The fate and migration of cyanide discharged by steel industries into groundwater

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ABSTRACT
Steel production industries dispose of large quantities of different pollutants including cyanide into the subsurface environment. In this research, the migration of cyanide was investigated using laboratory experiments, field measurement and modeling. Column tests showed that CN degradation followed a zero-order reaction rate mechanism with a rate of -3.45 to -3.6 1/d. Batch adsorption tests showed that adsorption of cyanide by soil was negligible and about 1 to 4 percent. Comparisons of filed measurement and model predictions showed that incorporating the degradation into modeling resulted in better prediction of concentrations of cyanide.

RÉSUMÉ
Les industries de production d'acier liquident de grandes quantités de polluants différents y compris le cyanure dans l'environnement de sous-sol. Dans cette recherche, la migration de cyanure a été examinée les expériences de laboratoire d'utilisation, la mesure de champ et le modelage. La colonne essaie a montré à cette dégradation de CN a suivi un mécanisme de taux de réaction de zéro-ordre avec un taux de -3.45 à -3.6 1/d. Adsorption de fournée essaie a montré à ce adsorption de cyanure par le sol était négligeable et environ 1 à 4 pourcent. Les comparaisons de mesure classée et de prédictions modèles ont montré qu'incorporant la dégradation dans le modelage a eu pour résultat la meilleure prédiction de concentrations de cyanure.

1 INTRODUCTION

Only 2% of the world's water is freshwater, out of which 87% is frozen, forming the polar ice caps, glaciers, and icebergs. Ground water accounts for more than 90% of the remaining freshwater supply. Therefore, water stored in the subsurface environment forms the largest available reservoir of fresh water. Population growth and industrial development have resulted in increasing demand for water. However, like other natural resources, water resources are limited and it is necessary to have an appropriate management system for usage and protection of groundwater resources.

One of the main sources of groundwater pollution is the discharge of industrial wastewaters, which has turned into one of the main environmental issues over the past few decades. Due to high temperatures in furnaces of iron and steel production industries carbon and nitrogen combine and produce cyanide, which finds its way to the industrial wastewater generated at these production plants, and eventually to groundwater when the effluent is discharged.

Cyanide and its compounds are very toxic and if released into environment could have adverse effect on surrounding environment. Cyanide is a non-carcinogenic priority pollutant, which has a highly effective lethal potency. It is designated as a hazardous substance under the USA Federal Water Pollution Control Act and further regulated by the Clean Water Act Amendments of 1977 and 1978 (Irwin, 1997). Due to its high degree of toxicity in certain forms, primarily HCN, acceptable levels of cyanide compounds in water and soil are generally low. The maximum level of free cyanide in drinking water in U.S. is set at 0.2 mg/l (Dzombac et al., 2006).

There have been numerous reported accidental releases of cyanide compounds into the environment and their consequent effects. In one case, accidental discharge of cyanide containing mine waste from a Canadian waste pond into a nearby creek killed more than 20,000 fish (Irwin, 1997). The failure of the tailing ponds at a gold mine near Baia Mare, Romania, in January 2000 is the most recent and significant release of cyanide. It is estimated that 50 to 100 tons of cyanide were released and entered Sasar River, and subsequently Lapus River and Somes River, and eventually Danube. As a result, massive fish kills were experienced in these rivers (Dzombac et al., 2006).

The lethal effect of cyanide on humans is also well documented through its use in genocidal programs in World War II making cyanide compounds responsible for more human deaths than any other chemicals known. Cyanide toxicity is essentially an inhibition of oxygen metabolism. In humans, cyanide can be inhaled, ingested, or absorbed through skin. First symptoms include headache, nausea, and vomiting followed by convulsions, falling, dilated pupils, clammy skin, and a weaker and more rapid pulse. In the final stage, heartbeat becomes irregular and slow, body temperature falls; there is cyanosis of lips, face, and extremities, coma, frothy bloody saliva flow from mouth, and death.

In aqueous solutions cyanide is mostly present in the free cyanide form, which is the sum of hydrocyanic acid (HCN) and cyanide anion (CN^-). The free cyanide dissociation reaction is as follows:

$$HCN = H^+ + CN^- \text{ , } pK_a = 9.24 \qquad [1]$$

Since the dissociation constant (pK_a) for HCN in about 9.2, the majority of free cyanide in natural conditions is usually in the form of HCN.

It is reported that cyanide can be biologically (naturally) degraded. Free cyanide is considered a good source of nitrogen and/or carbon for bacterial growth. Biodegradation of cyanide has been reviewed and reported by many researchers such as Knowles and Bunch (1986). A list of bacterial species that are capable of degrading cyanide and cyanogenic compounds is presented by Dzombac et al. (2006).

Shifrin et al. (1996) studied the chemistry, toxicity and health risk of cyanide compounds in soils at former manufactured gas plant sites. Kjeldsen (1998) presented a review on behavior of cyanides in soil and groundwater. Different cyanide compounds were investigated for their toxicity. He stated that pH and RP (redox potential) had significant effect on degradation of cyanide. Kunze and Isenbeck-Schröter (2000) studied the occurrence, species distribution and migration of cyanides in the groundwater of the Testfeld Sued. They observed that presence of heavy metals had a significant effect on reduction of cyanide. Lakatos et al. (2003) studied ecotoxicology and risk assessment of cyanide contamination in Tisza River. Sartaj et al. (2003) investigated the migration of cyanide in the vicinity of a gold mine. Several accidental releases of mine wastes from the tailing pond of the mine had resulted in the contamination of the surrounding environment. Soil concentration of cyanide down to a depth of about 1.5 m was negligible, and then increased with depth. They stated that enhanced volatilization and biological degradation of cyanide near the ground surface resulted in decontamination of the soil.

The main objective of this research study was to investigate the fate and migration of cyanide released through effluent of iron and steel production plants.

2 MATERIALS AND METHODS

Foulad Mobareke Steel Production Plant (FMSPP) is located in Isfahan province, central part of Iran. Cyanide is not removed from the industrial wastewater produced at the plant as it goes through the wastewater treatment system. The effluent is stored in two large ponds located to the east of the plant. These ponds were considered the main source cyanide release into the subsurface environment. An aerial photo of the plant is shown in Figure 1.

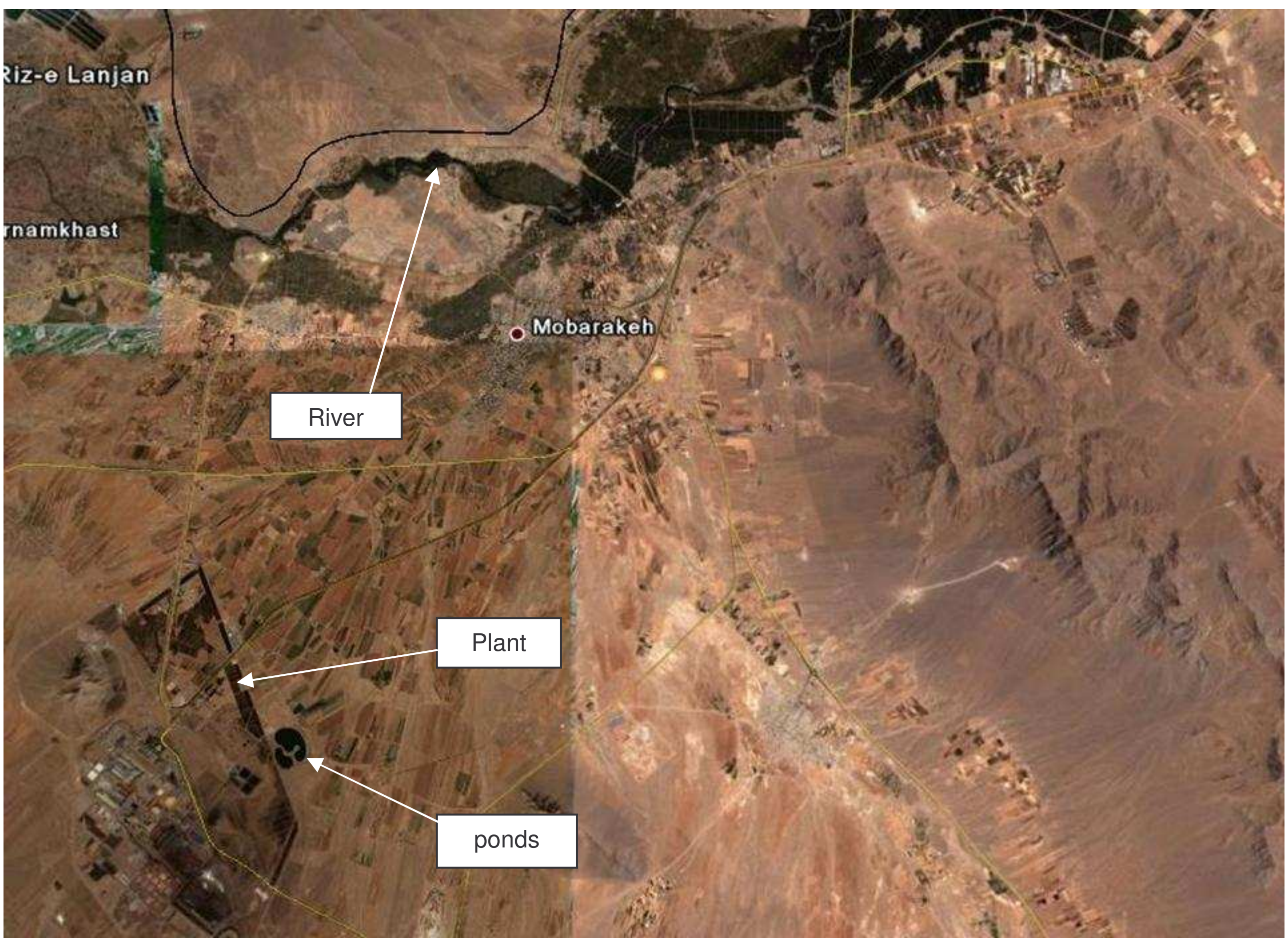

Figure 1. Aerial photo of the FMSPP plant

To assess the migration of cyanide, samples from holding ponds as well as 25 wells in the vicinity of the ponds inside the plant and downstream of the ponds were collected and analysed for concentration of free cyanide. The location of the pond and sampling points are shown in Figure 2.

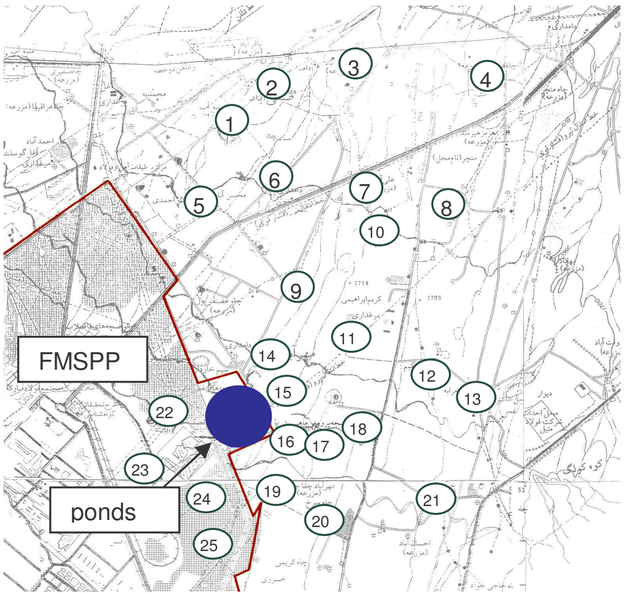

Figure 2. Location of holding ponds and sampling points

Column tests, see Figure 3, were carried out using the soil collected from near the wells 5 and 6, and water collected from a well close to the plant. Columns used for laboratory experiments were PVC pipes with internal diameter of 110 mm and a height of 1 m. Two reservoirs at the bottom and top of columns were provided to store and recirculate the effluent through the columns.

Figure 3. Column tests setup

Collected water was spiked for cyanide concentration and used as influent to the columns. Water was recirculated on a daily basis and free cyanide concentration was measured over time using a Hach Spectrophotometer (Model 2010).

In addition, some batch adsorption tests were carried out in the laboratory to investigate the potential for cyanide adsorption by the soil, see Figure 4. Three hundred grams of collected soil were added to 100 ml of synthetic cyanide solution made by dissolving enough KCN salt in distilled water. The containers were agitated by a laboratory shaker for 24 hrs. Then the solution was filtered and equilibrium concentrations of free cyanide were measured. Initial CN concentrations of 0.2, 0.5, 1, and 2 mg CN/l were investigated. Each test was replicated three times.

Figure 4. Batch Adsorption tests setup

The results of laboratory studies were incorporated into the groundwater and contaminant transport model of the aquifer and the results were compared with those obtained in the field.

3 RESULTS AND DISCUSSIONS

Concentration of free cyanide in samples collected from wells 14, 15 and 16 just downstream of the ponds were in the range of 0.6 - 0.7 mg/l. Water sample from well 17 contained 0.1 mg/l free cyanide and the concentration of cyanide in the rest of the wells was below detection limit. Water inside the pond contained 0.75 mg/l cyanide. The results show the extent of the cyanide migration in the vicinity of the plant. The concentration of cyanide decreases with distance downstream of the ponds.

Results from column tests are shown in Figure 5. They showed that for the first couple of weeks there was no change in concentration of cyanide. After the acclimatization period, the biological degradation started, which resulted in reduction of cyanide concentration.

Variation of pH and DO are shown in Figures 6 and 7. pH was in the range of 7.1 – 8.3 which was in the neutral range and was not a limiting factor for bacterial growth. DO of the effluent from the column was in the range of 11.7 – 14.6 mg/l showing that the column and any bacterial growth and biodegradation was aerobic.

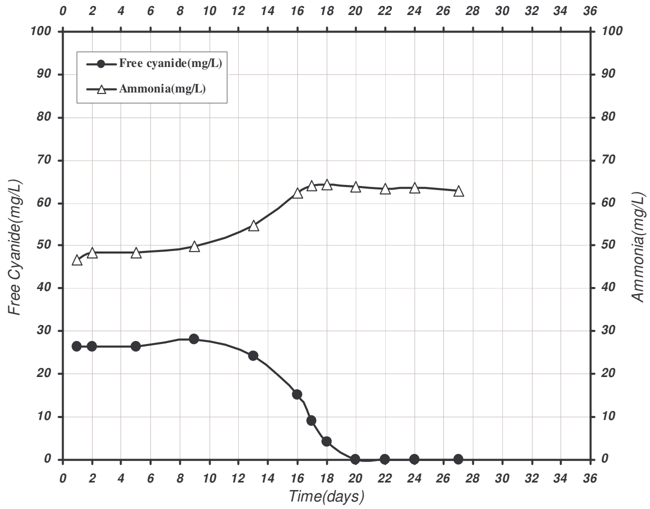

Figure 5. Variations of CN over time for column test

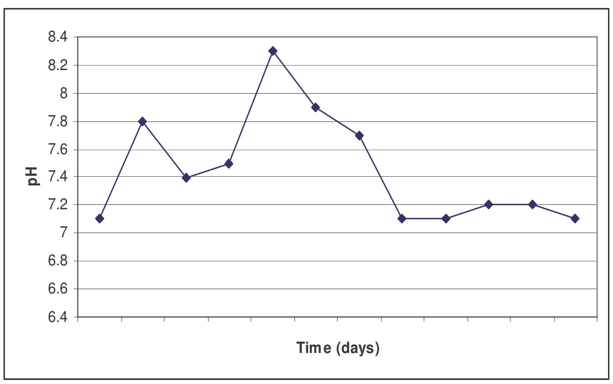

Figure 6. Variation of pH in the column tests

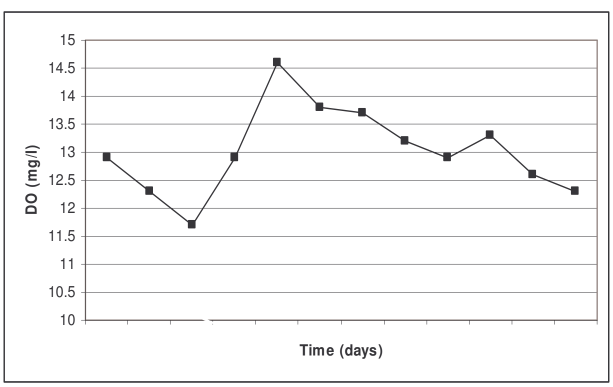

Figure 7. Variation of DO in the column tests

Figure 8 shows the linear variation of CN with time. Correlation factor for the fitted straight line and experimental points was 0.97. The linear trend showed that CN degradation followed a zero-order reaction rate mechanism. The slope of the fitted line obtained from two column tests were -3.45 1/d and -3.6 1/d, which is an

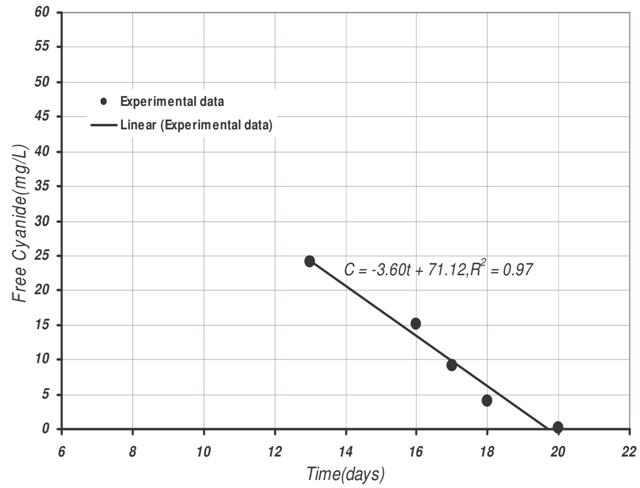

Figure 8. Linear trend of CN degradation showing a zero-order reaction rate mechanism

indication of the rate constant or how fast the degradation is proceeding.

Results of batch adsorption tests are presented in Table 1. The results show that the adsorption of cyanide by soil was negligible as after 24 hr of contact between soil and a solution containing cyanide only about 1 to 4 percent of cyanide was reduced. As a consequence, in modeling of the migration of cyanide adsorption was ignored.

Table 1. Results of Batch Adsorption Tests

Initial Concentration	0.2	0.5	1	2
Ce (#1)	0.197	0.486	0.975	1.935
Ce (#2)	0.192	0.488	0.964	1.942
Ce (#3)	0.198	0.481	0.976	1.937

In the next step the groundwater flow model of the aquifer was set up and calibrated. The results of the model for head are presented in Figure 9. Results of calibration of the groundwater flow model are illustrated in Figure 10. For cyanide transport modeling two cases were considered. In case one no biological degradation was assumed for cyanide while in case two it was assume that cyanide is degraded as it moves through the aquifer.

The results of modeling for both cases and the values measured in the field are presented in Table 2. As it can be seen, incorporating the degradation into modeling results in better prediction of concentrations of cyanide showing that degradation of cyanide is an important process, which has to be taken into account for assessment of cyanide migration.

Prediction of cyanide migration without and with degradation after 15 years is illustrated in Figures 11 and 12. As seen, degradation process has a significant effect on migration of cyanide and the extent of its plume.

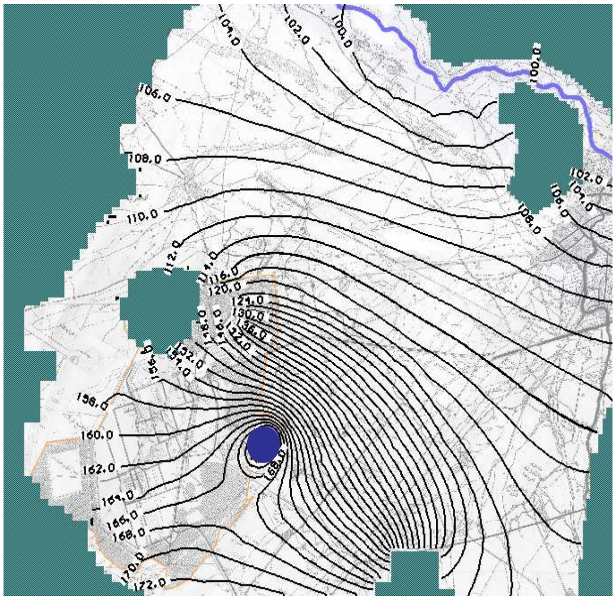

Figure 9. Results of modeling for head distribution

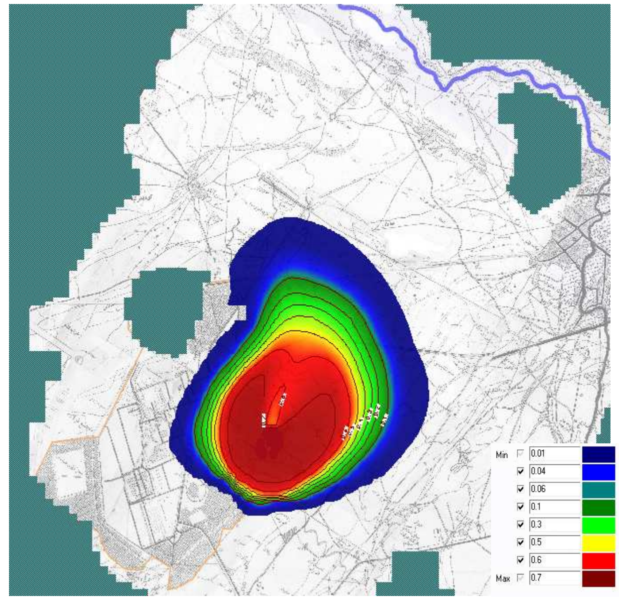

Figure 11. Migration of cyanide without degradation

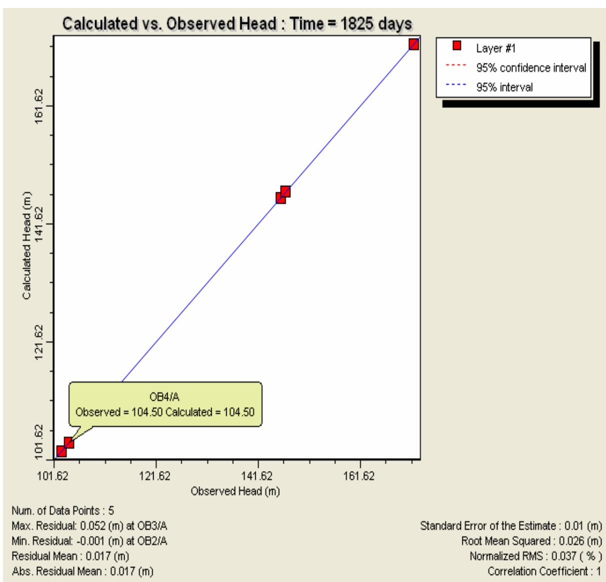

Figure 10. Calibration of groundwater flow model

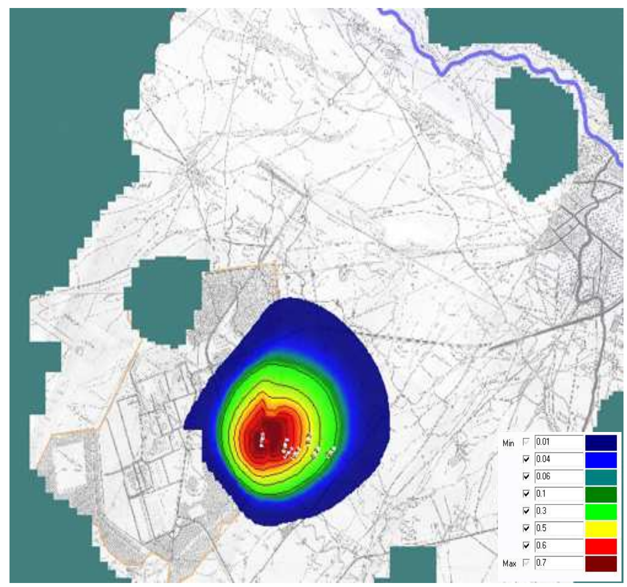

Figure 12. Migration of cyanide with degradation

Table 2. Comparison of the observed and predicted concentrations of cyanide

	Well 14	Well 15	Well 16	Well 17
Observed	0.7	0.61	0.65	0.1
Without degradation	0.74	0.74	0.73	0.73
With degradation	0.73	0.68	0.69	0.35

4 CONCLUSIONS

Groundwater is one of the major water resources used for domestic, agricultural and industrial purposes, especially in arid and semi-arid regions. Nowadays, in addition to quantity problems caused by excessive withdrawal, degradation of groundwater quality due to discharge of wastewater are an important issue for sustainable development of civil societies. Industrial wastewater generated at steel production plants usually contains cyanide. The industrial effluent at FMSPP is stored in two large ponds located to the east of the plant.

Field measurements showed that the holding ponds were the main source cyanide release into the subsurface environment. Column tests showed that CN degradation followed a zero-order reaction rate mechanism with a rate of -3.45 to -3.6 1/d. Batch adsorption tests showed that adsorption of cyanide by soil was negligible and about 2 to 4 percent. Groundwater flow modeling of the aquifer showed that incorporating the degradation into modeling results in better prediction of concentrations of cyanide. This shows that the degradation of cyanide is an important process, which has to be taken into account for the assessment of cyanide migration.

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