Preliminary study on vulnerability to water pollution in the cobalt-nickel ore treatment area of the Ambatovy project, Toamasina Madagascar

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Abstract

This work is part of the global study on the vulnerability of the water resources to industrial pollution from the cobalt-nickel treatment carried out in the East coast zone of Madagascar, province of Toamasina. This paper shows the first chemical and physical field work result in 2015. The main purpose of the study is to characterize the groundwater and surface water flow, to identify the origin of the pollution due to the industrial activity process that could lead to the water quality degradation with respect to the hydrological aspect, the relationship between surface water and groundwater interaction. The chemical results show that around the cobalt-nickel treatment area (ITACN), in the southern part of the site, the groundwater has the highest concentration of sulphate ion,300mg.L^{-1}, compared to that of North ITACN of which concentration is 60mg.L^{-1}. On the opposite the sulphate ion concentration is lower in the tailings, 45mg.L^{-1}. The respective electrical conductivity reinforces the latter results, since it is evaluated to 800µS.cm^{-1}in the south ITACN and 70µS.cm^{-1} in North ITACN, whereas it varies from 50 to 400µS.cm^{-1}in the tailings. The Piper Diagram shows that groundwater and surface water have four facies. Firstly, most of the water samples have the calcium bicarbonate type (Ca-HCO$_3$) facies, particularly those collected downstream the tailings, those in the eastern part of the site and downstream the ITACN area. Secondly, one sample has the calcium and sodium bicarbonate type (Na-Ca-HCO$_3$) facies, upstream the south-westpart of the ITACN. Thirdly, in the western part area of the ITACN, the groundwater sample has the sodium chloride type (Na-Cl) facies. And finally, the sulphated calcium chloride type (Ca-Cl-SO$_4$) facies is observed downstream the south of the ITACN and in the tailings. The relation betweenthe major ions and electrical conductivity show that the sulphate ion controls the water mineralization around the ITACNin both surface water and groundwater. The natural purification system seems to work properly since the groundwater mineralization is decreasing along the direction of water flow from the ITACN treatment area towards the tailings area.

Introduction

The Ambatovy project is an industrial cobalt-nickel deposit and processing area founded since 1960 by several companies such as a Japanese company «Sumitomo Corporation», South Korean society «Kores Corporation» and Dynatec Corporation of Canada[1]. The cobalt-nickel ore processing plant is located in the Atsinanana region, province of Toamasina. The study area is composed of 263,600 inhabitants according to the urban municipality of Toamasina, according to the Urban Municipality of Toamasina in 2009. The study area is about 7300 square meters.

This paper contributes on the water resources by analyzing their physical and chemical characteristics. The study is focused on the groundwater and surface water quality in two different places. First, the Tailings Management Facilities (TMF) also called zone 9600, is located in the West zone of the study area which is the upper altitude zone[2]. Secondly, the Industrial Treatment Area of the Cobalt-Nickel (ITACN) called zone

3300, which is located in the eastern part of the site, with a lower elevation (slightly above the sea level). The campaign occurred in November 2015, at the end of the dry season.

After the ore process treatment, the wastes of mud and water are pumped through a group of interconnected pipelines from the ITACN to the tailings. The pump stations are controlled and operated from the "control room" located in the ITACN factory. All data related to the field measurement are consolidated in the latter. Two natural decantation basins are located in between the ITACN and the tailings, in order to purify the waste water step by step until it reaches the tailings.

Description of the study area: Geographic location: The Ambatovy treatment project site is located in the Alaotra-Mangoro and Atsinanana region, particularly in the Mangoro and Toamasina economic zone. The study area is between Anambokatra and the city of Toamasina: respectively of latitude 18°9'42.77'' West and 18°10'8.01" East and between Ivondro

and Farafaty: respectively of longitude 49°23'50.85' 'South and 49°23'8.68'' North.

The water sampling points are located around the two places of interest, respectively downstream the TMF in the Western part of the site and in the surrounding of the ITACN located in the Eastern part of the site.

The mean slope fluctuation of the study area is low: 8%. The highest altitude area is located in the TMF (Figure-1), about 90 meters and the lowest altitude is surrounding the ITACN (Figure-2), about 10 meters.

In the TMF area, the collected groundwater samples are coded PW. In the ITACN, two water samples (00GWMW4 and 00GWMW5) of groundwater type were collected upstream in the North. The groundwater sample 00GWMW5, in particular, which is located at a distance of 200m from the raw material storage area is assigned to control the groundwater quality in the Northern part of the treatment plant. Three water sample points (00GWMW1, 00GWMW3 and 00GWMW6) were collected in the Southern part of the ITACN. One water sampling point 00GWMW2 is located downstream the sludge treatment and near a control pond.

Vegetation and climate: The Atsinanana region includes a tropical forest that has been severely deforested during the 1970s and 1980s because of the paddy field for subsistence purposes of the local population[3]. The basis of the diet is rice associated with cassava and sweet potato. The vegetation

consists of a secondary formation of Dalbergia pterocarpiflora, and Ravenala madagascariensis. Soil degradation was caused by the practice of Tavy and burning. Fortunately, plantations of coffee, banana and other fruit trees protect the soil against erosion. In addition, the study area consists of hills, valleys and coastal plains. The climate is hot and humid with an average temperature of 25°C. Seasonal cyclones are a high risk factor for flooding in the region. The maximum altitude in the east coast of Madagascar is 100 meters, especially in the western part of the site. The valleys of the Atsinanana region contribute to the evacuation of water. Most of the coastal plains of 10 meters height are occupied by swamps.
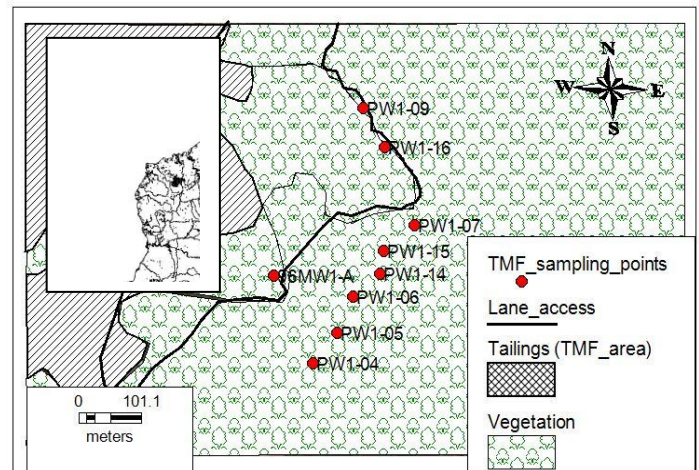

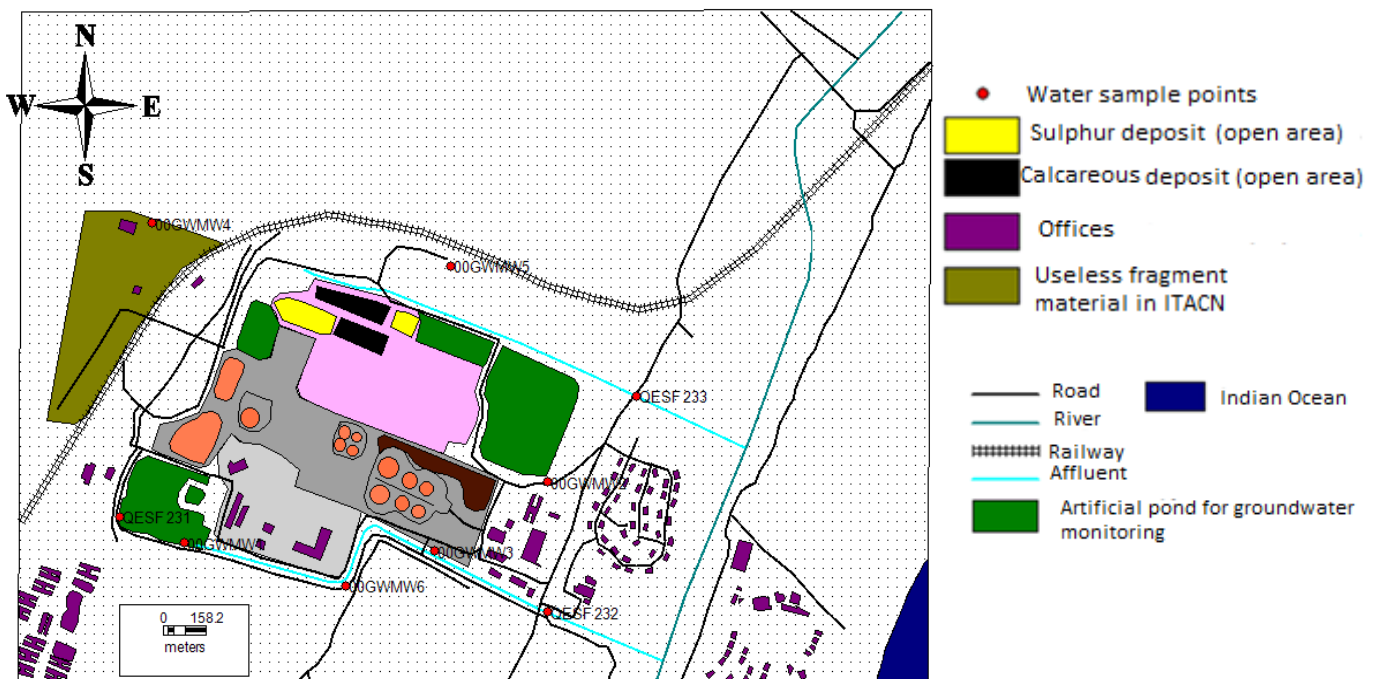**Figure-1:** Representation of the tailings[4].

Figure-2: Representation of the ITACN[4.]

Geology: The region consists of a hilly landscape with an average altitude of 80 to 60m and low hills of 50 to 40m above the sea level. The cobalt-nickel treatment plant is located in the sandy zone of the eastern part of the site. The western part of the site consists of silimanite and gneiss (Figure-3). The eastern and western parts of the study area are separated by bright dunes.

Materials and methods

Materials: All the values of the chemical parameters and isotope analysis are identified and achieved in the National Institute of Nuclear Sciences and Techniques (I.N.S.T.N.-Madagascar) laboratory, especially in the Isotope Hydrology Department. To obtain the values of the anions and cations, the integrated ion chromatography system: Dionex ICS 1100 is used. And, the Picarro L2120i is employed to determine the water stable isotopes (^{18}O and ^{2}H) values.

Sampling campaign: The sampling campaign is carried out in November 2015, at the end of the dry season. Then, twenty two (22) samples are collected surrounding the TMF and ITACN sites.

Measure in situ: By using the HACH HQd/IntelliCAL multimeter, the physical parameters of samples, such as the water temperature (T), electrical conductivity (EC), hydrogen potential (pH), total dissolved solids (TDS) and the concentration of the dissolved oxygen (DO), are measured.

To evaluate the alkalinity of the water samples, the alkalimetric method is used to estimate the concentration of the bicarbonate HCO_3^- ion in sample by manipulating the phenolphthalein and bromocresol indicator powder and the sulfuric acid (H_2SO_4).

Water sample: A polyethylene plastic bottle (PE-HD) of 50mL is filled for the anions (NO_3^-, SO_4^{2-}, Cl⁻), cations (Na^+, Mg^{2+}, Ca^{2+}, K^+) and stable isotopes (^{18}O and ^{2}H) analysis. And, one drop of the nitric acid (60%) is added to the cation samples. Also, apolyethylene plastic bottle (PE-HD) of 1000mL is utilized for the tritium analyse.

Results and discussion

The results of the physical and chemical parameters during the campaign period are shown below[6].

Physical parameters: To compare the results from Table-1 and Table-4, the highest value of electrical conductivity is observed in the ITACN for groundwater and surface water. The ITACN site is more mineralized than the tailings site.

The reason is that the maximum and minimum values of the same parameter for groundwater (Table-2) and surface water (Table-3) are high, in the ITACN, compared to the values in the tailings from Table-5 and Table-6.
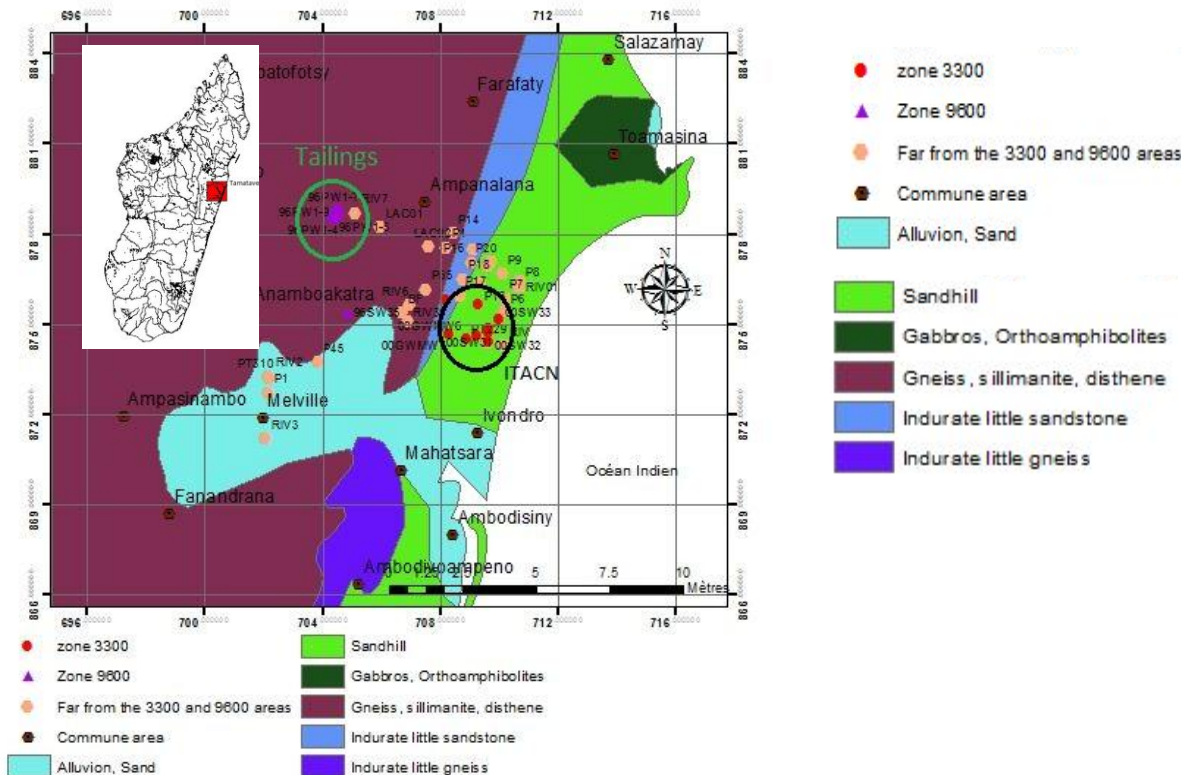
Figure-3: Geological representation of the area[5].

Table-1: Average value for groundwater and surface water. Around the ITACN area, zone 3300.

ITACN	Average elevation (m)	Average depth of well (m)	Average of the pH	Average of the T (°C)	Average of the Oxidation/Reduction Potential (Eh) (mV)	Average of the EC (μS.cm^{-1})	Average of the TDS (mg.L^{-1})	Average of the DO (mg.L^{-1})
Ground water	10.83 ±2.23	21.20 ±0.55	6.77 ±0.25	27.83 ±1.30	19.97 ±13.90	331.68 ±271.27	153.80 ±132.60	3.95 ±1.54
surface water	10.00 ±3.00	Not evaluated	7.10 ±0.51	26.00 ±1.90	0.93 ±27.82	482.67 ±396.45	229.9 ±193.25	4.67 ±2.10

Table-2: Maximum and minimum value of the physical parameter in the ITACN. Around the ITACN area, zone 3300.

Groundwater	pH	T (°C)	Eh (mV)	EC (μS.cm^{-1})	TDS (mg.L^{-})	DO (mg.L^{-1})
Maximum	7.13	28.8	36	794	386	5.94
Minimum	6.48	24.1	-0.1	53.8	23.5	1.24

Table-3: Surface water value of the physical parameter in the ITACN. Around the ITACN area, zone 3300.

Surface water	pH	T (°C)	Eh (mV)	EC (μS.cm^{-1})	TDS(mg.L^{-})	DO (mg.L^{-1})
Maximum	7.66	27.9	23.9	939	452	6.8
Minimum	6.67	24.1	-30	223	100.2	2.6

Table-4: Average value of the physical parameter. Tailings, zone 9600.

TMF	Average of the elevation (m)	Average depth of the well (m)	Average of the pH	Average of the T (°C)	Average of the Eh (mV)	Average of the EC (μS.cm^{-1})	Average of the DO (mg.L^{-1})
Ground-water	20.39±4.36	Not evaluated	6.46±0.55	24.89±0.65	34.72±34.16	170.30±118.22	3.20±1.97
Monitoring well	28±0.00	20.82±4.72	6.59±0.02	27.75±1.48	30.30±0.99	94.25±36.27	6.87±0.96
Surface water	19.00±2.83	Not evaluated	6.72±0.11	26.45±1.06	22.70±5.94	63.10±47.09	6.68±0.11

Table-5: Well maximum and minimum value of the physical parameter in tailings. Tailings, zone 9600.

Groundwater	pH	T (°C)	Eh (mV)	EC (μS.cm^{-1})	TDS (mg.L^{-1})	DO (mg.L^{-1})
Maximum	7.17	26.00	83	371	181.2	6.5
Minimum	5.63	24.10	-22	37	17.27	0.72

Table-6: Surface water maximum and minimum value in tailings. Tailings, zone 9600.

Surface water	pH	T (°C)	Eh (mV)	EC (μS.cm^{-1})	TDS (mg.L^{-1})	DO (mg.L^{-1})
Maximum	6.79	27.2	26.9	170	79.5	6.75
Minimum	6.64	25.7	18.5	103.4	46.7	6.6

Chemical parameters: The chemical results reinforce the previous hypothesis. The highest value of sulphate ion concentration is evaluated in the ITACN. The average value of the sulphate ion is 87.04±111.90mg.L^{-1} (Table-7). In the tailings, the average concentration is low 8.17±11.99mg.L^{-1} (Table-8).

Table-7: Major ion results in the ITACN zone with ionic balance of ±5%. ITACN, zone 3300.

ITACN	Na^+ (mg.L^{-1})	K^+ (mg.L^{-1})	Mg^{2+} (mg.L^{-1})	Ca^{2+} (mg.L^{-1})	HCO_3^- (mg.L^{-1})	Cl^- (mg.L^{-1})	NO_3^- (mg.L^{-1})	SO_4^{2-} (mg.L^{-1})
Maximum	125.58	2.36	16.54	115.05	203.98	26.57	28.92	277.34
Minimum	2.82	0.02	0.58	1.97	7.96	2.52	2.75	1.08
Average	31.84	1.04	6.13	38.78	87.34	12.1	8.92	87.04
Standard deviation	45.63	0.86	5.99	37.37	68.43	9.05	8.81	111.90

**Table-8:** Major ion results in tailings zone with ionic balance of ±5%. Tailings, zone 9600.

Tailings	Na^+ (mg.L^{-1})	K^+ (mg.L^{-1})	Mg^{2+} (mg.L^{-1})	Ca^{2+} (mg.L^{-1})	HCO_3^- (mg.L^{-1})	Cl^- (mg.L^{-1})	NO_3^- (mg.L^{-1})	SO_4^{2-} (mg.L^{-1})
Maximum	20.2	1.83	16.88	55.88	242.05	27.38	12.15	45.18
Minimum	1.43	0.08	0.48	0.96	9.49	3.35	0.01	0.97
Average	7.14	0.72	5.04	18.22	78.82	7.4	2.87	8.17
Standard deviation	5.55	0.53	5.17	15.59	72.91	6.25	3.08	11.99
Limit value	150 (French)	12 (French)	50 (French)	100 (French)	-	250 (O.M.S)	50 (O.M.S)	250 (O.M.S)

Discussion: Physical parameters: Kolmogorov-Smirnov test: In order to have a reliable value of pH, we try to verify that its distribution during the campaign sampling period is representative of the study area[7]. For such, we suppose that the pH sample water value follows either a normal distribution law (H_0) or not (H_a). According to the number of sample, twenty two (22) samples, the relative frequency distributions results corresponding to the tailings and ITACN is evaluated (Figure-4). The results show that the pH is less than the 5 values in the TMF. It can be estimated that the waste discharge progressively tends to acidify the water quality. The mean distribution value is: $\mu = 6.66$ with sigma = 0.45. Then, the test significance rate is 5%. So, according to the Kolmogorov-Smirnov test, we have the following results (Table-9):

Where D is the maximum distance value between the theoretical and empirical functions; p value is calculated from the two cumulative distributions for testing the null hypothesis; Alpha is the significance level of the test, used to detect the difference under the assumptions of the null hypothesis.

Table-9: Results of the Kolmogorov-Smirnov test[8]. **Figure-4:** The relative frequency distributions of pH for tailings and ITACN

D = 0.158;
p value = 0.586;
Alpha = 0.05
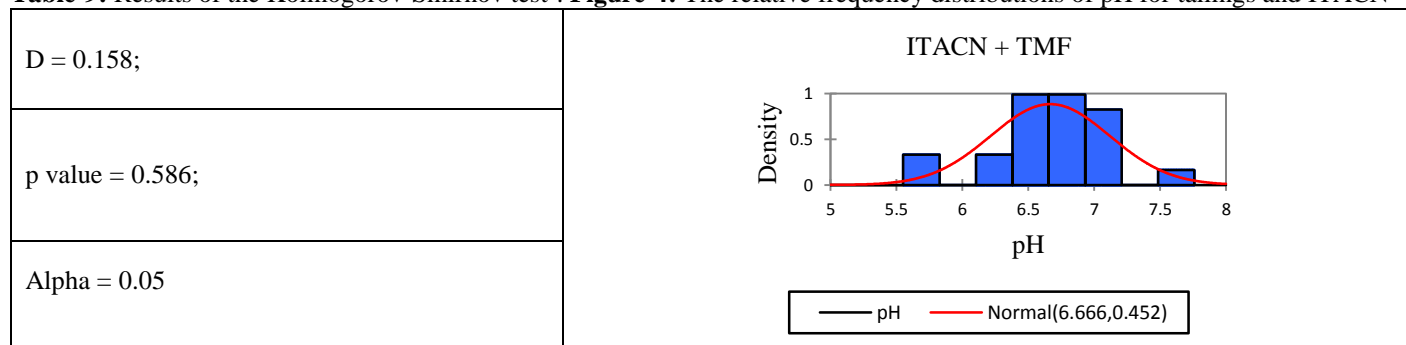
The objective is to calculate D by comparing both theoretical and empirical functions. According to the K-S table and the sample number equal to 22, we have D<D_α with D_α=0.281 for α=0.05.

Where, K-S test is the Kolmogorov-Smirnov test[9]. It is used to decide whether the water sample collected could represent the study area. D_α is the critical level read from the sample size table.

The value of p calculated, from XLSTAT, is 0.586 (more than alpha = 0.05). Thus, the null hypothesis H_0 cannot be rejected. The variation of pH value follows a normal distribution.

Consequently, the variation of pH and EC is relatively proportional according to the chemical process that may happen in the aquifers. The average value of the EC in the ITACN is 407.18 with a standard deviation of 284.38μS.cm^{-1}. The EC increases from the Northern part of the ITACN (70μS.cm^{-1}) to the Southern part (800μS.cm^{-1}). The standard deviation is relatively high because of the significant difference between the minimum and the maximum values respectively 53 and 1000μS.cm^{-1}. In the western part of the ITACN, the mineralization of ground water is slightly accentuated. In particular, the EC value of the surface water coded QESF231 is 286μS.cm^{-1}, whereas that of the groundwater coded 00GWMW2 is 380μS.cm^{-1}. The measured EC value of the surface water downstream the ITACN, in the southern part of the site is relatively high: 940μS.cm^{-1}. However, the mineralization is relatively less accentuated in the northern part of the site (less than 400μS.cm^{-1}). The gravitational migration of the artificial pollutants could be the reason of the mineralization in the latter part of the site after seepage into the layers[10].

Chemical parameters: Piper diagram: The Piper diagram[11] (Figure-5) below shows the dominance of the major ions: anions and cations[12]:

Group (1): The majority of samples have the calcium bicarbonate type (Ca-HCO$_3$) facies, in the northern part of the ITACN and for surface water type, downstream of the tailings;

Group (2): Only one sample has the calcium and sodium bicarbonate type (Na-Ca-HCO$_3$) facies, surface water type located in upstream and Western part of the ITACN[13];

Group (3): The sodium chloride type (Na-Cl) facies is composed of three samples, groundwater type located in upstream and Western part of the ITACN and Eastern part of the tailings;

Group (4): Two samples from the ITACN and three from the tailings have the sulphated calcium chloride type (Ca-Cl-SO$_4$) facies, in the Southern part of the ITACN.

Stiff diagram: The stiff diagram (Figure-6) directly assesses the concentrations of the major elements in water according to their anionic and cationic abundance[15].

The results of the stiff diagram (Figure-6) confirm those of the Piper Diagram and show in particular that the groundwater and surface water in ITACN plant are rich in sulphate, calcium and sodium ions. The origin of the high concentrations could be due to occasional contributions of the sulphate chemical wastes gathered in the surrounding of the ITACN.

The significant concentrations of sulphate, calcium and sodium are well reflected in the Stiff Diagram representation of 00GWMW1, 00GWMW2 and QESF232 water samples. The level of concentrations in the decreasing order is for the cations Na$^+$>> Ca^{2+}> Mg^{2+} and for the anion SO_4^{2-}>> Cl$^-$.

The major ion concentrations in samples 00GWMW5, 00GWMW6, PW1-06, PW1-09, PW1-16, QESF233 and 96MW1-A, 00GWMW4, QESF231, PW1-01, PW1-04, PW1-05, PW1-14, 96MW1-B, 96SW16 and 96SW35 water samples are relatively low (less than 2.5meq.L^{-1}). PW1-15 and PW1-16 are relatively high in hydrogen carbonates ion concentration. The dominance of cation is Na$^+$> Mg^{2+} and the dominance of anion is HCO_3^--.

Overall, the major ion concentrations of ground water and surface water around the tailings pond are relatively low compared to those in the ITACN. This assumes the existence of an effective infiltration process due to the geological and/or artificial nature of the environment[16].
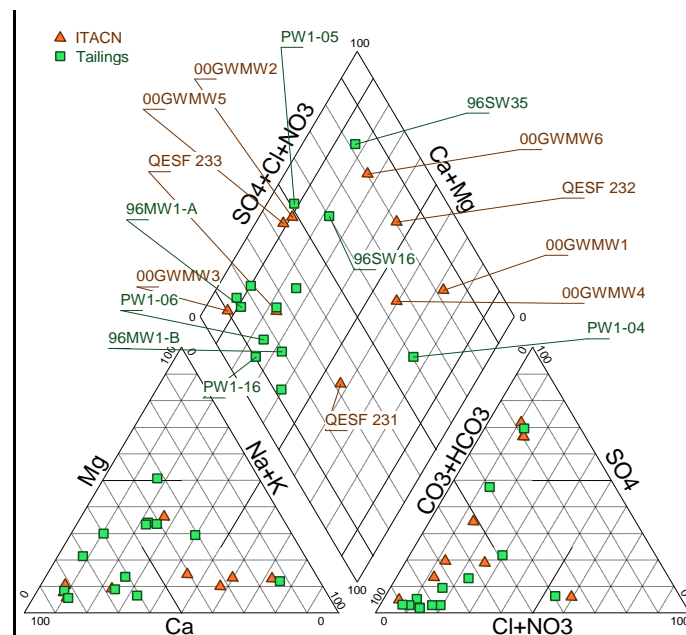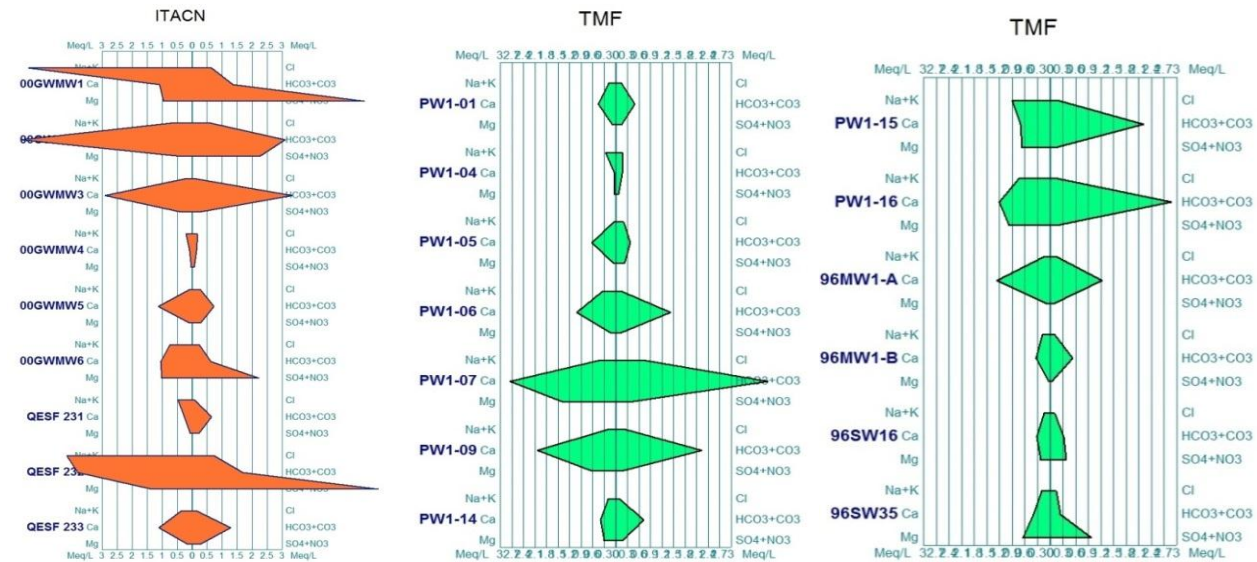

Figure-5: Facies of the water samples[14].

Figure-6: Abundance in major ions of water, in 2015[14].

Origin of the mineralization[17]: Origin of the mineralization of the study are explain on the basis of relationship of different ions which are shown in Figure-7,8,9.
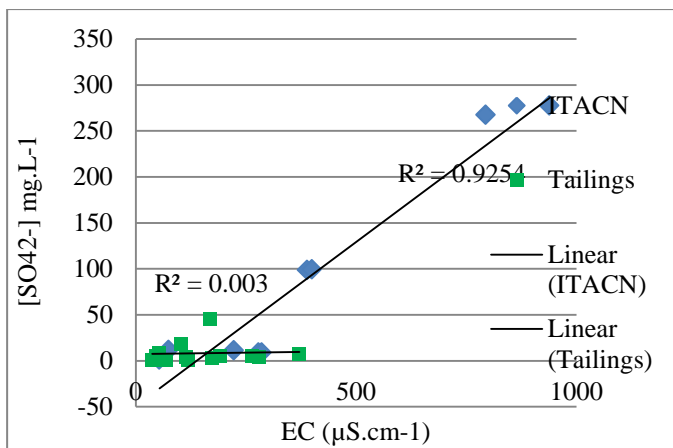
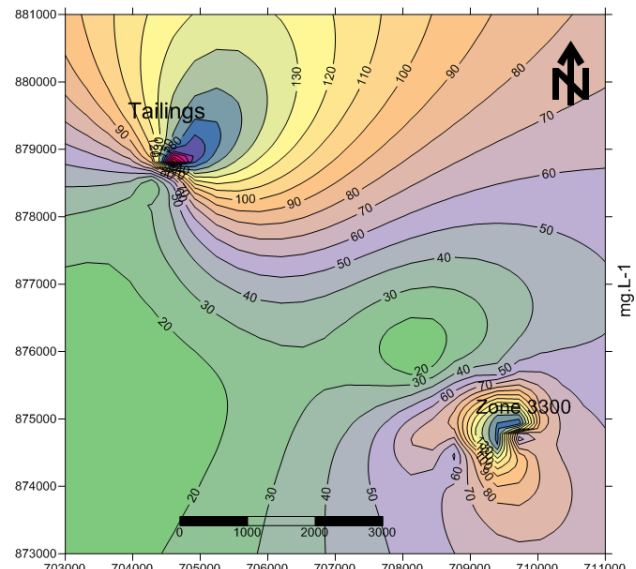

Figure-7: Relationship between sulphate ion and EC.

Figure-8: Relation between Mg^{2+} and Ca^{2+} vs bicarbonate ion.
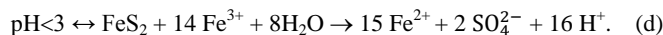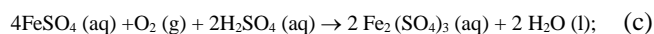

Figure-9: Estimation of the water mineralization[18].

Relationship between sulphate ion and EC: Figure-7 shows that the correlation between the sulphate ion and electrical conductivity around the tailings pond is low (R^2 =0.03). This result confirms the efficiency of the purification system used in the tailings area. On the other hand, in the ITACN, the correlation between the two parameters is relatively high, R^2 = 0.92. It can be inferred that the sulphate ion controls the groundwater mineralization in the surrounding of the cobalt-nickel treatment plant. This high mineralization could be due to the infiltration of the sulfur used as raw material for the treatment and stored in the open area in the treatment zone[19]. This phenomenon could be enhanced during the rainy season. The waste ore treatment seems to be the main source of pollutants. Actually, the presence of sulphate ion in the

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groundwater originates from the following chemical reactions (a), (b), (c) and (d)[20, 21]:

$$pH >4.5 \leftrightarrow FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe_2+ + 2SO_4^{2-} + 2\ H^+; \quad (a)$$
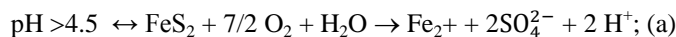
$3.5 < pH <4.5 \leftrightarrow$ same chemical reaction but the reaction duration is shorter;

$$pH<3.5 \leftrightarrow Fe_2+ + 1/4O_2 + H^+ \rightarrow Fe^{3+} + ½\ H_2O; \quad (b)$$

$$4FeSO_4\ (aq) + O_2\ (g) + 2H_2SO_4\ (aq) \rightarrow 2\ Fe_2\ (SO_4)_3\ (aq) + 2\ H_2O\ (l); \quad (c)$$

$$pH<3 \leftrightarrow FeS_2 + 14\ Fe^{3+} + 8H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+. \quad (d)$$
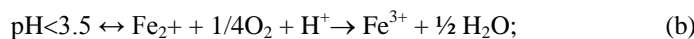
Relation between Mg^{2+} and Ca^{2+} versus bicarbonate ion: The correlation of magnesium ion plus calcium ion versus bicarbonate ion is relatively high (R^2=0.84) in the tailings (Figure-8). This strong correlation could come from the stability of the calcium-magnesium carbonate compound in the aquifer; according to the following reaction[22] (e):

$$CaMg(CO_3)_2 + 2\ H_2CO_3 \Leftrightarrow Ca^{2+} + Mg^{2+} + 4\ HCO_3^- \quad (e)$$
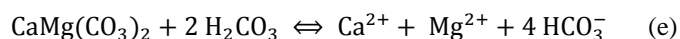
In fact, it is the dissolution of dolomite[23]. On the other hand, the correlation is low in the ITACN site (R^2=0.64) because of the alluvium geology of the latter.

Conclusion

Firstly, the groundwater and surface water quality in the tailings and ITACN is evaluated. The results of the chemical parameters during the campaign period show that the major ion concentrations in the TMF are low. The Stiff diagram shows that it is less than $2meq.L^{-1}$. On the contrary, in the ITACN, the latter concentrations can reach up to $3meq.L^{-1}$. The southern part of the ITACN is more mineralized than the northern one. The highest concentration of sulphate ion is particularly observed in the Southern part of this latter ($300mg.L^{-1}$), while it is evaluated as low in the north ($60mg.L^{-1}$).However, the origin of the water mineralization in the ITACN would be caused by the gradual infiltration of the sulphate deposit by rainwater from the surface of the soil to the aquifer.

Secondly, the electrical conductivity value of groundwater samples could reach up to $1000\mu S.cm^{-1}$ in the southern part of the ITACN. While it varies from 50 to $400\mu S.cm^{-1}$ in the tailings. Another origin of ground water mineralization in the same site could be the infiltration of wastewater from the cobalt-nickel treatment plant into the aquifers, due to the geological characteristics of the study area[24].

In addition, in the TMF pond, the mineralization of the sampled waters is relatively low ($<400\mu S.cm^{-1}$). This reinforces the previous hypothesis which explains the origin of the water mineralization in the study area.

As a confirmation of previous results, four facies type of water are evaluated according to the Piper diagram. First of all, the calcium bicarbonate type (Ca-HCO$_3$) facies, downstream the tailings, and in the Eastern part of the ITACN site. Then, the calcium and sodium bicarbonate type (Na-Ca-HCO3) facies are located in the upstream Western and Southern part of the ITACN. Whereas, the sodium chloride type (Na-Cl) facies in the Western part area of the ITACN is observed. Finally, downstream the southern part of the ITACN, the sulphated calcium chloride type (Ca-Cl-SO4) facies is characterized.

Thus, the results allow us to conclude that the natural system of groundwater and surface water purification is about fifty percent (50 %) efficient.

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