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Geochemical Characterization of the Spoil Heaps of the Ain Aouda Mine and its Impact on the Soil (Morocco)

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ABSTRACT

The exploitation of the Ain Aouda zinc lead mine in the Tazekka massif (Morocco) has abandoned spoil heaps stored directly on a karstified carbonated ground, without any means of precaution. The heaps were exposed to the weather agents, such as water infiltration and air circulation, which would generate a real source of pollution for the ecosystem. This pollution will inevitably produce effluents that can be loaded with metals and metalloids, which will have a significant negative influence on the soil and the environment. In this regard, the objective of this study was to confirm the existence of contamination of soils by using the technique of atomic emission spectrometry with inductively coupled plasma, and of spoil heaps by X-ray diffractometry, which confirmed the contamination by zinc, arsenic, lead and copper. Their maximum concentrations are 19858.800 (ppm), 1280.700 (ppm), 495.750 (ppm), and 328.65 (ppm), respectively. Nevertheless, it was noted that the pH of the majority of soils always remains basic, due to the significant presence of carbonates, the majority of soils are calcareous (15% to 30%) to very calcareous (> 30%). It was noticed that the phenomenon of neutralization occurs.

Keywords: calamine; contamination; content of zinc; neutralization; pollution.

INTRODUCTION

The mining sector forms an interesting part of the economy of countries. The mining activities that Morocco has known since the beginning of the last century constitute an axis of economic development of the country (Boushaba et al., 2008). However, mining sites are often contaminated by metallic elements; these contaminants affect the natural environment and may harm the environment; thus, the concentration of the majority of contaminants sometimes rises to the levels that are toxic for the ecosystem (Assabar et al., 2023).

According to (Akujobi, 2012), heavy metals are serious environmental pollutants, especially in the areas of high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in trace amounts, can cause serious problems for organisms.

Mining wastes/tailings are sources of contamination and environmental nuisance (Lakrim et al., 2011; 2012a; 2012b, 2015; El Hachimi et al., 2013). The same is true for the former Ain Aouda zinc mine, the subject of this study, which was operated for a period exceeding 15 years, with an estimated volume of 400 tons of calamine at 48% zinc, or about 2000 tons of zinc. The conducted study was aimed to assess the degree of metal contamination of the soils surrounding the Ain Aouda mine, as well as to specify the nature of the mine drainage from the physico-chemical and geochemical characterization of the samples.

MATERIALS AND METHODS

Study area

The Ain Aouda mine is located in the northeastern part of Morocco at the northeastern end of the Middle Atlas chain, it is located in the buttonhole of Tazekka, at an altitude of 1644 m (Figure 1).

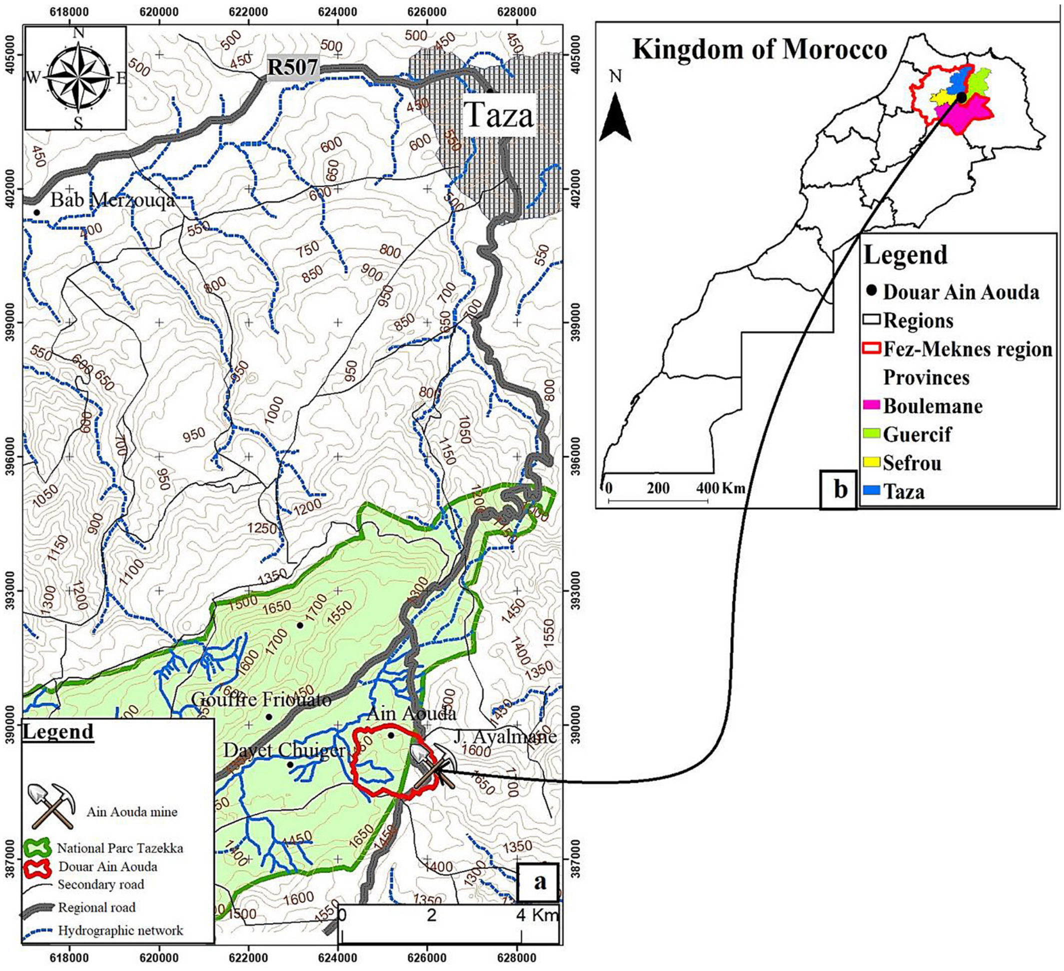

Figure 1. (a) Geographic location of the Ain Aouda mine (Taza, Morocco), (b) map of Morocco

The Tazekka massif and its Jurassic cover form a metallogenic province characterized by the presence of numerous Pb-Zn deposits composed of sulfides and oxidized lead-zinc ores with admixtures of Fe oxides. In the study area, at the Triassic-Liassic limestone contact, there is an abundance of iron mineralization of cluster vein type. They also seem to be distributed

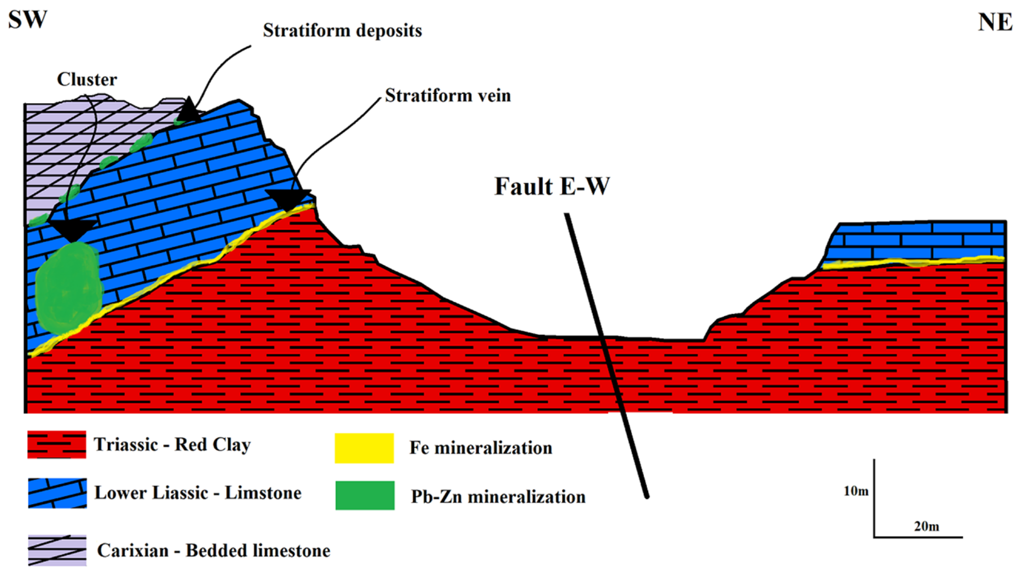

Figure 2. Geological structure section of Ain Aouda

along the accidents, parallel to the chain, affecting the Upper Triassic. However, in this contact there is the greatest possibility of encountering iron bodies associated with other types of mineralization.

The Ain Aouda deposit includes the most remarkable and the most interesting cluster of lead zinc (Pb-Zn) mineralization of the folded middle Atlas, it is located on the edge of a horst formed by Lower Lias limestones, oriented SSW-NNE. The deposit is composed of calamine, zinc carbonates (Smithsonite and hydrozincite), cerussite ($PbCO_3$) and traces of iron oxides, as well as the Pb-Zn mineralization is stratiform at the lower Lias and Carixian contact (Figure 2).

According to an excavation of 70 m length and 20 m width carried out by the office of mining research and participations (B.R.P.M), the calamine cluster is encountered at a depth of 25 m. The volume is estimated to be 4000 tons of scale with 48% zinc, or about 2000 tons of metal.

Primary mineralization of the Ain Aouda mine classified as a Mississippi Valley-type is composed of sulfides (galena, sphalerite, and pyrite) (Auajjar, 2000). As a result of Zn-bearing sulfides weathering, hemimorphite ($Zn_4Si_2O_7(OH)_2(H2O)$), and smithsonite ($ZnCO_3$) are formed.

Investigated calamines are also composed of hematite goethite and limonite with remnants of unweathered primary sulfides: galena and cerussite (Figure 3).

Sampling and preprocessing

In this study, a simple random sampling was performed. This well-known technique consists of taking samples from randomly selected locations over a large surface of the study area. We practiced it in different areas near the Ain Aouda zinc mine, from soils and spoil heaps.

This approach is not recommended for locating sampling stations. However, it can tolerate the evaluation of an average contamination of an environment. Therefore, it can only guarantee a high accuracy if there is a homogeneous contamination.

Soils and spoil heaps were sampled and packed in plastic bags and stored at low temperature (<10 °C).

The soil contains a small amount of hygroscopic water, it will be essential to dry it in the open air. Then, the samples are dried in the oven at 105 °C over 24 h (Lozet et al., 2002), in order to eliminate all the water.

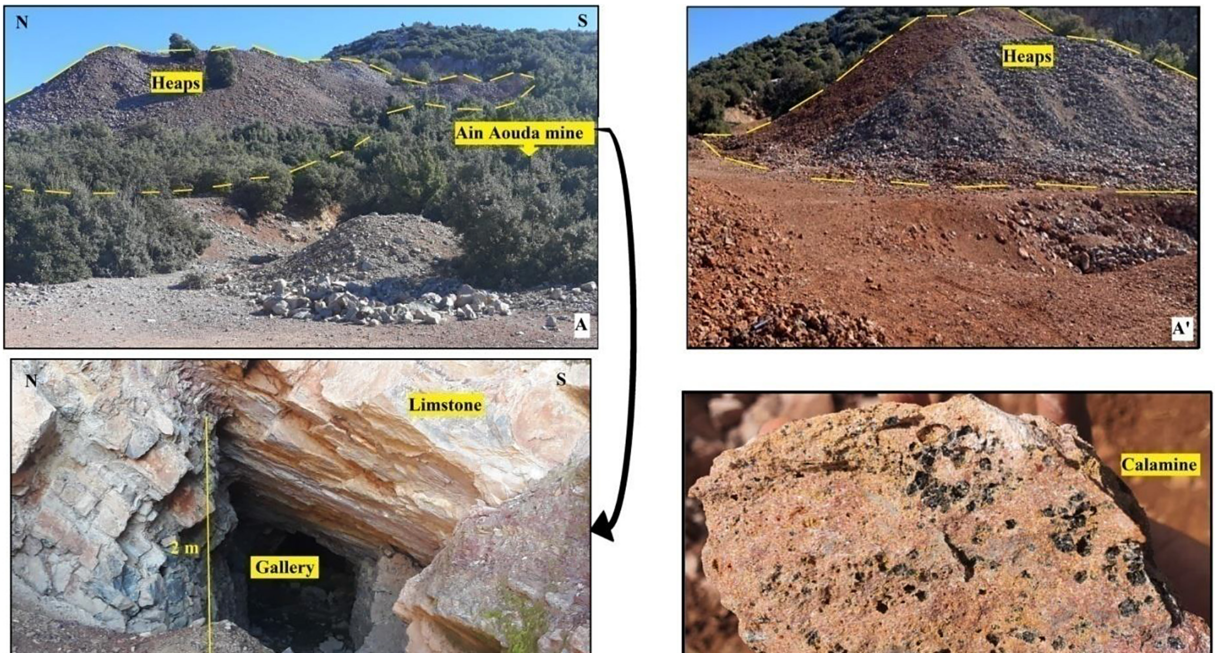

Figure 3. (A & A’) heaps of Ain Aouda mine, (B) Ain Aouda gallery, (C) Specimen of calamine from Ain Aouda mine

The sample of each soil underwent a quartering. It was separated into four equal quarters of which two opposite quarters are eliminated and the other two opposite quarters are combined. This selection is homogenized and a new quartering is performed, the operation was repeated three times. This gives a representative sample of the original material (Pauwels et al., 1992; Baba Ahmed, 2012).

Analytical techniques

Various physico-chemical analyses were performed by determining the pH (H_2O) and the electrical conductivity of the soil using a previously calibrated multiparameter, according to the ISO standard. The conductivity of water refers to the ability of water to conduct an electrical current depending on its salinity. It is important, because it can tell how much dissolved substances, chemicals, and minerals are present in the water (Lahmidi et al., 2023). Moreover, the total organic matter by loss on ignition (oven calcination) was measured at 450 °C for 24 hours. The residual moisture was measured by loss in mass at 105 °C for 48 hours according to ISO standard. In addition, the Bernard Calcimeter was used to calculate the $CaCO_3$ content in the examined solid samples.

The analysis of materials by X-ray diffraction (XRD) is a non-destructive analysis technique that allows the study and characterization of the structure in single crystals, as well as the qualitative and quantitative analysis of different crystalline forms present in the analyzed samples. The spoil heap samples were analyzed by the XRD technique after they were finely ground.

The chemical composition of soils was determined by ICP-AES at National Center for Scientific and Technical Research (Rabat) and the Regional University Center of Interface (Fez). This method is based on the identification and quantification of the mass percentage of metal(oid)s (Pb, Zn, Cu, As and Ni). Before starting this method, the soil samples underwent a very fine grinding (> 63 μm) by mortar grinder to succeed triacid attacks (HF, HNO_3, $HClO_4$).

The determination of heavy metal contents in soils, and their comparison with the values of normal contents of AFNOR standard could tolerate the estimation of the disputed contamination and determine its extent.

RESULTS AND DISCUSSION

Physico-chemical properties

In this study, the contamination of the soils surrounding the Ain Aouda mine in Taza was evaluate. The measurements of the physico-chemical parameters of the solutions of the solids consist in measuring the acidity (pH (H_2O)) and the electrical conductivity. For raw solids, the measurements concern the water content, the organic matter content, the $CaCO_3$ content. The results of all these measurements are listed in the table (Table 1).

Table 1 shows the results of the analyses carried out to determine the physicochemical characteristics of the samples. The hydrogen potential (H_2O) exceeds 7.4 in all samples of codified

Table 1. Physico-chemical parameters of the wastes and soils of the Ain Aouda mine

Sapmles	pH (H_2O)	Electrical conductivity μs/cm	Fireloss (%)	Moisture (%)	$CaCO_3$ (%)
S1	8.10	150.20	1.92	19.16	64.28
S2	7.42	81.90	2.04	4.22	55.01
S3	8.50	95.00	0.60	6.84	66.08
S4	7.60	86.00	2.76	4.00	46.17
S5	8.00	140.00	5.93	15.02	14.28
S6	8.20	91.00	3.97	5.61	37.50
S7	8.16	101.20	9.27	7.20	26.66
S8	7.66	52.60	8.86	18.50	0.33
H9	5.97	81.90	2.56	3.02	00.01
H10	5.346	127.50	2.36	9.12	00.12
H11	5.19	92.30	5.65	6.89	00.00
H12	5.05	76.40	7.84	1.02	01.23
H13	3.52	109.70	5.69	9.56	00.00
H14	4.04	142.80	2.00	7.83	00.00

soils (S1–S8) taken near the gallery of Ain Aouda., These samples have a slightly alkaline (7.4 < pH < 7.7) to alkaline (pH > 7.7) character. In turn, the samples from the numbered spoil heaps (T9–T14) have an acidic character (pH < 7).

The pH of soil samples shows values that range from neutrality to alkalinity, which is explained by the geological nature of the study area and the presence of $CaCO_3$ with high concentrations, likely originating from the encountered carbonate rocks such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) that promote the release of calcium ions (Ca_2^+) and bicarbonate ions (HCO_3^-), as well as minerals extracted from the lead-zinc mine in Ain Aouda, such as smithsonite, which is a zinc carbonate, and the abundant presence of cerussite, which is a lead carbonate. This is supported by the majority of soils (S1, S2, S3, S4, and S6) being either calcareous (15% to 30%) or highly calcareous (>30%). However, the tailings typically have a negligible $CaCO_3$ content (Fig. 4).

The spoil heaps (H9, H10, H11, H12, H13 and H14) show acidity in all samples (3.5 < pH < 5.9). The lowering of pH favors the mobility of trace metal elements, notably by the dissolution of metallic salts (Ekengele Nga et al., 2016). The leaching of these waste rock piles could contribute to the enrichment of neighboring soils in heavy metals.

The measurement of the electrical conductivity of soils and spoil heaps consists in measuring the quantity of ions present in them, which will have the capacity to dissolve in water. The conductivity values recorded are low and do not show significant variations. They are between 52.60 µs/cm and 150.20 µs/cm. The soils are not saline (0 < EC < 500 µs/cm at 25 °C).

The measured values of moisture vary between 4.00% and 19.60%, for the soils, and 1.02% and 9.56% for the spoil heaps. This can be explained by the nature of the sampled soils, while the soils have a clayey texture and the spoil heaps are in the form of coarse grain.

Mineralogical characterization of spoil heaps by XRD

X-ray diffraction technique was performed on the samples of mining waste from the Ain Aouda mine. The diffractograms (Figure 5) show the presence of net spectra of calcite and dolomite which confirm the carbonated nature of the bedrock.

They indicate that the spoil heaps contain zinc carbonates, such as smithsonite ($Zn CO_3$). Indeed, the calcareous environment gives rise to this mineral by the action of solutions containing zinc sulfate and due to the oxidation of sphalerite.

Also hemimorphite ($Zn_4 Si_2 O_7 (OH)_2 (H_2O)$) spectra were noticed, which are generally found in the oxidation zones of lead and zinc sulfides. Besides, the spoil heaps contain galena (PbS) which is always associated with cerussite, but by forming small-sized clusters (Auajjar, 2000). Iron oxyhydroxides are also present, they testify to the sulfide origin of the hypogene mineralization.

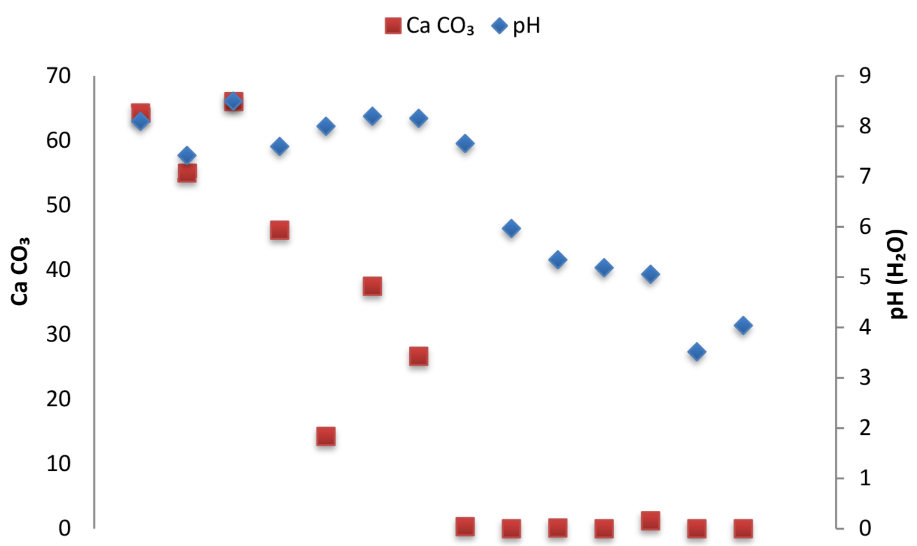

Figure 4. Relationship between the presence of carbonates in the samples analyzed and their pH

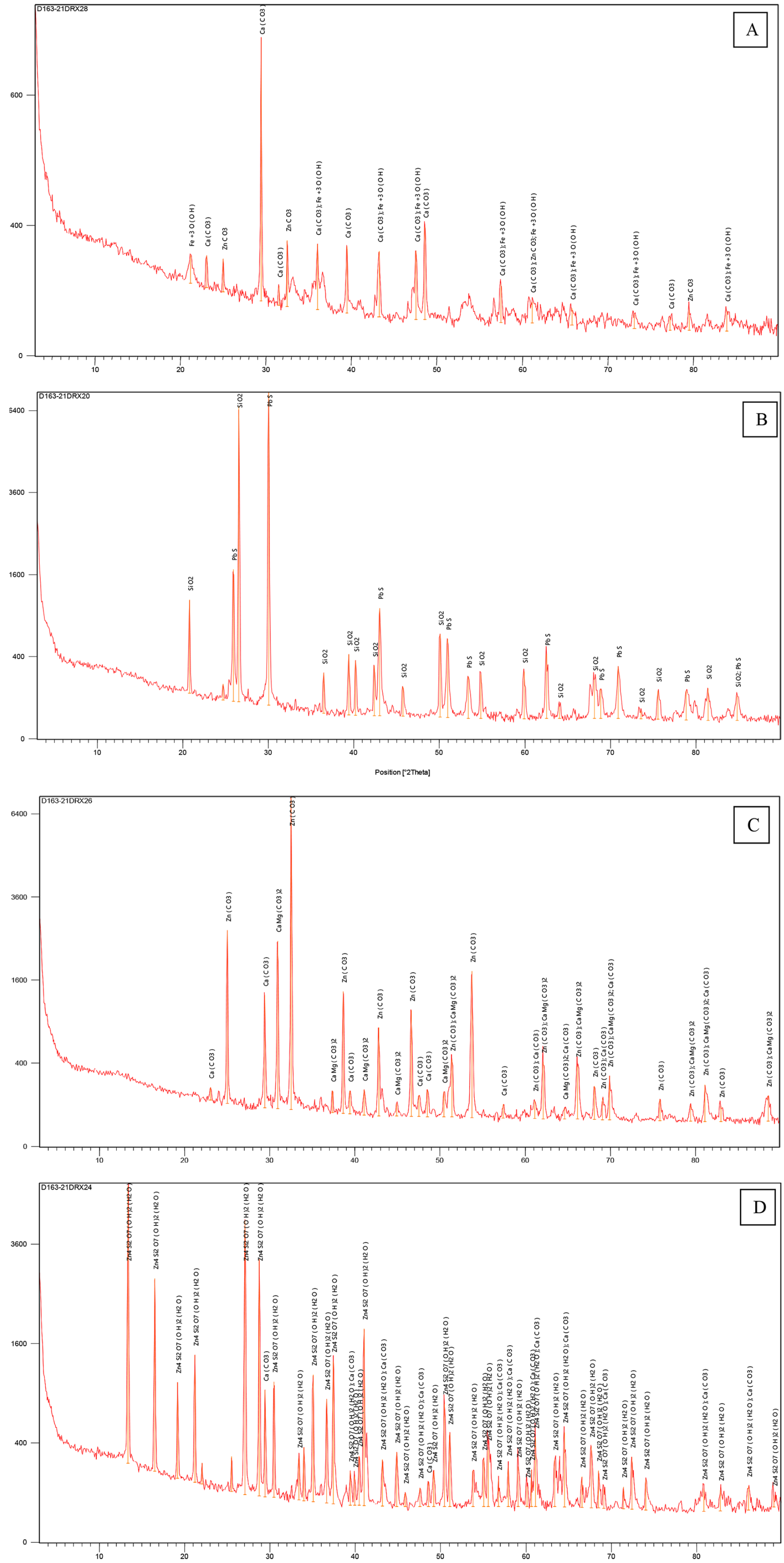

Figure 5. Principal mineral phases by X-ray diffraction (XRD) of the Ain Aouda spoil heaps

Bulk chemical composition of soils

The elements for which the measured contents are higher than the AFNOR standards are zinc, lead, copper and arsenic. This explains the positive anomalies with respect to the standards chosen to accomplish a comparative study (Table 2).

As, Pb and Zn are considered as metal(oid) pollutants resulting from the wastes disposed of mining heaps of the Ain Aouda mine. The majority of the solid samples collected from the study site are enriched with Zn and Fe. This is due to the presence of ferruginous calamine which is the ore extracted from the Ain Aouda mine as well as the dumping grounds. Zinc is present in all solid samples and it largely exceeds the maximum concentration admitted for a normal soil (Zn > 300 ppm, AFNOR standards) in the samples S1, S2, S3, S4, S5 and S8, it includes values between 1534.26 and 19858.80 ppm. In turn, in the same samples lead presents values between 150.30 and 1280.70 ppm, it should not exceed 100 ppm (AFNOR standards). Its presence is due to the existence of cerussite ($PbCO_3$) and galena (PbS). The release of lead from the spoil heaps was amplified in the presence of an acidic environment, noting that the the spoil heaps showed a pH below 6.

The range of copper content in the samples taken generally extends from 7.593 to 328.65 ppm, but samples S1, S2, S3, S5 and S8 show the highest content and exceed the normal content (Cu > 100 ppm, AFNOR standards). During the field investigations, traces of malachite were detected.

Arsenic exceeds the maximum value set by the World Health Organization in the soil (As > 40 ppm) in all samples except sample S6; their values are between 78.22 and 495.75 ppm. These levels provide evidence of the presence of arsenates in the study area (Table 2). The mining activities of Ain Aouda have generated large quantities of spoil heaps containing traces of arsenopyrite (FeAsS) which is in dissemination; when they are dissolved, they release arsenic (As) and generate mine drainage. Nickel concentrations remain ordinary. Iron is very abundant due to the association of calamine with goethite and hematite.

The contamination factor (CF) was calculated to express the level of contamination by each metal in the soil samples, is the ratio obtained by dividing the concentration of each heavy metal in the sediments ($C_{Heavy\ metal}$) by the concentration in the background ($C_{Background}$). According to the equation:

$$Contamination\ factor\ (CF) = \\ = C_{Heavy\ metal}/C_{Background} \tag{6}$$

North American Composite Shale (NACS) (Mclennan, 2001) were chosen as the geochemical background.

The interpretation of CF values was conducted as suggested by Rubio et al. (2000) where: CF < 1 is low contamination, 1 < CF < 3 is moderate contamination, 3 < CF < 6 is high contamination and CF > 6 is very high contamination.

The contamination factor of zinc and lead is greater than 6 in six samples (S1, S2, S3, S4, S5 and S8) reaching 279.70, and 75.34 in samples S5, and S1, respectively (Table 3).This ratio result justifies a very high contamination of soils. Moreover, Moreover, these high average contents are the result of the storage of mining heaps coming from the exploitation of calamine, cerussite, galena and other minerals (Assabar et al., 2023).

On the other hand, the analytical results of the contamination factor (CF) report show a high contamination (FC > 6) in arsenic in the

Table 2. Heavy metals contents (ppm) in soil samples from Ain Aouda mine

Samples	Zn (ppm)	Pb (ppm)	Fe (ppm)	As (ppm)	Cu (ppm)	Ni (ppm)
S1	6834.600	1280.700	16149.600	190.947	183.624	2.889
S2	1534.260	150.300	16155	117.348	175.056	1.473
S3	2795.130	903.690	16200	244.887	328.650	1.725
S4	2769.600	1051.500	15980.700	495.750	47.436	<0.5
S5	19858.800	422.020	3982.800	78.882	142.452	1.455
S6	273.900	62.637	4266.600	3.429	8.640	7.749
S7	94.671	59.709	7867.500	2.835	7.593	8.319
S8	17742.900	547.020	2188.650	28,581	183.390	<0.5
S9	296.010	65.140	98.210	2.690	54.200	0.560

Table 3. Average contamination factors of the soils sampled from the Ain Aouda mine

Samples	FC Zn	FC Pb	FC Cu	FC Ni	FC Fe	FC As
S1	96.26	75.34	7.34	0.07	3.30	38.19
S2	21.61	8.84	7.00	0.07	3.29	23.47
S3	39.37	53.16	13.15	0.05	3.31	48.80
S4	39.01	61.85	1.90	0.01	3.26	99.00
S5	279.70	24.82	5.68	0.02	0.81	15.60
S6	3.86	3.68	0.35	0.18	0.87	0.60
S7	1.33	3.51	0.30	0.20	0.85	0.40
S8	249.90	32.18	7.34	0.01	0.45	5.60
S9	4.17	3.83	2.17	0.01	0.02	0.40

majority of the samples S1, S2, S3, S4 and S5 (The values vary between 15.60 and 99.00). However, the contamination factor of copper is very high (CF > 6) in the samples S1, S2, S3 and S8, while iron presents a high contamination factor in the samples S1, S2, S3 and S4 (The values vary between 3.26 and 3.31). The nickel contamination factor is low in all samples (CF < 1) (Table 3).

CONCLUSIONS

The present study concerns the determination of the physico-chemical properties as well as the geochemical characterization of soil and spoil heaps samples of the abandoned Ain Aouda mine (Taza, Morocco) in order to evaluate the metallic contamination/pollution by zinc, lead, arsenic, copper and iron.

This study has shown the soil surrounding the mine is effectively contaminated by various metal(oid) elements (zinc, lead, arsenic, copper and iron). This contamination comes from the spoil heaps which contain sulfurous minerals and which are deposited without precaution on the substratum. Moreover, due to the acidic pH of spoil heaps, the oxidation of sulfide minerals, in the presence of water and air, generates acid which causes the dissolution of other minerals, but the neutralizing minerals (calcite and dolomite) present in the bedrock bring the pH back to be close to neutrality. The authors report that the soils surrounding the mine have a high pH and the concentrations of contaminants are higher than the limits of the environmental quality standards.

This study incites the authors to start other studies and analyses for the other environmental matrices (water and plants).

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