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Characterisation of sediments polluted by acid mine drainage in the northeast of Algeria

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Abstract

The present study investigates the composition and the mineralogy of sediments in the Essouk River, located in the Northeast of Algeria in Sidi Kamber mining zone at approximately 2km upstream Guenitra Reservoir. The mine is abandoned since 1976, but acidic drainage water is still a source of river contamination. Powder X-Ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive analyses (EDX), X -Fluorescence analyses and infrared spectroscopy analyses were used to characterize surface sediments sampled at various sites in the area near the mining effluents. The obtained results show that the composition of the sediments is mainly dominated by iron and sulphur. In the vicinity of the mine, jarosite and schwertmannite are the essential precipitates. Downstream, sediments are formed by various phases of iron oxyhydroxydes with the presence of adsorbed sulphate.

Key Words: Acid mine drainage, Sediments pollution, Sediments analyses, Iron oxyhydroxydes

1 Introduction

Mining activities generate a large amount of waste rocks and tailings; which deposit at the surface and become sources of pollution of ground and surface waters, by producing acid water that can generate important biogeochemical changes downstream (Filipek et al., 1987). The most common source of this phenomenon known as acid mine drainage (AMD) is the exposure of iron sulphide to air and water promoting the following chemical reactions (Rawat and Singh, 1983; Singh, 1987; Singh and Bahatnagar, 1985):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \xrightarrow{bacterialcatalysis} Fe^{3+} + \frac{1}{2}H_2O$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

The produced acid effluents are able to dissolve and transport important quantities of metals. Consequently, surface waters contaminated by acid mine drainage can be identified by low pH, elevated concentrations of iron, sulphate and heavy metals.

$Fe\ (OH)_3$ represents the secondary iron phase which plays an important role in the removal of several cations and anions by adsorption and coprecipitation (Benjamin, 1983; Dzombak and Morel, 1990; Boukhalfa et al., 2007a, 2007b).

After closing the mines, the acid mine drainage may persist for an extremely long time and may contribute to maintain a considerable contamination level. This is the case of Sidi-Kamber mine, located

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in the Northeast of Algeria at approximately 2km upstream Guenitra Reservoir. The mine is now abandoned but acidic drainage water is still a source of pollution of the Essouk River, which is the main stream in the area. The results of a previous study show a significant pollution of the river by metals (Boukhalfa, 2007c). Heavy metals upon entering into the water bodies may be quickly adsorbed onto suspended matter and ultimately move to bottom sediments (Sultan and Shazili, 2010). Consequently, sediments are considered as an additional source of pollution, they serve as a potential storage and a source of contaminants.

The objective of the present study is the identification and the characterization of the chemical precipitates formed in the Essouk River.

2 Study site

The Essouk River is located in Northeast of Algeria between Constantine and Skikda towns. It is an affluent of the Fessa River on which the Guenitra Reservoir is built (Fig. 1). Sidi Kamber mine is an abandoned zinc-lead mine. The modern work of the mine exploitation began in 1890 with a very weak production and rather frequent stops. It is only since 1913 that it started having a regular production (Beddai, 1976). In 1976, the mining of lead and zinc was stopped and barite was exploited by open-cast mining until 1984 when the mine was definitively closed (Oumdjbeur, 1986). The climate of the area is a semiarid, Mediterranean type; characterized by wet winters and dry and hot summers.

3 Experiment

3.1 Sample collection and preparation

Samples used in this study, were collected from the top 1-2cm of bed sediment at three locations (Fig. 1):

The sample SM1 came from a small channel carrying mine water. The channel was heavily coated with a yellowish mud and the water pH was 2.2;

The sample SM2 was sampled near the flow of a ground water;

The sample SR was taken below a confluence with an unpolluted tributary that joint the main stream.

In the two last locations, brownish red precipitates were observed, waters pH were 3.3 and 3.6 respectively.

Samples were transported to laboratory in cold, where excess water was evaporated by drying at 80°C. The dried samples were ground in an agate mortar, passed through a stainless steel sieve (<2mm) to obtain homogenous samples. Finally, the samples were conserved until analyses.

3.2 Analytical methods

Various analytical methods were used to characterize the sediments samples.

The weight compositions were semi-quantitatively determined by X-ray fluorescence spectrometry using a Magix-pro Panalytical-Philips spectrometer with rhodium radiation.

The particles morphology and the composition of the precipitates were examined with LEICA STEREO SCAN 440 Scanning Electron Microscope (SEM) equipped with EDAX KEVEX SIGMA analyses system. X-ray powder diffraction studies were performed on random powder diffraction mounts. Samples were prepared after grinding to a fine powder in an agate mortar. The Spectra were recorded from 5 to 80° 2θ with a scanning speed of 0.02° 2θ step size by using a Siemens D8 Diffractometer employing Cu-Kα1 radiation.

IR analyses were performed on the KBr pellets, scanning from 4,000 to 400cm^{-1} using a Hyper IR Shimatzu E spectrophotometer.

4 Results and discussion

4.1 XRF analyses

The chemical compositions (%) of the precipitates are presented in Table 1. If calculated as Fe_2O_3, iron constitutes 54%, 83% and 85.65% for SM1, SM2 and SR respectively; showing that iron oxyhydroxides are the major compounds. The sediment sampled at SM1 appears to be different from the two others.

The Fe/S molar ratio for the sample SM1 is about 1.7, which is close to the expected molar ratio for jarosite (Fe/S =1.5). Therefore, the sulphate rich mineral jarosite should be the prevailing constituent of the precipitate. The significant quantity of potassium implies that the jarosite should be K-jarosite. The two other samples seem to contain schwertmannite with Fe/S molar ratio in the range 4.6-8.0 recognised as characteristic of the mineral (Bigham et al., 1990).

Table 1 Concentrations (% weight) of compounds in sediments

Samples	Na	Al	Si	P	S	K	Fe	Ba	O
SM1	1.69	1.11	0.89	0.07	12.7	3.92	38.2	2.53	38.9
SM2	–	2.48	0.75	0.03	4.95	0.42	69.5	–	21.8
SR	–	0.34	–	–	5.16	0.35	59.9	–	33.9

Note: (–) not found

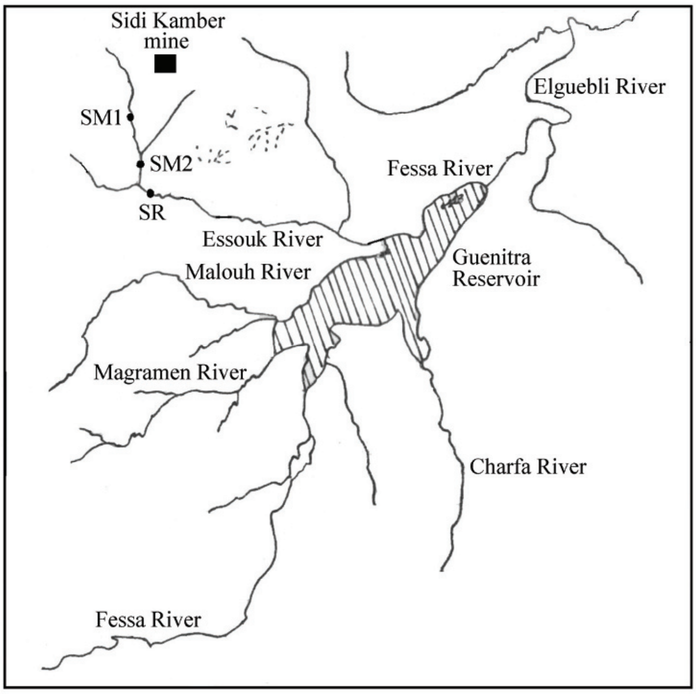

Fig. 1 Location of the Essouk River and sampling stations

4.2 EDX analyses

The obtained results from EDX analyses imply some differences with the XRF analyses, showing the heterogeneous character of the sediments. The spectrum of the SM1 sample shows the presence of aluminium and silicon phases in addition to jarosite. The SEM photographs of SM2 and SR samples (Fig. 2) reveal the predominance of the amorphous character. The same apparent composition is observed in their EDX spectra; the essential difference is in the silicon quantity, it is higher in the second sample with the presence of low amount of phosphorus. The significant iron quantity suggests the presence of ferrihydrite and or goethite with silicon. It has been reported that natural ferrihydrite contains silicon and strongly adsorbs silicic acid (Vempati and Loeppert, 1989).

4.3 XRD analyses

The obtained XRD patterns, show that the formed precipitates are seldom one pure phase but often contain two or more. By comparison with JSPDS 36-427, the peaks observed in the powder XRD pattern of the SM1 sample (Fig. 3a), show clearly that jarosite of the general formula $KFe_3(SO_4)_2(OH)_6$ is the major component. The peaks observed at 26.82°2θ and 20.97°2θ are assigned to quartz phase. However, the presence of a certain amount of poorly crystalline phases like schwertmannite and ferrihydrite is not ruled out. The peak occurred at 12.28°2θ can be attributed to the aluminosilicate phase of kaolinite.

Compared to the first sample, the samples SM2 and SR are of relatively low crystallinity with low peaks intensities in the XRD pattern (Figs. 3b, 3c). In SM2 sample (Fig. 3b), goethite (α-FeOOH) and schwertmannite ($Fe_8O_8(OH)_{4.8}(SO_4)_{1.6}$) are detected. The goethite exhibited line broadening indicative of poor ordering. It is difficult to detect all the characteristics peaks of schwertmannite. The presence of quartz is also observed. The powder XRD pattern of SR sample (Fig. 3c) shows the principal lines of quartz, lepidocrocite (γ-FeOOH) and goethite.

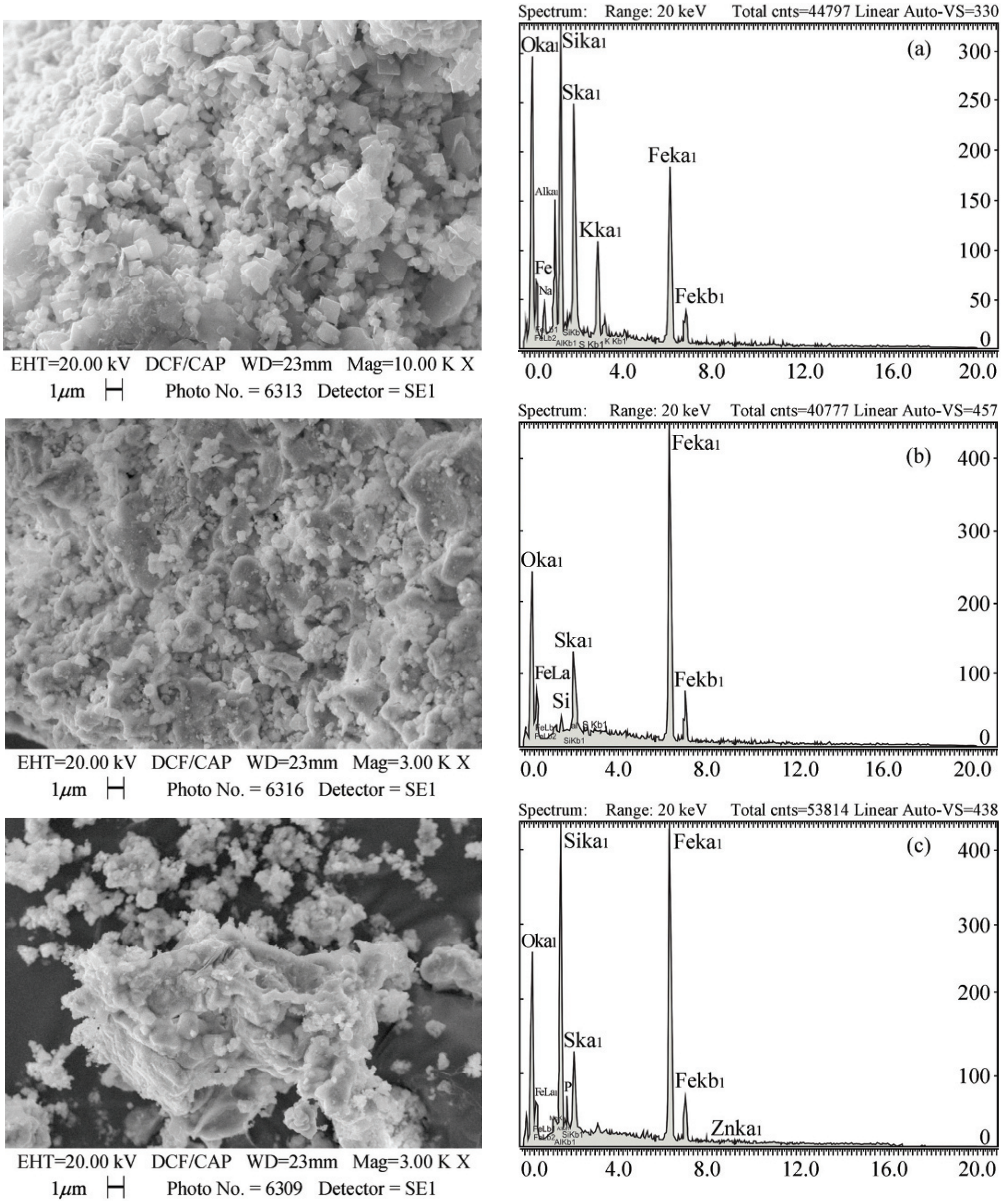

Fig. 2 SEM micrographs and EDX patterns of precipitates (a) SM1; (b) SM2; (c) SR

4.4 IR analyses

The results of IR analysis indicate that Fe-precipitates occurring at the studied sites are ferric oxy-hydroxides and oxy-hydroxysulfate. Bands in wave number range 1610-1635 cm^{-1}, originate from the stretching and bending vibrations of water molecules. Those in wave number region (900 to 1300 cm^{-1}), are associated to the vibrational modes of S-O bands in sulfoxyanions. The spectrum of the precipitate sampled at SM1 confirms the presence of jarosite (Sasaki, 2000). The spectra of SM2 and SR show the principal bands of goethite and schwertmannite (Schwertmann and Cornell, 2000). The band occurring at 756.0cm^{-1} in the spectrum of the last sample implies the formation of Lepidocrocite. The occurrence of oxy-hydroxides and oxy-hydroxysulfate implies that sulphate could be in the bulk structure and adsorbed at the surface. Bigham and co-authors (1990) suggest that it may be possible to distinguish structural and adsorbed SO_4 through the absorption bands at 610cm^{-1}. Consequently, the present results imply that sulphate ions are predominantly adsorbed. The absence of a band at around 980 cm^{-1} supports the formation of outer sphere complexes.

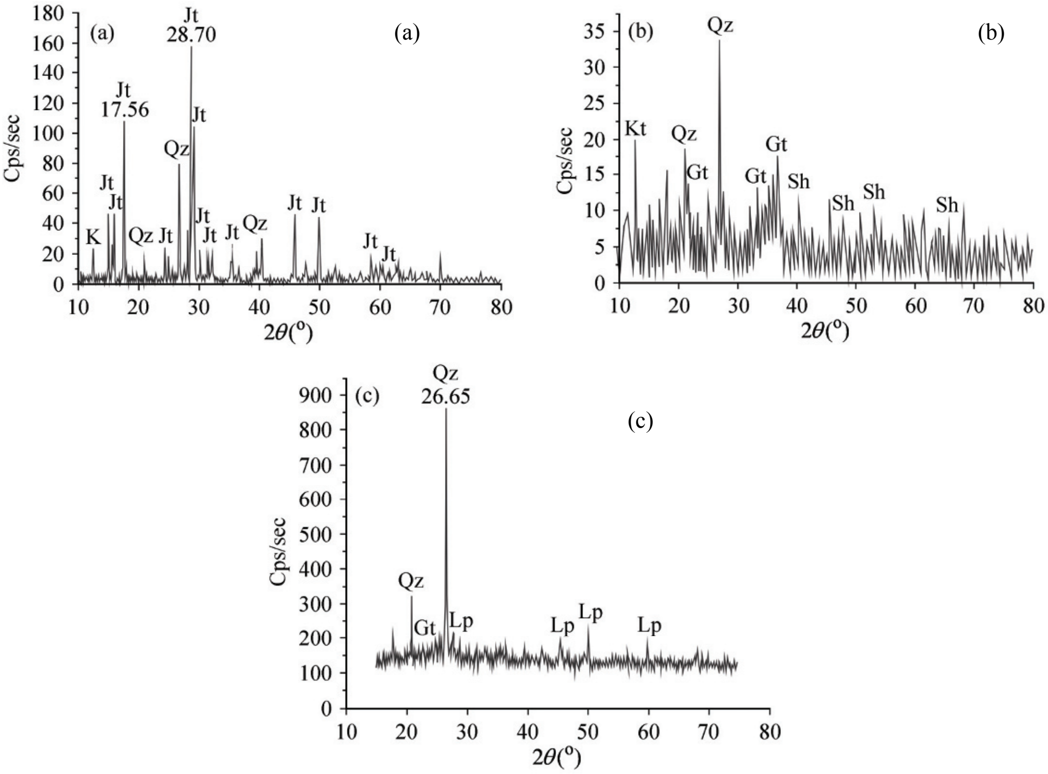

Fig. 3 XRD patterns of precipitates (a) SM1; (b) SM2; (c) SR
(Gt: goethite, Jt: jarosite, K: kaolinite, Lp: lepidocrocite, Qz: quartz, Sh: shwertmannite)

5 Conclusions

In the present study, several methods were used to characterize the mineral precipitates in the Essouk River. Some differences are observed in EDX and XRF results, showing the heterogeneous character of the sediments. In the two methods, the precipitates are composed mainly of iron and sulphur. More detail is given by DRX and IR analyses; the sediments mineralogy varies with waters pH. At very acidic pH (< 3), the principal mineral formed is jarosite. At pH > 3, schwertmannite, goethite and lepidocrocite are formed. Additional information about the sulphate complexation is illustrated in IR spectra. The significant presence of sulphate ion in the structure and on the surface of the formed precipitates suggests its removal from the river water. However, this is only a temporal sink; significant quantities can be released during minerals transformation or variation of various physicochemical conditions.

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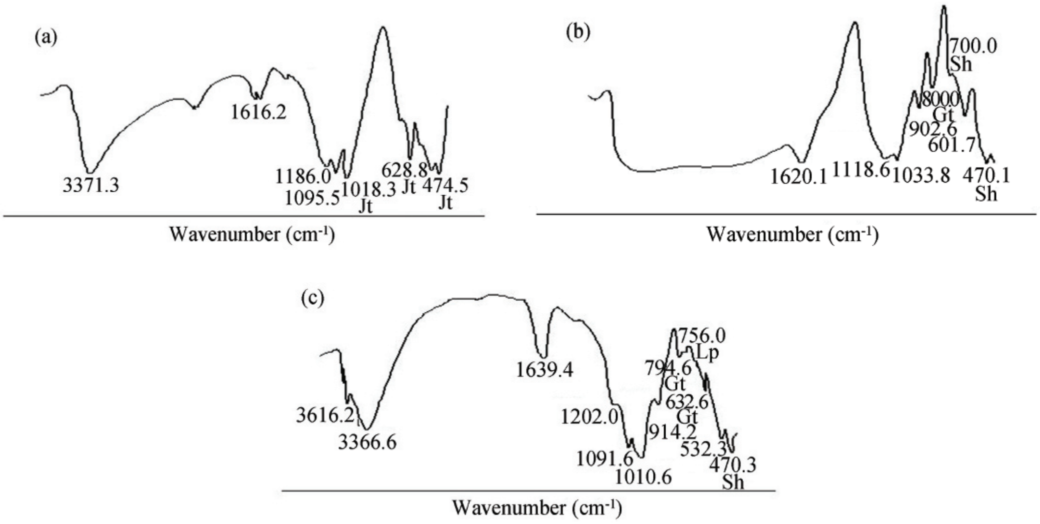

Fig. 4 Transmittance infrared spectra of the precipitates (a) SM1; (b)SM2; (c) SR (Gt: goethite, Jt: jarosite, Lp: lepidocrocite, Sh: shwertmannite)

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