DEVELOPMENT OF SIMPLIFIED MODELS OF WATER QUALITY IN LIGNITE MINING AREAS
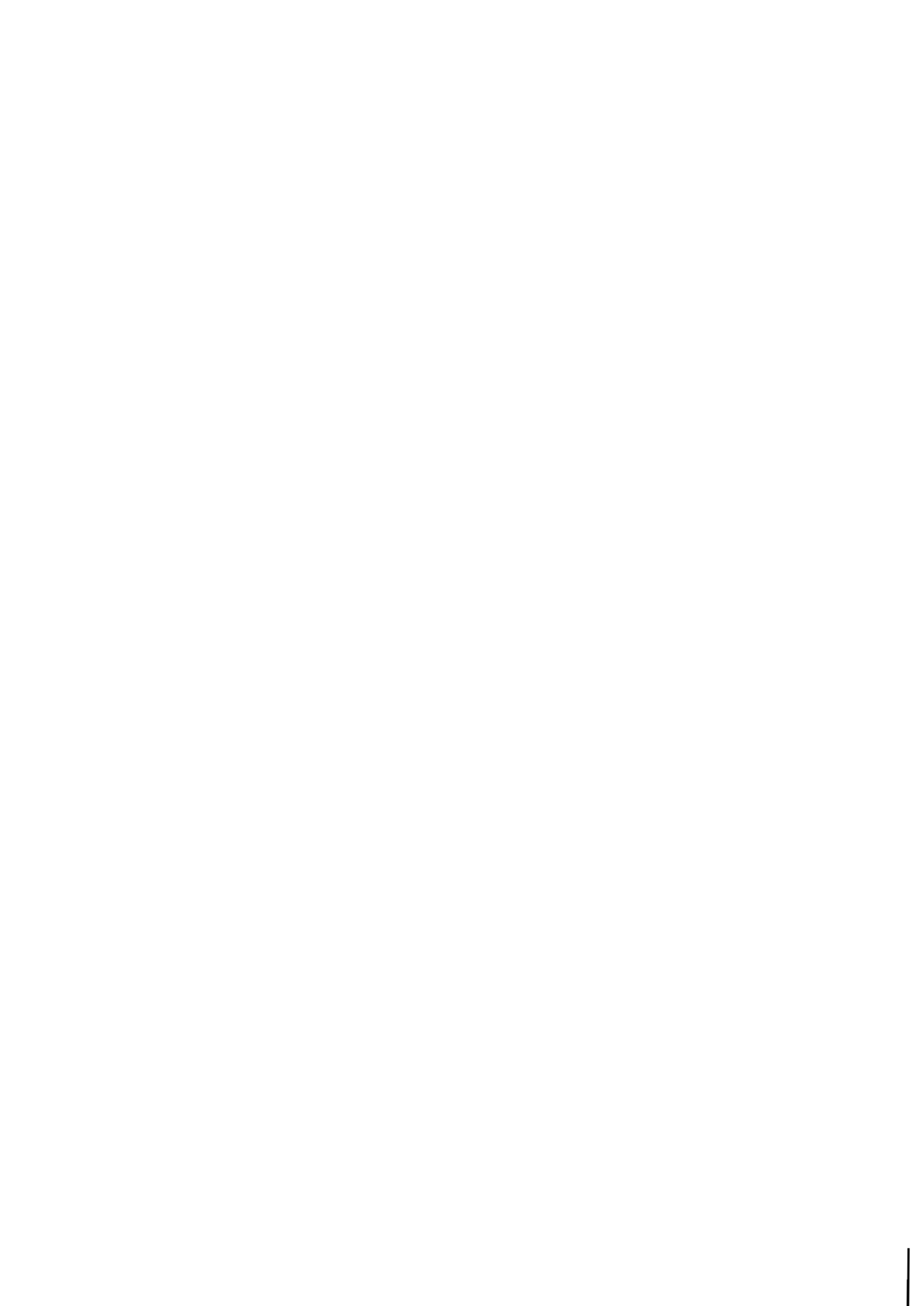
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PREFACE

The *Regional Water Policies* project of IIASA focuses on intensively developed regions where both groundwater and surface water are integrating elements of the environment. Our research is directed towards the development of methods and models to support the resolution of conflicts within such socio-economic environmental systems. For that reason complex decision support model systems are under development for important test areas. One of these test areas is an open-pit lignite mining area in the GDR.

A fundamental presumption for the development of such systems are appropriate submodels of the basic environmental processes to be considered. These submodels have to reflect the processes sufficiently accurately but should be on the other hand simple enough for their integration in complex model systems.

The paper deals with water quality processes. It presents a methodology for the development of simplified models with special regard to lignite mining areas.

The research has been done in the Joint Research Group "Open-pit Mine Dewatering Problems" of the Grossräschen Institute for Lignite Mining and the Dresden University of Technology. This research is part of a collaborative agreement between IIASA and the Institute for Water Management in Berlin. This paper is the final report for the second stage of collaboration.

Although the methodology has been developed with special regard to open-pit lignite mining areas the given approaches are intended to be more generally applicable.

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ABSTRACT

The development of complex decision support model systems for the analysis of regional water policies for regions with intense socio-economic development effecting and being affected by the water resources system is of increasing importance. One of the most illustrative examples are regions with open-pit lignite mining.

Such model systems have to be based on appropriate submodels e.g. for water quality processes. The paper describes submodel for groundwater and surface water quality with special regard to open-pit lignite mining regions.

We consider the discharge of acid ferruginous water into rivers as having the most important impact on water quality in open-pit lignite mining areas. One goal of the model system is the choice of the necessary degree of purification for mine water treatment plants, taking into account self-purification in rivers and remaining pits as well as the water quality demand of down-stream water users.

Based on comprehensive water quality models, the development of which is described in the paper, the possibilities for the derivation of reduced models are described. Those model have been elaborated 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. The computer program is included in the paper.

CONTENTS

DEVELOPMENT OF SIMPLIFIED MODELS OF WATER QUALITY IN LIGNITE MINING AREAS

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1. Introduction

Lignite mining leads to significant water quality problems , Luckner and Hummel 1982. Frequently the quality of mine drainage water is strongly affected by the oxidation of ferrousdisulphide minerals (pyrite, marcasite) in the drained ground. This results from the aeration in the subsoil of the cone of depression of one or several mines. With the recharge of the natural groundwater, the oxidation products are flushed out, and the percolated water becomes very acidic. Consequently, the acidity of the groundwater increases. In the post-mining period, the same effect occurs caused by the raising of the groundwater table and the leaching of all acid products. Especially the pH-value in spoils is very low, if the spoil material has not enough neutralization capacity. There are typically high sulphate-, iron(II)- and proton-concentrations in the groundwater in such areas, Starke 1980. The discharge of such polluted mine drainage water into streams also leads to the acidification of these surface water resources in mining regions, and may significantly effect down-stream water yields, see Kaden et.al. 1985.

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.

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This collaborative paper describes the methodology used to obtain such 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, based on comprehensive water quality models. This methodology, together with the included modular software package, should also be applicable to similar regional studies.

2. Comprehensive Water Quality Models

2.1. Components

The most comprehensive water quality models are the *systems descriptive models* of the dynamic water quality processes in the underground with distributed parameters, see Luckner and Mucha 1984. In comparison with water quantity problems (water flow problems), which are well-based from the methodological point of view, see e.g. Kaden et.al. 1985, difficulties of developing groundwater quality models for mining regions are tremendous.

The underground, the soilwater zone as well as groundwater zone, is a *three level multiphase system* (see Luckner and Schestakow, 1986):

The components of the mixed phases "soilair", "soilwater or groundwater", and "soil or rock" are in the lowest level. Under this consideration, the mixed phase "soilair" is composed of the gaseous components N_2, O_2, CO_2, Ar, H_2O, SO_2,... . One considers the main component of the air (nitrogen N_2) as the solvent and the other components as solutes. The same situation is given for the mixed phase "groundwater". Here water is the solvent, and the cations (e.g. H^+, Fe^{2+}, Ca^{2+},....), anions (e.g. SO_3^{2-}, SO_4^{2-}, Cl^-, HCO_3^-, CO_3^{2-}, OH^-,...), gases (e.g. O_2, CO_2, Ar,...), complexes and suspended gaseous, liquid or solid particles are the solutes. One can also consider the rock material in a similar way. In the loose-rock clay e.g. the SiO_4 - tetrahedrons and $Al(OH)_6$ - octahedrons are the solvents, in which the cations and anions are embedded (dispersed) as solutes.

Those solvents at the center of our consideration are called *"migrants"*. A migrant, therefore, can exist in each of the three mixed phases of the "underground". We distinguish *single-migrant models* of water quality from *multi-migrant models*.

The three mixed phases "soilair", "soil - or groundwater", and "soil or rock" in the middle level form together in the highest hierarchical level the multiphase system "underground". The fluid mixed phases "soilair" and "soilwater or groundwater" especially cause the mobility of the migrants in the "underground"! On the other hand the immobile mixed phase "rock" is often responsible for the significant migrant storage capability.

The multiphase system "underground" stands in the highest level. The smallest considerable part of such a system is the *representative elementary volume* (REV), and the least considerable time step is the so called *representative elementary time* (RET), see Luckner and Schestakow 1986. Figure 1 shows the hierarchical scheme of the three level multiphase system described above.

Only two hierarchical levels consist in surface water bodies. We can therefore consider surface water quality models as special cases of underground water quality models, and need no further separate description here for the surface water quality models.

MULTIPHASE SYSTEMS "UNDERGROUND"

MIXED PHASE "solair"	MIXED PHASE "soilwater or groundwater"	MIXED PHASE "soil or rock" (e.g. clay)
N_2	H_2O	$SiO_4-T;Al(OH)_6-O$
O_2 H_2O CO_2	Na^+ K^+ Ca^{2+}	Na^+ K^+ Fe^{2+}
CH_4 H_2S Ar	Mg^{2+} HCO_3^- H^+	Mg^{2+} Cl^- PO_4^{3-}
NO_2 NH_3 SO_2	NO_3^- O_2 SO_3^{2-}	SO_3^{2-} H^+ NO_3^-

MIGRANT (example)
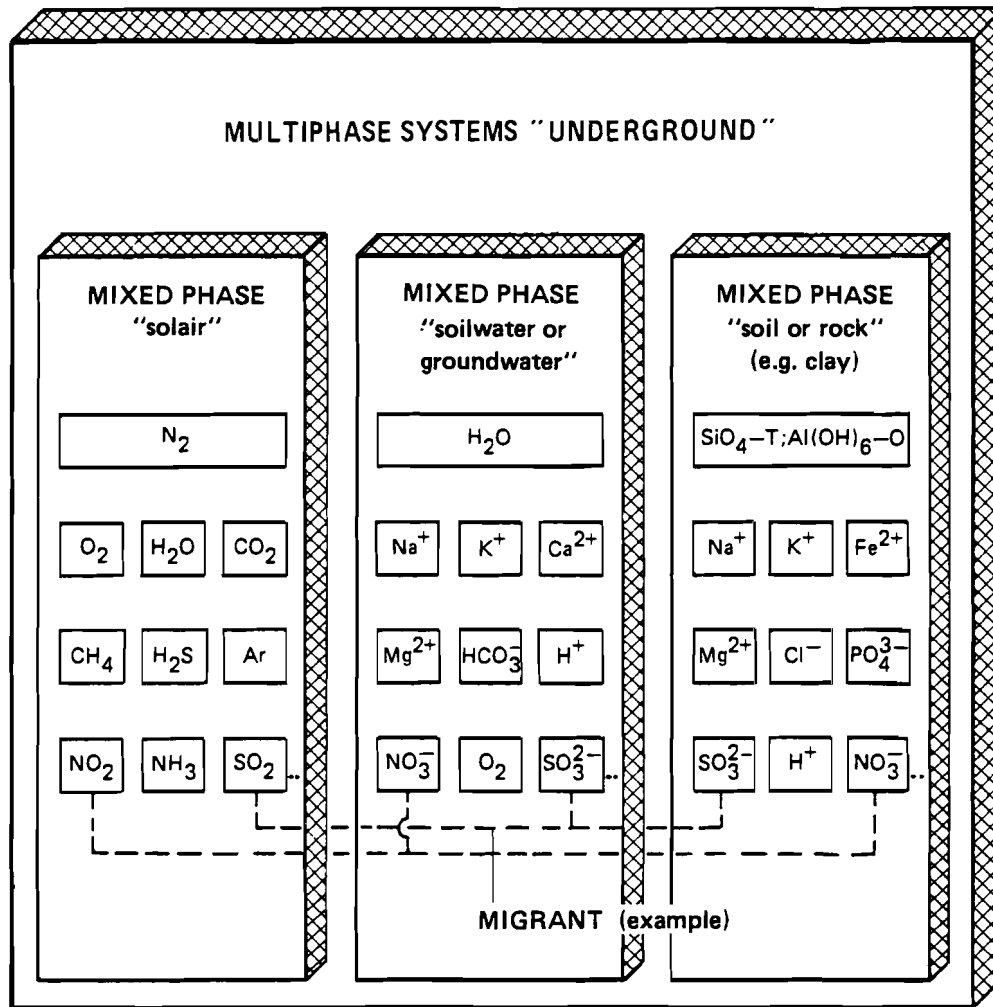
Figure 1: Hierarchical scheme of the three-level multiphase system "underground" for migration research purposes

2.2. Single Processes

The four main processes in which the migrants are subjugated are

- *transportation*
  - *storage*
    - *reactions* and
      - *exchange*.

We have to consider, therefore, the transportation phenomena in each and with each of the fluid mixed phases, the storage and the internal physico-chemical and bio-chemical reactions in each of the mixed phases and, last but not least, the exchange between the mixed phases of the multiphase system "underground" and the external exchange with other systems.

2.2.1. Transportation

The transport of migrants in the "underground" takes place (besides the purposive self-movement of some organisms) by means of:

- *molecular diffusion*
  - *convection* and
    - *hydrodynamical dispersion.*

Molecular diffusion is based on **Brown** 's molecular motion in solid, liquid and gaseous materials. This transport process is only important in the "soilair"-phase. In the "soil- or groundwater"-phase it is significant, when practically no convection exists (e.g. in clays).

The transportation of O_2 or CO_2 e.g. in the "soilair"-phase is mainly caused by molecular diffusion. This process can practically be stopped by saturation of the pores with water, because the diffusion coefficient in water is about one hundred thousand times less than in air. This fact can be used, e.g. to reduce the acidification of the mine water. The oxygen migrates to the sulphuric materials (e.g. pyrite), from the atmosphere to the coal-seams and other layers, in which the pyrite is embedded, through the "soilair"-phase by molecular diffusion. If we flood these layers or if we cover these layers by low permeable materials (e.g. silty materials), which are practically always water saturated, then the oxidation rate and therefore the acidification rate can be markedly reduced.

Convective transport and *hydrodynamic dispersion* are always coupled with the movement of a mobile mixed phase in the underground. The convection describes bulk movement of a mobile mixed phase. That means, the statistical averaged movement of all their components - the hydrodynamic dispersion - reflects all the deviations from this average.

The convective transport integrates in this way the flow process of water in the migration process. Therefore, one also often speaks of *"coupled water quantity and quality models"*, see e.g. Luckner and Gutt 1981. Without sufficient knowledge about the flow processes in the area under consideration, no water quality model can be quantified. Special difficulties arise in those cases, when more than one mobile immiscible phase exists in the underground, e.g. water and air in the unsaturated zone of a cone of depression. The convective transport model is then significantly more complex, see Luckner and Schestakow 1986. However, the transport of oxygen, for instance, in the unsaturated soil-water zone cannot be modeled with only a single moving phase.

The real velocities of migrants digress, of course, about the average bulk-movement of the mixed mobile phase. It is often supposed that these deviations are normally distributed about the convection movement. The values of the *hydrodynamic dispersion* depend on the convection (in the case of zero-convection no hydrodynamic dispersion appears) and on the gradient of the migrant-concentration. One distinguishes the longitudinal (in the direction of the bulk-movement) from the transversal hydrodynamic dispersion (perpendicular to the direction of the bulk-movement). The most difficult problem is the mathematical description of the *scale-dependency* of the dynamic dispersion, for details see Luckner and Schestakow 1986.

The *total transportation process* of the migrants in the underground is approximated by the superposition of the single processes described. This includes the assumption that these processes are linear. This assumption corresponds to the state-of-the-art in groundwater quality modeling.

2.2.2. Storage

Each mixed phase of the multiphase system "underground" is capable of storing migrants. The *specific storage* s_i is defined as the stored quantity of the migrant i in the considered mixed phase divided by the volume of the multiphase system. It depends on a *storage coefficient* ca_i and an *intensive state variable* P_i, with $s_i = ca_i \cdot P_i$. The storage-rate therefore amounts to

$$ds / dt = d(ca \cdot P) / dt.$$

The easiest measurable intensive state variable of the mixed phases in the underground is the concentration c_i of the considered migrant i in the mobile fluid phase after its extraction (separation). This variable c_i is, in water or air, a well-known function of the chemical potential μ_i, see Luckner and Schestakow 1986. Because it is also known that in the thermodynamic state of equilibrium in a multi phase system the chemical potential μ is equal in each of the mixed phases $\mu_1 = \mu_2 = \cdots$, the mathematical formulation is mostly based on c_i.
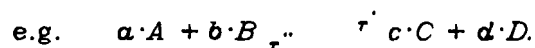
Generally the so called **Henry**-storage-isotherm, the **Freundlich**-storage-isotherm and the **Langmuir**-storage-isotherm are used as mathematical models of the storage processes in the multiphase system "underground". The *first* model is suitable to describe the storage process in water or air for low concentrations of migrants, the *second* e.g. for adsorption of sulphate, cadmium or herbicides on the solid phase, and the *third* when e.g. gases, cadmium or phosphate are adsorbed on the soil or rock. At this the **Henry**-storage-isotherm is an asymptote to the **Langmuir**-storage-isotherm in the case of low concentrations. Up till now we found the best results with the **Langmuir**-storage-isotherm, because it gives reasonable storage-rates in the case of very low as well as in the case of very high concentrations.

2.2.3. Reactions

In each of the mixed phases internal reactions may occur. The most important forms (see Luckner and Schestakow 1986) are:

- association/dissociation processes (complex formation, aggregation, dissolution, and precipitation with co-precipitation),
- oxidation/reduction processes,
- acid/base reactions and
- biological metabolizing.

The mathematical reaction model has to describe the stoichiometric balance as well as the reaction-rates of the migrants. The total reaction-rate r is formed by the forward rate r' describing the transformation velocity of the initial substances IS to the reaction products RP and the backward rate r'' the back transformation:

$$IS \underset{r''}{\overset{r'}{\rightleftharpoons}} RP$$

$$\text{e.g.} \quad a \cdot A + b \cdot B \underset{r''}{\overset{r'}{\rightleftharpoons}} c \cdot C + d \cdot D.$$

$\nu_i = a, b, c, d$ are stoichiometric coefficients and A, B, C, D substances. The thermodynamically-based reaction-rate is approximately

$$r = r' - r'' \approx k' \cdot \sum_{IS} \nu_j \cdot \mu_j - k'' \cdot \sum_{RP} \nu_i \cdot \mu_i = -k \cdot \Delta_R G \tag{1}$$

with

$\Delta_R G$ - free reaction enthalpy

k - velocity coefficient.

With the symbol $[i]$ for the concentration of the migrant i (substance i) in a mixed phase the easiest mathematical reaction model can be formulated as:

$$r = k \cdot \prod [i] \quad , \quad \text{e.g.} \quad r = k \cdot [A] \quad \text{or} \quad r = k \cdot [A] \cdot [B]. \tag{2}$$

This model holds only true, when the concentrations of the initial substances are significantly higher than those of the reaction products. Otherwise we have to formulate:

$$r = k' \cdot \prod [j] - k'' \prod [i] \quad , \quad \text{e.g.} \quad r = k' \cdot [A] \cdot [B] - k'' \cdot [C] \cdot [D]. \tag{3}$$

But these models do not reflect the thermodynamic equilibrium. This is only possible by introduction of the thermodynamic equilibrium constant given as $K_T \approx \prod [i] \, / \, \prod [j] = k' / k''$:

$$r = k' \cdot \left[\prod [j] - \prod [i] \, / \, K_T \right] \quad . \tag{4}$$

Often it is also useful to restrict the maximal reaction-rate to r_{max}. This is possible e.g. by means of Eq.(5), Luckner and Schestakow 1986:

$$r = \frac{r^* \cdot r_{max}}{r^* + r_{max}} \quad . \tag{5}$$

With $r^* = k^* \cdot [i] = (r_{max} \, / \, k_{max}) \cdot [i]$ appropriate to Eq.(2) the Eq.(5) represents e.g. the important **Michaelis-Menten**-kinetics.

All these reaction models ignore the necessity of an *activation energy* respectively enthalpy to start the reaction - see Figure 2. *Bio-catalyzers* can reduce this activation energy. These catalyzers are produced by microorganisms. They often enormously increase the velocity constant k and by this means the reaction-rate. On the other hand the variation of the equilibrium state k' / k'' is thereby negligible.

Consequently an important possibility to reduce the acidification of groundwater in mining areas is the development-stunting of microorganisms which are involved in the oxidation process of the sulphuric materials, see Luckner and Hummel 1982. In the range of pH>4 the activity of the most interesting microorganisms *thiobacillus ferrooxidans* and *ferrobacillus ferrooxidans* are negligible. Two ways are useful to increase the *pH*-values, by liming or to use ashes of coal-fired powerplants, which are spread out on the top of the ground surface and are mixed by the work of excavators. In such mixed spoils practically no acidification of groundwater takes place, only the sulphate concentration increases, see Fischer et.al. 1985.

2.2.4. Exchange

The most important forms of exchange between the phases are, see Luckner and Schestakow 1986:

-     the anion and cation exchange
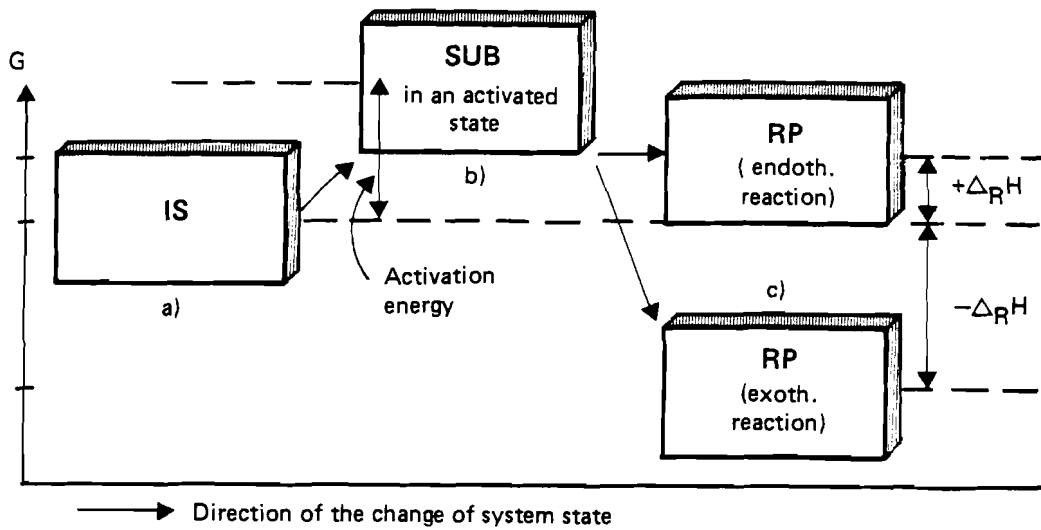-   the adsorption and desorption of migrants and

Figure 2: Scheme of energy respectively enthalpy change in chemical systems a)
migrants are in a metastable equilibrium b) migrants are in an instable
equilibrium c) migrants are for an exothermal reaction in a stable equili-
brium

- the external exchange e.g. due to abstraction of the root system.

The mathematical formulation of these processes in a multiphase system has to take
into account, that the exchange models do not contradict with the used storage-
process models. It is therefore recommended to use coupled exchange-storage
models, which turn over in the equilibrium state to the above mentioned storage
models, see Luckner and Schestakow 1986. This holds true for the storage of the
considered migrant in the mixed phase II exchanging migrants with the mixed
phase I. Typical models are:

- *the reversible linear kinetic model of 1st order*

$$\frac{ds_{II}}{dt} = k_I \cdot [i]_I - k_{II} \cdot s_{II}$$

for $\dfrac{ds_{II}}{dt} \to 0$ follows

$$s_{II} = (k_I \ / \ k_{II}) \cdot [i]_I = \alpha \cdot [i]_I \quad \textbf{(Henry—storage—isotherm)}$$

- *the reversible nonlinear kinetic model*

$$\frac{ds_{II}}{dt} = k_I \cdot [i]_I^q - k_{II} \cdot s_{II}$$

for $\dfrac{ds_{II}}{dt} \to 0$ follows

$$s_{II} = (k_I \ / \ k_{II}) \cdot [i]_I^q = K \cdot [i]_I^q \quad \textbf{(Freundlich—storage—isotherm)},$$

- *the bilinear kinetic model*

$$\frac{ds_{II}}{dt} = k_I \cdot [i]_I \cdot (s_{II,max} - s_{II}) - k_{II} \cdot s_{II}$$

for $\dfrac{ds_{II}}{dt} \to 0$ follows with $k_I / k_{II} = K'$

$$s_{II} = \frac{K' \cdot s_{II,max} \cdot [i]_I}{1. + K' \cdot [i]_I}$$ (**Langmuir**—storage—isotherm).

For practical purposes the same recommendations hold as for the storage-process-models.

2.3. Comprehensive Complex Model

The mathematical model of the complex dynamic water quality process, the *complex comprehensive water quality model*, should be developed based on figurative models. The elaboration of a chain of these models with graduated approximation-levels is often useful, see Luckner and Schestakow 1986.

Let us consider such a chain with three levels as shown in the upper part of Figure 3.

The *first figurative model* in this figure reflects the real distribution of the various mixed phases in a representative volume of the multiphase system "underground". Three mixed phases are considered:

- the mobile fluid phase marked by flow arrows, i.e. the mobile part of the groundwater,

- the immobile fluid phase adsorbed in thin films around the solid particles and entrapped in the small pores, the so called dead-end pores, and

- the solid skeleton (e.g. sand grains) marked by crosshatching.

The *second figurative model* reflects the ordered representative statistical average distribution of the three phases in the elementary volume. The storage symbols mark the storage-capability of each phase, and the exchange symbols mark the possible exchange-paths equivalent to the first figurative model.

Finally in the *third figurative model* the approximation is taken still further. The nodal points of the models characterize the mixed phases. Their number is reduced to two - to the *mobile phase* as before, and to an *immobile phase* formed by the solid phase and the immobile part of the liquid phase. Between both of them the *exchange* takes place. The vertical arrows on the left nodal point, which characterizes the mobile phase, symbolizes the *transportation* process and the diagonal arrows the *reaction* in respect to the considered migrant. Such a model must be developed for each migrant. In our example three migrants M_1, M_2, M_3 are considered, therefore the Figure 3 contains these three models. These models are the base for the mathematical formulation of the complex process.

As the next model the *stoichiometric balance* of the considered migrants has to be formulated. From this model we calculate the relations between the formation-rates and the decay-rates of the considered migrants. If we consider the three migrants Fe^{2+}, O_2 and $Fe(OH)_3$ and the well-known stoichiometric balance model relation of iron oxidation , compare Figure 3:

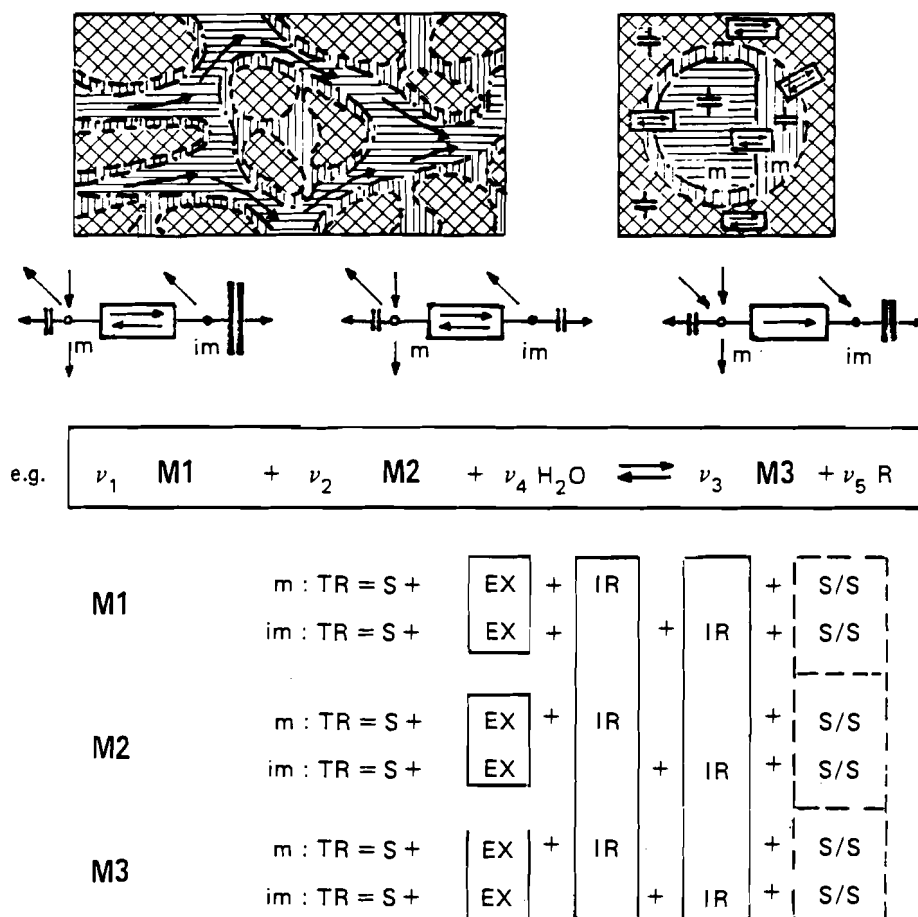$$4\ Fe^{2+} + 1\ O_2 + 10\ H_2O \to 4\ Fe(OH)_3 + 8\ H^+ \tag{9}$$
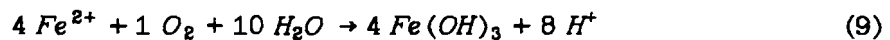
Figure 3: Scheme of a typical comprehensive systems-descriptive groundwater quality model

then we can easily find that e.g. the *formation-rate* of one mole $Fe\,(OH)_3$ is equal to the *decay-rate* of one mole Fe^{2+} and four times as much as the *decay-rate* of one mole disolved oxygen in the mobile groundwater phase.

The complex mathematical model consists finally of an equation system of $n*m$ equations (n - number of the considered phases and m - number of the considered migrants). Let us regard only the first equation in the Figure 3 reflecting the migration process of the migrant M_1 in the mobile phase. In this equation, *TR* symbolizes the *transportation process*, S the *storage process*, *EX* the *exchange process*, *IR* a *reaction process* internal of a phase, and S/S a *source/sink-term* reflecting an external reaction, e.g. the extraction of a migrant from the considered phase by the roots of plants, or in our case e.g. the intake of oxygen or lime hydrate in a mine water treatment plant or remaining pit.

The equations of the system are coupled with each other by the exchange process and internal reactions, see Figure 3. Of course, the external reaction can also have a couple effect, this will not be considered here (several typical examples are described in Luckner and Schestakow 1986).

Last but not least it is necessary to complete the equation system by *initial and boundary conditions*. This problem is described in more details in Luckner and Schestakow 1986. For each derivation of each of the dependent state-variables of the equation system one or two of those conditions appropriate to the

order of the derivation have to be formulate

3. Model Reduction

3.1. General Methods

The reduction of the comprehensive systems descriptive water quality models to box-models is possible in different ways. The following methods have been studied:

- *fitting* of a black-box model *by* means of *known* (measured) *input* - *and output-signals*, e.g. a deterministic trend-model, a convolution integral or an influence matrix, see Luckner and Mucha 1984,
- use of *analytical solutions* of approximated systems descriptive water quality models *as transition-functions* of box-models,
- *minimization of* the mixed *phases* of the multiphase system e.g. to a two- or to a one-single-phase model,
- *minimization of* the considered *migrants*, e.g. to Fe^{2+} and H^+, which have often the greatest importance in coal mining districts,
- *parameter-lumping* by averaging of the parameters in space as well as in time,
- *space-lumping* leading to the neglect of all the transportation processes, this also includes parameter-lumping,
- *time-lumping* leading to the neglect of all storage processes and the consideration of equilibrium exchange processes and reaction processes (this method also includes parameter-lumping).

For real situations it is usually necessary to use several of these approaches together.

In the following the development of reduced conceptual water quality models for typical subsystems in regions with open-cast lignite mines, which are coupled with each other will be demonstrated:

- the groundwater as the source of pollution,
- a mine water treatment plant as the control unit,
- a river section with an intake of acid ferruginous water, and
- a remaining pit, which can also be used as an effective control unit in mining areas.

These models may be used to estimate the necessary degree of purification for the acid ferruginous mine drainage water in the mine water treatment plant and the remaining pit, taking into account the self-purification process in rivers and remaining pits, as well as the water quality requirements of down- stream users.

To characterize the *model reduction procedure* in a uniform way for each of the four above mentioned subsystems, we are using a *box-symbol* reflecting the system under consideration with a *headline* marking the system's name. Around the box are symbolized all the *inputs* and *outputs* as well as the considered migrants (left and right) e.g. Fe^{2+} and H^+, and also the chemical control substances (on the top), e.g. lime hydrate or oxygen.

Figure 4 shows the connections between the four subsystems respectively the connections between their water quality models in mining areas with acid ferruginous mine water. The characteristic chemical species (migrants) in the whole system are Fe^{2+} and H^+. In the following the single models will be discussed in more detail.
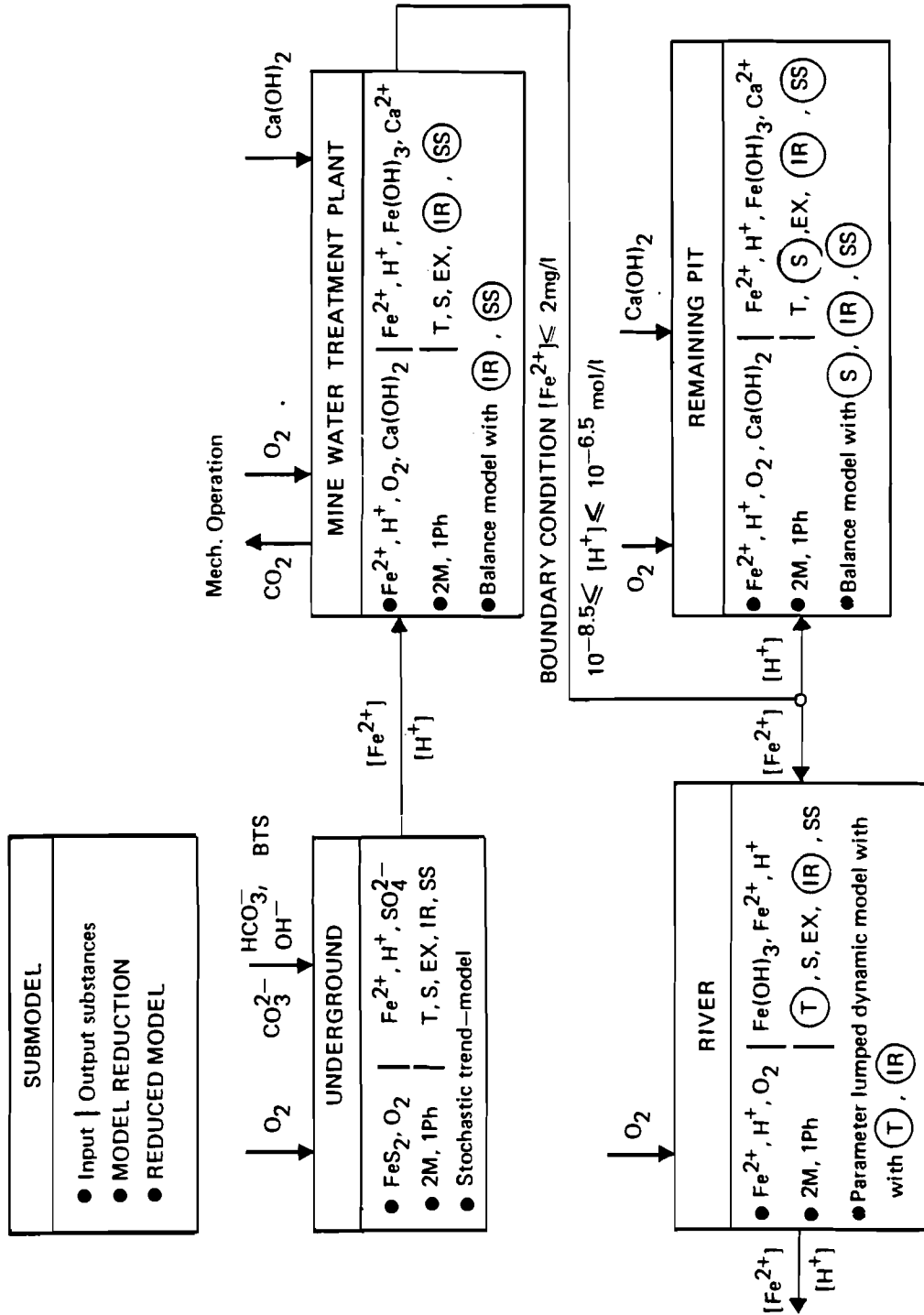
Figure 4: The complex scheme of the reduced conceptual quality models in a region with open-pit lignite mining

In the *first line* (internal of the box-symbol) are marked all the substances reacting with each other in the system, left the initial substances and right the reaction products. The stoichiometric balance equation quantifies their interactions.

In the *second line* are marked left the number of the considered migrants and the considered phases, and on the right hand side are specially marked the considered processes.

In the *third line* the names of the reduced models are given, e.g. "balance model with source/sink term and reaction" in the case of the mine water treatment plant.

3.2. Submodel "Groundwater"

A *stochastic trend model* for the prognosis of groundwater quality was developed based on the stoichiometric Eq.(10) and yearly series of measurements of the Fe^{2+}-and H^+-concentration in the drained mine water.

$$2 FeS_2 + 7 O_2 + 2 H_2O \rightarrow 2 Fe^{2+} + 4 SO_4^{2-} + 4 H^+ \quad . \tag{10}$$
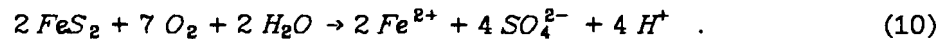
The trend models have the form, see Kaden et.al. 1985:

$$[Fe^{2+}] = a_{Fe} + b_{Fe} \cdot t + \varepsilon_{Fe} \quad , \quad \varepsilon_{Fe} \quad N(0, \sigma_{R,Fe}) \tag{11}$$

$$-lg[H^+] = a_H + b_H + \cdot t + \varepsilon_H \quad , \quad \varepsilon_H \quad N(0, \sigma_{R,H}) \quad . \tag{12}$$

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 5 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.

3.3. 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 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.
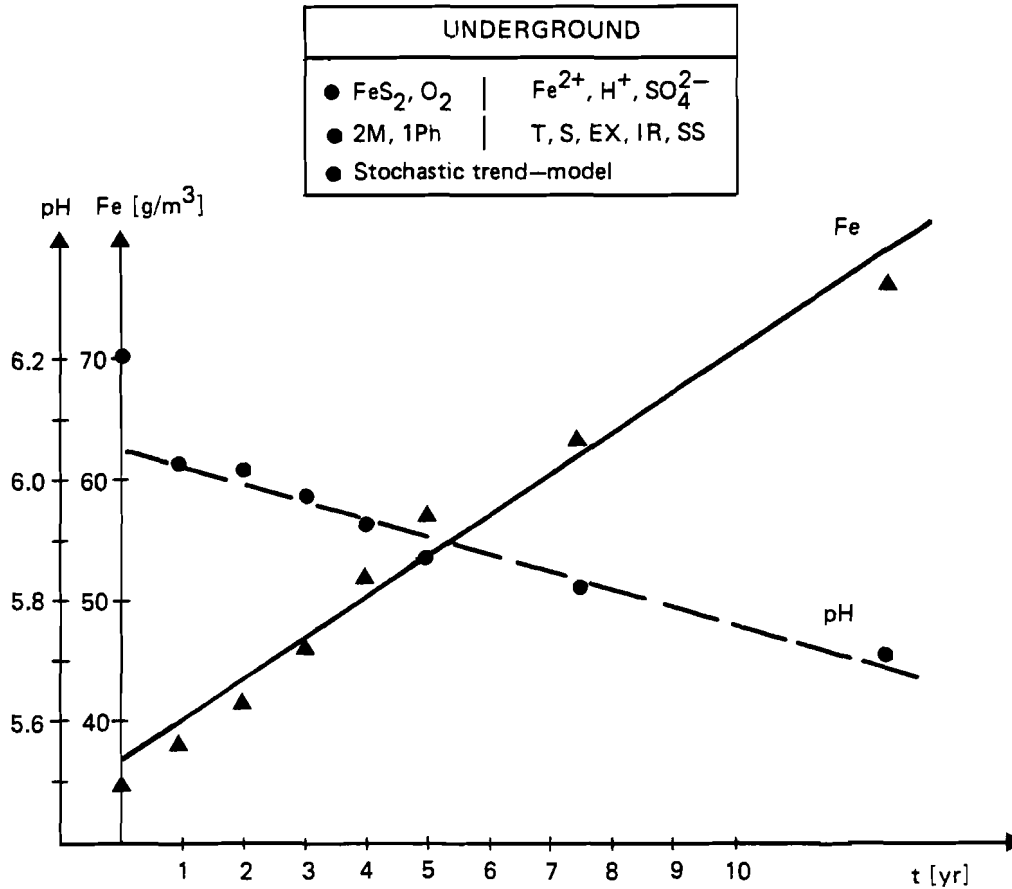
Figure 5: Scheme of the reduced model for the ground water pumped from an open-pit mine

- All the ferrous hydroxide formed is sedimented within the reaction time; no mathematical modeling is therefore necessary to reflect the *sedimentation process*.

- *Biochemical and chemical catalysis* of formed ferrous hydroxide and oxi-dehydrates are not considered in the coefficient *k* of the reaction rate model (see reactions).

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.(13). 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.(14). The total reaction is defined by Eq.(15).

$$Fe^{2+} + \frac{1}{4} O_2 + \frac{5}{2} H_2O \rightarrow Fe(OH)_3 + 2 H^+ \tag{13}$$

$$Ca(OH)_2(s) + 2 H^+ \rightarrow Ca^{2+} + 2 H_2O \tag{14}$$

$$Fe^{2+} + \frac{1}{4} O_2 + Ca(OH)_2 + \frac{1}{2} H_2O \rightarrow Fe(OH)_3 + Ca^{2+}. \tag{15}$$
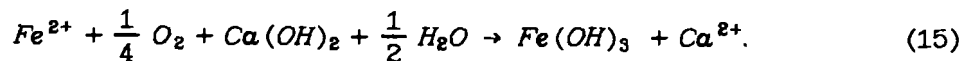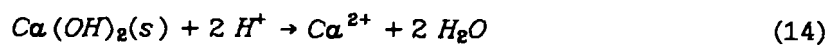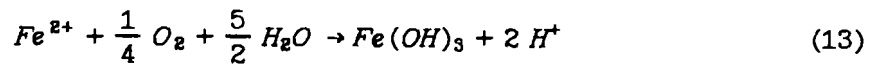
The *kinetics* of ferrous-ion oxygenation in laboratory systems has been previously

studied and the general rate law was found to be (see also Eq. (2)).

$$r_{Fe} = \frac{d[Fe^{2+}]}{dt} = -k \cdot [OH^-]^2 \cdot p_{O_2} \cdot [Fe^{2+}] \quad , \tag{16}$$

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.(16) reduces to a reaction rate model of pseudo-first-order kinetics:

$$r_{Fe} = -\frac{d[Fe^{2+}]}{dt} = k_1 \cdot [Fe^{2+}] \tag{17}$$

with

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

k_1 has the unit of inverse time.

Table 1: Velocity coefficients for the oxygenation kinetics of ferrous ions

Investigators	Velocity coefficient k $[mol^{-2} \cdot l^2 \cdot atm^{-1} \cdot min^{-1}]$	Temperature $[^0C]$
Stumm, Lee (1961)	$(8.0 \pm 2.5) \cdot 10^{13}$	$20.5\ ^0 C$
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 $10^0 C$ 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:

$$K_{H^+} = \frac{[H^+]}{[Ca(OH)_2]} \quad . \tag{18}$$

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:

$$K_{Fe} = \frac{[H^+]}{[Fe^{2+}]} = 3.58 \cdot 10^{-2} \, \frac{mol \, H^+}{g \, Fe^{2+}} \quad . \tag{19}$$

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 practically does not contain Fe^{2+} and has a pH-value of 7.

3.4. 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.(16)) and the external *sink* for protons (S/S) through a neutralization substance have to be considered. Under these assumptions the reduced model has the form:

$$Fe^{2+}: \quad -\frac{d\,[Fe^{2+}]}{dt} = \frac{k^{\,\prime}}{[H^+]^2}\cdot[Fe^{2+}] + \sum Q_A\cdot[Fe^{2+}] - \sum Q_Z\cdot[Fe^{2+}]_Z \qquad (20a)$$

$$H^+: \quad \frac{d\,[H^+]}{dt} = K_{Fe}\cdot\frac{d\,[Fe^{2+}]}{dt} + K_H\,[CA\,(OH)_2] + \sum Q_A\cdot[H^+] - \sum Q_Z\cdot[H^+]_Z. \qquad (20b)$$

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 $20°C$ in the case of *overdosage* because $Ca\,(OH)_2$ has a relatively low water solubility (1.6 $g\,/\,l$ in the case of $20°C$). In accordance with the limits for 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 $10^{-5.5} \le [H^+] \le 10^{-5.5}$ 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 6 shows the results of the submodel Eq. (20).

The graph in Figure 6 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 on the change of the $Fe\,(II)$-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 6 shows also that at *pH*-values less than 4 a substantially increased amount of lime hydrat is required for neutralization.

3.5. Submodel "River"

An intensive aeration of the river water provides enough oxygen to the *iron precipitation* according to Eq.(13). The formed protons will be neutralized up to the exhaustion of the buffer capacity of the carbonate and hydrogencarbonate ions. A *pH*-change occurs at about $3.58\cdot10^{-2}\ mol\ H^+$ 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 variation 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.

[Ca(OH)₂] [g/m³]
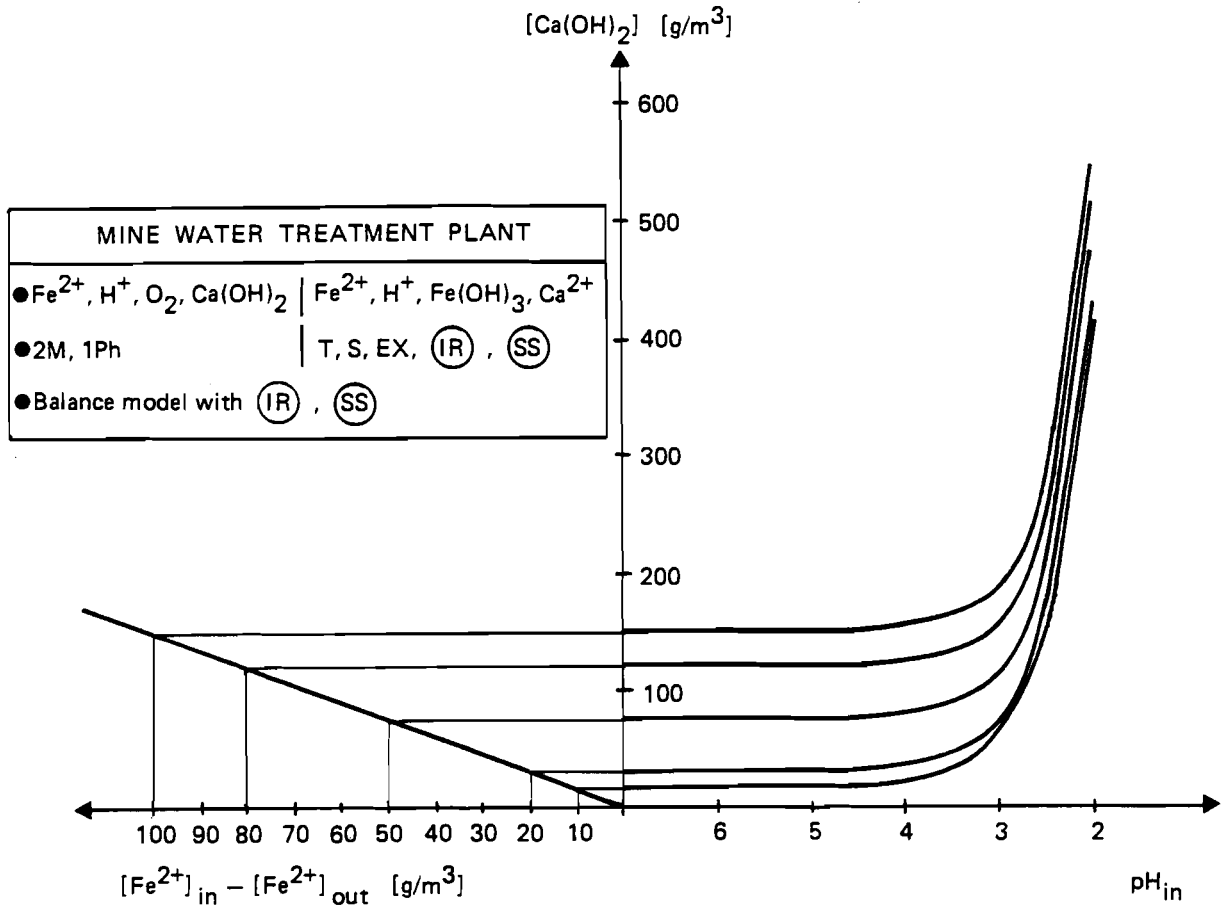
Figure 6: Demand of lime hydrate in dependency on the input *pH*-value and the difference of Fe^{2+}-input and -output concentration

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

$$Fe^{2+} : \quad -v\frac{d\,[Fe^{2+}]}{dx} = -\frac{d\,[Fe^{2+}]}{dt} = \frac{k}{[H^+]^2}\,[Fe^{2+}] \tag{21a}$$

$$H^+ : \quad -v\frac{d\,[H^+]}{dx} = \frac{d\,[H^+]}{dt} = K_{P_b}\,\frac{d\,[Fe^{2+}]}{dt} \quad . \tag{21b}$$

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

$$Q \cdot c = Q_Z \cdot c_z + \sum_{j=1}^{n} Q_{in,j} \cdot c_j - \sum_{l=1}^{m} Q_{out,l} \cdot c_l \quad . \tag{22}$$

Figure 7 shows typical results of the submodel "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.
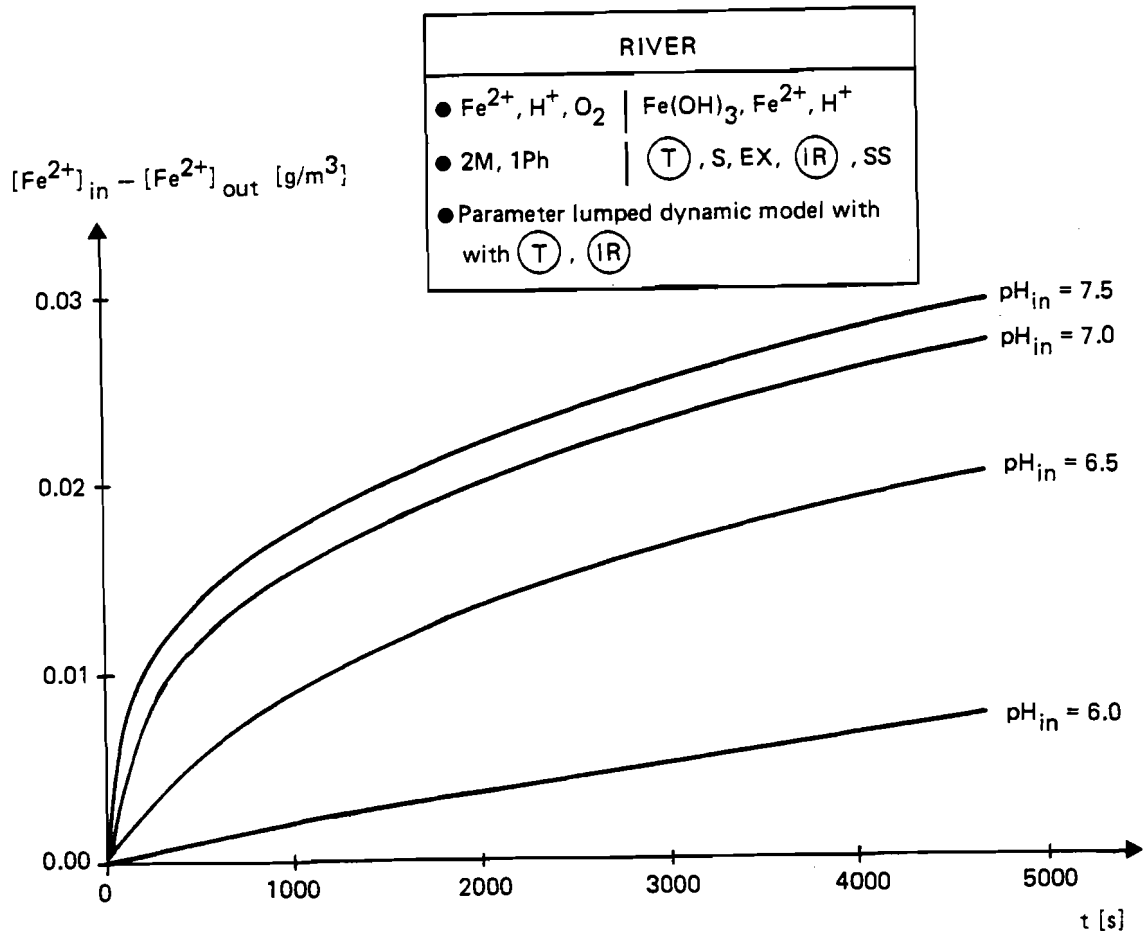
Figure 7: Changes of the ferrous ion concentration by oxygenation with air-oxygen
without neutralization in the river

3.6. 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 7)
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 6). 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 that we obtain:

$$Fe^{2+}: O = \frac{d(V \cdot [Fe^{2+}])}{dt} + \frac{k'}{[H^+]^2} \cdot V \cdot [Fe^{2+}] + \sum Q_A \cdot [Fe^{2+}] - \sum Q_Z \cdot [Fe^{2+}]_Z \quad (23a)$$

$$H^+: O = \frac{d(V \cdot [H^+])}{dt} + K_{Fe} \cdot V \frac{d[Fe^{2+}]}{dt} - K_H Ca(OH)_2 \cdot V + \quad (23b)$$

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

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.(23):

$$Fe^{2+}: \frac{d[Fe^{2+}]}{dt} = -\frac{k'}{[H^+]^2}[Fe^{2+}] - [Fe^{2+}] \cdot (\frac{\Delta V}{\Delta t \cdot V} + \frac{\sum Q_A}{V}) + \quad (24a)$$

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

$$H^+: \frac{d[H^+]}{dt} = -K_{Fe} \frac{d[Fe^{2+}]}{dt} - [H^+] \cdot (\frac{\Delta V}{\Delta t \cdot V} + \frac{\sum Q_A}{V}) + \quad (24b)$$

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

Figure 8 shows results of this model for an example with the following conditions: The conditions for an example are:

- $V = 10^7 \, m^3$,
- 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 $k' = 2 \cdot 10^{-13}$ 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.

4. Computer Model

4.1. Bases

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

$$\frac{dx}{dt} = -A \cdot \frac{x}{y^2} - G \cdot x + E \quad (25a)$$

$$\frac{dy}{dt} = -D \cdot \frac{dx}{dt} - G \cdot y + F \quad . \quad (25b)$$

The finite difference analogou of these equations is:

$$\frac{x^t - x^{t-\Delta t}}{\Delta t} = -x^t \cdot (\frac{A}{(y^t)^2} + G) + E \quad (26a)$$

$$\frac{y^t - y^{t-\Delta t}}{\Delta t} = -D \frac{x^t - x^{t-\Delta t}}{\Delta t} - G \cdot y^t + F \quad . \quad (26b)$$
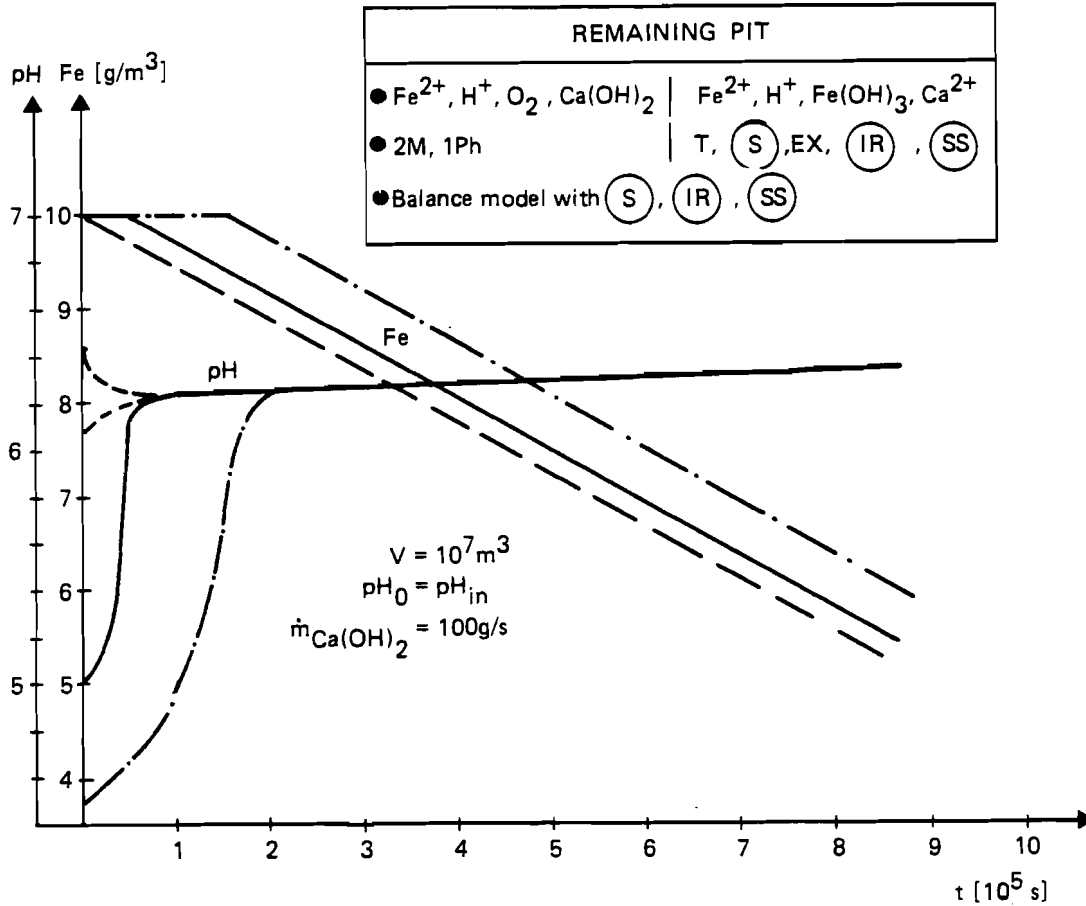
Figure 8: The change of the Fe^{2+}- and H^+- concentration in a remaining pit

From Eq.(26a) we obtain:

$$x^t = \frac{x^{t-\Delta t} + E \cdot \Delta t}{1 + \Delta t \cdot (\frac{A}{(y^t)^2} + G)}$$ (27)

A polynomial function of 3rd order results if we insert Eq.(27) into (26b). The solution is to be found in the range of $10^{-7} < y < 10$, this means in the range of $2 < pH < 10$.

$$0 = (y^t)^3 \cdot (1 + \Delta t \cdot G)^2 +$$ (28)

$$+ (y^t)^2 \cdot \left[D \cdot (x^{t-\Delta t} + \Delta t \cdot E) + (1 + \Delta t \cdot G) \cdot (-y^{t-\Delta t} - \Delta t \cdot F - D \cdot x^{t-\Delta t}) \right] +$$

$$+ y^t \cdot (1 + \Delta t \cdot G) \cdot A \cdot \Delta t + A \cdot \Delta t \cdot (-y^{t-\Delta t} - \Delta t \cdot F - D \cdot x^{t-\Delta t}).$$

4.2. Program Description

The computer program FEMO has been developed for the numerical solution of the generalized mathematical model for the three subsystems reflected by Eq.(28). 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 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 about pH-buffer reactions and catalytic reactions is possible.

The program source code is given in the Appendix 1. In Figure 9 a simplified flow chart of the program is depicted. In Appendix 2 test results are given.
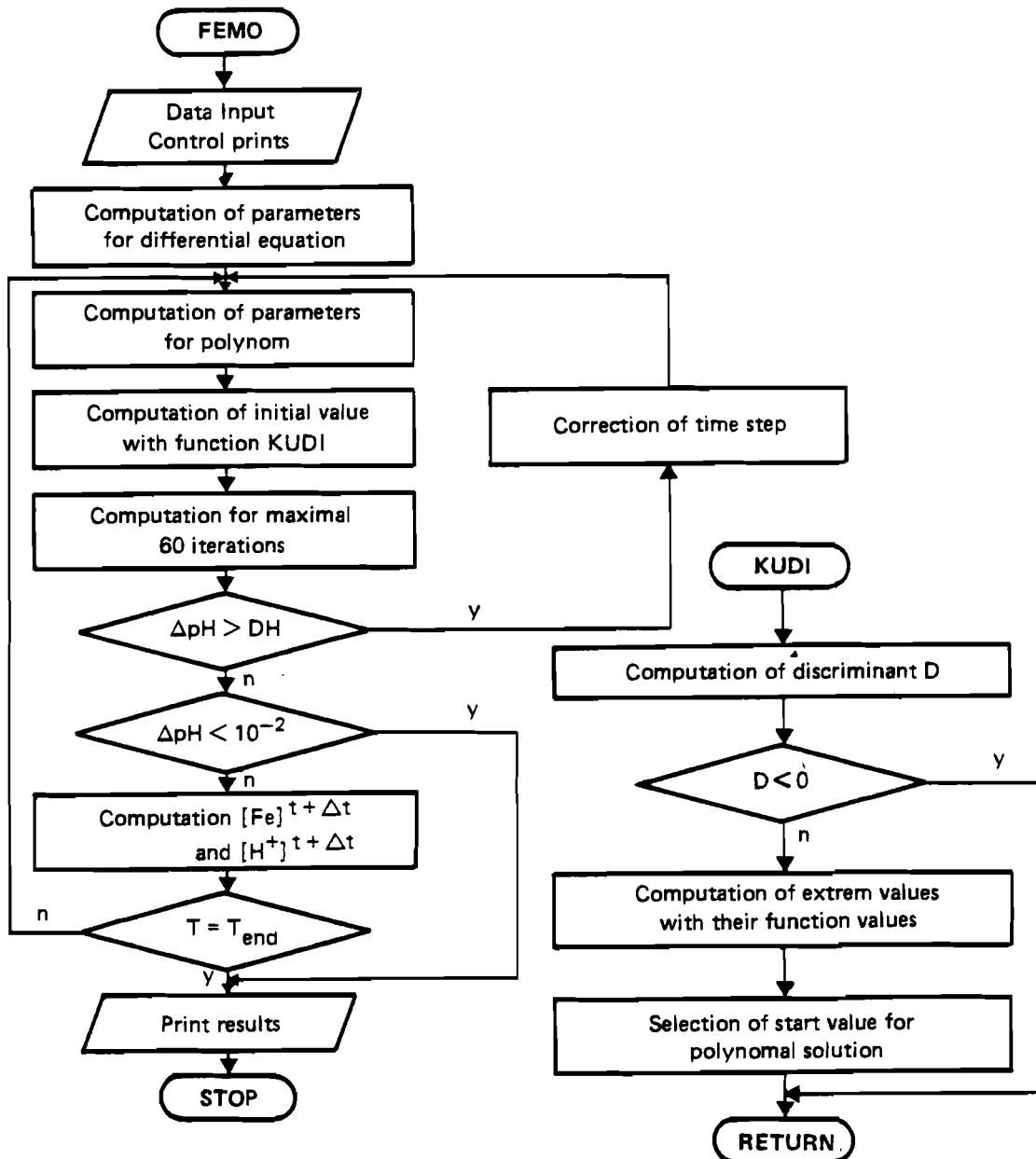
Figure 9: Flow chart of the model

The input data needed in applying the model are listed in Table 2. In Figure 10 the input data format is shown.

Table 2: List of input data

Record	Symbol	Description	Unit
1	text	text for heading	-
2	n	number of values	-
	im	number of model	-
		$(1\,\vert\,2\,\vert\,3)$	
	k	print after k time steps	-
3	rhk	reaction constant k_H	mol H^+/g $Ca(OH)_2$
	t	final time	sec.
	dh	maximum change of	-
		pH in one time step	
	v	volume	m^3
	a	reaction constant k^*	$mol^2 \cdot m^{-6} \cdot sec^{-1}$
4	qa	outflow	$m^3/sec.$
5	qz	inflow	$m^3/sec.$
6	$cfez$	concentration $[Fe^{2+}]$-input	g/m^3
7	phz	pH input	-
8	ck	demand of lime hydrate	$g/sec.$
9	$cfe0$	initial $[Fe^{2+}]$ concentration	g/m^3
10	$ph0$	initial pH-value	-

Figure 10: Input data format

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Appendix 1

```
c ********************************************************************************
c
c         Reduced Models for Water Quality by Oxidation of Fe(II) in
c         Mine Water Treatment Plants, Rivers and Remaining Pits
c
c ********************************************************************************
c
          program femo
c
c ***     a        - reaction constant k* [mol**2 m**-6 s**-1]
c ***               1.6... 13.6 * 10**-13
c ***     b        - ln(10)
c ***     b1..4    - parameters for polynom
c ***     b5,b6    - variable for pH**t,pH**(t+dt)
c ***     cah      - required dosage of lime hydrates [g/s]
c ***     cfez     - concentration [Fe2+]-input [g/m**3]
c ***     cfe0     - inital concentration [Fe2+] [g/m**3]
c ***     chz      - concentration [H+]-input [mol/m**3]
c ***     ck       - demand of lime hydrate [g/s]
c ***     d        - reaction constant kfe = 0.0358 [mol H+ /(g Fe2+) ]
c ***     dh       - maximum change of pH in one time step (0.05...0.3)
c ***     dt       - time step [s]
c ***     dta      - inintal time step [s]
c ***     e,f,g    - parameters for differential equation
c ***     f1,f2    - function values for extreme values
c ***     im       - number of model
c ***               im = 1    river
c ***               im = 2    mine water treatment plant
c ***               im = 3    remaining pit
c ***     k        - print after k time steps
c ***     kudi     - function to estimate start values of solution polynom
c ***     n        - number of values (max.10)
c ***     phz      - pH-input
c ***     ph0      - inital pH
c ***     qa       - outflow [m**3/s]
c ***     qz       - inflow [m**3/s]
c ***     rhk      - reaction constant kH(0.015...0.025) [mol H+ /(g Ca(OH)2)]
c ***     t        - final time [s]
c ***     text     - text for heading
c ***     ti       - actual time [s]
c ***     v,vp     - volume [m**3]
c ***     x0       - concentration [Fe2+**t] [g/m**3]
c ***     y0       - concentration [H+**t] [mol/m**3]
c ***     y1,y2    - extreme values
c ***     yd1,yd2  - approximate values for y0
c
          dimension cfe0(10),ph0(10),vp(11),ck(10),qa(10),
      *            qz(10),phz(10),cfez(10)
          real*8    a,b,d,d10,e,f,g,chz,yd1,yd2,y1,y2,
      *            b1,b2,b3,b4,b5,b6,x0,y0,t,ti,dt
          real*8    kudi
          character*72 text
          data      iin,iou/5,6/,d,d10/3.58d-02,1.0d+01/

c ***     iin      - standard input
c ***     iou      - standard output

c ***     IIASA-subroutine for assignment of input/output units,
c ***     has to be replaced by adaqute statements, e.g. open-statement
```

```
c ***    if data input/output is not done via standard i/o.

         call usearg

c ***    data input

         read(iin,'(a72)') text

         write(iou,2000) text
 2000    format(22x,'P R O G R A M   F E M O'//
     *           ,8x,'Reduced Water Quality Models By Fe(II)-Oxidation'
     *           //,3x,a72,/,3x,58('*')/)

         read(iin,*) n,im,k
         read(iin,1000) rhk,t,dh,v,a
         read(iin,1000) (qa(i),i=1,n)
         read(iin,1000) (qz(i),i=1,n)
         read(iin,1000) (cfez(i),i=1,n)
         read(iin,1000) (phz(i),i=1,n)
         read(iin,1000) (ck(i),i=1,n)
         read(iin,1000) (cfe0(i),i=1,n)
         read(iin,1000) (ph0(i),i=1,n)
 1000    format(5e10.4)

         write(iou,2001) n,im,k,rhk,t,dh,v,a
 2001    format('   n=',i2,' im=',i2,' k=',i4,' rhk=',f8.5,' t=',
     *          e8.2,' dh=',f8.2,' v=',e8.2,' a=',e8.2)
         write(iou,'(''   qa(i),i=1,n'')')
         write(iou,2002) (qa(i),i=1,n)
         write(iou,'(''   qz(i),i=1,n'')')
         write(iou,2002) (qz(i),i=1,n)
         write(iou,'(''   cfez(i),i=1,n'')')
         write(iou,2002) (cfez(i),i=1,n)
         write(iou,'(''   phz(i),i=1,n'')')
         write(iou,2002) (phz(i),i=1,n)
         write(iou,'(''   ck(i),i=1,n'')')
         write(iou,2002) (ck(i),i=1,n)
         write(iou,'(''   cfe0(i),i=1,n'')')
         write(iou,2002) (cfe0(i),i=1,n)
         write(iou,'(''   ph0(i),i=1,n'')')
         write(iou,2002) (ph0(i),i=1,n)
         write(iou,'(///)')
 2002    format(3x,10f8.2)

         vp(1)=v
         do 10 i=2,n+1
               vp(i)=vp(i-1)+t*(qz(i-1)-qa(i-1))
 10      continue
         b=dlog(d10)
         dta=t

c ***    computation

         do 180 i=1,n
               j1=0
               v=vp(i)
               e=0.
               f=0.
               g=0.
               if (im.eq.1) goto 20
```

```
                    if (im.eq.2) v=qz(i)*t
                    chz=d10**(-phz(i))*1000.
                    cah=qz(i)/rhk*(d*cfez(i)+chz-0.0001)
                    g=qz(i)/v
                    f=g*chz-rhk*ck(i)/v
                    e=g*cfez(i)

20                  write(iou,2100) i,a,g,e,d,g,f
2100                format('   differential equations for value ',i2//
     *                     '    dx/dt = - ',d10.4,' * x/y**2 - ',d10.4,
     *                     ' * x + ',d10.4/'    dy/dt = - ',d10.4,
     *                     ' * dx/dt  - ',d10.4,' * y + ',d10.4/)

                    ti=0
                    x0=cfe0(i)
                    y0=d10**(-ph0(i))*1000.
30                  dt=dta
35                  ti=ti+dt
                    ik=0
                    if (ti.le.t) goto 40
                    dt1=ti-t
                    ti=ti-dt
                    dt=dt-dt1
                    ti=ti+dt
40                  b1=1.+g*dt
                    b2=-y0-f*dt-d*x0
                    b3=dt*a
                    b4=d*x0+d*e*dt+b1*b2

c ***               discussion of curves / determination of start-values

50                  j=1
                    if (ik.gt.100) goto 110
                    yd1=kudi(b1,b2,b3,b4,ik)
                    if (ik.eq.1000) goto 110

c ***               first determination

60                  y1=b1*b1*yd1**3+b4*yd1*yd1+b1*b3*yd1+b2*b3
                    y2=3.*b1*b1*yd1*yd1+2.*b4*yd1+b1*b3
                    yd2=yd1-y1/y2
                    if (dabs(y1).lt.1.0d-14) goto 70
                    j=j+1
                    if (j.gt.60) goto 70
                    yd1=yd2
                    goto 60
70                  continue
                    if (yd2.lt.0.) goto 110
                    b5=-dlog(y0*0.001)/b
                    b6=-dlog(yd2*0.001)/b
                    y2=dabs(b5-b6)
                    if (y2.gt.dh) goto 110
                    if (ck(i).lt.0.001.and.y2.lt.0.01) goto 130
80                  if (j.ne.0) goto 90
                    dt=2.*dt
                    ti=ti+dt
90                  y0=(y0+yd2)/2.
                    x0=(x0+e*dt)/(b1+b3/y0/y0)
                    if (x0.lt.0.1) goto 130
                    y0=yd2
```

```fortran
                     j1=j1+1
                     if (j1.lt.k) goto 100
                     j1=0
                     write(iou,*) x0,y0,b6,ti,dt

100                  if (y0.lt.1.0d-07.or.y0.gt.10.) goto 50
                     if (ti.gt.(t-t*1.0e-4)) goto 120
                     goto 30


c ***                correction of timesteps

110                  ti=ti-dt
                     dt=dt/10.
                     if (dt.lt.1.0) dt=5.*dt
                     j=0
                     if (dt.gt.0.1) goto 35
                     if (yd2.lt.0.) goto 115
                     if (ik.gt.999) goto 170
                     goto 80


115                  write(iou,2200)
2200                 format('   no result for minimal time step 0.025 sec.')
                     stop


c ***                result  /  end of computation

120                  if (im.eq.2.and.b6.gt.8.5) goto 140
                     if (im.eq.2.and.b6.lt.6.5) goto 150
                     goto 160
130                  write(iou,2300) b6
2300                 format('   pH =',f5.2,
     *                        ', there is no more Fe-oxidation,')
                     write(iou,2400) ti
2400                 format('   reduction process is closed after ',
     *                        d12.6,' sec.'/)
                     goto 160
140                  write(iou,2500) cah
2500                 format('   pH greater then 8.5, overdosage of lime',
     *                        ' hydrate'/,'   recommendation: ',e10.4,
     *                        ' g/sec.'/)
                     goto 160
150                  write(iou,2600) cah
2600                 format('   pH less then 6.5, underdosage of lime',
     *                        ' hydrate'/,'   recommendation: ',e10.4,
     *                        ' g/sec.'/)
160                  write(iou,2700)
2700                 format('       [Fe2+]-input    [Fe2+]-output'
     *                        ,'   pH-input    ph-output')
                     write(iou,2701) cfe0(i),x0,ph0(i),b6
2701                 format(2(9x,f6.2),10x,f5.3,7x,f5.3//)
                     goto 180
170                  write(iou,2800)b6
2800                 format('   for ph =',f5.2,' no result of the',
     *                        ' system of differential equations exists'/)
180             continue


          stop
          end
```

```
          real*8 function kudi(b1,b2,b3,b4,ik)
c
c ***     discussion of curves  /  determination of startvalues
c
          real*8 b1,b2,b3,b4,y1,y2,f1,f2,d,d1,dd,kudi1
          data dd/1.0d-04/

          if(ik.ne.0) goto 20
          ph0=10.
          kudi1=ph0
          d1=3.*b1*b1
          d=b4*b4-d1*b1*b3
          if(d.gt.0) goto 10.
          ik=1000
          goto 40
10        y1=(-b4+dsqrt(d))/d1
          y2=(-b4-dsqrt(d))/d1
          f1=b1*b1*y1**3+b4*y1*y1+b1*b3*y1+b2*b3
          f2=b1*b1*y2**3+b4*y2*y2+b1*b3*y2+b2*b3
          ik=2
          if(f1.lt.0..and.f2.lt.0.) ik=1
          if(f1.gt.0..and.f2.gt.0.) ik=3
          if(ik.eq.1) kudi1=y1+dd
          if(ik.eq.3) kudi1=y2-dd
          if(kudi1.ne.ph0) ik=100+ik
          if(ik.gt.99) goto 40
          kudi1=y2+dd
          goto 40
20        if(ik.gt.10) goto 30
          ik=ik+10
          kudi1=y1+dd
          goto 40
30        ik=2000
          kudi1=y2-dd
40        kudi=kudi1
          return
          end
```

Appendix 2

                    P R O G R A M   F E M O

        Reduced Water Quality Models By Fe(II)-Oxidation

    Model test - River (im=1)
    ****

    n= 3 im= 1 k= 100 rhk= 0.02500 t=0.40d+04 dh=   0.10 v=0. e+00 a=0.20d-12
    qa(i),i=1,n
         1.00   1.00   1.00
    qz(i),i=1,n
         1.00   1.00   1.00
    cfez(i),i=1,n
        10.00   10.00   10.00
    phz(i),i=1,n
         5.00   5.50   6.00
    ck(i),i=1,n
         0.   0.   0.
    cfe0(i),i=1,n
        10.00   10.00   10.00
    ph0(i),i=1,n
         5.00   5.50   6.00

    differential equations for value   1

    dx/dt = - 0.2000d-12 * x/y**2 - 0.   d+00 * x + 0.   d+00
    dy/dt = - 0.3580d-01 * dx/dt - 0.   d+00 * y + 0.   d+00

    pH = 5.00, there is no more Fe-oxidation,
    reduction process is closed after 0.400000d+04 sec.

       [Fe2+]-input   [Fe2+]-output   pH-input   ph-output
         10.00   10.00   5.000   5.000

    differential equations for value   2

    dx/dt = - 0.2000d-12 * x/y**2 - 0.   d+00 * x + 0.   d+00
    dy/dt = - 0.3580d-01 * dx/dt - 0.   d+00 * y + 0.   d+00

    pH = 5.50, there is no more Fe-oxidation,
    reduction process is closed after 0.400000d+04 sec.

       [Fe2+]-input   [Fe2+]-output   pH-input   ph-output
         10.00   10.00   5.500   5.496

    differential equations for value   3

    dx/dt = - 0.2000d-12 * x/y**2 - 0.   d+00 * x + 0.   d+00
    dy/dt = - 0.3580d-01 * dx/dt - 0.   d+00 * y + 0.   d+00

       [Fe2+]-input   [Fe2+]-output   pH-input   ph-output
         10.00   9.99   6.000   5.921

P R O G R A M   F E M O

Reduced Water Quality Models By Fe(II)-Oxidation

Model test - Mine Water Treatment Plant (im=2)
****

n= 1 im= 2 k= 100 rhk= 0.02500 t=0.90d+04 dh=   0.10 v=0. e+00 a=0.20d-12
qa(i),i=1,n
      3.00
qz(i),i=1,n
      3.00
cfez(i),i=1,n
     20.00
phz(i),i=1,n
      5.00
ck(i),i=1,n
     50.00
cfe0(i),i=1,n
     20.00
ph0(i),i=1,n
      5.00

differential equations for value 1

$dx/dt = - 0.2000d-12 * x/y**2 - 0.1111d-03 * x + 0.2222d-02$
$dy/dt = - 0.3580d-01 * dx/dt - 0.1111d-03 * y + -.4519d-04$

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
20.00	10.04	5.000	7.558

P R O G R A M   F E M O

Reduced Water Quality Models By Fe(II)-Oxidation

Model test - Remaining Pit (im=3)
****

n= 5 im= 3 k= 100 rhk= 0.02000 t=0.86d+06 dh=   0.20 v=0.10e+08 a=0.20d-12
qa(i),i=1,n
      1.00   1.00   1.00   1.00   1.00
qz(i),i=1,n
      1.00   1.00   1.00   1.00   1.00
cfez(i),i=1,n
     10.00   10.00   10.00   10.00   10.00
phz(i),i=1,n
      5.00   5.50   6.00   6.50   7.00
ck(i),i=1,n
     10.00   10.00   10.00   10.00   10.00
cfe0(i),i=1,n
     10.00   10.00   10.00   10.00   10.00
ph0(i),i=1,n
      4.50   5.00   5.50   6.00   6.50

differential equations for value 1

dx/dt = - 0.2000d-12 * x/y**2 - 0.1000d-06 * x + 0.1000d-05
dy/dt = - 0.3580d-01 * dx/dt - 0.1000d-06 * y + -.1900d-07

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
10.00	10.00	4.500	4.865

differential equations for value 2

dx/dt = - 0.2000d-12 * x/y**2 - 0.1000d-06 * x + 0.1000d-05
dy/dt = - 0.3580d-01 * dx/dt - 0.1000d-06 * y + -.1968d-07

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
10.00	9.84	5.000	5.710

differential equations for value 3

dx/dt = - 0.2000d-12 * x/y**2 - 0.1000d-06 * x + 0.1000d-05
dy/dt = - 0.3580d-01 * dx/dt - 0.1000d-06 * y + -.1990d-07

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
10.00	9.67	5.500	5.742

differential equations for value 4

dx/dt = - 0.2000d-12 * x/y**2 - 0.1000d-06 * x + 0.1000d-05
dy/dt = - 0.3580d-01 * dx/dt - 0.1000d-06 * y + -.1997d-07

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
10.00	9.32	6.000	5.760

differential equations for value 5

dx/dt = - 0.2000d-12 * x/y**2 - 0.1000d-06 * x + 0.1000d-05
dy/dt = - 0.3580d-01 * dx/dt - 0.1000d-06 * y + -.1999d-07

[Fe2+]-input	[Fe2+]-output	pH-input	ph-output
10.00	9.40	6.500	5.760