IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

Potentiometric analysis of metastable carbonate water coolants of thermal power plants and heat supply systems

To cite this article: A A Chichirov *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **288** 012004

View the article online for updates and enhancements.

This content was downloaded from IP address 94.180.208.21 on 15/01/2020 at 17:04

IOP Conf. Series: Earth and Environmental Science **288** (2019) 012004 doi:10.1088/1755-1315/288/1/012004

Potentiometric analysis of metastable carbonate water coolants of thermal power plants and heat supply systems

A A Chichirov, A A Filimionova, B A Gilfanov, A A Gafiatullina and N D Chichirova

Kazan state power engineering university, Russia, 420066 Kazan, Krasnoselskaya, 51

b_gilfanov@bk.ru

Abstract. The paper describes a new method for studying the structure of metastable carbonate solutions, based on obtaining pK- and pH-spectra of solutions from potentiometric titration data. The decoding method is used to obtain the equations for calculating the coordinates of the spectra. In the production of thermal and electrical energy in modern thermal power plants (TPP) operate with water systems that have a constantly producing phase instability. Such systems include (1) water systems in intermediate stages of water treatment, in particular lime-coagulated or clarified water after pre-treatment, (2) cooling water in the circulating cooling system (COO) of the station, (3) water heat transfer medium in conjugated heat networks , (4) boiler water. All these systems are characterized by the presence of a stabilized (metastable) solid phase, mainly calcium carbonate, capable of forming a crystalline phase of calcite under certain conditions. The crystallization process is undesirable, since it can lead to dense deposits on the heat exchange surfaces. Approximately the instability of such systems is characterized by the value of ΔQw - by changing the total alkalinity of water in time (hours, days). The method of quantitative determination of stabilized calcium carbonate in water systems of TPPs is currently lacking. Development of a technique for potentiometric analysis of carbonate-alkaline solutions.

The experimental part

The initial solutions Na2CO3, NaHCO3, CaCl2, NaOH were prepared on the basis of bidistillate and dry chemically pure substances. Model solutions were obtained by mixing the starting solutions in a certain proportion. About 10 minutes after the preparation, potentiometric titration of model solutions with 0.1 N HCl solution was carried out. Titration was carried out in a potentiometric cell, closed from the atmosphere, with a working glass electrode and a silver chloride reference electrode. During the titration, the solution was stirred with a magnetic stirrer. Before and after the experiment, the electrode was calibrated using standard buffer solutions.

To find the equivalence point, a differential curve is frequently constructed in the coordinates δE / δV - V, (δpH / δV - V). The maximum of the obtained curve indicates the point of equivalence, and the reading along the abscissa axis corresponding to this maximum gives the volume of the titrant consumed for titration up to the point of equivalence. The definition of the equivalence point along the differential curve is much more accurate than the simple E-V (pH-V) dependence.

The obtained results were presented in the form of dependences in the coordinates pH-V (HCl), pH-f, δpH / δf-f, and δpH / f-pH, q-pKa. Here, f = nt / n0 is the degree of titration, which is equal to the ratio of the quantity of the currently tipped substance (nt) to the original quantity (n0), pKa is the acid dissociation constants. The obtained experimental curves were compared with the results of

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

calculation of chemical equilibria in model solutions using the previously written applied computer program (PP) "Structure Analysis and Classification of Water" [2 ± 5].

Results and discussion

The formation of calcium carbonate can occur according to different mechanisms, depending on the total concentration of calcium ions with (Ca2 +) in solution [3]:

with (Ca2 +) ≥ 10 mM - spontaneous precipitation;

with (Ca2 +) ≥ 3 mM - delayed homogeneous formation of nucleation centers (embryos);

with (Ca2 +) ≥ 2.5 mM - deposition on solid microparticles;

with (Ca2 +) ≤ 2,5 mM - formation of supersaturated solution and subsequent precipitation of precipitate**.**

In this case supersaturated (metastable) solutions retain phase stability up to several days. A study of the kinetics of the process showed [4, 5] that the precipitation of CaCO3 proceeds in two stages: the formation of calcium carbonate and its subsequent crystallization. Moreover, the first stage - the formation of salt as a result of ionic transformations - proceeds rapidly during a time of 1 to 10 minutes.

The structure of metastable solutions was studied by the potentiometric method. For guaranteed entry into the region of supersaturated solutions, the measurements were started 10 minutes after the initial solutions were drained. In alkaline carbonate solutions that do not contain hardness ions, there are three potential jumps - at pH 3.5 ÷ (I), pH 8.2 (II) and pH 10 ÷ 11. When calcium ions with a concentration of more than 1 mM are introduced into the solution, which corresponds to an excess of PR (CaCO3), there are four jumps.

On the concentration-logarithmic diagram calculated by means of PP (Fig. 1), it is possible to visually determine the coordinates of the titration curves and the reactions corresponding to them.

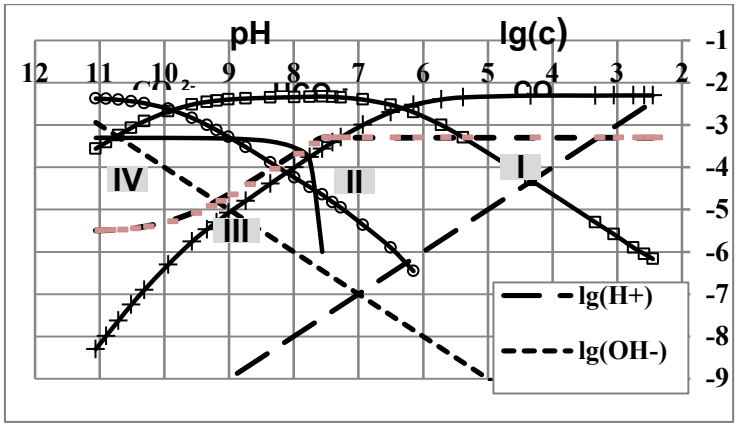


Figure1. Concentration-logarithmic diagram of CaCl2 solution (1 mM), Na2CO3 (10 mM), NaOH (1mM).

For the I point of equivalence (pH 3 ÷ 5), the potential-determining reaction-neutralization of bicarbonate ions

$$H^+ + HCO_3^- \Leftrightarrow H_2CO_3, \quad (1)$$

which is characterized by the dissociation constant of weak carbonic acid in the first stage (K1)

$$K_1 = \gamma_1^2 \frac{[\mathbf{H^+}] \cdot [\mathbf{HCO_3^-}]}{[\mathbf{H_2CO_3}]}. \quad (2)$$

At the equivalence point: [HCO3-] = [H +]

For the II equivalence point (pH 7 ÷ 8,2), the potential-determining reaction is the carbonate-bicarbonate-ion transition, including ions, formed during the dissolution and dissociation of calcium carbonate. The diagram (Figure 1) shows that in the region between the II and III equivalence points, complete dissolution of CaCO3 occurs.

$$\mathbf{H^+ + CO_3^{2-} \Leftrightarrow HCO_3^{2-}} \quad (3)$$

$$\mathbf{CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}}. \quad (4)$$

The equilibrium is characterized by a dissociation constant of carbonic acid in the second stage (K2) and PR (CaCO3)

$$K_2 = \gamma_2 \frac{[\mathbf{H^+}] \cdot [\mathbf{CO_3^{2-}}]}{[\mathbf{HCO_3^-}]}. \quad (5)$$

At the equivalence point [CO32-] = [CO2] or max [HCO3-].

For the III equivalence point (pH 6.5 ÷ 8.2), the potential-determining reaction is the carbonate-bicarbonate-ion transition, with the exception of the main part of calcium carbonate, which remains in the insoluble state

$$\mathbf{ПР_{CaCO_3}} = \left[\mathbf{Ca^{2+}}\right] \cdot \left[\mathbf{CO_3^{2-}}\right]. \quad (6)$$

In the third point of equivalence of [Ca2 +] = [CO32-] under the condition with (CO2) ≥ s (Ca2 +).

For the IV equivalence point (pH 10.5 ÷ 11.5), the potential-determining reaction-neutralization of hydroxyl ions:

$$\mathbf{OH^- + HCO_3^- \Leftrightarrow H_2O + CO_3^{2-}}. \quad (7)$$

In the fourth point of equivalence, [OH-] = [HCO3-].

In the equations (2) and (5), the ion activities are equated to their concentrations or to the coefficients γ = 1.

The results show that in the pK spectrum only the maximum of the peak is observed in the region of the characteristic value of pK0 (coincides with pK2). The peaks of other peaks lie in the region pK = pH (α = 1/2). Therefore, for practical purposes, the use of pH values (α = 1/2) seems preferable to us.

In Fig. 4 represents the experimental and calculated theoretical pH spectra of the solution under study. Good agreement with the concentration-logarithmic diagram indicates the correctness of the correlation of peaks and reactions. The number of peaks and their coordinates (pHeq) unambiguously characterize the composition and structure of the solution.

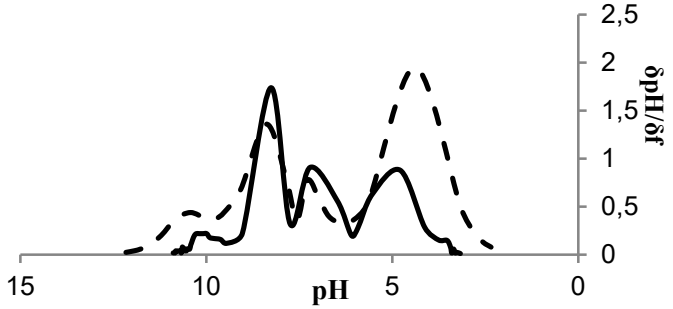


Figure 2. The pH spectrum of a model solution of CaCl2 (2 mM), Na2CO3 (10 mM), NaOH (2 mM).

For an approximate calculation of the characteristics of potentiometric curves and pH spectra, we use the basic equation obtained by summing the expressions (2), (5), (6).

$$a_{\mathbf{H}^+}^2 \cdot \frac{\sqrt{\mathbf{\Pi P}}}{K_1 \cdot K_2} + a_{\mathbf{H}^+} \cdot \frac{\sqrt{\mathbf{\Pi P}}}{\gamma_1 \cdot K_2} + \frac{\sqrt{\mathbf{\Pi P}}}{\gamma_2} = c_{\mathbf{CO_2^-}}; \tag{8}$$

Taking the activity coefficients γ = 1, we obtain an expression for the concentration of hydrogen ions:

$$\left[\mathbf{H}^+\right] = \frac{-\frac{\sqrt{\mathbf{\Pi P}_{KK}}}{K_2} \pm \sqrt{\frac{\mathbf{\Pi P}_{KK}}{K_2^2} - \mathbf{4} \cdot \frac{\sqrt{\mathbf{\Pi P}}}{K_1 K_2} \cdot \left(\sqrt{\mathbf{\Pi P}_{KK}} - c_{\mathbf{CO_2}}\right)}}{\mathbf{2} \cdot \frac{\sqrt{\mathbf{\Pi P}}}{K_1 \cdot K_2}}. \tag{9}$$

For regions near the peaks on the curve of the pH spectrum, after appropriate simplifications, we obtain expressions for finding the coordinates of the spectrum (Table 1).

Table 1. Characteristics of pH-spectra in systems CO32- - OH - - Ca2 +

Peak	Value pH	Formula for calculating the pH of ECB	
		$\mathbf{Na_2CO_3 + NaOH}$	$\mathbf{Na_2CO_3 + NaOH + CaCl_2}$
1	3-5	$\frac{1}{2}\left(\mathbf{p}K_1 - \mathbf{lg}c_{\mathbf{CO_2}}\right)$	$\frac{1}{2}\left(\mathbf{p}K_1 - \mathbf{lg}c_{\mathbf{CO_2}}\right)$
2	7-8,2	$\frac{1}{2}\left(\mathbf{p}K_1 + \mathbf{p}K_2\right)$	$\frac{1}{2}\left(\mathbf{p}K_1 + \mathbf{p}K_2 - \mathbf{lg}C_{\mathbf{Ca^{2+}}} - \frac{1}{2}\mathbf{p\Pi P}\right)$
3	6,5-9,5	-	$\mathbf{p}K_2 - \mathbf{lg} \cdot \left(c_{\mathbf{CO_2}} - c_{\mathbf{CaCO_3}}\right) - \frac{1}{2}\mathbf{p\Pi P}$
4	10,5-11,5	$\frac{1}{2}\left(\mathbf{p}K_w + \mathbf{p}K_2 + \mathbf{lg}c_{\mathbf{CO_2}}\right)$	$\frac{1}{2} \cdot \left(\mathbf{p}K_w + \mathbf{p}K_2 + \mathbf{lg} \cdot \left(c_{\mathbf{CO_2}} - c_{\mathbf{CO_3}}\right)\right)$

Here c (CO2) is the total content of all equilibrium forms of carbonic acid; with (CaCO3) - concentration of all forms of calcium carbonate; KW is the water constant equal to [H +] · [OH-].

$$\mathbf{ПР}_{\mathbf{CaCO_3}} = \mathbf{5 \cdot 10^{-9}}.$$

By the potentiometric titration curves, the content of metastable calcium carbonate in the solution can be quantitatively determined by the formula:

$$c(CaCO_3) = c(HCl)\cdot(V_{III}(HCl) - V_{II}(HCl))/V\text{p-pa}. \quad (10)$$

In a series of 20 experiments with metastable solutions, a good agreement was obtained between the experimental and calculated values of the CaCO3 content. The standard deviation was ± 15 rel. %, which can be considered acceptable for metastable equilibrium and small concentrations.

It should be noted that in the chemical laboratories of TPP, the hydrate alkalinity, acidity and carbon dioxide content are determined by titration in the presence of indicators of phenolphthalein and methylorange, which change their color depending on the pH of the solution. Moreover, the phenolphthalein color transition occurs in the pH range of 8.5 ÷ 10.0. Meanwhile, as can be seen from the pH spectrum of a metastable solution, a part of the carbonate bound to calcium is not titrated. But this part of carbonates is titrated in the area of methylorange (pH 3,0 ÷ 4,0). Thus, a systematic error occurs.

The results in the article allow us to draw some conclusions:

- Potentiometric and pH-spectroscopic analysis of metastable alkaline solutions containing carbonates and stiffness ions allows qualitative and quantitative determination of their structure and ion-molecular composition, including stabilized calcium carbonate;
- the method of potentiometric titration can be used for the analysis of metastable solutions, including turbid or colored, which is difficult or impossible, since the use of color indicators gives a systematic error.

References

[1] Garmash A V, Vorobyova O N, Kudryavtsev A V and Danchenko N N 1998 *Journal of Analytical Chemistry* **4** 411-417
[2] Chichirov A A, Chichirova N D, Khusainov R R, Filimonov A G and Filippov I E 2006 *Energysaving and watertreatment* **2** 31-34
[3] Filimonov A G, Chichirov A A, Gainutdinova L I and Chichirova N D 2012 *Energy problems* **5-6** 11-16
[4] Boskey A L, Posner A S J/ Phys. Chem. 1973. v.77, p. 2313.
[5] Khoroshilov A V, Semenova I V and Simonova S V 2004 *Energysaving and watertreatment* **3** 20-22