Chapter 2
Methods

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To simulate numerical reactive transport problems, *OpenGeoSys(OGS)*, a scientific open-source software, is coupled to the *IPhreeqc* module of the geochemical solver *PHREEQC(PQC)*. This new coupling scheme (hereinafter referred to as "*OGS#IPhreeqc*") is capable of simulating various chemical reactions alongside different processes such as water flow and solute mass transport. After a brief description of both codes, *OGS* (Sect. 2.1) and *PQC* (Sect. 2.2), the coupling interface *OGS#IPhreeqc* will be introduced (Sect. 2.3), verified on the basis of an benchmark example (Chap. 5), and applied to two different reactive transport problems (Chaps. 6 and 7).

2.1 OpenGeoSys (OGS)

OGS is a scientific open-source initiative based on the Galerkin finite element method (FEM), and is able to simulate multidimensional THMC (thermo-hydro-mechanical-chemical) coupled processes in porous and fractured media (Kolditz et al., 2012). This code has been applied in environmental science, such as in the fields of contaminant hydrology, water resources management, waste deposition, geothermal systems, and energy storage. *OGS* also has been participating several international benchmarking initiatives, such as DECOVALEX (with applications mainly in radioactive waste repositories), CO2BENCH(CO_2 storage and sequestration), HM-Intercomp (coupled hydrosystems), and SeSBENCH (reactive transport processes). A large number of benchmarks have been developed for the source code and algorithm verification over the time.

OGS is based on an object-oriented (C++) FEM concept to provide a flexible numerical framework (Fig. 2.1). It gives various possibilities to simulate a broad range of different processes which include flow process such as groundwater flow, overland flow, density-driven flow, unsaturated flow, and two-phase as well as multiphase flow processes. Picard and Newton–Raphson schemes can be applied to solve nonlinear problems such as Richards flow and density-dependent flow processes.

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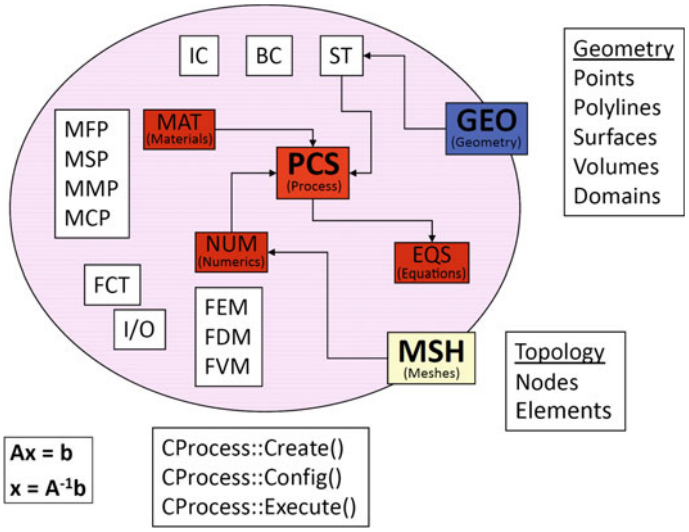

Fig. 2.1 Object-oriented structure of *OpenGeoSys* Version 5 (Kolditz et al., 2012)

Mass transport in the fluid phase is calculated based on the advection–dispersion equation (ADE). For the simulation of flow and transport processes, both implicit and explicit time discretization schemes can be applied. To couple different processes, such as flow, mass, and heat transport, either the monolithic or staggered approach can be used (Wang et al., 2011). *OGS* also can handle a random walk particle tracking (RWPT) methods for Euler–Lagrange simulations (Park et al., 2008). To increase the computational efficiency, the *OGS* code has been parallelized (Wang et al., 2009). This helps to deal with computationally intensive tests in the modeling of complex problems such as the present 3D model of the Nankou area in China (Sun et al., 2011) and nitrate reduction processes under coupled physical and chemical aquifer heterogeneity (Jang et al., 2017).

There are two possible ways to simulate reactive transport modeling (RTM) with *OGS*. One is to use its internal KinReact modules which is able to simulate kinetically controlled biogeochemical reactions (Ballarini et al., 2014). The other way is to couple the external geochemical solvers such as *OGS-PHREEQC* (Xie et al., 2006; He et al., 2015), *OGS-GEMs* (Kosakowski and Watanabe, 2014), *OGS-BRNS* (Centler et al., 2010), and *OGS-ChemApp* (Beyer et al., 2012; Li et al., 2014).

More detailed information regarding *OGS* developments, code resources, and benchmarks can be found at http://www.opengeosys.org/.

2.2 PHREEQC and IPhreeqc Module

PHREEQC is a geochemical solver to simulate a variety of aqueous geochemical calculations in natural waters or laboratory experiments (Parkhurst and Appelo, 1999). It is freely available and one of the most widely used open-source geochemical solvers in the fields of hydrochemistry and chemical modeling (Lucia and Kühn, 2013). *PHREEQC* offers a wide range of equilibrium reactions and kinetic formulations for modeling nonequilibrium mineral dissolution and precipitation, microbial reactions, decomposition of organic compounds, and other kinetic reaction (Charlton and Parkhurst, 2011). *PHREEQC* can simulate batch reaction and one-dimensional (1D) transport calculations with reversible and irreversible reactions. Inverse modeling for interpretation of different processes is also provided (Parkhurst and Appelo, 2013). Several databases provide a variety of possibilities for aqueous speciation calculations, such as Debye–Huckel formations (*phreeqc.dat, wateq4f.dat, llnl.dat, minteq.dat, minteq.v4.dat* and*iso.dat*); the Pitzer specific-ion interaction model (*pitzer.dat*) and the specific-ion interaction theory (SIT) model (*sit.dat*). All databases include temperature dependence of activity coefficient constants and van's Hoff or analytical expressions for equilibrium constants (Parkhurst and Appelo, 1999).

IPhreeqc, where"I" stands for interface, is a C++ *PHREEQC* module designed for coupling *PHREEQC*'s capabilities to other software programs (e.g., multi-dimensional transport simulators) (Charlton and Parkhurst, 2011). There are several works to couple *IPhreeqc* with other codes such as *COMSOL Multiphysics* (Wissmeier and Barry, 2011), *OpenGeoSys* (He et al., 2015; Kolditz et al., 2012), *UTCHEM* (Korrani et al., 2015), and *Matlab* (Muniruzzaman and Rolle, 2016). The interested reader is referred to Charlton and Parkhurst (2011) for the detailed information on *IPhreeqc* and its data manipulation methods.

2.3 OGS#IPhreeqc Coupling Scheme

In this tutorial, we use the coupling scheme developed by He et al. (2015). The nonchemical processes such as flow process and mass transport part are simulated by *OGS*, and *PHREEQC* is then applied to handle the local chemical system in each time step (Fig. 2.2). The coupling scheme is realized at source code level. It means that *IPhreeqc* functions can be accessed directly in the coupling interface. This is the major difference between *OGS#IPhreeqc* and the existing coupling between *OGS* and *PHREEQC*, in which *PHREEQC* is executed externally with a system call (Xie et al., 2006). The Sequential Non-Iterative Approach (SNIA) for Operator Splitting (OS) is applied for the coupling between *OGS* and *IPhreeqc*. *PHREEQC* input data can be prepared as either a file or a character string in the client program (e.g., *OGS*). Both file and character string based approaches are available for data exchange between *OGS* and *IPhreeqc*.

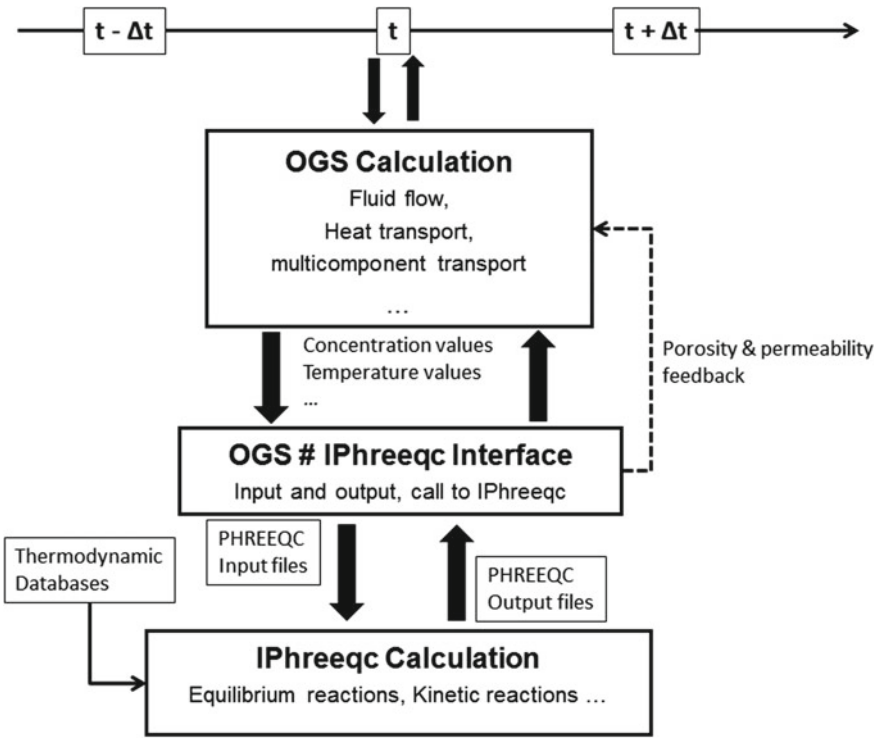

Fig. 2.2 General concept of the coupling between *OpenGeoSys* and *IPhreeqc* (He et al., 2015)

The coupling between *OGS#IPhreeqc*'s main advantages is listed below.

1. Open-source softwares: Both codes are available free of charge for scientific use.
2. Easy to update: The coupling interface itself is version independent and can stay unchanged after any updates. For example, a new release version from *IPhreeqc* is given, it can be integrated efficiently by updating the source code the *IPhreeqc* side. When new *IPhreeqc* files are added (or old files are removed) in the new version, only a reconfiguration of the build system is required. This allows user to benefit continuously from code developments of both sides (He et al., 2015).
3. Capability of simulating a variety of geochemical reactions with dynamic scale/different processes: Coupled with the geochemical code by utilizing the *IPhreeqc* module, thus enabling to perform the variety of geochemical reactions included in the *PHREEQC*'s reaction package. Moreover, multi-dimensional scale can be provided by *OGS*.
4. Computational performance: A significant reduction of the computation time is achieved by using a parallelization scheme based on the message passing interface (MPI). MPI grouping techniques are applied for the parallelization to enable a flexible distribution of different amounts of computer resources for the calculation of two kinds of tasks, i.e., geochemical reactions and the domain decom-

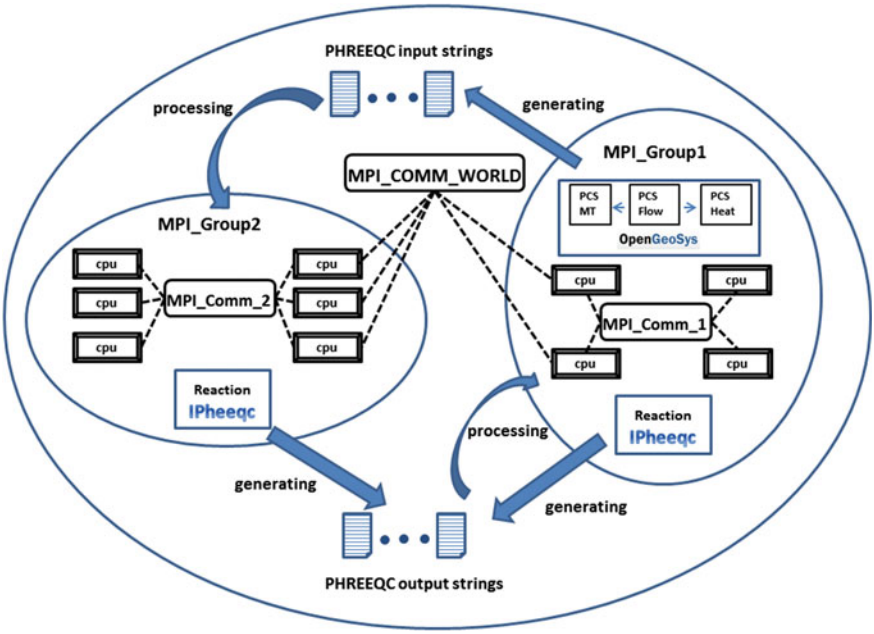

Fig. 2.3 Parallelization scheme for *OGS#IPhreeqc* (He et al., 2015)

position (DDC) related processes. As geochemical reaction is solved locally on each finite element node, its parallelization procedure is independent of the DDC approach implemented in *OGS* (Wang et al., 2009), which is applied to partition the computational tasks of the global assembly and the linear solver for the calculation of processes such as flow and transport. Figure 2.3 represents the general idea of the parallelization scheme. Two different MPI groups, i.e., MPI_Group1 and MPI_Group2, and related intercommunicators are created. The compute cores which belong to MPI_Group1 will be assigned to calculated DDC related processes (groundwater flow, mass, and heat transport) as well as geochemical reactions; whereas those of MPI_Group2 will only take a small part in the calculation of geochemical simulation. By using this method, optimized allocation of the number of compute cores for both types of processes can be realized.

More detailed information about the *OGS#IPhreeqc* interface and benchmarks can be found in (He et al., 2015).

References

O. Kolditz, S. Bauer, L. Bilke, N. Böttcher, J.O. Delfs, T. Fischer, U.J. Görke, T. Kalbacher, G. Kosakowski, C.I. McDermott, C.H. Park, F. Radu, K. Rink, H. Shao, H.B. Shao, F. Sun, Y.Y. Sun, A.K. Singh, J. Taron, M. Walther, W. Wang, N. Watanabe, Y. Wu, M. Xie, W. Xu, B. Zehner, OpenGeoSys: an open-source initiative for numerical simulation of thermo-hydro-mechanical/chemical (thm/c) processes in porous media. Environ. Earth Sci. **67**, 589–599 (2012), http://doi.org/10.1007/s12665-012-1546-x

W. Wang, T. Schnicke, Parallel finite element method and time stepping control for non-isothermal poro-elastic problems. Comput. Mater. Contin. **21**(3), 217 (2011), https://doi.org/10.3970/cmc.2011.021.217, http://www.techscience.com

C.H. Park, C. Beyer, S. Bauer, O. Kolditz, A study of preferential flow in heterogeneous media using random walk particle tracking. Geosci. J. **12**(3), 285–297 (2008), http://doi.org/10.1007/s12303-008-0029-2

W. Wang, G. Kosakowski, O. Kolditz, A parallel finite element scheme for thermo-hydro-mechanical (thm) coupled problems in porous media. Comput. Geosci **35**(8), 1631–1641 (2009). ISSN 0098-3004, http://doi.org/10.1016/j.cageo.2008.07.007

F. Sun, H. Shao, T. Kalbacher, W. Wang, Z. Yang, Z. Huang, O. Kolditz, Groundwater drawdown at nankou site of beijing plain: model development and calibration. Environ. Earth Sci. **64**(5), 1323–1333 (2011). ISSN 1866-6299, https://doi.org/10.1007/s12665-011-0957-4

E. Jang, W. He, H. Savoy, P. Dietrich, O. Kolditz, Y. Rubin, C. Schüth, T. Kalbacher, Identifying the influential aquifer heterogeneity factor on nitrate reduction processes by numerical simulation. Adv. Water Resour. **99**, 38–52 (2017), https://doi.org/10.1016/j.advwatres.2016.11.007

E. Ballarini, C. Beyer, R.D. Bauer, C. Griebler, S. Bauer, Model based evaluation of a contaminant plume development under aerobic and anaerobic conditions in 2d bench-scale tank experi. Biodegrad **25**(3), 351–371 (2014). ISSN 1572-9729, https://doi.org/10.1007/s10532-013-9665-y

M. Xie, S. Bauer, O. Kolditz, T. Nowak, H. Shao, Numerical simulation of reactive processes in an experiment with partially saturated bentonite. J. Contam Hydrol **83**(1—-2), 122–147 (2006). ISSN 0169-7722, https://doi.org/10.1016/j.jconhyd.2005.11.003, http://www.sciencedirect.com/science/article/pii/S0169772205002093

W. He, C. Beyer, J.H. Fleckenstein, E. Jang, O. Kolditz, N. Dmitri, T. Kalbacher, A parallelization scheme to simulate reactive transport in the subsurface environment with ogs#iphreeqc 5.5.7-3.1.2. Geosci. Model Dev. **8**(10), 3333–3348 (2015), https://doi.org/10.5194/gmd-8-3333-2015

G. Kosakowski, N. Watanabe, Opengeosys-gem: A numerical tool for calculating geochemical and porosity changes in saturated and partially saturated media. Phys. Chem. Earth, Parts A/B/C **70—-71**, 138–149 (2014). ISSN 1474-7065. Mechanisms and Modelling of Waste-Cement and Cement-Host Rock Interactions, http://dx.doi.org/10.1016/j.pce.2013.11.008

F. Centler, H. Shao, C. De Biase, C. H. Park, P. Régnier, O. Kolditz, M. Thullner. Geosysbrns—a flexible multidimensional reactive transport model for simulating biogeochemical subsurface processes. Comput. Geosci. **36**(3), 397 – 405 (2010). ISSN 0098-3004, http://dx.doi.org/10.1016/j.cageo.2009.06.009

C. Beyer, D. Li, M. De Lucia, M. Kühn, S. Bauer, Modelling co2-induced fluid-rock interactions in the altensalzwedel gas reservoir. part ii: coupled reactive transport simulation. Environ. Earth Sci. **67**(2), 573–588 (2012), https://doi.org/10.1007/s12665-012-1684-1

D. Li, S. Bauer, K. Benisch, B. Graupner, and C. Beyer. Opengeosys-chemapp: a coupled simulator for reactive transport in multiphase systems and application to co2 storage formation in northern germany. Acta Geotech. **9**(1), 67–79 (2014). ISSN 1861-1133, http://doi.org/10.1007/s11440-013-0234-7

D.L. Parkhurst, C.A.J. Appelo. User's guide to phreeqc (version 2) : a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Technical report, U.S. DEPARTMENT OF THE INTERIOR U.S. GEOLOGICAL SURVEY (1999), http://pubs.er.usgs.gov/publication/wri994259

M. De Lucia, M. Kühn, Coupling r and phreeqc: Efficient programming of geochemical models. Energy Procedia **40**, 464–471 (2013). ISSN 1876-6102, http://doi.org/10.1016/j.egypro.2013.08.053

S.R. Charlton, D.L. Parkhurst, Modules based on the geochemical model phreeqc for use in scripting and programming languages. Comput. Geosci. **37**(10), 1653–1663 (2011). ISSN 0098-3004, https://doi.org/10.1016/j.cageo.2011.02.005

D.L. Parkhurst, C.A.J. Appelo. Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods (2013), https://pubs.usgs.gov/tm/06/a43/

L. Wissmeier, D.A. Barry, Simulation tool for variably saturated flow with comprehensive geochemical reactions in two- and three-dimensional domains. Environ. Model. Softw. **26**(2), 210–218 (2011). ISSN 1364-8152, https://doi.org/10.1016/j.envsoft.2010.07.005, https://www.sciencedirect.com/science/article/pii/S1364815210002094

A.K.N. Korrani, K. Sepehrnoori, M. Delshad, Coupling iphreeqc with utchem to model reactive flow and transport. Comput. Geosci **82**, 152–169 (2015).ISSN 0098-3004, http://dx.doi.org/10.1016/j.cageo.2015.06.004, https://www.sciencedirect.com/science/article/pii/S0098300415001351

M. Muniruzzaman, M. Rolle, Modeling multicomponent ionic transport in groundwater with iphreeqc coupling: Electrostatic interactions and geochemical reactions in homogeneous and heterogeneous domains. Adv. Water Res. **98**, 1–15 (2016). ISSN 0309-1708, https://doi.org/10.1016/j.advwatres.2016.10.013

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