УДК 628+546.264

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CALCIUM CARBONATE FORMATION IN THE WATER TREATMENT SYSTEMS AND ON THE 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. Determined the solubility of calcium carbonate, depending on the ratio of hydrogen ions activity and product concentrations of calcium and carbonate ions without and with presence of scale inhibitors.

Removing of compounds calcium carbonate hardness in clarifiers and settling tanks systems performance, the intensity of deposits formation on heat transfer surfaces in the power equipment and, consequently, efficiency and reliability reducing 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]. Data on fig. 1 shows the change in the rate of crystallization at various concentrations of calcium ions. Obviously, to prevent scale formation needed to find a solution – time in the heating zone must be less than induction period of crystallization. In contrast, the reagent water softening in clarifiers or settling basins time of water residence in the reaction zone should be more of the latent period of crystallization.

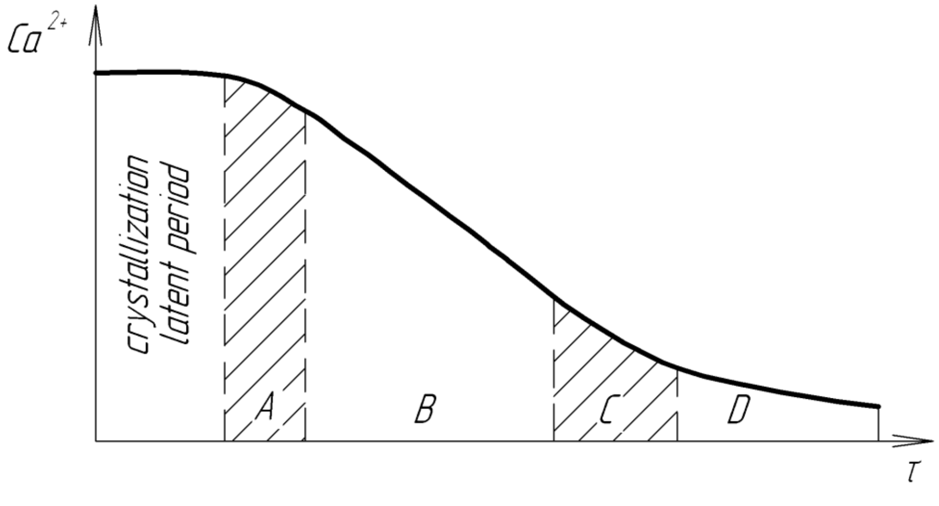


Fig.1 – Change in the rate of calcium carbonate crystallization over time

Area A: $$\frac{dCa^{2+}}{d\tau} = -\frac{S}{V} k_T \left[\left(Ca^{2+} \right) - \left(Ca^{2+} \right)_S \right] \qquad (1)$$

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

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

AreaД: $\frac{dCa^{2+}}{dt} = 0$ (4)

whereCa^{2+}, CO_3^{2-} – accordingly, calcium ions and carbonates concentration in volume of solution, mol/l;

S – surface, where is calcium carbonate form deposits, m^2;

V – solution volume, m^3;

κ_τ – constant of crystallization rate on the surface, m/hr;

κ – constant of crystallization rate in solution volume, mol/hr^2;

C_1 – bimolecular reaction rate constant, m^3/hr mol.

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

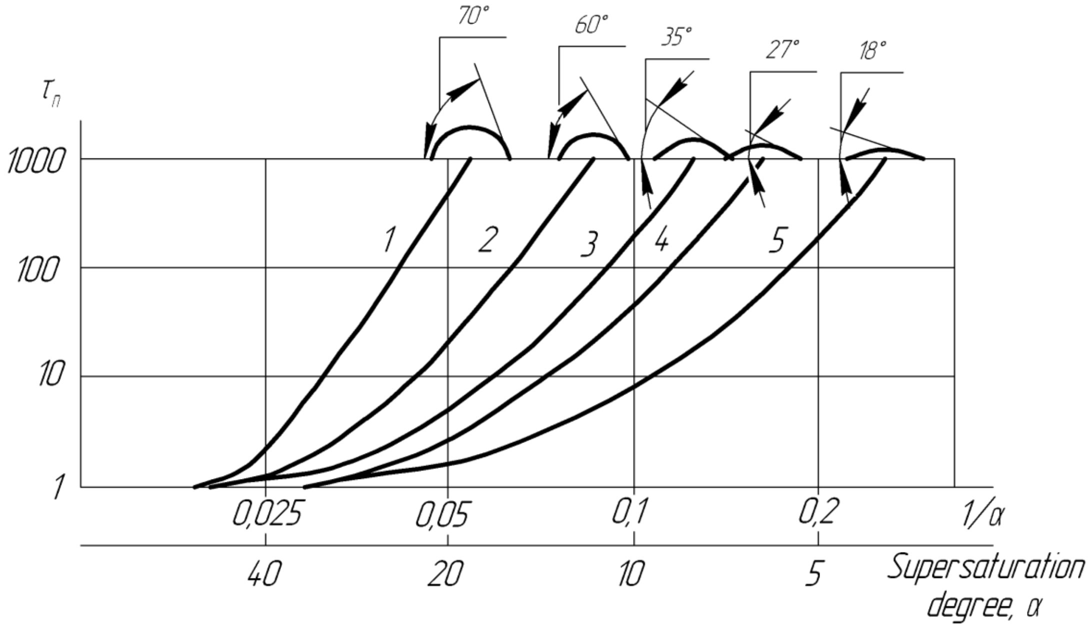


Fig.2 – Dependence of crystals nucleation τ_3 on the degree of supersaturationα and surface type

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

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

$$A = \frac{1}{3}\cdot\pi\cdot r^2\cdot\sigma\cdot\left[2\cdot\left(1-\cos\Theta\right)-\sin^2\Theta\cdot\cos\Theta\right], \qquad (5)$$

whereA – energy of the crystal nucleus formation on the wall, N · m;

r – crystals particular size, m;

σ – surface energy of the crystal face, N/m;

Θ – limiting wetting angle, degrees.

From this expression follows, that the ratio of the energy of the isothermal formation of the solid phase from a supersaturated solution on a solid surface, and the surface free energy of crystallization in the bulk solution depends on the contact angle of the surface. Obviously, with the boundary wetting angle Θ = 0 ° crystallization starts with a slight supersaturation. At Θ = 90 ° energy of nucleation on the wall surface and in the bulk solution are equal, therefore, the intensity of the bulk solution crystallization as calcium carbonate encrustation on the surface of the wall, are equally probable.

In the study of calcium carbonate crystallization conditions on a variety of surfaces, the dependence of the rate of formation of deposits on the surface type received. The data are given in table. 1.

Table 1 – Heat transfer surfaces materials research

Material	Wetting angle Θ, degree	Scaleformation intensityV, g/(m^2·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, the lower the rate of crystallization of the particles on the surface heating. Fig. 3 shows the effect of the free energy of calcium carbonate crystallization particles in the bulk solution and the intensity of crystallization of calcium carbonate on the heat transfer surface.

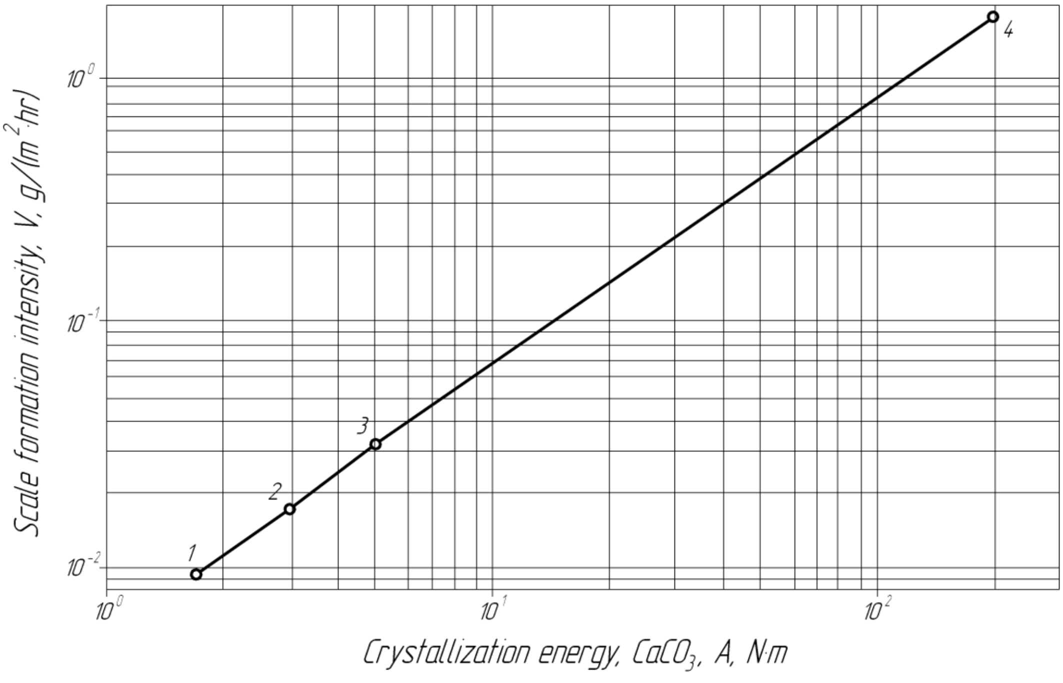


Fig.3 – Dependence of crystallization rate from the type of material, on which calcium carbonatecrystallization is going, and the energy of nucleation

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 management and water treatment practice, there are several approaches to assessing the stability of the water in terms of intensity scaling 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, based on the theoretical solubility of $CaCO_3$ at different temperatures depending on the salinity of water proposed, a method to assess the stability depending on the degree of saturation of water with calcium carbonate for the calculation of water at saturation (the so-called value pHs) and pH. If the actual pH of the water is below the calculated value pHs, 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 pHs, the water will have a positive Langelier index and will be repleted with $CaCO_3$. This water probably will facilitate scaling. The greater the difference between the actual pH and pHs, the more pronounced its instability with respect to the formation of deposits.

$$\text{Langelier Index} = I_L = pH - pH_s \qquad (6)$$

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

$$\text{Stability Index} = 2pH_s - pH \qquad (7)$$

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

Langelier index is particularly well used to predict the risk of malfunction 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.

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

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

wherepH– determined experimentally;

pCa = logI/[Ca];

pAlk = logI/[Alk];

K – 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 open cooling water circulation systems with zero discharge level.

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

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

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

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

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

where T – temperature, °K.

This solubility decrease essentially ends above a pH of 10.5, where most of the added CO_3^{2-} remains as CO_3^{2-} because of 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 a soluble salt, Na_2CO_3 to a simple solution ($CaCO_3$ in deionized water) sets up the equilibria

$$Na_2CO_3 \leftrightarrow 2Na^{+} + CO_3^{2-}$$

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

$$SP = [Ca^{2+}]\ ([CO_3^{2-}]_{Na2CO3})$$

where the subscripts indicate the introduction of the carbonate ion from either $CaCO_3$ or Na_2CO_3 . Because $[Na_2CO_3] > [CaCO_3]$, the following expression applies:

$$[Ca^{2+}] = SP / [Na_2CO_3]$$

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:

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^{+} + HCO_3^{-}$$
$$HCO_3^{-} \leftrightarrow H^{+} + CO_3^{2-}$$
$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3,$$

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

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

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

After simple transformations of this dependence, we obtain:

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

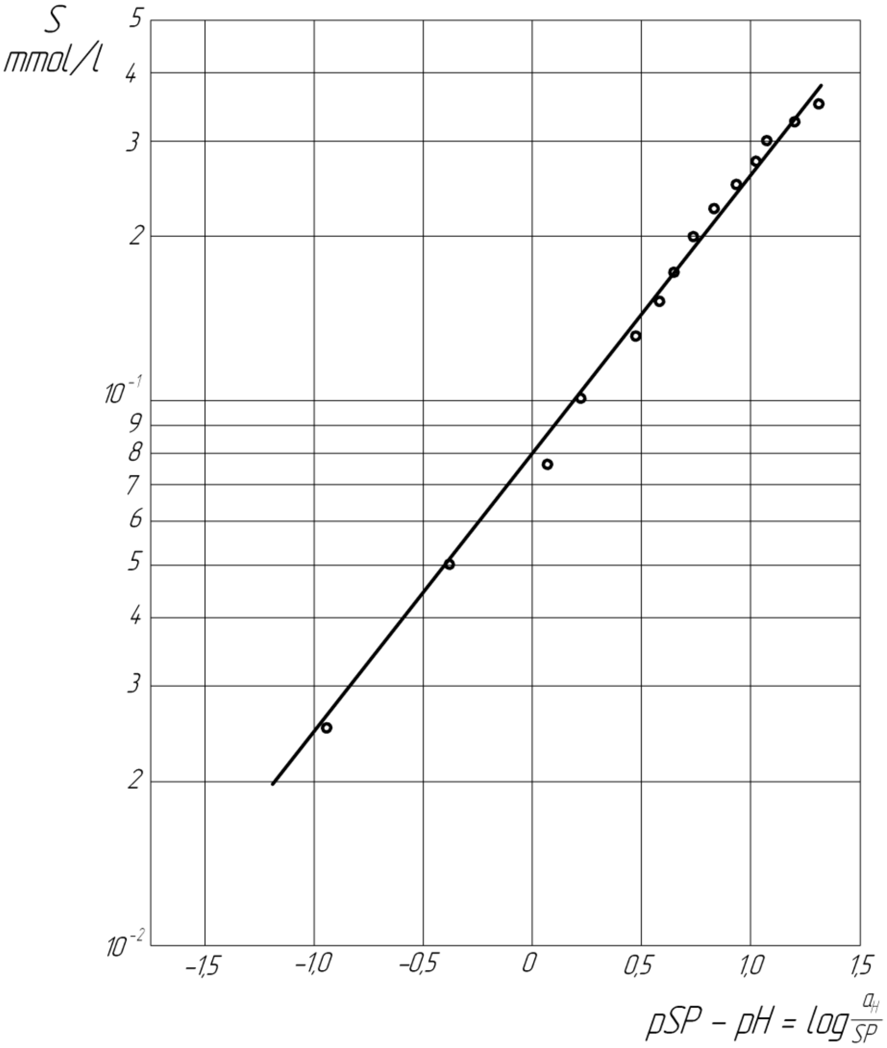


Fig.4 – Dependence of calcium carbonate solubility from the difference (pSP–pH)

In laboratory conditions experiments were performed to determine the intensity of scale formation at various concentrations and the pH of the product solution. The solution temperature was maintained 93 ± 2°C. From the Fig. 5 data, the intensity scaling is well described by an exponential dependence on the parameter (pCP–pH).

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

In the application of polyphosphates, with the value of water (pH–pCP) <6 or index Stability Rizner over 4,0 can be used at temperatures up to 93 °C with a slight amount of scale.

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

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

Dependence of deposits amount on the heating surface with 1,7mg/kgpolyphosphate

$Na_9P_7O_{22}$dosing is given by:

$$G = 1,2 \cdot 10^{-8} exp2,72\left(pH - pCP\right) = 1,2 \cdot 10^{-8} \left(\frac{a_{Ca} \cdot a_{CO_3}}{a_H}\right)^{1,18}, mmol/hr \qquad (13)$$

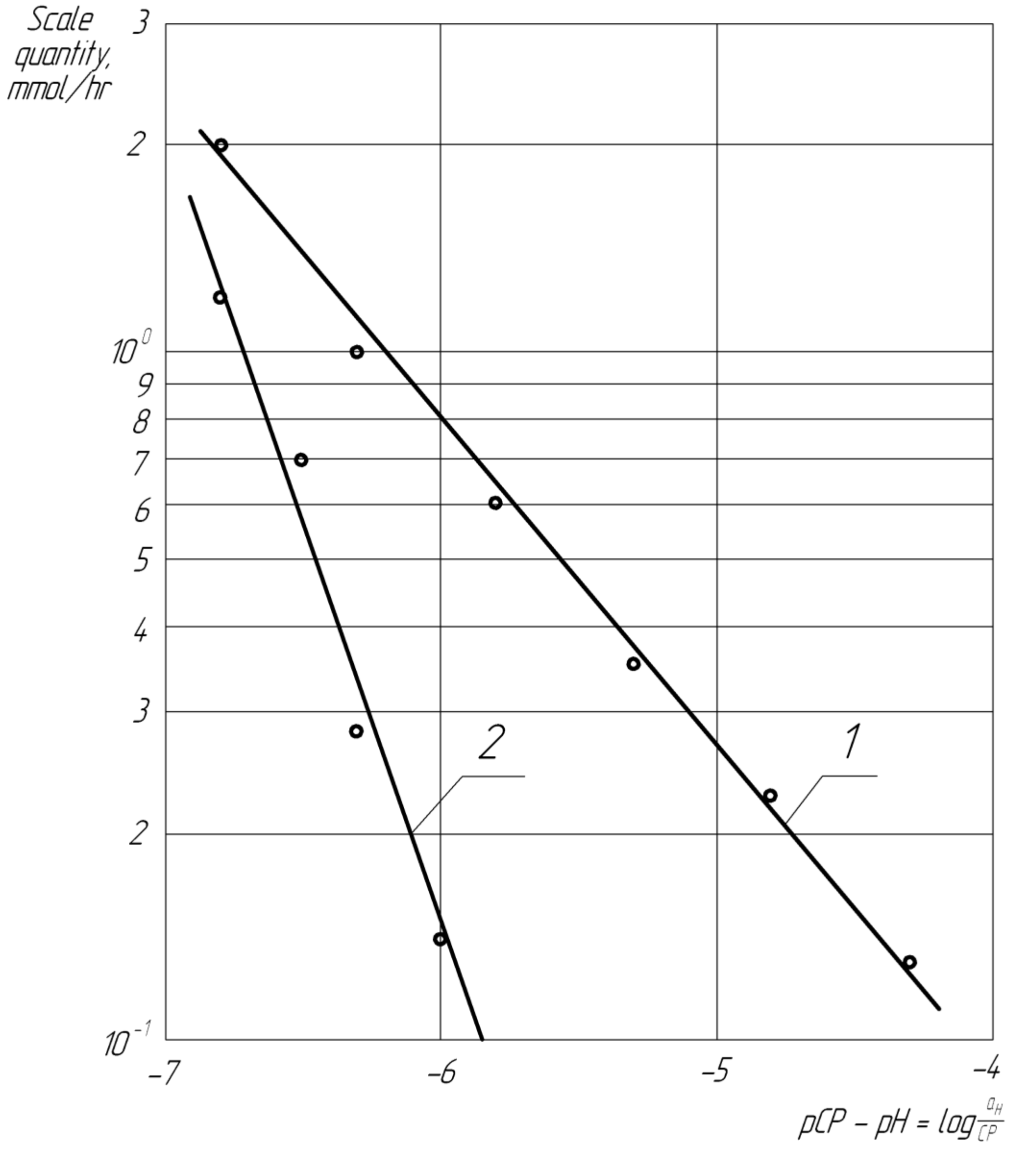


Fig.5 –Dependence of deposits amount on the heating surface from the rate (pCP–pH)
1 – amount of deposits with heating without scale stabilizers (antiscalant);
2 –amount of deposits with a polyphosphate $Na_9P_7O_{22}$dosage of 1,7 mg / kg

Thus, for the same value of the indicator (pH–pCP) = 6 adding of antiscalant additive reduces the formation of scale about in 5,5 times. Along with this increase in pH and, consequently, the difference (pH–pCP) to 6,5 times reduces the efficiency of antiscalant additives. The intensity of scale formation in these conditions reducing in 2,4 times.

It should be noted, that these data were considered the formation of calcium carbonate with equilibrium conditions. Duration of calcium carbonate crystals nucleation depends on the degree of supersaturation and the solution temperature.

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

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

whereDS – the degree of supersaturation is equal to the ratio of product concentration "ПК" to the product solubility.

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

From the data at double supersaturation the calculated induction period is 3,400 years, the triple - 6,86hr, and at 10 - 10 sec.

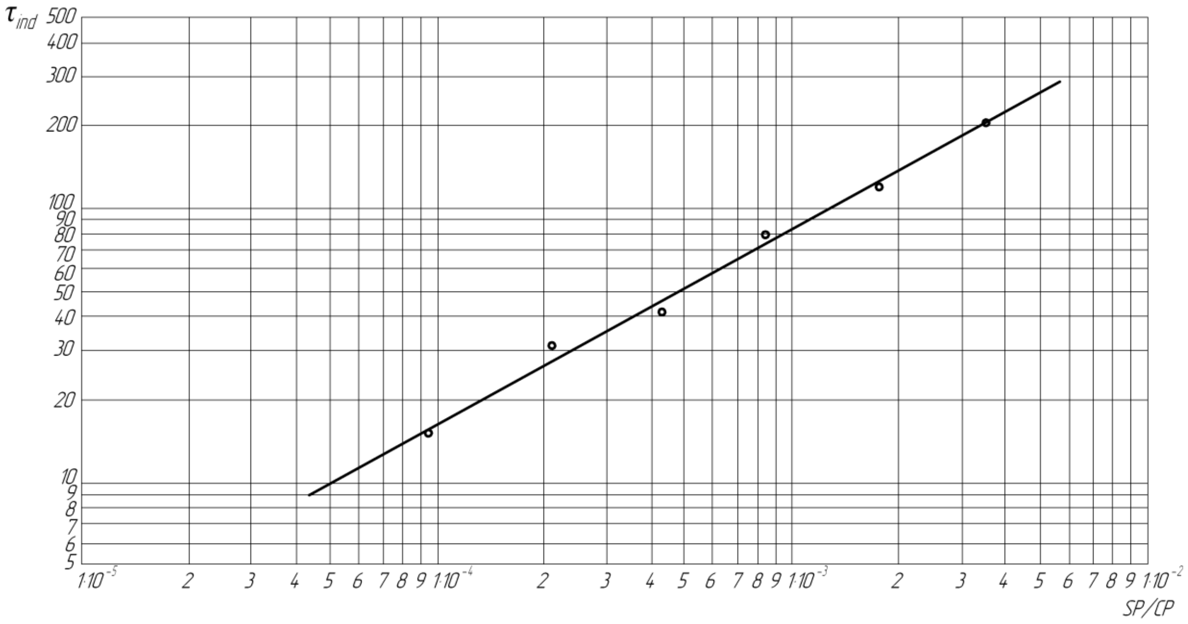
The formation of crystals in the solution is the result of processes capable of growing submicroscopic size embryo, to further – increase and make it a particle.

In determining the induction period used an optical method using a microscope MBS-10. On a microscope slide were mixed equal volumes of calcium chloride and lithium carbonate solutions various concentrations. Magnification levelwas selected 56 times. Given the fact that the human eye is able to distinguish the size to 0,06 mm, created the possibility of registering the appearance crystal size 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 determination results, τ_{ind}, sec

№	Temperature, °C	Product concentration, $(\text{mg-eqv/l})^2$	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

The dependence of the induction period of calcium carbonate crystallization at different temperatures shows at fig. 6–8.



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

Fig.6 – The dependence of the calcium carbonate crystallization induction period on the ratio of the product solubility to a product concentrations of given matter at 297 °K(24 °C)

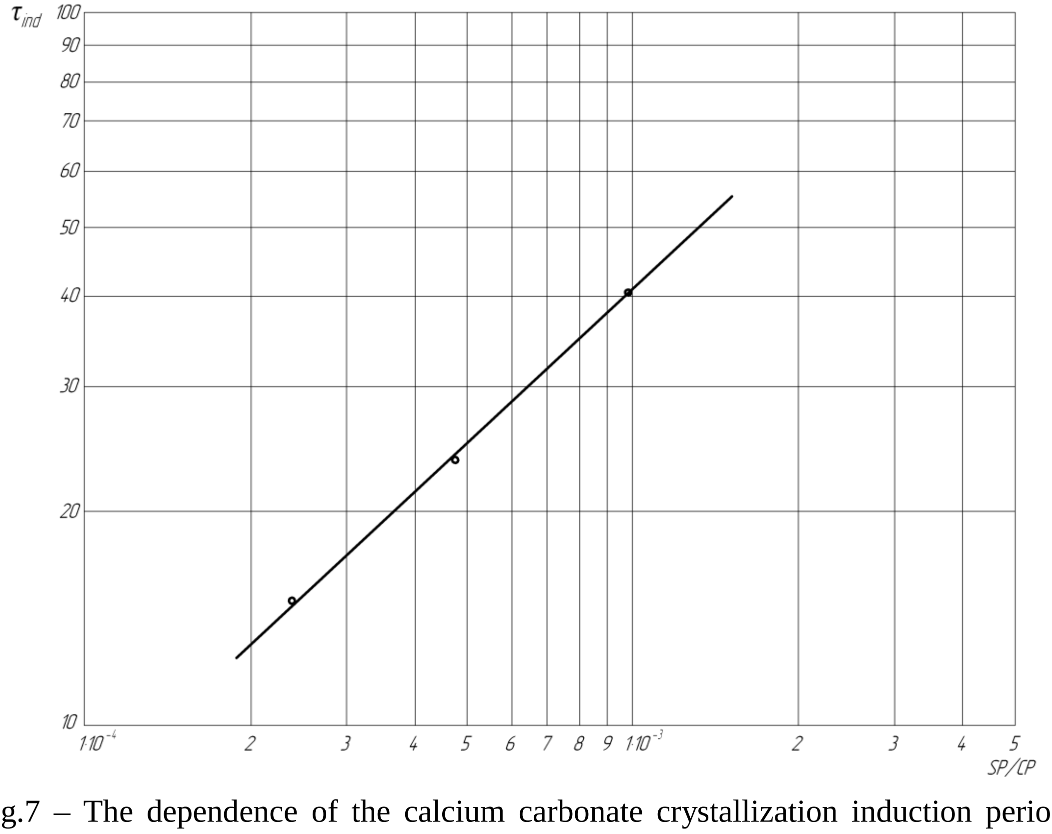


Fig.7 – The dependence of the calcium carbonate crystallization induction period on the ratio of the product solubility to a product concentrations of given matter at 313 °K(40 °C)

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

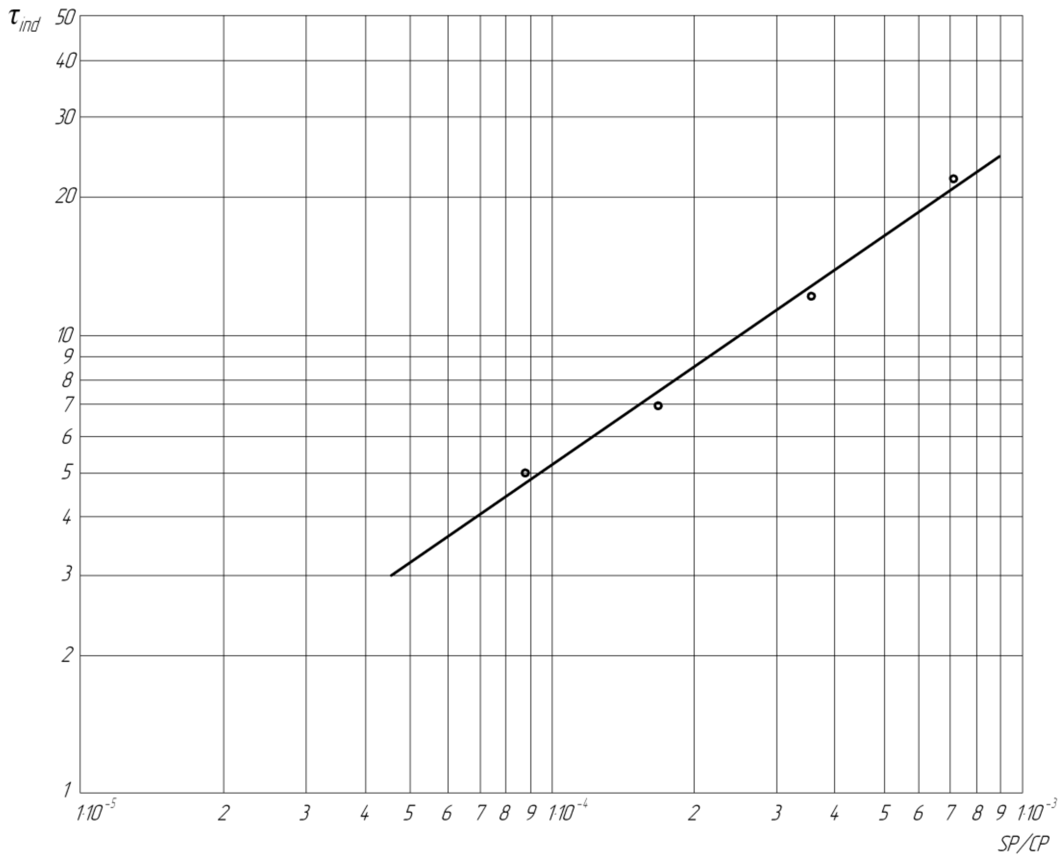


Fig.8 – The dependence of the calcium carbonate crystallization induction period on the ratio of the product solubility to a product concentrations of given matter at 343 °K(70 °C)

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

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

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

Conclusions

1. Quantitative characteristics of the solubility of calcium carbonate in solution at different temperatures and the degree of supersaturation is determined.
2. Shown that the main parameter affecting the solubility is: $\left(pSP - pH\right) = \log\frac{a_H}{SP}$
3. Calcium carbonate crystallization induction period is an exponential function of the magnitude is inversely proportional to the absolute temperature and the ratio of the exponential function and the product concentration solubility product.
4. It is shown, that the phosphate additive at low concentrations provides increase of the equilibrium concentration of calcium carbonate in 5,5 times at (pH–pCP)=6.

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