Introduction to BEM
(Batch Equilibrium Model)

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Abstract

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BEM is a computer program for the calculation of coupled chemical equilibria in aqueous electrolyte systems. The equilibria may include complexation, acid/base reactions, dissolution/precipitation of salts and cation exchange. Changing total concentrations in consecutive batch experiments can be modelled. Several such models may be linked to give a rough representation of transport processes (batch cascade).

The concepts of BEM are introduced and the equations on which the program is based are documented completely.

Particular models are specified to BEM via files. These files are readable, concise definitions of models. The elements of these files are explained.

Two examples are presented. The first is a titration of aluminum ions with hydroxide in the presence of a complexing ligand. The second is an acidification model for "topsoil", "subsoil" and "creek" in a watershed.

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1 Introduction

If everything were at equilibrium the world would be a deadly boring place — dead indeed, because life is essentially a non–equilibrium phenomenon. Nevertheless there are subsystems in the world which reach a state of rest which can be explained by the thermodynamic equilibrium theory. The theory of the chemical equilibrium is by no means boring because these states depend in a complicated manner on the composition of systems. The student of this theory has to move in rather abstract spaces of chemical variables — the real space and the time being of little importance.

Studying equilibria is worthwhile also from a more practial point of view. The more ambitious type of theory is the kinetic approach which describes how processes develop in time. The modest equilibrium theory says only where the asymptotic final state will be. But for many systems we do not have the choice of a kinetic theory because it is not developed for the system and because the necessary experiments have not been done. Often there is also no demand for the knowledge of all transient states. This depends on ratios of velocities between the processes studied and other processes in the system of interest.

Consider as an example a glass of sparkling mineral water. It would be a tremendous task to predict the change in pH as function of time during the degasing process. This had to be, among other things, a function of the form of the glass. But using equilibrium calculations we can say from existing knowledge and quite generally where the pH finally will be, which is a function of the ambient carbondioxide pressure and of the minerals dissolved in the water.

What the equilibrium approach is lacking in detail about the development of processes in time may be outweighed by the complexity of chemical interactions it can handle. The special form of the chemical equilibrium theory makes it possible to combine knowledge about single reactions into rather complicated models. BEM has been developed for this combination process. The results are somtimes surprising — the effect of the combination is often not easily foreseen.

The program BEM is presently used at this institute in a variety of projects like cation exchange experiments with soils, studies on the organic complexation of aluminum and modelling of watershed acidification within 200 years. This paper is intended as a convenient reference for publications which include results from BEM. It aims at a complete explanation of the assumptions and equations which form the model. It does not explain how to use BEM actively. For that purpose further information will be needed.

We start by introducing the concepts of chemical thermodynamics on which BEM as an *equilibrium* model is built. Next, the concept of a *batch* model is introduced which is also able to model some dynamic behaviour, if the concentrations in the batch vessel are changed from outside. In any modelling effort one must be aware of the assumptions which may limit the success of the model as *model* of reality. Some general remarks on the limitations of batch equilibrium models are included.

The mathematical equations which form the core of BEM are documented completely.

BEM is a generalized chemical equilibrium model. Only a few specific chemical assumptions are fixed, everything else is communicated to the program via a file, called the model file. The notation in this file is an almost readable description of the particular model. These files may be used as shorthand documentation of specific models. Therefore this notation is explained in this introduction.

A first example describes the titration of Al^{3+} with base in the presence of an organic ligand.

A second example is a model of the acidification of a watershed under the impact of acid precipitation. The soil moves from the carbonate buffer range (pH $\approx$ 8) to the aluminum buffer range and below (pH $\approx$ 3). The model has 3 "compartments": topsoil, subsoil and creek.

2 Concepts

2.1 Chemical equilibria

The theory of the chemical equilibrium is a well established branch of Physical Chemistry. We can only give a superficial introduction at this point and must refer the reader to the many excellent textbooks for details, citing only [7, 15, 16] where further references may be found.

Consider a closed reaction vessel. That is, a system which can not exchange matter with its surroundings. But let the system exchange energy with its environment if this exchange is restricted to the transfer of heat to or from a “heat reservoir” which is at constant temperature and to the transfer of work of volume change to or from a “pressure reservoir” which is at constant pressure. In reality the atmosphere may serve as either of the reservoirs. Let us call such a system a *G–system*.

Chemical reactions within the vessel will, by definition, change the concentrations of the substances involved. Transport processes as driven by concentration gradients or bulk movements may change the distribution of substances within the vessel. Experience shows that chemical reactions and transport processes in G–systems eventually cease so that the macroscopic concentrations of all substances in all parts of the system become constant. An infinitely continued reaction in a G–system is as seldom as a *perpetuum mobile* in mechanics.

The theory of thermodynamics explaines this finding from its second law. For G–systems this law states that the thermodynamic function G, or Gibbs energy, can only decrease.

$$dG \leq 0 \tag{1}$$

It follows that at a global miniumum of G no more changes, which could only increase G, are possible. This state is called the equilibrium state of the system. The purpose of BEM is to predict equilibrium states for G–systems.

This is possible only because the relationship between G and the concentrations within a reaction vessel are found to be simple in many cases. These relations are studied as partial derivates of G with respect to the concentration c_i of a single substance i

$$\mu_i = \frac{\partial G}{\partial c_i} \tag{2}$$

μ_i is called the chemical potential of i. For aqueous electrolyte solutions BEM uses the following form for μ_i of an ion i

$$\mu_i = \mu_i^0(P,T) + RT\ln(c_i\gamma_i) \tag{3}$$

where P is the pressure, T is the temperature, R is a constant, c_i is the concentration of i and γ_i is the so called activity coefficient of i. This equation splits the chemical potential in two parts, one that depends on the chemical composition and one that depends on temperature and pressure only. The part μ_i^0 is the chemical potential of the substance i where the product $c_i\gamma_i$ is unity ("state of unit activity").

In sufficiently dilute solutions γ_i is close to 1.

$$\mu_i = \mu_i^0(P,T) + RT\ln c_i \tag{4}$$

This relation is simple because the change of G with changing concentrations depends at given P and T only on c_i alone.

Consider the following example: Let a G–system contain the Elements A, B and C which form the compounds AB and CB

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \tag{5}$$
$$\mathrm{C} + \mathrm{B} \rightleftharpoons \mathrm{CB} \tag{6}$$

At given temperature, pressure and *total* concentrations of A, B and C (sum of A and AB; B and AB and CB; C and CB respecitively) the *single* concentrations of A, B, C, AB and CB can vary till with a minium in the Gibbs energy an equilibrium state is reached. Experience shows that the same state of equilibrium is approached, regardless what the initial *single* concentrations are, if the *total* concentrations are the same. If form 4 is valid, we see that the relationship betwen the Gibbs energy and each concentration is fully defined if the term $\mu_i^0(P,T)$ is known. It is possible to study experimentally the chemical potential of each substance in simplified systems and to transfer this knowledge in the form of tabulated μ_i^0 values to more complicated ones. In our example it would be sufficient to study the systems $\{$ A, B, AB $\}$ and $\{$B, C, CB$\}$ seperately in order to predict equilibria in the more complicated system $\{$A, B, C, AB, CB$\}$.

This operation is essential to programs like BEM. They facilitate, by using the power of the computer, the building of models with many chemical components. The specific parameters for these models often can be derived from experiments which are chemically simpler.

If the electrolyte solution is not very dilute eqn. 3 has to be used. But we can take advantage of a well established theory (Debye-Hückel theory) [15, 16] which relates the activity coefficient γ to the overall electrolyte level in the solution. The possibility to predict complicated situations from simple ones exists in this case also.

Eq. 1 together with 3 leads to the *law of mass action.* For reaction 5 and 6 we would have expressions

$$\frac{c_{\mathrm{AB}}\gamma_{\mathrm{AB}}}{c_{\mathrm{A}}\gamma_{\mathrm{A}}c_{\mathrm{B}}\gamma_{\mathrm{B}}} = K_1 \tag{7}$$

$$\frac{c_{\mathrm{CB}}\gamma_{\mathrm{CB}}}{c_{\mathrm{C}}\gamma_{\mathrm{C}}c_{\mathrm{B}}\gamma_{\mathrm{B}}} = K_2 \tag{8}$$

where the K_ν depend only on the terms $\mu_i^0(P,T)$.

The theory outlined so far has dealt only with homogeneous phases, that is in the case of BEM an aqueous ionic solution. If minerals (salts) in equilibrium with this solution are to be included we need an expression for the chemical potential of a salt. If we assume that each salt, if present in the system at all, is present in a seperate phase of fixed properties, we get

$$\mu_j = \mu_j^0(P,T) \tag{9}$$

where j denotes a salt. This equation means that the composition of the salt phase is not changing and therefore there is no dependence of μ_j on a concentration term. The formation of *solid solutions* [2, 16] is excluded. Eq. 1 together with 9 leads to the *solubility product* [7] equation. If, e.g., in reaction 5 the compound AB were a salt we had

$$c_{\mathrm{A}}\gamma_{\mathrm{A}}c_{\mathrm{B}}\gamma_{\mathrm{B}} = K_{sp} \tag{10}$$

instead of 7.

Another solid phase which may be present in BEM models is the *cation exchanger*. It is understood as seperate phase with a fixed total negative charge. An equivalent positive charge is supplied by cations which can be exchanged against other cations from the solution phase. If we denote the cation exchanger by X an exchange reaction could read

$$\frac{1}{a}\mathrm{A}^{+a} + \frac{1}{b}\mathrm{BX} \rightleftharpoons \frac{1}{b}\mathrm{B}^{+b} + \frac{1}{a}\mathrm{AX} \tag{11}$$

We assume that the chemical potential of a cation bound to the exchanger is given by

$$\mu_k = \mu_k^0(P,T) + RT\ln x_k \tag{12}$$

where k denotes a cation and x_k is the equivalent concentration of the cation on the exchanger. This equation leads to the *selectivity coefficient* [5, 6] for cation exchange.

Let A^{+a} and B^{+b} be cations which are present on the exchanger and in solution. At equilibrium we then would have from eqn. 1 with 3 and 12

$$\frac{(c_{\mathrm{A}}\gamma_{\mathrm{A}})^{1/a}x_{\mathrm{B}}^{1/b}}{(c_{\mathrm{B}}\gamma_{\mathrm{B}})^{1/b}x_{\mathrm{A}}^{1/a}} = K_{sel} \tag{13}$$

A similar form, the *Gapon coefficient* [5, 6] may be used as an alternative with BEM:

$$\frac{(c_{\mathrm{A}}\gamma_{\mathrm{A}})^{1/a}x_{\mathrm{B}}}{(c_{\mathrm{B}}\gamma_{\mathrm{B}})^{1/b}x_{\mathrm{A}}} = K_{Gapon} \tag{14}$$

2.2 Batch equilibrium models

If we want to calculate the equilibrium in a chemical system we need to know what chemical *substances* there are in the system and what *reactions* are possible between them. Some of the substances will be elementary in the sense that they will be neither formed nor transformed by the reactions considered possible in the system. We will call such substances *(elementary) components*. All other substances then must be compounds which are formed in the reactions considered.

The equilibrium is found as minimum of the Gibbs energy G. We therefore need the dependence of G on the system composition. It is sufficient to know the change in G which is associated with the formation of any of *compounds* from its *components*. (Any other reactions are linear combinations of these and so are the corresponding changes in G.) In BEM this information is supplied as one equilibrium constant (cf. eqs. 7, 8, 10, 13, 14), for each [1] component.

A list of components, compounds and equilibrium constants for the formation of the latter sets up the *structure* of a chemical equilibrium model. In order to enable quantitative calculations we must supply in addition the *total concentrations of the components*. These are numbers which will not be changed in the course of any of the reactions considered in the model. The task of equilibrium calculation can be described as finding the unknown concentrations of compounds from the known total concentrations of components or to find the equilibrium distribution of components

[1]The case of a cation exchanger needs special attention here: Formally, it is possible to see the exchanger as a *component* X which forms complexes with cations like an anion (cf. eqn. 11). But, in contrast to free anions, X^- is not existent. The exchanger is always saturated with cations. We can understand AX, BX, and so on, as *compounds* but we have equilibrium equations only for *exchange* reactions and not for a *formation* reaction from "free" X because this has a concentration of zero imposed on it. This gives one equilibrium equation less than the number of cations which can bind to the exchanger. A similar argument would hold for the concentration of electrons in redox reactions.

among compounds. [2]

It is quite possible to keep the structure of the model while allowing for changes in total component concentrations. In this way a series of equilibrium distributions is calculated which resembles dynamical change. But one must keep in mind that each of the calculated states of equilibrium is, by definition, time invariant. The dynamics is imposed from outside on the structure of the model. A well known example is the *titration*: stepwise a solution of known composition is added to the system giving rise to new equilibrium compositions. BEM can handle titrations. As an example one might think of the titration of an acid with base. The pH dynamics in such a case is not a function of time but of the amount of added base.

An other way to change the total component concentrations is the *consecutive batch experiment* (Fig.1). In such experiments part of the liquid phase, that is for BEM: an aqueous solution, is replaced in each step while the solid phases, that is: salts and cation exchanger, remain in place. Chemical analysis of the removed solution makes the calculation of the changes in total concentrations possible. BEM is prepared to handle such systems as series of equilibrium calculations. Again, one can say that the dynamics of such a system is not really a function of time but rather of change in total component concentrations associated with the input and output operations.

It is possible to link several consecutive batch experiments in such a way that the output from one vessel becomes the input to the next one. We call such a chain of vessels a *batch cascade* (Fig.2). This arrangement can be seen as a crude approximation of "transport with chemical reaction", e.g. in a soil column. BEM can handle batch cascades.

[2] The concentrations of the *single* components are also unknown. But they are fixed as difference to the *total* component concentrations as soon as all compound concentrations are known.

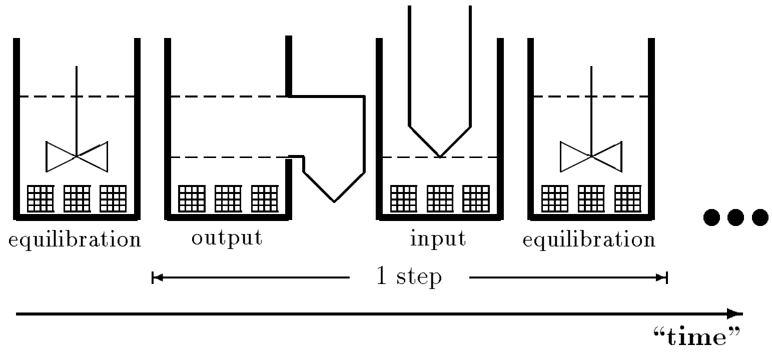

Figure 1: **Consecutive batch experiments.** *The heavilly outlined box symbolizes a chemical system with one liquid phase (stirred) and several solid phases. After equilibration part of the liquid phase is removed and replaced by the same volume of a solution of known composition. This sequence is repeated.*

2.3 Model validity considerations

Like any theoretical scientific statements models are hypothetical and have to be subjected to empirical testing (Popper). This has, of course, to be done for specific batch equilibrium models as models of specific classes of real world objects. In this introduction we only can discuss in a general manner critical points where the inherent assumptions of these models may be invalid.

2.3.1 Kinetics

The theory of thermodynamics can not say anything about the speed of processes. It only deals with equilibrium states and it can say that these states are approached in the long run (asymp-

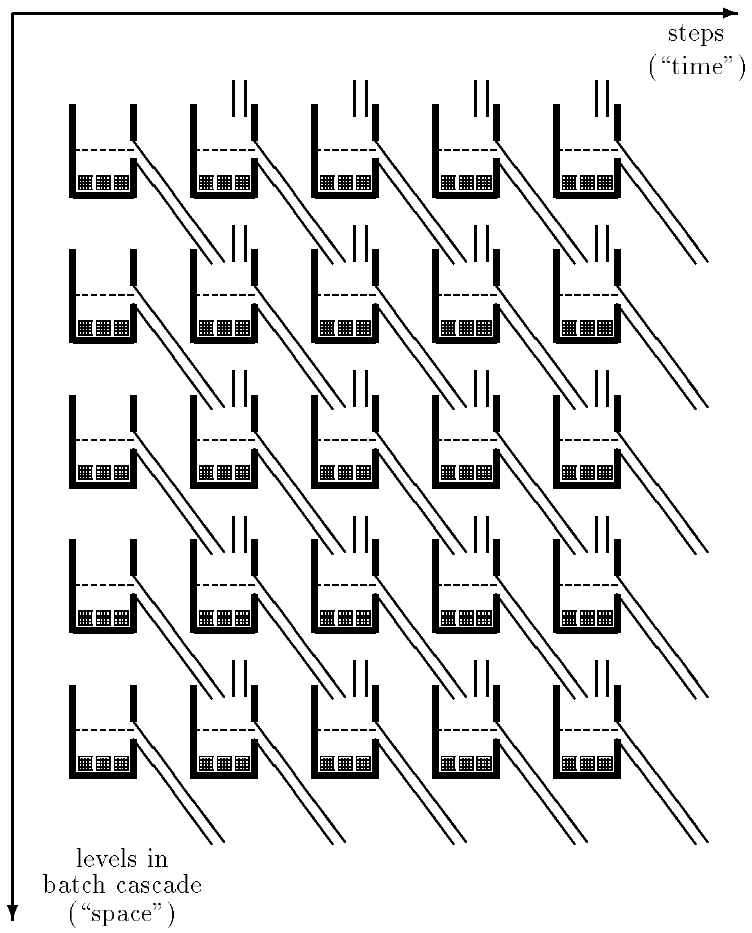

Figure 2: **Batch cascade.** *Each row represents a batch reaction vessel which is subjected to a consecutive batch experiment. "output", "input" and "equilibration" (cf. fig. 1) are symbolized jointly as one step. The vessels are connected through output and input from top on downwards. Exept from the beginning (left hand side) and from the top of the system the vessels receive their input from the next higher vessel and from the preceding step. Each vessel can receive additional input from outside.*

Table 1: **A classification of reaction velocities** *sometimes enables the use of equilibrium models where overall thermodynamic equilibrium is not attained.*

reaction speed	model assumptions
high	equilibrium
medium	unknown
low	kinetics defined via input or output
very low	ignored

totically). In a consecutive batch experiment (fig. 1) the description of this experiment as a sequence of equilibrium states is only valid, if the time allowed for "equilibration" is long enough for the equilibria to be reached. If a certain time interval is fixed we may say such a description is valid only for reactions which are quick enough. The classification of a reaction as quick enough will not only depend on the time interval but also on the changes in total component concentrations brought about by "input" and "output". A larger change will need a longer time for the new equilibrium to be attained.

In any real system there may be possible chemical reactions of quite different speeds. It is often found helpful [14] to classify these as shown in table 1.

Such classification helps in setting up a strategy of using an equilibrium model even if some reactions in the system are known to be not at equilibrium. We can give some possible examples here but the success of such strategy has to be judged for specific cases against empirical evidence.

A *very low* reaction speed may be assumed for the microbial oxidation of an organic ligand in a laboratory system, provided the growth of organisms has been excluded. In this case it is valid to study the equilibrium of complexation reactions of this ligand, ignoring the fact that the overall equilibrium is on the side of carbondioxide and water for the oxidation of the ligand.

The kinetics of a *low* velocity reaction sometimes may be simple enough to be included explicitly in the "input" or "output" specification of a consecutive batch experiment. This seems to be the case if the reaction velocity is independent of the concentrations in the system itself. This case is called a *zero order* reaction. This is often assumed for the silicate weathering reaction in soil systems. This reaction is taken into account simply as input flux.

The class of *medium* velocity reactions should be empty: For each reaction it must be decided whether it is quick enough to be treated as being at equilibrium or whether a kinetic description can be included into the model. In soils the formation of secondary minerals are possible *medium* velocity reactions

Among the *high* speed reactions for which the assumption of equilibrium is a good approximation are often homogeneous ionic reactions, that is complexation and acid/base reactions in aqueous solution. Also cation exchange seems to be near equilibrium in many systems.

2.3.2 Transport

The concept of equilibrium demands that all (net) transport processes within the system cease and therefore all concentrations at all points are constant at equilibrium. A real system may be closer to this concept if it is stirred or shaken. With soils, a suspension with an excess of solution over solid is more likely to be at equilibrium than a structured, aggregated soil.

One can try to use the batch equilibrium concept also for systems where continuous transport processes are going on. In this case the transport effect is included in the "output" and "input" operations of consecutive batch experiments (fig. 1). This idea is similar to the treatment of low speed reactions (table 1) as explained above. In the dimension of time this would mean to identify a consecutive batch experiment, which is composed of discrete operations (fig. 1), with a system where a continuous flow of solution moves through a reaction vessel. In this case one is free to choose a discrete *time step*.

If transport processes develop in space, e.g. in the porous medium soil, one can also try to identify such a process with a chain of consecutive batch experiments, that is with a batch cascade (fig. 2). So far with BEM, this is only possible for one–dimensional transport. In this case a *space step* can be chosen.

If we compare this approach with the convection–dispersion differential equation for transport in porous media [4, 8] we see that we have ignored the dispersion part of the equation (pure piston flow). It is not to be expected that this scheme will give very accurate descriptions of transport processes. The advantage of using BEM for continuous processes can only lie in the flexibility of the chemical part of the model. There are examples for the combination of a numerical solution for the transport differential equation with an equilibrium approach to chemical reactions [8], but these models are more restricted in the kind of chemistry they can handle.

2.3.3 Activity coefficients

For ions in aqueous solution we already have introduced the activity coefficient γ in eqs. 3, 7 and 8. The Debye–Hückel theory and its semi–empirical extensions can predict these activity coefficients with remarkable success. In BEM the *Davies equation* is used which is believed to be valid for salinities at least up to the level of sea water [15, 16]. There is no doubt that the chemical potential in the bulk solution can be described by a theory for electrolyte solutions — if it is clearly enough seperated from the solid phases which may be present in the system. So called suspension effects may put the validity of a model for aqueous solutions into question in the vicinity of solids.

For solubility equilibria we have made a stringent restriction: Solid salts in equilibrium with the solution are assumed to be of constant and known composition and internal structure. This then leads to the simple equations 9 and 10. But this simplicity is by no means granted for real world systems like soils. More realistic would be to allow for the formation of *solid solutions* [2, 16]. Unfortunately there is no tested *general* theory for the chemical potential of components in solid solutions comparable to the Debye–Hückel theory. The validity of the simplistic approach used in BEM can be studied by calculating the ion activity product IAP in natural or experimental solutions believed to be in equilibrium with the minerals in question [12].

Our treatment of cation exchange in eqs. 12 and 13 is equally simplistic. We assume the cation exchanger to be an ideal solution of cation equivalents and we do not introduce activity coefficients as amendments in this concept (cf. [3, 15]) because, again, there is no *general* theory for the calculation of the latter. In other words, we take our *selectivity coefficients* as constants while in many studies it has been shown that they depend on the exchanger composition [2, 15]. This means, on the other hand, that BEM can give more realistic results where the composition of the exchanger does not change too much.

2.3.4 Chemical structure

We have introduced the structure of a batch equilibrium model as being defined by a list of *components* and of *compounds* together with *thermodynamic equilibrium constants* for the formation of the latter from the former ones.

If any components are already chosen the selection of the compounds and of additional components is, of course, not arbitrary. It is necessary to include all compounds whose formation (or disintegration) will influence any of the components in reality and within given limits of precision. Additional components must be included if they are needed in the formation reaction of that compounds. Reactions which have been placed in the categories of *low* or *very low* reaction velocities (section 2.3.1) must not be included in the model structure.

The choice of thermodynamic equilibrium constants is a crucial one for any chemical equilibrium model. [16] includes a short list of standard reference tabulations. For soil science [9] is a convenient source of data. For BEM use can be made of the parameter data files for the program WAKO [12] which has an almost identical format as needed for BEM and is available at the same computer installation.

Difficulties arise with minerals which may form slowly. In this case different solubility product constants will be reported for the *amorphous* modification which is formed quicker and for *cristalline* forms which will be formed instead of the amorphous ones after longer periods of time. Any further *cristal modifications* will have also different thermodynamic constants in general. If *solid solutions* are formed (see last section) it may be that for different mixture states different solubility product constants are used.

There are hundreds of studies on the cation exchange equilibria of soils or soil materials [6], most of them on purified soil materials where only two cations are involved. It is not clear whether the results from this existing work can be transfered to programs like BEM, where a prediction of exchange behaviour is sought. The *exchange selectivity coefficients* are at present best treated as *free parameters* in a data fitting procedure of BEM output against evidence from suitable experiments.

3 Specifications

3.1 Special components and limitations

3.1.1 Water and electroneutrality

From the general definitions of *elementary components* and of *compounds* (section 2.2) one would expect the ions H^+ and OH^- to be components and water, H_2O, to be a compound in aqueous solutions. But in BEM these are exceptions to the general rule: H^+ and OH^- are treated as components but they do not have a *total concentration* as a model parameter attached to them. The reasons for this are

1. In making up an electrolyte solution from its ionic components the total concentrations of the components must obey the rule of *electroneutrality*: the sums of positive and negative charges must cancel each other. If there are n ionic components you need only $n-1$ to calculate the last one. In BEM H^+ has been chosen to be this last one.

2. The concentration of water usually is assumed to be constant in aqueous solutions. BEM adopts this convention and does not treat H_2O as compound formed from H^+ and OH^-. From this assumption it follows that the activity of OH^- can be directly calculated from the activity of H^+ via the *ionic product of water*. This makes the introduction of OH^- as a component unneccessary.

In both cases the introduction of an additional condition leads to the canceling of an independent model parameter. Without such regulations there would be too many degrees of freedom in the model. The present rule means that each electrolyte solution which is defined as an input to a BEM model is implicitly complemented to electroneutrality with either H^+ or OH^-. So "1 mol sulfate" (without accompanying cation) means "1 mol sulfuric acid" and "1 mol sodium" (without anion) means "1 mol sodiumhydroxide".

3.1.2 Carbondioxide and other gases

In general, a gas phase is not considered in BEM. In systems without a gas phase there can exist the *component* CO_3^{2-} with its *compounds* HCO_3^- and H_2CO_3. In this case there must be given a *total component concentration* for CO_3^{2-} (which means for carbonic acid in all its forms). But often it is more realistic to allow for the passage of carbondioxide between the aqueous solution and a neighbouring gas phase. It is possible in BEM to specify a *partial pressure of carbondioxide*, P_{CO_2}, assumed to be in equilibrium with the solution. The introduction of CO_3^{2-} as a component is a neccessary consequence but there can not be a specification of a total concentration for this component at the same time.

3.1.3 Redox and temperature

BEM has not been prepared to handle redox reactions.

The effect of temperature is not included in BEM. But it is possible to use sets of thermodynamic constants for other temperatures than the usual 25 °C. The only influence of temperature which is fixed in the structure of BEM is the coefficient in the Davies equation. But the variation of this parameter between 0 and 30 °C [15] seems to be negligable.

3.2 The defining equations

This section gives a complete definition of BEM in the language of mathematical equations.

The structure of a batch equilibrium model is defined by sets of *components* and *compounds* while the single equilibrium within such structure is determined by *total component concentrations.*

Let $\mathbf{E}$ be the set of components. Let $\mathbf{E^t}$ be the set of those components for which total concentrations must be specified. Let other components be called *special components* and let $\mathbf{E}^*$ be the set of special components. $\mathbf{E}^*$ will always include H^+ and OH^-

and also CO_3^{2-}, if P_{CO_2} is specified. Some components will be cationic. Let the set of these be $\mathbf{E}^+$. We then have the relations

$$\mathbf{E}^+ \subset \mathbf{E}\,, \qquad \mathbf{E}^* \cap \mathbf{E^t} = \emptyset\,, \qquad \mathbf{E^t} \cup \mathbf{E}^* = \mathbf{E}$$

Let the set of those compounds which are present in the solution phase be $\mathbf{L}$ and let the set of salts which may be present in the system be $\mathbf{S}$. The stoichiometry of the compounds can be defined by matrices

$$(l_{ij})_{\substack{i\in\mathbf{E}\\ j\in\mathbf{L}}} \qquad \text{and} \qquad (s_{ik})_{\substack{i\in\mathbf{E}\\ k\in\mathbf{S}}}$$

As units for concentrations we choose $\boxed{\text{mol / L (solution)}}$ It is possible to express also the amounts of salts and exchangeable ions relative to a unit volume of solution as long as the ratio of solid phase to aqueous solution is known.

For exchangeable cations we use the symbol c_i^x for the concentration of exchangeable component i in mol (i) / L (solution).

We now can write the general component balance for all $i \in \mathbf{E^t}$:

$$t_i = c_i + \sum_{j\in\mathbf{L}} l_{ij} c_j + \sum_{k\in\mathbf{S}} s_{ik} c_k + c_i^x \tag{15}$$

where t_i are the total component concentrations and

$$c_i^x = 0 \qquad \text{for} \qquad i \notin \mathbf{E}^+$$

We assume that all cationic components compete for the cation exchanger, if that phase is present. We exclude all compounds (e.g. complexes) from the exchanger. The cation exchange capacity is denoted by t_x and has the dimension of mol (equivalents) / L (solution). Let z_i denote the charge of component i. We then have

$$t_x = \sum_{i\in\mathbf{E}^+} c_i^x z_i \tag{16}$$

The charge of a compound in solution ($j \in \mathbf{L}$) is given by

$$z_j = \sum_{i\in\mathbf{E}} l_{ij} z_i$$

Let $\mathbf{U}$ be the set of all species in solution

$$\mathbf{U} = \mathbf{E} \cup \mathbf{L}$$

The ionic strength of the solution then is defined as

$$I = \frac{1}{2} \sum_{m \in \mathbf{U}} z_m^2 \, c_m$$

The acitivity coefficents (γ_m) for all species in solution ($m \in \mathbf{U}$) are then defined by the Davies equation [15, 16]

$$\log_{10} \gamma_m = -0.5 \, z_m^2 \, \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \, I\right) \tag{17}$$

The law of mass action (cf. eqs. 7, 8) yields for all soluble compounds ($j \in \mathbf{L}$)

$$K_j = \frac{\prod_{i \in \mathbf{E}} (c_i \gamma_i)^{l_{ij}}}{c_j \gamma_j} \tag{18}$$

While concentrations of possible chemical species in solution never become zero, salts can be either present or not present in the equilibrium system. If they are not present the solution must be undersaturated with respect to the salt. We first define the *ion activity product* for a salt $k \in \mathbf{S}$:

$$Q_k = \prod_{i \in \mathbf{E}} (c_i \gamma_i)^{s_{ik}}$$

For Q_k we then have the following set of conditions (cf. eq. 10)

$$\left.\begin{array}{l} \big(Q_k < K_k^{sp} \quad \text{and} \quad c_k = 0\big) \\ \text{or} \\ \big(Q_k = K_k^{sp} \quad \text{and} \quad c_k > 0\big) \end{array}\right\} \tag{19}$$

The upper line corresponds to undersaturation and the lower line corresponds to saturation for salt k.

To prepare the treatment of cation exchange equilibria we define the saturation fraction x_i for each cation ($i \in \mathbf{E}^+$) by

$$x_i = \frac{c_i^x \, z_i}{t_x}$$

We single out the cation H^+ which is present in each BEM model as a common reference cation. The user then may choose between two equilibrium equations ($i \in \mathbf{E}^+$, $i \neq H^+$):

$$K_i^{sel} = \frac{(c_i \gamma_i)^{1/z_i} \; x_{H^+}}{c_{H^+} \gamma_{H^+} \; {x_i}^{1/z_i}} \tag{20}$$

$$K_i^{Gapon} = \frac{(c_i \gamma_i)^{1/z_i} \; x_{H^+}}{c_{H^+} \gamma_{H^+} \; x_i} \tag{21}$$

The choice of either eq. 20 or 21 can only be made once in a model structure for all cations.

As mentioned earlier the charged species in an aqueous solution must obey the electroneutrality rule:

$$0 = \sum_{m \in \mathbf{U}} z_m c_m \tag{22}$$

The concentrations of H^+ and OH^- in aqueous solutions are coupled by the ion product equation for water:

$$K_W = c_{H^+} \gamma_{H^+} \, c_{OH^-} \gamma_{OH^-} \tag{23}$$

If P_{CO_2} is specified we must include the following definitions:

$$CO_3^{2-} \in \mathbf{E}^* , \quad HCO_3^- \in \mathbf{L} , \quad H_2CO_3 \in \mathbf{L}$$

and we get one additional equation:

$$K_H \, P_{CO_2} = c_{H_2CO_3} \tag{24}$$

where K_H is the Henry constant for CO_2.

This equation completes the definition of BEM.

3.3 The numerical task

The equations of the preceding section form a system which implicitly defines the equilibrium state of the model. We will outline the structure of this system of equations in short. For the sake of clarity let us assume that P_{CO_2} is *not* specified and that cation exchange is described by *selectivity* coefficients. Let us use the same symbols as in the preceding section.

The model structure is defined by matrices (l_{ij}) and (s_{ik}). The elements of these matrices are clearly known parameters. The equilibrium constants K_j, K_k^{sp}, K_i^{sel} and K_W are also part of the model structure and therefore known parameters. Further, the *total* concentration t_x and t_i are known parameters. The t_i may change between different equilibria in a consecutive batch experiment.

The *single* concentrations (c_i, c_j, c_k and c_i^x) are unknowns. The task is to find a set of non–negative numbers for these concentrations that complies with eqns. 15 – 20 and 22 – 23.

At present BEM uses an optimization procedure that is based on the aggregation of all equations into one sum of squared residues and searching the minimum of this sum of squares by a modified NEWTON method [10].

3.4 The BEM model file

The user of BEM has to prepare a file, called the model file, that contains all definitions and technical information for a particular model. The specifications for a possible consecutive batch experiment (fig. 1) are also included in that file. (If a batch cascade (fig. 2) is to be calculated one model file has to be prepared for each layer.)

For the purpose of the present introduction we will stress those chemical definitions which make up the model proper and determine the outcome of the calculations. Technical information which has no influence on the calculated equilibria (but may change the speed of convergence) will be only mentioned in passing and will be marked by small print .

The program BEM in a first step performs the numerical calculation of the equilibrium or the equilibria demanded by the model file. The results are stored in an internal format and any output in tabular or graphical form is produced in further steps. Therefore no options for output formats are found in model files.

In the following we will use `typescript` as indication of text which has to be included exactly in that lettering into the model file. In describing the model file we will further use *italics* as indication of symbolic variables, that are places where some text has to be filled in.

Each line in the model file starts with a header that identifies the line. We will refer to types of of lines by the name of the header: if the header is `xyz` we call such a line a `xyz`–line. Table 2 lists all possible line types.

3.4.1 Defining the chemical structure

Cations are specified as components by `cat`–lines which have the format

`cat` *name* *charge*

Anions or uncharged components are specified by `ani`–lines which have the format

`ani` *name* *charge*

The charge on `ani`–lines is given as absolute value. The `cat`– and `ani`–lines together define the set $\mathbf{E^t}$ (section 3.2). The *names* can be chosen freely.

Examples:

```
cat   Al    3
ani   Citro   3
```

The ions H^+ and OH^- are defined automatically with *names* `H` and `OH` and must not be specified on `cat`– or `ani`–lines.

Compounds in solution are defined on `cpl`–lines which have the format

Table 2: **Syntax overview for model files.** *The lines which may be used in BEM model files with pages where these lines are introduced.*

line definition	page
`*` *comment*	32
`ani` *name* *charge*	24
`cat` *name* *charge*	24
`cec` `typ:`eqn $cat_1 : pK_1$ $cat_2 : pK_2$ $\cdots$ $cat_n : pK_n$	26
`cex` $cat_1 : val_1$ $cat_2 : val_2$ $\cdots$	34
`co2` pK_H pK_1 pK_2	27
`cpl` $(e_1)l_1(e_2)l_2\cdots(e_n)l_n$ $pK\text{–}value$	26
`ctin` $elt_1 : val_1$ $elt_2 : val_2$ $\cdots$	30
`ctl0` $elt_1 : val_1$ $elt_2 : val_2$ $\cdots$	28
`end`	32
`estcon` $elt_1 : con_1$ $elt_2 : con_2$ $\cdots$	32
`estslt` $slt_1 : cst_1$ $slt_2 : cst_2$ $\cdots$	32
`exp` `nrep:`$rpts$ `flow:`$chgvol$ `volinp:`$inpvol$	30
`pkw` pK_W	27
`plus` $elt_1 : val_1$ $elt_2 : val_2$ $\cdots$	31
`run` `relerr:`err `trace:`trc `tracun:`iou	33
`run` `maxit1:`$mx1$ `maxit2:`$mx2$	33
`slt` $(e_1)s_1(e_2)s_2\cdots(e_n)s_n$ $pK\text{–}value$	26
`vls` `cec:`$value$	29
`vls` `estph:`ph `estxsh:`xH `eststr:`I	32
`vls` `pco2:`$value$	29
`vls` `ssr:`$value$	29
`wptslt` $slt_1 : val_1$ $slt_2 : val_2$ $\cdots$	33

`cpl` $(e_1)l_1(e_2)l_2\cdots(e_n)l_n$ $pK\text{–}value$

for a compound that contains n different components e_ν. The l_ν are the stoichiometric coefficients. If the value is 1, it may be omitted. $pK\text{–}value$ is defined as $-\log_{10} K$, where K is the equilibrium constant (eqs. 7, 8, 18) for the complete dissociation reaction of the compound into the components.

Examples:

```
cpl     (Al)(Citro)     9.33
cpl     (H)2(PO4)     17.53
cpl     (X)3(Y)4(Z)5     123.
```

The definition of salts which are defined as possible parts of the equilibrium system is similar:

`slt` $(e_1)s_1(e_2)s_2\cdots(e_n)s_n$ $pK\text{–}value$

defines a salt with n different components e_ν and stoichiometric coefficients s_ν. The $pK\text{–}value$ in this case is $-\log_{10} K^{sp}$ where K^{sp} is the solubility product constant (eqns. 10, 19)for the salt.

Example:

```
slt     (K)(Al)3(SO4)2(OH)6     85.6
```

defines alunite.

The presence of a cation exchanger in the system is indicated by a `cec`–line:

`cec` `typ:`eqn $cat_1 : pK_1$ $cat_2 : pK_2$ $\cdots$ $cat_n : pK_n$

The variable eqn has to take either of the values `sel` or `gap`. It decides which of the two forms of cation exhange equations (eqns. 13/20 or 14/21) is used. The list of n cations cat_ν must include all cationic elementary components of the model, except H^+. The pK_ν are $-\log_{10} K_\nu$, where K_ν is either of the two exchange equilibrium constants.

Example:

```
cec      typ:sel   Ca:0   K:0
```

defines a cation exchanger in a system with cations `Ca`, `K` and `H` which follows the selectivity coefficient equation and has no preference for any of the three cations ($K_\nu^{sel} = 1$).

If the specification of a partial pressure for CO_2 is to be part of the model structure, this has to be indicated by a `co2`–line:

`co2` $\quad pK_H \quad pK_1 \quad pK_2$

where pK_H is the Henry constant for CO_2 (eqn. 24). pK_1 and pK_2 are the negative decadic logarithms of the first and second acidity constant of carbonic acid.

```
co2      1.5   6.4   10.3
```

are the usual values for 25 °C.

It is possible to specify the ion product constant of water by

`pkw` $\quad pK_W$

This line is only necessary if the temperature differs from 25 °C. For that standard temperature

```
pkw      14
```

is already included by default.

3.4.2 Specifying the total concentrations

If the system contains different phases (if salts or a cation exchanger are defined) the specification of the total component concentrations t_i (eqn. 15) can be made through the different phases seperatly in whatever way is more convenient. For the purpose of this specification the phases are thought to be seperate, not in equilibrium with each other. One can imagine the phases as seperate materials on the laboratory desk, without contact. The amount or, in the case of the cation exchanger, the composition, of these phases will determine the total concentrations also in the equilibrium system. The composition of the solution "before equilibration" is specified by

`ctl0` $elt_1 : val_1 \quad elt_2 : val_2 \quad \cdots$

where the elt_ν are members of the set $\mathbf{E^t}$ as defined on `cat`– and `ani`–lines. The val_ν are concentrations in

$$\mu\text{mol/ L} .$$

The amounts of salts "before equilibration" are specified as

`cslt0` $salt_1 : val_1 \quad salt_2 : val_2 \quad \cdots$

where the $salt_\nu$ are salts as defined on `slt`–lines and the val_ν are concentrations in

$$\text{mmol (salt) / kg (solid material)} .$$

The composition of a cation exchanger "before equilibration" is specified by

`xs0` $cat_1 : val_1 \quad cat_2 : val_2 \quad \cdots$

where the cat_ν are cations defined on `cat`–lines and the val_ν are saturation fractions (x_i as defined above). In the following example

```
vls    ssr:1    cec:10     pco2:0.35
ctl0   Na:100   Ca:100     Cl:300
cslt0 (Ca)(CO3):3
xs0    Na:1
```

total concentrations are defined for Na as 100 μmol/L plus 10000 μmol at the exchanger which is introduced as Na–saturated "before equilibration". (There is an exchange capacity of 10 mmol/kg at a soil/solution ratio of 1 kg/L.) For Ca we have 100 μmol plus

3000 μmol in the form of calciumcarbonate. For Cl there is 300 μmol in solution. The partial pressure of CO_2 is specified as near the present atmospheric value. A definition of the total components as a hypothetical solution would be equivalent:

```
ctl0     Na:10100   Ca:3100   Cl:300
```

if the above `cslt0`– and `xs0`–line were omitted.

Some further specifications are made on `vls`–lines. These lines can assemble different items, but here we treat one item at a time:

The ratio of solid material to solution is specified by

`vls` `ssr:`*value*

where *value* has the unit of

kg / L .

The exchange capacity of a cation exchanger is given by

`vls` `cec:`*value*

where *value* has the unit of

mmol (p^+) / kg (solid material) .

A partial pressure of CO_2 is specified by

`vls` `pco2:`*value*

where *value* has the unit

mbar .

We now have described all specifications which are necessary to define any single chemical equilibrium that can be handled in BEM.

3.4.3 Arranging equilibria in series

In section 2.2 we have introduced *titrations, consecutive batch experiments* and *batch cascades*.

Titrations and consecutive batch experiments are defined by groups of lines, starting with an `exp`–line and followed by `ctin`–lines. There may be several of these groups of lines in sequence.

`exp` `nrep:`*rpts* `flow:`*chgvol* `volinp:`*inpvol*

where *rpts* says how often this instruction is to be repeated. *chgvol* defines a consecutive batch experiment where in each step the fraction *chgvol* is exchanged (fig. 1. The unit of *chgvol* is

L / L .

For titrations *inpvol* defines the volume of titrant added in each step in

mL / L (original volume) .

The concentrations in the input solution of either experiment are specified as

`ctin` $elt_1 : val_1 \quad elt_2 : val_2 \quad \cdots$

where elt_ν is one of the components defined on `cat`– or `ani`–lines and val_ν is the concentration in

μmol/L .

If these concentrations change during the course of the experiment a new specification has to be started with an `exp`–line again.

Examples:

```
exp     nrep:5   flow:0.5
ctin     Na:1000   Cl:1000
exp     nrep:5   flow:0.5
ctin     Ca:500   Cl:1000
```

describes a consecutive batch experiment where half the solution of the system is replaced first 5 times by a 1 mmol/L sodium chloride solution and then 5 times by an equivalent calcium chloride solution.

```
exp     nrep:25   volinp:10
ctin     SO4:0.5e6
```

defines a titration where 1 sufuric acid ($0.5\,10^6$ μmol of sulfate without accompanying cation) is added in each of 25 steps.

A batch cascade is a chain of consecutive batch experiments (fig. 2). For each of these a seperate *model file* has to be prepared. The first layer (starting batch vessel) has to have the full set of definitions for a consecutive batch experiment, including the `exp`– and `ctin`–lines. In the following layers (vessels) these lines can be omitted. The linkage between the layers is defined in a special file, the *linkinfo* file. This file contains at least two lines for each link between layers:

```
exp   flow:chgvol
end
```

where *chgvol* has the same meaning as above. *chgvol* refers to the *receiving* layer. It may differ from layer to layer, if the volume of solution present is different between layers, while the volume transported is equal. The concentrations in the transported solution are results of the calculation of equilibria in the preceding layer of the batch cascade. But it is possible to specify a so called *source function*. This is an input of chemical components to the layer, that is additional to the output from the preceding one. In fig. 2 these special inputs have been indicated by the short vertical pipes. This input function is invoked by including `plus`–lines following the `exp`–lines in the linkinfo file.

`plus` $\quad elt_1 : val_1 \quad elt_2 : val_2 \quad \cdots$

where elt_ν and val_ν have the same meaning and units as on `ctin`–lines.

```
exp     flow:0.9
plus     Na:40
end
```

would define the transfer between two layers where 90 % of the volume of the lower layer would be exchanged in each step and an additional input of 40 μmol/L of sodium would be assumed in the input to the lower layer.

3.4.4 Miscellaneous and technical elements

The *model files* may and indeed must contain some informations which do not influence the outcome of the calculations in the end. The reader who wants only to deal with the assumptions and the results of BEM may ignore these elements.

Lines starting with an asterix are *comments* and are ignored by BEM

> * *comment*

The model files have to be structured into 3 sections, each ended by

```
end
```

The first section contains the chemical structure definitions, the second one contains all concentrations needed to define the first equilibrium, the third one defines titrations or consecutive batch experiments. The third one may be empty.

It is very important to have a resonable guess for many of the unknown concentrations as a starting point for the numerical procedure. The format of these specifications is

> **vls** **estph:**ph **estxsh:**xH **eststr:**I
> **estcon** $elt_1 : con_1$ $elt_2 : con_2$ $\cdots$
> **estslt** $slt_1 : cst_1$ $slt_2 : cst_2$ $\cdots$

where ph stands for pH, xH for the saturation fraction of H^+, I for the ionic strength, con_ν for the concentrations of the single components and cst_ν for the amount of a salt in the (first) equilibrium state. These estimates must only be supplied for the first equilibrium if a consecutive batch experiment or titration is performed.

There is alternative method for the specification of estimates which uses intervals instead of single numbers. The intervals are specified as pairs of number in () brackets. Example:

```
vls     estph:(3,7)
```

A specification of an interval for any one estimate invokes an improved search algorithm for the starting point, which is often much simpler to use than the standard method.

Another estimate has to be supplied for the solubility of the salts. This has to be an order of magnitude estimate that indicates to BEM what concentrations in solution are to be expected for the components of a salt. It is called the working point for the salt.

`wptslt` $slt_1 : val_1 \quad slt_2 : val_2 \quad \cdots$

where val_ν has the unit of

$$\mu\text{mol} \ / \ \text{L} \ .$$

The behaviour of the program can be influenced by specifications on `run`–lines.

`run` `relerr:`err `trace:`trc `tracun:`iou
`run` `maxit1:`$mx1$ `maxit2:`$mx2$

The number err specifies a relative error as criterion for convergence. Care is necessary if this is set to a much higher value than the default which is 10^{-6}. trc and iou are parameters that influence the output from BEM during the numerical procedure. This output is mainly for diagnostic purposes while the interpretation of BEM results is performed by different steps after completion of the numerical task. $mx1$ and $mx2$ influence the performance of the numerical procedures.

There is a special form of BEM which facilitates sensitivity tests: If braces {} are used in a model file, this means that BEM has to be called once for each of the items in the braces. Example:

```
cpl     (Al)(Citro)    {8 10 12}
```

would have three versions of the model file executed, with stability constants (pK) for the Al–Citro complex of 8, 10 and 12 respectively. The output from all three runs would be available for comparative representation.

3.4.5 Indirect specification of selectivity coefficients

Instead of specifying the equilibrium constants K^{sel} or K^{Gapon} as numbers one can specify the right hand sides of eqn. 20 or 21 respectively. We go one step further and do not specify the x_i but rather the c_i^x, thereby implicitly defining the cation exchange capacity t_x also.

This method is invoked by a `cex`–line:

`cex` $cat_1 : val_1 \quad cat_2 : val_2 \quad \cdots$

where the val_ν have units of

mmol (p^+) / kg (solid material) .

These specifications are not only used for the definition of cation exchange selectivity constants but also replace the `xs0`–line and the `cec`–specification in defining the total component concentrations for the (first) equilibrium state.

The concentrations in solution and the activity coefficients which appear on the right hand sides of eqns. 20 and 21 are taken from the estimates I, pH and val_ν in

`vls` `eststr:`I `estph:`pH
`estcon` $elt_1 : val_1 \quad elt_2 : val_2 \quad \cdots$

The specifications $cat_\nu : pK_\nu$, `cec:`$value$ and `estxsh:`$value$ on `cec`– and `vls`–lines respectiively and all `xs0`–lines have to be omitted if this method is used.

By this method it is possible to start with a system that does not contain a cation exchanger, make sure that the `est`–values really reflect the composition of the first equilibrium, and then to add a cation exchanger to the system which is by definition already in equilibrium with the specified solution.

3.5 State and availability of the program

The program BEM is at present in update level 3.1 . It is implemented at the computer center of the University of Göttingen on an IBM 3090 computer under VM/CMS. It is a FORTRAN program that has a framework of REXX procedures built arround it. E.g., the organization of batch cascades is mainly written in REXX. (REXX is a command execution language for the operating system VM/CMS). The tabular output makes use of the editor XEDIT. Graphical output is based on this institutes graphical software UNIPLOT.

BEM may be used with the authors consent for scientific purposes at the Göttingen University computing center free of charge.

4 Examples

4.1 Titration of $AlCl_3$ with NaOH in the presence of an organic ligand

An experiment like this may be used to study the stability of an organic aluminum complex. We suppose that the acidity constants of the organic ligand are known and we assume that only the 1–1 complex is formed. The observed parameter in this experiment would be the pH as it increases with hydroxide addition.

4.1.1 Model definition

The *model file* for this example reads:

```
************ The titration model file
cat Na 1
cat Al 3
ani Lig 3
ani Cl  1
cpl (Al)(OH)       9.03
cpl (Al)(OH)2      18.7
cpl (Al)(OH)3      27.0
cpl (Al)(OH)4      33.0
cpl (Al)2(OH)2     20.3
cpl (Al)3(OH)4     42.06
cpl (Al)13(OH)32   349.27
cpl (Lig)(H)     7
cpl (Lig)(H)2   12
cpl (Lig)(H)3   15
cpl (Lig)(Al)      {8 9 10}
slt (Al)(OH)3   33.
end
ctl0 Na:1    Lig:1000   Al:1000   Cl:3001
vls  estph:3.5   eststr:8000
estcon Na:1  Al:829  Lig:.1e-2   Cl:3001
estslt  (Al)(OH)3:0
```

```
wptslt  (Al)(OH)3:1000
end
exp  nrep:40  volinp:10
ctin Na:10000
end
```

The file starts with a `*`–line as heading. `cat`– and `ani`–lines define Na^+, Al^{3+} and Cl^- as components of the system. The organic ligand is introduced as anion Lig^{3-}.

The next seven lines define hydroxo–complexes of aluminum. This is the set of such complexes that has been published by BAES & MESMER [1, 12].

The next three `cpl`–lines define the acidity of the ligand. The pK values on `cpl`–lines have to be specified for the *complete dissociation* reaction of the complex. In this example the hypothetical ligand has pK^s values of 3, 5 and 7 respectively.

$$\begin{array}{lclcll} \mathrm{LigH_3} & \rightleftharpoons & \mathrm{LigH_2^-} & + & \mathrm{H^+} & ; \quad pK_1^s = 3 \\ \mathrm{LigH_2^-} & \rightleftharpoons & \mathrm{LigH^{2-}} & + & \mathrm{H^+} & ; \quad pK_2^s = 5 \\ \mathrm{LigH^{2-}} & \rightleftharpoons & \mathrm{Lig^{3-}} & + & \mathrm{H^+} & ; \quad pK_3^s = 7 \end{array}$$

For the model definition in BEM we can accept only the last reaction and pK_3^s without change. For the complete dissociation of $LigH_2^-$ and $LigH_3$ we have to combine the lower two or all three reactions respecitively. With combining the reactions chemically the pK values have to be added algebraically. The values in the model file are therefore 12 and 15 for $LigH_2^-$ and $LigH_3$ respectively.

The last `cpl`–line defines the 1–1 complex between aluminum and the ligand. Braces {`8 9 10`} indicate that three variants of the model have to be run in sequence with values of 8, 9 and 10 respectively for the pK value of this complex.

The next line is a `slt`–line that introduces a salt with the formula of gibbsite as possible solid in the equilibrium system. The pK^{sp} value of 33 lies between values for amorphous and cristalline aluminumtrihydroxide [9].

An `end`–line concludes the definition of the chemical structure.

The total component concentrations for the first equilibrium are given as concentrations in solution on the `ctl0`–line. This solution is composed of 1 mmol/L of aluminumchloride, 1 mmol/L of ligand as $LigH_3$ and 1 μmol/L of sodiumchloride. The latter is necessary only because BEM does not accept total concentrations of zero for any of the components defined in the model.

The following four lines (`vls`–, `estcon`–, `estslt` and `wptslt`–line) carry technical parameters which do not belong to the model definition proper (cf. section 3.4.4). An `end`–line concludes this section of the model file.

The titration experiment is defined next. The `exp`–line specifies 40 steps. In each step a volume equal to 1 % (10 mL / L) of the original solution volume is added. The `ctin`–line says that the titration solution contains 10 mmol/L of sodium ions. Because no anion is defined this means a solution of 10 mmol/L of sodiumhydroxide. The third `end`–line concludes the model file.

4.1.2 Results

In this model a relatively high stability of the organic complex has a twofold influence on pH: (i) it furthers the deprotonation of the organic acid (lower pH) and (ii) it hinders the hydroxilation of Al^{3+} (higher pH). Either mechanism dominates in different ranges of the titration.

The calculated pH values are shown in fig. 3. At about step 25 the precipitation of aluminumhydroxide starts in the pK=8 case and the other cases follow suit. From this point on, the calculation is presumably far from the real experiment because the precipitation reaction in reality takes a long time to come to equilibrium.

But if we interpret only the first 20 steps, one may find a suitable method here for the indirect determination of stability constants for aluminum–organo–complexes.

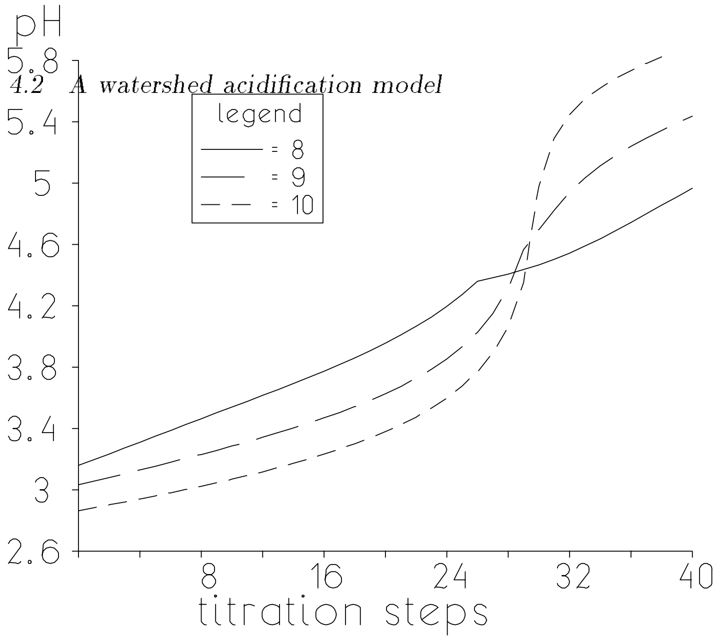

Figure 3: **Titration model.** *A solution of 1 mmol/L aluminum-chloride and 1 mmol/L of an organic acid is titrated with sodium hydroxide. A 1–1 complex between the organic acid and aluminum is assumed with stability pK values of 8, 9 and 10 respectively. The calculated pH is shown for each variant.*

4.2 A watershed acidification model

Acid deposition can change the state of a soil because the soil materials react with acids. We assume the soil to contain calciumcarbonate, a cation exchanger and aluminumhydroxide (as a product of silicate weathering). According to the theory of buffer ranges [17, 11] these materials will react one after another in the order mentioned above with the incoming acidity. We distinguish a topsoil , a subsoil that has no calciumcarbonate at the beginning and a creek which receives the percolating water. This arrangement leads itself to the form of a BEM *batch cascade*.

Let us assume for the sake of simplicity that the only relevant neutral cation in the system is Ca^{2+}. It may represent to a certain degree also Na^+, K^+ and Mg^{2+}. Let us also assume the Cl^- is the only relevant neutral anion, that means that HCl is the only relevant strong acid.

4.2.1 Model definition

We have to define three different *model files* for topsoil, subsoil and creek respectively. The one for the topsoil reads:

```
**************** The topsoil model file
cat Ca 2
cat Al 3
ani Cl 1
co2 1.4  6.4  10.3
cpl (Al)(OH)       9.03
cpl (Al)(OH)2      18.7
cpl (Al)(OH)3      27.0
cpl (Al)(OH)4      33.0
cpl (Al)2(OH)2     20.3
cpl (Al)3(OH)4     42.06
cpl (Al)13(OH)32   349.27
slt (Ca)(CO3)  8.3
slt (Al)(OH)3  33.
cec typ:sel Ca:-2.   Al:-1.0
end
vls   cec:100   ssr:0.6    pco2:8
ctl0 Ca:400   Al:1 Cl:3
xs0 Ca:1.0 Al:0
cslt0 (Ca)(CO3):90    (Al)(OH)3:100.
vls   estph:7.5   eststr:1600  estxsh:.69e-5
estcon Ca:1210 Al:.15e-7  CO3:6.92 Cl:1
estslt (Ca)(CO3):100000     (Al)(OH)3:1000
wptslt (Ca)(CO3):100000     (Al)(OH)3:1000
end
exp nrep:300 flow:1
ctin Ca:180   Cl:1300
end
```

After a `*`–line as heading the ions Ca^{2+}, Al^{3+} and Cl^- are defined as model components. The `co2`–line defines CO_3^{2-}. The following complex definitions are the same as in section 4.1.1 above.

The two `slt`–lines define calciumcarbonate and aluminumhydroxide. The pK^{sp} values are literature values for 25°C [9, 12, 5].

The `cec`–line specifies that the cation exchanger is described by *selectivity coefficient equations* in this model. The selectivity coefficients used indicate that Al is less favourably bound than H and Ca less favourably than Al. These pK^{sel} values should be seen only as examples. It is beyond the scope of this introduction to discuss the suitability of specific exchange coefficients in BEM models. An `end`–line concludes the first section of the model file.

The following `vls`–line specifies the cation exchange capacity as 100 mmol(p^+) per kg of solids at a ratio of 0.6 kg of solids per litre of solution. The partial pressure of CO_2 is set to 8 mbar.

The specification of total concentrations of components in this model file is accomplished by the following `ctl0`–, `xs0` and `cslt0`–line. The hypothetical solution "before the first equilibrium" is composed of 400 μmol/L of Ca and 1 μmol/L of aluminumchloride. The Ca may be thought to be present as hydroxide or as bicarbonate. Both forms are equivalent at this point because the defined reservoir of carbondioxide is an unlimited buffer for all forms of carbonic acid. The cation exchanger is specified as calcium saturated, at least as far as the total component specification is concerned. Both salts are supplied in certain amounts in the "recipe" for the first equilibrium: 90 and 100 mmol per kg of solid material for calciumcarbonate and aluminumhydroxide respectively.

The next four lines are again of technical nature and do not change the model definition proper (cf. section 3.4.4). An `end`–line concludes the second section of this model file.

The `exp`– and the `ctin`–line define the input and output fluxes of the topsoil model.

Let the system have the following chracteristics: The topsoil is 30 cm thick and has a density of 1 kg (dry matter) / L. The seepage is 500 $\mathrm{L\,m^{-2}\,a^{-1}}$. We choose a time step of 1 year. This means that we equilibrate one year's total seepage with the soil matrix in one step. The parameter `ssr` then becomes

$$\frac{0.3\,\mathrm{m}\cdot 1\,\mathrm{m}^2\cdot 1\,\mathrm{kg}\,(10^{-3}\,\mathrm{m}^3)^{-1}}{500\,\mathrm{L}\,\mathrm{m}^{-2}} = \frac{300\,\mathrm{kg}\,\mathrm{m}^{-2}}{500\,\mathrm{L}\,\mathrm{m}^{-2}} = 0.6\,\mathrm{kg/L}$$

as has been already specified. This amount of solution is exchanged completely in each step. The parameter `flow` therefore becomes `1`.

The deposition of acidity amounts to $5\,\mathrm{kmol(p^+)ha^{-1}\,a^{-1}}$ This has to be solved in the input solution flux:

$$\frac{5\cdot 10^3\,\mathrm{mol}\,(10^4\mathrm{m}^2)^{-1}\,\mathrm{a}^{-1}}{5\cdot 10^2\,\mathrm{L}\,\mathrm{m}^{-2}\,\mathrm{a}^{-1}} = 10^{-3}\mathrm{mol/L}$$

The rate of silicate weathering is $1\,\mathrm{kmol\,ha^{-1}\,a^{-1}\,m^{-1}}$. This amounts to $0.3\,\mathrm{kmol\,ha^{-1}\,a^{-1}}$ for a 30 cm compartment of soil. With an analogous calculation as for the acidity input the weathering impact amounts to 60 μmol(p^+)/L in the input solution.

The input of neutral salts into the system may be represented by 300 μmol/L of $CaCl_2$ in the input solution.

In all this reasoning we ignore the influence of the vegetation. It may be assumed to be in a steady state without net effects in the time scale considered. We are therefore not concerned with the precipitation volume flux. We need only that volume minus the evapotranspiration, which is the seepage.

The concentrations on the `ctin`–line are now explained: 180 μmol/L of Ca^{2+} (150 from neutral salt and 30 from silicate weathering) and 1300 μmol/L of Cl^- (300 from neutral salt and 1000 as acidity input).

An `end`–line concludes the model file for the topsoil.

We let the subsoil have almost the same properties. We only assume that there is no calciumcarbonate and that the partial pressure of CO_2 is lower. The model file reads

```
**************** The subsoil model file
cat Ca 2
```

```
cat Al 3
ani Cl 1
co2 1.4  6.4  10.3
cpl (Al)(OH)       9.03
cpl (Al)(OH)2      18.7
cpl (Al)(OH)3      27.0
cpl (Al)(OH)4      33.0
cpl (Al)2(OH)2     20.3
cpl (Al)3(OH)4     42.06
cpl (Al)13(OH)32   349.27
slt (Ca)(CO3)  8.3
slt (Al)(OH)3  33.
cec typ:sel Ca:-2.   Al:-1.0
end
vls   cec:100   ssr:0.6   pco2:4
ctl0 Ca:400 Al:1 Cl:3
xs0 Ca:1.0 Al:0
cslt0 (Ca)(CO3):0 (Al)(OH)3:100.
vls   estph:7.09   eststr:1246  estxsh:0.04
estcon Ca:415  Al:0.72e-6   CO3:0.59   Cl:3
estslt (Ca)(CO3):0  (Al)(OH)3:1000
wptslt (Ca)(CO3):100000  (Al)(OH)3:1000
end
end
```

We can compare this with the topsoil model file. The first difference is given by `pco2:4`. This specifies half the partial pressure of CO_2 as in the topsoil. This may reflect the site of the production of carbondioxide which is mainly the topsoil. The second difference is the specification `cslt0 (Ca)(CO3):0`. This means that no calciumcarbonate is introduced as a source of calcium into the first equilibrium. Such a situation may result from the deposition of loess on top of non-calcareous material. The formation of calciumcarbonate remains possible in this model.

The third section of this file is empty because this is the model file for a lower layer (not the top layer) of a *batch cascade* model.

The input and output specifications in these cases come from the next higher level of the cascade together with specifications in the *linkinfo* file (see below).

The following layer in the batch cascade is the creek. This is a batch vessel which receives the output solution from the subsoil layer. It has no cation exchanger and no salts at the beginning. But the precipitaion of salts is possible. The partial pressure of CO_2 is that of the free atmosphere (0.3 mbar). The model file accordingly reads:

```
**************** The creek model file
cat Ca 2
cat Al 3
ani Cl 1
co2 1.4  6.4  10.3
cpl (Al)(OH)       9.03
cpl (Al)(OH)2      18.7
cpl (Al)(OH)3      27.0
cpl (Al)(OH)4      33.0
cpl (Al)2(OH)2     20.3
cpl (Al)3(OH)4     42.06
cpl (Al)13(OH)32   349.27
slt (Ca)(CO3)  8.3
slt (Al)(OH)3  33.
end
vls  pco2:0.3
ctl0   Ca:400   Al:1   Cl:3
cslt0 (Ca)(CO3):0   (Al)(OH)3:0.
vls  estph:8.2   eststr:1200
estcon Ca:400    Al:0.13e-9    CO3:7    Cl:3
estslt (Ca)(CO3):0    (Al)(OH)3:0
wptslt (Ca)(CO3):100000    (Al)(OH)3:1000
end
end
```

To complete the definition of a batch cascade the *linkinfo file* is necessary (cf. p 31). In this example it reads:

```
********** The linkinfo file
exp  flow:1
plus Ca:30
END
exp  flow:1
END
```

It specifies that in both, the subsoil and the creek, the volume of solution is exchanged completely in each step (`flow:1`). Now, the volume of solution that is transported between layers has to be the same. This means that the amount of solution present in these layers is assumed to be the same as in the topsoil, that is the total seepage volume of one year. The subsoil receives an additional input of Ca which is specified on the `plus`–line. It represents the silicate weathering which is assumed to be equal in top– and subsoil.

These specifications conclude the definition of the batch cascade which is our watershed acidification model.

4.2.2 Results

The pH in all three layers of the model (fig. 4) is constant for a certain time from the start on. This can be understood if we look at the distribution of calciumcarbonate in the model (fig. 5). Despite the lack of $CaCO_3$ in the subsoil and in the creek at the start, it forms during the first some tens of pore volumes (years). This is due to the fact that we have decreasing partial pressures of CO_2 from topsoil to subsoil to creek. Higher partial pressures result in dissolution of carbonate which is precipitated again when carbondioxide degases from the solution. The pH during the existence of calciumcarbonate is lower where the partial pressure of CO_2 is higher. At that point in time where the calciumcarbonate is used up we get a steep decrease in pH. This is especially spectacular in the creek where the pH drops from 8.2 to 4.2 at a time when the topsoil remains constant in pH. This result has been found also using equilibrium models similar to BEM [13].

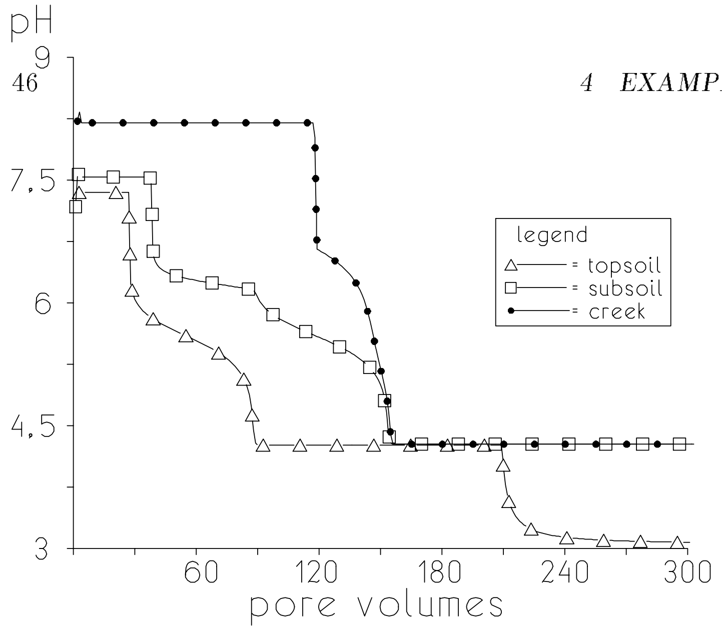

Figure 4: **Watershed acidification.** *The pH decreases at the fastest rate in the topsoil where, after passing the carbonate and aluminum buffer range, it reaches the pH value of the input solution (3).*

There is another part of the pH plots where pH is constant for some time. This part can be identified with the dissolution of aluminumhydroxide (fig. 6). We can say that the using up of the $Al(OH)_3^{(s)}$ lets the pH drop further. This is the case in the topsoil at about 210 pore volumes (years). Near the x–axis in fig. 6 it is indicated that a small amount of aluminumhydroxide is formed in the creek from about year 120 on. This is due to the fact that a solution saturated with $Al(OH)_3^{(s)}$ enters the creek where the pH is at that time higher than in the subsoil. At the same time the amount of aluminumhydroxide in the subsoil also increases slightly, for the same reason.

The curvilinear parts of the pH plots must be attributed to exchange processes: first Ca^{2+} is displaced by Al^{3+} and later (only in the topsoil) Al^{3+} is displaced by H^+. In the end the pH in the

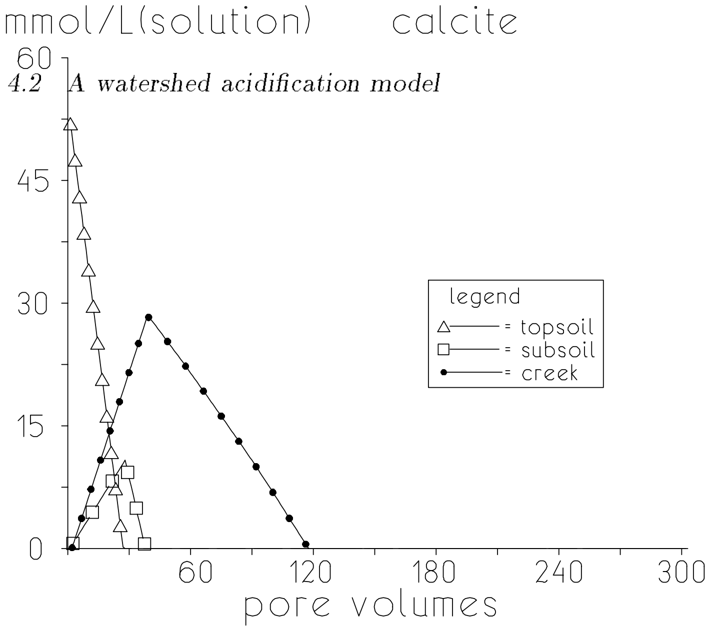

Figure 5: **Watershed acidification.** *The carbonate is redistributed from the topsoil to the subsoil and to the creek. This is due to lower partial pressures of carbondioxide in lower levels.*

topsoil approaches that of the input solution: all buffer mechanisms are exhausted.

Fig. 7 shows the aluminum concentration in solution. It increases very steeply as soon as a certain pH is reached. At this point a change in pH of less than 0.1 units has dramatic effects on the aluminum concentration. We can say that this point is reached when the Ca^{2+} saturation of the exchanger has dropped to a low level, so that the exchange buffer mechanism is exhausted.

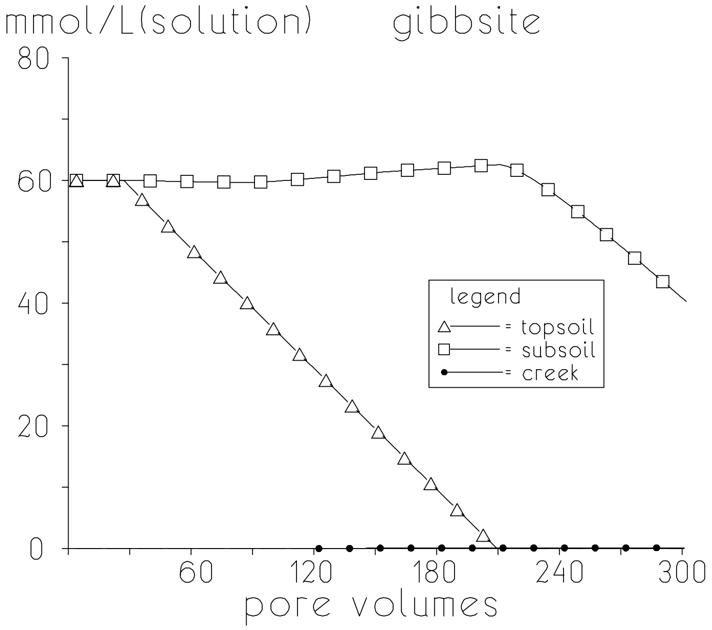

Figure 6: **Watershed acidification.** *Aluminumhydroxide begins to dissolve in the topsoil soon, in the subsoil it is first formed and later dissolved, in the creek a tiny amount is formed.*

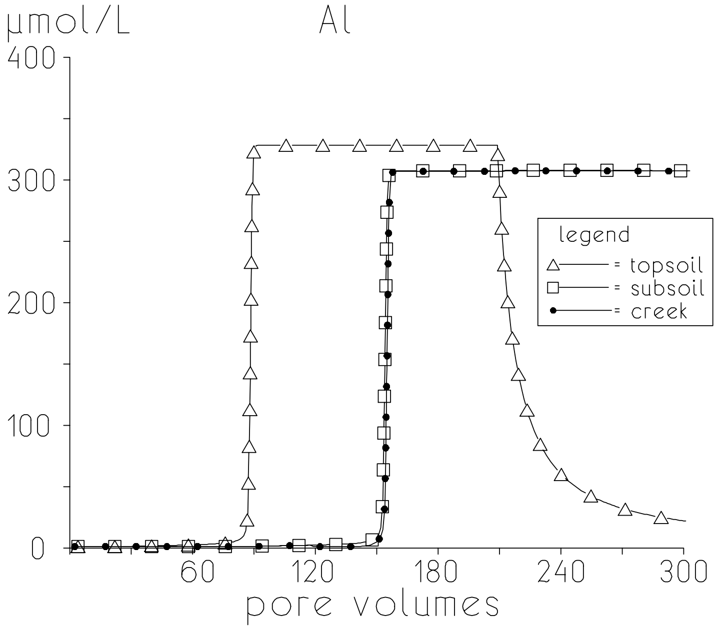

Figure 7: **Watershed acidification.** *The total aluminum in solution increases sharply as the exchange buffer mechanism is exhausted.*

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