CORELAȚII ÎNTRE CONDUCTIVITATEA ELECTRICĂ RELATIVĂ ŞI VULNERABILITATEA LA ÎNGHEȚ-DEZGHEȚ A CĂRĂMIZILOR AUTOCLAVIZATE, PE BAZĂ DE CENUŞĂ ZBURĂTOARE

RELATIONSHIP BETWEEN RELATIVE ELECTRICAL CONDUCTIVITY AND FREEZE-THAW DAMAGE OF AUTOCLAVED FLY ASH BRICK

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The electrical conductivity of the cement based materials mainly depends on the properties of its pore solution, and its freeze-thaw cycling damage properties are related to the pore size and distribution definitely. This paper has studied on the relationship between the electrical resistivity variation and the freeze-thaw cycling damage behavior of the autoclaved fly ash brick. Test results show that, the hysteresis effect of the electrical conductivity of the autoclaved fly ash brick has been changed significantly, whereas its frost-resistance ability decrease in quantity with increasing amount of fly ash added. Bricks with more cement added give high frost-resistance ability, such that the remarkable descent stage of them change from -10~0 ^{0}C to -20~0 ^{0}C. The addition of air entraining agent has little or undesirable effect on the frost-resistance ability of the autoclaved fly ash bricks.

Conductivitatea electrică a materialelor pe bază de ciment depinde, în principal de proprietățile soluției din pori, iar rezistența la îngheț-dezgheț ciclic este corelată cu distribuția şi dimensiunea porilor. Această lucrare a studiat relația dintre variația rezistivității electrice şi rezistența la îngheț-dezgheț ciclic a cărămizilor autoclavizate pe bază de liant de cenuşă zburătoare. Rezultatele testelor arată că efectul de histerezis al conductivității electrice a soluției din porii carămizii autoclavizate pe bază de liant de cenuşă zburătoare, s-a modificat în mod semnificativ, în timp ce rezistența la îngheț-dezgheț a scăzut cu creşterea cantității de cenuşă în liant. Creşterea dozajului de ciment a dus la mărirea rezistenței la îngheț, astfel încât temperatura de îngheț a scăzut de la -10 ~ 0 ^{0}C până la -20 ~ 0 ^{0}C. Adăugarea de aditiv antrenator de aer are un efect redus sau nedorit asupra rezistenței la îngheț a cărămizilor autoclavizate pe bază de liant de cenuşă zburătoare.

Keywords: *Fly ash brick, electrical conductivity, frost-resistance, electrical resistance.*

1. Introduction

In China, the traditional building bricks industry is a great waste of clay. About 1.3 billion m^2 cultivated area has been destroyed and 70 million tons coal has been consumed owing to the production of burnt clay bricks in the past fifty years [1]. The autoclaved brick from fly ash is a kind of new building materials which can consume large quantities of the industrial by-product fly ash. Since 2003, along with the new policy has been set up by Chinese government to forbid producing the burnt clay bricks as building materials, autoclaved fly ash brick (AFAB) is considered as the hopeful building materials which offer very high potential for exploitation in the 21 century [2]. However, in the cold areas, the frost-resistance of the building materials is the key indexes in evaluating the durability of them for application in the construction [3]. Therefore, in relation to the mechanical and mass variation during the freeze-thaw cycling, the design of mix proportion, the moulding craft, the water absorption and the curing condition of the AFAB have been extensively addressed [4-5].

The freeze-thaw cycling damage of porous materials is not only related to the crystallization in pores, but also to the interaction between the pore solution and the pore structures, the purity of the liquid water and the supercooling phenomenon [6-7]. Studying ice formation process through the change of electrical conductivity of concrete has been proved as a suitable technique; however it has not been applied to representative the frost-resistance behavior of AFAB. The damage evolution during freeze-thaw cycling of cement mortar was found by electrical resistivity measurement to involve damage accumulating gradually cycle by cycle until failure. Further D. D. L. Chung [8] has first proposed the theory that the resistivity decrease exhibited hysteresis, which grew as cycling processed. Since the damage caused by freeze-thaw cycling is expected to affect the electrical conductivity properties, the basic electrical resistance features of the AFAB with designed freeze-thaw cycle are preliminarily discussed in this paper. Investigation the influence of the mix proportion on the frost-resistance of the AFAB is the secondary objective of this work.

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2. Materials and Experimental

2.1. Materials

Composite cement used was from Harbin Cement Factory. The river sand with a fineness modulus of 2.4 and calcium hydroxide ($Ca(OH)_2$) were used in this study. Fly ash was obtained from Harbin SanFa Building Materials Ltd., China. SJ-2 were prepared and used as entraining agent in AFAB. The compositions of materials used in this research are given in Table 1.

2.2. Moulding technique

Firstly, optimum water demand, brick forming pressure, steam pressure and autoclaving time were determined. Ten different types of brick specimens were produced as shown in Table 2. Brick specimens were prepared with 75% water demand for normal consistency of the resultant cement and formed with the aid of a hydraulic press of 26 MPa into mold with 120×240×53 mm. The specimens were steam autoclaved in an autoclave with constant operating pressure of 1MPa and curving temperature of 160~170^{0}C for 12 hours. Autoclaved specimens were curved under the circumstance of 20±2 ^{0}C, RH 60%. And then the specimens were rectangular bars of size 100×100×53 mm for testing their properties. Specimens were stored in water until they reached constant weights.

2.3 Electrochemical test

The electrical resistivity measurements were performed by RST5200 electrochemical system using the two-probe AC impedance method as shown in Figure 1 [9, 10]. The electrical contacts were stainless steel plate in conjuction with copper wires. To further eliminate the negative influence of interface, two pieces of wet sponge contain 3% NaCl solutions were put between the surface of specimens and electrodes.

The test frequencies ranged from 0.1 Hz to 10 KHz, and the potential amplitude was 10 mV. For each mix proportion (MU1 to Mu19), all the electrochemical parameters were measured six times and the result in the paper was an average value of six measurements. Temperature was gradually lowered and raise in the refregerator between 0 to 30 ^{0}C to simulate a freeze-thaw cycle. The electrical conductivity of the specimens was measured after every 10 ^{0}C interval during freezing and thawing processes.

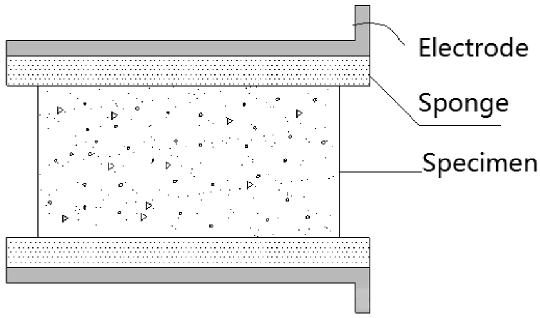

Fig.1- Test arrangement/ *Metoda de încercare a rezistivității electrice*.

Table 1

Chemical composition of materials used in this research/ *Compoziția chimică a materialelor utilizate în lucrare*

Oxide *Oxid*	Composite Cement *Ciment compozit* (%)	Fly Ash *Cenuşă zburătoare* (%)	Calcium Hydroxide *Hidroxid de calciu* (%)
SiO_2	21.08	66.57	1.32
Al_2O_3	5.47	18.95	1.01
Fe_2O_3	3.96	4.44	0.79
CaO	62.28	3.05	67.12
MgO	1.73	1.22	3.22
SO_3	2.63	0.31	4.21
Loss on ignition(LOI)	1.61	3.10	21.12

Table 2

Mix proportion of AFAB/*Compoziția amestecurilor pentru cărămizi autoclavizate, pe bază de liant de cenuşă*

Specimens *Probe*	Fly Ash *Cenuşă zburătoare*	Calcium Hydroxide *Hidroxid de calciu*	Cement *Ciment*	Gypsum *Gips*	Sand *Nisip*	SJ-2
MU 1	51	8	4	2	35	0
MU 3	49	8	6	2	35	0
MU 5	45	8	10	2	35	0
MU 7	41	8	14	2	35	0
MU 9	51	4	8	2	35	0
MU 11	39	16	8	2	35	0
MU 13	40	15	8	2	35	0
MU 15	40	8	15	2	35	0
MU 17	51	8	4	2	35	0.04
MU 19	51	8	4	2	35	0.08

3. Results and Discussion

3.1. Electrical Resistance under Room Temperature

Figure 2 a shows the Nyquist curve of AFAB with different cement content under the room temperature. The cusp between 50 kHz and 20 kHz in the Nyquist plot is used to determine the cement-based materials' resistance. At this point, the value of Z″ is at a minimum, which is the cutoff frequency (f_{cutoff}) which has a considerable range and has been observed to range from 100 Hz to 100 kHz [11]. The influence of the cement content can be clearly distinguished by observing the electrical resistance data in Figure 2 b. In the range from 6 to 14 wt. % cement, the electrical resistance increase monotonically with the increasing cement content. This means that the hydration products of cement improve the pore structure and decrease the porosity of the AFAB because of its filling effect. This effect of the cement is more significant when the cement content exceeds 10 wt. % of the total mixture (the electrical resistance increase from 18.29 to 59.5K·Ohm).

Figure 3 illustrates the Nyquist curve of AFAB with different proportion of calcium hydroxide and cement at room temperature. The electrical resistance of AFAB increases slightly with increasing proportion of calcium hydroxide and cement (from 1:2 to 2:1). The weak effect of the different ratio of them on the electrical resistance indicates that the structure development and hydration of the AFAB are mainly governed by the total content of cement and the calcium hydroxide. However, the secondary hydration products of cement can influence the pore structure and the secondary interface microstructure. Thus, the frost-resistance may reveal their difference in the further discuss.

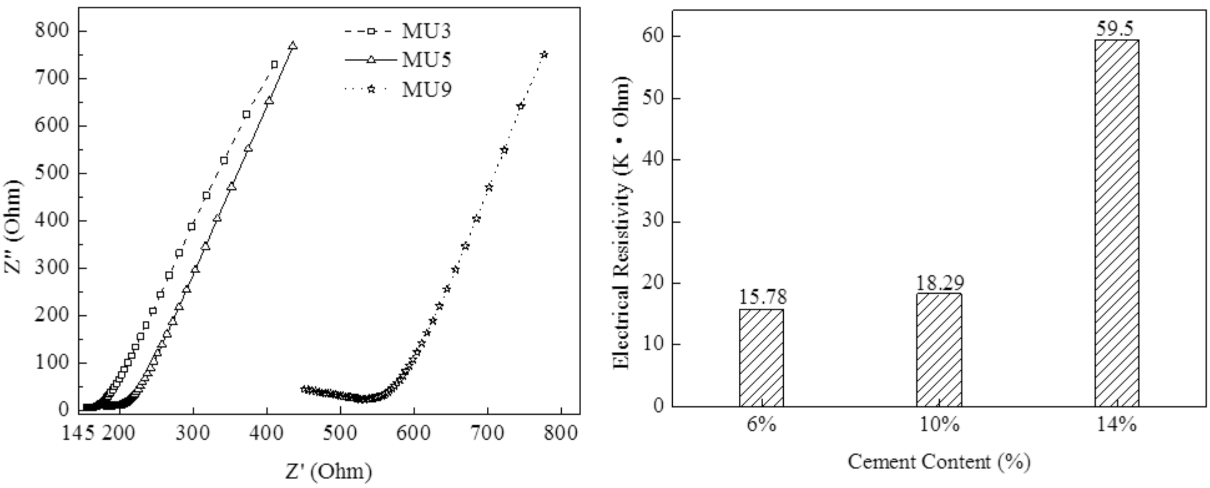

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Fig. 2-Effect of cement content on the Nyquist curve and electrical conductivity of AFAB/ *Efectul conținutului de ciment asupra funcției Nyquist şi a conductivității electrice a AFAB.*

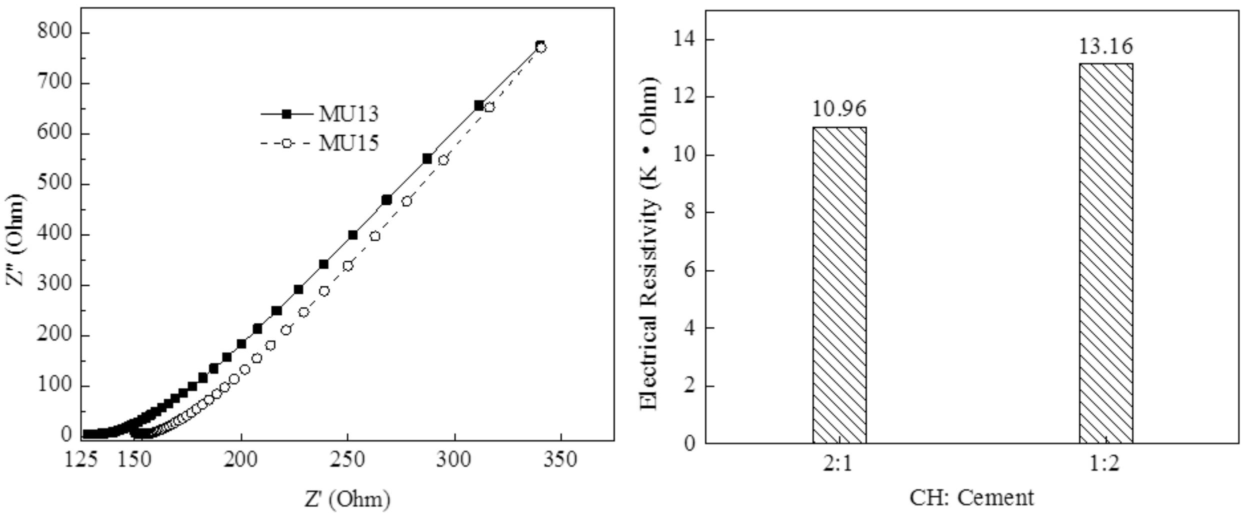

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Fig. 3- Effect of lime to cement ratio on the Nyquist curve and electrical conductivity of AFAB/ *Efectul raportului var /ciment asupra funcției Nyquist şi a conductivității electrice a AFAB.*

As shown in Figure 4, the addition of the entraining agent in AFAB decreased its electrical resistance sharply. Since the addition of the entraining agent in AFAB correspond to a substantial amout of porosity, increase the conductivitity of the AFAB. Since both a larger amount of porosity and a better porosity distribution correspond to the addtion of the entraining agent, the two treads appear to be contraditory. The apparent contradiction suggests that the addtion of entraining agent is sensitive to the frost-resistance, such that the relationship between these two quantities is not simple.

3.2. Relative electrical conductivity under freeze-thaw cycling

3.2.1 Cement content

Figure 5-8 shows the relationship between temperature and the relative electrical conductivity of different mixing ratio, lime content and cement content. The relative electrical conductivity is defined as the ratio of the electrical conductivity under a certain temperature to the one at 0 ^{0}C of the same specimen [3]. The same hysteresis behavior of ice formation in freezing process has been observed in all these Figures.

Figure 5 presents the influence of the cement content on the relative electrical conductivity of AFAB under freeze-thaw cycling. As shown in Figure 5, the electrical conductivity in freezing process is always higher than that in thawing process under the same temperature, which indicates more ice exists in AFAB in the thawing process. Test results showed that the electrical conductivity deceases along with the temperature reduction. This is due to the weak mobility of ions existed in the pore solution of the AFAB, which has lower ionic shifting activation energy at lower temperature [12,13]. After the temperature reduced to near zero, the phase transition of the pore solution in the big capillary has been occurred. Subsequently the same

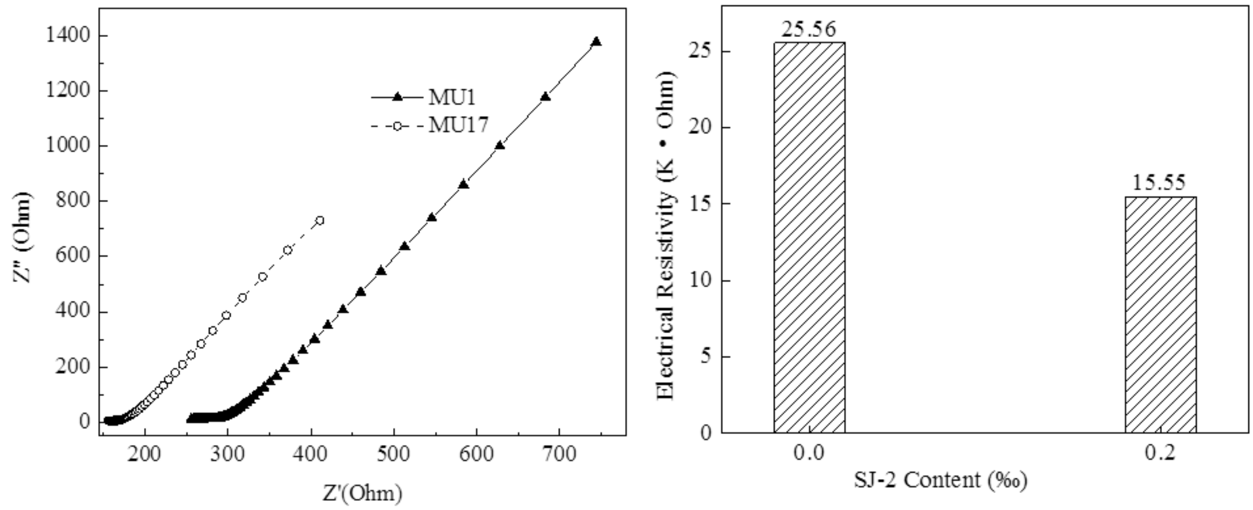

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Fig.4-Effect of air entraining agent content on the Nyquist curve and electrical conductivity of AFAB / *Efectul aditivului antrenator de aer asupra funcției Nyquist şi a conductivității electrice a AFAB.*

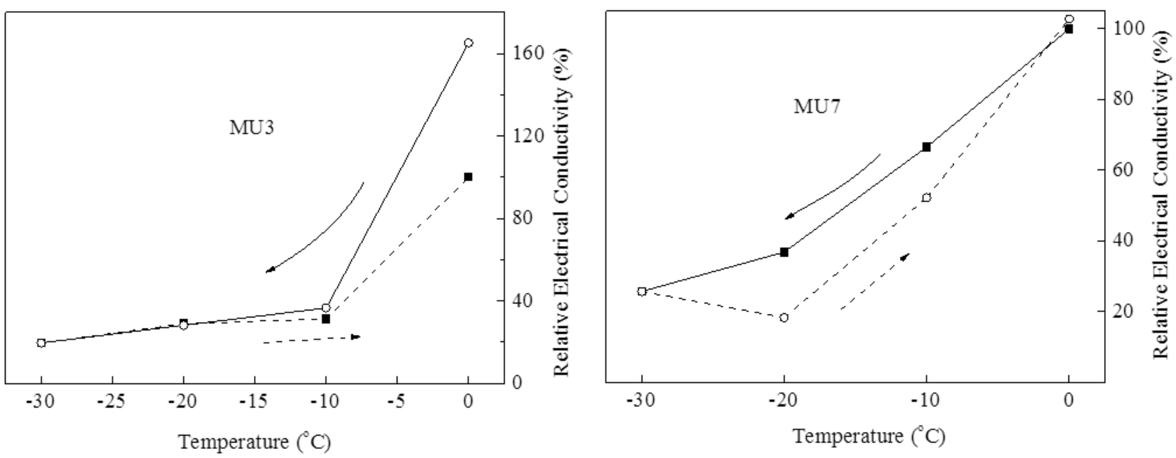

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Fig.5-Relative electrical conductivity of AFAB with different cement content vs. temperature/ *Conductivitatea electrică relativă a AFAB în funcție de conținutul de ciment şi temperatură.*

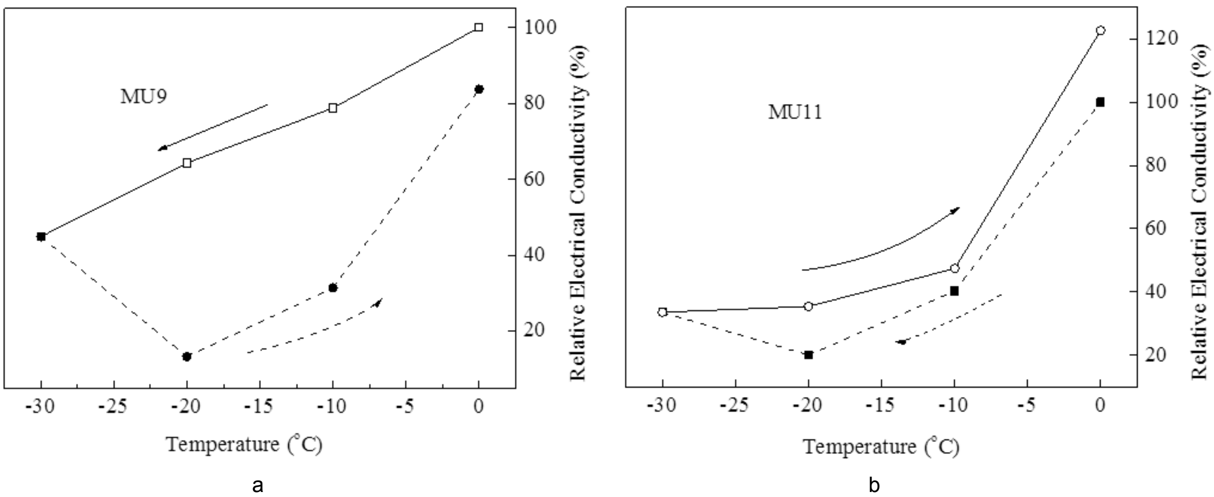

Fig.6- Relative electrical conductivity of AFAB with different fly ash content vs. temperature / *Conductivitatea electrică relativă a AFAB în funcție de conținutul de cenuşă şi temperatură.*

phenomenon is happening for the pore solution in smaller capillary and air pore with temperature decline. Note that both of these processes reduced a portion of the electrical conductivity of the AFAB. This also means that the decrease rate of the electrical conductivity has a strong correlation with the pore size distribution. The faster electrical conductivity decreases, the more pore has occurred the phase transition and vice versa.

Generally, the electrical conductivity of the AFAB is proportional to the volume of the unfrozen pore solution. As shown in Figure 5, the increase of cement content contributed to an apparent drop in electrical conductivity of AFAB from -10~0 ^{0}C to -20~0 ^{0}C. This is mainly because the hydrated product of the cement had a relatively high alkaline to improve the hydration activity of Fly ash. Further the hydrates and crystalline phases of cement can improve the structure of the AFAB. Together, they account for the main reason the frost-resistance of AGAB increases with the increasing cement content.

3.2.2. Fly ash content

The correlation of the fly ash content with the relativity electrical conductivity of AFAB is shown in Figure 6. The combination of Figure 5 and Figure 6 shows a significant hysteresis of ice formation in freezing process along with the increasing fly ash content in the mixture. These results mean that both the volcanic effect and the hydratability of Fly ash could be blocked by the over high ratio of fly ash, and thus insufficient cement and lime as alkaline agent in the mixture. The hysteresis also indicates that the lack of litter pore and higher porosity in the MU 9 as shown in Figure 6. As a result, the effective diffusivity increases rapidly due to the higher porosity of the MU9. Because the decrease of the temperature may unite larger pores, which makes the degree of the channel curving of harden paste decline. The higher effective diffusivity corresponds to the higher relative electrical conductivity all along with the freezing process of MU9.

Based on Figure 6 b, the mirco structure and the freezing resisting of AFAB can be improved greatly by adding sufficient alkaline agent and appropriate fly ash to the mixture and activating its activation. The behavior is consistent with the notion that it is more difficult for pore solution to diffusion under full hydration condition in AFAB system. And appropriate fly ash content also enables the AFAB to fulfill the conditions for full hydration and speed up the AFAB to harden.

3.2.3. Lime/Cement ratio

Figure 7 illustrates the relative electrical conductivity change of AFAB with different lime to cement ratio under freeze-thaw cycling. In Figure 7, the electrical conductivity in freezing process is lower than that in thawing process under the same temperature for L/C is 2:1. Conversely, the electrical conductivity in freezing process is higher than that in thawing process for L/C is 1:2. These results mean that the cement and the lime have different results to excite the activity of fly ash. For the L/C is 2:1, the excess lime could accelerate secondary hydration reaction during the thawing process. After that degree of second hydration on fly ash's surface is improved, and integration about fly ash to hydration production of activator. Due to the optimization of the secondary pore structure of the higher lime content specimen, the electrical conductivity of the AFAB increasing accordingly. For the L/C is 1:2, proper raising the cement content is not so useful to give fly ash activity in full play at short term. The hysteresis of ice formation in the freezing process indicates the early hydration process of cement pastes is not as good as lime. This suggests that the initial addition of cement results in better pore distribution. However, as cement is further added, the lime becomes

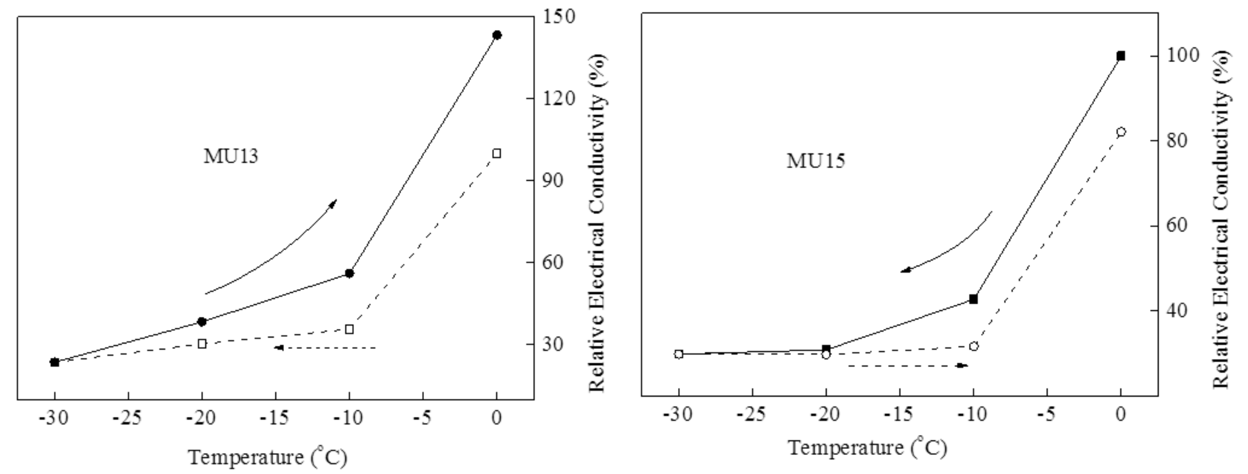

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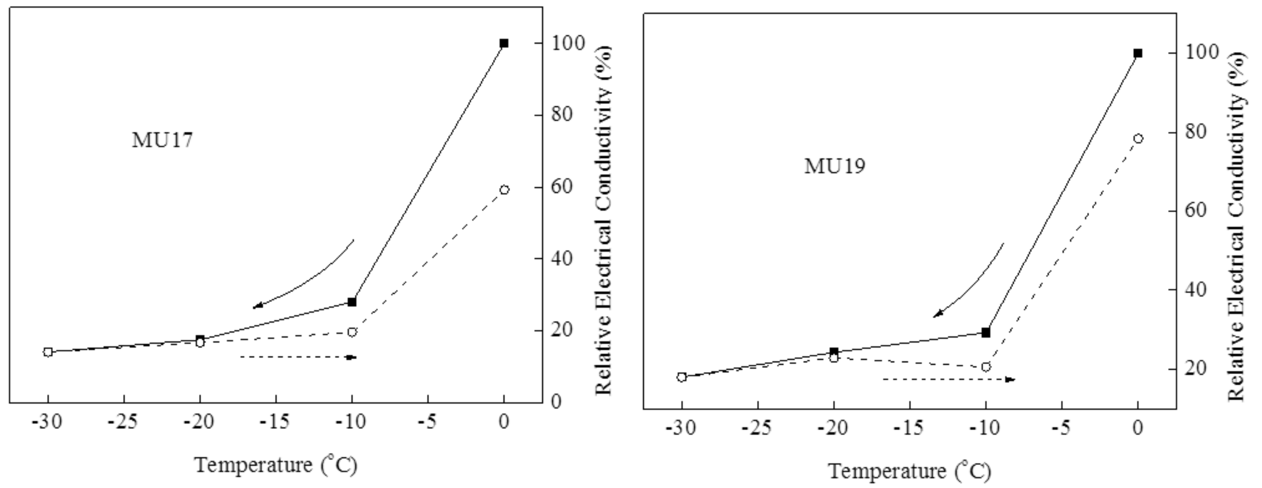
Fig.7-Relative electrical conductivity of AFAB with different lime to cement ratio vs. temperature / *Conductivitatea electrică relativă a AFAB în funcție de raportul var/ciment şi temperatură.*



a) b)

Fig.8-Relative electrical conductivity of AFAB with different air entraining agent content vs. temperature / *Condudtivitatea electrică relativă a AFAB în funcție de conținutul de aditiv antrenator de aer şi temperatură.*

more insufficient, thus resulting in slight reduction in the early hydration. This confirms that lime is much more effective that cement in enhancing the frost-resistance character of AFAB.

3.2.4 Air entraining agent

Figure 8 illustrates the influence of air entraining agent on the relative electrical conductivity of AFAB under freeze-thaw cycling. Due to the low water-solid ratio (13~14%), the air entraining agent can't lead into air to produce lots of little and stable bubbles in the processing of mixing mixture. The combination of Figure 6 and Figure 8 shows that the apparent drop in electrical conductivity of AFAB is still at -10~0 ^{0}C, which indicates that the addition of entraining agent does not change the behavior of pore solution. In contract, it increases the entire volume of the pore and low the phase transition temperature. As shown in Figure 8, there is no obvious difference of relative electrical conductivity of AFAB, with more or less addition of air entraining agent.

4. Conclusions

4.1 AFAB with added sufficient cement gives much higher values of the electrical resistance, and contributes to an apparent drop in electrical conductivity of AFAB from -10~0 ℃ to -20~0 ℃. This means that AFAB with added cement is effective for improving its structure and porosity.

4.2 Positive effect of excess fly ash addition on the electrical resistance and frost-resistance of AFAB were observed. 40 to 45% of fly ash addition was estimated as optimum.

4.3 With both lime and cement added to the AFAB, cement enhances the porosity distribution, whereas lime enhances the early hydration. However, the effect of lime is more significant to confirm the frost-resistance ability when the total content of lime and cement is fixed. The optimum lime to cement ratio was determined as 2:1.

4.4 It is found that, due to the low water-solid ratio, the addition of air entraining agent couldn't improve the spacing factor or pore structure of AFAB. The phase transition temperature doesn't change anymore, thus the addition of air entraining agent has no effect on improving the frost-resistance ability of AFAB as usual.

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