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Evaluation of Pollution Linked to Open-Air Storage of Black Shale by the Company Frontier S.A in Sakania in the South-East of the DR. Congo

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Abstract:- The black shale from the company "Frontier S.A" in Sakania is impregnated with sulphide minerals such as pyrite which is an iron sulphide (FeS2) and chalcopyrite which is a double sulphide of copper and iron (Cu FeS2). Due to its storage in the open air, these sulphides are particularly oxidized. In addition, this black shale presents a certain physical and chemical instability which can be the basis of the degradation of the nearby surrounding environments (watercourses, soils, groundwater, etc.).

It results from our chemical characterization tests that this black shale contains 0.05% Cu, 0.007% Co, 1.3% Fe, 0.007% Ni, 0.001% As; 0.0012% Pb; 0.0021 Cd; 1.75% of S.The mineralogical analysis reveals that the sample contains the main minerals: sulphides, in the form of chalcopyrite and pyrite; oxidized, in the form of quartz; carbonates, in the form of dolomite and calcite, and graphitic material (C).

For the determination of the character of acid mine drainage, the static tests for predicting the AMD on the one hand, gave values for the net neutralization potential (NNP) and the ratio between the neutralization and acidification potentials (RPN). respectively 37.5 and 41.39, that is to say values classifying the black shale of Frontier as not generating ADM. And on the other hand, during the kinetic tests using the principle of testing periodic leaching of the sample over a long period, the percolates obtained made it possible to monitor the pH (between 6.2 to 7.07), the redox potential (between -39.8 to 92mV), the electrical conductivity (between 640 to 672µS/Cm), as well as the concentration rate of metals (low mobilization). This made it possible to conclude that the AMD did not exist on the site.

Keywords:- *Black Shale, AMD, Pollution*

I. INTRODUCTION

The exploitation of mines and the processing of supplied ores in the Democratic Republic of Congo cause many environmental problems. They generate mining deposits, as well as supplied discharges which, unfortunately, are not managed rationally and safely in order to protect the environment. These mining discharges and deposits often constitute a source of environmental contamination, linked to their physical and chemical instability, following their interactions with water and oxygen in the air.

The black shale of the mining deposit coming from the KISHIBA open-cast mine in SAKANIA is impregnated with pyrite and chalcopyrite, which contain around 1.75% sulfur. These iron sulfides, when naturally exposed to the action of open air and water, oxidize and generate sulfuric acid. This phenomenon, called acid mine drainage (AMD), can be the cause of pollution and ecological imbalance [1,2]

Mining discharges and deposits containing large quantities of acid-eating minerals do not generate AMD, following the neutralization of acidic waters [3,4,5]

In this article, we set ourselves the objective of characterizing the AMD of this site where the sulfurs of the black shale have already undergone partial environmental oxidation, to see how to propose a sustainable management solution in the event of confirmed pollution.

➢ *This characterization involves on-site sampling followed by all recommended DMA tests:*

- Static tests for PA determination; PN; PN/PA and PNN by Sobek law. improved [6]
- Kinetic tests using the principle of testing periodic leaching of a sample over a long period and recovery of leachates or percolates which are analyzed. [7]

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As these black shales are partly oxidized, leaching of the oxidized part is necessary to be able to determine the PN neutralization capacity. [8]

II. MATERIAL, METHOD AND SAMPLING

- *Sampling*

The samples submitted to this study are black shale from the open-air quarry of the company Frontier S.A. Systematic sampling with a 10m x10m mesh and 3m depth was carried out.

A composite sample of 30Kg was made up of 60 individual samples. Part of the composite sample was intended for chemical, mineralogical and particle size characterization. The other part of the sample was kept for actual testing of the DMA tests.

- *Material and Method*

- The following equipment was used during our study: glassware, a Metteler Toledo brand analytical balance, a hot plate, an AGILENT technology 200 series AA brand atomic absorption spectrometer, an atomic emission spectrometer with coupled plasma Varian induction (ICP), a series of standardized sieves and a polarizing optical microscope;
- The following reagents were used: mineral acids (HCl, HClO4, HNO3) to dissolve the mineral elements present in the sample;
- Hydroxide (HCl 0.1N) to determine the neutralization potential (PN) in static DMA prediction tests.

The elementary chemical analyzes were carried out using an atomic absorption spectrometer whose principle is based on measuring the characteristic absorbance of an element in the liquid state excited by its own light [6]. Non-elemental chemical analyzes were carried out using an atomic emission spectrometer with inductively coupled plasma. [9]

The characterization of the DMA of the sample was carried out in its static part using the method which was used in particular by. [2, 10, 11] The kinetic part followed the periodic wetting method explained by Hasan. [12]

III. PRESENTATION OF THE RESULTS

In this point, we present the results of the experimental tests obtained and their analyses. These are the results of the chemical, mineralogical, granulometric characterization; of the capacity of the DMA by static tests, which allow to determine indices of the DMA (PA and PN) and, by kinetic tests which, by making the black shale contact with water and air by wetting and drying cycles in controlled conditions in the laboratory, allow to follow the evolution of several parameters as function of time.

Let us also note the presence of the results of the aqua regia leaching test which will make it possible to determine the oxidized fraction of the black shal.

Table 1 Chemical Composition of the Sample

Element	Content %	Element	Content %
Pb	0,0012	Zn	0,021
Na	0,023	Ni	0,0071
Cd	0,0021	Cu	0,05
K	0,41	Co	0,0074
Ca	0,40	Mm	0,
Mg	0,46	As	0,001
Al	0,602	Cuox	0,01
Si	0,51	S	1,75
Fe	1,30		

Chemical analysis of the composite tells us that Frontier S.A.'s black shale does indeed contain ETMs. Copper and cobalt are present at respective levels of 0.05 and 0.0074%. However, there are also high concentrations of iron (1.3%), magnesium (0.46%), aluminum (0.602%), silica (0.51%), calcium (0.40%) and potassium (0.41%). Frontier's black shale contains pyrite and chalcopyrite, which confirms the presence of 1.75% total sulfur capable of generating acid mine drainage.

Mineralogical analysis provides information on the mineralogical composition of the composite sample after observation under an optical microscope.

Table 2 Results of Mineralogical Analysis

Class	Minerals	Formula
Sulfide	Pyrite	FeS_2
	Chalcopyrite	$Cu FeS_2$
Oxide	Quartz	SiO_2
Carbonate	Dolomite	$CaMg(CO_3)_2$
	Calcite	$Ca CO_3$
Graphite material		C

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From this analysis it appears that black shale is made up of minerals such as chalcopyrite, pyrite, dolomite, quartz and graphitic material.

- Pyrite and chalcopyrite are sulfide minerals characterized by physical and chemical instability, following their interaction with water and oxygen in the air, and as a result, they are responsible for the production of acidic waters.
- Dolomite and calcite are carbonates that have a great neutralizing power in an acidic environment and therefore, they can be responsible for the neutralization of acidic waters.

Table 3 Results of the particle size analysis of the composite sample of black shale

Sieve (Water)	Weights (g)	Refusal (%)	Cumulative Refusal (%)	Cumulative Passers (%)
+250	1,93	0,18	0,18	99,82
-250 +180	53,72	5,14	3,42	96,4
-180 +150	153,35	14,68	6,18	90,22
-150 +106	23,4	23,25	4,19	86,03
-106 +75	99,61	9,54	18,81	67,22
-75 +53	36,19	3,46	12,10	55,12
-53 +45	21,04	2,01	3,43	51,69
-45 +38	11,46	1,10	2,11	49,58
-38	219,46	40,64	49,58	0,0
TOTAL	**620,16**	**100**	**100**	

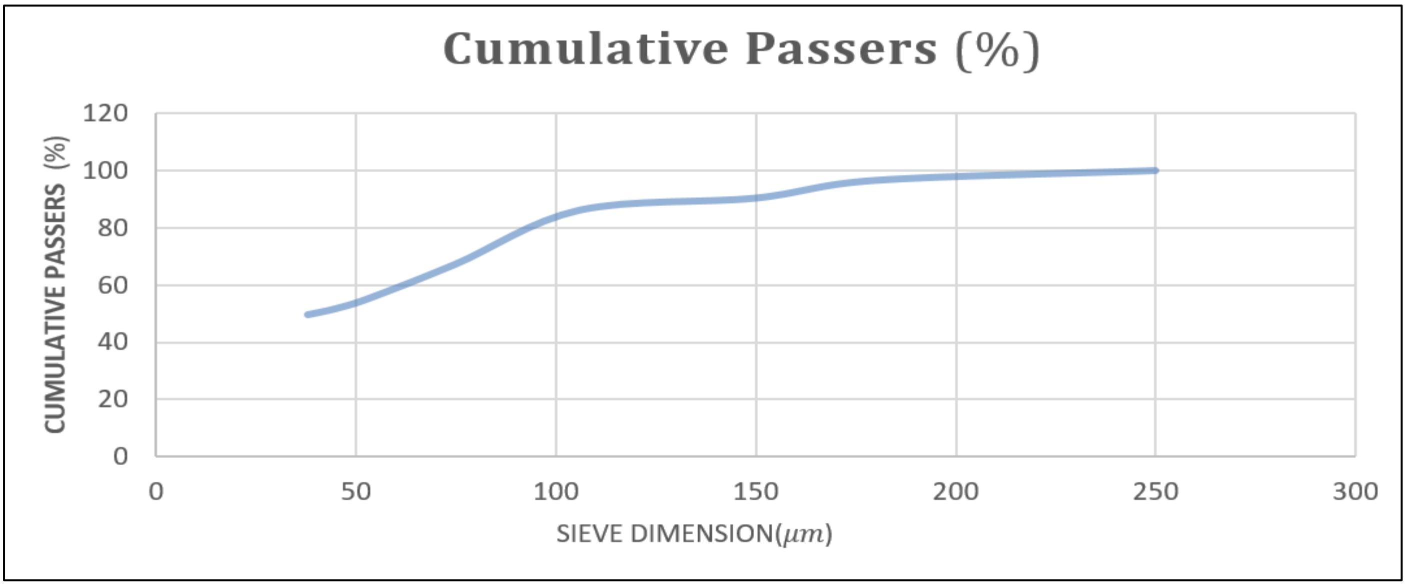

Fig 1 Curve Representing the Cumulative Weights of Passers-by in Granulometric Slices of the Granulometric Distribution.

The variation curve of the distribution of elements in the different particle size ranges shows that it is in the finest ranges that we find the majority of elements. These fine particles have a large specific surface area, would be able to easily undergo oxidation and therefore be the basis for the production of acidic waters. This curve indicates that the fractions between 150µm and 250 µm are those which contain the least elements.

Table 4 Leaching Test Results

	Elements										
Solutions	**Cd**	**Cu**	**Co**	**Ca**	**Mg**	**Fe**	**Zn**	SO_4^{2-}	**S**	**AS**	**Insoluble**
Leaching (g/l)	0,0012	2,6	0,008	0,63	0,55	2,05	0,028	0,001	-	0,02	
Wash water (g/l)		0,99	0,02	0,52	0,001	0,21	0,002	-	-		
Residue (%)	0,0009	0,04	0,006	0,32	0,30	1,24	0,012	-	1,75	0,0009	72,8

The leaching test was initiated with the aim of quantifying the oxidized fraction of black shales. 700g of the composite was used for leaching, which contains 0.05% copper and 0.0074% cobalt. After leaching, we obtained a residue that weighs 680g containing 0.04% copper and 0.006% cobalt. From the contents before leaching, we note that the 700g of black shale contains 0.35g of copper and 0.0518g of cobalt. The contents in the black shale make it possible to determine the remaining quantities, either 0.272g of copper and 0.0408g of cobalt.

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The percentage of oxidized copper and cobalt are given by:

- For copper : $\left(\frac{0,35-0,272}{0,35}\right).100 = 22,28\%$
- For cobalt $\left(\frac{0,0518-0,0408}{0,0518}\right).100 = 21,2\%$

A. Results of the Static Characterization of Acid Mine Drainage

➢ *Determination of Acid Potential (AP)*

- *Calculation of Sulfur Capable of Producing DMA*

Taking the simplest form of copper supplied CuS, the simple rule of three indicates that the sulfur which accompanies copper is given by the expression: $\frac{0.35g.32}{63.5}$ = 0.176 of sulfur.

Likewise for cobalt, we have $\frac{0,0518.32}{58,9}$ either 0.02814 of sulfur. The total metallic sulfur is therefore equal to 0.2041g. The sulfur sulfide capable of producing DMA is equal to $\frac{0.2041.100}{700}$ *or* 0.029%.

- *Calculation of Acidity Potential*

The PA is determined to assess the amount of acid likely to be generated by black shale in the event of DMA.

✓ PA = 31.25% Sulphide. [6]
✓ PA = 31.25.0.029 = 0.906Kg CaCO3/t

➢ *Determination of Acid Neutralization Potential (NP)*

The PN is calculated to be able to determine the capacity of black shale to neutralize the acid possibly produced in the case of DMA. The principle of the PN determination is based on the acid-base titer, hydrochloric acid (HCl) was used to titrate the black shale.

$$PN = \frac{50a\left[x - y\left(\frac{y}{a}\right)\right]}{m}$$

- a and b: normal concentrations of acid and base solutions;
- x and y: the volumes of the acid and base solutions;
- m: the mass of the sample;
- 50: the conversion factor;
- PN = 37.5Kg CaCO3/t

➢ *Interpreting Static Test Results*

Many authors consider that materials with a negative PNN (Net Neutralizing Potential) value or an RPN (Neutralizing Potential to Acidity Ratio) value less than 1 would present the obvious risks of DMA. [13, 14, 15, 16]

The Congolese mining code sets the threshold value of the PNN at 20Kg CaCO3 to establish the non-existence of DMA risks. As for the criterion based on the RPN, based on similar considerations, the risk of DMA is established when the RPN is less than 1. [17]

Table 5 Summary of the Results of Static Tests on the Composite Sample

Normality of acid (N)	0,1
Normality of base (N)	0,1
Volume of base used (ml)	10
Volume of acid used (ml)	25
PN, KgCaCO3/t	37,5
Sulfur sulfide (%)	0,029
PA, KgCaCO3/t	0,906
PNN, KgCaCO3/t	36,59
RPN = PN/PA	41,39

The PNN and RPN values obtained classify the Frontier SA black shale in the non-acid mine drainage generator zone.

B. Results of the Kinetic Characterization of Acid Mine Drainage

➢ *Sample Wetting Cycle*

90g of the composite sample placed dry in a Buchner funnel equipped with filter paper, and the Buchner is placed in the Erlenmeyer thus creating a mini-alternating cell. The latter is subjected to rinsing cycles in the open air, using 75ml of distilled water on the composite sample, according to the method explained by. [18, 19, 20, 21] After each rinsing, the solutions used are collected for various measurements and chemical analyses.

The values obtained are analyzed according to the values indicated to characterize the water flows from acid mine drainage. [22]

The main characteristics of acid mine drainage associated with water from a tailings pond or a waste dump are:

- pH < 6;
- Redox potential (E) up to 0.8V;
- Electrical conductivity between 800 and 6500µs/Cm;
- Iron concentration of the order of 100 to 4000ppm;
- Possible presence of elements (Cu, Zn, As, Cd, Pb, etc.);
- Very poor in organic matter.

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Table 6 pH values after Different Rinses

Rinse	pH
	Black Shale
1	7.07
2	6.54
3	6.89
4	7.58
5	7.40
6	6.2

The pH measurements were made directly on the percolates of the different rinses using a pH meter. The results are presented in Table 6.

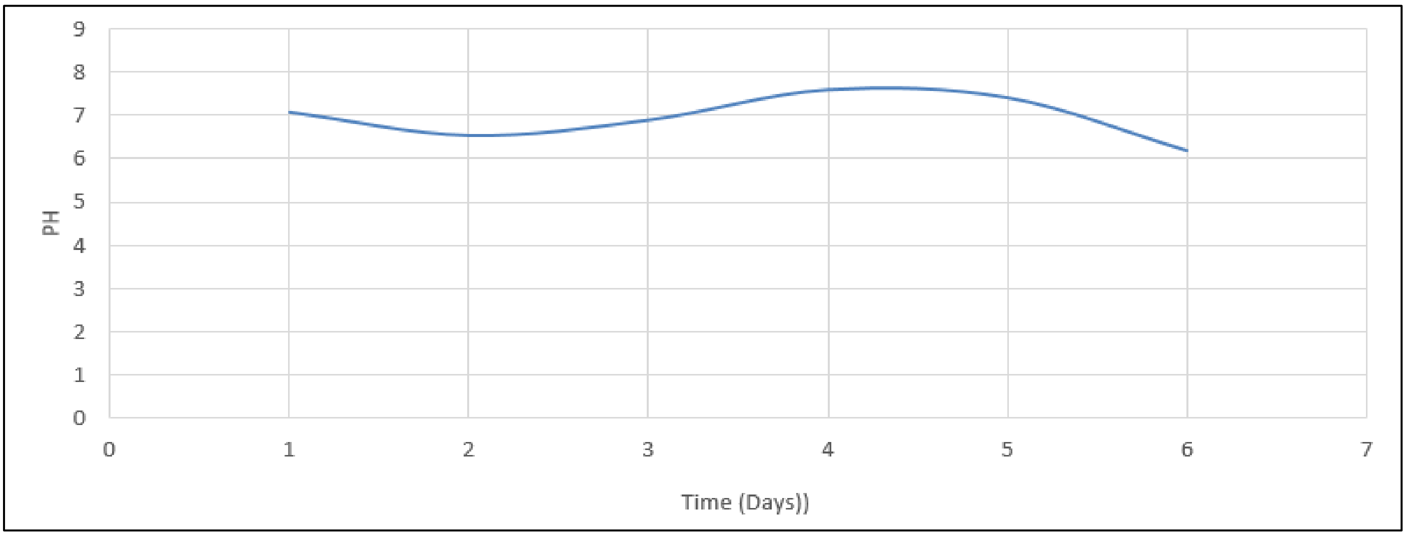

Fig 2 Curve Representing the pH Variation in the Percolate Collected after Different Rinsing's

According to the results obtained, from the first to the fifth rinse the oxidation and acid generation processes are weak, the pH around neutrality. In the sixth rinse, the pH has dropped to 6.2 but the oxidation process still remains weak, which makes it difficult to generate acid.

C. Variations in Conductivities and Redox Potentials

Since conductivity and redox potential are proportionally related to the concentration of trace metal elements in the percolates, it is easy to understand the similarity of the variations of these values. These values, shown below, confirm the hypothesis that the Frontier black shales do not generate acidic waters. The values of electrical conductivities are low, that is to say that the concentration of metals in the percolates is also low. In addition, the low values of redox potential which are lower than 0.8V confirm that the medium is not oxidizing.

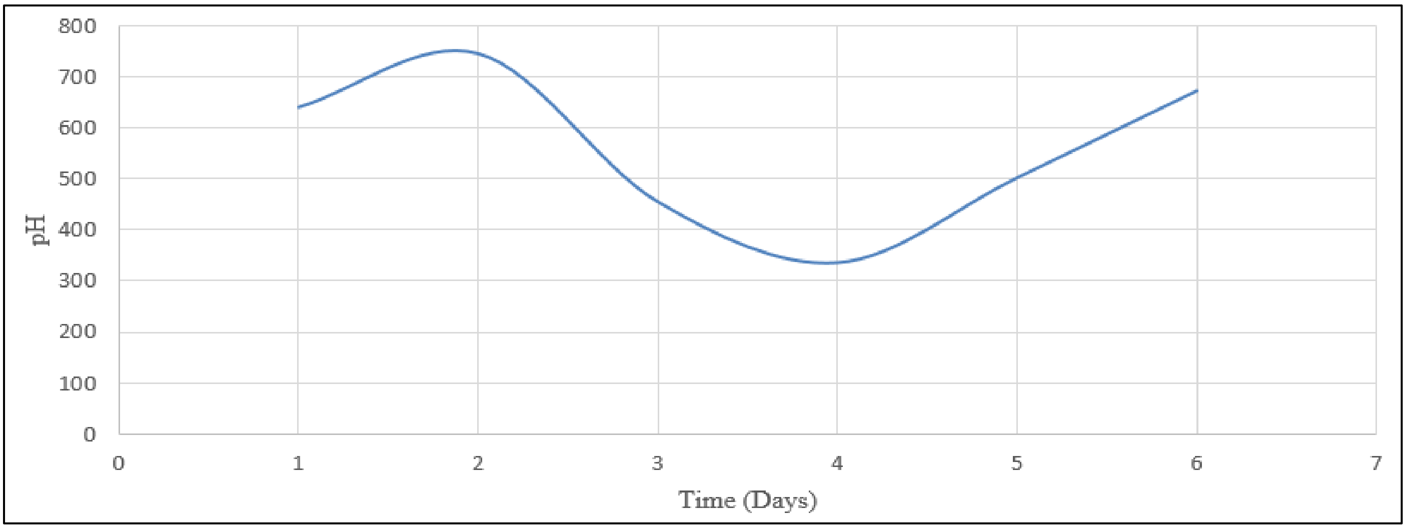

Fig 3 Curve Representing the Variation of Conductivity in Percolates

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Table 7 Concentrations and release rates of elements in percolates during the first rinse

Elements	Concentrations (mg/L)	Element release rates (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,002	$1{,}66.10^{-3}$	0,200
Na	16,00	13,330	-
Cd	0,0347	0,0289	-
K	78,371	65,300	-
Ca	40,371	33,642	-
Mg	34,882	29,068	-
Al	0,211	0,175	-
Si	2,649	2,200	-
Fe	0,057	0,0475	3,000
Zn	0,0372	0,0310	0,5000
Ni	0,008	$6{,}66.10^{-3}$	0,5000
Cu	10,00	8,330	0,5000
Co	0,0552	0,046	-
Mn	0,553	0,460	-
As	0,001	$8{,}33.10^{-3}$	0,5000

The results of the analysis of the first percolate show that the acid mine drainage are uncertain. It was found that the pH of the percolate is almost neutral (pH=7.07), due to high concentrations of (Ca = 40.371mg/L) and (Mg = 38.183mg/L) in the percolate. In addition, the release of ETM is low (Pb = 1.66.10-3), (AS = 8.33.10-4mg/L) and (Ni = 6.66.10-3), due to the low redox potential value in the percolate (E=1.8mV).

Table 8 Concentration and release rates of elements in second rinses

Elements	Concentrations (mg/L)	Element release rates (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,02	$5{,}5.10^{-3}$	0,2000
Na	8,013	2,22	-
Cd	0,0198	0,0055	-
K	49,310	13,69	-
Ca	27,770	7,71	-
Mg	18,482	5,13	-
Al	0,0245	0,0068	-
Si	2,139	0,59	-
Fe	0,002	$5{,}5.10^{-4}$	3,000
Zn	0,013	0,0035	0,5000
Ni	0,000	0,000	0,5000
Cu	44,320	12,310	0,5000
Co	0,0552	0,015	-
Mn	0,553	0,153	-
As	0,001	$2{,}77.10^{-4}$	0,5000

The analysis of the second percolate also shows that the acid mine drainage are uncertain. The pH of the percolate has slightly decreased (pH = 6.54), following the decrease in the values of the concentrations of (Ca = 27.7 mg/L) and (Mg = 18.4 mg/L. The results of the concentrations and release rates of the elements are almost the same as in the first flushing.

Table 9 Concentration and release rate of elements at the third rinse

Elements	Concentrations (mg/L)	Element release rate (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,130	0,027	0,200
Na	1,960	0,408	-
Cd	0,015	0,0031	-
K	29,730	6,190	-
Ca	45,700	9,375	-
Mg	24,690	5,140	-
Al	0,0200	0,00416	-
Si	3,670	0,76	-

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Fe	0,005	$1,04.10^{-3}$	3,000
Zn	0,056	0,0116	0,500
Ni	0,043	$8,958.10^{-3}$	0,500
Cu	0,0626	0,013	0,500
Co	0,000	0,000	-
Mn	0,101	0,021	-
As	0,001	$2,08.10^{-4}$	0,500

The results of the analysis of the third percolate confirm again that, the acid mine drainage still remains uncertain. However, the pH of the percolate is close to that of the first test (pH = 6.89), following the values of Ca and Mg which are also close to that of the first test (Ca = 45.7mg / L and (Mg = 24.69mg / L). The results of the concentrations and release rates are also almost the same as the previous ones.

Table 10 Concentration and release rate of elements at the fourth rinse

Elements	Concentrations (mg/L)	Element release rate (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,420	$5,8.10^{-2}$	0,200
Na	5,850	4,870	-
Cd	0,090	$1,2.10^{-3}$	-
K	17,130	2,370	-
Ca	50,20	6,970	-
Mg	48,800	6,660	-
Al	0,200	$2,77.10^{-2}$	-
Si	1,070	0,148	-
Fe	0,900	$1,25.10^{-1}$	3,000
Zn	0,063	$8,75.10^{-3}$	0,500
Ni	0,004	$5,55.10^{-4}$	0,500
Cu	44,000	4,500	0,500
Co	0,000	0,000	-
Mn	0,040	$5,55. .10^{-1}$	-
As	0,001	$1,38.10^{-4}$	0,500

The high values of the releases observed in the percolate show that the agent that guides the oxidation during the kinetic tests is mainly oxygen. The measured pH (pH = 7.58) does not allow the bacteria to effectively catalyze the indirect oxidation of black shale by ferric iron which is much more powerful than oxygen. Furthermore, the value of the redox potential is negative (E = -39.8mV), the environment becomes reducing as in a poorly aerated soil, the mobility of the ETM increases sharply and, the mechanisms involved, are the tendency of conversion of soluble species into gaseous species; acid mine drainage remains uncertain.

Furthermore, the analysis shows that the concentrations of dissolved calcites and that of dolomitic limestone are very high in the percolate (Ca = 50.2 mg/L) and (Mg = 48.8 g/L).

Table 11 Concentration and release rate of elements at the fifth rinse

Elements	Concentrations (mg/L)	Element release rate (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,410	0,043	0,200
Na	10,86	1,130	-
Cd	0,099	$1,041.10^{-3}$	-
K	46,060	4,800	-
Ca	48,400	5,040	-
Mg	39,200	4,080	-
Al	0,300	$3,125.10^{-2}$	-
Si	1,280	0,130	-
Fe	0,800	$8,333.10^{-2}$	3,000
Zn	0,0106	0,010	0,500
Ni	0,010	$1,04.10^{-3}$	0,500
Cu	0,360	0,038	0,500
Co	0,000	0,000	-
Mn	0,044	$4,791.10^{-3}$	-
As	0,001	$2,08.10^{-3}$	0,500

The analysis of the fifth percolate also shows that the medium is reducing with a negative redox potential (E = -31.3mV); the results of the concentrations and release rates are almost the same as in the fourth rinse**.**

Table 12 Concentration and release rate of elements at the sixth rinse

Elements	Concentrations (mg/L)	Element release rate (mg/L)	Directive 019 standards maximum concentration (mg/L)
Pb	0,002	2.10^{-3}	
Na	3,148	0,330	
Cd	0,0097	$3{,}02.10^{-3}$	
K	27,691	2,880	
Ca	19,80	2,060	
Mg	14,200	1,480	
Al	0,0159	0,00165	
Si	1,977	0,205	
Fe	0,049	$5{,}1.10^{-3}$	3,00
Zn	0,0223	0,0223	0,500
Ni	0,000	0,000	0,500
Cu	9,900	1,030	0,500
Co	0,026	0,0027	-
Mn	0,340	0,035	-
As	0,031	$3{,}23.10^{-3}$	0,500

From the analysis of the results of the sixth rinse, it appears that the DMA remains uncertain. The pH of the percolate decreases to 6.2 due to the low values of the concentrations of (Ca = 19.8 mg/L).

IV. CONCLUSION

This study was conducted with the aim of quantifying acidic waters produced by the black shale of chalcopyrite processed by the Frontier Company in SAKANIA, in order to assess environmental pollution in this city. To do this, several tests were recommended on the black shale samples in order to determine acid mine drainage on the site.

Chemical analysis of the composite sample showed that this black shale contains a certain proportion of metals likely to be released into the environment; these include 0.05% Cu, 0.21% Zn, 0.0071% Ni, 0.0021% Cd, 0.0012% Pb to name a few. The static DMA prediction test gave results with no DMA risk, PNN = 36.5 and RPN = 41.39.

Kinetic tests showed that the pH values measured on the percolates from the rinsing of black shale from the first to the fifth day are not acidic. On the sixth day of rinsing we obtained a slightly acidic pH (pH=6.2), but the oxidation process still remains weak on this sixth day, which makes it difficult to oxidize the sulfur contained in the black shale. In addition, the analysis showed that the different metals were not mobilized.

The study of the kinetic characterization carried out therefore does not confirm the existence of DMA on the site and that the reactions based on pH = 6.2 have zero kinetics in view of the evolution of the different parameters during this characterization (low redox potential). This allowed the neutralizing minerals present on the site to neutralize the protons from these waters at pH = 6.2. It also emerges from the results of these kinetic tests that the black shales of Frontier do not generate DMA and that they do not pollute the environment of SAKANIA.

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