

**EFFECT OF ADMIXTURE (LITHIUM NITRATE) TO INHIBIT ALKALI SILICA
REACTION**



SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

Master of Philosophy in Chemistry

By

FAIZA QURBAN

Roll No. SU92-MSCHW-F22-022

Session: 2022-2024

Faculty of Sciences

Author's Declaration

I hereby state that my M.Phil. thesis titled “**Effect of admixture (lithium nitrate) to inhibit alkali silica reaction**” is my work and has not been submitted previously by me for taking any degree from this University,

The Superior University, Lahore,

or anywhere else in the country/world.

At any time if my statement is found to be incorrect even after my graduation, the university has the right to withdraw my M.Phil. degree.

Name of Student: Faiza Qurban

Date: _____

Plagiarism Undertaking

I solemnly declare that research work presented in the thesis titled “**Effect of admixture (lithium nitrate) to inhibit alkali silica reaction**” is solely my research work with no significant contribution from any other person. Small contribution/help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and University,

The Superior University, Lahore,

towards plagiarism. Therefore, I as author of the above-titled thesis declare that no portion of my thesis has been plagiarized and any material used as a reference is properly referred/cited. I undertake that if I am found guilty of any formal plagiarism in the above-titled thesis, even after awarding of M.Phil. degree, the University reserves the rights to withdraw/revoke my M.Phil. degree and that HEC and the University have the right to publish my name on the HEC/University website on which names of students are placed who submitted a plagiarized thesis.

Student/Author Signature: _____

Name: Faiza Qurban

Research Completion Certificate

This is to certify that the thesis entitled “**Effect of admixture (lithium nitrate) to inhibit alkali silica reaction**” submitted by “**Faiza Qurban**” has been accepted towards the partial fulfillment of the requirement for M.Phil. “**Chemistry**”. The quality of the work contained in this thesis is adequate for the award of degree.

Supervisor Name: Dr Shaukat Ali
Designation: Assistant Professor

Signature: _____

Certificate of Approval

This is to certify that the research work presented in this thesis, titled “**Effect of admixture (lithium nitrate) to inhibit alkali silica reaction**” was conducted by “**Faiza Qurban**” under the supervision of “**Dr Shaukat Ali**”

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of “**Chemistry**” in Faculty of Sciences at The Superior University, Lahore.

Student Name: Faiza Qurban

Signature: _____

Examination Committee:

Session Chair:

Signature: _____

a) External Examiner:

Signature: _____

b) Internal Examiner:

Signature: _____

c) Supervisor Name:

Signature: _____

d) Name of HOD: Prof. Dr. Uqba Mehmood

Signature: _____

e) Name of Dean: Prof. Dr. Mohammad Naveed Babur

Signature: _____

f) Controller Examination: Dr. Muhammad Haris

Signature: _____

DEDICATION

I dedicate this thesis to my mentors and advisors, whose guidance and wisdom have been invaluable throughout this journey. To my friends, family and colleagues, whose support and camaraderie made this journey bearable. Special thanks to Dr Shaukat Ali for your unwavering belief in my abilities and your endless encouragement.

ACKNOWLEDGEMENT

All praises thanks for Allah Almighty, Who bestowed us with the heart to feel and brain to think, so that we know, what we don't indeed. He is the best knower, the wisest, peace and blessing of Allah be upon the Holy prophet Hazrat Muhammad (S.A.W.W) who is the real role model for the mankind.

I feel highly indebted to my intellectual supervisor Dr. Shaukat Ali for their kind and affectionate attitude, guidance and keen interest throughout my research work. Their support has been instrumental in my success, I appreciate their mentorship and the opportunity they have provided. Thank you for believing in me and pushing me to excel. Their leadership has made significant impact on our teams' achievements. And I'm thankful for the trust they have placed in me and for their continued support.

I acknowledge with deep reverence all honorable teachers especially Prof. Dr. Naveed Babar, Dean faculty of Allied Health Sciences, Prof. Dr. Uqba Mehmood, Head of Department, Biological Sciences, Prof. Dr. Muhammad Mudassir Iqbal, Program Leader, Department of Chemistry, Superior University Lahore for providing me help, guidance and necessary research facilities.

I dedicate my research work to my beloved and respectful parents for his countless prayers, salutary advices and emboldening attitude that kept my spirit alive. I am unable to show my gratitude to my loving and encouraging sisters and my whole family. It's the symbol of love, prayers, support, and encouragement which provided by my whole family.

Faiza Qurban

TABLE OF CONTENTS

	Page
AUTHOR’S DECLARATION.....	i
PLAGIARISM UNDERTAKING.....	ii
RESEARCH COMPLETION CERTIFICATE.....	iii
CERTIFICATE OF APPROVAL.....	iv
DEDICATION.....	v
ACKNOWLEDGEMENT.....	vi
TABLE OF CONTENTS.....	vii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
LIST OF ABBREVIATION.....	x
ABSTRACT.....	xi
CHAPTER 1.....	01
INTRODUCTION.....	01
1.1 ALKALI SILICA REACTION.....	01
1.2 IMPACT OF ALKALI SILICA REACTION	04
1.3 ADMIXTURES AND SCMs.....	05
AIM AND OBJECTIVES-----	17
CHAPTER 2.....	18
LITERATURE REVIEW.....	18
CHAPTER 3.....	30
METHODOLOGY.....	30
3.1 MATERIALS.....	30
3.2 APPRATUS.....	30
3.3 GENERAL PROCEDURE FOR PREPARATION OF CONCRETE CUBE.....	31
3.4 COMPRESSIVE STRENGTH TEST.....	32
3.5 GENERAL PROCEDURE OF ACCELERATED MORTAR BAR TEST.....	32
3.6 GENERAL PROCEDURE FOR CONCRETE PRISM AND ACCELERATED CONCRETE PRISM TEST.....	33

CHAPTER 4.....	35
RESULTS.....	35
CHAPTER 5.....	40
DISCUSSION.....	40
CHAPTER 6.....	44
CONCLUSION.....	44
REFERENCES.....	46

LIST OF TABLES

Chapter	Description	Page
4	Table 4.1 Determined compressive strength against specified crushing strength 2000 psi@ 07 Days as per BS 1881 part 225.	35
4	Table 4.2 Determined compressive strength against specified crushing strength 3000 psi@ 28 Days as per BS 1881 part 225.	36
4	Table 4.3 Classification of cement, aggregate and water combination with varying dose of LiNO_3 and ASR expansion	37
4	Table 4.4 Results of concrete prism test	38
4	Table 4.5 Results of accelerated concrete prism test	39

LIST OF FIGURES

Chapter	Description	Page
1	Figure 1. Schematic representation of ASR mechanism	2
1	Figure 2. A representative diagram of ASR mechanism in concrete	4
1	Figure 3. Factors affecting ASR	5

LIST OF ABBREVIATIONS

ASR	Alkali silica reaction
OPC	Ordinary Portland Cement
LiNO ₃	Lithium Nitrate
SCM	Supplementary cementitious material
SiO ₂	Silica
≡Si-OH	Silanol group
Al ₂ O ₃	Alumina
CaO	Lime
MK	Metakaolin
GGBFS	Ground Granulated Blast Furnace Slag
RHA	Rice Husk Ash
FA	Fly Ash
PSA	Pore solution alkalinity
(C-S-H)	Calcium silica hydrate
MICP	Microbially induced calcium carbonate
DEF	Delayed ettringite formation
CNS	Colloidal nano silicate
SSC	Specialist sustainable cement
MBT	Mortar bar test
ACPT	Accelerated concrete prism test
CS	Compressive Strength

BRS	Building Research Station
ASTM	American Society For Testing Materials
SEM	Scanning electron microscope
BS	British Standard

ABSTRACT

The alkali-silica reaction (ASR) produces expansive alkali silica gel which is chemical hazardous leading to develop crack and damage the concrete structure. This research work is being designed to explore the mitigation potential of lithium nitrate with varying percentage for minimizing the intensity of ASR reaction in concrete. For this purpose different laboratory investigation were made with combination of reactive aggregate, ordinary Portland cement, water and LiNO_3 to evaluate lithium nitrate compound in mitigating expansion due to ASR reaction through compressive strength test, mortar bar test(MBT), concrete prism test(CPT) and accelerated concrete prism test(ACPT). It was revealed from the obtained result concrete composite containing LiNO_3 upto 3.5% is non significant to inhibit alkali silica reaction. Whereas, usage of lithium nitrate ranging from 4 to 5% in concrete composite is effective to control alkali silica reaction. The SEM analysis was performed on the surface microstructure which also proved that adding lithium nitrate as an additive helped refine and densify the concrete microstructure by enhancing the interfacial transition zone of the cement-aggregate mix.

CHAPTER 1

INTRODUCTION

Concrete is a popular construction material that adds strength, durability, and versatility to structures and infrastructure. It is a composite material consisting of cement, sand, stone aggregate, and which sets over time. One of the most significant characteristics of concrete is its ability to endure enormous loads and compressive stresses, making it perfect for foundations, pillars, walls, and slabs. Its compatibility can be adjusted by modifying the concrete mix proportions, and it hardens with time [1-3].

Concrete is also extremely durable, as it can survive harsh weather conditions, chemical attacks, and natural calamities. And it has a long life. Concrete's sustainability makes it a great alternative for buildings, bridges, dams, and other building projects [4].

Another important feature of concrete is its flexibility. Because it can be molded into different forms and sizes to fulfill the precise needs of a construction project. Concrete can also be poured, sprayed, or prefabricated for faster and more efficient construction procedures. Its inflexibility allows for the creation of exclusive architectural designs as well as the construction of complex-shaped structures. However, the adaptability of concrete is substantially reduced due to the alkali-silica reaction. And it causes structural damage, which affects the integrity and durability of buildings [5, 6].

1.1 ALKALI-SILICA REACTION (ASR)

The alkali-silica reaction, commonly known as "concrete cancer," is a gradual swelling reaction that develops over time between highly alkaline cement paste and reactive amorphous silica present in various aggregates. Although, ASR produced structural strain in nuclear power plants and dams. ASR-induced concrete deterioration is a gradual and extensive process. Over time, ASR forms an alkali-silica gel, which causes gradual deformation in the concrete due to inner stresses, eventually leading in diminished serviceability and durability [7-10].

ASR induced strain can cause substantial damage to concrete structures, demanding their demolition. This phenomena and its mechanisms have been thoroughly

described in many research works [11]. The ASR mechanism is depicted schematically in figure.1

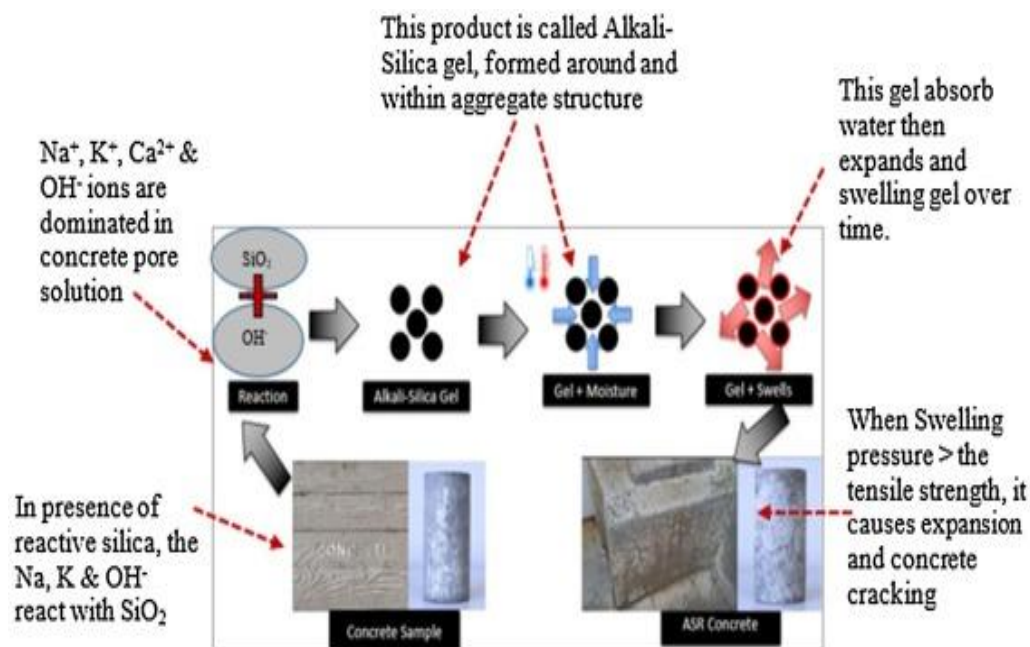


Figure 1: Schematic representation of ASR mechanism

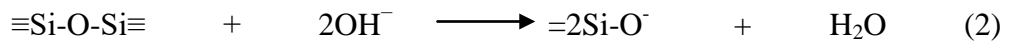
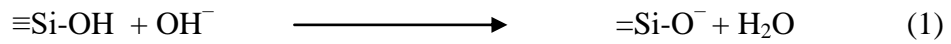
Alkali-silica reaction (ASR) is a chemical process that occurs between reactive silica in aggregates and hydroxyl ions (OH^-) present in concrete pore solution. Silica (SiO_2) in aggregates is chemically inert and often exists as quartz with a siloxane group structure ($\equiv\text{Si-O-Si}\equiv$). Imperfections or surface flaws on crystalline silica particles increase their attraction for water, forming amorphous hydrous silica containing silanol groups ($\equiv\text{Si-OH}$). This change, known as silica hydration, or silanol production, begins the ASR process.

The reaction between silicon atoms and water molecules results in the formation of silanol groups on the surfaces of crystalline silica particles. The silicon atoms on the surface have unfilled bonds, making them reactive to water. When water molecules interact with the surface of crystalline silica, they establish hydrogen bonds with the silicon atoms, resulting in the formation of silanol groups [12, 13].

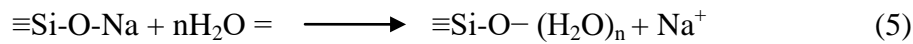
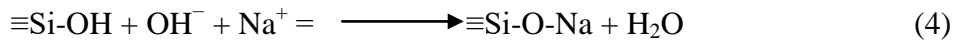
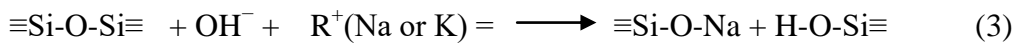
The presence of these groups on the surface of crystalline silica particles increases their hydrophilicity, which makes them more likely to attract and interact with water molecules. The surface hydration process can alter the physicochemical

characteristics of silica particles, as their charge on the surface, reactivity, & adsorption characteristics. The amorphous hydrous silica that forms on the outermost layer of crystalline silica particles different from the initial crystalline structure, as it lacks the long-range order and periodic arrangement of atoms that characterize crystalline materials.

Silica hydration is the process by which $\equiv\text{Si-OH}$ develop on the crystalline silica particles due to disorder and imperfections. As a result, amorphous hydrous silica with a stronger water affinity is formed. The silica (SiO_2) dissolves when exposed to high concentrations of hydroxyl ions. This method requires neutralizing the silanol groups ($\equiv\text{Si-OH}$) and then the siloxane groups ($\equiv\text{Si-O-Si}\equiv$) as depicted in equations 1 and 2.



The structures ($\equiv\text{Si-OH}$, $\equiv\text{Si-O-Si}\equiv$) attract water soluble alkali hydroxides especially NaOH and KOH which are most prevalent in the concrete pore solution as they degrade. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, in the pore solution react and increased OH^- concentration during cement hydration. Equation 3 shows how the reaction of siloxane groups ($\equiv\text{Si-O-Si}\equiv$) with hydroxyl ions form an alkali-silicate solution and gel at different moisture contents. Then, Si-OH reacts with hydroxyl ions and alkali metals to form alkaline silicate hydrate in a process that releases water. Equations(4) and (5) are also shown in Fig. 3 [14, 15].



The hydrated gel diffuses from the aggregates into the cement paste, where it reacts with calcium ions in the paste to generate Ca^{+2} silicate gel. When moisture is present, the finished product expands. Excessive expansion causes cracking in mixture and results in tension and cracks in concrete structures [16].

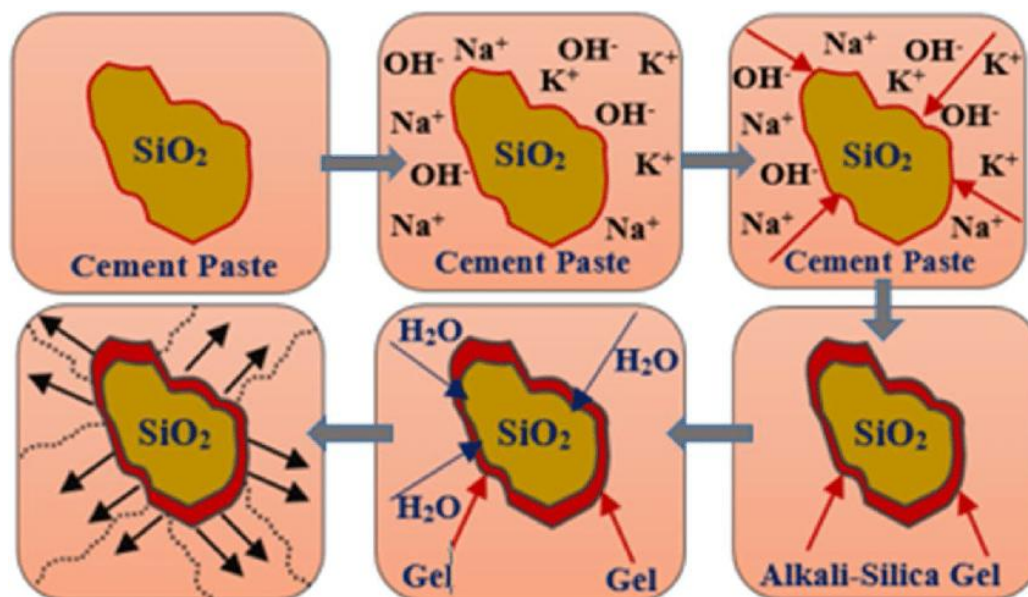


Figure 2: A representative diagram of ASR mechanism in concrete.

1.2 IMPACT OF ALKALI-SILICA REACTION (ASR)

The ASR gel itself causes no direct damage to the concrete, but swells with moisture from its environment causing internal stress and expansion. These can exceed the tensile strength of concrete, leading to longitudinal cracks and ultimately to cumulative distress. The three key ingredients commonly believed to be essential for ASR in concrete materials are:

1. Siliceous components reactive in aggregates (fine and coarse fractions)
2. Highly alkaline content from cementing material
3. Moisture is present, as are other contributing elements such as temperature and additives.

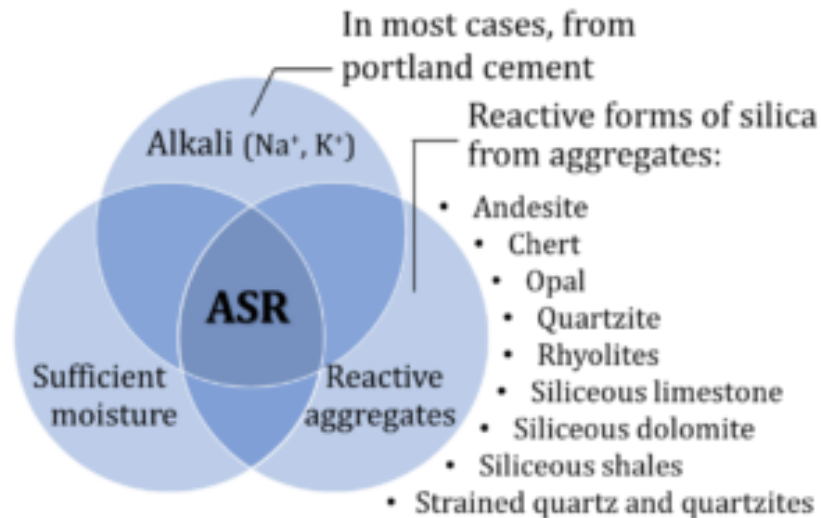


Figure 3: Factors affecting ASR

Admixtures such as supplementary cementitious materials (SCMs) can help reduce ASR by lowering the accessible alkalis and refining the pore structure of concrete. Furthermore, chemical admixtures, such as lithium compounds, have shown beneficial in interrupting the reaction of alkalis and reactive silica, preventing the formation of perilous ASR gel [7].

1.3 ADMIXTURE AND SCMS

An admixture is any element other than water, aggregates, cement, or fiber that is added to a concrete mixture while it is being mixed. It is used to change the mixing, setting, and hardening qualities of concrete. Mineral admixtures that fulfill the requirements to enhance the characteristics of both freshly mixed and hardened concrete are known as supplemental cementitious materials, or SCMs. SCMs help improve the strength, permeability, longevity, unit weight, reliability, and hydraulic the functionality of concrete [17, 18].

Supplementary cementitious materials such fly ash(FA), ground granulated blast furnace slag(GGBFS), silica fume(SF), calcined clays or metakaolin, and natural pozzolans are often added to the original Portland Cement or used in part of a replacement for Portland design concrete. The use of SCMs has also been increasing — the worldwide average clinker content in cement dropped from 85 percentage (2003) to 77 %age (2010), and is expected to drop further down to 71 percent [19].

1.3.1 FLY ASH

To identify the optimal fly ash dosage, performance-based approaches for determining fly ash effectiveness in moderating the alkali-silica reaction (ASR) must be studied over a range of replacement levels. The present ASR evaluation methods fall short as a mix design tool for new concrete construction when it comes to estimating the optimal fly ash dosage for ASR mitigation. To address this issue, this study describes a screening method for predicting the optimal fly ash dosage required to reduce ASR in concrete mixtures. This approach calculates pore solution alkalinity (PSA) by taking into account the water-soluble alkalis given by both fly ash and cement at various amounts of fly ash replacement [20].

Although many studies have shown that fly ash (FA) is an effective pozzolanic material for inhibiting ASR expansion, the substantial decrease in expansion could also be attributed to other reasons, such as the influence of filler or a decrease in OPC content in the mix. Furthermore, the present literature does not provide a clear picture of how the impact of filler and FA fineness affect ASR growth. Therefore, this study aims to investigate that how replacing OPC with FA at varied fineness levels affects mortar ASR growth. Two different fineness levels of FA were investigated to determine their influence on ASR growth [21].

Furthermore, ground river sand (RS) of the same fineness as FA was used to replace OPC at the same rates to assess the filler effects of FA and RS on ASR growth in mortar. The researchers discovered that FA did not always inhibit ASR formation in mortars containing highly reactive components. According to their findings, the control mortar had an ASR growth of 0.70% after 14 days of replacing 20% of the OPC with Class C. During the same time span, FA did not restrict ASR expansion to less than 0.20% [22].

1.3.2 SILICA FUME

Similarly, silica fume (SF) is utilized as a supplementary cementitious material (SCM) to reduce ASR. Research has consistently shown that concrete containing silica fume with low water content can be stronger and more robust than concrete built exclusively from Portland cement [23].

Incorporating silica fume can considerably decrease the risk of ASR by enhance pozzolanic characteristics of the concrete. According to research, silica fume is most efficient at controlling ASR when used to replace 5% to 12% of the cement weight. At these rates of substitution, silica fume efficiently suppress ASR-induced expansion compared with other supplementary cementitious materials such as fly ash or slag [24].

This silica-enriched process adds more reactive silica to the concrete that reacts with the alkalis to redress their effectiveness to cause harmful reactivity with the reactive aggregates. Also, this reaction produces additional C-S-H matrix thus improving the overall toughness and longevity of the concrete. Although silica fume is positive, it may cause ASR if the fume clumps or is not correctly disposed into the concrete. Thus, proper handling and mixing of the silica fume need to be very careful so that silica fume can be effective in stopping ASR. Conclusively, silica fume can be efficaciously used in control of ASR in concrete but if it is integrated into a properly prepared mix [25].

1.3.3 SLAG CEMENT

Slag cement is an effective tool in restricting the potential for the alkali-silica reaction (ASR) in concrete use. The alkali levels inherent in the slag cement are, on the average, lower than for Portland cement, being on the order of 0.5 to 0.7% Na₂O equivalents. The reduced alkali content is that there are fewer compounds of alkali to react with the reactive aggregates. In addition, the hydration products of slag cement adsorb a greater quantity of alkalis relative to Portland cement hence lowers the concentration of hydroxyl ions in the pore solution. This practice becomes more effective in avoiding ASR reduction in the number of reactive encounters between alkalis and silica [26].

Research proves that the addition of slag cement at levels ranging from 30 to 60% of the total amount of cementitious materials is an effective method of reducing ASR, in particular where the concrete is characterized by highly reactive silica. The necessary ratio can only be established after testing, while at the same time evaluating the features of the materials and prevailing climatic conditions. Using of the slag cement is efficient way to prevent ASR influences in concrete. By lowering the availability of accessible alkalis and by adsorbing alkali ions in its hydration

products, slag cement has the potential to improve the life and application length of concrete components threatened by ASR [27].

1.3.4 METAKAOLIN

Metakaolin is obtained by high-temperature calcination of a kaolin clay and a pozzolan material is produced. Its use as a partial replacement for cement under concrete significantly minimizes ASR expansion risk. Such research examples included that fact that the use of metakaolin reduced the ASR expansion, yet still increased the mechanical properties of concrete to make them appropriate for construction in those areas where ASR is an issue [28].

The metakaolin has lesser alkalis content compared to the Portland cement, hence fewer alkalis being available. Calcium-silicate-hydrate emerges from one of the hydration products of metakaolin as being prominently significant. This specific binding action of (C-S-H) gel attracts more alkalis, lowering its concentration in the pore solution and limiting its ASR contribution [29].

Metakaolin improves microstructure of the concrete by reducing capillary porosity and pore size distribution. Reduced permeability because of metakaolin utilization reduces its susceptibility to dampness and prevents the penetrating of adverse chemicals that may cause ASR expansion. Research proves that addition of metakaolin at ratios varying between 8% and 20% by mass of cement is adequate in limiting ASR, with high percentages at times providing additional protection. The efficiency of metakaolin in controlling the ASR expansion is dependent upon particle sizes, reactivity of metakaolin, the extent of alkalinity in the cement and the aggregates reactivity [30, 31].

1.3.5 CALCIUM CARBONATE

Calcium carbonate has various actions in neutralising alkali-silica reaction. Firstly, it decreases the number of alkalis in pore water. The dissolution of reactive silica will be blocked by calcium ions (Ca^{2+}), so the risk of gel will be minimized. Research findings indicate that calcium ions alter the chemistry of the pore solution making it less suitable for ASR to take place. Experiments have shown that when calcium carbonate is introduced to concrete, the ASR-induced water expansion can be

prevented by altering the nature of the gel produced as a result of the reaction. Such a gel also has a lower expansion and weaker resistance to stresses [32].

Furthermore, calcium carbonate is able to strengthen concrete microstructure. It helps in the production of calcium silicate hydrate gel (C-S-H) resulting in denser and lower permeable matrix. Its impact also calms the moisture and alkali infiltration, two factors that have been known to cause ASR. The densification advantages of calcium carbonate used to considerably reduce ASR and enhance the mechanical performance and toughness of the concrete [33].

Recently, application of calcium carbonate has undergone innovation, especially in the use of microbially induced calcium carbonate precipitation (MICP), a technology that uses microorganisms to precipitate calcium carbonate directly onto aggregate surface. This method of inhibition proves the ability to build a protective seal around aggregates so as to minimise the risk of ASR by blocking the contact between reactive aggregates and alkalis. Adding calcium carbonate to the formulation of concrete is a proven way to reduce ASR risk. Reduction of alkali availability, change in gel chemistry, and improvement of microstructure through the introduction of calcium carbonate increase durability and survival time in concrete structures [32, 34].

1.3.6 CALCIUM SULFATE

A number of strategies are used in the battle by calcium sulfate against ASR. The reactive silica adsorption reaction is impeded by the presence of calcium ions (Ca^{2+}) in the pore solution. Increased calcium ions in the potential hydrogen of pore solution reduce silica reactivity, which favors gel formation. The findings of the academic work show that calcium sulfate has the ability to control ASR-induced expansion as a result of the alteration of the chemical setting of the reaction which will prevent silica rupture and expansive gels [33].

Also, calcium sulfate is used to enhance the microstructural features of concrete. Encourage the formation of calcium-silicate-hydrate, gel. The addition enhances the density of the concrete matrix; thereby reducing permeability while limiting exposure to moisture and alkalis. The increased density ensures that ASR is avoided, but at the same time improves mechanical performance of concrete [35].

Although the calcium sulfate can overcome ASR, definite limitations of its effectiveness exist. The risk of delayed ettringite formation (DEF) is of concern particularly when calcium sulfates react with aluminates in the presence of moisture. This reaction is the reason of concrete to expand and crack, particularly in areas with significant humidity or temperature variations. On top of that, the efficiency of calcium sulfate in suppressing ASR relies on the type of aggregate, its reactivity and the alkaline content of the cement. It is important to assess the dosage and the actual conditions of concrete application to maximize its applicability as an ASR mitigation approach [36].

As a result, calcium sulfate appears to be a promising strategy for minimizing ASR by delivering calcium ions while also enhancing the microstructure of concrete. Its application must be carefully monitored to avoid any problems [37].

1.3.7 RICE HUSK ASH

Rice husk ash (RHA) is a byproduct of rice milling. It has the ability to help inhibit the alkali-silica reaction (ASR) in concrete. RHA's high silica content (usually 80-90%) has been shown to minimize ASR-induced development due to its pozzolanic characteristics. Silica in RHA combines with calcium hydroxide generated during cement hydration, forming additional calcium - silicate - hydrate (C-S-H) gel. This pozzolanic reaction not only strengthens and boosts the longevity of the concrete, but it also decreases the availability of alkalis that lead to ASR [38].

However, introducing RHA into the concrete mix reduces the total alkali content. RHA typically has lower alkali levels than Portland cement, therefore its inclusion reduces the overall quantity of alkalis available via reacting with reactive silica in aggregates. Furthermore, finer RHA particles are more effective at reducing ASR expansion because they have a higher surface area for pozzolanic reactions and can fill holes in the concrete matrix, so improving its microstructure. This densification decreases permeability, preventing the passage of moisture and alkalis, that can increase ASR [39].

Despite its potential benefits, RHA has limits in reducing ASR. Some studies indicate that RHA may not reliably inhibit ASR growth. The study discovered that higher RHA replacement levels (over 10-15% by mass). This resulted in increasing

expansions. This suggested that RHA's vesicular structure could generate channels for external alkalis to penetrate, or that its chemical makeup could negatively interact with reactive silica and alkalis [40].

The size of RHA particles is a determinant to the extent that RHA is capable of limiting ASR expansion. Results have indicated that finer RHA particles provide greater efficacy than the coarser ones as a result of greater pozzolanic action. The bigger RHA particles have been known to serve as a better alkali penetrator. It is also necessary to keep in mind the fact that characteristics of RHA vary not only depending on its source and processing, which in turn affects its pozzolanic activity and its action on ASR. Therefore, correct identification of the RHA in use for concrete applications is important [39]. Result of its pozzolanic properties, and ability to improve microstructural features, the rice husk ash provides a realistic remedy to ASR, in concrete. Nevertheless, its efficiency is defined by such factors as particle size, quality, and a specific thing in concrete mix preparation. Further research is needed to optimize the practice of using RHA against alkali-silica reaction. [41].

1.3.8 CALCIUM NITRATE

Calcium nitrate contained within the chemical formula $\text{Ca}(\text{NO}_3)_2$ has been found to be a positive ingredient for the concrete to reduce the alkali-silica reaction (ASR). Major part of its usefulness is due to its capabilities to establish a layer of protection on reactive aggregate surfaces. The incorporation of calcium nitrate into concrete causes its solution in water and thus causing a reaction between calcium ions and reactive silica. The resulting compounds, such as calcium-silicate-hydrate (CSH) and calcite, are non expansive and they serve to limit the dissolution of reactive aggregates and ASR future [42].

The additional aspect of calcium nitrate is its influence on the processes of hydration of cement. Researchers have shown that calcium nitrate causes early hydration and short setting times. It is critical to ensure that no promotion of early hydration is conducted at the expense of other concrete property completeness or associated schedule. Further, if acceleration becomes too fast, it can make the concrete harder to put and finish [43].

Furthermore, the long-term strength of concrete containing calcium nitrate may not improve when compared to a reference mix without the addition. The reduction in ASR growth is mostly due to lower dissolution of reactive aggregates, not greater strength or stress resistance. While calcium nitrate improves its durability, and is also necessary to evaluate its applicability for applications that require high strength [44].

Another consideration is the calcium nitrate concentration used. Because higher dosages often result in bigger decreases in ASR growth, and the appropriate level of calcium nitrate has unfavorable effects. As a result, the optimal dosage should be determined through testing for each individual concrete mix design and set of components [42].

Finally, calcium nitrate is seen as a more cost-effective alternative to other ASR mitigation strategies. The additional expense of the admixture must still be considered. If the benefits of utilizing calcium nitrate, such as increased durability and reduced chance of ASR-related damage, are evaluated against the increased cost [45].

1.3.9 CALCIUM HYDROXIDE

Calcium hydroxide has the ability to lessen the alkali - silica reaction (ASR) in concrete. Calcium hydroxide can aid by interacting with silica to form calcium silicate hydrates, which are less extensive than the gels formed during the ASR. This reaction decreases the quantity of reactive silica accessible for potentially hazardous interactions with alkali. Furthermore, calcium hydroxide can assist buffer the potential hydrogen of the pore solution by potentially decreasing the solvability of reactive silica, lowering the likelihood of ASR [46].

Several factors influence Ca(OH)_2 's effectiveness in avoiding ASR, including the concentration of reactive silica in the aggregates and the overall composition of the concrete mix. While calcium hydroxide can aid to minimize ASR growth, it is frequently combined with other supplemental cementitious materials like fly ash or slag. Such materials increase performance through the stimulation of more pozzolanic reactions which exploit alkalis and reactive silica [47].

Concrete use of calcium hydroxide $\text{Ca}(\text{OH})_2$ help tout them salkali-silicas react id ASR. However, using calcium hydroxide deserves much caution. A possible problem arises when calcium hydroxide, as opposed to reducing the activity of silica, facilitates silica reactivity in some cases, and particularly in alkali-activated ones. Moreover, the use of calcium hydroxide in the control of ASR largely depends on the composition of the concrete and the character of theses particles. Mismanagement of calcium hydroxide may cause poor ASR control, that may cause continuous expansion and damage to structures. As such, much research and rigorous tests are essential to ensure that calcium hydroxide is indeed able to control the ASR while not saddening it with the occult potential risks [48].

1.3.10 LITHIUM BASED ADMIXTURES

Lithium-based admixtures provide opportunities for improving the properties of materials. Results of studies show that the use of lithium-based compounds could greatly increase the mechanical strength and resilience of concrete. These admixtures are known for their distinct ability to decrease tASR thus extending the lifespan and general structural performance of the concrete. Common lithium-based admixtures to be used in controlling ASR in concrete include LiOH , Li_2CO_3 , LiCl and LiNO_3 [49].

1.3.11 LITHIUM SULFATE

Lithium sulfate (Li_2SO_4) is one of the multiple lithium materials used to inhibit ASR in concrete usage. It means that lithium compounds such as lithium sulfate can help to mitigate ASR when they slow the reaction's rates. Their impact is realized through their ability to alter the chemical flow that leads to the synthesis of the gel that is responsible for the ASR. By replacing Na and K ions in the pore solution, lithium ions facilitate stabilization of the reaction by reducing the total expansion caused by ASR [50].

Thus, lithium sulfate acts as an efficient admixture for ASR prevention in the newly developed concrete recipes. It is normally used in conjunction with lithium nitrate or other compounds of lithium to raise its ability. For structures that have already experienced ASR, lithium sulfate treatments can help to limit additional damage, making them especially useful for infrastructure maintenance and rehabilitation operations [51].

Lithium sulfate, when combined with other lithium salts, has been shown in studies to successfully prevent ASR-induced expansion in various concrete mixes [52].

1.3.12 LITHIUM CARBONATE

Through changing the chemistry of the gel and diminishing its expansiveness, lithium carbonate (Li_2CO_3) successfully avoids ASR. It inserts lithium ions (Li^+) into the pores solution of the concrete. These ions can partially replace sodium and potassium ions in alkali-silica gel. The substitution of lithium for Na^+ and K^+ resulting production of a gel with a different chemical makeup, which is less expansive and less likely to absorb water. This minimizes the overall volume expansion caused by ASR. [53].

It reacts with the alkali hydroxides present in the pore solution (e.g., sodium hydroxide and potassium hydroxide), thereby lowering their concentration. This prevents the high alkaline environment required for ASR from being maintained. Lower alkali concentrations inhibit the breakdown of reactive silica in aggregates, reducing or stopping the ASR process. Lithium carbonate decreases the amount of hydroxide ions and lowers the pH of the pore solution. Since a high pH environment is necessary for the ASR reaction to take place, this pH reduction serves to prevent silica dissolution and succeeding gel formation. It can mix with dissolved silica to generate stable lithium silicates. These silicates are less reactive and non-expansive, which reduces the negative impacts of ASR [54].

There are some limitations when using lithium carbonate. It has lower solubility than lithium nitrate. This can make it less effective in dispersing lithium ions throughout the concrete matrix, limiting its efficacy in mitigating ASR. The effectiveness of lithium carbonate is strongly dose-dependent. If not utilized in sufficient quantities, it may not offer adequate protection against ASR. Lithium carbonate works by chemically changing the alkali-silica gel and reducing the concentrated amount of alkalis in the concrete pore solution, resulting in reduced expansion and cracking. Despite its lesser solubility, lithium nitrate is frequently favored in practical applications.[55].

1.3.13 LITHIUM NITRATE

Lithium nitrate (LiNO_3) is widely recognized as an efficient chemical agent for lowering ASR in concrete. According to research, lithium nitrate can effectively minimize ASR growth by preventing the creation of harmful gel products that cause concrete deterioration. Furthermore, adding lithium nitrate to concrete compositions has been demonstrated to considerably limit expansion rates related with ASR, emphasizing its value as a preventative measure. [49].

Lithium ions can replace sodium and potassium ions by forming reactive silica gels. This gel limits the possibility for expansion. By changing the solubility of reactive silica, lithium ions restrict the quantity of silica accessible for reactivity with alkalis, lowering the overall extent of ASR. According to research, lithium nitrate produces less expansive reaction products than standard ASR methods. And this adds to the reduced damage in concrete constructions. [50].

Hence the Alkali-silica reaction remains a significant challenge in concrete infrastructures, leading to expansion, cracking, and eventual degradation. Current practices to mitigate ASR are rarely long term viable, especially under high moisture and alkali percentages. Despite the valued low greenhouse gas emission of geopolymer concretes, they become more susceptible to ASR due to increased alkali activators. The attempts to create a single, effective strategy for inhibiting ASR for Portland and geopolymer concrete have not yet led to large scale global application. Lithium nitrate admixtures provide a glimmer of hope in addressing ASR but the extent to which they prove effective in a variety of formulations and contexts remains to be determined.

The understanding of how lithium nitrate provides control over the ASR is paramount for producing this kind of infrastructure made of durable, and environmentally friendly concrete. The aim of this investigation is to provide a reliable way of controlling ASR caused problems by in-depth analysis of the effects of Lithium Nitrate in reactive aggregates present in both Portland and geopolymer concretes. The results of the research may encourage the wider use of admixture from lithium nitrate, thus prolonging life of the infrastructure, reducing maintenance needs, and promoting more sustainable construction. The results of this research may

provide valuable data on the expanded use of lithium-based admixtures in the next generation concrete techniques.

The use of a numerous extra cementitious materials in concrete is becoming increasingly desirable in an attempt to reduce damage resulting from the alkali silica reaction. Because of many harmful chemical interactions that occur between reactive silica of aggregate and alkali hydroxide of concrete, concrete expands, subsequent in the progressive formation of cracks in concrete and causing damage to infrastructure development. As a result, the use of LiNO_3 as a potential alkali silica reaction inhibitor must be investigated in order to limit the impacts of alkali silica reaction (ASR) in concrete building and improve compressive strength, performance, & durability of the concrete structure.

AIM AND OBJECTIVES

Following are the aim and objective of this research as under:

- To evaluate reduction in expansion resulting from lithium nitrate admixture application in concrete mixtures prone to alkali silica reaction.
- To quantify optimal lithium nitrate dosage for suppressing alkali silica reaction.
- To determine the compressive strength (CS) of concrete matrix made up reactive aggregate and cement.
- To observe concrete performance variation with different dosages of lithium nitrate.

CHAPTER 2

LITERATURE REVIEW

Isabel *et al.*, (2013) demonstrated that the concrete has been one of the most extensively utilized building materials since the eighteenth century. It is composed of a binder (cement), aggregates, water, and maybe additional additives. Although concrete was exceedingly adaptable and durable in the early twentieth century. Since the 1940s, substantial study has been performed in order to identify the components of rocks and minerals that contribute to the chemical processes that occur during the deterioration process. This study found that, despite its benefits, the material in issue can have a negative impact on the endurance and functionality of structures. Among these concrete problems, different mechanisms caused the concrete to deteriorate. The mechanism was alkali silica reaction (ASR) [56].

Ivan and coworkers (2021) explained that the ASR is generally recognized as a damaging mechanism in concrete. This resulted in the early loss of serviceability of the afflicted structures. Furthermore, a large number of research investigations have been undertaken on the underlying mechanisms, as well as the reduction and prevention of the reaction. However, additional research has been undertaken on the role of moisture and temperature. These were the key reasons that affected the reaction. As a result, these constraints hindered the comprehensive assessment of ASR-induced damage. Furthermore, the accessible moisture in concrete initiates and sustains the reaction, which was predominantly estimated using relative humidity due to difficulties in employing alternative measurements, such as capillary saturation. This study examined the current understanding of moisture measurement in concrete, the impact of moisture and temperature in the reaction's kinetics, and the moisture threshold required for the reaction [57].

Mark (2022) demonstrated that the reaction that formed a highly hygroscopic silica gel that expanded into the pores of concrete. This resulted in a significant drop in mechanical performance for the damaged structures. Various strategies were studied to limit the expansion within a specific threshold, including the use of different compounds for mitigation. However, the mechanics remained problematic. This study attempted to establish a method that was consistent with existing information,

therefore it used Larive's chemo mechanical model and curve-fitting techniques. Furthermore, these results obtained precision in respect to the experimental measurements from multiple methods and indicated the necessity for future research [58].

Stephen *et al.*, (2022) demonstrated that the alkali-silica reaction is a chemical degradation process that causes cement and aggregate particles to expand and break, eventually deteriorating the concrete. Several factors influence ASR, including aggregate reactivity, cement alkali concentration, and moisture availability. According to this study, geopolymer concrete may be more susceptible to ASR due to the high alkali concentration of the activator than Portland cement concrete [59].

Tsuneki and coworkers (2007) explored the experimental studies were carried out to acquire a better understanding of the soft and fluid alkali silicate gel generated alkali-silica reaction between aggregate and alkaline pore solution. This gel formation causes expanding pressure within the concrete, resulting in fractures in both the aggregate and the surrounding concrete. Elemental study of aggregates embedded in cement paste revealed that the alkali silicate could only provide expanding pressure if the aggregate was closely bonded by a reaction edge. This reaction edge developed gradually around the ASR - affected aggregate. The study showed that consuming alkali hydroxide during ASR lowered the solubility of Ca^{2+} ions in the pore solution. When interacting with Ca^{2+} ions, the alkali silicate formed a stiff and insoluble reaction edge. The reaction edge progressively formed around the ASR-affected material. The study discovered that using alkali hydroxide during ASR decreased the solubility of Ca^{2+} ions in the pore solution. When interacting with Ca^{2+} ions, the alkali silicate formed a stiff and insoluble edge. This border allowed alkaline solutions to pass through while keeping viscous alkali silicate from escaping, allowing later-formed alkali silicate to collect within the aggregate. This accumulation created enough expanding pressure to fracture both the aggregate and the surrounding concrete [12].

Gopakumar et al., (2021) searched for new ways to reduce ASR, with the particulars of additives and admixture in concrete. The difference between "additive" and "admixture" was discussed, with "additive" usually defining powdered materials and "admixture" designating liquid dispersants, but the terms are commonly used interchangeably. Although LiSO_3 was considered, researchers discovered that these

alternatives were not only cheaper, but also easily available. Also, LiOH admixtures proved to be of higher quality consistency, availability, and performance compared to the extra cementitious materials. Researchers found an analytical method to determine the additives that help control ASR by reducing the pH of concrete pore solution. The approach revealed the mechanism that caused the pH reduction and presented a logical formalism of evaluating possible additions. The impact of their application for concrete performance was assessed by applying ASTM C1293 testing on the chosen chemicals [60].

Dip *et al.*, (2024) demonstrated that alkali silica reactivity (ASR) was a major concern for the durability of concrete constructions. Thus, they minimized this deleterious reaction by replacing significant amounts of cement with supplemental cementitious materials (SCMs) [25].

Andria and coworkers (1999) illustrated the use of low-level mineral admixtures to minimize mortar bar expansion caused by the ASR. In addition, SF, powdered bottle glass, FA, and slag cement were tested their ability to reduce ASR in Portland cement concrete incorporating reactive-waste glass aggregate. As a result, different mineral admixtures were investigated to determine their capacity to inhibit ASR expansion. Few of these admixtures were successful, with expansions of less than 0.20 percent. ASTM C-1260 also established the detrimental expansion. As a result, in this study, they looked at efficient cement alternatives for lowering expansion below this threshold, such as silica fume, specific fly ashes, and powdered glass. Furthermore, fineness was discovered as a critical aspect in determining the usefulness of fly ashes in minimizing ASR expansion. In this investigation, silica fume was investigated to be the most suitable for pavement patch applications. Powdered glass also revealed that the possibility for opposing the ASR, although it did not acquire full strength within 24 hours [61].

Muhammad and coworkers (2016) examined in his study that the use of rice husk ash (RHA) instead of cement to minimize contraction caused by the alkali-silica reaction. They demonstrated mortar bar examples are varied RHA doses (10%, 20%, 30%, and 40% by weight as a replacement for cement) and assessed them in compliance with the American standard ASTM C-1260. RHA's strength activity index was also analyzed. These results showed that RHA met ASTM's strength

activity standards. Furthermore, the RHA substitution (10-40% by cement weight) was discovered and beneficial to overcome the alkali-silica reaction growth [62].

Andres and his coworkers (2023) examined that the new sources of high-class non-crystalline silica for use in optimized concrete. They demonstrated that highly efficient silica could be generated by ash from rice, a common agricultural waste that is widely offered globally. They discovered that manufacturing RHA by reaction with HCl for burning. They increased the reactivity by eliminating M^+ contaminants & forming a framework with a larger external surface. Hence, in this study focused on the excellent activity of this ash. This was developed & tested an alternative to PC in high-performance concretes. RHA's effectiveness was compared to typical silica fume (SF). These outcomes of this investigation revealed a significant high in compressive strength across all ages. In general, the strength of the control concrete out performed 20%. Furthermore, increase in flexural strength was greater, with concrete containing RHA & SF increasing with 30% and 40% corresponding. Using polyethylene, polypropylene fiber in concrete with TRHA and SF resulted in a synergistic effect. The data indicated chloride ion penetration. It also showed that TRHA behaved similarly to SF. Based on these statistical analyses, TRHA's performance was shown to be identical to that of SF [63].

Tandre and coworkers (2020) described that the study delves into the effect of alkali-silica reaction (ASR) on the corrosion of concrete structures. ASR is a chemical reaction that occurs between basic OH^- in cement and reactive silica in aggregates, causing substantial expansion and breaking in concrete over time. The study found that Li-containing chemical compounds can effectively mitigate the negative impacts of ASR. The critical effect of such admixtures is to introduce them into the concrete mix to prevent the alkali-silica reaction, which consequently reduces both the expansion as well as ASR-induced damage. In order to demonstrate how such admixtures function, calcium nitrate becomes a reactive aggregate for the tests. Research has shown that calcium nitrate increases ASR induced-expansion and can therefore be used as a medium to assess chemical therapy against ASR. By adding lithium based admixtures to the mixes of concrete with calcium nitrate, the researchers observed significant control over ASR expansion. The findings emphasize the need for employing appropriate chemical admixtures to inhibit ASR-

induced failures of concrete. The investigation also provides a low-cost solution to avoid ASR by mixing soluble alkaline-earth compounds into concrete mixes. Added such additives to concrete mixes significantly reduces active aggregate deterioration and the development of ASR. The use of such techniques is a more cost-effective way to avoid the occurrence of ASR on concrete and enhance appropriate resilience and durability in concrete-based infrastructures [44].

Rui *et al.*, (2024) demonstrated that Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ was capable of reducing the alkali-silica reaction (ASR) in concrete. Shallow appearance of a precipitate or barrier or passivation layer formed through ASR mitigation hindered the dissolution of reactive aggregate surfaces. The ability of CN to control ASR was evaluated in this investigation by the use of the two types of cements (I & II, Portland Limestone Cement), aggregates with different reactivities, and several types and dosages of QSus, such as amorphous steel. Based on ASTM C-1260/C-1567 expansion measurements, CN, when used in various amounts, significantly diminished ASR in mortar preparations comprising several types of aggregates. Additionally, intensive investigations by microstructural analysis and dissolving tests, as well as thermo calculations indicated that CN caused the formation of C-S-H, portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3) on aggregate surfaces and displaced conventional ASR gels. The formation of these precipitates established a protective barrier that was able to stop ASR in both formulations, irrespective of the presence of a SCM. The experimental results confirmed that CN was a suitable and economical ASR mitigant, especially in the face of limited supply of the fly ash and increasing lithium price [42].

Terrence *et al.*, (2000) demonstrated a recent study investigated the Ability of high-reactivity metakaolin to inhibit expansion in both concrete and in mortar applications. The research involves replacement of up to 10 to 30 percent of the ordinary Portland cement with HRM and the analysis of results using a modified accelerated mortar bar method. By this method, employing it, we can deeply examine the influence of HRM concerning controlling expansion as it grows with age. In addition, this work measured the chemical attributes of pore solutions taken from cement pastes containing 0.1%, 11.2%, and 30% HRM. The determination of the amount of K^+ , Na^+ and OH^- ions in the extracts was the major aspect under consideration in this investigation. Since these ions are involved in the alkali-silica

reaction (ASR), they are critical as this reaction causes expanding and cracking on concrete. When 20% HRM was added to cement paste, long-term accumulation of OH^- , Na^+ and K^+ ions significantly decreased. The measured decline in the levels of ion clearly associated with substantial decrease in expansion clearly indicated the efficiency of HRM in regulating ASR. The work shows how introducing HRM can significantly help in the durability of concrete and mortars, despite the issues caused by expansion [64].

Dayou and his colleagues (2022) analyzed the a detailed understanding of the mitigation processes was gained when aggregate silica dissolution was researched along with material assessment using various compositions. Furthermore, considerable reductions in ASR expansion and cracking density were observed at 80.2% and 73.5%, respectively. This trial also indicated the high efficacy of MIC in the ASR, outperforming metakaolin or lithium administered alone. The combination usage of MIC and lithium resulted in a synergistic impact that addressed many ASR prerequisites. This study described the complimentary efficiency of lithium and aluminum by reducing silica dissolution, lowering water uptake by 55.7%, lowering inflammation potential of ASR gel upto 90.3%, and transforming the expansive ASR (Q3) gel into the non- expansive C -S -H (Q2). This resulting the potential strategy for building durable concrete [65].

Jiaying and coworkers (2023) demonstrated that the super sulfated cementitious system. This gained popularity due to the lowering of carbon emissions in the construction industry. Furthermore, that study looked at characteristics & suppression mechanisms of ASR in super-sulfated cement (SSC). Even with 100% glass aggregates, there was essentially no ASR-induced growth in SSC. In the context of the alkali-silica reaction (ASR), the study evaluated the performance of specialist sustainable cement (SSC) vs conventional ordinary Portland cement (OPC). When compared to SSC, OPC was found to have a larger growth ratio of expansion connected to ASR. Remarkably, it was discovered that SSC was 20 times more successful at reducing the impacts of ASR. This notable difference demonstrates how well SSC performs in limiting expansion's and enhancing the concrete's overall durability. SSC showed excellent hydration characteristics during ASR testing, which improved the pore size distribution inside the matrix. This improvement improved the mortar's structural integrity by increasing its

compressive strength. Alkali ion concentration and aggregate interaction decreased as a result of the SSC's capacity to absorb alkali ions from the pore solution. Because it reduces the quantity of reactive alkali available to react with silica in aggregates, this reduction is essential for minimizing acid-base reactivity (ASR). Moreover, SSC had a vital bulk electrical resistance, which hindered the alkali ion's ability to flow through the mortar. Because of this feature and the higher Al/Si ratio, the negatively charged surface of SSC enhanced the adsorption of sodium ions. Furthermore, the SSC pore solution's high sulfate ion concentration (SO_4^{2-}) impeded the flow of hydroxide ions (OH^-), which increased its efficiency in regulating ASR. All things considered, SSC shows great promise as a low-carbon substitute for cementitious materials, providing better performance in concrete applications as well as increased resistance to ASR [27].

Dip *et al.*, (2024) demonstrated The introduction of supplemental cementitious materials (SCMs) to increase durability has been driven by the problem of alkali-silica reactivity (ASR) in concrete. Since it works well even at low dosages, nano- SiO_2 has become one of these alternatives that shows possibility. The ASTM C1260 accelerated mortar bar test, which measures ASR susceptibility under controlled circumstances, was employed in this work to evaluate the efficacy and mechanisms of colloidal nano- SiO_2 (CNS). The study showed that the size of the CNS particles was critical in determining the rate of the pozzolanic reaction. CNS2 and silica fume reacted with comparable pozzolanic behavior, but CNS2 showed higher pozzolanic reactivity than CNS1. When CNS was added to the mortar, porosity was increased and reactive silica was decomposed, leading to less ASR expansion. CNS enhanced the resistance to electrical currents and flexural strength of the mortar in general but response varied with the nature and concentration of CNS used. In addition, the research proved that CNS increased calcium hydroxide consumption and increased alkaline binding in ASR gel, insight into its function. These results indicate that CNS is very effective in reducing ASR and provides great opportunities for use in buildings of concrete structures. It is suggested by the study, based on these results, that CNS may be a promising solution to reduce ASR issues in the real-world construction context [25].

Mohammad and coworkers (2024) investigated by producing ash is a common by-product obtained when burning sewage sludge, which is a water treatment process. It

was researched for its potential use as a cement replacement material to improve its durability. The features of SSA varied according to its source, composition, and combustion procedures. This lengthy study demonstrated the ability of CSRs to reduce the ASR, a damaging phenomena that jeopardized concrete viability. This study looked at the effectiveness of SSA with two different fineness levels and three replacement levels, as well as triadic blends with trass or pumice (natural pozzolans), in controlling ASR. The results showed that SSA considerably reduced ASR growth. Furthermore, it only succeeded in controlling the ASR at a 50% replacement level, regardless of fineness. Furthermore, the ternary mixes greatly increased resistance to ASR expansion by allowing for ASR management at lower SSA replacement levels. As a result, the Silicon/Calcium ratio was identified as the important component in SSA's ability to manage the ASR, as it included 2.5 and 4.5 times more SiO_2 & Al_2O_3 , respectively, than Portland cement, and roughly one-third of its CaO. In addition, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and mapping validated the relative quantities of Si, Al, and Ca in the SSA [66].

Wenhui and co-workers (2022) demonstrated that the alkali-silica reaction (ASR) is a major stability concern. While Ca-rich supplemental cementitious materials (SCMs), such as ground granulated blast furnace slag (GGBS), enhanced mechanical performance. And it caused critical ASR-induced destruction, especially when high-reactive aggregates were involved. In this work, alum sludge, a byproduct of drinking water treatment procedures, was identified to be particularly effective at reducing ASR in mortars containing GGBS as a cement replacement and waste glass as a high-reactive aggregate. In this work, raw alum sludge was calcined for 3 hours at 900°C and crushed through a $80\text{-}\mu\text{m}$ sieve. The ternary blended binders were generated by substituting 20.1%, 30.10%, and 40.1% of the cement with a 1:1 mix of alum sludge & GGBS. When 30% of cement was substituted with an alum sludge and GGBS mixture, the mortar samples showed significantly higher CS and ASR resistance than the reference samples. This study investigated microstructural characterisation by X-ray diffraction, backscattered electron imaging, and energy-dispersive X-ray spectroscopy. It was discovered that raising the Al content of the alum sludge efficiently prevented the composition of harmful Calcium-rich, low-flowing ASR gels. Furthermore,

inhibitory impact was ascribed to the alkaline binding capacity and the extra precipitation of calcium aluminum silicate hydrate phases, which occurs from plentiful aluminum into the binder [67].

Weiwei *et al.*, (2023) investigated the alkaline-activated materials (AAMs). It was also advanced as a carbon-reducing alternative binder to cement. However, because of their high alkaline content, AAMs based on GGBS have a elevated risk of ASR when used with amorphous silica-rich aggregates. The purpose of the study was to determine whether alkali-silica reaction (ASR) in mortars containing highly reactive glass aggregate might be reduced by using alum water treatment residue (AWTR) as a precursor in slag-based alkali-activated materials (AAM). After 28 days of accelerated testing, the results indicated that adding 40% AWTR increased the mortars' compressive strength and decreased the expansion brought on by ASR. Backscattered electron imaging and energy-dispersive X-ray spectroscopy were used in the investigation to better understand the nature of ASR products. These microscopic investigations demonstrated that ASR products generated in two stages: first, the reaction induced cracking, and then the ASR gel extruded into the existing fractures, causing severe damage to the mortar matrix. AWTR was integral in minimizing the amount of silica integrity loss. To attain this, an aluminium (Al) coating was added to the surface of the aggregate. The Al layer served to protect the ASR gel from volatile transformation into calcified forms and produced lesser possibilities of harmful crystalline ASR products [26].

Thomas (2001) explained that Silica fume (SF) is the method of control of harmful damage caused by Alkali-Silica reaction (ASR) in concrete. It was held that the use of silica fume depends on both nature of reactive aggregates as well as the alkaline content available in the concrete. This study used blown cement, low-alkali po nders Stone cement and silica fume. This method provided a reasonable solution to reducing expansions in concrete with possibly reactive particles [24].

Gisli *et al.*, (1999) demonstrated that The properties of silica fume, obtained from the production of ferrosilicon alloy, were not uniform. Further, carbon concentration of the silica fume in each production cycle demonstrated great discrepancies. Hence, this caused significant changes to the color of the silica fume produced, based on carbon content fluctuation. The darker shades of colors were found due to a higher carbon-content in the silica-fume whereas less carbon in silica was found to be gray.

In this work, concrete and mortar specimens were developed using undensified silica fume that was collected from various phases of the production cycle at Icelandic Alloys Ltd. ferrosilicon plant in Grundartangi, Iceland. The concrete and mortar samples used aggregates that have been extensively characterized and their ASR behaviour is documented. The experiments used Portland cement CEM I with silica fume application between 3.5% and 7.5%. Testing according to the ASTM C1260 procedure does not affect the pozzolanic effectiveness of silica fume as amount of carbon in it. The tests also proved that undensified silica fume would produce results equivalent to the densified silica fume pozzolanic action [68].

Stokes (2013) demonstrated a methodology with which to produce concrete free of adverse impacts associated with alkali-silica reactivity. This procedure comprised incorporating admixture into the concrete mixture, which included water, firstly lithium-containing materials in an amount adequate to control the ASR, and secondly lithium-containing materials in an amount sufficient to control the set time. Optionally, mineral and chemical admixtures with enhanced qualities unrelated to ASR mitigation and/or set time should be managed. This method resulted in the stabilized concrete. An additive for stabilizing concrete against ASR has also been provided [69].

Thomas and his colleagues (2003) explained the capacity of lithium-based chemicals to reduce the harmful expansion produced by the alkali-silica reaction (ASR) in mortar and concrete. This study explored the use of a chemical admixture to prevent the ASR. This investigation was conducted to identify a chemical additive based on lithium admixture. This altered the characteristics of both fresh and hardened concrete of administered dose levels necessary to control ASR growth. That was accomplished by comparing the fresh and cured concrete qualities of various combinations containing and excluding the admixtures. Furthermore, the study used constituent materials and concrete mixture proportions permitted for structural Concrete in a large highway projects. That materials consisted of Type II Portland cement, Class F FA, a reactive aggregate, & water-reducing & air-entraining additives. Concrete had a H₂O-to-cementitious material ratio of around 0.35. That tested concretes had whichever no air entrainment or air contents ranging from 6% to 8%, slump values of 100 millimeter to 125 millimeter, and strengths ranging from 32 MPa to 36 MPa. This study looked at the

amounts required to effectively prevent ASR expansion and found that even at dosages more than 10 liters per cubic meter, there was no negative influence on their characteristics of fresh & hardened concrete. Furthermore, the measured slump, air content, and setting time of plastic concrete were all insignificant [70].

Zdzisława and his co-workers (2022) explained that the efficacy of specific chemical admixtures and mineral additions in reducing the alkali-silica reaction. This was evaluated to reactive gravel aggregates. The Li compounds, in the form of polysilicate, were utilized as chemical additives. Natural pozzolans with zeolites acted as mineral additives. Modifying these compounds with ammonium ions improved their efficiency. Linear changes in mortars containing crushed gravel aggregates were examined utilizing both expedited and long-term approaches. In addition, SEM were utilized to observe microstructures. It was explained that the used lithium compounds gave superior shield at elevated temperatures. Beneath field-like conditions, 20-30% age natural pozzolans found to be more effectual in mitigating growth. Regardless of the protective strategy, alkali-silica reaction products have been identified in the microstructure of the mortars [71].

Dayou *et al.*, (2024) illustrated that There are numerous strategies for mitigating ASR; lithium salts have proven the most effective, albeit they can interfere with cement hydration and influence shrinkage behavior. Magnesium nitrate was investigated as a possible option. Experiments were carried out on mortar mixes containing reactive aggregate, with magnesium-to-alkali (Mg/alkali) ratios ranging from 2 to 3.0. The results showed that a Mg/alkali ratio of 0.74 significantly reduced the detrimental effects of ASR. ASR-induced expansion was reduced by 21.1% age, whereas surface fracture density decreased by 34.3percent. The study also discovered that the production of ASR gel, which is the primary source of the harmful expansion, aids in the management of silica dissolution from reactive aggregates. This shows that magnesium nitrate not only alleviates the physical symptoms of ASR, but also influences the chemical events that occur. The underlying mechanisms were subsequently investigated at various length scales to better understand how $MgNO_3$ affects ASR, shedding light on its potential as an alternative chemical therapy for ASR in concrete [72].

Kaladharan (2023) and his coworkers demonstrated in recent study, eight feasible calcium and magnesium salts were found from over 700 probable candidates

utilizing a systematic approach for their ability to mitigate the alkali-silica reaction (ASR) by lowering the pH of concrete pore solution. This research assessed the performance of these admixtures in paste, mortar, and concrete mixtures. Paste mixtures were utilized to determine the long-term pH of pore solutions over a six-month period, as well as pore size distribution. Flow, flow retention, setting time, and drying shrinkage were all measured using mortar mixtures. The ASR mitigation capacity of these admixtures was evaluated in a concrete prism test using a highly reactive material. Concrete mixtures were then created to meet specified performance goals and tested for slump, plastic air content, compressive strength, and bulk resistivity. The salts successfully maintained a lower pore solution pH throughout time. The pore size properties were found to be comparable to or better than those of the control mixture. The salts efficiently reduced ASR and had little effect on workability, air content, or compressive strength (CS). Most of the salts functioned as set accelerators. Drying shrinkage was slightly higher than the control, although it remained in limitations set by the regulations. Overall, it was summarized that these pH-reducing admixtures may be employed with little changes to the concrete mixture proportioning to consistently reduce ASR [47].

Yuhai and his co-workers (2014) illustrated that lithium salts were recognized to have a remarkable effect in suppressing the alkali-aggregate reaction, but their impact on cement paste strength and setting time was unknown. The goal of this study was to use electrical resistivity measurements and other methods to explore the effect of lithium sulfate strength & setting time of regular Portland cement paste. It was demonstrated that lithium sulfate expedited the cement hydration reaction, reduced setting time, and increased strength at both early and long-term ages. Furthermore, the development of electrical resistivity in different samples with varying dosages of lithium sulfate was indicated as a set and hardening accelerator in conventional Portland cement paste, with greater dosages having a stronger effect. Thus, moderate quantities of lithium sulfate were discovered to be useful in modifying the setting time and boosting both early and long-term strength [73].

CHAPTER 3

METHODOLOGY

All the experimental work was done with Shaukat's research group in Building Research Station Communication and Works Department, Government of the Punjab Lahore and in the office of Geological Survey of Pakistan at Lahore. This chapter deals of three portion, having selection of material, experimental section and methodology for evaluation of engineering properties.

3.1 MATERIALS

The following materials were used in this research work:

3.1.1 LITHIUM NITRATE

Lithium nitrate of analytical Sigma Aldrich having purity 99% was used.

3.1.2 CEMENT

Ordinary Portland Cement (OPC) of Pioneer brand having grade 46 was provided by BRS which fulfilled British standard BS 12 [74]. The term "grade 46" refers to the cement's compressive strength, which was at least 46 MPa.

3.1.3 AGGREGATES

Two type of aggregate were being used. One is fine aggregate which was obtained from Ravi River near Ravi Toll Plaza, Lahore. Whereas, Coarse Aggregate from the Sargodha quarry was sourced during execution of Multi-Storey Flats/Suites project near the Building Research Station Lahore. This aggregate was selected for its strength, workability, durability, and appropriate grading, which ensured minimal voids in the concrete mix.

3.1.4 WATER

Fresh water was used during the experiment

3.2 APPARATUS

Te following apparatuses were used during the experiment, as listed below:

- Weighing Balance
- Iron mould having dimensions 6x6x6

- Mechanical full load mixture
- Water curing tank
- Compressing Testing machine
- SEM
- Petroleum Ether Extraction
- Mortar Bar Test
- CPTs
- ACPT

3.3 GENERAL PROCEDURE FOR PREPARATION OF CONCRETE CUBE

The procedure followed was based on the protocol outlined in the literature, specifically British Standard BS 1881, for making concrete cubes to determine their compressive strength [75]. The step-by-step procedure is described as follows:

3.3.1 PREPARATION OF CONCRETE MIX

The first step involved preparing a homogenized concrete mixture composed of cement, sand, and aggregate in a 1:2:4 ratio, respectively. Tap water free from salt (hard water) was added to these ingredients to create a concrete paste. The concrete matrix was thoroughly mixed in a full-load mechanical concrete mixer to ensure uniform distribution of materials.

3.3.2 CASTING OF CONCRETE CUBES

Once the concrete mix was ready, it was poured into iron molds to form concrete cubes of standard dimensions, typically adhering to specifications such as 6x6x6. The molds were filled with the concrete mix in three layers, each compacted with 25 hammer strokes to remove air voids and leveled off to create a smooth surface. The cast cubes were left at room temperature for 24 hours to allow for initial setting.

3.3.3 CURING OF CONCRETE CUBES

After 24 hours, the cast concrete cubes were removed from the iron molds and placed in a water tank for curing. The cubes were cured under controlled conditions at room temperature for 7 and 14 days. The moist condition of the environment can be maintained using water curing to help hydrate and increase the durability of the concrete.

3.3.4 COLLECTION OF CONCRETE CUBES

After the provided curing period of 7, 14 and 28 days were over, the concrete cubes were gently pulled out of the water tank. Particular care was provided to lift them without risking any damage that could affect the test results.

3.4 COMPRESSIVE STRENGTH TEST

The concrete specimens were transported to the laboratory for testing. The first test performed was the compressive strength evaluation where the strength of a given concrete cube breaking under pressure was measured. Maintaining the structural integrity and qualities of the concrete, therefore, is one of the key objectives of this test.

3.4.1 DETERMINATION OF COMPRESSIVE STRENGTH

In the laboratory, each concrete cube was placed in a Compression Testing Machine. The machine applied a gradual and uniform load on the cube until it fractured. The load at which the cube failed was recorded, and the compressive strength was calculated using the formula:

Compressive strength in psi = Maximum load in lbs / Cross-sectional area of the cube in inches

3.4.2 ANALYSIS AND REPORTING

Once the compressive strength tests were completed for all concrete cubes, the results were analyzed to assess the performance of the concrete mix. Compressive strength values obtained were compared against relevant standards or specifications to determine compliance, and comprehensive results were calculated.

3.5 GENERAL PROCEDURE OF ACCELERATED MORTAR

BAR TEST

This test was performed according to procedure as reported in ASTM C 1260 [76]. For this purpose, the aggregate collected from sakhi sarwar quarry retained sieve no 8,16,30 was obtained and crushed it like sand particle size to mixed with ordinary Portland cement to prepare mortar bar having size 25mmX285mm with different %age of LiNO_3 . The casted mortar bar were removed from iron mould after 24 hours. The un moulded samples were placed in water curing tank for 24 hours at 72-80°C to accelerate alkali silica reaction. Then the immersed sample were removed from water after 24 hours to measure initial reading by comparator. To provide the more severe condition then field environment, the mortar bar than stored in 1N NaOH solution to provide the media of instant source hydroxyl and sodium ion. The final length of mortar bar was measured for 7, 14 and 28 days. Percentage expansion of mortar bar was calculated with the help of following formula:

$$\text{Mortar bar expansion(\%)} = (L_n - L_o) / L_c * 100$$

3.6 GENERAL PROCEDURE FOR CONCRETE PRISM AND ACCELERATED CONCRETE PRISM TEST

The CPT and ACPT was carried out to evaluate the concrete mixture sustainability towards alkali silica reaction as reported in literature protocol. Step wise procedure as follow:

3.6.1 MATERIAL SELECTION

Material like aggregate was collected from sakhi sarwar quarry . The ordinary Portland cement of pioneer company was used, and LiNO_3 was used as a admixture to measure the effectiveness of ASR mitigation.

3.6.2 CONCRETE MIX DESIGN

The concrete mix was obtained by mixing cement aggregate and additive. The water was added to maintain the water cement ratio in range of 0.422:5.0 to prepare various badges of concrete mix.

3.5.3 PRISM CASTING

Concrete mix was moulded into prism having size 75x75x285mm by maintaining compaction. The mould was covered to prevent moisture loss and put them at room temp for 24 hours.

3.6.4 PRISM CURING

The prisms were cured after demoulding in water curing tank at room temp for 24 hours.

3.6.5 MEASUREMENT OF LENGTH

The prism initial length was measured with the help of length comparator which was recorded as a base line for further expansion measurement.

3.6.6 ACCELERATED CONDITION FOR PRISM

The cured prism were placed in 1N NaOH solution. To accelerate ASR process at room temperature.

3.6.7 MONITORING & MEASUREMENT

The prism length was measured periodically at the age of 7, 14, 28, 56days and 3 months by using length comparator.

3.6.8 CALCULATION OF RESULTS

The expansion % of each prism was calculated to compare prism expansion results with and without lithium nitrate additive to assess the potential for ASR damage.

The demand of the use of various SCMs is increasing day by day in the concrete to mitigate the potential effect of alkali silica reaction. Because different deleterious chemical reactions occur between reactive silica of aggregate and alkali hydroxide of concrete. Due to these reactions expansion in concrete take place which lead to devolp gradually by damaging the infrastructure devolpment (building structure).

CHAPTER 4

RESULTS

Table 4.1: Determined compressive strength against specified crushing strength 2000 psi@07
Days as per BS 1881 part 225.

Cube No	Mix Ratio	Cross Sectional Area in inches	Addition of LiNO ₃ by weight in %age	Load Applied in lbs	Determined Compressive Strength in psi
1	1:2:4	36	—	61,700	1714
2	1:2:4	36	0.5	64,700	1797
3	1:2:4	36	0.75	66,000	1835
4	1:2:4	36	1	68,300	1897
5	1:2:4	36	1.5	68,800	1911
6	1:2:4	36	2	69,500	1930
7	1:2:4	36	2.5	70,000	1944
8	1:2:4	36	3	70,600	1961
9	1:2:4	36	3.5	71,600	1988
10	1:2:4	36	4	72,200	2005
11	1:2:4	36	4.5	72,800	2022
12	1:2:4	36	5	73,300	2036

Table 4.2 : Determined compressive strength against specified crushing strength 3000 psi@28
Days as per BS 1881 part 225.

Cube No	Mix Ratio	Cross Sectional Area in inches	Addition of LiNO ₃ by weight in %age	Load Applied in lbs	Determined Compressive Strength in psi
1	1:2:4	36	—	93,600	2600
2	1:2:4	36	0.5	95,800	2662
3	1:2:4	36	0.75	100,100	2781
4	1:2:4	36	1	100,800	2800
5	1:2:4	36	1.5	102,000	2834
6	1:2:4	36	2	103,200	2865
7	1:2:4	36	2.5	104,000	2888
8	1:2:4	36	3	104,400	2900
9	1:2:4	36	3.5	106,200	2950
10	1:2:4	36	4	108,100	3001
11	1:2:4	36	4.5	109,800	3050
12	1:2:4	36	5	110,300	3066

Table 4.3: Classification of cement, aggregate and water combination with varying dose of LiNO_3 and ASR expansion.

Material Combination	% Lithium Nitrate	% expansion after 7 days	% expansion after 14 days	% expansion after 28 days
Agg. + OPC + water	—	0.15	0.191	0.412
Agg. + OPC + water	0.50	0.14	0.189	0.324
Agg. + OPC + water	0.75	0.11	0.160	0.30
Agg. + OPC + water	1.00	0.10	0.160	0.280
Agg. + OPC + water	1.50	0.90	0.154	0.275
Agg. + OPC + water	2.00	0.80	1.150	0.270
Agg. + OPC + water	2.50	0.75	0.130	0.260
Agg. + OPC + water	3.00	0.7	0.140	0.256
Agg. + OPC + water	3.50	0.1	0.123	0.248
Agg. + OPC + water	4.00	0.068	0.076	0.196
Agg. + OPC + water	4.50	0.016	0.024	0.168
Agg. + OPC + water	5.00	0.008	0.019	0.152

Table 4.4: Results of concrete prism test

% Lithium Nitrate	% expansion after 7 days	% expansion after 14 days	% expansion after 28 days	% expansion after 56 days	% expansion after 3 Month
—	0.18	0.211	0.440	0.520	0.620
0.50	0.17	0.208	0.352	0.440	0.540
0.75	0.14	0.181	0.328	0.380	0.440
1.00	0.13	0.181	0.308	0.370	0.430
1.50	0.12	0.175	0.303	0.365	0.420
2.00	0.11	0.171	0.298	0.360	0.415
2.50	0.10	0.166	0.291	0.355	0.410
3.00	0.09	0.161	0.288	0.350	0.405
3.50	0.07	0.151	0.284	0.345	0.400
4.00	0.04	0.144	0.276	0.330	0.385
4.50	0.02	0.094	0.224	0.260	0.310
5.00	0.015	0.041	0.196	0.220	0.270

4.5: Results of accelerated concrete prism test

% Lithium Nitrate	% expansion after 7 days	% expansion after 14 days	% expansion after 28 days	% expansion after 56 days	% expansion after 3 Month
—	0.100	0.19	0.35	0.48	0.58
0.50	0.081	0.16	0.28	0.40	0.50
0.75	0.072	0.14	0.24	0.35	0.45
1.00	0.063	0.12	0.20	0.30	0.38
1.50	0.054	0.10	0.18	0.28	0.35
2.00	0.045	0.08	0.16	0.25	0.30
2.50	0.036	0.06	0.14	0.22	0.28
3.00	0.037	0.05	0.12	0.20	0.25
3.50	0.021	0.04	0.08	0.14	0.18
4.00	0.010	0.02	0.05	0.08	0.10
4.50	0.010	0.02	0.04	0.06	0.08
5.00	0.010	0.01	0.03	0.05	0.061

CHAPTER 5

DISCUSSION

The mitigation effect of lithium nitrate with various percentage on alkali silica reaction in concrete composite is discussed in this chapter. The expansion magnitude of reactive aggregate is being measured through rigorous laboratory investigation. Different trials were made on the same type of aggregate collected from Sakhi Sarwar quarry and ordinary Portland cement along with various percentage of lithium nitrate. For this purpose different laboratory tests such as compressive strength test, mortar bar test, concrete prism test, accelerated concrete prism test are performed to measure the percentage expansion in concrete specimen due to formation of lysilica gel in response of alkali silica reaction. The surface microstructure of selected concrete specimen was examined by scanning electron microscopy. Test wise discussion is depicted as under.

5.1 COMPRESSIVE STRENGTH

The twelve concrete matrixes were prepared containing lithium nitrate from 0-5%. The 24 concrete cubes were casted in order to determine their compressive strength through CTM in laboratory. The compressive strength of 12 concrete cubes was determined at the age of 7 days whereas 12 cubes were evaluated at the age of 28 days. The result of compressive strength of prepared sample at the age of 7 days and 28 days are depicted in table 4.1 and 4.2 respectively. The cube number 1 was casted with concrete matrix without the addition of lithium nitrate which was referred as controlled sample and its compressive strength was determined as 1714 psi which is too much less than standard strength 2000psi at the age of 7 days. However cube no 2-9 containing lithium nitrate ranging from 0.5 to 3.5% exhibited compressive strength 1797psi to 1988 psi. Whereas, cube no 9-12 showed compressive strength 2005 to 2035 psi fulfilling the specified compressive strength. It was observed that the addition of lithium nitrate admixture in concrete matrix did not remarkably affect the concrete strength. However it is useful to reduce the potential rate of alkali silica reaction which is chemically hazardous for concrete. It was observed that the use of lithium nitrate in ranging of 0.5 – 3.5 revealed meager effect on alkali silica reaction whereas the dosage percentage of lithium nitrate from

4-5% was very significant to control the alkali silica reaction by arresting expansion formed due to OPC aggregate combination reaction.

Similarly at the age of 28 days the compressive strength of prepared concrete cube was evaluated the specified compressive strength of concrete cube is 3000 psi at the age of 28 days. 12 cubes were prepared containing lithium nitrate from 0 to 5% and their compressive strength was determined at the age of 28 days. Cube no 13 was casted without lithium nitrate referring as controlled sample which showed less compressive strength 2600 psi as compared with standard strength. Cube no 14-21 having percentage of lithium nitrate from 0.5 to 3.5 revealed 2662psi to 2950psi against 3000psi. The compressive strength of these cubes did not meet the specified crushing strength as per BS 1881. However, cube no 22-24 gave 3001 to 3066 psi compressive strength which meet the standard specification. It was noted that the results mentioned in table 4.1 and 4.2 showed similar trend in increasing compressive strength at the age of 7 and 14 days respectively. The addition of LiNO_3 did not increase compressive strength. It only inhibited the rate of alkali silica reaction which reduces the compressive strength of concrete.

5.2 ACCELERATED MORTAR BAR TEST

The laboratory investigation was carried out to measure the percentage expansion cause by reactive aggregate in mortar bar. LiNO_3 in various %age was used with the same category of aggregate and OPC. Different attempts were performed to explore the mitigating potential of lithium nitrate through AMBT method. The percentage expansion in mortar bar specimen containing 0 to 5 % LiNO_3 was measured after specified days. The test results of percentage expansion with different %age of lithium nitrate for 7, 14 and 28 days are mentioned in table 4.3. The test results reveals that the effect of using LiNO_3 from 0.5 to 3.5% has non significant to inhibit alkali silica reaction at the age of 7 days. The alkali silica mitigation effect is seen significantly in mortar bar containing 0.4 to 5%.

Likewise %age expansion in mortar bar along with lithium nitrate percentage ranging 0 to 5% was measured at the age of 14 days and 28 days to explore the inhibiting ability of alkali silica reaction. The mortar bar of concrete composite made up of OPC aggregate and water was considered as reference sample. Whereas, other mortar bar containing 0.5 to 5% LiNO_3 were referred as test sample. The measured

percentage expansion of all the prepared mortar bar specimen indicates that alkali silica mitigation effect remain non significant upto 3.5% lithium nitrate at the age of 14days and 28 days. Whereas, it becomes significant between 4 to 5% LiNO_3 . In accordance to obtained my research results, Ravi and coworker (2017) have reported that the combination of reactive aggregate OPC water containing 10-20% lithium nitrate are effective to mitigate alkali silica reaction at the age of 14 days [77]. They recommended that the use of high %age of lithium nitrate is significant to inhibit ASR reaction. It might be due to high content of reactive silica present in aggregate which they used. In comparison to literature reported result only 4 to 5% lithium nitrate is sufficient to mitigate the effect of alkali silica reaction which might be due to presence of less reactive silica content in used aggregate.

5.2 CONCRETE PRISM TEST

The data from the Concrete Prism Test reveal that expansion decreases as the dosage of lithium nitrate increases, as shown in Table 4.4. At 0% lithium nitrate (control), the expansion is considerable, starting at 0.18% after 7 days and expanding to 0.620% after 3 months. As the dosage of lithium nitrate is steadily increased, the expansion continuously decreases, showing successful suppression of the Alkali-Silica Reaction (ASR). For instance, at 0.50% lithium nitrate, the expansion is slightly reduced than the control, at 0.17% after 7 days and 0.540% after 3 months. As the dosage rises to 3.00%, the expansion after three months decreases to 0.405%. The most significant reduction occurs at 5.00% lithium nitrate, where the expansion is reduced to 0.015% after 7 days and remained low at 0.270% after 3 months. It indicates that greater doses of lithium nitrate are more effective in reducing ASR, with the effect increasing over time.

In the Accelerated Concrete Prism Test, the decrease in expansion with increasing lithium nitrate dosage is considerably more prominent, most likely due to the accelerated conditions emphasizing the impact of lithium nitrate more immediately. The control (0% lithium nitrate) reveals an early growth of 0.10% after 7 days, which increases to 0.58% after three months. At 0.50% lithium nitrate, the growth decreases to 0.08% after 7 days and 0.50% after 3 months. As the dosage increases to 3.00%, the expansion after 3 months decreases to 0.25%. The most substantial reduction occurs at 5.00% lithium nitrate, with expansion nearly eliminated at 0.01%

after 7 days and 0.06% after 3 months. This shows that accelerated testing conditions may better demonstrate the ability of lithium nitrate to suppress ASR, with larger dosages resulting in significantly smaller expansions over time.

CHAPTER 6

CONCLUSION

The research work presented in this thesis is about the “Effect of lithium nitrate to inhibit alkali silica reaction. In this dissertation, four different laboratory tests comprising of compressive strength test, mortar bar test, concrete prism test and accelerated concrete prism test were performed to exploit the inhibiting effect of LiNO_3 on alkali silica reaction occurring between reactive aggregate and ordinary Portland cement. Scanning electron microscopy was applied for surface micro structural analysis on selected concrete specimens.

24 concrete cubes were casted by using a combination of ordinary Portland cement (OPC), aggregate, water and varying percentages of lithium nitrate (0-5%) to assess their compressive strength at the ages of 7 and 28 days. The obtained results indicated that concrete cube without lithium nitrate exhibited lower compressive strength 1714 psi after 07 days curing and 2600 psi after 28 days against 2000 psi and 3000 psi respectively. Particularly up to 3.5% dosage of LiNO_3 showed did not meet standard criteria. However, concrete containing 4-5% lithium nitrate achieved higher compressive strength that fulfills 3000 psi requirement. Addition of lithium nitrate only effectively reduced potential effect of ASR.

The reactivity of the aggregate and the effect of using OPC and lithium nitrate were further evaluated by using AMBT. The results showed that a 0.5-3.5% dosage of lithium nitrate had a non-significant affect on ASR. However, at higher dosages (4-5%), lithium nitrate was effective in controllinn g ASR, reducing expansion caused by the aggregate-OPC reaction by 90% to 95%.

Both the Concrete Prism Test (CPT) and Accelerated Concrete Prism Test (ACPT) demonstrated the efficiency of lithium nitrate in reducing expansion. The control sample, containing 0% lithium nitrate, exhibited the highest expansion, reaching 0.620% after 3 months. As the lithium nitrate dosage increased, the expansion significantly decreased, with a 5% dosage showing a much lower expansion of 0.270%. Particularly effective dosages were between 4% and 5%, which significantly reduced expansion from 0.385% to 0.270%. The ACPT results mirrored

the CPT, with the control sample expanding by 0.580% after 3 months, while 5% lithium nitrate dosage reduced expansion to just 0.061%. This consistent reduction in expansion with increasing lithium nitrate dosage highlights its effectiveness in controlling ASR, thereby enhancing the durability of concrete.

REFERENCES

1. Dahyabhai PM, Jayeshkumar RP. Introducing the self-curing concrete in construction industry. *J IERT*. 2014;3(3).
2. Jin R, Chen Q, eds. An investigation of current status of “green” concrete in the construction industry. 49th ASC Annu Int Conf Proc; 2013.
3. Demirboğa R, Gül R. Production of high strength concrete by use of industrial by-products. *Build Environ*. 2006;41(8):1124-7.
4. Gjorv OE. Durability of concrete structures. *Arab J Sci Eng*. 2011;36:151-72.
5. Mackechnie J, Alexander M. Using durability to enhance concrete sustainability. *J Green Build*. 2009;4(3):52-60.
6. Esposito R, Hendriks M. Literature review of modelling approaches for ASR in concrete: a new perspective. *Eur J Environ Civ Eng*. 2019;23(11):1311-31.
7. Beaver J, Jiang L, Sherman M. Inspection and monitoring of ASR-affected structures at Seabrook Station, NH. 2013.
8. Diamond S. Alkali aggregate reactions in concrete. An annotated bibliography 1939-1991. 1992.
9. Venkatachalam S, Raja K, Vishnuvardhan K, Suchithra S, Maniarasan S, Saravanan M, et al. The ASR mechanism in concrete and the influence of lithium in mitigating it: A critical review. *Mater Today Proc*. 2022;65:A1-A6.
10. Stanton TE. Expansion of concrete through reaction between cement and aggregate. 1940.
11. Wang X, Nguyen M, Stewart M, Syme M, Leitch A. Analysis of climate change impacts on the deterioration of concrete infrastructure—Part 1: Mechanisms, practices, modelling and simulations—A review. Published by CSIRO, Canberra; 2010. ISBN: 9780(4310365):8.
12. Ichikawa T, Miura M. Modified model of alkali-silica reaction. *Cem Concr Res*. 2007;37(9):1291-7.
13. Hair ML. Hydroxyl groups on silica surface. *J Non-Cryst Solids*. 1975;19:299-309.
14. Swamy RN. The alkali-silica reaction in concrete. Blackie Glasgow; 1992.
15. Godart B, de Rooij MR, Wood JG. Guide to diagnosis and appraisal of AAR damage to concrete in structures. Springer; 2013.

16. Dron R, Brivot F. Thermodynamic and kinetic approach to the alkali-silica reaction. Part 1: Concepts. *Cem Concr Res.* 1992;22(5):941-8.
17. Asadollahfardi G, Yahyaei B, Salehi AM, Ovesi A. Effect of admixtures and supplementary cementitious material on mechanical properties and durability of concrete. *Civ Eng Des.* 2020;2(1-2):3-11.
18. Snellings R, Mertens G, Elsen J. Supplementary cementitious materials. *Rev Mineral Geochem.* 2012;74(1):211-78.
19. Schneider M, Romer M, Tschudin M, Bolio H. Sustainable cement production—present and future. *Cem Concr Res.* 2011;41(7):642-50.
20. Saraswatula P, Mukhopadhyay A, Liu K-W. Development of a screening tool for rapid fly ash evaluation for mitigating alkali silica reaction in concrete. *Transp Res Rec.* 2022;2676(11):583-95.
21. Hay R, Ostertag CP. New insights into the role of fly ash in mitigating alkali-silica reaction (ASR) in concrete. *Cem Concr Res.* 2021;144:106440.
22. Ramjan S, Tangchirapat W, Jaturapitakkul C, Chee Ban C, Jitsangiam P, Suwan T. Influence of cement replacement with fly ash and ground sand with different fineness on alkali-silica reaction of mortar. *Mater.* 2021;14(6):1528.
23. Hooton R. Influence of silica fume replacement of cement on physical properties and resistance to sulfate attack, freezing and thawing, and alkali-silica reactivity. *Mater J.* 1993;90(2):143-51.
24. Thomas M. Using silica fume to combat ASR in concrete. *Indian Concr J.* 2001;75(10):671-6.
25. Banik D, He R, Lu N, Feng Y. Mitigation mechanisms of alkali silica reaction through the incorporation of colloidal nanoSiO₂ in accelerated mortar bar testing. *Constr Build Mater.* 2024;422:135834.
26. Duan W, Zhuge Y, Chow CW, Keegan A, Liu Y, Merta I. Mitigation of alkali-silica reaction in blast-furnace slag-based alkaline activated material through incorporation of alum water treatment residue. *Constr Build Mater.* 2023;406:133383.
27. Ban J, Fan D, Li K, Yao J, Lu J-X, Wang Z, et al. Mechanisms on the inhibition of alkali-silica reaction in supersulfated cement. *Cem Concr Compos.* 2024;145:105320.

28. Li C, Ideker JH, Drimalas T, editors. The efficacy of calcined clays on mitigating alkali-silica reaction (ASR) in mortar and its influence on microstructure. *Calcined Clays for Sustainable Concrete: Proceedings of the 1st International Conference on Calcined Clays for Sustainable Concrete*. 2015: Springer.
29. Demir İ, Sivrikaya B, Sevim O, Baran M. A study on ASR mitigation by optimized particle size distribution. *Constr Build Mater*. 2020;261:120492.
30. Ferreira R, Castro-Gomes J, Costa P, Malheiro R. Effect of metakaolin on the chloride ingress properties of concrete. *KSCE J Civ Eng*. 2016;20:1375-84.
31. Tapas MJ, Sofia L, Vessalas K, Thomas P, Sirivivatnanon V, Scrivener K. Efficacy of SCMs to mitigate ASR in systems with higher alkali contents assessed by pore solution method. *Cem Concr Res*. 2021;142:106353.
32. Bu S-z, Zheng Y-l, Lu C-h, Cheng L. Efficient inhibition of ASR by microbially induced calcium carbonate precipitation on aggregates at a low degree of saturation. *J Build Eng*. 2024;84:108516.
33. Ong F, Seiler P, Myers M, Bury M, Larch T, Atienza J, et al. Comparison of ASR mitigating effects of Ca²⁺ using three different test methods.
34. Lu C-H, Bu S-z, Shahin MA, Zheng Y-l, Cheng L. Mitigation of alkali-silica reaction by microbially induced CaCO₃ protective layer on aggregates. *Constr Build Mater*. 2022;328:127065.
35. Balouchkhaneh SA, Shahnava B, Moghaddam AM, Karrabi M. Mitigating alkali-silica reaction in cement mortars through microbial carbonate precipitation technique. *Constr Build Mater*. 2023;367:130155.
36. Tapas MJ. Role of supplementary cementitious materials in mitigating alkali-silica reaction: *Univ Technol Sydney (Australia)*; 2020.
37. Doğruyol M. Determination of ASR in concrete using characterization methods. *Buildings*. 2024;14(3):657.
38. Yang Y, Lu P, Shao R, Zhao Q, Yang T, Wu C. A comprehensive review of multisource solid wastes in sustainable concrete: From material properties to engineering application. *Constr Build Mater*. 2024;435:136775.

39. Ahmed A, Ameer S, Abbas S, Abbass W, Razzaq A, Mohamed AM, et al. Effectiveness of ternary blend incorporating rice husk ash, silica fume, and cement in preparing ASR resilient concrete. *Mater.* 2022;15(6):2125.
40. Barreto Santos M, De Brito J, Santos Silva A. A review on alkali-silica reaction evolution in recycled aggregate concrete. *Mater.* 2020;13(11):2625.
41. Attoh-Okine N, Atique F. Service life assessment of concrete with ASR and possible mitigation. Del Cent Transp, Univ Delaware: Newark, DE, USA. 2006.
42. Xiao R, Prentice D, Collin M, Balonis M, La Plante E, Torabzadegan M, et al. Calcium nitrate effectively mitigates alkali-silica reaction by surface passivation of reactive aggregates. *J Am Ceram Soc.* 2024.
43. Falzone GD, Oey T, Franke W, Seiler P, La Plante EC. Mitigation of alkali-silica reaction in concrete using readily-soluble chemical additives. Google Patents; 2022.
44. Oey T, La Plante EC, Falzone G, Hsiao Y-H, Wada A, Monfardini L, et al. Calcium nitrate: A chemical admixture to inhibit aggregate dissolution and mitigate expansion caused by alkali-silica reaction. *Cem Concr Compos.* 2020;110:103592.
45. Wang W, Noguchi T, Maruyama I. Mitigation effect of lithium nitrate on the alkali-silica reaction in alkali-activated slag mortars. *Cem Concr Compos.* 2022;130:104532.
46. Kim T, Olek J, Jeong H. Alkali-silica reaction: kinetics of chemistry of pore solution and calcium hydroxide content in cementitious system. *Cem Concr Res.* 2015;71:36-45.
47. Kaladharan G, Rajabipour F. Performance evaluation of novel alkali-silica reaction inhibiting chemical admixtures in cementitious systems. *J Mater Civ Eng.* 2023;35(9):04023310.
48. Zhou J, Yu B, Kong Y, Yang W, Cheng B, Wu J. Effect of calcium hydroxide on the microstructure and performance of super sulfated cement. *Ceram-Silikaty.* 2022;66(1):85-94.
49. Sathya S, Manju R. Effect of lithium-based admixtures on alkali silica reaction in concrete and flexural behavior of reinforced concrete rectangular beams. *Asian J Eng Appl Technol.* 2018;7(S1):52-9.
50. Collins C, Ideker JH, Willis G, Kurtis K. Examination of the effects of LiOH, LiCl, and LiNO₃ on alkali-silica reaction. *Cem Concr Res.* 2004;34(8):1403-15.
51. Lumley J. ASR suppression by lithium compounds. *Cem Concr Res.* 1997;27(2):235-44.

52. Ekolu S, Thomas M, Hooton R. Dual effectiveness of lithium salt in controlling both delayed ettringite formation and ASR in concretes. *Cem Concr Res.* 2007;37(6):942-7.
53. Owsiak Z, Zapala-Slaweta J. The course of the alkali-aggregate reaction in the presence of lithium nitrate. *Ceram-Silikaty.* 2013;57(2):138-45.
54. Folliard KJ, Thomas MD, Fournier B, Kurtis KE, Ideker JH. Interim recommendations for the use of lithium to mitigate or prevent alkali-silica reaction (ASR). US Fed Highway Admin Off Infrastruct; 2006.
55. Mo X, Zhang Y, Yao J, Li G, Feng Y. Influence of various parameters on Li_2CO_3 against alkali-silica reaction. *Constr Build Mater.* 2008;22(8):1668-74.
56. Fernandes I, Broekmans MA. Alkali-silica reactions: an overview. Part I. *Metallogr Microstruct Anal.* 2013;2:257-67.
57. Duvnjak I, Klepo I, Serdar M, Damjanović D. Damage assessment of reinforced concrete elements due to corrosion effect using dynamic parameters: A review. *Buildings.* 2021;11(10):425.
58. Vacher M, Jacobsen S. Empirical modelling of lithium mitigation for alkali-silica reactivity. *Nord Concr Res.* 2022;67(2):1-14.
59. Ekolu S, Tchadjié L, Naghizadeh A, editors. Alkali-silica reaction resistance versus susceptibility of geopolymer binders. *MATEC Web Conf*; 2022: EDP Sci.
60. Kaladharan G, Szeles T, Stoffels SM, Rajabipour F. Novel admixtures for mitigation of alkali-silica reaction in concrete. *Cem Concr Compos.* 2021;120:104028.
61. Carpenter AJ, Cramer SM. Mitigation of ASR in pavement patch concrete with highly reactive fine aggregate. *Transp Res Rec.* 1999;1668(1):60-7.
62. Munir MJ, Kazmi SMS, Khitab A, Hassan M, eds. Utilization of rice husk ash to mitigate ASR in concrete. *Proc 2nd Int Multidisc Conf*; 2016: Univ Lahore, Gujrat Campus Pakistan.
63. Salas Montoya A, Chung C-W, Kim J-H. High performance concretes with reactive rice husk ash and silica fume. *Mater.* 2023;16(11):3903.
64. Ramlochan T, Thomas M, Gruber KA. Effect of metakaolin on ASR in concrete. *Cem Concr Res.* 2000;30(3):339-44.

65. Luo D, Sinha A, Adhikari M, Wei J. Mitigating ASR through metakaolin-based internal conditioning: Insights into property evolution and mitigation mechanism. *Cem Concr Res.* 2022;159:106888.
66. Amirjani MJ, Maleki A, Ramezani-pour AM. Effectiveness of sewage sludge ash and natural pozzolans in controlling ASR. *Struct Concr.* 2024.
67. Duan W, Zhuge Y, Liu Y, eds. Effect of blending alum sludge and GGBFS as cement replacement to mitigate ASR. *Int Conf Variability Sun & Sun-like Stars; 2022: Springer Nature Singapore.*
68. Gudmundsson G, Möller JS, Halfdanarson J, eds. Effect of silica fume properties on ASR reactivity. *11th Int Conf Alkali Aggregate Reaction; 2000: Québec City, Canada.*
69. Stokes DB. Lithium-based concrete admixtures for controlling ASR with enhanced set-time control. *Google Patents; 2013.*
70. Brower LE, Ferraris CF. Comparison of concrete rheometers. *Concr Int.* 2003;25(8):41-7.
71. Owsiak Z, Czapik P, Zapała-Sławeta J. Methods of mitigating alkali reactivity of gravel aggregate. *Struct Environ.* 2022;14(3):102-9.
72. Luo D, Wei J. Elucidating the role of magnesium in alkali-silica reaction: Performance and mechanisms. *Constr Build Mater.* 2024;437:136935.
73. Deng Y, Zhang C, Wei X. Influence of lithium sulfate addition on the properties of Portland cement paste. *Constr Build Mater.* 2014;50:457-62.
74. Arimanwa M, Onwuka D, Arimanwa J. Effect of chemical composition of ordinary portland cement on the compressive strength of concrete. *Int J Eng Appl Sci.* 2016;5:20-31.
75. Ingham J, Barnes EIR. Briefing: Testing times for concrete structures—is BS 1881-124 still fit for purpose? *Proc Inst Civ Eng-Const Mater.* 2015;168(6):253-8.
76. Rangaraju PR, Olek J. Evaluation of the potential of densified silica fume to cause alkali-silica reaction in cementitious matrices using a modified ASTM C 1260 test procedure. *Cem Concr Aggregates.* 2000;22(2):150-9.
77. Agarwal R, Vidyarthi U, Gupta U, Sivakumar N. Alkali silica reaction (ASR) mitigation in concrete by using lithium nitrate. *Int J Eng Appl Sci.* 2017;4(3):257516.

PLAGERISM REPORT

thesis
by FAIZA QURBAN

Submission date: 06-Sep-2024 03:28PM (UTC+0500)

Submission ID: 2446454854

File name: CHAPTER_1_2.docx (405,98K)

Word count: 12458

Character count: 71206

thesis

ORIGINALITY REPORT

8%

SIMILARITY INDEX

3%

INTERNET SOURCES

7%

PUBLICATIONS

1%

STUDENT PAPERS

PRIMARY SOURCES

1

Gopakumar Kaladharan, Farshad Rajabipour. "Performance Evaluation of Novel Alkali-Silica Reaction Inhibiting Chemical Admixtures in Cementitious Systems", Journal of Materials in Civil Engineering, 2023

Publication

1%

2

vtechworks.lib.vt.edu

Internet Source

1%

3

Luo, Dayou. "Nanoengineered Clay-Based Internal Conditioning: Cement Hydration and Alkali-Silica Reaction Mitigation", University of Massachusetts Lowell, 2024

Publication

1%

4

opus.lib.uts.edu.au

Internet Source

<1%

5

Mukesh C Limbachiya, Hsein Y. Kew. "Excellence in Concrete Construction through Innovation - Proceedings of the conference held at the Kingston University, United Kingdom, 9 - 10 September 2008", CRC Press, 2019

<1%