Intense Quench Process in Slow Agitated Water Salt and Polymer Solutions

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ABSTRACT

In the paper it is shown that quenching in slow agitated water salt solution of optimal concentration and in low concentration of inverse solubility polymers is intensive quenching creating maximal temperature gradients at the beginning of cooling. The evidence to support such idea were collected by analyzing quenching process in liquid media where any film boiling process was completely absent. In this case, surface temperature at the beginning of cooling drops closely to saturations temperature of a liquid within the interval 1–2 seconds, independently on nature of water solution, and then during transient nucleate boiling process maintains at the level of boiling point of a liquid which is often called self-regulated thermal process. The computer modeling of such cooling processes provided Kondrat'ev numbered Kn which are strongly linear function of time. At the beginning of cooling Kondrat'ev number is almost equal to 1 while average Kondrat'ev number $Kn \geq 0.8$. According to US Patent, intensive quenching starts when $Kn = 0.8$. Based on achieved results, it is possible to perform intensive quenching in slow agitated of low concentration water salt and polymer solutions, usually initiated by hydrodynamic emitters. Along with liquid agitation, emitters generate resonance wave effect which destroys film boiling processes making cooling very uniform and intensive. The proposed IQ process works perfectly when martensite starts temperature $M_s > T_s$. If saturation temperature $T_s \geq M_s$, intensive austempering process via cold liquids can be successfully performed to replace slow cooling of molten salts and alkalis by intensive quenching in liquid media.

Keywords: Low water concentration, IQ process, low agitation, Kondrat'ev numbers, hydrodynamic emitters, new technology.

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I. INTRODUCTION

In last decade, several important findings were made concerning study of the transient nucleate boiling process. One of them is duration of transient nucleate boiling that is proportional to thickness squared, depends on form coefficient, initial temperature, cooling intensity of quench system and is inversely proportional to thermal diffusivity of a material (see (1)) [1], [2]:

$$\tau_{nb} = \bar{\Omega} k_F \frac{D^2}{a} \quad (1)$$

It was also established that surface temperature during quenching in water salt and alkali solutions drops within 1 – 2 seconds close to boiling point of a liquid (see (2)) which is calculated as:

$$T_{sf} = T_s + \frac{g_I + g_{II}}{2} \approx const \quad (2)$$

The value Ω depends on initial temperature T_o and convective heat transfer coefficient α_{conv} as shown by (3) [3], [4]:

$$\bar{\Omega} = 0.48 + 3.21 \ln \frac{g_I}{g_{II}} \quad (3)$$

Here

$$g_I = 0.293 \cdot \left[\frac{2\lambda (g_o - g_I)}{R} \right]^{0.3} \quad (4)$$

$$g_{II} = 0.293 \cdot [\alpha_{conv} (g_{II} + g_{th})]^{0.3} \quad (5)$$

$$\beta = \frac{75\lambda \odot (\rho \odot - \rho'')^{0.5} g^{0.5}}{\sigma^{0.5} (\rho'' r^* W'')^{0.7} Pr^{0.2}} \quad (6)$$

$$\frac{1}{\beta} = 0.293 ;$$

$Pr = \frac{\nu}{a}$ is Prandtl number.

According to Tolubinsky, the bubble growth rate is function of pressure and does not depend on concentration of water salt solutions (see (7)) [5]:

$$\frac{W''}{W_{0.1}} = \left(\frac{\rho_{0.1}}{\rho''} \right)^{2.3+0.5 \lg \frac{P}{P_{cr}}} \quad (7)$$

$W_{0.1}$ is bubble growth rate at normal pressure P ; P_{cr} is critical pressure in Pa; α is heat transfer coefficient at nucleate boiling ($W/m^2 K$); λ is thermal conductivity of liquid ($\frac{W}{mK}$); σ is surface tension ($\frac{N}{m}$); g is gravity acceleration ($\frac{m}{s^2}$); ρ' is liquid density (kg/m^3); ρ'' is vapor density (kg/m^3); q is heat flux density (W/m^2); r^* is heat of vapor formation (J/kg); W'' is steam bubble growth rate (m/s); T_o is initial temperature; ν is kinematic viscosity (m^2/s); a is thermal diffusivity of a liquid (m^2/s).

In this paper the author is going to find out what is difference between water solutions of optimal concentration such as NaCl; NaOH; NaNO₂; NaNO₃; Na₂CO₃; CaCl₂; MgCl₂ and low concentration of inverse solubility polymers when any film boiling process is completely absent. The idea consists in possibility of switching from given solution to any listed quenchant that provides identical and stable result of cooling, temperature fields, stress distribution, and super strengthening effect. All of this is fulfilled if temperature field during quenching in mentioned solutions are identical. It can be done analyzing equations which are provided above.

For liquid in still condition, the convective heat transfer coefficient (HTC) is evaluated by (8) [6]:

$$\alpha_{conv} = 0.135\lambda \cdot \left(\frac{g\beta' \Delta T}{a\nu} \right)^{1/3} \quad (8)$$

In contrast to (6), here β' is volumetric expansion. Convective HTC in still liquids are approximately equal to 500-1000 W/m²K while for agitated bath with 1 m/s it is equal to 4000 W/m²K. For still liquid condition the convective Biot number Bi is equal to 0.136 while for agitated liquid Bi = 1 when standard probe 12.5 mm is used. According to Ref. [7], for given convective Biot numbers $\overline{\Omega} = 5.1$ and $\overline{\Omega} = 3$. The flow and spray convention are considered in [7], [8].

II. EFFECT PHYSICAL PROPERTIES OF QUENCHANT ON NUCLEATE BOILING PROCESS DURATION

The value β in (6) presents physical properties of water and water salt solutions which also includes vapor cooling rate grows W'' . The last does not depend on water salt concentration (see Table I).

As one can see from Table I, in case of boiling high-concentration solutions of NaCl and Na₂CO₃, their vapor bubble growth rates are the same as for water. In [5] it is noted that the vapor bubble growth rate for boiling aqueous

solutions is determined by properties of the solvent (water) and its vapor and is very weakly affected by properties of solved substances, viscosity and Prandtl number of a solution.

TABLE I: COMPARISON OF PARAMETERS OF BOILING PROCESS FOR WATER AND AQUEOUS SALT SOLUTIONS AT NORMAL PRESSURE [5]

Substance	d_0 , mm	f , 1/s	W'' , mm/s
Water	2.5	62	155
25% NaCl solution	2.4	64.5	155
29% Na ₂ CO ₃ solution	2.4	65	156

TABLE II: VALUE β VERSUS PRESSURE AT CONSTANT TEMPERATURE OF A LIQUID

Pressure, MPa	0.1	0.2	0.3	0.4	1
β	3.41	3.89	4.20	4.44	5.39

For all water salt solutions of optimal concentration, the value β varies between 3 and 4 while during quenching in liquid media under pressure β exceeds 5 (see Table II). Let us consider how varying β within 3 and 6 impacts the duration of transient nucleate boiling process. Calculations show very weak effect (see Table III).

TABLE III: DURATION OF TRANSIENT NUCLEATE BOILING PROCESS IN SECONDS VERSUS PARAMETER β AND DIAMETER OF CYLINDER WHEN COOLING FROM 850 °C IN STILL WATER SALT SOLUTION AT 20 °C

Diameter of Cylinders, mm	Duration, s			
	$\beta = 3$	$\beta = 3.41$	$\beta = 4.44$	$\beta = 6$
12.5	6.292	6.316	6.358	6.516
25	21.94	22.04	22.17	22.15
50	75.305	75.37	75.45	75.73

The reason for such small effect is extremely large HTC during boiling process. Transient nucleate boiling process in this case depends on convective HTC or convective Biot number [7].

It should be noted that the duration of the self-regulated thermal process was considered when developing processes for interrupted cooling to monitor conveyor speeds and also is used for developing the new quenching technologies [4]. It considerably depends on convective HTC (see Table IV).

TABLE IV: DURATION OF TRANSIENT NUCLEATE BOILING PROCESS IN SECONDS VERSUS CONVECTIVE HEAT TRANSFER COEFFICIENT AND PARAMETER β WHEN COOLING CYLINDER 50 MM DIAMETER FROM 850 °C IN STILL WATER SALT SOLUTION AT 20 °C

HTC W/m ² K	Duration, s			
	$\beta = 3$	$\beta = 3.41$	$\beta = 4.44$	$\beta = 6$
500	75.305	75	75.45	75.73
3000	39.26	39.6	40.3	40.9
5000	29.14	29.34	30.4	31

In contrast to duration of transient nucleate boiling process, β essentially effects overheat of a boundary layer during nucleate boiling (see (4) and (5)).

Authors [9] came to conclusion that temperature fields during quenching in 14% NaCl water solution and 1% water solution of polyalkylene glycol (PAG) are identical when $\beta = 3.41$. That is also true for larger β because increase β results in decreasing $\mathcal{G}_I$ and $\mathcal{G}_{II}$ (see (4) and (5)). It means that NaCl; NaOH; NaNO₂; NaNO₃; Na₂CO₃;

CaCl_2 , MgCl_2 and low concentration of inverse solubility polymers can replace each other to provide almost the same temperature fields during quenching in listed liquid media if film boiling is completely absent. This fact is very important for the practice.

The idea is supported by experimental data below (see Fig. 1 and Fig. 2).

Fig. 1. Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in water solution of polyoxyethylene (0.001%) at 23°C [10].

The film boiling in this experiment was absent due to presence of very thin insulating polymeric layer that decreases initial heat flux density q_0 below its critical value q_{cr1} (see (7)) and Table V [11]:

$$q_{in} = \frac{q_0}{\left(1 + 2 \frac{\delta}{R} \frac{\lambda}{\lambda_{coat}}\right)} \quad (7)$$

Similar results were obtained during quenching the same probe in 5% water NaOH solution (see Fig. 2).

Fig. 2. Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in water solution of NaOH (5%) at 20 °C.

TABLE V: COOLING TIME COMPARISON WHEN QUENCHING STANDARD PROBE 12.5 MM DIAMETER IN 1% WATER SOLUTION OF PAG AND 5% WATER SOLUTION OF NaOH AT 20 °C

Cooling condition	Cooling time from 850 °C to 700 °C	Cooling time from 850 °C to 600 °C	Cooling time from 850 °C to 400 °C	Cooling time from 850 °C to 300 °C	Cooling time from 850 °C to 200 °C
Cooling time in s (Polymer)	3.8	5.5	7.6	9.9	15.8
Cooling time in s (5% NaOH)	2.5	4.45	6.8	7.8	11.3

In the second experiment, the film boiling was absent due to presence electrical forces in the double electrical layer. According to the classical statistical thermodynamic, the pressure created by free electrons in metal is directly proportional to the absolute temperature T and is calculated as [12]:

$$P = nkT \quad (8)$$

where n is a number of electrons in one sm^3 of metal; k is the Boltzmann constant which is equal to $k = 1.3806488(13) \times 10^{-23} [\text{JK}^{-1}]$.

As a result, in the double electrical layer [13], [14] a high electrical force appears when quenching metal in electrolyte of optimal concentration (see Fig. 3). Maximal electrical forces are observed in solutions of optimal concentration where critical heat flux densities are maximal.

Fig. 3. A double electrical layer taking place during quenching metal in electrolytes.

As seen from Fig. 1, Fig. 2 and Table IV, temperature curves are similar when any film boiling process is completely absent. It does not matter what was a reason for absence of film boiling process: thin polymeric insulating layer or electrical forces in the double electrical boundary layer.

III. ANALYSIS OF KONDRAT'EV NUMBERS FOR WATER SOLUTIONS OF OPTIMAL CONCENTRATION

As known, Kondrat'ev number Kn is responsible for intensity of cooling process and it varies within $0 \leq Kn \leq 1$ [15]-[17].

According to US Patent [18], cooling process is intensive when Kn varies within $0.8 \leq Kn \leq 1$.

Let us see what cooling curves and Kondrat'ev numbers Kn are during quenching probes 12.5 mm and 50 mm diameter in water salt and alkali solutions of optimal concentration. The same consideration will be contributed to low concentration of polymer solutions.

Fig. 4 below shows cooling curves and cooling rates during quenching in 5% water NaOH solution at 20 °C. For standard Inconel 600 probe 12.5 mm diameter the self – regulated thermal process is clearly visible and it lasts more than 5 seconds. During the first second, the shock boiling takes place those results in maximum heat flux density (see Fig. 5).

Fig. 4. Cooling curves and cooling rate versus time during quenching cylindrical probe 12.5 mm diameter in 5% water solution of NaOH at 20 °C.

Fig. 5. Heat flux density versus time during quenching cylindrical probe 12.5 mm diameter in 5% water solution of NaOH at 20 °C.

Fig. 6 presents real and effective Kondrat'ev numbers versus time during quenching cylindrical probe 12.5 mm diameter in 5% water solution of NaOH at 20 °C.

Fig. 5. Real and effective Kondrat'ev numbers versus time during quenching cylindrical probe 12.5 mm diameter in 5% water solution of NaOH at 20 °C.

Similar results were received for cylindrical probe 50 mm diameter quenched in 5% water NaOH solution at 20 °C (see Fig. 6 and Fig. 7).

Fig. 6. Cooling curves and cooling rate versus time during quenching cylindrical probe 50 mm diameter in 5% water solution of NaOH at 20 °C.

From both experiments one can come to conclusion that nucleate boiling process develops very intensive quenching and creates huge temperature gradients. Unfortunately, investigators who use only one thermocouple at the core of probe cannot come to conclusion that IQ process can be performed in still quenching media. Especially it refers to those who operate with effective heat transfer coefficients.

Fig. 7. Real and effective Kondrat'ev numbers versus time during quenching cylindrical probe 50 mm diameter in 5% water solution of NaOH at 20 °C.

Table VI compares real and effective Kondrat'ev numbers Kn related to quenching 12.5 mm and 50 mm cylindrical probes in 5% water solution of NaOH at 20 °C to see whether cooling belongs to intensive quenching (IQ) process.

TABLE VI: REAL AND EFFECTIVE KONDRAT'EV NUMBERS Kn FOR CYLINDRICAL PROBES QUENCHED FROM 850 °C IN 5% WATER SOLUTION OF NaOH AT 20 °C WHEN CONVECTIVE HTC IS 500 W/m²K

Dia, mm	Type of Kn	Kn_i	Kn_{II}	$(Kn_i + Kn_{II})/2$	HTC, W/m²K
12.5	Real	0.95	0.81	0.88	20420
	Effective	0.90	0.225	0.562	3956
50	Real	1.0	0.87	0.935	9660
	Effective	0.96	0.3	0.63	1288

As seen from Table VI, average real Kondrat'ev numbers for both 12.5 mm and 50 mm probes are higher than 0.8 that belong to intensive quenching process as it was mentioned above. Note that real Kondrat'ev numbers Kn are responsible for temperature gradient evaluation while effective Kondrat'ev number can be used only for

approximate core cooling time evaluation. It cannot be used for a temperature gradients calculation.

Thus, cooling from high temperatures in NaCl; NaOH; NaNO_2 ; NaNO_3 ; Na_2CO_3 ; CaCl_2 ; MgCl_2 of optimal concentration and in low concentration of inverse solubility polymers is intensive quenching process within initial temperature T_o and saturation temperature T_s . Moreover, listed solutions can replace each other to provide almost the same temperature fields during quenching if any film boiling process is completely absent. Differences between listed solutions are critical heat flux densities. More information is provided below (see Table VII and Tabler VIII).

TABLE VII: CORE TEMPERATURE, COOLING RATE, REAL AND EFFECTIVE KONDRAT'EV NUMBERS VERSUS TIME DURING QUENCHING STANDARD PROBE 12.5 MM IN ELECTROLYTES OF OPTIMAL CONCENTRATION WHEN HTCCONV IS EQUAL 500 W / m² K

Time, s	Temperature, °C	Cooling rate, °C/s	Kn_{eff}	Kn_{real}
0	850	0	0	0
0.5	835	135	0.850	0.928
1.0	715	278	0.802	0.931
1.5	583	245	0.771	0.947
2	472	198	0.694	0.930
2.5	485	154	0.619	0.912
3.0	317	118	0.543	0.893
3.5	266	89	0.467	0.872
4.0	227	67	0.397	0.851
4.5	198	51	0.333	0.831
5.0	176	38	0.278	0.815
5.5	160	29	0.232	0.803
5.7	181	26.4	0.217	0.801

TABLE VIII: CORE TEMPERATURE, COOLING RATE, REAL AND EFFECTIVE KONDRAT'EV NUMBERS VERSUS TIME DURING QUENCHING CYLINDRICAL PROBE 50 MM IN ELECTROLYTES OF OPTIMAL CONCENTRATION WHEN HTCCONV IS EQUAL 500 W / m² K

Time, s	Temperature, °C	Cooling rate, °C/s	Kn_{eff}	Kn_{real}
0	850	0	0	0
10	797	15	0.867	0.973
20	620	16.9	0.787	0.958
30	472	12.7	0.703	0.943
40	365	9.10	0.611	0.925
50	288	6.43	0.515	0.906
55	258	5.38	0.469	0.897
60	234	4.50	0.423	0.887
65	213	3.78	0.381	0.879
70	19.6	3.17	0.341	0.871
75	181	2.67	0.305	0.865

In heat treating industry cooling characteristic of quenchant is represented by core cooling curve and core cooling rate of standard cylindrical Inconel 600 probe 12.5 mm diameter [19]. Thermocouple is located at the center of the standard probe that creates certain difficulties when solving inverse problem to evaluate heat transfer coefficients. Authors [4] used regular thermal condition theory and cooling rate curves to evaluate average HTC's which allow approximately calculate core cooling time of different steel parts during quenching in liquid media. It was underlined many times that such approach cannot be used for accurate temperature fields' calculations. Now, there is an opportunity to see what average HTC's are. We will use cooling curve rates of standard probe (see Fig. 4).

As known, cooling rate is evaluated by (9) [4], [15], [16]:

$$v = \frac{aKn}{K}(T - T_m) \quad (9)$$

or

$$Kn = \frac{vK}{a(T - T_m)}$$

The real Kondrat'ev number Kn is calculated as:

$$Kn = \frac{vK}{a(T - T_s)}$$

In heat treating industry, historically, engineers use effective HTC's which could be low enough to satisfy condition $q \leq 0.2$ where core temperature and surface temperature are approximately equal. In fact, it cannot be because transient nucleate boiling process is very intensive.

Currently, as a rule, intensive quenching (IQ) is performed using powerful pumps and electro motors with powerful propellers. During batch quenching water solution flow, developed by rotating propellers, eliminates film boiling process and increases convection. Unfortunately, due to hydrodynamic resistance, liquid flow does not eliminate completely film boiling processes. In 2012 author [20], [21] come to conclusion that thin surface polymeric layer, formed during quenching in low concentration of inverse solubility polymers, decreases initial heat flux density below its critical value that eliminates any film boiling process without pumping and rotating propellers. Moreover, in this paper it is shown that water salt solutions of optimal concentration and low concentration of PAG solution (usually 1%) develop of IQ process during nucleate boiling mode. Temperature fields during quenching in all mentioned solutions are similar. First, that means dropping surface temperature within 1–2 seconds close to boiling point of a liquid and maintaining surface temperature relatively a long time at the level of boiling point, often called the self-regulated thermal process (SRTP). The duration of SRTP does not depend on inner characteristics of nucleate boiling process.

Due to developed new approach in exploring water polymer solutions, the new problem is arising such as:

- Requirements in investigation behavior of thin surface insulating polymeric layer during steel quenching.
- Requirements in investigation thermal and physical properties of polymeric insulating layer.
- Requirements in investigation of critical heat flux densities during quenching in liquid media.
- Need in designing new database for quenchants and quenching technology.

Experimental and numerical calculations support discussion above. Using French's experimental data [22] regarding cooling different samples from 875 °C to 150 °C and equations (1)–(5), core cooling curve and core cooling rate were calculated which are shown in Fig. 8.

Fig. 8. Core cooling curve and cooling rate curve versus time obtained by computer simulation of quenching cylindrical probe 50 mm diameter in 1% water PAG solution at 23 °C.

Core cooling curve and core cooling rate during quenching probe 50 mm diameter in 1% water PAG solution, obtained by authors [9], are shown in Fig. 9 which coincides well with calculated data shown in Fig. 8.

Fig. 9. Core cooling curve and cooling rate curve versus time obtained during quenching cylindrical probe 50 mm diameter in 1% water PAG solution at 23 °C [9].

Thus, intensive quenching processes one can perform in still or low agitated water salt solutions of optimal concentration and low concentration of PAG solutions if any film boiling is completely absent and critical heat flux densities are maximal [23]-[25]. The principal scheme for performing IQ process in slow agitated water solutions is shown in Fig. 10 and Fig. 11.

Fig. 10. Quench tank with emitters for slow quenchant agitation and generating resonance effect: 1 is hydrodynamic emitter; 2 is quench tank; 3 is quenchant; 4 is vapor film; 5 is steel part; 6 is lifting system.

Fig. 11. Platform for placement emitters: 1 is platform; 2 is liquid flow; 3 are hydrodynamic emitters.

The proposed IQ process works perfectly when martensite starts temperature $M_s > T_s$. If saturation temperature $T_s \geq M_s$, intensive austempering process via cold liquids can be successfully performed to eliminate slow cooling of molten salts and alkalis [7].

Note that many types of hydrodynamic emitters can be used for quenching purposes.

IV. CONCLUSION

Intensive quenching process can be performed in still or low agitated water salt solutions of optimal concentration or in low concentration (1%) water PAG polymer solutions if any film boiling process is completely absent. There is a need to investigate critical heat flux densities of different quenchants as a main parameter of cooling liquid to eliminate effectively film boiling processes during quenching.

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