Numerical simulation and prediction of groundwater pollution caused by the leakage of sulphuric acid storage tank with GMS model

Yimin Liang¹, Junkang Lan¹*
¹ College of Environmental Science and Engineering, Guilin University of Technology, Guilin City, China
*Corresponding author’s e-mail: 1269431898@qq.com

Abstract. Because of the concentration of SO₄²⁻ in the sulfuric acid tank is extremely high, the leakage of sulphuric acid storage tank is great harm to groundwater environment. Once the accident of leakage take place, the drinking water sources of residents around the leak point will be greatly polluted. In order to find out the severity of groundwater pollution and the migration of pollutants after leakage, a GMS software was used to simulate and predict. During simulation, the scope of the simulation area and its hydrogeological conditions were determined by hydrogeological surveying, mapping and drilling. The parameters used in the simulation are obtained from field tests. The simulation results show that the concentration of SO₄²⁻ at the central pollution halo is as high as 788050 mg/L after 27.39 years of the leakage accident happened. Due to the low permeability of the formations, the decontamination effect of the polluted halo mainly depends on the slow dilution of aquifer. The process of the completely purifying pollutants in groundwater will takes a long time.

1. Introduction
Sulfuric acid has corrosion and oxidization. Once the sulfuric acid tank leaks, it may cause fire, explosion, poisoning and other accidents. So far, there have been few studies to predict the damage to the groundwater environment after the leakage of sulfuric acid tanks. But the tank leaks will cause great pollution to the groundwater environment. It is necessary to study and predict it so that people can take scientific measures to prevent groundwater pollution. In this paper, a feed factory in Nanning city is taken as an example to study.

2. Geological environment conditions
There is plenty of rain in the study area. The annual rainfall is about 1430 millimeters and the main rainfall occurs from April to September. The study area is a low mountain and hilly area. The ground elevation is about 60 ~ 120 m. The area is also a interriver block area. On the east and west sides of the study area, there are Yujiang River and Gantangjiang River, respectively.

The strata in the study area are as follows: (1)Quaternary layers, including loose surface soil, and residual or slope alluvial soil. These soils are mainly composed of clay or silty clay. (2) Eogene stratum, mainly composed of sandstone, mudstone or conglomerate. (3)Cretaceous straum which is consisted of gray-yellow, brown-red siltstone or argillaceous siltstone.

According to the water-bearing medium, there are two types of groundwater in the study area. One is pore water which is stored in the loose layers and the other is fissure water which is stored in clastic
rocks. Both of them are mainly recharged by atmospheric rainfall. Affected by terrain, the groundwater flows from the middle of interriver blocks to both sides. However, at the potential leakage points, the groundwater flows from west to east (i.e. drain to Gantang River).

In the simulation area, there is no well. The discharge of the groundwater is carried out by the runoff to the river and phreatic evaporation (The phreatic water table in the area is shallow).

3. Water Quality Assessment
Groundwater sample monitoring was carried out from 5 boreholes. These five boreholes are drilled in advance near the potential leakage point and its upstream, west and downstream respectively. The water quality monitoring results showed that the current quality of groundwater in 4 holes has exceeded the standard of water quality before leakage accident happened. Especially, the groundwater in the upstream hole has been seriously polluted. The concentration of COD $\text{Mn}$ in the upstream hole has exceeded 5.15 times and its Nitrite (NO$_2$) exceeded 299 times. After detailed investigation and study, the pollution of the groundwater in the study area is thought to be caused by the enterprises near the feed factory.

4. Numerical Simulation of Groundwater

4.1. Mathematical model
The groundwater flow model of the area can be expressed by the following equations[1]:

\[
\frac{\partial}{\partial x} \left[ K_x \frac{\partial h}{\partial x} \right] + \frac{\partial}{\partial y} \left[ K_y \frac{\partial h}{\partial y} \right] + \frac{\partial}{\partial z} \left[ K_z \frac{\partial h}{\partial z} \right] + W = \mu_s \frac{\partial h}{\partial t} \quad (x, y, z \in \Omega, t = 0)
\]

\[
h(x, y, z, t) = h_0(x, y, z) \quad (x, y, z \in \Omega, t \geq 0)
\]

\[
h_{1_{\Gamma_1}} = h_1(x, y, z, t) \quad (x, y, z \in \Gamma_1, t \geq 0)
\]

\[
k \frac{\partial k}{\partial n} |_{\Gamma_2} = q(x, y, z, t) = 0 \quad (x, y, z \in \Gamma_2, t \geq 0)
\]

In the above equations, $K_x$, $K_y$, $K_z$ are hydraulic conductivities along $x$, $y$, $z$ direction respectively (m/d); $h$ is groundwater head (m); $h_1$ is the river water levels (m); $W$ is the source and sink intensity (d$^{-1}$), is the simulation area; $\mu_s$ is water storage rate (m$^{-1}$) and its empirical value of 0.0005 is used in the simulation. $\Gamma_1$ is the specified head boundary (i.e. the first kind of boundary); $\Gamma_2$ is the barrier boundary (i.e. the second boundary);

4.2. Boundary Conditions
In the view of horizontal direction: The watershed is considered to be the second kind of boundaries in the north and the south of the simulation area. Gantang River and Yujiang River are thought to be the the first kind of boundaries[2].

In the view of vertical direction: The top boundary is phreatic water, their height is got by the monitoring data (including groundwater level in boreholes and river levels) and calculated by interpolation[3]. The bottom boundary is thought to be the thick, slightly weathered sandstone top (because slightly weathered sandstone is a water tight stratum).

4.3. Hydrogeological parameters
(1) The initial infiltration coefficient of the aeration zone: The value is used as 0.10 according to regional hydrogeological survey report. The final value is obtained by simulation inversion calculation.

(2) The initial permeability coefficients of the aquifers: According to borehole water injection tests, the simulated initial of permeability coefficients of the following aquifers are: The filling and topsoil 0.75 m/d, residual silty clay 0.075 m/d, strong weathered sandstone 0.65 m/d, middle weathered layer 0.03 m/d. The final permeability coefficients of these aquifers are also got by simulation inversion.
4.4. Mesh generation
The simulation area is about 5.54 km². The planar grid was divided into 60 rows and 60 columns. The vertical profile was divided into three layers: (1) The first layer: including the fill soil, surface soil and residual silty clay; (2) The second layer: strong weathered sandstone; (3) The third layer: medium weathered sandstone. Due to the weak weathered sandstone is an impermeable layer, it is not considered to be an aquifer and was not included in the grid.

4.5. Hydrogeological Parameters Verification
The initial parameters obtained from field tests, the monitoring groundwater levels (10 points) and the variable river water levels were all input into the model. During simulation, the relevant parameters were slightly adjusted. When the calculated groundwater levels were coincided with the measured groundwater level at each observation point, the adjusted parameters were considered to be credible and can be used in subsequent simulation (water quality prediction).

5. The quality of groundwater simulation and prediction

5.1. The solute transport mathematical model
The mathematical model of three-dimensional hydrodynamic dispersion problem is[1]:

\[ R \theta \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j} \left( \theta D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_j} \left( \theta V_j C \right) - WC - WC - \lambda_1 \theta C - \lambda_2 \rho_b C \]  

(2)

\[ C(x, y, z, t) = C_0(x, y, z), (x, y, z) \in \Omega_1, t = 0 \]  

(3)

\[ C(x, y, z, t)|_{\Gamma_1} = C(x, y, z, t), (x, y, z) \in \Gamma_1, t \geq 0 \]  

(4)

\[ (\theta D_{ij} \frac{\partial C}{\partial x_j} - q_j(C)) |_{\Gamma_3} = g_j(x, y, z, t), (x, y, z) \in \Gamma_3, t \geq 0 \]  

(5)

In (2) to (5) formulas: \( R \) is hysteresis coefficient, \( R = 1 + \rho_b \frac{\partial C}{\partial C} \); \( \rho_b \) is medium density (kg/(dm³)); \( \theta \) is porosity of medium; \( C \) is the concentration of pollutants in groundwater (g/L); \( \overline{C} \) is solute concentration adsorbed by medium (g/kg); \( t \) is time (d); \( D_{ij} \) is hydrodynamic diffusion coefficient (m²/d); \( V_j \) is seepage velocity of groundwater (m/d); \( W \) is sources and sinks of water (l/d); \( \overline{C} \) is the concentration of components (g/L); \( \lambda_1 \) is primary reaction rate of dissolved phase (l/d); \( \lambda_2 \) is adsorption phase reaction rate (l/d).

The hydrodynamic diffusion coefficient: Based on field dispersion tests carried out by YU, H. K. and others in 2016, the longitudinal dispersion in the mixture of fine sand, silt and silty clay is about 0.0058 ~ 0.0064 m⁴. Therefore, the longitudinal dispersion adopted in simulation is 0.006 m, and the transverse dispersion is used as 1/8 of the longitudinal dispersion (according to empirical value).

5.2. Prediction Method
Estimation of leakage volume in sulphuric acid tanks: Suppose the leakage area of the tank is 0.01 m² (the value only occurred in the most serious accident) and all corresponding effective measures were taken to stop the accident after leakage happened in 20 minutes. The leakage of sulphuric acid is about 552 kg. Conversion by volume, 30 L of the leakage of sulphuric acid is adopted in the prediction.

5.3. The Range of Contamination Halos
Because areas with over 250 mg/L of sulphate concentrations are defined as contaminated areas according to Chinese “Sanitary Standard of Drinking Water” (GB 5749-2006) and the background
value of $SO_4^{2-}$ is 2.37mg/L in drilling hole of ZK1 at the project site, 247.6mg/L was used as the demarcation line of $SO_4^{2-}$ pollution area after leakage accident happens.

5.4. Prediction results
After the accident of leakage of the sulphuric acid tanks, the simulation and prediction results of the pollution in the aquifer are shown in Fig. 1 to Fig. 3.

Concentration of $SO_4^{2-}$ in leakage liquid: According to the concentration of 98.3%, the density is 1.84g/cm³, the concentration of $SO_4^{2-}$ in the leaked liquid is calculated as 1766400mg/L.

The simulation results showed that the concentration of $SO_4^{2-}$ at the central pollution halo is still as high as 788050 mg/L after 10000d (about 27.39 years) of the leakage accident. This means the purification of pollutants are mainly depended on the dilution of the aquifer. Once the aquifer is polluted, the groundwater in the area will be difficult to be purified by the circulation of groundwater.
Table 1 Characteristic table of transport of pollutants in aquifers during leakage of sulphuric acid tanks under abnormal conditions

| Time (d) | Pollutants | Pollution halo forward maximum distance (m) | Vertical migration maximum distance (m) |
|---------|------------|-------------------------------------------|---------------------------------------|
| 100     | SO₄²⁻      | 43.15                                     | Reach the bottom                       |
| 1000    | SO₄²⁻      | 83.5                                      | Reach the bottom                       |
| 10000   | SO₄²⁻      | 469.74                                    | Reach the bottom                       |

6. Conclusions and suggestions

(1) Thought the pollution of SO₄²⁻ in the aquifer is very serious after leakage accident, there will no any serious consequences occurs to the local residents. The reason is that there is no well in the study area.

(2) Numerical simulation results showed that the aquifer in the study area will be heavily polluted after the leakage accident occurred. What’s more, the pollutants in the aquifer move very slowly. The forward distances of SO₄²⁻ pollution halos front are only 43.15 m, 83.5 m and 470 m respectively after 100 days, 1000 days and 10000 days of the leakage accident. Once the groundwater in the area is polluted, it is difficult to be purified through groundwater natural circulation.

(3) To ensure safety in production process, it is necessary to strengthen the management of sulfuric acid tanks in production. At the same time, checking the pollution sources regularly is also necessary.

(4) In order to prevent groundwater polluted by leakage of sulphuric acid tanks, all enterprises with sulphuric acid tanks should establish effective emergency response systems. The effective emergency response systems should included measures and steps such as stopping production, plugging leakage point, intercepting sewage and treating sewage as soon as heavy leakage accident happened.

References

[1] Technical guidelines for environment impact appraisal — groundwater environment (HJ 610-2016). (In Chinese)
[2] Xue, Y. Q. (1997) Groundwater dynamics. Geological publishing, Beijing. (In Chinese)
[3] LI, Y. G., LAN, J. K., LI, R. L. et al. (2016) Permeability coefficients of weathering zones in Huashan granite of Guangxi. Journal of Guilin University of Technology, 36:681-687. (In Chinese)
[4] YU, H. K., GUO, Q., LUO, B., et al. (2016) Dispersion test of unconfined aquifers in northeast of Dingbian County. Environmental Chemistry, 35: 575-580. (In Chinese)