

Univerza v Ljubljani



**INFLUENCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS ON
HYDRATION, MICROSTRUCTURE DEVELOPMENT, AND DURABILITY
OF CONCRETE**

DOCTORAL THESIS

Tina Simčič

Supervisors:

prof. dr. Stane Pejovnik

prof. dr. ir. Geert De Schutter

Ljubljana, july 2015

Izjavljam, da sem avtorica predložene doktorske disertacije in da je opisano delo rezultat mojega raziskovalnega dela.

Tina Simčič

Ljubljana, 23.06.2015

Zahvala

Opravljeno raziskovalno delo se je izvajalo na različnih ustanovah in laboratorijih, in sicer na Fakulteti za kemijo in kemijsko tehnologijo na Katedri za materiale in polimerno inženirstvo, na Fakulteti za gradbeništvo in geodezijo na Katedri za preskušanje materialov in konstrukcij, v podjetju Primorje d.d. ter na Ghent University v Magnel Laboratory for Concrete Research. Za možnost dela na tako raznolikih lokacijah in sodelovanjem z različnimi ljudmi se zahvaljujem vsem, ki ste mi to omogočili.

Mnogi so prispevali k uspešnem zaključku te doktorske disertacije. Težko bi vse naštela. Med najzaslužnejšimi so:

Mentorju prof. dr. Stanetu Pejovnik, se zahvaljujem za strokovno pomoč, usmeritve in vspodbudo. V ključnem trenutku me je znal motivirati in podpreti, da sem doktorsko nalogo zaključila. Posebno se mu zahvaljujem za organizacijo izmenjave na univerzi v Ghentu.

I would like to express my gratitude to my co-supervisor prof. dr. Geert De Schutter for giving me the opportunity to work at Ghent University. Thanks for your excellent supervision, support and encouragement throughout the duration of this thesis. I want to thank the whole staff at Magnel Labo, for great technical and intellectual support and for making my stay in Ghent unforgettable.

Posebna zahvala gre tudi skupini Primorje, ki me je seznanila z znanstvenim pristopom pri obravnavi betona. Posebna zahvala gre Zvonku Cotiču za vse diskusije in odpiranja novih idej za reševanje problemov. Njegova vnema pri problematiki betona mi je bila mnogokrat vzor. Hvala tudi Karmen Koglot za njeno mentorstvo v času njenega dela na Primorju.

Zahvala vsem sodelavcem Katedre za materiale na FKKT, še posebej Marjanu Marinšku za delo na elektronskem mikroskopu, Vojmirju Francetiču za vse pogovore in napotke za raziskovalno delo, Klementini Zupan in Barbari Novosel ter tudi Amaliji Golobič za pomoč pri XRD vzorcih.

Posebna zahvala gre tudi prof. dr. Violeti Bokan Bosiljkov, ki mi je bila skozi celoten študij v veliko pomoč. Z njenim obiskom v Ghentu je pokazala pomembnost naloge. Po povratku mi je omogočila delo v laboratoriju na Katedri za preskušanje materialov in konstrukcij, kjer sem spoznala tudi odlične sodelavce in prijatelje. Hvala Petri, Davidu, Franciju, Meti za vse prijetne urice na katedri.

Nazadnje pa posebna zahvala družini, ki me je podpirala in spodbujala skozi celoten študij.

POVZETEK

Uporaba dodatnih materialov s hidravličnimi ali pucolanskimi lastnostmi (supplementary cementitious material - SCM) v betonu se je v zadnjih letih močno razširila zaradi težnje po trajnostnem razvoju. Glavni razlog za to je v zmanjševanju specifične potrebe po energiji in emisij ogljikovega dioksida pri proizvodnji cementa (OPC). Okolju prijazen SCM material je tudi elektrofiltrski pepel (EFP), ki nastaja kot stranski produkt v termoelektrarnah.

V prvem delu disertacije smo spremljali hidratacijo OPC in EFP s pomočjo kalorimetrije in termogravimetrije. V prvih urah EFP upočasni začetno hidratacijo cementa, še posebej hidratacijo belita. V obdobju med 21 in 28 dnevi smo v cementnih pastah z dodatkom EFP zaznali zmanjšanje vsebnosti kalcijevega hidroksida (CH) ter posledično povečanje vsebnosti vezane vode, glede na vsebnosti pri OPC, zaradi pucolanske reakcije. To kaže na spremembo nastalih produktov hidratacije v sistemu OPC-EFP, in sicer zmanjšana vsebnost CH, povečanje C-S-H faze ter AF_m faze glede na vsebnosti v OPC. V obdobju enega leta je poraba CH 50% večja pri cementnih pastah, ki vsebujejo 30% EFP kot v primeru cementne paste brez dodatka. Ta pojav se odraža v opaznem povečanju mehanskih trdnosti veziva v daljšem časovnem obdobju. Po 90 dneh tlačne trdnosti betonov z 20% zamenjavo cementa z EFP presegajo vrednosti tlačnih trdnosti betonov s čistim cementom. V primeru 50% zamenjave OPC z EFP, pa so vrednosti 90 dnevih tlačnih trdnosti skoraj primerljive.

Pri vrednotenju mehanskih lastnosti dveh betonskih mešanic pripravljenih z različno vrsto karbonatnega agregata, vendar z enako recepturo, smo opazili, v primeru betonske mešanice z dolomitnim agregatom, znatno povečanje tlačnih trdnosti (24%) ter elastičnega modula (13%), v primerjavi z betonsko mešanico pripravljeno z apnenčastim agregatom. Te razlike so vodile nadaljnjo raziskavo alkalno-karbonatne reakcije (ACR), ki nastane ko karbonatni minerali reagirajo v alkalnem okolju, kar se kaže s pričetkom reakcije imenovane dedolomitizacija. Ugotovili smo, da v nasprotju z dosedanjim prepričanjem v literaturi, proces ACR poteče po 6-ih mesecih v maltah potopljenih v vodni medij, pripravljenih z zelo čistim dolomitnim agregatom brez vsebnosti reaktivnega silicija. To pomeni, da ne potrebujemo katalizatorja, kot je močno alkalna raztopina oziroma reaktivnih primesi, za pričetek reakcije. Poleg tega, smo opazili na meji med dedolomitiziranim agregatom ter sekundarnim kalcitom novo fazo, bogato s Si, Al in Mg atomi. Domnevamo, da je ta pojav vzrok za izboljšanje mehanskih lastnosti betonske mešanice pripravljene z dolomitnim agregatom, zaradi gostejše medfazne prehodne cone ter boljše povezave cementnega veziva in zrn agregata.

Preiskovali smo obnašanje betona z dodatkom EFP v agresivnih okoljih, v primerjavi z betonom z OPC. Rezultati preiskav kažejo na pozitiven učinek betona z dodatkom EFP v kloridnem okolju, tudi v primeru, ko smo 50% OPC nadomestili z EFP. Višji odstotek t.i. »ink-bottle« poroznosti smo eksperimentalno potrdili za betone z dodatkom EFP. Zaradi tega se tem betonom zniža efektivna poroznost, kar se odraža v večji odpornosti betona na prodor kloridov. Učinek zamenjave OPC z EFP na vezavo kloridov ni bil posebej izrazit, čeprav smo s kalorimetrijo potrdili večjo vsebnost AF_m faze za cementno pasto z EFP v primerjavi z vsebnostjo te faze v OPC. Odpornost betona z dodatkom EFP je bila slabša v primerjavi z betonom z OPC v primeru karbonatizacije in zmrzlinke odpornosti betona v prisotnosti soli. Raziskave procesa karbonatizacije so pokazale, da se globina karbonatizacije poveča s povečanjem vsebnosti zamenjave OPC z EFP v betonih, ki so bili 18 tednov izpostavljeni 10 vol% atmosferi CO₂. Kljub temu, pa je globina karbonatizacije pri betonih z 20% zamenjavo OPC z EFP na koncu življenjske dobe betona še vedno sprejemljiva v normalnih okoljih. Pri betonskih konstrukcijah, ki so izpostavljene kombiniranemu delovanju zmrzali in soli, dodatek EFP ne sme biti večji od 20%. Čeprav betonske mešanice z dodatkom EFP lahko dosežejo visoko tlačno trdnosti, ima betonska mešanica, ki vsebuje 50% EFP, izrazito slabšo odpornost površine betona proti zmrzovanju/tajanju v prisotnosti soli.

Ključne besede: elektrofiltrski pepel, beton, alkalno karbonatna reakcija, prodor kloridov

ABSTRACT

In recent years the use of supplementary cementitious materials in the production of concrete has become an ever more frequent trend, since such use contributes to a sustainable concrete industry. The main reason for this lies in the reduction of the specific energy requirement and of carbon dioxide emissions in the production of cement (OPC). One such environmentally friendly product is fly ash (FA), which occurs as a by-product of coal-fired thermal power plants.

In the first part of the thesis the hydration of OPC and FA at early ages, as well as at later ages, was monitored by means of calorimetry and thermogravimetry. During the first hours the FA retarded the hydration of OPC, particularly the belite hydration. Up to an age of 28 days, the FA exerted a physical nucleation effect on the OPC hydration, which did not compensate for the dilution effect. Furthermore, between 21 and 28 days, a decrease was observed in the amount of calcium hydroxide (CH), and a corresponding increase in the amount of bound water relative to the OPC content, due to a pozzolanic reaction, indicating a change in the hydration products that are formed in the FA blended cement, i.e. less CH and more C-S-H and AF_m phases relative to the OPC content. Comparing the two investigated types of FA, siliceous and calcareous FA, no clear difference can be observed with regard to the decrease in the amount of CH. On the other hand, the amount of hydrated products increased significantly up to 28 days, and then not changed much up to one year in the case of the cement paste with siliceous FA. In contrast, in cement paste made by using calcareous FA, the amount of hydrated products increased gradually up to one year. Over a period of one year the consumption of CH was 50% greater in the case of cement pastes containing 30% FA than in the case of cement paste without such an addition. This phenomenon was reflected over time in the observed increase in the mechanical strength of the binder. After 90 days, the compressive strength of concrete in which 20% of the OPC was replaced by FA exceeded the compressive strength of the unmodified concrete. Furthermore, when the replacement level was 50%, the 90 day compressive strengths were almost comparable.

When characterizing the mechanical properties of two concrete mixtures made with different types of carbonate aggregate but with identical mix designs, it was found that, in the case of concrete made by using dolostone aggregate, there was a considerable increase in the compressive strength (24%) and modulus of elasticity (13%), compared with the values which corresponded to concrete made by using limestone aggregate. These differences initiated a further investigation into the alkali-carbonate reaction (ACR) which occurs when carbonate minerals react in an alkaline environment. The first process of the mechanisms of ACR is called dedolomitization. In contrast to statements which can be found in the literature, in the case of the used high-purity dolostone aggregate, which did not contain any reactive silica, the dedolomitization was observed after a 6-month exposure period in water. That means that no accelerators in the form of highly alkaline solutions or reactive components are needed to initiate the reaction. Moreover, a new phase which was rich in Si, Al and Mg atoms, was observed between the dedolomitized aggregate and the secondary calcite. It is supposed that this phenomenon may be responsible for the improvement in the mechanical characteristics of the concrete made by using dolostone aggregate, due to the denser interfacial transition zone and better interlocking of the cement binder and the aggregate grains.

The behaviour of the FA modified concrete in aggressive environments was also investigated, and compared to that of unmodified concrete. The study of chloride ingress showed that the FA modified concretes achieved smaller penetration depths, and thus required smaller cover depths. The test results indicated a beneficial effect of FA modified concrete, even when 50% of the OPC was replaced by FA. The results correspond well with measured porosity by means of mercury porosimetry. A higher percentage of ink-bottle porosity was confirmed experimentally in the case of the FA modified concrete. This leads to a lower effective porosity, which means that a higher resistance of the concrete to chloride penetration was achieved. Not only the porosity but also the chemical composition of the FA plays an important role in chloride diffusion in concrete. The concrete with siliceous FA, which had a lower content of calcium, showed better resistance to chloride penetration up to 90 days than the concrete with calcareous FA. On the other hand, after 126 days the concrete with

calcareous FA showed better chloride resistance characteristics than the concrete with siliceous FA. This phenomenon seemed to correlate with experimentally observed compressive strength results. The chloride binding was also tested by means of the differences between the amount of water and total-soluble chloride content. The effect of the replacement of OPC by FA on chloride binding capacity was not particularly pronounced. However, the assumption that FA blended cements containing higher amounts of AF_m phases relative to the OPC content, which are favourable for chloride binding, was confirmed by calorimetry.

The performance of FA modified concrete was poorer in the case of carbonation and frost/salt attack by de-icing salts. With regard to carbonation, the carbonation depth increased with increasing FA content in the concrete mixture that was exposed for 18 weeks to a 10 vol% CO₂ environment. Nevertheless, the depth of carbonation at the end of the FA modified concrete's life could still be acceptable in normal environments in the cases when 20% of the OPC is replaced by FA. In the case of concrete structures that are exposed to the combined action of frost and de-icing salts, the addition of FA should not be greater than 20%. Although FA modified concrete mixtures can achieve a high compressive strength class, the concrete mixture containing 50% of FA proved to have poorer resistance to frost/salt attack. Also the impact of the type of chloride salts on frost/salt scaling was discussed. The test results indicated that sodium, magnesium, and calcium chloride at solution concentrations of 3% showed no significant differences of the unmodified concrete mixture. Otherwise, more rapid scaling rate was observed in the case when the solution concentration of CaCl₂ was increased to 24%.

SAMENVATTING

Het gebruik van alternatieve cementvervangende materialen voor de productie van beton is de laatste tijd sterk toegenomen, wegens de positieve bijdrage tot het beperken van de milieu impact. Door het vervangen van portlandcement (PC) kan de vereiste productie-energie immers verminderd worden, evenals de emissie van koolstofdioxide. Vliegashuis (VA) is een dergelijk cementvervangend poeder, beschikbaar als bijproduct van elektriciteitsproductie met kolencentrales.

In het eerste deel van de thesis wordt de hydratatie van PC en VA bestudeerd, op jonge ouderdom en op langere termijn, door middel van calorimetrie en thermogravimetrie. Tijdens de eerste uren vertraagt VA de hydratatie van PC, door een vertraging van de reactie van beliet. Tot een ouderdom van 28 dagen bevordert VA de nucleatie van hydratatieproducten van portland cement, wat echter het verdunningseffect (dilutie) niet kan compenseren. Tussen 21 en 28 dagen is door een puzzolane reactie een vermindering merkbaar van het gehalte calciumhydroxide (CH), en een overeenstemmende toename in het gehalte gebonden water relatief ten opzichte van het gehalte portland cement. Dit wijst op een wijziging in de gevormde hydratatieproducten, i.e. minder CH en meer C-S-H en AF_m zijn gevormd ten opzichte van het gehalte portland cement. Wanneer de twee verschillende types VA (kwartshoudend en kalkhoudend) vergeleken worden, kan geen duidelijk verschil waargenomen worden betreffende de reductie in het gehalte CH. Echter, het gehalte hydratatieproducten stijgt op significante wijze tot op een ouderdom van 28 dagen, waarna geen opmerkelijke wijziging meer optreedt in het geval van cementpasta met kwartshoudende VA. Hiertegenover staat dat in het geval van cementpasta met kalkhoudende VA nog een geleidelijke stijging waargenomen wordt van het gehalte hydratatieproducten tot op een ouderdom van 1 jaar. Over een periode van een jaar wordt de consumptie van CH 50% groter in het geval van cementpasta met 30% VA in vergelijking met een cementpasta volledig gebaseerd op portland cement. Dit fenomeen uit zich ook in de waargenomen sterktoename van het bindmiddel. Na 90 dagen overstijgt de sterkte van een beton met 20% PC-vervanging deze van het referentiebeton zonder vervanging. Voor een vervangingsniveau van 50% worden nagenoeg identieke sterktes bekomen.

Bij de karakterisering van de mechanische eigenschappen van twee betonsamenstellingen met verschillende types granulaten doch met voor het overige dezelfde samenstelling werd vastgesteld dat het beton met dolomiet een substantiële sterkte winst vertoont (met ongeveer 24%) evenals een winst in stijfheid (met ongeveer 13%) ten opzichte van het beton vervaardigd met kalksteengranulaten. Deze vaststellingen hebben verder onderzoek geïnitieerd betreffende de alkali-carbonaat-reactie (ACR) die kan optreden wanneer carbonaatmineralen reageren met alkaliën uit het omgevende milieu. Het eerste reactieproces in het kader van ACR wordt in de literatuur gedefinieerd als dededolomitiseren. In tegenstelling tot beweringen gevonden in de literatuur werd deze reactie effectief vastgesteld in het geval van dolomiet met een zeer hoge zuiverheid en zonder reactief silica na 6 maanden blootstelling in water. Dit betekent dat een oplossing met hoog alkaligehalte of met reactieve componenten niet vereist is om de reactie effectief te initiëren. Een nieuwe fase, rijk aan Si, Al en Mg, werd waargenomen in de zone tussen het gededolomitiseerd granulaat en het secundaire calciëet. Er wordt aangenomen dat dit fenomeen verantwoordelijk is voor de toename van de mechanische eigenschappen van het beton met dolomietgranulaten, door een hogere dichtheid van de overgangszone tussen het granulaat en de matrix, en een betere aanhechting tussen het bindmiddel en de granulaatkorrels.

Het gedrag van VA-gemodificeerd beton in agressieve omgevingen werd eveneens bestudeerd, en vergeleken met het gedrag van het referentiebeton zonder VA. De studie van de chloridepenetratie toont aan dat het VA-gemodificeerd beton geringere chloridepenetratiedieptes vertoont, en bijgevolg kleinere betondekkingen vereist. De proefresultaten wijzen op een gunstig effect van VA, zelfs indien 50% van het Portland cement vervangen wordt door VA. De resultaten stemmen goed overeen met experimentele studie van de porositeit, opgemeten door middel van kwikporosimetrie. Een hoger aandeel van de zogenaamde 'ink-bottle'-porositeit werd experimenteel bevestigd in het geval van VA-gemodificeerd beton. Dit leidt tot een lagere effectieve porositeit, zodat een hogere weerstand

tegen chloridepenetratie bekomen wordt. Niet alleen de porositeit, doch ook de chemische samenstelling van het VA speelt een belangrijke rol bij de chloridediffusie in het beton. Beton met kwartshoudend VA, met een lager gehalte aan calcium, vertoont een betere weerstand tegen chloridepenetratie tot op een ouderdom van 90 dagen in vergelijking met het beton met kalkhoudend VA. Anderzijds vertoont het beton met kalkhoudend VA na 126 dagen een betere weerstand tegen chloridepenetratie dan het beton met kwartshoudende VA. Dit fenomeen leek ook gecorreleerd met waargenomen druksterkteresultaten. De chloridebinding werd ook experimenteel bestudeerd door de studie van het verschil tussen het vrij oplosbaar chloridegehalte en het totaal oplosbaar chloridegehalte. Het effect van de vervanging van portland cement door VA op de chloridebinding was niet uitgesproken. Echter, de aanname dat VA-gemodificeerde bindmiddelen een hoger gehalte aan AF_m-fasen bevatten relatief ten opzichte van het gehalte portland cement, wat gunstig is voor de binding van chloriden, werd experimenteel bevestigd.

De prestaties van VA-gemodificeerd beton zijn meer gematigd in het geval van carbonatatie of vorst-dooizout-aantasting. De carbonatatie diepte na 18 weken blootstelling aan een 10% CO₂-omgeving neemt toe met toenemend gehalte aan VA. Nochtans worden, met het oog op de te behalen gebruiksduur, aanvaardbare carbonatatie dieptes bekomen voor gehalten aan VA oplopend tot 20%. In het geval van een gecombineerde blootstelling aan vorst-dooizout-aantasting en carbonatatie wordt het gehalte aan VA best beperkt tot 20%. Alhoewel VA-gemodificeerd beton een hoge sterkteklasse kan vertonen, tonen de proeven aan dat het beton met 50% VA een beperkte weerstand heeft tegen vorst-dooizout-aantasting. Tevens werd de invloed van het type chloorzout op de vorst-dooi-weerstand bestudeerd. De experimentele resultaten geven aan dat oplossingen van natrium-, magnesium- en calciumchloride met concentratie gelijk aan 3% geen significante verschillen opleveren betreffende het vorst-dooigedrag van het referentiebeton. Anderzijds werd een snellere degradatie door afschilfering waargenomen in het geval van een calciumchloride-oplossing met een concentratie verhoogd tot 24%.

TABLE OF CONTENTS

1	INTRODUCTION.....	12
1.1	GENERAL INTRODUCTION.....	12
1.1.1	<i>Background of the research project.....</i>	<i>12</i>
1.2	LITERATURE REVIEW.....	14
1.2.1	<i>Ordinary Portland Cement.....</i>	<i>14</i>
1.2.2	<i>Fly ash blended cement.....</i>	<i>16</i>
1.2.3	<i>Mechanical characteristics of fly ash modified concrete.....</i>	<i>20</i>
1.2.4	<i>Alkali carbonate reaction.....</i>	<i>22</i>
1.2.5	<i>Carbonation.....</i>	<i>24</i>
1.2.6	<i>Chloride ingress.....</i>	<i>26</i>
1.2.7	<i>Resistance to freezing and thawing in combination with de-icing salts.....</i>	<i>28</i>
2	SCOPE AND STRATEGY OF THE RESEARCH PROJECT	30
2.1	OBJECTIVES	30
2.2	RESEARCH STRATEGY.....	30
3	EXPERIMENTAL STUDY.....	32
3.1	THE EFFECT OF FLY ASH BLENDED CEMENT ON THE CHEMICAL PROPERTIES OF THE BINDER 32	
3.1.1	<i>Materials.....</i>	<i>32</i>
3.1.2	<i>Binder proportion.....</i>	<i>35</i>
3.1.3	<i>Test procedures.....</i>	<i>36</i>
3.2	THE EFFECT OF FLY ASH ON THE CHARACTERISTICS OF FRESH AND HARDENED CONCRETE 38	
3.2.1	<i>Materials.....</i>	<i>38</i>
3.2.2	<i>Concrete mixture proportion.....</i>	<i>40</i>
3.2.3	<i>Testing fresh concrete.....</i>	<i>41</i>
3.2.4	<i>Testing hardened concrete.....</i>	<i>41</i>
3.3	ALKALI CARBONATE REACTION.....	42
3.3.1	<i>Materials.....</i>	<i>42</i>
3.3.2	<i>Test procedures.....</i>	<i>42</i>
3.4	THE EFFECT OF FLY ASH MODIFIED CONCRETE ON DURABILITY	45
3.4.1	<i>Concrete mixture proportion.....</i>	<i>45</i>
3.4.2	<i>Test procedures.....</i>	<i>46</i>
4	RESULTS AND DISCUSSION	51
4.1	THE EFFECT OF FLY ASH BLENDED CEMENT ON THE CHEMICAL PROPERTIES OF THE BINDER 51	

4.1.1	<i>Isothermal calorimetry</i>	51
4.1.2	<i>Thermal Analysis</i>	54
4.1.3	<i>Discussion</i>	59
4.2	THE EFFECT OF FLY ASH ON THE CHARACTERISTICS OF FRESH AND HARDENED CONCRETE 60	
4.2.1	<i>Fresh concrete properties</i>	60
4.2.2	<i>Hardened concrete properties</i>	61
4.2.3	<i>Discussion</i>	63
4.3	ALKALI CARBONATE REACTION.....	65
4.3.1	<i>Measurements of length change</i>	65
4.3.2	<i>Results on the stone prisms</i>	65
4.3.3	<i>Results on the mortar prisms</i>	67
4.3.4	<i>Discussion</i>	74
4.4	CARBONATION	78
4.4.1	<i>Properties of the hardened concrete</i>	78
4.4.2	<i>Influence of the concrete composition</i>	78
4.4.3	<i>Discussion</i>	79
4.5	CHLORIDE INGRESS.....	81
4.5.1	<i>Cyclic immersion and drying test</i>	81
4.5.2	<i>The NSSM tests</i>	89
4.5.3	<i>Discussion</i>	91
4.6	FROST/SALT SCALING	93
4.6.1	<i>Properties of fresh and hardened concrete</i>	93
4.6.2	<i>Type and concentration of de-icing salts</i>	93
4.6.3	<i>Influence of concrete composition</i>	95
4.6.4	<i>Discussion</i>	98
5	CONCLUSION	99
5.1	MAIN RESEARCH FINDINGS	99
5.2	RESEARCH PERSPECTIVES	103
	REFERENCE	105
	UVOD	111
	ZAKLJUČEK	112
	NADALJNJE RAZISKAVE	116

LIST OF SYMBOLS

%	All percentages in the thesis are expressed in weight percentage
AAS	Atomic Absorption Spectrometry
ACR	Alkali Carbonation Reaction
AF _m	Monosulphate phase
AF _t	Ettringite phase
AS	Aluminosilicate
ASR	Alkali-Silica Reaction
B	Binder
C-(A)S-H	Calcium Silicate Aluminate Hydrates
C-A-H	Calcium Aluminate Hydrates
CEM	Cement
CH	Calcium hydroxide or Portlandite
CO ₂	Carbon Dioxide
C-S-H	Calcium Silicate Hydrates
D/H	Diameter/Height
DTG	Differential Thermogravimetric Analysis
EDS	Energy-Dispersive X-ray Spectroscopy
FA	Fly Ash
H	H ₂ O, water
IR	Infrared Spectroscopy
Mon	Months
OPC	Ordinary Portland Cement
S	Slag
SCM	Supplementary Cementitious Materials
SEM	Scanning Electron Microscopy
TG	Thermogravimetric Analysis
W/B	Water/binder ratio
W/C	Water/cement ratio
XRD	Powder X-Ray Diffraction
XRF	X-Ray Fluorescence

1 INTRODUCTION

1.1 GENERAL INTRODUCTION

1.1.1 Background of the research project

Among all building materials used throughout the world, concrete is the commonest. Its resistance to both fire and water, the fact that it can be produced in different shapes, its relatively low production costs, the good availability of raw materials, and its high compressive strength all help to facilitate its widespread use. High durability can also be achieved in the case of certain compositions. However, during its production a total of approximately 0.13 ton of CO₂ is emitted per ton of concrete produced, depending on the cement type, as well as the strength and durability class of the concrete. The major part of the CO₂ embodied in concrete originates from the clinker in the cement. The cement industry is indeed responsible for about 5-8% of global man-made CO₂ emissions [1]. Sustainable development trends require a reduction in greenhouse gas emissions, so that in recent years much attention has been paid to the search for methods which could be used to reduce the clinker content in cement by replacing it with supplementary cementitious materials - SCMs.

SCMs are mostly by-products of other industries. The most significant advantage of the use of SCM in concrete production, apart from the fact a certain amount of clinker is replaced, is the reduction in the amount of waste materials dumped in landfills. Furthermore, if high durability behaviour of the concrete can be achieved, then the service life of concrete is increased so that the consumption of natural resources is reduced. The use of SCMs in concrete mixture has also been shown to be efficient from the economical point of view.

The use of SCMs depends strongly on their availability and quality. In the case of concrete production, the most promising type of industrial waste must be available in large quantities. In Slovenia, this is surely fly ash (FA), which is collected from exhaust by electrostatic or mechanical precipitation in the thermal power plants at Trbovlje and Šoštanj. The use of this waste material as a mineral addition to concrete has, however, increased only in recent years. In Slovenia it was only fairly recently that a start was made to the controlled use of FA in the role of a mineral addition to concrete, after the SIST EN 206-1 standard was introduced to construction practice,

and first certificate of conformity was issued for FA. Before that rather non-controlled use of FA resulted in several failed applications and even increased radioactivity of structural elements in buildings, which resulted in the belief that FA is too problematic to be used as a concrete addition.

FA from Trbovlje had already obtained a certificate of conformity according to the standard SIST EN 450-1:2005. Due to its varying chemical composition, its effect on the hydration process is yet not entirely known and not many data can be found in the literature concerning the reaction of calcareous FA with cement and its durability behaviour [2].

1.2 LITERATURE REVIEW

1.2.1 Ordinary Portland Cement

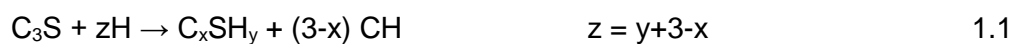
Ordinary Portland Cement (OPC) is produced by burning finely ground raw meal mainly consisting of limestone, and to a lesser extent marl, clay or even shale, at about 1450 °C in a rotary kiln. The product of such burning is called clinker. The clinker is cooled down very fast and is then ground into a fine powder with a small amount of gypsum in order to obtain OPC.

The main oxides of the ordinary Portland clinker are: CaO (60-70%), SiO₂ (18-22%), Al₂O₃ (4-6%) and Fe₂O₃ (2-4%). They represent about 95% of the clinker, and the remaining 5% includes MgO, K₂O, Na₂O, TiO₂, Mn₂O₃, and SO₃. The main mineralogical phases of OPC are listed in Table 1.1 [3].

Table 1.1: The main phases of OPC and their characteristics [3]

Parameter	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Chemical formula	3·CaO·SiO ₂	2·CaO·SiO ₂	3·CaO·Al ₂ O ₃	4·CaO·Al ₂ O ₃ ·Fe ₂ O ₃
Technical name	alite	belite	aluminate	ferrite
Amount in CEM I [%]	55-65	15-25	3-15	4-15
Reactivity	high	low	very high	low
Heat of hydration [J/g]	500	250	1340	420
Contribution to strength	high at early ages	high at late ages	high at very early ages	very low

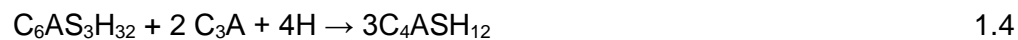
Alite and belite react with water to form C-S-H gel and CH according to Equations 1.1 and 1.2 respectively [4].



Z typically falls within the range 3-4.

Alite is essential for concrete hardening. Belite reacts slowly, so that a large part of it can remain unreacted even after one year of hydration.

The aluminate phase is very important for the rheological behaviour during the first hours of cement hydration. It reacts with water and gypsum (CSH_2) to form ettringite ($\text{C}_6\text{AS}_3\text{H}_{32}$) (Equation 1.3). Within the first day, the gypsum is consumed and the ettringite starts to react with the remaining aluminate to form calcium monosulfoaluminate ($\text{C}_4\text{ASH}_{12}$) (also referred to as monosulfate) as described by Equation 1.4 [4].



The hydration of the ferrite phase is analogous to the hydration of the aluminate phases. The hydration of C_4AF is slower compared to that of C_3A . The Al in the ettringite and monosulfate can be partly replaced by Fe. The phases derived from pure monosulfate and pure ettringite with partial substitution of Al by Fe, and SO_4^{2-} by other ions are referred to respectively as the AF_m and AF_t phases [4].

The clinker contains alkalis, which are easily soluble or incorporated in the clinker phases. Together with the formation of CH, this results in high pH pore solution in the hydrated paste [4].

1.2.2 Fly ash blended cement

Fly ash is a by-product of coal-fired thermal power plants. It is the residuum of the coal particles, which are collected from the exhaust by electrostatic or mechanical precipitation. During the combustion of powdered coal in thermal power plants, as coal passes through the high-temperature zone in the furnace (1000-1600) °C most of the mineral components contained in the coal melt and form small fused droplets which upon rapid air cooling transform into spherical glassy particles [5]. They predominantly consist of SiO₂, Al₂O₃, Fe₂O₃ and alkalis. Their chemical composition can vary considerably and depends on the composition of the inorganic fraction of the coal and technological conditions. Table 1.2 shows the chemical composition of two types of FA depending on the fuel used [6].

Table 1.2: The average values for the chemical composition of two FA [6]

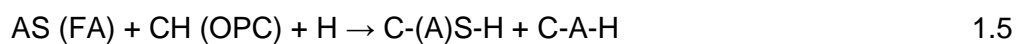
Oxide [%]	FA generated when burning anthracite and hard coal	FA generated when burning lignite and brown coal
SiO ₂	48 (34-60)	38 (25-40)
Al ₂ O ₃	28 (17-31)	22 (8-17)
Fe ₂ O ₃	9 (2-25)	4 (5-10)
CaO	4 (0,5-10)	24 (10-38)
MgO	2 (1-5)	5 (1-3)
SO ₃	1	3
LOI	5	1

FA can be classified as siliceous or calcareous FA depending on its chemical composition based on the reactive calcium oxide content according to the standard SIST EN-197-2 [7]. Both types of FA are often referred to as pozzolanic materials. Calcareous FA is considered to be partially hydraulic. Siliceous FA contains less than 10% of reactive calcium oxide, whereas calcareous FA contains more. It should also contain more than 25% of reactive silicon oxide if it is to be used in blended cements to conform with SIST EN-197-2 [7]. The American standard ASTM C618 uses two classes: class F and class C FA. This classification distinguishes between the total reactive SiO₂, Al₂O₃ and Fe₂O₃ content of the FA, requiring a total content higher than 70% for the former and higher than 50% for the latter.

The FA used in cement production generally has a glass content which varies between (50-90)% in the form of alumina-silicate (AS) gel, whereas the remainder consists of crystalline phases and often some left over unburnt carbon particles such as free lime (CaO) and periclase (MgO) [5]. The crystalline phases which can be found in FA are mullite (24 to 34%), quartz (2.8 to 8.5%), hematite (1.1 to 2.7%), magnetite (0.8 to 2.6%), and a small residue of incompletely modified clay materials.

In cementitious systems, FA can act as an active filler, because of its pozzolanic properties; this contributes to the increased strength and durability behaviour of the concrete. Part of the FA can be considered to act as an inert filler, and thus be able to reduce the porosity of concrete due to its high specific surface area. The denser structure of the material reduces the diffusion of aggressive substances into the binder and improves the quality of the material's microstructure.

The hydration of FA blended cement is a complex process: both materials have their own hydration reactions which are also influenced by each other [4]. Pozzolanic materials principally consist of a reactive, glassy aluminosilicate component which reacts with CaO in an alkaline solution thereby forming reaction products. When a pozzolan is combined with OPC, CH is provided by the hydration of the cement and the high alkaline solution activates the pozzolanic reaction. The pozzolanic reaction can be qualitatively described as [8]:

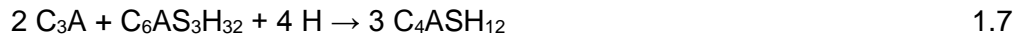


FA that contains high alumina glassy particles reacts with the silica content of the particle and excess calcium from the cement hydration to produce C-A-S-H phases which can be described as [9]:



Approximately after 28 days the pozzolanic reaction begins to take place, which is manifested in a change of the hydrated products [10]. Reaction products, such as calcium silicate hydrate (C-S-H), strätlingite and hydrogarnet (C₃AH₆), may be formed. The C-S-H present in FA blended cement shows a significant variation in its composition. The Ca/Si molar ratio of the C-S-H formed in FA blended cement pastes decreases when the percentage of the blending component is increased [11].

Based on the literature review described in [12], alite appears to react faster in cement pastes with FA up to 7 days. The remaining aluminates react with the ettringite to form monosulfate after all the gypsum has been consumed according to the equation 1.7:



The conversion of ettringite into monosulfate depends on the amount of SO_3 available, and on the CO_2 content of the cement paste. A faster reaction of aluminate and ferrite in FA containing mixtures is indicated. Furthermore, it has also been observed that FA blended cements have a higher proportion of AF_m phases relative to the OPC content due to the additional alumina provided by reaction of the FA and due to the acceleration of the hydration of the aluminate phases of the OPC [12].

Figure 1.1 illustrates the volume of the different phases as functions of time in a FA blended cement modelled by using GEMS [12]. The formation of monosulfate is predicted and a reduction in the amount of ettringite over time. Additionally, the formation of hydrogarnet is predicted after a longer hydration time. The additional alumina provided by the FA lowers the SO_3 -alumina ratio. For this reason larger proportions of AF_m than of AF_t phases are formed over time.

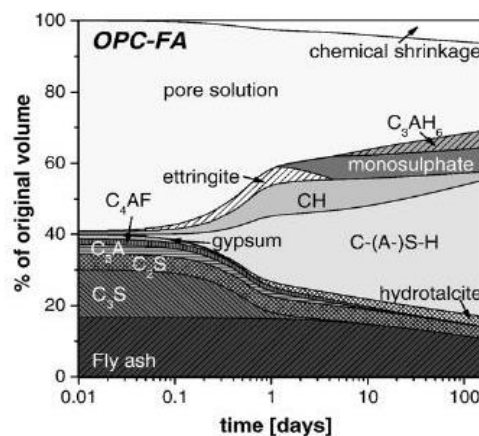


Figure 1.1: The volume of the different phases as functions of time in an FA blended cement [12].

Damidot et al. distinguish the hydration of an FA blended cement with (0-50)% FA replacing OPC by thermodynamic modelling [13]. Figure 1.2 presents the modelled changes in a hydrated FA blended cement. The use of silica-rich SCMs influences the amount and kind of hydrates that are formed, and thus also the volume, porosity, strength, and ultimately durability. At the substitution levels which are normally used, the major changes are: a decrease in the CH content, and a lowering of the Ca/Si

ratio in the C-S-H phase. Alumina-rich SCMs (like FA) increase the Al-uptake in the C-S-H phase and the proportion of aluminate hydrates [13].

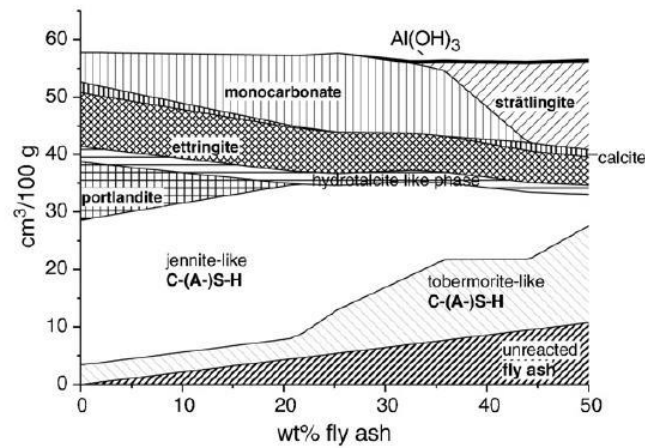


Figure 1.2: Modelled changes in a hydrated FA blended cement [13].

All of the above-mentioned products affect the sustainability and durability of mineral binders and concrete. Opinions about the reduction of chloride ingress and about improvements in the resistance to alkali-silica reaction in FA modified concrete are quite similar [14, 15]. Furthermore, the presence of FA also improves resistance to sulfate corrosion [16]. By replacing cement with FA the amount of CH and C_3A (tricalcium aluminate) is reduced in the cement mixture. A smaller proportion of both components have a positive effect on the resistance of concrete to sulfate corrosion.

1.2.3 Mechanical characteristics of fly ash modified concrete

1.2.3.1 Microstructure permeability

FA blended cements usually have a lower permeability than plain ones. Moreover, permeability decreases when the pozzolana content is increased and the curing time is extended. When the FA starts reacting, it fills up the pores. The volume of the precipitating mass is small and is therefore unable to fill the larger pores, but it is sufficient to obstruct the thinner channels which connect the larger pores together [8]. FA modified concrete usually has a higher total porosity than unmodified concrete (i.e. concrete not containing FA). However, the proportion of coarser pores ($> 0.1 \mu\text{m}$) in FA modified concrete is lower than in unmodified concrete. On the other hand, an increase in the proportion of finer pores ($< 0.01 \mu\text{m}$) has been observed.

With the progress of the pozzolanic reaction, a gradual decrease occurs in both the size of the capillary pores and the crystalline hydration products in the transition zone, thereby reducing the latter's thickness and eliminating the weak link in the microstructure of the concrete [5].

1.2.3.2 Strength

The development of strength in FA modified concrete depends mostly on the behaviour, replacement level, curing time and reactivity of the FA. Up to an age of 28 days, the FA usually only has a filler effect, which does not compensate for the dilution effect [17]. De Weerd et al. [12] observed that replacing part of the OPC by FA results in slower strength development up to 28 days. After 28 days the FA starts to react, which is manifested in an increase in strength. However, depending on the characteristics of the added FA, small replacements of the latter (up to approximately 15%) with respect to the OPC can also improve the 3-day strength, and this improvement can persist as long as 91 days [8]. To sum up, in general, FA reduces the short-term strength while improving the long-term strength.

1.2.3.3 Durability

Durability defines the suitability of the concrete for the preservation of its structural performance, as defined by the designer, over time; hence it plays a fundamental role in determining the service life of a structure. It depends on both the concrete properties and on the environmental conditions [8].

The durability of concrete changes dramatically when it is exposed to various aggressive substances (carbon dioxide, chloride and sulfate ions) and therefore requires a lot of attention. Many studies have been focused on this subject, but no well defined explanation yet exists. The fact that the chemical composition of FA varies has led to different observations and conclusions [5].

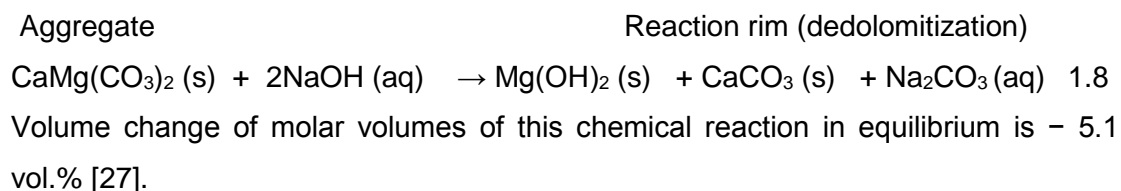
In conclusion, a combination of the particle packing effect, a low water content and a pozzolanic reaction accounts for the eventual disappearance of the interfacial transition zone in FA modified concrete, resulting in the development of a highly crack-resistant and durable product. While it is true that the addition of FA cannot remove all durability problems, it can nevertheless make a significant contribution to the solving of most of them provided that it is appropriately used.

1.2.4 Alkali carbonate reaction

This chapter is based on the paper [18] “Observation on dedolomitization of carbonate concrete aggregates, implications for ACR and expansion” which was published in the Cement and Concrete Research journal in 2013.

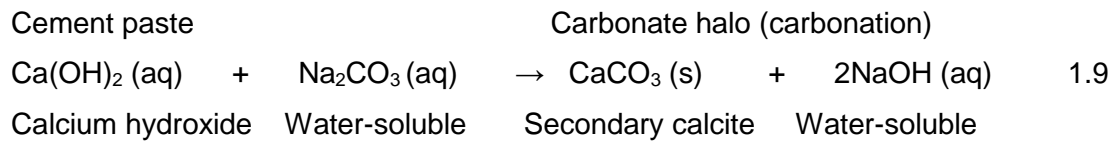
In spite of the fact, that alkali carbonation reaction (ACR) appears to be rare, it has been observed and reported by many researchers [19-22]. The ACR is usually divided into two types of reaction: (1) the reaction of carbonate minerals (dolomite) in an alkaline environment, developing dedolomitization, and (2) the reaction of silica associated minerals in carbonate rocks, i.e. alkali-silica reaction [21].

In the past [23, 24] damages caused by the ACR were often attributed to other processes like frost, leaching or sulfate attack, because the ACR could not be detected properly. Researchers, when studying the ACR, focused mostly on expansion [25, 26], but Katayama [27] pointed out that a very effective method to determine the ACR is combined examination of SEM, quantitative EDS analysis and the mapping of the reaction products. At ICAAR 2008, a number of cases of the ACR were identified as the alkali silica reaction of cryptic silica, by selective digestion of bulk carbonate aggregate [19]. However, on the contrary, it has been an established fact that dolostone is unstable in contact with the average alkaline pore solution of Portland cements [28, 29]. Due to high alkalinity and the presence of alkali ions in the pore solution, ion exchange between the Ca^{2+} , Mg^{2+} and CO_3^{2-} ions in the solid phase (stone aggregates) and ions in the pore solution is occurring. This reaction is called dedolomitization and could be written as follows in Eq. 1.8:



The molar volume change associated with the dedolomitization reaction is negative. It means that no expansion will take place, but the porosity will increase, which has a negative effect on the durability of the material.

Further reaction still is the formation of the secondary calcite or carbonate halo in the transition zone of the carbonate aggregate. This can be simplified as Eq. 1.9.



Volume change of molar volumes of this chemical reaction in equilibrium is + 10.2 vol.% but this is a dissolution-precipitation process which leaves no expansion [27].

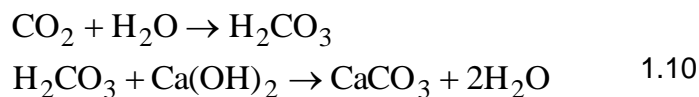
In literature [30, 31], different test methods for the ACR on mortar prisms can be found. Already Milanesi et al. [32] pointed out that a large increase in the concentration of the solution may not only alter the rate but also the type of the chemical reactions involved. There is also controversy about the mechanism of the dedolomitization at different temperatures. For example, Garcia et al. [28] concluded that the mechanism is different at 25 °C as it is at 75 °C. Nevertheless, Xu et al. [26] obtained no obvious modification in the nature of the ACR products at 40 °C and at 80 °C. In our study, the real temperature conditions to which concrete will be exposed in service were simulated.

1.2.5 Carbonation

The carbonation process consists of gaseous diffusion combined with a chemical reaction, and is known to cause a lowering of alkalinity, which can lead to the corrosion of re-bars. In order to minimize the risk of corrosion of the reinforcement, the concrete must be dense and the cover sufficiently thick. [8]

Carbon dioxide in the atmosphere diffuses through the empty pores of concrete and reacts with the hydration products, which is known as a "carbonation process". The carbonation of concrete is commonly defined as the chemical reaction between CO₂ and the cement hydration products such as calcium hydroxide, as well as the calcium silicate hydrates (C-S-H) and C-A-H. [33]

During the carbonation reaction Eq. 1.10 [8], the CH phase is primarily attacked, hydroxyl-ions are withdrawn from the pore solution, the pH value of the pore water decreases, and the steel re-bars are no longer passivated when the pH becomes lower than 9. The reinforcing steel may start to rust, together with spalling of the concrete cover.



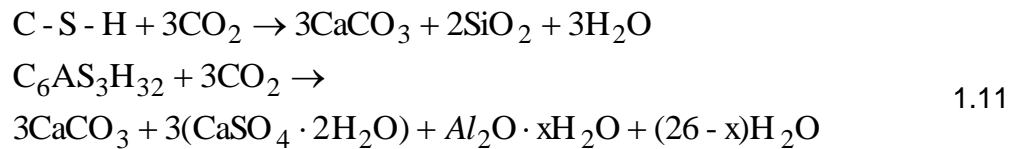
The formed CaCO₃ has a very low solubility, and is therefore precipitated into the empty pores so that in general a denser structure is obtained. [9]

The depth of carbonation in concrete increases with time, and depends on the following parameters: the partial pressure of CO₂, the temperature, the ambient humidity, the presence of microcracks, the cement content, the water/cement ratio and duration of curing.

With regard to carbonation, there are two determining factors [34]:

- Gas permeability: the lower the permeability, the slower the CO₂ diffusion is, and the lower the carbonation rate.
- Amount of carbonatable material: the more CH is available, the more CO₂ molecules can react, which leads to slower ingress of CO₂.

In FA modified concrete, the amount of CH is limited since the pozzolanic reaction which takes place between the calcium hydroxide and the reactive silica from the FA decreases the CH content and increases the proportion of the C-S-H phase. It is thus likely that CO₂ also affects the other phases (especially the C-S-H phases, but the aluminate hydrates - ettringite, ferrite hydrates, and sodium and potassium ions can also react with CO₂) which are presented in equation 1.11 [9].



Mechanically, the pozzolanic reaction is considered as beneficial since it results in the clogging up of bigger capillary pores and refining the microstructure or the filling of cracks. Nevertheless, such FA modified concretes may become more sensitive to the presence of carbon dioxide due to reduced ability of the matrix to bind CO₂ into CH. [35]

The most significant disagreement is associated with the carbonation of FA modified concrete. Some researchers have observed increased carbonation in FA modified concrete [34, 36], but this has not always been in line with conclusions drawn by other researchers, who were of the opinion that such comparisons have to be made between concretes having the same 28-day strength [8]. The degree of carbonation in concretes containing 15-30 % FA as a replacement for OPC is approximately the same as that found in unmodified concretes; however, the rate of carbonation of concretes containing 50 % FA carbonates is significantly higher than in unmodified concretes of the same strength grade [8]. However, the carbonation of pozzolana-containing cement is greater when the curing time is shorter, because of the slow rate of the pozzolanic reaction [33].

1.2.6 Chloride ingress

One of the problems in reinforced concrete structures is their degradation due to the corrosion of steel re-bars, due to which the mechanical characteristics and service life of such structures is reduced [37]. In the case of concrete structures that are located in a marine environment, wetting-drying cycles can accelerate the deterioration of concrete because two actions are combined, i.e. capillary suction and diffusion [38]. During a wetting period, sea water containing chloride ions penetrates into the concrete by means of capillary suction, up to a considerable depth, whereas during the following drying period water evaporates from the concrete, leaving chloride ions inside the concrete, which diffuse in all directions into the concrete. During the next wetting period further chloride ions will penetrate into the concrete. Since the quantity of chloride ions in the concrete at any particular penetration depth has a tendency to continuously increase due to capillary suction, a relatively steep chloride concentration gradient is created inside the remaining concrete. As a result of this process a relatively high diffusion velocity can occur. [39]

Chloride can harmfully affect the durability of both concrete and reinforcement. They dissolve in water and increase the rate of leaching of CH, thus increasing the porosity of mortar and concrete [8].

The rate and depth of penetration of chloride ions into concrete depend on the ionic diffusion coefficient that is on the permeability of concrete. So, when the risk of chloride attack occurs, concrete must be compact and the cover thickness must be adequate to the environmental conditions. Thus FA blended cements proved to be able to reduce the depth of penetration of chloride [8].

It is generally considered that it is possible, in the case of concrete structures in marine environments, to improve the performance of such concrete by replacing part of the cement with a reactive pozzolan such as FA. From the literature it is well-known that the pozzolanic reaction of FA in concrete reduces chloride ingress and improves chloride binding in comparison with unmodified concrete made by using OPC [37, 40, 41]. Due to the activation of the aluminosilicate component, which is the main constituent of FA, by the calcium hydroxide produced by the hydrating cement, secondary (pozzolanic) calcium silicate hydrate (C-S-H) is formed, which, to some extent, fills the pore spaces [8]. The diffusion process is also affected by other

factors, including ion exchange and chloride binding into the C–S–H and AF_m phase(s) [42]. The underlying mechanisms of chloride binding in cement system are complex as several different processes act simultaneously. For example, chloride ions may interact with hydrated cement forming chloroaluminate phases, such as Friedel's, Kuzel's salt and solid solutions with other AF_m phases but can also be chemisorbed by C-S-H. Chloride binding depends on the content of aluminium in pozzolanic addition. [43]

There are a lot of different techniques to determine the chloride penetration in concrete [44]. A method which can be successfully used to simulate a tidal zone was developed at the Magnel Laboratory for Concrete Research [45]. Although this technique is relatively time-consuming, very accurate results can be obtained when analyzing the total and water-soluble chloride profiles. In order to reduce the duration of such tests, a different type of test was applied to determine the resistance of concrete to chloride penetration, using the non-steady state migration test (NSSM), as described in NT Build 492 [46]. This test method is fairly well established, even though it has certain limitations, which have been reported in the literature [47, 48].

1.2.7 Resistance to freezing and thawing in combination with de-icing salts

Concrete structures exposed to the combined action of frost and de-icing salts undergo superficial degradation, with the removal of small chips or flakes from the surface, which is called (frost-) salt scaling. Five negative effects have been mentioned [5]:

- an increase in the degree of saturation of the concrete due to the hygroscopic character of the salt,
- an increase in the disruptive effect when the cooled water in the pores eventually freezes,
- the development of differential stresses as a result of layer-by-layer freezing of the concrete due to salt concentration gradients,
- temperature shock as a result of the dry application of de-icing salts on concrete covered with snow and ice,
- salt crystallization in saturated solutions in the pores.

Researchers [49] have pointed out the importance of various parameters such as air entrainment, mixture composition, characteristics of the freezing cycles, and the microstructure of the surface layers. Although all of these factors have their own effect, and although it is clear that the de-icing salts are in contact with a layer of concrete that is often very different from the bulk of the material, it is not possible to identify which factors have the greatest importance, or to predict with any degree of certainty the resistance to scaling of any type of concrete. [49]

For winter road maintenance, different types and concentrations of de-icing salts, i.e. sodium, magnesium, and calcium chlorides are currently used in Slovenia. However, since the Slovenian standard SIST 1026 [50] for determining the resistance of concrete surface to frost/salt scaling requires sodium chloride for de-icing salt, the effect of all used de-icing salts on the frost damage of concrete is presently not known. A study about the effect of the type and concentration of de-icing salts on the surface scaling of concrete can be found in the literature [51]. Figure 1.3 presents the effect of the amount and type of de-icing salts, i.e. calcium chloride, sodium chloride, urea, and ethyl alcohol on surface scaling. From Figure 1.3 it can be seen that, for the majority of the de-icing salts, the most critical concentration range is between (2.0 and 5.0)%. In the case of higher concentrations of de-icing salts, the damage tends to be smaller. This is not the case for calcium chloride. With an increasing number of

cycles of freezing/thawing from 50 to 200 cycles, the amount of material scaled from the concrete surface increased rapidly, with increasing concentrations of calcium chloride over 8%.

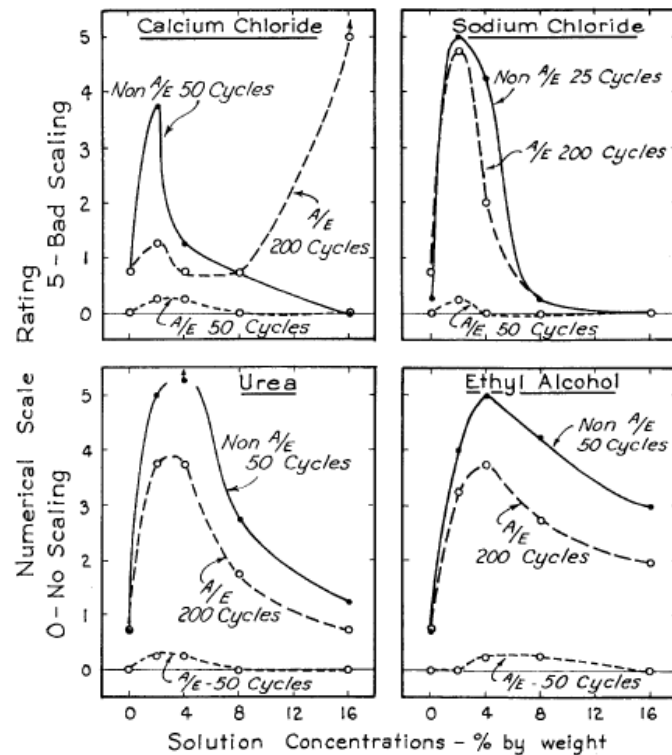


Figure 1.3: Effect of the amount of de-icing salts on surface scaling [51].

The influence of pozzolanic material on the (frost) salt resistance of concrete depends on the replacement level. Pigeon et al. [49] observed that, in general, if the amount of FA in the mixture is increased (from 20% to 40%), the scaling residues in the first 10 cycles are also increased. This phenomenon can be related to the thickness of the porous layer as observed under SEM. In some cases the use of pozzolanic material requires special care, because the carbon remaining in the FA requires an additional amount of air-entraining admixture in order to obtain the specified air content in the concrete [8].

2 SCOPE AND STRATEGY OF THE RESEARCH PROJECT

2.1 OBJECTIVES

Each mineral addition to a concrete mixture influences the formation of hydration products, which results in changes in the complex physico-chemical properties of hydraulic binders [3]. Without understanding how such mineral additions interact with cement, it is not possible to predict or guarantee the durability of (Slovenian) fly ash modified concrete.

The aim of this thesis was to examine the interaction between fly ash and other components in cementitious systems, and explain the durability behaviour in various situations when Slovenian fly ash is used in concrete mixtures as a partial replacement for cement. By increasing the fly ash content and subjecting the same concrete mixture to different types of corrosive attack (chloride, carbon dioxide, and de-icing salts) the optimal replacement level was investigated in order to achieve the desired durability of the concrete.

2.2 RESEARCH STRATEGY

The research work is divided into three parts, which are:

- the effect of FA blended cement on the chemical properties of the binder,
- the effect of FA on the characteristics of fresh and hardened concrete, including alkali carbonate reaction, and
- the effect of FA modified concrete on durability.

The aim of the research in the first part was to study the effect of FA blended cement on the chemical properties of the binder. In order to illustrate the influence of the addition of two types of fly ash, silicious and calcareous, on the hydration process of fly ash blended cement paste, different instrumental methods was monitored, such as isothermal calorimetry, thermogravimetry (TG), and derivative thermogravimetry (DTG).

In the second part, the effect of fly ash on the characteristics of fresh and hardened concrete was treated with following methods: on the fresh concrete slump tests, flow table tests, and air content tests were performed, while on the hardened concrete compressive strength and static modulus of elasticity tests, as well as tests to

determine the depth of penetration by water under pressure were performed. The type of used aggregate was found to be of particular importance. For this reason the research work was extended in order to examine the alkali carbonate reaction (ACR). To simulate the real conditions, we used local highly-purity aggregates exposed to water media at 20 °C and 60 °C (60 °C is temperature of flue gasses in thermal power plant). In order to study the influence of accelerating solution on implications of the ACR the 1 M NaOH was chosen. The process of ACR was investigated by measuring length change, and by using optical and electron microscopy as well as atomic absorption spectrometry and the X-ray diffraction method.

In the third part of the thesis, the durability behaviour of fly ash modified concrete was studied. The effect of exposure time, FA content, and FA composition on carbonation, chloride ingress, and frost/salt scaling were examined. For this reason seven types of concrete mixtures were designed, with a different OPC - FA replacement level, respectively 0%, 20%, 50% and 65% and the type of fly ash, silicious and calcareous. Regarding chloride ingress we wanted to simulate a tidal zone and to obtain the required concrete cover depth, thus we used the cyclic immersion and drying test. For comparing the results about chloride penetrations we used also standard method, the non-steady state migration test (NSSM). The porosity was found to be of particular importance, thus mercury porosimetry was also included in this study. Last but not least durability test was frost/salt scaling. We wanted to examine the influence of concrete composition and the different types and concentrations of de-icing salts on frost/salt scaling resistance of concrete, which are used for winter road maintenance.

3 EXPERIMENTAL STUDY

3.1 THE EFFECT OF FLY ASH BLENDED CEMENT ON THE CHEMICAL PROPERTIES OF THE BINDER

3.1.1 Materials

3.1.1.1 Ordinary Portland Cement

Ordinary Portland Cement CEM I 42.5R, complying with the European standard EN 197-2 [7] was used in all the pastes, mortars, and concrete mixtures as a hydraulic binder. Table 3.1 lists the chemical composition of the cement determined by XRF analysis. The OPC contained 0.85 % Na₂O equivalent.

Table 3.1: Chemical composition of the used OPC in the weight percent of its oxides

Oxide [%]	CEM I
Na ₂ O	0.35
K ₂ O	0.75
CaO	62.06
MgO	2.07
Fe ₂ O ₃ -tot	2.70
Al ₂ O ₃	5.62
SiO ₂	19.33
Cl ⁻	0.009
SO ₃	3.23
LOI	3.70
	Calculated (wt%)*
C ₃ S, %	64.07
C ₂ S, %	7.09
C ₃ A, %	10.33
C ₄ AF, %	8.22
Blaine specific surface area [cm ² /g]	3760
Density [g/cm ³]	3.09

*By Bogue equations.

3.1.1.2 Fly ash

Three different types of FA were used as a partial OPC replacement material in the FA blended cement pastes. Table 3.2 lists the chemical composition of the studied FA as determined by XRF analysis according to the standard SIST EN 197-2 [7].

Based on the calcium oxide (CaO) content in the FA according to SIST EN 197-2 [7], FA I can be classified as siliceous FA, whereas both FA II and FA III can be classified as calcareous FA. Only FA I met all the criteria prescribed in the standard SIST EN 450-1 [52]. FA II had a higher content of reactive CaO. The content of reactive CaO as required by the a fore mentioned standard should not exceed 10.0% by mass content, whereas in fact FA II and FA III contained 15.20% and 25.04% of it, respectively. FA III also had a higher content of magnesium oxide (MgO) and a lower total content of silicon dioxide, aluminium oxide, and iron oxide ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$). In FA more than 4% of MgO is considered undesirable since MgO can cause the hydration of brucite in the cement paste, which is manifested in an increased volume of the cement paste, and can lead to the formation of cracks.

Table 3.2: Chemical composition of the investigated FA in the weight percent of its oxides

Chemical composition (%)	Sample		
	FA I	FA II	FA III
	Measured (wt%)*		
SiO ₂ , %	47.71	41.98	27.92
Al ₂ O ₃ , %	26.67	18.51	11.27
Fe ₂ O ₃ , %	9.23	9.67	15.52
CaO, %	5.99	15.20	25.04
SO ₃ , %	1.88	2.38	1.74
MgO, %	2.06	2.62	8.22
Na ₂ O, %	1.34	1.06	0.24
K ₂ O, %	2.12	1.91	1.00
Cl ⁻ , %	0.006	0.023	0.026
Na _{equiv.} , %	2.74	2.32	0.90
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , %	83.61	70.16	54.71
Loss of ignition, LOI, %	1.28	4.19	n.a.
Fineness, %	36.8	42.0	n.a.
Glass content, %	72.0	71.8	n.a.

* By XRF, n.a. not available.

Based on the obtained experimental results, it was found that FA III contained high contents of MgO and CaO, and low contents of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$). For this reason it was estimated that FA III was not suitable for use in concrete, so it was not used in this study.

For the determination of the glass phase (amorphous or non-crystalline fraction), quantitative XRD was performed (Rietveld Analysis). An internal Zincite-standard (10 wt.%) was added to the sample as a reference. With XRD, the crystalline phases can be analysed. The Rietveld analysis data was used for quantification the identified

crystalline phases. However, at the end, 100% minus the crystalline phases is considered to be the amount of glass phase. The quantities of the crystalline phases of the selected FA are listed in Table 3.3. In Figure 3.1 and Figure 3.2 two XRD patterns are given for the crystalline phases of FA I and FA II.

Table 3.3: The quantity of crystalline phases of the investigated FA

Crystalline phases	Sample	
	FA I*	FA II*
Quartz (SiO ₂), %	5.8	7.2
Hematite (Fe ₂ O ₃), %	2.7	1.4
Anhydrite (CaSO ₄), %	2.1	2.5
Lime (CaO), %	0.8	1.7
Mullite (Al ₆ Si ₂ O ₁₃), %	13.8	1.4
Magnetite (Fe ₃ O ₄), %	0.9	2.5
Feldspar (NaCaAlSi ₃ O ₈), %	1.9	7.3
Gehlenite (Ca ₂ Al ₂ SiO ₇), %	0.0	4.1
Periclase (MgO), %	0.0	0.1
Glass content, %	72.0	71.0

* By XRD.

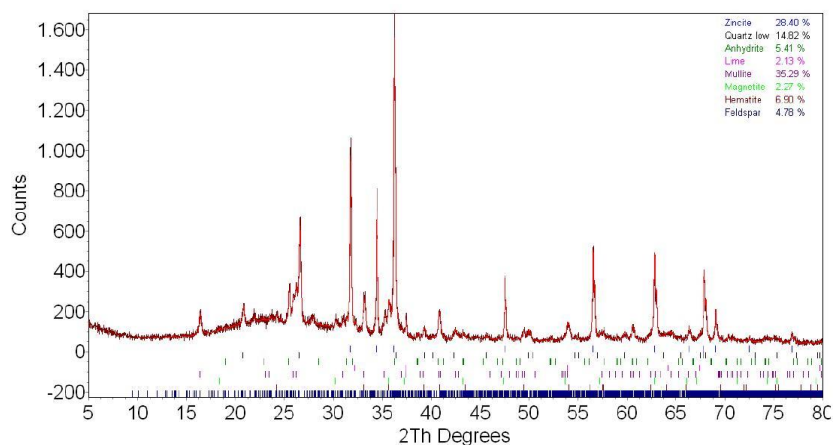


Figure 3.1: XRD pattern of (untreated) FA I and the modeled pattern. Zincite was added as internal standard. The black curve is the measured pattern; the red curve is the modeled pattern. The lines below indicate the peak positions for each mineral in the same order in which they are listed in the right corner.

Both of the FA had almost the same proportion of the glass amorphous phase. The main crystalline phases of FA I were mullite, quartz, and hematite, whereas in the case of FA II feldspar, quartz, and gehlenite were found.

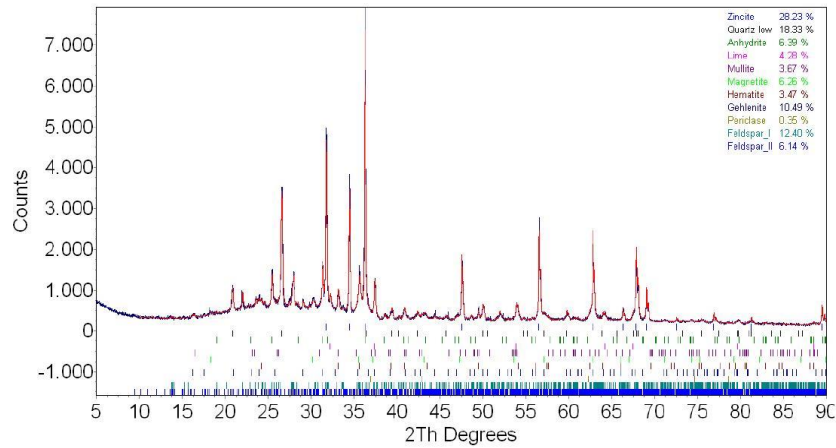


Figure 3.2: XRD pattern of (untreated) FA II I and the modeled pattern. Zincite was added as internal standard. The blue curve is the measured pattern; the red curve is the modeled pattern. The lines below indicate the peak positions for each mineral in the same order in which they are listed in the right corner.

The particle size distribution of the FA, as obtained by the laser scattering technique (MICROTRAC-FRA9200), is shown in Figure 3.3. As regards FA, the particle size distribution is quite wide, FA I being finer and better graded than FA II and FA III.

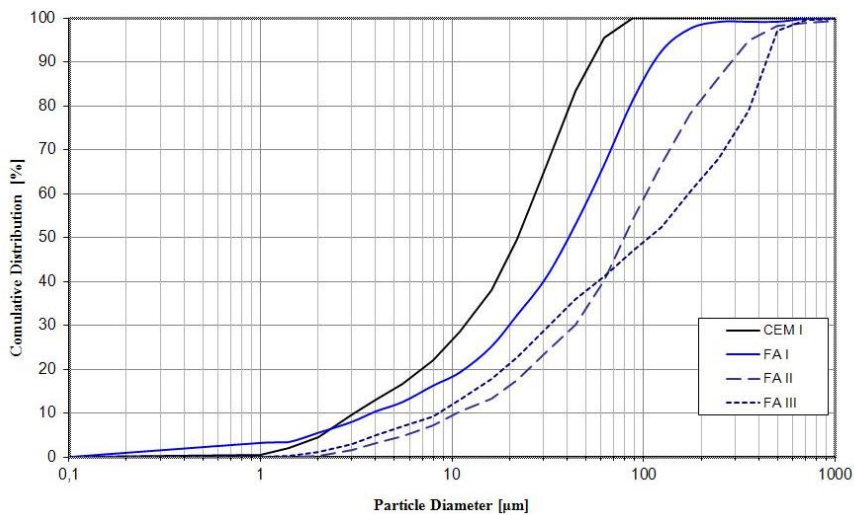


Figure 3.3: The particle size distribution of the FA and OPC

3.1.2 Binder proportion

Cement pastes with a water-to-binder (w/b) ratio of 0.45 and FA-to-binder ratios of 0, 0.20, 0.50 and 0.65 were prepared. Table 3.4 lists the mix proportions for seven binder mixtures for the isothermal calorimetry test. The chemical properties of the

OPC (CEM I) are given in paragraph 3.1.1.1, whereas the chemical and physical properties of FA I and FA II are given in paragraph 3.1.1.2.

Table 3.4: Mixture proportions per batch of cement paste for isothermal calorimetry test

	CEM [g]	FA I [g]	FA II [g]	water [g]
CEM100FA0W45	100.00	0.00	0.00	45.00
CEM80FA(I)20W45	80.00	20.00	0.00	45.00
CEM50FA(I)50W45	50.00	50.00	0.00	45.00
CEM35FA(I)65W45	35.00	65.00	0.00	45.00
CEM80FA(II)20W45	80.00	0.00	20.00	45.00
CEM50FA(II)50W45	50.00	0.00	50.00	45.00
CEM35FA(II)65W45	35.00	0.00	65.00	45.00

Cement pastes with a water-to-binder (w/b) ratio of 0.5 and FA-to-binder ratios of 0 and 0.3 were prepared in order to be able to study the hydration reaction by means of thermogravimetric analysis. Table 3.5 lists the mix proportions for the three binder mixtures. Generally, the components were mixed for 2 minutes.

Table 3.5: Mixture proportions per batch of cement paste for thermal analysis

	CEM [g]	FA I [g]	FA II [g]	water [g]
CEM100FA0W50	100.00	00.00	00.00	50.00
CEM70FA(I)30W50	70.00	30.00	00.00	50.00
CEM70FA(II)30W50	70.00	00.00	30.00	50.00

3.1.3 Test procedures

3.1.3.1 Isothermal calorimetry

Isothermal calorimetry provides continuous measurement of the heat released by a cementitious binder from the very early stage of hydration. The hydration heat of the FA blended cement was determined by means of a TAM AIR isothermal heat conduction calorimeter (TA instruments). The measurements were performed on cement pastes containing different amounts of FA at 20 °C and 35 °C during the first 120 hours after water addition. Each test was performed in duplicate.

3.1.3.2 Thermal Analysis (DTA/TG)

The amount of calcium hydroxide (CH) and bound water (H) were determined by thermogravimetric analysis using Netzsch STA 409 equipment by measuring the weight loss of a 100 mg sample. The tests were carried out at a heating rate of 10 °C/min, going from 25 °C to 1100 °C, and were performed in a non-oxidized atmosphere (argon) in order to avoid the superposition of peaks which could be attributed to the combustion of coals in the FA and to calcium hydroxide decomposition.

3.2 THE EFFECT OF FLY ASH ON THE CHARACTERISTICS OF FRESH AND HARDENED CONCRETE

3.2.1 Materials

3.2.1.1 Aggregates

Two different types of crushed carbonate aggregate were used. The aggregates were taken via concrete aggregate supplier and were sampled according to the standard EN 932-1 [53] and reduced according to the standard EN 932-2 [54]. A petrographic examination with optical microscope and X-ray diffraction, including a quantitative determination of the chemical composition, was done on stone aggregates. The aggregate A is the middle and upper Paleocene, the lower Eocene limestone, on the other hand the aggregate B is the lower Triass dolostone. The aggregates have different and independent paleogeographic and tectonic histories. Figure 3.4A shows the result of petrographic analysis of thin section of the stone aggregate A. The Figure 3.4A clearly shows the limestone with predominantly micritic texture, rich in fossil fragments. In the middle of the sample, a thin vein crossed the micritic texture and was filled with calcite sparite cement. The aggregate A was a highly homogeneous limestone, comprising of calcite (98.4 wt.%) and dolomite (1.6 wt.%). It had a relative density of 2.69 g/cm³ and water absorption of 0.8%. The second one, the aggregate B, was also homogeneous and had a calculated composition of dolomite (96.6 wt.%) and calcite (3.4 wt.%). The parent rock was late diagenetic dolostone crosscut with tectonic cracks filled with calcite or dolomite vein as it is visible on Figure 3.4B.

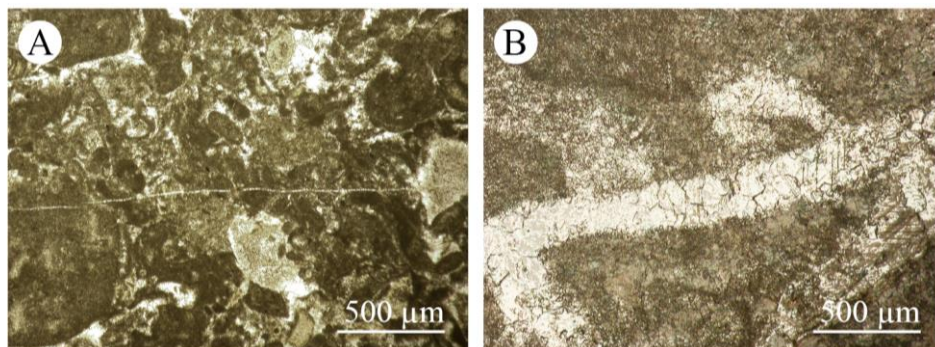


Figure 3.4: Thin sections of stone aggregates; PPT, x50: (A) aggregate A, (B) aggregate B.

It had a relative density of 2.85 g/cm³ and water absorption of 0.5%. Figure 3.5 shows the XRD pattern of investigated aggregates. The chemical composition of the aggregates was determined by the XRF analysis and is given in the Table 3.6.

Table 3.6: Chemical composition of carbonate aggregates materials in weight percent oxides

Oxide [%]	Limestone	Dolostone
Na ₂ O	0	0
K ₂ O	0	0
CaO	55.97	31.67
MgO	0.66	19.49
Fe ₂ O ₃ -tot	0	0.04
Al ₂ O ₃	0	0.07
SiO ₂	0.06	0.18
Cl ⁻	0	0
SO ₃	0	0

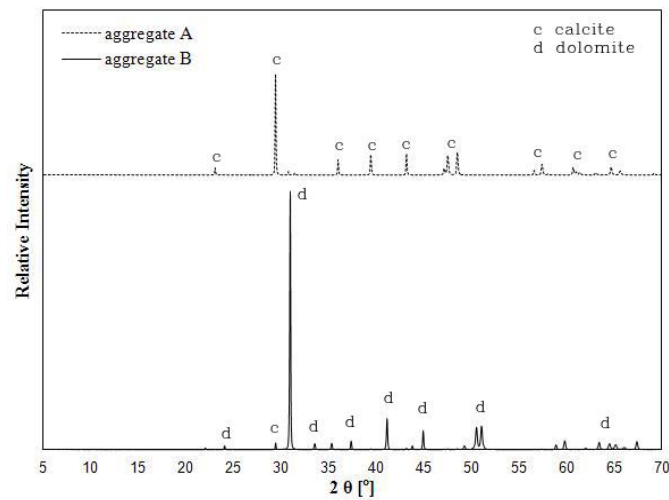


Figure 3.5: XRD pattern of investigated aggregates.

3.2.1.2 Admixtures – water reducers

To improve the workability of concrete, a superplasticizer based on a polycarboxylate was used.

3.2.2 Concrete mixture proportion

Table 3.7 lists the mixture proportions for the four investigated concrete mixtures. The chemical properties of the OPC are given in paragraph 3.1.1.1. The difference between concrete mixtures 1 and 2 was in the composition of the binder. The concrete mixtures with the added number 1 were unmodified concretes, i.e. without mineral additions, whereas the mixtures with the added number 2 contained 20% of FA II as the OPC replacement. The chemical and physical properties of FA II are given in paragraph 3.1.1.2. The difference between concrete mixtures A and B was in the type of used aggregate. Concrete mixtures A were made using limestone aggregate, while concrete mixtures B were made using dolostone aggregate. The chemical and physical properties of aggregates A and B are given in paragraph 3.2.1.1.

Table 3.7: Concrete mixture proportion

	A1	A2	B1	B2
aggregate 0/2 [kg/m ³]	620	601	620	601
aggregate 0/4 [kg/m ³]	413	401	413	401
aggregate 4/8 [kg/m ³]	188	182	188	182
aggregate 8/16 [kg/m ³]	657	638	657	638
cement [kg/m ³]	380	304	380	304
fly ash [kg/m ³]	0	76	0	76
water [kg/m ³]	171	171	171	171
SP [l/m ³]	2.64	2.92	2.64	3.04
W/B	0.45	0.45	0.45	0.45
W/C	0.45	0.56	0.45	0.56
B [kg/m ³]	380	380	380	380

To obtain an optimal particle packing of the aggregate, four different fractions of aggregates were used, i.e. coarse and fine aggregate. The coarse aggregate was divided into 36% of fraction 8/16 mm and 10% of fraction 4/8 mm, whereas the fine aggregate was divided into 22% of fraction 0/4 mm and 32% of fraction 0/2 mm.

All the concrete mixtures were prepared in the same way. After blending the dry materials for one minute (i.e. the aggregate, the OPC, and the FA), water was added. The fresh concrete was mixed for one minute before the superplasticizer was added. After this had been done, the concrete was mixed for another two minutes and finally tested for its workability.

3.2.3 Testing fresh concrete

The workability of the concrete mixtures was determined according to the standard SIST EN 12350-2 (Slump test) [55] and SIST EN 12350-5 (Flow table test) [56]. A total of four measurements were performed on each concrete mixture, the measurements being performed at 20 minute intervals. The first measurement was carried out at the end of the mixing. The air content was measured in accordance with the standard SIST EN 12350-7 [57] immediately after mixing and one hour after mixing.

3.2.4 Testing hardened concrete

3.2.4.1 Compressive strength

The compressive strength of the hardened concrete was determined on test specimens which consisted of concrete cubes with a side of 150 mm, following the specifications of the standard SIST EN 12390-3 [58]. These tests were triplicated.

3.2.4.2 Static modulus of elasticity

The static modulus of elasticity was determined by means of tests that were performed on test specimens which consisted of concrete cylinders with the dimensions of $D/H = 100/200$ mm, in accordance with the provisions of the standard JUS UM1.025 (1982). These tests were carried out in triplicate on days 3, 28, and 90.

3.2.4.3 Depth of penetration of water under pressure

The depth of penetration of water under pressure into the hardened concrete was carried out according to the standard SIST EN 12390-8 [59]. Water was applied under pressure to the surface of hardened concrete. The specimen was then split and the depth of penetration of the waterfront was measured in triplicate on days 3, 28, and 90.

3.3 ALKALI CARBONATE REACTION

3.3.1 Materials

Two different types of crushed carbonate aggregate were used in this study, namely limestone and dolostone. The properties of both aggregates are given in the paragraph 3.2.1.1, the properties of the used OPC are given in the paragraph 3.1.1.1.

In this study, we considered the highly aggressive chemical environment XA3 [60] for the mortar mix design. The cement-to-aggregate ratio and the w/c ratio were 1:3 and 0.45, respectively. The maximum aggregate size was 4 mm and designed porosity was 3%. The moulds with the test specimens (40x40x160 mm) were placed in the storage room (20±1 °C; relative humidity above 90%) for a period of 24±2 h. After demoulding, the specimens were cured in water bath for 28 days. After curing for 28 days, the specimens were soaked in distilled water and 1 M NaOH solution at the room temperature 20 °C and the elevated temperature 60 °C for 9 months. Benchmarking between samples is possible if one compares samples being exposed at the same time.

3.3.2 Test procedures

3.3.2.1 Length change measurements

Length comparator consisting of a high-grade dial micrometer, graduated to read in 5 µm units and accurate to within 5 µm was used to measure change of length of the specimens over time. The measuring range of the micrometer is ± 10 mm. An Invar® reference bar (40x40x160 mm) was used for checking the measuring device, before and after each set of readings. The initial length (l_0) of the specimens was measured using the caliper accurate to within 10 µm, just before their exposure to the water or NaOH solution.

The measurements of the bars' change in length over time were carried out for 6 months in intervals of 7 days. For each combination of stone or mortar and exposing condition, three specimens were measured. The bars were removed one at a time from the solution and their surfaces were dried with a towel. Immediately after the surface dried, measuring of the length change was carried out.

3.3.2.2 Thin sections petrography

Thin sections of the test specimens taken from mortar prisms were prepared for optical microscopy to examine the presence of reaction products in the carbonate aggregate and interface transition zone. The polarizing optical microscope with transmitted light Nikon Eclipse E200 was used. The thin sections were prepared according to the chapter “Thin section specimen preparation” in [61].

3.3.2.3 Chemical analysis by XRF and AAS

The XRF analyses were done by NITON, model XL3t GOLDD 900-He. The atomic absorption spectrometer (AAS) PerkinElmer AAnalyst 600 was used to determine the content of magnesium ions in the water and NaOH solution at 20 °C, where stone prisms were placed in an equal volume of solution.

3.3.2.4 Scanning Electron Microscopy

All samples were characterized on the FE-SEM Zeiss Ultra Plus microscope equipped with EDS (Oxford X-Max SDD 50 mm² detector and INCA 4.14 X-ray microanalysis software) in working condition of 20 kV accelerating voltage, vacuum environment of $1\text{-}2 \times 10^{-6}$ mbar, beam current around 20 nA. The EDS spectra were recorded on flat regions of the Au coated samples using process time 5, livetime 120 s and 20 kV accelerating voltage. Using the Anderson-Halser estimation [62] the X-ray production depth was approximately 3 μm . Qualitative analysis of the X-ray spectra was performed with respect to the standard procedure provided by the software manufacturer (ZAF-based method [63]). For statistically reliable data in each case 5-7 different fields of view in various regions of interest were analyzed.

3.3.2.5 X-Ray power Diffraction

In all cases samples were homogenized and grounded with an agate mortar and pestle for 5 minutes. The X-ray powder diffraction data were collected on PANalytical X'Pert PRO MPD diffractometer with θ - 2θ Bragg-Brentano reflection geometry using CuK α 1 radiation ($\lambda = 1.54059 \text{ \AA}$) and with operation conditions of 45 kV and 40 mA. The diffractometer is equipped with Ge(111) Johannson type monochromator in the primary beam. The specimen mounting was flat plate. The data were collected at room temperature in the 2θ range from 5 to 70° in steps of 0.034° with a total integration time of 100 s per step (the full range of the 128 channel linear RTMS detector was used, so that each channel integrated the intensity for about 0.78 s at each step). The total scan time was approximately 25 minutes. The detectability limit is less than 1%. Qualitative analyses of powder diffraction patterns were performed

by using the X'Pert HighScore Plus Ver. 2.1.2 program equipped with a database PDF-2, Release 2008 (International Center for Diffraction Data, Newtown Square, PA). Program suite Topas Ver. 2.1 [64] was used for quantitative phase analyses of the phases with known structures, by Rietveld refinement method. Since background of the diffraction patterns was in all cases very low, we ignored the contribution of the amorphous phase in these samples. We assumed that mass fractions resulted from Rietveld refinement (which in principal represent mass fractions of phases in the crystalline part of the sample) represents mass fractions of phases in the whole sample.

3.4 THE EFFECT OF FLY ASH MODIFIED CONCRETE ON DURABILITY

3.4.1 Concrete mixture proportion

The chemical properties of the OPC are given in paragraph 3.1.1.1, whereas the properties of FA I and FA II are given in paragraph 3.1.1.2 and those of the used limestone aggregate A in paragraph 3.2.1.1. Table 3.8 shows the proportions of the unmodified concrete mixture (made without FA) and of the FA modified concrete containing 20%, 50% and 65% FA I as a replacement for the OPC.

Table 3.8: The proportions of the unmodified concrete mixture and of the concrete containing 20%, 50% and 65% FA I as a replacement of the OPC

	C(I)100FA(I)0W45	C(I)80FA(I)20W45	C(I)50FA(I)50W45	C(I)35FA(I)65W45
	M1	M2	M3	M4
aggregate 0/2 [kg/m ³]	620	601	587	649
aggregate 0/4 [kg/m ³]	413	401	392	433
aggregate 4/8 [kg/m ³]	188	182	178	197
aggregate 8/16 [kg/m ³]	657	638	623	688
cement [kg/m ³]	380	304	190	133
fly ash [kg/m ³]	0	76	190	247
water [kg/m ³]	169.0	168.3	168.8	168.8
SP [l/m ³]	2.01	2.66	2.20	2.20
FA/B	0.00	0.20	0.50	0.65
W/B	0.45	0.45	0.45	0.45
W/C	0.44	0.55	0.89	1.27
B [kg/m ³]	380	380	380	380

In all the concrete mixtures a constant amount of binder (PC + FA) was taken into consideration, i.e. 380 kg/m³; as well as a constant water-to-binder ratio, i.e. 0.45. The amount of superplasticizer was determined in order to obtain suitable flowability.

Table 3.9 lists the proportions of the concrete containing 20%, 50% and 65% FA II as a replacement for the OPC.

Table 3.9: The proportions of the concrete containing 20%, 50% and 65% FA II as a replacement of the OPC

	C(I)80FA(II)20W45 M5	C(I)50FA(II)50W45 M6	C(I)35FA(II)65W45 M7
aggregate 0/2 [kg/m ³]	601	587	649
aggregate 0/4 [kg/m ³]	401	392	433
aggregate 4/8 [kg/m ³]	182	178	197
aggregate 8/16 [kg/m ³]	638	623	688
cement [kg/m ³]	304	190	133
fly ash [kg/m ³]	76	190	247
water [kg/m ³]	168.3	167.3	168.8
SP [l/m ³]	2.66	3.66	2.20
FA/B	0.20	0.50	0.65
W/B	0.45	0.45	0.45
W/C	0.55	0.88	1.27
B [kg/m ³]	380	380	380

Slump (SIST EN 12350-2) [55], as well as flow table tests (SIST EN 12350-5) [56], density tests (SIST EN 12350-6) [65] and air content tests (SIST EN 12350-7) [57] were performed on all the fresh concrete mixtures.

3.4.2 Test procedures

3.4.2.1 Carbonation

Seven different concrete mixtures (M1, M2, M3, M4, M5, M6, and M7, as defined in section 3.4.1) were produced. The cubes with a side length of 100 mm were demoulded after one day and cured in a climate room at a temperature of (20±2) °C and a RH higher than 95% for 28 days. An epoxy coating was applied to all surfaces of specimens just before the start of the carbonation test, except on the surface that

was exposed to CO₂ in order to obtain correct measurements of the one-dimensional penetration of CO₂. On day 28, the three concrete specimens for each concrete mixture were placed in a climate chamber with a 10% enriched CO₂ atmosphere (temperature 20±2 °C, R.H. 60±5%). After 3, 6, 12, 15, and 18 weeks of exposure, the carbonation depth was determined by spraying a phenolphthalein solution onto a freshly sawn cut. Since the colour of the indicator turns purple at pH values higher than 8.3 – 10 [66], the non-carbonated zones are coloured whereas the carbonated zones are colourless. The carbonation depth was measured at different places (the distance between individual measurements was 10 mm) to the nearest millimeter.

3.4.2.2 Chloride ingress

The experimental research was performed on five concrete mixtures (M1, M2, M3, M5, and M6, as defined in section 3.4.1) which contained 0%, 20% and 50% of FA I and FA II as a replacement of the OPC.

For each of the concrete mixtures 5 cylindrical specimens with a diameter of 230 mm and a thickness of 70 mm were prepared for the cyclic immersion and drying method, whereas 6 cylindrical specimens with a diameter of 100 mm and a thickness of 50 mm were prepared for the non-steady state migration test (NSSM test), and 6 concrete cubes with sides of 150 mm for the compression strength tests.

Four concrete mixtures (M1, M2, M3, and M5) were tested using the cyclic immersion and drying method. Mixture M6 was not tested due to limitations of the available testing device. The general arrangement of the testing apparatus is shown in Figure 3.6. A more detailed description of the test apparatus can be found in the literature [39].



Figure 3.6: The test set-up for cyclic immersion and drying test.

The concrete specimens were exposed cyclically (one rotation per hour) to wetting in a 10% NaCl solution (immersion in the solution during one third of the time) and drying (the surface was exposed to air for two thirds of the time). For each of the concrete mixtures, 5 cylindrical specimens were made and stored for 28 days in a climatic chamber at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at a RH greater than 90%. Before the specimens were mounted on the testing device, the two side faces were coated in order to obtain one-dimensional penetration of the chloride ions, from the outside of the cylinders. The concrete specimens were then exposed to the wetting-drying cycles. After 21, 42, 84, 105, and 126 days of exposure to these wetting-drying cycles, the water-soluble and total-soluble chloride contents, and the chloride penetration depths, were determined. At the same time the porosity of each concrete was determined after 84 and 126 days.

The total and water-soluble chloride profiles were determined experimentally by means of potentiometric titration at the freshly split section. For this reason powder samples first have to be obtained by grinding the material in layers. The thickness of each layer was 2 mm, and 10 successive layers were considered, in order to obtain an accurate chloride profile. The dust, coming from each layer, was collected separately and sieved through a 160 μm sieve. Subsequently, a sample of about 6 g was dried at a temperature of 80°C for 24 hours. In order to determine the total-soluble chlorides, 2 g of the sample was dissolved in diluted nitric acid and heated until it boiled. In order to determine the water-soluble chlorides, 2.5 g of the sample was dissolved in distilled water and stored for 24 hours. The solution was then filtered, and diluted nitric acid was added to the extracted liquid before determining the total and water-soluble chlorides by potentiometric titration. The applied procedure was based on the work described in [67].

The second test method was NSSM test [46]. Five of the concrete mixtures (M1, M2, M3, M5, and M6) were tested. For each of the concrete mixtures, 6 cylindrical specimens with a diameter of 100 mm and a thickness of 50 mm were prepared. Half of cylindrical specimens were stored for 21 days, and the second half for 56 days in a climate chamber at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and a RH greater than 90%. The concrete specimens were then vacuum saturated in a $\text{Ca}(\text{OH})_2$ solution (4 g/l) for 18 hours. Following this, an external electrical potential was applied axially across the specimen, forcing the chloride ions to migrate from the solution into the specimen. The catholyte solution was a 10% NaCl solution, whereas the anolyte solution was a 0.3 N NaOH solution.

Finally, the test specimens were split and a 0.1 M silver nitrate solution was sprayed on one half. The penetration depth could be measured visually by checking the color change boundary induced by the precipitation of visible white silver chloride.

The compressive strengths of the investigated concretes were determined on standard concrete cubes with a side of 150 mm (SIST EN 12390-3) at 7, 28, and 90 days.

In order to characterize the porosity of the concrete, small-cored samples, 25 mm in diameter and with lengths of 15-25 mm, were removed from the concrete cylinders at a depth of 20 mm. These small cores were dried in an oven at (105-110) °C for 24 hours until testing, which was performed on an automatic mercury porosimeter (Autopore IV 9500 series – Micromeritics) within the pressure range from (0.003 to 414) N/mm².

3.4.2.3 Frost/salt scaling

The standard procedure according to the standard SIST EN 1026 [50] was used to measure the resistance of the investigated concretes to frost/salt scaling. According to this standard, a 3% sodium chloride solution has to be used. The sample consisted of three (15x15x15) cm concrete cubes, which were cured for 21 days at 20 °C and 100% relative humidity, and were then exposed to conditioning at ambient conditions of 20±2 °C and 65±5% relative humidity for 7 days. After conditioning, the samples were exposed to 25 and further to 50 freeze-thaw cycles, in which the temperatures of the air in the testing chamber reached -20±2°C in the freezing phase, and 20±2 °C in the thawing phase. The freezing and thawing phases were 16 to 18, and 6 to 8 hours long, respectively. [68] In our study the frost/salt scaling test was performed using three de-icing salts with different concentrations on four different concrete mixtures. The properties of the de-icing salts are presented in Table 3.10. A de-icing salt solution was poured over the surface of the test sample before exposure. The liquid height was maintained at 3 mm throughout the test.

Table 3.10: The properties of solutions of de-icing salts

De-icing salt	Mark	Concentration [%]	Molarity Cl ⁻ [mol]
NaCl	solution A	3,0	0,0517
CaCl ₂	solution B	2.8	0.0517
CaCl ₂	solution C	24	0.4364
MgCl ₂	solution D	2.4	0.0517
MgCl ₂	solution E	30	0.6383

The mass of the material scaled off the surface of the test samples was determined every 5 cycles. The criterion for scaling resistance was a maximum of 0.20 mg/mm² for the average cumulative mass loss after 25 freeze-thaw cycles, where the average value was obtained from the measurements on the 3 specimens. After 50 freeze-thaw cycles, the criterion for scaling resistance was changed to a maximum of 0.40 mg/mm² for the average cumulative mass loss.

The resistance of the investigated concretes to frost/salt scaling was determined for four concrete mixtures (M1, M2, M3, and M5, as defined in section 3.4.1). Since the used aggregate had a maximum grain size D_{max} of 16 mm was used, an air content in the fresh concrete of between (5.0 and 7.0)% is recommended according to the standard SIST EN 1026 [50]. In order to achieve the required properties of the fresh concrete a varied amount of the air entraining agent was added. Table 3.11 lists the amount of the added superplasticizer and of the air entraining agent.

Table 3.11: The amount of the added superplasticizer and air entraining agent

Mixture	Water [kg/m ²]	SP [kg/m ²]	Air entraining agent [kg/m ²]
M1	167	3.00	0.75
M2	167	3.04	1.08
M3	168	2.28	1.58
M5	167	2.86	1.50

4 RESULTS AND DISCUSSION

4.1 THE EFFECT OF FLY ASH BLENDED CEMENT ON THE CHEMICAL PROPERTIES OF THE BINDER

4.1.1 Isothermal calorimetry

Hydration of OPC is an exothermic process. The reaction kinetics were monitored by means of isothermal calorimetry on the paste mixtures with varying percentages of the incorporated FA.

Figure 4.1 and Figure 4.2 show typical curves of heat evolution which were obtained during the early hydration of the cement binders. Immediately after the first contact of the OPC with water various reactions occur. Four stages can be identified by measuring the heat flow: an initial hydration period, a dormant period, an acceleration period, and a deceleration period. During the initial hydration easily soluble component like alkalis, calcium sulfate phases, and free lime are dissolved by the surrounding water, and ettringite is formed around the C_3A containing surfaces. Then follows the dormant period, which lasts 2-3 hours. During this time, the concrete has to be transported and placed. This period is characterized by very low heat flow. The heat flow starts to rise again during the acceleration period, which is associated with the setting of the OPC. The intense hydration of C_3S is associated with the formation of C-S-H gel and calcium hydroxide. [3]

After the maximum peak at about 9-12 hours typically, another maximum occurs. In Taylor [69], the third peak, which occurs after about 16 hours of hydration at 20 °C, can be attributed to the renewed formation of ettringite. A further, less distinct shoulder, which can sometimes be observed, is then associated with the hydration of the ferrite phases [69] or the conversion of the AF_t to AF_m phases [70]. Due to lack of sulfate ions in the pore water, the ettringite is converted into monosulfate. After that the rate of heat release gradually reduces.

Figure 4.1 and Figure 4.2 show the hydration curves of the pastes containing different amounts and types of FA at 20 °C. The isothermal calorimetric curves are plotted per gram of OPC in order to be able to more easily assess the change in the OPC hydration. A reduction in the initially produced heat was observed in the case of the FA blended cements. This phenomenon leads to retardation of the hydration

during the first day, especially that of belite. The replacement of OPC by FA results in an increase and delay of the maximum rate of heat of hydration relative to the OPC content. The shape of the heat evolution curves is also influenced by the presence of the FA. An increase in the volume of the hydration reactions of the alumina phases was observed, which can be attributed to the increased aluminium content, which entered into the system by means of the added FA.

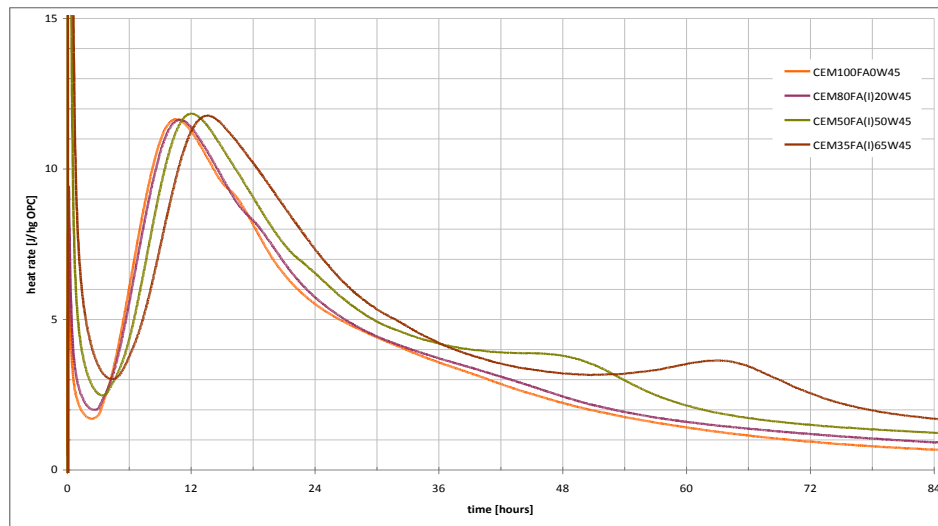


Figure 4.1: Isothermal calorimetric curves for cement paste with different percentage of FA I at 20 °C expressed per gram of OPC.

As an increasing replacement level of the OPC content by FA is reached, the OPC hydration retards, and the third hydration peak becomes more pronounced and delayed. Even a 65% replacement level of OPC with a low C_3A content by FA can cause a third peak, which confirms the assumption that this peak is related to C_3A hydration.

The same observation can be made in the case of the use of another type of FA (Figure 4.2).

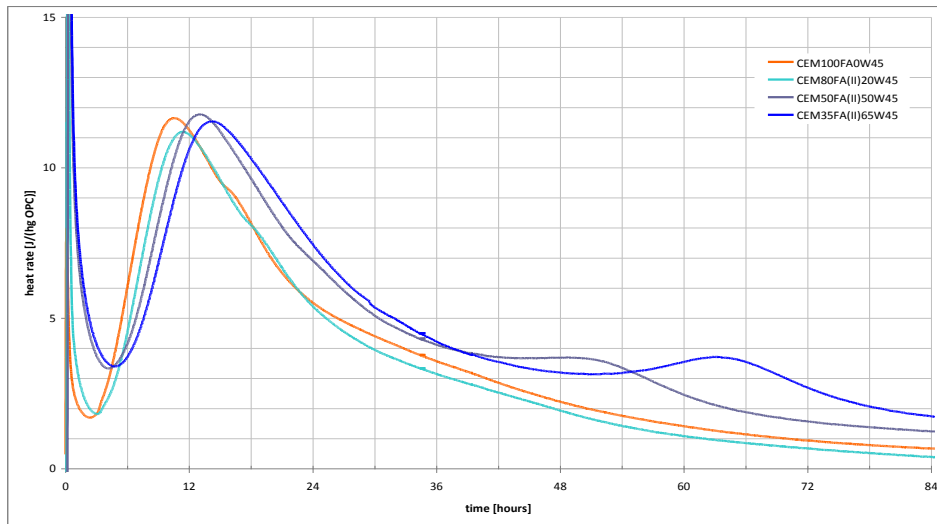
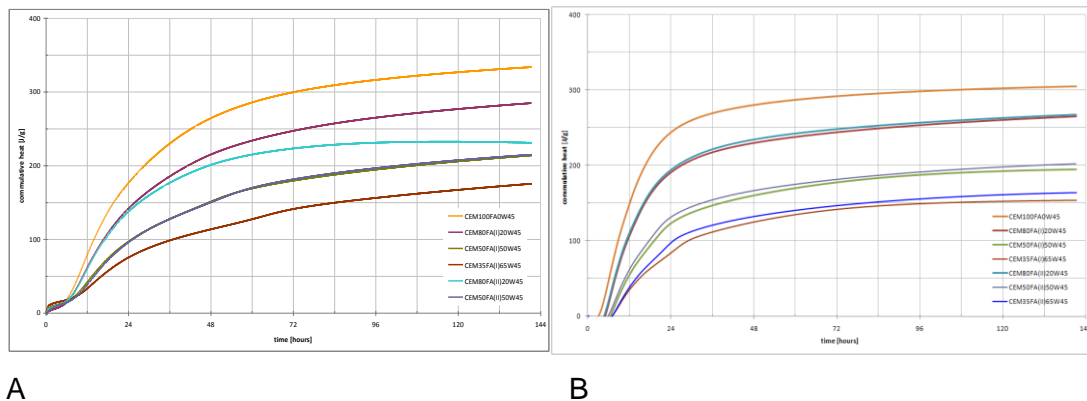
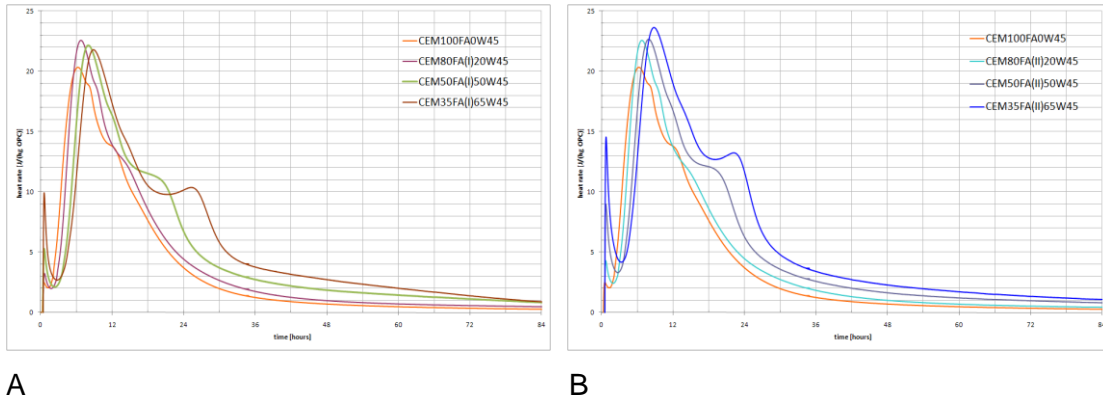


Figure 4.2: Isothermal calorimetric curves for cement paste with different percentage of FA II at 20 °C expressed per gram of OPC.

In order to study the effect of temperature on hydration, the isothermal calorimetry test was also performed at a temperature of 35 °C. As can be deduced from Figure 4.3, such a higher curing temperature accelerates the hydration of both binders (i.e. of the cement paste without FA, and of the FA blended cement pastes). The second hydration peak appears earlier at 35 °C (Figure 4.4) than at 20 °C (Figure 4.2). The higher ambient temperature initiates an earlier reaction.



A B
Figure 4.3: Cumulative heat of hydration expressed per gram of the investigated specimen for cement pastes of different types and with different percentages of FA at 20 °C (A) and 35 °C (B).



A **B**

Figure 4.4: Isothermal calorimetric curves for cement pastes of different types and with different percentages of FA at 35 °C; (A) is the isothermal heat rate expressed per gram of OPC for the cement paste made with FA I, whereas (B) is the isothermal heat rate expressed per gram of OPC for the cement paste made with FA II.

4.1.2 Thermal Analysis

The influence of the incorporation of FA in cementitious systems on hydration was studied. The release of water from the dehydration of calcium hydroxide and hydrated products by thermogravimetry and derivative thermal analysis (TG and DTG) over time was investigated.

Figure 4.5 presents a typical graph of the mass change as a function of the temperature as a result of a TG experiment, i.e. the DTG and DTA curves. The mass change is clearly visible with the first derivative of the TG curve (DTG) plotted on the ordinate with dm/dt and temperature on the abscissa for the sample CEM100FA0W50 at three days of hydration.

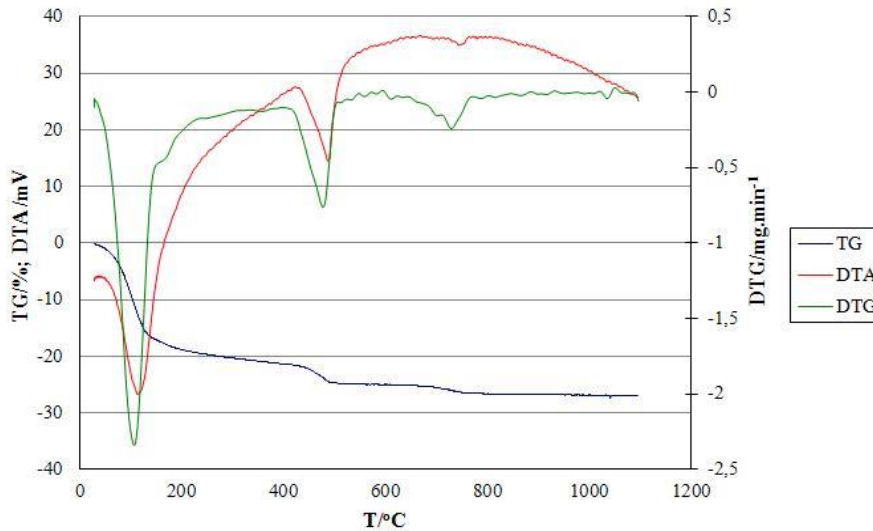


Figure 4.5: TG, DTG and DTA measurements of the cement paste CEM100FA0W50 at 3 days of hydration.

In the temperature range generally between 450 °C and 550 °C the CH decomposes into CaO and H₂O. The start and ending of each temperature interval is determined for each sample based on the DTG curve. A mass loss is recorded due to the loss of water. Taking into account the molecular weights of calcium hydroxide ($M_{CH} = 74,08 \text{ g/mol}$) and water ($M_{H_2O} = 18 \text{ g/mol}$), the weight loss during CH dehydration (WL_{CH} in %) could be converted to the amount of CH (in %) [71] according to the formula (4.1). In order to compare results, the CH content is expressed per gram of OPC.

$$CH = \frac{W_{450} - W_{550}}{W_{550}} \cdot \frac{M_{CH}}{M_{H_2O}} = WL_{CH} \cdot \frac{M_{CH}}{M_{H_2O}} = WL_{CH} \cdot 4,12 \quad 4.1$$

$$\frac{CH}{OPC} = CH \cdot \frac{100}{\% OPC}$$

Furthermore, the mass loss recorded in the temperature range between 40 °C and 550 °C corresponds to the release of water from different hydrates and possibly some absorbed water. This weight loss will be referred to as the bound water (H) (equation 4.2). H is measured from 40 °C and not from about 100 °C as is generally the case, since the AF_i phases and the C-S-H already start to decompose at 100 °C [71].

$$H = \frac{W_{40} - W_{550}}{W_{550}}$$

$$\frac{H}{OPC} = H \cdot \frac{100}{\% OPC}$$

4.2

Figure 4.6 shows the DTG curves for the specimen CEM100FA0W50 up to 90 days. The third peak reveals the development of the CH content over time due to the hydration of the alite and belite.

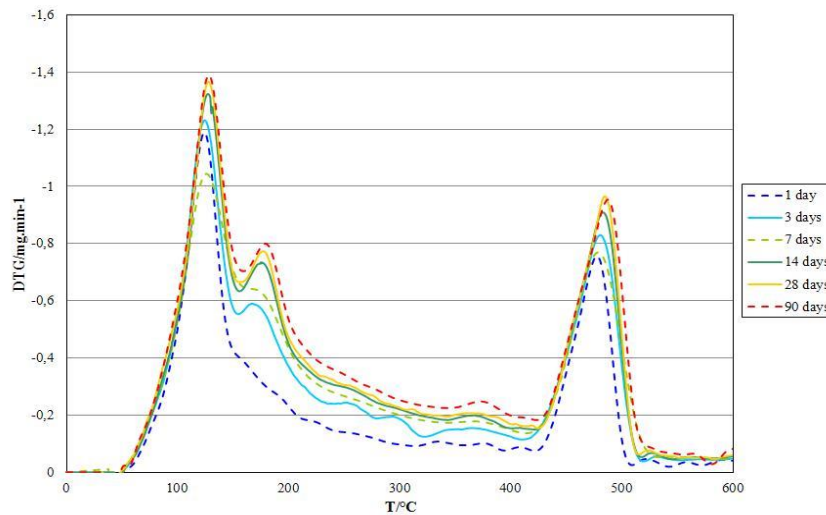


Figure 4.6: Development of the CH content for the specimen CEM100FA0W50.

The evolution of CH for cement paste and FA blended cement paste, as shown in Figure 4.7, is expressed per gram of OPC, since all the CH originates from the hydration of the OPC clinker. Figure 4.7 shows that, up to the end of day 1, the CH content of all the samples does not significantly differ for the different pastes. From day 7 until day 21, the FA blended cement pastes exhibit a higher CH content than the cement paste without additions. This finding is in agreement with the theory that FA, from days 7 until days 21, serves as a thermodynamically favourable nucleus due to the additional surface provided resulting in an acceleration of the OPC hydration [71].

By replacing part of the OPC with FA, the content of the main reactive component in the OPC, i.e. the clinker, is reduced. This is known as the dilution effect. It has also been observed by other researchers [17] that FA exerts a physical nucleation effect on the OPC hydration, which does not compensate for the dilution effect up to day 28. This is confirmed by the slightly increasing amounts of H and CH expressed per

gram of the OPC, although there is a decrease when the CH is expressed per gram of the dry content, as presented in Figure 4.8.

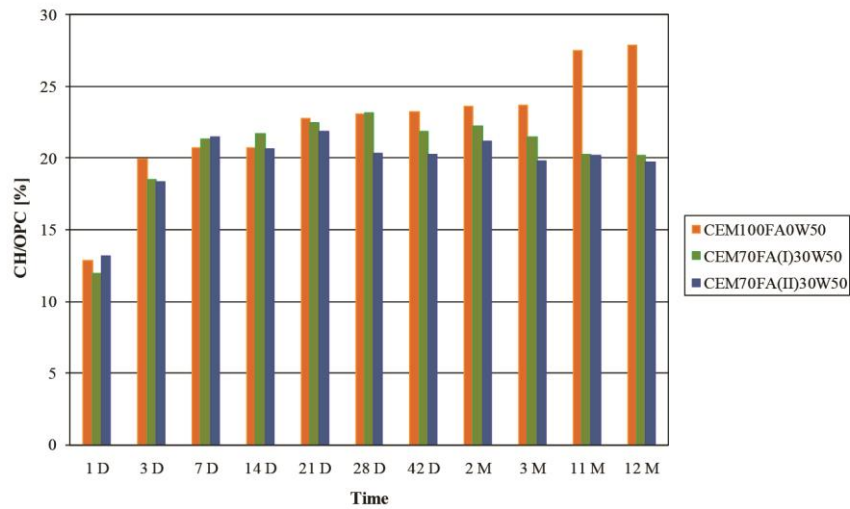


Figure 4.7: The amount of calcium hydroxide (CH) expressed per gram of OPC.

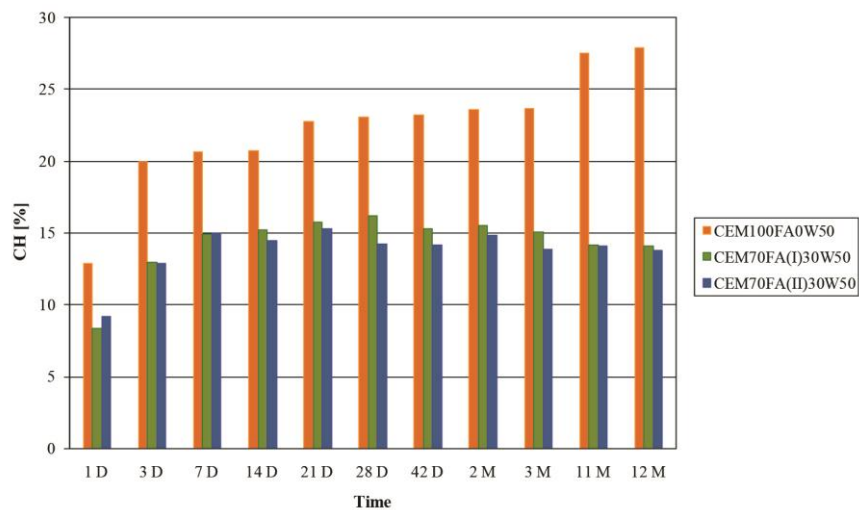


Figure 4.8: The amount of calcium hydroxide (CH) expressed per gram of the dry content.

After reaching its maximum, the CH content starts to decrease between days 21 and 28, due to the on-going pozzolanic reaction. The relatively low consumption of CH over one year shows the low reactivity of the FA. The results show that in one year the consumption of CH was 50% greater in the case of cement pastes containing 30% FA than in the case of cement paste without such an addition. That means that the unreacted particles of FA act as an inert filler.

The amount of hydrated products or bound water (H) was determined over the period up to one year. The results are plotted in Figure 4.9. The main part of the bound

water is bound during the first day. The amount of bound water increases slightly up to day 90, but thereafter, in general, does not change. In the FA blended cement pastes, the decrease in the amount of CH, together with the corresponding increase in the amount of bound water after 28 days, indicates a change in the nature of the formed hydration products, i.e. less CH, and more C-S-H gel and AF_m phases relative to the OPC content.

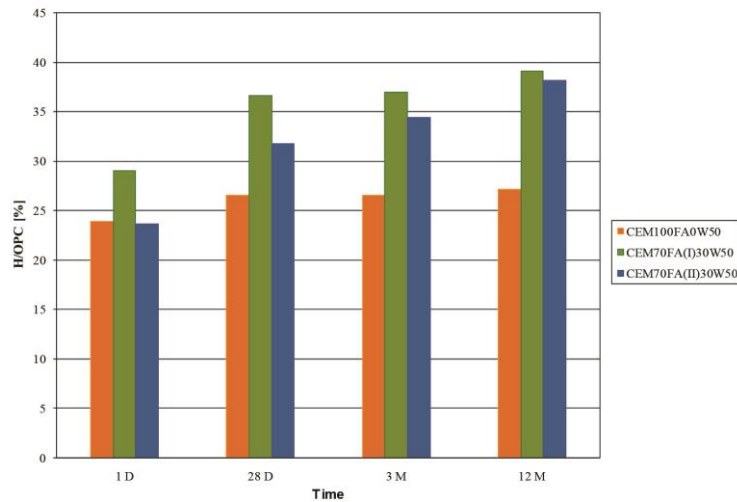


Figure 4.9: The amount of chemically bound water (H) expressed per gram of OPC.

When comparing Figure 4.7 and Figure 4.9, it is clear that the reduction in the amount of CH is related to the amount of hydration products formed. This confirms the assumption that CH is consumed during the pozzolanic reaction of the FA.

Furthermore, it is also possible that the dissolved aluminosilicate from the FA reacts directly with already formed C-S-H gel rather than precipitating in the reaction with CH. This reaction leads to the formation of C-S(A)-H gel with a lower Ca/Si ratio and an increased Al/Si ratio.

Comparing the two investigated types of fly ash, FA I and FA II, no clear difference can be observed with regard to the decrease in the amount of CH in periods up to one year. On the other hand, a slight difference can be seen with regard to the increase in the amount of hydrated products. In the case of the cement paste with FA I, the amount of such products increased significantly up to 28 days, and then not change much up to one year. In contrast, in the case of the cement paste with FA II the amount of hydrated products increased gradually up to one year.

4.1.3 Discussion

The replacement of OPC by FA resulted in an increase and delay of the maximum rate of heat of hydration relative to the OPC content up to 120 hours. This indicated that FA retarded the OPC hydration in the first hours. Furthermore, the higher amounts of AF_m phases relative to the OPC content was detected for FA blended cements due to the additional alumina provided by reaction of the FA. This was indicated by the appearance of the third hydration peak which became even more pronounced with an increasing replacement level of the OPC content by FA. Despite the fact that, with an increasing percentage of FA in the cement paste, the content of C_3A decreases, C_3A hydration was still observable.

The release of water from the dehydration of calcium hydroxide (CH) and hydrated products (H) by thermogravimetry as well as derivative thermal analysis (TG and DTG) over time was determined. From day 7 until day 21, the FA blended cement pastes exhibited a higher CH content relative to the OPC content than the cement paste without additions. This physical effect was generally attributed to the increased nucleation possibilities due to additional surface supplied by the powder replacing the OPC [71]. However, up to day 28 the H and CH expressed per gram of the OPC increased, although when expressed per gram of the dry content it decreased.

Between days 21 and 28, a decreased in the amount of CH and a corresponding increased in the amount of bound water relative to the OPC content were observed, which indicated a change in the nature of the hydration products formed. The CH content expressed per gram of OPC decreases in the FA blended cements as it was consumed by the pozzolanic reaction of the FA. Based on the literature review reported in [12] it was observed that the presence of FA increased the amount of ettringite per gram of OPC, and decreased the amount of CH over time.

The relatively low consumption of CH in the period of up to one year demonstrated the low reactivity of the FA. The results show that in one year the consumption of CH was 50% greater in the case of cement pastes containing 30% FA than in the case of cement paste without such an addition. This is in agreement with [9] where a similar decrease in the amount of CH over four years was reported. At later ages, the process of hydration of the clinker minerals of the OPC, as well as the pozzolanic reaction between the mineral additions and the CH, continues at a low intensity.

4.2 THE EFFECT OF FLY ASH ON THE CHARACTERISTICS OF FRESH AND HARDENED CONCRETE

4.2.1 Fresh concrete properties

Slump tests, flow table tests, and air content tests were performed on the fresh concrete mixtures A1, A2, B1, and B2 at different time intervals. The properties of the fresh concrete mixtures are presented in Table 4.1.

Table 4.1: The fresh concrete properties corresponding to the concrete mixtures A1, A2, B1, and B2

Slump test [mm]	A1	A2	B1	B2
t = 0 min	185	230	210	250
t = 20 min	170	210	180	240
t = 40 min	170	205	155	235
t = 60 min	120	195	90	220
Flow table test [mm]				
t = 0 min	430	505	450	535
t = 20 min	410	470	425	570
t = 40 min	410	470	380	500
t = 60 min	370	455	345	470
Air content [%]				
t = 0 min	4.5	2.1	3.6	2.2
t = 60 min	4.3	2.1	3.4	2.7

The targeted consistence class S3 was achieved for the concrete mixture A1, and this concrete mixture maintained the same consistence class after 60 minutes, too. On the other hand, concrete mixture B1 dropped to consistence class S2 after 60 minutes. The achieved consistence class for concrete mixtures A2 and B2 was S4 according to the standard SIST EN 206-1:2000 [60]. Larger quantities of the superplasticizer had been added to these two mixtures. A similar trend in the behaviour of concrete workability was observed in the results of the flow table tests.

4.2.2 Hardened concrete properties

Compressive strength and static modulus of elasticity tests, as well as tests to determine the depth of penetration by water under pressure, were performed on the hardened concrete mixtures A1, A2, B1, and B2 at 3, 28, and 90 days.

4.2.2.1 Compressive strength

Compressive strength was measured on the hardened concrete mixtures at 3, 28, and 90 days. The results are presented in Table 4.2.

Table 4.2: Compressive strength of the investigated concrete mixtures A1, A2, B1, and B2

Comp. strength [MPa]	A1	A2	B1	B2
3 days	48.3	45.0	49.7	44.5
28 days	67.1	64.0	73.1	67.4
90 days	67.4	74.6	83.5	80.2

All the concrete mixtures were made solely from very pure crushed limestone or dolostone aggregate with a relatively high content of fine particles below 0.125 mm. Because of the presence of such fine particles in the used limestone aggregate, it is possible to talk about a ternary cement-FA-limestone system.

Comparison of the unmodified concrete mixtures (i.e. concrete which did not contain FA) with different type of aggregate (A1: B1)

Despite the fact that mixtures A1 and B1 differed only with regard to the types of carbonate aggregate, mixture B1 had a different rate of increase of its compressive strength. Concrete mixture A1 reached 99.6% of its compressive strength at 90 days already after 28 days. Based on this result, it is supposed that the process of hydration was almost over after 28 days. On the other hand, in the case of concrete mixture B1, an increase in the compressive strength was observed also after day 28. These differences were initially attributed to the physical-chemical processes in the transition zone between the cement paste and the aggregate grains.

Comparison of the concrete mixtures with and without FA (A1:A2 and B1: B2)

The FA modified concrete mixtures achieved a slightly lower compressive strength at early ages (measured on day 3) in comparison with that achieved by the unmodified concrete mixtures. On day 28, the differences were similar as for 3 days. The

addition of FA appeared to improve the compressive strength between days 28 and 90. The concrete mixture A2 achieved a higher compressive strength on day 90 than the mixture A1, which did not contain FA. These results can be explained by the pozzolanic reaction of the FA with the products of OPC hydration. The reaction begins when the alkalinity of the solution is above pH 13.2. At higher pH values the reactivity of the FA increases. At the beginning of the hydration process, the OPC reaches a pH-value of about 12, so the speed of the initial pozzolanic reaction is very low and increases over time. This is reflected in the subsequent increase in compressive strength.

4.2.2.2 Static modulus of elasticity

Static modulus of elasticity was measured on the hardened concrete mixtures on days 3, 28, and 90. The results are presented in Table 4.3.

Table 4.3: Static modulus of elasticity of the investigated concrete mixtures A1, A2, B1, and B2

Static modulus of elasticity [GPa]	A1	A2	B1	B2
3 days	37.3	31.5	34.5	28.3
28 days	42.5	43.8	42.6	40.4
90 days	44.0	42.0	49.6	43.9

The static modulus of elasticity of the FA modified concrete mixtures was about 17% lower than that of the unmodified concrete mixtures, measured on day 3. The largest value was measured in the case of concrete mixture A1 (37.3 GPa).

On day 90, the concrete mixtures A1, A2, and B2 achieved comparable values of the elastic modulus. On the other hand, the value of the elastic modulus for concrete mixture B1 increased by 13% in comparison with the other mixtures when measured on day 90. A similar effect was noticed in the case of the measured compressive strength.

4.2.2.3 Depth of penetration of water under pressure

The depth of penetration by water under pressure was measured on the hardened concrete mixtures after 3, 28, and 90 days. Table 4.4 lists the results of the measured penetration depths.

Table 4.4: Depth of penetration by water under pressure

Penetration depth [mm]	A1	A2	B1	B2
3 days	15	16	19	20
28 days	14	12	19	15
90 days	17	16	18	17

Each value of the penetration depth was the average of that measured on three specimens. The dispersion of the results was very high on day 3, which indicates non-homogeneity of the concrete mixture. This was also reflected in the measurements of the static modulus of elasticity.

On days 28 and 90, the dispersion of the results was smaller. Despite some scattering of the results, the average value of the measurements achieved the target penetration depth of water under pressure of 500 ± 50 kPa according to the standard EN 12390-8 [59]. The maximum permissible penetration depth of water for level PV III is 20 mm (SIST 1026:2008). The results indicate that all the investigated concrete mixtures can be classified as dense concrete with low permeability.

4.2.3 Discussion

Investigations of the characteristics of the fresh and hardened concrete were performed. The selection of the mixture was made in order to consider two important parameters: the addition of FA, and the type of aggregate (limestone and dolostone). The following conclusions were drawn:

In the case of the investigated FA modified concrete mixtures, a higher amount of superplasticizer was added in order to obtain the desired workability. The addition of FA decreased the compressive strength at early ages (measured on day 3). Compressive strengths are reduced due to the retardation in the belite hydration, which was confirmed experimentally by means of the results of the performed isothermal colorimetric study. After 90 days, the compressive strength of the concrete in which 20% of OPC had been replaced by FA exceeded the compressive strength of the unmodified concrete (concrete mixture A2). The reason for the observed increase in the compressive strength when FA was added was the on-going pozzolanic reaction, which was confirmed by the results of the thermogravimetric analysis accompanied by evolution of the hydrated phases, and the observed decrease in the amount of calcium hydroxide. The experimental data which were

obtained in this study about water penetration depth showed that there was no significant difference in permeability for the investigated concrete mixtures, all of which, however, provided excellent water-tightness, which is an important parameter for durability.

The two concrete mixtures (A1 and B1) which were made with different types of carbonate aggregate but whose mix design was identical were found to have different rates of increase of their mechanical characteristics over time. The concrete with dolostone aggregate attained a 90 day compressive strength which was 24% higher, and a modulus of elasticity which was 13 % higher than that of the concrete with limestone aggregate, although after 28 days these differences were only 9% and 0.2%, respectively. These differences were initially attributed to the physical-chemical processes in the transition zone between the cement paste and aggregate grains, which might have been caused by alkali-carbonate reaction (ACR). This question is studied hereafter.

4.3 ALKALI CARBONATE REACTION

This chapter is based on the paper [18] “Observation on dedolomitization of carbonate concrete aggregates, implications for ACR and expansion” which was published in the Cement and Concrete Research journal in 2013.

4.3.1 Measurements of length change

By studying the time dependent change of the stone and mortar prisms length, we did not observe significant difference in length up to 6 months on 3 replicate samples of carbonate stone and mortar prisms (Figure 4.10) in water as well in NaOH solution. The difference in expansion of samples exposed to 20 and 60 °C is due to the temperature expansion (Figure 4.10). This corresponds with the theory proposed by Katayama [20] that the process of dedolomitization does not cause significant expansion. The changes are reflected predominantly in the material structure and, therefore, the determination of the ACR requires a microscopic approach.

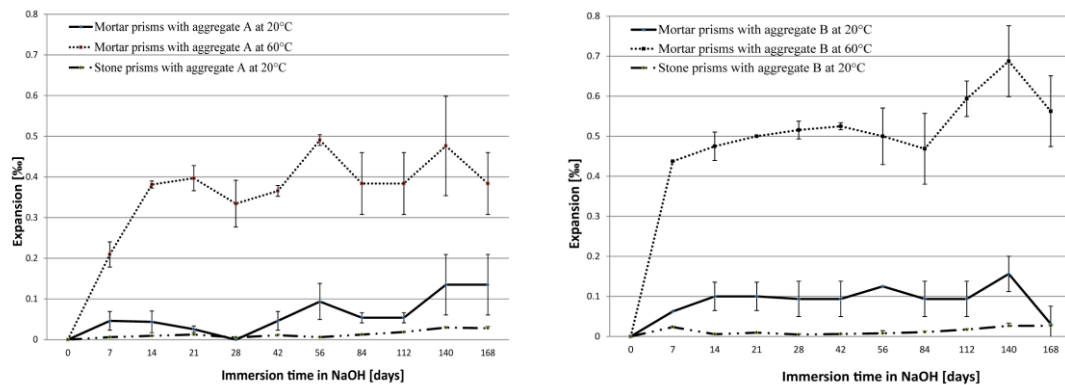


Figure 4.10: Stone and mortar prisms expansion in 1M NaOH at 20 °C and 60 °C; aggregate A (A) and aggregate B (B).

4.3.2 Results on the stone prisms

Using the atomic absorption spectrometry, we determined the content of magnesium ions in the water and NaOH solution at 20 °C that were leached from the limestone (A) and the dolostone (B) prisms. The Table 4.5 represents the results of concentration of magnesium ions.

Table 4.5: Concentration of magnesium ions dissolved from carbonate rocks into the water and NaOH solution

	Mg [mg/L]
A_H ₂ O	1.37
A_NaOH	1.69
B_H ₂ O	3.09
B_NaOH	155.20

Three phases (calcite, dolomite, brucite) were observed in the X-ray powder pattern to cover all the peaks (Figure 4.11). A model using the Rietveld program Topas was created to determine the content of these three phases in the stone prisms after the 9-month exposure period to the 1M NaOH. The structure of the selected phases were taken from the Inorganic Crystal Structure Database – code 079673 (calcite), 202162 (dolomite) and 079198 (brucite). Contents of all three phases in the carbonate rocks after 9-month exposure period are shown in the Table 4.6.

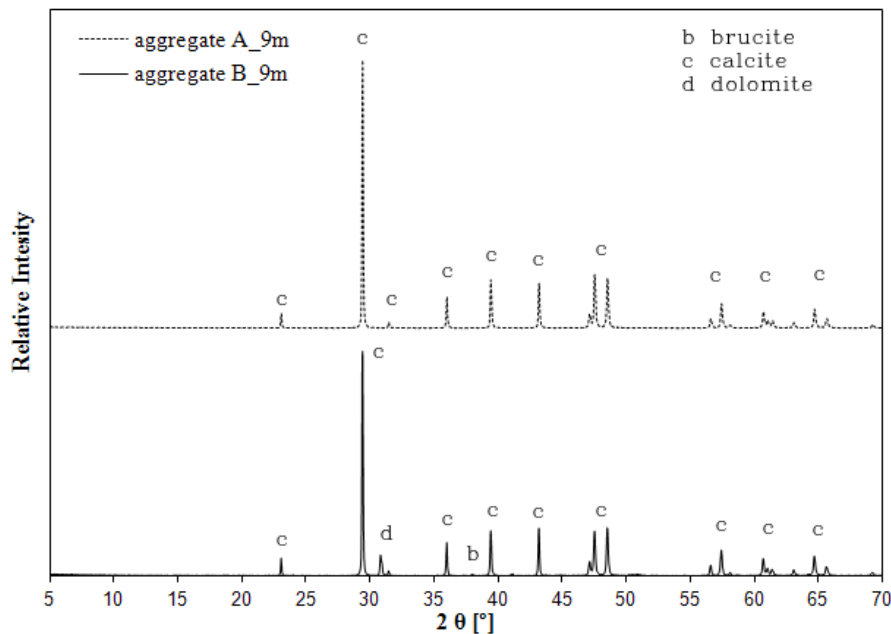


Figure 4.11: XRD pattern of investigated aggregates after the 9-month exposure period to 1M NaOH.

Based on the results obtained with the AAS and the XRD, we observed that the limestone, the aggregate A, after 9-month exposure period to 1M NaOH showed no alteration. This confirms the fact that the limestone is stable in a high alkaline solution. On the contrary, the dolostone showed a significant alteration after 9-month

exposure period. As can be seen from the XRD result, almost all the dolomite transformed into calcite through the process of dedolomitization (Table 4.6). Only 1 wt.% of brucite was detected with the XRD in the samples. From this result, we suppose that the Mg ions are predominantly carried away into the solution during the process of dedolomitization. This is confirmed by the results of the AAS (Table 4.5). The results are also in accordance with Katayama [72].

Table 4.6: Rietveld analysis of investigated aggregates before and after 9-month exposure period to 1M NaOH

	Limestone, A		Dolomite, B	
	before exposure	after exposure	before exposure	after exposure
Calcite	98.47	99.89	3.12	91.58
Dolomite	1.59	0.11	96.02	7.25
Brucite	0	0	0.26	1.17

The quantities are in wt.%

4.3.3 Results on the mortar prisms

In order to obtain the first view of the microstructure of all investigated mortar specimens, polarizing microscopy was used. The Figure 4.12A,B show that none of the mortar prisms containing the aggregate A have shown alteration of the structure or of the aggregate itself at all conditions. The 3-month exposure period to the water causes no alteration on the dolostone aggregate (Figure 4.12C). On the other hand, Figure 4.12D shows that after 6 months at 60 °C the reaction on the aggregate occurred in the water.

An evident alteration of the aggregate occurred in the alkaline solution already after 3 months for mortar prisms containing the aggregate B, at the margin of a coarser aggregate ($D > 1$ mm) and at the whole surface of a finer aggregate (D_{max} around 1 mm), respectively (Figure 4.12E). Over time, the alteration has spread over almost all aggregates; coarser and finer (Figure 4.12F).

In order to obtain more detailed information about the formed reaction products, a microstructure analysis with the SEM-EDS was also performed.

Replicate determinations on the samples taken from the mortar prisms were performed with the back-scattered electrons (BSE) image mode of the SEM and the EDS.

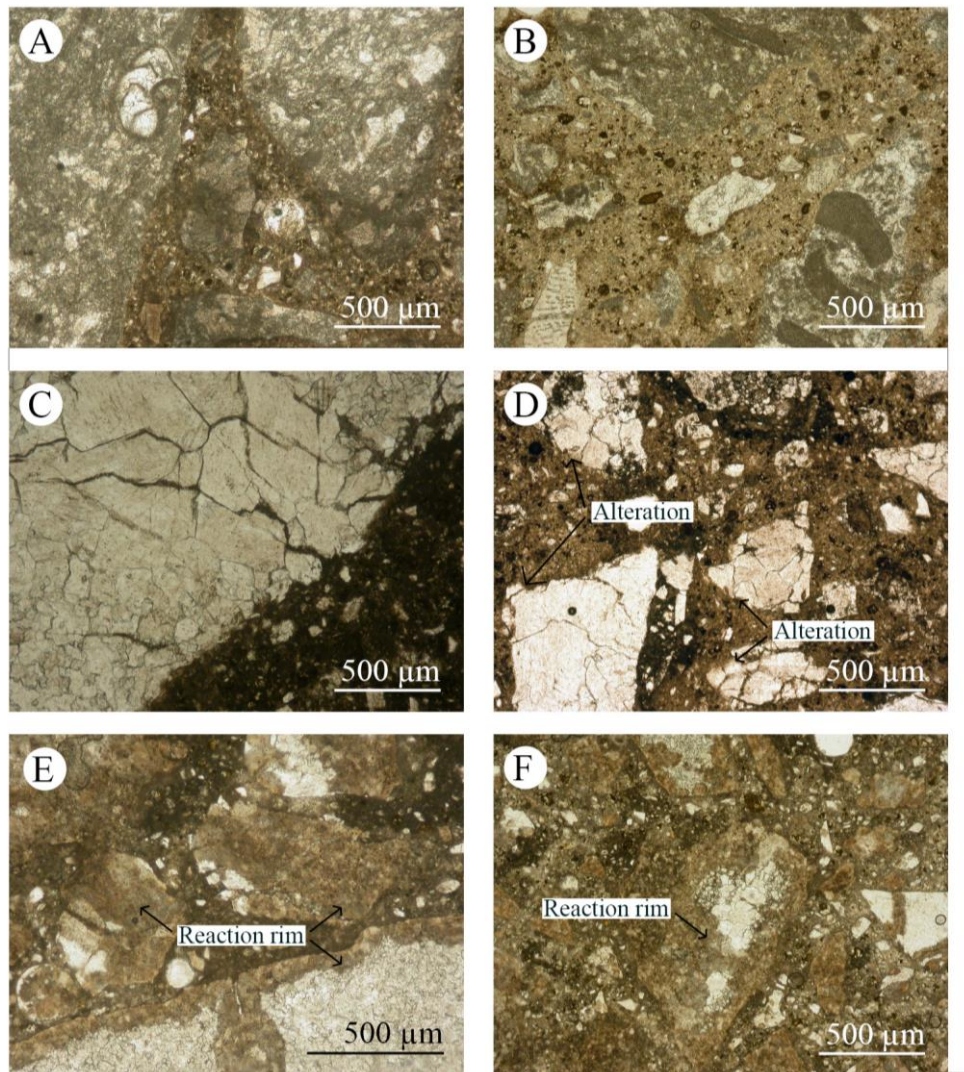


Figure 4.12: Thin sections of mortar prisms; PPT, x50: (A) Limestone, NaOH 60 °C 3 months, (B) Limestone, NaOH 60 °C 6 months, (C) Dolostone, H₂O 60 °C 3 months, (D) Dolostone, H₂O 60 °C 6 months, (E) Dolostone, NaOH 60 °C 3 months and (F) Dolostone, NaOH 60 °C 6 months.

4.3.3.1 Water solution, 60 °C, 3 months

Figure 4.13 shows the samples of the limestone and the dolostone mortar prisms after 3 months in water solution. On the sample with the limestone aggregates (Figure 4.13A,B) no reaction could be seen. The boundary between the cement binder and the limestone aggregates is clearly visible.

In general, also the sample with the dolostone aggregates (Figure 4.13C,D,E) has almost no alteration in the structure. The sample has a homogeneous texture as is visible from the mapping analysis in the Figure 4.13C. The only difference is that the aggregate has many calcite or dolomite veins. Some of them are filled with calcite sparite cement (Figure 4.13D), which is in agreement with the petrographic analysis (Figure 3.4B). In addition, the cement binder diffuses inside the aggregate. The diffusion of the silicon atoms between the calcite vein that fills the tectonic crack and the surrounding host dolomite is clearly visible in Figure 4.13E. Nevertheless, the process of dedolomitization was not evident.

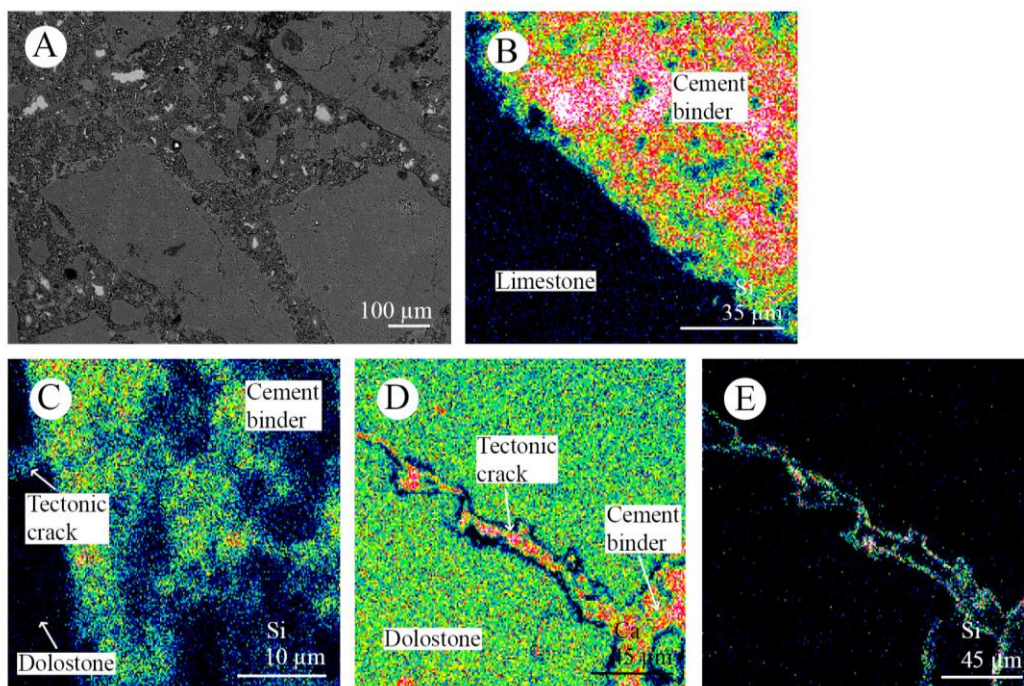


Figure 4.13: Mortar prism made with the limestone aggregate in H₂O 60 °C 3 months. (A)–(B) Relative concentration maps for selected elements by EDS for mortar prism made with the dolostone aggregate in H₂O 60 °C 3 months (C)–(E).

4.3.3.2 NaOH solution, 60 °C, 3 months

In the case of mortar with the limestone aggregate in 1 M NaOH solution no alteration was noticed. On the other hand, evident alteration was observed on the samples with dolostone aggregates. The Figure 4.14 shows that all fine aggregate grains and the margin of coarse dolostone aggregates tend to dedolomitization. At low magnification, the dedolomitization was readily recognizable as a characteristic texture at the margin of the coarse dolostone aggregates, but inside the aggregate remained unaltered and composed of the dolomite phase (Figure 4.14A). A mottled

mixture shown in the Figure 4.14A was observed at high magnification. The elemental composition of the mottled mixture detected by the EDS (Figure 4.14B,C,D) was rich in magnesium, calcium and silicon atoms. The Figure 4.14D shows the presence of silicon atoms between brucite and calcite.

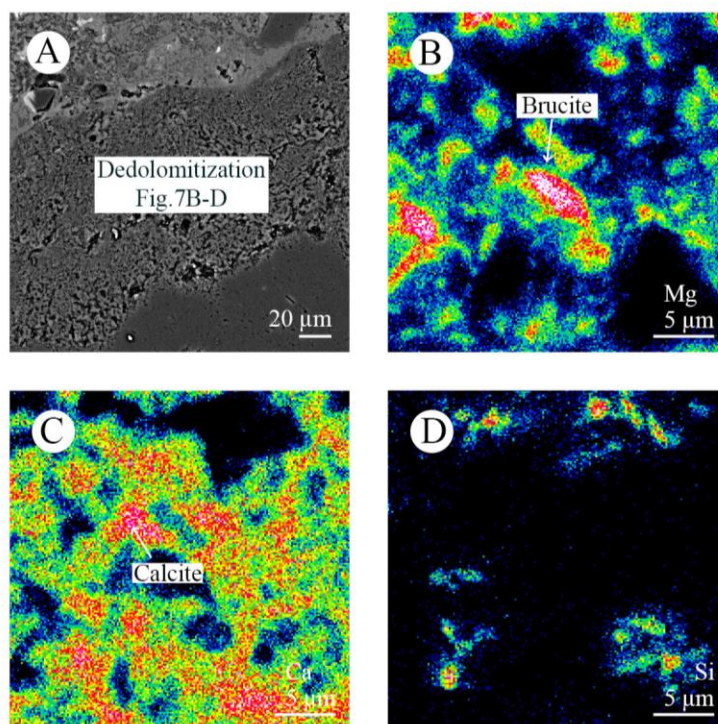


Figure 4.14: Relative concentration maps for selected elements by the EDS. (A)–(D): mortar prism made with the dolostone aggregate in NaOH 60 °C 3 months.

The third product of dedolomitization is a soluble phase that contains liberated CO_3^{2-} ions. These ions react with calcium ions and form a secondary calcite (Figure 4.15A, B) in the transition zone along the aggregate grain. The use of the CAMEO function in the INCA software that enables coloring of grains according to their chemical composition, distinguishing between dolostone aggregate and secondary calcite, became feasible (Figure 4.15A). From such colorized pictures, different gray values for calcite and dolomite can be easily obtained. On the border between the interior of the aggregate and the secondary calcite, Si and Al atoms were enriched. This is supported by an element linescans analysis (Figure 4.15C). On the left side of the image Figure 4.15C is a dolostone aggregate rich in Mg and Ca, then a narrow rim – 2 μm – of Si and Al is concentrated. On the right side of the image, secondary calcite is formed as it is shown from the linescans analysis (Figure 4.15D). This part is rich in calcium atoms.

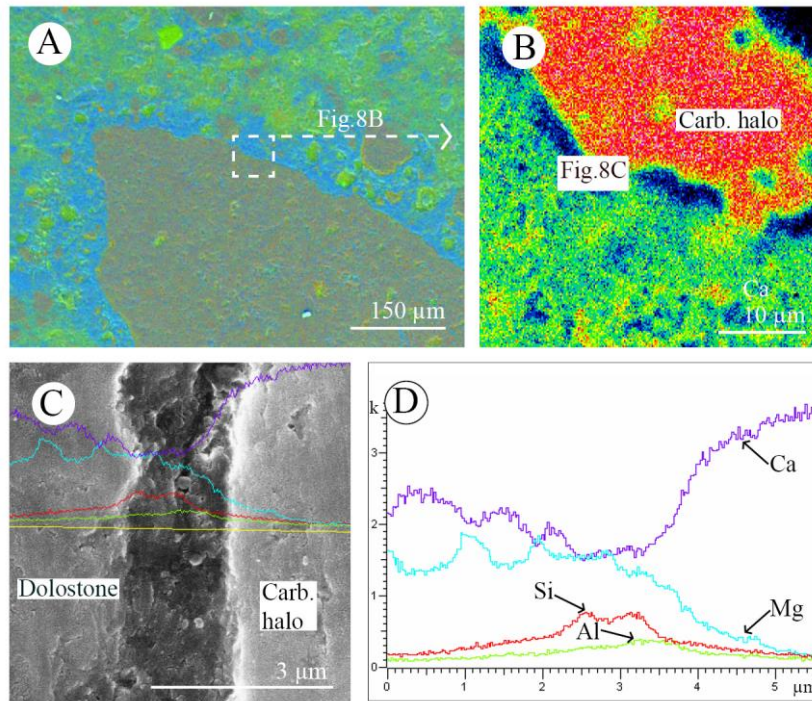


Figure 4.15: Relative concentration maps for selected elements by EDS. (A)–(D): mortar prism made with the dolostone aggregate in NaOH 60 °C 3 months.

4.3.3.3 Water solution, 60 °C, 6 months

According to the results of the microstructural analysis, the morphology of the limestone aggregate altered neither in the water nor in the 1 M NaOH. This in turn means that the considered limestone is stable in high alkaline media after the 6-month exposure period.

Figure 4.16 indicates that the process of dedolomitization had already taken place in mortar with the dolostone aggregate in non-accelerated solution – water after 6-month exposure period. The dedolomitization exhibits evidently in the range of the detected dolomite vein (Figure 4.16A). We noticed the increase of calcium atoms in the cement binder, which is in agreement with Katayama [27]. A characteristic texture composed of the mottled mixture of brucite and calcite was observed also at the margin of some aggregate grains (Figure 4.16D). The darker the reaction zones appear in the reflected light, the more Mg-rich phase can be identified in the SEM-EDS and the lighter the reaction zone is the more Ca-rich phase was created (Figure 4.16). Based on the literature review described in [27], it is supposed that the dark zones correspond to brucite and the lighter zones correspond to calcite. The Figure 4.16E shows that the cement binder did not completely alter.

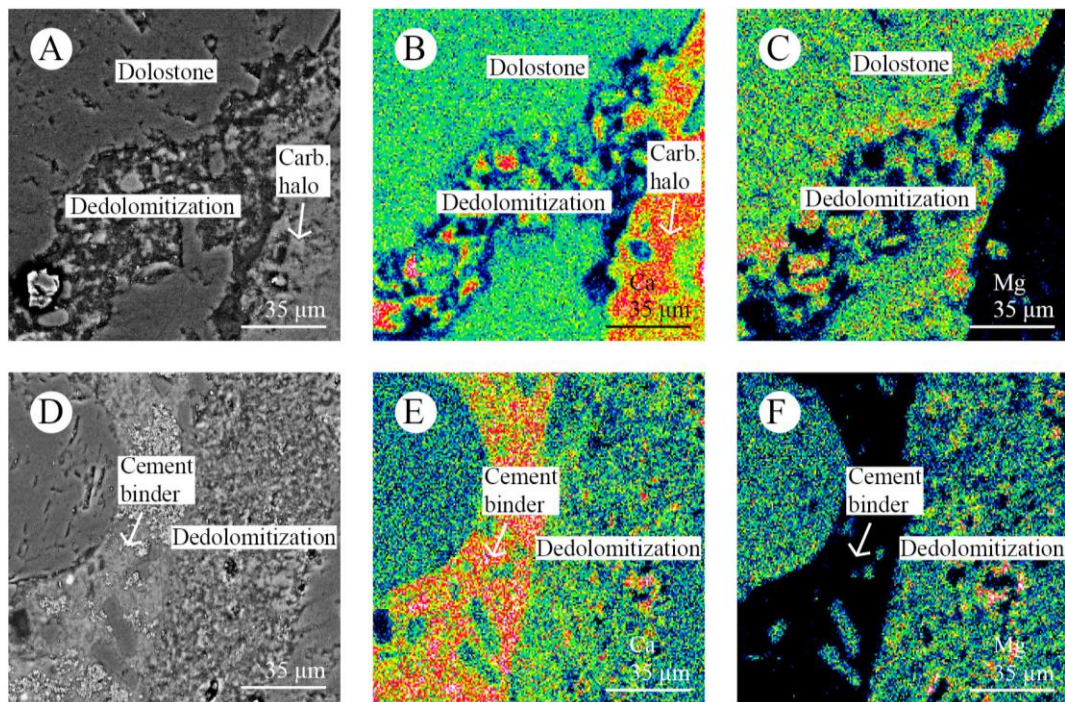


Figure 4.16: Relative concentration maps for selected elements by EDS. (A)–(F): mortar prism made with the dolostone aggregate in H₂O 60 °C 6 months.

4.3.3.4 NaOH solution, 60 °C, 6 months

The strong effect of the alkaline solution becomes even more apparent after 6 months of exposure at 60 °C. All dolostone aggregate grains, finer and coarser, and cement binder have shown a distinct alteration. The Figure 4.17 shows an evident formation of secondary calcite. In order to confirm the formation of the secondary calcite, the point analysis with silicon standard was used. The EDS point analysis shows that the part of the secondary calcite is mainly composed of calcium (average 36% by weight) and oxygen (average 63.6% by weight) with a minor concentration of silicon (average 0.4% by weight) (Figure 4.17B). The analysis was also carried out on the part of the aggregate that dedolomitized, precisely in the area where we assumed the formation of brucite would be. The analysis shows that the part of the brucite is mainly composed of magnesium (average 39% by weight) and oxygen (average 54% by weight) with a minor concentration of calcium (average 7% by weight) (Figure 4.17C).

In order to confirm the same mechanism of dedolomitization after 6-month exposure period to the alkaline solution, an element linescans was used to identify the boundary between aggregate and cement paste. The Figure 4.17D show that on the

boundary secondary calcite is formed. Between the secondary calcite and the aggregate, a narrow rim – 2 μm – of Si, Al and Mg is concentrated. This phenomenon was also visible after 3 months.

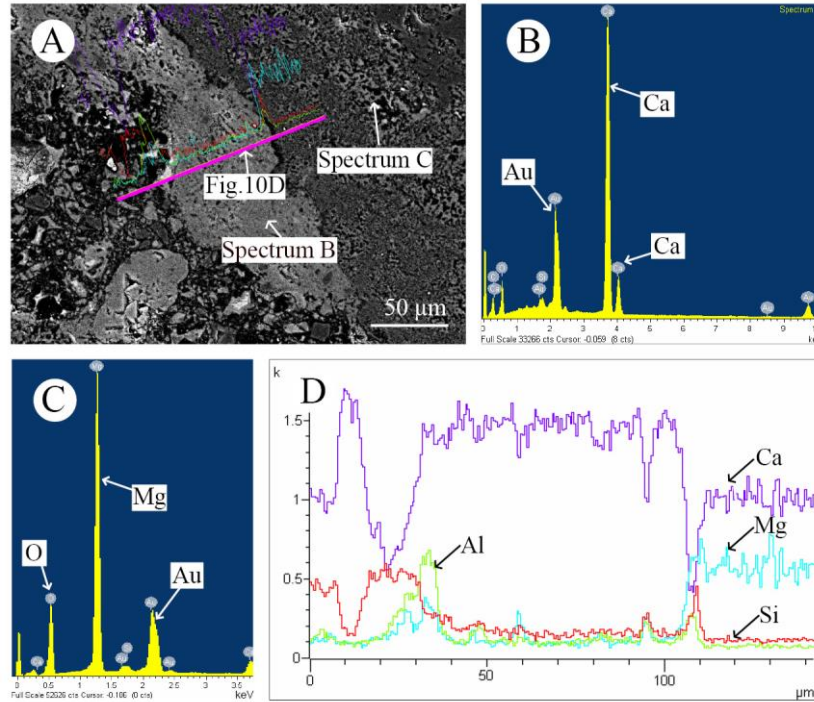


Figure 4.17: Completely dedolomitized dolostone aggregate grain in mortar in NaOH 60 °C 6 months, producing carbonate halo (A-D). (B) Point analysis on the area where the secondary calcite formed. (C) Point analysis on the area where the brucite formed.

Figure 4.18 shows the composition of the cement binder near the dolostone aggregate. Over time in the alkaline solution, the cement binder showed an evident alteration, especially near the dolostone aggregate grains where secondary calcite is formed. C-S-H gel is concentrated in small areas, at the distance of the aggregate.

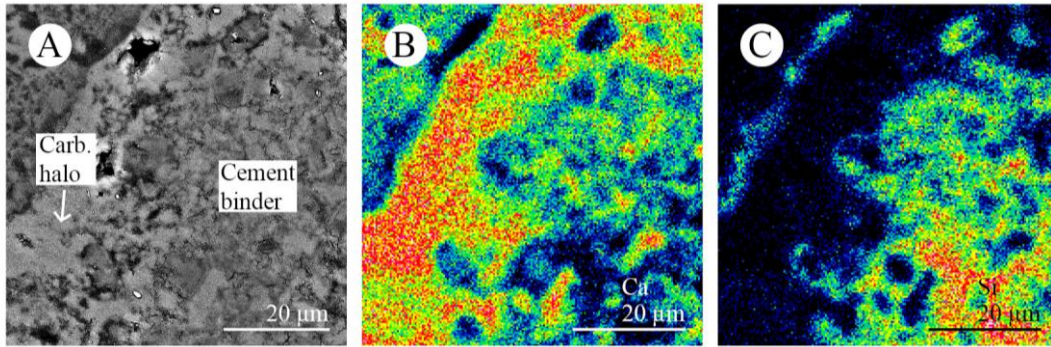


Figure 4.18: Relative concentration maps for selected elements by EDS. (A)–(C): mortar prism made with the dolostone aggregate in NaOH 60 °C 6 months.

4.3.3.5 Water solution and NaOH solution, 20 °C, 6 months

Based on the test results obtained after 3 months at 60±2 °C, the examination for macroscopic evidence of the carbonate rock reaction at 20±2 °C was made only after 6 months. Figure 4.19A shows that the sample of mortar with dolostone aggregate remained unaltered after 6-month exposure period in the water at 20 °C. This means that the pore solution does not have enough alkali ions and hydroxyl ions. The rate of reaction proceeded also very slowly in the alkaline solution, where at the margin of the aggregates a small alteration was observed (Figure 4.19B). This is in agreement with [73], where it was found that at room temperatures the alkali in the solution reduces the dissolution rate of dolomite.

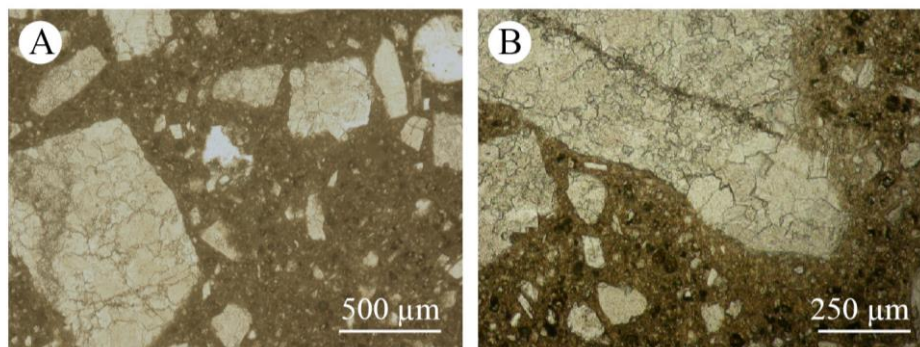


Figure 4.19: Samples of mortar prisms made with the dolostone aggregate in NaOH and H₂O 20 °C 6 months: Thin sections of the dolostone aggregate in H₂O, PPT, x50 (A), and of the dolostone aggregate in NaOH, PPT, x100 (B).

4.3.4 Discussion

In the referenced literature, observations ACR in concrete have been made mostly on carbonate aggregates including reactive silica and in accelerated solutions [19-23, 25-27, 32]. In our research we wanted to study the process of ACR on local

carbonate aggregates and at real conditions. The considered carbonated rocks do not include silica, clay minerals or other reactive minerals. Aggregate petrography, the XRD and the XRF confirmed that the aggregates are virgin limestone and dolostone. Most researchers use high alkaline solution when studying the ACR. To simulate the real conditions, we used water media at 20 °C and 60 °C. In order to study the influence of accelerating solution on implications of the ACR the 1 M NaOH was chosen.

The microscopic observation after three months exposure period presents that the dedolomitization proceeded in the dolostone aggregates in the alkaline solution. By the EDS analysis we observed the Si and Al atoms in the pores between two formed phases, calcite and brucite (Figure 4.14). This agrees well with the Eq. (1.8). The decrease of the volume of products causes an increase in porosity. This higher porosity increases the ionic mobilization capability and could enable a diffusion of Si and Al atoms from the cement binder into the dedolomitized aggregate. According to the calculations Eq. (1.8 and 1.9), the dedolomitization is a dissolution-precipitation process which leaves no expansion. Long term measurements of length change of mortar bars with dolostone aggregate confirmed no expansion. On the other hand, significant chemical and mineralogical alteration of studied dolostone aggregate grains occurred in the concrete over time.

According to the Eq. (1.9), the liberated CO_3^{2-} ions, from the Eq. (1.8), diffuse from the dolostone into the cement paste and react with the calcium ions in the cement paste. Along all dedolomitized aggregates formation of a secondary calcite or carbonate halo was observed in the hydrated cement paste (Figure 4.15B). This phenomenon manifests in dense cement binder in the transition zone. However, a narrow rim between the dedolomitized aggregate and the secondary calcite was observed after 3 and 6 months. It is supposed that the rim is composed of a phase rich in Si, Al and Mg atoms and there is also the possibility that it contains a Mg-silicate gel [27].

The rate of reaction proceeded very slowly even in alkaline solution after a 6-month exposure period at 20 °C. This means that both the temperature and the pH value of the solutions play an important role on the rate of the ACR reaction. The higher the temperature and the pH value, the larger the rate. Already Min et al. pointed out [29] that the reaction will proceed very slowly or may even not take place when the temperature is below 25 °C and the pH value is lower than 12.

Therefore, it is difficult to conclude that the considerable increase in compressive strength (24%) and the increase in the modulus of elasticity (13%) in case of concrete prepared with the dolostone aggregate, compared with those from the limestone aggregate, are the result of the reaction of dedolomitization. However, formation of the secondary calcite in the ITZ and diffusion of the Si and Al atoms from the cement binder along the calcite or dolomite veins are changes in the concrete structure that can increase mechanical characteristics of concrete under consideration, due to the denser ITZ and better interlocking of the cement binder and the aggregate grains. Thus, we can only suppose that the detected processes may influence the mechanical characteristics of concrete even before being detected with the applied testing methods.

By taking the results from the studied process of dedolomitization on the mortar prisms with the carbonate aggregates, a table has been prepared (Table 4.7) summarizing the alteration of the aggregates A and B over time in various solutions. It is obvious that the tested limestone is more stable than dolostone at high alkaline solution even after 6 months at 20 °C and 60 °C. Thus, in our case the limestone should be favorable when used as an aggregate.

Table 4.7: The alteration of the carbonate aggregates A and B over time in various solutions taken under SEM over time

Position of dedolomitization	Limestone			
	H ₂ O	H ₂ O	NH-	NH-
	60°C	60°C	60°C	60°C
	3mon	6mon	3mon	6mon
Rim of aggregate	N	N	N	N
Carbonation halo	N	N	N	N

Position of dedolomitization	Dolomite					
	H ₂ O	H ₂ O	NH-	NH-	H ₂ O	NH-
	60°C	60°C	60°C	60°C	20°C	20°C
	3mon	6mon	3mon	6mon	6mon	6mon
Rim of aggregate	R	CM	CM	C	N	R
Carbonation halo	N	R	CM	C	N	R

NH: NaOH; N: None; R: Rare; CM: Common; C: Conspicuous

When designing building structures with an increased service life, where the structural elements will be exposed to increased temperatures, we should be careful with selection of type and source of carbonate aggregate.

4.4 CARBONATION

4.4.1 Properties of the hardened concrete

The development of the compressive strength of the concrete mixtures M1, M2, M3, M4, M5, M6, and M7 is shown in Figure 4.20. The FA modified concrete mixtures achieved a slightly lower compressive strength at early ages (i.e. at an age of 2 days) in comparison to the unmodified concrete mixtures. On day 28, the differences were smaller. The addition of FA up to 50% appeared to improve the compressive strength between days 28 and 90. On day 90, the concrete mixture with 20% of FA had achieved a higher compressive strength than the unmodified concrete mixture. These results can be explained by the pozzolanic reaction of the FA with the products of the OPC hydration.

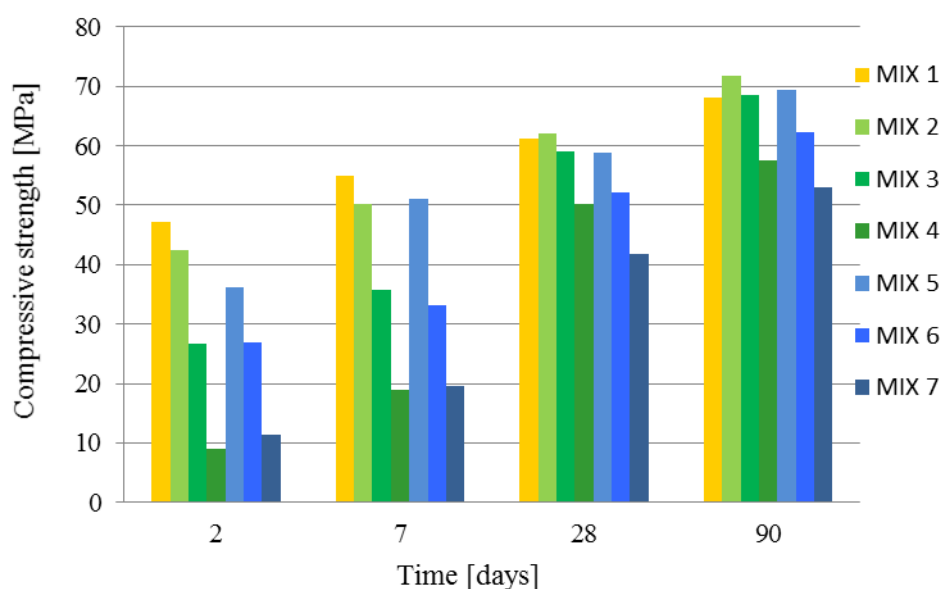


Figure 4.20: Development of the compressive strength of the concrete mixtures M1, M2, M3, M4, M5, M6, and M7.

4.4.2 Influence of the concrete composition

Figure 4.21 presents the evolution of carbonation depth as a function of exposure time for the concrete mixtures M1, M2, M3, M4, M5, M6, and M7, which contained different amounts of FA, were cured for 28 days at 20 °C and a RH > 95%, and were

subsequently exposed to a 10 vol% CO₂ environment. The carbonation front was determined after spraying phenolphthalein solution on a freshly sawn surface.

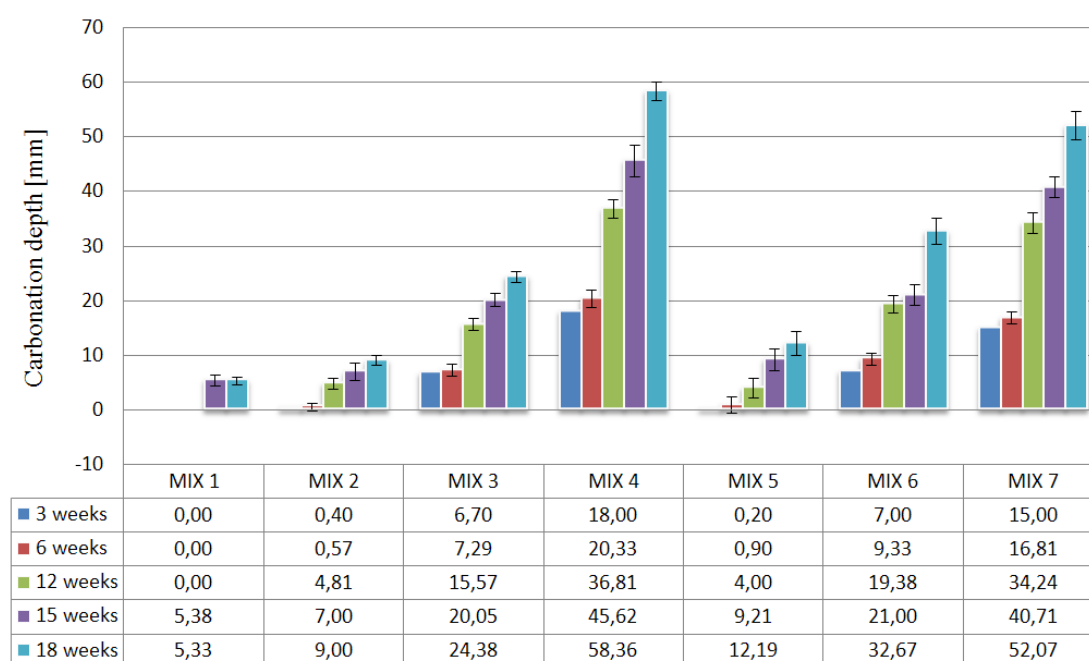


Figure 4.21: Evolution of carbonation depth as a function of exposure time for the concrete mixtures M1, M2, M3, M4, M5, M6 and M7, containing different amounts of OPC and FA exposed to an environment containing 10 vol% CO₂ at different ages.

As presented in the Figure 4.21, the reference, unmodified concrete mixture M1 showed no carbonation after a 15-week exposure to the selected CO₂ atmosphere. However, the carbonation depths increased with increasing FA content. This is not surprising since the pH of the pore solutions in the FA modified concrete is already low and CO₂ preferentially reacts with CH (which is only present to a small extent), so that the pH is rapidly reduced below the end point of the phenolphthalein indicator. These results are in line with those reported by Gruyaert [74].

4.4.3 Discussion

The carbonation process was studied in the concrete mixtures with different types and levels of FA replacement (up to 65 %) and a constant w/b ratio. The carbonation depth in concrete mixture M2 containing 20% FA as replacement for OPC was slightly higher than that found in the unmodified concrete mixture M1. In the case of the concrete mixture M5, which contained the same replacement level as M2, a higher carbonation depth was obtained. These results were in line with the achieved 28 days compressive strength. The concrete mixture M2 achieved a higher

compressive strength on day 28 than the mixture M1, whereas the mixture M5 reached a lower compressive strength. However, the mixture M3, which contained 50% FA, achieved almost the same 28 days compressive strength as the mixture M5 which contained 20% FA, although the carbonation depth for the mixture M3 was clearly higher. This means that in the concrete mixture containing 50% FA as a replacement for the OPC the rate of carbonation was significantly higher despite the same strength grade.

Based on the results a higher carbonation depth with increasing FA content was observed in the concrete with a constant w/b ratio. Already De Belie et al. pointed out [34] that greater carbonation depths are most likely due to higher permeability and a lower amount of carbonatable material in high-volume FA modified concrete.

Carbonation of pozzolana-containing cements is also deeper when accelerated carbonation methods are used instead of long-term exposure on site [8]. The used accelerated procedure makes use of a CO₂-enriched atmosphere (10 vol% CO₂ and 60±5 % relative humidity), whereas this gas is present in the atmosphere only to the extent of 0.03 vol%. This means that the concentration in the used procedures was circa 330 times higher than under normal conditions. If the concentration of CO₂ is increased it is possible that not only the rate may be altered but also the type of chemical reactions involved. The suitability of procedures using a CO₂-enriched atmosphere is therefore questionable since it is possible that they will not provide values similar to those obtained under natural exposure conditions.

4.5 CHLORIDE INGRESS

This chapter is based on the paper [75] “Chloride ion penetration into fly ash modified concrete during wetting-drying cycles” which was accepted in the journal Construction & Building Materials in April 2015.

4.5.1 Cyclic immersion and drying test

The results of the cyclic immersion and drying tests were used to investigate the effect of the exposure time, the FA content, and the composition of the FA.

4.5.1.1 Exposure time

In order to study the time-dependent change in the chloride profiles, four concrete mixtures were exposed to the chloride solution under wetting-drying cycles for 21, 42, 84, 105 and 126 days. Care was taken to study the total and water-soluble chloride penetration profiles. Since chlorides that can bind in the form of a complex salt such as calcium monochloroaluminate hydrate cannot initiate corrosion, the water-soluble chloride contents were measured in order to determine the free chloride contents.

The acid-(total) soluble chloride content (c_{as}) and water-soluble chloride concentration (c_{ws}) (% Cl^- relative to the concrete mass) can be calculated according to formula 4.3 [67]:

$$c_{as(ws)} = \frac{f_d \cdot M(Cl^-) \cdot c(AgNO_3) \cdot V(AgNO_3)}{m(\text{sample})} \cdot 100 \quad 4.3$$

c_{as} is the acid-(total) soluble chloride content by the mass of sample (%), f_d is the dilution factor (= 10), M is the atomic mass of chlorides (= 35.45 g/mol), $c(AgNO_3)$ is the concentration of the titration liquid (= 0.01 mol/l $AgNO_3$ or the exact value obtained by calibration), $m(\text{sample})$ is the mass of the concrete powder in the extraction liquid (= 2 g and 2.5 g, respectively, for the determination of the acid-soluble and water-soluble chloride content) and $V(AgNO_3)$ is the titrated volume $AgNO_3$ (l). [67]

Figure 4.22 shows the total and water-soluble chloride penetration profiles for the two concrete mixtures M1 and M2. The chloride penetration depth was greater over time in the case of both mixtures, due to capillary suction and diffusion of the chloride ions. A relatively large penetration depth was observed in the case of the unmodified

concrete mixture M1 when compared to mixture M2 already on day 84, which further increased by day 126.

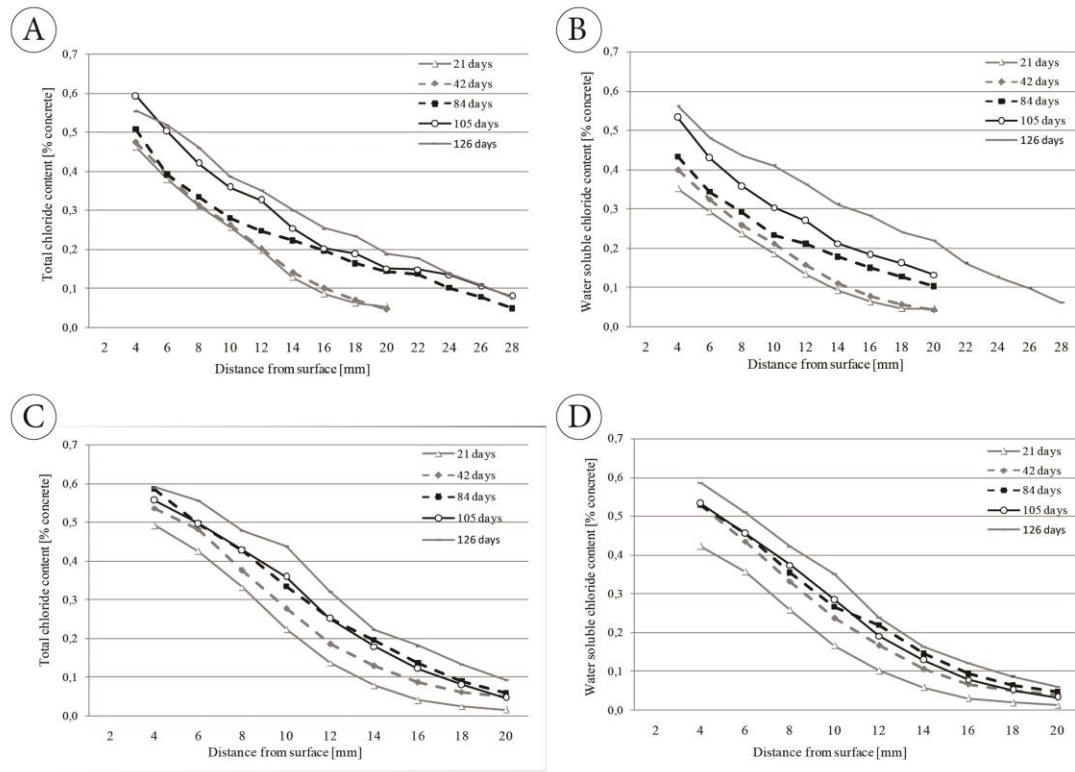


Figure 4.22: Total and water-soluble chloride penetration profiles for the two concrete mixtures M1 (A and B) and M2 (C and D) to wetting-drying cycles on days 21, 42, 84, 105 and 126.

The chloride content when compared to the mass of the sample was lower when the water-soluble chlorides were measured compared to the total-soluble chlorides. It seems that the binding capacity of concrete with 20% of cement replacement by FA I in mixture M2 was quite similar to that of the unmodified mixture M1.

4.5.1.2 Replacement level

The influence of material characteristics, concerning concrete composition, on chloride profiles in a tidal zone was studied. Four concrete mixtures were made where FA was used as a partial replacement of OPC at 0%, 20% and 50% by weight of the binder. The total and water-soluble chloride penetration profiles for concrete mixtures M1, M2, M3, and M5 are presented in Figure 4.23. They correspond to day 21 of the exposure of the mixtures to chlorides in the wetting-drying cycles. From the chloride profiles presented in Fig. 4.23 it can be seen that at early ages (21 days) the

chloride penetration for concrete containing 20% and 50% FA has a similar chloride ion diffusivity to that of the unmodified concrete mixture M1.

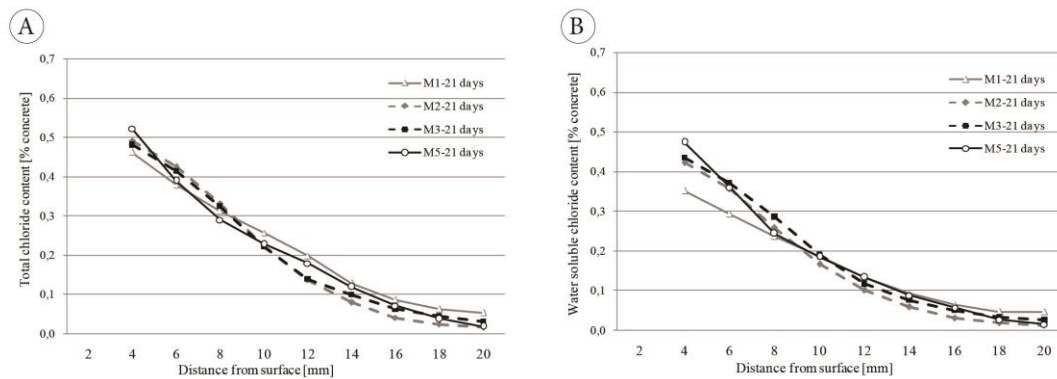


Figure 4.23: Total (A) and water-soluble (B) chloride penetration profiles of the FA modified concretes on day 21 of exposure to wetting-drying cycles.

For comparison purposes, the total-soluble chlorides as well as the water-soluble chlorides are plotted in Fig. 4.24. The concrete with 50% of cement replacement in mixture M3 has the lowest binding capacity (Fig. 4.24B). However, the effect of cement replacement by FA on the chloride binding capacity is not particularly pronounced. For this reason only the influence of the total-soluble chloride over time will be analyzed.

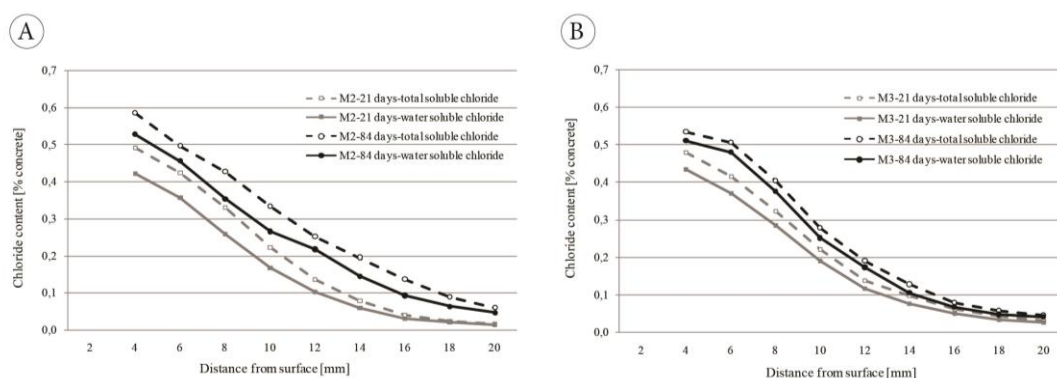


Figure 4.24: Comparison between the total and water-soluble chloride penetration profiles of the FA modified concretes on days 21 and 84 of exposure to wetting-drying cycles for mixture M2 (A) and mixture M3 (B).

On day 84 the difference in the chloride penetration depth becomes evident for the FA modified concrete mixtures compared to the unmodified concrete mixture M1 (Figure 4.25). All the FA modified mixtures show a higher resistance compared to the

unmodified concrete mixture M1 (Figure 4.25). This in turn means that the pozzolanic reaction of the FA in the concrete leads to a lower permeability, thus leading to lower chloride ingress compared to the unmodified concrete, which was also experimentally observed in previous studies [37, 44, 76].

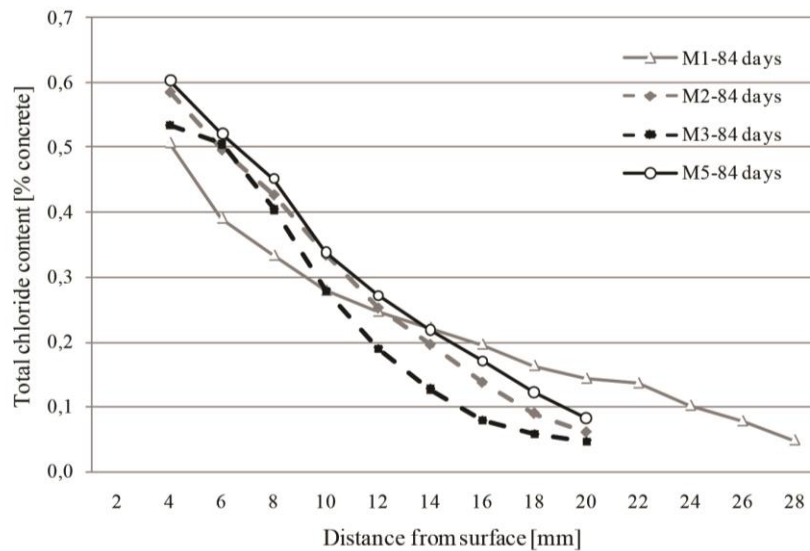


Figure 4.25: Total-soluble chloride penetration profiles of all the concrete mixtures on day 84 of exposure to wetting-drying cycles.

It is clear that the transport properties of ions in the concrete are related to porosity. For this reason mercury porosimetry (MIP) was carried out on samples taken from the concrete after 84 and 126 days of exposure in order to gain information about pore-size distribution. Table 4.8 presents the experimental data for total porosity measured by MIP for the concrete mixtures M1, M2, M3, and M5 on day 126.

Table 4.8: Experimental data for total porosity measured by mercury porosimeter for concrete mixtures M1, M2, M3, and M5 on day 126

Mixture	Total porosity [%]
M1	6.800
M2	10.010
M3	9.540
M5	6.420

It was observed that the total porosity increases slightly in the case of the FA modified concretes, but in the same (FA) mixtures the effective porosity is reduced because of ink-bottle porosity (Figure 4.26).

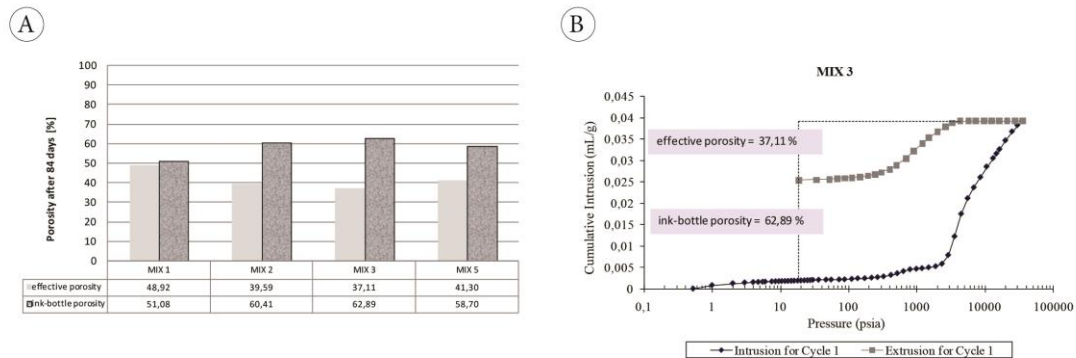


Figure 4.26: Effective and ink-bottle porosity for all the mixtures on day 84 of exposure to wetting-drying cycles (A). The relationship between the cumulative intrusion of mercury and pressure for mixture M3 (B).

Ink-bottle porosity defines the ratio between the volume of mercury which remains in the specimen after an intrusion and extrusion cycle, and the bulk density of the test specimen. Ink-bottle pores have a narrow neck and a wide body. Chloride ions are entrapped in these pores and cannot penetrate further. As pointed out previously, FA particles change the shape of pores, which results in increased ink-bottle porosity and reduced effective porosity. This phenomenon manifests itself in increased resistance of the concrete to chloride penetration, because the changed shape of the pores blocks ion penetration. To illustrate the effect of the porosity characteristics of the concrete, mercury porosimetry was also carried out after 126 days of exposure to the chloride solution. Fig. 4.27A shows the pore-size distribution curves for four different concrete mixtures, plotting the differential volume of the intruded mercury as a function of the pore diameter. On day 126 the lowest porosity was achieved in the case of mixture M5, which is in agreement with the results obtained for the chloride profile where the mixture M5 was the most resistant of the FA modified concretes. The same effect of increased ink-bottle porosity for the FA modified concrete was detected also after 126 days of exposure. The results are shown in Fig. 4.27B. A higher percentage of ink-bottle porosity and a lower effective porosity of the concrete mixture means a higher resistance of the concrete to chloride penetration.

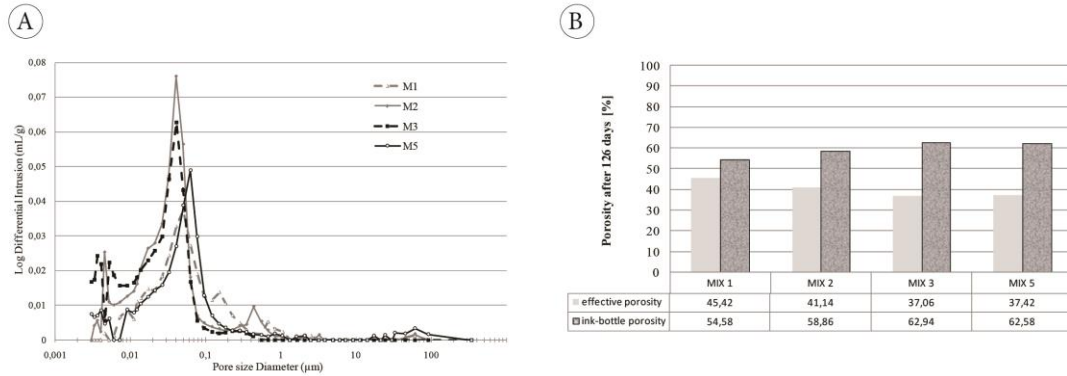


Figure 4.27: (A) Pore-size distribution curves for all mixtures on day 126 of exposure under the effect of wetting-drying cycles. (B) Effective and ink-bottle porosity for all mixtures on day 126 of exposure to wetting-drying cycles.

In order to present the difference in chloride penetration for concrete modified by different replacement levels of FA over time, the concrete cover depth was determined. The cover depth of concrete required to protect steel reinforcement from the initiation of corrosion was defined by the penetration depth of the threshold value for the chlorides in concrete [77]. The threshold value for chlorides was determined from the FIB model code for service life design [78], where C_{crit} is defined by a beta-distribution with a lower boundary of 0.6% by weight of cement. The parameter C_{crit} was expressed as the chloride content which is related to the weight of the concrete and then transferred to the weight of the binder. Table 4.9 lists the experimental data for penetration depths at the threshold values.

Table 4.9: Experimental data for penetration depths at threshold values after 21, 84 and 126 days of exposure to a chloride solution in cyclic wetting and drying of concrete

		M1	M2	M3	M5
FA replacement (%)		0	20	50	20
Density of fresh concrete (kg/m ³)		2450	2406	2344	2394
Binder (kg/m ³)		380	380	380	380
Factor (concrete/binder)		6.447	6.332	6.168	6.300
Threshold (C_{crit} by weight of binder [%])		0.093	0.095	0.097	0.095
Penetration depth [mm]	21-day exposure	15.7	13.7	14.0	14.3
	84-day exposure	24.5	19.0	16.6	21.0
	126-day exposure	27.0	20.0	20.0	19.0

The FA modified concretes achieved smaller penetration depths, and thus require smaller cover depths, which indicates the beneficial effect of FA on the service life of reinforced concrete structures. The incorporation of FA may have only a minor impact on the ion transport properties determined at early ages, but it can lead to improvements of the order of one magnitude in the long term, this range being in agreement with the limits observed in previous studies [79].

4.5.1.3 Composition of the fly ash

The difference between the unmodified concrete and the FA modified concrete with regard to chloride penetration depth becomes even more apparent on day 126, which is shown in Figure 4.28.

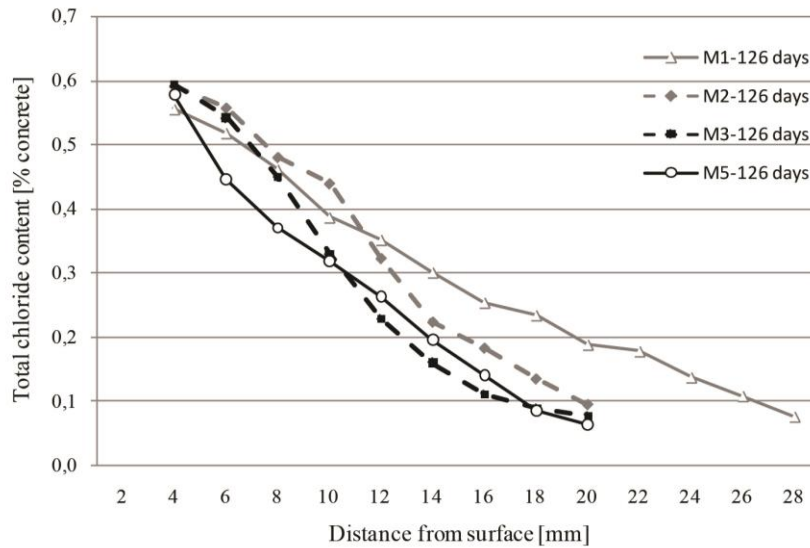


Figure 4.28: Total-soluble chloride penetration profiles of all the concrete mixtures on day 126 of exposure to wetting-drying cycles.

By day 126 the resistance of mixture M5 had increased and was even better than that of mixture M2, which has the same FA replacement level as mixture M5. The only difference between these two mixtures is the type of FA. Based on these results, it was assumed that the hydration of the cement with FA II was slower than that of the cement with FA I up to a period of 90 days. The same effect was observed in the case of the measurements of compressive strength (Table 4.10).

Table 4.10: Compressive strength.

Mixture	Compressive strength [MPa]		
	7 days	28 days	90 days
M1	55.05	61.16	68.16
M2	50.20	62.07	71.90
M3	35.74	59.01	68.64
M5	51.16	58.83	69.36
M6	33.20	52.24	62.40

The mixtures with FA I rapidly gained compressive strength up to 28 days compared to the concrete mixtures with FA II. Between 28 and 90 days in the case of the mixture with FA II (M5) a slight increase was observed in the speed of the reaction relative to the mixture with FA I (M2). Analysing the chemical composition of FA, it

was observed that in FA I the content of calcium was lower than in FA II. In the literature review which is described in [80] it was observed that, with a higher content of calcium in the FA, the pozzolanic reaction in the concrete was slower up to 90 days of hydration. This means that the reactivity of FA II is slower up to 84 days compared to FA I, and that it increased after 90 days.

4.5.2 The NSSM tests

The resistance to chloride penetration was also determined by the non-steady state migration test as described in NT Build 492 [46]. The chloride migration coefficient (D_{nssm}) was calculated according to formula 4.4.

$$D_{nssm} = \frac{RT}{zFE} \left(\frac{x_d - \alpha \sqrt{x_d}}{t} \right) \quad \text{where} \quad 4.4$$

$$E = \frac{U - 2}{L} \quad \text{and} \quad \alpha = 2 \sqrt{\frac{RT}{zFE}} \operatorname{erf}^{-1} \left(1 - \frac{2c_d}{c_0} \right)$$

D_{nssm} is non-steady-state migration coefficient (m^2/s), z is absolute value of ion valence, F is the Faraday constant ($9.648 \times 10^4 \text{ J}/(\text{V}\cdot\text{mol})$), U is the absolute value of applied voltage (V), R is the gas constant ($8.314 \text{ J}/(\text{K}\cdot\text{mol})$), T is the average value of the initial and final temperatures in the anolyte solution (K), L is the thickness of the specimen (m), x_d is the average value of penetration depths (m), t is the time of test duration (s), c_d is the chloride concentration at which the colour changes, c_0 is the chloride concentration in the catholyte solution ($\sim 2 \text{ N}$).

The chloride migration coefficient (D_{nssm}) was calculated according to formula (4.4). The number of specimens for each concrete mixture was six. The coefficient D_{nssm} is the most dependent on the average temperature in the anolyte solution, on the absolute value of applied voltage, and on the average value of penetration depths. The experimental parameters are summarized in Table 4.11.

Table 4.11: Experimental data for applied average temperature in anolyte solution, applied voltage and measured penetration depths for concrete mixtures M1, M2, M3, M5 and M6, after 21 and 56 days.

Mixture	Temperature [°C]		Voltage [mV]		Depth [mm]	
	after 21	after 56	after 21	after 56	after 21	after 56
M1	24.0	24.5	30	25	27.21	26.57
M2	24.0	26.2	30	30	12.08	11.83
M3	22.5	26.2	50	60	15.43	9.45
M5	22.5	23.8	25	30	21.40	20.04
M6	24.2	24.5	30	40	15.44	7.57

Figure 4.29 shows the values of the non-steady-state migration coefficient for the different concrete mixtures after 21 and 56 days of curing of the specimens.

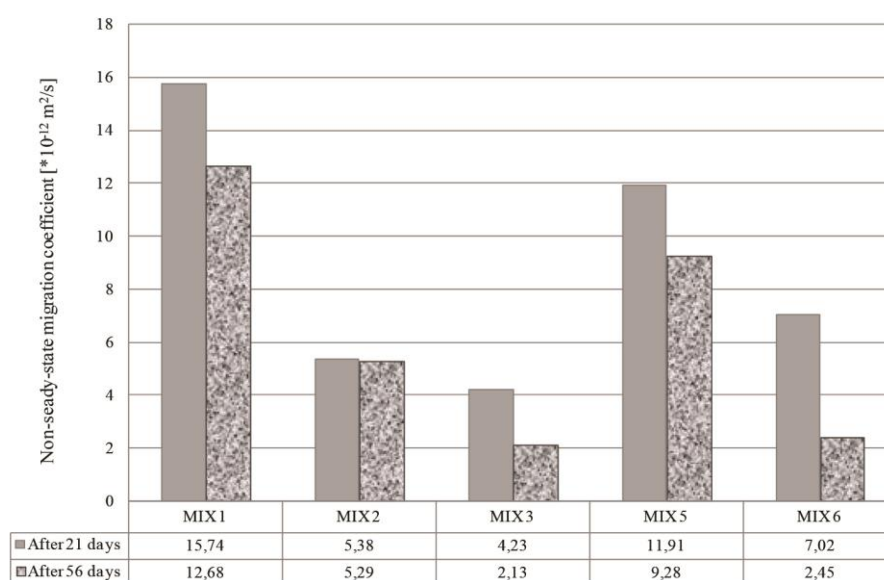


Figure 4.29: The non-steady-state migration coefficient for concrete mixtures M1, M2, M3, M5 and M6, after 21 and 56 days.

Although the cyclic immersion and drying tests and the non-steady state migration tests are not directly comparable, it is clear that the trend of decreasing chloride diffusion for all concrete mixtures is the same. The FA modified concrete has a lower migration coefficient than the unmodified concrete. This can be attributed to the slower migration of chloride ions through FA modified concrete. Additionally, the mixtures with FA II (M5 and M6) show a significant decrease in the migration coefficient after 56 days compared to mixtures with FA I (M2 and M3). Moreover, the

value of the migration coefficient for concrete was, in the case of FA II (M6), reduced by more than half from 21 to 56 days. That could be attributed to the different reactivity of the FA. This agrees well with the experimental observations made when using the previous method.

4.5.3 Discussion

The subject of this study was the extent to which, during wetting-drying cycles, chloride ions penetrate into fly ash modified concrete. Detailed chloride profiles were recorded which show how the total and water-soluble chloride contents vary with the depth of penetration of these ions into the concrete. In order to study the effect of exposure time, fly ash content, and fly ash composition on such penetration, two different types of fly ash were used as a partial replacement of OPC, their proportions amounting to 0%, 20% and 50% by weight of the binder.

Based on our experimental work, the results indicate that the fly ash modified concretes exhibited lower chloride penetration depths when compared to the unmodified concrete. Over time this difference becomes even more apparent. It could be attributed to the lower effective porosity in the case of FA modified concretes, which was defined by means of mercury porosimetry. A higher percentage of the ink-bottle porosity and a lower effective porosity of a concrete mixture means a higher resistance of the concrete to chloride penetration.

By taking into account the chloride content for total-soluble chlorides, the required concrete cover depth was determined. The FA modified concretes achieved smaller penetration depths, and thus require smaller cover depths, which indicates the beneficial effect of FA on the service life of reinforced concrete structures.

For the concrete with FA I, as well as for concrete with FA II, the chloride resistance was higher compared to that of the unmodified concrete. Not only the porosity but also the chemical composition of the FA plays a key role in chloride diffusion in concrete. The concrete with FA I, which had a lower content of calcium, showed better resistance to chloride penetration up to 90 days than the concrete with FA II. On the other hand, after 126 days the concrete with FA II showed better chloride resistance characteristics than the concrete with FA I. This phenomenon was confirmed also by the results of the compressive strength tests. A higher content of

calcium in the investigated FA means a lower reactivity of FA in the early ages up to 90 days.

Good agreement was observed between the results of the cyclic immersion and drying tests and those of the NSSM tests. Both methods showed the same trend for all of the concrete mixtures.

4.6 FROST/SALT SCALING

4.6.1 Properties of fresh and hardened concrete

The workability and air content of the fresh concrete mixtures were comparable for all four of the investigated concrete mixtures. The results are presented in Table 4.12. To achieve the given properties it was necessary to use different amounts of chemical admixtures (Table 3.8). After 28 days, all the concrete mixtures achieved the designed compressive strength class C 30/37.

Table 4.12: The properties of the fresh and hardened concrete mixtures

Mixture	Slump [mm]	Air content [%]	Density [kg/m ³]	Comp. strength, 28 days [MPa]
M1	183	5.3	2384	60.5
M2	200	5.0	2353	54.5
M3	214	5.7	2283	43.6
M5	195	5.3	2308	55.2

4.6.2 Type and concentration of de-icing salts

Assessments of frost/salt scaling are based on the amount of material which is scaled from the concrete surface after a given number of freeze-thaw cycles, when the concrete surface is saturated with an aqueous solution of a selected type and salt concentration. The results of the tests which were performed on the unmodified concrete mixture M1, when exposed to five different de-icing salts, are presented in Table 4.13.

Table 4.13: Results of the scaling tests performed on the concrete mixture M1, exposed to different de-icing salts

Mixture	Solution	Scaling [mg/mm ²]	
		25 cycles	50 cycles
M1	A	0.00	0.01
M1	B	0.01	0.03
M1	C	0.61	0.88
M1	D	0.00	0.02
M1	E	0.01	0.01

The corresponding cumulative losses of mass are presented in Figure 4.30. The concrete which was exposed to solution A (3% NaCl) was resistant to frost/salt scaling, the amount of material scaled from the concrete surface after 50 freeze-thaw cycles amounting to less than the prescribed threshold of 0.40 mg/mm². This phenomenon can also be seen in Figure 4.32, where the surface after the completion of the test appears to be almost unchanged.

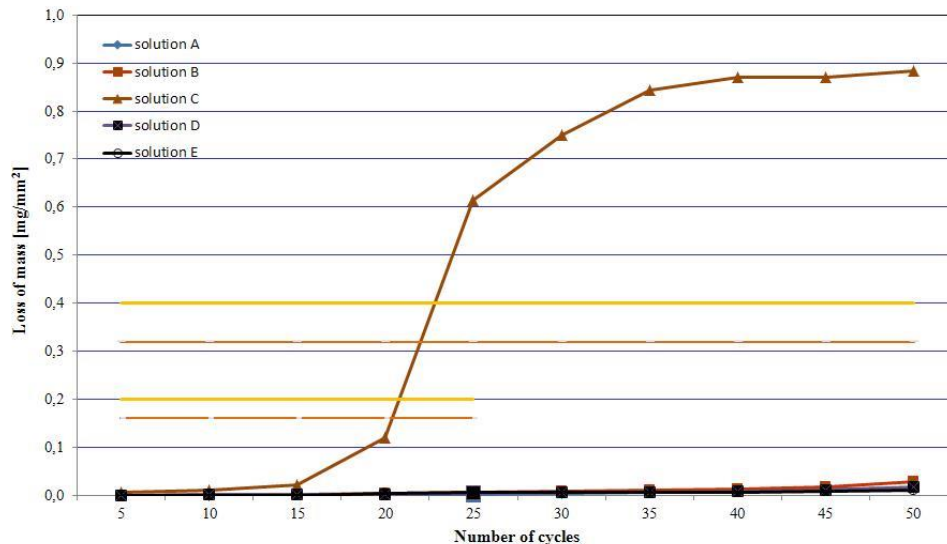


Figure 4.30: The scaling resistance of the concrete mixture M1 when exposed to five different de-icing salts.

The results of the study of different type of chloride salts at the same concentrations of chloride ions (solutions A, B, and D) showed the same behaviour with regard to scaling of the concrete surface. This means that the type of cation in the chloride solution at a concentration of 3% does not have a significant effect on the scaling in the case of concrete mixture M1. Otherwise, a more rapid scaling rate was observed in the case when the solution concentration of CaCl₂ was increased to 24% (solution C) for the unmodified concrete mixture. Solution C does not freeze in the chamber at a temperature (-20±2) °C. Based on this phenomenon it was supposed that the reason for the scaling was not the mechanical incompatibility between the frozen ice layer and the concrete, but was most likely due to the crystallization of salt beneath the surface, which causes internal shocks to the concrete. This phenomenon was observed in the case of two specimens, whereas the third specimen of the concrete had a relatively intact surface.

4.6.3 Influence of concrete composition

In order to study the impact of the binder composition on the frost/salt scaling resistance, four different concrete mixtures were investigated. The scaling test results are presented in Table 4.14. All mixtures were eligible for the degree of exposure of concrete XF4 according to the standard SIST 1026 [50]. The binder was varied with different replacement levels of OPC by FA and different types of FA.

Table 4.14: Scaling test results for concrete mixture M1, M2, M3, and M5

Mixture	Solution	Scaling [mg/mm ²]	
		25 cycles	50 cycles
M1	A	0.00	0.01
M2	A	0.16	1.02
M3	A	0.88	/
M5	A	0.03	0.14

The results of the average mass losses for the concrete mixtures M1, M2, M3, and M5 when exposed to solution A are presented in Figure 4.31. The unmodified concrete mixture M1 was the most frost/salt scaling resistant.

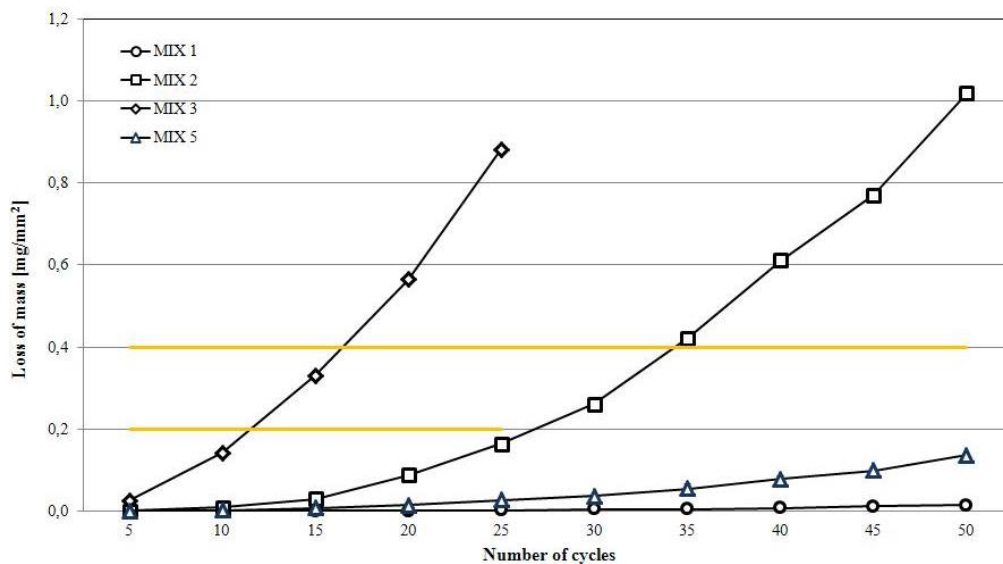


Figure 4.31: The scaling resistance of concrete mixtures M1, M2, M3, and M5 when exposed to solution A.

The amount of material scaled from the concrete surface after 50 freeze-thaw cycles was less than the prescribed threshold for the concrete mixture M5, despite the fact that in mixture M5 20% of the OPC had been replaced by FA.

On the other hand, the concrete mixture M2 had reduced frost/salt scaling resistance when compared with mixture M5. The concrete mixture M2 did not exceed the prescribed threshold value after 25 freeze-thaw cycles, but after the 30th freeze-thaw cycle the scaling rates increased sharply. The effect on the surface of the concrete mixture M2, which was severely damaged after 50 freeze-thaw cycles, can be seen in Figure 4.32. The reason perhaps lies in the spacing of air voids in the concrete. The mixture M2 had the smallest content of air pores in the fresh concrete in comparison with the other mixtures. Moreover, the amount of the added air-entraining admixture was lower in the case of the mixture M2 than in the case of mixture M5. It has been established fact that the carbon remaining in the FA requires an additional amount of air-entraining admixture in order to achieve a specified air content in the concrete [8].

The concrete mixture M3, which contained 50% of OPC replaced by FA, exceeded the prescribed threshold amount of material scaled from the concrete surface already after 25 freeze-thaw cycles, and consequently the scaling test was discontinued. This result indicates that with an increasing amount of FA (from 20% to 50% of OPC replaced by FA) in the mixture, a drastic decrease in the frost/salt scaling resistance of the concrete occurs. These results are in agreement with those reported by Pigeon et al. [49].

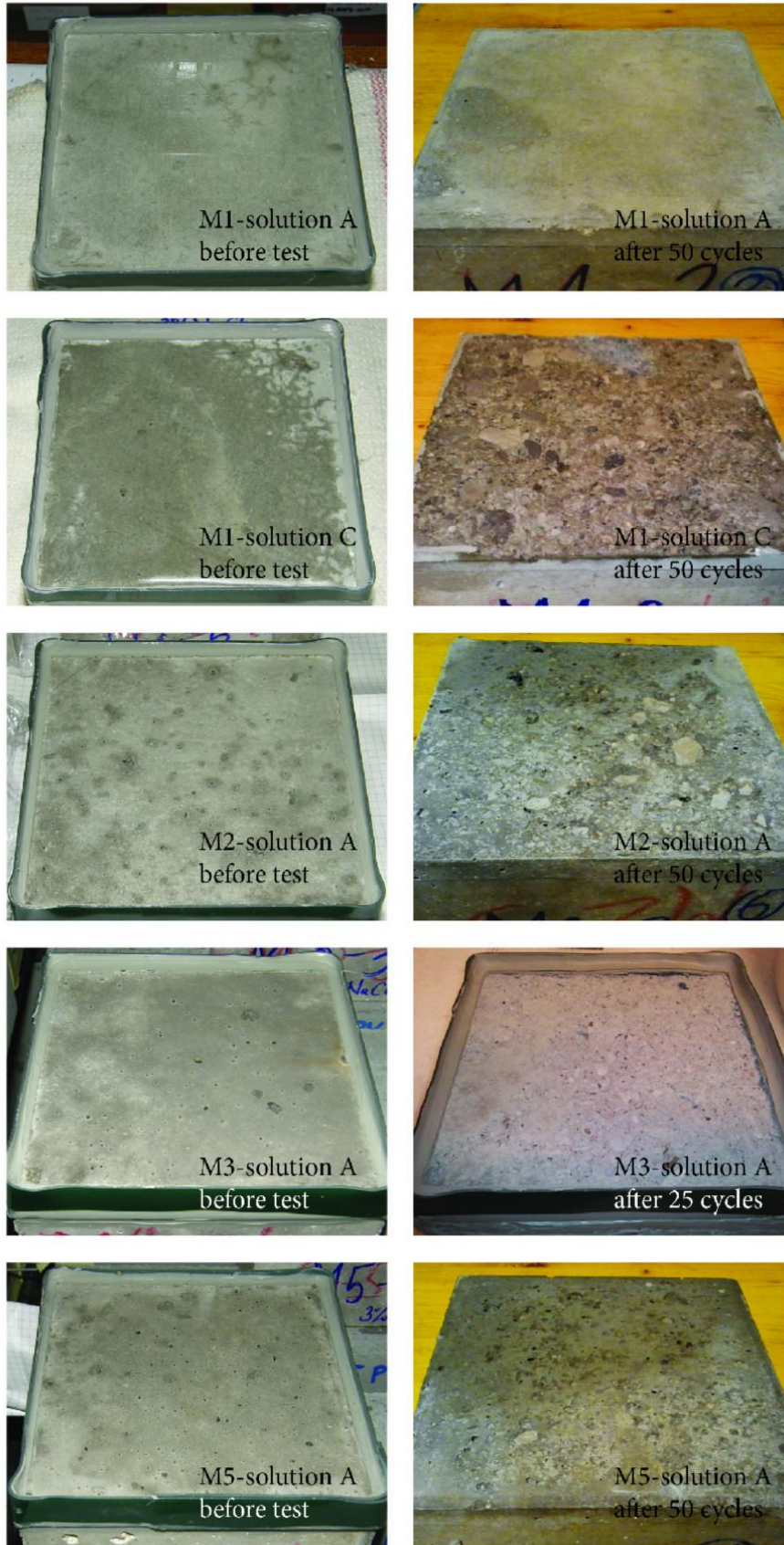


Figure 4.32: The appearance of test specimens made from concrete mixtures M1, M2, M3, and M5 at the beginning of the tests and after 25 or 50 freeze-thaw cycles.

4.6.4 Discussion

Based on the obtained results of the study of the impact of the type of chloride salts and concrete composition on frost/salt scaling, the following main conclusions can be drawn:

The impact of sodium, magnesium, and calcium chloride at solution concentrations of 3% showed no significant differences with regard to the scaling of the unmodified concrete mixture M1 which was designed for a XF4 rate exposure after 50 freeze-thaw cycles.

Otherwise, more rapid scaling rate was observed in the case when the solution concentration of CaCl_2 was increased to 24% for the unmodified concrete mixture M1. It was assumed that this was due to the fact that the crystallization of salts caused internal stresses in the concrete.

Not only the type of de-icing salts, but also the concrete composition, is an important parameter for the frost/salt scaling resistance of concrete. Although all the investigated concrete mixtures achieved a high compressive strength class, the concrete mixture containing 50% of FA proved to be less frost/salt resistant. Additionally, it was observed that concrete mixtures with two types of FA but otherwise an identical replacement level (20% of OPC replaced by FA) were found to have different frost/salt scaling resistances. The reason for this is not just the composition of the FA, but also the spacing of air voids, which plays an important role in frost scaling resistance.

5 CONCLUSION

5.1 MAIN RESEARCH FINDINGS

The use of high-quality by-products as materials for the replacement of cement can result in a significant reduction in the need for clinker production, and thus contribute to a more sustainable cement industry. The main advantages are reduced energy consumption and lower carbon dioxide emissions in the production of cement. By replacing cement with mineral additions, the quantity of waste material can be reduced, and thus the environmental burden is eased. One of these mineral additions is fly ash (FA), which occurs as a by-product of coal-fired thermal power plants.

FA is a mineral addition which can act either as an active component or as an inert filler in cementitious systems. FA consists of a reactive aluminasilicate component, which reacts with CaO in an alkaline solution, and forms binding reaction products. This process is called pozzolanic reaction. Moreover, FA has a high specific surface area, which can reduce the porosity of the concrete, resulting in a denser structure of the material. This effect can reduce the diffusion of aggressive substances into the binder.

Experience has shown that the properties of Slovenian concretes often differ significantly from the commonly accepted behaviour of concrete with a certain composition. One reason is that, in Slovenia, the majority of concrete mixtures are made solely of very pure crushed limestone or dolostone aggregate, with a relatively high content of fine particles below 0.125 mm (in the aggregate fractions 0/2 and 0/4). Furthermore, the FA used also has its own specific properties.

The replacement of Ordinary Portland Cement (OPC) by FA alters the hydration processes and the microstructural development of concrete. Moreover, the mechanical characteristics as well as the durability properties of the concrete are influenced. In the current PhD thesis, a complete study with regard to the effect of the addition of FA has been performed.

The effect of fly ash blended cement on the chemical properties of the binder

The hydration of OPC and FA was monitored by calorimetry and thermogravimetry. In combination, the results of these tests showed that:

- FA retarded the OPC hydration in the first hours due to the retarding of belite hydration.
- FA blended cements contained higher amounts of the AF_m phases related to the OPC due to the additional alumina provided by the reaction of the FA and, to a lesser extent, due to the acceleration of the hydration of the aluminate phase of the cement.
- Up to an age of 28 days, the FA exerted a physical nucleation effect on the OPC hydration, which did not compensate for the dilution effect. Between an age of 21 and 28 days, the observed decrease in the amount of CH and the corresponding increase in the bound water relative to the OPC content indicated a change in the hydration products formed. In the period up to one year the consumption of CH was 50% greater in the case of cement pastes containing 30% FA than in the case of plain cement pastes without any such additions.

The effect of fly ash on the characteristics of fresh and hardened concrete

Investigations into the characteristics of fresh and hardened concrete were performed. The following main findings were made:

- In the case of FA modified concrete mixtures, a higher amount of superplasticizer was needed to be used in order to obtain a workability which was similar to that of unmodified concrete.
- Obtained water penetration depths showed that all investigated concrete mixtures (without and with the FA) provided excellent water-tightness, which is an important parameter for durability.
- The beneficial effect of FA addition on compressive strength can be due to both a physical effect known as the filler effect, and a chemical effect, i.e. a pozzolanic reaction. The addition of FA decreased the compressive strength at early ages (on day 3), but increased it after 90 days in the case of FA modified concrete mixtures where 20% of the OPC was replaced by FA.
- Concrete with dolostone aggregate attained a 24% higher 90 day compressive strength, and a 13% higher 90 day modulus of elasticity compared to the concrete made with limestone aggregate, although after 28 days these differences were only 9% and 0.2%, respectively. These differences were initially attributed to the physical-chemical processes in the transition zone between the cement paste and the aggregate grains, possibly caused by alkali-carbonate reaction (ACR).

Alkali-carbonate reaction

Alkali-carbonate reaction (ACR) was monitored by measuring length change, and by using optical and electron microscopy as well as atomic absorption spectrometry and the X-ray diffraction method. Examination of the tests results showed that:

- ACR reflects in the process of aggregate grains' dedolomitization, the formation of secondary calcite in binder and the formation of new reaction products rich in Mg, Al and Si atoms along the dedolomitized parts of the grains.
- Dedolomitization caused no expansion. However, a significant chemical and mineralogical alteration of the studied dolostone aggregate grains occurred in the concrete over a period of 6 months, which was not observed in the petrographic examinations of the parent rock.
- In contrast to statements given in the literature, the results showed that a process of ACR had taken place also in the dolostone aggregate of high purity and without reactive silica involvement, which was confirmed by XRD and XRF.
- The process of dedolomitization was observed after a 6-month exposure period in water at 60 °C. That means that no accelerators in the form of high alkaline solutions are needed to initiate the process of dedolomitization for the used dolostone aggregate.
- A phase rich in Si, Al and Mg atoms, between the dedolomitized aggregate and the secondary calcite, was observed.

The effect of fly ash modified concrete on durability

In connection with the durability characteristics of FA modified concrete, three test methods which were related to carbonation, chloride ingress, and frost/salt scaling were used.

Carbonation

- A higher carbonation depth with increasing FA content (from 0% to 65%) in the concrete mixture with a constant w/b ratio, exposed for 18 weeks to a 10 vol% CO₂ environment, was confirmed experimentally.
- Although the investigated concrete mixtures containing 20% and 50% FA as a replacement for the OPC had the same compressive strength grade after 28 days, the rate of carbonation was significantly higher in the case of the concrete mixture containing 50% FA. This in turns means that the use of

more than 50% FA in concrete mixtures could cause poor performance of FA modified concrete with regard to carbonation.

- The question arises regarding the suitability of such methods and regarding the using a CO₂-enriched atmosphere giving similar values to natural exposure.

Chloride ingress

In order to study the effect of exposure time, FA content, and FA composition on chloride penetration, two test methods were used: the cyclic immersion and drying test, and the non-steady state migration test (NSSM). Based on the results of the performed experimental work, the results indicated the following:

- The FA modified concretes exhibited lower chloride penetration depths when compared to the unmodified concrete, even when 50% of the OPC was replaced by FA. This could be attributed to the lower effective porosity in the case of the FA modified concretes, as measured by mercury porosimetry. A higher percentage of the ink-bottle porosity and a reduced effective porosity of a concrete mixture mean a higher resistance of the concrete to chloride penetration.
- By taking into account the chloride content for total-soluble chlorides, the required concrete cover depth was determined. The results indicated the beneficial effect of FA on the service life of reinforced concrete structures due to the smaller cover depths required for FA modified concretes in case of chloride induced corrosion.
- The chemical composition of the FA plays a key role in the chloride diffusion in concrete. A higher content of calcium in the investigated FA means a lower reactivity of FA at early ages up to 90 days.
- Good agreement was observed between the results of the cyclic immersion and drying tests and those of the NSSM tests.

Frost/salt scaling

The impact of the type of chloride salts and concrete composition on frost/salt scaling was studied for four different concrete mixtures exposed to 50 freeze-thaw cycles. The following conclusions can be drawn:

- The impact of sodium, magnesium, and calcium chloride at solution concentrations of 3% showed no significant differences in the scaling of the unmodified concrete mixture. Otherwise, a more rapid scaling rate was observed in the case when the solution concentration of CaCl₂ was increased

to 24% for the unmodified concrete mixture, which was most likely due to the crystallization of salts, causing internal stresses in the concrete.

- Although all of the FA modified concrete mixtures achieved a high compressive strength class, the concrete mixture containing 50% of FA proved to be the least frost resistant. Additionally, concrete mixtures with two types of FA but otherwise having an identical replacement level (20% of the cement was replaced by FA) were found to have different levels of frost scaling resistance.

To sum up

The "safe level" of FA depends on a number of factors, including the composition and replacement level of the FA, the level of alkali in the concrete, the nature of the reactive aggregate, and the exposure conditions. It is difficult to assess the effect of FA on the service life of a concrete structure, partly due to the highly uncertain material parameters. However, some general conclusions can be drawn. The performance of the investigated FA modified concrete was better than that of the corresponding unmodified concrete with regard to:

- ink-bottle porosity,
- compressive strength,
- chloride ingress.

On the other hand, the resistance to carbonation and frost/salt scaling was lower in the case of FA modified concrete. Nevertheless, all the above characteristics apply to concrete where less than 50% FA was used as a replacement for OPC. The positive effect decreases with increased cement replacement levels up to 50%. It is difficult to provide an optimal replacement level for FA modified concrete since this also depends on the environmental conditions. As mentioned above, in the presence of chloride ions a beneficial effect due to FA was recorded even when 50% of the OPC was replaced by FA. In the case when concrete structures are exposed to the combined action of frost and de-icing salts, it is recommended that no more than 20% of FA should be added.

5.2 RESEARCH PERSPECTIVES

Hydration and microstructure

The fineness of the FA plays an important role due to its contribution to the pozzolanic reaction. It might be useful to study the impact of FA fineness and

different replacement levels (less than 50%) on the hydration of FA blended cement, and to find the optimal value of fineness of the FA.

Durability

More research is needed with regard to carbonation. As indicated in Chapter 4.4, the suitability of the used method needs to be investigated with regard to the maximum concentration of CO₂, giving similar values to natural exposure.

Another point of interest is the study of the behaviour of FA modified concrete under sulfate ingress, and also under the combined action of chloride and sulfate ions. It is once again recommended that the replacement level in FA modified concrete should be less than 50%.

REFERENCE

- [1] Damtoft JS, Lukasik J, Herfort D, Sorrentino D, Gartner EM. Sustainable development and climate change initiatives. *Cem Concr Res.* 2008;38(2):115-27.
- [2] Lothenbach B, Scrivener K, Hooton RD. Supplementary cementitious materials. *Cem Concr Res.* 2011;41(12):1244-56.
- [3] Griesser A. Cement-Superplasticizer Interactions at Ambient Temperatures. Zurich, Swiss Federal Institute of Technology; 2002.
- [4] De Weerd K. Blended Cement with Reduced CO₂ Emission - Utilizing the Fly Ash-Limestone Synergy. Trondheim, PhD thesis; 2001.
- [5] Mehta PK, Monteiro PJM. *Concrete: Microstructure, Properties and Materials.* 3rd ed. New York: The McGraw Hill Companies; 2006.
- [6] Đureković A. *Cement, cementni kompozit i dodaci za beton.* Zagreb: Nacionalna i sveučilišna biblioteka; 1996.
- [7] SIST EN 197-2:2005, Cement - Part 1: Composition, specifications and conformity criteria for common cements.
- [8] Lea FM. *Lea's Chemistry of Cement and Concrete.* 4th ed. London: Arnold; 1998.
- [9] Lilkov V, Rostovsky I, Petrov O, Tzvetanova Y, Savov P. Long term study of hardened cement pastes containing silica fume and fly ash. *Construction and Building Materials.* 2014;60(0):48-56.
- [10] Rahhal V, Talero R. Influence of two different fly ash on the hydration of Portland cement. *Journal of Thermal Analysis and Calorimetry.* 2004;78:191–205.
- [11] Shehata MH, Thomas MDA, Bleszynski RF. The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes. *Cem Concr Res.* 1999;29(12):1915-20.
- [12] De Weerd K, Haha MB, Le Saout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. *Cem Concr Res.* 2011;41(3):279-91.
- [13] Damidot D, Lothenbach B, Herfort D, Glasser FP. Thermodynamics and cement science. *Cem Concr Res.* 2011;41(7):679-95.
- [14] Zuquan J, Wei S, Yunsheng Z, Jinyang J, Jianzhong L. Interaction between sulfate and chloride solution attack of concretes with and without fly ash. *Cem Concr Res.* 2007;37(8):1223-32.
- [15] Baert G, Gruyaert E, Audenaert K, De Belie N. Chloride ingress in high-volume fly ash concrete. *Rilem proceedings 2008.*

- [16] Malhotra VM, Mehta PK. High-Performance Fly-Ash Concrete: Materials, Mixture Proportioning, Properties, Construction practice and Case Histories, Supplementary Cementing Materials for Sustainable Development Inc. Ottawa2002.
- [17] De Weerd K, Kjellsen KO, Sellevold E, Justnes H. Synergy between fly ash and limestone powder in ternary cements. *Cement and Concrete Composites*. 2011;33(1):30-8.
- [18] Prinčič T, Štukovnik P, Pejovnik S, De Schutter G, Bokan Bosiljkov V. Observations on dedolomitization of carbonate concrete aggregates, implications for ACR and expansion. *Cem Concr Res*. 2013;54(0):151-60.
- [19] Grattan-Bellew PE, Mitchell LD, Margeson J, Min D. Is alkali-carbonate reaction just a variant of alkali-silica reaction ACR = ASR? *Cem Concr Res*. 2010;40(4):556-62.
- [20] Katayama T. How to identify carbonate rock reaction, in concrete. *Materials Characterization*. 2004;53(2-4):85-104.
- [21] Lopez-Buendia AM, Climent V, Verdu P. Lithological influence of aggregate in the alkali-carbonate reaction. *Cem Concr Res*. 2006;36(8):1490-500.
- [22] Lu DY, Mei LB, Xu ZZ, Tang MS, Fournier B. Alteration of alkali reactive aggregates autoclaved in different alkali solutions and application to alkali-aggregate reaction in concrete (I) - Alteration of alkali reactive aggregates in alkali solutions. *Cem Concr Res*. 2006;36(6):1176-90.
- [23] Leemann A, Holzer L. Alkali-aggregate reaction - identifying reactive silicates in complex aggregates by ESEM observation of dissolution features. *Cement & Concrete Composites*. 2005;27(7-8):796-801.
- [24] Mittermayr F, Klammer D, Köhler S, Leis A, Höllen D, Dietzel M. Dissolution of Dolomite in Alkaline Cementitious Media. *Proceedings of the 13th International Congress on the Chemistry of Cement*. Madrid2011.
- [25] Tong L, Tang MS. Correlation between reaction and expansion of alkali-carbonate reaction. *Cem Concr Res*. 1995;25(3):470-6.
- [26] Xu ZZ, Lan XH, Deng M, Tang MS. A new accelerated method for determining the potential alkali-carbonate reactivity. *Cem Concr Res*. 2002;32(6):851-7.
- [27] Katayama T. The so-called alkali-carbonate reaction (ACR) - Its mineralogical and geochemical details, with special reference to ASR. *Cem Concr Res*. 2010;40(4):643-75.
- [28] Garcia E, Alfonso P, Labrador M, Gali S. Dedolomitization in different alkaline media: Application to Portland cement paste. *Cem Concr Res*. 2003;33(9):1443-8.
- [29] Min D, Mingshu T. Mechanism of dedolomitization and expansion of dolomitic rocks. *Cem Concr Res*. 1993;23:1397-408.

- [30] RILEM TC 191-ARP, RILEM Recommended Test Method AAR-0: Detection of potential alkali-reactivity in concrete - Outline guide to the use of RILEM methods in assessments of alkali-reactivity potential. *Materials and Structures*. 2003;36(261):8.
- [31] ASTM C 586-05, Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks as Concrete Aggregates. United States 1986.
- [32] Milanese CA, Marfil SA, Batic OR, Maiza PJ. The alkali-carbonate reaction and its reaction products an experience with Argentinean dolomite rocks. *Cem Concr Res*. 1996;26(10):1579-91.
- [33] Sisomphon K, Franke L. Carbonation rates of concretes containing high volume of pozzolanic materials. *Cem Concr Res*. 2007;37(12):1647-53.
- [34] De Belie N, Lammertijn S. Gas transport and carbonation in high-volume fly ash concrete versus age at testing. *Proceedings of the International Symposium Non-Traditional Cement & Concrete III 2008*.
- [35] Morandea A, Thiéry M, Dangla P. Impact of accelerated carbonation on OPC cement paste blended with fly ash. *Cem Concr Res*. 2015;67(0):226-36.
- [36] Baert G, Van den Heede P, Audenaert K, De Belie N. Microstructure of high-volume fly ash concrete. *Rilem proceedings 2008*.
- [37] Andrade C, Bercke N. Reinforcement durability. *Proceedings of the 13th International Congress on the Chemistry of Cement*. Madrid 2011.
- [38] Gao J, Yu Z, Song L, Wang T, Wei S. Durability of concrete exposed to sulfate attack under flexural loading and drying–wetting cycles. *Construction and Building Materials*. 2013;39(0):33-8.
- [39] Audenaert K, De Schutter G. Study of chloride penetration in self-compacting concrete by simulation of tidal zone. *Concrete Repair, Rehabilitation and Retrofitting II – Alexander et al (eds)*. London 2009.
- [40] Chalee W, Jaturapitakkul C. Effects of W/B ratios and fly ash finenesses on chloride diffusion coefficient of concrete in marine environment. *Materials and Structures*. 2009;42(4):505-14.
- [41] Yuan Q, Shi CJ, De Schutter G, Audenaert K, Deng DH. Chloride binding of cement-based materials subjected to external chloride environment - A review. *Construction and Building Materials*. 2009;23(1):1-13.
- [42] Balonis M, Lothenbach B, Le Saout G, Glasser FP. Impact of chloride on the mineralogy of hydrated Portland cement systems. *Cem Concr Res*. 2010;40(7):1009-22.
- [43] Andrade C, Bercke N. Reinforcement durability. *Proceedings of the 13th International Congress on the Chemistry of Cement*. Madrid 2011.

- [44] Jain JA, Neithalath N. Chloride transport in fly ash and glass powder modified concretes - Influence of test methods on microstructure. *Cement & Concrete Composites*. 2010;32(2):148-56.
- [45] De Belie N, Monteny J, Taerwe L. Apparatus for accelerated degradation testing of concrete specimens. *Materials and Structures*. 2002;35(251):427-33.
- [46] NT Build 492: Concrete, mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments. Nordtest; 1999. p. 8.
- [47] Baroghel-Bouny V, Belin P, Maultzsch M, Henry D. AgNO₃ spray tests: advantages, weaknesses, and various applications to quantify chloride ingress into concrete. part 1: Non-steady-state diffusion tests and exposure to natural conditions. *Materials and Structures*. 2007;40(8):759-81.
- [48] Baroghel-Bouny V, Belin P, Maultzsch M, Henry D. AgNO₃ spray tests: advantages, weaknesses, and various applications to quantify chloride ingress into concrete. part 2: Non-steady-state migration tests and chloride diffusion coefficients. *Materials and Structures*. 2007;40(8):783-99.
- [49] Pigeon M, Talbot C, Marchand J, Hornain H. Surface microstructure and scaling resistance of concrete. *Cem Concr Res*. 1996;26(10):1555-66.
- [50] SIST EN 1026:2004, Concrete - Part 1: Specification, performance, production and conformity - Rules for the implementation of SIST EN 206-1.
- [51] Verbeck G, Klieger P. Studies of "Salt" Scaling of Concrete. *Highway Research Board Bulletin*. 1956;150.
- [52] SIST EN 450-1:2005+A1:2008, Fly ash for concrete - Part 1: Definition, specifications and conformity criteria.
- [53] EN 932-1:1997, Tests for general properties of aggregates. Methods for sampling
- [54] EN 932-2:1999, Tests for general properties of aggregates. Methods for reducing laboratory samples.
- [55] SIS EN 12350-2:2009, Testing fresh concrete - Part 2: Slump-test.
- [56] SIST EN 12350-5:2009, Testing fresh concrete - Part 5: Flow table test
- [57] SIST EN 12350-7, Testing fresh concrete - Part 7: Air content - Pressure methods.
- [58] SIST EN 12390-3, Testing hardened concrete - Part 3: Compressive strength of test specimens
- [59] SIST EN 12390-8, Testing hardened concrete - Part 8: Depth of penetration of water under pressure

- [60] SIST EN 206-1:2003, Concrete - Part 1: Specification, performance, production and conformity.
- [61] St John DA, Poole AB, Sims I. Concrete Petrography. New York: Arnold 1998. p. 17-20.
- [62] Friel JJ, Lyman CE. X-ray Mapping in Electron-Beam Instruments. Microscopy and Microanalysis. 2006;12:2–25
- [63] Goldstein J. Scanning Electron Microscopy and X-Ray Microanalysis. Springer. New York 2003.
- [64] Topas2.1: General Profile. Structure analysis software for powder diffraction data. Bruker AXS. Karlsruhe:Germany 2003.
- [65] SIST EN 12350-6: 2009, Testing fresh concrete - Part 6: Density
- [66] RILEM CPC 18, Measurement of hardened concrete carbonation depth, RILEM draft recommendation. Materials and Structures 17. 1984. p. 435-40.
- [67] Yuan Q. Fundamental studies on test methods for the transport of chloride ions in cementitious materials doctoral. Ghent, University of Ghent and Central South University; 2008.
- [68] Šelih J. Performance of concrete exposed to freezing and thawing in different saline environments. Journal of civil engineering and management. 2010;16(2):306-11.
- [69] Taylor H. Cement chemistry, 2nd edition. London: Thomas Telford Publishing; 1997.
- [70] Bullard JW, Jennings HM, Livingston RA, Nonat A, Scherer GW, Schweitzer JS, et al. Mechanisms of cement hydration. Cem Concr Res. 2011;41(12):1208-23.
- [71] De Weerd K, Sellevold E, O. Kjellsen K, Justnes H. Fly ash–limestone ternary cements: effect of component fineness Advances in Cement Research. 2011;23(4):203 - 14.
- [72] Katayama T. So-called alkali-carbonate reaction - Petrographic details of field concrete in Ontario. In: Mauko A, Kosec T, Kopar T, Gartner N, editors. Proceedings of the 13th Euroseminar on Microscopy Applied to Building Materials (EMABM). Ljubljana, Slovenia 2011. p. 15.
- [73] Gali S, Ayora C, Alfonso P, Tauler E, Labrador M. Kinetics of dolomite-portlandite reaction - Application to Portland cement concrete. Cem Concr Res. 2001;31(6):933-9.
- [74] Gruyaert E. Effect of Blast-Furnace Slag as Cement Replacement on Hydration, Microstructure, Strength and Durability of Concrete Doctoral thesis. Ghent, Ghent University, Belgium; 2010 - 2011.

- [75] Simčič T, Pejovnik S, De Schutter G, Bokan Bosiljkov V. Chloride ion penetration into fly ash modified concrete during wetting-drying cycles. *Construction & Building Materials* 2015;accepted.
- [76] Chalee W, Ausapanit P, Jaturapitakkul C. Utilization of fly ash concrete in marine environment for long term design life analysis. *Materials & Design*. 2010;31(3):1242-9.
- [77] Angst U, Elsener B, Larsen CK, Vennesland O. Critical chloride content in reinforced concrete - A review. *Cement and Concrete Research*. 2009;39(12):1122-38.
- [78] Model code for service life design, fib Bulletin No. 34. 2006.
- [79] Thomas MDA, Bamforth PB. Modelling chloride diffusion in concrete - Effect of fly ash and slag. *Cem Concr Res*. 1999;29(4):487-95.
- [80] Schulze S.E, Rickert J. Influence of the chemical composition of fly ashes on their reactivity. *Proceedings of the 13th International Congress on the Chemistry of Cement*. Madrid 2011.

UVOD

Beton je med najbolj razširjenimi materiali na svetu. Odpornost na prisotnost vode in zraka, možnost oblikovanja poljubnih oblik konstrukcijskih elementov, relativno nizka cena in dobra dostopnost materialov ter visoka tlačna trdnost omogočajo njegovo široko uporabo. Pri določenih sestavah betona pa lahko dosega le ta tudi visoko trajnost. Pri proizvodnji betona se sprosti približno 0.13 ton CO₂ na tono betona, odvisno od vrste uporabljenega cementa, trdnosti ter trajnostnega razreda. Največji izpusti CO₂ so povezani s proizvodnjo cementnega klinkerja, ki lahko predstavlja tudi tretjino sestave betona. Zaradi velike proizvodnje betona predstavljajo izpusti iz cementne industrije 5-8 % svetovne emisije CO₂ [1]. Težnja po trajnostnem razvoju zahteva zmanjšanje emisij toplogrednih plinov, zato se danes posveča veliko pozornost zmanjšanju količine cementnega klinkerja v betonu in uporabo dodatnih materialov s hidravličnimi ali pucolanskimi lastnostmi (supplementary cementitious material - SCM) v betonu.

SCM materiali so večinoma stranski produkti drugih industrij. Z uporabo SCM v betonu ne zmanjšamo samo količine klinkerja, temveč tudi količino odpadkov in s tem obremenjenost okolja. V primeru, da uspemo betonom z vključenim večjim deležem mineralnega dodatka, zagotoviti tudi visoko trajnost, lahko še dodatno znižamo porabo naravnih virov, saj povečamo življenjsko dobo objekta, navkljub agresivnim vplivom okolja.

Uporaba SCM je odvisna od razpoložljivosti in kvalitete le teh. S stališča proizvodnje betona so najbolj perspektivni tisti industrijski odpadki, ki jih je količinsko veliko. V Sloveniji je to zagotovo elektrofiltrski pepel (EFP), ki se ga izloča pri čiščenju dimnih plinov v termoelektrarni Šoštanj in termoelektrarni Trbovlje. Uporaba EFP kot mineralnega dodatka v betonu se je povečala šele v zadnjih letih. V Sloveniji se je kontrolirana uporaba EFP v betonu pričela z uvedbo standarda SIST EN 206-1 ter izdajo certifikata o skladnosti za EFP. Pred tem je nekontrolirana uporaba EFP povzročila več neuspešnih aplikacijah in celo povečala radioaktivnost strukturnih elementov v stavbah, kar je prevedlo v prepričanje, da je EFP preveč problematičen za uporabo kot mineralni dodatek v betonu.

EFP Trbovlje je že pridobil certifikat o skladnosti proizvoda s standardom SIST EN 450-1: 2005. Zaradi spreminjanja kemijske sestave EFP, njegov vpliv na proces

hidratacije še ni v celoti raziskan. Poleg tega le malo raziskav na tem področju je usmerjenih v študij kalcijskega EFP s stališča hidratacije in trajnosti betona.

ZAKLJUČEK

Uporaba kakovostnih stranskih proizvodov kot surovina za zamenjavo cementa lahko znatno zmanjšanja količino klinkerja v proizvodnji cementa, in tako prispevati k bolj trajnostni proizvodnji cementa. Glavni prednosti sta manjša poraba energije ter manjše emisije ogljikovega dioksida v proizvodnji cementa. Z zamenjavo cementa z mineralnimi dodatki lahko zmanjšamo količino odpadnega materiala, in s tem zmanjšamo obremenjenost okolja. Primer mineralnega dodatka je tudi elektrofiltrski pepel (EFP), ki nastaja kot stranski produkt v termoelektrarnah na premog.

EFP je mineralni dodatek, ki v cementnem sistemu lahko predstavlja tako aktivno kot tudi inertni polnilo. EFP sestoji iz reaktivne, steklaste alumosilikatne komponente, ki reagira s kalcijevim hidroksidom (CH), ki je produkt hidratacije cementa, in tvori hidratacijske produkte. Ta proces imenujemo pucolanska reakcija. Del EFP deluje kot inertno polnilo in zaradi velike specifične površine lahko zmanjša poroznost betona. Z gostejšo strukturo materiala se zmanjša difuzija agresivnih snovi v vezivo in s tem do armature, ter izboljša kvaliteta cementnega kamna in s tem tudi betona.

V Sloveniji je večina betonskih mešanic pripravljena izključno iz zelo čistega drobljenega apnenega ali dolomitnega agregata, ki ima relativno visoko vsebnost finih delcev pod 0,125 mm. Izkušnje so pokazale, da se lastnosti slovenskih betonov pogosto bistveno razlikujejo od splošno sprejetih opažanj betona z določeno sestavo. Zaradi tega ima tudi tako pripravljena betonska mešanica z mineralnim dodatkom EFP posebne lastnosti.

Zamenjava Portlandskega Cementa (OPC) z EFP spremeni proces hidratacije in razvoj mikrostrukture betona. Poleg tega ima ta dodatek tudi vpliv na mehanske lastnosti kot tudi na trajnost betona. V doktorski disertaciji je bila opravljena celovita študija vpliva dodatka EFP na lastnosti betonske mešanice z izbranim dodatkom.

Vpliv cementa z elektrofiltrskim pepelom na kemijske lastnosti takega veziva

Hidratacijo OPC in EFP smo spremljali s kalorimetrijo in termogravimetrijo. Rezultati teh preiskav so pokazali sledeče:

- V prvih urah EFP upočasnijo začetno hidratacijo OPC, še posebej hidratacijo belita.
- Cementi z dodatkom EFP vsebujejo večje količine AF_m faze kot cement brez dodatka zaradi dodatnega aluminijevega oksida, ki je sestavni del EFP ter zaradi pospešene hidratacije aluminatne faze cementa.
- V obdobju med 21 in 28 dnevi smo v cementnih pastah z dodatkom EFP zaznali zmanjšanje vsebnosti kalcijevega hidroksida (CH) ter posledično povečanje vsebnosti vezane vode glede na vsebnost OPC, zaradi pucolanske reakcije. To kaže na spremembo nastalih produktov hidratacije v sistemu OPC-EFP, in sicer zmanjšana vsebnost CH, povečanje C-S-H faze ter AF_m faze glede na vsebnost OPC, kar je bilo eksperimentalno potrjeno z rezultati termogravimetrije. V obdobju enega leta je poraba CH 50% večja pri cementnih pastah, ki vsebujejo 30% EFP kot v primeru cementne paste brez dodatka.

Vpliv elektrofilitnega pepela na lastnosti svežega in strjenega betona

Na podlagi izvedenih preiskav lastnosti svežega in strjenega betona lahko podamo naslednje glavne ugotovitve:

- V primeru betonskih mešanic z dodatkom EFP je potrebna večja količina superplastifikatorja za doseg primerljive obdelavnosti betona kot za betonske mešanice brez dodatka.
- Rezultati tlačnih trdnosti kažejo na pozitiven učinek dodatka EFP v betonu kar je lahko posledica tako polnilnega učinka kot tudi kemijskega učinka, t.j. pucolanska reakcija. Dodatek EFP sicer zmanjša tlačno trdnost v zgodnji starosti (3 dni), vendar poveča 90-dnevne tlačne trdnosti v primeru betonskih mešanic z 20% zamenjavo OPC z EFP.
- Preiskava mehanskih lastnosti strjenega betona je pokazala, da betonska mešanica z dolomitnim agregatom doseže 24% višjo 90-dnevno tlačno trdnost in 13% višji 90-dnevni modul elastičnosti v primerjavi z betonsko mešanico pripravljeno z apnenim agregatom, čeprav so bile po 28 dneh te razlike le 9% in 0,2%. Ta pojav pripisujemo fizikalno-kemijskim procesom v prehodnem pasu med cementno pasto in zrni agregata, ki so lahko posledica alkalno-karbonatne reakcije (ACR).

Alkalno-karbonatna reakcija

Alkalno-karbonatno reakcijo (ACR) smo spremljali z različnimi metodami in tehnikami, in sicer z eksperimentalnimi meritvami sprememb dolžine kamnin in

maltnih prizem, optično in elektronsko mikroskopijo, atomsko absorpcijsko spektrometrijo ter rentgensko difrakcijo. Na podlagi eksperimentalnih podatkov je mogoče podati naslednje pomembnejše sklepe:

- Dedolomitizacija ni povzročila ekspanzije, kar je bilo potrjeno z eksperimentalnimi rezultati. Kljub temu smo opazili znatne kemijske in mineraloške spremembe na proučevanih dolomitnih agregatih v cementnih maltah s časom, katere niso bile prisotne pri petrografski analizi kamnine pred pričetkom testiranja.
- V nasprotju z dosedanjim prepričanjem v literaturi, proces ACR poteče po 6-ih mesecih v maltah potopljenih v vodni medij, pripravljenih z zelo čistim dolomitnim agregatom brez vsebnosti reaktivnega silicija, kar smo potrdili s XRD in XRF analizo. To pomeni, da niso potrebni nobeni pospeševalci v obliki visokih alkalnih raztopin oziroma reaktivnih komponent, da sprožijo proces dedolomitizacije. Sproži jo že alkalnost cementnega veziva v obdobju šestih mesecev pri temperaturi 60 °C.
- Temperatura in pH vrednost raztopin igrata ključno vlogo pri hitrosti procesa dedolomitizacije. Izbrana temperatura 60 °C, ki je značilna za nekatere gradbene konstrukcije, znatno poveča proces dedolomitizacije, v primerjavi s temperaturo 20 °C.
- Na meji med dedolomitiziranim agregatom in sekundarnim kalcitom smo opazili ozek rob – novo fazo. Faza je bogata s Si, Al in Mg atomi, ki bi lahko predstavljal Mg-silikatni gel.

Vpliv betonske mešanice z elektrofiltrskim pepelom na trajnost betona

Trajnost betonske mešanice z dodatkom EFP smo spremljali pri treh različnih pogojih, katerim je beton najpogosteje izpostavljen, in sicer izpostavljenost CO₂ (karbonatizacija), kloridnim ionom ter zmrzali in talilnih soli.

Karbonatizacija

- Zaznali smo povečanje globine karbonatizacije s povečanjem vsebnosti zamenjave OPC z EFP (od 0% do 65%) v betonskih mešanicah s konstantnim vodo vezivnim razmerjem, ki so bile 18 tednov izpostavljene 10 vol% atmosferi CO₂.
- Kljub temu da sta preučevani betonski mešanici z 20% in 50% zamenjave OPC z EFP dosegli enak razred tlačne trdnosti po 28 dneh, je bila stopnja karbonatizacije bistveno višja pri betonski mešanici, ki je vsebovala 50% EFP. To pomeni, da več kot 50% zamenjava OPC z EFP povzroči slabšo odpornost betona na karbonatizacijo.

Prodor kloridov

Vpliv časa izpostavljenosti, vsebnosti EFP in sestave EFP na prodor klorida smo preiskovali z dvema preskusnima metodama: ciklično namakanje in sušenje vzorcev v kloridni raztopini ter nestacionarno migracijski test (NSSM). Na podlagi opravljenega eksperimentalnega dela lahko zaključimo sledeče:

- Betonske mešanice z dodatkom EFP so dosegle nižji prodor klorida v primerjavi z betonsko mešanico brez dodatka, tudi v primeru, ko smo 50% OPC nadomestili z EFP. To lahko pripišemo eksperimentalno določeni nižji efektivni poroznosti za betonske mešanice z dodatkom EFP. Posledično so te betonske mešanice dosegle višji odstotek t.i. »ink-bottle«, kar se odraža v večji odpornosti betona na prodor kloridov.
- Zahtevano zaščitno plast betona smo določili z upoštevanjem eksperimentalno določene celokupne vsebnosti topnega klorida v vzorcih. Rezultati so pokazali pozitiven učinek EFP na življenjsko dobo armiranobetonskih konstrukcij v kloridnem okolju, saj je v primeru betonskih mešanic z dodatkom EFP potrebna manjša zaščitna plast betona, ki zadostuje za preprečitev iniciacije korozije.
- Kemijska sestava EFP predstavlja pomembno vlogo pri prodoru kloridov v beton. Višja vsebnost kalcija v proučevanem EFP je predstavljala manjšo reaktivnost EFP v zgodnji starosti do 90 dni.
- Obe uporabljeni metodi, in sicer ciklično namakanje in sušenje vzorcev ter nestacionarno migracijski test (NSSM), sta pokazali enak trend prodora kloridov v betonske mešanice z različno sestavo.

Odpornost površine betona proti zmrzovanju/tajanju v prisotnosti soli

Predstavljeni so rezultati študije vpliva vrste in koncentracije kloridnih soli ter sestave betonske mešanice na luščenje površine betona izpostavljene 50-im ciklom izmeničnega zmrzovanja/tajanja v prisotnosti soli.

- Vpliv raztopin natrijevega, magnezijevega in kalcijevega klorida na osnovi enakega števila molov kloridnih ionov pri 3% koncentraciji raztopin ni pokazal razlik v luščenju betona. V nasprotnem primeru pa je povečana koncentracija CaCl_2 na 24% povzročila znatno luščenje betona, kar je najverjetneje posledica kristalizacije soli, ki povzroča notranje pritiske v betonu.
- Čeprav so vse betonske mešanice z in brez dodatka EFP dosegle visok razred tlačnih trdosti, se je betonska mešanica s 50% deležem zamenjave cementa z EFP izkazala kot najmanj odporna na luščenje betona. Poleg tega je bilo ugotovljeno, da so betonske mešanice z enakim deležem zamenjave

cementa z EFP (20%), le z različno vrsto EFP, dosegle različno odpornosti površine betona proti zmrzovanju/tajanju v prisotnosti soli.

Če povzamemo

"Varna uporaba" EFP je odvisna od številnih faktorjev, in sicer sestave in deleža zamenjave EFP, stopnje alkalnosti v betonski mešanici, narave reaktivnosti agregata ter stopnje izpostavljenosti. Zaradi tega je težko določiti splošen vpliv EFP na življenjsko dobo betona, delno zaradi zelo negotovih parametrov materiala in okolja. Vsekakor pa lahko podamo nekaj splošnih ugotovitev. Na podlagi rezultatov se je izkazalo, da boljše lastnosti betona z dodatkom EFP dosežemo za naslednje karakteristike:

- »ink-bottle« poroznosti,
- tlačnih trdnosti,
- kloridnega napada.

V nasprotnem primeru, pa je odpornost na karbonatizacijo ter zmrzlinško odpornost betona ob prisotnosti soli bila slabša za betonske mešanice z dodatkom EFP kot za betonsko mešanico brez dodatka. Upoštevati je potrebno dejstvo, da so navedene karakteristike veljale za betonske mešanice z zamenjavo OPC z EFP pod 50%. Pozitiven učinek EFP se zmanjšuje, ko povečujemo delež zamenjave, še zlasti nad 50%. Težko je zagotoviti splošno optimalno zamenjavo OPC z EFP, saj je pomemben namen uporabe betona. Kot je že bilo navedeno, se izkaže betonska mešanica z dodatkom EFP, tudi do 50%,

učinkovitejša na prodor kloridov kot betonska mešanica brez dodatka. V primeru betonske konstrukcije izpostavljene delovanju zmrzali in soli je priporočljivo uporabiti betonsko mešanico z dodatkom EFP manj kot 20%.

NADALJNJE RAZISKAVE

Hidratacija in mikrostruktura

Neraziskano vprašanje, ki ima tudi pomembno vlogo pri hidrataciji OPC je finost EFP. Morda bi bilo koristno, da bi se preučilo vpliv finosti EFP in različen odstotek zamenjave OPC z EFP (manj kot 50%) na hidratacijo OPC z EFP in poiskati optimalno finost uporabljenega EFP.

Trajnost

Potrebno bi bilo razširiti študijo karbonatizacije. Kot je navedeno v poglavju 4.4, je potrebo raziskati ustreznost uporabljene metode, še posebej glede uporabljene

visoke koncentracije CO₂ ter ujemanje teh rezultatov z rezultati, ki bi jih podali testi izpostavljeni naravni atmosferi CO₂ v zraku.

Druga zanimivost bi bila študija vpliva odpornosti betonske mešanice z dodatkom EFP na vdor sulfatnih ionov ter kombinacija kloridnih in sulfatnih ionov.