Inverse geochemical modelling of pit lake waters in the Zeida abandoned mine (Morocco)

L El Alaoui, A Dekayir, M Rouai
ER Geotech, Faculty of Sciences, Moulay Ismail University, Meknes, Morocco

Abstract. In the high Moulouya watershed, the exploitation of the Zeida mine between 1972 and 1985 generated huge masses (millions of tons) of mining waste (Pb, Zn). This activity created large pits currently filled with stagnant water which are in permanent contact with remaining ore deposit.
The interaction of rainwater with rocks and minerals lead to the enrichment of Water Lake with heavy metals.
An inverse geochemical modelling carried out on water sampled in ZA and ZL1 lakes made it possible to highlight the chemical reactions occurring between rainwater and ore deposit and which would control the chemistry of these waters.
KEYWORDS: Contamination, Heavy metals, Inverse Modelling, Zeida, Morocco.

1. Introduction
In water geochemistry, many methods have been used to study, evaluate and characterize the variation of water composition. These methods include multivariate statistical techniques and inverse geochemical modelling [1:9].
Phreeqc inverse geochemical modelling [7] is based on a geochemical model of molar balance, which quantifies the mole transfer of phases (mole of minerals and liquid to be reacted in a solution) taking into account differences in the initial and final composition of the water along a flow path.
At least two chemical analysis of water sampled at different point of the pathway and a set of phases are necessary to perform the calculation.
This study aims to determine the chemical mechanism that controls the chemical composition of ZA and ZL1 pit lakes waters from the Zeida abandoned mine located in high Moulouya.

2. Material and methods
In the eastern part of Morocco, the Zeida abandoned mine is located in a semi-arid to arid climate (300mm/year) with a scarcity of water resources. The pit lakes are used by people to support their domestic and agricultural needs. In this study two samples were collected from ZA and ZL1 pit lakes. Some of these samples were filtered at 0.22µm using a Nalgene filtration tool and then frozen in a dry ice. The parameters pH, T and C.E of waters were measured during the sampling.
Figure 1. Situation Of the studied lakes in Zeida mining area

For the inverse modelling calculation, Phreeqc has been used [7]. The calculation of the mass balance during water infiltration is the number of moles of minerals that must dissolve or precipitate to account for the difference in composition between the initial water (rain water tab.1) and the final water (lake ZA or ZL1 waters, Tab.2) [5-8].

The analysis of the metallic traces elements were carried out on the filtered water by the ICP-AES technical then the main cations, anions, and the total organic carbon were carried out by ion chromatography (Dionew ICS-1000), and a carbon analyser organic (Shimadzu TOC-VCSH) according to a high temperature catalytic oxidation process [2] in hydrosiences laboratory, Montpellier in France [5].

Figure 2. Geological section showing the disposition of tailing (tailing I and II) in relation to pit lakes ZA and Oued Moulouya (O.M)
3. Results and discussion

The chemical data of the studied waters are presented in table 2. These waters are generally alkaline with pH between 9.02 and 9.08. The conductivity (EC) varies between 5630 µS/cm in ZL1 Lake at 16°C as evidenced by the precipitation of salt on the edges of ZL1 Lake. The ZA water shows a weak (pe) compared to that of ZA one reflecting a more reducing environment (Tab.1).

The ZA water show lower values of sodium, potassium, magnesium, calcium, chloride and sulphate than ZL1 water. In ZL1, bicarbonate show high value (1864 ppm) followed by chloride with a value of 2703.79 ppm and the (SO$_4^{2-}$) with a value of 1397.59 ppm (Tab.2).

The rainwater used in this calculation as an input solution in the system shows an alkaline pH with an average chemical composition given in Table 1. This water is enriched in SO$_4$, in chloride and calcium with a (pe) of 4 reflecting oxidative conditions.

Table 1. Physical and chemical properties of rainwater (ppm) (Solution 1)

| pH | Pe | Ca | Cl | K | NO3- | SO4 |
|----|----|----|----|---|------|-----|
| 7  | 4  | 21 | 9  | 0.8 | 1.6  | 9.5 |

Table 2. Physical and chemical properties of ZA and ZL1 water (Solution 2) (ppm)

| pH   | Pe  | Ca | Cl     | K     | NO3-  | SO4$^{2-}$ | Al   | As  |
|------|-----|----|--------|-------|-------|------------|------|-----|
| ZA Lake | 9.02 | 0.35 | 29 | 943.12 | 33.12 | 0 | 96.51 | 0.01109 | 0.04389 |
| ZL1 Lake | 9.08 | 1.189 | 16020 | 2703.79 | 118.37 | 0 | 1397.59 | 0.0024 | 0.09705 |

| B | Ba | U | Br | CH$_4$ | Cd | Cs | Cu | F | Fe |
|---|----|---|----|--------|----|----|----|---|----|
| ZA Lake | 0.05595 | 0.06437 | 0.02363 | 0 | 82.82 | - | 0.000219 | 0.001844 | 0 | 0.003621 |
| ZL1 Lake | 2.461 | 0.0768 | 0.2764 | 0 | 480.15 | 0.000323 | 0.00333 | 0.000515 | 0 | 0.007661 |

| Li  | Mg  | Mn | Pb  | Rb  | Sr  | Zn  | HCO$_3$ |
|-----|-----|----|-----|-----|-----|-----|---------|
| ZA Lake | 1.851 | 42.27 | 0.0252 | 0.000022 | 0.02578 | 2.823 | 0.02961 | 450.7 |
| ZL1 Lake | 11.16 | 187.07 | 0.008253 | 0.000021 | 0.2101 | 3.473 | 0.2899 | 1864 |

Hydrochemistry of studied waters: The Piper diagram show the composition of major hydrochemical facies identified for each lake waters ZA and ZL1. From the piper plot (Fig.3), major hydrochemical facies identified were Na$^+$,K$^+$,SO$_4$,$\text{Cl}^-$,NO$_3$ with minor amount of Ca and Mg.
Figure 3. Representation of ZA and ZL1 water compositions in the piper diagram

Water saturation index: Calculation of the saturation index (SI) of waters consists in predicting the mineral phases which must precipitate or dissolve. The PhreeqC aqueous speciation model [7] was used for this. It’s equal to log10 of the product of the ionic activity of a mineral component divided by the equilibrium constant for the considered mineral. Indeed, an SI>0 indicates a precipitation in water (saturated) SI<0 indicates an under saturation of the water while an SI=0, indicates a state of equilibrium of the mineral constituents with the aqueous solution.

The values of the saturation index calculated in the two water are shown in (Fig.3). These waters show over-saturation for hematite, aragonite and dolomite and under-saturation of the halite, cerussite, calcite and arsenic phases (Fig.4)

Figure 4. Water saturation index of ZA and ZL1 waters
Table 3. Result of the inverse geochemical modelling of ZA water

| Mineral/Phases | Calcite  | Cerussite | Halite  | Hematite | Scorodite | Aragonite |
|----------------|----------|-----------|---------|----------|-----------|-----------|
| Model-I        | -9.86e-05| 9.89e-05 | 2.66e-02| -2.61e-07| 5.88e-07 | -         |
| Model-II       | -9.89e-05| 9.89e-05 | 2.66e-02| -        | -         | -9.86e-05|
| Model-III      | -        | 9.89e-05 | 2.66e-02| -2.61e-07| 5.88e-07 | -         |
| Model-IV       | -9.89e-05| 9.89e-05 | 2.66e-02| -        | 6.50e-08 | -         |
| Model-V        | -5.24e+05| 5.24e+05 | 2.66e-07| -5.88e-07| -         | -         |
| Model-VI       | -2.67e-02| -1.74e-10| 6.54e-08| -        | -         | -         |
| Model-VII      | -        | 9.89e-05 | 2.66e-02| -6.50e-08| -         | -9.89e-05|

Table 4. Results of the inverse geochemical modelling of ZA water

| Mineral | Anhydrite | Calcite  | Cerussite | Halite  | Hematite | Scorodite | Aragonite |
|---------|-----------|----------|-----------|---------|----------|-----------|-----------|
| Model-I | 1.08e-01  | -1.08e-01| 1.08e-01  | 7.6e-02 | -5.8e-07 | 1.30e-06  |           |
| Model-II| 1.08e-01  | *        | 1.08e-01  | 7.6e-02 | *        | *         | -1.08e-01 |
| Model-III| 2.23e-04 | *        | 3.21e-04  | 7.6e-02 | -5.8e-07 | 1.30e-06  | *         |
| Model-IV | 1.08e-01  | 1.08e-01  | 7.6e-02  | *       | 1.38e-07 | -1.08e-01 |           |
| Model-V  | 2.23e-04  | *        | 3.21e-04  | *       | -5.8e-07 | 1.30e-06  |           |
| Model-VI | 2.23e-04  | *        | *         | 7.6e-02 | -1.7e-10 | 1.38e-07  |           |
| Model-VII| 1.08e-01  | 1.08e-01  | 7.6e-02  | -5.8e-07| -1.08e-01|           |           |
Inverse geochemical modelling: The minerals used in the calculation of the inverse geochemical modelling are those present in the study area. The positive values of mass transfer indicate dissolution of the minerals or gases while the negative values indicate a precipitation or degassing. According to the inverse calculation, the primary mineral phases used are calcite, cerussite, halite, hematite, scorodite, and aragonite. In ZA water from I to VII models, minerals such as hematite, calcite and aragonite show precipitation, while cerussite, halite and scorodite show dissolution (Tab. 3). The inverse geochemical modelling calculated for ZL1 water, shows 7 (Table 4), from which minerals such as calcite, hematite and aragonite show a precipitation while halite, anhydrite, scorodite and cerussite show a dissolution (Tab.4). The calculation of saturation index along the flow path between the input solution (rainwater) and the final solution (water lake) fit perfectly with the inverse calculation data [4].

Conclusion
The saturation index calculations and inverse geochemical modelling applied along the precipitation (rainwater) – pit lakes water pathways show that the chemical compositions of these waters results from the interaction between the rainwater and the primary minerals of rocks and sediments crossed by these waters. This chemical mechanism is characterized by dissolution of minerals such as anhydrite, cerussite, scorodite, halite and the precipitation of calcite, hematite and aragonite. Metal minerals based on lead (galena) and arsenic show essentially dissolution in these waters.

ACKNOWLEDGEMENT
This work has been supported by the grant in the framework of CNRST Projet Prioritaires N° 34/2015.

References
[1] Belkhiri L, Boudoukha A, Mouni L, and Baouz T 2010 Geoderma. 159(3-4), 390-398.
[2] Casiot C, Egal M, Elbaz-Poulichet F, Bruneel O, Bancon-Montigny C, Cordier M A, and Aliame C 2009 Applied geochemistry. 24 (5), 787-799.
[3] Charlton S R, MacKlin C L, and Parkhurst D L 1997 Water-Resources Investigations Report. 9, 7- 4222.
[4] Dhiman S D, and Keshari A K 2006 Environmental geology. 50(8), 1211-1219.
[5] EL Alaoui, L., Dekayir, A. (2018) E3S Web of Conferences 37,01007.
[6] Kenoyer G J, & Bowser C J 1992 Water Resources Research. 28(2), 591-600.
[7] Parkhurst D L 1999 Water-Resources Investigations Report 99-4259. US Geological Survey.
[8] Plummer L N, Parkhurst D L, & Thorstenson D C 1983 Geochimica et cosmo chimica Acta. 47(4), 665-685.
[9] Suma C S, Srinivasamoorthy K, Saravanaan K, Faizalkhan A, Prakash R, & Gopinath S 2015 Aquatic Procedia. 4, 986-992.