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SUBMODELS OF WATER QUALITY FOR THE ANALYSIS OF REGIONAL WATER POLICIES IN OPEN-PIT LIGNITE MINING AREAS

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ABSTRACT

The paper outlines the approach to water quality submodels for the analysis of regional water policies in open-pit lignite mining areas, with special regard to a test region in the German Democratic Republic.

Reduced conceptual water quality models have been developed for the concentrations of the substances $[Fe^{2+}]$ and $[H^+]$ in mine water treatment plants, rivers and remaining pits.

The resulting system of differential equations is solved numerically. First results are presented. The applied methodology to obtain simplified models of groundwater and surface water quality processes suitable for decision support model systems for regional water policies in open-pit lignite mining areas is assumed to be applicable to similar regional studies.

INTRODUCTION

Lignite mining leads to significant water quality problems. These problems are caused both by the mine dewatering which results in the weathering of the ferrousdisulphide minerals and salt water intrusion, and contamination due to waste disposals, etc.

The design of water management policies and water use technologies as well as that of mine drainage can only be done properly when it is based on appropriate mathematical models, Kaden and Luckner (1984). These models have to be built up as submodels for a complex model system; this implies that they have to be as simple as possible, Kaden et al. (1985). On the other hand, they also have to reflect the real water quality processes in mining regions with the required accuracy for the planned model-supported decision making.

Based on comprehensive water quality models, see Luckner (1985), the possibilities for the derivation of reduced conceptual models are described for a few examples. Models are demonstrated for groundwater, as the source of pollution, mine water treatment plants as control units, river sections with an intake of acid ferruginous water, and remaining-pits, which can also serve as effective control units. Related with each other, these models form the complex system model, a system of differential equations. They were numerically solved.

We consider the discharge of acid ferruginous mine water into rivers as the most important impact on water quality. The chemical reactions which take a leading part by the formation and treatment of acid ferruginous mine water are schematically described in Figure 1.

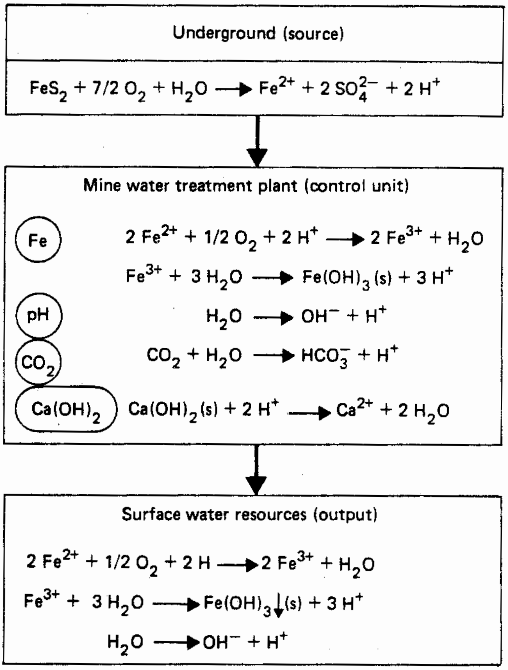

Figure 1: Important reactions of the weathering of ferrous-disulphide caused by lignite mine dewatering.

Underground ferrousdisulphide will be oxidized by oxygen in the air. At the same time iron(II)-, sulphate-ions and protons originate. The acidity increases in the groundwater. The reaction products will be flushed out with the perculated water from aerated zones and transported by the rise of groundwater. The iron and acid concentration is especially high in the perculated water in spoils. Furthermore, the groundwater is characterized by increased concentrations of CO_2 resulting from biochemical degradation processes. All of these parameters will be influenced in the mine water treatment plant by adding lime hydrate. The remaining iron(II)-concentration in the treated water will be oxidized by air in the river, the remaining pit respectively, hydrolized and precipitated according to the kinetics of reactions and residence times. The kinetics of all these reactions depends among others on the pH-value.

The model of the substance exchange, transport and storage processes is a comprehensive migration model for coupled components. It is based on the well-known differential equation:

$$div\ ((D + D_0)\,\nabla C - v \cdot C) = n\frac{\partial C}{\partial t} + R + Ex + SS \qquad (1)$$

$$T = S + R + Ex + SS$$

with T - transport term (convection, diffusion, dispersion)
S - storage term
R - reaction processes
Ex - exchange processes
SS - sinks and sources.

The paper of Luckner (1985) describes different ways for model reduction of such comprehensive models. Generally, this model reduction is done by the neglection of terms of the comprehensive model. In the following the model reduction is demonstrated for typical subprocesses in lignite mining areas. For an overview see Figure 4 in Luckner (1985).

SUBMODEL "GROUNDWATER"

A ***stochastic trend model*** for the prognosis of groundwater quality was developed based on the stoichiometric Eq.(2) and yearly series of measurements of the Fe^{2+}-and H^+-concentration in the drained mine water.

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \qquad (2)$$

The trend models have the form, see Kaden et.al. 1985:

$$[Fe^{2+}] = a_{Fe} + b_{Fe} \cdot t + \varepsilon_{Fe} \quad , \quad \varepsilon_{Fe} \sim N(0, \sigma_{R,Fe}) \qquad (3)$$

$$-lg\,[H^+] = a_H + b_H + \cdot t + \varepsilon_{H^+} \quad , \quad \varepsilon_{H^+} \sim N(0, \sigma_{R,H}) \qquad (4)$$

The coefficients a_{Fe}, b_{Fe}, $\sigma_{R,Fe}$ and a_H, b_H, $\sigma_{R,H}$ e.g. are tabulated for the GDR mining test area in Kaden et al. (1985). Figure 2 shows these trends for the mine water of the mine A in this test area.

The ***oxygen-rate*** diffusing vertical through the dewatered zone depends on the oxygen concentration in soil-air and groundwater (see transportation), the content of ***buffer ions*** , especially CO_3^{2-}, HCO_3^- and OH^- (see reactions), and biotoxic substances to retard effectively the activity of microorganisms. The oxygenation process may be controlled by all these factors as it is usually done worldwide. The use of ***coal-fire power-plant-ashes*** is a particularly effective method of buffering the system and to prevent *pH*-falldown, Fischer (1985).

BASES OF THE SURFACE WATER MODELS

The submodels reflecting the water quality processes in the mine water treatment plant, the river system and the remaining pit are developed under the following

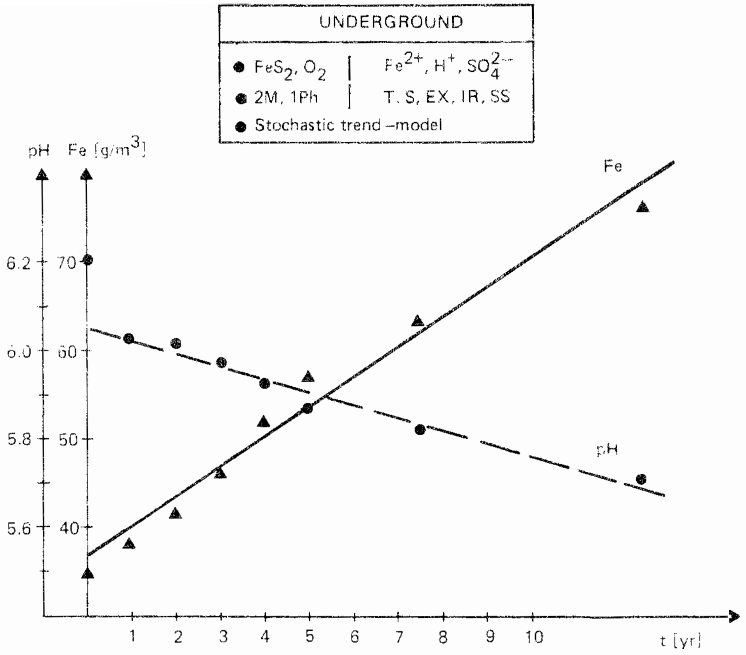

Figure 2: Scheme of the reduced model for the ground water pumped from an open-pit mine

assumptions:

- The *chemical reactions* in the water bodies are considered as non-equilibrium reactions with complete stoichiometric turnover of the initial substances.
- The *dissolved carbonic acid* of the drained groundwater is removed in the mine water treatment plant by mechanical de-acidification and in the rivers by de gasification during the flow processes. Similar reactions are also given in the remaining pit. These processes are not considered here.
- The *buffer capacity* of water with reference to hydrogen carbonate is neglected. This is only allowable for water with low carbonate hardness. Such conditions are typical for the GDR test area.
- In the surface water bodies is enough *oxygen for oxidation* processes, and the partial pressure is constant ($p_{O_2} = 0.21$ *bar*).
- The *transport processes* are one dimensional.
- All the ferrous hydroxide formed is sedimented within the reaction time; no mathematical modeling is therefore necessary to reflect the *sedimentation process*.

Bio-chemical and chemical catalysis of formed ferrous hydroxide and oxidehydrates are not considered in the coefficient k of the reaction rate model.

The characteristic chemical reactions for all further submodels in the one-phase-system "water" are the *oxygenation* reactions of $Fe(II)$ and the *hydrolysis* of $Fe(III)$, Eq.(5). The protons formed will be neutralized in the mine water treatment plant, and, if necessary and possible, in the remaining pit by means of the treatment with lime hydrat, Eq.(6). The total reaction is defined by Eq.(7).

$$Fe^{2+} + \frac{1}{4}\,O_2 + \frac{5}{2}\,H_2O \rightarrow Fe(OH)_3 + 2\,H^+ \tag{5}$$

$$Ca\,(OH)_2(s) + 2\,H^+ \rightarrow Ca^{2+} + 2\,H_2O \tag{6}$$

$$Fe^{2+} + \frac{1}{4}\,O_2 + Ca(OH)_2 + \frac{1}{2}\,H_2O \rightarrow Fe(OH)_3\downarrow + Ca^{2+} \tag{7}$$

The *kinetics* of ferrous-ion oxygenation in laboratory systems has been previously studied and the general rate law was found to be:

$$r_{Fe} = \frac{d\,[Fe^{2+}]}{dt} = -\,k \cdot [OH^-]^2 \cdot p_{O_2} \cdot [Fe^{2+}] \quad , \tag{8}$$

where k is the velocity constant in $mol^{-2}\,l^2\,min^{-1}\,bar^{1}$. $[OH^-]$ denotes the concentration of hydroxyl ions, and $[Fe^{2+}]$ denotes the concentration of ferrous ions. In Table 1 the velocity constant is given from the literature. At constant p_{O_2} Eq. (8) is reduced to a reaction rate model of pseudo-first-order kinetics:

$$r_{Fe} = -\,\frac{d\,[Fe^{2+}]}{dt} = k_1 \cdot [Fe^{2+}] \tag{9}$$

with

$$k_1 = \frac{k \cdot p_{O_2} \cdot K_W}{[H^+]^2} = \frac{k^*}{[H^+]^2}$$

k_1 has the unit of inverse time.

Table 1: Summary of previous results concerning oxygenation kinetics of ferrous ions

Investigators	Velocity coefficient k $[l^2.mol^{-2}.atm^{-1}.min^{-1}]$	Temperature ^oC
Stumm, Lee (1961)	$(8.0 \pm 2.5) \cdot 10^{13}$	20.5
Morgan, Birkner (1966)	$2.0 \cdot 10^{13}$	25
Schenk, Weber (1968)	$(2.1 \pm 0.5) \cdot 10^{13}$	25
Theis (1972)	$1.36 \cdot 10^{14}$	25

For a water temperature of about 10°C and a oxygen partial pressure near $p_{O_2} = 0.21 bar$ k^* will be in the range of $k^* = 1.6 \cdots 13.6 \cdot 10^{-13}$ in $mol^2\,m^{-6}\,s^{-1}$.

The weathering of pyrite or marcasite forms protons. They can be neutralized by a corresponding quantity $Ca(OH)_2$. The neutralization capacity K_{H^+} is stoichiometrical:

$$K_{H^+} = \frac{[H^+]}{[Ca(OH)_2]} \tag{10}$$

For a ***technical lime hydrate*** the constant K_{H^+} is in the range of

$0.015 \cdots 0.025\ mol\ H^+/g\ Ca(OH)_2$. The exact value has to be determined in the laboratory. This means the effective substance of technical lime hydrate amounts to between 56% and 93%.

In the transposition of $Fe(II)$ into $Fe(III)$-hydroxide, the stoichiometric ratio between protons- and ferrous mass-formation rate K_{Fe} is:

$$K_{Fe} = \frac{[H^+]}{[Fe^{2+}]} = 3.58 \cdot 10^{-2} \frac{mol\ H^+}{g\ Fe^{2+}} \quad . \tag{11}$$

The shown connections are an important base for the development of the following submodels. By optimal dosage of $Ca(OH)_2$, the treated mine water does not contain Fe^{2+} and has a pH-value of 7.

SUBMODEL "MINE WATER TREATMENT PLANT"

In the mine water treatment plant the precipitation of $Fe(III)$ occurs by simultaneous neutralization through dosage of lime hydrate. The reduced model allows to simulate the output concentration and dosage of $Ca(OH)_2$. The mass transport is neglected.

Internal reaction processes (Eq. 8)) and the external sink for protons (SS) through a neutralization substance have to be considered. Under these assumptions the reduced model has the form:

$$Fe^{2+}: \quad -\frac{d[Fe^{2+}]}{dt} = \frac{k^*}{[H^+]^2} \cdot [Fe^{2+}] + \sum Q_A \cdot [Fe^{2+}] - \sum Q_Z \cdot [Fe^{2+}]_Z \tag{12a}$$

$$H^+: \quad \frac{d[H^+]}{dt} = K_{Fe} \cdot \frac{d[Fe^{2+}]}{dt} + K_H[CA(OH)_2] + \sum Q_A \cdot [H^+] - \sum Q_Z \cdot [H^+]_Z . \tag{12b}$$

An *underdosage* of lime hydrate results in incomplete neutralization of protons, that means only a partial precipitation of the ion occurs and the pH-values remain less than 7.

The alkalinization substance $Ca(OH)_2$ guarantees a definite saturation pH-value of 12.6 for $20^\circ C$ in the case of *overdosage* because $Ca(OH)_2$ has a relatively low water solubility ($1.6\ g/l$ in the case of $20^\circ C$). In accordance with the limits for the discharge of water into public surface water systems the pH-value should be held in the range of $6.5 < pH < 8.5$, which is equivalent to $10^{-5.5} \leq [H^+] \leq 10^{-3.5}$ if $[H^+]$ is given in mol/m^3. In mine water treatment plants the residence time is usually in the range of 2.0 ... 2.5 hours. Typically in the GDR e.g. are sedimentation tanks with a capacity of $3\ m^3/s$ and a volume of $27000\ m^3$.

Figure 3 shows the results of the submodel Eq. (12).

The graph in Figure 3 shows the required demand of calcium hydroxide in the case of a reference pH-value of 7.0 in the discharge depending on the input pH-value and the input $Fe(II)$-concentration. For the graph a neutralization capacity of the lime hydrate (as technical product) of 0.025 mol H^+ per $g\ Ca(OH)_2$ is presumed. Figure 3 shows also that at pH-values less than 4 a substantially increased amount of lime hydrat is required for neutralization.

SUBMODEL "RIVER"

An intensive aeration of the river water provides enough oxygen to the *iron precipitation* according to Eq. (5). The formed protons will be neutralized up to the exhaustion of the buffer capacity of the carbonate and hydrogencarbonate ions. A pH-change

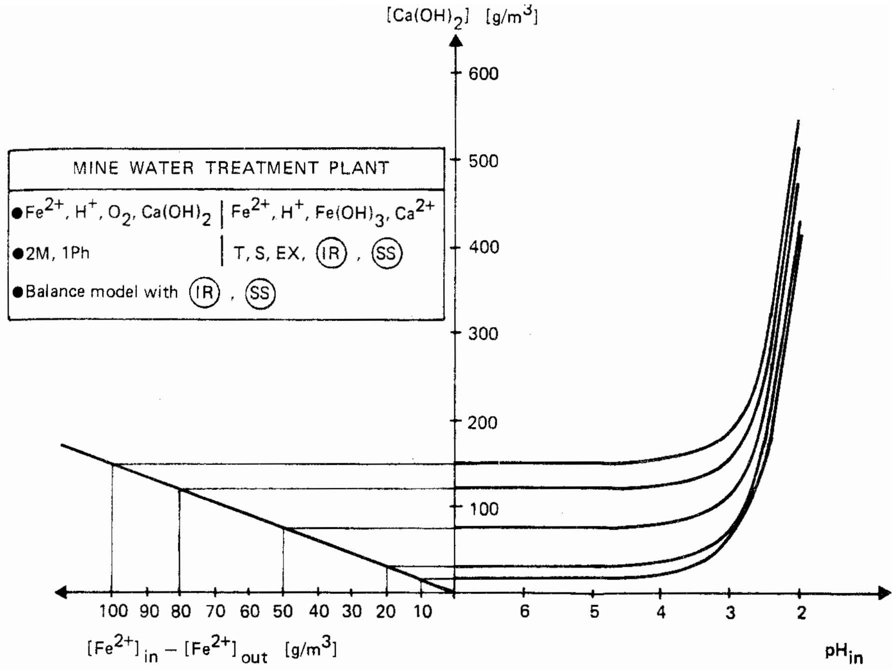

Figure 3: Demand of lime hydrate in dependency on the input pH-value and the difference of Fe^{2+}-input and output concentration

occurs at about $3.58 \cdot 10^{-2}$ $mol\ H^+$ per each $g\ Fe^{2+}$ if all CO_3^{2-}- and HCO_3^--ions are converted.

The river water e.g. in the Lusatian lignite mining district (the GDR test area, see Kaden et.al. (1985), has a low buffer capacity, so that it can be neglected in order to simplify the river submodels. In the opposite way to Baumert et.al. 1981 in the submodel "River" the hydrodynamic dispersion and diffusion is also neglected.

The river system is subdivided into *balance profiles* and *river segments* between them. External sinks and sources (water diversion and intake) are arranged on the balance points (junctions). Storage changes will be neglected. The conversion of the Fe^{2+}-concentration in the river by oxidation and hydrolysis is approximated as a reaction of the 1st order, and the variation of the H^+-concentration is regarded as a reaction of the 0th order.

Based on the assumption that $v\frac{dc}{dx} = \frac{dc}{dt}$ holds true in the river segments, the submodel "River" has the form:

$$Fe^{2+}: -v\frac{d[Fe^{2+}]}{dx} = -\frac{d[Fe^{2+}]}{dt} = \frac{k}{[H^+]^2}[Fe^{2+}] \tag{13a}$$

$$H^+: -v\frac{d[H^+]}{dx} = -\frac{d[H^+]}{dt} = K_{Fe}\frac{d[Fe^{2+}]}{dt} \tag{13b}$$

On the junction the Fe^{2+} or the H^+ concentration in the river water will be determined under the assumption that perfect mixing exists:

$$Q\cdot c = Q_z\cdot c_z' + \sum_{j=1}^{n} Q_{in,j}\cdot c_j - \sum_{l=1}^{m} Q_{out,l}\, c_l \quad . \qquad (14)$$

Figure 4 shows typical results of the submodel "river".

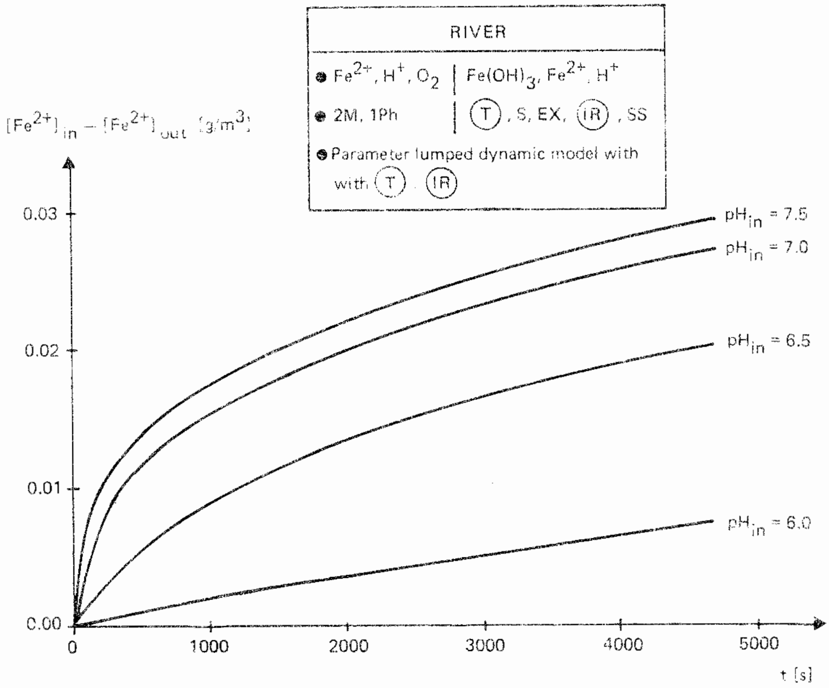

Figure 4: Changes of the ferrous ion concentration by oxygenation with air-oxygen without neutralization in the river

Obviously, the *oxidation rate* depends on the input *pH* values. It increases by higher *pH*. Figure 7 shows further low changes of $Fe\,(II)$-concentrations ($\leq 1\ g\,/\,m^3$) for long residence times. The formed protons vary between *pH*-values of 5.9...and 6.0. For $pH < 5.9$ to 6.0 no important oxidation rate exists. In reality, higher oxidation rates often take place. This is caused by the neglected buffer capacity and catalyzes of formed ferrous hydroxides.

SUBMODEL "REMAINING PIT"

In remaining pits the *oxidation* of Fe^{2+} by air-originated oxygen takes place as well as an additional *hydrolysis* of the produced Fe^{3+}. The reactions depend on the *pH* value. For *pH* less than 6.0 no important oxidation rate (see Figure 4) exists. By adding *lime hydrate* to the water body of a remaining pit, protons which are in the water and are formed by Fe^{2+} - oxidation will be neutralized. If the *pH* value is less than 4.0 a large amount of lime hydrate is needed to neutralize the water (see Figure 3). Under those conditions this method is uneconomical. Another possibility for neutralization is the flooding of the remaining pit with surface water, which has a higher pH value.

All transportation processes are neglected in the submodel "Remaining Pit". Only the following processes are taken into account:

- storage processes,
- reaction processes with
  - reaction kinetics of 1st order for Fe^{2+}-oxidation
  - reaction kinetics of 0th order for the neutralization process,
- external inputs and outputs (external exchange).

Based on this, we obtain:

$$Fe^{2+}: O = \frac{d(V\cdot[Fe^{2+}])}{dt} + \frac{k^*}{[H^+]^2}\cdot V\cdot[Fe^{2+}] + \sum Q_A\,[Fe^{2+}] - \sum Q_Z\cdot[Fe^{2+}]_z \qquad (15a)$$

$$H^+: O = \frac{d(V\cdot[H^+])}{dt} + K_{Fe}\cdot V\,\frac{d[Fe^{2+}]}{dt} - K_H\,Ca(OH)_2\cdot V + \qquad (15b)$$

$$+ \sum Q_A\cdot[H^+] - \sum Q_Z\,[H^+]_Z \quad .$$

With $d\ (V\cdot[i\,])/\,dt = V\cdot d\,[i\,]/\,dt\ +\ \Delta V/\,\Delta t$ the following differential/difference equations can be formulated based on Eq.(15):

$$Fe^{2+}: \frac{d[Fe^{2+}]}{dt} = -\frac{k^*}{[H^+]^2}[Fe^{2+}] - [Fe^{2+}]\cdot\left(\frac{\Delta V}{\Delta t\cdot V} + \frac{\sum Q_A}{V}\right) + \qquad (16a)$$

$$+ \frac{\sum Q_Z\,[Fe^{2+}]_Z}{V}$$

$$H^+: \frac{d[H^+]}{dt} = -K_{Fe}\,\frac{d[Fe^{2+}]}{dt} - [H^+]\cdot\left(\frac{\Delta V}{\Delta t\cdot V} + \frac{\sum Q_A}{V}\right) + \qquad (16b)$$

$$+ \frac{\sum Q_Z[H^+]_Z}{V} - K_H\,[Ca(OH)_2] \quad .$$

Figure 5 shows results of this model for an example with the following conditions:

- $V = 10^7\ m^3$,
- input pH- and input Fe^{2+}-concentration are equal to the initial $pH = pH_0$ and initial Fe^{2+}-concentration.
- the capacity of technical lime hydrate is 0.02 $mol\ H^+/\,g\ \ Ca(OH)_2$ (tech.).
- reaction coefficient $k^* = 2\cdot10^{-13}$ in $mol^2\ m^{-6}\ s^{-1}$,
- lime hydrate dosage 100 $g/s = 8{,}6\ t/d$.

Independent of the input pH, if it is greater then 4.0, the equilibrium pH value is in the range of 6.2 ... 6.3. Under such conditions 50% of the Fe^{2+} will be oxidized within 10 days.

The influence of the storage change rate dV/dt which couples the water quantity model with the dynamic water quality model of a remaining pit or other big surface water reservoirs can be significant.

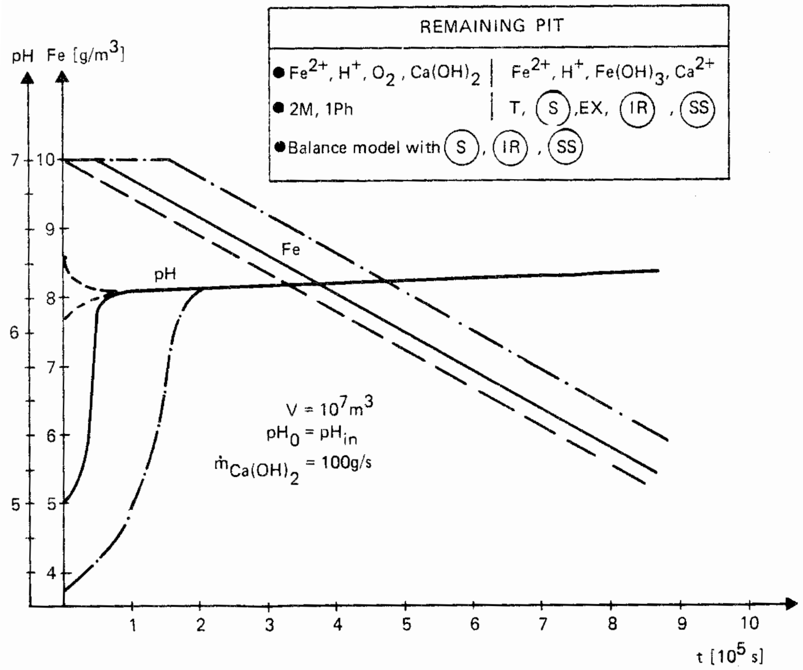

Figure 5: The change of the Fe^{2+} and H^{+} - concentration in a remaining pit (example)

COMPUTER MODEL

The last three reduced submodels can be described in a general form with $x = [Fe^{2+}]$, $y = [H^{+}]$:

$$\frac{dx}{dt} = -A \cdot \frac{x}{y^2} - G \cdot x + E \tag{17a}$$

$$\frac{dy}{dt} = -D \cdot \frac{dx}{dt} - G \cdot y + F \tag{17b}$$

The finite difference analogon of these equations is:

$$\frac{x^t - x^{t-\Delta t}}{\Delta t} = -x^t \cdot \left(\frac{A}{(y^t)^2} + G\right) + E \tag{18a}$$

$$\frac{y^t - y^{t-\Delta t}}{\Delta t} = -D \, \frac{x^t - x^{t-\Delta t}}{\Delta t} - G \cdot y^t + F \tag{18b}$$

From Eq.(18a) we obtain:

$$x^t = \frac{x^{t-\Delta t} + E \cdot \Delta t}{1 + \Delta t \cdot \left(\frac{A}{(y^t)^2} + G\right)} \tag{19}$$

A polynomial function of 3rd order results if we insert Eq.(19) into (18b). The solution is to be found in the range of $10^{-7} < y < 10$, this means in the range of $2 < pH < 10$.

$$
\begin{aligned}
0 = {} & (y^{t})^{3} \cdot (1 + \Delta t \cdot G)^{2} + \\
& + (y^{t})^{2} \cdot \left[D \cdot (x^{t-\Delta t} + \Delta t \cdot E) + (1 + \Delta t \cdot G) \cdot (-y^{t-\Delta t} - \Delta t \cdot F - D \cdot x^{t-\Delta t}) \right] + \\
& + y^{t} \cdot (1 + \Delta t \cdot G) \cdot A \cdot \Delta t + A \cdot \Delta t \cdot (-y^{t-\Delta t} - \Delta t \cdot F - D \cdot x^{t-\Delta t}).
\end{aligned}
\tag{20}
$$

The computer program FEMO has been developed for the numerical solution of the generalized mathematical model for the three subsystems reflected by Eq.(20). The solution of the polynomial function is executed with **Newtons**-approximation method for a given range. If no solution with the assumed time step is possible, than it is to be corrected. The time step will be also corrected, when the change of pH is greater as a given value. The program stops if

- the changes of pH are less than 0.01 pH units,
- the Fe^{2+}-concentrations are less than 0.1 g / m^{3},
- the end of residence time is reached, and
- in the submodel "Mine Water Treatment Plant" the pH limits are exceeded.

An expansion of the model including pH-buffer reactions and catalytic reactions is possible. The program is given in Luckner et al. (1985).

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