Plant wide chemical water stability modelling with PHREEQC for drinking water treatment

A.W.C. van der Helm*/, O.J.I. Kramer*, J.F.M. Hooft* and P.J. de Moel***/****

* Waternet, PO Box 94370, 1090 GJ, Amsterdam, the Netherlands
(E-mail: alex.van.der.helm@waternet.nl, Tel: +31 6 5248 0203)
** Delft University of Technology, Faculty of Civil Engineering and Geosciences, Department of Water Management, PO Box 5048, 2600 GA, Delft, the Netherlands
*** Omnisys, Eiberlaan 23, 3871 TG, Hoevelaken, the Netherlands

Abstract
In practice, drinking water technologists use simplified calculation methods for aquatic chemistry calculations. Recently, the database stimela.dat is developed especially for aquatic chemistry for drinking water treatment processes. The database is used in PHREEQC, the standard in geohydrology for calculating chemical equilibria in groundwater. The development of a graphical user interface for PHREEQC in Microsoft Excel has made it possible to easily incorporate complicated chemical calculations for use by technologists of drinking water treatment plants. By making use of PHREEQC the calculations performed are more accurate because of inclusion of ionic strength, ion pairs and most recent determined chemical equilibrium constants. Due to this development it is possible to for instance validation of laboratory measurements and on-line sensors. The use of PHREEQC is demonstrated in a simulation of the chemical water stability at drinking water treatment plant Weesperkarspel of Waternet.

Keywords
Chemical equilibrium; drinking water treatment; modelling; phreeqc; stimela

INTRODUCTION

PHREEQC (USGS, 2014) has become the ‘de facto’ standard in geohydrology for calculating chemical equilibria in groundwater. It is developed by the US Geological Survey (USGS), starting in 1980 with regular updates and extensions to date. Major aspects contributed to its success are:

- scientific base, fully traceable;
- adapted to newest scientific knowledge;
- users can modify and extend the basics;
- freely available;
- availability of an MS COM module for communication with e.g. MS Excel.

Recently de Moel et al. (2014) developed the stimela.dat database for PHREEQC which is specifically designed for water treatment. The stimela.dat database is based on the phreeqc.dat database (de Moel et al., 2013) that is available in PHREEQC. Adaptation of the phreeqc.dat database is necessary because, on the contrary to geochemistry, in water treatment processes thermodynamic equilibrium of all redox reactions cannot be assumed. Therefore, inert elements are defined for a number of parameters such as:

- non N(+5) oxidation states of nitrogen, with species NH_4^+, N_2 and NO_2^-;
- typical anaerobic groundwater species, such as Fe^{2+}, Mn^{2+} and NH_4^+;
- all anaerobic gases such as CH_4, H_2S, NH_3 (already implemented in PHREEQC version 3).

Waternet, the water cycle utility of Amsterdam and surrounding areas in the Netherlands, is adopting the use of stimela.dat in PHREEQC in their operation through the use of a Microsoft Excel user interface with PHREEQC. This paper describes the use of stimela.dat through Excel for calculation of chemical stability in drinking water treatment.

MATERIALS AND METHODS

Data is used from the Loenderveen-Weesperkarspel drinking water treatment, see Figure 1. The pre-treatment Loenderveen consists of an intake of seepage water from the Bethune polder and a consecutive treatment of coagulation and sedimentation, self-purification in a lake-water reservoir and rapid sand filtration. The pre-treated water is transported over 14 kilometers to the Weesperkarspel treatment plant without chlorination. The first process at the treatment plant Weesperkarspel is ozonation for disinfection purpose and oxidation of organic matter. Thereafter, pellet reactors are used to reduce hardness (softening) and biological activated carbon filtration is applied to remove natural organic matter and organic micro-pollutants. The last step in the treatment is slow sand filtration. The drinking water is transported and distributed without residual chlorine.

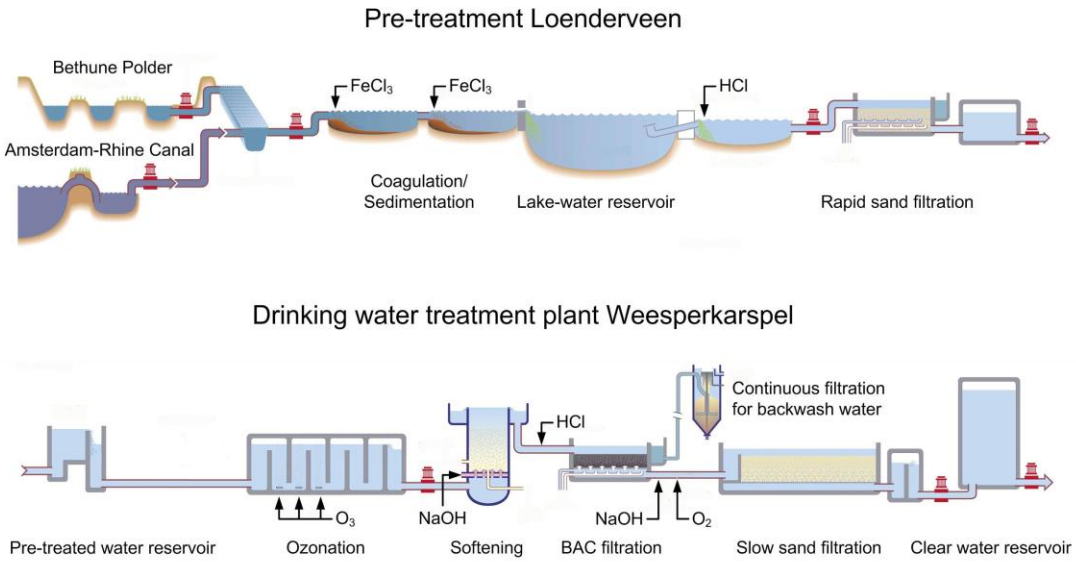

Figure 1 Process scheme of drinking water treatment plant Loenderveen-Weesperkarspel of Waternet

In the model, the water from the lake-water reservoir, with a detention time of about 100 days, is used as influent. The used laboratory measurements are temperature, pH, calcium, magnesium, alkalinity, ammonium, natrium, kalium, ferric iron, chloride, sulfate, nitrate, phosphae, oxygen, silica and total organic carbon. In Table 1 an overview is given of the relevant chemical reactions within the treatment plants. All these chemical reactions are defined within the PHREEQC/Stimela database, as equilibrium reactions with all related equilibrium constants and compound characteristics.

Table 1 Chemical reactions included in the PHREEQC/Stimela water treatment model

Process	Item	Reaction
pH control	HCl-dosing	$HCO_3^- + H^+ + Cl^- \text{ -- > } CO_2 + H_2O + Cl^-$
Filtration	NH_4-oxidation	$NH_4^+ + 2\ O_2 + 2\ HCO_3^- \text{ -- > } NO_3^- + 2\ CO_2 + 3\ H_2O$
Ozone	O_3-reduction	$2\ O_3 \text{ -- > } 3\ O_2$
Softening	NaOH-dosing	$CO_2 + OH^- + Na^+ \text{ -- > } HCO_3^- + Na^+$
	NaOH-dosing	$HCO_3^- + OH^- + Na^+ \text{ -- > } CO_3^{2-} + Na^+$
	$CaCO_3$-crystallization	$Ca^{2+} + CO_3^{2-} \text{ -- > } CaCO_3(s)$
pH control	HCl-dosing	$CO_3^{2-} + H^+ + Cl^- \text{ -- > } HCO_3^- + Cl^-$
AC filtration	DOC-oxidation	$CH_2O + O_2 \text{ -- > } CO_2 + H_2O$
pH control	NaOH-dosing	$CO_2 + OH^- + Na^+ \text{ -- > } HCO_3^- + Na^+$
O_2 control	O_2-dosing	$O_2 \text{ -- > } O_2$
SS filtration	DOC-oxidation	$CH_2O + O_2 \text{ -- > } CO_2 + H_2O$

The input file for the model only defines the quantity of dosed chemicals or the quantity of the converted compounds. In this case the operation of the plant is simulated for the caustic soda and hydrochloric acid dosages at Loenderveen and Weesperkarspel based on the set-points used in the plants for the calcium carbonate saturation index (SI) and total hardness (TH) after pellet softening. The calculated dosages are obtained within the model by iterative calculations, by specific algorithms or by 'normal' functionality of PHREEQC.

The output of the model is fully in compliance with all related equilibria as defined within the chemical database. The model calculates the content of all compounds, after each treatment step, as well as typical calculated values for e.g. pH, SI and electrical conductivity.

The model set-up allows for the incorporation of non-chemical compounds such as turbidity and UV-extinction. In this particular model these non-chemical compounds were not included, as the prime goal for this model was the prediction of acid and base dosing levels.

The computer program PHREEQC version 3.1.4 (phreeqci-3.1.4-8929.msi) was used to solve the mathematical equations which are generated from the chemical database stimela.dat and an input file (.pqi), both adjustable by the user (Parkhurst and Appelo, 2013). For use of PHREEQC through Excel the communication module version 3.0.6 (IPhreeqcCOM-3.1.4-8929-win32.msi) was used.

RESULTS

In Figure 2 the TH and the SI of the influent and the set-points in the plants are shown, as well as the calculations results for the acid and base dosages to meet the set-points. These are the results of the dataset of one day as they are presented in MS Excel and calculated with PHREEQC. In Figure 3 the calculation results for 4 years are shown.

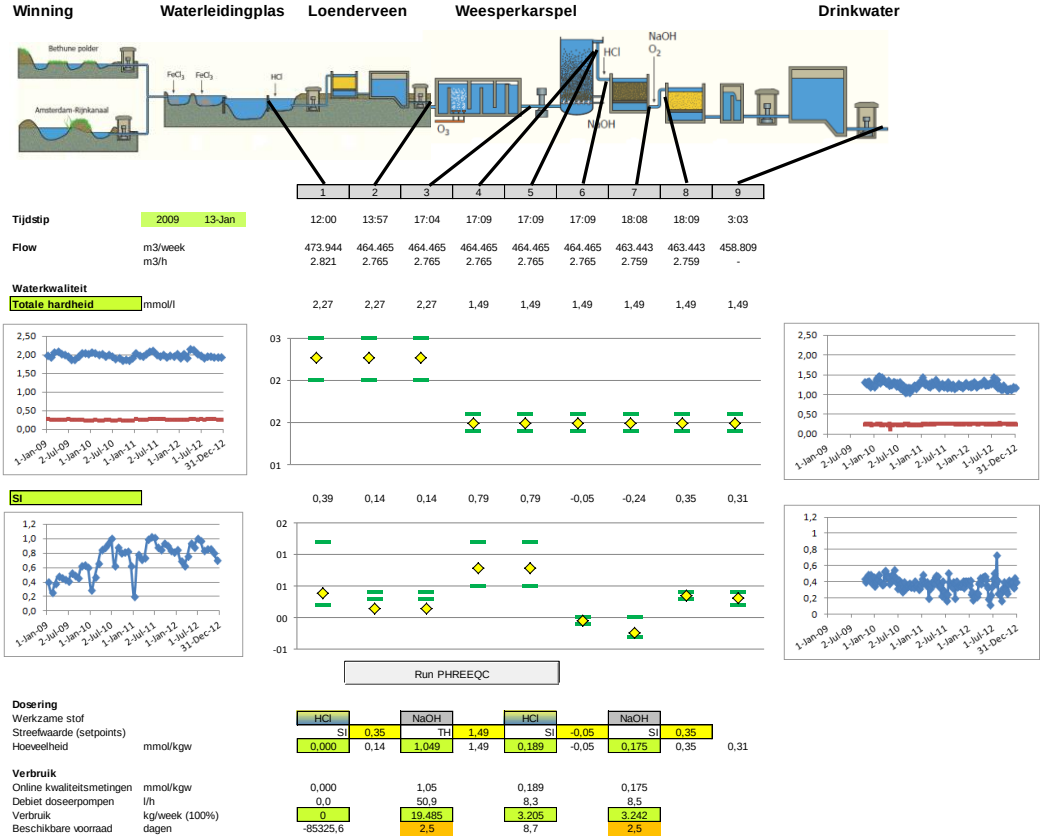

Figure 2 Simulation results for chemical dosages at drinking water treatment plant Weesperkarspel for January 13th 2009

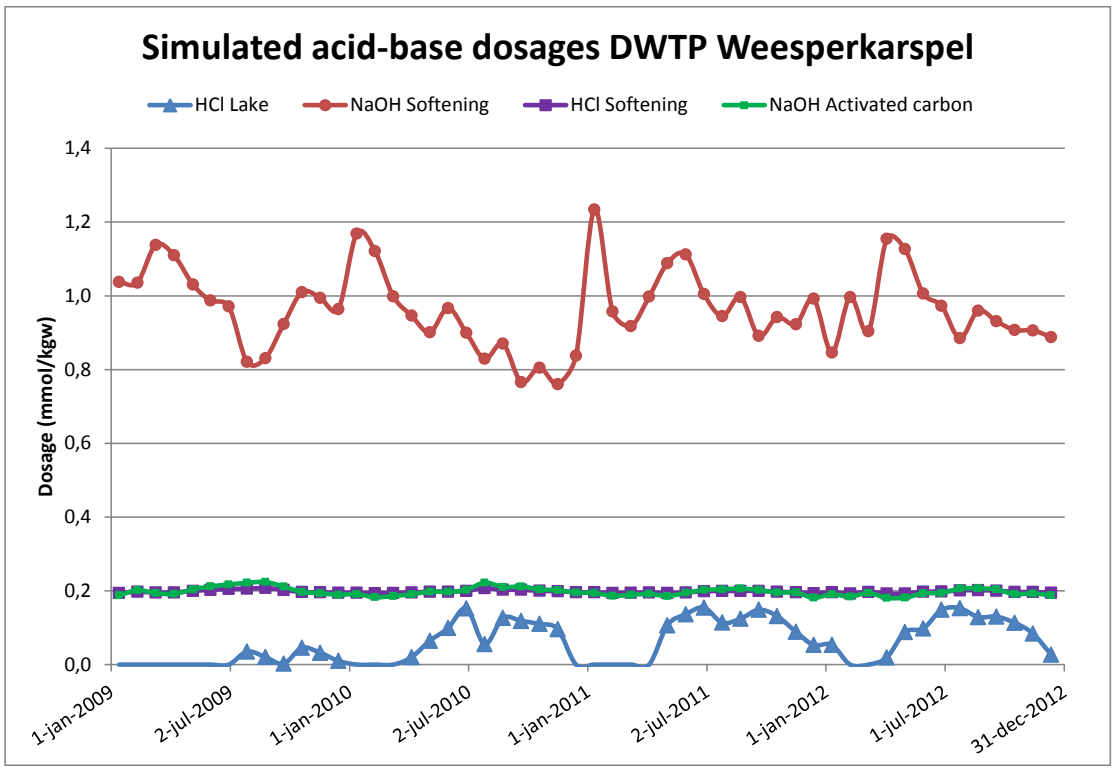

Figure 3 Simulated chemical dosages based on Phreeqc modelling

CONCLUSIONS

The development of a graphical user interface in Excel has made it possible to incorporate complicated chemical calculations in daily operation of drinking water production for technologists. By using PHREEQC the calculations performed are more accurate, because effects of ionic strength and ion pairs are included and most recent determined chemical equilibrium constants are used. Furthermore the dosing of chemicals with regard to the calcium carbonate saturation can be optimised. Important for practice of technologists is the availability of a tool that can work with data arrays instead of for instance average year values. This gives better insight in the processes and leads to better decisions by process technologists.

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