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Energy



Energy Procedia 50 (2014) 685 - 691

The International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES14

Mobility of chromium and tin associated with geochemical dynamics in groundwater in Meboudja plain

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Abstract

In the region of Sidi Amar Annaba South. Storage of industrial waste from the Arcelor-Mittal steel complex directly on the floor produced an infiltration of heavy metals to the under saturated and groundwater area. To know the exact origin of some pollutants and their evolution in time, monthly monitoring of water chemistry (potential hydrogen, potential of oxydo-reduction, temperature, conductivity, Oxygen, Calcium, Magnesium, Sodium, Potassium, Chlorine, sulfate, bicarbonate, Nitrate, Strontium, total Chrome, total Tin) was performed on wells for water cycle.

Statistical analysis shows a common origin of chromium and tin that would be due to electroplating waste. The temporal evolution of these elements highlights the influence of several factors (potential hydrogen, potential of oxydo-reduction, rainfall and pumping) in the dissolution of these species and the evolution of the dominant aqueous species. There presentation of water points on the Eh-pH equilibrium diagram indicates that chromium may appear in the water table in two complex forms, trivalent and hexavalent by against the tin is in the hexavalent form.

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"Keywords: pollution, surface water, chromium, tin, redox ;"

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O ₂ Dissolved oxygen	Ľ
EH Redox potential]
T Temperature	ſ
EC Conductivity]
NO ₂ Nitrite]
NO ₃ Nitrate]
NH ₄ ⁺ Ammonium]
SO ₄ ²⁻ Sulphate	
Fe (T) Iron. total]
Mn ²⁺ Manganese]

1. Theorical considerations

The natural chemical quality of groundwater depends mainly on their origin, the nature of the alluvium and rocks that store water, as well as physic-chemical conditions of the environment. These have been the subject of this study, given their important role in changing the chemical form of the elements. The presence of bacteria in a medium result in consumption of oxygen for their metabolism and oxyanions (NO₃⁻, SO₄²) are important sources for them. The sequence of decomposition of organic matter in the environment causes the zoning of redox reactions. Thus, the denitrification space between disappearance and appearance of dissolve oxygen of significant levels of metal cations in solution. Changes typically observed in the field are illustrated, see Fig. 1. To characterize the environmental conditions, it is possible to emphasize the study of the dominant presence and / or absence of certain species, including dissolve oxygen and NO₃⁻, strong oxidizing, or metals such as iron and manganese, insoluble in oxidizing conditions. This characterization can be performed:

- A spatial distribution in the study of physic-chemical conditions on a hydro geological profile showing the captive setting of the aquifer,
- · Then study the time variation of some characteristic features of two holes.



Fig. 1. Hydrogeochemical typical profile of the phenomenon of denitrification during the passage of the water in captivity (Edmunds, 1982)

In this study, we will examine the evolution of three chemical elements (iron, manganese, nickel and nitrogen) according to the variation of redox potential (EH) and oxygen in a natural passage of groundwater between the oxidizing environments and reduces the middle of the water gravel.

1.1. Geological and hydrogeological context

Hydro geological study of the area is very interesting because it allows to consider the underground trade (meaning water outlet, transfers of pollutants) (Djabri L 2003) [1] that may occur in aquifers based on geological description of land and hydro geological characteristics each training, we can distinguish a set of filling Miocene Pliocene Quaternary can be two kinds of aquifers:

- Shallow aquifer,
- Deep aquifer.

1.2. Aquifer Geometry

Both aquifers identified in our study area are `one` aquifer system with hydraulic transfer's drainance communicating the surface water and groundwater of gravies (Hani A 2003 Kherici N 1993) [2, 3].

The description of the various aquifers, see Fig. 2. According to a North-South orientation: The surface water is in direct contact with the deep aquifer, its thickness is estimated 15m. This sheet is represented by alluvial clay loam, and covers most of the area for investigation of an area of 320 km².

More than one 's moving towards the North, the semi-permeable layer appears between the unconfined and confined aquifer with an average thickness of around 40m. Deep aquifer (groundwater metamorphic formations, gravel layer) extends below; increasing its thickness reaches the 45m area, to the sea.



Fig. 2. Cross section through the plain of Annaba showing groundwater of gravel (in Hani 2003) [4]

Legend: 1: silty clay with sand past (surface water) 2: Plio-Quaternary detrital clay, 3 lenses sands 4: Pebbles and gravel (deep water), 5: Clay Numidia or Paleocene; 6: Drilling, 7: Direction of flow; 8 piezometric surface of the gravel layer.

2. Results and interpretation

2.1. Space Evolution

A sampling campaign was carried out in 13 boreholes. The samples were taken in a north-south profile consistent with the groundwater flow direction. It took place in August 1999, according to a north-south profile consistent with the groundwater flow direction.

The parameters measured in situ are: dissolved O₂, redox potential (EH), pH, temperature (T) and conductivity (EC). For large items, analyzes carried out nitrite (NO₂⁻), nitrate (NO₃⁻), ammonium (NH₄⁺) and sulphate (SO₄²⁻). Other analyzes related metals (iron (Fe (T) and manganese Mn²⁺).

On the north- south profile, see Fig. 2. The gravel layer is gradually transferred under pressure in a waterproof cover, which induces consumption without renewal of the oxidizing species (Hani A) [5]. We observe, from south to north, joint lower levels of NO_3^- , SO_4^{2-} and dissolved oxygen. We also note a sharp drop in values of EH in the F9 and F13 drilling where the thickness of the clay layer reaches twenty meters. In detail, nitrate levels go quickly around 70 mg/l (F3) to 0 mg/l (F9 to F13) and sulphate of 350 mg/l F2 least 100 mg/l in water drilling F8 to F13. Fluctuations in oxygen levels are also notable because they spend about 3.5 mg/l to 1.5 mg/l in the direction of flow. Meanwhile, the concentrations of iron, manganese, nickel and ammonium, relatively low upstream of the hydraulic flow from the rapidly increasing drilling F10.

The distribution of oxygen levels (3.6 mg/l), nitrate (70 mg/l), sulphate (342 mg/l) and values of EH (389 mV) in the sector of Chihani Drean indicates oxidative phase (Hani A) [6] drilling F1, F2 and F3. In contrast, the presence of ammonium, reduced form of nitrogen, iron, manganese and nickel right drilling F10, F1, F12, F13 indicates more reducing conditions than on all points, see Fig. 3.





2.2. Temporal evolution

The evolution of the chemical forms of chromium and tin is presented using two Eh-pH diagrams, see Fig. 4. (Debieche TH.2002 [7])

2.2.1. Chromium:

In nature, it appears in three oxidation levels: divalent Cr (OH)₂, trivalent Cr (OH)₃ and hexavalent represented by two species: $HCrO_4^-$ and CrO_4^{-2} . The high water period (February, March, April), with a pH range of 7.51 to 7.64 and redox potentials of 426-462 mV, however, during the low water period (June, August, and October): the decrease in EH (431 to 370-366mV).

2.2.2. Tin:

The most common complex forms in nature are derived from Sn^{2+} species (Sn(OH)+ and Sn (OH)₆²⁻) and those derived from Sn⁴⁺ (SnO₂ and HSnO₂). The projection of the plain water on the equilibrium Eh-pH diagram of tin (see Fig. 4) shows that the samples are in equilibrium with the only form Sn(OH)₆²⁻. The latter is produced by the following equation: Sn⁴⁺ + OH⁻⁶ Sn (OH)₆²⁻ due the cessation of aerated water flows to the water.



Fig. 4. Equilibrium diagram's (a) Chromium (b) Tin (in (Debieche TH.2003 [8])

Conclusion

The passage of the water from the gravel plain Annaba shows denitrification with the appearance of high levels of NO_3 , SO_4 , O_2 and high in redox potential in conditions where the water is only a few meters from the surface (Debieche TH.2002) [8] values floor (area from Chihani to upstream Chbaita Mokhtar). At the contrast, the downstream of the water where the gravels are captives (the roof of the water is 40m) sector, there are high levels of iron, manganese, ammonium nickel in enough net reducing conditions. Between the two develop a transition zone characterized by the presence sometimes such low levels of NO_3 and high values of iron. This study has allowed us to highlight the presence of contamination superficial layer of the low plain of Seybouse by two trace elements (chromium and tin); causing these two elements according to the relationship Cr-Sn is related to the storage residues of the industry on the aquifer.

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