn content, and when the mine water reached the nearest creek, almost all the fish population disappeared. In 1997 the water authorities took remedial actions diverting the mine water to a pond where Fe hydroxides are effectively removed (Iribar et al. 1999).

3 Data and methods

In this study three different kinds of data sets were used: flow, piezometric, and water quality data. Data pre 1993 was collected by the mining company and data between 1993 to 2001 was collected by personnel of the Diputación Foral de Gipuzkoa (the local water authority).

3.1 Flow measurements

From March, 1995 to May, 1997, the flow from the North decline was gauged weekly using the "time-volume" method, whereas from May, 1997 to 2001, the flow was continuously recorded in a weir constructed at the mine portal (Fig. 2a).

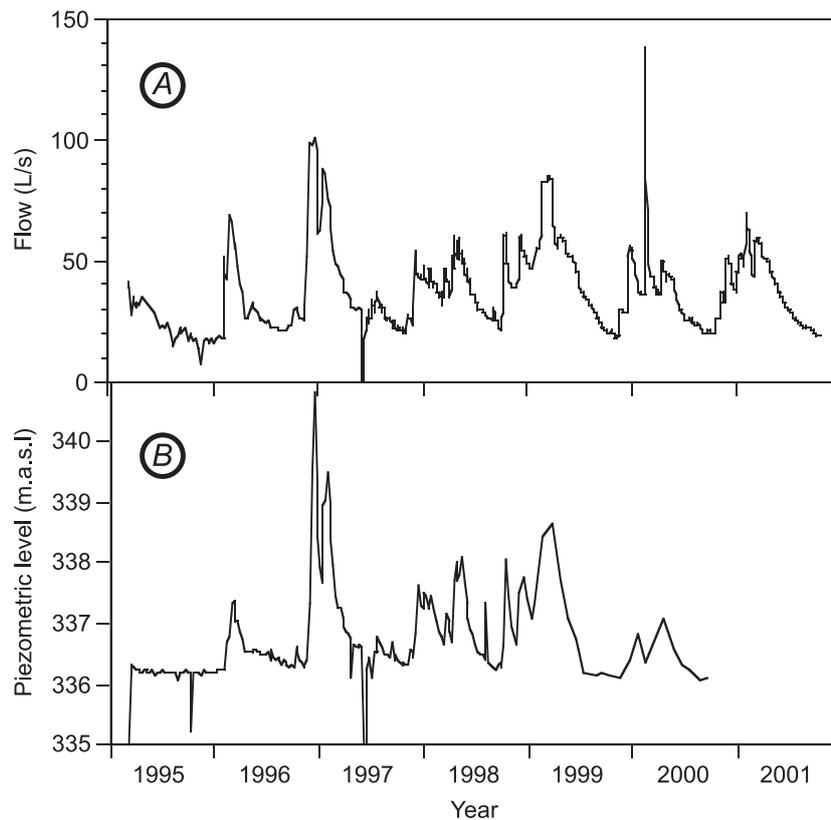


Fig. 2. a) Flow record at the North decline. b) Piezometric level evolution near the mine void

3.2 Piezometric data

There are no data concerning the water level in the flooded mine. However, the piezometric level of the karstic aquifer is recorded at a piezometer located 18 m from the mine void. Since the aquifer is highly permeable

around the mine (the permeability at the site calculated in a pumping test is about 50 m/d), it is expected that the water level position inside the mine must be very similar to the level recorded in the piezometer. From 1995 to November 1998, piezometric level were recorded weekly, and later every two weeks or monthly (Fig. 2b).

3.3 Chemical analysis

There are three data sets on water quality at the Troya mine and in the limestone aquifer, these relate to:

- the spring that drained the aquifer before the mine activity started
- the water pumped during mining activity
- the water flowing from the North decline

The median values of the three data sets are shown in Table 1, and the temporal changes of the water quality flowing from the North decline are shown in Fig. 3. The pH of the water flowing from the North decline is neutral and relatively constant, and water comes out from the mine without any turbidity. Turbidity increases soon (in a few seconds) by iron hydroxide precipitation. The metal contents shown in Table 1 and Fig. 3 are referred to non-filtered samples.

Table 1. Chemical analysis of the Troya system (median values)

mg/L	Karstic spring (1976)	Drainage wells (1983-1993)	North decline (1995-2001)
HCO ₃	220	350	358
SO ₄	46	126	1260
Cl	5	16	17
Ca	68	110	552
Mg	11	25	54
Fe	0.006	0.03	31
Mn	-	0.16	0.6
Zn	-	0.166	1.0
pH	7.2	7.6	6.8
n of samples	5	112	255

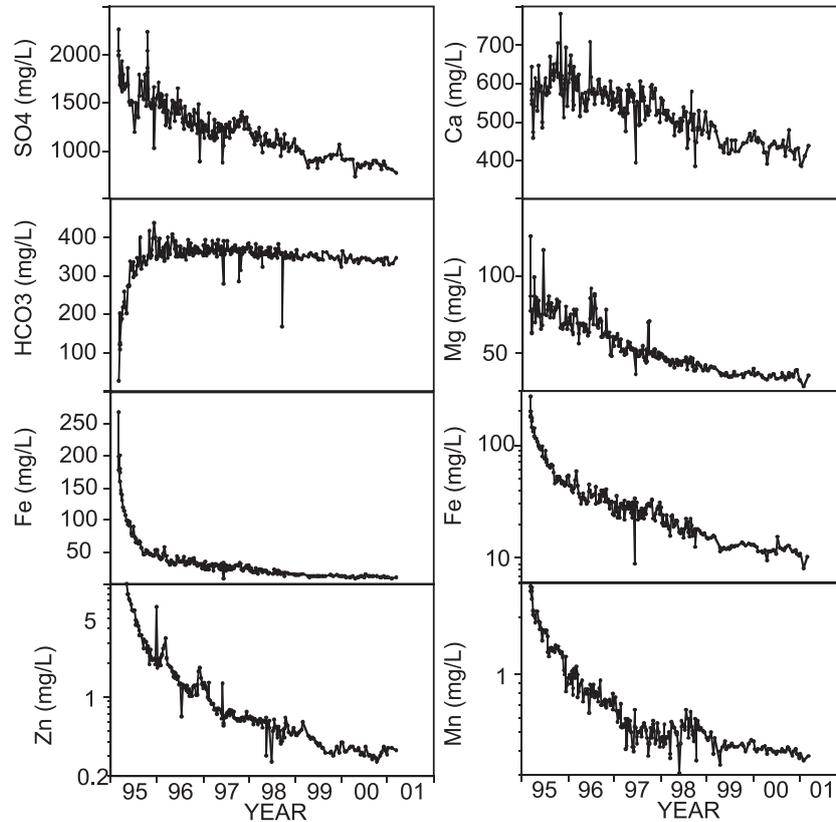


Fig. 3. Hydrochemical evolution of North decline water. SO_4 , HCO_3 , Ca and Mg concentrations are in normal scale. Fe concentration in normal and logarithmic scale. Zn and Mn concentrations in logarithmic scale

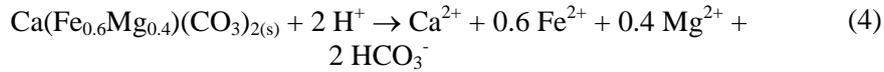
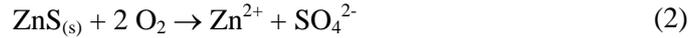
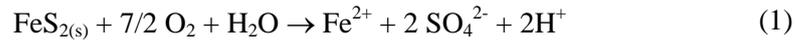
3.4 Geochemical modeling

Equilibrium modeling of 255 water analyses from the North decline allows a possible examination of the reactions that may influence mine water chemistry. Modeling has been done using the PHREEQC program and the PHREEQC thermodynamic database (Parkhurst and Appelo 1999). Ankerite was added to the thermodynamic database used for the simulations. The solubility product adopted for ankerite was $\text{Log } K = -17.40$ (Al et al. 2002). The redox potential was not measured in the field, and in order to test the influence of pe in equilibrium, the calculations were done using values of pe = 0, 4, and -3.

3.5 Mass balances

The mass balances were performed by comparison of the quality of the karstic spring water with the quality of waters from the North decline, and also by taking into account the flow of the North decline. The principal condition to make the balances was that dissolved ions can only come from dissolution of the minerals present at the mine. The increase in SO_4 , Ca, Mg, HCO_3 , Fe, and Zn is explained by the following mineral reactions.

It is assumed that SO_4 comes from pyrite/marcasite and sphalerite dissolution (Eqs. 1 and 2). Galena and chalcopyrite are not considered in the balances because Pb and Cu concentrations in water are below detection limits (0.002 mg/L). Ca, Mg and HCO_3 come from calcite and ankerite dissolution (Eqs. 3 and 4). And finally, ferrous iron oxidation and ferric hydroxide precipitation (Eq. 5), and CO_2 degassing (Eq. 6) are allowed.



4 Results and discussion

The ionic concentration of water from North decline follows in general a downward trend except for HCO_3 . The reduction in concentration is the result of a decreasing rate of pyrite oxidation. In NMD this decreasing rate is interpreted as the result of Fe hydroxide accumulation on the pyrite surfaces (Nicholson et al. 1990; Hölmström et al. 1999). Nevertheless the results obtained with the geochemical modeling and the mass balances allow greater examination of the process.

4.1 Geochemical modeling

Mean values of calculated saturation indices for minerals that are present in the mine or can precipitate or dissolve in similar environments are presented in Table 2. For each mineral the saturation index was calculated with different pe of input water. The temporal changes in saturation indices for selected minerals are shown in Fig. 4.

During 1995, water from the North decline was in equilibrium with gypsum, but later it becomes progressively more undersaturated. The water is always subsaturated with respect to melanterite, and the subsaturation degree has increased with time. However, during the first months of 1995, the rate of reduction of the subsaturation degree of water with respect melanterite was more important than in the following months.

In the first three months of 1995, water was undersaturated with respect to calcite and ankerite, and later water is near equilibrium with both minerals, although the degree of saturation is higher for calcite than for ankerite. Also, the $P_{CO_2(g)}$ increased from -2.5 to -1.5. Water is always supersaturated with respect siderite, the other carbonate present in the mine.

Table 2. Mean values of saturation indices for selected minerals, calculated with different pe in input water

Mineral	Formula	pe = 4	pe = 0	pe = -3
Calcite	CaCO ₃	0.25	0.25	0.25
Dolomite	CaMg(CO ₃) ₂	-0.25	-0.25	-0.25
Ankerite	Ca(Fe _{0.6} Mg _{0.4})(CO ₃) ₂	-0.28	-0.27	-0.27
Siderite	FeCO ₃	1.07	1.12	1.12
Gypsum	CaSO ₄ ·2H ₂ O	-0.14	-0.14	-0.14
Melanterite	FeSO ₄ ·7H ₂ O	-4.02	-3.96	-3.96
Ferrihydrite	Fe(OH) ₃	2.86	-1.11	-4.11
Goethite	FeOOH	8.61	4.63	1.63
Smithsonite	ZnCO ₃	-1.44	-1.44	-1.44
Zn(OH) ₂	Zn(OH) ₂	-3.16	-3.16	-3.16
Rhodochrosite	MnCO ₃	-0.24	-0.24	-0.24
Pyrolusite	MnO ₂	-11.91	-19.91	-25.91
Manganite	MnOH	-6.11	-10.11	-13.11
CO _{2(g)}	$P_{CO_2(g)}$	-1.54	-1.54	-1.54

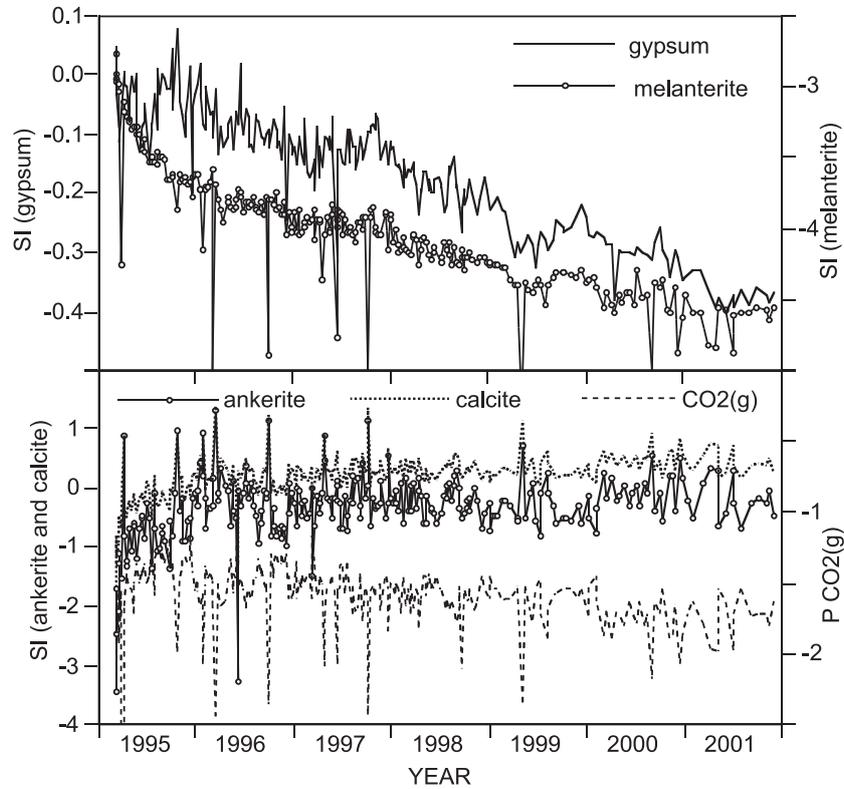


Fig. 4. Time evolution of saturation indices of gypsum, melanterite, calcite, ankerite, and P_{CO_2} of the North decline water.

From Table 2, it can be realized that water is always supersaturated with respect to goethite, but saturation state with respect to ferrihydrite is constrained by the p_e of water. Thus, the solubility of Fe can be controlled by the p_e , and the mineral phase in equilibrium with water.

Water is undersaturated with respect to Mn and Zn bearing oxides, hydroxides and carbonates present in the PHREEQC database.

4.2 Mass balances

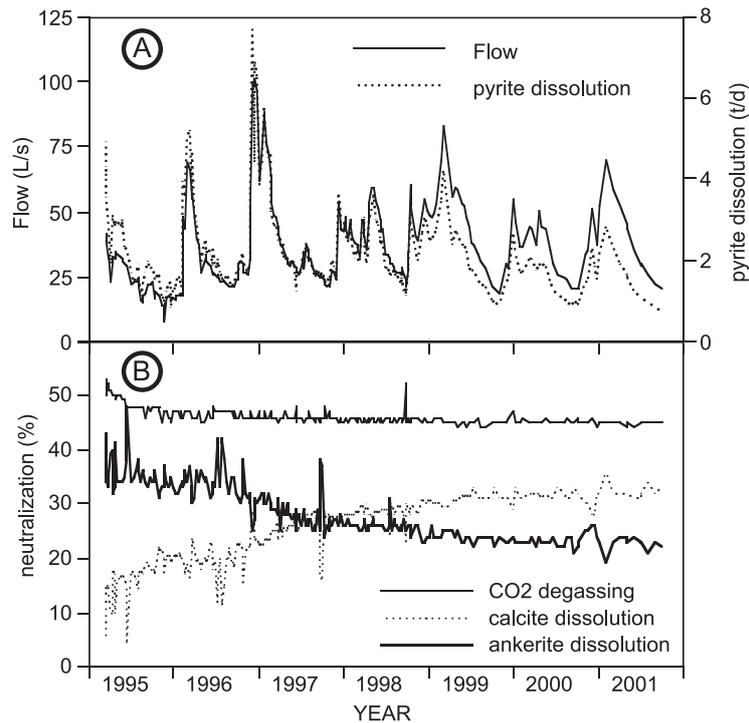
The mean results of mass balances are presented in Table 3, and temporal changes of selected aspects of mass balances are shown in Figs. 5 and 6.

The time evolution of the rate of pyrite dissolution is parallel to the flow evolution in the North decline (Fig 5a), parallel trends are observed for cal-

Table 3. Mean mineral dissolution (-) or precipitation (+) rate calculated with mass balances in the 1995-2001 period

Mineral	Formula	Process	Rate (kg/d)
Pyrite	FeS ₂	dissolution	-2078
Sphalerite	ZnS	"	-5.9
Ankerite	Ca(Fe _{0.6} Mg _{0.4})(CO ₃) ₂	"	-2410
Calcite	CaCO ₃	"	-2224
Goethite	FeOOH	precipitation	+2047

cite and ankerite dissolution (not shown here). This evolution shows that neutralization by carbonate dissolution is always effective. Since reaction of carbonate dissolution is faster than pyrite oxidation, (Banwart and Malmström, 2001) this is the expected trend. On the other hand, dilution is not seen at high flow periods. The lack of dilution can be the result of the combination of a high residence time of the water in the mine void, and to an increase in the rate of pyrite oxidation in high water periods.

**Fig. 5.** Time evolution of results of mass balances. a) Rate of dissolved pyrite vs. North decline flow. b) Relative importance in (%) of neutralization mechanisms

The acidity neutralization processes change with time (Fig. 5 b). During the first 3 months of 1995, CO₂ degassing was the most important neutralizing mechanism, and later its relative importance has remained constant. This fact can be explained because during the first 3 months of 1995, the water was saturated with respect to gypsum, and there was not the possibility of calcite dissolution without gypsum precipitation. Thus, the mechanism of acidity neutralization was the CO₂ degassing. This is reflected in the low HCO₃ concentration observed in the first months of 1995 (Fig. 3). In addition, the importance of calcite dissolution with respect to ankerite dissolution increases with time, suggesting that progressively there is less relative availability of ankerite. Since ankerite and calcite are very abundant with relation to pyrite, it is possible that the drop of relative availability of ankerite is due to selective action of Fe hydroxide coatings precipitated on ankerite surfaces.

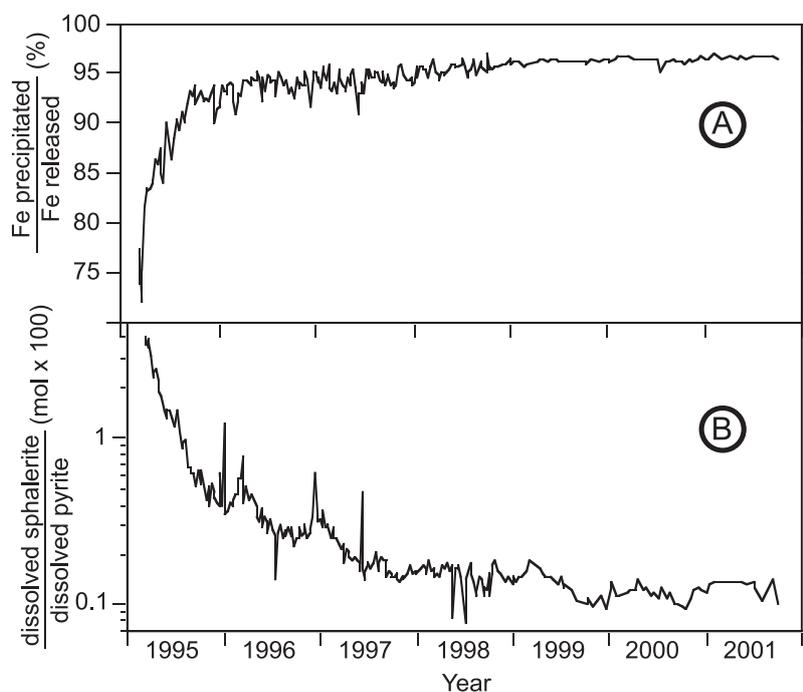


Fig. 6. Time evolution of results of mass balances. a) Relation in (%) between Fe precipitated as hydroxide and Fe released from pyrite and ankerite dissolution. b) Relation between sphalerite and pyrite dissolution

As regards the behaviour of Fe, the downward trend in the concentration of dissolved Fe shown in Fig. 3 could be interpreted as if progressively there is less pyrite and ankerite dissolution. Nevertheless, mass balances show that the relation of the Fe that precipitates with respect to the Fe that is released by pyrite and ankerite dissolution is increasing with time (Fig. 6a). As the pH of the water remains constant there are other processes that might be the cause of this phenomenon. One of them is the transformation of ferrihydrite to goethite with time (Bigham et al. 1996; Jambor and Duztriac 1998).

By comparing the relationship between sphalerite and pyrite dissolution (Fig. 6b), it is observed that this relation is descending since 1995, but that there are 3 relative maxima in this trend. One happened in March, 1995, the second in February, 1996, and third in December, 1996. These 3 events are coincident with the maxima in the position of the piezometric level (Fig. 2b). This suggests that the process that originated the Zn content increase was the washing of sulfate soluble salts located in the walls of the mine during periods of high water level, instead of an increase in the rate of sphalerite dissolution. Many of these salts are a temporary storage of Zn that is washed in the periods of high water (Frau 2000, Buckby et al. 2003). In the case of the maximum of March, 1995, with an ascent of the water level from 190 m a.s.l. to 335 m a.s.l., washing of important amounts of gypsum should have happened, suggested by the evolution of the saturation index of gypsum and melanterite (Fig. 4).

5 Conclusions

The combined use of equilibrium modeling techniques along with hydrochemical balances has allowed to identify geochemical processes occurring within the Troya mine that are not directly observable because the underground mine is flooded. In addition to pyrite oxidation and neutralization of acidity by carbonate dissolution, other processes that can be identified with these techniques are:

The washing and dissolution of iron-sulphates and likely of gypsum from the mine walls during the ascent of the water level.

The change of the neutralization mechanisms with time, depending on the state of saturation with respect to gypsum and the variations of relative availability of calcite and ankerite.

The increase in time, of the amount of Fe hydroxide that precipitates within the mine, in relation to the Fe that is released by dissolution of pyrite and ankerite.

Nevertheless, equilibrium modeling and hydrochemical balances neither explain the origin of the variations of ankerite availability, nor the greater effectivity of Fe hydroxide precipitation with time. The origin of these phenomena can be related to kinetic reasons constrained with the selective precipitation of the Fe hydroxide on ankerite, and by the transformation or aging of Fe hydroxides from ferrihydrite to goethite.

Acknowledgements

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References

- Al TA, Martin CJ, Blowes DW (2002) Carbonate-mineral/water interactions in sulfide-rich mine tailings. *Geochim Cosmochim Acta* 64 (23): 3933-3948
- Alpers CN, Nordstrom DK (1999) Geochemical modeling of water-rock interactions in mining environments. In: Plumlee GS, Logsdon MJ (eds) *The Environmental Geochemistry of Mineral Deposits*. *Rev Econ Geol*, vol 6A. Soc Econ Geol, pp 289-323
- Balistrieri LS, Box SE, Bookstrom AA, Ikramuddin M (1999) Assessing the influence of reacting pyrite and carbonate minerals on the geochemistry of drainage in the Coeur d'Alene mining district. *Environ Sci Technol* (33): 3347-3353
- Banks D, Younger PL, Arnesen RT, Iversen ER, Banks S (1997) Mine-water chemistry: the good, the bad and the ugly. *Environ Geol* (32): 157-174
- Banwart SE, Malmström ME (2001) Hydrochemical modelling for preliminary assessment of minewater pollution. *J Geochem Exploration* (74): 73-97
- Benvenuti M, Mascaro I, Corsini F, Ferrari M, Lattanzi P, Parrini P, Costagliola P, Tanelli G (2000) Environmental mineralogy and geochemistry of waste dumps at the Pb(Zn)-Ag Bottino mine, Apuane Alps, Italy. *Eur J Mineral* (12): 441-453
- Bigham J M, Schwertmann U, Carlson L (1996) Mineralogy of precipitates formed by the biogeochemical oxidation of Fe(II) in mine drainage. *Catena supplement* (21): 219-232
- Buckby T, Black S, Coleman ML, Hodson ME (2003) Fe-sulphate-rich evaporative mineral precipitates from the Río Tinto, southwest Spain. *Min Mag* 67 (2): 263-278
- Cravotta III CA, Trahan MK (1999) Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. *Appl Geochem* (14): 581-606

- Fernández-Martínez J, Velasco F (1996) The Troya Zn-Pb carbonate hosted SEDEX deposit, Northern Spain. *Soc Econ Geol. Special Publication* (4): 364-377
- Frau F (2000) The formation-dissolution-precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: environmental implications. *Min Mag* (64): 995-1006
- Holmström H, Ljungberg J, Öhlander B (1999) Role of carbonates in mitigation release from mining waste. Evidence from humidity cell tests. *Environ Geol* 37 (4): 267-280
- Iribar V, Izco F, Tames P, da Silva A, Antigüedad I (2000) Water contamination and remedial measures at the Troya abandoned Pb-Zn mine (The Basque Country, Northern Spain). *Environ Geol* 39 (7): 800-806
- Jambor JL, Dutrizac JE (1998) Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chem Rev* (98): 2549-2585
- Jurjovec J, Ptacek CJ, Blowes DW (2002) Acid neutralization mechanisms and metal release in mine tailings: A laboratory column experiment. *Appl Geochem* 66 (9): 1511-1523
- Nicholson RV, Gillham RW, Reardon EJ (1990) Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. *Geochim Cosmochim Acta* (54): 395-402
- Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ (eds) *The Environmental Geochemistry of Mineral Deposits. Rev Econ Geol*, vol 6A. *Soc Econ Geol*, pp 133-160
- Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *USGS Water-Resources Investigations Report* 99-4259
- Perry EF (2001) Modelling rock-water interactions in flooded underground coal mines, Northern Appalachian Basin. *Geochemistry: Exploration, Environment, Analysis* (1): 61-70
- Shevenell L, Connors KA, Henry CD (1999) Controls on pit water quality at sixteen open-pit mines in Nevada. *Appl Geochem* (14): 963-987
- Scharer JM, Pettit CM, Kirkaldy JL, Bolduc L, Halbert BE, Chambers DB (2000) Leaching of metals from sulphide mines wastes at neutral pH. In: *ICARD 2000 Proc from the Fifth Intl Conf on Acid Rock Drainage*, vol 1. Society for Mining, Metallurgy, and Exploration, Inc, pp 191-201
- Schmiermund RL, Drozd MA (1997) Acid mine drainage and other mining influenced waters (MIW). In: Marcus JJ (ed) *Mining environmental handbook*. ICP, London, pp 599-617
- Webb JA, Sasowsky ID (1994) The interaction of acid mine drainage with a carbonate terrane: evidence from the Obey River, north-central Tennessee. *J Hydrol* 161: 327-346
- Younger PL (2000) Nature and practical implications of heterogeneities in the geochemistry of zinc-rich, alkaline mine waters in an underground F-Pb mine in the UK. *Appl Geochem* (15): 1383-1397