# SURFACE COMPLEXATION MODEL OF AQUIFER POLLUTION WITH HEAVY METALS ON AN ASH AND SLAG DUMP NEAR TIMIŞOARA

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**ABSTRACT**

For modelling of the pollutants transport process in aquifer a very important aspect has the analysis of aquifer pollution with heavy metals. The surface complexation process of heavy metals on the grains of porous-media is reversible similar to the adsorption-desorption in transport processes, in aquifer pollution, but strongly dependent of pH value. High pH values determine increasing heavy metals complexation and consequently decrease their concentration in the groundwater. Decreasing pH value leads to liberation of heavy metals from the formed complex and so an increased concentration of heavy metals in the groundwater appears. This paper presents the results obtained by using a numerical experiment using PhreeqC and PMWIN software package for the spreading of the heavy metals pollution in the aquifer of an ash and slug dump, as pollution source, near village Utvin, Timiş County, Romania.

## 1. INTRODUCTION

It is known that heavy metals are metals with a higher density than $\mu g/m^3$. These metals as well as their residues are pollutants in the environment; some of them are even toxic. Some of these elements are actually necessary for humans in minimal amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper), the skin, bones, or teeth (nickel, cadmium, copper, chromium).

Mentioned items that reach the aquifer are spread by advection, dispersion and other transport processes. Heavy metals found in the environment have the ability to form complexes on the surface of particles; this process is known as surface complexation. This process is influenced by different parameters, but we study only the influence of pH.

The process of surface complexation is shown schematically in the following Fig.:

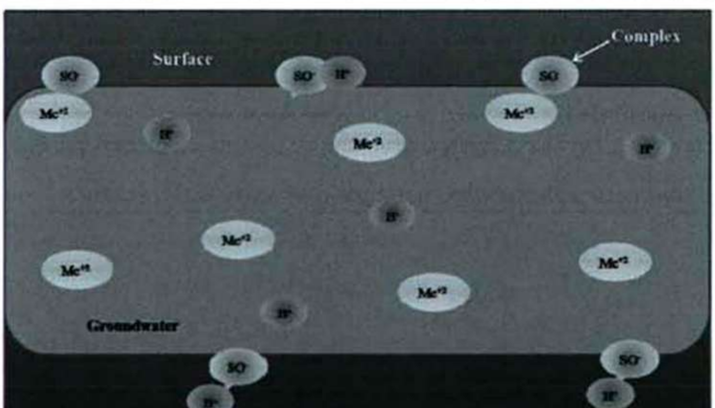


***Figure 1. Surface complexation model***

The reactions responsible for surface complexation presented in Fig. 1 can be written:

$$SOH_2^+ \Leftrightarrow SOH^0 + H^+$$

$$SOH^0 \Leftrightarrow SO^- + H^+$$

$$SOH_0 + Me^{2+} \Leftrightarrow SOMe^+ + H^+$$

The surface complexation is reversible, meaning that the complex bands can decay if the environmental conditions change.

## 2. TOOLS, DATA AND DOMAINS

### 2.1. Modelling tools

Surface complexation is highlighted by the software PhreeqC that enables forecasting chemical processes that occur naturally in studied aquifers. PhreeqC version 2 (Parkhurst, D. L., Appelo, C.A.J., 1999) uses mole fraction for the activity of surface species. Surface complexation processes are included in the model through heterogeneous mass-action equations, mole-balance equations for surface sites, and charge-potential relations for each surface.

For transport modelling, meaning spreading of pollutants in aquifer, which in our case are heavy metals are modelled using PMWIN, a MODFLOW based software (Chiang, W.H., Kinzelbach, W., 2001). MODFLOW is a simulation system for modelling groundwater flow and pollution transport processes. This software allows modelling of underground water flow and extension of pollutants plume in aquifer in space and time.

### 2.2. Data

All data used were provided by CET SUD Timişoara, and it represents the analysis performed during the years 2007-2010 from wells of the slag and ash dump. Wells from which samples were taken are represented in Fig. 2, and they are marked with: PJ1, PJ2, PJ10, PJ11 and PJ12.

For our study we used an average concentration of heavy metals. Average was calculated for 2010, because these were the last analysis results we obtained at this moment.

### 2.3. Analysed Domain

The analysed site is a slag and ash dump located near Utvin village in Timiş county. There we find stored ash and slag produced from the combustion of coal at CET SUD. Coal combustion is used to produce heat and domestic hot water, provided to Timişoara City. Utvin slag and ash dump is a deposit of lowland, which occupies an area of 150 hectares. The dump has a trapezoidal form with the large base of 1100 m, a lower base of 900 m and the trapezoidal height of 500 m.

The dump is located at:

- 1,5 km SW of Utvin Village
- And about 4 km West of Timişoara City

The dump is located at approx. 2 km SE of Bega River and near the Nivelda creek, which passing approximately 500 m south of the deposit.

The deposit is designed for a total capacity of 4 821 000 m$^3$. (Ministry of Environment and Sustainable Development, 2008)

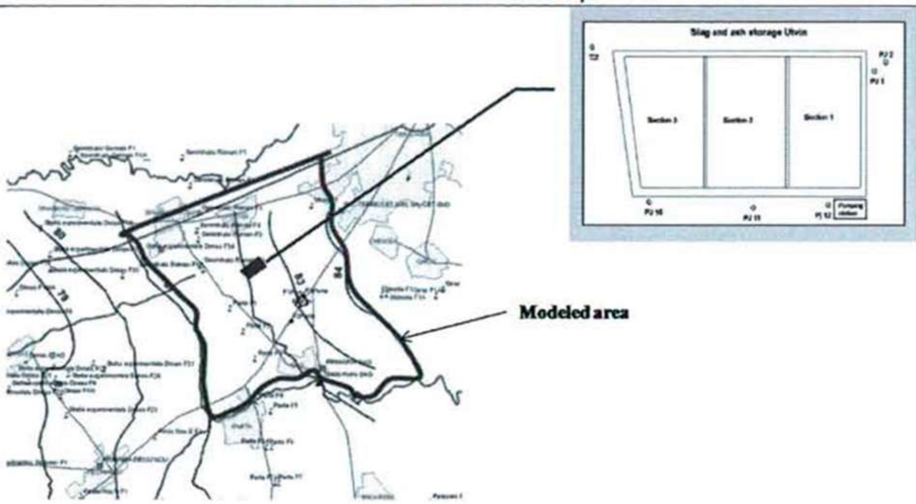


*Figure 2. Localization and shape of the studied slag and ash dump* (*David I. et all, 2007*)

Waterproofing system

According to the hydro geological survey, slag and ash dump Utvin is located on a clay layer of 3,5 to 6,5 m thickness, which has an average permeability of $k = 0,05$ m / day ($k = 5 \times 10^{-5}$ cm/s ).

## 3. RESULTS

The first step of the research was to determine surface complexation at different pH values using PhreeqC software. The results obtained are shown below.

Molality at different pH values:

Initial concentration of Zn is 0,001898 mol/kg. We can see in Fig.3 that the concentration decreased with increasing pH: for a pH of 8,5 the Zn concentration become 0. That indicates that it has been fixed entirely by surface complexation.

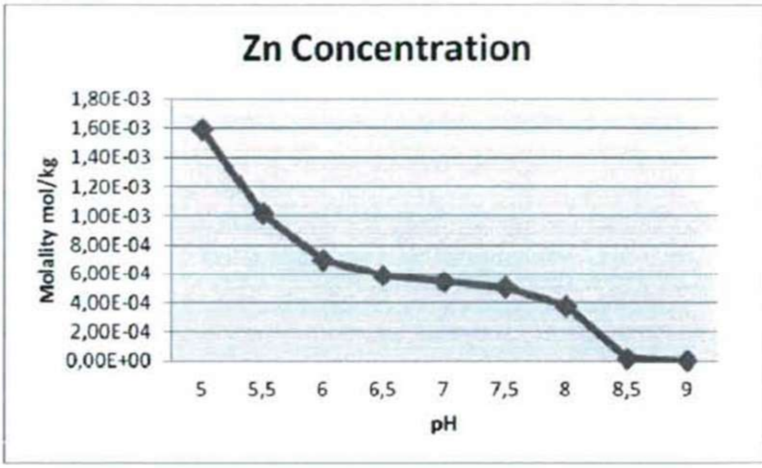


*Figure 3. Zn Concentration of Zn at different pH values*

In the case of lead we started from a lower concentration than zinc, namely 0, 00003943 mol/kg. Initial concentration was lower but in Fig. 4 we can see that removing the whole quantity of Pb from the groundwater, by surface complexation, is reached at pHvalue of 8,5.

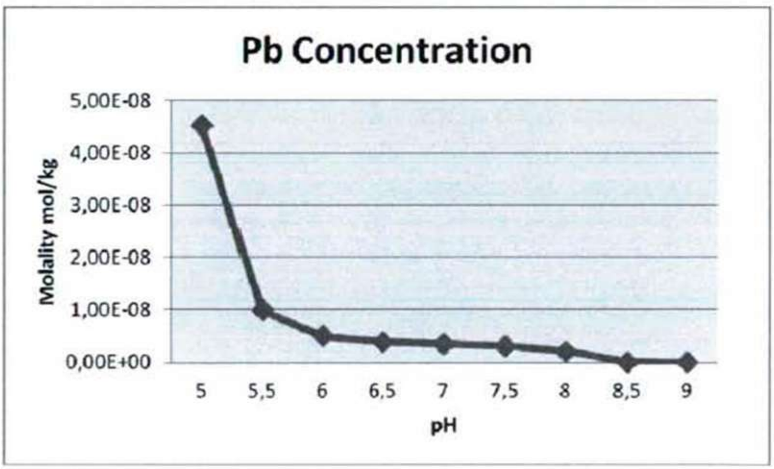


*Figure 4. Concentration of Pb at different pH values*

Copper appeared with two different valences, (1) and (2), the concentration of these two forms being 0, 00000005157 mol / kg Cu (1) and 0,000001074 mol / kg Cu (2). Cu (2) behaves like Zn and Pb, meaning that at a pH value of 8,5 it reaches a concentration of 0 in solution. But in contrast Cu (1) disappears at a pH value of 8, but this may be due the small amount of Cu (1) of the solution. Fig. 5 is a graphic representation of the two concentrations Cu (1) and Cu (2) and their evolution in function of pH.

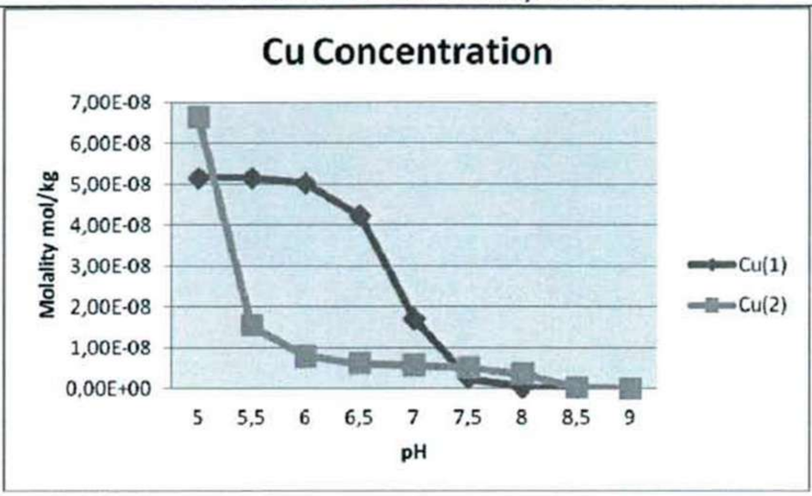


*Figure 5. Concentration of Cu (1) and Cu (2) at different pH values*

The 4-th studied element is cadmium. In this case we start the study at a concentration of 0.0001444 mol / kg. We can see in Fig. 6 that this heavy metal, Cd, is removed from the groundwater, and fixed by surface complexation at a pH value between 8.5 and 9. This indicates that Cd disappears later from the aquifer than previously studied items. The difference is not great but is visible.

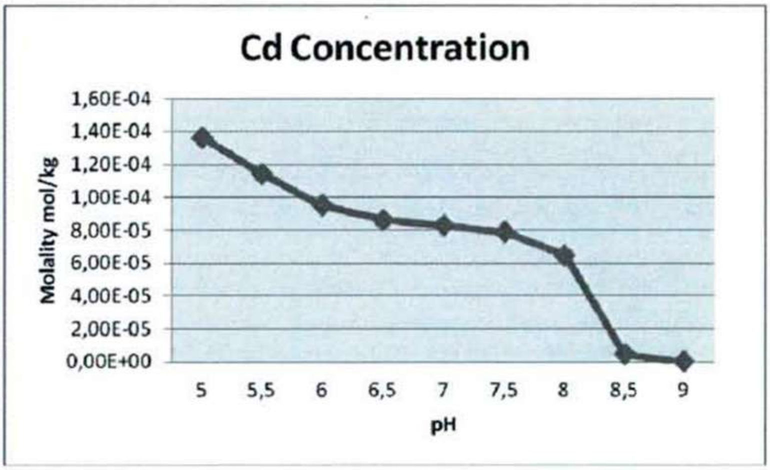


*Figure 6. Cd concentration at different pH values*

The next step of the study was to introduce the data, obtained using the software PhreeqC, in the development of a transport model using PMWIN. The stabilised heavy metals concentration under the pollutant source (*ash and slug dump as pollution source near village Utvin, Timiş County, Romania)* determined by the pH value can be used as a fixed boundary concentration for modelling the spreading of the heavy metals pollution in the aquifer.

By creating a model based on obtained data we want to show, that the fixation of heavy metals by surface complexation, leads to modified spreading of pollution into the environment.

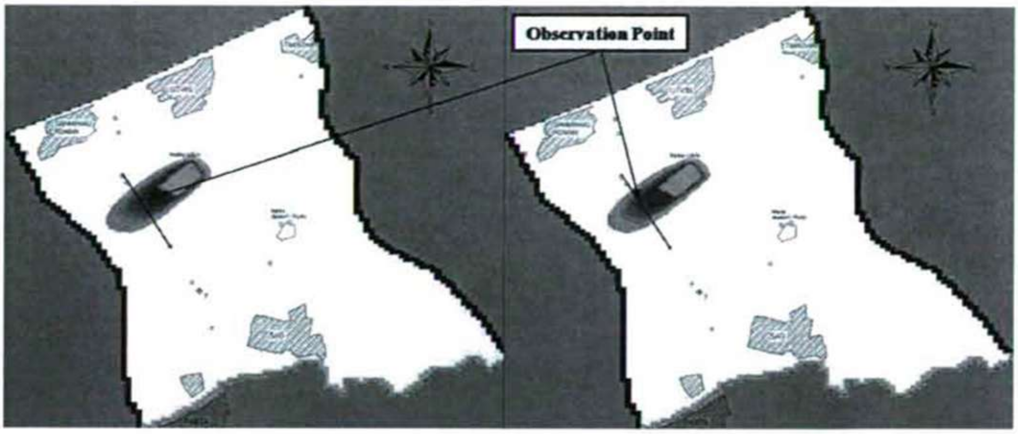


*Figure 7. Pollution plum after 30 years (initial concentration and pH=7,)*

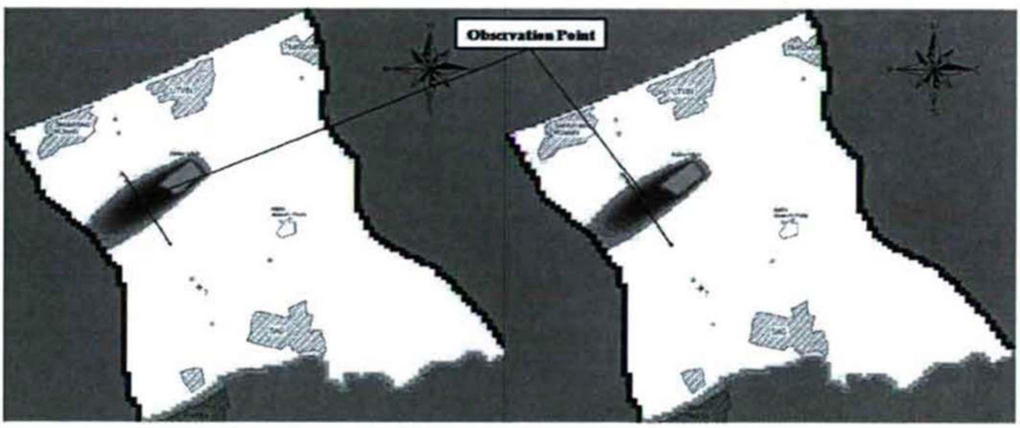


*Figure8. Pollution plum after 50 years (initial concentration and pH=7)*

The obtained differences by surface complexation are not that visible. For this reason we used an observation point in which, with the use of PMWIN software, we can highlight the space and time evolution of pollutant concentrations. (Fig. 9)

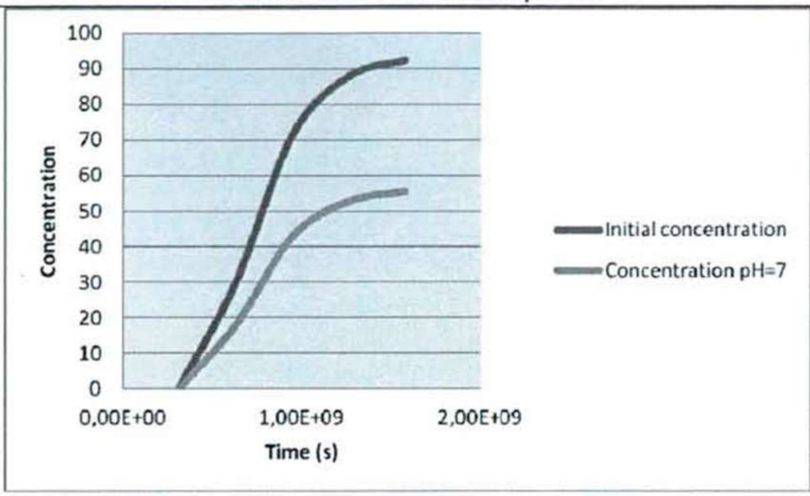


*Figure 9. Concentration in the observation point after surface complexation*

## 4. CONCLUSION

Based on PhreeqC modelling relevant conclusions can be formulated on the state of heavy metals concentration in the groundwater.

The surface complexation process of heavy metals on the grains of porous-media in the aquifer is reversible similar to the adsorption-desorption transport processes but strongly dependent of pH values. High pH values determine increasing heavy metals surface complexation and consequently decreased concentrations in the groundwater. Decreasing pH value leads to release of heavy metals from the formed complexes and so an increased concentration of heavy metals in the groundwater appears. At pH values between 8 and 8,5 we found out that the concentration of heavy metals have minimum values (Fig. 5-6). Having a pH value of 8.5 reduces heavy metals concentration to zero (0). Thereby an alkaline pH favours the surface complexation process. In order to forecast the evolution of pollutant plume we must take into consideration natural attenuation and surface complexation as a part of these natural processes which takes place without the application of engineering technologies. Only such we can determine true and correct the concentrations under the source of pollution which are the essential boundary conditions needed for modelling pollutant extension.

Fixing processes of heavy metals described above can be considered natural attenuation only if a stabile natural pH value is maintained in order to avoid the reversibility of surface complexation processes.

Monitoring of contaminated sites can reduce the threat to environment, because by exact monitoring we reduce the risk of unwanted events. In case unwonted situation would appear we can take action soon to remove the danger to human health and the environment.

## ACKNOWLEDGMENT

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