

ОХОРОНА НАВКОЛИШНЬОГО СЕРЕДОВИЩА ТА ЕКОЛОГІЧНА БЕЗПЕКА

UDC 628+546.264

S. VYSOTSKY (doctor of technical sciences, prof.),
A. FATKULINA (candidate of technical sciences, senior lecturer)
Auroad institute DonNTU

CALCIUM CARBONATE FORMATION IN WATER TREATMENT SYSTEMS AND ON HEATING SURFACES

The paper studies the processes of calcium carbonate formation in various water treatment systems and heat transfer surfaces, when water is heated. It is shown, that the intensity of scale formation depends mainly on the temperature and degree of supersaturation of the solution. We defined the solubility of calcium carbonate, depending on the ratio of hydrogen ions activity and product concentrations of calcium and carbonate ions without and with the presence of scale inhibitors.

Keywords: *watertreatment, calcium carbonate, induction period, scaling.*

The performance of the systems of removing calcium carbonate hardness compounds in clarifiers and settling tanks, the intensity of deposits formation on heat transfer surfaces in the power equipment and, consequently, the reduction of the efficiency and reliability of this equipment are mainly connected with the conditions of calcium carbonate formation.

The intensity of calcium carbonate formation in the systems of heat transfer in condensers and heat exchangers at different stages of the process is determined by different equations and depends mainly on the degree of supersaturation of the solution and temperature [1]. The data on fig. 1 show the change in the rate of crystallization at various concentrations of calcium ions. Obviously, for scale formation prevention the time of the solution staying in the heating zone should be shorter than the induction period of crystallization. In contrast, during reagent water softening in clarifiers or settling tanks the time of water staying in the reaction zone should exceed the latent period of crystallization.

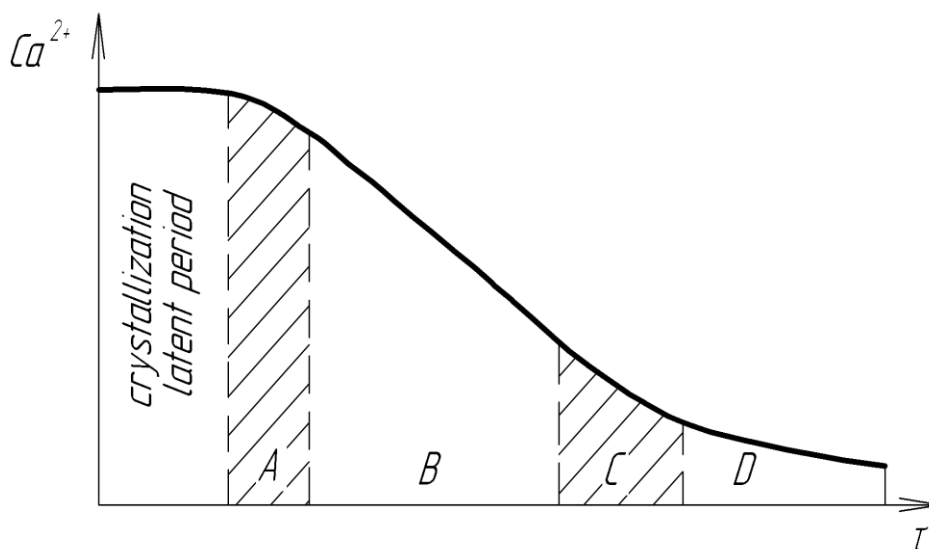


Figure 1 – Change in the rate of calcium carbonate crystallization in time

Area A:
$$\frac{dCa^{2+}}{d\tau} = -\frac{S}{V}k_{\tau} [Ca^{2+} - Ca^{2+}_s] \tag{1}$$

Area B:
$$\frac{dG}{dt} = a - k \cdot \tau \tag{2}$$

Area C:
$$\frac{dCa}{dt} = -C_1 [CO_3^{2-} \cdot Ca^{2+}] \tag{3}$$

Area D:
$$\frac{dCa^{2+}}{dt} = 0 \tag{4}$$

where Ca^{2+} , CO_3^{2-} are calcium ions and carbonates concentrations in the volume of solution, mol/l;
 S – surface, where calcium carbonate forms deposits, m^2 ;
 V – solution volume, m^3 ;
 k_{τ} – constant of crystallization rate on the surface, m/hr;
 k – constant of crystallization rate in solution volume, mol/hr²;
 C₁ – bimolecular reaction rate constant, $m^3/hr \text{ mol}$.

Additionally, the duration of crystals nucleation depends on the type of surface on which crystallization occurs. [2]

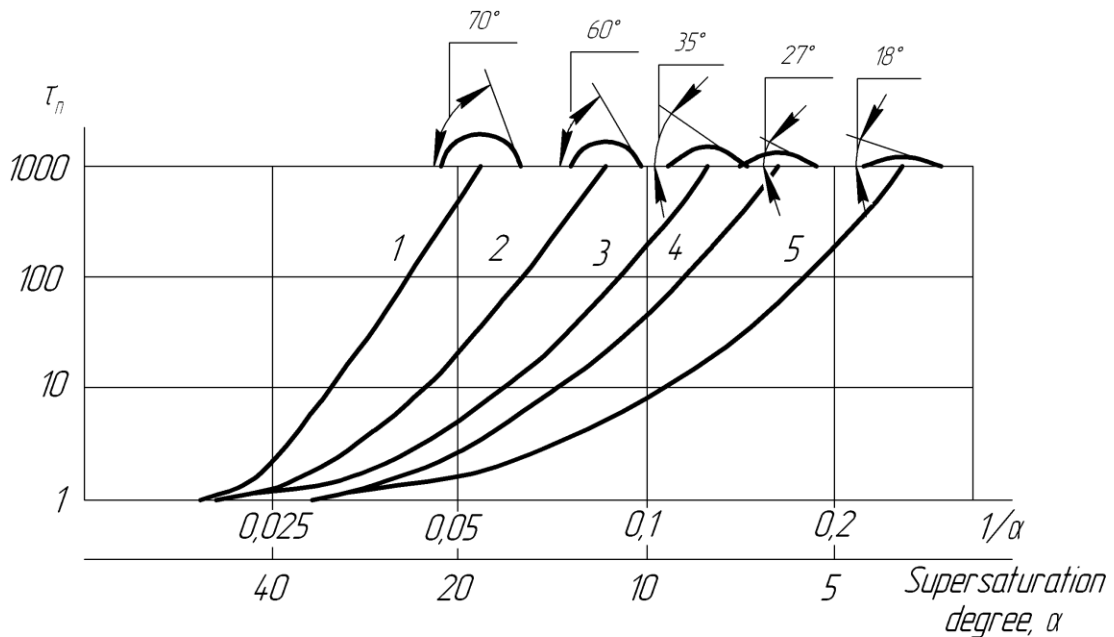


Figure 2 – Dependence of crystals nucleation τ_3 on the degree of supersaturation α and surface type:

1 – PVC, 2 – plexiglass, 3 –glass, 4 – frozen plexiglas, 5 – polished stainless steel

According to M. Vollmer, solid phase formation is largely dependent on the type of a wall or physical state of the interface surface. The energy of nucleus crystal formation is defined as:

$$A = \frac{1}{3} \cdot \pi \cdot r^2 \cdot \sigma \cdot [2 \cdot 1 - \cos\Theta - \sin^2\Theta \cdot \cos\Theta], \tag{5}$$

where A is the energy of the crystal nucleus formation on the wall, N m;
 r – crystals particles size, m;
 σ – surface energy of the crystal face, N/m;

Θ – limiting wetting angle, degrees.

From this expression it follows that the ratio of the energy of the isothermal formation of the solid phase from the supersaturated solution on the solid surface, and free surface energy of crystallization in solution volume depends on the contact angle of the surface. Obviously, with the limiting wetting angle $\Theta = 0^\circ$ crystallization starts with a slight supersaturation. If $\Theta = 90^\circ$ the energies of nucleation on the wall surface and in solution volume are equal, therefore, the intensity of crystallization in solution volume and calcium carbonate incrustation on the wall surface are equally probable.

When studying the conditions of calcium carbonate crystallization on different surfaces we obtained the dependence of the rate of deposits formation on the type of surface. The data are given in table 1.

Table 1 – Heat transfer surfaces materials research

Material	Wetting angle Θ , degree	Scaleformation intensity V , $g/(m^2 \cdot hr)$
Polyethylene	87	0,0088
Fiberglass	71	0,0194
Fiberglass Cloth	57	0,032
Asbestos cement	24	1,74

Scale formation intensity on different surfaces depends on the expences of energy to overcome the threshold of "instability". The higher the energy is, the lower is the rate of crystallization of the particles on the surface of heating. Fig. 3 shows the effect of free energy of calcium carbonate particles crystallization in solution volume and on the heat transfer surface on the intensity of calcium carbonate crystallization.

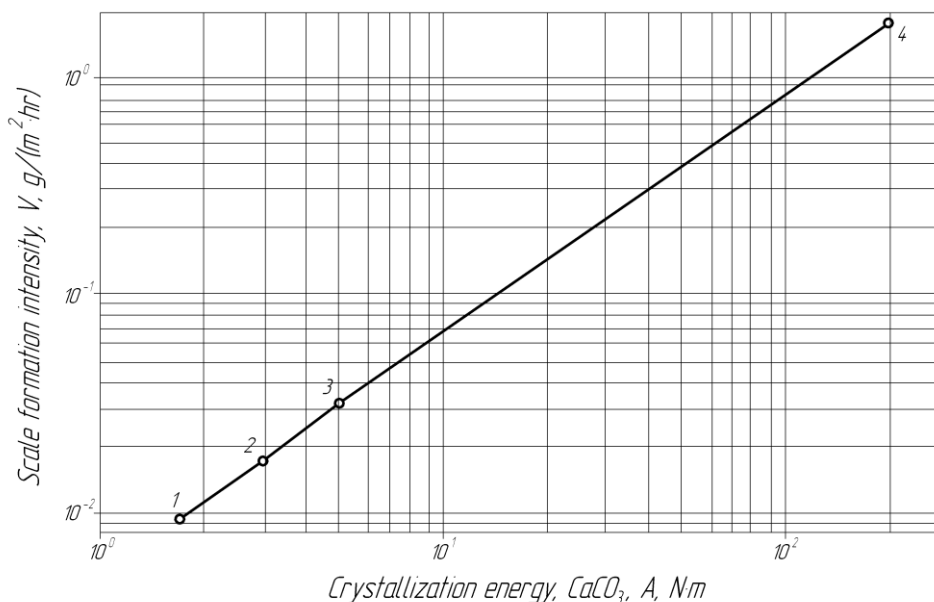


Figure 3 – Dependence of crystallization rate on the type of material, on which calcium carbonate crystallization occurs, and nucleation energy:

1 – polyethylene; 2 – fiberglass; 3 – fiberglass cloth; 4 – asbestos cement

Analyzing these results, it is necessary to take into account that the value of "instability" threshold is dependent on the physical state of the surface. If the surface is porous, has narrow cracks (as, for example, asbestos-cement plates), calcium incrustation can occur even in an

unsaturated solution.

In water consumption and water treatment practice, there are several approaches to assessing water stability in terms of scaling intensity and corrosion properties of aqueous solutions.

Langelier, studying the equilibrium values for CaCO_3 according to the degree of dissociation of carbonic acid, bicarbonate and carbonate, on the basis of the theoretical solubility of CaCO_3 at different temperatures depending on water salinity, proposed a method to assess the stability depending on the degree of saturation of water with calcium carbonate for the so-called value pH_s and pH . If the actual pH of water is below the calculated value pH_s , the water has a negative Langelier index and will dissolve CaCO_3 . Typically, this means that the water can be aggressive to steel in the presence of oxygen. If the measurements show that the pH value exceeds pH_s , the water will have a positive Langelier index and will be oversaturated with CaCO_3 . This water will probably facilitate scaling. The greater is the difference between the actual pH and pH_s , the more pronounced is its instability with respect to the formation of deposits.

$$\text{Langelier Index} = I_L = \text{pH} - \text{pH}_s \quad (6)$$

Analyzing the conditions of scale and corrosion formation in several municipal systems, Rizner modified Langelier index for a more reliable estimate of scaling and corrosion probability, proposing to use the stability index (Rizner index).

$$\text{Stability Index} = 2\text{pH}_s - \text{pH} \quad (7)$$

Rizner index is a characteristic of semi-quantitative estimation of the scaling intensity. If Rizner index > 6 , the aqueous solution is considered to be aggressive, and if < 6 , then there is a high probability of scaling.

Langelier index is successfully used to predict malfunction risk in large circulating systems with low flow rates. Rizner index is an empirical value and is used in most cases for systems with running water, in which the conditions of mass and heat transfer near the pipes are different from those in the water flow.

Stiff and Davis modified Langelier index to analyze mineralized oilfield (reservoir) water, high salinity of which has an impact on the ionic strength and solubility of CaCO_3 . In this case, the index is calculated by the formula:

$$\text{Index} = \text{pH} - K - \text{pCa} - \text{pAlk}, \quad (8)$$

where pH is defined experimentally;

$$\text{pCa} = \log I/[\text{Ca}];$$

$$\text{pAlk} = \log I/[\text{Alk}];$$

K is a constant that depends on the total ionic strength and temperature.

Such data for oil mineralized (reservoir) water can be used to develop processing technologies for open cooling water circulation systems with zero discharge level.

To calculate stability index, it is necessary to know the temperature, pH and ion concentration of HCO_3^- and SO_3^{2-} . Additionally we need a complete analysis of water to calculate ionic strength and activity coefficients of the corresponding ions.

In the above indexes there is qualitative (Langelier index, the index of Stiffy and Davis) or semiquantitative (Rizner index) assessment of the impact of water quality on scaling intensity. This makes it difficult to quantify the water quality both on scaling intensity and on the degree of scale formation removal in water treatment equipment.

The purpose of the study is to define the effect of temperature, pH and calcium carbonate solubility product on scale formation rate and calcium carbonate solubility at different temperatures, as well as on the induction (latent) period of crystallization.

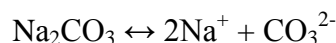
The presentation of basic research material. Since carbonate and bicarbonate ions are conjugate with weak acids, they are involved in equilibrium with the hydronium ion (H_3O^+) and their concentration will be fixed depending on pH. The effect of this relationship is shown in Figure 3. The solubility product of calcium carbonate is defined according to previously derived dependence [3]:

$$SP = 5,77 \cdot 10^{-5} \exp\left(\frac{3,4 \cdot 10^3}{T}\right) - 0,095 \quad (9)$$

where T is temperature, °K.

Essential decrease of solubility stops when pH exceeds 10.5, where most of added CO_3^{2-} ions remain unchanged due to the high alkalinity of the solution.

Another important example of how the composition of an aqueous solution will affect the solubility of CaCO_3 is the common-ion effect. Adding soluble salts Na_2CO_3 to a simple solution (CaCO_3 in deionized water) sets up the equilibria



With pH 11, the effect of hydronium ions can be neglected, and the amount of CaCO_3 that dissolves can be expressed by rewriting as:

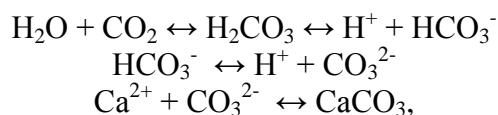
$$SP = [\text{Ca}^{2+}] ([\text{CO}_3^{2-}]_{\text{Na}_2\text{CO}_3})$$

where the subscripts indicate the introduction of the carbonate ion from either CaCO_3 or Na_2CO_3 . As $[\text{Na}_2\text{CO}_3] > [\text{CaCO}_3]$, the following expression is:

$$[\text{Ca}^{2+}] = SP / [\text{Na}_2\text{CO}_3]$$

This equation means that the amount of CaCO_3 that will dissolve in an aqueous solution is strongly dependent on the amount of Na_2CO_3 present. For example, the solubility of CaCO_3 at 25 °C in a 10 g/L (0.094M) solution of Na_2CO_3 is less than 0,1% of its solubility in pure water! In other words, the addition of Na_2CO_3 to a system dramatically decreases the solubility of CaCO_3 , and it should be noted that any other source of carbonate would have the same common-ion effect on solubility.

The main factor determining the displacement of equilibrium in the system



is water temperature, pH and calcium ions concentration, as well as the partial pressure of CO_2 . According to our experimental data and (9) for the dependence of solubility product on temperature we plotted a dependence (see fig. 4).

The analytical expression of this dependence of dissolved calcium carbonate amount on the parameter (pSP–pH) is:

$$S = 7,97 \cdot 10^{-2} \exp 1,18 \text{ pSP} - \text{pH} = 7,97 \cdot 10^{-2} \exp \left[\left(\log \frac{a_H}{SP} \right)^{1,18} \right], \text{ mmol} / \text{ l} \quad (10)$$

After simple transformations of this dependence we obtain:

$$S = 7,97 \cdot 10^{-2} \left(\frac{a_H}{SP} \right)^{0,51}, \text{ mmol / l} \quad (11)$$

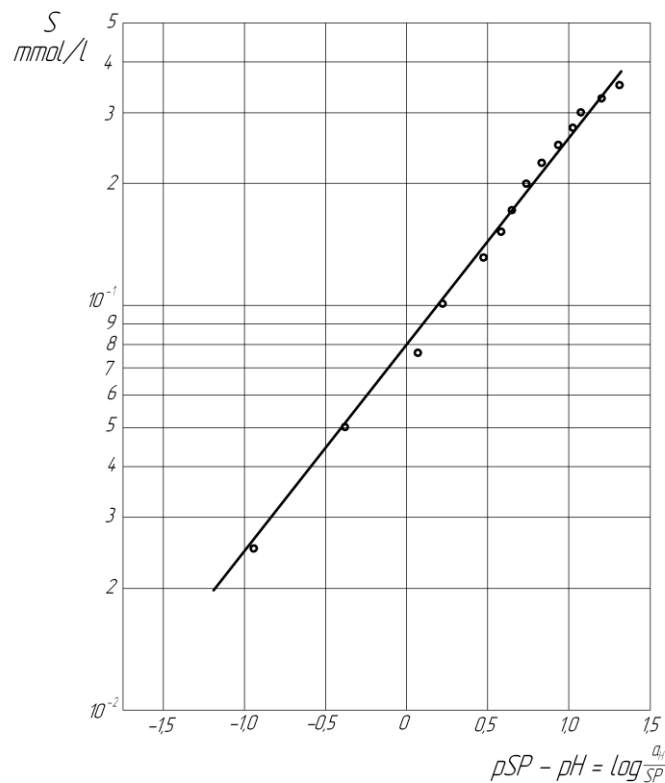


Figure 4 – Dependence of calcium carbonate solubility on the difference (pSP–pH)

In laboratory conditions experiments were performed to define the intensity of scale formation with various concentrations and pH product of the solution. The solution temperature was maintained $93 \pm 2^\circ\text{C}$. The data on Fig. 5 show that scaling intensity is well described by an exponential dependence on the parameter (pCP–pH).

Without stabilizing treatment, water, having the value $(pH - pCP) > 4$ or Rizner stability index less than 6,0 is prone to deposits formation. With the value $(pH - pCP) < 4$ or the index over 7,0 (Rizner) the formation of the protective coating in the form of calcium carbonate is not guaranteed. Corrosion will become a more and more serious problem when the value $(pH - pCP) > 4$ or Rizner stability index increase up to 7,5–8,0.

In polyphosphates application, the water with $(pH - pCP) < 6$ or Rizner stability index over 4,0 can be used at temperatures up to 93°C with a small amount of deposits.

The dependence of deposits amount on the heating surface without stabilizers is given by:

$$G = 1,09 \cdot 10^{-3} \cdot \exp 1,1 \cdot pH - pCP = 1,09 \cdot 10^{-3} \cdot \left(\frac{a_{Ca} \cdot a_{CO_3}}{a_H} \right)^{0,45}, \text{ mmol / hr} \quad (12)$$

Dependence of the deposits amount on the heating surface with 1,7mg/kg polyphosphate $\text{Na}_9\text{P}_7\text{O}_{22}$ dosing is given by:

$$G = 1,2 \cdot 10^{-8} \exp 2,72 \cdot pH - pCP = 1,2 \cdot 10^{-8} \left(\frac{a_{Ca} \cdot a_{CO_3}}{a_H} \right)^{1,18}, \text{ mmol / hr} \quad (13)$$

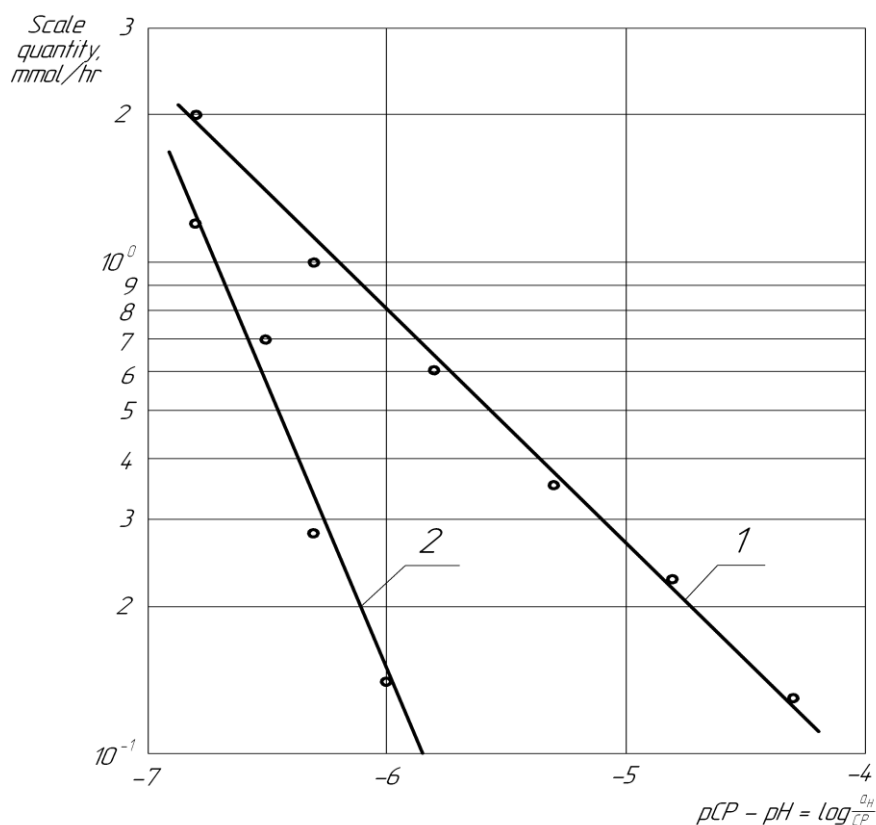


Figure 5 – Dependence of deposits amount on the heating surface on (pCP–pH)
 1 – amount of deposits during heating without scale stabilizers (antiscalant):
 2 –amount of deposits with 1,7 mg / kg dosing of polyphosphate $\text{Na}_9\text{P}_7\text{O}_{22}$

Thus, for the same value of $(\text{pH} - \text{pCP}) = 6$ the addition of antiscalant additive reduces scale formation by approximately 5,5 times. Besides the increase in pH and, consequently, the difference $(\text{pH} - \text{pCP})$ up to 6,5 times reduces the efficiency of antiscalant additives. The intensity of scale formation in these conditions reduces by 2,4 times.

The duration of calcium carbonate crystals nucleation depends on supersaturation degree and solution temperature.

In 1920 Vollmer derived the classical formula of the dependence of the induction time of nucleation on the degree of solution supersaturation:

$$\log \tau_{ind} = (\log^2 DS)^{-1}$$

where DS is the degree of supersaturation equal to the ratio of "TIK" concentration product to the solubility product.

In accordance with this formula there is the following series of relationships between DS and latent - induction period:

DS=CP/SP	2	3	4	5	10	20
τ_{ind}, sec	$1,08 \cdot 10^{11}$	$2,47 \cdot 10^4$	$5,74 \cdot 10^2$	111,4	10	3,89

According to these data when supersaturation is double the calculated induction period is 3,400 years, when triple - 6,86 hr, and when tenfold - 10 sec.

When defining the induction period we used an optical method which employs microscope MBS-10. On the microscope slide we mixed equal volumes of calcium chloride and lithium carbonate solutions of different concentrations. Magnification level was 56 times. As the human eye is capable of distinguishing the objects up to 0,06 mm, it was possible to record the appearance of crystals with sizes up to 1,1 microns. The experiments were performed at 24 °C, 40 °C and 70 °C. The results of the experiments are shown in table 2.

Table 2 – Induction period results, τ_{ind} , sec

№	Temperature, °C	Product concentration, (mg-eqv/l) ²	Induction period, sec
1	24 °C	6	210
2		12	120
3		25	80
4		49	43
5		100	32
6		225	15
7	40 °C	6	41
8		12	24
9		25	15
10	70 °C	6	22
11		12	12
12		25	7
13		43	5

Fig. 6–8 show the dependences of the induction period of calcium carbonate crystallization at different temperatures.

$$\tau_{ind} = 1,12 \cdot 10^4 \left(\frac{SP}{CP} \right)^{0,707} \quad (14)$$

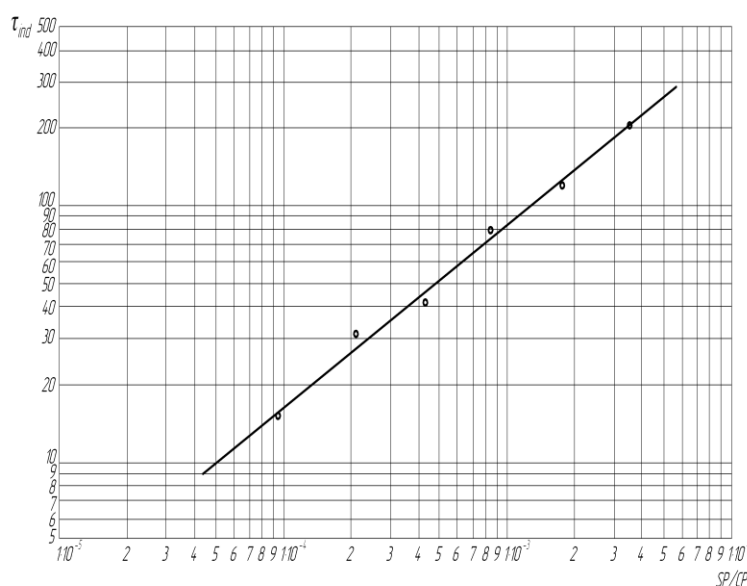


Figure 6 – The dependence of the calcium carbonate crystallization induction period on the

ratio of the solubility product to the given matter concentrations product at 297 °K(24 °C)

$$\tau_{ind} = 1,12 \cdot 10^4 \left(\frac{SP}{CP} \right)^{0,707} \quad (14)$$

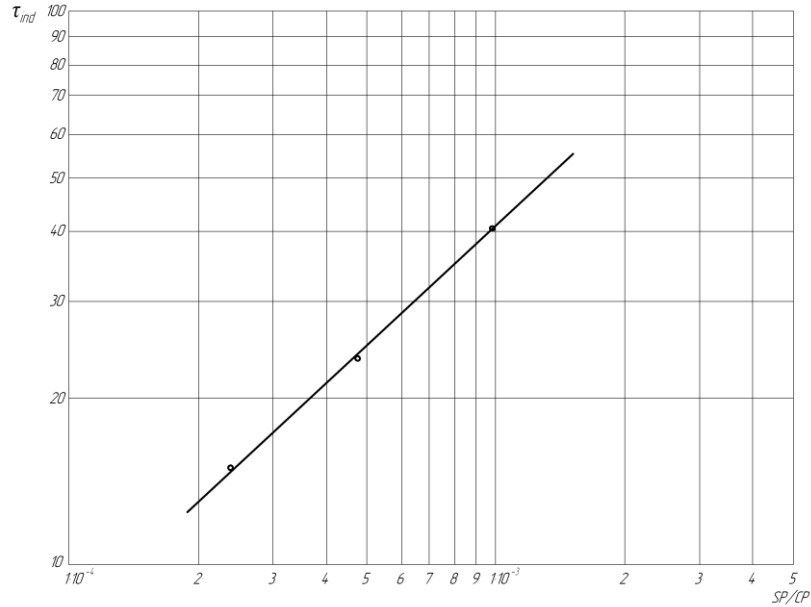


Figure 7 – The dependence of the calcium carbonate crystallization induction period on the ratio of the solubility product to the given matter concentrations product at 313 °K(40 °C)

$$\tau_{ind} = 5,79 \cdot 10^3 \left(\frac{SP}{CP} \right)^{0,714} \quad (15)$$

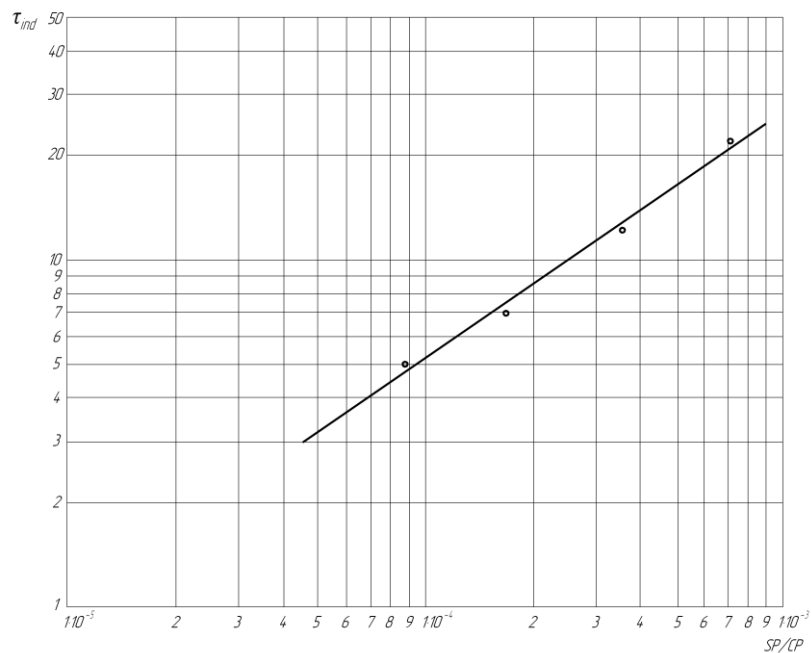


Figure 8 – The dependence of the calcium carbonate crystallization induction period on the ratio of the solubility product to the product of given matter concentrations at 343 °K(70 °C)

$$\tau_{ind} = 3,56 \cdot 10^3 \left(\frac{SP}{CP} \right)^{0,710} \quad (16)$$

General dependence τ_{ind} on temperature and supersaturation degree is calculated by the formula:

$$\tau_{ind} = 2,93 \exp \left(\frac{2,422 \cdot 10^3}{T} \right) \left(\frac{CP}{SP} \right)^{0,71} \quad (17)$$

Conclusions.

1. Quantitative characteristics of calcium carbonate solubility in the solution at different temperatures and the degree of supersaturation have been defined.

2. It has been shown that the main parameter, which affects solubility, is:

$$pSP - pH = \log \frac{a_H}{SP}$$

3. Calcium carbonate crystallization induction period is an exponential function of a value, which is inversely proportional to the absolute temperature, and the exponential function of the ratio of concentration product and solubility product.

4. It has been shown that the phosphate additive at low concentrations leads to the increase in the equilibrium concentration of calcium carbonate by 5,5 times if $(pH - pCP) = 6$.

References

1. Rogues H. Kinetics of the formation condition of carbonate tartars / H. Rogues, A. Girou // Water Reseach. - vol. 8. - P. 907-920.
2. Висоцький С. П. Кристаллізація карбоната кальція в оборотних системах охолодження води / С. П. Висоцький, С. Канда // Хімія і технологія води. - 1994. - №5. - С. 541-544.
3. Applied water technology
4. Висоцький С. П. Накипоутворення в теплофікаційних системах / С. П. Висоцький, Г. В. Фаткуліна // Вісник Донбаської національної академії будівництва і архітектури : збірник наукових праць: інженерні системи та техногенна безпека. - 2009. - Вип. 2(76). - С. 99-105.
5. Висоцький С. П. Надежность работы систем теплофикации и технология обработки подпиточной воды / С. П. Висоцький, Д. Н. Бут // Сантехніка, опалення, кондиціонування (СОК): Щомісячний спеціалізований журнал. - 2007. - № 7. - С. 12-15.
6. Справочник по свойствам, методам анализа и очистке воды в: 2-х ч. / [Л. А. Кульський, И. Т. Горюновский, А. М. Когановский, М. А. Шевченко]. - Киев: «Наукова думка», 1980. - 1206 с.

Надійшла до редакції 20.02.2013

С.П. ВИСОЦКИЙ, А.В. ФАТКУЛИНА

ОБРАЗОВАНИЕ КАРБОНАТА КАЛЬЦИЯ В СИСТЕМАХ ВОДОПОДГОТОВКИ И НА ПОВЕРХНОСТЯХ НАГРЕВА

Статья посвящена изучению процессов образования карбоната кальция в различных системах водоподготовки и на теплопередающих поверхностях при подогреве воды. Показано, что интенсивность накипеобразования зависит в основном от температуры и степени пересыщения раствора. Определены растворимость карбоната кальция в зависимости от соотношения активности ионов водорода и произведения концентраций ионов кальция и карбонатов без ингибиторов накипеобразования и в их присутствии.

Ключевые слова: водоподготовка, карбонат кальция, индукционный период, накипеобразование.

С.П. ВИСОЦЬКИЙ, А.В. ФАТКУЛІНА

УТВОРЕННЯ КАРБОНАТУ КАЛЬЦІЯ В СИСТЕМАХ ВОДОПІДГОТОВКИ І НА ПОВЕРХНЯХ НАГРІВАННЯ

Стаття присвячена вивченню процесів утворення карбонату кальцію в різних системах водопідготовки і на теплопередаючих поверхнях при підігріві води. Показано, що інтенсивність накипеутворення залежить в основному від температури і ступеня пересичення розчину. Визначено розчинність карбонату кальцію залежно від співвідношення активності іонів водню і добутку концентрацій іонів кальцію і карбонатів без інгібіторів накипеутворення і в їхній присутності.

Ключові слова: *водопідготовка, карбонат кальцію, індукційний період, накипоутворення.*

© Vysotsky S., Fatkulina A., 2013