MONIKA METRYKA-TELKA
Kielce University of Technology
e-mail: monikatelka11@gmail.com

ROBERT KOWALIK
Kielce University of Technology
e-mail: robert2099290@gmail.com

JAROSŁAW GAWDZIK
Kielce University of Technology

BARBARA GAWDZIK
Jan Kochanowski University in Kielce

ALICJA GAWDZIK
University of Opole

Manuscript submitted 2020.03.11 – revised 2020.03.17,
initially accepted for publication 2020.03.21, published in March 2020

APPLICATION OF THE PHREEQC PROGRAM TO ASSESS THE CHEMICAL STABILITY OF TAP WATER IN KIELCE

ZASTOSOWANIE PROGRAMU PHREEQC DO OCENY STABILNOŚCI CHEMICZNEJ WODY WODOCIĄGOWEJ W KIELCACH

DOI: 10.30540/sae-2020-005

Abstract

The research was conducted on samples of water in Kielce from two intakes: Białogon and Zagnańsk. The results of selected indicators for these waters were presented, among others, the most important ones influencing its chemical stability i.e. calcium or magnesium. Then, using the PHREEQC program, stability indices were calculated for water in Kielce from the two shots in question. In the next stage, the correctness of the water test method was checked by means of a program through the ionic balance of the water and comparison of pH of the water determined with the value determined by calculation. For the above mentioned activities, tables and calculations were prepared on the basis of which appropriate conclusions were made.

Keywords: PHREEQC, water chemical stability, stability index.

Streszczenie

Badania przeprowadzono na próbkach wody w Kielcach pochodzące z dwóch ujęć: Białogon i Zagnańsk. Przedstawiono wyniki wybranych wskaźników dla tych wód, m.in. najważniejszych wpływających na ich stabilność chemiczną, tj. wapnia lub magnezu. Następnie, za pomocą programu PHREEQC, obliczono wskaźniki stabilności dla wód w Kielcach z dwóch ujęć, o których mowa. W kolejnym etapie sprawdzono poprawność metody badania wody za pomocą programu poprzez bilans jonowy wody i porównanie pH wyznaczonej wody z wartością wyznaczoną w wyniku obliczeń. Dla wyżej wymienionych czynności przygotowano tabele i obliczenia, na podstawie których wyciągnięto odpowiednie wnioski.

Słowa kluczowe: PHREEQC, stabilność chemiczna wody, wskaźnik stabilności.

1. INTRODUCTION

The chemical stability of water is one of the main problems associated with tap water quality. The chemical stability of water is usually determined by based on its carbonate-calcium balance. Water with a tendency to precipitate large amounts of $CaCO_3$ tends to accumulate deposits of significant amounts of sediment on pipeline walls. On the other hand, water with the ability to dissolve $CaCO_3$ is described as aggressive, which proves its corrosive properties [1].

Water, which is chemically stable, prevents the formation of deposits on the inner surfaces of pipes and their destruction. Substance appearing in water, they often react with the plastic of the water pipes, which negatively affects the chemical stability of the water. The most important factors for this stability are, among others, aggressive carbon dioxide, various types of sulphates, as well as chlorides, dissolved oxygen and detergents used for disinfection, and the carbonate-calcium balance is also of great importance for maintaining stability [2].

When water, which is not chemically stable, is introduced into the water supply system, electrochemical corrosion of the pipes can be caused, as well as the penetration of substances resulting from it into the water, especially metal compounds of released materials used for their construction [3, 4]. As a result, water becomes cloudy and has a visible colour. In water characterized by its corrosivity, deposits inside the pipes may be released, and with them further microbiological as well as chemical impurities develop [5].

PHREEQC is a program that originates from FORTRAN PHREEQE. This program is used to perform various calculations of water quality indicators. Its wide possibilities allow to predict the state of water in water supply systems under certain conditions, which may increase its chemical stability [6].

2. THE PHREEQC PROGRAMME AND ITS CAPABILITIES

The PHREEQC geochemical model has the ability to simulate the equilibrium reaction between water and minerals, ionic substitutes, solid and gaseous solutions. The kinetic formula used in the program allows to model unbalanced dissolution and precipitation of minerals, microbiological reactions, decomposition of organic compounds and other kinetic reactions [7]. The PHREEQC program includes the possibility of reactive transport, including multi-component diffusion and transport of surface compound species.

Currently, computer programs can be used to simulate the ionic composition of water. The calculation takes into account the degree of dissociation of a given compound depending on the ionic strength of the water. For the calculation, the PHREEQC program was used, which is applicable in the temperature range from 0°C to 50°C and the ionic strength of water below 0.1 mol/dm^3. The calculations are based on the Debye-Huckle rule and ion association theory in aqueous solutions [8]. The program can be used for:

- calculation of saturation indices of inorganic compounds that may precipitate from or be dissolved by water;
- determination of the forms of occurrence of chemical compounds in water, i.e. the ionic composition of water and the concentrations of compounds remaining in the non-ionic form;
- calculation of reversible and irreversible equilibriums at the water-solid, water-gas interface, including ion exchange;
- determination of stability of inorganic compounds during water mixing with different water quality or temperature changes;
- searching for groups of inorganic compounds or gases responsible for changes in the composition of water during its flow through an aquifer or technological equipment;
- distribution of redox elements in speculative calculations, when they are in the valencian states;
- estimate the correct mass of water in the aqueous phase during the reaction and transport calculations;
- analysis of complex reactions;
- of mixing solutions, reverse calculations for modelling that may have an acceptable uncertainty in the analytical data [9, 10].

3. TEST METHODOLOGY

On the basis of the values of water indices listed in Table 1, using the PHREEQC programme, stability indices have been calculated for selected minerals that may precipitate from water. The results of these tests are presented in the Table 2.

The possibilities of the programme were presented using the composition of water supply water in Kielce from the intake in Białogon and Zagnańsk. Table 1 presents the values of selected indicators for water intakes in Kielce.

The values of selected indicators of tested water at the temperature of 10°C for two of the discussed intakes in Kielce are higher for most substances for the Kielce – Białogon intake. This is particularly visible on the example of calcium, which in the Zagnańsk intake is over 30g/m^3 less than in Białogon. The calcium content in water affects its hardness.

4. RESULTS

The water stability index can be most simply determined on 3 levels:

a) solubility – the mineral has a negative index;
b) stability – the mineral has an index close to or equal to zero;
c) precipitation – the mineral has an index with a positive value.

Table 1. Values of selected water indicators supplied to the city of Kielce from the intake in Zagnańsk and Białogon

Index name	Symbol	Kielce – Białogon	Zagnańsk	Unit
Calcium	Ca^{+2}	90.19	62.2	g/m^3
Magazine	Mg^{+}	8.53	12.2	g/m^3
Sodium	Na^{+}	10	5	g/m^3
Potassium	K^{+}	1.2	2	g/m^3
General Iron	Fe	0.01	0.04	g/m^3
Sulphates	SO_4^{-2}	41.6	45.3	g/m^3
Chlorides	Cl^{-}	27.9	15.4	g/m^3
Nitrates	NO_3^{-}	22	17.3	g/m^3
Fluoride	F	<0.10	<0.10	g/m^3
pH	–	7.78	7.42	–
Temperature	–	10	10	°C
pe	–	4	4	–

Table 2. Value of stability indices for precipitated minerals

Mineral	Chemistry formula	Zagnańsk	Białogon
Anhydride	$CaSO_4$	-2.3	-2.39
Argonit	$CaCO_3$	0.19	-0.32
Kalcyt	$CaCO_3$	0.34	-0.18
Dolomite	$CaMg(CO_3)_2$	-0.22	-0.91
Hydrated iron (III) Hydroxide	$Fe(OH)_3$	1.58	1.49
Geothyt	FeOOH	6.90	6,82
Gypsum	$CaSO_4 \cdot 2H_2O$	-1.83	-1.92
Hausmannit	Mn_3O_4	-19.94	-21.64
Hematite	Fe_2O_3	15.74	15.57
Manganite	MnOOH	-6.08	-7.10
Melatrit	$FeSO_4 \cdot 7H_2O$	-8.66	7.57
Hydixyapatyk	$Ca_5(PO_4)_3OH$	-7.70	-10.00
Pirochroit	$Fe(OH)_3$	-7.72	-8.38
Pyroluzite	MnO_2	-12.87	-14.25
Rhodochrosyt	$MnCO_3$	-2.25	-2.54
Syderite	$FeCO_3$	-1.93	-1.28

environment

The Table 2 summarises the stability indices calculated for water in the water supply network in Kielce from a shot in Zagnańsk and Białogon. In the analysed waters, calcium carbonate, which may precipitate in the form of aragonite or calcite, indicates stability. In case of water contact with anhydrite, dolomite (in case of water from Zagnańsk), gypsum, melaniterite, hausmannite, manganite, pyrochroite, pyrolysite, rhodochrosite and syderite will dissolve these minerals. Geothite, hematite and hydrated iron(III) hydroxide can be precipitated. It is noteworthy that the corrosion products (geothite and hydrated iron(III) hydroxide) were not dissolved by flowing water.

5. CHECKING THE CORRECTNESS OF THE METHOD

The correctness of the water analysis by the programme can be assessed on the basis of:

a) ionic balance of the water – the analysis is correct when the condition is met:

$$\frac{|Kt - An|}{Kt + An} \cdot 100 \leq 10\% \qquad (1)$$

here:

$$Kt = \sum_{i=1}^{n} m_i^{Kt} z_i^{Kt} \qquad (2)$$

$$An = \sum_{j=1}^{n} m_j^{An} z_j^{An} \qquad (3)$$

where:

m_i^{Kt} – concentration of cations, mol/dm³,

m_j^{An} – anion concentration, mol/dm³,

z_i^{Kt} – the value of cations,

z_j^{An} – the value of anions.

If this condition is not met, the analysis is highly flawed and absolutely cannot be used for further calculations of the ionic composition of the water, the most common reason being the lack of determination of sodium and potassium content.

b) comparison of the water pH (pH_{ozn}) with the value determined by calculation (pH_{obl}). The water analysis is correct when there is inequality:

$$|pH_{ozn} - pH_{obl}| \leq 0.2 \qquad (4)$$

When the condition I_S^M>0 is met, the compound precipitates. If I_S^M c (-0.5;0.5) then we are talking about chemical balance between water, and the substance precipitated from it. Knowing the concentration values of ions present in water we can determine the stability indices of the compounds precipitated or dissolved in water [11].

6. SUMMARY

Computer programs enable simulation of ionic composition of water and calculation of stability indices of the compounds contained in it. Analyses carried out by means of the PHREEQC programme have the possibility to take into account a considerable number of different factors influencing chemical balance, which results in much more precise forecasts and can therefore be used for diagnostic purposes for water supply plants. Maintaining chemical stability in water supply systems will allow for a long service life of their pipes.

For two examined water intakes in Kielce – Zagnańsk and Białogon, the tests of selected indicators showed slightly higher values for water intake from Białogon, which may influence its hardness. In these waters, however, calcium carbonate showed stability. The substances tested whose stability index presented in Table 2 has a positive result will precipitate out of the water, while those whose values are negative will dissolve in it.

REFERENCES

[1] Wolska M., Mołczan M.: *Assessment of stability of water entering the water supply system*.

[2] Palomo A., Blanco-Varea M.T., Granizo M.L., Puertas F., Vazqez T., Grutzeck M.W.: *Chemical stability of cementitious materials based on methacaolin*. Cement and Concrete Research (1999), Vol. 29, No. 7, pp. 997-1004.

[3] Tartara M.: *Secondary pollution of tap water during its distribution in terms of deterioration of the physico-chemical quality of water*. Gas, Water and Sanitary Technology (2001), No. 6, pp. 201-205.

[4] Sarin P., Snoeyink V.L., Lytle D.A., Kriven W.M.: *Iron corrosion scales: Model for scale growth, iron release, and colored water formation*. Journal of Environmental Engineering (2004), Vol. 130, No. 4, pp. 364-373.

[5] Volk C., Dundore E., Schiermann J., Le-Chevallier M.W.: *Practical evaluation of iron corrosion control in a drinking water distribution system*. Water Research (2000), Vol. 34, No. 6, pp. 1967-1974.

[6] Wingender J., Flaming H.C.: *Potencjał zanieczyszczeniowy biofilmów sieci dystrybucji wody pitnej*. Water Science and Technology (2004), Vol. 49, No. 11-12, pp. 277-286.

[7] Adrien R., Ellway M., Lin J.: *Study of corrosion material accumulated on the inner wall of steel water pipe*. Corrosion Science (2001), Vol. 43, No. 11, pp. 2065-2081.

[8] Balcerzak W., Knapik K., Kubała K.: *Changes in water quality in the distribution system*. Mat. Conf. "Water supply and water quality". PZITS, Gdańsk (2002), pp. 615-823.
[9] Łomotowski J., Siwoń Z.: *Utilization of programs stimulating ionic composition of water for evaluation of chemical stability of tap water*. "Ochrona Środowiska" (2004).
[10] Smith A. L.: *Causes and prevention of quality changes in water supply systems*. "Ochrona Środowiska" (2003), No. 4, pp. 3-6.
[11] Łomotowski J., Radosz M.: *Stabilność wody w systemach wodociągowych*. Matthew Conf. „Wspomaganie komputerowe w projektowania i eksploatacji systemów wodociągowych", Świnoujście-Copenhagen 2002.

Acknowledgments:
The work was financed by Jan Kochanowski University in Kielce, University in Opole and Kielce University of Technology

Podziękowania:
Praca była finansowana przez Uniwersytet Jan Kochanowski w Kielcach, Uniwersytet w Opolu oraz Politechnikę Świętokrzyską w Kielcach