

ALKALI-SILICA REACTION RESISTANT CONCRETE
USING PUMICE BLENDED CEMENT

by

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A dissertation submitted to the faculty of
The University of Utah
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Civil and Environmental Engineering

The University of Utah

August 2014

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ABSTRACT

Durability of structures is a major challenge for the building industry. One of the many types of concrete deterioration that can affect durability is alkali-silica reaction (ASR). ASR has been found in most types of concrete structures, including dams, bridges, pavements, and other structures that are 20 to 50 years old. The degradation mechanism of ASR produces a gel that significantly expands in the presence of water as supplied from the surrounding environment. This expansion gel product can create high stresses and cracking of the concrete, which can lead to other forms of degradation and expensive structural replacement costs. The four essential factors that produce an expansive ASR gel in concrete are the presence of alkalis, siliceous aggregate, moisture, and free calcium hydroxide (CH). If concrete is starved of any one of these essential components, the expansion can be prevented. Reducing CH through the use of a supplementary cementitious material (SCM) such as natural pozzolan pumice is the focus of this research.

By using a pozzolan, the amount of CH is reduced with time based on the effectiveness of the pozzolan. Many pozzolans exist, but one such naturally occurring pozzolanic material is pumice. This research focuses on determining the effect of a finely ground pumice as a SCM in terms of its resistance to ASR expansion, as well as improving resistance to other potential concrete durability mechanisms. In spite of having high alkali contents in the pumice, mixtures containing the SCM pumice more effectively

mitigated the ASR expansion reaction than other degradation mechanisms. Depending on the reactivity of the aggregates and fineness of the pumice, 10-15% replacement of cement with the pumice was found to reduce the ASR expansion to the acceptable limits.

The amount of CH remaining in the concrete was compared to the ASR expansion in order to improve understanding of the role of CH in the ASR reaction. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis were used to quantify the relative amount of CH across time. From analyzing mortar specimens in an aggressive ASR environment for 14 days, specimens with 15% of cement replaced by a finely ground pumice showed up to 40% lower CH content and 95% reduction in ASR expansion compared to 100% cement specimens. Instead of using low alkali cement, this type of pumice can be utilized in longer durable service-life structures despite whether highly reactive siliceous aggregates are used in the concrete mixtures.

I dedicate this dissertation to my family, especially...
to my supporting hubby Ram, lovely daughter Harshini,
and interminably encouraging parents.

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ACKNOWLEDGMENTS

I would like to thank Dr. Paul Tikalsky and Dr. Amanda Bordelon for their guidance and support throughout my research. In addition to research guidance, from Dr. Tikalsky, I learned the skills to execute work independently. I thank Dr. Bordelon for her valuable time, quick turnarounds, and high availability. Also, I thank Dr. Larry Reaveley for being a mentor and all the support he has given. I also thank Dr. Terry Ring for his time and effort in helping me understand the chemical engineering aspect of the research. I thank Dr. Pedro Romero for his contribution as committee member.

I thank Hess Pumice Products for funding of this research and for the material supply. Also, I thank CMT Engineering Laboratories for their time, providing space in their lab, and help in conducting experiments.

A special thanks to Shannon Hanson for being a friend in my life. She guided and taught the basics every student should know in a concrete lab. Also, she helped in making specimens for the research. Further thanks go to Wade Stinson and Mark Bryant in civil engineering department, as well as Dana Overacker in chemical engineering department, for their assistance in conducting experiments.

Most of all, I give a special thanks to my husband Ramiah Natarajan for his incredible support in every aspect. Without my family support, I wouldn't have completed the research. I also appreciate the support I received from my parents and in-

laws for staying with us, traveling all the way from India, to support my studies and help take care of my family.

CHAPTER 1

INTRODUCTION

1.1 Introduction to Alkali-Silica Reaction

Structures with poor durability can require substantial costs to repair, rehabilitate, or replace. One of the many types of concrete deterioration that can affect durability is alkali-silica reaction (ASR). ASR is the reaction between alkalis primarily from cement and reactive siliceous minerals in the aggregate. The product of the reaction is called ASR gel, which has the ability to imbibe water. When the gel intakes water, eventually it swells and exerts pressure on the cement paste and aggregate. The swelling pressures can lead to cracking of concrete. ASR is the most common alkali aggregate reaction in concrete, compared to alkali carbonate reaction found with dolomitic aggregates.

Since the late 1930s (Stanton, 1940; PCA, 1940) ASR has been recognized as a potential distress in concrete structures. ASR occurrence has been identified in more than 33 states in the United States (Mielenz, 1994). A petrographic analysis was initially used to identify the problematic aggregates by their mineral content. It was found that alkalis in the cement were the key contributor to produce ASR expansion (Stanton, 1940). Since then, the Na_2O alkali content in manufactured hydraulic cement has been limited to less than 0.6 % (ASTM C150) as a means to prevent ASR. Despite this limitation, ASR continues to occur even now because of other contributing factors like siliceous aggregate

and free calcium hydroxide.

1.2. Mechanisms for ASR

The ASR chemical reaction mechanism has been analyzed since the 1940s, and the following three conditions have been proposed by past researchers to result in the ASR expansion.

High Alkali: The pore solution in concrete is concentrated by dissolved alkali hydroxides, such as NaOH and KOH. These hydroxides contribute to a high pH (typically 13.2 to 14) environment in the pore solution.

High pH + Reactive Silica: At a high pH, the OH⁻ ions in the pore solution react with the reactive silica components on the surface of certain amorphous siliceous aggregates. From this reaction, the silica is dissolved into the pore space. The dissolution of reactive silica can be represented by the following equations (Dent et al., 1981).

- $R_3\text{-Si-OH} + \text{OH}^- + \text{Na}^+ \rightarrow R_3\text{-Si-O-Na} + \text{H}_2\text{O}$
- $R_3\text{-Si-O-Si-R}_3 + 2\text{OH}^- + 2\text{Na}^+ \rightarrow 2(R_3\text{-Si-O-Na}) + \text{H}_2\text{O}$

A weak poorly crystalline hydrous silanol group Si-OH on the surface of the aggregate can be readily dissolved by the hydroxide ion as shown in the first equation. Even stronger siloxane Si-O-Si links near the surface of the aggregate can also be dissolved as shown in the second equation.

Alkali-Silica Reaction: The dissolved silica precipitates with any free Ca²⁺ ions also found in the pore space to produce an alkali-silica gel. The specific gel structure is not known but presumed amorphous, different from the C-S-H gel also formed during the cement hydration reaction.

Although the above combined conditions have been accepted by many researchers, other mechanisms have been proposed for the cause of cracking seen in the concrete.

Osmotic Pressure Theory: The alkali-silica gel absorbs water through osmosis from the surrounding environment and expands. The volumetric expansion can lead to pressure on the existing hydrated cement and aggregate particles. If this pressure exceeds the strength of the surrounding paste or aggregates, then cracking will occur (Hansen, 1944).

ASR Widens Existing Cracks: McGowan and Vivian in 1952 and Diamond in 1975 contradicted the osmotic pressure theory proposed by Hansen in 1944 on the basis that the cracking of a semipermeable membrane would relieve the pressure and prevent additional cracking. Under such conditions, osmotic pressures cannot exist. Instead, reaction products will absorb water and swell, and lead to further mortar cracks. They reported that the expansion due to ASR was primarily because of widening of cracks. They proposed a correlation between expansion of the specimen with the mean number of cracks and width of cracks. Ming-shu in 1981 supported the McGowan and Vivian theory while also determining additional factors that created the expansion. These additional factors were tensile strength of cement paste, number of reactive particles, amount of alkalis per unit area of reactive particle, and the expansive force induced by each particle due to ASR. Nielsen in 1984 further suggested that ASR is incapable of initiating cracks, but rather can lead to widening of cracks in the concrete when reaction takes place in an already existing crack.

Hydraulic Pressure from Fluid Alkali and Silica Components: Power and Steinour in 1955 suggested that if enough water is absorbed, the alkali-silica product is transformed

from a gel to fluid, then the expansion is caused by hydraulic pressure as Hansen suggested. If the gel remains solid, Power and Steinour proposed that the expansion occurs due to swelling. In this way, they accept both the theory that no semipermeable membrane is required to produce expansion and also cement paste in concrete can act as an osmotic pressure membrane. These theories have not been confirmed by experimental results. Struble and Diamond in 1981 studied ASR using a synthetic silica gel, prepared as a model gel simulated to be like that expected for concrete with ASR. An unexpected behavior was noted when the gel exhibited little expansion in an unloaded state, yet exerted great expansion in a loaded state and exposed to water. From the above behavior, they suggested that localized regions in the concrete can be affected by alkali-silica reaction expansion. Some other gels which expanded greatly became liquefied upon loading. This liquefying behavior explains that a fluid reaction product can form under applied pressure of the concrete.

1.3 Supplementary Cementitious Materials (SCM) for ASR Mitigation

More than 2000 years ago, Romans used the natural pozzolans in their structures. Some of their structures without reinforcement are still durable, while some of the mid-20th century constructed concrete structures with reinforcement are already starting to show degradation. The success of pozzolans in producing long-lasting structures should be considered, emphasized, and incorporated in future constructed concrete structures.

In the mid-1930s, fly ash was used in the market for concrete applications. The first large-scale concrete project that specified use of fly ash was at Hungry Horse Dam in Montana in 1948 (FHWA). Today, the most common mitigating techniques to reduce

ASR expansion are a combination of low alkali cement as according to ASTM C150 standards, and use of either class F fly ash or ground-granulated blast furnace slag pozzolans as a percentage replacement of the total cementitious content. Compared to class C fly ash, a class F fly ash has been shown to mitigate ASR more effectively due to its lower calcium content (Dunstan, 1982). Class F fly ash and slag blended-cements can be used to effectively mitigate ASR at cement replacement rates of 15-30% and 25-70%, respectively, by weight of total cementitious content (Bartojay, 2013; Thomas and Innis, 1997). Other pozzolans such as silica fume and metakaolin have also been effectively utilized to mitigate ASR by forming a denser and stronger concrete or reducing the pH of the pore solution after entrapping free alkalis (Hasparyk et al., 2000; Duchesne and Berube, 1994; Ramlochan et al., 2000). Additionally, combinations of SCMs can be used in ternary cement blends to also be very effective in mitigating ASR expansion (Sheata and Thomas, 2002; Lane and Ozyildirim, 1999). In general, as the amount of supplementary cementitious material (SCM) content increases, the ASR expansion decreases (Carrasquillo and Farbiaz, 1989). Some limitations on the effectiveness to mitigate ASR have been noticed for these pozzolans (Malvar et al., 2002). Silica fume can be prone to clumping and, in which case, can act more like a reactive fine aggregate and therefore initiate ASR formation. Hence, for ASR reduction, it is necessary to have either finely-ground unglomerated powder forms of these SCMs, or to use extended mixing to facilitate dispersion is compulsory (Glauz et al., 1996).

1.4 Influence of Calcium Hydroxide on ASR

Past experimental studies reported that adequate amounts of calcium in the form of Ca(OH)_2 is necessary for significant expansion. In the presence of sufficient amounts of silica and alkalis other than calcium, silica dissolves and remains in the solution without causing any distress to concrete. Wang and Gillott in 1991 concluded that the calcium acts as a buffer to maintain the high OH^- concentration in pore solution and thus to maintain a high pH environment. The presence of this free calcium promotes “alkali recycling”, i.e., Ca^{2+} may be exchanged for other alkali ions (commonly Na^+ or K^+) within the ASR gel formation. Due to this exchange mechanism, the free alkali ions can react further with silica in aggregates and promote further ASR gel formation (Thomas, 2001; Wang and Gillott, 1991).

Chatterji in 1979 stated that presence of free Ca(OH)_2 is the essential condition to have expansive ASR. Later, Struble in 1987 studied a system similar to concrete undergoing alkali-silica reaction but lacking any calcium source. Without calcium ions, reactive silica dissolves in alkali hydroxide, but remains in solution. Additional research has confirmed that the alkali-silica gel formation occurs only in presence of calcium hydroxide (Kilgour, 1988; Thomas, 2001; Wang and Gillott, 1991; Diamond, 1989; Thomas, 1998). Larbi in 1992 suggested that complete removal of Ca(OH)_2 is not necessary, but limiting the calcium hydroxide content such as with fly ash helps in arresting further ASR formation. Bhattu in 1985 suggested that if the Ca to Si mole ratio in the calcium-silica-hydrate (C-S-H) phase was maintained below 1.5, then there is negligible alkali-silica reaction. By forming lower Ca to Si ratios in the hydrated paste, alkalis can be retained in the calcium-silica-hydrate phase, thus reducing the amount of

alkali available for future reaction. Pozzolans react with the calcium hydroxide and water present in hardened concrete to form additional C-S-H gel. Thus, pozzolans can be used to reduce the free CH present in the concrete and mitigate potential ASR (Larbi, 1992; Bhatta, 1985; Chatterji, 1979). Calcium hydroxide can also reduce due to natural leaching, as enhanced through salts such as CaCl_2 (Chatterji, 1986).

1.5 Other ASR Mitigation Techniques

Suggestions for ASR mitigation also involve utilizing cements that are high in dicalcium silicate content are more resistant with reactive aggregate, or using less cement contents in the concrete (Chatterji, 1979). Another mitigation technique is use of lithium compounds, which has been reported first in 1951 after a comprehensive study of over 100 chemical admixtures (McCoy and Caldwell, 1951). Lithium nitrate, compared to other lithium compounds, has been found most effective in mitigating ASR (though all lithium compounds require higher dosage) by not increasing the pore solution pH (Folliard et al., 2003).

1.6 Research Motivation

Pumice is a natural material that has been deposited due to volcanic eruption. Properties of this pumice, as used as a SCM in mortar and in concrete specimens, were initially investigated to determine its feasibility as a pozzolanic and cementitious product. From the preliminary testing found in Chapter 2, pumice exhibited pozzolanic properties in terms of excellent durability characteristics. The pumice was able to mitigate the ASR expansion more effectively, in spite of having high alkali contents in the pumice, than in

mitigating other degradation conditions such as sulfate attack. Then the research shown in Chapter 3 focused on using alternative reactive aggregates and different grades of pumice, to check its effectiveness in mitigating ASR expansion. After optimizing the cement replacement with pumice for specific reactive aggregates and pumice grade, research in Chapter 4 focused on investigating how this particular pumice arrests the ASR expansion so effectively. By better understanding the mechanisms and response of pumice, it may be economically and environmentally more feasible in the future to utilize pumice blended cements for preventing ASR and other concrete durability problems.

Furthermore, a correlation was found to confirm that as the amount of CH is reduced, the ASR expansion of the mortar or concrete was also mitigated.

1.7 Organization of Dissertation

Chapter 1 gives the overall introduction of ASR, mechanism involved, mitigation techniques, and the importance of CH content in ASR. It also includes the motivation and organization of thesis section. Chapter 2 describes the physical and chemical material characterization of pumice and cement, the hydration kinetics, the fresh properties, and the hardened properties of mortar and concrete blended with pumice. Durability characteristics including resistance to ASR expansion, sulfate attack for pumice blended mortar mixtures are also illustrated in Chapter 2. Additional statistical verification of the strength for such pumice and control mixtures is also illustrated in Chapter 3. Due to the unique effectiveness of the pumice blended mortar in resisting ASR expansion, specific alternative reactive aggregates and different grades of pumice used in the mortar and in concrete samples were then tested, with results shown in Chapter 3. Chapter 3 also shows

some more statistical verification of durability performance of pumice and control mixtures. From the literature, the magnitude of calcium hydroxide was hypothesized to be a major contributor for the effectiveness witness for this pumice blended mortar and concrete system. Thus, the amount of calcium hydroxide and the correlated reduction in ASR expansion is monitored and reported in Chapter 4. The final Chapter 5 indicates the key conclusions of this research, along with proposed recommendation and future work ideas related to testing the effectiveness of pozzolanic materials.

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CHAPTER 2

ENHANCED CONCRETE WITH PUMICE BLENDED CEMENTS*

2.1 Abstract

High-grade pumice is a volcanic mineral which exists in select locations of the western United States. Pumice used in this research has the potential to be both pozzolanic and a hydration nucleation substrate to improve the hydration of portland cement. Pumice is a white-colored porous material that can be used in combination with hydraulic cements to improve the durability of concrete and its environmental sustainability. Commercially available pumice from the mountain west was found to meet the standardized tests for chemical and physical characteristics of a pozzolanic material. Three grades of pumice (DS200, DS325, and Ultrafine) varying in particle size were tested in this research. The research included the hydration kinetics of blended cements and the mixture design properties of concrete containing these pumice grades. The durability results of this research showed enhanced resistance against common concrete distress mechanisms of sulfate attack and alkali-silica reaction (ASR). Ultrafine pumice showed the highest improved performance over other grades of pumice because of its greater surface area. The use of 20% pumice as a part of total cementitious material produced required strength gain for most applications, and showed excellent performance

* U. Ramasamy, P. J. Tikalsky, and A.C. Bordelon, "Enhanced Concrete with Pumice Blended Cements," submitted to *American Concrete Institute Materials Journal*, (2014).

in durability characteristics.

2.2 Introduction

Pumice is a natural material of volcanic origin, produced during volcanic eruption followed by the rapid cooling of magma. It is composed mainly of aluminosilicates and has a final formation of either glassy, or vitreous phases with a disordered structure. These disordered aluminosilicates do not remain stable when exposed to a saturated lime environment. This reaction with lime is the basis for the pozzolanic property of volcanic glasses¹. Pumice is a white porous volcanic glass, consisting of interlocking vitreous fibers filled with tiny air bubbles. The abundant small bubbles give pumice a unique porosity that can be useful in certain applications. The mining operations of pumice products often crush and process the pumice into finer particle sizes for use in a wide variety of products and industries.

The pumice used in this research project originates from the largest producer of finely-ground processed pumice, located in Southeastern Idaho near the community of Malad City. In the past, it has been found that concrete containing pozzolanic materials exhibited desirable properties like improved workability, lower temperature rise, and lower cost². Generally, a portion of portland cement is reduced and pozzolans are added to not only reduce cost, but also to improve the technical properties. It has been shown that water adsorbed by porous fine aggregate particles is helpful in maintaining a high relative humidity within the concrete, which creates an environment conducive to cement and pozzolan hydration. Due to the lower heat of hydration and other benefits, pozzolans were used in mass construction applications such as dams and other large structures in the

1920s and 1930s². Many durability problems can be addressed by the addition of suitable pozzolans to portland cement^{3,4}. Pozzolans are able to mitigate alkali-silica reaction through the consumption of hydrated lime, eliminate expansions related to sulfate exposures, and greatly reduce the permeability of concrete, which assists in resisting the ingress of chlorides and other salt species⁵. Because of its ability to resist sulfate attack from sea water, portland-pozzolan cement was used in many bridge constructions⁶. Despite the above benefits, replacement of pumice in portland cement is limited due to a perceived slower rate of strength gain. The blending of portland cement, slags, fly ash, processed pozzolans, and/or natural pozzolans produces ASTM C595⁷ and ASTM C1157⁸ cements for ready-mix and/or precast concrete products. Extensive use of natural pozzolans in multiple projects in the past has been reported in the literature^{2,9,10}.

This research was conducted to determine pozzolanic activity and complimentary cementitious capability of pumice labeled DS200, DS325, and Ultrafine pumice products for use in combination of portland and hydraulic cements. According to ASTM C 618¹¹, pozzolans are a siliceous and aluminous material in finely divided form, which in the presence of moisture, at ordinary temperatures, chemically reacts with calcium hydroxide to form compounds possessing cementitious properties. Complimentary cementitious materials are the materials that provide microsubstrate materials for the more efficient hydration of other cementitious material. Pumice is characterized by understanding its base chemical and physical characteristics, hydration kinetics, and the mixture design properties of concrete with pumice. Five combinations of mixture designs of pumice blended with a Type II/V were examined: a control mixture with 100% cement, three mixtures with 20% cement replaced by DS200, DS325, or Ultrafine (different grades

pumice), and one mixture with 30% replacement by DS325.

2.3 Research Significance

Pozzolanic materials have been used in concrete applications in the past for various reasons. In this research, pumice has been identified as one of the natural pozzolans that can be extensively used as cementitious material to produce durable concrete. Concrete containing finely-ground pumice were shown to have improved characteristics in terms of strength, hydration, and durability characteristics such as sulfate resistance and alkali-silica reaction resistance. In addition to improved performance properties, using pumice in concrete can lead to environmental benefits from the reduced demand of cement, and thus a potential lower carbon footprint.

2.4 Chemical and Physical Material Characterization

It is necessary to understand the chemical and physical characteristics of the pumice materials to predict and optimize the use of these materials. The materials were evaluated using X-ray diffraction (XRD) to determine the mineralogical crystalline composition and the chemical composition was determined using X-ray fluorescence (XRF). The particle size distribution of each of the products was determined using a laser diffractometer, providing a size spectrum from $0.02\mu\text{m}$ (0.7874×10^{-3} in) to $2000\mu\text{m}$ (78.74 in). The particle shape of each pumice grade was characterized using a 600x magnification controlled optic microscope combined with images from a scanning electron microscope (SEM).

2.4.1 Mineralogical Composition of Pumice

X-ray diffraction was performed on a sample of each pumice grade from a range of 5 to 90 degrees (0.087 to 1.571 rad) 2Φ . It has been confirmed by XRD analyses that pumice tested are more than 99% amorphous by the halo-shaped diffraction band. There is no peak in the signature, which indicates the pumice has no well-defined crystalline minerals. It also shows the vitreous/glassy nature of material, whereas in cement, well defined peaks were observed along a level baseline. The amorphous nature of pumice is corroborated by XRD results of different grades of pumice. X-ray diffraction patterns of DS200 pumice and cement are shown in Fig. 2.1(a) and (b), respectively.

2.4.2 X-Ray Fluorescence

The total chemical composition of different grades of pumice and cement are given in Table 2.1. The chemical analysis shows that pumice is mainly composed of silica (~70%), whereas cement is mainly calcium oxide (~62%).

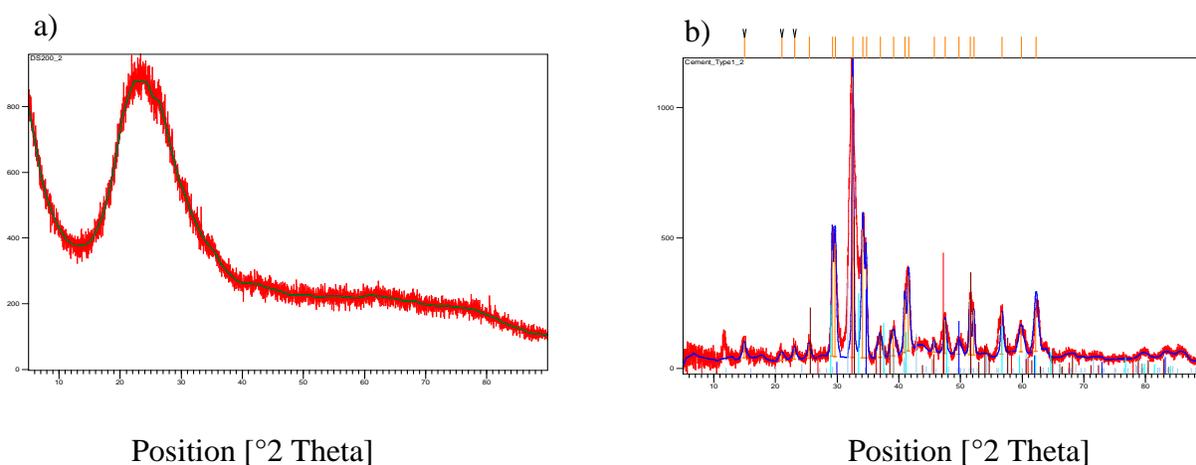


Fig. 2.1 XRD Signature (a) DS200 Pumice (b) Cement

This pumice is classified according to ASTM C 618¹¹ as a Class N pozzolan (for raw or calcined natural pozzolan) based on its specific physical and chemical characteristics. Class N pozzolan has a minimum $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content of 70%; pumice has approximately 80% of these materials. Presence of siliceous and aluminous compounds is evident from chemical analysis results of pumice. From the chemical analysis result, it is evident that all grades of pumice composed of more or less the same percentage of elements differ only in particle size, which can be inferred from the particle size distribution analysis and scanning electron microscopy. From Table 2.1, it is inferred that pumice has significantly higher silica, significantly lower calcium oxide, more alumina, and more alkali contents compared to Type I and II cements.

2.4.3 Particle Size Distribution and Scanning Electron Microscopy

The particle analysis results for different grades of pumice are shown in Table 2.2. It is clear from the mean diameter of particle, the finest is Ultrafine and coarsest is DS200. Ultrafine pumice is approximately four times finer than the portland cement. Scanning electron micrographs for DS200 and cement with two different magnifications are shown in Fig. 2.2. From the image, the glassy nature of pumice is evident and it also illustrates the crushed nature of the material.

2.5 Hydration Kinetics of Pumice Blended Cements

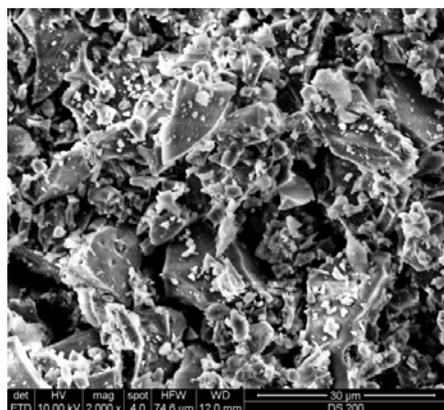
Cementitious materials generate heat through exothermic hydration reaction. The kinetics of pozzolanic and cementitious reactions can be measured with an isothermal heat conduction calorimeter.

Table 2.1 Chemical Analysis Result from XRF Test in %

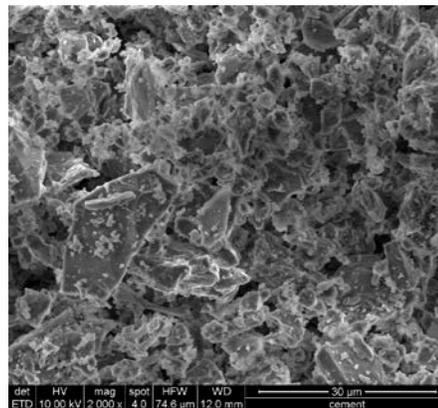
	Type I Cement	Type II Cement	DS200 Pumice	DS325 Pumice	Ultrafine Pumice
SiO₂	20.02	20.67	69.09	69.16	69.75
Al₂O₃	5.37	3.97	10.63	10.79	11.18
Fe₂O₃	2.35	3.65	1.01	1	1.04
CaO	61.67	63.57	0.93	0.93	0.97
MgO	2.46	1.55	0.09	0.16	0.25
SO₃	3.81	2.81	-0.04	-0.04	-0.04
Na₂O	0.25	0.06	2.49	2.13	2.34
K₂O	1.18	0.72	4.77	5.08	4.79
Cl	0.055	0.018	Nil	Nil	Nil
Total	99.4	98.43	89.12	89.33	90.42

Table 2.2 Particle Size Details of Pumice

Sample	Ultrafine	DS325	DS200
Single Particle Area, cm ² /cm ³ (in. ² /in. ³)	18093 (45956.3)	5921.2 (15039.9)	4375.4 (11113.5)
Median, μm (in.)	3.755 (0.148 x10 ⁻³)	17.788 (0.700 x10 ⁻³)	31.725 (1.249 x10 ⁻³)
Mean, μm (in.)	3.995 (0.157 x10 ⁻³)	21.292 (0.838 x10 ⁻³)	45.369 (1.786 x10 ⁻³)
Standard Deviation, μm (in.)	1.695 (0.067 x10 ⁻³)	16.158 (0.636 x10 ⁻³)	60.756 (2.392 x10 ⁻³)
Mode, μm (in.)	4.711 (0.185 x10 ⁻³)	24.373 (0.960 x10 ⁻³)	41.895 (1.649x10 ⁻³)
Refractive Index	1.5	1.5	1.5



DS200



Cement

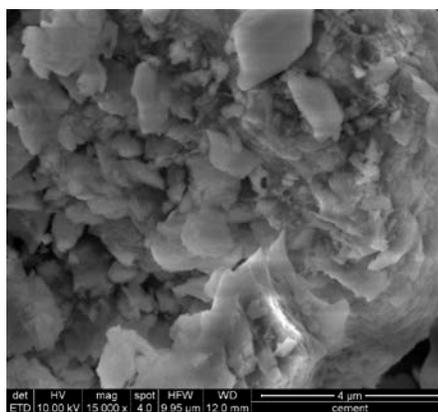
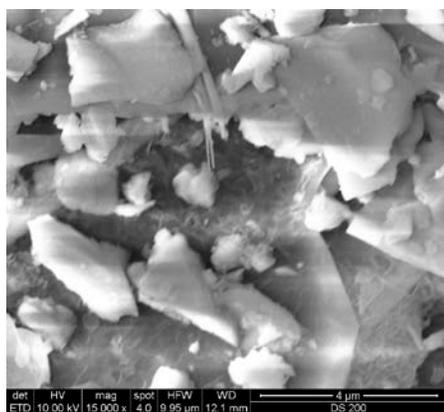


Fig. 2.2 Scanning Electron Microscope images for DS200 and Type 2 cement at 2000X and 1500X magnification.

An air-isolated heat conduction calorimeter was used to analyze 8 pumice combinations with a control cement. The eight combinations used were 100% portland cement, ASTM Type II/V; 20 and 30% DS200; 10, 20, and 30% DS325; 20 and 30% Ultrafine pumice. Pumice replacement percentages are done by mass. Each of the tests was conducted at 21° C (70° F) for 30 days.

A sample of 10 g (0.022 lb) per ampoule with a reference of 10 g (0.022 lb) per ampoule was used with w/cm ratio of 0.5. The eight combination results are shown for the first 225 hours in Fig. 2.3 (0 to 75 hours) and Fig. 2.4 (75 to 225 hours). The 100% cement mixture produces more heat as compared to the mixtures containing pumice. As the pozzolanic content increases, the main peak of heat flow decreases. Depending on the grades of pumice, the height of the main hydration peak varies for the same percentage combination of cement and pozzolanic material. For example, the 70% cement and 30% DS200 and DS325 combinations produce the lowest heat flows among the 8 mixtures, whereas the 70% cement and 30% Ultrafine pumice combination produces heat comparable to the 80% cement and 20% DS200 and DS325 mixtures. Similarly, the 90% cement and 10% DS325 produces a heat flow comparable to 80% cement and 20% Ultrafine pumice. The calorimeter testing shows that there is no appreciable pozzolanic activity in the first 100 hours for DS200 or DS325. However, the Ultrafine pumice impacts the early age hydration characteristics. After 100 hours, hydration of the 100% cement mixture starts declining, whereas for mixtures containing pumice, there seems to be continuous hydration. This shows the pozzolanic reaction of different grades of pumice is dependent on the fineness.

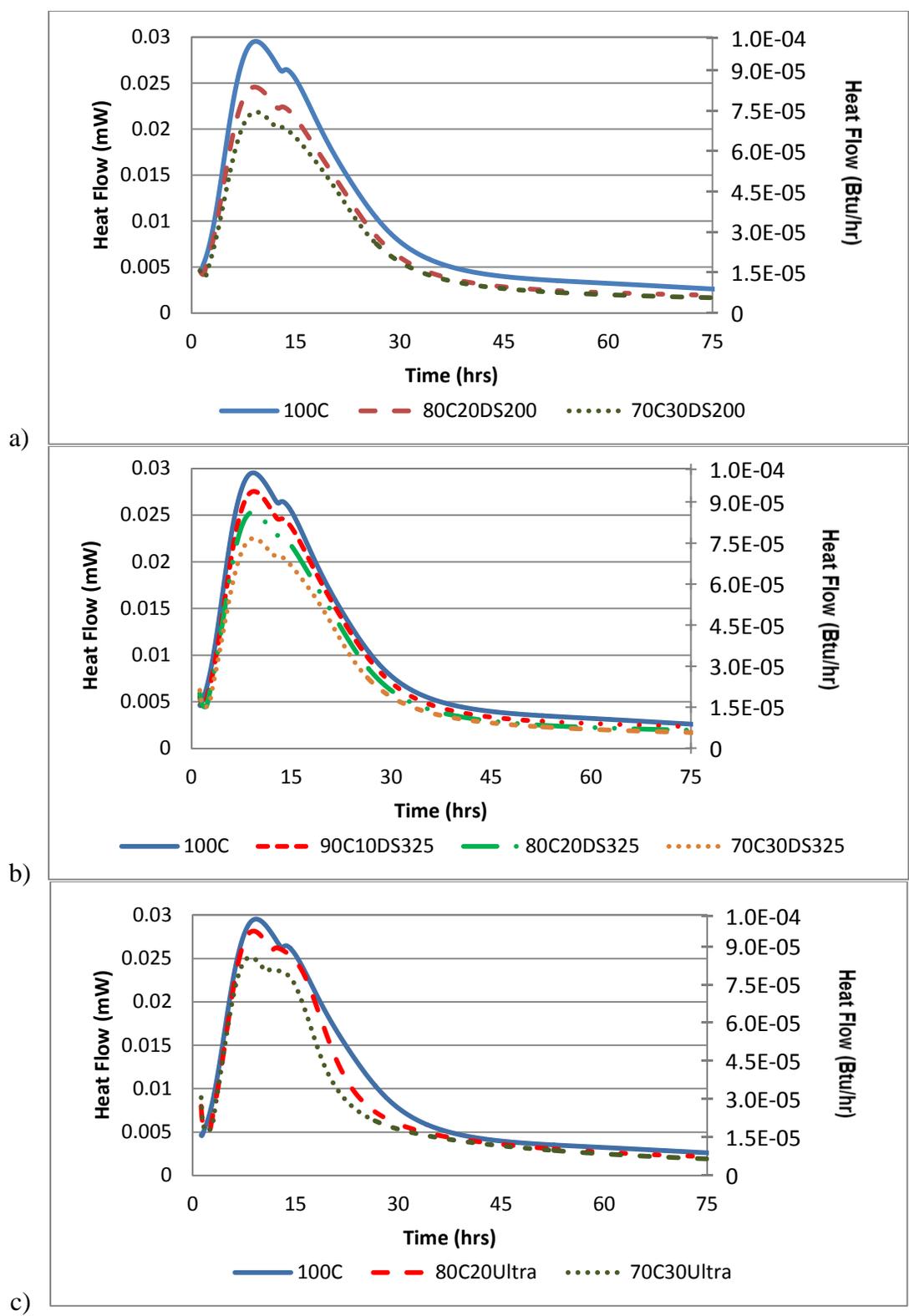


Fig. 2.3 Hydration heat flow for different mixture combinations of Type II/V cement versus a) DS200, b) DS325, and c) Ultrafine pumice during first 75 hrs.

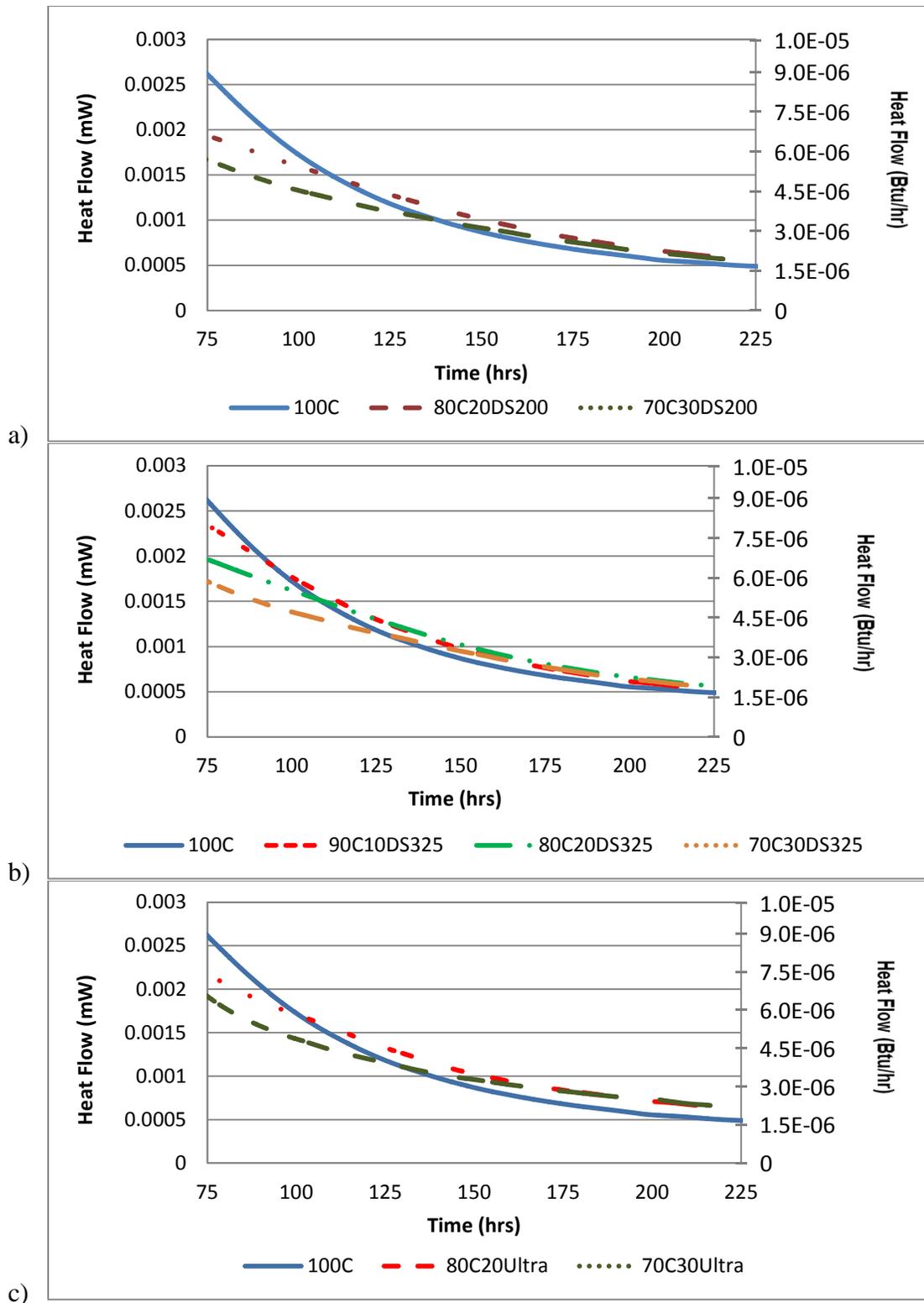


Fig. 2.4 Hydration heat flow for different mixture combinations of Type II/V cement versus a) DS200, b) DS325, and c) Ultrafine pumice during 75 to 225 hrs.

2.6 Concrete Mixture Designs with Pumice

By replacing a portion of cement with pumice, many properties of the cementitious system can be influenced by physical effects associated with small finer particle size distributions than portland cement, as well as by the pozzolanic and cementitious reactions. Since pozzolans have the ability to influence the durability and strength development properties, it is important to study these properties with the pumice blended cement mixtures.

2.6.1 Setting Time

Setting times of five mixtures were determined by a Vicat needle test method according to ASTM C191¹². The variation of setting time and water requirement for different mixture are presented in Table 2.3 and Fig. 2.5. There is an increase in initial and final setting time for the mixtures containing pumice compared to 100% cement (ASTM Type II/V) when tested at a constant flow without admixtures. The increases are well within the limits of ASTM C595⁷ specification for blended hydraulic cement, which is likely attributed to the increased water demand. Water demand was more for mixtures containing pumice compared to 100% cement. The percentage increase in water demand is shown in Table 2.3. The grade of pumice that has very small particles (Ultra) requires more water compared to grades with comparatively larger particles (DS200 and DS325). Also, the mixture that has 30% replacement consumed more water due to increase in surface area and also due to the porous nature of pumice. The increase in water demand can be addressed by addition of common water-reducing admixtures.

Penetration resistance indicates the setting characteristic of cement mixture paste.

Table 2.3 Effect of Pumice on Setting Time and Water Demand

Mixture	Setting Time (min)		Water Used, g (lb)	% Increase in water
	Initial	Final		
100C	117	242	173 (0.381)	
80C20DS200	143	286	181 (0.399)	4.6
80C20DS325	148	271	195 (0.430)	12.7
70C30DS325	159	315	201 (0.443)	16.2
80C20Ultra	129	323	199 (0.439)	15

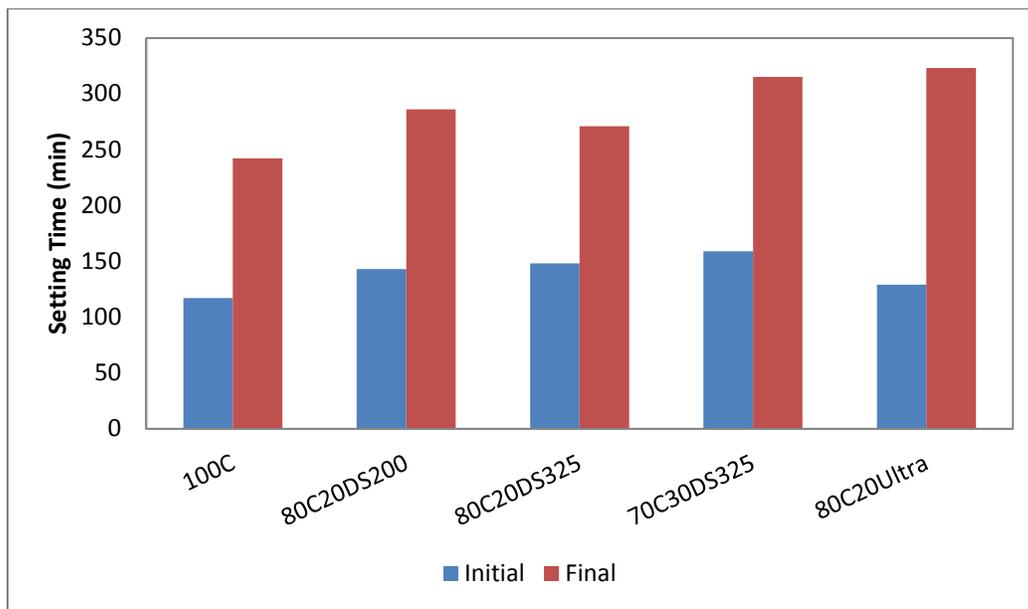


Fig. 2.5 Effect of pumice on initial and final setting time according to Vicat test.

The penetration resistance for different mixture combinations over a time period is shown in Fig. 2.6. From Fig. 2.6, it is clear that 100% cement (100C) mixture had rapid setting characteristics compared to other mixtures. The 80% cement with 20% Ultrafine (80C20Ultra) mixture setting characteristic was closer to 100C compared to other pumice mixtures. The penetration resistances, along with Vicat and hydration heat flow curve, indicate that the 80C20Ultra mixture has the ability to set faster than other mixtures.

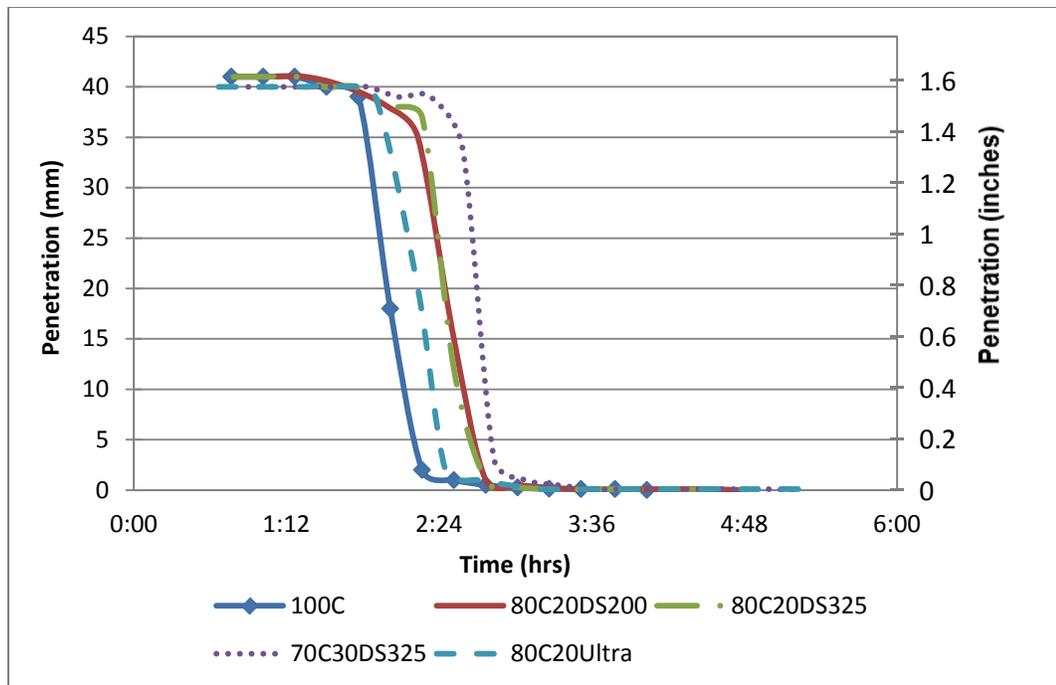


Fig. 2.6 Penetration resistance of different cement and pumice blended mixtures.

2.6.2 Strength Development

The compressive strength of concrete is one of the primary considerations in concrete mixture design. Following ASTM C39¹³, compressive strength of 4" (101.6 mm) x 8" (203.2 mm) cylinders was tested with different grades of pumice for five mixtures commonly used for 4 ksi (281.2 kg /cm²) specifications. The five concrete mixtures included either 100% Type II/V cement, 20% of DS200, DS325, or Ultrafine pumice with 80% cement, or 30% DS325 with 70% cement. All mixtures had a w/cm ratio of 0.485. ASTM C192¹⁴ is followed for preparing concrete test specimens and the basic mixture proportions used to produce 1 cubic feet (0.0283 m³) concrete is shown in Table 2.4. A polycarboxylate-based water reducer admixture was used in the mixtures to maintain a slump of 3-5 inches (76.2 mm-127 mm). Compressive strength results were

Table 2.4 Basic Mixture Designs to Produce 1 Cubic Foot (0.0283 m³) of Concrete

Ingredients	Mix-1	Mix-2	Mix-3	Mix-4	Mix-5
Type II/V Cement, kg (lb)	9.48 (20.9)	7.58 (16.7)	7.58 (16.7)	6.62 (14.6)	7.58 (16.7)
Pumice, kg (lb)	0 (0)	1.91 (4.2)	1.91 (4.2)	2.86 (6.3)	1.91 (4.2)
Coarse Aggregate, kg (lb)	30.39 (67)	30.39 (67)	30.39 (67)	30.39 (67)	30.39 (67)
Fine Aggregate, kg (lb)	24.49 (54)	24.04 (53)	24.04 (53)	23.59 (52)	24.04 (53)
Water, kg (lb)	4.54 (10)	4.54 (10)	4.54 (10)	4.54 (10)	4.54 (10)

shown in Table 2.5 and Fig. 2.7.

The mixtures containing pumice had lower compressive strengths than the control mixture; however, all mixtures exceeded 28-day 4000 psi (280 kg/cm²) design strength. The minimum strength achieved by all mixture combinations at age 7 days was greater than 3300 psi (230 kg/cm²) and at age 28 days was greater than 4800 psi (340 kg/cm²). Mixtures containing Ultrafine pumice reached higher early strength compared to mixtures containing the DS200 and DS325 grade pumice. This trend is supported by the results from hydration heat flow behavior of the same blended cements, for which the Ultrafine pumice mixture showed rapid hydration characteristics. The 80C20DS200 mixture

Table 2.5 Average Compressive Strengths of 4" (101.6 mm) x 8" (203.2 mm) Cylinders

Mixture Design	Strength at age 7, psi (kg/cm²)	Strength at age 28, psi (kg/cm²)
Cement (Mix-1)	5636 (396)	7400 (520)
80% C+20% DS200 (Mix-2)	4214 (296)	5749 (404)
80% C+20% DS325 (Mix-3)	3343 (235)	4860 (342)
70% C+30% DS325 (Mix-4)	3398 (239)	5359 (377)
80% C+20% Ultrafine (Mix-5)	4648 (327)	7083 (498)

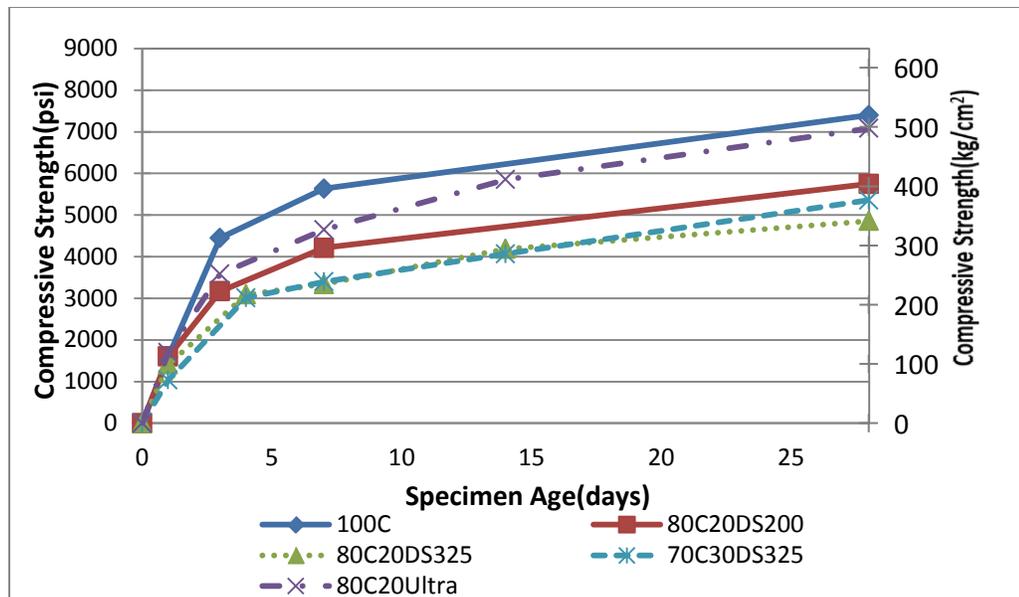


Fig. 2.7 Average compressive strengths of 4'' (101.6 mm) x 8'' (203.2 mm) cylinders.

reached a higher strength at 7 and 28 days compared to 80CDS325 mixture, which also mimicked the hydration behaviors exhibited by these different grades of pumice.

2.6.3 Repeatability of Compressive Strength Results

Two additional mixtures (A2 and A3) were attempted but with a different source of Type II/V cement, and different source of the limestone coarse and natural sand fine aggregates used. For these new mixtures, the 100% cement mixture and the 80% cement with 20% Ultrafine pumice mixture were tested for compressive strength at 3, 7, 14, and 28 days. Another variation between these new mixtures was the type of mixer utilized: either by using a 9 cubic foot counter planetary pan mixer versus a 2 cubic foot drum mixer. Despite having the above difference, the strength results shown in Fig. 2.8 indicated low variation between the cylinders (max COV was 0.09 at 28 days). Compared

to the previous results where the 100% cement mixture strength at 28 days was greater than the 80% cement with 20% Ultrafine pumice mixture, in this new attempt, the mixture containing pumice indicated greater 28 day strength. By taking into account the expected variation in the strength curve, it can be concluded that the addition of up to 20% pumice does not significantly change the measured strength of the concrete. Comparable strength can be obtained between control and pumice replacement mixture.

2.6.4 Sulfate Mitigation

Following the procedures of ASTM C1012¹⁵, five mortar mixture designs were tested for sulfate resistance. The cementitious combinations were the same as used in the compressive strength testing. The specimens were tested through 6 months and the percentage length change of mortar specimens for different mixtures is shown in Table 2.6 and Fig. 2.9. Test values below 0.05% at 6 months indicate high sulfate resistance and test values below 0.10% at 6 months indicate moderate sulfate resistance. All the pozzolanic mixtures are within the limit of 0.05%, hence qualified to be HS (High Sulfate resistance). The control mixture with 100% Type II/V cement is classified as MS (Moderate Sulfate resistant) since the length change is still less than 0.10% by 6 months, but greater than the 0.05% limit for high sulfate resistance.

2.6.5 Alkali-Silica Reaction

The same five mortar mixture designs were tested for alkali-silica reaction resistance according to a modified ASTM C1567¹⁶ procedure. The mixture proportions were the same as for sulfate resistance and strength test except that an ASTM Type I

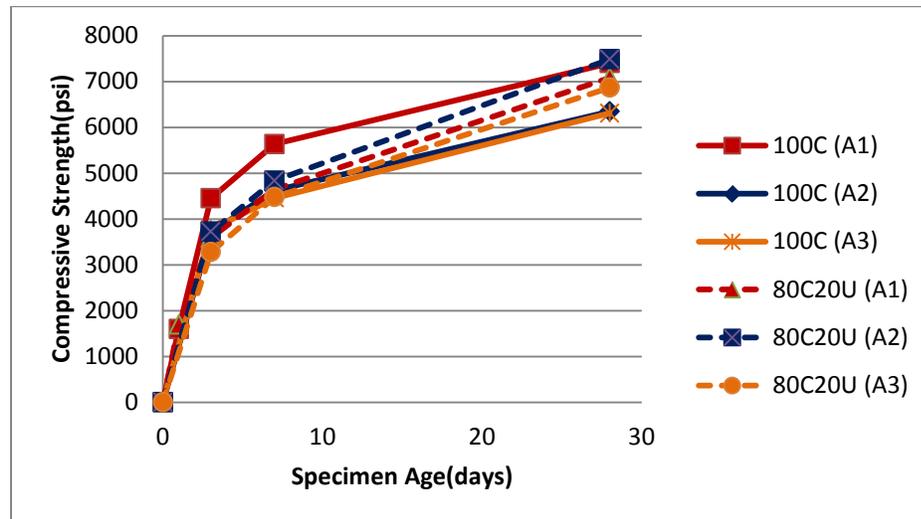


Fig. 2.8 Compressive strength of 100C and 80C20U mixture tested at different periods.

Table 2.6 Length Change (%) of Mortar Specimens in Sulfate Environment

Weeks	Length change (%)				
	Mix-1	Mix-2	Mix-3	Mix-4	Mix-5
1	0.004	0.006	0.006	0.016	0.016
2	0.007	0.014	0.012	0.013	0.011
3	0.014	0.015	0.013	0.016	0.012
4	0.019	0.016	0.014	0.017	0.012
8	0.032	0.027	0.026	0.034	0.026
13	0.039	0.029	0.028	0.035	0.023
15	0.045	0.031	0.028	0.039	0.028
Month 4	0.053	0.033	0.031	0.038	0.027
Month 6	0.070	0.046	0.045	0.048	0.034

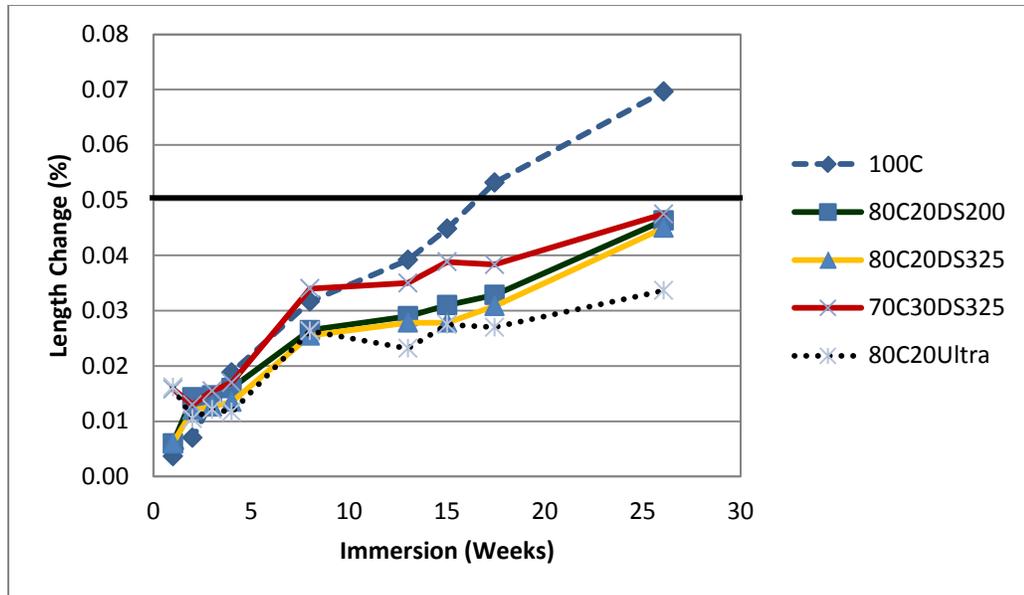


Fig. 2.9 Length change (%) of mortar specimen in sulfate environment.

cement was used instead of Type II/V cement, along with a 25% replacement of the fine aggregate natural sand with ground cullet glass and no coarse aggregate. The fine sand and glass aggregates were blended to meet ASTM C1567 gradation requirements. The percent length change of mortar specimens for different mixtures is shown in Fig. 2.10 and summary is given in Table 2.7. The percent length change for acceptable expansion according to ASTM C1567 is less than 0.10% at 14 days of immersion in an aggressive environment. Any percent length change over 0.10% is considered deleterious expansion. Results showed that the usage of pumice is very effective in mitigating the expansion.

2.7 Conclusion

Pumice tested in this research was determined to be pozzolanic and well-suited for concrete applications. The various grades of pumice behave differently in the

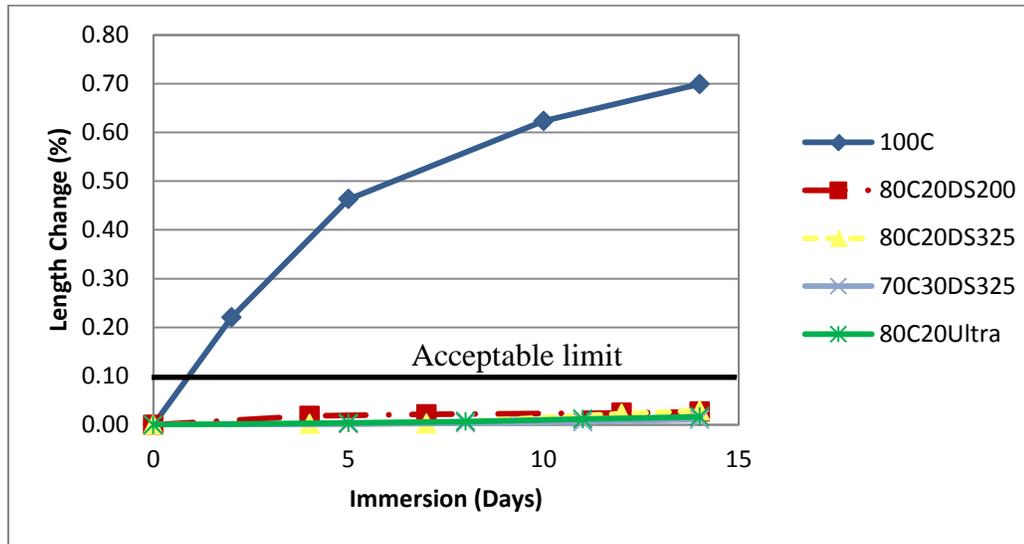


Fig. 2.10 Length change (%) of mortar specimen due to alkali-silica reaction.

Table 2.7 Summary of ASR Resistance

Mixture	ASR % Length Change	Rating
100C 25% Glass	0.699	Deleterious Expansion
80C20DS200 25% Glass	0.027	Acceptable Expansion
80C20DS325 25% Glass	0.029	Acceptable Expansion
70C30DS325 25% Glass	0.011	Acceptable Expansion
80C20Ultra 25% Glass	0.017	Acceptable Expansion

hydration characteristic even with the same chemical composition, which may be due to varying particle size distribution. Ultrafine pumice showed improved performance compared to other grades of pumice in terms of hydration, strength, sulfate resistance, and alkali-silica reaction resistance. The improved hydration characteristics of Ultrafine pumice were also supported by the compressive strength and the penetration resistance results of the same.

The exothermic heat produced from mixtures containing pumice was reduced compared to mixtures with 100% cement, which makes it advantageous in mass concrete placements. The water demand is higher for all the mixtures containing porous finely-ground pumice, yet improved performance in durability makes it a valuable addition to design for exposed concrete elements. Midrange water reducer can be used to reduce the water demand, which may help in reducing the setting time to the equivalent of 100% cement mixture.

DS200 and DS325 pumice showed improved performance compared to 100% cement in durability characteristics. If the application requires primarily an improved durability, i.e., high sulfate resistance and high ASR resistance, then DS200, DS325, or Ultrafine pumice can be recommended as a part of cementitious material. But, if the requirement is maintaining similar compressive strength and improved durability, then Ultrafine pumice would be recommended. When pumice is used as a supplementary cementitious material in concrete, it is possible to produce an enhanced concrete with improved durability properties along with potential environmental benefits from a reduced cement demand.

To check its resistance towards various levels of reactive aggregates and also to

find the minimum amount of pumice required to resist ASR expansion, a detailed study has been conducted in the next chapter.

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CHAPTER 3

REDUCTION OF ALKALI-SILICA REACTION USING PUMICE AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL*

3.1 Abstract

Pozzolans have been used in concrete applications for centuries to produce long-lasting durable structures. This study looks at a finely ground pumice as a natural pozzolan to mitigate the alkali-silica reaction (ASR). Different particle sizes of the pumice and various percentages of replacement of cement in mortar were investigated in this research study. Previous research on mortar using pumice as a supplementary cementitious material (SCM) was found to exhibit good resistance to ASR expansion, sulfate attack, and chloride intrusion. The ASR resistance of using pumice was found to be uniquely more effective than other durability tests responses. Further experimental investigation of the pumice as a SCM was conducted in this study to understand the potential ASR resistance for different reactive aggregates. All ASR testing has been conducted on mortar and concrete specimens according to ASTM C1567 and a modified ASTM C1293, respectively. Depending on the reactivity of the aggregates and fineness of the pumice, rates of 10-15% replacement of cement with the pumice were found to

* U. Ramasamy, A.C. Bordelon, and P. J. Tikalsky, "Reduction of Alkali-Silica Reaction using pumice as a supplementary cementitious material", submitted to *Cement, Concrete and Research Journal*, (2014).

reduce the ASR expansion to the acceptable limits. A finer particle size of the pumice was found to require a lower amount of cement replacement compared to coarser particles for the same expansion limits of the ASR mortar test. Pumice produced an enhanced resistance to ASR expansion and was shown to be a market-ready SCM for durable and strong concrete.

3.2 Introduction

Alkali-silica reaction (ASR) has been recognized as a potential distress in concrete structures since the late 1930s [1, 2]. The most common alkali aggregate reaction in concrete is alkali-silica reaction, compared to alkali carbonate reaction which is found with dolomitic aggregates. ASR is a chemical reaction in concrete or mortar caused by the presence of certain reactive siliceous minerals in aggregate, hydroxyl ions, and alkalis in hydraulic cement. This reaction leads to an “alkali-silica gel” formation which has the tendency to imbibe water and swell. Under significant moisture conditions, swelling builds up pressure and the expansion causes cracking of the concrete.

Pozzolans are siliceous and aluminous materials that react with soluble calcium oxides from hydrated cement to form calcium silicate hydrate (C-S-H) amorphous gel structures, as well as other stable silica aluminate compounds [3]. A supplementary cementitious material (SCM) is implemented to replace a portion of portland cement with a finely ground pozzolan or other hydraulic reacting material to potentially reduce demand and cost associated with portland cement, while also maintaining or improving the long-term strength, workability, or durability properties. Some naturally occurring and artificially produced materials can demonstrate this pozzolanic reaction and, thus,

can be used as a supplementary cementitious material (SCM) in producing concrete. Naturally-occurring pozzolans are extensively used in the locations where such siliceous materials are abundantly available. A variety of natural pozzolans have been used in concrete projects as reported in the past [4-9]. Artificial pozzolans can be produced deliberately or can be obtained as waste or by-products such as fly ash, granulated slag, silica fume, metakaolin, rice husk ash, etc. Artificial pozzolans are often utilized in a wider variety of applications based on the reduced economics of the processing and transportation combined with their increased performance benefits to concrete. Ground-granulated blast furnace slag or pozzolans can be preblended with portland cement by the cement manufacturers and are classified as “Blended Hydraulic Cements” according to ASTM C595 [10]. In the mid-1930s, fly ash was used in the market for concrete applications. The first large-scale concrete project specified use of fly ash was at Hungry Horse Dam in Montana in 1948. Research conducted on using fly ash or silica fume as SCMs has shown that they are proven to produce durable ASR resistant concrete [11]. Today, the most common mitigating technique to reduce ASR expansion is to use both a low alkali cement as according to ASTM C150 standards and use either class F fly ash or ground-granulated blast furnace slag as a percentage replacement of the total cementitious content. Compared to class C fly ash, a class F fly ash has been shown to mitigate ASR more effectively due to its lower calcium content [12]. Class F fly ash and slag blended-cements can be used to effectively mitigate ASR at cement replacement rates of 15-30% and 25-70%, respectively, by weight of total cementitious content [13, 14]. Other pozzolans such as silica fume and metakaolin have also been effectively utilized to mitigate ASR by forming a denser and stronger concrete or reducing the pH of

the pore solution after entrapping free alkalis [15-17]. Combinations of SCMs can be used in ternary cement blends to also be very effective in mitigating ASR expansion [18, 19]. In general, as the amount of supplementary cementitious material (SCM) content increases, the ASR expansion decreases [11].

Some limitations on the effectiveness to mitigate ASR have been noticed for these pozzolans [20]. Silica fume can be prone to clumping and, in which case, can act more like a reactive fine aggregate and therefore initiate ASR formation. Hence, for ASR reduction, it is necessary to have either finely-ground unglomerated powder forms of these SCMs, or to use extended mixing to facilitate dispersion is compulsory [21].

Currently, the industry has utilized many of the by-products or waste-based pozzolans due to cost-saving, but with diminishing supply of such materials. Now is the time that researchers and contractors are beginning to seriously consider using natural or other artificial pozzolans. **Pozzolans should be either economically viable or provide superior performance enhancements to be considered as a SCM for a construction project.** Pumice is an example of a naturally-occurring pozzolan formed from volcanic activity. There have been few publications documenting the usage of pumice as a SCM in concrete. Furthermore, there have been no publications prior to this research about the usage of pumice to specifically arrest ASR expansion.

The majority of pozzolan materials are volcanic in origin, composed of volcanic glass, volcanic ashes, or pumices [3]. Pumice is created during a volcanic eruption as the rapidly cooling and depressurizing alumino-silicate magma releases gases while forming a vitreous phase material that has a highly porous vesicular structure. Pumice appears as a white porous volcanic glass with interlocking vitreous fibers filled with tiny air bubbles.

These abundant small internal bubbles give pumice its unique material properties. When exposed to saturated lime, the disordered alumino-silicate's structure does not remain stable. This instability in the presence of lime is the basis for the pozzolanic property of volcanic glasses [22]. Pumice has been verified to be pozzolanic and, thus, potentially complementary in its reactions in portland cement concrete [23]. The use of a finely-ground pumice added as a SCM to mortar reduced the effects of high alkali or high sulfate ion expansion reactions [23]. Pozzolans that are ground finer are expected to react faster, and thus demonstrate excellent durability characteristics, increased hydration rates, and higher early compressive strengths. The resulting ASR expansion was negligible when finely ground pumice was used as a SCM despite the use of 25% highly reactive silica glass as a fine aggregate along with moderately reactive aggregate in the mortar [23].

Among all the durability benefits, the reduction in ASR expansion was considered significant, especially due to the presence of high amounts of silica and alkalis in the pumice. The scope of this research is to check effectiveness of pumice as an SCM in reducing ASR expansion for other various reactive aggregates and to determine an optimal level of replacement of portland cement in mortar and concrete.

3.3 Materials and Methods

The hydraulic cement used in this research was an ASTM C150 Type I portland cement, manufactured in Mississauga, Ontario. The pumice used as a SCM originated from a volcanic deposit in Malad City, Idaho. The chemical composition of the Type I cement and three fineness grades of pumice (DS200, DS325, and Ultrafine) are shown in

Table 3.1. The particle sizes for each grade of pumice are described in Table 3.2. Three different grades of pumice and four different sources of fine aggregate were used to make mortar bars. Based on the magnitude of mortar bars expansion, aggregates were named as either moderately or highly reactive. Out of four fine aggregates, one of them was moderately reactive aggregate blended with 25 % pyrex glass (MRA1+25% glass), two of them were moderately reactive aggregate (MRA2 and MRA3), and one highly reactive aggregate (HRA). All aggregates or aggregate blends met ASTM C1567 ASR test gradation requirements and are summarized in Table 3.3.

3.3.1 Mortar Tests

The variables studied in creating mortar samples to test for ASR resistance were the following:

- The amount of pumice to replace portland cement varied from 0, 5, 10, 15, and 20%.
- The three different grades of pumice were of variable fineness levels.
- Different aggregate types (MRA2, MRA3 and HRA) or combinations of aggregate types (MRA1+25%glass) were studied with the same pumice grade.

The ASTM C1567 [24] “Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)” was used to study the effectiveness of pumice in mitigating ASR. All the test specimens were kept in an accelerated ASR reaction environment of at 80 °C and submerged in 1 N NaOH solution after demolding at 1 day age, and then submerged in tap water at 80 °C (176 °F) for an additional day. These

Table 3.1 Chemical Oxide Analysis (in percent) of Cement and Pumice Grades

Oxide	Type I Cement	DS200 Pumice	DS325 Pumice	Ultrafine Pumice
SiO ₂	19.7	69.09	69.16	69.75
Al ₂ O ₃	5.1	10.63	10.79	11.18
Fe ₂ O ₃	2.5	1.01	1	1.04
CaO	62.6	0.93	0.93	0.97
Na ₂ O	-	2.49	2.13	2.34
K ₂ O	-	4.77	5.08	4.79

Table 3.2 Particle Size Details of Pumice Grades

Sample	Ultrafine	DS325	DS200
Surface Area (cm ² /cm ³)	18093	5921.2	4375.4
Mean (μm)	3.995	21.292	45.369
Standard Deviation (μm)	1.695	16.158	60.756

Table 3.3 Different Aggregate Sources

Aggregate classification*	Source Location
Crushed pyrex glass	Corning, New York
MRA1 (fine)	Point of the Mountain, SLC, Utah
MRA2 (fine)	Beck Street, SLC, Utah
MRA3 (fine)	Rupert, Idaho
HRA (fine)	Snake River Valley, Idaho
HRA (coarse)	

*Aggregates were named after ASTM C1567 mortar test results based on the magnitude of expansion.

specimens are considered “acceptable” to prevent ASR if the expansion is limited to \leq 0.1 % of the specimen length after an age of 16 days. All of the mixtures were measured at intervals up to 16 days, and many of them were measured beyond the 16 days of being in the accelerated environment condition.

3.3.2 Concrete Tests

Concrete samples were created using only the Ultrafine pumice grade as an SCM and with highly reactive fine and coarse aggregates as per ASTM C1293 [25] aggregate gradation requirements. Similar to the mortar samples, concrete prisms were created and tested in an accelerated environment condition. A modified ASTM C1293 “Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction” was used. The modified environment for these concrete prisms was to use 80 °C (176 °F) instead of 38 °C (100 °F), while still submerged in 1 N NaOH solution to accelerate the ASR. Although the ASTM C1293 standard describes a test carried out over a year, the other modification to the test was to measure the length change for the shorter duration of 50 days. It has been shown by past literature that the higher temperatures will produce the ASR gel more rapidly [26].

3.4 Results and Discussion

Effectiveness of pumice in mitigating ASR expansion was studied. Overall, pumice samples, regardless of the amount of pumice or aggregate type, showed reduced expansion in the accelerated ASR environment compared to 100% cement mixture samples. The necessary amount of pumice as a SCM to produce the maximum acceptable

expansion level depended on the reactivity level of the aggregate.

3.4.1 Mortar with Moderately Reactive Aggregate (MRA)

3.4.1.1 MRA1 with 25% Glass vs. Pumice Content

An aggregate blend with 75% moderately reactive aggregate (MRA1) and 25% glass was tested with all three grades of pumice (at 0, 5, 10, 15, or 20% replacement of cement). The 0% pumice mixture (100% cement) showed a length change of 0.7% by 16 days, which is 7 times greater than the acceptable limit. In order to produce acceptable length change values, the minimum pumice contents for the DS200 and DS325 coarser grade pumices was 15% replacement (Fig. 3.1a and 3.1b) and 10% replacement for the Ultrafine grade pumice (Fig. 3.1c). Smaller particle sizes of the pumice resulted in faster hydration and likely helped in pore structure refinement. The densification of the mortar due to pumice can reduce further moisture intrusion, and mitigate ASR expansion. For the Ultrafine grade pumice, a reduced amount of cement replacement was sufficient to produce the acceptable ASR resistance compared to coarser grade pumice. Furthermore, even at 5 and 10% replacement of finer or coarser grade pumices, the magnitude of expansion was reduced.

At 20% pumice replacement of cement, influence of the pumice particle size was negligible and all grades of pumice were equally effective at resisting ASR. Whereas when the level of replacement reduced from 20% to 5%, the finer grade pumice was able to reduce ASR expansion more effectively compared to the coarser grade pumices (Fig. 3.2). The particle size of pumice definitely played a role in determining the amount of replacement, but the extent of influence of pumice particle size was significant when the

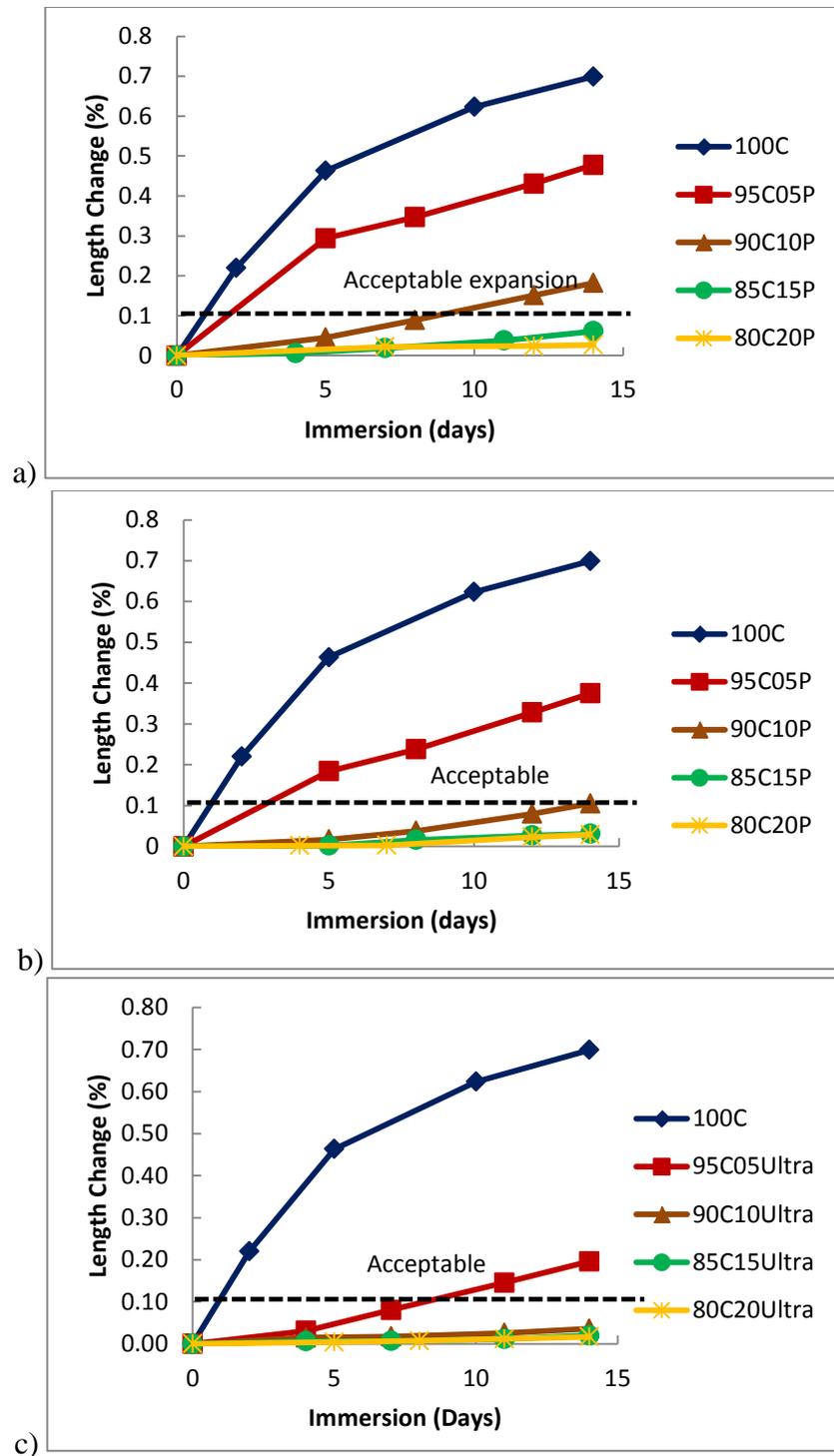


Fig. 3.1 ASR expansion of mortar specimens at 16 days containing a) DS200 pumice, b) DS325, and c) Ultrafine pumice (at varying replacement amounts of 0, 5, 10, 15 and 20%) and a blend of moderately reactive aggregate (MRA1) with 25% glass fine aggregates.

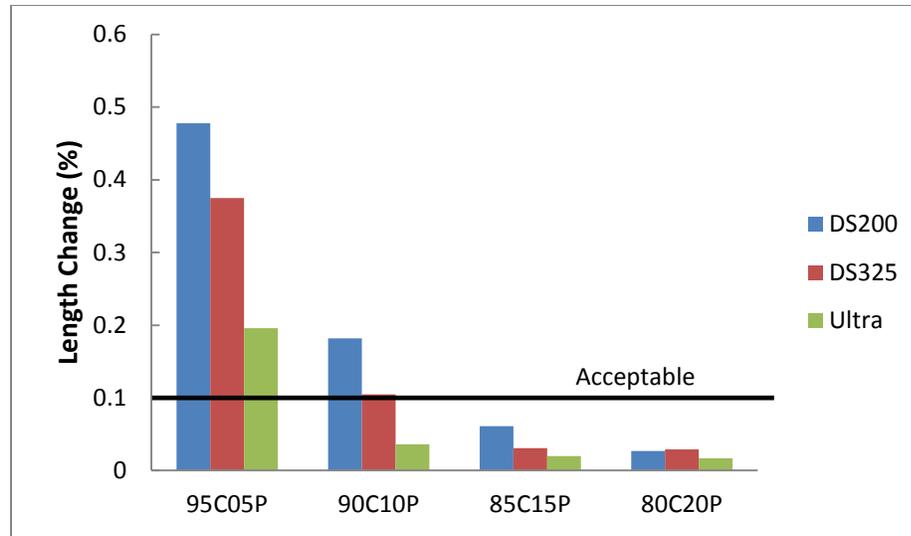


Fig. 3.2 Comparison between different grades of pumice against ASR expansion of mortar bars made with moderately reactive aggregate (MRA1) with 25% glass and measured by 14 days in an accelerated ASR environment.

replacement amount was low (Table 3.4). Among the three grades of pumice studied, the Ultrafine pumice resisted ASR expansion most efficiently. Therefore, the remainder of this study investigated the effectiveness of pumice in the presence of other types of aggregates, while using only the Ultrafine pumice grade as a replacement of 0 to 15% of the cement.

3.4.1.2 MRA2 vs. Ultrafine Pumice Content

Moderately reactive aggregates from SLC, Utah were tested with 0, 5, 10, or 15% Ultrafine pumice replaced mortar mixture. The 0% pumice mixture (100% cement) showed a length change of 0.58% at 16 days. For this fine aggregate, the minimum pumice replacement of 15% is required to produce an acceptable length change of 0.03% in the accelerated ASR environment (Table 3.5). The 15% replacement was able to

Table 3.4 ASR Expansion of 75% MRA1+25% Glass at 16 days

Mixture	ASR % Length Change	Rating
100C 25%Glass	0.699	Deleterious Expansion

Mixture ID	ASR % Length Change	Rating
80C20DS200 25%Glass	0.027	Acceptable Expansion
85C15DS200 25%Glass	0.061	Acceptable Expansion
90C10DS200 25%Glass	0.182	Deleterious Expansion
95C05DS200 25%Glass	0.478	Deleterious Expansion

Mixture ID	ASR % Length Change	Rating
80C20DS325 25%Glass	0.029	Acceptable Expansion
85C15DS325 25%Glass	0.031	Acceptable Expansion
90C10DS325 25%Glass	0.105	Deleterious Expansion
95C05DS325 25%Glass	0.375	Deleterious Expansion

Mixture ID	ASR % Length Change	Rating
80C20Ultra 25%Glass	0.017	Acceptable Expansion
85C15Ultra 25%Glass	0.020	Acceptable Expansion
90C10Ultra 25%Glass	0.036	Acceptable Expansion
95C05Ultra 25%Glass	0.196	Deleterious Expansion

Table 3.5 ASR Expansion of MRA2 at 16 days

Mixture ID	ASR % Length Change	Rating
100C	0.578	Deleterious Expansion
95C05U	0.499	Deleterious Expansion
90C10U	0.133	Deleterious Expansion
85C15U	0.034	Acceptable Expansion

reduce the expansion from 0.78% to 0.09% at 28 days. Furthermore, at this amount of pumice replacement, the expansion stayed lower than the ASTM limit even for an extended period. However, the control mixture (0% pumice) with MRA2 produced less expansion (Fig. 3.3) compared to MRA1 (Fig. 3.1). At 15% pumice, the difference in expansion was both below the limit and similar between moderately reactive aggregates

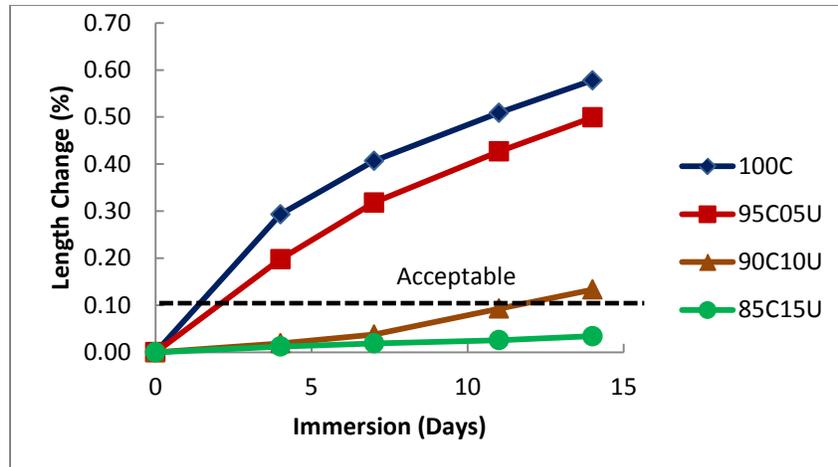


Fig. 3.3 ASR expansion of mortar specimens containing Ultrafine pumice at 0, 5, 10, or 15% replacement of cement and moderately reactive fine aggregate (MRA2).

MRA1+glass and MRA2. As seen previously with the MRA1+glass, an increase in the amount of pumice replacement for cement in a mixture will reduce the ASR expansion up to the optimum level.

3.4.1.3 MRA3 vs. Ultrafine Pumice Content

The 100% cement mixture (0% pumice) specimens showed a length change of 0.48% at 16 days (Fig. 3.4) with MRA3 (from Rupert, Idaho) and Ultrafine pumice. The fine aggregate MRA2 caused higher expansion in the accelerated ASR environment compared to MRA3. For this fine aggregate, a minimum pumice replacement of 10% is required to produce acceptable length change of 0.07% (Table 3.6). The 15% replacement was able to reduce the expansion from 0.65% to 0.09% at 28 days, which again indicates a low expansion level even for an extended period of time. Even though the minimum pumice replacement amount is different to accommodate for the reactivity levels of slightly different fine aggregate sources (MRA2 versus MRA3), at 15% pumice

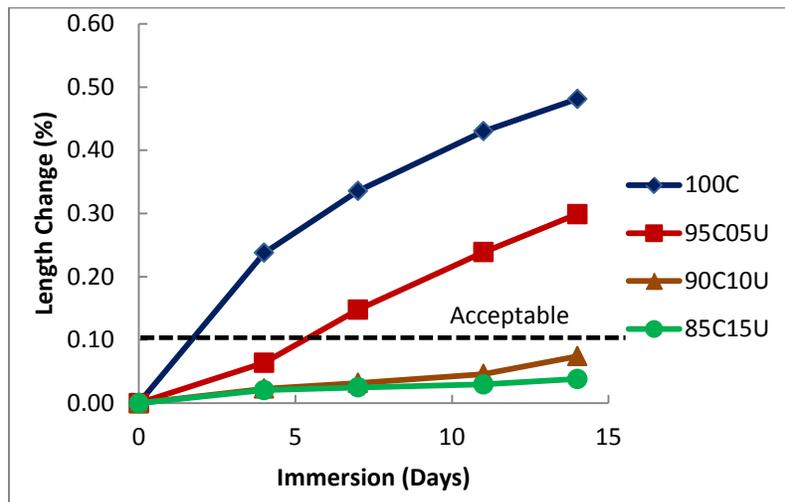


Fig. 3.4 ASR expansion of mortar specimens containing Ultrafine pumice at 0, 5, 10, or 15% replacement of cement and moderately reactive fine aggregate (MRA3).

Table 3.6 ASR Expansion of MRA3 at 16 days

Mixture ID	ASR % Length Change	Rating
100C	0.481	Deleterious Expansion
95C05U	0.299	Deleterious Expansion
90C10U	0.074	Acceptable Expansion
85C15U	0.038	Acceptable Expansion

replacement, the magnitude of ASR expansion is similar and below the limit despite the type of fine aggregate (Fig. 3.5). The results confirm that each reactive aggregate source can require different levels of pumice replacement to produce acceptable ASR resistance.

There is no further increase in ASR resistance when excess amounts of pumice used than required to produce acceptable expansion.

3.4.2 Mortar with Highly Reactive Aggregate (HRA) vs. Ultrafine Pumice

Highly reactive aggregate from Snake River Valley, Idaho was tested with 0, 10, and 15 % Ultrafine pumice replaced mixtures until 5 months. The 100% cement mixture (0% pumice) showed a length change of 1.04% at 16 days. This aggregate when used without pumice in a mortar specimen produced an expansion of 10 times higher than the acceptable limit in the accelerated ASR environment. For these highly reactive fine

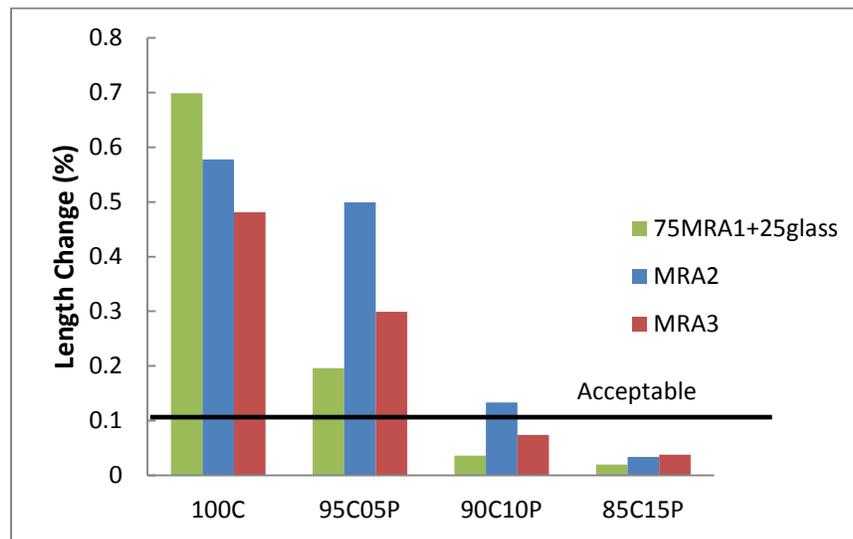


Fig. 3.5 Comparison of ASR expansion after 16 days between different moderately reactive fine aggregates and Ultrafine pumice at 0, 5, 10, and 15% replacement of cement in mortar.

aggregate mixtures, a minimum pumice replacement of 15% is required to produce acceptable length change of 0.09% (Table 3.7). Even at 10% pumice replacement, there is significant reduction in the expansion compared to control mix containing 100% cement. This shows the effectiveness of pumice in reducing the ASR expansion. Ideally,

the percentage of cement replacement can be chosen based on the reactivity of aggregate.

The 100% cement mixture showed a higher expansion rate at initial age compared to pumice mixtures for all aggregates including HRA (Fig. 3.6). This shows that the ASR reaction slowed down or majority of the reaction completed at later age in 100% cement.

Table 3.7 ASR Expansion of HRA at 16 days

Mixture ID	ASR % Length Change	Rating
100C	1.041	Deleterious Expansion
90C10U	0.247	Deleterious Expansion
85C15U	0.089	Acceptable Expansion

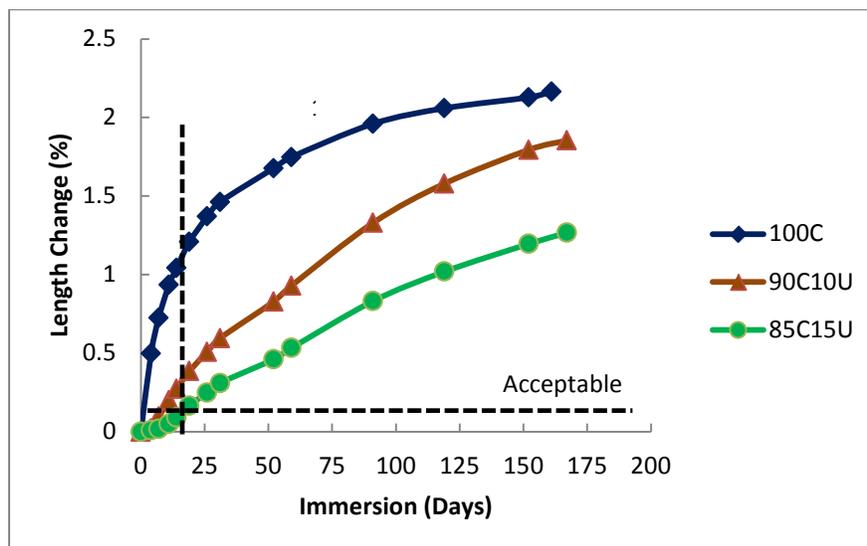


Fig. 3.6 ASR expansion of mortar specimens containing Ultrafine pumice (at 0, 10, or 15% replacement of cement) and highly reactive fine aggregate.

3.4.3 Concrete with Highly Reactive Aggregates vs. Pumice

Among the three different aggregate sources tested, the Snake River valley fine aggregates demonstrated the highest reactivity in the aggressive ASR environment. This same source was selected to study the ASR resistance of pumice blended cement in concrete in addition to mortar samples. Concrete prism specimens of 3''x3''x11.25'' were created with 100% cement and 15% Ultrafine pumice replacement of cement. From ASTM C1567 mortar test results, this 15% pumice replacement was the minimum required amount to produce acceptable ASR resistance. These concrete samples were introduced to the same accelerated ASR environment (80° C and 1 N NaOH solution) as that of the mortar samples.

A similar trend as the mortar samples was found in that the ASR expansion was reduced in the concrete specimens with the presence of the pumice as a SCM. The ASTM C1293 standard method for concrete ASR testing sets an acceptance limit at 0.04% after the concrete specimens are in solution for 1 year of time and at a lower temperature environment. Because this test procedure is modified from the ASTM C1293 to a higher temperature, there is no fixed limit value that would indicate the acceptance level of this pumice blended concrete. Still, the pumice at 15% replacement of cement in concrete specimens showed negligible expansion compared to 100% cement in concrete mixture, even up to 50 days of immersion. The expansion levels were 0.77% for 100% cement and 0.06% for the 15% pumice mixture by 50 days of immersion in the accelerated ASR solution (Fig. 3.7). The result shows that using 15% pumice as an SCM is very effective in resisting the ASR expansion.

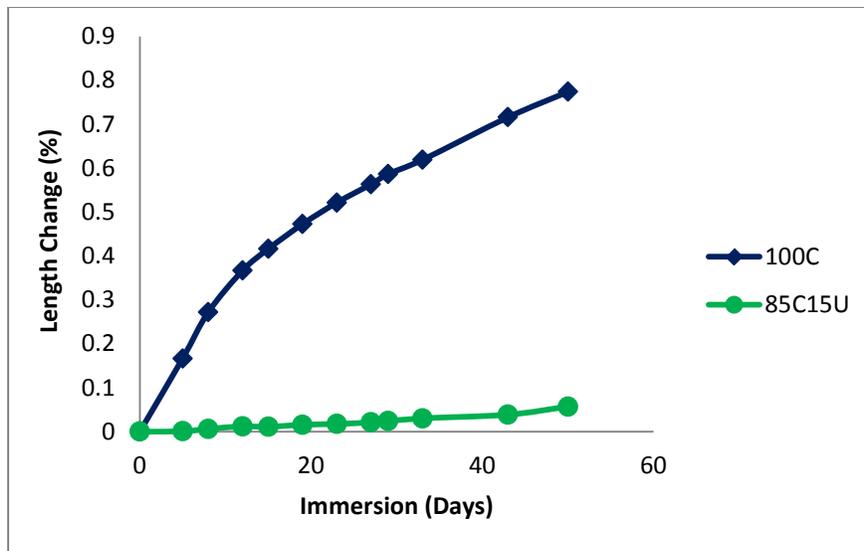


Fig. 3.7 ASR expansion of concrete specimens containing Ultrafine pumice (0 and 15% cement replacement) and highly reactive coarse and fine aggregates.

3.4.4 Repeatability of Test Results with Pumice Blended Cement

The 100% cement and 85% cement 15% Ultrafine pumice mortar specimens were tested with highly reactive aggregate for ASR expansion according to ASTM C1567. An old set of data was tested in spring 2013 until 14 days and the new data were tested in summer 2013 until 15 days. All the data showed 15% pumice replaced mixture reduced the ASR expansion from 1.04% to an acceptable limit ($\leq 0.1\%$) at 14 days (Fig. 3.8). All the data showed a similar trend in resisting the ASR expansion.

3.4.5 Reason for ASR Mitigation

The four factors which influence ASR in a concrete structure are alkali content, moisture, siliceous aggregate, and free calcium hydroxide (CH). If the system is starved from any of these influencing factors, it is possible to mitigate ASR. In this research, high

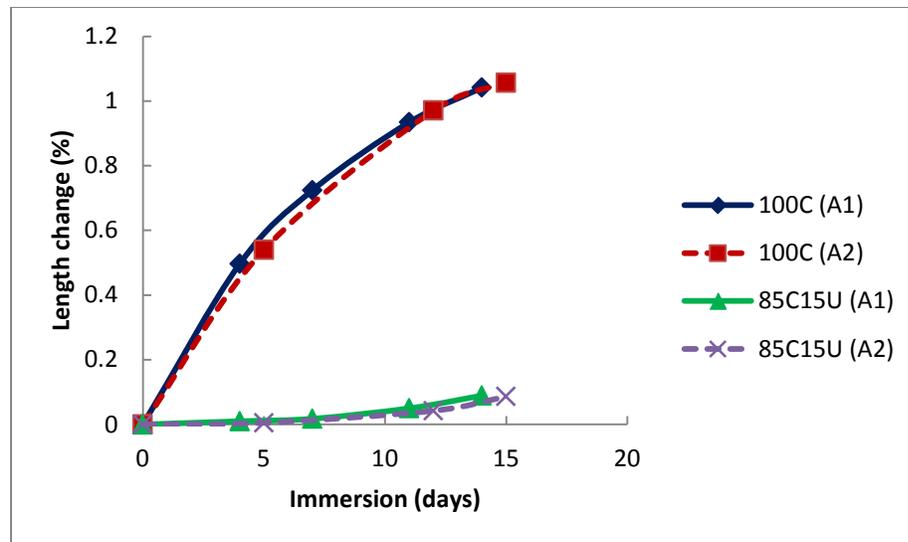


Fig. 3.8 ASR expansion of 0 and 15% pumice blended concrete mixtures tested at different time period. Pumice mixture showed negligible expansion compared to 100% cement mixture.

alkali content from the cementitious material, along with highly reactive siliceous aggregate and adequate moisture content, were used. Substantial ASR mitigation was witnessed when pumice was utilized as an SCM.

A possible reason could be the reduction of free calcium hydroxide in the system through pozzolanic reaction. The importance of CH in ASR mitigation was indicated and supported by the several other researchers in the past [27-30]. It has been stated that a minimum amount of calcium in the form of CH can lead to the ASR expansion [31]. Also, it has been concluded that complete removal is not necessary to mitigate ASR, but limiting the CH content helps in mitigating ASR expansion [32]. Additional research presented by the authors investigated the amount of CH content variation and the corresponding length change (ASR expansion) across time, by blending cement with the Ultrafine grade pumice [33]. It was found that mixture with less CH produced less

expansion compared to the one with higher CH content at similar age [33]. Hence, the anticipated reason for the pumice success in mitigating ASR expansion is the reduction of CH content across time through pozzolanic reaction.

3.5 Conclusion

The ASR resistance of using pumice as a supplementary cementitious material was studied according to ASTM C1567 and a modified ASTM C1293 on mortar and concrete specimens, respectively. Various percentages of cement replacement (0, 5, 10, 15, and 20%) with pumice were tested to find the minimum amounts of pumice necessary to reduce ASR expansion to acceptable limits, despite the use of potentially reactive fine and coarse aggregates. The study indicated that as the amount of pumice replacement increased in the mixture, the ASR expansion was reduced. The particle size of pumice definitely plays a role in determining the amount of replacement of cement necessary to produce acceptable expansion. The exact minimum amount of pumice replacement needed to reduce the expansion to acceptable limit depends on the reactivity of the specific aggregate type or aggregate blend used in the mixture, as well as the fineness of pumice grade. Finer pumice was found to be more effective at reducing ASR expansion than coarser pumice grades. For the pumice grades and specific aggregates used in this study, a 10-15% amount of pumice replacement of cement in mortar was required to produce an acceptable ASR expansion of <0.1% in an aggressive environment. When added in concrete with highly reactive coarse and fine aggregate, while also submerged in a high alkaline solution environment and high temperature of 80 °C, a 15% replacement of pumice for cement was found to significantly reduce the expansion of ASR.

Even though the reactive aggregates were from different sources, the pumice studied here as an SCM was able to resist ASR expansion. Effectiveness of pumice in reducing ASR expansion for various reactive aggregates was studied, but it may also be important to study the role of the high alkali content of pumice for reducing the ASR expansion. If an excessive amount of pumice replacement is used in a mixture, more than is required for ASR resistance, it may not provide any additional benefits on reduced expansion. Depending on the reactivity of the aggregate and strength requirements, an optimum percentage of pumice replacement needs to be found. The test conducted in this research showed 15% replacement is sufficient even for very high reactive aggregates. By using a pumice blended mixture in the industry, it is possible to produce durable concrete structures.

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CHAPTER 4

INFLUENCE OF PUMICE ON CALCIUM HYDROXIDE CONTENT IN AN AGGRESSIVE ALKALI-SILICA REACTION*

4.1 Motivation

The previous research in Chapters 2 and 3 indicated a substantial reduction in ASR expansion occurred for various reactive aggregates in concrete with the use of the natural pozzolan pumice. Despite having a high alkali and silica content, pumice was able to resist the ASR expansion. It is essential to investigate why this particular pumice is effective in mitigating ASR expansion, and especially effective compared to other durability mechanisms. By understanding the mechanism, it is possible to effectively design with other pumice deposits or other materials to resist ASR expansion.

4.2 Abstract

The four essential factors that produce an expansive alkali-silica reaction (ASR) in concrete are the presence of alkalis, siliceous aggregate, moisture, and free calcium hydroxide. If concrete is starved of any one of these essential components, the expansion can be mitigated. For economical and long-term durability reasons, the most common

* U. Ramasamy, A.C. Bordelon, T.A. Ring, and P. J. Tikalsky, "Influence of Pumice on Calcium Hydroxide Content in an Aggressive Alkali-Silica Reaction," submitted to *Journal of American Ceramic Society*, (2014).

solution to reduce ASR expansions is through the use of pozzolans that consume the calcium hydroxide (CH) and reduce the moisture migration in concrete. The research on use of a finely ground pumice as a pozzolan or supplementary cementitious material (SCM) indicated a significant reduction in ASR expansion. This project quantified the amount of CH and determined its importance on the ASR expansion of mortar bars using pumice, especially in an aggressive environment (1 N NaOH solution and 80 °C). Thermo-gravimetric analysis and X-ray diffraction were used to quantify the relative amount of CH across time. Mortar specimens containing pumice as SCM and 100% cement tested at various ages for determining how much of CH and the length changes across time. Pumice specimens showed lower CH content and less expansion compared to 100% cement specimens in an aggressive environment.

4.3 Introduction

The durability of structures is a major issue for the concrete industry, which has led to substantial rehabilitation and consequentially substantial expenses. A special type of concrete deterioration identified as alkali-silica reaction (ASR)¹ occurs in various types of concrete structures, including dams, bridges, pavements, and other structures. ASR is the reaction between alkalis in cement paste and certain unique siliceous minerals in aggregate in the presence of sufficient moisture. The product of alkali-silica reaction called ASR gel may cause significant expansion as it draws water from the surrounding environment and creates cracking of the concrete.

The four essential factors that produce an expansive ASR in concrete are the presence of alkalis, siliceous aggregate, moisture, and free calcium hydroxide (CH). If

concrete is starved of any one of these essential components, the expansion can be mitigated. Starving alkalis from cement is challenging because of the high energy cost for reducing alkalis in the production of cement. Moisture is always present in concrete and is a key component in making the concrete stronger with time. The siliceous aggregates can be avoided if identified as problematic for ASR durability. Starving free calcium from the system can also be advantageous for improving durability of the concrete. Reducing free calcium hydroxide has been achieved by using a pozzolan.

Fly ash or other pozzolans are commonly one of the mitigation materials added to concrete that reduce the calcium hydroxide present in hardened concrete.²⁻³ Past experimental studies reported that a minimum amount of calcium in the form of CH is necessary for significant expansion. It has been stated that presence of free CH is the essential condition for destructive ASR.⁴ Struble⁵ concluded that in the presence of a sufficient amount of silica and alkalis other than calcium, silica dissolves and remains in the solution without causing any distress to concrete. Additional research has confirmed that the alkali-silica-gel formation occurs only in the presence of calcium hydroxide.⁶⁻¹⁰ A previous study suggested that complete removal of CH is not necessary, but limiting the calcium hydroxide content helps in arresting further ASR formation². The previous research indicated a substantial reduction in ASR expansion occurred for various reactive aggregates in concrete with the use of the natural pozzolan pumice.¹¹ Information on how this particular pumice reduces the ASR expansion and how it influences the CH content will benefit the cement and concrete industry.

The research scope of this paper is to quantify the amount of CH in mortar containing pumice as a pozzolan, as well as determine the CH content relation to the

amount of expansion both for the mortar exposed to an accelerated ASR environment. Thermo-gravimetric analysis (TGA) and X-ray diffraction (XRD) were used to quantify the relative amount of CH across time. These analyses are used to demonstrate how the amount of pumice replacement of cement correlates to the rate of CH reduction and a subsequent reduction in ASR expansion.

4.4 Materials and Methods

4.4.1 Materials

The chemical composition of Type I portland cement and pumice used in this research is shown in Table 4.1. Pumice used in this research had an average particle size of 3.9 μm , which is approximately four times finer than the portland cement. The mortar samples contained a highly reactive fine aggregate from Snake River Valley, Idaho. Two mixtures variations were made for the mortar samples: with either 100% cement (labeled as “100C”) or with 85% cement and 15% Ultrafine pumice (“85C15U”) as the total cementitious component in the mortar. The mixtures followed the recommended proportioning from ASTM C1567 accelerated mortar bar test¹² and had water to cementitious ratio of 0.47.

4.4.2 Experimental Methods

4.4.2.1 Mortar Bar Specimen Preparation

For each mixture set studied, six mortar bars were prepared, such that four bars were used for length change measurements across time, and two were used for measuring calcium hydroxide content over time. The mortar bars of size 25.4 mm x 25.4 mm x

Table 4.1 Chemical Analysis Result from XRF test ¹⁴

	Type I Cement	Ultrafine Pumice
SiO₂	19.7	69.75
Al₂O₃	5.1	11.18
Fe₂O₃	2.5	1.04
CaO	62.6	0.97
MgO	2.4	0.25
SO₃	3.8	-0.04
Na₂O	-	2.34
K₂O	-	4.79
Total	98.43	90.42

285.75 mm (1 inch x 1 inch x 11.25 inch) were prepared in accordance to ASTM C1567. Sets of the mortar specimens were cured in two different conditions: at a room temperature with a continuous water saturation environment or at a high temperature (80 °C) accelerated ASR environment of 1 N NaOH mixed with di-ionized water solution.

4.4.2.2 ASR Environment Specimens

Specimens with each aggregate cementitious combination were stored in separate storage containers. Storage containers were filled with 1 N NaOH solution and kept in an oven at 80 °C to create the accelerated ASR environment. Four 100% cement specimens for length measurement were stored in one container C1 and the two used for measuring calcium hydroxide were stored in a different container C2. The same procedure was followed for storing 85C15U mixture specimens in containers C3 and C4, respectively. At the designated test days, samples selected for length measurements were removed and quickly measured within 10 seconds. Samples for the TGA and XRD tests were allowed to cool to room temperature after sitting outside the oven for a ½ hour.

4.4.2.3 Control Environment Specimens

A separate set of storage containers were filled with de-ionized water and were kept at room temperature to be used for the control environment specimens. Similar to those samples in the accelerated ASR environment, specimens of each mixture type were stored in separate containers and placed in the container after 24 ± 2 hours of casting. At the test days, length measurements and calcium hydroxide analysis measurements were done after samples were temporarily removed from the containers.

4.4.3 Analytical Tools

X-ray diffraction can be used to track the relative amount of CH across time in concrete specimens, whereas the thermo-gravimetric analysis can be used to quantify the actual CH amount at a given time. The calcium hydroxide content was quantified at 7, 14, 28, 56, and 93 days across time from casting. Three replicates were tested with the TGA and one sample was tested with the XRD analysis technique.

4.4.3.1 Sample Preparation for TGA and XRD

A specimen size of 25.4 mm x 25.4 mm x 38.1 mm (1 in x 1 in x 1.5 in) was cut from the mortar bar 25.4 mm x 25.4 mm x 285.75 mm (1 in x 1 in x $11^{1/4}$ in) at one end to eliminate any potential effects of chemical intrusions. The remaining part of the mortar bar was then sawed and a 25.4 mm x 25.4 mm x 25.4 mm (1 in x 1 in x 1 in) sample was cut and crushed into smaller pieces using a chisel and hammer. The sample was manually crushed into a powder form using a mortar and pestle. Roughly 25-35 mg of the crushed powder was collected and used in each TGA and XRD analysis. During the time of

running one sample for TGA or XRD, the remaining powder sample was covered in an airtight system to reduce outside humidity effects to be used in concurrent aged test samples.

4.4.3.2 Thermo-Gravimetric Analysis

TGA measurements were performed with a Simultaneous DSC (differential scanning calorimetry) -TGA Q Series instrument (SDT Q600, TA Instruments). The device measures the weight change and heat flow associated with the phase transitions and reactions of materials over a temperature range. By measuring TGA and DSC simultaneously in the same instrument, sampling variability can be reduced in data analysis. Nitrogen gas was used as a purging gas to eliminate heating-induced carbonation, which will otherwise cause a mass increase at a given temperature and affect other decomposition reactions. For the analysis, a sample was placed in a quartz pan and heated up to 650 °C with a constant heating rate of 10 °C/min. The sample was heated to remove water and then there were some relatively distinct intervals where specific phases decompose. The decomposition of CH of hardened cement occurs approximately between 350 °C and 550 °C.¹³ The weight of the TGA sample reduces as the temperature increases due to the transition and associated reaction of that sample.

4.4.3.3 Interpretation of TGA Curve

There is no universally accepted procedure to determine the CH content from the TGA curve. The minimum negative peak of the DSC curve between the temperature ranges of 350 to 550 °C corresponds to the breaking down of CH. The associated weight

change was due to loss of water molecules bound in the CH. A more specific temperature range that corresponds to the start and end points of each sample's local minimum peak of DSC curve was estimated, and then used to determine the corresponding change in weight from this starting temperature and ending temperature. Alternatively, a fixed temperature approach to determine CH content would be considered inaccurate because several variable factors such as crystallinity of material, fineness, quantity of sample, and the instrument pressure would alter the actual temperature of the CH decomposition each time.¹⁴

The calculated weight loss for each sample gives the amount of water loss associated with decomposition of CH. Equation 4.1 was used to determine the Ca(OH)₂ or CH content in g/g of mortar sample¹⁵:

$$CH = \frac{74.1}{18.0} \frac{(M_{start}^s - M_{end}^s)}{M_c} \quad (\text{Equation 4.1})$$

where M_{start}^s and M_{end}^s are the start and end point mass (mg), respectively, of TGA curve corresponding to the Ca(OH)₂ decomposition, and M_c is initial mass (mg) of sample taken for TGA analysis. The ratio 74.1 to 18.0 is the molar weight ratio of Ca(OH)₂ to water, included to determine the amount of CH that is bound to the mortar sample.

4.4.3.4 X-Ray Diffraction

XRD measurements were performed using a X-ray diffractometer (Philips X'Pert, PANalytical) using CuK α radiation (wavelength $\lambda = 1.54 \text{ \AA}$). The samples from the aggressive ASR environment were scanned between 5° and 80° 2 θ with an X'celerator detector. No samples were analyzed from the control environment. The powder samples of each mixture were tested in the XRD at 7, 14, 28, and 56 days age. Due to a specific

powder diffractometer detector malfunction, a thin film analysis was performed at the 93rd day.

4.4.3.5 Interpretation of XRD Graph

X'Pert Highscore Plus (version 2.2d) software was used to identify and match angles corresponding to peaks of quartz and calcium hydroxide. Trace amounts of other compounds were found in some samples, but those were not included in the analysis. Quantification of those compounds across time was performed using software based on a Rietveld refinement method. The Rietveld refinement quantification is based on the relative amount of the identified compounds. At later sample ages, the concrete was found dominated by silica so CH cord number was used to identify calcium hydroxide compound.

4.5 Results

Pumice-replaced mixtures immersed in an aggressive environment of 80 °C and 1 N NaOH show less calcium hydroxide contents and negligible ASR expansion, primarily at the initial ages, compared to 100% cement mixtures in the same environment. The length change results from the ASR mortar test were used to examine how the aggressive ASR expansion may have had a correlation on the CH content, determined from both the TGA and XRD analysis in a mixture with and without pumice at an elevated temperature.

4.5.1 Length Change Measurements for ASR and Control Environment Specimens

All specimens in the aggressive ASR environment showed increasing expansion across time, especially with a higher expansion rate at earlier ages of cement hydration.

Among these specimens, those with 15% pumice replacement of cement showed a lower magnitude of expansion compared to those without any pumice (Fig. 4.1). The specimens in the control environment showed negligible expansion, compared to the ASR environment specimens (Fig. 4.1). Among the control environment samples, those with 15% pumice replacement for cement showed lower magnitudes of expansion compared to 0% pumice replacement (Fig. 4.2).

4.5.2 Thermal Gravimetric Analysis (TGA)

4.5.2.1 TGA Curve

The mass change associated with the CH decomposition was identified using the minimum negative peak in the heat flow curve. As the time continued, the magnitude of associated weight loss from the TGA decreased (Fig. 4.3) for the samples in an aggressive ASR environment, which implies the reduction in CH content as the time passes. Samples in the control environment were interpreted to have almost the same magnitude of weight loss associated with CH content for each age. For both environment conditions, those samples with 15% pumice replacement of cement showed reductions in the CH content compared to those with 0% pumice. The decomposition of CH happened between 390 °C and 460 °C for all mortar specimens across time. Details on the measured temperatures and CH contents for each sample can be found in the Appendix. A summary of the CH content versus time for both mixtures is shown in Fig. 4.4 and Fig. 4.5.

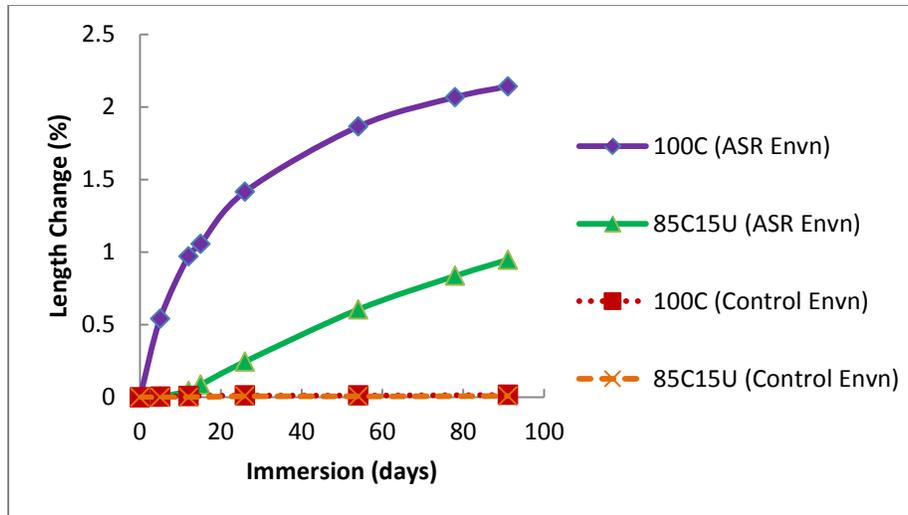


Fig. 4.1 Average length change results of mortar bars in an aggressive ASR environment (80 °C and 1 N NaOH) and control environment (water saturated and room temperature). Mortar bars made with highly reactive aggregate and either 100% Type I cement or 85% Type I cement and 15% pumice. Solid lines show the specimen in ASR environment, and 100C specimen expansion rate was substantially higher than 85C15U specimen. Dotted line shows the specimens in water curing environment, and negligible expansion compared to ASR environment specimens.

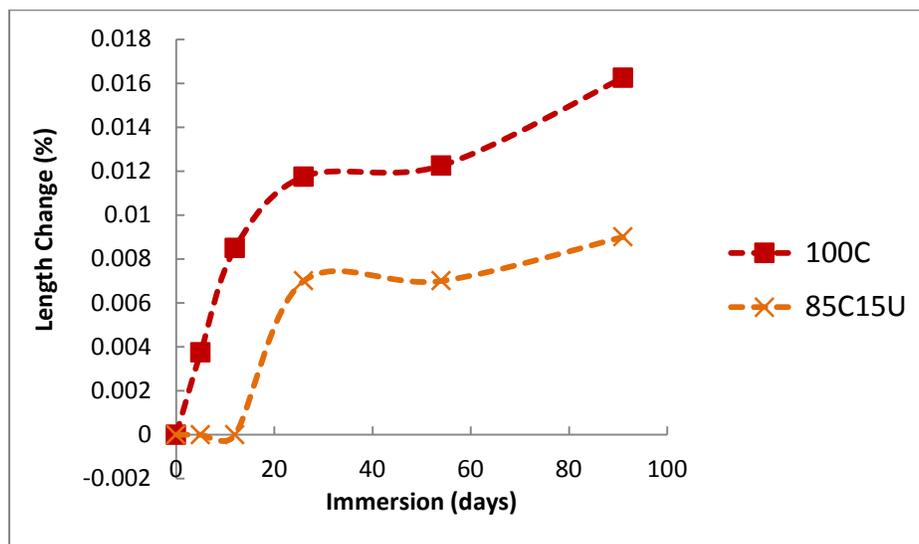


Fig. 4.2 Length change results of control environment specimens (zoomed view of Fig. 4.1). Pumice replaced specimens showed lesser length change compared to 100C specimens.

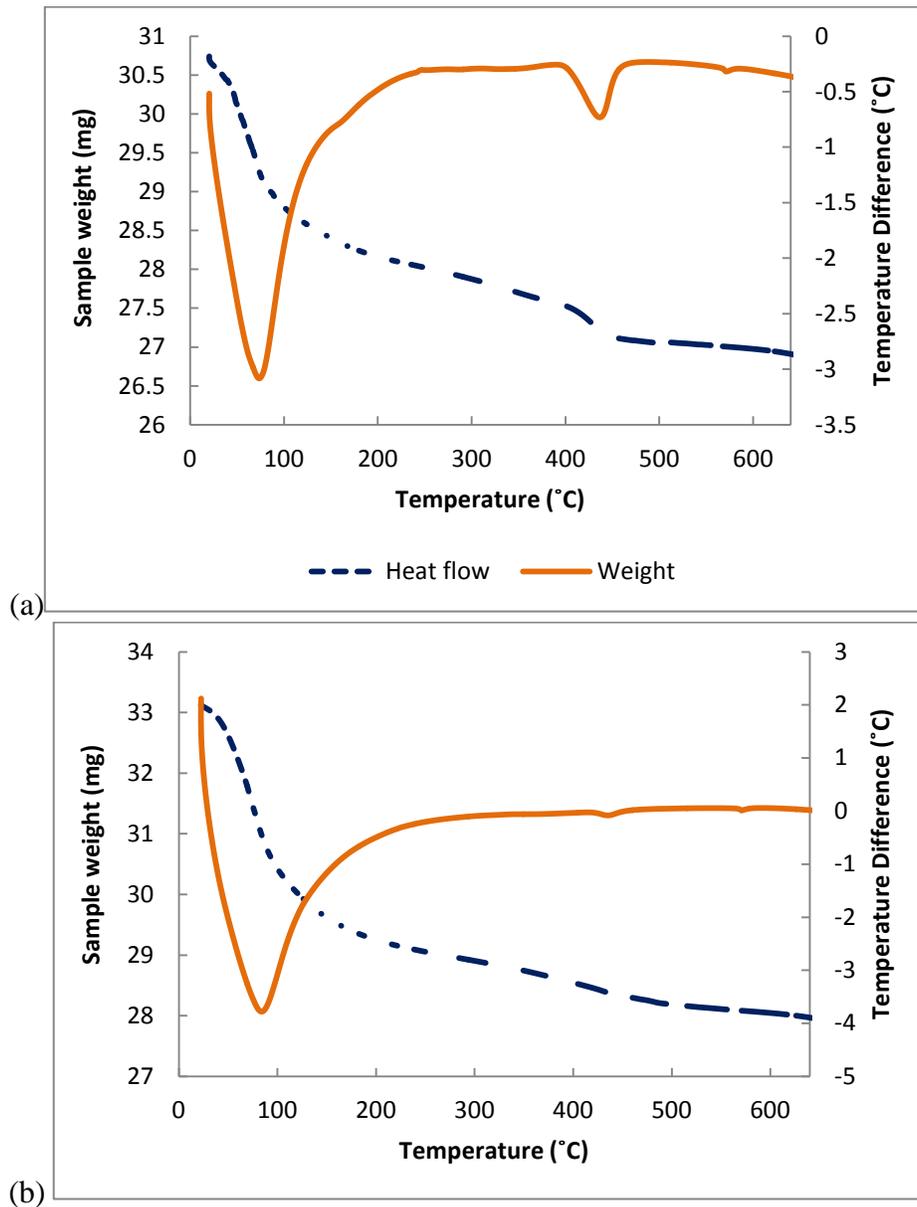


Fig. 4.3 TGA heat flow (plain line) and weight change (dotted line) of 100C specimen in ASR environment (80 °C and 1 N NaOH) for (a) 7 days and (b) 91 days for the first replicate. The local minimum peak of heat flow curve decreased across time implies the reduction in CH content.

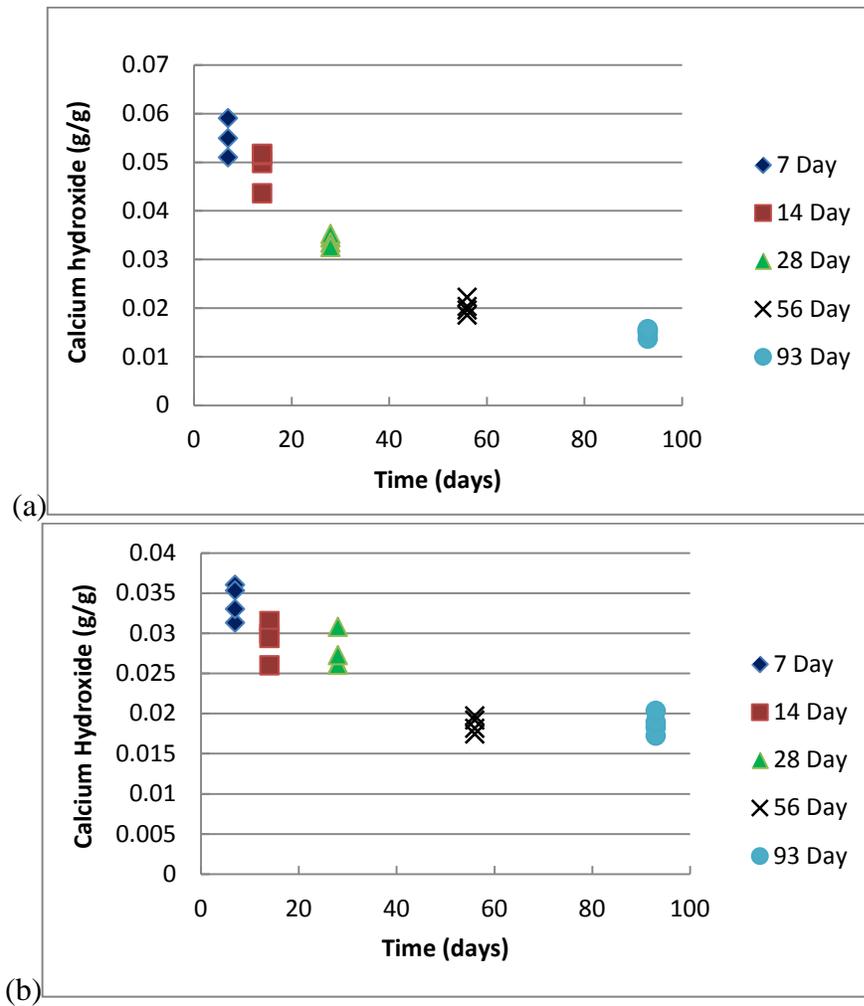


Fig. 4.4 The CH content of (a) 100C specimens and (b) 85C15U specimens in ASR environment (80 °C and 1 N NaOH) across time. At each test day, four samples were tested and CH was calculated using TGA data. Maximum coefficient of variation between the 100C replicates was 0.077 and 85C15U was 0.080.

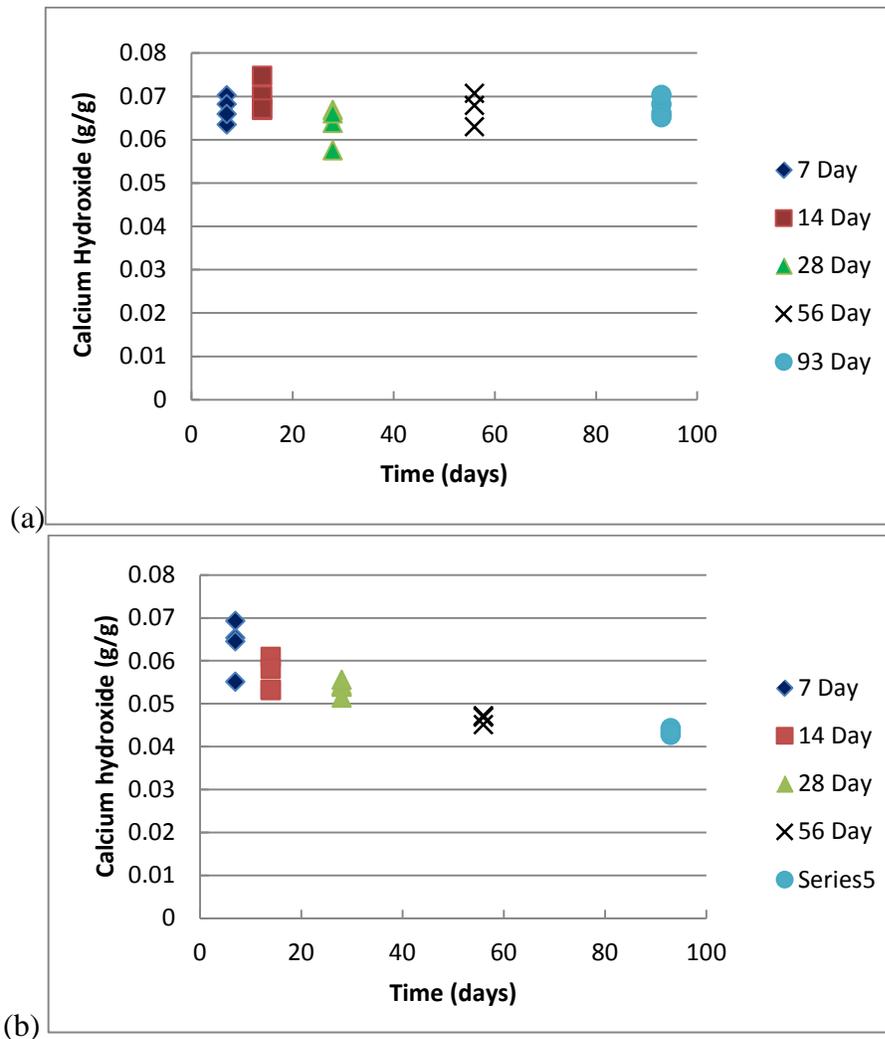


Fig. 4.5 The CH content of (a) 100C specimens and (b) 85C15U specimens in control environment across time. At each test day, four samples were tested and CH was calculated using TGA data. Maximum coefficient of variation between the 100C replicates was 0.066 and 85C15U was 0.095.

4.5.2.2 Variability between Replicates

At each day, four replicates samples were tested from both an aggressive ASR and control environment with TGA. In the aggressive ASR environment, the maximum coefficient of variation between the four replicate samples of the 0% pumice mixture (Fig. 4.4) was 0.077 and for 15% pumice mixture was 0.080. For the specimens in the control environment (Fig. 4.5), the maximum coefficient of variation of the 0% pumice mixture was 0.066 and 15% pumice mixture was 0.095.

4.5.2.3 Calcium Hydroxide Content

(a) ASR Environment Specimens: The amount of CH content decreased across time for both the 100% cement and pumice blended cement specimens in the ASR environment. Due to the reduced cement content of the pumice blended mixture, a reduced CH content was analytically calculated based on the 100% cement TGA curve. The pumice-replaced specimens showed less CH content compared to 100% cement specimens at initial age (Fig. 4.6). At later ages, the CH content of pumice-containing mixture remained similar to that of 100% cement mixtures.

(b) Control Environment Specimens: The CH contents of control environment specimens (both 100% cement and 85% cement 15% pumice) were higher than specimens cured in an aggressive ASR environment. The CH content remained fairly constant with time in the 100% cement mixture specimens. The addition of pumice replacement in this control environment, like the ASR environment, showed reduced CH contents compared to the 100% cement specimens (Fig. 4.7). In the pumice-containing mixture, CH content slightly decreased across time and showed a lesser CH content than

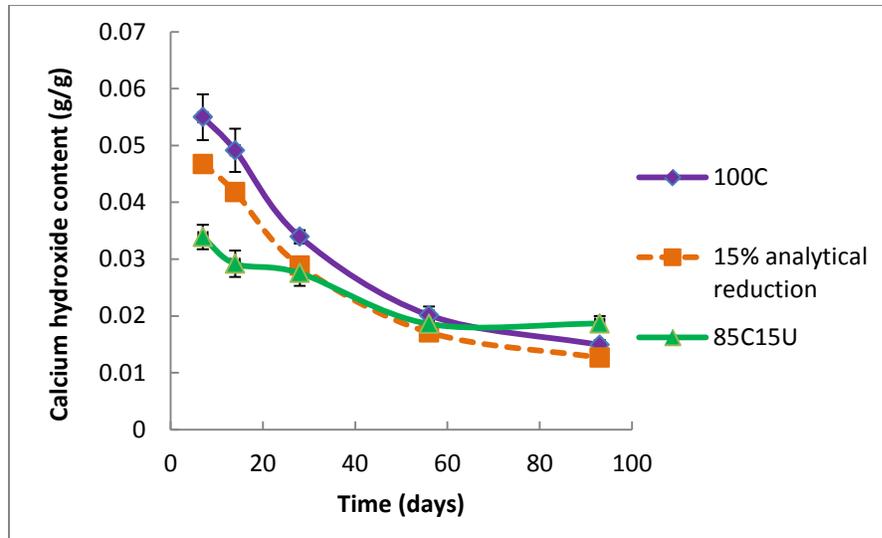


Fig. 4.6 Average CH content determined from TGA of mortar specimens in an alkali-silica reaction (ASR) environment (80 °C and 1 N NaOH) across time. The 15% cement replaced specimens (85C15U) showed less CH content compared to 100C (100% cement) at initial age. The CH content decreased across time in 100C by participating in ASR and 85C15U by participating in pozzolanic reaction and ASR. A calculated 15% analytical reduction (dotted line) was shown to represent the potential 85% cement content in the pumice replacement samples. Error bar with standard deviation was plotted for 100C and 85C15U curve to show the possible variation in the data.

the 15% analytically reduced curve.

4.5.3 X-Ray Diffraction (XRD)

Data evaluated from the XRD (Table 4.2) confirmed the CH trend obtained from the TGA for the aggressive ASR environment. The CH content of 15% pumice-containing specimens was lower than 0% pumice mixtures at initial age. For the later ages of the mortar, the CH content of pumice-containing specimen remained almost the same, whereas the 100% cement specimen showed CH decreasing with age.

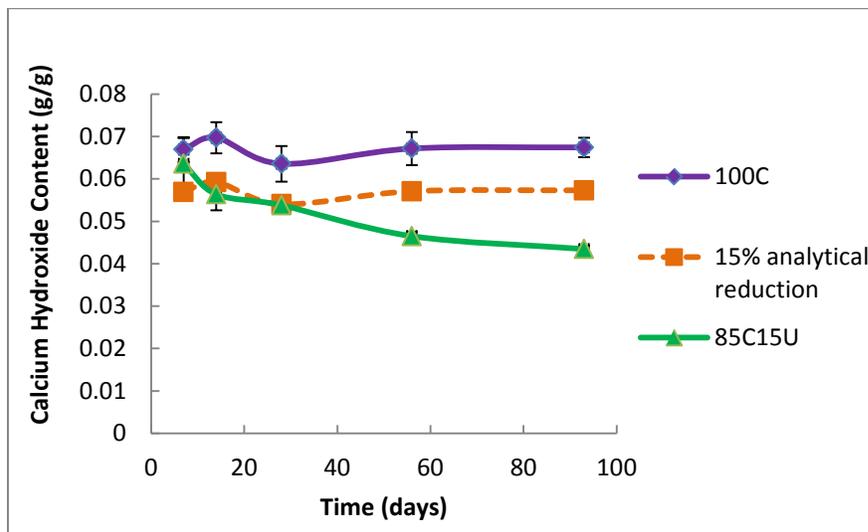


Fig. 4.7 Average CH content determined from TGA of mortar specimens in control environment across time. The 15% pumice specimens (85C15U) showed less CH content compared to 100C (100% cement). A calculated 15% analytical reduction (dotted line) was shown to represent the potential 85% cement content in the pumice replacement samples. Error bar with standard deviation was plotted for 100C and 85C15U curve to show the possible variation in the data.

Table 4.2 Calcium hydroxide content of ASR environment specimens

Specimen Age (Days)	100% Cement		85% Cement 15% Ultra	
	Quartz (%)	Ca(OH) ₂ (%)	Quartz (%)	Ca(OH) ₂ (%)
7	75.8	24.2	88.5	11.5
14	83.1	16.9	87.6	12.4
28	87.4	12.6	89.1	10.9
56	92.4	7.6	91.2	8.8
93	96.8	3.2	92.9	7.1

*Calcium hydroxide content of mortar specimens in an ASR environment (80 °C and 1 N NaOH) across time from XRD analysis.

4.6 Discussion

The mortar samples with 15% pumice replacement of cement had lower CH content compared to those with 0% pumice as confirmed quantitatively by TGA and indicated by XRD. Due to higher temperature and presence of NaOH solution, the expansion of mortar bars in ASR environment was substantially higher than control environment specimens.

4.6.1 ASR Expansion

The ASR length change of 100% cement specimens showed a steeply increasing expansion at early age. The initial gel formation from the ASR is highly accelerated because of higher CH content in the mixture. It is presumed that once the majority of the CH content has been utilized in precipitating ASR gel, any remaining CH content in the mixture slowly contributes to further expansion, thus reducing the expansion rate at later ages. The pumice replaced mixture showed a lower expansion rate at the initial ages possibly due to formation of C-S-H gel instead of ASR gel because of lower CH content. The expansion rate increase at the later age may be because complete utilization of pumice led to increased CH content, as CH content was produced continuously from hydration reaction. When the CH content increased to a certain level, increased expansion rate was observed compared to early age.

4.6.2 TGA Analysis

The TGA shows pumice played a significant role in limiting the CH content. The start point and end point selection of temperature is very critical in determining the CH

decomposition. TGA data interpretation is subjective because of selection of start and end point temperature based on the minimum negative peak in the heat flow curve. Due to uncertainty with each data point, replications to demonstrate the findings are definitely needed. Ambiguity in the TGA data is because of sample heterogeneity, smaller size, fineness, and particular sample composition. By having four replicate tests of the same sample in both the environments, the maximum coefficient of variance was less than 0.095.

4.6.3 XRD Analysis

XRD data qualitatively confirm the CH trend obtained from TGA for 100C and 85C15U specimens in ASR environment. Reason for the early age and later age CH trend in the XRD data was the same as discussed in TGA data. In the XRD analysis, the quantification was based on the relative intensity of CH and quartz peaks rather than the quantity of one particular compound. The method used to quantify CH assigns 100% among the selected compounds. Neglecting the trace of other compounds in the sample may induce error in quantifying the exact amount. By tracking the intensity of CH peak with respect to quartz peak across time, the trend in CH content was predicted.

4.6.4 Role of Calcium Hydroxide Content

4.6.4.1 ASR Environment

The pumice-replaced mixture showed less CH content than 100C at the initial age because of early pozzolanic reaction. Pumice starts to react from the time it is introduced in the mixture. The CH content of 100C and 85C15U specimens in ASR environment

decreases across time by participating in ASR and pozzolanic reaction, respectively. The 15% analytically reduced curve (Fig. 4.5) accounts for reduced CH production due to reduced cement content in 85C15U mixture. Still, CH content of 85C15U mixture was less than 15% analytically reduced curve at early age that shows pumice plays a significant role in reducing the CH content by participating in early pozzolanic reaction. Once the replaced pumice has been utilized in the mixture at early age, reactive aggregate in 85C15U mixture may start to take part in ASR reaction at later age. However, the length change of 85C15U specimens was less than 100C specimens. The other reasons could be ASR gel in 85C15U specimens may not consume enough CH for its growth as it does in 100C specimens and the pozzolanic reaction may become slow at later age. In other words, a limited amount of CH availability (from lower cement contents or from the pumice pozzolanic reaction) may not be enough to grow the ASR gel to a level such that it produces unacceptable expansion. The accelerated environment (80 °C) will also accelerate the cement hydration reaction that results in the majority of hydration reaction and the associated CH production completed at the early stage. By participating in ASR reaction, CH content reduced across time for 100C mixture and by pozzolanic reaction for 85C15U mixture. The reduction rate of CH content was higher at initial age because of higher availability of CH in the mixture, while at later ages, the ASR expansion rate was reduced due to lower CH production rate from the remaining hydration reaction.

4.6.4.2 Control Environment

Even in the control environment, pumice-replaced specimens showed less CH content, which shows its participation in the pozzolanic reaction at early age. The CH

content of 100C and 85C15U specimens in control environment was higher than the ASR environment specimens because of nonparticipation in ASR reaction. At early age, the CH content of 100C samples gets leveled off because of various hydration reactions occurring at different time intervals and then it is almost the same at later age. The CH content of pumice replaced specimens at 7 days was high compared to 15% analytically reduced curve (Fig. 4.6) because pumice has been waiting for the cement to produce enough CH for the pozzolanic reaction to take place. At later age, the CH production due to hydration reaction is counteracted by pozzolanic reaction of pumice-replaced mixture, which results in less CH content compared to 100C and 15% analytically reduced curve. Also, at later age, the reason for leveled CH content in both the mixtures may be due to the diffusion of excess CH (produced from various hydration reactions) in the water. Control environment specimens show the real case scenario, whereas ASR environment specimens (accelerated condition) were studied to demonstrate the importance of CH content in ASR expansion.

4.6.5 Correlation Between ASR Expansion and CH Content with Pumice

At an initial age, the use of pumice limited the expansion of mortar bars in the ASR environment while continuously decreasing the CH content. Specimens with a higher initial CH content (those with 100% cement and no pumice) showed greater expansion compared to mixtures with pumice that exhibited lower CH contents. It appears that at later ages, the CH content in the pumice-containing mixtures reached a minimum plateau and at which time the ASR expansion began to occur in the same sample. This may be due to the availability of sufficient CH content to take part in ASR

gel precipitation at later age, after the majority of pozzolanic reaction was completed.

Thus, the role of pumice may delay ASR expansion by primarily consuming the CH until

low amounts of CH are achieved and then ASR is mitigated.

4.7 Conclusion

The influence of pumice on calcium hydroxide content and ASR expansion of mortar bars was studied by measuring the CH content and ASR expansion simultaneously for 100% cement and 15% pumice-replaced mixture. The amount of CH in a specimen is quantified using TGA and XRD across time and the respective ASR expansion of mortar bars were measured at the same time according to ASTM C1567. The following conclusions were determined:

1. In an aggressive ASR environment (1 N NaOH solution and 80 °C), 15% pumice-replaced cement in mortar specimens containing highly reactive fine aggregates showed less CH content and less ASR expansion compared to 100% cement specimens.
2. In a typical curing environment (water submersion and room temperature), 15% pumice-replaced specimens showed less CH content and length change compared to 100% cement specimens. This indicates pumice is an early pozzolan.
3. It was found that a pozzolan such as Ultrafine pumice used as a replacement of cement at 15% reduced the CH content by 40% amount, and also exhibited a reduced ASR length change by 95% after 14 days in an aggressive environment. By knowing how this pumice helps in mitigating ASR expansion, it is possible to efficiently design other materials to resist ASR.

4. Among analysis tools, the TGA and DSC technique were found to be the best methods to quantify the CH content. Despite the subjectivity of interpreting data, the TGA method had a low variability between four replicate samples of the same mortar mixture. XRD can be used with samples to predict a CH reduction trend across time from the addition of such pozzolans.
5. Tools such as TGA and XRD can be used to determine the remaining CH content in existing structures that either have or do not show signs of ASR. This will provide insight into what the minimum amount of CH is that might be present in the concrete that leads to ASR susceptibility. This can also be used as a test method in future for determining the existing structures ASR susceptibility.

The results from this research indicates CH content plays a significant role in ASR expansion and pumice helps in reducing the CH content in a mixture at an elevated temperature. Hence, if concrete can be designed or altered in a way that has the ability to reduce CH content in the hardened mixture, the structure made with this concrete will have a long-lasting durable service life.

4.8 References

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

To understand the influence of using pumice as a pozzolan in concrete, material characterization of the pumice and properties of concrete containing different grades of pumice as a supplementary cementitious material were studied in this research. The use of a finely-ground pumice that is approximately four times finer than cement was found effective at a cement replacement of approximately 15% in order to provide excellent concrete ASR resistance. At these amounts, the pumice blended mortar and concrete samples were found to be highly effective to reduce alkali-silica reaction gel formation even in the presence of different highly reactive aggregates and high alkali content within the mixture. Some key findings are summarized as follows:

1. The pumice used in this research was determined to be a pozzolanic material and well suited for concrete applications. Mortar containing each grade of pumice (DS200, DS325, and Ultrafine) was found to exhibit significant resistance to ASR expansion, sulfate attack, and chloride intrusion, though the effectiveness of resistance varied with the pumice particle size.
2. The finest grade of pumice ($\sim 4\mu\text{m}$ in diameter) showed superior performance in terms of higher strengths, higher heat of hydration, and improved durability characteristics

when compared to coarser grades (~21 and 45 μm) of the pumice. The 20% replacement of the finest grade of pumice demonstrated statistically similar compressive strengths as 100 % cement, yet the pumice blended mixture had improved durability characteristics.

3. Depending on the reactivity of aggregates and fineness of the pumice, the required minimum amount of pumice replacement to mitigate ASR expansion can vary. The test conducted in this research showed that 15% replacement was sufficient even when using a highly reactive aggregate. An increase in the amount of pumice replacement of cement was found to reduce the ASR expansion. Beyond an optimum amount of pumice, it appeared that no further reduction in ASR expansion was exhibited.
4. To produce similar ASR expansion levels, the required amount of pumice replacement was less for the finest grade compared to the coarser grades of pumice available. For the finest grade of pumice and with the specific aggregates used in this study, a 10-15% replacement of cement by pumice was required to produce an acceptable expansion of $<0.1\%$ according to ASTM C1567.
5. A 15% finely ground pumice replacement of cement showed 40% reduced CH contents and 95% less expansion at 14 days compared to specimens with 0% pumice, both tested at an elevated temperature (80 °C) and high alkali solution environment.
6. At a given specific environment, either at 80 °C with 1 N NaOH solution, or at room temperature with water submersion, the pumice blended mixtures showed lower CH contents and lesser expansion levels compared to cement only mixtures.
7. The CH content plays a significant role in ASR expansion. Hence, if concrete can be

designed or altered in a way that has the ability to reduce CH content in the hardened mixture, the structure made with this concrete is expected to have a long-lasting durable service life.

5.2 Recommendations

1. The minimum amount of pumice needed for a concrete mixture to have ASR resistance, or effective optimization of the pumice for other performance measures, should be determined for each specific case by using the locally utilized cements, aggregates, and appropriately selected curing conditions.
2. If the amount of pumice used in the concrete is more than the minimum requirement for ASR resistance, any additional amount of pumice in the mixture may not provide additional benefits on reduced ASR expansion.
3. Rather than using low alkali cements or avoiding use of siliceous aggregates in a concrete mixture, the use of pumice that is finely-ground and used as a SCM can provide an alternative highly effective solution for durable longer service-life concrete structures.
4. The amount of calcium hydroxide content across time in pumice blended mortar samples was determined using analytical tools like thermogravimetric analysis and X-ray diffraction. TGA can be used to quantify the calcium hydroxide content with an accuracy of $\pm 2\%$ and XRD can be used to qualitatively confirm the presence and relative amount of CH compared to other crystalline materials such as SiO_2 .

5.3 Future Work Suggestions

1. The specific physical structure of the reactions that occur within the pumice blended cement samples can be studied at different time periods under a scanning electron microscope and chemical analysis from energy dispersive spectroscopy. This information may be helpful in verifying that certain formations, possibly ASR gel or calcium-silica-hydrate gel, occur and quantifying the extent of these formations within the pumice blended mixtures.
2. It is hypothesized that the ASR reduction in pumice mixtures may be due to limited availability of CH content; the available amount of CH in the mixtures may not be enough to grow the ASR gel to a level such that it produces unacceptable expansion. The role of CH on ASR resistance can be further studied through mixtures originating with the same cement content and varying pumice amounts.
3. One can use tools such as TGA and XRD analysis to determine the remaining CH content in existing structures that either have or do not show signs of ASR. This will provide insight into what the minimum amount of CH that might be present in the concrete that leads to ASR susceptibility. This can also be used as a test method in future for determining the existing structures ASR susceptibility.
4. Some variation in the CH content using the TGA method is anticipated to be related to the sample preparation. The influence of particle size of the TGA sample and the method of sample preparation, either crushed by hand or mechanical crushing, for quantifying the CH content can be studied in order to provide recommendations to reduce variation for future analysis.

APPENDIX A

CALCULATION OF CH CONTENTS

Table A.1 CH Content of 100% Cement in ASR Environment at Different Times

Sample Name	Mstart (g)	Mend (g)	Mc (g)	CH (g/g)	Average	Standard Deviation	Coefficient of Variation
ASR_100C_7D_1	27.52	27.11	30.74	0.054907	0.0549852	0.004024	0.073185
ASR_100C_7D_2	34.21	33.75	37.13	0.051001			
ASR_100C_7D_3	29.64	29.18	32.07	0.059048			
ASR_100C_7D_4							
ASR_100C_14D_1	31.18	30.81	34.94	0.043594	0.0491504	0.003799	0.077289
ASR_100C_14D_2	27.81	27.43	31.4	0.049820			
ASR_100C_14D_3	27.44	27.05	31.19	0.051475			
ASR_100C_14D_4	27	26.62	30.25	0.051713			
ASR_100C_28D_1	29.4	29.12	33.42	0.034490	0.0339306	0.001173	0.034569
ASR_100C_28D_2	27.88	27.61	31.547	0.035233			
ASR_100C_28D_3	28.46	28.2	32.01	0.033438			
ASR_100C_28D_4	32.59	32.3	36.664	0.032562			
ASR_100C_56D_1	26.85	26.71	31.06	0.018555	0.0201394	0.001526	0.075777
ASR_100C_56D_2	26.43	26.28	30.43	0.020292			
ASR_100C_56D_3	29.2	29.04	33.7	0.019545			
ASR_100C_56D_4	30.8	30.61	35.289	0.022165			
ASR_100C_93D_1	28.44	28.33	33.12	0.013673	0.0149004	0.000875	0.058695
ASR_100C_93D_2	27.5	27.38	32.21	0.015337			
ASR_100C_93D_3	28.21	28.09	33.11	0.014920			
ASR_100C_93D_4	28.89	28.76	34.147	0.015672			

Table A.2 CH Content of 85% Cement and 15% pumice in ASR Environment at Different Times

Sample Name	Mstart (g)	Mend (g)	Mc (g)	CH (g/g)	Average	Standard Deviation	Coefficient of Variation
ASR_85C15U_7D_1	29.17	28.92	32.88	0.031301	0.033897	0.002150	0.063432
ASR_85C15U_7D_2	27.62	27.37	31.18	0.033007			
ASR_85C15U_7D_3	29.85	29.56	33.16	0.036002			
ASR_85C15U_7D_4	27.6	27.34	30.34	0.035278			
ASR_85C15U_14D_1	27.63	27.4	31.68	0.029887	0.029186	0.002315	0.0793165
ASR_85C15U_14D_2	25.14	24.92	28.77	0.031480			
ASR_85C15U_14D_3	30.96	30.74	34.86	0.025980			
ASR_85C15U_14D_4	28.38	28.15	32.21	0.029396			
ASR_85C15U_28D_1	27.77	27.57	31.485	0.026150	0.027551	0.002220	0.0805819
ASR_85C15U_28D_2	26.49	26.3	30.034	0.026043			
ASR_85C15U_28D_3	26.99	26.76	30.758	0.030783			
ASR_85C15U_28D_4	29.38	29.16	33.26	0.027230			
ASR_85C15U_56D_1	27.75	27.6	32.2	0.019177	0.018602	0.001012	0.054418
ASR_85C15U_56D_2	29	28.84	33.48	0.019673			
ASR_85C15U_56D_3	27.59	27.45	31.8	0.018124			
ASR_85C15U_56D_4	28.97	28.83	33.06	0.017433			
ASR_85C15U_93D_1	27.02	26.88	31.58	0.018250	0.018674	0.001290	0.0690698
ASR_85C15U_93D_2	26.43	26.3	31.06	0.017230			
ASR_85C15U_93D_3	28.04	27.89	32.66	0.018907			
ASR_85C15U_93D_4	29.74	29.57	34.46	0.020309			

Table A.3 CH Content of 100% Cement in Control Environment at Different Times

Sample Name	Mstart (g)	Mend (g)	Mc (g)	CH (g/g)	Average	Standard Deviation	Coefficient of Variation
Control_100C_7D_1	29.94	29.42	33.74	0.063446	0.066926	0.002903	0.043371
Control_100C_7D_2	25.08	24.6	28.15	0.070195			
Control_100C_7D_3	28.68	28.15	32.02	0.068140			
Control_100C_7D_4	26.55	26.08	29.35	0.065923	0.0697001	0.003657	0.052468
Control_100C_14D_1	27.33	26.826	31.03	0.066864			
Control_100C_14D_2	28.11	27.55	30.85	0.074727			
Control_100C_14D_3	25.98	25.49	28.78	0.070089	0.0635668	0.004210	0.06623
Control_100C_14D_4	26.43	25.95	29.44	0.067120			
Control_100C_28D_1	29	28.498	32.39	0.063803			
Control_100C_28D_2	28.55	28.03	32.015	0.066864	0.0671564	0.003925	0.058442
Control_100C_28D_3	28.42	27.91	31.79	0.066043			
Control_100C_28D_4	27.84	27.4	31.47	0.057557			
Control_100C_56D_1					0.0674248	0.002291	0.033974
Control_100C_56D_2	28.85	28.31	32.76	0.067857			
Control_100C_56D_3	32.24	31.69	35.98	0.062928			
Control_100C_56D_4	27.91	27.37	31.45	0.070684	0.0674248	0.002291	0.033974
Control_100C_93D_1	28.61	28.07	32.61	0.068169			
Control_100C_93D_2	29.41	28.88	33.018	0.066080			
Control_100C_93D_3	31.17	30.62	34.75	0.065156	0.0674248	0.002291	0.033974
Control_100C_93D_4	28.41	27.86	32.21	0.070294			

Table A.4 CH Content of 85% Cement and 15% pumice in Control Environment at Different Times

Sample Name	Mstart (g)	Mend (g)	Mc (g)	CH (g/g)	Average	Standard Deviation	Coefficient of Variation
Control_85C15U_7D_1	29.17	28.73	32.88	0.055089	0.06357	0.006022	0.094733
Control_85C15U_7D_2	25.84	25.37	29.6	0.065366			
Control_85C15U_7D_3	27.36	26.88	30.62	0.064533			
Control_85C15U_7D_4	26.79	26.28	30.3	0.069290			
Control_85C15U_14D_1	24.55	24.13	28.39	0.060902	0.05638	0.003817	0.0676942
Control_85C15U_14D_2	25.12	24.71	29.01	0.058181			
Control_85C15U_14D_3	27.26	26.86	30.9	0.053290			
Control_85C15U_14D_4	25.66	25.29	28.66	0.053146			
Control_85C15U_28D_1	28.86	28.43	32.61	0.054283	0.053778	0.001748	0.0325009
Control_85C15U_28D_2	27.17	26.76	31.31	0.053907			
Control_85C15U_28D_3	28.53	28.09	32.61	0.055545			
Control_85C15U_28D_4	27.28	26.89	31.25	0.051376			
Control_85C15U_56D_1	31.81	31.41	36.54	0.045065	0.046501	0.000967	0.0207922
Control_85C15U_56D_2	28.08	27.71	32.5	0.046867			
Control_85C15U_56D_3	30.32	29.92	34.91	0.047169			
Control_85C15U_56D_4	29.68	29.29	34.23	0.046903			
Control_85C15U_93D_1	27.79	27.46	31.807	0.042711	0.043465	0.000778	0.0179057
Control_85C15U_93D_2	26.51	26.18	30.69	0.044265			
Control_85C15U_93D_3	26.18	25.86	30.34	0.043419			
Control_85C15U_93D_4	27.51	27.08	31.83	0.055613			

APPENDIX B

TGA CURVE OF ASR ENVIRONMENT SPECIMENS

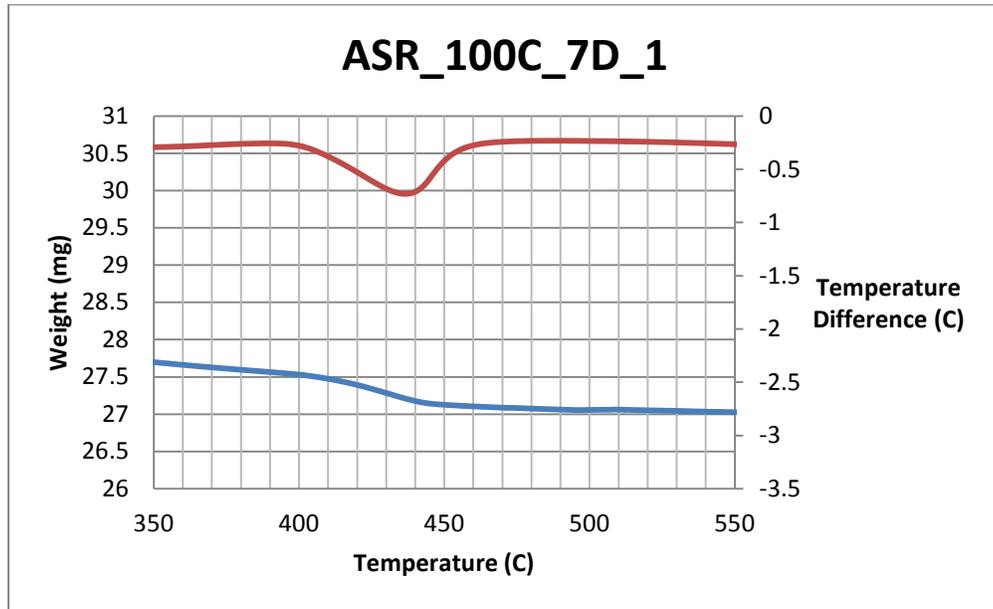


Fig. B.1 TGA curve of mortar sample1 with 100% cement in ASR environment at 7 days

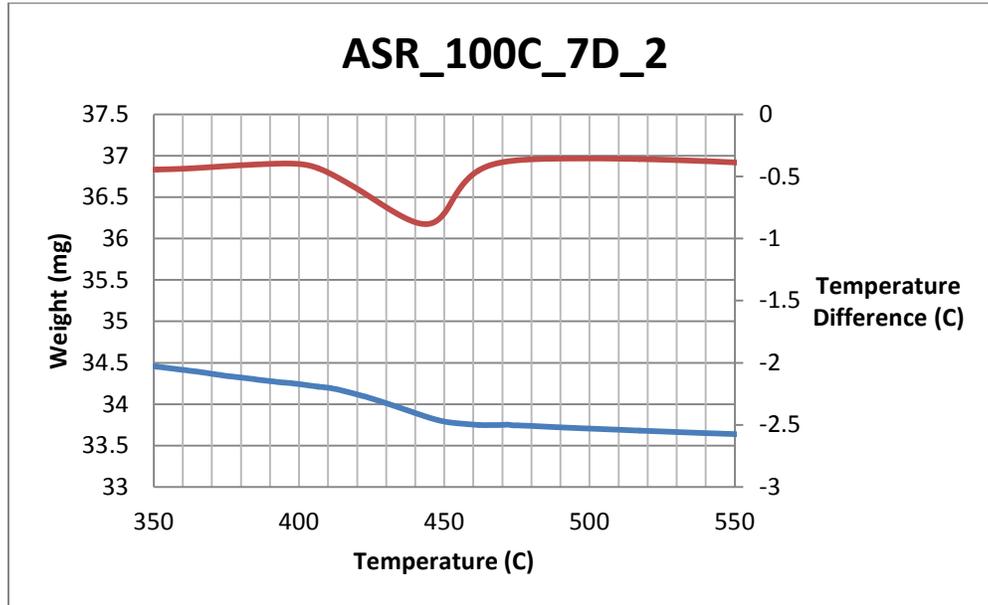


Fig. B.2 TGA curve of mortar sample2 with 100% cement in ASR environment at 7 days

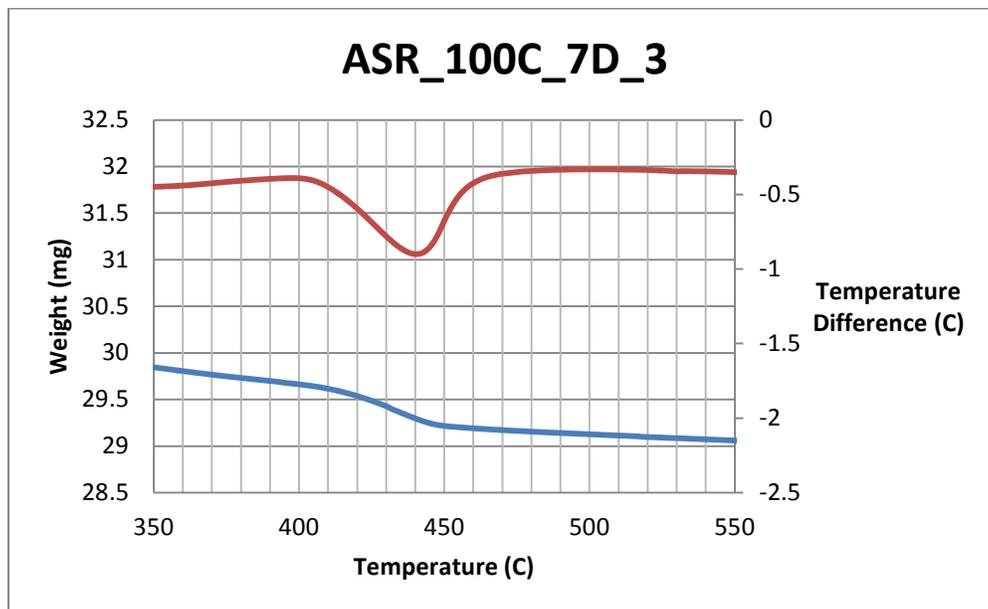


Fig. B.3 TGA curve of mortar sample1 with 100% cement in ASR environment at 7 days

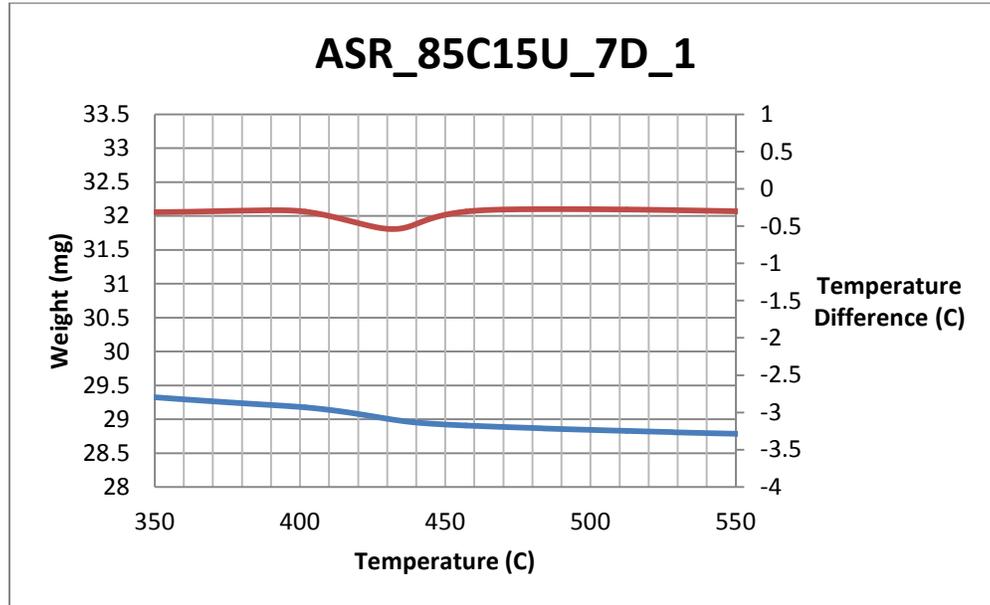


Fig. B.4 TGA curve of mortar sample1 with 85% cement and 15% pumice in ASR environment at 7 days

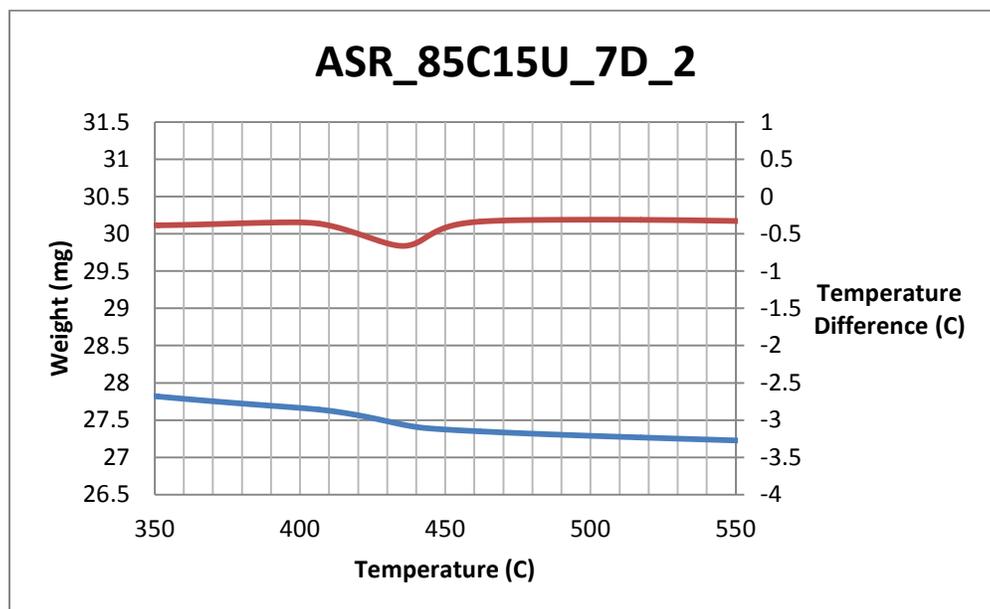


Fig. B.5 TGA curve of mortar sample2 with 85% cement and 15% pumice in ASR environment at 7 days

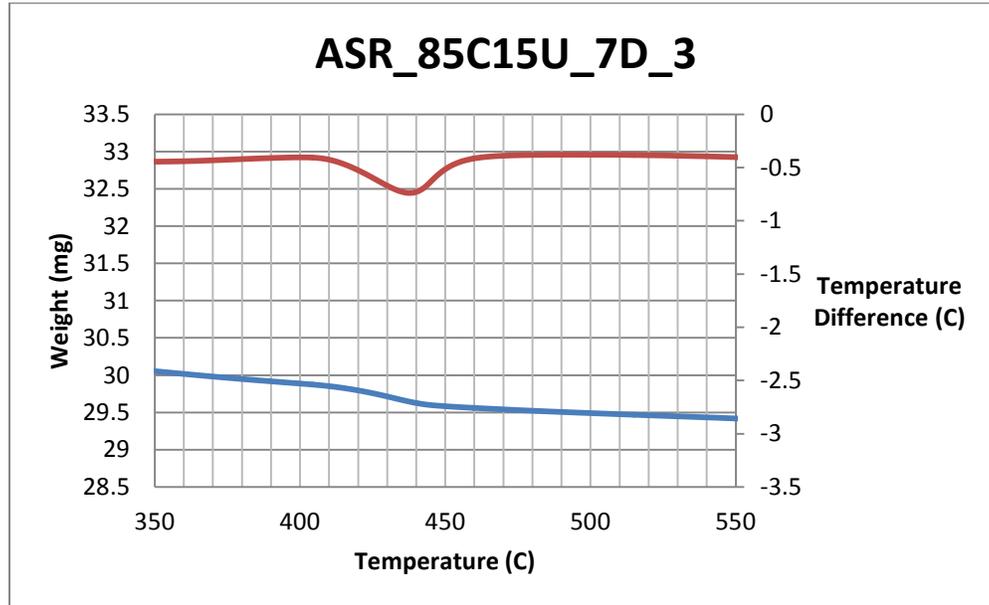


Fig. B.6 TGA curve of mortar sample3 with 85% cement and 15% pumice in ASR environment at 7 days

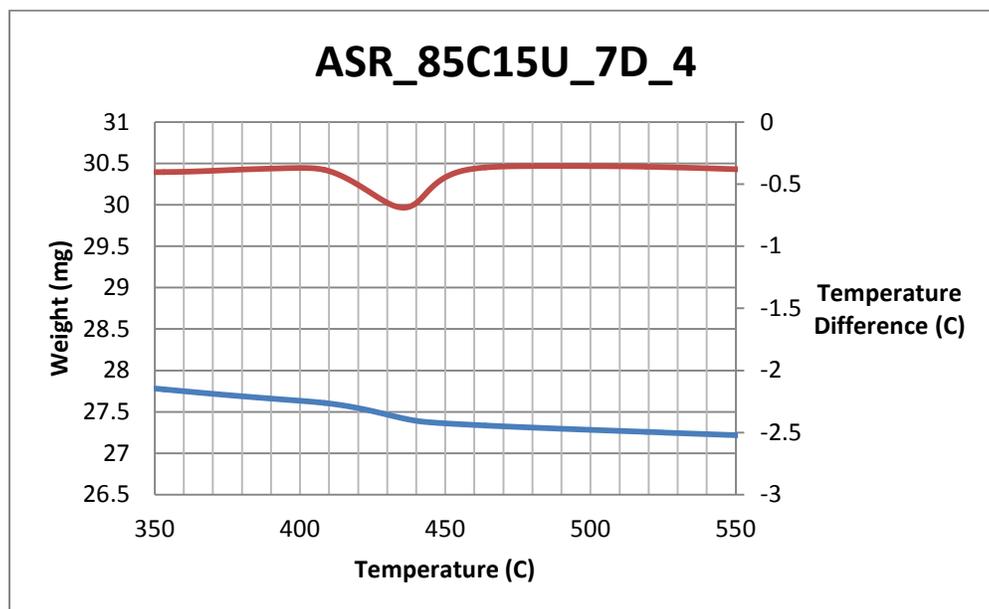


Fig. B.7 TGA curve of mortar sample4 with 85% cement and 15% pumice in ASR environment at 7 days

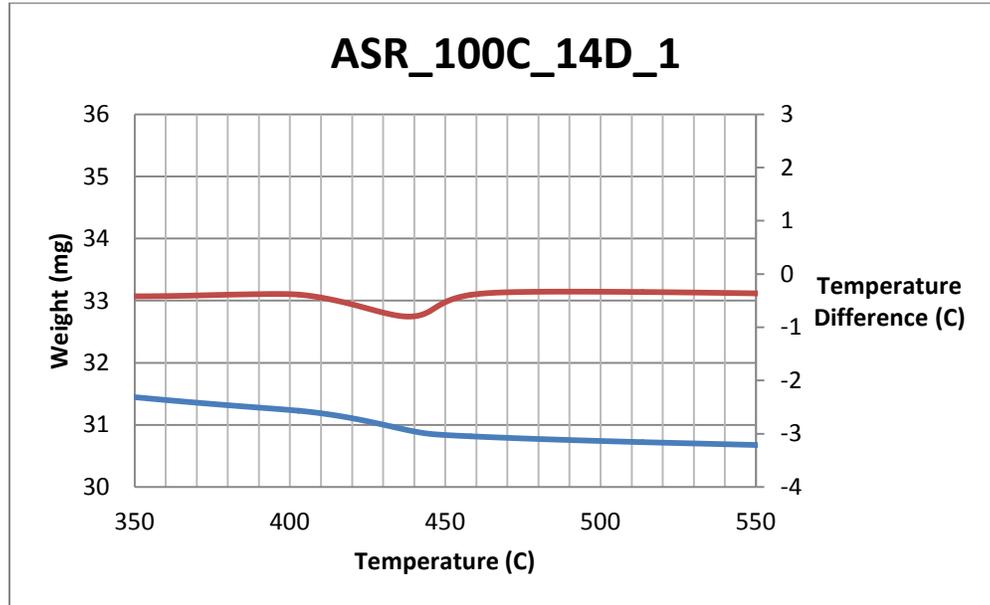


Fig. B.8 TGA curve of mortar sample1 with 100% cement in ASR environment at 14 days

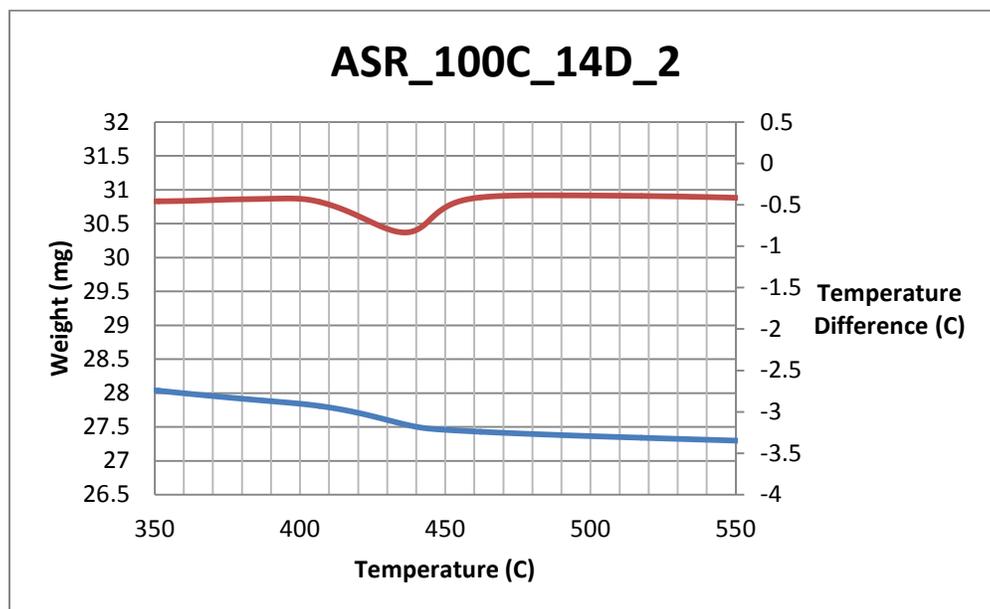


Fig. B.9 TGA curve of mortar sample2 with 100% cement in ASR environment at 14 days

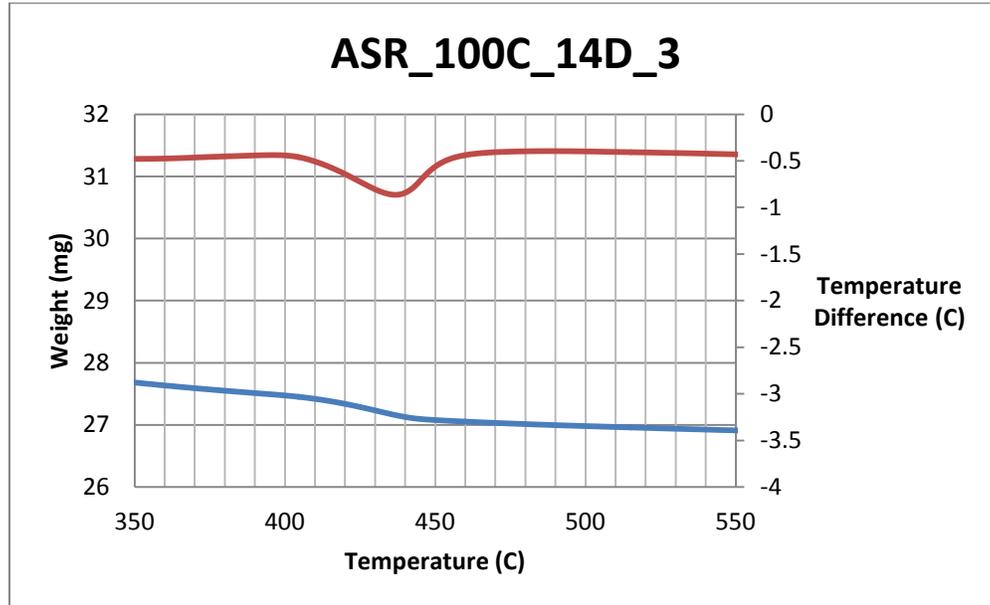


Fig. B.10 TGA curve of mortar sample3 with 100% cement in ASR environment at 14 days

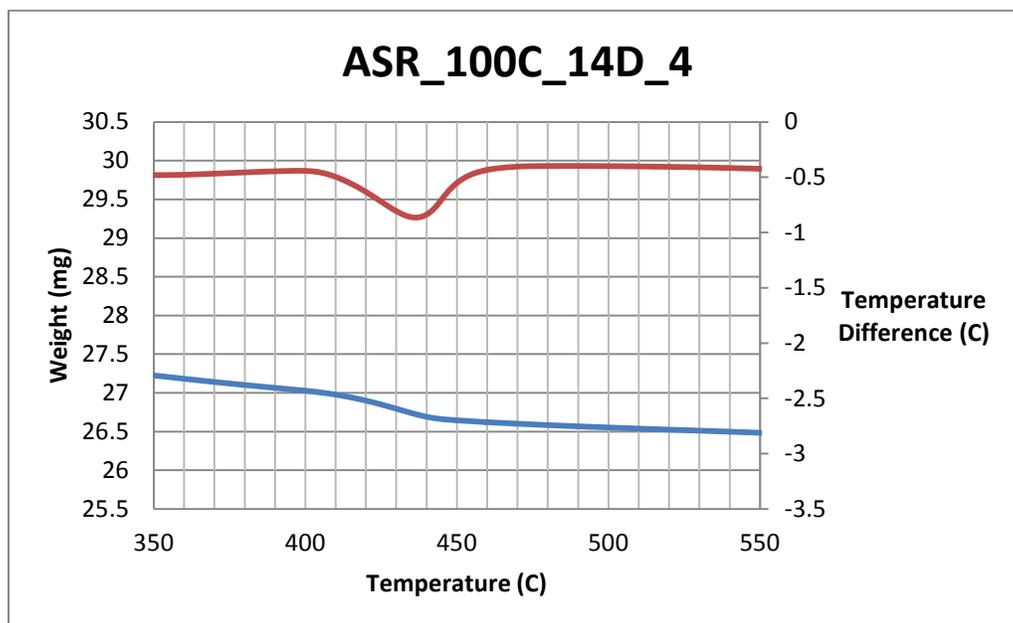


Fig. B.11 TGA curve of mortar sample4 with 100% cement in ASR environment at 14 days

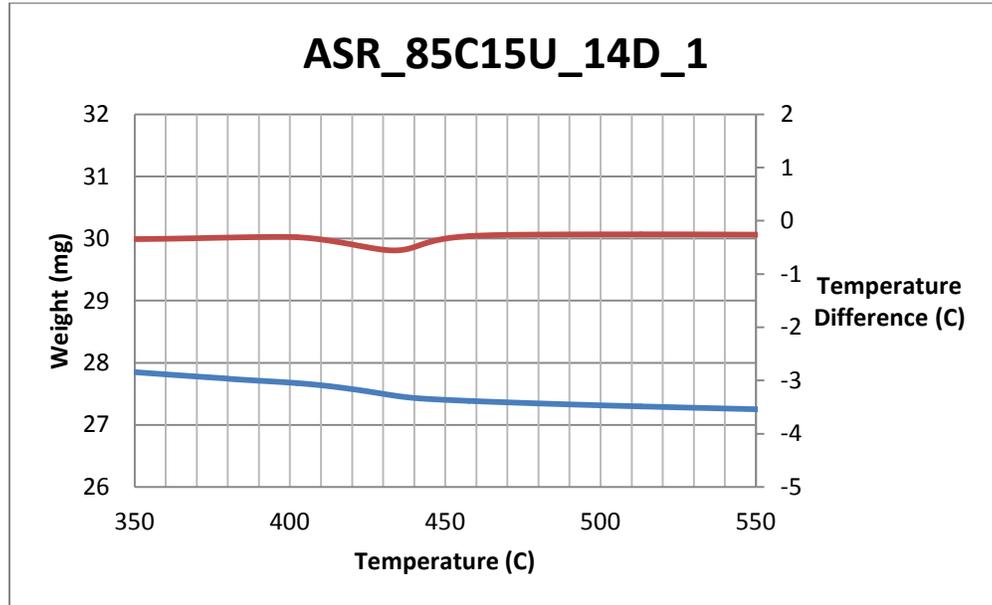


Fig. B.12 TGA curve of mortar sample1 with 85% cement and 15% pumice in ASR environment at 14 days

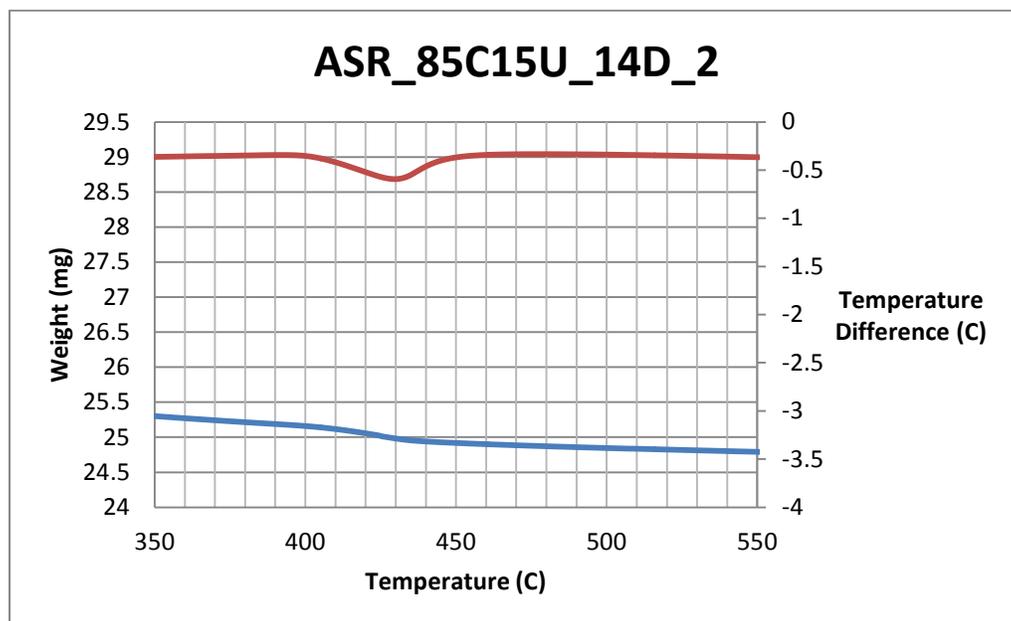


Fig. B.13 TGA curve of mortar sample2 with 85% cement and 15% pumice in ASR environment at 14 days

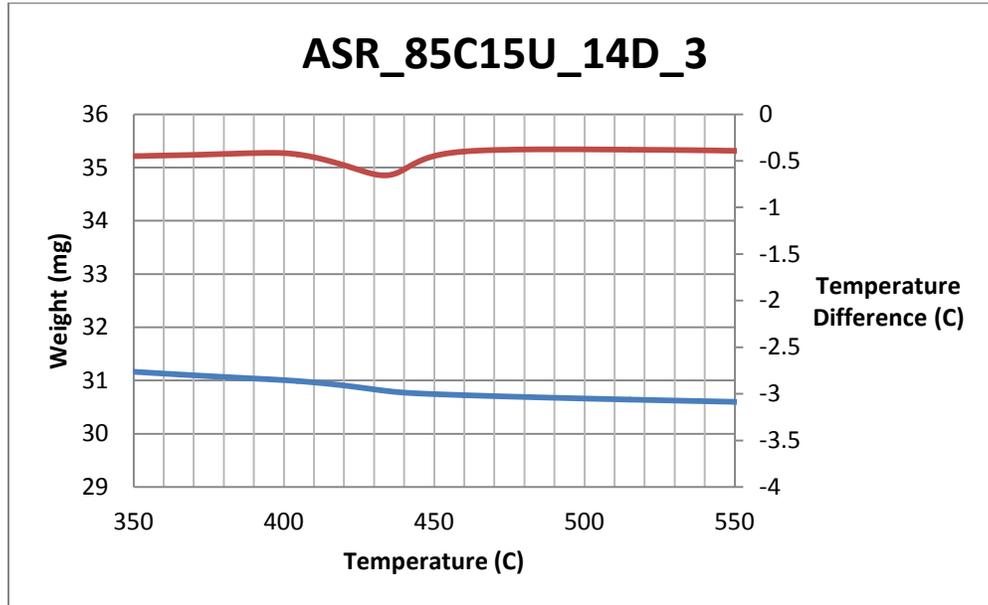


Fig. B.14 TGA curve of mortar sample3 with 85% cement and 15% pumice in ASR environment at 14 days

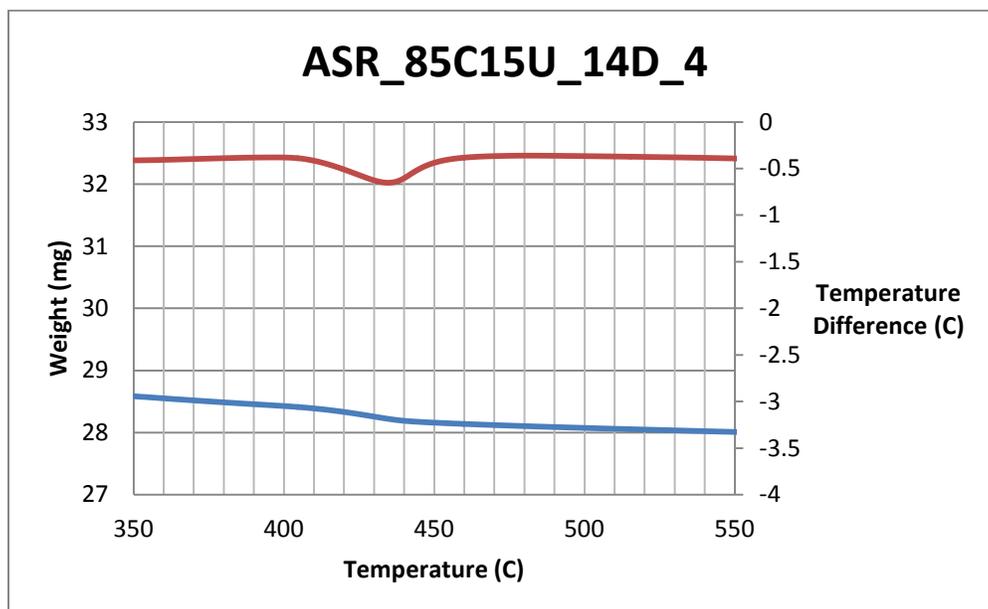


Fig. B.15 TGA curve of mortar sample4 with 85% cement and 15% pumice in ASR environment at 14 days

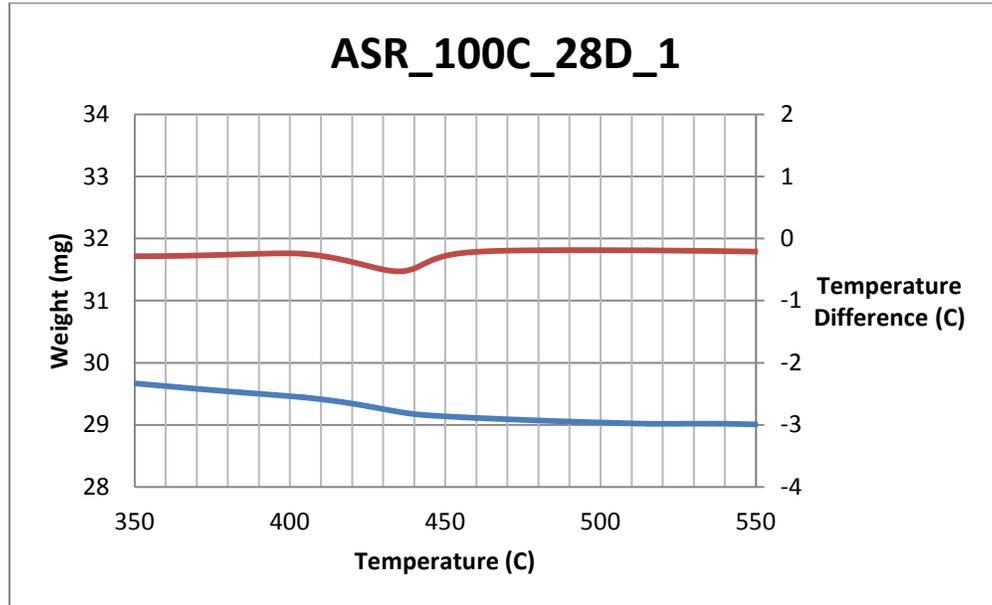


Fig. B.16 TGA curve of mortar sample1 with 100% cement in ASR environment at 28 days

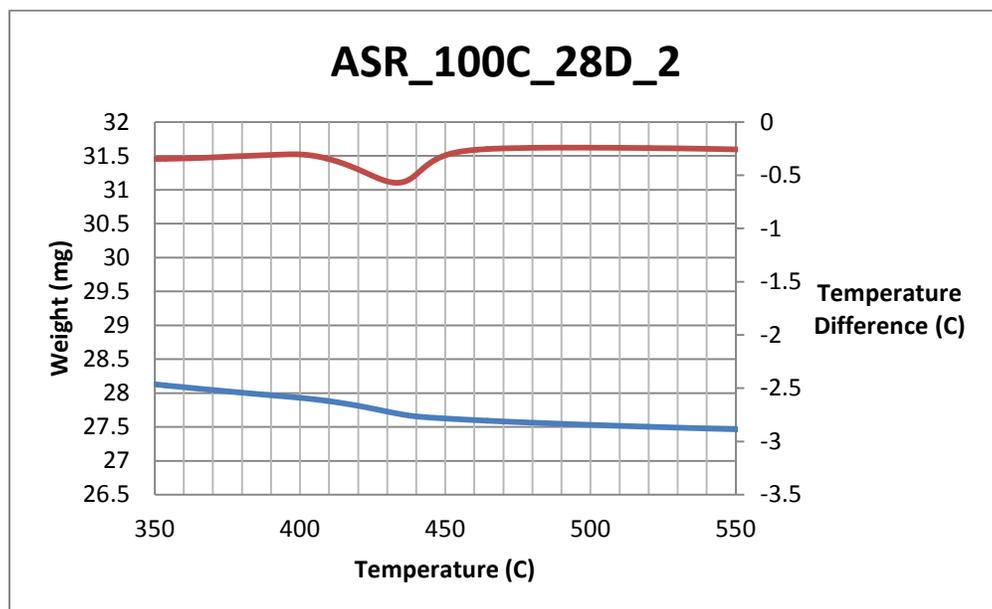


Fig. B.17 TGA curve of mortar sample2 with 100% cement in ASR environment at 28 days

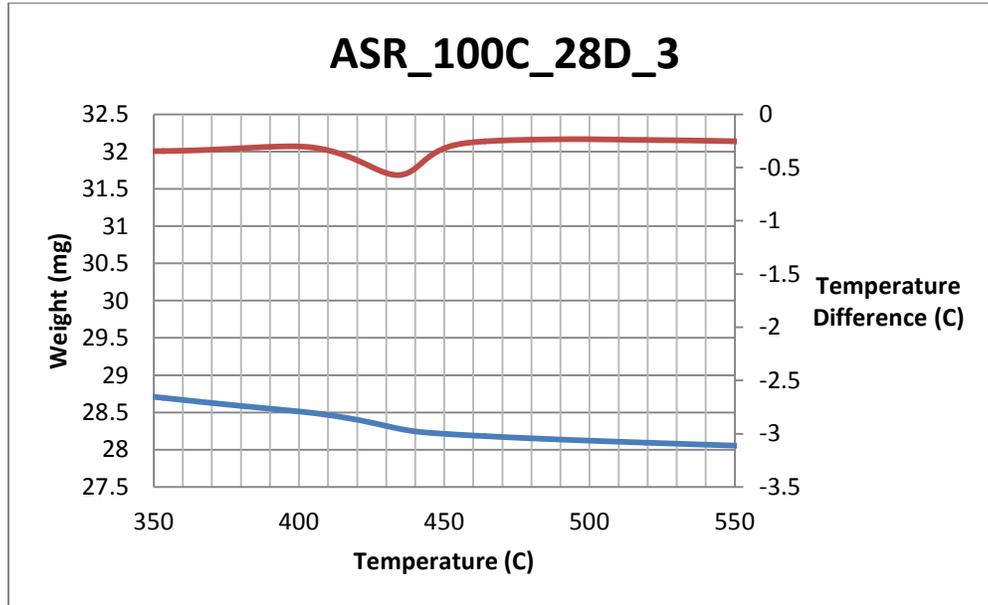


Fig. B.18 TGA curve of mortar sample3 with 100% cement in ASR environment at 28 days

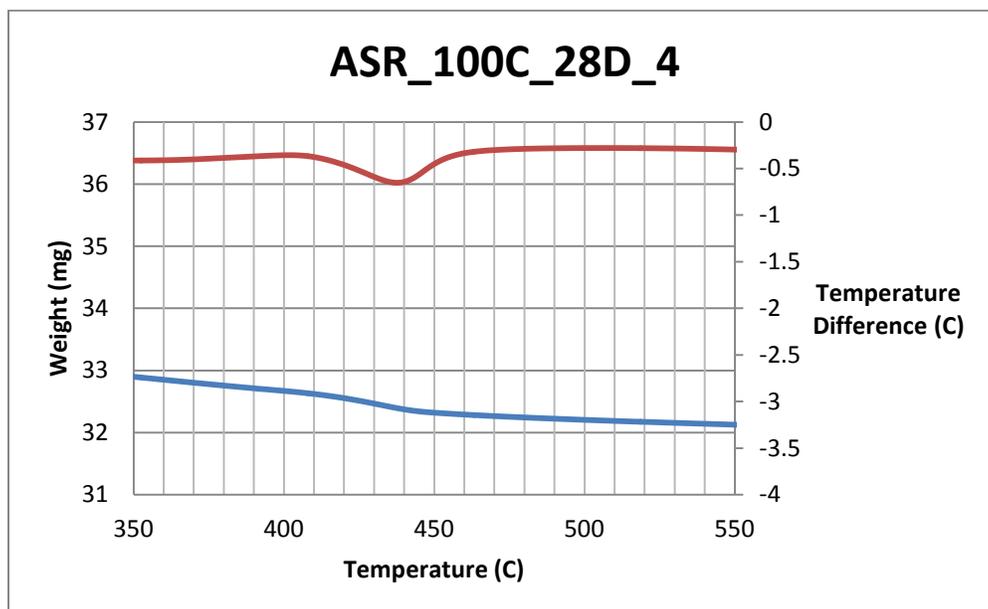


Fig. B.19 TGA curve of mortar sample4 with 100% cement in ASR environment at 28 days

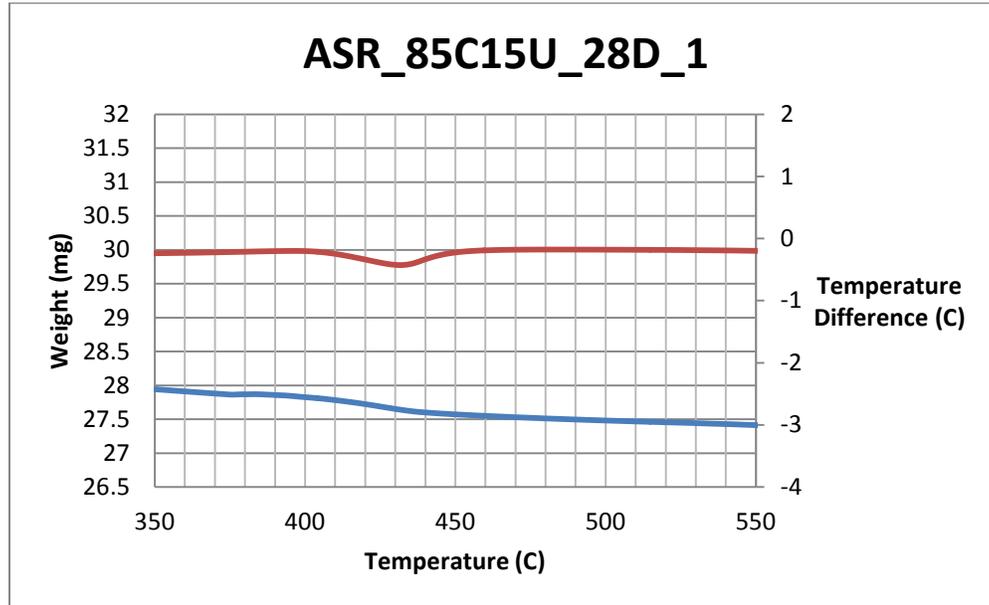


Fig. B.20 TGA curve of mortar sample1 with 85% cement and 15% pumice in ASR environment at 28 days

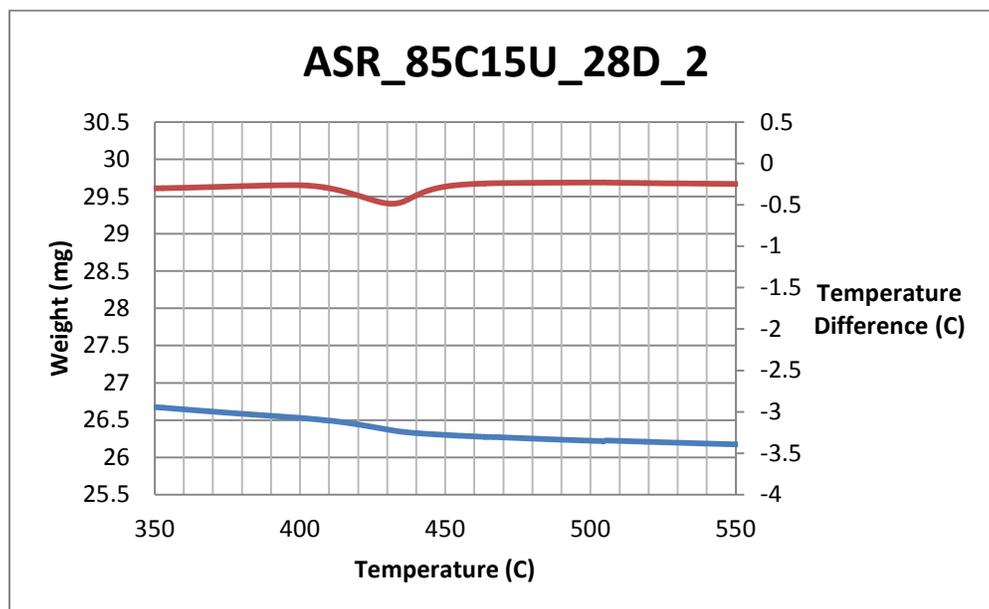


Fig. B.21 TGA curve of mortar sample2 with 85% cement and 15% pumice in ASR environment at 28 days

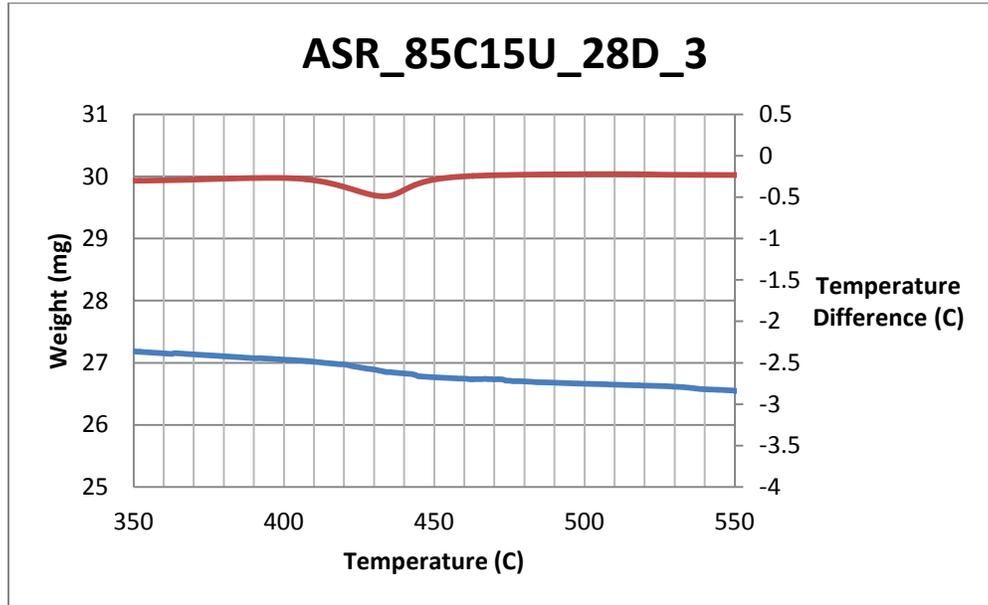


Fig. B.22 TGA curve of mortar sample3 with 85% cement and 15% pumice in ASR environment at 28 days

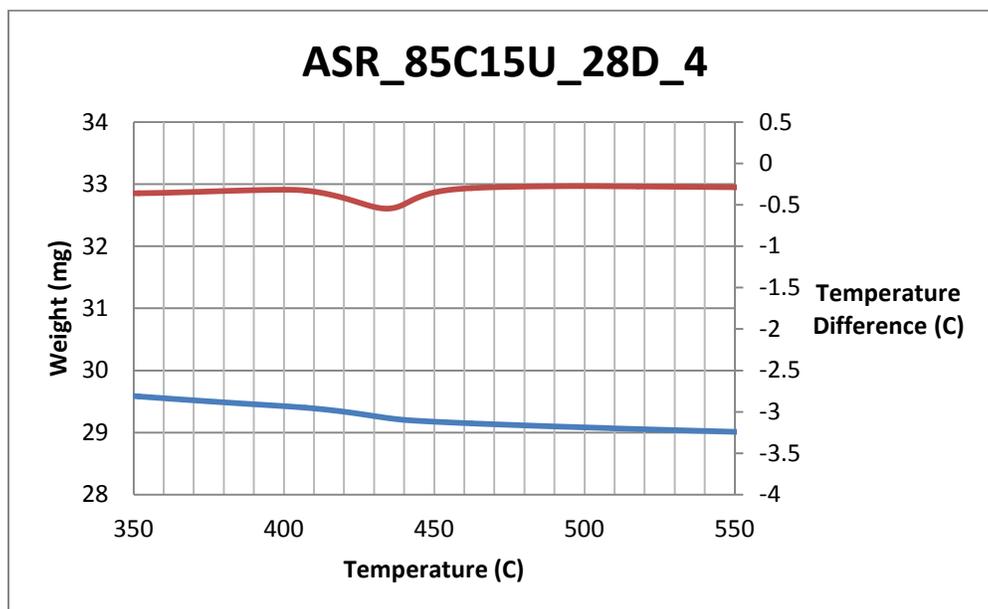


Fig. B.23 TGA curve of mortar sample4 with 85% cement and 15% pumice in ASR environment at 28 days

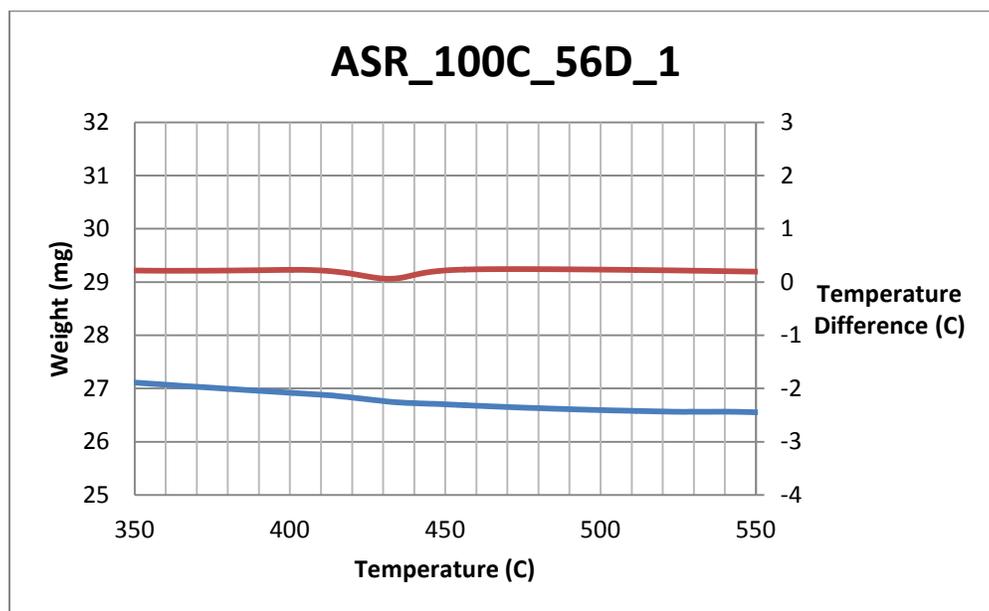


Fig. B.24 TGA curve of mortar sample1 with 100% cement in ASR environment at 56 days

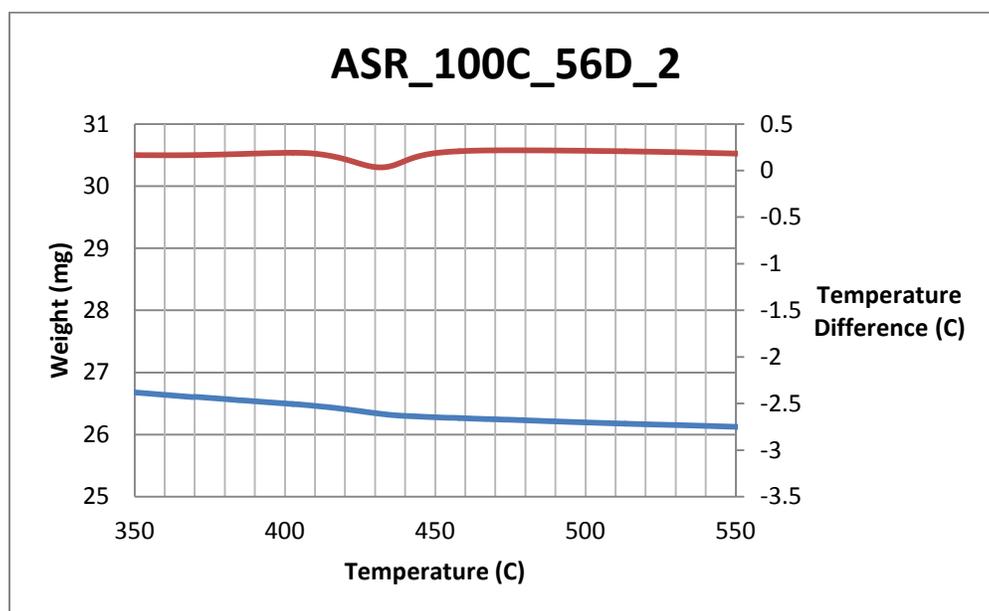


Fig. B.25 TGA curve of mortar sample2 with 100% cement in ASR environment at 56 days

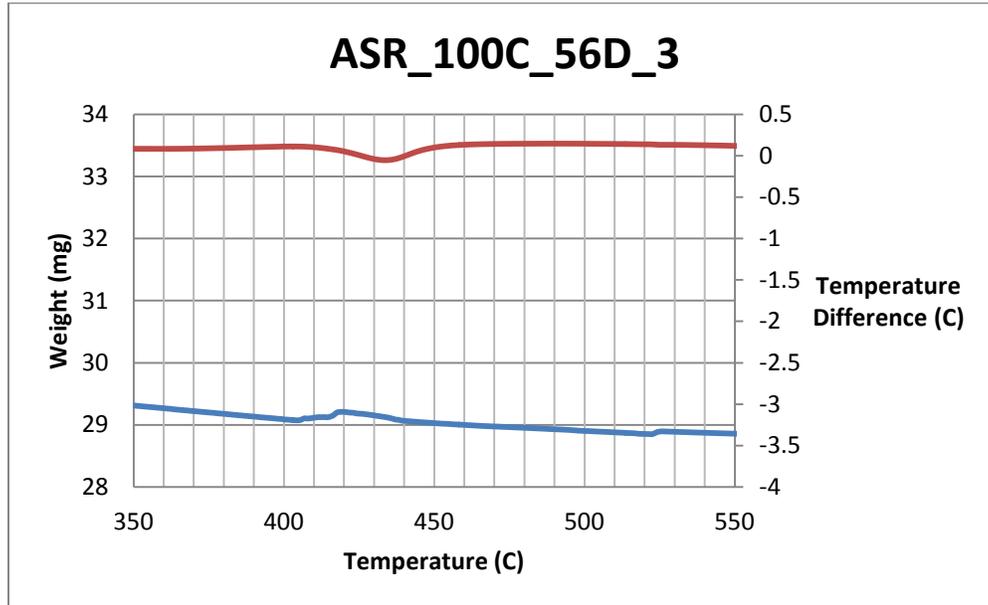


Fig. B.26 TGA curve of mortar sample3 with 100% cement in ASR environment at 56 days

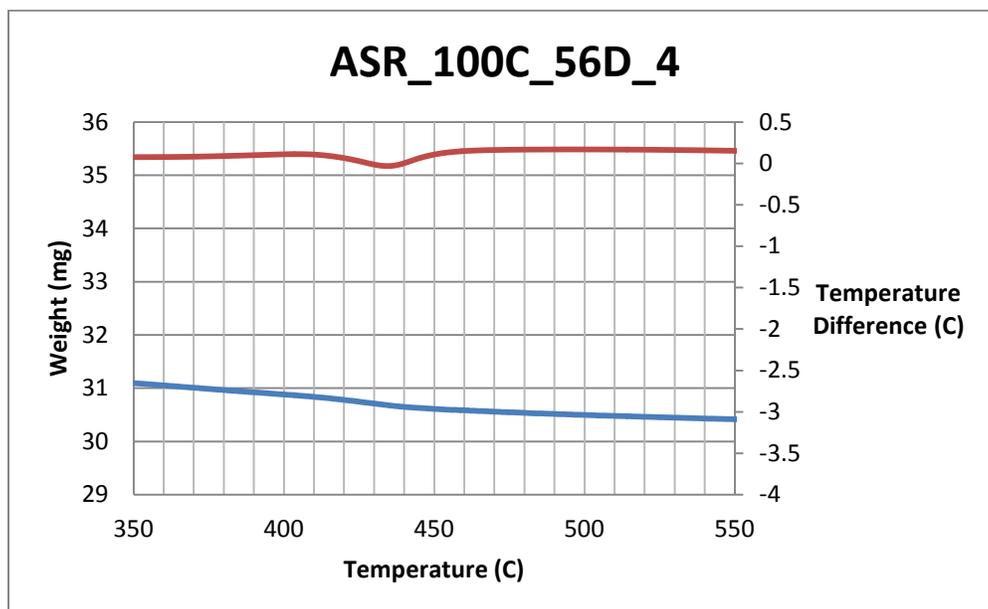


Fig. B.27 TGA curve of mortar sample4 with 100% cement in ASR environment at 56 days

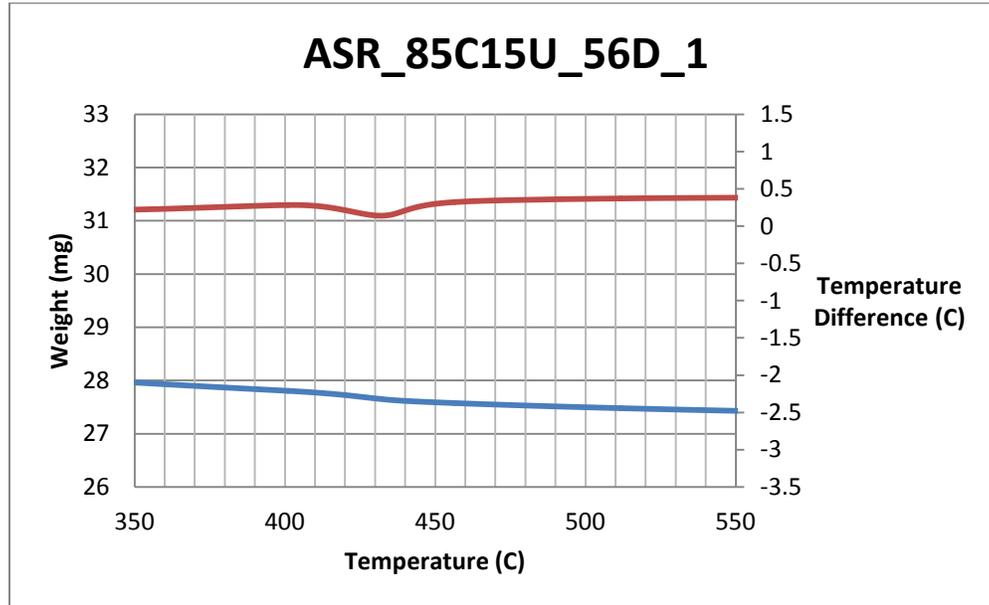


Fig. B.28 TGA curve of mortar sample1 with 85% cement and 15% pumice in ASR environment at 56 days

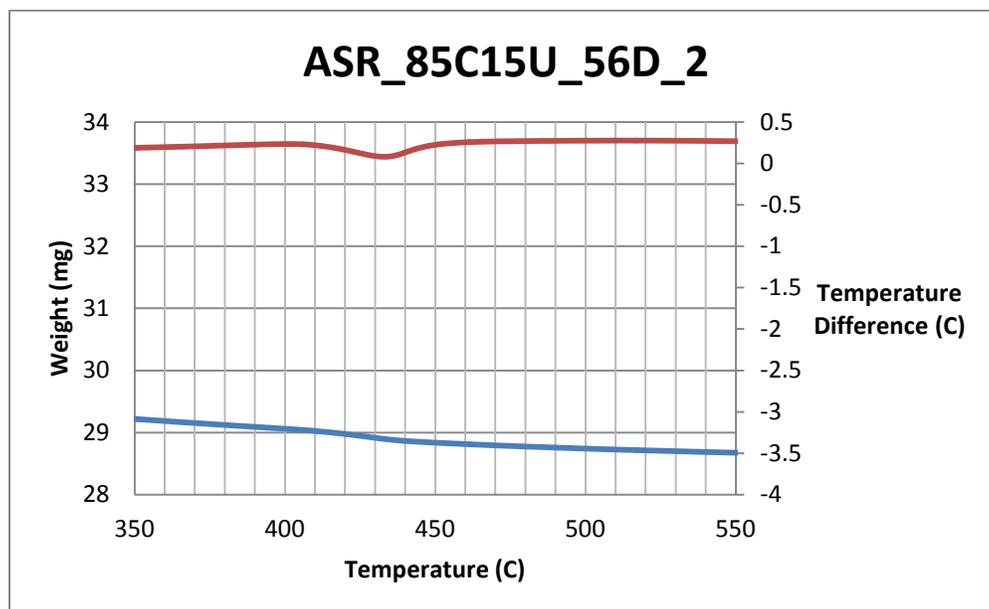


Fig. B.29 TGA curve of mortar sample2 with 85% cement and 15% pumice in ASR environment at 56 days

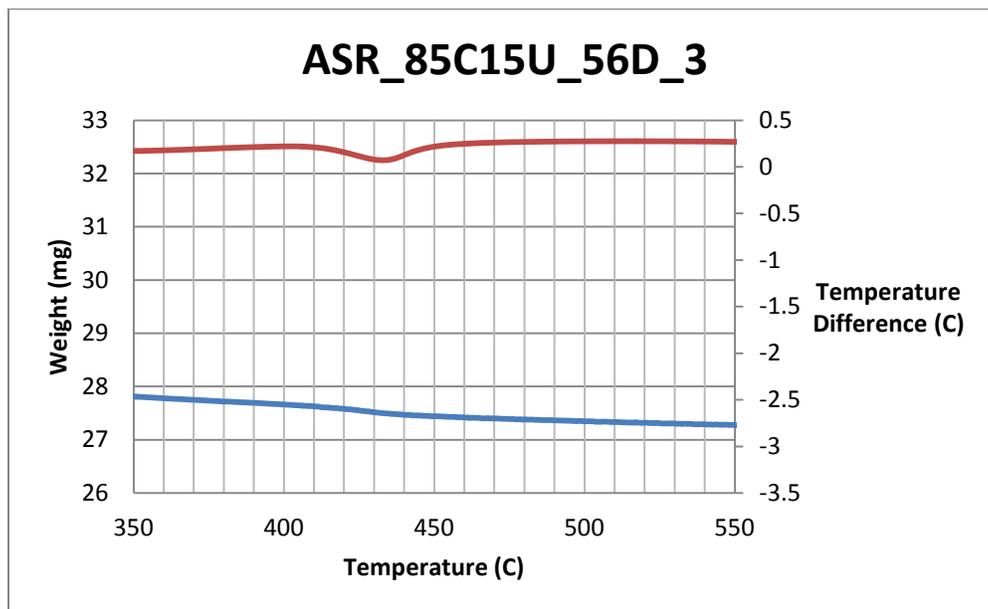


Fig. B.30 TGA curve of mortar sample3 with 85% cement and 15% pumice in ASR environment at 56 days

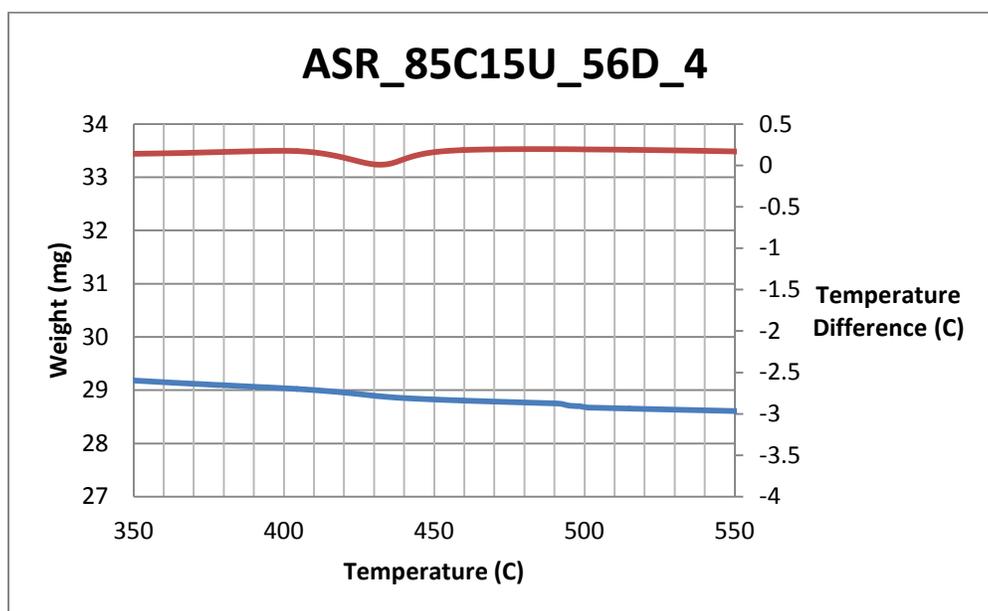


Fig. B.31 TGA curve of mortar sample4 with 85% cement and 15% pumice in ASR environment at 56 days

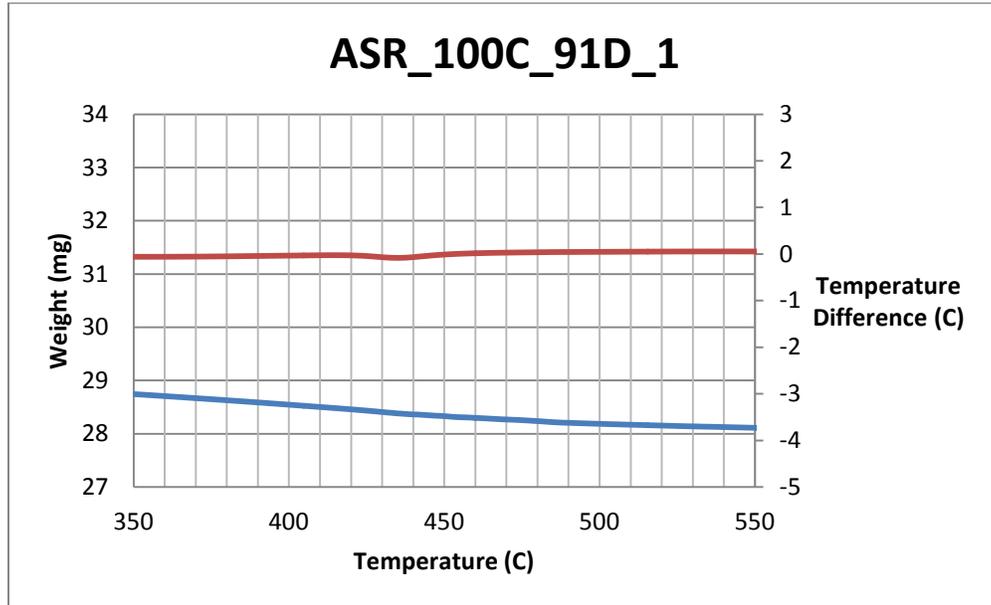


Fig. B.32 TGA curve of mortar sample1 with 100% cement in ASR environment at 91 days

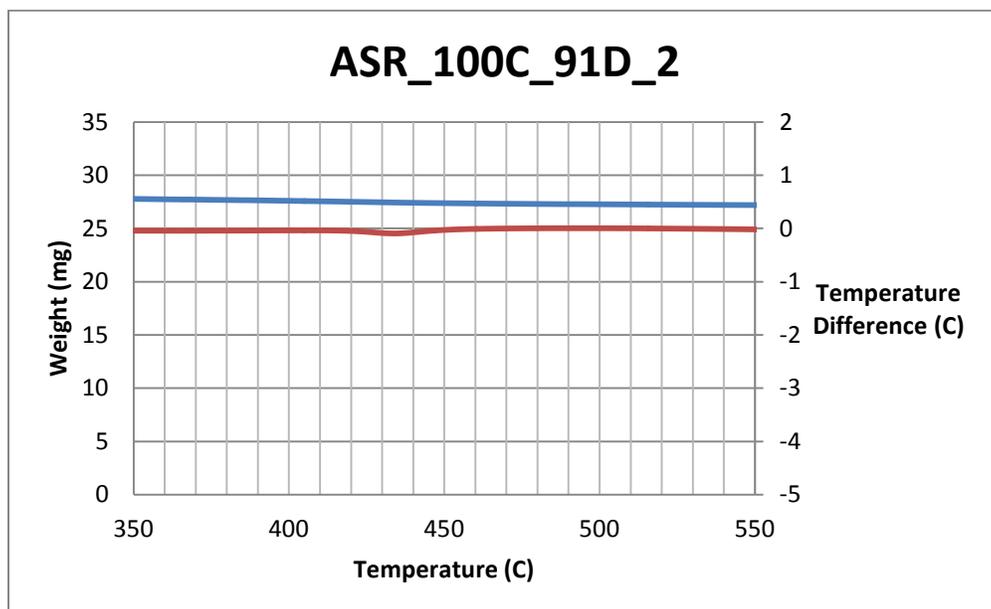


Fig. B.33 TGA curve of mortar sample2 with 100% cement in ASR environment at 91 days

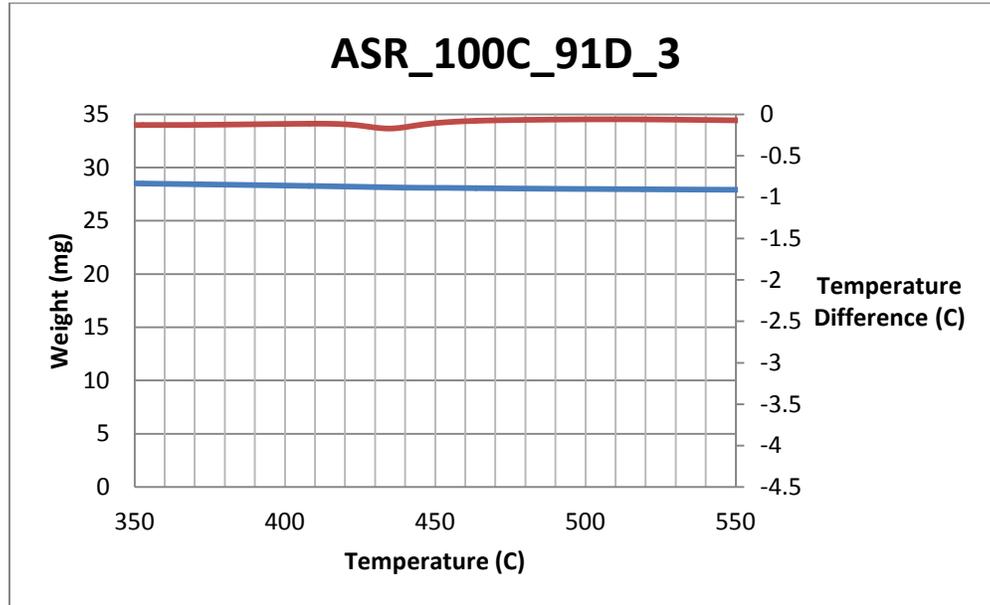


Fig. B.34 TGA curve of mortar sample3 with 100% cement in ASR environment at 91 days

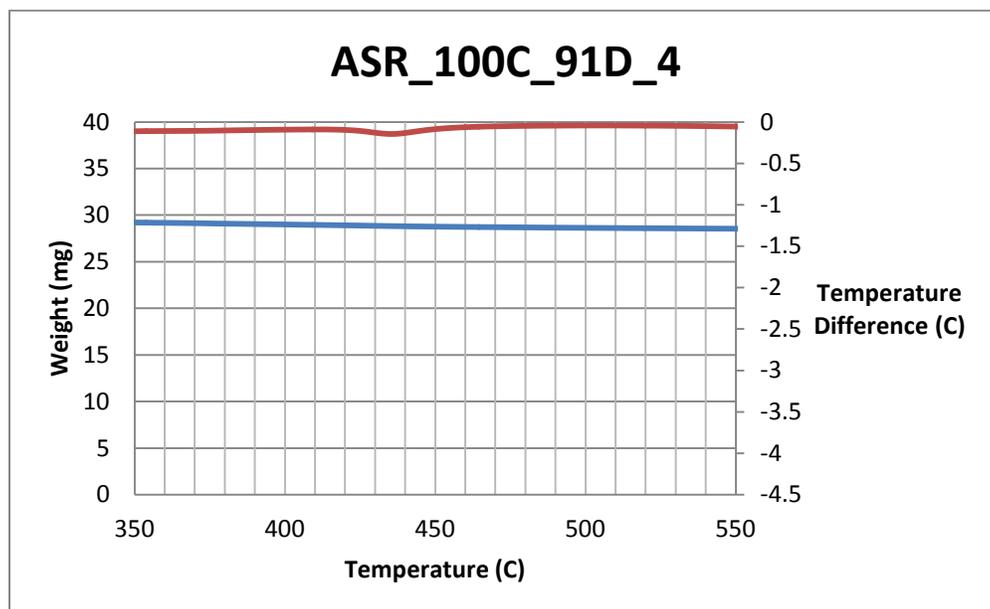


Fig. B.35 TGA curve of mortar sample4 with 100% cement in ASR environment at 91 days

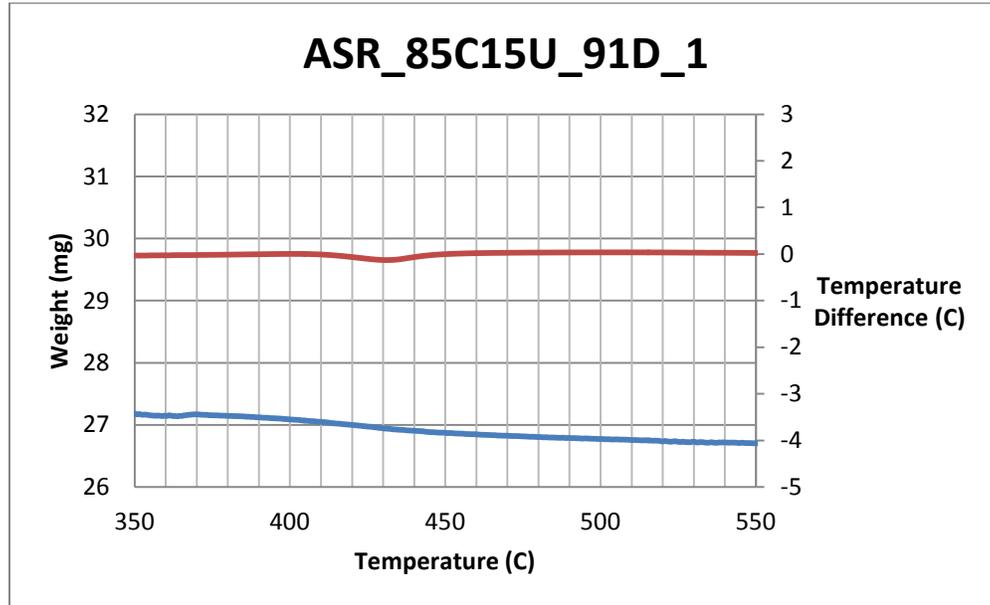


Fig. B.36 TGA curve of mortar sample1 with 85% cement and 15% pumice in ASR environment at 91 days

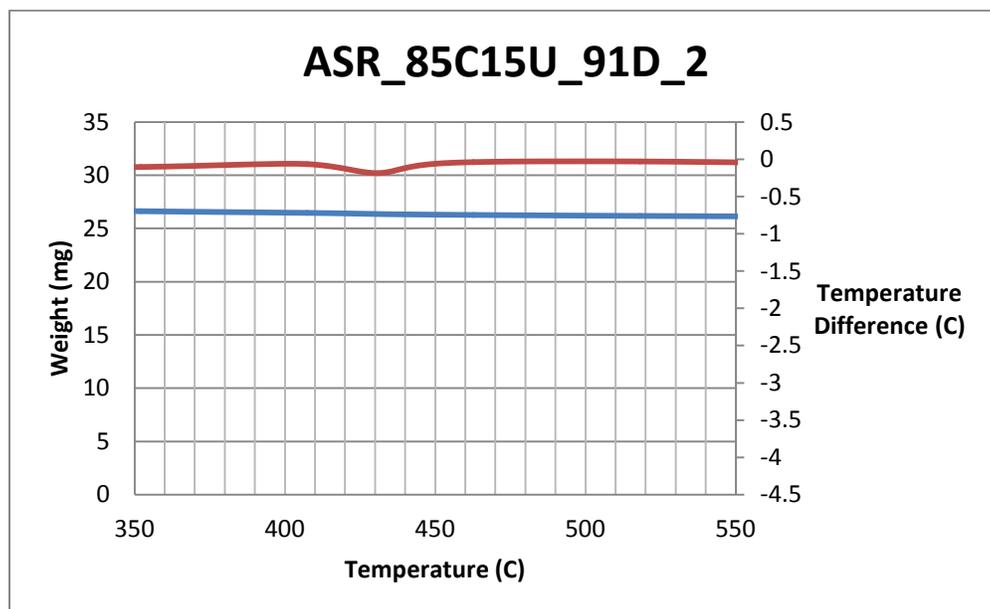


Fig. B.37 TGA curve of mortar sample2 with 85% cement and 15% pumice in ASR environment at 91 days

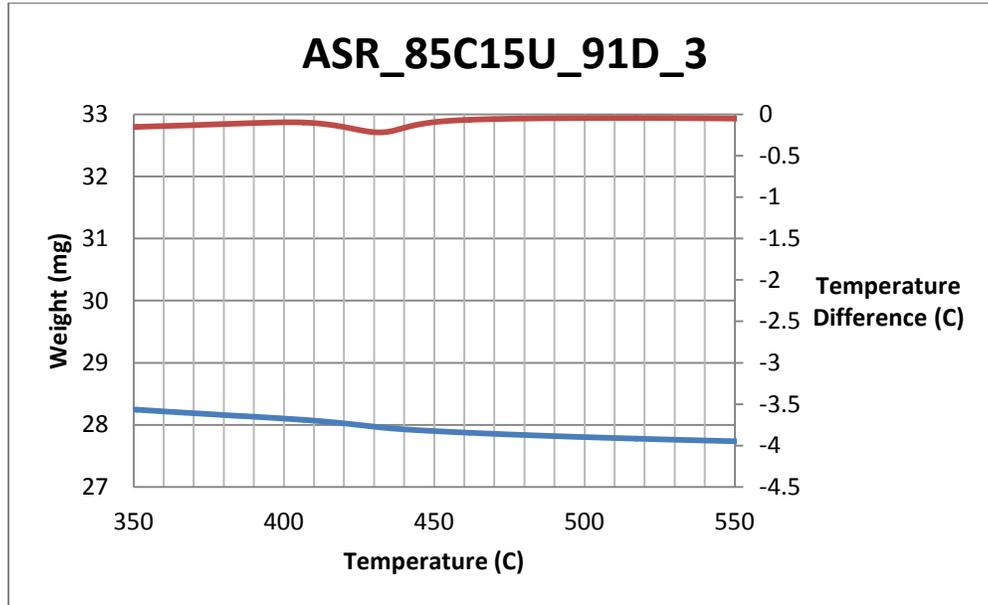


Fig. B.38 TGA curve of mortar sample3 with 85% cement and 15% pumice in ASR environment at 91 days

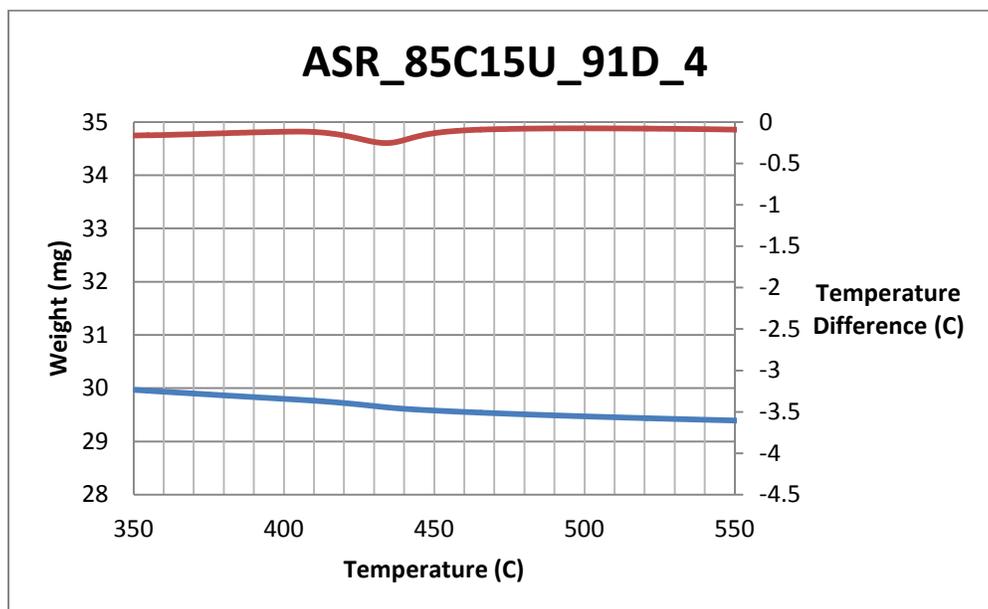


Fig. B.39 TGA curve of mortar sample4 with 85% cement and 15% pumice in ASR environment at 91 days

APPENDIX C

TGA CURVE OF CONTROL ENVIRONMENT SPECIMENS

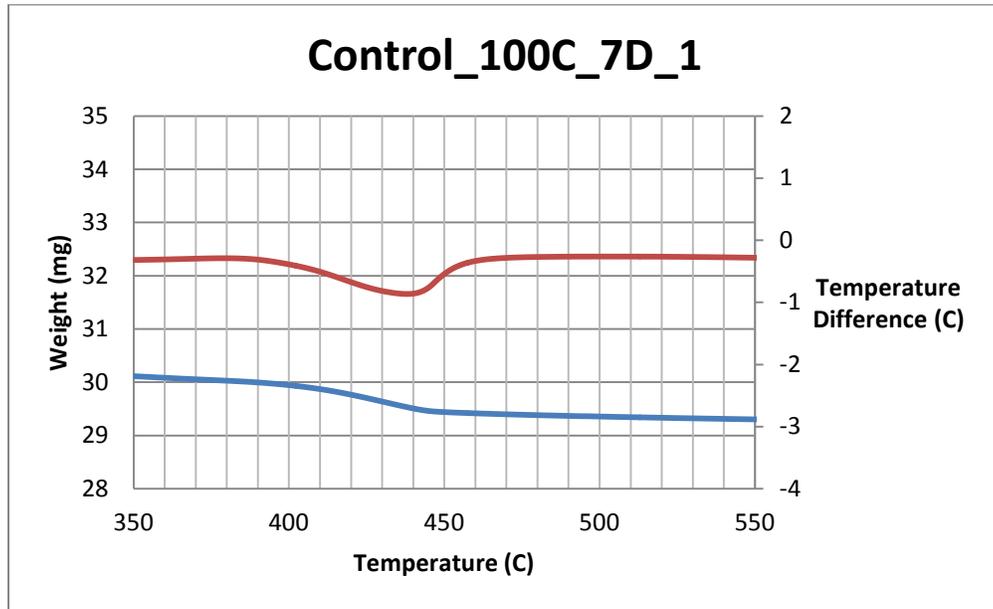


Fig. C.1 TGA curve of mortar sample1 with 100% cement in control environment at 7 days

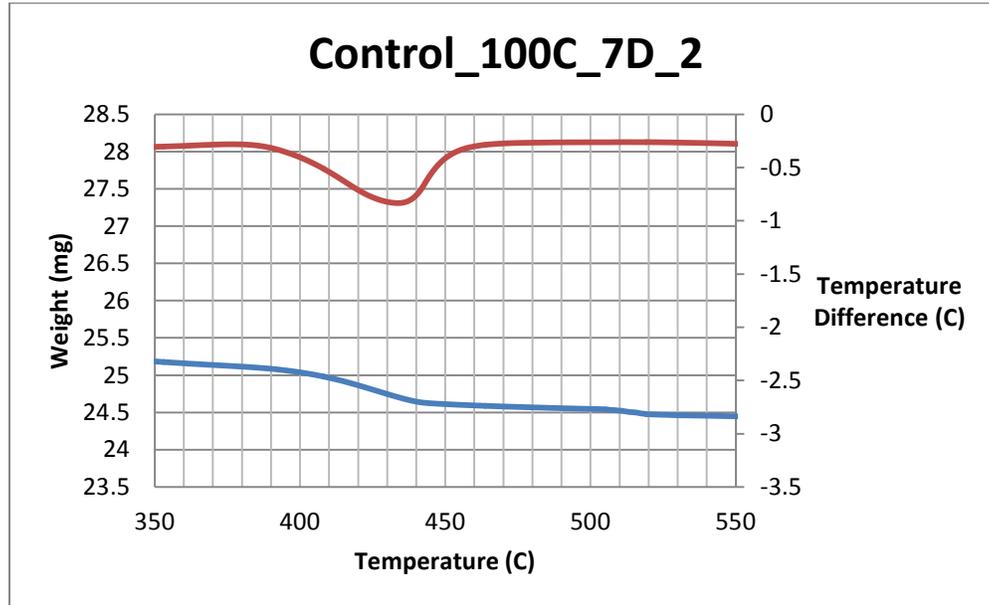


Fig. C.2 TGA curve of mortar sample2 with 100% cement in control environment at 7 days

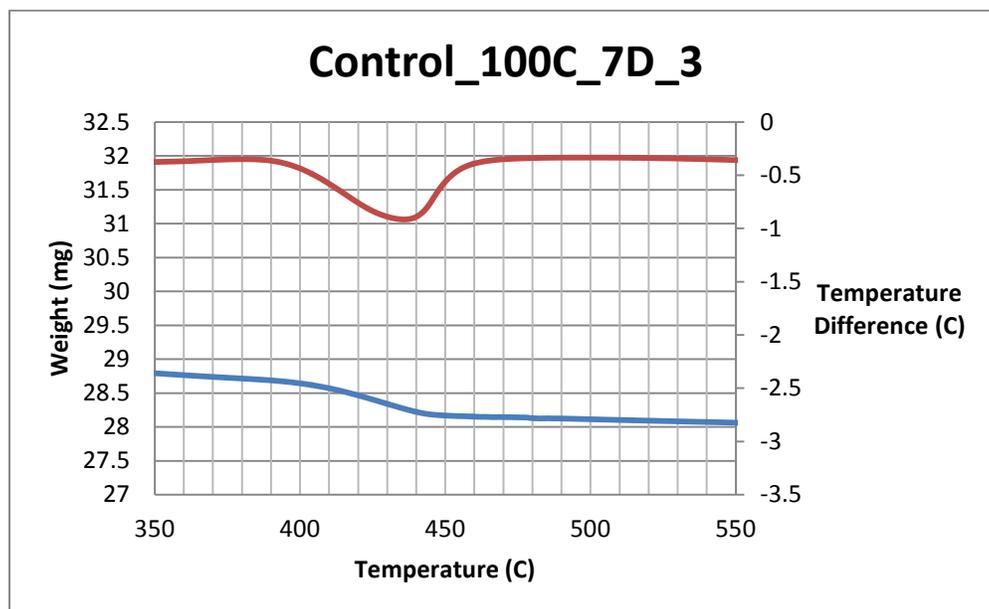


Fig. C.3 TGA curve of mortar sample3 with 100% cement in control environment at 7 days

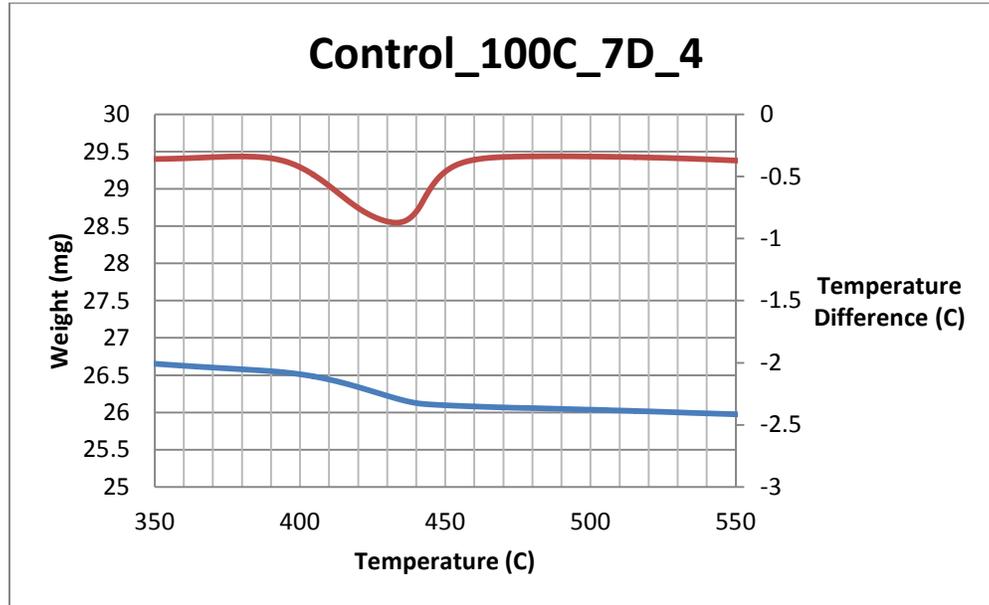


Fig. C.4 TGA curve of mortar sample4 with 100% cement in control environment at 7 days

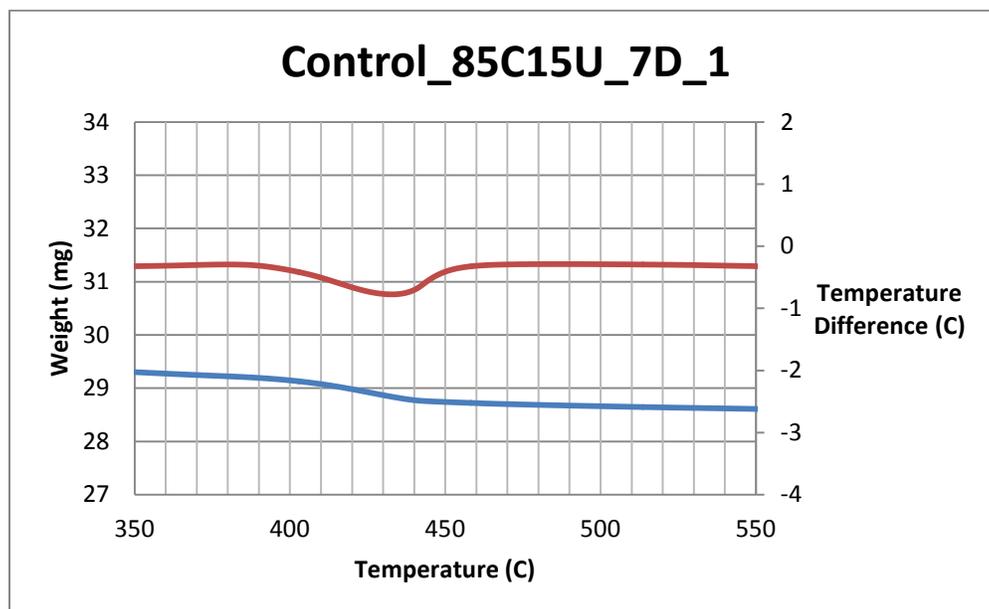


Fig. C.5 TGA curve of mortar sample1 with 85% cement and 15% pumice in control environment at 7 days

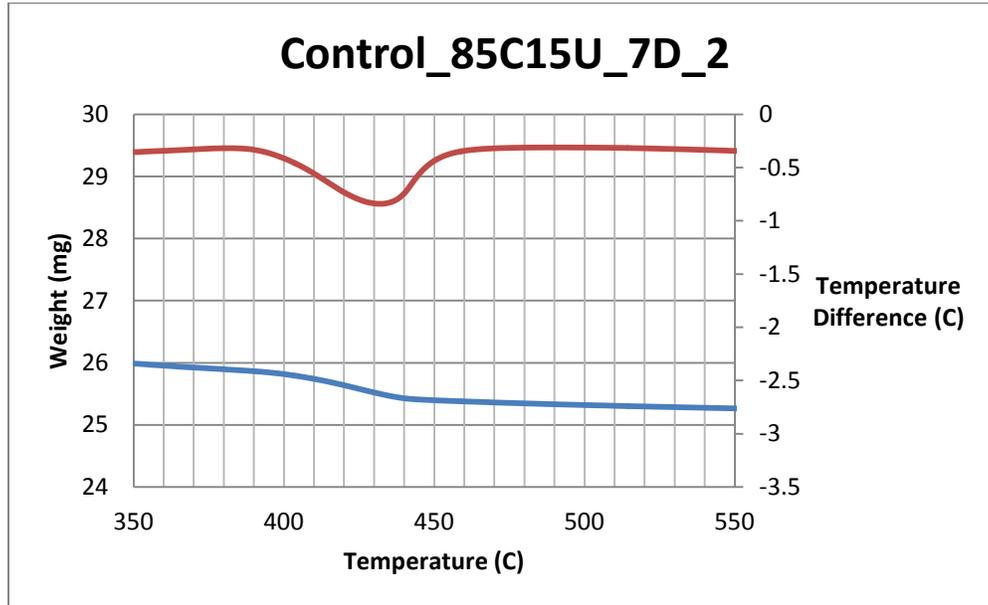


Fig. C.6 TGA curve of mortar sample2 with 85% cement and 15% pumice in control environment at 7 days.

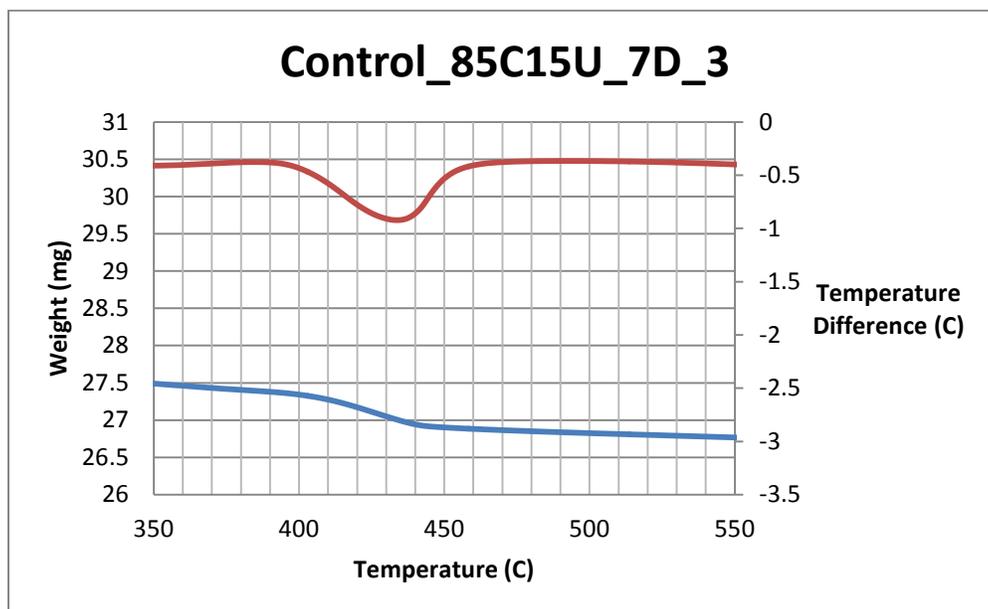


Fig. C.7 TGA curve of mortar sample3 with 85% cement and 15% pumice in control environment at 7 days

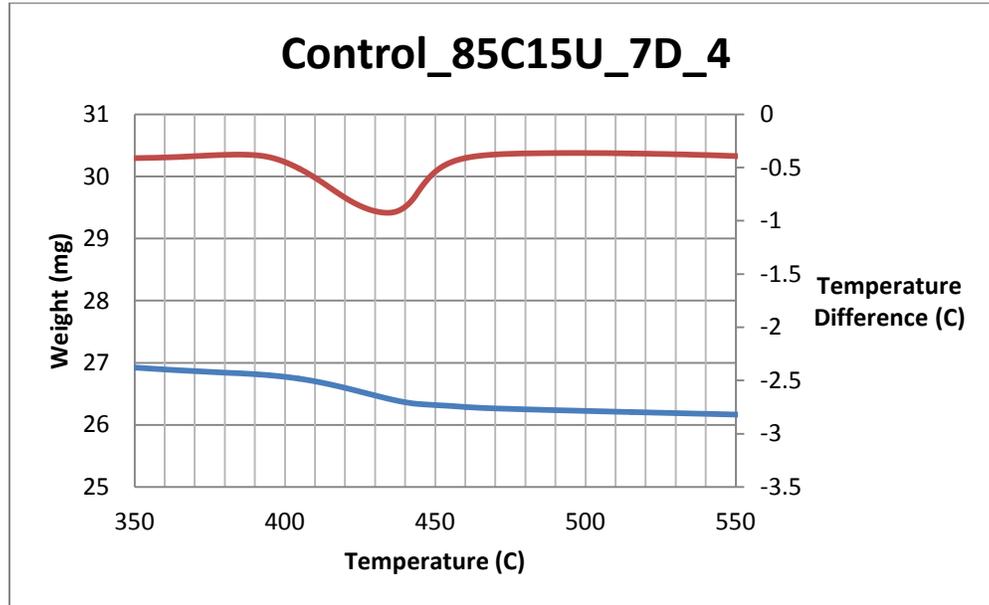


Fig. C.8 TGA curve of mortar sample4 with 85% cement and 15% pumice in control environment at 7 days

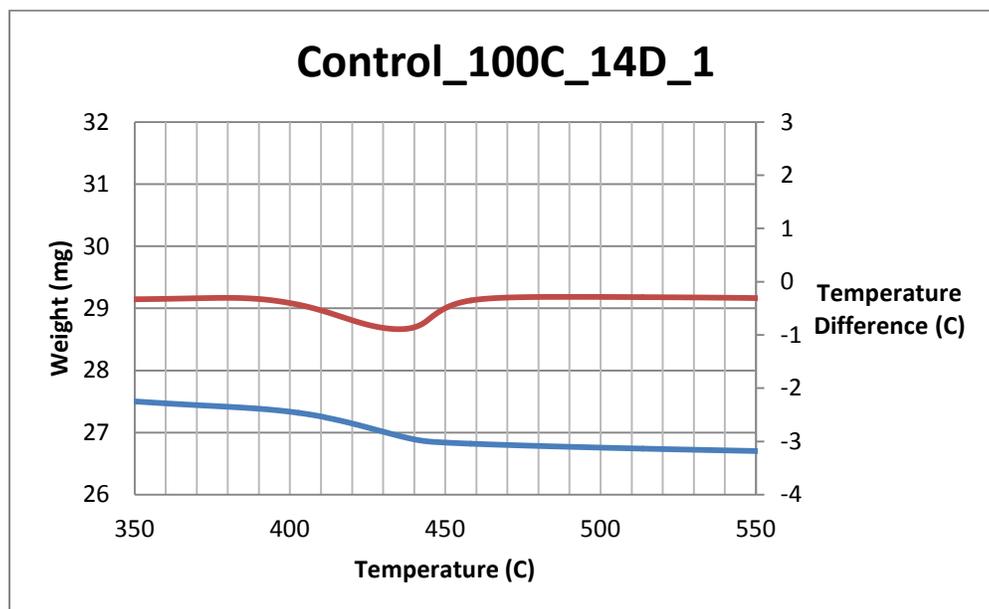


Fig. C.9 TGA curve of mortar sample1 with 100% cement in control environment at 14 days

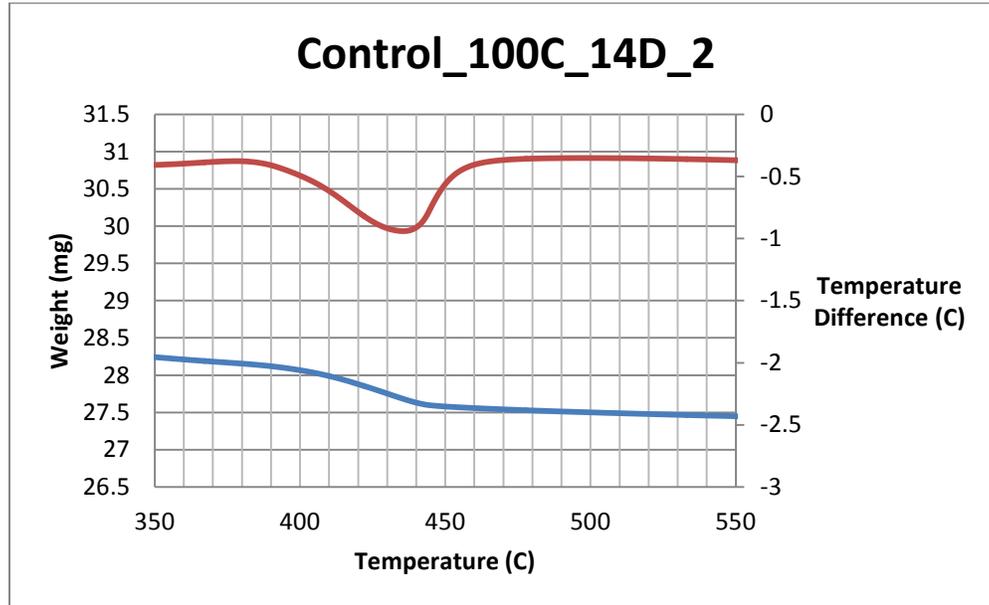


Fig. C.10 TGA curve of mortar sample2 with 100% cement in control environment at 14 days

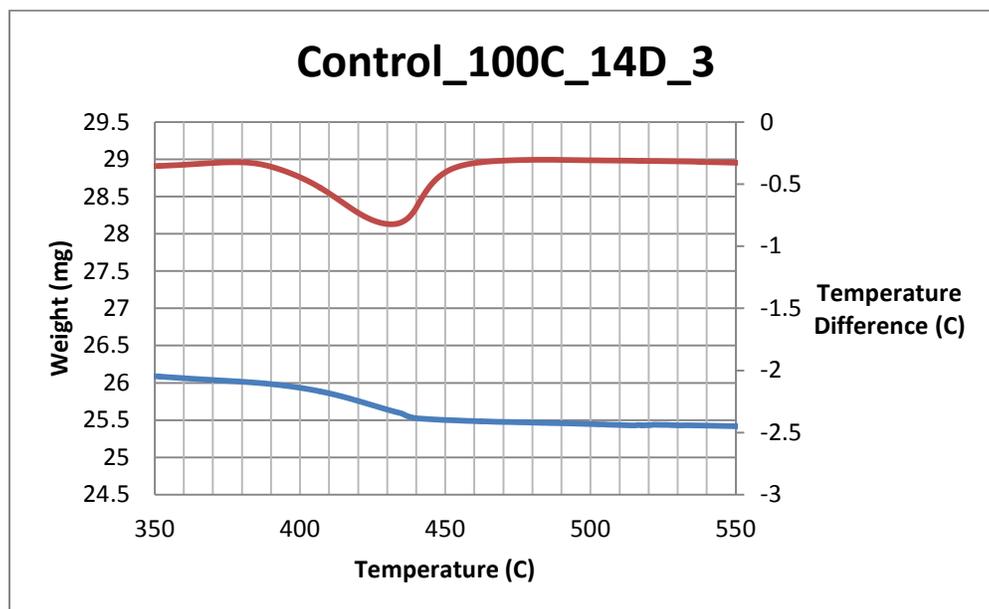


Fig. C.11 TGA curve of mortar sample3 with 100% cement in control environment at 14 days

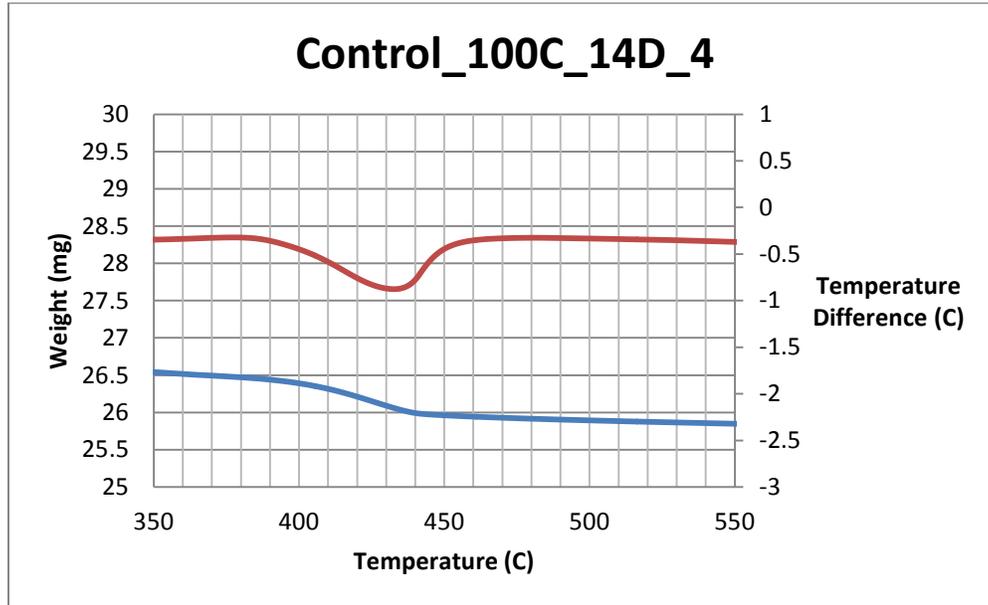


Fig. C.12 TGA curve of mortar sample4 with 100% cement in control environment at 14 days

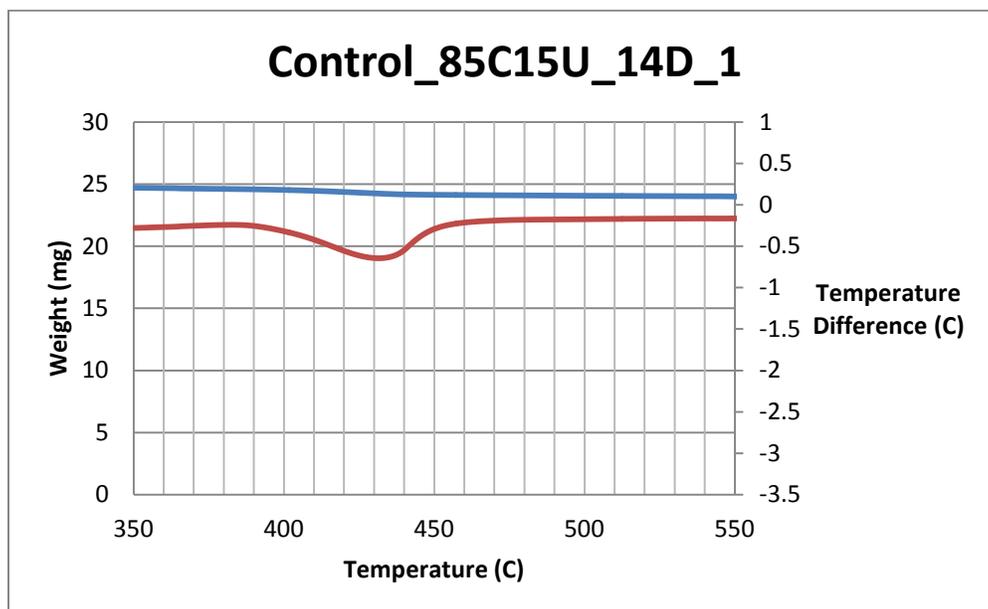


Fig. C.13 TGA curve of mortar sample1 with 85% cement and 15% pumice in control environment at 14 days

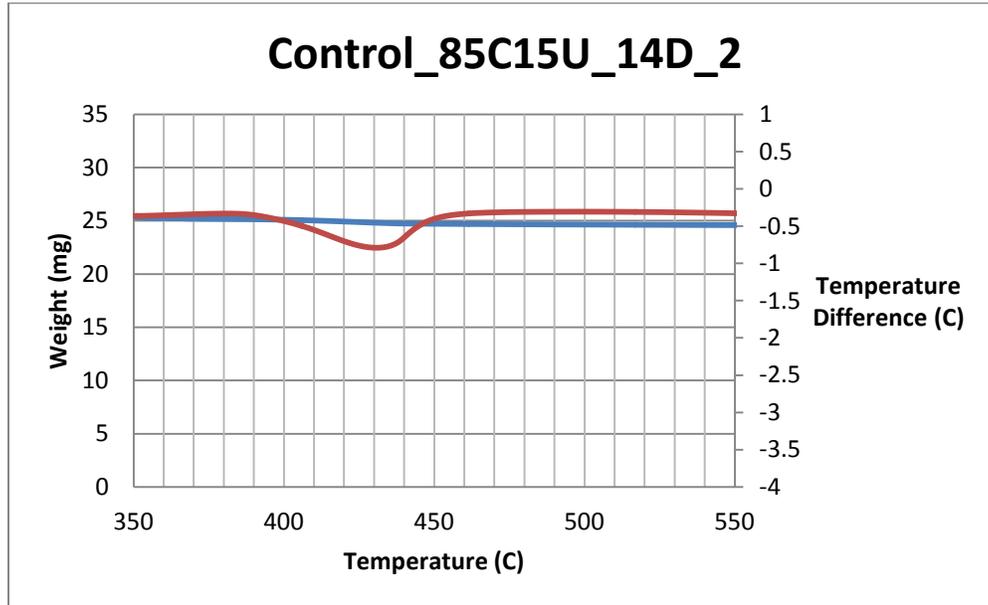


Fig. C.14 TGA curve of mortar sample2 with 85% cement and 15% pumice in control environment at 14 days

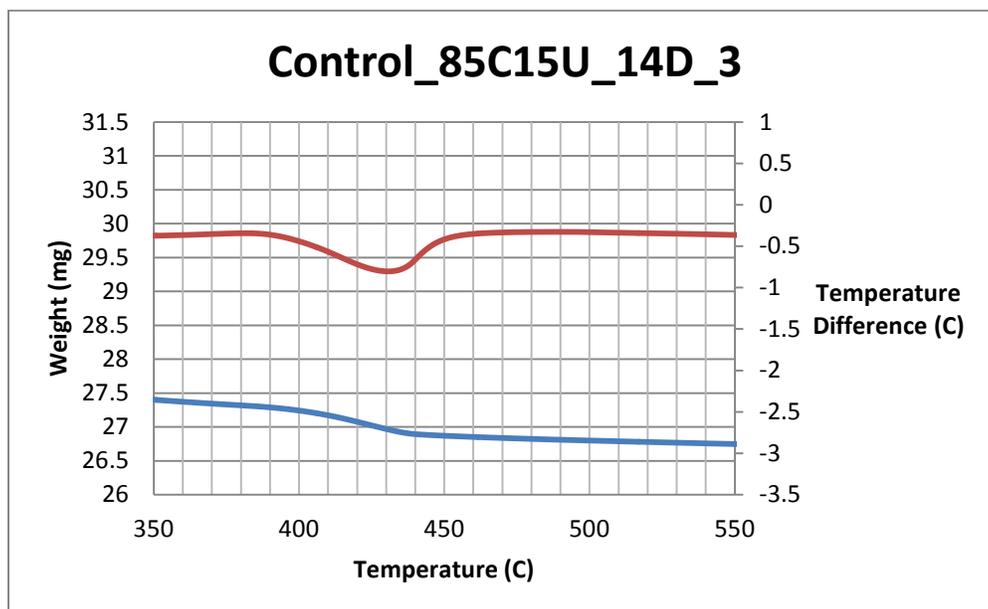


Fig. C.15 TGA curve of mortar sample3 with 85% cement and 15% pumice in control environment at 14 days

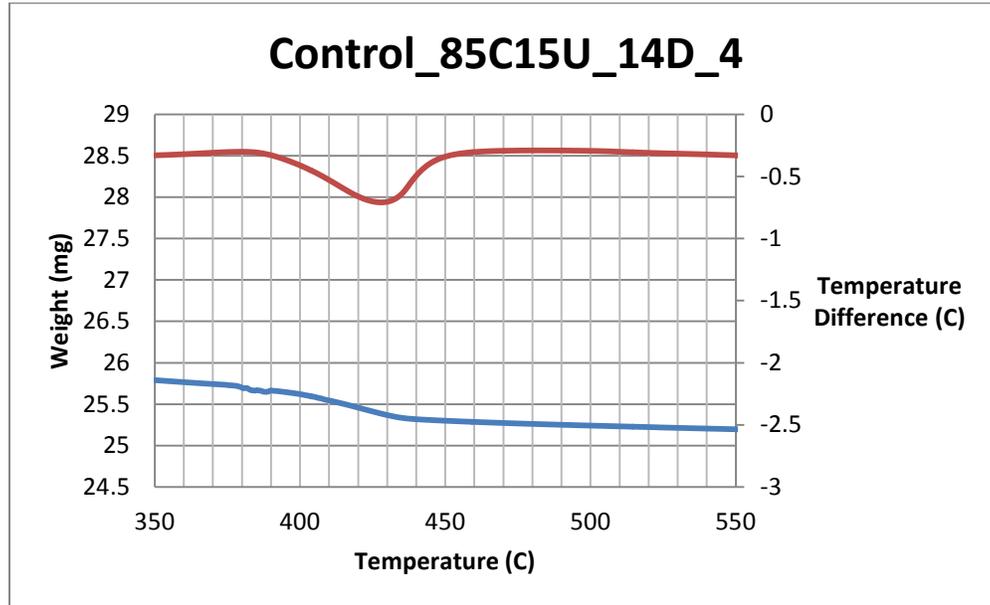


Fig. C.16 TGA curve of mortar sample4 with 85% cement and 15% pumice in control environment at 14 days

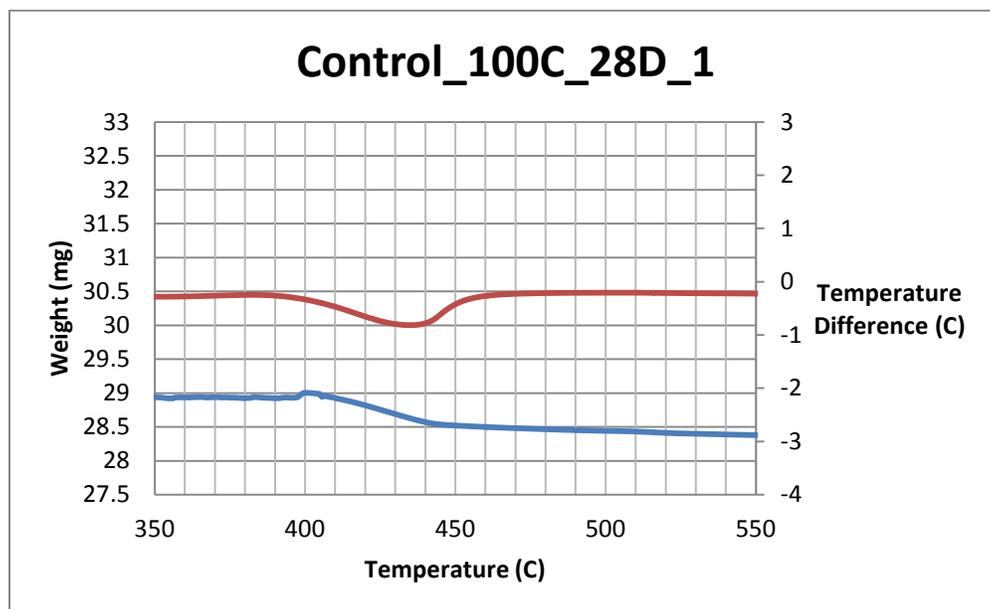


Fig. C.17 TGA curve of mortar sample1 with 100% cement in control environment at 28 days

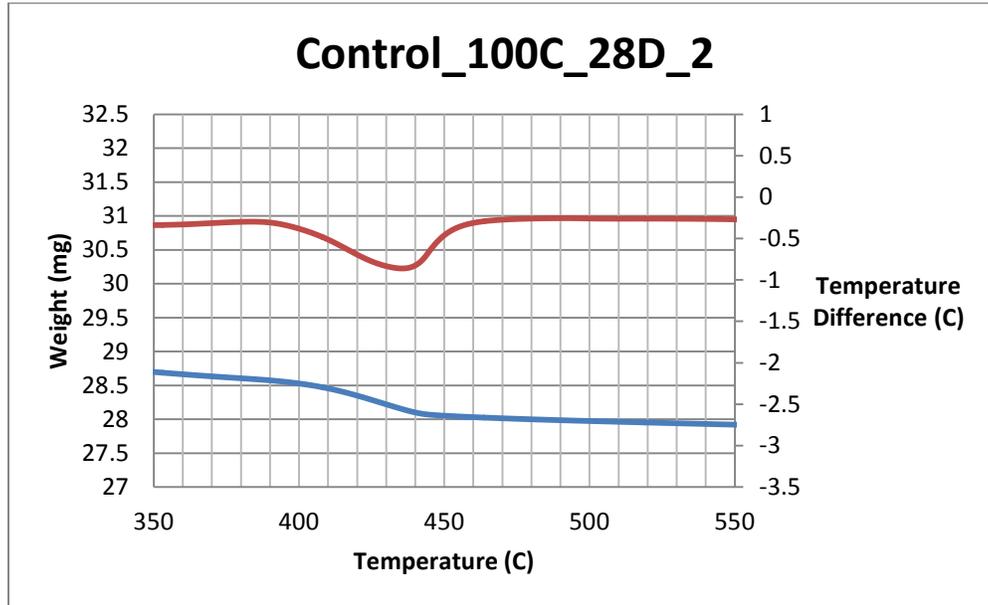


Fig. C.18 TGA curve of mortar sample2 with 100% cement in control environment at 28 days

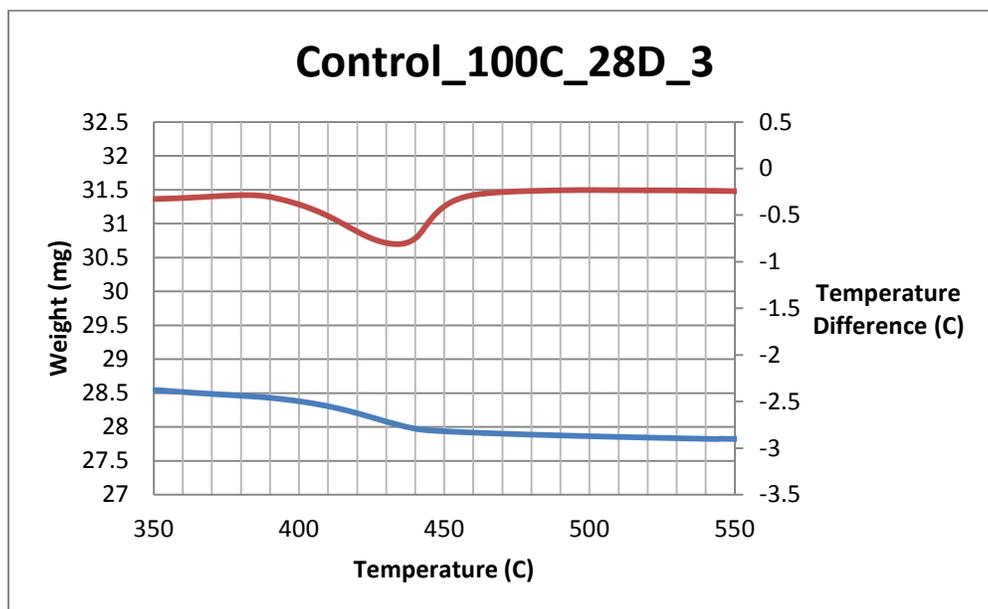


Fig. C.19 TGA curve of mortar sample3 with 100% cement in control environment at 28 days

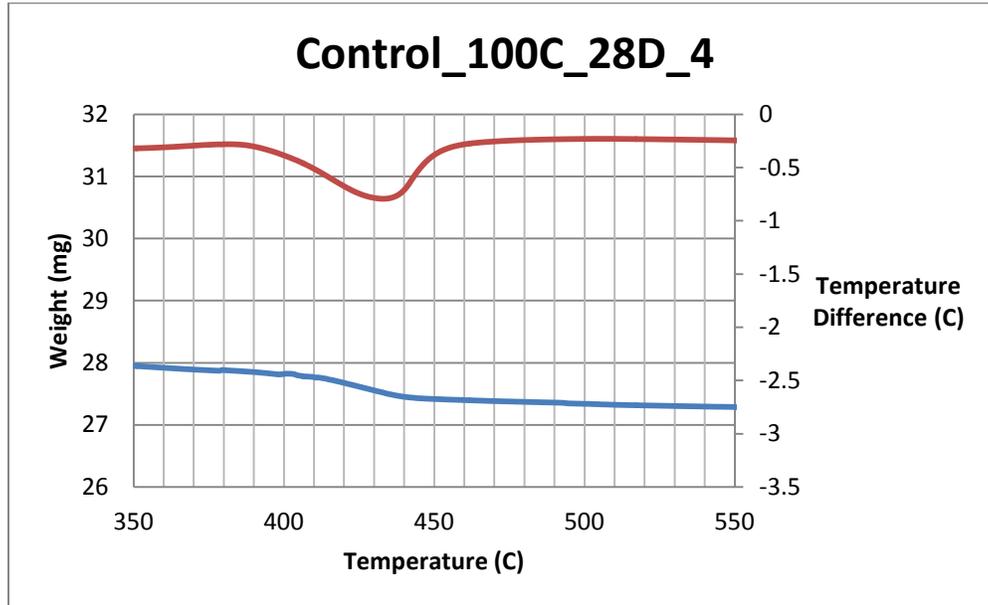


Fig. C.20 TGA curve of mortar sample4 with 100% cement in control environment at 28 days

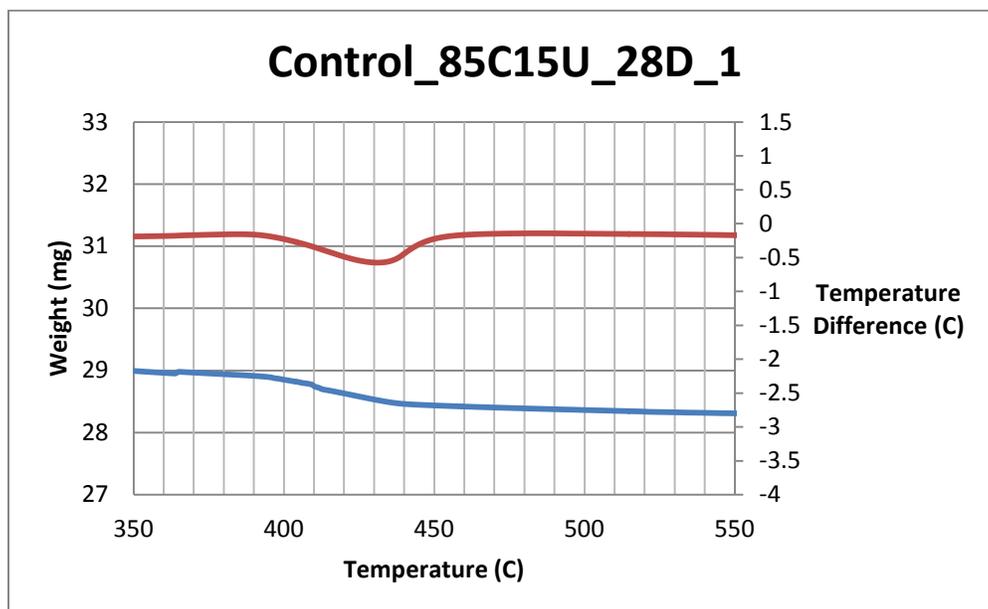


Fig. C.21 TGA curve of mortar sample1 with 85% cement and 15% pumice in control environment at 28 days

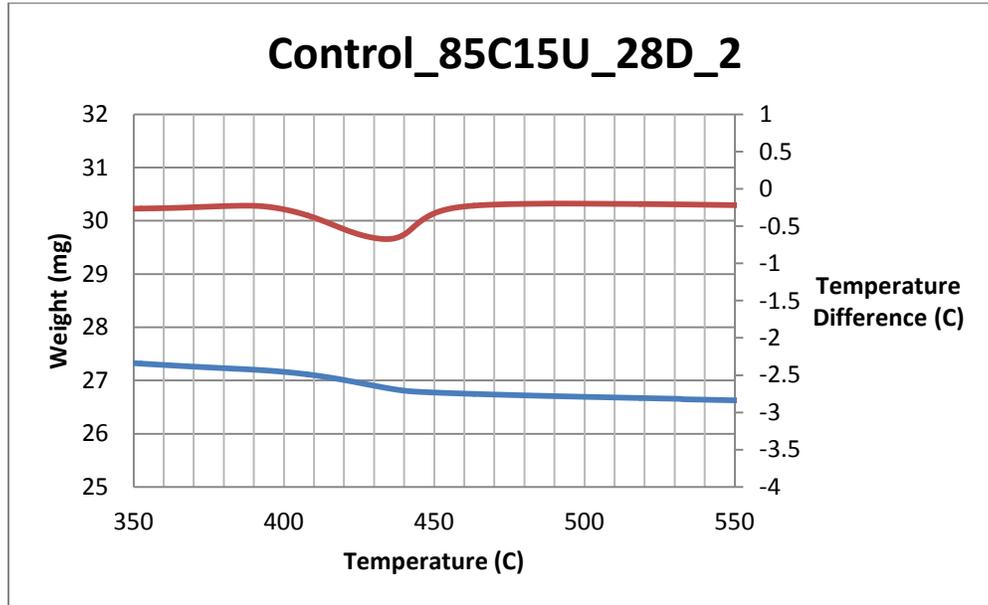


Fig. C.22 TGA curve of mortar sample2 with 85% cement and 15% pumice in control environment at 28 days

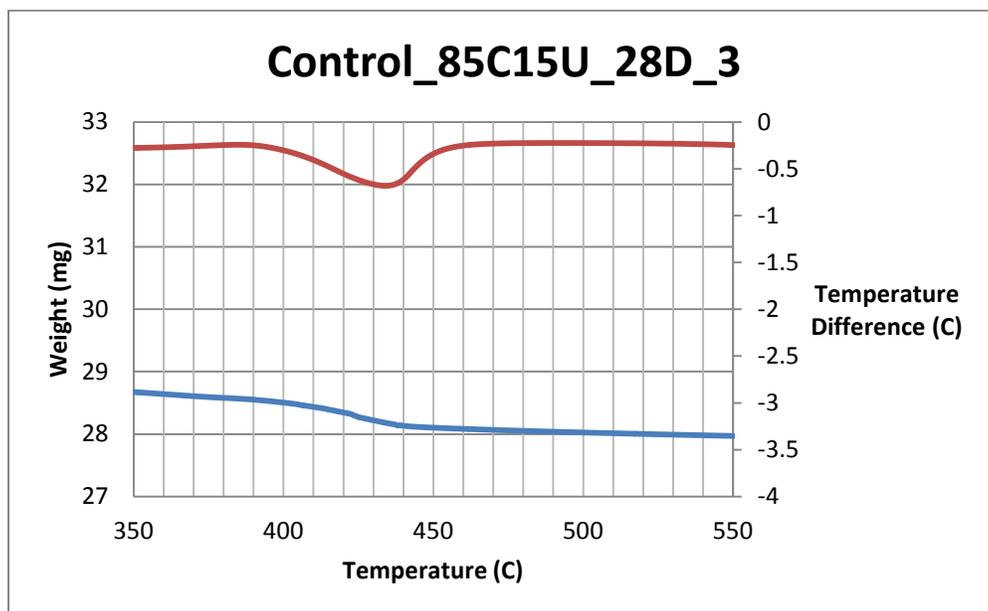


Fig. C.23 TGA curve of mortar sample3 with 85% cement and 15% pumice in control environment at 28 days

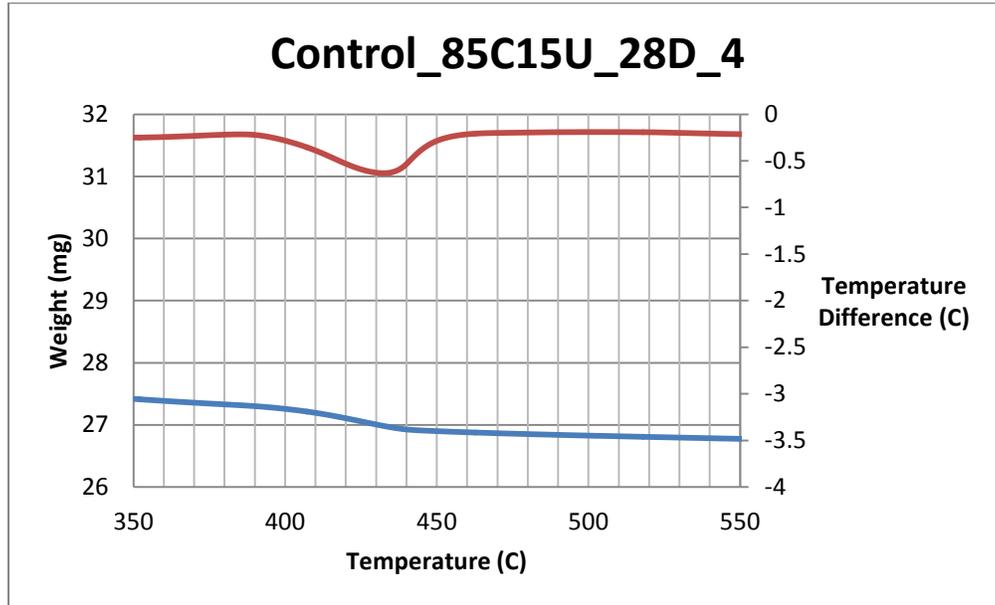


Fig. C.24 TGA curve of mortar sample4 with 85% cement and 15% pumice in control environment at 28 days

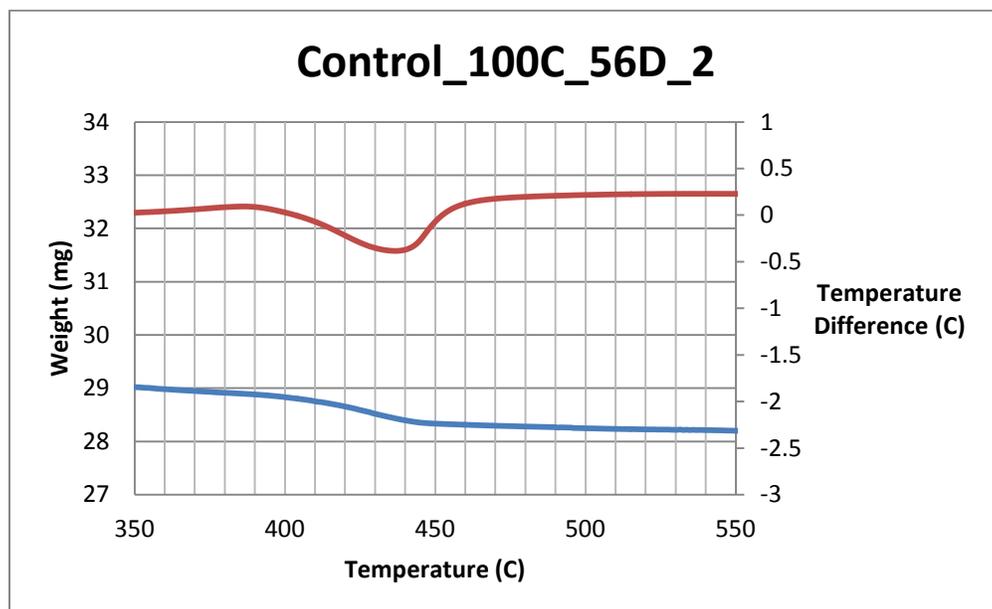


Fig. C.25 TGA curve of mortar sample2 with 100% cement in control environment at 56 days

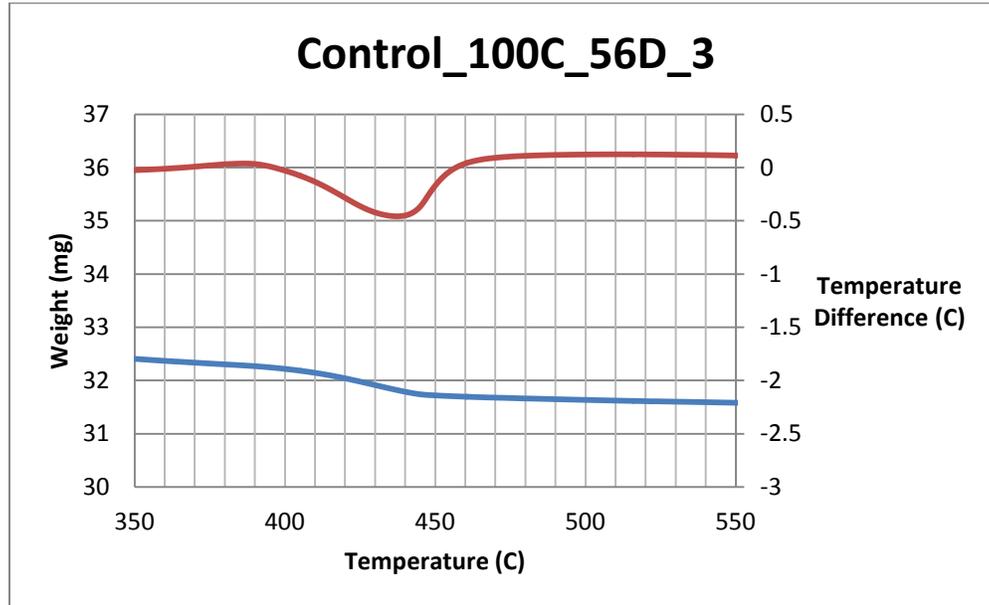


Fig. C.26 TGA curve of mortar sample3 with 100% cement in control environment at 56 days

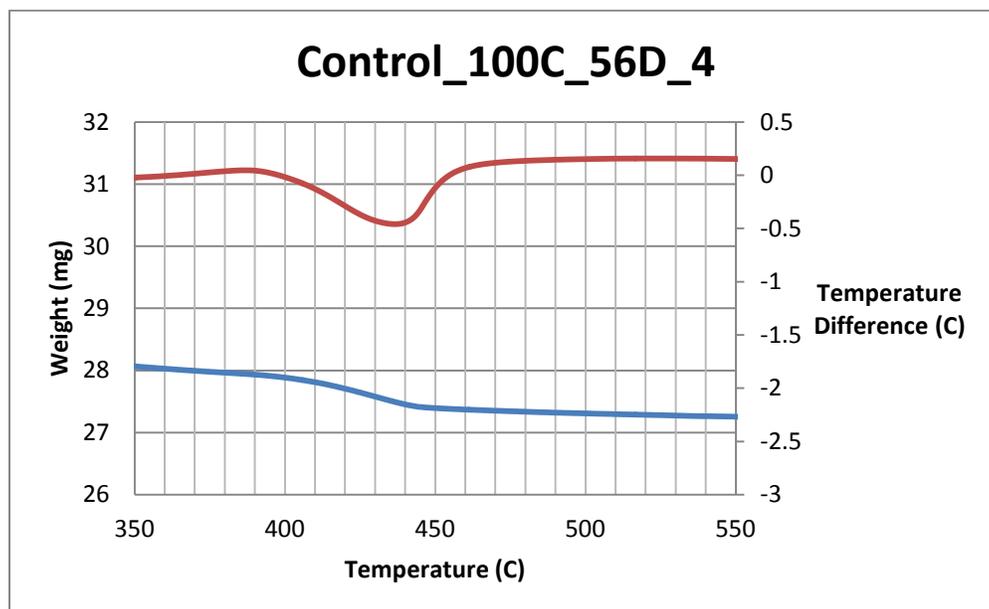


Fig. C.27 TGA curve of mortar sample4 with 100% cement in control environment at 56 days

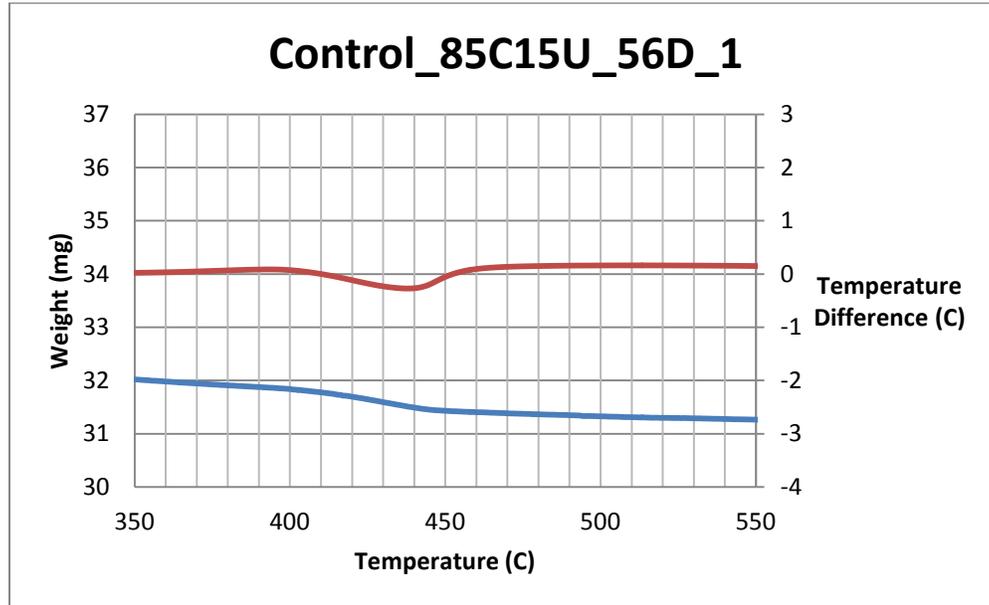


Fig. C.28 TGA curve of mortar sample1 with 85% cement and 15% pumice in control environment at 56 days

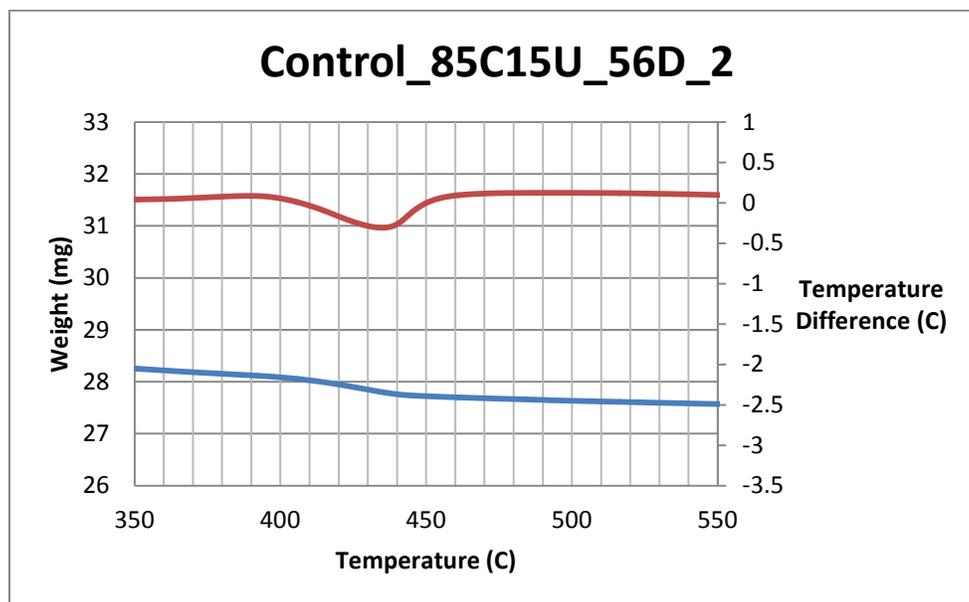


Fig. C.29 TGA curve of mortar sample2 with 85% cement and 15% pumice in control environment at 56 days

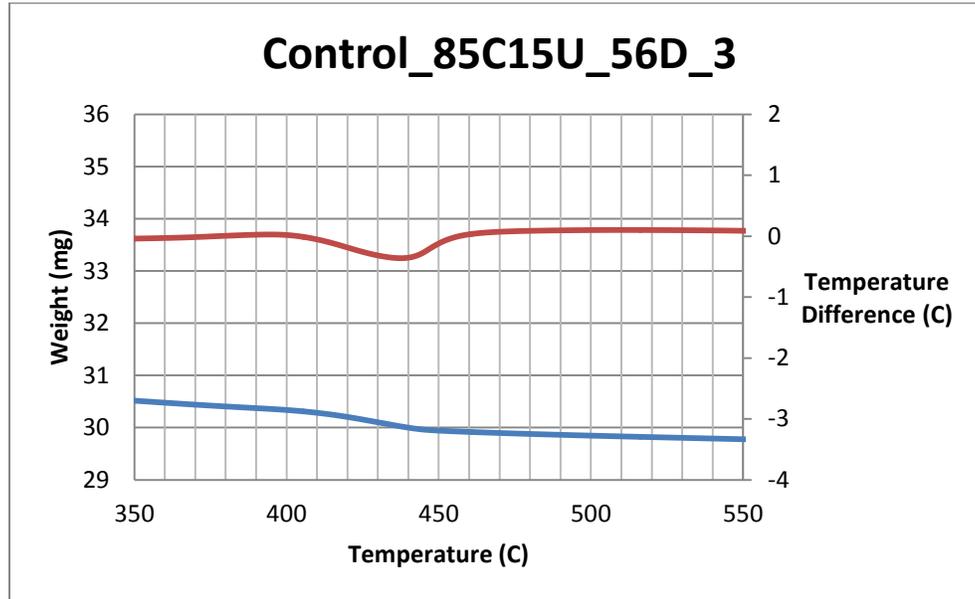


Fig. C.30 TGA curve of mortar sample3 with 85% cement and 15% pumice in control environment at 56 days

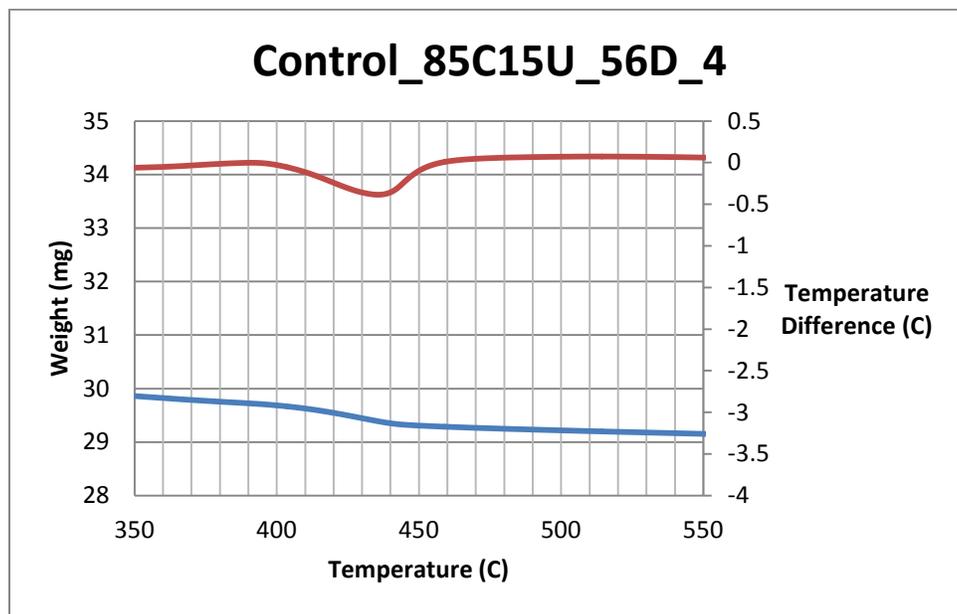


Fig. C.31 TGA curve of mortar sample4 with 85% cement and 15% pumice in control environment at 56 days

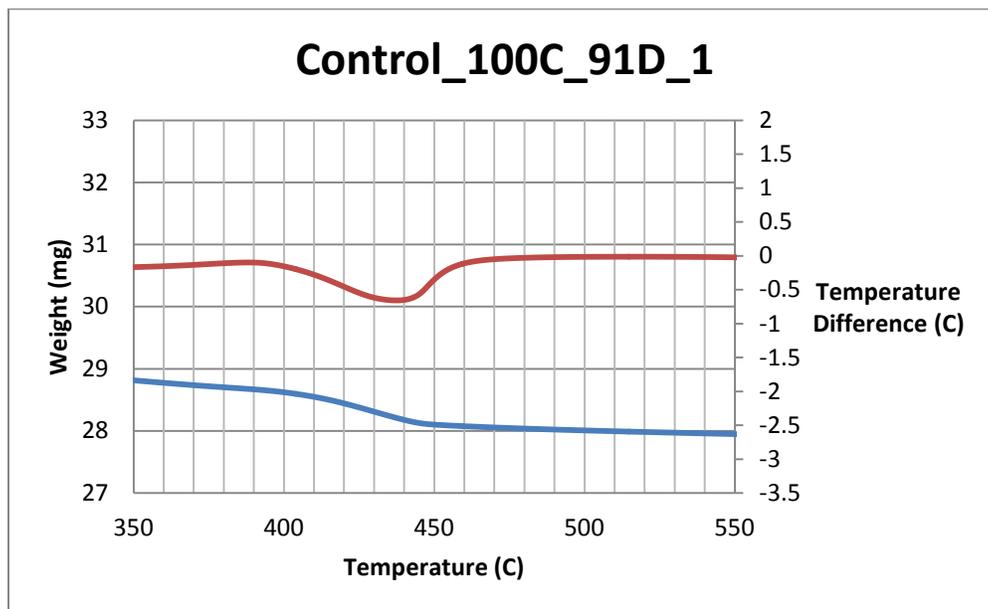


Fig. C.32 TGA curve of mortar sample1 with 100% cement in control environment at 91 days

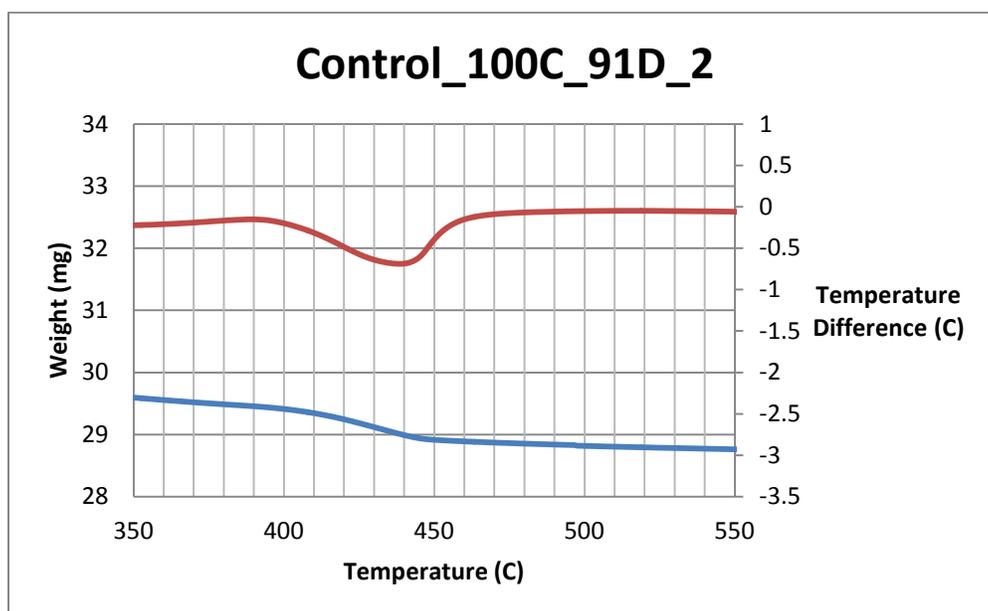


Fig. C.33 TGA curve of mortar sample2 with 100% cement in control environment at 91 days

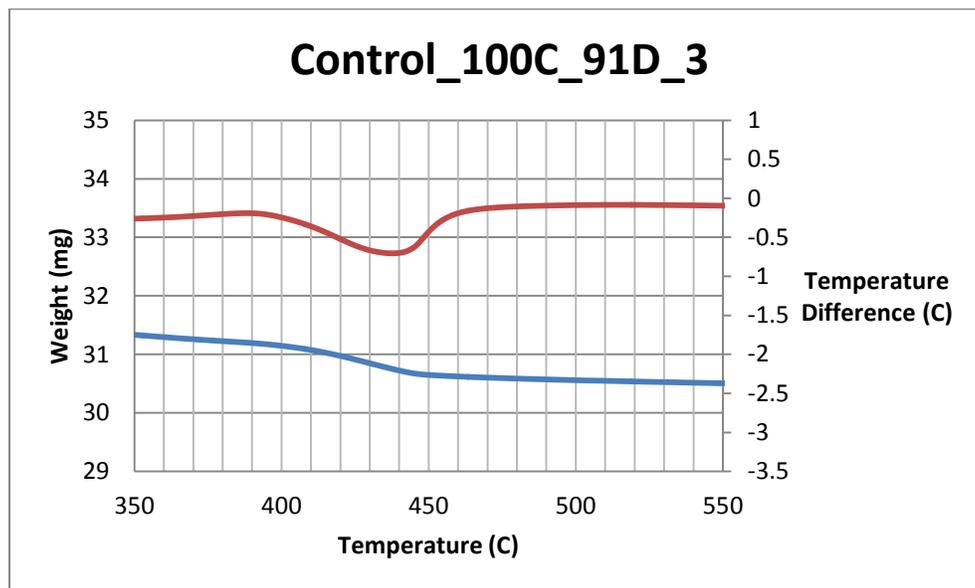


Fig. C.34 TGA curve of mortar sample3 with 100% cement in control environment at 91 days

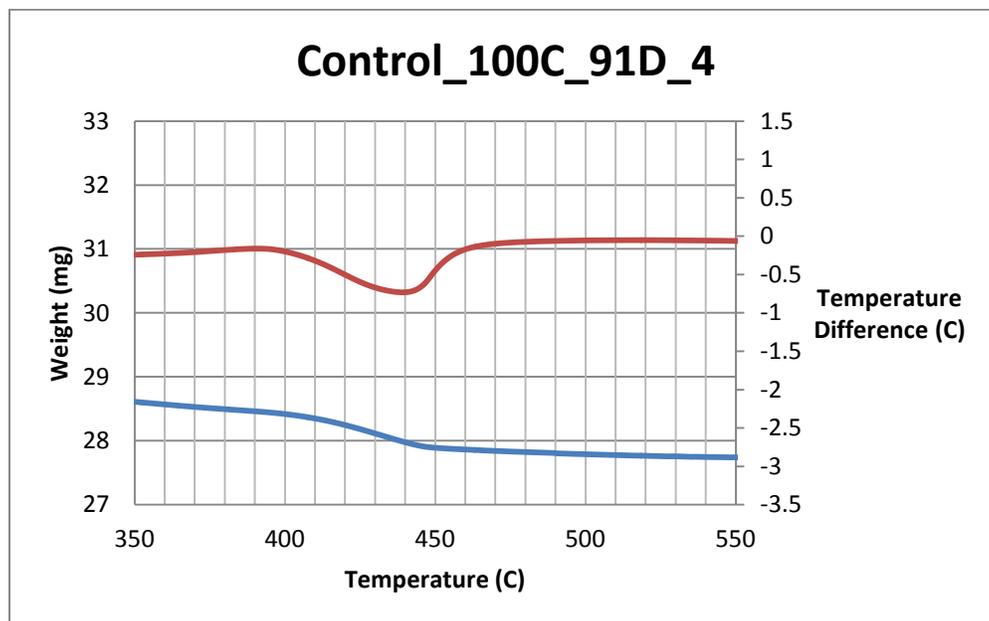


Fig. C.35 TGA curve of mortar sample4 with 100% cement in control environment at 91 days

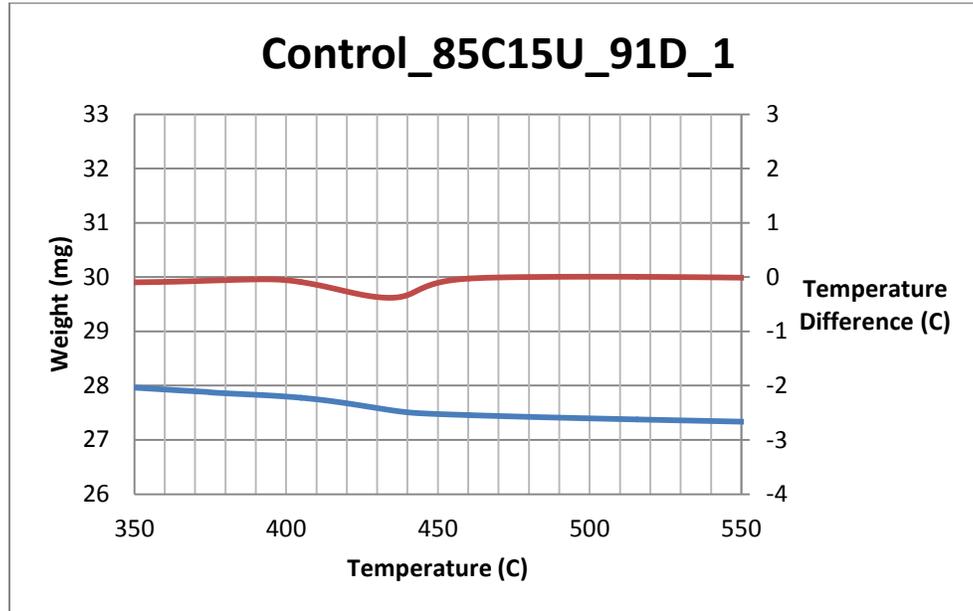
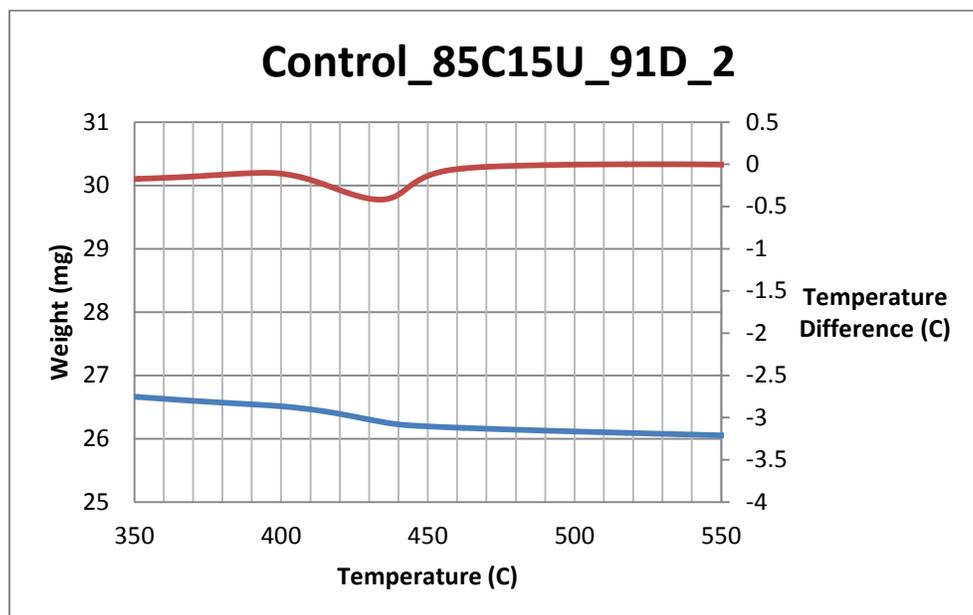


Fig. C.36 TGA curve of mortar sample1 with 85% cement and 15% pumice in control environment at 91 days



. Fig. C.37 TGA curve of mortar sample2 with 85% cement and 15% pumice in control environment at 91 days

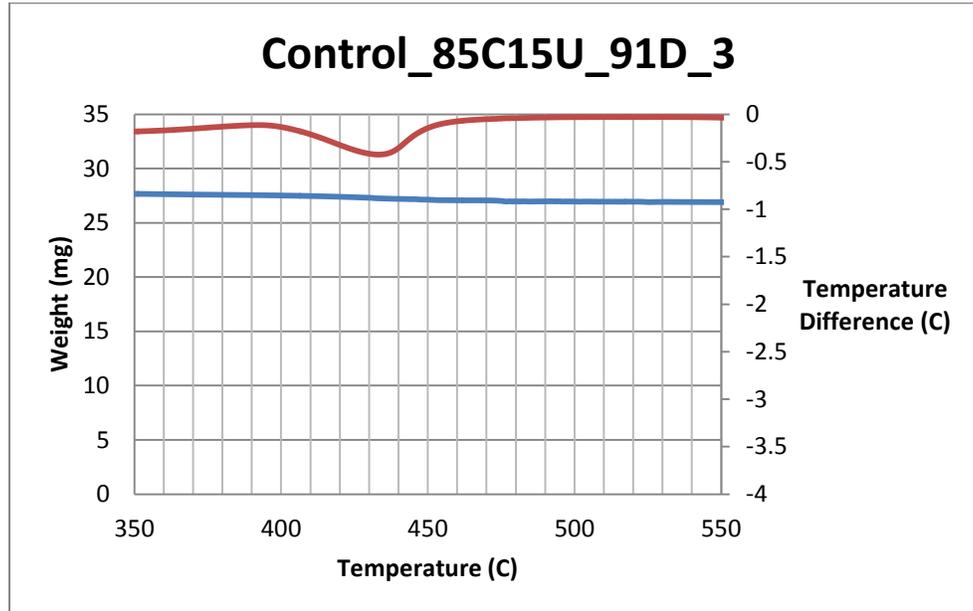


Fig. C.38 TGA curve of mortar sample3 with 85% cement and 15% pumice in control environment at 91 days

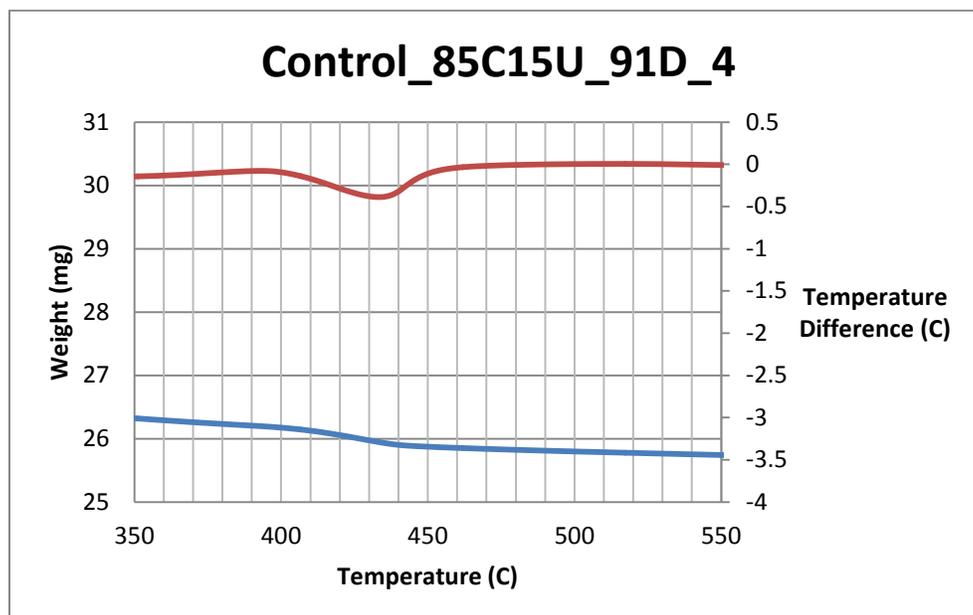


Fig. C.39 TGA curve of mortar sample4 with 85% cement and 15% pumice in control environment at 91 days