

MINE WATER. GRANADA, SPAIN. 1985

**MODELING OF MIGRATION PROCESSES WITH
COUPLED MIGRANTS AND THEIR REDUCTION
TO CONTROL MODELS**

L. Luckner

Research Group for Open-Pit Mine
Dewatering Problems of the Grossräschen
Institute for Lignite Mining and the
Dresden University of Technology
GDR-8027 Dresden, Mommsenstr. 13
German Democratic Republic

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. We consider the discharge of acid ferruginous mine 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 users.

The paper describes the state-of-the-art of comprehensive water quality models with special regard to lignite mining areas. Based on this, approaches for model reduction are explained. These models are described in detail in the paper by Hummel et al. (1985).

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 dewatered 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 ground-water 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).

Comprehensive water quality have to consider several coupled migrants which may occur in several mixed phases in the underground. Such multi-migrant and multi-phase migration models as they are explained below are highly complicated and practically not to be used for complex model systems. Their reduction to conceptual box-models is necessary and in most cases reasonable.

COMPREHENSIVE WATER QUALITY MODELS

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, the 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). In Figure 1 a scheme of this hierarchical system is depicted.

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 the 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 centre 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.

Only two hierarchical levels consist in surface water bodies. We can therefore consider surface water quality models as special cases of underground water quality

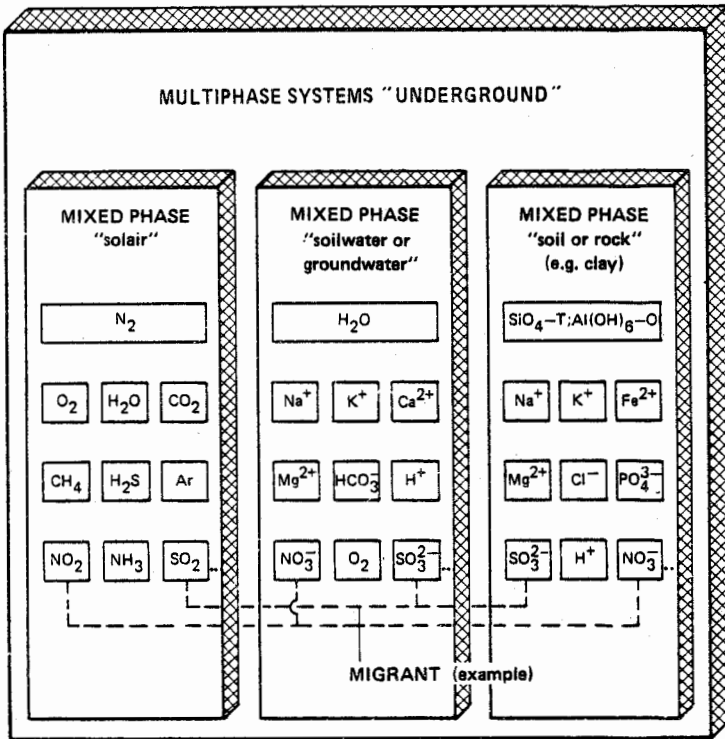


Figure 1: Hierarchical scheme of the three-level multiphase system "underground" for migration research purposes

models, and need no further separate description here for the surface water quality models.

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.

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 clay).

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, 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 the 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.

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

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

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 $\mu_1 = \mu_2 = \dots$, the mathematical formulation is mostly based on c_i .

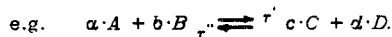
Generally the so called **Henry-storage-isotherm**, the **Freundlich-storage-isotherm** and the **Langmuir-storage-isotherm** are used as mathematical models of the storage processes in the multiphase system "underground". The *first* model is suitable to describe the storage process in water or air for low concentrations of migrants, the *second* e.g. for adsorption of sulphate, cadmium or herbicides on the solid phase, and the *third* if 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.

Reactions

In each of the mixed phases internal reactions may occur. The most important forms 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:



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

$$r = r' - r'' \approx k' \cdot \sum_{IS} v_j \cdot \mu_j - k'' \cdot \sum_{RP} v_i \cdot \mu_i = -k \cdot \Delta_R G \quad (1)$$

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:

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

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:

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

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

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

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):

$$r = \frac{r' \cdot r_{\max}}{r' + r_{\max}} \quad (5)$$

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 power-plants, 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).

Exchange

The most important forms of exchange between the phases are:

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

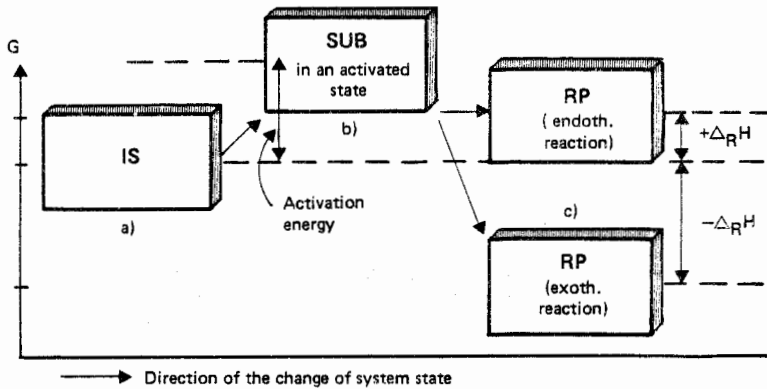


Figure 2: Scheme of energy respectively enthalpy change in chemical systems
 a) migrants are in a metastable equilibrium
 b) migrants are in an instable equilibrium
 c) migrants are for an exothermal reaction in a stable equilibrium

- 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 $\frac{ds_{II}}{dt} \rightarrow 0$ follows

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

- the reversible nonlinear kinetic model

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

for $\frac{ds_{II}}{dt} \rightarrow 0$ follows

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

- 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 $\frac{ds_{II}}{dt} \rightarrow 0$ follows with $k_I/k_{II} = K'$

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

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

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 (1966).

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

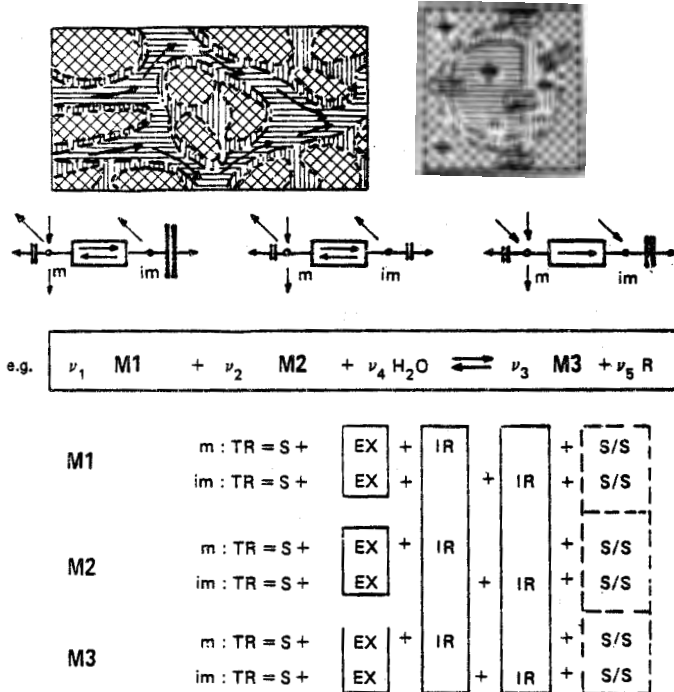


Figure 3: Scheme of a typical comprehensive systems-descriptive groundwater quality model

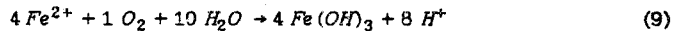
The *first figurative model* in this figure reflects the real distribution of the various mixed phases in a representative volume of the multiphase system "underground". Three mixed phases are considered:

- 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* of Figure 3, 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* with respect to the considered migrant. Such a model has to 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:



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 dissolved oxygen in the mobile groundwater phase.

The complex mathematical model consists finally of an equation system of $n \cdot m$ 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 formulated.

MODEL REDUCTION

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 paper by Hummel et al. (1985), the development of reduced conceptual water quality models for typical subsystems in regions with open-cast lignite mines, which are coupled with each other, are demonstrated in detail:

- 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.

At this point, only an overview is given. 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.

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^+ .

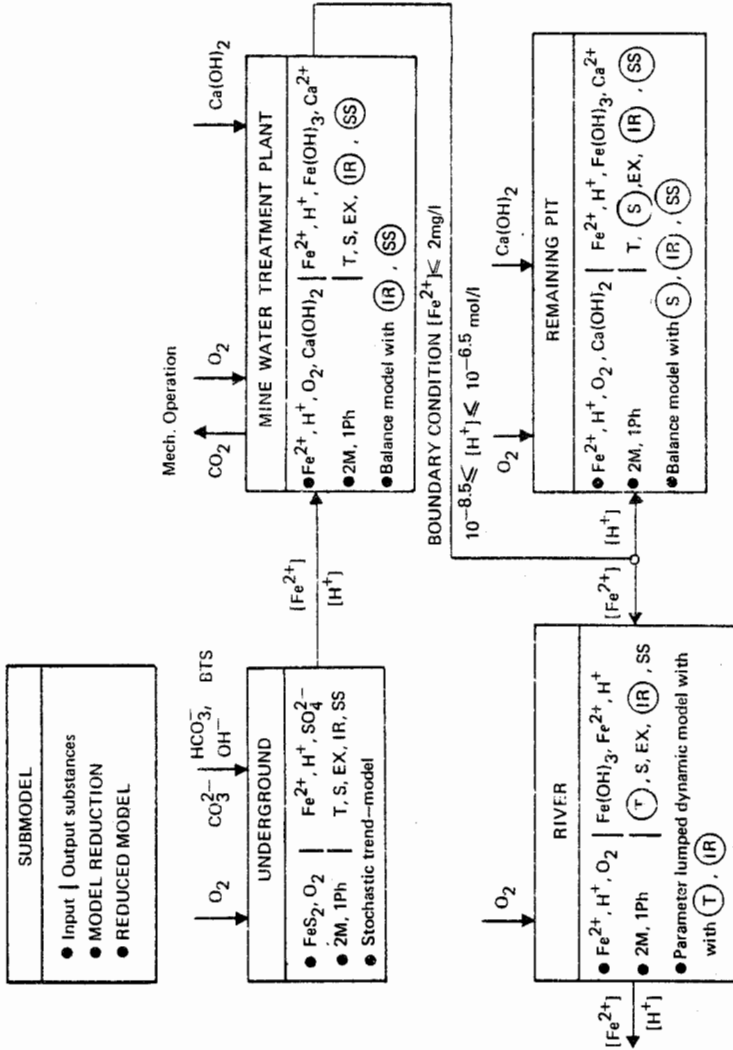


Figure 4: The complex scheme of the reduced conceptual quality models in a region with open-pit lignite mining

To characterize the *model reduction procedure* in a uniform way for each subsystem, 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.

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

References

- Fischer, R. et al. 1985, The problem of weathering of markasite and pyrit (in German). Leipzig, *Neue Bergbautechnik* (forthcoming).
- Hummel et al. 1985, Submodels of Water Quality for the Analysis of Regional Water Policies in Open-Pit Lignite Mining Areas. *Proceedings of the 2nd Congress of the IMWA*, Granada, September 1985.
- Kaden, St. et al. 1985, Decision Support Model System for the Analysis of Regional Water Policies in an Open-Pit Lignite Mining Area of the GDR. *Proceedings of the 2nd Congress of the IMWA*, Granada, September 1985.
- Luckner, L., Gutt, B. 1981, State-of-the-art and possibilities of groundwater quality management with computer support in the GDR (in German), Final report of the first part of the Intern. Hydrogeological Program 1975-80, Vol. 4, pp. 66-74.
- Luckner, L., Hummel, H. 1982, Modelling and predictions of the quality of mine drainage water used for the drinking water supply in the GDR. *1st Intern. Mine Water Congress of the IMWA*, Budapest, Hungary, Proc. D, pp. 25-36.
- Luckner, L., Mucha, I. 1984, Theory and methods of hydrogeological modelling in connection with the solution of major practical problems on regional and local scales, *27th Intern. Geological Congress*, Proc. Vol. 16 (Hydrogeology), pp. 91-106, *VNU Science Press*, Utrecht, The Netherlands.
- Luckner, L., Schestakow, W.M. 1986, *Migration processes in the soil- and groundwater zone* (in German and in Russian), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig and Isdateilstvo Nedra Moscow, planned for 1986.
- Starke, W. 1980, Utilization of mine water of open-cast lignite mines for drinking water supply (in German), *Wasserwirtschaft/Wassertechnik* Berlin, 30(1980), No. 7, pp. 219-222.