Piezoelectric photoacoustics application possibility for concrete hydration stages determination has been analyzed. Cement sample placed on a transparent base was irradiated by laser beam. The acoustic signal from base transformed by piezoelectric converter into electric signal and through the amplifier moved in recorder device. The accent was on research and transient modelling with a pulse laser irradiation.

Mathematical model of transient for the given system with a single laser impulse was developed. The results of mathematical modelling were experimentally checked up and are well coincided.

Keywords: Photoacoustics, piezoelectric, cement, hydration

1. Introduction

Photoacoustic method, first revealed by A. Bell, evolved from interaction of intensity modulated light with substance. It causes acoustic wave generation due to thermal expansion, produced by the absorbed radiation. Great number of scientific works are devoted to this subject, different aspects of photoacoustic application for piezoelectric registration are considered in [1, 2, 3]. Most part of these works describe established generation rate [1, 2, 3]. In this case, radiation intensity of laser beam represents as [1, 2, 3]

\[ I(t) = \frac{2P_0}{\pi a^2} e^{-\beta/a^2} e^{-\omega t} (1 + \cos(\omega t)) \]  

where \( P_0 \) - laser power, \( a \) – beam radius, \( \beta \) – absorbing coefficient, \( \omega \) – modulation frequency. Temperature field considered quasiperiodic and described by next equation

\[ T = \tilde{T} e^{-i\omega t} \]  

Transition process forestalls rate establishing. Experimentally received transition process view is shown on Fig. 1.

This work is devoted to experimental and theoretical transition process description and opportunity of its application for time changes diagnostics of optical radiation thermal absorption and thermal conductivity of cement during hydration process.

2. Piezoelectric effect by thermal deformation influence

Photoacoustic measurements by this method are based on voltage detection, caused by deformation of piezoelectric attached with sample. Piezoceramics, consists of several layers of pressed powdered ferroelectric crystals (like BaTiO\(_3\) [4]) alternated with conducting layers, are widely used in our times (Fig. 2).
Let's use known dependence for electric charge, which is fair for all piezoelectric sensors [5]

\[ q = C_0 U - k \varepsilon u \]  

(3)

where \( C_0 = \frac{q}{U} \bigg|_{u=0} \) - capacity without deformation (clamped sensor), \( U \) - voltage from sensor, \( u \) - deformation, \( k \) - constant (dimensionless quantity if \( u \) - absolute deformation, or has length dimension if \( u \) - relative deformation), \( \varepsilon = Ed \), \( E \) - Young’s modulus of piezoceramic sensor in case of zero electric field, \( d \) - piezoelectric modulus. Voltage measurement is usually hold after signal amplifying. Substitutive electric scheme of detecting device is shown on Fig. 3, where \( R \) - input resistance, \( V \) - measurement device. For this scheme we could use an equation

\[ U + RC_0 \frac{dU}{dt} = RkE \frac{du}{dt} \]  

(4)

While \( R \rightarrow \infty \), we get an equation like in Jackson, Amer and Blonskij works [1, 2]. Detection voltage describes like solution of equation (4)

\[ U(t) = \frac{kE}{C_0} \int_0^t e^{\frac{RC}{C_0}} u'(t')dt' \]  

(5)

Let’s take the sample, one surface of which is inflexibly tied with piezoceramics surface, and another is free. Blending of sample is ignored in our case, because it is essential for very thin samples only [1]. Considering the fact, that low power laser was used in our experiment (25mW), we have a case of small deformations, that could described by next equation

\[ u'(t) = \frac{\int_S (u_x + u_y)_{\text{sam}p} dA}{dt} \]  

(6)

where \( S \) - sample square, covered with piezoceramics, \( u = \frac{\partial u_i}{\partial x_i} \) – deformation tensor for small deformation case from Landau work [6]. Axes \( x \) and \( y \) are laying on sample surface. According to [1], ignoring blending, we can get

\[ \int_S (u_x + u_y)_{\text{sam}p} dA = 2\alpha \int_S T_{\text{sam}p} dA \]  

(7)

Obtained experimental data (Fig. 4.) confirm that in case of detection devices with input resistance less than 10G\( \Omega \), equation (5) should be used. While \( R \rightarrow \infty \), voltage asymptotically increased till defined value, that not coincide with our experimental data. Photoacoustic signal voltage dependence vs. time (Fig. 4.) we could proper characterized by two values: maximum voltage amplitude \( U_{\text{max}} \) and time for its achievement \( t_{\text{max}} \).

3. Temperature field

For transition process investigation we irradiate the sample with the impulses, which described by
\[ I(t) = \begin{cases} 0, & t < t_0 \\ \frac{P_0}{\alpha_0}, & t \geq t_0 \end{cases} \] (8)

For temperature field determining we used the sample model (Fig. 5) of parallelepiped form for simplest computer modeling. Temperature field in sample, according with Lykov [7], has to satisfy next equation

\[ \frac{\partial T}{\partial t} - a_i \Delta_i T = q \] (9)

where \( a_i \) - thermal diffusivity, \( q \) - increasing temperature rate in light spot on sample. For laser beam that spot describes with

\[ \frac{2P_0}{\pi^2 a^2} e^{-r^2/a^2} e^{-j\omega} \] (9')

For our model it is simplest to take spot of square evenly irradiated form (Fig. 5) with a side length \( s \). If sample material has great absorption (with very big value of \( \beta \)), then increasing temperature rate in light spot on sample could be represented as

\[ q = \frac{(1-\gamma)P_0\delta(z-\ell)}{s^2C\rho} \bigg|_{z=\ell} \]

If \((1-\gamma)\) excludes from (10), it could used for any materials, which are heated only on surface. Though \((9')\) not coincide with (10), it is not always important, as it would be shown next. Irradiation of sample begins at time \( t=0 \). At that moment sample and environment temperatures are equal \( T(0)=0 \) (11) Heat exchange on the sides \( z=0, \ z=l \) is going due to convection by Newton law \( \frac{\partial T}{\partial z} = kT \bigg|_{z=\ell} \) (12), \( \frac{\partial T}{\partial z} = -kT \bigg|_{z=0} \) (13). We could ignore heat exchange from side borders if \( 4A \ll A^2 \). In that case \( \frac{\partial T}{\partial x} = 0 \bigg|_{x=0, x=a} \) (14), \( \frac{\partial T}{\partial y} = 0 \bigg|_{y=0, y=a} \) (15).

According to handbook of linear partial differential equation for engineers and scientists [8] solution of equation (9):

\[ T(x, y, z, t) = \int_{A-y}^{A+y} \int_{A-z}^{A+z} \int_{0}^{l} qG(x, y, z, \xi, \eta, \zeta, \ell')d\xi d\eta d\ell', \] (16)

\[ G(x, y, z, \xi, \eta, \zeta, \ell') = G_x(x, \xi, \ell')G_y(y, \eta, \ell')G_z(z, \zeta, \ell') \cdot G_t(t, \ell') = \frac{1}{A} \left[ 1 + 2 \sum_{n=1}^{\infty} \cos \left( \frac{\pi x}{A} \right) \cos \left( \frac{\pi y}{A} \right) \exp \left( -\frac{\pi^2 n^2 A t}{A^2} \right) \right]. \]

\[ G_x(x, \xi, \ell') = \frac{1}{A} \left[ 1 + 2 \sum_{n=1}^{\infty} \cos \left( \frac{\pi x}{A} \right) \cos \left( \frac{\pi y}{A} \right) \exp \left( -\frac{\pi^2 n^2 A t}{A^2} \right) \right] \cdot G_t(t, \ell') = \frac{\rho_n(z) \rho_n(\zeta)}{\| \rho_n \|^2} \exp(-a v^2 t), \]

\[ \rho_n(x) = \cos(v_n x) + \frac{k_n}{v_n} \sin(v_n x) \cdot \| \rho_n \|^2 = \frac{k_n v_n^2 + k_n^2}{2 v_n^2 + k_n^2} + \frac{k_n}{2 v_n^2} + \frac{l}{2} (1 + \frac{k_n^2}{v_n^2}). \]

Where \( v_n \) - positive roots of transcendental equation \( \tan(\ell') = \frac{k_1 + k_2}{v^2 - k_1 k_2} \).

Mathematical modeling of (16) gives next results. Example of temperature field for plate size 20x20x1 mm with heat exchange coefficient \( k_1 = k_2 = 0.0005 \text{ mm}^{-1} \), thermal diffusivity \( \alpha = 15 \text{ mm}^2/\text{s} \) (like sapphire, according to hand-book [9]), heat spot size - 2x2 mm, increasing temperature rate in light spot - 1 K/s or \( q = \delta(z-l) \) after 1 second from heating start is shown on Fig. 6. Ignoring the fact, that heat source has square form, equitemperature lines in a brief time got a circle form with heat source centre in their centres. (Fig. 7).
By placing (16) and (10) in (7), the voltage is finding like

\[
U(t) = \frac{2\alpha(1-\gamma)P_0}{s^2C\rho} k\varepsilon \left[ \sum_{i=0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \delta(z-l)G(x,y,z,\xi,\eta,\zeta,t')dx dy dz dt dl d\zeta d\xi d\eta \right] dt',
\]

(17)

Analyzed (17), we could made the following conclusions:

- Linear dependence of voltage vs. light source power and reflection index is stable.
- There is no dependence of \(U_{\text{max}}\) and \(t_{\text{max}}\) vs. light spot size.
- There is the dependence of \(U_{\text{max}}\) and \(t_{\text{max}}\) vs. discharge constant \(RC_0\).
- There is the dependence of \(U_{\text{max}}\) and \(t_{\text{max}}\) vs. heat exchange coefficients \(k_1\) \(k_2\).

On Fig. 8 calculated dependences of \(U_{\text{max}}\) and \(t_{\text{max}}\) vs. thermal diffusivity for different value of \(k_1\) are shown. Initial conditions are: plate size 20x20x1 mm, \(k_2=0.0005\text{mm}^{-1}\), \(RC_0 = 4\) and \(\frac{2\alpha(1-\gamma)P_0}{s^2C\rho} k\varepsilon \left[ \sum_{i=0}^{\infty} \right] \frac{C_0}{0} = 1.\)

![Fig. 8. Calculated dependences of \(U_{\text{max}}\) and \(t_{\text{max}}\) vs. thermal diffusivity for different value of \(k_1\).](image)

Lets take transparent base with high thermal diffusivity (sapphire in our case) tightly hold with piezoceramics with constant value sample placed on base, that covers the same square of base in every experiment. So thermal diffusivity of base is a constant value. If the same amplifier is always used, then \(RC_0=\text{const}). Then values of \(t_{\text{max}}\) and \(\frac{U_{\text{max}}}{P_0}\) would be defined by radiation reflection index of sample and its influence on heating exchange of one side of base. According to Ramachandran and Beaudoin [10], it is known that thermal diffusivity of cement during hydration increases. It’s logical to suggest that radiation reflection index is changing too according to the previous researches [11]. Mass and heat capacity of hydration cement in hermetic vessel keep unchanged [10]. So, while cement hydration process investigation by long impulses photoacoustic method, according to our computer modeling, we could made some conclusions:

- Changing of \(U_{\text{max}}\) would be happen due to changes of sample reflection index and heat exchange coefficient \(k_1\) of base. According to Fig. 8, while \(k_1\) decreases, \(U_{\text{max}}\) and \(t_{\text{max}}\)
increase.

- Changing of $t_{\text{max}}$ occurs due to $k_1$ changes only, if $R_0=\text{const.}$

4. Experiment

Experimental setup (Fig. 9) consists of sample 1, sapphire base 2, piezoceramics 3, beam splitter 4, laser 5, photodiode 6, amplifiers 7, ADC 8, PC 9. Laser 5 ($\lambda = 633\,\text{nm}$) irradiate the sample 1, absorbing light heats the sample, that heats transparent base 3, deformation of which is registered by piezoceramics 3, signal from what pass through amplifiers 7 and ADC 8 and store in PC 9. Radiation power pass through beam splitter 4 and is controlled by photodiode 6, signal from what pass through amplifiers 7 and ADC 8 and store in PC 9. For light spot diameter changes a lens 10 was used.

For cement hydration process investigation we take two samples of one kind of cement mixed with different quantity of water (10g of cement mixed with 3 or 3.5 ml of water). Experimental results are shown on Fig. 10.

![Experimental results](image)

Fig. 10. Normalized $U_{\text{max}}$ and $t_{\text{max}}$ vs time of hydration.

5. Discussion

On Fig. 10 one can see that during cement hydration $t_{\text{max}}$ value increasing is observed that complies cement thermal diffusivity decreasing and coincide with [10]. In the same time fast decreasing of $\frac{U_{\text{max}}}{P_0}$ is seen, that could be explained with decreasing of cement reflection index only. So our method opens new opportunities of cement hydration investigation.

References