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Multicomponent reactive transport modeling at the Ratones uranium mine, Cáceres (Spain)

Modelación de transporte reactivo multicomponente en la mina de uranio Los Ratones, Cáceres (España)

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Abstract

Flooding of abandoned mines may have a major impact in groundwater quality. Predicting the long-term evolution of the water quality is, therefore, a relevant matter for environmental management. The Ratones uranium mine was abandoned and flooded in 1974. Due to its reducing underground environment uranium concentration is very low, although some points show high concentration in Fe and As. Within the works prior to a remediation strategy, reactive transport modelling were performed of the mine and surrounding groundwater system. The results of the calculations were compared with analyses of groundwater samples collected in selected points.

Modelling based on water-rock reactions taking place only in the mine galleries indicates the rapid exhaustion of dissolved oxygen and predicts solute concentrations that are much lower than those measured in the boreholes. In contrast, modelling that includes weathering processes taking place in the unsaturated zone of the surrounding rock indicates high dissolution of minerals (even if present in small amounts) and concentrations of solutes and values of pH and redox potential that better match the measured values. Therefore, current models based only on water-rock reactions in the walls of the mine galleries may clearly underestimate the impact of mineralization in groundwater, and processes taking place in the shallow surrounding rock must also be considered

Keywords: mine water, uranium, reactive transport, granite hydrochemistry, Ratones mine.

Resumen

La inundación de minas abandonadas puede dar lugar a impactos importantes en la calidad del agua subterránea. Por lo tanto, predecir la evolución de la calidad del agua es un tema clave para la gestión medioambiental. La mina Los Ratones es una mina de uranio subterránea, que fue abandonada e inundada en 1974. Gracias al ambiente reductor del subsuelo, la concentración de uranio en el agua es muy baja, pero algunos puntos muestran concentraciones importantes de hierro y arsénico. En el marco de los trabajos previos a una estrategia de remedio, se ha realizado un modelo de transporte de solutos reactivos, que comprende la mina y su entorno. Los resultados de los cálculos se han comparado con los análisis de aguas subterráneas recogidas en puntos seleccionados.

Según los cálculos, las reacciones entre el agua y la roca que tienen lugar en las galerías de la mina llevan a un agotamiento rápido del oxígeno, las reacciones apenas progresan y las concentraciones de solutos resultantes son muy inferiores a las medidas en los sondeos. Por el contrario, las reacciones de meteorización que tienen lugar en la zona no saturada del granito encajante producen una

disolución mineral importante y las concentraciones de solutos, el pH y el Eh resultantes son muy semejantes a los medidos. Por lo tanto, los modelos que se están usando comúnmente, y que están basados en las reacciones que tienen lugar en las galerías inundadas subestiman claramente el impacto de las mineralizaciones en el agua subterránea. Estos modelos deberían considerar también los procesos que tienen lugar en la superficie de la roca encajante.

Palabras clave: agua de mina, uranio, transporte reactivo, hidroquímica de granito, mina Los Ratones

1. Introduction

The flooding of galleries as mining activity ceases has major consequences on groundwater, such as modifications of the regional flow regime, and degradation of the water quality. The management of water resources and decisions on remediation actions require prior understanding of the natural processes involved in pollution generation and long-term predictions of its qualitative and quantitative evolution.

Some studies are available regarding groundwater quality modifications after flooding underground mines. They consist of models based on the structure and connection between galleries and shafts, and the hydrogeological parameters of this type of system (Therrien and Sudicky, 1996; Bochenska *et al.*, 2000; Burke and Younger, 2000; Adams and Younger, 2001). Some of these models have been applied to abandoned coal mines and predict decreasing iron concentrations with time along a century. These models, however, are mainly hydrodynamic with only basic treatment of geochemical processes.

In contrast, a number of models with comprehensive treatment of geochemical reactions have been used to predict the impact of mining activities on water quality. Most of them, however, have been developed for mine tailings and wastes, which are considered porous media (Elberling *et al.*, 1994; Wunderly *et al.*, 1996; Xu *et al.*, 2000; Gerke *et al.*, 2001; Zhu *et al.*, 2001; Neumann and Sami, 2002). Bain *et al.* (2000, 2001) used the MIN3P reactive transport model to predict the evolution of the water quality after the flooding of a uranium mine. Nonetheless, the models capable of simulating metal release in abandoned underground mines are scarce.

The Ratones mine is an underground uranium mine that was exploited between 1955 and 1974. The mining works created a hole of 147,000 m³ that rapidly filled and overflowed after closure. No important fluctuations of water level have been observed since then because groundwater level is controlled by a ventilation shaft. Mine waters discharge at the surface into a small river. There are no acidity pollution problems, and uranium concentrations are very low, (below 0.1 mg/L), but some points show high values in Fe (up to 20 mg/L) and As (up to 3 mg/L). Both iron and arsenic are oxidation products of sulphides associated with the mineralization of uranium.

The present work is an application of reactive transport modelling to understand the hydrogeochemical system in an underground mining setting: to localize the sources of water pollution, to quantify the extent of water flow and mixing, and to predict the amount and quality of groundwater discharge to the surface ecosystem. By characterizing and modelling the mechanisms controlling the chemistry of the water, we should be able to determine how the chemistry of the groundwater is expected to evolve and for how long, and, therefore, to devise the most convenient remediation method.

2. Geological and hydrogeological setting

The Ratones mine is located in the Albalá granitic pluton (SW of Iberian Massif, Spain). The pluton is a concentrically zoned body, elongated in a NNW-SSE direction and formed by ten different intrusive units. Granite outcrops in 40% of the pluton surface, the remainder being lehm (surface weathered granite). According to Escuder (1999), the granite was affected by three deformation phases, the last one being post-Hercynian in age and generating a dense network of brittle deformation structures (Fig. 1).

The four major structures in the mine area are two N-S trending vertical quartz dykes (27 and 27') and two E-W trending faults, the Northern fault and the Southern fault. The Southern fault is subvertical, whereas the Northern fault dips gently southwards (Fig. 2). The uranium deposit is concentrated in the two dykes (0.4-1.8 m wide, 360 m large and 160 m deep), and consists of pitchblende with iron sulphides that contain variable amounts of arsenic, oxides and carbonates. The deposit was mined by four levels of horizontal galleries interconnected by vertical shafts, the main one being the Pozo Maestro. A total of 125.000 t of ore with 0.23% U_3O_8 was extracted from 1959 to 1975. Then, the galleries were filled up with material from the rock wastes, pumping was stopped, and the mine was flooded with about 0.15 hm³ of water.

Based on the physical properties of the granite and the hydraulic parameters derived from hydraulic testing, five geological units have been defined vertically (Ortuño *et al.*, 2001). A shallow unit of lehm, with a heterogeneous distribution, 3-8 m deep; an upper weathered unit, 20-49 m deep, intensively fractured, with a hydraulic transmis-
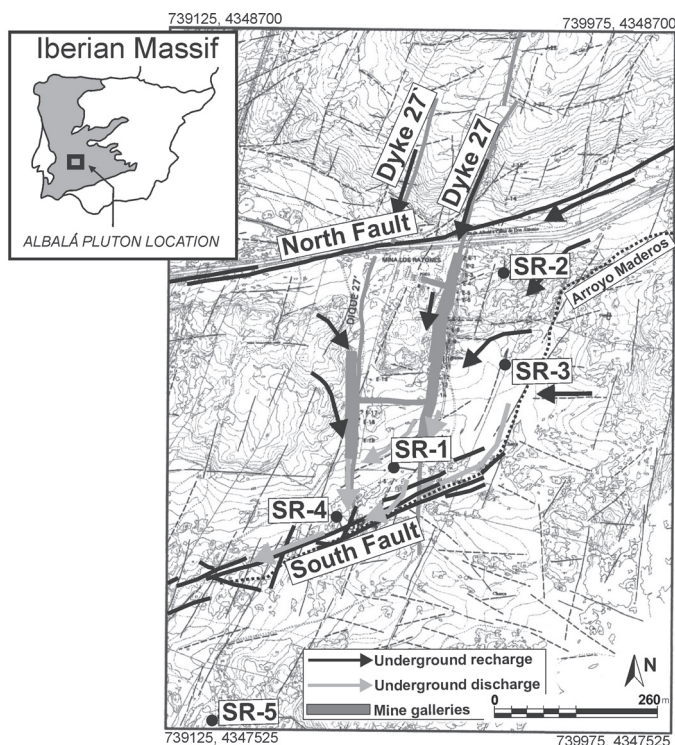
Fig. 1.- Location, geology and structure of Los Ratones mine: Dykes 27 and 27'. SR: stands for borehole location.

Fig. 1.- Localización, geología y estructura de la mina Los Ratones: diques 27 y 27'. SR: localización de los sondeos.

sivity in the range 1E-5 and 1E-4 m²/s; a fractured unit, with high porosity and fractures, 100-150 m deep, with a transmissivity of approximately 1E-6 m²/s; a deep granite with low deformation (granitic matrix), from 150 m deep and transmissivity of 1E-9 to 1E-11 m²/s approximately. Finally a brittle fracture system, with a decametric width, and transmissivity ranging between 1E-5 and 1E-7 m²/s decreasing with depth, superimposes the four previous units.

A network of four packered boreholes (SR1, SR2, SR3 and SR4), 101 mm of diameter, length from 77 to 195 m, and inclination between 0° and 30°, was installed in the mine area, to monitor groundwater levels and collect groundwater and solid samples (see location in figure 1). The four research boreholes, (SR), intercept a main structure: SR1-T1 crosses Dyke 27 between 76 and 50 m depth; SR2-T1 crosses the Northern fault between 79 and 37 m depth; SR3-T1 crosses the Northern Fault between 195 and 137 m depth and SR4-T1 intercepts the Southern Fault between about 125 and 75 m depth. There is one more borehole, (SR5), which was drilled far from the mine and will not be used for this study. The five boreholes were rotary drilled with continuous core recovery. Fresh water with a different tracer in each borehole was used as drilling fluid. Moreover, two mine shafts (the access shaft or Pozo Maestro and the ventilation shaft) were

also monitored and used for groundwater sampling.

In a regional setting, water flows from NE to SW, controlled by the topography and the conductive structures of the granite pluton. There are no significant aquifers, and granite materials provide sparsely vegetated soils. The mean annual rainfall is about 578 mm/year and the estimated recharge about 20-30 mm/year. At mine scale and under natural conditions, groundwater levels to the north are always higher than in the mine shafts. A previous local flow model showed that the mine is recharged from the north, from the lehm and from the E-W fracture system (Martínez-Landa *et al.*, 1999). It discharges to the south through the dykes, and through the southern fault where the Maderos River is located. Gradients to the north and south, (recharge and discharge), are about 0.10-0.11, whereas from the east, the recharge gradient is about 0.03-0.06, and within the mine it is estimated as 0.001. The mine basically controls the piezometry, because the galleries act like a drain due to their high transmissivity.

3. Lithological and hydrochemical setting

An exhaustive solid phase characterization was carried out by Buil (2002). The mineralogy of the granite is composed of quartz, alkaline-plagioclase (0.97 albite), K-feldspar, muscovite and biotite. Pyrite, uraninite, cordierite, andalucite, monacite and zircon were also found as minor phases. More interesting from the water-rock-interaction point of view are fracture filling phases. Inherited minerals of the granite are present in all the samples from fractures, showing dissolution textures (particularly albite). Moreover, secondary minerals formed from alteration of granite minerals are ubiquitous in fractures, and their abundance varies between fractures. Among carbonates, an ankerite phase of variable composition with average around $CaFe_{0.3}Mg_{0.7}(CO_3)_2$ is present throughout the entire fracture system. Apatite, and a silica gel phase are also described in many fissure fillings (Pérez del Villar *et al.*, 1999). In addition, kaolinite in the shallow part of the system (<50 m depth) and smectite in the deeper part are also abundant. Uraninite and occasionally coffinite are the U(IV) phases present in the veins and fractures throughout the system, whereas U(VI)-phosphates and gummites are found in shallow weathered zones of borehole SR4 and the Southern Fault. As already pointed out by Arribas (1962), uraninite is partially oxidized. This seems a common feature in uranium mines. Thus, Ahonen *et al.* (1993) suggest that groundwater samples from Palmottu uranium mine in Finland, are equilibrated with U_3O_7. Similarly, Gómez (2002) describes that groundwater samples from Ratones mine show better equilibration
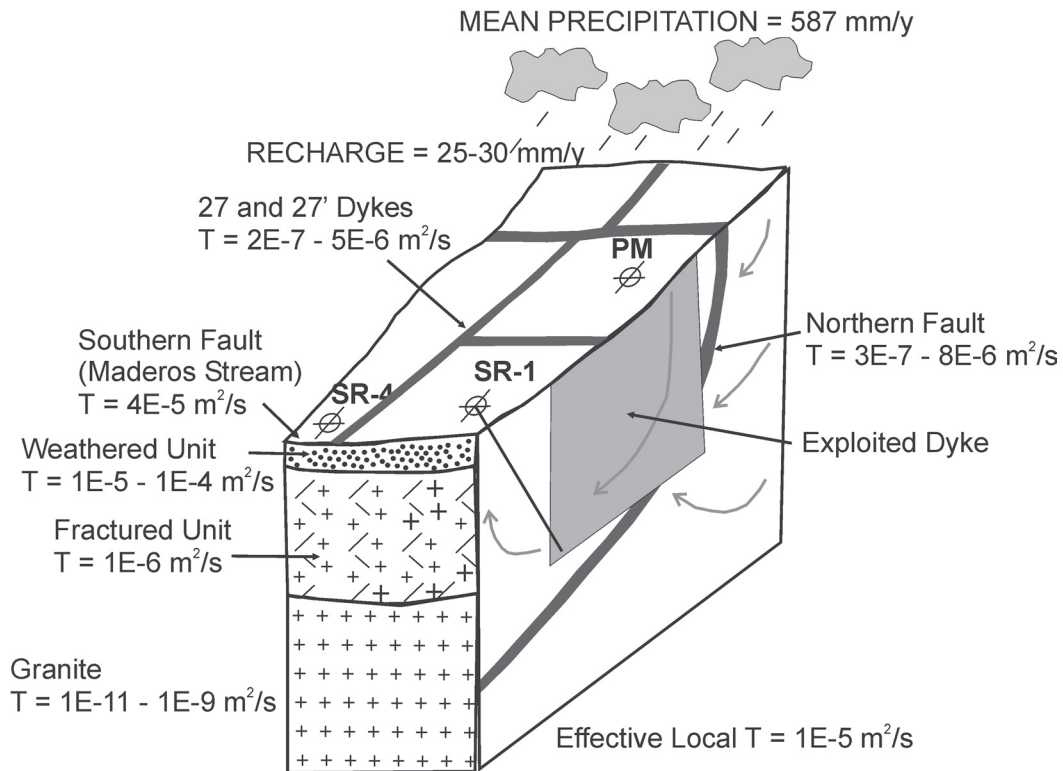
MEAN PRECIPITATION = 587 mm/y

RECHARGE = 25-30 mm/y

27 and 27' Dykes
T = 2E-7 - 5E-6 m²/s

PM

Southern Fault
(Maderos Stream)
T = 4E-5 m²/s

Northern Fault
T = 3E-7 - 8E-6 m²/s

SR-1

SR-4

Weathered Unit
T = 1E-5 - 1E-4 m²/s

Exploited Dyke

Fractured Unit
T = 1E-6 m²/s

Granite
T = 1E-11 - 1E-9 m²/s

Effective Local T = 1E-5 m²/s

Fig. 2.- Vertical zonation, main structures and conceptual flow model of Los Raones mine. SR: stands for borehole location.
Fig. 2.- Zonación vertical, estructuras principales y modelo de flujo conceptual de la mina Los Ratones. SR: localización de los sondeos.

with U_4O_9 and U_3O_7 than with uraninite. Pyrite and minor amounts of arsenopyrite and chalcopyrite are present in fissures, but are particularly abundant in the mineralized veins. Ferrihydrite is found in many solid samples and is present as a colloidal phase in the filters using during groundwater samples (Gómez, 2002). It is particularly abundant in precipitates around the groundwater discharges under atmospheric conditions. Ferrihydrite is found in many solid samples and is present as a colloidal phase in the filters used during groundwater sampling (Gómez, 2002). It is particularly abundant in precipitates around groundwater discharges under atmospheric conditions. Ferrihydrite contains minor amounts of As and U (up to 10^{-4} molar). At the Southern Fault (102.67 m) the presence of autunite, indicative of oxidizing conditions, and the presence of U-silicophosphates, indicative of more reducing conditions, seems to indicate that it is a transition redox zone in the oxidation of U(IV) to U(VI), although their coexistence with altered pyrite indicates dominant oxidizing conditions.

An exhaustive hydrochemical characterization was carried out by Gómez *et al.* (1999, 2000, 2001), and summarized by Gómez (2002). No important seasonal variations in the water chemistry were observed, and Table 1 shows analyses of representative samples used in the calibration of the reactive transport calculations. As explained above, the mine water under natural conditions discharges through the dyke and Southern Fault. Therefore, water at sampling points SR1 and SR4 is a mixture of mine water and dyke water. To ensure that SR1-T1 sample is representative of the dyke water and SR4-T1 of the Southern Fault, samples collected during long-term pumping in September 2000 were chosen.

Most of the samples are HCO_3-Ca type evolving to HCO_3-Na type waters at depth upstream of the mine. Only the shallow samples of SR1 and SR4 boreholes are SO_4-Mg type. Conductivity values are low (<760 µS/cm), pH circum-neutral (from 6.2 to 8.4), and Eh reducing in general (from 0 to –300 mV). A plot of the groundwater analyses in a pH-Eh diagram suggests that the redox system is controlled by the $Fe^{2+}/Fe(OH)_3$ and SO_4^{2-}/S^{2-} equilibria (Gómez, 2002).

Uranium concentrations range from the detection limit to 104 ppb, which are quite low taking into account that the mine was exploited for uranium. Two groundwater types are distinguished by looking at the Fe and As data. High Fe and As concentrations can be found in points directly related to the mine (SR1, Pozo Maestro and some-
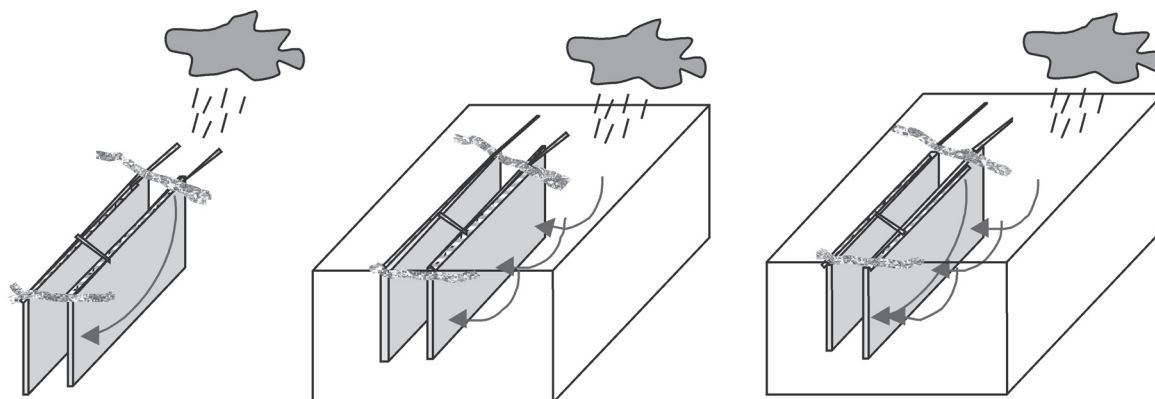
Fig. 3.- Three conceptual models for groundwater flux depending on the flow path and water-rock interaction options: A) Mine Oxidation Model; B) Rock Oxidation Model; C) Mixed Oxidation Model.

Fig. 3.- Tres modelos conceptuales para el flujo de agua subterránea dependiendo de las vías de flujo y de la interacción agua-roca: A) Modelo de Oxidación de la Mina; B) Modelo de Oxidación de la Roca; C) Modelo de Mezcla de Oxidación.

what lower in SR4), with Fe as high as 28 mg/l (most of it Fe^{2+}) and arsenic at 2.5 mg/l (see Table 1, Pozo M). The other groundwater type shows low iron and arsenic concentrations as observed in points not related to the mineralized dykes (SR2, SR3).

4. Reactive transport modeling

4.1. Conceptual models

Three conceptual models of the hydrogeochemistry of the mine area are analyzed. The models differ in terms of flow and hydrochemistry (Fig. 3):

1.- Mine oxidation model: In this model, rainwater equilibrated with atmospheric O_2 and CO_2 infiltrates from the surface along the dyke where the mined galleries act as preferential conduits. Dissolution-precipitation reactions are assumed to take place between water and the walls and the loose fragments that fill the galleries. This is the conceptual model currently assumed for predicting the quality of discharges from abandoned mines (Adams and Younger, 2001).

2.- Rock oxidation model: In the second case, rainwater infiltrates through the weathered granite. As the rainwater infiltrates through the unsaturated lehm the recharge wa-

ter becomes partly evaporated, equilibrates with the pCO_2 of the soil (estimated as $10^{-2.5}$), and atmospheric oxygen. Because of the high porosity of the lehm, the surface area in contact with O_2 is greater than in the previous model. Finally carbonates are assumed to have been dissolved in the upper granite zone. This is supported by the fact that shallow groundwater analyses are clearly undersaturated with respect of carbonates, whereas they are equilibrated in the rest of the system (Gómez, 2002).

3.- The third case is a mixture of these two cases described above, with a flow line of meteoric water infiltrating directly along the dyke and with lateral recharge into the dyke of groundwater which previously infiltrated through the lehm and the granite.

4.2. Numerical models

The flow systems of the three conceptual models were simplified as 1D numerical grids of 250 m long discretized into 100 elements. A stationary flow with prescribed head was imposed as a boundary condition in the mine and rock oxidation models (Fig. 4). A hydraulic conductivity of 1 m/y and a gradient of 0.02 were inferred from the regional hydrogeological setting, resulting in a flow of 0.02 m/y (20 mm/y). In the mixed model, however, a

Borehole	Depth (m)	Date (m/d/y)	pH	Eh (mV)	pe	HCO$_3$ (mol/L)	SO$_4$	Ca	Mg	Na	Fe	SiO$_2$	As	U
Pozo M	0.0-164	9/19/00	7.0	-200	-3.38	2.34E -03	6.46E -04	7.38E -04	5.69E -04	6.09E -04	5.05E -04	6.31E -04	2.04E -05	1.68E -08
SR1 -T1	50.1-76.1	9/20/00	7.65	-200	-3.38	2.74E -03	1.72E -03	8.21E -04	1.26E -03	1.35E -03	1.83E -04	6.76E -04	1.08E -05	4.20E -09
SR1 -T2	25.3-49.1	9/21/00	7.05	-200	-3.38	1.51E -03	2.20E -03	7.46E -04	1.24E -03	1.52E -03	4.70E -05	6.10E -04	5.23E -07	2.52E -08
SR1 -T3	0.00-24.3	9/26/00	7.23	-165	-2.79	1.46E -03	2.53E -03	8.29E -04	1.25E -03	1.32E -03	1.79E -04	6.86E -04	1.93E -07	4.20E -08

Table 1.- Chemistry of representative groundwater analyses used in model calibration.

Tabla 1.- Composición química de las aguas subterráneas utilizadas para la calibración del modelo.
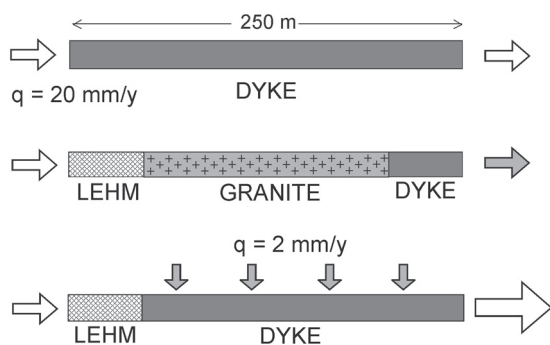
Fig. 4.- Sketch of the reactive transport models corresponding to the three conceptual models of figure 3.

Fig. 4.- Esquema de los modelos de transporte reactivo correspondientes a los tres modelos conceptuales de la figura 3.

constant flow of 0.02 m/y was imposed at the upstream boundary, and a lateral recharge of 0.002 m/y was also assumed for each numerical element. A longitudinal dispersivity of 2.5 m was assumed in all cases.

The geochemical model has been built up with 13 primary species (H^+, e^-, H_3AsO_3, HCO_3^-, Fe^{2+}, Mg^{2+}, SO_4^{2-}, Ca^{2+}, Al^{3+}, Mn^{2+}, $SiO_{2(aq)}$, Na^+, UO_2^{2+}), 34 additional aqueous complexes (OH^-, $H_2AsO_3^-$, $H_4AsO_3^+$, $H_2AsO_4^-$, $H_3AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, $CO_{2(aq)}$, $CaHCO_3^+$, $MgHCO_3^+$, $MnHCO_3^+$, CO_3^{2-}, Fe^{3+}, $FeSO_{4(aq)}$, $Fe(OH)_2^+$, $Fe(OH)_4^-$, $Fe(OH)_{3(aq)}$, $MgSO_{4(aq)}$, $O_{2(aq)}$, $H_2S_{(aq)}$, HS^-, $CaSO_{4(aq)}$, $Al(OH)_{3(aq)}$, $AlOH^{2+}$, $Al(OH)_4^-$, $Al(OH)_2^+$, $U(OH)_5^-$, $U(OH)_{4(aq)}$, U^{4+}, UO_2OH^+, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2CO_{3(aq)}$), 8 minerals (ankerite, pyrite, arsenopyrite, albite, chalcedony, ferrihydrite, siderite and U_3O_7), and 2 gases (O_2 and CO_2). Although present, K-feldspar, biotite, kaolinite and smectite have been omitted to simplify the calculations. Some calculations show that including these phases does not significantly modify the conclusions. The equilibrium constants of the different species are those from the EQ3NR thermodynamic database (Wolery, 1992), with the exception of ankerite (Al *et al.*, 2000). The kinetic laws and dissolution rate constants at 25°C for the minerals are listed in Table 2. Reactive transport calculations were performed with the code RETRASO (Saaltink *et al.*, 2004). The initial mineral composition of each lithology composing the three reactive transport models is described in Table 3.

The meteoric water of the region (Gómez, 2002) was assumed as boundary water for the Mine Oxidation Model (Table 4). For the boundary water of the Rock Oxidation Model and the Mixed Model, meteoric water was arbitrarily evaporated ten times in the pores of the unsaturated zone, and equilibrated with a P_{CO2} of $10^{-2.5}$ bar, typical of a poorly vegetated soil. Finally, in coherence with the conceptual model (Figs. 3 and 4) the water recharging laterally into the Mixed Model was assumed similar to the water resulting from the Rock Oxidation Model (Table 3).

Mineral	Stoichiometry	Dissolution rate law $(mol \cdot m^{-2} \cdot s^{-1})$	Ref.
Ankerite	$CaFe_{0.3}Mg_{0.7}(CO_3)_2$	$2.2 \times 10^{-8} \cdot (\Omega-1)$ (=dolomite)	(1)
Pyrite	FeS_2	$[6.4 \times 10^{-9} \cdot a_{O2}^{0.5} + 10^{-5} \cdot a_{Fe+3}^{0.9} \, a_{Fe+2}^{-0.4}] \cdot (\Omega-1)$	(2)
Arsenopyrite	$FeAsS$	(=pyrite)	(2)
U_3O_7	UO_2	$[1.4 \times 10^{-8} \cdot a_{H+}^{0.53} + 4 \times 10^{-12}] \cdot (\Omega-1)$ (= uraninite)	(3)
Albite	$NaAlSi_3O_8$	$[4 \times 10^{-10} \cdot a_{H+}^{0.5} + 0.8 \times 10^{-14} \cdot a_{H+}^{-0.3}] \cdot (\Omega-1)$	(4)
Chalcedony	SiO_2	precipitation in equilibrium	
Ferrihydrite	$Fe_{0.91}As_{0.09}(OH)_3$	$1.7 \times 10^{-13} \cdot a_{HCO3-}^{0.26} \cdot (\Omega-1)$	(7)
Siderite	$FeCO_3$	$4.64 \times 10^{-7} \cdot (\Omega-1)$ (= calcite)	(8)

Table 2.- Stoichiometry of minerals included in the model and experimental dissolution rate constant (Ω accounts for saturation). References: (1) Chou *et al.* (1989); (2) Nicholson (1994); (3) Bruno *et al.* (1991); (4) Chou and Wollast (1985); (7) Grivé (2005); (8) Inskeep and Bloom (1985).

Tabla 2.- Estequiometría de los minerales incluidos en el modelo y ley de disolución experimental (Ω representa el estado de saturación). Referencias: (1) Chou *et al.* (1989); (2) Nicholson (1994); (3) Bruno *et al.* (1991); (4) Chou and Wollast (1985); (7) Grivé (2005); (8) Inskeep and Bloom (1985).

	Weathered granite		Granite		Mineralized dyke	
Mineral	V_x	σ	V_x	σ	V_x	σ
Ankerite	0	0	10^{-2}	10^{-4}	0.4	0
Pyrite	10^{-2}	1	10^{-2}	1	10^{-2}	1
Arsenopyrite	10^{-2}	0.1	10^{-2}	0.1	10^{-2}	1
U_3O_7	10^{-3}	0.1	10^{-3}	0.1	10^{-2}	1
Albite	0.2	10	0.2	10^{2}	0.2	10
Chalcedony	0	0	0	0	0	0
Ferrihydrite	10^{-3}	1	10^{-3}	1	10^{-3}	1
Siderite	0	0	0	0	0	0
Porosity	0.1		10^{-2}		10^{-2}	

Table 3.- Initial volume fraction of minerals and reactive surface area (m^2 m^{-3} of rock) of the three lithologies used in the calculations.

Tabla 3.- Fracción volumétrica inicial de minerales y área superficial reactiva (m^2 m^{-3} de roca) de las tres litologías utilizadas en los cálculos.
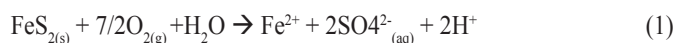
5. Results and discussion

The results of the reactive transport calculations are compared with selected analyses of groundwater. The samples from Pozo Maestro have been selected as representative of the water contained in the galleries of the mine (Mine Oxidation Model). In the regular groundwater regime Pozo Maestro discharges into the Southern Fault through borehole SR4, and water sampled in SR4-T1 (the deepest part from SR4) is usually representative of the water retained in the galleries. However, in September 2000 Pozo Maestro was intensively pumped, and the groundwater flux was reversed from SR4-T1 towards Pozo Maestro. Therefore, waters sampled in September 2000 at different depths of borehole SR1 were considered representative of water infiltrating through the weathered rock surrounding the veins (Rock Oxidation Model).
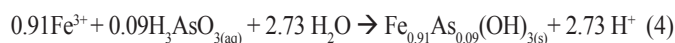
5.1. Mine Oxidation Model

The modelling results from varying solid phase volumes (dissolution/precipitation) and the evolution of the chemistry of the groundwater are plotted in figures 5, 6 and 7, respectively. The results are compared with groundwater sampled in Pozo Maestro, representative of the bulk water retained in the gallery system.

In the Mine Oxidation Model, rainwater infiltrates directly into the mine and reacts with the dyke-forming minerals exposed on the walls of the gallery. The oxidizing agent is the dissolved oxygen which oxidizes the arsenic and iron sulphides:

$$FeS_{2(s)} + 7/2 O_{2(g)} + H_2O \rightarrow Fe^{2+} + 2SO4^{2-}_{(aq)} + 2H^+ \qquad (1)$$

$$FeAsS_{(s)} + 11/2 O_{2(g)} + 3/2 H_2O \rightarrow Fe^{2+} + SO4^{2-}_{(aq)} + H_3AsO_{3(aq)} \qquad (2)$$

If oxygen is still available Fe(II) is oxidized to Fe(III) and ferrihydrite precipitates, co-precipitating some As with it. Ferrihydrite has been described as a common fracture-filling mineral (Buil, 2002). Since the inventory of dissolved oxygen is limited most of the Fe(II) is carried downstream and only a minor fraction precipitates as ferrihydrite:

$$Fe^{2+} + \tfrac{1}{4} O_{2(g)} + 2H^+ \rightarrow Fe^{3+} + \tfrac{1}{2} H_2O \qquad (3)$$

$$0.91 Fe^{3+} + 0.09 H_3AsO_{3(aq)} + 2.73 H_2O \rightarrow Fe_{0.91}As_{0.09}(OH)_{3(s)} + 2.73 H^+ \quad (4)$$

U(IV) in U_3O_7 is oxidized to U(VI). No U(VI) phases have been included in the model due to poor thermodynamic data. Therefore, all the U(VI) in solution is carried downstream by water. As oxygen is exhausted by pyrite and pe decreases, dissolved U(VI) is reduced again to U(IV). No coffinite is assumed to be precipitated in the reducing part of the system.

	MINE MODEL BOUNDARY WATER	ROCK MODEL BOUNDARY WATER	MIXED MODEL BOUNDARY WATER 1	MIXED MODEL BOUNDARY WATER 2
pH	5.30	4.30	4.30	7.60
pe	15.27	15.57	15.57	3.56
As	1.00E-14	1.00E-14	1.00E-14	1.32E-07
TIC	1.20E-5 (1)	1.10E-4 (2)	1.10E-4 (2)	2.83E-03
Fe	8.93E-07	8.93E-06	8.93E-06	1.01E-05
Mg	1.90E-05	1.90E-04	1.90E-04	1.04E-04
SO$_4$	2.50E-05	2.70E-04	2.70E-04	1.66E-03
Ca	4.50E-05	4.50E-04	4.50E-04	1.60E-03
Al	1.00E-09	1.00E-09	1.00E-09	1.40E-07
Mn	5.45E-08	5.45E-07	5.45E-07	5.45E-06
SiO$_2$	8.33E-07	8.33E-06	8.33E-06	4.88E-04
Na	3.50E-05	3.50E-04	3.50E-04	1.65E-03
U	1.00E-14	1.00E-14	1.00E-14	1.40E-11

Table 4.- Chemical compositions (mol/L) of boundary water solutions used in the calculations. TIC= total inorganic carbon. (1) Calculated in equilibrium with a CO$_2$ partial pressure of $10^{-3..5}$ bar. (2) Calculated in equilibrium with a CO$_2$ partial pressure of $10^{-2.5}$ bar.

Tabla 4.- Composición química (mol/L) del agua de contorno utilizada en los cálculos. TIC= carbono inorgánico total. (1) Calculado, en equilibrio con una presión parcial de CO$_2$ de $10^{-3..5}$ bar. (2) Calculado, en equilibrio con una presión parcial de CO$_2$ de $10^{-2.5}$ bar.

The acidity contained in the rainwater as carbonic acid plus the acidity produced during sulphide oxidation and ferrihydrite precipitation induces the dissolution of ankerite present in the dyke. This process raises pH to values higher than neutral and liberates Fe(II), Ca and Mg to the water (Mn is excluded for simplicity):

$$CaFe_{0.3}Mg_{0.7}(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + 0.3\ Fe^{2+} + 0.7\ Mg^{2+} + 2HCO_3^- \quad (5)$$
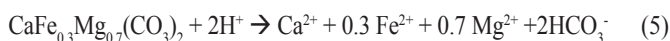
Bicarbonate released in ankerite dissolution reacts with Fe(II) released in the sulphide oxidation, and saturation and precipitation of siderite takes place:

$$HCO_3^- + Fe^{2+} \rightarrow FeCO_{3(s)} + H^+ \quad (7)$$

Bicarbonate released during ankerite dissolution reacts with Fe(II) released in the sulphide oxidation, and saturation and precipitation of siderite takes place:

$$HCO_3^- + Fe^{2+} \rightarrow FeCO_{3(s)} + H^+ \quad (6)$$

Secondary siderite has not been observed in the fracture filling of Los Ratones dyke, although it is commonly described phase in tailings and in near-neutral sulphide oxidation environments (Dubrovsky *et al.*, 1985; Al *et al.*, 1994; Blowes and Ptacek, 1994).

The acidity of the recharge also causes albite dissolution, as evidenced in many samples observed under Scanning Electron Microscopy (Buil, 2002):

$$NaAlSi_3O_8 + 4H^+ \rightarrow Na^+ + Al^{3+} + 3SiO_2(aq) + 2\ H_2O \quad (7)$$
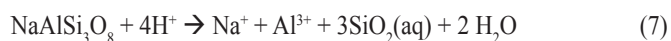
The dissolution rate of albite depends on pH and saturation of the solution (Table II). The dissolution rate is initially high (Fig. 5), although it decreases as pH increases and equilibrium is approached due to ankerite (and albite) dissolution. The concentration of dissolved silica increases and reaches the saturation of chalcedony, which precipitates (Fig. 5). Chalcedony and mainly silica gel are found in fracture filling throughout the Ratones system (Pérez del Villar *et al.*, 1999). Precipitation of chalcedony removes silica from water, decreases saturation with respect to albite, and enhances the dissolution of this mineral.

Because of water flow and the water-mineral reactions described above, pH increases rapidly up to values close to 9. These values are clearly higher than measured values, and are due to the low Ca and TIC (total inorganic carbon) content of the inflow water. Thus, due to the low concentration of Ca, Mg, Fe(II) and TIC in the rain water,
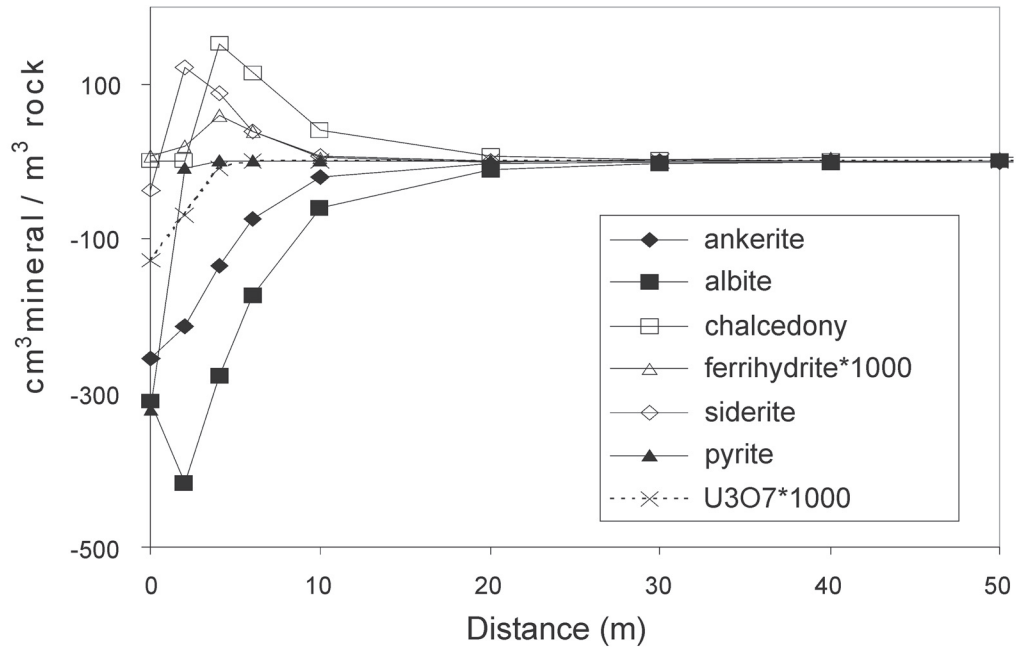
Fig. 5.- Mineral dissolution/precipitation as calculated for the Mine Oxidation Model, after 10^4 years of elapsed time.

Fig. 5.- Disolución/precipitación de minerales calculadas para el Modelo de Oxidación de la Mina, después de un lapso de tiempo de 10^4 años.
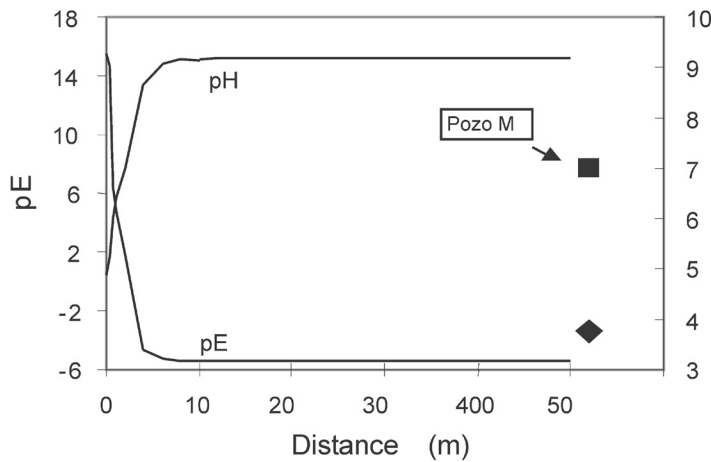

Fig. 6.- pH and pe values of groundwater as calculated by the Mine Oxidation Model. Results are compared with the values measured in Pozo Maestro.

Fig. 6.- Valores de pH y pe del agua subterránea calculados para el Modelo de Oxidación de la Mina. Los resultados se comparan con los valores medidos en el Pozo Maestro.
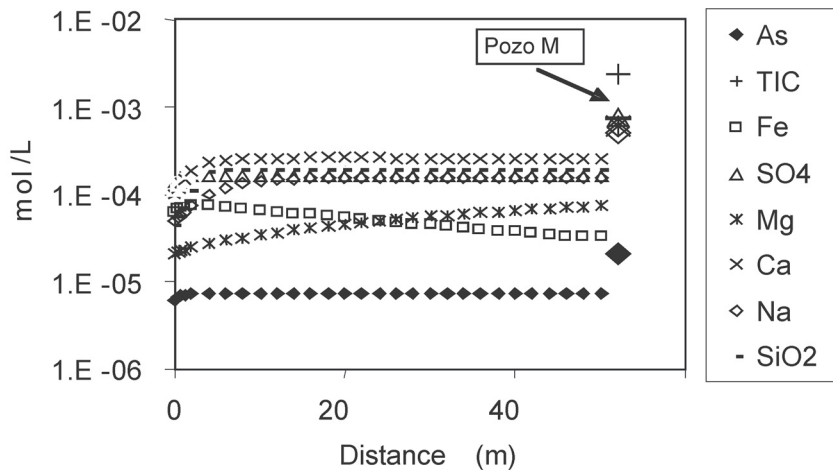
Fig. 7.- Concentration of major elements of groundwater as calculated for the Mine Oxidation Model. Uranium concentrations are always below 1.0E-7 mol/L. Results are compared with values measured in Pozo Maestro.

Fig. 7.- Concentración de elementos mayoritarios en el agua subterránea calculados para el Modelo de Oxidación de la Mina. Las concentraciones de uranio están siempre por debajo de 1.0E-7 mol/L. Los resultados se comparan con los valores medidos en el Pozo Maestro.

stoichiometric proton consumption required in reaction 5 causes pH to increase to a high value as the water reaches equilibrium with ankerite.

Due to the high concentration in the solution, Fe is assumed to control the redox system. Therefore, high pH values lead to low pe values, at Fe^{2+}-$Fe(OH)_3$(s) equilibrium. As observed in figure 6, water reaches highly reduced conditions after 20 m of circulating through the dyke because sulphide oxidation rapidly consumes dissolved oxygen. Reducing conditions in most of the system allow U_3O_7 preservation and justify the low uranium concentrations in groundwater. With the exception of As, the predicted concentrations of the rest of solutes is at least one order of magnitude lower than those measured in Pozo Maestro (Fig. 7).

5.2. Rock Oxidation Model

In contrast to the previous Mine Oxidation Model, water is assumed to infiltrate also through the surroundings of the mine. In accordance with field observations, a zone of 5 m of weathered granite with unsaturated water flux is assumed as an uppermost layer (lehm). Below that, water flows into weathered granite and finally recharges laterally the galleries in the dyke. Water flows from the surface to the dyke through the fractures and through the granite. As the rainwater infiltrates through the lehm it becomes partly evaporated, equilibrates with the P_{CO2} of the soil (estimated as $10^{-2.5}$ bar) and with atmospheric oxygen. Therefore, unlike the Mine Oxidation Model, the oxidizing and acid carbonic capacity of the water is not only based on atmospheric oxygen and CO_2, but on the gas phase in the unsaturated zone. Finally, since the shallow water samples are highly unsaturated in carbonates (Gómez, 2002), ankerite has been assumed to be absent in fracture fillings for the uppermost 30 m of the Rock Oxidation Model.

Water-rock interaction processes are very similar to those described in the Mine Oxidation Model: pyrite oxidation, albite and ankerite dissolution, and ferrihydrite, chalcedony and siderite precipitation (Fig. 8). Compared to the previous model, however, and due to the higher oxidation capacity, pyrite dissolves more intensively and dissolved SO_4 and Fe increase to higher values. The thickness of the zone where mineral-water reactions take place is greater, and the amount of mineral involved is higher, than in the Mine Oxidation Model (note the scales of figure 5 and figure 8). Moreover pH remains lower in the shallower part where ankerite is absent and water remains unsaturated in albite, in accordance with analyses (Gómez, 2002). Due to this and to the higher reactive surface, albite dissolution is enhanced and silica, sodium and aluminium concentrations increase to values that are close to measured concentrations (Fig. 10). The model probably overestimates precipitation of chalcedony. This is because for simplicity the model has not considered kaolinite and smectite formation. Alternative calculations including these two minerals indicate the formation of kaolinite in the shallow few metres and of smectite in deeper zones, in accordance with observations (Buil, 2002). Since arsenopyrite has only been found in the dyke, only a minor amount is assumed in the lehm and granite, and when water reaches the dyke it is too reduced for arsenopyrite to dissolve. Therefore, the As concentration predicted with the Rock Oxidation model is much lower than observed.

When water reaches ankerite it already contains higher concentrations of TIC (total inorganic carbon), Ca, Mg and Fe due to higher soil P_{CO2}, evaporation and pyrite dissolution. Thus equilibrium with ankerite is reached in the model at lower pH values, very close to those observed (Fig. 9). Evolution of pe decreases in accordance with the pH increase along the Fe^{2+}-$Fe(OH)_3$(s) equilibrium boundary, and reaches values that are also close to measured values.

5.3. Mixed Oxidation Model

The high arsenic concentrations measured at some points directly connected with the mine or the mineralized dyke, and the presence of arsenopyrite in percent concentrations in the dyke mineralogy, motivated the generation of the Mixed Oxidation Model. It is similar to the Rock Oxidation Model, although the oxidizing water also infiltrates through the dyke from the surface and through the E-W conductive structures that cross the dyke. The oxidative dissolution of arsenopyrite also takes place. Results are very similar to the Rock Oxidation Model, and measured solute concentrations, including those of arsenic, are comparable.

6. Conclusions

The main hydrochemical trends are similar in the three models: acidic and oxidizing conditions at surface trending to neutral and reducing water at depth. However, as can be observed in figures 11 and 12, the Mine Oxidation Model underestimates the measured solute concentrations in groundwater by an order of magnitude, overestimates pH by more than a unit and calculates pe to be too negative. The Rock Oxidation and Mixed Oxidation Models match the measured concentrations and the pH and pe
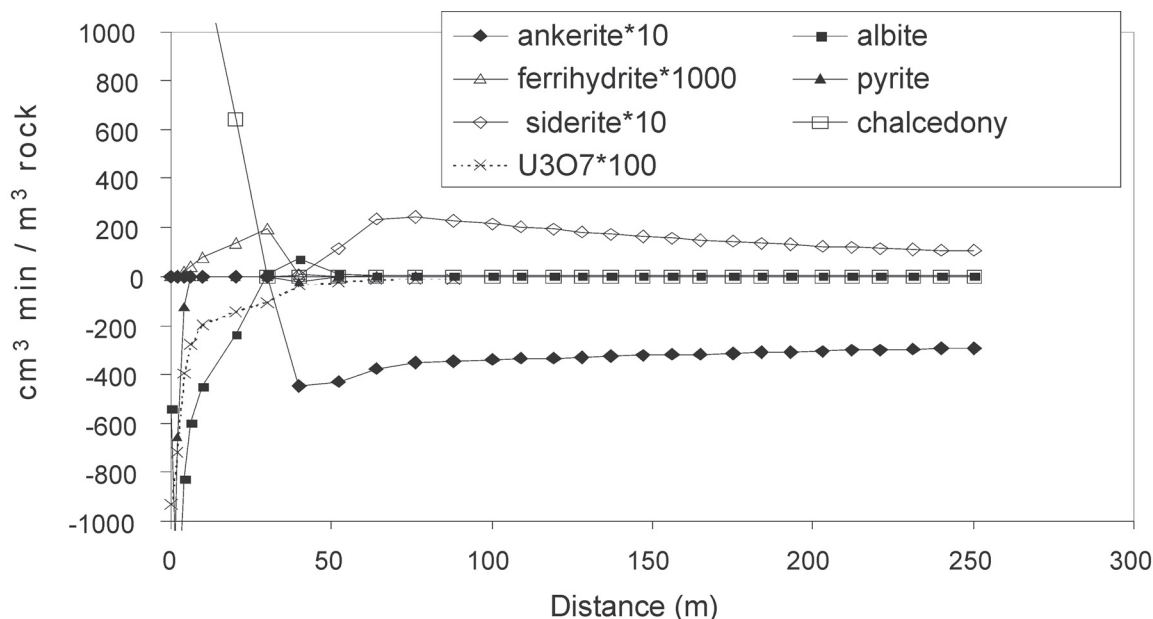
Fig. 8.- Mineral dissolution/precipitation as calculated for the Rock Oxidation Model, after 10^4 years of elapsed time.

Fig. 8.- Disolución/precipitación de minerales calculadas para el Modelo de Oxidación de la Roca, después de un lapso de tiempo de 10^4 años.
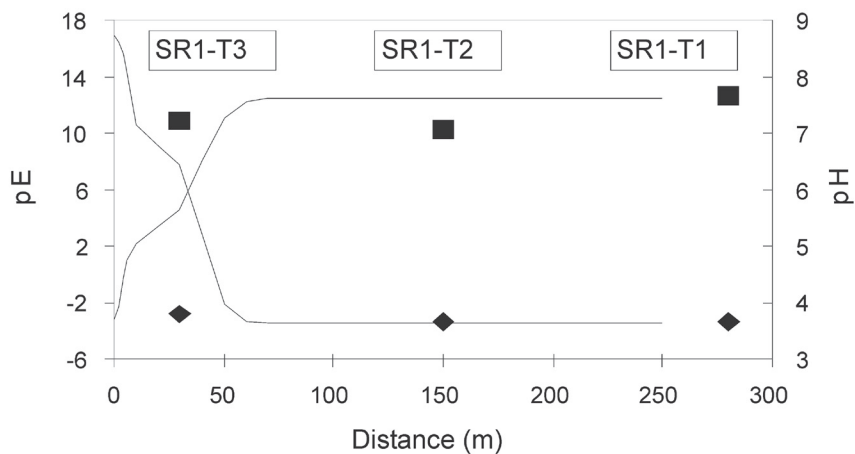

Fig. 9.- pH and pe values of groundwater as calculated for the Rock Oxidation Model. Results are compared with the values measured in the SR1 borehole.

Fig. 9.- Valores de pH y pe de las aguas subterráneas calculados para el Modelo de Oxidación de la Roca. Los resultados se comparan con los valores medidos en el sondeo SR1.
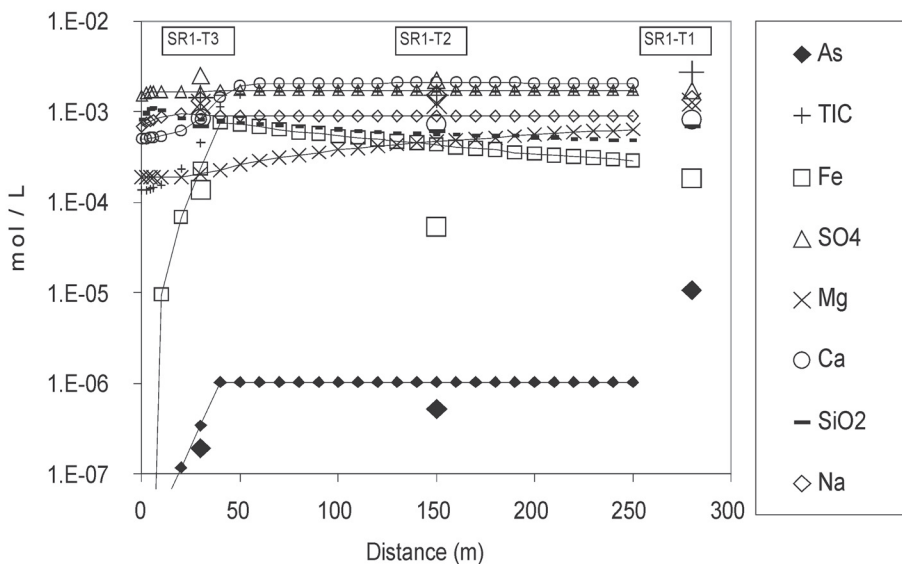

Fig. 10.- Concentration of major elements of groundwater as calculated for the Rock Oxidation Model. Uranium concentrations are always below 1.0E-7 mol/L. Results are compared with the values measured in the SR1 borehole.

Fig. 10.- Concentración de elementos mayoritarios del agua subterránea calculados para el Modelo de Oxidación de la Roca. Las concentraciones de uranio están siempre por debajo de 1.0E-7 mol/L. Los resultados se comparan con los valores medidos en el sondeo SR1.
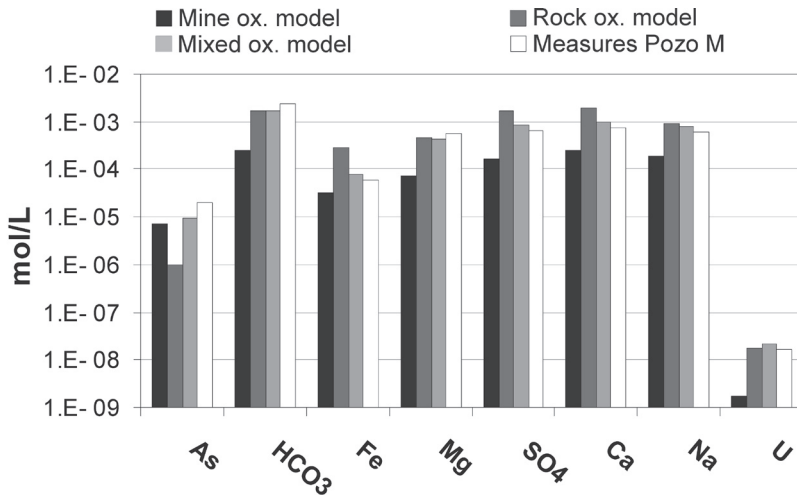
Fig. 11.- Comparison of the modeled solute concentra-
tions with values measured at Pozo Maestro.

Fig. 11.- Comparación de las concentraciones de solu-
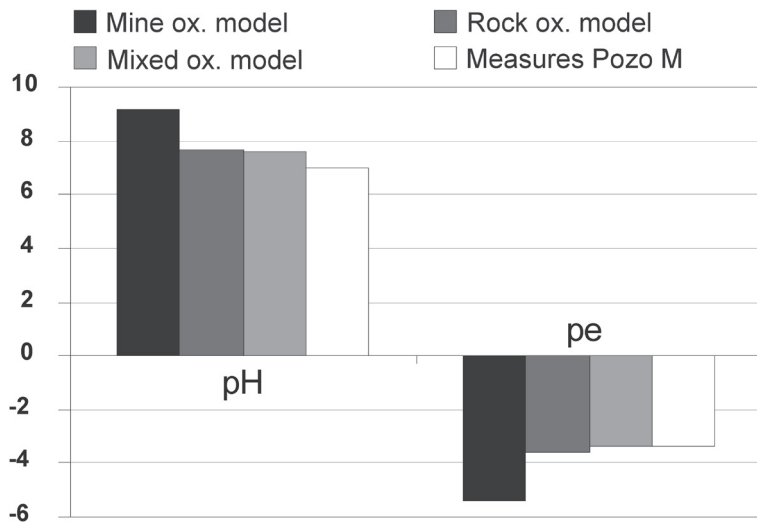tos calculadas y medidas en el Pozo Maestro.

Fig. 12.- Comparison of the modeled pH and pe values
with values measured at Pozo Maestro.

Fig. 12.- Comparación de los valores de pH y pe cal-
culados y medidos en el Pozo Maestro.

values. The Mixed Oxidation Model also matches arsenic concentrations. The main uncertainties of the calculations are in the reactive surface areas assumed from minerals. Additional calculations including variations of initial surface area values lead to modifications in the amount of dissolution and in the thickness of the dissolution zone for each mineral. These changes, however, do not modify significantly the pH and pe and the solute concentrations resulting from the calculations. This is due to the fact that equilibrium is eventually reached for the different minerals involved in the reactions.

Water-rock reactions are similar in all three models, main differences being the intensity of oxidation-disso-lution processes taking place in the shallow part of the surrounding granite. The rapid exhaustion of oxygen and the low concentration of the recharge water in the Mine Oxidation Model are the cause of low predicted solute concentrations. In contrast, processes in the unsaturated zone of the Rock Oxidation and Mixed Oxidation models cause higher dissolution of minerals and solute concen-

trations that better match the measured composition of groundwater.

Therefore, unlike the models which predict the quality of mine water based on reactions within the galleries, our modelling exercise in Los Ratones mine shows the key role of water infiltrating through the surrounding rock and the water-rock interaction processes taking place in the shallow subsurface.

Acknowledgements

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