Nuclear magnetic resonance analysis of concrete-lined channel freeze-thaw damage

Wang XIAOXIAO, Shen XIANGDONG,† Wang HAILONG and Gao CHU

College of water conservancy and civil engineering, Inner Mongolia Agricultural University, Hohhot 010018, China

The channel lining of Inner Mongolia hetao irrigation is set in the research background, which was used by natural pumice concrete as the raw material. In the present study, based on the existing research and analysis methods of air entraining natural pumice concrete freeze-thaw damage, a nuclear magnetic resonance detection technique was introduced. From the research of essence of freeze-thaw coupling-induced concrete damage in saline solution, natural pumice concrete porosity and transversal relaxation time were used as criteria. Nuclear magnetic resonance imaging (NMRI) technology, an intuitive method, was used to quantitatively determine the freeze-thaw damage. Furthermore, the nuclear magnetic resonance results were compared and demonstrated, combined with ultrasonic testing methods and the capillary water absorption test. Based on the study results, it may be concluded that four peaks were present in the $T_2$ distribution of air entraining natural lightweight aggregate concrete after 200 cycles of freezing and thawing, the porosity increased with the increase of the air-entraining agent, and $T_2$ spectrum area increased. The freeze-thaw cycle of frost resistance was improved by a moderate quantity of air entraining agent. An excess of the air-entraining agent caused large pores, which accelerated the freeze-thaw damage. NMRI was used to analyze the pore damage propagation characteristics of the air-entraining concrete, which provides information for freezing thawing damage analysis of concrete, and also represents the unique advantages of NMR techniques.

Key-words : Channel lining, Air entraining natural pumice concrete, Freeze-thaw damage, Nuclear magnetic resonance (NMR).

Porosity, Relaxation time

1. Introduction

In this paper, the natural pumice stone in the Inner Mongolia area is taken as the research object. Natural pumice stone is a type of porous vitric extrusive rock. There is a large quantity of natural pumice stones in the Inner Mongolia area, where there are abundant and widely-distributed available volcanic resources, as well as abundant raw materials of natural lightweight aggregate.1) Lightweight aggregate concrete has been widely used in recent years due to its high porosity, low density, frost resistance and favorable heat retaining property.1-6) It was developed to adapt to the cold areas of farmland channel lining of the new material - natural pumice concrete by making full use of local resources.

Natural pumice concrete is a type of complex porous material, and its interior structure contains a large number of irregular and cross-dimensional aperture gaps. These pores directly affect the concrete strength, elastic modulus, wave velocity, permeability, frost resistance, permeability resistance and other physical and mechanical properties. Due to the fact that air-entrained concrete has strong anti-permeability, anti-frost and anti-corrosion performances, it is often applied to practical engineering. Due to the introduction of the air-entraining agent, a large number of micro-bubbles with uniform distribution, stability and closed states were produced in the preparation process of the concrete. Therefore, air-entraining concrete is considered to be a rather complex system of porous material.7,8) Furthermore, the air-entraining agent will affect the changes in the pore structure and interface transition zone of hardened paste, and these have been considered important factors affecting the durability and macro-mechanics of concrete.9) In northern China, due to the prolonged duration of the winter season and large day-night temperature difference, the cold damage of the channel hydraulic structures is more serious, the changes of the internal pore structure of concrete caused by cycles of freezing and thawing affect the physical and mechanical properties of concrete. Therefore, it is very meaningful to analyze and explore the effects of the characteristics of the pore structure and interfacial transition zone on the damage laws of air-entraining concrete freeze-thaw.

Currently, indoor test methods which are used to describe and evaluate the concrete pore structure and interface transition zone mainly include the mercury method, optical microscope, micro-hardness testing, scanning electron microscope (SEM) and CT scanning technique. Scholars from throughout the world have carried out relevant research work, and achieved fruitful results. Sidney Mindess9) and Yang Shuyan7) found that the introduction of an appropriate amount of air-entraining agent improved pore structure and the interfacial transition zone of high performance concrete by using the mercury intrusion method, optical microscope, micro hardness testing and scanning electron microscope testing, which would allow high bonding strength of high performance concrete. Mehta PK et al.10-12) believed that not only porosity, but pore size distribution and connectivity also controlled concrete permeability. Huwien Wan,13) by using the mercury intrusion and optical microscopy methods, discovered that a certain dosage of air-entraining agent affected the pore size distribution and connectivity of concrete. Morgan et al.13) and Oral Buyukozturk14) obtained concrete section void clear images of aggregate and mortar, and believed that X-CT was an effective method for studying the internal structure of concrete. John

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et al.\textsuperscript{15}) and Houqun Chen\textsuperscript{16}) concluded that there were problems in judging three-dimensional crack characteristics and morphology by using the CT scanning and digital image correlation techniques.

NMR has been maturely used in fields such as medical diagnosis, petroleum exploration and development, agriculture, food and bio-pharmaceutical, and it has nondestructive testing, samples can be repeated use, test speed etc.\textsuperscript{17}) However, in the field of the concrete, using NMR technology research and not to the relevant literatures. NMR technology in the field of geotechnical engineering has made a lot of achievements, at present this technology has become a new method and means of core physical property analysis.\textsuperscript{18),19} In this paper, the air-entrained natural pumice concrete is taken as the research object; then, we conduct ultrasonic testing and water absorption testing after freeze-thaw damage; next we apply an NMR analyzer for relaxation measurement and imaging measurement; finally, we analyze and discuss the distribution of the $T_2$ spectrum, variation of $T_2$ spectrum area, and internal pore distribution characteristics of air-entrained natural pumice lightweight aggregate concrete.

2. Test Profile

2.1 Test materials and instruments

Cement: Jidong P.O42.5 Ordinary Portland Cement; coarse aggregate: pumice aggregate of central Inner Mongolia, China, bulk density 690 kg/m$^3$, apparent density 1,593 kg/m$^3$, water absorption in 1 h 16.44%; fine aggregate: natural river sand, fineness modulus 2.56, silt content 1.98%, bulk density 1,465 kg/m$^3$, apparent density 2,645 kg/m$^3$, moisture content 1.987%, favorable grain composition; fly ash: I-grade fly ash of Jinqiao Thermal Power Plant, Hohhot; water reducing agent: RSD-8 type superplasticizer, dominant ingredient $\beta$-sodium naphthalene formaldehyde high-condensation, admixture amount 3%, water-reducing rate 20%, no corrosive action on the rebar; water: ordinary tap water. The performance of coarse aggregate and fine aggregate were checked by Lightweight aggregates and its test methods-Part1: Lightweight aggregates (GBT17431.1-2010) and Sand for construction (GB/T14684-2011) respectively.

Key instruments in the test: freeze-thaw cycle test machine, ultrasonic testing analyzer, vacuum saturation device, NMRI analysis system, etc.

2.2 Test method and program

The channel lining was made in Inner Mongolia Hetao irrigation district, by using air entraining natural pumice concrete as material (see Fig. 1). In order to better analysis the damage mechanism of air entraining natural pumice concrete under freezing and thawing in saline solution, the mesoscopic material performance experiment of concrete was tested. In the test, LC30 strength grade lightweight aggregate concrete is taken as the research object. Mix proportion is m (cement):m (water):m (pumice lightweight aggregate):m (sand):m (fly ash):m (water reducing agent) = 360:180:530:730:90:9, Air-entraining agent was joined to 0, 0.01, 0.02% with binding material quality, which was 0, 45, 90 g respectively, and, was named the group of LCA,LCB,LCC. The technological process follows the mixing procedure in Technical Specification for Lightweight Aggregate Concrete (JGJ51-2002), we take the “fast freezing method” freeze-thaw cycle test in the saline solution in the Hetao Irrigation District, the cycle indexes are 200. The ultrasonic test follows Technical specification for concrete strength by ultrasonic-Rebound combined method (CECS 02: 2005). In order to more comprehensively understand the interior pore structure of lightweight aggregate concrete before and after the freeze-thaw, we remove the test piece before freeze-thaw and after 200 freeze-thaws. We then core the test piece with a cutting machine. In order to eliminate the uneven freeze-thaw influence at the ends, we cut off 100 $\times$ 100 $\times$ 170 mm at both ends of the test piece. Then we cut off the four formed surfaces of the test piece equivalently, and leave the residual size at about 40 $\times$ 40 $\times$ 60 mm. This helps to eliminate the uneven distribution of formed surface and the underside aggregate, as shown in Fig. 2.
Then, we conduct the NMR test on the test pieces of 40 mm × 40 mm × 60 mm before and after the freeze-thaw cycles. First, we apply the vacuum saturation device to saturate the concrete sample. The vacuum pressure value is 0.1 MPa and the pump-down time is 4 h. Next, we steep the sample in distilled water for 24 h and conduct the process again for the NMR relaxation measurement for comparison analysis by the MiniMR-60 type NMRI analysis system. In order to eliminate the effects of moisture evaporation on the test results, when removing the sample from the water, we wipe off the moisture on the surface and wrap it with a preservative film for the NMRI test.

In order to get the size of the sample 100 mm × 20 mm × 50 mm, the sample of 100 mm × 100 mm × 170 mm was cut off. The capillary water absorption tests were conducted in accordance with ASTM C1585-04 standard. Put the sample into the oven of 50°C, it was baked 4 days until the specimen quality off. The capillary water absorption tests were conducted in the oven of 50°, it was baked 4 days until the specimen quality off. The capillary water absorption tests were conducted in the oven of 50°, it was baked 4 days until the specimen quality off. The capillary water absorption tests were conducted in the oven of 50°, it was baked 4 days until the specimen quality off.

### Table 1. Ultrasonic test results of freeze-thaw damage

| The groups | The ultrasonic wave velocity before freeze-thaw v/(m·s⁻¹) | The ultrasonic wave velocity after freeze-thaw v(’)/(m·s⁻¹) | The wave dropping rate η/% | The damage degree D |
|------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------|---------------------|
| LCA        | 4588                                                    | 2500                                                    | 45.5                       | 0.70                |
| LCB        | 3727                                                    | 2266                                                    | 39.2                       | 0.63                |
| LCC        | 3137                                                    | 1861                                                    | 40.7                       | 0.65                |

3.2 Analysis of capillary water absorption

The pores appearing in hardened concrete include gel holes, capillary porosity and air bubbles. The hole diameter of gel is 15–100 Å, and it does not freeze above ~78°C. Air bubbles are either inhaled naturally or artificially introduced by adding an air entraining agent during the stirring and vibrating of concrete. Air bubbles generally show a closed spherical shape and are favorable to the frost resistance of concrete, thus capillary porosity is the only pore which is harmful to the frost resistance of concrete. Therefore, the capillary water absorption test can be used to quantitatively analyze the water absorption characteristics of concrete.

The capillary water absorption model of porous cement material is based on the theory of capillary absorption of the parallel capillary porous media transmission. As can be seen from the capillary water absorption kinetics model, in theory there is a linear relationship between water penetration depth and square of time.

For the relationship between water invasive capacity and time of porous cement base material, a constant parameter B is assumed to represent the capillary water absorption permeability coefficient, under the conditions of not considering the cement-based material internal aperture, water surface tension, contact angle or viscosity coefficient change. Under the condition that the above assumed conditions are met, capillary water absorption per unit area and square of time also show a linear relationship. The equation is as follows:

\[
\Delta W = C \cdot S_C \cdot \sqrt{t}
\]

where C is the mass absorption coefficient of concrete \( [\text{kg/(m}^2 \cdot \text{h}^{1/2}] \); and \( S_C \) is the correction coefficient of water absorption with the changing of time; the value in early water absorption is 1; \( \Delta W \) is the water invasion amount per unit area on the contact surface of concrete and water \( [\text{kg/m}^2] \); \( t \) is time; and \( h \) includes 0.25h, 0.5h, 0.75h, 1h, 1.5h, 2h, 3h, 3.5h, 4h, 6h, 8h, 12h, 24h, 32h, 48h, 72h, 96h and 120h. Furthermore, \( A = C \cdot S_C \) is the capillary absorption coefficient; \( A \) can reflect the water absorption property of concrete, by which the durability of concrete can be assessed. In addition to the weighing and measurement of mass changes during the water invasive process for the previous frozen specimens, the water absorbing capacity change of the sample with time was also obtained (Fig. 3). The water absorbing capacity change of the sample which experienced 200 cycles of freezing and thawing was also determined, and the results are shown in Fig. 4.
As illustrated in Fig. 3, the capillary water absorption in the LCC group was the largest, followed by LCA, and the water absorption quantity in the LCB group was the smallest. Compared with that of the LCA without air entraining agent, the capillary water absorption in the LCB group decreased by 5.5–13.7% from the initial stage of water invasion into the concrete, while the capillary water absorption in the LCC group increased by 8.0–24.6%. The capillary water absorption coefficient can be demonstrated by using the traditional linear model; the capillary water absorption coefficient decreased by 14.1% in the LCB group, and that in the LCC group increased by 11.1%. Therefore, it can be concluded through the capillary absorption coefficient that the freezing resistance in the LCB group was better, and that the frost resistance of the LCC group was the worst. Moreover, it can be seen from the capillary water absorption that the adding of 0.01% air entraining agent in the LCB group introduced a large number of tiny air bubbles into the interior of the concrete. The bubbles are uniform, dispersed and independent in the concrete, thus impeding the transmission path of moisture in the cement matrix to a certain extent, along with a corresponding delay in the water penetration quantity. With the increase of time, the water absorption curve becomes more flat, which is mainly related to the pore size distribution and the gravity of the concrete material itself. Capillary firstly attained saturated water absorption, after which the absorption of the pore water of the pore wall of both small and large bubbles was relatively slow.

It can be clearly seen from Fig. 4 that the capillary water absorption of light weight aggregate concrete displayed an increasing trend compared with that of non-freezing and thawing for the samples with 200 times of saline of freezing and thawing. The increase of the LCB group was the smallest, and that in the LCC group was the greatest. The capillary absorption coefficient in the LCB group was the smallest, and its frost resistance was the best. The introduction of the proper amount of air entraining agent produced air bubbles, which provided pore water “pressure relief space”, thereby reducing pore water flow length and hydrostatic pressure, so that the frost resistance of concrete was greatly improved.\(^{23}\)

### 3.3 Natural pumice concrete porosity

Porosity refers to the specific value between the pore volume and the total volume of the concrete. After applying the NMR technology, the porosity of the samples which are the groups of LCA, LCB, LCC before the freeze-thaw and after 200 freeze-thaw cycles are measured (see Table 2, Table 3 for the results). With the data of porosity and pore distribution provided by the

| The groups | Porosity /% | The bound fluid saturability /% | The free fluid saturability /% | Permeability /mD | The cut-off value of \( T_2 \) |
|------------|-------------|---------------------------------|--------------------------------|-----------------|--------------------------|
| LCA-0      | 4.037       | 46.736                          | 53.264                         | 225.775         | 10                       |
| LCB-0      | 4.412       | 49.462                          | 50.538                         | 199.404         | 10                       |
| LCC-0      | 4.832       | 52.517                          | 47.843                         | 485.772         | 10                       |

| The groups | Porosity /% | The bound fluid saturability /% | The free fluid saturability /% | Permeability /mD | The cut-off value of \( T_2 \) |
|------------|-------------|---------------------------------|--------------------------------|-----------------|--------------------------|
| LCA-200    | 4.464       | 39.811                          | 60.189                         | 743.161         | 10                       |
| LCB-200    | 4.692       | 45.464                          | 54.537                         | 697.373         | 10                       |
| LCC-200    | 5.435       | 17.723                          | 82.277                         | 1880.683        | 10                       |
NMR, the permeability and movable fluid content can be calculated. The cut-off value of $T_2$ is related to the pore size and is the boundary value between the bound fluid and free fluid. In order to better compare the pores of natural pumice light-weight aggregate concrete with different air-entraining agent, it is decided that $T_2 = 10$, according to the empirical value. The bound fluid corresponding to values smaller than this value exists in the small pores; the free fluid corresponding to values of 10–500 exists in the medium-sized pores; and the free fluid corresponding to values larger than 500 exists in the large pores.

As illustrated in Table 2, the porosity of the natural pumice concrete increased with the increase of air-entraining before freezing and thawing, and the change rates in the LCB group and LCC group were 9.3 and 19.7% compared with that of the LCA group. It is demonstrated in Table 3 that the change rates of the pores in the LCB group and LCC group were 5.1 and 21.8% after 200 cycles of freezing and thawing compared with the LCA group, thus it may be concluded that the incorporation of an air-entraining agent could not prevent the reduction of porosity. Furthermore, it may also be concluded, through comparison between Tables 2 and 3, that the respective change rates of porosity in the LCA group, LCB group and LCC group before and after freezing and thawing were 10.6, 6.34 and 12.5%, thus indicating that the damage rate of the pores in the LCB group was the smallest.

As demonstrated in Table 2, the free fluid saturations in the LCB group and LCC group were decreased to some extent before freezing and thawing compared with that of the LCA group, and the decrease trend of the pores in the LCB group and LCC group were 5.1 and 21.8% after 200 cycles of freezing and thawing compared with the LCA group. At the same time, 11.7% of the permeability in the LCB group was decreased, while 115.1% of the permeability in the LCC group was increased. Combined with the results after freezing and thawing, shown in Table 3, the free fluid saturation and permeability decreased and the bound fluid saturation increased in the LCB group compared with those of the LCA group. The reason for this may be that the air-entraining agent created bubbles, and at the same time a portion of the free water was released, so that the extent of hydration was higher in the samples with a greater amount of air-entraining agent addition to the concrete with the same hydration period. With the increased degree of hydration and age, the volume of the large pores decreased and those of the medium- and small-sized pores increased, thereby increasing the distribution of the micro-pores. After the addition of the excess air-entraining agent, the free fluid saturation and permeability in the LCC group increased suddenly, the reasons for which may be that the increased and evenly distributed bubbles were connected, and that the number of large pores increased.

As demonstrated in Figs. 5 and 6, the increased extent of porosity and permeability of the air entraining the natural pumice concrete was different before the freeze-thaw and after 200 cycles of freezing and thawing, the permeability in the LCB group was the lowest, and porosity in the LCA group was at its minimum. This is due to the fact that concrete permeability is controlled not only by porosity, but also by pore size distribution and connectivity, which are involved in the addition of the air-entraining agent.\(^{3,39}\)

### 3.4 Distribution of $T_2$ spectrum of NMR

According to the NMR principle,\(^{33,38}\) distribution of $T_2$ spectrum of NMR is relative to the pore size, this process may be expressed simplify as follows:

$$\frac{1}{T_2} = \rho \left(\frac{S}{V}\right)_{\text{pore}}$$

where $\rho$ is the lateral surface relaxation strength of porous medium (\(\mu m/\text{ms}\)); $S/v$ is the specific surface of the pore (\(cm^2/cm^3\)).

The smaller the $T_2$ is, the smaller the pore is; Otherwise, the larger the pore is, the larger the $T_2$ is. Therefore, the distribution of the $T_2$ spectrum can reflect the distribution of the pores. The position of the peak is related to the pore size and the area of the peak is related to the number of pores with the corresponding pore size. Figures 7 and 8 show the distribution of the $T_2$ spectrum of air-entrained natural pumice concrete before freeze-thaw and after 200 numbers of freeze-thaw cycles respectively.

As demonstrated in Fig. 7, the $T_2$ spectrum in the LCA group before freezing and thawing mainly exhibited a 4-peak chart. After the addition of air-entraining agents, the LCB group and LCC group showed a 3-peak chart, the reason for which was that the range of the first peak did not change fundamentally, and the introduction of a large number of bubbles incurred, so that the second peak value and third peak value in the LCA group were shortened to a single peak value. Compared with the distribution pattern of the $T_2$ spectrum in the LCB group, both the first peak value and third peak values in the LCC group were larger, and the second peak value underwent a right shift, namely shifting to the direction of the $T_2$ spectrum of the large pore direction, thus indicating that the incorporation of excess air entraining agents
resulted in the formation of connected from the micro-pores, thereby leading to large total pore spaces in the LCC group.

Figure 8 shows that the $T_2$ spectrum distribution of the air-entraining natural pumice concrete mainly demonstrated four peaks after 200 freeze-thaw cycles. Relative to the LCA-200 group, the value of the first peak in the LCB group was the maximum, and the values of the second and third peaks decreased, indicating that the addition of the amount of the air-entraining agent increased the number of small pores and decreased the number of large pores in the concrete after freezing and thawing, which suggests that an appropriate amount of air-entraining agent is helpful for the frost resistance of pumice concrete. The value of the first peak in the LCC group decreased, while the values of the other three peaks all increased, indicating that the incorporation of excessive air-entraining agent made it easier for the connection and formation of large pores from small pores. After freezing and thawing, the solution transformed into ice, thus allowing the volume expansion of concrete solution to ice. Cracks were produced in the internal concrete after repeated frost boiling, which caused the tensile force produced in the process of expansion of the ice body to exceed the tensile strength of the concrete. Cracks were more easily extended, and the number of aperture gaps was increased, thus exacerbating the freeze-thaw damage. Therefore, nuclear magnetic resonance signal intensity increases, LCC group aggravate natural pumice concrete freeze-thaw damage.

### 3.5 Analysis of $T_2$ spectrum area

The nuclear magnetic resonance $T_2$ spectrum area is directly proportional to the total amount of fluid contained in concrete. The total $T_2$ spectrum area is generally equal to or less than the active porosity of concrete, which can intuitively reflect the changes of the internal structure of pores. The change characteristics of the $T_2$ spectrum area of the air-entraining natural pumice concrete and each peak area ratio before freeze-thaw and after 200 freeze-thaw cycles are shown in Tables 4 and 5.

Tables 4 and 5 demonstrates the nuclear magnetic resonance spectrum area of the air-entraining natural pumice concrete. It can be seen from before freeze-thaw and after 200 cycles of freezing and thawing that the $T_2$ spectrum area increased with the increase of air entraining agent quantity. The reasons for this are that the addition of the air-entraining agent may introduce a large amount of bubbles, thus causing freeze-thaw prior to LCB group and LCC group of the first, second peak area increased. And that pore distribution is more obvious after freezing and thawing. In the LCB group to which an appropriate amount of air entraining agent was added, the value of the first peak area increased, but the values of the second and third peak areas decreased, indirectly suggesting that the addition of large quantities of air-entraining agent induced uniformly distributed, stable and closed tiny bubbles, and also eased the frost resistance. After adding the excess air-entraining agent, the first peak area in the LCC group decreased by 50%, while the remaining three peak areas...
increased, suggesting that the excessive air-entraining agent contributed to the coalescence of a large amount of bubbles being introduced, thus resulting in increased porosity after freezing and thawing, as well as an accelerated freeze-thaw damage speed.

### 3.6 Analysis of NMRI

Figure 9 shows the results of the NMRI of the air-entrained natural pumice concrete before freeze-thaw and after 200 numbers of freeze-thaw cycles. However, firstly, due to the fact that the concrete material contains a paramagnet substance which may interfere with the signals of the NMR, level-selective imaging is impossible; secondly, because the concrete pores is not absolutely ideal sphere, the imaging region can be obtained more comprehensive from two surface imaging, thus overall imaging of the concrete is performed. The two-dimensional imaging of the cross-section in the two axial directions along the concrete is achieved.

**Table 4.** The NMR spectrum area of the air-entrained natural pumice concrete before freeze-thaw cycles

| The groups | $T_2$ spectrum area | The first peaks occupies of the total area/% | The second peaks occupies of the total area/% | The third peaks occupies of the total area/% | The four peaks occupies of the total area/% |
|------------|---------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------|
| LCA-0      | 13956               | 37.28                                       | 18.54                                       | 38.63                                       | 5.55                                       |
| LCB-0      | 14023               | 45.48                                       | 40.66                                       | 13.86                                       | —                                         |
| LCC-0      | 14218               | 51.74                                       | 30.64                                       | 17.62                                       | —                                         |

**Table 5.** The NMR spectrum area of the air-entrained natural pumice concrete after 200 numbers of freeze-thaw cycles

| The groups | $T_2$ spectrum area | The first peaks occupies of the total area/% | The second peaks occupies of the total area/% | The third peaks occupies of the total area/% | The four peaks occupies of the total area/% |
|------------|---------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|--------------------------------------------|
| LCA        | 14329               | 28.11                                       | 26.52                                       | 36.37                                       | 9.00                                       |
| LCB        | 14812               | 35.81                                       | 23.21                                       | 28.96                                       | 12.02                                      |
| LCC        | 14902               | 13.57                                       | 28.63                                       | 44.25                                       | 13.55                                      |

(a) The front images of LCA-0  
(b) The front images of LCA-200  
(c) The front images of LCB-0  
(d) The front images of LCB-200  
(e) The front images of LCC-0  
(f) The front images of LCC-200

Fig. 9. The result of nuclear magnetic resonance image.
In the image square light area is the sample image, the white spots are the semaphores of the water molecules. The more white spots in the image there are, the more moisture in the corresponding air-entrained natural pumice concrete material there is; in addition, the more pores in the area there are, the larger the pore size is. Otherwise, the pore size is small. The surrounding black area is the background color, so as to form a sharp contrast in favor of viewing. Using this feature, NMRI can directly see the pore size distribution inside the concrete. Figures 9(a), 9(c) show the pore size nuclear magnetic resonance (NMR) imaging before freezing and thawing, and Figs. 9(b), 9(d) and 9(f) show the imaging after 200 cycles of freezing and thawing.

Figures 9(a), 9(c) and 9(e) show the images in the LCA group, LCB group and LCC group before freezing and thawing, respectively. The bright spot zone of the pumice concrete without freezing and thawing was small, and that in the LCC group was the largest, followed by those of the LCB group and LCA group, which is consistent with the results of the capillary water absorption before freezing and thawing.

Figure 9(b) shows the natural pumice concrete without air-entraining agent (LCA group) after 200 freeze-thaw cycles. The image is dark, indicating that there is less water content, porosity is smaller. The area with bright spots on both sides is small, while a small number of bright spots are large. This indicates that several large pores exist in a small area, but small pores occupy most parts. The reason for this is that natural pumice concrete is a porous medium itself.

Figure 9(d) shows the LCB group of the image after 200 freeze-thaw cycles, where the brightness increases slightly, highlight the regional distribution more uniform. From the front and side images it can be mainly with small bright spot, this shows that the NMR signal increases. The freeze-thaw cycle of frost resistance was improved by a moderate quantity of air entraining agent. Larger than air entraining agent of 0.02% binding material quality caused large pores, which accelerated freeze-thaw damage.

5. NMRI results showed air-entraining agent of natural pumice concrete of internal damage after 200 cycles of freezing and thawing. An appropriate amount of air-entraining agent can alleviate the freeze-thaw damage of concrete, and it is mainly oriented to the formation of small pores. But too much of air-entraining agent makes the NMR signal increased dramatically and highlight areas increase, made large pore and cracks accelerated expansion, it has played a negative role to the concrete freezing and thawing.

4. Conclusions

1. Through ultrasonic testing after the air-entrained natural pumice concrete after the freeze-thaw cycles, wave dropping rate $\eta$ and damage degree of $D$ were both decreased, indicating that addition of a certain amount air entraining agent improves frost resistance of natural pumice concrete

2. It can be seen from the capillary water absorption capacity and capillary absorption coefficient that the incorporation of the proper amount of agents can reduce the capillary water absorption capacity and coefficient and enhance the frost resistance. In addition, excess air entraining agent can increase the capillary water absorption and coefficient, thereby reducing the frost resistance.

3. Before freeze-thaw and after 200 cycles of freezing and thawing, the porosity of natural pumice concrete is advanced with the growth of air-entraining agent, indicating that addition of air entraining agent cannot stop decreasing of porosity. And the growing rate of porosity and permeability are not same proportion.

4. The $T_2$ spectrum distribution of air entraining natural pumice concrete mainly demonstrated four peaks after freeze-thaw cycles. With the increase of air-entraining agent quality, $T_2$ spectrum area increases. The freeze-thaw cycle of frost resistance was improved by a moderate quantity of air entraining agent. Larger than air entraining agent of 0.02% binding material quality caused large pores, which accelerated freeze-thaw damage.

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