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ANALYSIS OF THE COOLING CHARACTERISTICS OF 2% CARBOXYMETHYL CELLULOSE SOLUTIONS IN WATER AT VARIOUS INITIAL TEMPERATURES

BY

GHEORGHE LEONTE, CARMEN NEJNERU, MANUELA-CRISTINA PERJU*, IONELA-ANDREEA PINTILIE and MARIAN FANARAGIU

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering, Iași, Romania

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Abstract. Cooling for tempering as the final operation is of particular importance for obtaining the properties required in operation, such as hardness, mechanical strength and a state of internal stresses corresponding to the demands that the part must withstand in function. Cooling for tempering involves the use of a generally liquid tempering medium such as water, oil, emulsions or solutions from synthetic media. Carboxymethyl cellulose is a substance that results as a secondary product in the manufacture of paper and is used as a cooling medium dissolved in water in percentages of 1.5% to 5%. In the work, the cooling curves of a 2% carboxymethyl cellulose solution in water with initial ambient temperatures of 20°C, 40°C and 60°C were analysed.

Key words: carboxymethyl cellulose, heat transfer coefficient, cooling capacity, cooling speed.

*Corresponding author; *e-mail*: manuela-cristina.perju@academic.tuiasi.ro

1. Introduction

Heat treatments are widely used in the manufacturing industry because they seek to obtain new structures, change the state of stress in the parts and therefore change the mechanical properties of mechanical resistance, hardness, refractility and chemical resistance of a material (Ashish *et al*., 2011).

An important component of the heat treatment stages is represented by cooling technologies. For a cooling corresponding to the type of thermal treatment of quenching or annealing chosen, a static or recirculated quenching medium must be used to achieve the objectives imposed by the treatment (Malakootian *et al*., 2019).

They are used for cooling during tempering such as water, thermal treatment oil, salt baths, emulsions and also synthetic media such as polymer solutions, mineral solutions etc (Fanfan *et al*., 2023).

Classic tempering media present problems such as flammability (heat treatment oil), toxicity, perishability (organic solutions), high cost price, high cooling speeds dangerous for the integrity of the parts (Hashmi *et al*., 2021). That is why, as an alternative to the classic tempering media, synthetic tempering media have been tested and used, usually chosen from the residual substances obtained from the chemical industry of paper processing, petroleum products or other industrial branches of processing biological products. By mixing certain substances with water, gels are formed (Guangxu *et al*., 2024). Among these substances we also mention carboxymethyl cellulose whose cooling properties are the object of study of the work (de Britto and Assis, 2009). This substance is used in a 1-5% solution dissolved in water for the quenching heat treatment of large and very large parts that require cooling baths with agitators and large recirculation systems (Achachlouei *et al*., 2011).

Carboxymethyl cellulose is found in the form of bundles of threads and present in the form of gels forms in the liquid of the tempering bath whose surface tension changes a large number of vaporization centers that accelerate the formation of vapors and reduce the rate of condensation of the accessor (Park *et al*., 2019). The beginning of the cooling of the parts takes place through the heating period, when a film of vapor forms around the part, the stability of which depends on the initial temperature of the tempering medium. As a result, the resistance of the vapor film increases a lot, the critical boiling temperatures move into the low temperature range and the cooling capacity of the water is considerably reduced (Abdel-Galil *et al*., 2014).

2. Materials Used for the Experiment

Solutions of carboxymethyl cellulose dissolved in water and undissolved carboxymethyl fibrous were used for the experiment.

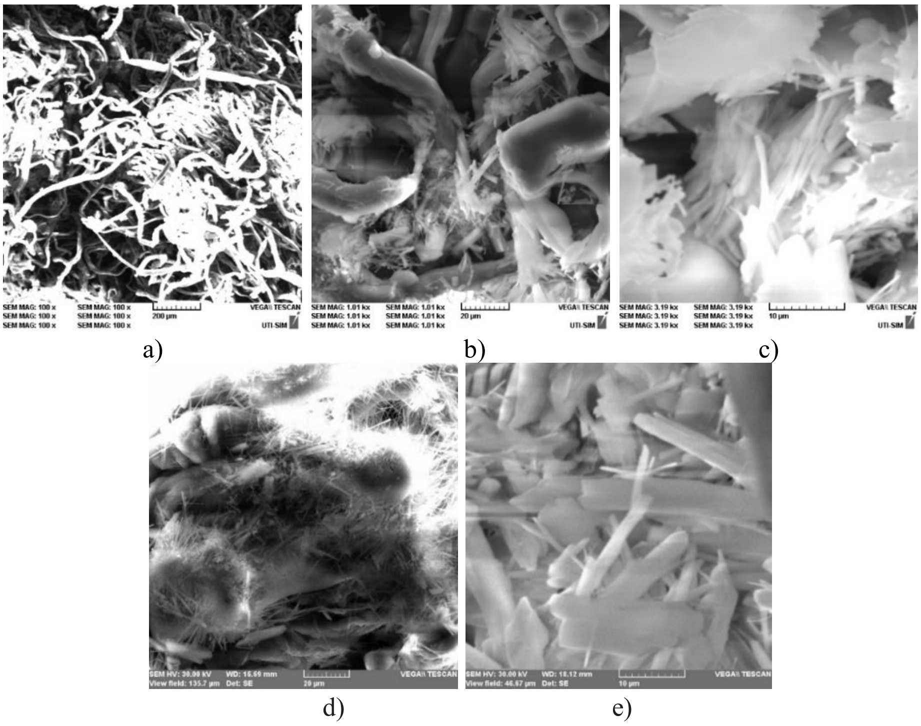
The microstructure of carboxymethyl cellulose Carboxymethyl cellulose (CMC) is a secondary product resulting from the manufacture of cane paper, but it can also be found in the textile industry as well as in the pharmaceutical and food chemical industries.

The chemical substance results from the processing of vegetable products, so it has an organic origin and for this reason it is risk-free, being ecological and non-toxic for the natural environment.

Carboxymethyl cellulose (CMC) has good solubility, forming colloidal solutions in water and changing cooling parameters and the contact angle with metal surfaces (Tan *et al*., 2017).

As the primary substance, it has a fibrous appearance similar to the vegetable form, has a density of 1.6 g/cm^3 and melts at 274°C. The pH of the 2% CMC solution in water is 10.19.

In Fig. 1 shows the basic structure of the carboxymethyl cellulose used for the experiment, easily observing the characteristics of vegetable fibers because the substance was collected as waste from a paper factory that used cane as a raw material.



a) b) c)

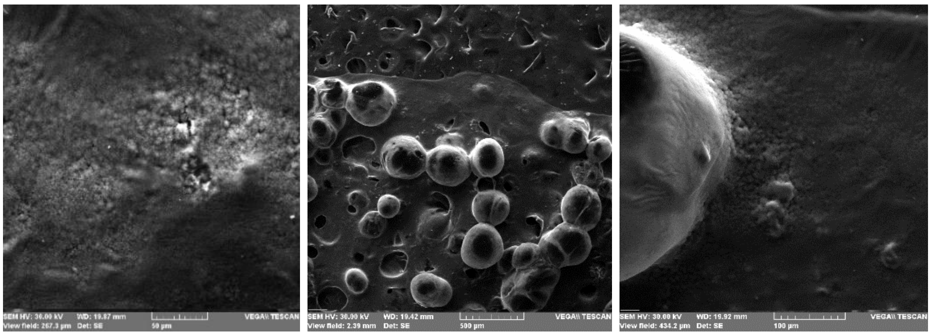
d) e)

Fig. 1 – Carboxymethyl cellulose diverse fibrous structure not dissolved in water at various magnifications: a) general view structure; b) coarse fibrous structure; c) hybrid acicular structure; d) area with small connecting fibers; e) woody structure.

Preliminary results on the microstructure of CMC carboxymethyl cellulose and the combined water-dissolved carboxymethyl cellulose solution are shown in Fig. 2.

The experiments were done under vacuum and the film remaining after the evaporator was analyzed. The structure has a compact appearance with well-defined bonds, particles and even bubbles, consisting of films of continuous and coherent films.

EDX experiments were performed on the dry cooling medium. Table 1 shows the results of the EDX analysis for the medium with 2% CMC.



a) b) c)

Fig. 2 – Carboxymethyl cellulose 2% dissolved in water after drying at various magnifications: a) compact area, 50 μm; b) uniform film structure, 500 μm; c) coherent structure 100 μm.

Table 1

Chemical composition of carboxymethyl cellulose solution in water after drying

Chemical element	Cooling medium (CMC)	
	% mass	% atom
Oxygen	80.40	89.54
Nitrogen	15.53	11.63
Chloride	3.45	1.67
Sodium	0.85	0.24
Carbon	1.23	1.84
Iron	0.62	0.19

3. Determination of the Cooling Characteristics of 2% Carboxymethyl Cellulose Solutions in Water at Various Initial Temperatures

In the paper, the cooling curves of a standardized cylindrical silver sample were drawn. The installation used for the experimental determination of the quenching cooling curves consists mainly of:

- air bubbling system;

- the heating system of the silver sample (cylindrical furnace with electrical resistance Fig. 3;
- measurement system represented by a y-t recorder (with a device for changing the speed of movement of the recorder).

Fig. 3 – Ag cylindrical specimen of standardized dimensions with chromel-alumel type thermocouple embedded in the center having the following characteristics: Ø = 13 [mm]; h = 28 [mm]; S = 1408 [mm^2]; m = 39.9 [g]; ρAg = 10.5 g/cm^3; λAg = 418.5 W/m·K.

The specimen was heated to a temperature higher than 800°C and inserted into the container with the analyzed quenching medium, the cooling curve was recorded with a "y-t recorder".

For each cooling medium were calculated:
- cooling rate per interval [°C/s];
- the thermal transfer coefficient on intervals.

$$\alpha_i = \frac{3600 \cdot m \cdot c}{\Delta t_i \cdot S} ln \frac{T_i - T_o}{T_f - T_o} \text{ [W/m}^2\text{·K]} \quad (1)$$

where: m = 0.0399 [kg] mass of the sample;
c = 0.056 [kcal/kg·grd] the specific heat of silver;
S = 0.001408 [m^2] the surface of the sample;
Δt [s] time interval;
T_i, T_f [°C] initial and final temperature of the working interval;
T_0 initial temperature of the cooling medium.

The obtained results were tabulated and based on them the following were drawn:
- Cooling curves T = f (t);
- Variation of cooling rate with temperature v_r = f(T);
- Variation of the heat transfer coefficient with temperature α_i = f(T).

Table 2

Parameters cooling curves in solution of CMC 2% - 20°C

CMC 2% - 20°C					
T [°C]	ΔT [ºC]	t [s]	Δt [s]	V_r [ºC/s]	α [W/m^2 K]
800	0	0	0	0	0
700	100	12.50	12.50	8.00	72.70
600	100	20.00	7.50	13.33	140.60
500	100	21.00	1.00	100.00	1254.10
400	100	24.25	3.25	30.77	476.40
300	100	28.00	3.75	26.67	539.70
200	100	31.25	3.25	30.77	900.90
100	100	38.00	6.75	14.81	796.20
60	50	67.50	29.50	1.69	155.70

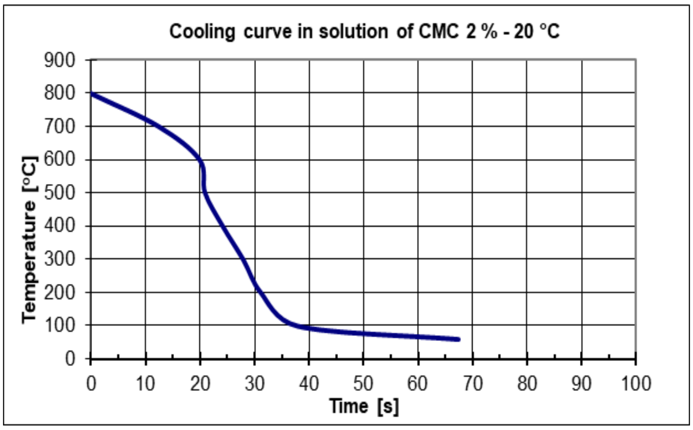


Fig. 4 – Cooling curves in solution of CMC 2% - 20°C.

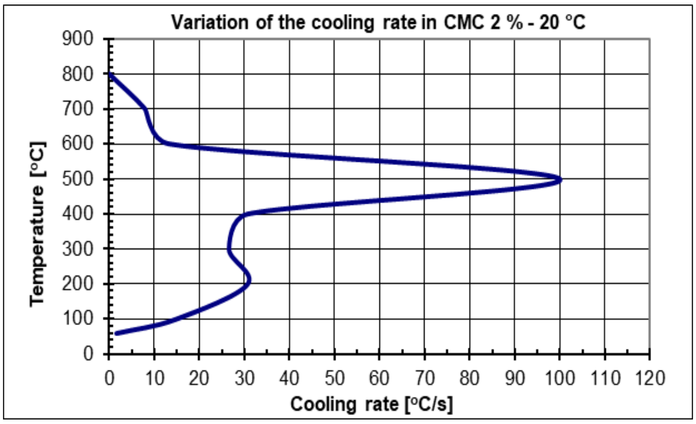


Fig. 5 – Variation of cooling rate in CMC 2% - 20°C.

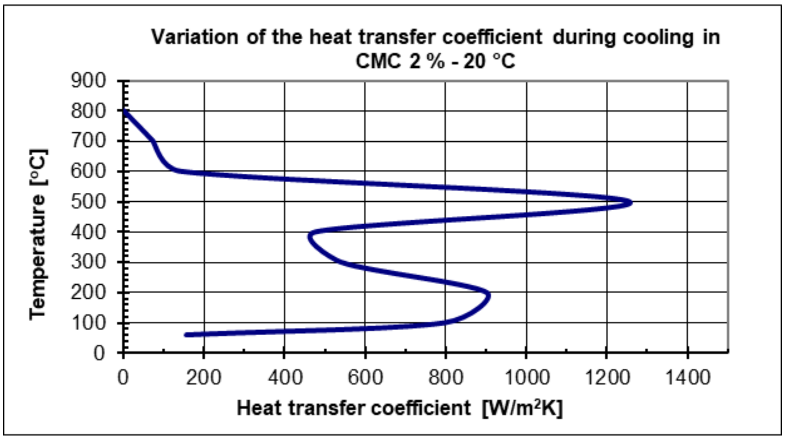


Fig. 6 – Variation of the heat transfer coefficient during cooling in CMC 2% - 20°C.

Table 3

Parameters cooling curves in solution of CMC 2% - 40°C

CMC 2% - 40°C					
T [°C]	ΔT [°C]	t [s]	Δt [s]	V_r [°C/s]	α [W/m^2 K]
800	0	0	0	0	0
700	100	20.00	20.00	5.00	45.50
600	100	33.25	13.25	7.55	79.60
500	100	39.25	6.00	16.67	209.00
400	100	42.00	2.75	36.36	563.00
300	100	47.25	5.25	19.05	385.50
200	100	52.00	4.75	21.05	616.40
100	100	65.00	13.00	7.69	413.40
60	50	72.50	7.50	6.67	612.50

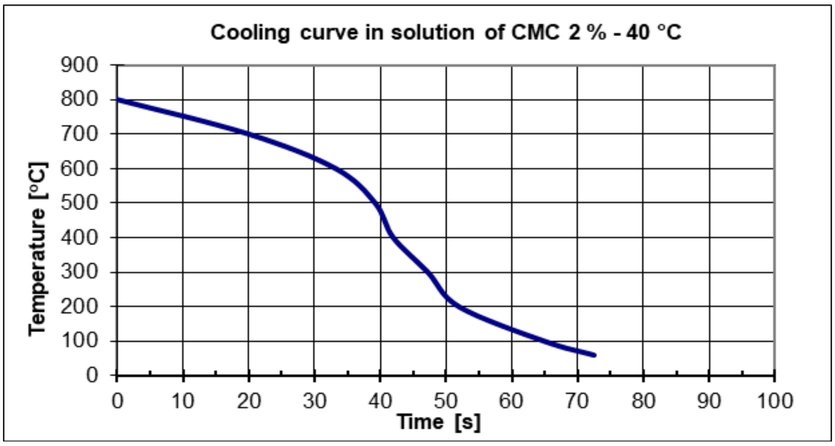


Fig. 7 – Cooling curves in solution of CMC 2% - 40°C.

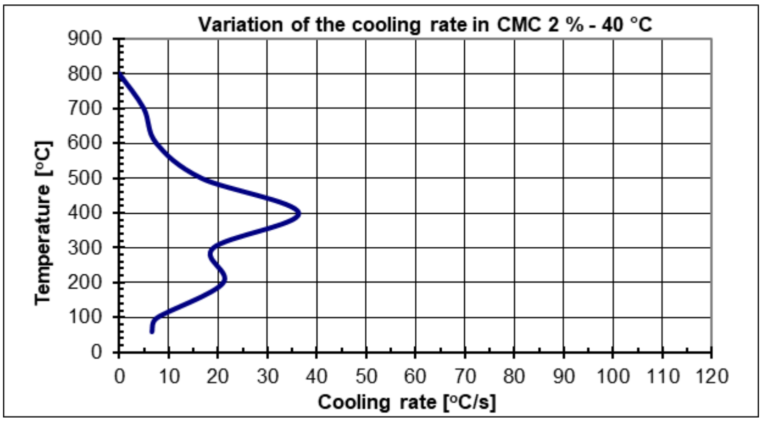


Fig. 8 – Variation of cooling rate in CMC 2% - 40°C.

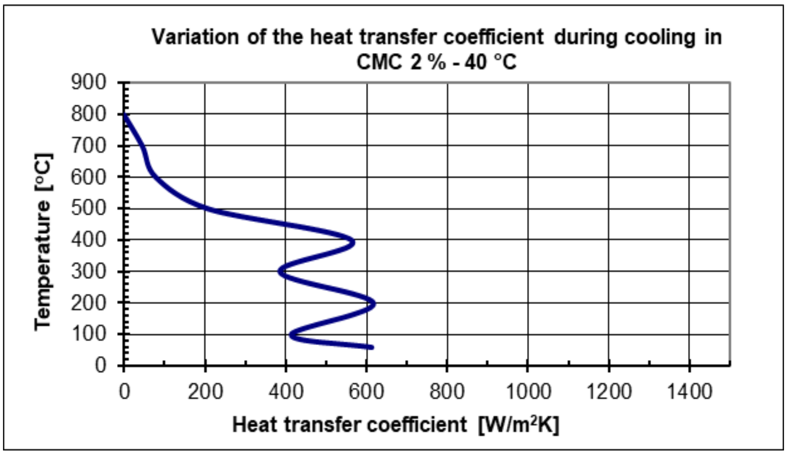


Fig. 9 – Variation of the heat transfer coefficient during cooling in CMC 2% - 40°C.

Table 4

Parameters cooling curves in solution of CMC 2% - 60°C

CMC 2% - 60°C					
T [°C]	ΔT [°C]	t [s]	Δt [s]	V_r [°C/s]	α [W/m^2 K]
800	0	0	0	0	0
700	100	19.50	19.50	5.13	46.60
600	100	32.75	13.25	7.55	79.60
500	100	51.25	18.50	4.41	67.80
400	100	56.75	5.50	18.18	281.50
300	100	62.50	5.75	17.39	352.00
200	100	67.50	5.00	20.00	585.60
100	100	77.50	10.00	10.00	537.40
60	50	97.50	20.00	2.50	229.70

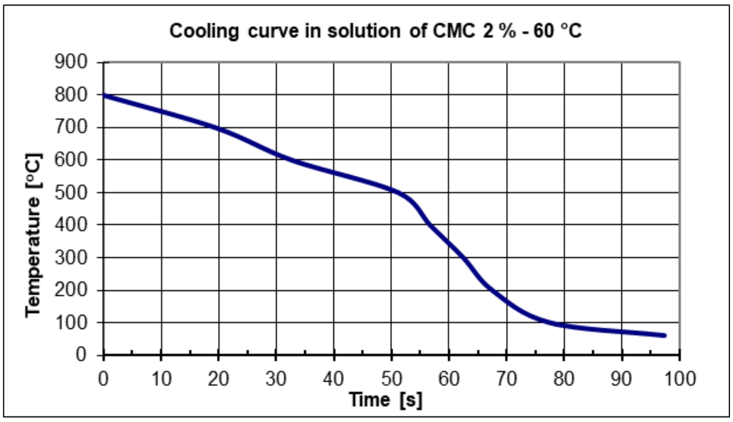


Fig. 10 – Cooling curves in solution of CMC 2% - 60°C.

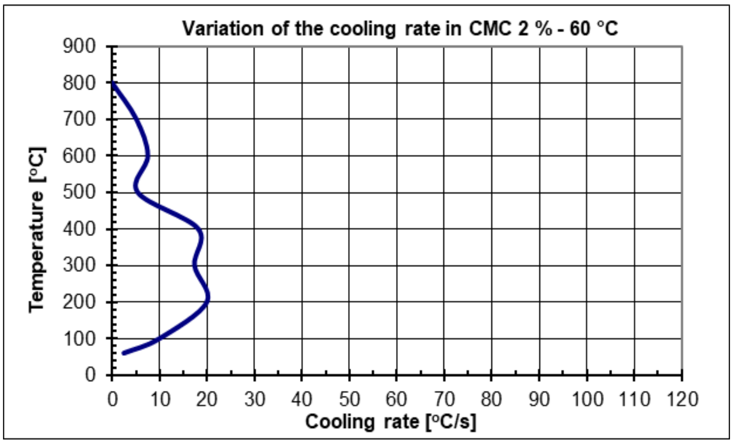


Fig. 11 – Variation of cooling rate in CMC 2% - 60°C.

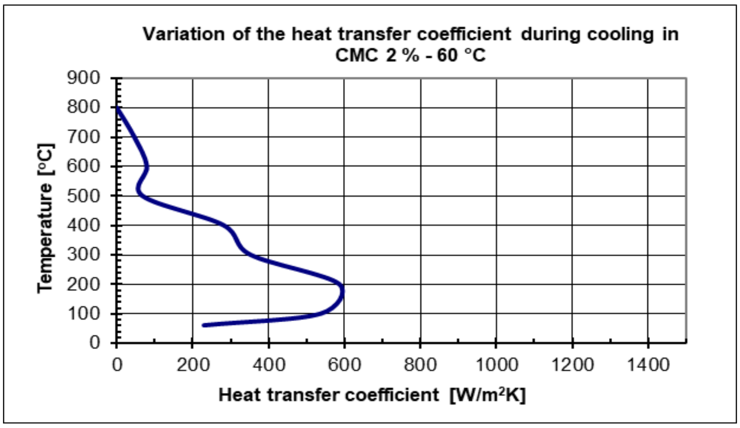


Fig. 12 – Variation of the heat transfer coefficient during cooling in CMC 2% - 60°C.

4. Results and Discussion

The initial temperature of the cooling medium during tempering influences all stages of cooling, changing its temporal values.

A first stage of cooling, namely heating, which represents the formation of vapors of the tempering solution around the part and which isolates the part from the liquid through the gas film formed, is prolonged when the initial temperature of the cooling medium increases. At temperatures of 60°C, the heating lasts more than 30 seconds, while at 20°C it lasts less than 20 seconds, something highlighted on the cooling graphs (Nejneru *et al*., 2014). The boiling period that follows the breaking of the gas film around the part is 23 seconds at 60°C, so much longer than 14 seconds at 20°C.

It is also observed that within the initial temperature of 40°C we have a change in the properties of the medium which is a solution of an organic polymer and has a partial amorphization point at that temperature, a fact that leads to the reduction of the maximum cooling speed and implicitly to the change in the character of the cooling and expected structural transformations. From the point of view of the uniformity and smoothness of the cooling curve, the curve obtained when cooling the sample in CMC solution with an initial temperature of 20°C is recommended.

5. Conclusion

1. The initial temperatures influence the shape and the values on the cooling curves and are important for achieving a quality tempering heat treatment.
2. At the initial temperature of 20°C, a CMC solution has the cooling time of the silver sample in 67 seconds, while an environment with an initial temperature of 60°C cools in 97.5 seconds.
3. The initial cooling period, i.e. the heating period, is extended by 10 seconds, which extends the start of the structural transformation period.
4. The 2% carboxymethyl cellulose solution in water at a temperature of 20°C has a cooling speed during the boiling period 3 times higher than the speed of the same medium at a temperature of 60°C.
5. The maximum cooling speed decreases from the environment with an initial temperature of 20°C having a value of 100°C/s to one with an initial temperature of 60°C having a value of 21°C/s.

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ANALIZA CARACTERISTICILOR DE RĂCIRE A SOLUȚILOR DE CARBOXIMETIL CELULOZĂ 2% ÎN APĂ LA DIVERSE TEMPERATURI INIȚIALE

(Rezumat)

Răcirea pentru călire ca operație finală are o importanță deosebită pentru obținerea proprietăților necesare în exploatare, adică duritate, rezistență mecanică și o stare de tensiuni interne corespunzătoare solicitărilor la care piesa trebuie să reziste în funcționare. Răcirea pentru călire implică folosirea unui mediu de călire în general lichid cum ar fi apă, ulei, emulsii sau soluții din medii sintetice. Carboximetil celuloza

reprezintă o substanță ce rezultă ca produs secundar la fabricarea hârtiei și se folosește ca mediu de răcire dizolvată în apă în procente de 1,5% până la 5%. În lucrare au fost analizate curbele de răcire a unei soluții de 2% carboximetil celuloză în apă cu temperaturi inițiale ale mediului de 20°C, 40°C și 60°C.