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Non-destructive evaluation of concrete mixtures for direct LNG containment

Reginald B. Kogbara [a,*], Srinath R. Iyengar [a], Zachary C. Grasley [b], Eyad A. Masad [a,b], Dan G. Zollinger [b]

[a] Mechanical Engineering Program, Texas A&M University at Qatar, P.O. Box 23874, Education City, Doha, Qatar
[b] Zachry Department of Civil Engineering, Texas A&M University, College Station, TX 77843, USA

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ABSTRACT

The suitability of six concrete mixtures for use in direct containment of liquefied natural gas (LNG) was assessed using nuclear magnetic resonance (NMR), X-ray computed tomography (XRCT) and acoustic emission (AE). The mixtures were prepared with river sand as fine aggregate using different coarse aggregates. The mixtures were cooled from ambient to cryogenic temperatures at a cooling rate of 3 °C/min. Proton NMR measurements and XRCT imaging were carried out before and after cooling to monitor changes in porosity and pore size distribution, and internal microstructure, respectively. AE sensors monitored damage evolution during cooling and warming. NMR results indicated porosity increases of 0%, 0.3%, 1.4% and 3.3% in the non-air-entrained trap rock aggregate, limestone aggregate, sandstone aggregate and lightweight aggregate concrete mixtures, respectively. The air-entrained trap rock and limestone mixtures showed porosity increases of 0% and 1.9%, respectively. There was a strong positive correlation between AE cumulative energy and NMR porosity change. XRCT imaging generally showed no frost-induced cracking in the concrete mixtures. Thus, pore structure changes and apparent damage were in the form of microcracks less than the XRCT resolution (22 microns). The results highlight the utility of trap rock aggregate in production of durable concrete for direct LNG containment.

1. Introduction

Traditional liquefied natural gas (LNG) tank construction utilizes 9% Ni steel walls and floor for the inner containment tank as it has greater ductility at cryogenic temperatures (⩽−165 °C) compared to normal carbon steel. Nevertheless, this construction method is becoming increasingly expensive. However, available literature on concrete properties at cryogenic temperatures shows that most properties of concrete generally improve above their ambient temperature values at cryogenic temperatures [1]. Utilization of concrete for direct LNG containment would lead to huge cost savings. Moreover, the development of the American Concrete Institute (ACI 376-11) standard on concrete structures for containment of refrigerated liquefied gases [2] may increase the impetus for tank designs utilizing concrete for primary LNG containment. Therefore, a thorough understanding of the properties of concrete related to its ability to maintain liquid tightness and structural integrity required for LNG tanks is necessary.

Concrete utilized for direct LNG containment must be dense, durable, nearly impermeable, and resistant to chemicals, with limited deflections and cracking. Its serviceability requirements must include gas-tightness to prevent leakage of LNG vapor and loss of product, and to promote durability [3]. It is evident from the foregoing that the permeability of concrete is of utmost importance in the design of concrete for use in direct LNG containment as it controls the rate by which LNG is lost from the primary container [1]. The permeability of concrete depends on the porosity, pore size distribution, pore roughness, constrictions of the pore space, and the tortuosity and connectivity of the internal pore channels [4,5]. Moreover, the pore size distribution has a significant influence on the formation of ice and its expansion ability when concrete is cooled to cryogenic temperatures. This in turn affects the development of internal stresses in concrete due to freezing water [1]. One promising technique for quick and reliable determination of pore size distribution and porosity in porous materials like concrete is nuclear magnetic resonance (NMR). Proton NMR (also ^{1}H NMR) is a fast, potentially non-invasive technique for the characterization of the internal structure of a porous material based on its mobile water molecule content [6]. Similarly, X-ray computed tomography (XRCT) allows for non-destructive 3D visualization of the internal microstructure of materials. XRCT is capable of viewing deeply buried microstructures that 2D surface imaging techniques – e.g. scanning electron microscopy (SEM) – may not observe. Thus, XRCT is a

* Corresponding author.
E-mail address: regkogbara@cantab.net (R.B. Kogbara).

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valuable tool used for visualization of internal microcracks and cracks in materials [7]. Furthermore, upon cracking, some of the strain energy of thermally stressed concrete is converted to wave energy, which flows through the material and is eventually released into the air making a sound [8]. This sound can be recorded by appropriately placed acoustic emission (AE) sensors. AE is a well-established, non-destructive technique for damage detection in concrete [9]. It has been successfully deployed for studying frost-induced cracking in rock and concrete [8,10].

A ^{1}H NMR experiment provides information on the amount of hydrogen in the pore spaces of concrete and is thus a measure of porosity as the porosity can be obtained by comparison of the ^{1}H NMR signal of concrete with that of an equivalent volume of water. Moreover, NMR relaxation times give information on the pore size distribution of porous media as the decay of the proton (from water molecules) magnetization depends on the length scales of the pores and on the pore-fluid-grain interactions [11]. For instance, it is well known that the transverse relaxation rate ($1/T_2$) is directly proportional to the surface to volume ratio (S/V) of the pore system. Thus, if the constant of proportionality, ρ_2 – the T_2 surface relaxivity (relaxing strength of the pore surfaces) – is known alongside the T_2 relaxation time, the pore size distribution of a material can be determined. Nevertheless, the presence of paramagnetic ions in concrete components (Portland cement and aggregates) such as Fe^{3+} presents difficulties. Paramagnetic impurities may shorten relaxation times or prevent observation of some of the ^{1}H signal, as well as increase the surface relaxivity of materials [12]. Despite the challenge presented by impurities, NMR relaxometry has been deployed for different applications in cement-based materials. These include hydration kinetics of cement, compressive strength development, the physicochemical characteristics of water molecules according to their confinement level, study of the formation of the microstructure of hydration products, alongside porosity, pore size distribution and pore connectivity within the cement matrix [13–17]. Similarly, XRCT has been successfully deployed for related studies on frozen concrete mortars and cement paste. These include examination of cracking in non-air entrained mortars subjected to 35 freeze–thaw cycles between 25 °C and −25 °C. The study showed that cracks attempt to follow the weaker interfacial transition zone between sand and cement paste in frost-damaged mortars [18]. XRCT has also been deployed for characterization of the formation and distribution of ice crystals inside and around air voids in air-entrained hydrated cement paste. These investigations revolved around development of air-entrainment admixtures for prevention of frost damage in concrete [19].

Furthermore, as non-destructive techniques, NMR and XRCT have the advantage of investigating the internal structure of the same specimen before and after environmental changes or mechanical stress. In spite of their enormous advantages, there is a paucity of literature on the aforementioned non-destructive techniques in the study of the microstructure of concrete subjected to cryogenic temperatures, or for evaluating concrete suitability for LNG storage. The majority of previous investigations on concrete behavior for cryogenic applications have focused on mechanical and thermal properties such as compressive and tensile strengths, Young's modulus, creep, coefficient of thermal expansion (CTE) and thermal conductivity [20]. However, Bamforth [21] measured water and gas permeability at cryogenic temperatures using permeability cells, as well as porosity and pore size distribution of frozen concrete using mercury intrusion porosimetry. A similar study in this direction considered the effects of cryogenic temperatures on hydrating white cement pastes using NMR [22]. Albeit, this study mainly investigated pore structure evolution (pore size distribution) as a function of hydration times with a view to understanding cement hydration in the lunar environment.

The present work sought to evaluate the potential of different concrete mixtures for LNG storage by complementing other assessment techniques with XRCT imaging, NMR and AE measurements of the mixtures. It builds on the findings of a previous related study [8], which showed the utility of AE for studying the potential of frost-induced microcracking in concrete during cryogenic cooling only, in relation to water and chloride permeability testing and XRCT imaging on replicate specimens. However, the present work studied the same concrete specimens before and after cryogenic cooling using NMR and XRCT, while AE measurements were made during the cooling process as well as during warming to ambient temperature. The aim of the study was to relate observed changes in porosity, pore size distribution and internal microstructure to cracking determined from cumulative energy emissions from the materials during the cooling and warming processes. It is thought that even though paramagnetic ions affect NMR relaxation times, changes in relaxation time distributions after cryogenic cooling can be attributed to pore size distribution changes since cooling is unlikely to change the paramagnetic content of a given concrete mixture. It was the object of the study to investigate the potential of the different aggregates to produce frost-damage-resistant concrete.

2. Materials and methods

2.1. Production of concrete specimens

Concrete specimens were produced using river sand as fine aggregate, and coarse aggregates with different CTE values, namely, limestone, sandstone, trap rock and TXI Streetman expanded shale lightweight aggregate. All aggregates were obtained from quarries in Texas, USA. Key physical properties and mineralogical composition of the aggregates have been detailed elsewhere [8]. Type I portland cement was used for casting of all concrete specimens. Table 1 shows the composition, mixture proportions and selected properties of the six concrete mixtures studied. Four of the six concrete mixtures were without air-entrainment, while two mixtures were air-entrained with 6% air content. Cubes (150 mm) of the non-air-entrained mixtures produced with ⩽12.5 mm aggregates were initially tested after 28 and 56 days of water curing. The findings of the AE measurements, XRCT imaging and water and chloride permeability carried out have been reported elsewhere [8]. Thus, the air-entrained mixtures were produced with only limestone and trap rock aggregates, using Master Air AE 200 air-entraining admixture (*BASF*, Ohio, USA), based on the findings of the initial experiments. The grain size distributions of the aggregates used here are shown in Fig. 1. The non-air-entrained mixtures had a water/cement (w/c) mass ratio of 0.42, while a w/c ratio of 0.35 was used for the air-entrained mixtures.

The exact dimensions of the concrete specimens used were 75 mm diameter by 150 mm long for molded cylinders, and 23 mm diameter by 50 mm long for cores drilled from replicate 150 mm cubes for each mixture. The non-air-entrained and air-entrained specimens were cured under water for 365 and 28 days, respectively, before testing. The non-air-entrained specimens were all casted at the same time while the air-entrained specimens were casted 11 months later. Hence, as the difference in curing age might have some influence on experimental results, the non-air-entrained mixtures should only be compared qualitatively with the air-entrained mixtures. The 28-day compressive strengths (tested on cylinders according to ASTM C39 [23] as recommended by ACI code 376 [2]) of the non-air-entrained samples were >34.5 MPa, while those of the air entrained samples were >27.6 MPa (Table 1). The strength values correspond to the