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ADVANCEMENT OF THE HARDENING FRONT IN FORMS AND CORES MADE OF QUICKLY BONDING COMPOSITES – ULTRASONIC ANALYSES

PRZEMIESZCZANIE FRONTU UTWARDZANIA W FORMACH I RDZENIACH WYKONANYCH Z MAS SZYBKOWIĄŻĄCYCH – BADANIA ULTRADŹWIĘKOWE

In this paper a new method of analysing the kinetics of hardening of quickly bonding composites, allowing to monitor the advancement of the composite hardening front in the form (core) was presented. The method was based on a patented measuring method, utilising the ultrasonic technology. In the paper, a new measuring workstation was presented, and the idea behind the measurement methodology was described. The results of analyses of the formaldehyde resin, hardened after aerating with CO_2 was presented. The velocity of the advancement of the hardening front as a function of parameters such as: composite permeability, size of the base kernels, the degree of densification measured by the ostensible density was analysed. The influence of each of the factors was described by a function. The results of the analyses, apart from its cognitive character, also have a utilitarian value. The research goes towards determining the dependencies, on the basis of which the optimum time for hardening (aerating) of cores with reactive gas can be specified. This in turn shall lead to reducing the consumption of the hardening gases and improving the efficiency of the core manufacturing process, produced in the "cold box" technology with the use of various types of bonding materials and various hardening gases.

Keywords: quickly bonding composites, ultrasonic technique, hardening front, bonding kinetics

W artykule zaprezentowano nową metodę badań kinetyki utwardzania mas szybkowiążących, pozwalającą monitorować przemieszczanie się frontu utwardzania mas w formie (rdzeniu). Metoda oparta jest na opatentowanym sposobie pomiarów wykorzystującym technikę ultradźwiękową. W pracy przedstawiono nowe stanowisko pomiarowe, opisano ideę metodyki pomiarów. Zamieszczono wyniki badań mas z żywicą formaldehydową, utwardzaną przez przedmuchiwanie CO_2. Wyznaczono prędkość przemieszczania się frontu utwardzania w funkcji takich parametrów jak: przepuszczalność masy, wielkość ziaren osnowy, stopień zagęszczenia mierzony gęstością pozorną. Wpływ każdego z czynników opisano funkcją. Wyniki badań, oprócz cech poznawczych mają również wartość utylitarną. Badania zmierzają do wyznaczenia zależności, w oparciu o które można by wyznaczyć optymalny czas utwardzania (przedmuchiwania) rdzeni reaktywnym gazem. To z kolei powinno pozwolić ograniczyć zużycie gazów utwardzających i podnieść sprawność procesu produkcji rdzeni wykonywanych w technologii cold box, z zastosowaniem różnych rodzajów spoiwa i gazu utwardzającego.

1. Introduction

In foundry engineering, more and more often a tendency to use elements of sand forms (cores) made of composites with chemical bondings, made with the use of the cold box technology, can be observed. The process of hardening (bonding) of such composites involves the creation of the bonding bridges between the kernels of the sand mass, strengthened as a result of chemical reactions. This process can be achieved by aerating the composite, condensed in the core box, with active gas. The bonding process is a complex, physic – chemical process. During the composite hardening the main roles are played by chemical reactions, however the physical processes, occurring during the transport of gases within the form are also important.

The speed of chemical reactions depends on the concentration of the reacting substances and on the temperature. In case the reacting substances assume -) one a liquid state and the other a gaseous state, the reaction progresses mainly on the boundary between the two mediums: liquid bonding – gaseous hardener. In general, the speed of the chemical reactions can be determined by the diffusion in the liquid medium of composites which react with the gas or by the participation of the reactive component in the gaseous constituent.

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Binding material distributed on the surface of the base kernels – usually quartz – create a strongly developed surface. The thickness of the binding layer does not exceed several microns, what leads to diminishing the importance of the diffusion factor in the liquid reacting substance. Instead the factor controlling the speed of the process is the time of diffusion of the active component of the gas in the porous medium [1].

Transport of gas in the porous medium, as well as the velocity of its flow, depends (in accordance to the H. Poiseuille equations (1) and (2)) on pressure differences (Δ P), gas viscosity (η), porosity scale of the medium (V_p), linked with the size of the inter kernel capillaries (D_p), length of the capillaries channels (L) and the area of the pores walls (S) [3, 4].

$$\bar{\upsilon} = \frac{D_p^2 \cdot \Delta P}{32 \cdot \eta \cdot L} \tag{1}$$

$$\bar{\upsilon} = \frac{V_p^2 \cdot V_l \cdot \Delta P}{(1 - V_p)^2 \cdot S^2 \cdot \eta \cdot 2L} \tag{2}$$

In case of moulding sands, the flow of active gas by the layers of the composite involves the process of forcing out the air which filled the inter kernel areas. The flow of the reactive gas through the composite is associated with its simultaneous wear as a result of a reaction with the binding material. The advancement of the front of the hardened layer is a complex physic - chemical process. The determination of the velocity of the advancement of the hardening front with the use of theoretical analysis is difficult, however the utilisation of a new, ultrasonic research method allows to determine this velocity with relative ease.

The flow of gas through a composite thickened in the core box leas to its gradual hardening in the consecutive layers – as shown in Fig. 1. The velocity of the growth of the thickness of the hardened composite (or the velocity with which the hardening front is advancing) is different from the velocity of gas flow in the porous medium (which can be calculated from the H. Poiseuille equations). The velocity of the advancement of the hardening front determines the time necessary for the aeration of cores (forms) with the reactive gas, what means that it also determines the technological cycle [6].

Three variants of relations between the velocity of the advancement of the hardening front and the velocity of the gas flow can be determined in the hardened composite: [1]:

1. The velocity of the advancement of the hardening front is **equal** to the velocity of gas flow;
2. The velocity of the advancement of the hardening front is **lower** than the velocity of gas flow;
3. The velocity of the advancement of the hardening front is **higher** than the velocity of gas flow.

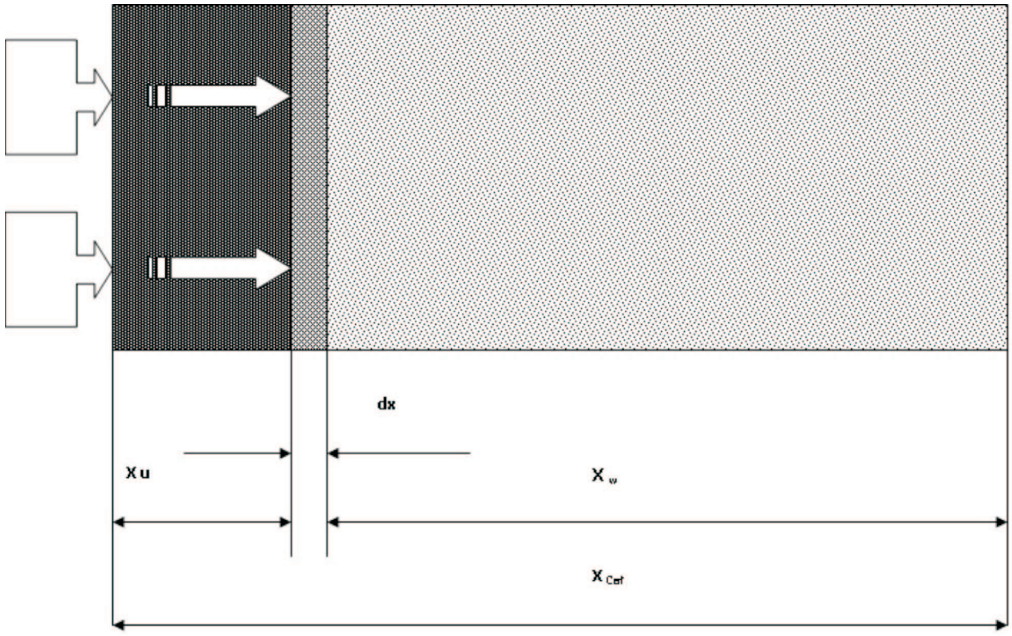

Fig. 1. Model of the process of hardening composite mass with chemical bonding material by blowing with active gas. X_u – hardened layer, d_x – layer, in which the hardening process is currently in progress, X_w – layer of non-hardened composite, $X_{całb}$ – total thickness of the hardened layer [2, 5]

The most beneficial arrangement is the first case. In the second case, part of the gas will be evacuated outside the hardened element. In the third case, the hardening process will be unnecessarily lengthened. In order to control the afore described velocities, it is necessary to [1]:

- Change the velocity of hardening of the composite by adjusting the concentration of the reactive substances, including the concentration of the reactive gas flowing through the hardened composite;
- Change the velocity of the gas flow by influencing the permeability of the composite itself and by adjusting the pressure of the gas pumped into the composite.

Until now, conducting the analysis of the velocity of the advancement of the composite hardening front was not possible due to the lack of the appropriate measuring method. In the real life, the optimisation of the hardening process shall be done by measuring time, after which the satisfactory hardening of the composite, at the constant supply of the reactive gas, was achieved. The professional literature however states that often the amount of gas used for the hardening process is exceeding the necessary minimum [7]. The authors state that the excess of used gas, due to the constant supply, when compared to the amounts derived from the stoichiometric calculations for the reaction, exceeds the necessary amount by 200% or even by 700%.

2. The author's own studies

2.1. Purpose and methodology of the studies

Hardening of a composite aerated with reactive gases occurs when the gas particles are transported to the place where a bridge is forming between the kernels and providing that they remain in contact with the binding material for the sufficiently long period of time. In time, the thickness of the hardened layer, measured from the surface, through which the gas is delivered, increases. The velocity with which the thickness of the hardened layer increases depends on various factors. In this paper, a method of determining the velocity of the advancement of the hardening front was presented.

The workstation designed for the determination of the kinetics of the composite hardening, what is the first step towards the determination of the the velocity of the advancement of the hardening front was presented in Fig. 2.

The study of the process of composite hardening was conducted in the following way. The prepared moulding sand was placed in the core box (11). The factor causing the composite hardening was gas – CO_2 – transported to the core box from the gas bottle (1) via a reducer equipped with a manometer (2) and a heater (3). The time of the gas flow was adjusted by the electro-valve (4). During the process of hardening, the moulding sand by the CO_2 the time necessary for the passage of the ultrasonic wave through the layer of composite, the thickness of which was the thickness of the core, was measured.

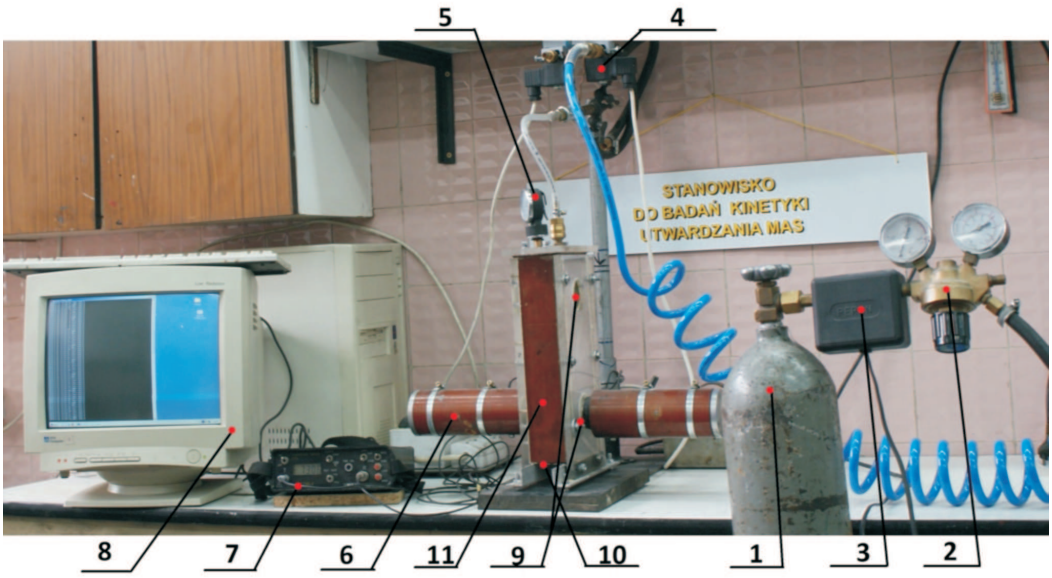

Fig. 2. Workstation for taking measurements and conducting ultrasonic studies of the kinetics of the hardening process of the quickly binding composites

The measurements were taken in 2 locations on the height of the core (9) – in the top section of the core, in the vicinity of the surface, and in the bottom section of the core, in the vicinity of the perforated bottom of the core (10), through which the excess of gas is evacuated outside the core box. The ultrasound wave was generated and received by the generator (7) with the use of the transmitting and receiving heads (6). The time necessary for the passage of the ultrasonic wave through the core was registered by the receiver and next it was acquired and saved in an external workstation (a computer) (8), with the use of a special software application. During the measurement process the excessive gas pressure in the core box, above the top layer of the composite was also registered with the use of a manometer (5).

In order to determine the velocity of the advancement of the hardening front, it was necessary to read from the graphs of the previously determined composite hardening kinetics for the particular degree of hardness S_x, the time which passed from the time the flow of CO_2 begun – that is from the time the hardening process commenced to the time the composite reached the pre-determined degree of hardness. The method of reading the results was presented in Fig. 3.

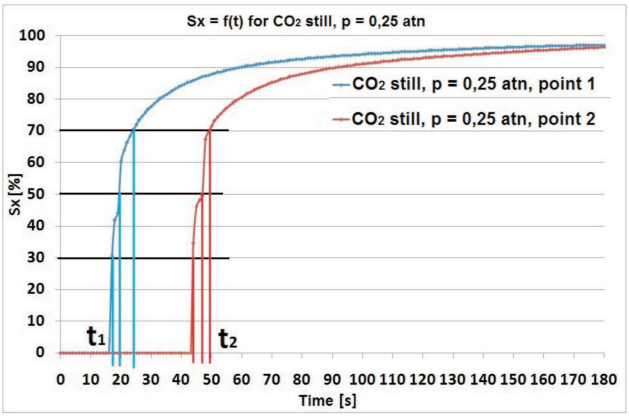

Fig. 3. Method of reading times $t_{1,2}$ – necessary for calculating the velocity of the advancement of the hardening front from the graphs presenting the kinetics of composite hardening, determined with the use of an ultrasonic wave

After reading from the graph times: t_1 – time for measurements taken in point 1 and t_2 – for measurements taken in point 2, it is possible to determine the velocity of the advancement of the hardening front, in accordance to formula 3.

$$v = \frac{d}{t_2 - t_1} \tag{3}$$

where:
v – velocity of the advancement of the hardening front [cm/s]
t_2, t_1 – times, read from the hardening kinetics graph [s]
d – distance between the measurement points – d = 17 cm

The velocity of the advancement of the hardening front depends on the permeability of the composite. The assessment of the actual permeability was conducted with the use of samples, cut from the previously hardened cores. In order to determine the permeability, ostensible density and strength of the composite, the samples for analyses were cut from the hardened cores with the use of a cutter of an appropriate diameter and then they were subjected to further processing in order to obtain standard dimensions of 50×50. The hardened core before and after cutting the samples as well as the samples themselves were presented in Fig. 4.

Fig. 4. Core, before and after cutting the samples for the analyses

2.2. Results of the analyses

The analyses were conducted with the composites based on "Szczakowa" quartz sand, of a various average kernel diameter: d_L = 0,24; 0,27; 0,34 mm.

A single stage phenol - formaldehyde, SuperEko NFC resin was used as a binding material. The resin was applied in the amount of 2,5%, and the cores were aerated with CO_2, applied at the pressure of 0,25; 0,50; and 1,0 atn. CO_2 blowing time through the core boxes was 5 minutes.

2.3. Velocity of the advancement of the hardening front

The dependence between the velocity of the advancement of the hardening front and the diameter of the sand base kernels d_L for the active gas (CO_2) applied at the pressure of p = 0,25 atn was presented in Fig. 5.

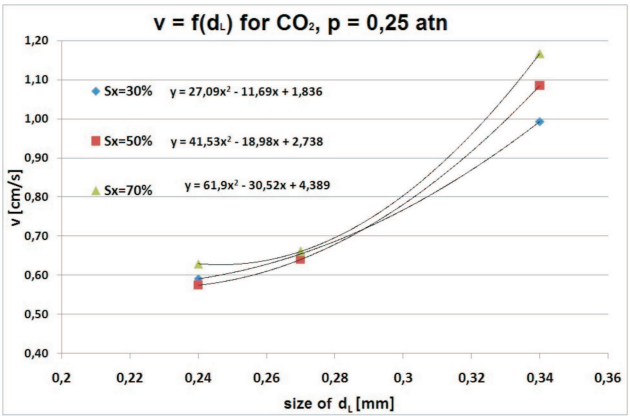

Fig. 5. Velocity of the advancement of the hardening front and the diameter of the sand base kernels d_L for the active gas (CO_2) applied at the pressure of p = 0,25 atn for various degrees of composite hardening

The velocity of the advancement of the hardened composite layer is described using the quadratic equations, regardless of the hardening stage selected for the comparison of the process.

From the analysis of Fig. 5 one can see that as the diameter of the kernel increases, the velocity of the advancement of the hardening front increases – at every stage of the composite hardening process. For every size of the sand base kernels, the velocity of the advancement of the head of the gas wave is lower than the velocity of the advancement of the head of the hardened composite. This is due to the fact that the initial hardening of the composite S_x=30% is slower (lower velocity of the front, low active gas concentration, which in the initial phase is mixed with air filling the inter-kernel cavities), than the full hardening of the composite S_x=70% (higher velocity of the front, higher concentration of the reactive gas – the hardening reaction progresses faster). This means that the hardening process is controlled by the velocity of the flow of reactive gas to the particular layer of the composite and not by the velocity of the hardening reaction.

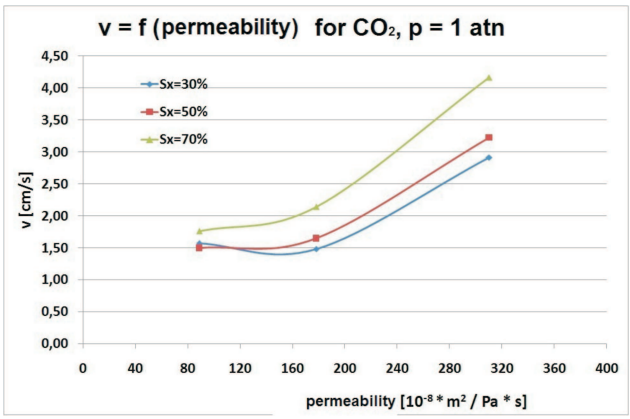

Fig. 6. Velocity of the advancement of the hardening front as a function of gas permeability for CO_2 applied at the pressure of 1 atn for various degrees of the composite hardening

The influence of the condensed composite permeability on the velocity of the advancement of the hardening front was presented in Fig. 6. The analyses were conducted with the use of the hardening gas (CO_2) applied at the pressure of 1 atn. The velocity of the advancement of the hardening front for various degrees of the composite hardening S_x was determined.

As we can see from the conducted analyses, the velocity of the advancement of the hardening front is similar for the composite hardening stages S_x= 30 and 50%, yet for S_x=70% it was higher. The figure also shows that the velocity of the advancement of the hardening front for every stage of the composite hardening S_x, increases in line with the increase of the composite permeability. Particularly significant increase of the velocity was observed when the permeability was greater than around 160 units.

The runs of the changes of the velocities of the advancement of the hardening front depending on the permeability of the composite, for the hardening degree S_x=30%, for various pressures of the applied reactive gas were compared in Fig. 7.

The graph shows that for a specific permeability of the composite, the velocity of the advancement of the hardening front increases in line with the increase of the pressure of the applied reactive gas. This increase was even more extreme for greater composite permeabilities.

The analysis of the measurement data showed that the velocity of the advancement of the composite hardening front depends on the pressure of the applied gas as well as on the permeability of the composite – closely associated with its degree of condensation.

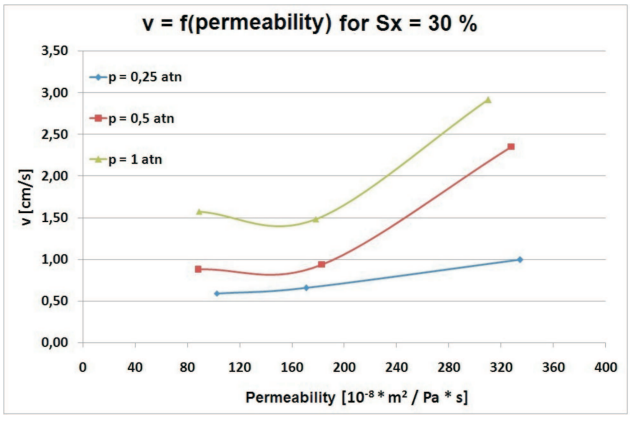

Fig. 7. Velocity of the advancement of the hardening front as a function of composite permeability (composite hardening degree S_x=30%, reactive gas pressure 0,25-1,0 atn.)

The changes in the velocity of advancement of the hardening front depending on the composite permeability and pressure of the reactive gas, determined for composite hardening degree S_x=30% was presented in Fig. 8. The graph shows that as the

pressure of the reactive gas increased, the velocity of the advancement of the hardening front for lower permeabilities (90 and 175) rose with the same intensity. However for greater composite permeabilities (322 units) the intensity was much greater. This means that only after exceeding the certain level of composite permeability, its significant influence on the velocity of the advancement of the hardening front can be observed. This border value was determined to be around 200 units.

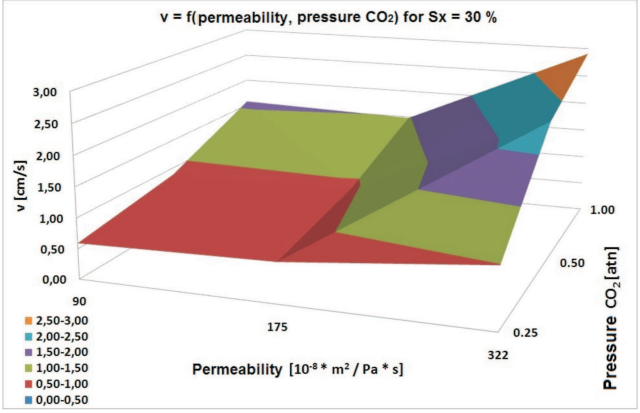

Fig. 8. Velocity of the advancement of the hardening front as a function of permeability and pressure of the reactive gas for the composite hardening degree S_x=30%

3. Summary and conclusions

The conducted studies regarding the application of the ultrasonic technology for the control of processes associated with manufacturing of cores allowed the author to derive the following conclusions:

- The ultrasonic technology allows to control "on line" the kinetics of composite hardening with chemical binding material, aerated with reactive gases,
- On the basis of the ultrasonic measurements the velocity of the advancement of the hardening front of the composite can be determined,
- The velocity with which the composite layers grow (harden) depends on the velocity of the advancement of the reactive gas in the porous medium; thus intermediately, it depends on the composite permeability,
- The determined dependencies of the velocity of the advancement of the composite hardening front on the composite permeability and gas pressure can be applied in real life for controlling the hardening times of cores or moulds of the specific thicknesses made of composites containing the single stage phenol – formaldehyde, SuperEko NFC resin.

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