

# Physicochemical Substantiation of the Technology of a Decrease in the Level of Natural Water Acidation with Calcite-Containing Reagents

V. N. MAKAROV, I. P. KREMENETSKAYA, T. N. VASILIEVA and O. P. KORYTNAYA

*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,  
Kola Scientific Centre, Russian Academy of Sciences,  
Ul. Fersmana 26a, Apatity 184269 (Russia)*

*E-mail: kreme\_vg@chemy.kolasc.net.ru*

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## Abstract

Experimental data on the dissolution of calcite in water and in the solution of sulphuric acid were treated with the help of the generalized equation of heterogeneous kinetics. The possibility of using this method to determine the kinetic characteristics of the process was demonstrated. The data on the limiting stage were obtained; rates constants of calcite dissolution under different conditions were calculated. A procedure to calculate technological parameters of the process leading to a decrease in the level of acidation of natural water was proposed.

## INTRODUCTION

Acidation of natural water in industrial regions and adjacent territories is an essential ecological problem [1, 2]. The concentration of hydrogen ions in water is one of the main abiotic environmental factors for fresh-water animals [3]; it can vary, depending on the chemical composition of environment and underlying rocks, as well as on the biological processes going on in a water body (photosynthesis, decomposition of the organic matter). The pH value is unstable and exhibits diurnal and seasonal variations in the same water body. In summer, during daylight hours, when photosynthesis is most intensive, the concentration of hydrogen ions in the medium decreases several ten or hundred times. *Vice versa*, in winter, when the prevailing processes are those involving decomposition of organic matter with the formation of carbon dioxide and acidic products, water acidation is observed, and pH decreases. As a rule, pH varies within the range

6.5–8.5, which is safe for normal vital activities of the major part of invertebrates [4]. The number of fresh-water reservoirs with pH variations beyond this range has been accounting for only 10–15 % of their total number till recently. However, this number is sharply increasing during the recent decades due to atmospheric pollution with non-purified gaseous industrial wastes and acid rain [3].

In Russia, a complex investigation of the effect of atmospheric acid precipitation on the status of surface water bodies and water streams was carried out for the territory of Murmansk Region. Biogeocenoses of water sources of the Kola Peninsula under the existing climatic and geological conditions of water body formation are mainly sensitive to acidation processes [5], which are due also to the trans-boundary transfer of atmospheric pollution from West Europe [6]. A sharp decrease in pH was revealed during the snow-melting period in some rivers of the Kola Peninsula (the so-called pH-shock). The period of low pH

(4.4–4.7) is short (5–7 days) but it can cause disastrous consequences for the subarctic fauna [7].

A number of works dealing with the problem of acidic precipitation over the territory of West Siberia was published. In particular, the authors of [1] obtained the data on the composition of atmospheric aerosol, precipitation and surface water for different natural climatic zones. It was established that the character of atmospheric precipitation and the conditions of the formation of surface water composition in the southern territories of West Siberia do not promote acidation of water bodies, unlike for the northern territories where some lakes of the tundra zone are acidified not only in spring but all year round under the conditions of low water mineralization.

It should be noted that water acidation causes not only a decrease in the pH of water but also changes in water composition with respect to other ion and non-ion chemical forms. The stability of water to acidation is determined first of all by the concentration of hydrocarbonates. Another important parameter determining pH and its variations in the bogged lakes is the concentration of humic acids.

The worldwide-accepted criteria for the evaluation of acidation processes are such parameters as pH, alkalinity, acid-neutralizing capacity (ANC) of water, the ratio of molar concentrations of  $\text{HCO}_3^-/\text{SO}_4^{2-}$  ions *etc.* [8]. A number of authors stress that the ANC is one of the main indices of interest for the evaluation of efficiency of the recovery of acidated lakes because this parameter depicts the ability of water to neutralize the arrival of strong acids and its sensitivity to an acid (low ANC value points to the low buffer capacity and therefore to the high sensitivity) [9].

In spite of the measures aimed at a decrease in the level of sulphur dioxide emission into the atmosphere, the degree of acidation of water bodies remains high in some regions. The authors of [9] explain this fact by a depletion of the buffer capacity of the flood basin territory.

Another aspect of the problem of surface water acidation was marked by the authors of [2] who considered the hydrochemical regime of a permanently acidated Yellow Creek brook (West Virginia, USA). The water of the brook was characterized as a diluted solution of

sulphuric acid unsuitable for maintaining the vital activities of fish populations. The acidated brook flows into the Otter Creek where trout fish lives. Extremely unfavourable conditions arise for fish in the mixing zone. The authors believe this is connected with the fact that water gets supersaturated with aluminium with respect to the mineral phases; aluminium is afterwards deposited in the organs of fish.

The measures aimed at an improvement of the indices of natural water acidation are most frequently reduced to the introduction of neutralizing reagents, mainly calcium carbonate, into the water. In the opinion of the author of [1], it is necessary to investigate the efficiency of operations and technologies of natural water alkalization that are used in a number of countries to eliminate the negative consequences of acid precipitation. Below we will describe some examples of this approach.

The authors of [10] describe an automatic doser feeding calcite suspension in order to maintain the necessary water quality during heavy rain. The addition of calcite allowed one to eliminate temporary increase in water acidity.

Three alternative approaches to controlling pH and ANC were tested with mountain trout brooks with pH 4.5–5.3 and negative ANC [11]. Such versions as hanging the pieces of limestone across a brook on a wire barrier, or soda briquettes on baskets made of metal mesh. In the former case pH increased by about 0.5 within 2 weeks, then the effect of limestone became negligible.

The method involving the use of ground limestone with particle size from 14 (fine fraction) to 40  $\mu\text{m}$  (coarse fraction) is of interest [12]. Immediately after water treatment, a notable increase in pH, ANC and calcium concentration was observed. The required water characteristics (pH > 6.5, ANC > 100  $\mu\text{eq/l}$ ) were achieved within the initial period of time in the upper water layers of the lake and after two months in the lower layers.

The authors of [13] discussed the efficiency of adding a reagent by different methods: directly into a lake and onto the lakeside. The direct introduction of calcite into a lake causes a large and short-time increase in pH and water alkalinity in the lake outflow immediately after the treatment. In the case if the territory

is treated, a longer and more gradual increase in pH and alkalinity of the outflow from the lake and soil are observed.

The works considered above and describing the methods of decreasing the level of natural water acidation are mainly empirical in their character. We did not find any publications dealing with the determination of the technological parameters of water deacidification process depending on the conditions of a specific water body. Calculations of these parameters should be based on the data on the interaction of the reagent with water components.

A number of works dealt with the questions of chemical thermodynamic modeling in solving the complex tasks of describing the states of water ecosystems [14–16, *etc.*]. Starting from the analysis of the data of field observations, it was concluded that pH of natural water is governed by the concentrations of bicarbonate ions  $\text{HCO}_3^-$  and aqueous carbon dioxide which is in equilibrium with the atmospheric carbon dioxide [14]. Atmospheric precipitation and any other water bodies in which there is no high bicarbonate ion concentration (formed either by the dissolution of carbonate rocks or by any other way) can be rather acidic. In addition, a significant decrease in pH is possible due to the protonation of a noticeable part of  $\text{HCO}_3^-$  under the action of local man-made sources of strong acids [15]. Both factors are characteristic of natural water during snow thaw in the vicinity of plants emitting acid-forming compounds into the atmosphere.

The present work deals with the calculation of a set of chemical equilibria modeling the state of water with an increased acidation level (due to the arrival of sulphuric acid) in equilibrium with the atmosphere while the interaction with calcite proceeds. The data on the composition of the formed solutions are necessary to develop the technology of natural water deacidification. Calcite was chosen as a model reagent because it is the major component of the assumed reagent, *i.e.* comminuted carbonate.

#### DISSOLUTION OF CALCITE IN WATER

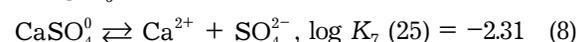
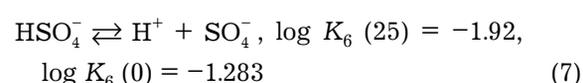
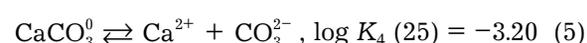
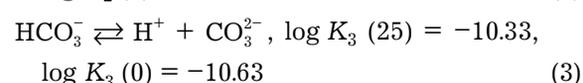
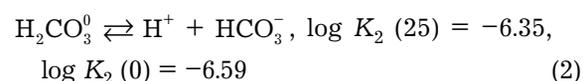
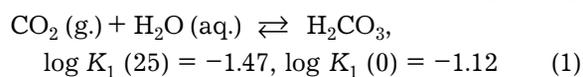
Determination of the composition of solutions formed after calcite dissolution in water,

as well as the determination of the distribution of calcium and carbon ion forms depending on pH are necessary in order to master the experimental procedure and reveal admissions that can be made for the calculations of a more complicated system.

It was shown in [17] that the pH of a system composed of calcite in water in equilibrium with the atmosphere is 8.4; the major components are  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ .

After the addition of calcite to the melted snow water, the resulting water may be considered as weakly mineralized calcium hydrocarbonate water. In this case  $\text{Ca}(\text{HCO}_3)_2$  is known to account for more than 70 % of total mineral content [15].

When investigating the carbonate system of natural water, the following forms should be taken into account, according to [16]:  $\text{H}_2\text{CO}_{3\text{aq}}$ ,  $\text{H}_{\text{aq}}^+$ ,  $\text{HCO}_{3\text{aq}}^-$ ,  $\text{CO}_{3\text{aq}}^{2-}$ ,  $\text{Ca}_{\text{aq}}^{2+}$ ,  $\text{CaHCO}_{3\text{aq}}^+$ ,  $\text{CaCO}_{3\text{aq}}$ . The reference data on equilibrium constants  $K$  used in the calculations are [17–19]:

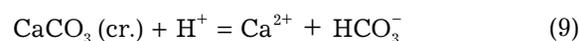


The results of calculations shown in Table 1 suggest that the main part in calcium balance is played by calcium ion  $\text{Ca}^{2+}$ , while the concentrations of  $\text{CaHCO}_3^+$  and  $\text{CaCO}_3$  can be neglected in subsequent calculations. The main species in carbon balance is  $\text{HCO}_3^-$ . In addition, the amount of  $\text{Ca}^{2+}$  within the pH range 5.8–8.0 is 2–3 times smaller than the amount of  $\text{HCO}_3^-$  (see Table 1). Therefore, at least a half of  $\text{HCO}_3^-$  ions present in solution was formed due to the absorption of carbon dioxide from the air, formation of carbonic acid followed by its dissociation, and consumption of the protons:

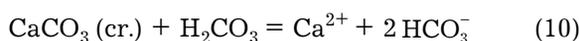
TABLE 1

Composition of solutions formed after calcite dissolution in water in equilibrium with atmospheric CO<sub>2</sub> ( $P_{\text{CO}_2} = 3.16 \cdot 10^{-4}$  atm [14],  $t = 25$  °C)

pH	Concentration, mol/l					
	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Ca <sup>2+</sup>	CaHCO <sub>3</sub> <sup>+</sup>	CaCO <sub>3</sub> <sup>0</sup>	HCO <sub>3</sub> <sup>-</sup> / Ca <sup>2+</sup>
5.8	$2.81 \cdot 10^{-6}$	$8.31 \cdot 10^{-11}$	$6.15 \cdot 10^{-7}$	$3.14 \cdot 10^{-11}$	$8.09 \cdot 10^{-14}$	4.57
6.0	$4.45 \cdot 10^{-6}$	$2.09 \cdot 10^{-10}$	$1.73 \cdot 10^{-6}$	$1.40 \cdot 10^{-10}$	$5.72 \cdot 10^{-13}$	2.57
6.4	$1.12 \cdot 10^{-5}$	$1.32 \cdot 10^{-9}$	$5.40 \cdot 10^{-6}$	$1.10 \cdot 10^{-9}$	$1.13 \cdot 10^{-11}$	2.07
6.8	$2.81 \cdot 10^{-5}$	$8.31 \cdot 10^{-9}$	$1.40 \cdot 10^{-5}$	$7.14 \cdot 10^{-9}$	$1.84 \cdot 10^{-9}$	2.01
7.2	$7.05 \cdot 10^{-5}$	$5.24 \cdot 10^{-8}$	$3.53 \cdot 10^{-5}$	$4.53 \cdot 10^{-8}$	$2.94 \cdot 10^{-9}$	2.00
7.6	$1.77 \cdot 10^{-4}$	$3.31 \cdot 10^{-7}$	$8.90 \cdot 10^{-5}$	$2.87 \cdot 10^{-7}$	$4.66 \cdot 10^{-8}$	1.99
8.0	$4.45 \cdot 10^{-4}$	$2.09 \cdot 10^{-6}$	$2.24 \cdot 10^{-4}$	$1.81 \cdot 10^{-6}$	$7.41 \cdot 10^{-7}$	1.99



Taking this fact into account, we may depict the dissolution of calcite in water in an open system by reaction (1) and



#### DISSOLUTION OF CALCITE IN WATER WITH INCREASED ACIDATION LEVEL

The goal of calculations of the concentrations of solution components formed as a result of calcite dissolution in acid water is to determine the amount of reagent which is necessary to be introduced into a brook with increased level of acidation. During this period, the low water of a brook gets diluted with melted snow water [7], and its chemical composition is determined by the chemical composition of melted snow water.

As a first approximation, we assume water temperature to be 0 °C, and the main components to be carbonate- and sulphate-containing species. According to equilibria (1)–(3), the concentrations of carbonate components at the constant partial pressure of carbon dioxide are unambiguously connected with pH, while this value itself and the concentrations of sulphates are determined by the accumulation of H<sub>2</sub>SO<sub>4</sub> during long winter on the territory adjacent to the brook. Contamination of snow cover may be considered to be constant along the whole brook length, so the concentration of sulphuric acid in the brook can be considered con-

stant, too. The total sulphate content does not change with the addition of calcite to the stream, because, as preliminary calculations showed, the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are insufficient for calcium sulphate to get precipitated. So, water flow is characterized by a definite pH value with the corresponding concentrations of SO<sub>4</sub><sup>2-</sup>-containing forms which are constant along the whole stream.

When calculating the dissolution of calcite in water, in addition to Ca<sup>2+</sup> concentration we took into account the concentrations of its carbonate forms CaHCO<sub>3</sub><sup>+</sup> and CaCO<sub>3</sub><sup>0</sup>. The concentrations of the latter forms were determined to be 3–6 orders of magnitude smaller than the concentration of Ca<sup>2+</sup>. It was shown in [19] that in the case if the concentration of SO<sub>4</sub><sup>2-</sup> is less than that of HCO<sub>3</sub><sup>-</sup> by an order of magnitude, the fractions of CaHCO<sub>3</sub><sup>+</sup> and CaSO<sub>4</sub><sup>0</sup> among all the calcium-containing forms are approximately the same. In the case under our consideration, SO<sub>4</sub><sup>2-</sup> concentration is larger than HCO<sub>3</sub><sup>-</sup> concentration, so the fraction of CaSO<sub>4</sub><sup>0</sup> will be much larger than that of CaHCO<sub>3</sub><sup>+</sup>. In addition, the Ca<sup>2+</sup> accounts for the major fraction in the overall balance of calcium-containing chemical forms, while the fraction of CaSO<sub>4</sub><sup>0</sup> is notable in the balance of SO<sub>4</sub><sup>2-</sup>-containing species ([CaSO<sub>4</sub><sup>0</sup>] is only one order of magnitude less than [SO<sub>4</sub><sup>2-</sup>]). Taking the above considerations into account, we may state that calculations of calcite dissolution in water acidified with sulphuric acid are to take into

account partial binding of  $\text{SO}_4^{2-}$  into  $\text{CaSO}_4^0$ , while the data on  $[\text{CaHCO}_3^+]$  and  $[\text{CaCO}_3^0]$  ( $[\text{CaHCO}_3^+] < [\text{CaCO}_3^0]$ ) can be neglected.

In addition to the concentrations of solution components, we also determined acidation indices – the molar ratio of bicarbonate to sulphate ions  $\text{HCO}_3^-/\text{SO}_4^{2-}$  and ANC:

$$\text{ANC} = [\text{HCO}_3^-] - [\text{H}^+] \quad (11)$$

#### MAIN RESULTS OBTAINED IN THE CALCULATION OF CHEMICAL EQUILIBRIA IN THE SYSTEM CALCITE–SULPHURIC ACID–WATER

For the development of the technology of a decrease in natural water acidation level, one should determine the conditions which are necessary for water quality to correspond to the standard requirements (for example, pH 6.5, ANC = 20  $\mu\text{eq/l}$ ,  $\text{HCO}_3^-/\text{SO}_4^{2-} > 1$ ). The calculated indices are shown in Table 2.

Since a definite  $[\text{HCO}_3^-]$  value which is constant under the given conditions (temperature, equilibrium with atmospheric carbon dioxide and its partial pressure) corresponds to a definite final  $\text{pH}_f$  of the solution, the ANC value depends only on the solution pH and does not depend on pH of the initial acid water ( $\text{pH}_{\text{in}}$ ). Therefore,  $\text{pH}_f$  and ANC in rather simple system under consideration duplicate each other. In addition, the standard pH 6.5 corresponds to ANC = 20  $\mu\text{eq/l}$ , accepted for the Kola North in [5] as the limiting load on water bodies.

Because of this, further we did not analyze the ANC value under calcite introduction.

Unlike for ANC, the  $\text{HCO}_3^-/\text{SO}_4^{2-}$  ratio depends not only on  $\text{pH}_f$  but also on  $\text{pH}_{\text{in}}$  or, in the case considered by us, on the concentration of sulphate ions in the initial water. For  $\text{pH}_{\text{in}} \geq 4.5$   $\text{HCO}_3^-/\text{SO}_4^{2-} > 1$  if pH corresponds to the standard value (6.5). In the case when  $\text{pH}_{\text{in}}$  is 3, 3.5 and 4, it is necessary to increase  $\text{pH}_f$  to 8, 7.5 and 7, respectively, in order to make the  $\text{HCO}_3^-/\text{SO}_4^{2-}$  ratio more than unity. It is evident that developing the technology of a decrease in water acidation one should first of all determine which index or a set of indices is the criterion of water quality.

A change in  $\text{HCO}_3^-$  concentration causes a shift in the sequence of equilibria between carbonate species; either the removal of carbon dioxide from solution or its absorption will take place, depending on the conditions. Therefore, it is more convenient to monitor the amount of the dissolved reagent on the basis of calcium concentration but not the concentration of carbonates. The values of  $\text{Ca}^{2+}$  concentration, which is necessary for water quality indices to correspond to the chosen values, are listed in Table 3.

#### CONCLUSIONS

Thus, calculation results allow us to determine what should be the concentration of calcium in water under the corresponding chosen acidation indices. However, calcite

TABLE 2

Indices of water acidation level after treatment with calcite ( $P_{\text{CO}_2} = 3.16 \cdot 10^{-4}$  atm [14],  $t = 0$  °C)

$\text{pH}_f$	ANC, $\mu\text{eq/l}$	$\text{HCO}_3^-/\text{SO}_4^{2-}$ for $\text{pH}_{\text{in}}$ equal to					
		3	3.5	4	4.5	5	5.5
3.5	-316	$3.68 \cdot 10^{-5}$	–	–	–	–	–
4	-100	$1.17 \cdot 10^{-4}$	$3.84 \cdot 10^{-4}$	–	–	–	–
4.5	-31	$3.70 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$	$3.82 \cdot 10^{-3}$	–	–	–
5	-9	$1.17 \cdot 10^{-3}$	$3.84 \cdot 10^{-3}$	$1.21 \cdot 10^{-2}$	$3.97 \cdot 10^{-2}$	–	–
5.5	-1	$3.71 \cdot 10^{-3}$	$1.22 \cdot 10^{-2}$	$3.82 \cdot 10^{-2}$	$1.25 \cdot 10^{-1}$	$4.18 \cdot 10^{-1}$	–
6	5	$1.17 \cdot 10^{-2}$	$3.85 \cdot 10^{-2}$	$1.21 \cdot 10^{-1}$	$3.97 \cdot 10^{-1}$	132	$1.09 \cdot 10^1$
6.5	20	$3.71 \cdot 10^{-2}$	$1.22 \cdot 10^{-1}$	$3.83 \cdot 10^{-1}$	126	419	$3.46 \cdot 10^1$
7	63	$1.18 \cdot 10^{-1}$	$3.87 \cdot 10^{-1}$	126	4.00	$1.33 \cdot 10^1$	$1.10 \cdot 10^2$
7.5	200	$3.77 \cdot 10^{-1}$	124	390	$1.28 \cdot 10^1$	$4.26 \cdot 10^1$	$3.53 \cdot 10^2$
8	633	124	410	$1.28 \cdot 10^1$	$4.23 \cdot 10^1$	$1.41 \cdot 10^2$	$1.16 \cdot 10^3$

TABLE 3

Concentration of dissolved calcium after a decrease in the level of water acidation

pH <sub>in</sub>	Ca <sup>2+</sup> content, mg/l	
	pH <sub>c</sub> 6.5	HCO <sub>3</sub> <sup>-</sup> / SO <sub>4</sub> <sup>2-</sup> = 1
3	21.96	29.60
3.5	6.96	9.60
4	2.50	3.00
4.5	1.03	0.90
5	0.59	0.50
5.5	0.42	0.00*

\*In the initial water: HCO<sub>3</sub><sup>-</sup> / SO<sub>4</sub><sup>2-</sup> > 1.

dissolves slowly, and the time of reagent residence in water can turn out to be insufficient for the whole introduced amount of calcite to get dissolved. The required rate of calcium arrival into water is determined by the hydrodynamic regime of the acid water flow and by the chemical composition of water before and after its treatment with the reagent. Since dissolution rate depends not only on the type of material but also on the specific surface, material grinding method and other factors, at the next stage it will be necessary to choose a reagent and a method of its preliminary treatment to provide the required rate of calcium arrival into the water under treatment.

## REFERENCES

- 1 B. S. Smolyakov, *Chem Sust. Dev.*, 10, 5 (2002) 497. <http://www.sibran.ru/English/csdw.htm>
- 2 R. D. Fitzhugh, T. Furman, J. R. Webb *et al.*, *Biogeochemistry*, 47 (1999) 39.
- 3 N. A. Berezina, *Ekologiya*, 5 (2001) 372.
- 4 I. V. Stebaev, Zh. F. Pivovarova, B. S. Smolyakov, S. V. Nedelkina, *Biogeosistemy lesov i vod Rossii*, Nauka, Novosibirsk, 1993.
- 5 T. I. Moiseenko, *Zakisleniye i zagryazneniye tyazhelymi metallami poverkhnostnykh vod Kol'skogo Severa*, Apatity, 1991.
- 6 T. I. Moiseenko, *Teoreticheskiye osnovy normirovaniya antropogennykh nagruzok na vodoemy Subarktiki*, Apatity, 1997.
- 7 T. I. Moiseenko, *Vod. Resursy*, 25 (1998) 16.
- 8 T. I. Moiseenko, V. A. Yakovlev, *Antropogennyye preobrazovaniya vodnykh ekosistem Kol'skogo Severa*, Nauka, Leningrad, 1990.
- 9 J. L. Stoddard, C. T. Driscoll, J. S. Kahl, J. H. Kellogg, *Environ. Monitoring Assessment*, 51 (1998) 399.
- 10 A. Janicki, H. Greening, *Gov. Rep. Announcement Index (US) 1989*, 89 (9), Abstr. No. 923,024.
- 11 D. E. Arnold, W. D. Skinner, D. E. Spotts, *Water, Air, Soil Pollut.*, 41 (1988) 385.
- 12 D. C. McAvoy, C. T. Driscoll, *Res. J. Water Pollut. Control Fed.*, 61 (1989) 1552.
- 13 J. E. Davis, R. A. Goldstein, *Water Resour. Res.*, 24 (1988) 525.
- 14 V. I. Belevantsev, S. A. Sukhenko, *Vod. Resursy*, 22 (1995) 85.
- 15 V. I. Belevantsev, L. V. Gushchina, A. A. Obolenskiy *et al.*, *Chem. Sust. Dev.*, 3 (1995) 3.
- 16 V. I. Belevantsev, V. I. Malkova, A. P. Ryzhikh *et al.*, *Ibid.*, 12 (2004) 731.
- 17 R. M. Garrels, C. L. Christ, *Solutions, Minerals, and Equilibria*, Harper and Row, New York, 1965.
- 18 *Spravochnik khimika, Khimiya*, Moscow-Leningrad, 1965.
- 19 A. P. Endovitskiy, M. B. Minkin, *Gidrokhim. Mat.*, 74 (1978) 58.