Modelling of Arsenic Removal from Water

Means and Limitations

Broder J. Merkel

TU Bergakademie Freiberg, Lehrstuhl für Hydrogeologie, Gustav-Zeuner-Straße 12, 09596 Freiberg/Sachsen,
Email: merkel@geo.tu-freiberg.de

1 Introduction

Arsenic is an element which has proven to be one of the most hazardous elements in surface and ground water. It may occur naturally in elevated concentrations but as well due to man made sources. Mining activities are often associated with significantly increased arsenic concentrations in mine water.

Arsenic is present in aquatic systems in inorganic and organic species with oxidation states +5, + 3 and -3. However, in Arsenopyrite (FeAsS) arsenic has the formal oxidation state of 0 and in Loellingite $FeAs_2$ the nominal oxidation state is -1. Organic, mainly methylated, species may occur dissolved in water and as volatile gaseous species.

It has been proven that the toxicity of arsenic is depending on its oxidation state and the species in particular. The most toxic form of As is gaseous arsine, followed by inorganic and organic As(III), inorganic As(V), organic As(V) compounds, and elemental arsenic. Arsenosugars, Arsenobetaines, or Arsenocholines are the least toxic forms of arsenic. Thus, removal strategies of arsenic from water have to take into account the species both for toxicity reasons and for their individual migration behaviour in the environment.

Removal of arsenic from water may be managed by precipitation, co-precipitation, ion exchange, sorption, plant uptake, and volatilization. The common assumption that arsenic(V) is always more easily removed from water is wrong. The pH value is a master variable, since the solubility of many arsenic minerals is strongly dependent on it. Furthermore, one has to distinguish between technical treatment processes, where the precipitated or sorbed arsenic compounds can be further treated and stabilized before dumping at a land fill site, and passive treatment systems, where the reaction products remain in the environment. In the latter case, sustainability is only reached if the solid arsenic bearing compound is stable on the long run and will not be resolved or desorbed.

Modelling the remediation measure, experiments with pilot plants, and finally constructing the treatment plant will be the chronological sequence. Modelling removal of arsenic or any other constituent from water may be straight forward or inverse. This paper briefly reviews the possibilities and limitations of modelling arsenic removal from water.

2 General remarks on Modelling

Since modelling nowadays is a routine task and models with graphical user interfaces (GUI´s) are available for everybody, quality control and criteria for quality control have to cover all steps during a modelling procedure. Quality control has to focus in particular on the modeller (the person), system analysis, data collecting, conceptual and mathematical model, verification, calibration, validation, sensitivity analysis, prognosis, and heuristics. Data collection consists of field work (sampling and documentation) and analysis in the laboratory. While high quality standards are applied for laboratory work (GLP) they are frequently neglected during field work, which has to be seen as a big challenge. Another shortage has often to be addressed to data treatment. Although statistical methods are known and could by readily applied, analytical errors and uncertainties are often not taken into account during modelling procedures. Another trap a modeller might step in is the system analysis and the conceptual model: Using a thermodynamic approach will produce poor results if the process to be described is obviously not in thermodynamic equilibrium.

Assuming that thermodynamic parameters have been determined correctly and are recalculated to

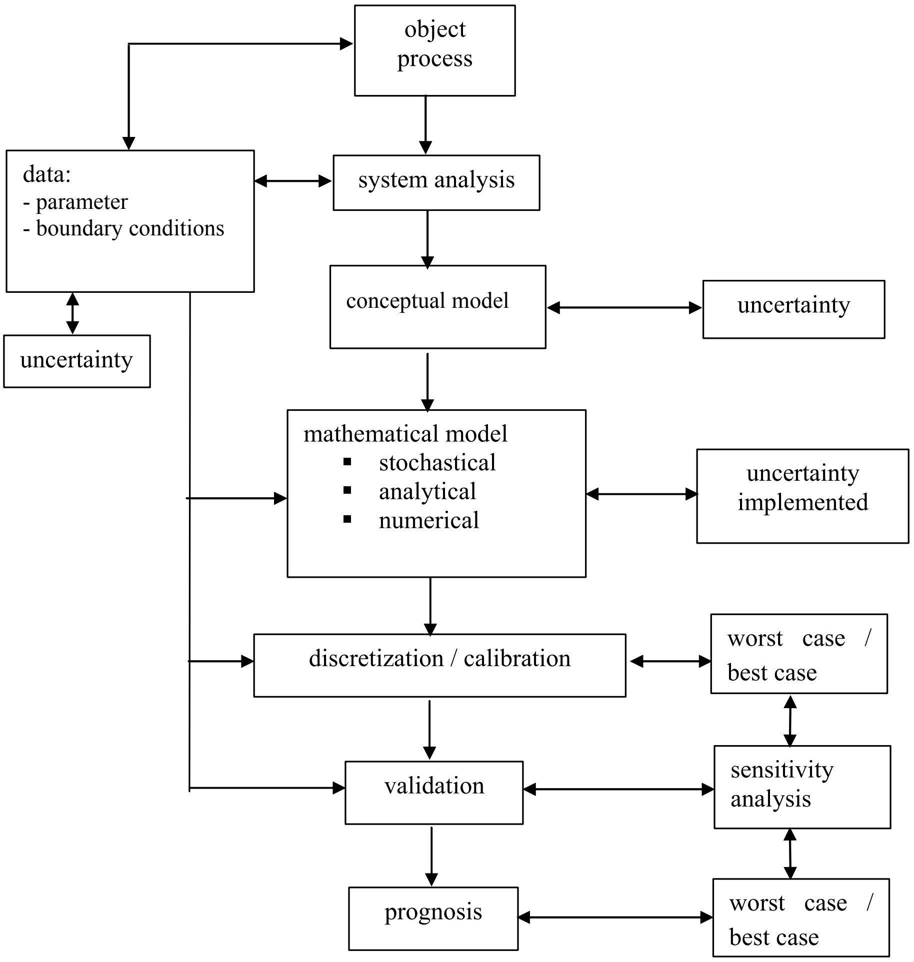

Figure 1: Work flow diagram of modelling steps taking into account data and uncertainties.

ionic strength of zero they are natural constants and thus not subject to a calibration procedure. However, this is not true for solid solution minerals, ion exchange, sorption, and kinetically controlled reaction (e.g. redox reactions).

Mathematical approaches to model chemical reactions in aquatic systems may either be based on equilibrium constants or on minimizing free enthalpies of formation. Programs based on equilibrium constants are e.g. WATEQ4F (BALL & NORDSTROM 1991), MINTEQA2 (ALLISON et al. 1991), SOLMINEQ (KHARAKA et al. 1988, EQ 3/6 (WOLERY et al. 1990), and PHREEQC (PARKHURST 1995). These 5 programs are frequently and commonly used by geoscientists and environmental scientists. ChemSage (N.N.a) is a direct descendant of a Gibbs energy minimizing program (SOLGASMIX) developed by Dr. Gunnar Eriksson. ChemSage was released in 1987 and represented a significant development of the former program. The ChemSage 'engine' also forms the basis for a number of other commercial software programs. EQS4WIN (N.N.b) solves equilibrium problems by minimizing the overall Gibbs free energy of systems involving up to 4 multi-species ideal-solution phases (a gas phase and up to 3 condensed liquid or solid solutions) and any number of pure (condensed) phases. Both minimizing-codes have not yet found significant usage and distribution in the geo- and environmental research community.

Verification of software according to ISO 9000-3 2000 (Guidelines for Applying ISO 9001 1994 to Computer Software) means that it has to be proven that software is doing fine in any cases and with any boundary conditions which is in the end impossible for a numerical code. Benchmarks and standard data sets might be used to test and compare different codes (NORDSTROM 2004; NORDSTROM et al. 1979).

While WATEQ4F may only calculate speciation and saturation index but is very convenient in maintaining excel files, MINTEQA2 offers the option to calculate the distribution of dissolved and adsorbed species (on solid phases). The application spectrum of SOLMINEQ, PHREEQC and EQ 3/6 is far greater. PHREEQC and EQ3/6 are the most versatile of the three, but Solmineq has more capabilities regarding high pressure and high salinities. EQ3/5 and phrqpitz are also better models for high salinities.

3 Modelling arsenic speciation and removal

3.1 Speciation

Thermodynamic data about inorganic arsenic species are well known as long as the system As – H_2O is considered. Several analytical determination techniques are known to distinguish between As(III) and As(V). Thus, by means of a reliable pH determination it is possible to calculate the distribution of species like $H_3AsO_3^0$, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}, $H_4AsO_3^+$, $H_3AsO_4^0$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}.

However for species like AsO_3F^{2-}, $HAsO_3F^-$, AsF_3, AsF_5, AsF_6^-, or $AsCl_3$, $AsCl_6^-$ which may form at elevated concentrations of F or Cl reliable thermodynamic data are not available. Under reducing conditions and neutral to alkaline pH thioarsenites (AsS_3^{3-}) might form (CULLEN & REIMER 1989), but thermodynamic data are not available as well. Volatile and methylated arsenic species are neither considered. Thus, the means of thermodynamic modelling of arsenic species distribution is limited, especially for aquatic environments where microbiological processes have to be taken into account modelling. While considerable progress is being made on the analytical methods for As speciation (on site species separation, HG-AAS under varying HG-conditions, HPLC-ICP-MS, CZE), the information can not be processed in nowadays hydrogeochemical modelling codes due to the described lack of thermodynamic data.

Considering aquatic systems where neither halogens, thioarsenites, nor methylated arsenic species have to be taken into account hydrogeochemical modelling can be applied in terms of speciation and based on this as well water rock interactions: solution and precipitation, ion exchange and sorption.

3.2 Precipitation

Solubility products of potential limiting arsenic minerals listed in common thermodynamic data bases are not always reliable (ZHU & MERKEL 2001; MERKEL et al. 2003). While the PHREEQC data base has no arsenic minerals, others list realgar, orpiment, and e.g. the arsenic oxides arsenolite and claudetite. WATEQ4F und MINTEQ present Ba-, Al, Ca-, Cu, Fe-, Mn-, Ni-, Pb- und Zn-Arsenates, the LLNL-data set additional Cd-, Co- und Sr-Arsenates and a couple of As-U-minerals. Since iron-arsenate and barium-arsenate might be a limiting mineral the significant differences found in common data bases will be discussed in the following for both iron-arsenate and barium-arsenate:

Solubility products for scorodite ($FeAsO_4*2H_2O$) vary between logK -19.86 (CHUKHLANTSEV 1956) and logK -24.60 (ALLISON et al. 1991) for the following equation

$FeAsO_4{:}2H_2O = Fe^{3+} + AsO_4^{3-} + 2H_2O$

This is due to fact that boundary conditions (pH, ionic strength, experimental setup, concentrations etc) were pretty different and the experiments at that time were not performed with the objective of creating a consistent thermodynamic data set. It could be shown by (ZHU & MERKEL 2001) that if recalculation to ionic strength is done in a consistent way scorodite seems to be less stable than assumed before (logK -22.77).

As a second example barium arsenate data will be discussed briefly. A groundwater from Rioverde, Mexico was modeled; the water with a pH of 7.2, a temperature of 25.9 °C, a total mineralization of 7 mmol·L^{-1} showed an arsenic concentration of 7 µg·L^{-1} and 160 µg·L^{-1} for barium (PLANER-FRIEDRICH 2000). PHREEC results using the recent WATEQ4F data base showed a significant over saturation (SI 8.3) with respect to $Ba_3(AsO_4)_2$

$Ba_3(AsO_4)_2 = 3\ Ba^{2+} + 2\ AsO_4^{3-}$ $\log K = -50.110$ (CHUKHLANTSEV 1956)

While PHREEQC, CHEMVAL, and LLNL offer no barium-arsenate-minerals MINTEQ uses the following equation and solubility product:

$Ba_3(AsO_4)_2 + 6H^+ = 3Ba^{2+} + 2H_3AsO_4$

log K -8.91

By using the MINTEQ data the saturation index is calculated to be SI 8.4 and from this the assumption that $Ba_3(AsO_4)_2$ being a limiting mineral sounds plausible. A thorough literature review, however, showed that already RAI et al. (1984) assumed the solubility constant for $Ba_3(AsO_4)_2$ being deadly wrong by comparing the data with solubility products from magnesium-arsenate (log K -30.32), calcium-arsenate (log K -18.48) and strontium-arsenate (log K -18.79). ROBINS (1985) and ESSINGTON (1988) proved with their experiments (log K -16.58, respectively log K -21.62, that $Ba_3(AsO_4)_2$ is by far less stable. Using this data the calculated SI showed to be -25.3 respectively –20.2 instead of +8.3 or +8.4.

Furthermore Essington (1988) showed that presumably BaHAsO4·H2O with a solubility product of log k -24.64 may be a limiting phase. However, for the Rio Verde groundwater SI was calculated -0.4 with respect to $BaHAsO_4 \cdot H_2O$. If the arsenic and barium concentrations would by 4 times higher over saturation would occur. Despite the fact that Essington already in 1988 published the mistake, databases in 2004 still contain the erroneous data.

Thus a thorough data check is recommended before using reported thermodynamic data. This, however, is a task a common user of any geochemical code will not be able to do. From this point of view the general availability of geochemical modelling codes carry a certain risk.

If solid solution minerals might be the limiting phase the situation is getting worse since very few reliable data are available. A similar situation appears if ion exchange or sorption is the governing process.

3.3 Sorption

Data from Chukhlantsev (1956) may be used for sorption on iron hydroxides (table 1), however, experiments have shown that behaviour of iron hydroxides may differ significantly from these data. Thus, own time consuming laboratory experiments are mandatory, since data fitting or calibrating procedures do not solve the problem.

Modelling sorption e.g. by means of PHREEQC is not complicated as can be seen from the example listed in Figure 1. In this simple case only the impact of different phosphate concentrations was modelled using the published data from (Dzombak & Morel 1990) without any site specific changes. The results are shown in Figure 2 and they appear to be logically. However, more than this can not be derived from the results without site specific investigations. Furthermore, it has to be considered that in this kind of forward modelling uncertainties of both input data (pH, measured concentrations etc.), thermodynamic data, and site specific sorption data are not implemented.

Table 1: Surface data from Chukhlantsev (1956)

Reaction Arsenate	Log K
Hfo_wOH + AsO_4^{3-} + $3H^+$ = Hfo_wH_2AsO_4 + H_2O	29.31
Hfo_wOH + AsO_4^{3-} + $2H^+$ = Hfo_w$HAsO_4^-$ + H_2O	23.51
Hfo_wOH + AsO_4^{3-} = Hfo_w$OHAsO_4^{3-}$	10.58
Arsenite	
Hfo_wOH + H_3AsO_3 = Hfo_wH_2AsO_3 + H_2O	5.41

```
SOLUTION 2
units mmol/l
pH 8
temp 10
pe 12
Ca  4
S(6) 2.2
C    4
P   0.1
Ba  30   ug/l
As  1    mg/l

REACTION
Fe Cl3
0.0001 0.0003 0.0005  0.0008 0.001

EQUILIBRIUM_PHASES 2
Fe(OH)3(a)  0   0
CO2(g) -3.5
```

```
SURFACE 2
Hfo_wOH Fe(OH)3(a) equilibrium_phase
0.1 0.0001

KNOBS
-step_size     10
-pe_step_size  2
-diagonal_scale true
-tolerance 1e-18
-iterations 600


SELECTED_OUTPUT
-file  surf_complex.csv
-reset false
-pH
-pe
-reaction
-totals   As S(6) P
```

Figure 2: Example of modeling sorption on weak binding sites considering different phosphate concentrations by means of PHREEQC.

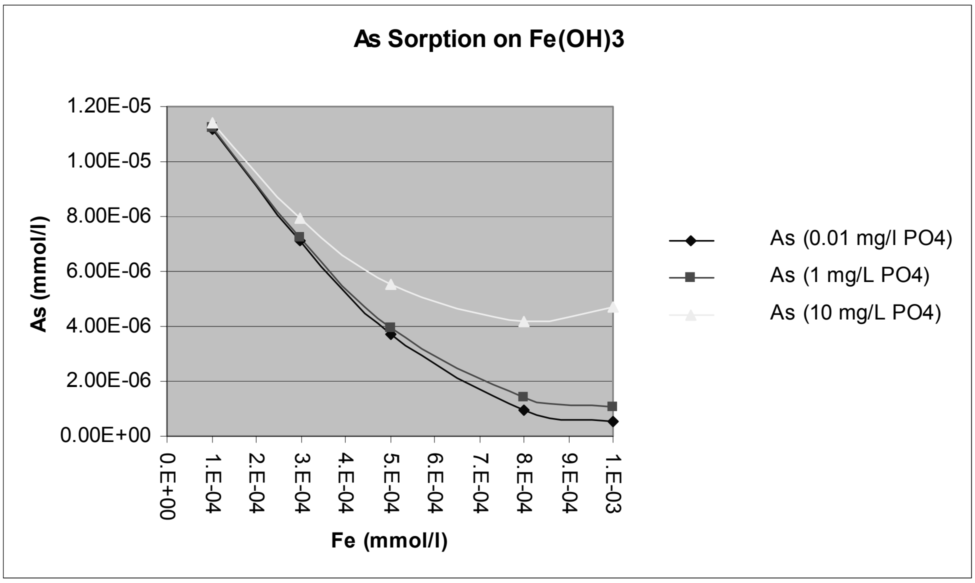

Figure 3: Sorption of arsenic(V) on iron hydroxide in relation to phosphate in solution.

3.4 Kinetics

For a more realistic scenario, PHREEQC offers the option of kinetically modelling. But again, the main problem is not how to model a kinetically controlled reaction but how to get reliable reaction rates including information about the uncertainty of the data obtained. Once both reaction rates and information about their uncertainty are available, the next problem is that codes nowadays available can not handle uncertainties (MEINRATH et al. 2002). Thus, improving hydrogeochemical codes in this direction will be a major task for the future.

4 References

BALL, J.W. & NORDSTROM, D.K. (1991): User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91-183: 189 p. (Revised and reprinted August 1992.)

ALLISON, J. D., BROWN, D. S. & NOVO-GRADAC, K. J. (1991): MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. EPA/600/3-91/021, U.S. Environmental Protection Agency, Athens, Georgia, March 1991.

KHARAKA, Y.K., GUNTER, W.D., AGGARWAL, P.K., PERKINS, E.H., & DEBRAAL, J.D. (1988): SOLMINEQ.88: a computer program for geochemical modelling of water-rock interactions. – U.S. Geol. Survey Water Resour. Invest. Rept. 88-4227; Menlo Park, CA, pp. 207.

WOLERY, T.J., JACKSON, K.J., BOURCIER, W.L., BRUTON, C.J., VIANI, B.E., KNAUSS, K.G. & DELANY, J.M. (1990): Current Status of the EQ3/6 software package for geochemical modelling. – In: MELCHIOR, D.C. & BASSET, R.L. (eds): Chemical modelling of aqueous systems II. – Am Chem Soc Symp., **416**: 104 —116.

PARKHURST, D.L. (1995): User's guide to PHREEQC - a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 95-4227, 143 p.

N.N.a: ChemSage http://gttserv.lth.rwth-aachen.de/~sp/tt/chemsage/cs4.htm

N.N.b: EQS4WIN http://thermo.hotbox.ru/pubs.htm

CULLEN, W.R. & REIMER, K.J. (1989): Arsenic Speciation in the Environment. – Chem Rev, 89: 713—764.

ZHU, Y. & MERKEL B. (2001): The dissolution and Solubility of Scorodite, $FeAsO_4$:H_2O - Evaluation and simulation with PHREEQC. – Wiss. Mitt. Inst Geol.TU BAF, Vol. 18, 72—87 (ISSN 1433-1284).

MERKEL, B.J., MEINRATH, G. & PLANER-FRIEDRICH, B. (2003): Fehler in thermodynamischen Datensammlungen.– Jahrestagung Wasserchemische Gesellschaft. – Fachgruppe in der GDCh (Gesellschaft Deutscher Chemiker), Mai 2003, Stade / Deutschland.

CHUKHLANTSEV, V.G. (1956): Solubility products of arsenates. – J. Inorg. Chem. (USSR) 1: 1975—1982.

KRAUSE, E. & ETTEL, V.A. (1988): The solubility of scorodite, FeAsO4*2H2O: New data and further discussion. – American Mineralogist, **73**: 850—854.

PLANER-FRIEDRICH, B. (2000): Hydrogeological and hydrochemical investigations in the Rioverde basin, Mexico. – FreibergOnlineGeoscience III; http://www.geo.tu-freiberg.de/fog/issues.phtml (ISSN 1434-7512).

RAI, D., ZACHARA, J.M., SCHWAB, A.P., SCHMIDT, R.L., GAVIN, D.C. & ROGERS, J.E. (1984): Chemical attenuation rates, coefficients and constants in leachate migration - A critical review. – EPRI (Electric Power Research Institute) Rep. EA 3356; Vol.1; Palo Alto, California.

ROBINS, R.G. (1985): The solubility of barium arsenates: Sherritt´s barium arsenate process. – Metall Trans B, **16B**: 404—406.

ESSINGTON, M.E. (1988): Solubility of barium arsenate. – Soil Science Society of America, 52 Division S-2 – Soil Chemistry: 1566—1570.

DZOMBAK, D.A. & MOREL, F.M.M. (1990): Surface complexation modelling – Hydrous ferric oxide: New York, John Wiley.

MEINRATH, G., MERKEL, B., SCHNEIDER, P. & DELAKOWITZ, B.(2002): The Role of Metrology and Statistics in Making Geochemical Modelling Defensible. – In: Uranium in the aquatic environment, p 355—358; Springer (ISBN 3-540-43927-7).

NORDSTROM, K.D. (2004): Modelling Low-temperature Geochemical Processes. – Treatise on Geochemistry, **5**: pp. 37—72; Elsevier.

NORDSTROM, D.K., PLUMMER, L.N., WIGLEY, T.M.L., WOLERY, T.J., BALL, J.W., JENNE, E.A., BASSETT, R.L., CRERAR, D.A., FLORENCE, T.M., FRITZ, B., HOFFMAN, M. JR, HOLDREN, G.R., LAFON, G.M., MATTIGOD, S.V., MCDUFF, R.E., MOREL, F., REDDY, M.M., SPOSITO, G. & THRAILKILL, J. (1979): Chemical Modelling of Aqueous Systems: A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems. – Am. Chem. Soc.: pp 857—892.