SCS: Specific Chemical Simulators dedicated to chemistry-transport coupled modelling: Part I. Design and construction of an SCS

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BRGM approach in geochemical modelling

In the design of facilities in which hazardous materials are handled (e.g. waste disposal sites) or when determining preventive or remedial action to be taken into account in groundwater quality management, it is critical to be able to simulate coupling between hydrodynamic, transport and geochemical processes. Those kind of complex simulations can only be carried out with adapted numerical tools. Because numerical codes of that sort are scarce BRGM decided to develop its own modelling tools.

Basic equations and numerical methods describing hydrodynamic and transport processes are well known. In contrast, chemical interactions occurring (or potentially occurring) in natural systems are many and have not been utterly described and characterized in the literature. Therefore, it is not possible to develop a definitive fully-coupled general 3D hydro-transport-geochemistry code.

A number of all-purpose geochemical codes such as EQ3NR (Wolery, 1992), MINEQL+ (Schecher and McAvoy, 1992), or PHREEQC (Parkhurst, 1995) are available but none was specifically designed for coupled modelling. As a result, they lack the kind of computing efficiency required for 3D coupled modelling. In addition, as knowledge of geochemical processes occurring in natural systems changes and improves continuously, codes such as those quoted above cannot necessarily deal with the variety of geochemical problems that may have to be considered in environmental modelling studies.

In order to meet the requirements of computing efficiency and of ability to deal with varying chemical processes, BRGM based its geochemical modelling strategy on the concept of Specific Chemical Simulators (SCS). The baseline of this approach is that a new SCS is developed for each new specific study. This can only be done by use of adapted tools which greatly facilitate the process of code writing. The choice made at BRGM is the ALLAN-NEPTUNIX 4 software package distributed by CISI. Combined use of these two softwares permits to generate simulators automatically, as long as the processes involved in the system being modelled can be described by a set of algebraic and/or ordinary differential equations.

Because a SCS only takes into account those specific processes relevant to the problem being studied, computing efficiency is greatly improved. The code generated for any SCS is much smaller than that of the general softwares mentioned above. In addition, the rapidity and the ease with which SCS can be generated with ALLAN-NEPTUNIX 4 allows to add or suppress processes readily in order to produce a tailor-made simulator.

Construction of an SCS with the ALLAN-NEPTUNIX 4 integrated simulator generation system

NEPTUNIX 4 is a general solver which, at the end, automatically generates a FORTRAN code that solves the selected set of algebraic and differential equations. ALLAN functions include graphical interface, high-level description language, translator for NEPTUNIX 4, graphical assembling of individual models, exploitation of simulators and post-processing of generated data.

The first step in constructing an SCS is to list the relevant processes to be considered. This wok is done by the investigator on the basis of his knowledge of the geological-geochemical context and of the hydro-geochemical scenario(s) to be simulated. The second step consists in writing the corresponding algebraic and differential equations describing the processes selected. Up to this stage, no numerical or coding effort is required. The third step is the construction of the SCS itself within the ALLAN environment. This work is carried out by a specialist of this tool and mainly consists in graphical assembling tasks and in coding of equations using the high-level ALLAN

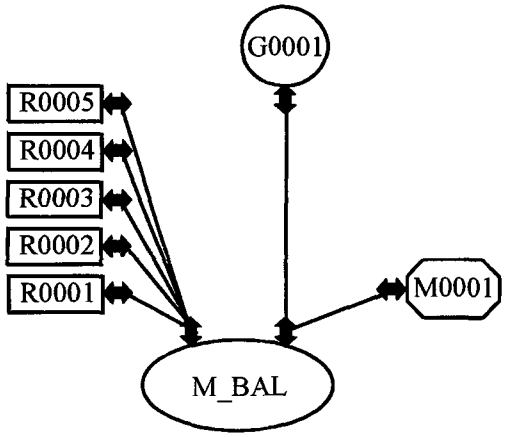

FIG. 1. General ALLAN structure of an SCS.

description language (i.e. nearly mathematical language). The generation of the final SCS and the associated FORTRAN code is then automatically done by ALLAN and NEPTUNIX 4.

The SCS developed in that manner can be run alone within the ALLAN environment or as a conventional FORTRAN routine embedded in a larger computer program. The latter option allows us to conveniently export an SCS from the ALLAN environment and include it (as a subroutine) in any of the hydro-transport codes available at BRGM to perform coupled modelling.

Internal structure of an SCS

All specific chemical simulators are constructed following the same general structure. The corresponding ALLAN representation of such a simulator is illustrated in Fig. 1.

The SCS is composed of a number of elementary modules, each of which corresponds to either an aqueous reaction (*Rxxxx*), a mineral reaction (*Mxxxx*) or a gaseous phase (*Gxxxx*). Equations in *Mxxxx* and *Gxxxx* modules can take into account kinetic laws, if necessary. All of those modules are linked to a mass balance (*M_BAL*) module. The equations specific to a particular SCS are placed in the *M_BAL* module. The other elementary modules only contain general equations which are not simulator-dependent. Once constructed, the latter modules can then be stored in a model-library for future use when needed. Therefore, the equation writing task (steps 2 and 3) is limited to the *M_BAL* module and to those reaction modules that are not yet available in the library. Despite the fact that each SCS is different, the equation writing process is usually quite straightforward since the nature of the variables and the general form of the balance equations are recurrent.

TABLE 1. Example of speciations calculated with EQ3NR and the *CARBO* SCS

Species	EQ3NR	*CARBO* SCS
$CaCO_3(aq)$	7.0307e−06	7.0307e−06
$CaHCO_3^+$	4.3546e−06	4.3547e−06
$CaOH^+$	1.1372e−08	1.1372e−08
Ca^{2+}	4.8631e−04	4.8630e−04
CO_3^-	9.6159e−06	9.6161e−06
H_2CO_3	1.0742e−05	1.0742e−05
HCO_3^-	9.5574e−04	9.5576e−04
H^+	5.5405e−09	5.5406e−09
OH^-	1.9899e−06	1.9899e−06
Ionic strength	1.47290390e−03	1.47290033e−03

As an example, we present here a very simple SCS (named *CARBO*) designed to calculate the aqueous speciation of carbonates and simulate equilibrium with $CO_2(g)$ and Calcite. The activity model considered in *CARBO* is based on Davies formulation. *CARBO* is constituted of 5 aqueous reactions combining 9 aqueous species, 1 reaction with $CO_2(g)$ and 1 reaction with Calcite (ALLAN structure presented on Fig. 1).

The numerical soundness of *CARBO* is illustrated in table 1. Speciation calculations were carried out for equilibrium of pure water with $CO_2(g)$ and Calcite at pH=8.275, with *CARBO* and with EQ3NR for comparison. Results show excellent agreement between the two codes (Table 1).

An SCS such as *CARBO* can then be integrated in a higher level ALLAN model in order to construct a chemical reactor and finally a Network of Chemical Reactors capable of simulating coupled chemistry-transport processes in a simplified way (Baranger and Kervévan, part II of present abstract). Another option for coupled simulations is to extract the SCS from the ALLAN environment and use it as a FORTRAN subroutine in a hydro-transport code (Kervévan *et al.*, part III of present abstract).

References

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