

## EFFECT OF ADMIXTURE LITHIUM NITRATE (LiNO<sub>3</sub>) TO INHIBIT ALKALI SILICA REACTION

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### Abstract

Large-scale cracking and structural degradation over time are caused by the alkali-silica reaction (ASR), which poses a serious threat to concrete infrastructure globally. ASR in concrete structures is thoroughly examined in this review article, along with its processes, effects, and mitigating techniques. The concrete pore solution's alkalis react with reactive silica in aggregates to generate expanding gel, which starts the ASR process. Temperature, humidity, and aggregate reactivity are a few examples of variables that affect the rate and intensity of expansion spurred by ASR. ASR has a significant effect on replacing and repairing infrastructure. Additionally, corrosion and freeze-thaw damage are two more deterioration mechanisms that can be made worse by ASR-induced cracking. ASR inhibition techniques being investigated, such as the use of chemical admixtures, non-reactive aggregates, and additional cementitious materials. Due to its ability to stop ASR gel formation and silica dissolution, LiNO<sub>3</sub> presents itself as a potentially effective mitigation method when used alone or in conjunction with other approaches. Certain variables, like the composition of the concrete, the reactivity of the aggregate, and the exposure circumstances, affect how effective LiNO<sub>3</sub> is. Although it looks promising in terms of lessening ASR-induced expansion, more research and attention in concrete construction procedures are necessary given its long-term performance and cost-effectiveness. Overall, this review emphasizes the complexity of ASR in concrete structure and stresses the need of preventive mitigation techniques to guarantee the resilience and lifespan of infrastructure systems.

### Keywords

Concrete, Infrastructure, Admixture, Cracking, Aggregate.



## 1. Introduction

Cement have a crucial role in the development of buildings and economic growth. It is the primary basic component of infrastructure, an essential construction material in concrete manufacturing. However, cement-based materials are widely used in construction have numerous advantages, including high compressive strength, low manufacturing cost, thermal conductivity, sound insulation, fire resistance, and durability. But due to its disadvantages such as the permeability of concrete, thermal movement, creep movement, corrosion of reinforcement, moisture movement, improper structural design and specifications, poor maintenance the cracking occurs in any type of building which allows the penetration of moisture and alkalis into the concrete, and which in turn will accelerate the chemical reaction which is called alkali-silica reaction (ASR) which is the reaction of the reactive silica-rich aggregates when come in contact with water and alkaline solution in

the micro pores of concrete, that causes in the concrete to expands and cracks which is one of main and severe deterioration of concrete structures (Chitte & Sonawane, 2018; Ichikawa & Miura, 2007; Thagunna, 2014). A number of concrete buildings in the USA were reported to exhibit serious cracking in 1923; the cause was unknown. Stanton initially identified the "alkali-silica reaction" (ASR), a harmful reaction involving alkalis, Na, and K in the paste mixed with silica from the aggregate, in 1940 (Diamond, 1992). Since its initial discovery, deleterious ASR has been identified in numerous concrete structures and is a global issue in the field of concrete technology (Broekmans, 2012). ASR has reportedly caused damage to a number of different structures. For instance, bridge parts in Finland, Denmark, the USA, Japan, and Canada. Similarly, it has been reported that ASR has damaged a number of dam structures in Pakistan (Abbas, 2023).



**Figure 1:** Building affected due to ASR

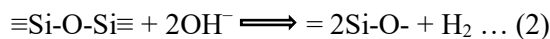
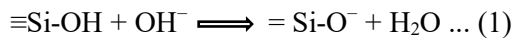
In Alkali silica reaction the expansion is the factor which is greatly affected by its surrounding

environment and local weather condition and other parameters, such as temperature and humidity which

in turn influence the chemical reaction between alkalis and silica, and causes subsequent expansion (Rahman & Lu, 2023). In the humidity environment the reactive silica and alkalis interaction results in chemical process that produces a gel that expands as moisture is absorbed and causes induced expansion and cracking in the concrete is impacted. Although ASR-affected structure collapse is rare, it can raise a number of issues with dependability and serviceability (Tragardh & Lagerblad, 1996).

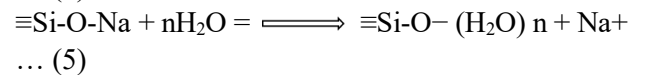
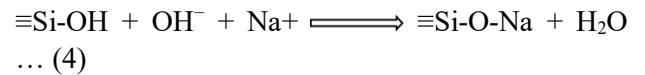
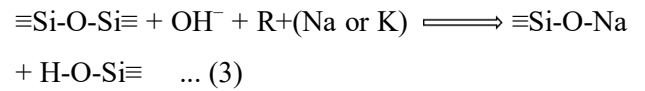
### 1.1 Mechanism of ASR

Reactive silica in aggregates and hydroxyl ions in the concrete pore solution react chemically to produce the ASR. In the aggregates, silica (SiO<sub>2</sub>) is primarily organized as siloxane groups (≡Si-O-Si≡) and is chemically inactive in the form of quartz. But because of their surface disorder, crystalline silica has a strong attraction to water, which results in the formation of amorphous hydrous silica (silanol group [≡Si-OH]) (Ichikawa & Miura, 2007). The silica(s) then tends to dissolve in the presence of highly concentrated hydroxyl ions by first neutralizing the siloxane groups (≡Si-O-Si≡) and subsequently the silanol groups (≡Si-OH), as equations 1 and 2 show (MDA Thomas, Fournier, & Folliard, 2012).



When the Si-OH and Si-O-Si structures gradually disintegrate, they also draw in the soluble alkali hydroxides, such as NaOH or KOH, that are widely distributed in the concrete pore solution (Godart, de Rooij, & Wood, 2013). The hydroxyl ions (OH<sup>-</sup>) in

the pore solution are also increased by the calcium hydroxide that is created during cement hydration. The first products of the reaction between these siloxane groups (≡Si-O-Si≡) and hydroxyl ions are alkali-silicate solution and gel (based on the moisture content) (Eq. 3). After that, as shown in Eqs. 4 and 5, the Si-OH interacts with additional OH<sup>-</sup> and alkali metals to generate alkali silicate hydrate and water (Bazant & Steffens, 2000; Godart et al., 2013; Ichikawa & Miura, 2007; Swamy, 1991).



This hydrated alkali-silicate gel diffuses through the aggregates to the cement paste, where it combines with the calcium ions in the paste to generate an alkali-calcium-silicate hydrate gel. This finished product swells as it becomes wet. The interfacial transition zone (ITZ) between the aggregate and cement paste is where an excess expansion causes cracks, which compound to cause stress and fissures in concrete structure (Dron & Brivot, 1992, 1993; Thaulow, Jakobsen, & Clark, 1996). The schematic representation of ASR chemistry in concrete structures is shown in Fig.2, which was taken from (Talley, 2009).

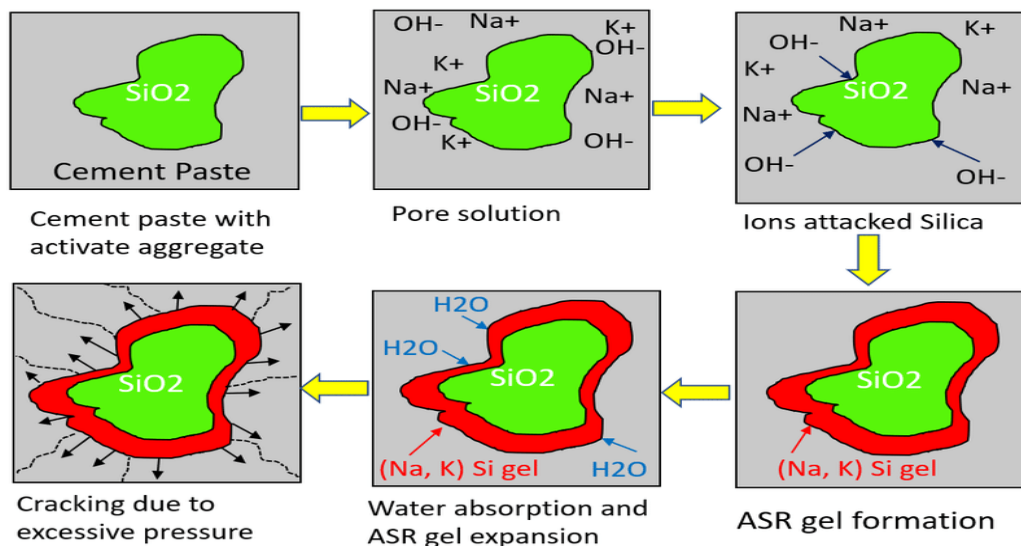


Figure 2: Schematic diagram of ASR

ASR damage not only affects the functionality of a structure but also its structural performance. Cracking that often results from ASR can also contribute to further deterioration mechanisms, such as freeze-thaw damage and corrosion(Fernandes & Broekmans, 2013; Fournier, Bérubé, Folliard, & Thomas, 2010).

1.2 Alkali-silica reaction (ASR)-affecting factors

Although the ASR gel does not directly create discomfort in concrete, it does produce internal tensions by expanding when it absorbs ambient moisture. Such stresses may be greater than the

concrete's tensile strength, which leads to progressive cracking and related degradation. The three primary elements that are generally accepted as being necessary for ASR in concrete materials are:

- Reactive siliceous components (coarse and fine fractions) present in aggregates
- Sufficient alkali content in cementitious materials
- Moisture content in combination with other elements like temperature and additives(Fanijo, Kolawole, & Almakrab, 2021).

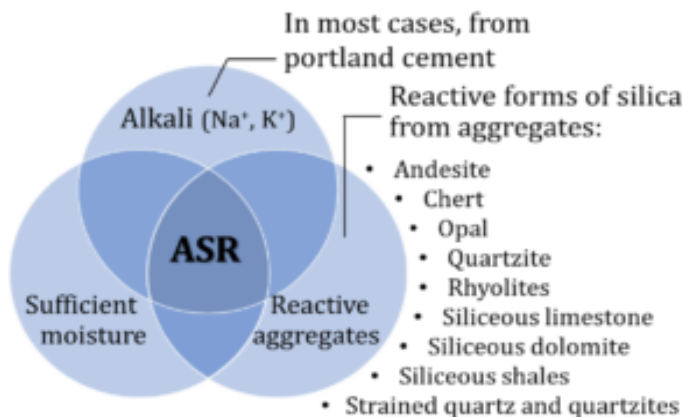


Figure 3: Factors that affects ASR

### 1.3 Impact of ASR on Infrastructure

There is a lot we know about ASR and its effects on concrete. The reaction happens gradually, years or even decades after construction (Mehta & Monteiro, 2006). As of 2017, reports of the response were received from 60 nations. Roughly forty states in the US had recorded ASR as of 2003 (Sims & Poole, 2017). Five dams and five hundred bridges in France are impacted (Martin, Bazin, & Toutlemonde, 2012). Safety risks arise from ASR damage, particularly in nuclear installations and dams (Acevedo & Serrato, 2010; Hayes *et al.*, 2018; William, Xi, & Naus, 2013).

## 2. Methods to inhibit Alkali silica reaction

This ASR can cause damage to the concrete by reducing its strength and stiffness with the progression of time because it is greatly affected by its surrounding environment and local weather conditions which causes global warming and other parameters, such as temperature and humidity influence the chemical reaction between alkalis and silica, and the subsequent expansion (Rahman & Lu, 2023). So in concrete building materials for the mitigation of alkali silica reaction the usage of admixture which is sustainable for environment as lithium nitrate  $\text{LiNO}_3$  (Deng, 2022) in order to reduce the environmental impact and improves durability. Other approaches to mitigating alkali-silica reaction (ASR) include the utilization of non-reactive aggregates, lowering the alkali loading of concrete (by employing cements with low alkali concentration, for example), and adding more cementitious materials (Kaladharan, Szeles, & Rajabipour, 2022). Theoretically, reducing the alkalinity of the pore solution, using non-reactive aggregates, and lowering the concentration of

calcium and portlandite ions can all suppress the conditions that lead to silica dissolution and exchange alkali in the formed ASR gel, recycling alkalis back into the concrete pore solution and maintaining the alkaline environment. However, in some areas where reactive aggregates predominate in the rock resource and non-reactive aggregate availability is restricted, using non-reactive aggregates is not a workable solution. The processes and requirements indicate that ASR mitigation techniques have been thoroughly studied to prevent concrete deterioration. ASR's most significant reactant, after reactive silica, is alkali. Consequently, lowering the alkali content of concrete is an achievable method to lower ASR (Rajabipour, Giannini, Dunant, Ideker, & Thomas, 2015). Supplementary cementitious materials (SCMs) are the most often used strategy to control ASR. SCM has the ability to efficiently consume CH through pozzolanic processes, improve the microstructure of the cement matrix, decrease the porosity and permeability of concrete, and help in the formation of more calcium silicate hydrates (C-S-H), which will bind more alkali ions and aid in lowering the alkali content of concrete. As previously stated, in order to optimize their efficacy, SCM's calcium (CaO) and alkali contents had to be restricted (Michael Thomas, 2011). Research has demonstrated that fly ashes, slag, silica fume, ground clay bricks, and rice husk ashes are beneficial at reducing the impacts of ASR. (Abbas, Kazmi, & Munir, 2017; Afshinnia & Poursaee, 2015; Aquino, Lange, & Olek, 2001; Chen, Soles, & Malhotra, 1993; Shafaatian, Akhavan, Maraghechi, & Rajabipour, 2013). Soon after this effect was discovered in the 1940s, concrete expansion caused

by the alkali-silica reaction was first reported to be prevented using chemical admixtures, such as lithium salts, and mineral cement additives more than 80 years ago. Using cement with mineral additives (containing primary components other than Portland clinker) to lower the pH and the concentration of sodium and potassium ions in the concrete's pore solution is an efficient way to minimize the risk of damage to the elements during the production process from the alkali-silica reaction. Low pH levels and soluble sodium and potassium concentrations decrease the likelihood of producing alkali-silica reaction (ASR) products (Shi, Park, Lothenbach, & Leemann, 2020), which also slow down the reaction by preventing the dissolution of the silica's reactive phases (Bagheri, Lothenbach, Shakoorioskooie, Leemann, & Scrivener, 2021). Admixtures made of minerals derived from natural sources, like zeolite or metakaolin, are utilized since it might be challenging to obtain mineral additions in the form of waste products from other industrial processes, like fly ash or blast-furnace slag. Lithium salt solutions, in contrast to mineral additives, which can only be added when concrete is being produced, can be used as a chemical admixture, or directly applied to a concrete structure to show the effects of an alkali-silica reaction. In the past, various lithium salt formulations have been investigated to mitigate the consequences of the alkali-silica reaction (Demir & Arslan, 2013; McCoy & Caldwell, 1951; Mitchell, Beaudoin, & Grattan-Bellew, 2004; Zapala-Slaweta & Owsiak, 2016). Alkali-silica reaction (ASR) growth has been inhibited and mediated by  $\text{LiNO}_3$  (Schneider, Hasparyk, Silva, & Monteiro, 2008).  $\text{LiNO}_3$  is added to the concrete mixture during the procedure. The type of cement system and

the concentration of  $\text{LiNO}_3$  are two parameters that affect how well  $\text{LiNO}_3$  mitigates ASR. It has been discovered that  $\text{LiNO}_3$  effectively reduces the expansion brought on by ASR in ordinary Portland cement systems (Doria & Barreto, 2021).  $\text{LiNO}_3$  addition can prevent silica from dissolving and the production of ASR products (Zapala-Slaweta, 2022). Glass and five reactive alkali-silica aggregates were chosen as the materials of interest at  $38^\circ\text{C}$  and  $80^\circ\text{C}$ , various lithium dosages were used to examine the effects of  $\text{LiNO}_3$  on ASR expansion, silica dissolving, and concrete pore solution. In the concrete-prism and concrete microbar experiments, when bigger size aggregate was utilized, the aggregates' reactivity to lithium differed. However, the results revealed that  $\text{LiNO}_3$  could effectively inhibit the detrimental expansion for all five reactive aggregates when they were crushed to sand size.  $\text{LiNO}_3$  was able to drastically lower the total amounts of dissolved silica, but it was unable to distinguish between different aggregates. The ASR reaction products were examined for the mechanistic work using several sophisticated analytical techniques, including SEM, XRD, and LA-ICP-MS. The findings demonstrated that Ca ions were crucial to the development of ASR gel products. Na ions might reach the reactive aggregate particle surface before Li ions because they had a higher effective diffusion coefficient than Li ions, according to an MRI study on the diffusion of Na and Li ions. A novel mechanism for  $\text{LiNO}_3$  suppressive effects on limiting ASR-induced expansion is put forth considering the findings. The formation of Li-bearing, low-Ca ASR gel products with a CIS ratio below 0.2, which have denser gel structure, stronger bond with the aggregate particles, and lower

mobility than conventional ASR gel, is thought to be the cause of  $\text{LiNO}_3$  suppressive effects on ASR expansion. Another reason is the formation of a layer of Li-Si crystals intimately at the reactive  $\text{SiO}_2$  particle surface, which acts as a diffusion barrier and protective layer to keep the reactive aggregate particles safe from additional attack by alkalis. As the reaction products get sufficiently thick, the amount of  $\text{OH}^-$  ions that can diffuse through the barriers decreases. Consequently, the expansion that follows the alkali silica reaction will be totally inhibited (Feng, 2008). In a different study, the efficiency of natural pozzolans with zeolite and lithium compounds was examined. It was discovered that while natural pozzolans were more successful in preventing expansion in field settings, lithium compounds offered superior protection at higher temperatures (Owsiak, Czapik, & Zapała-Sławeta, 2022). However, it was discovered that applying  $\text{LiNO}_3$  in conjunction with microwaves prevented silica from dissolving and caused a coating to form on the surface of the aggregate, which reduced ASR (Doria & Barreto, 2021). Furthermore, it was discovered that using metakaolin and  $\text{LiNO}_3$  together had a synergistic impact on preventing the expansion of ASR (Zapała-Sławeta, 2022). All things considered, the application of  $\text{LiNO}_3$ , either by itself or in conjunction with other techniques, exhibits promise in reducing ASR in concrete constructions.

### *2.1 Effectiveness of $\text{LiNO}_3$ to inhibit ASR*

Depending on the circumstances,  $\text{LiNO}_3$ 's ability to mitigate the alkali-silica reaction (ASR) varies. Studies suggest that because of the high alkalinity and dense microstructure of alkali-activated slag (AAS) systems,  $\text{LiNO}_3$  may not be a very effective

way to mitigate ASR in these systems (Wang, Noguchi, & Maruyama, 2022). However, lithium nitrite solutions, especially those with a lithium-sodium molar ratio of 0.6 or higher, can dramatically lower expansion rates when pressure-injected into concrete during the ASR propagation stage (Kobayashi & Takagi, 2020). Furthermore, by preventing aggregate dissolution, calcium nitrate has demonstrated potential in lowering ASR-induced expansion, offering a practical means of suppressing ASR (Oey *et al.*, 2020). Studies conducted over an extended period of time indicate that  $\text{LiNO}_3$ 's ability to mitigate ASR might decrease over time, increasing the production of ASR gel (Zapała-Sławeta & Owsiak, 2017).  $\text{LiNO}_3$ -induced acoustic emission analysis verifies slower ASR advancement in mortars using reactive opal aggregate (Zapała-Sławeta & Świt, 2018).

### *2.2 Cost and Availability of $\text{LiNO}_3$ for ASR Inhibition*

Lithium nitrate ( $\text{LiNO}_3$ ) for the inhibition of the alkali-silica reaction (ASR) varies in price and availability depending on the particular materials and conditions. Research have demonstrated that a variety of factors, including the type of aggregate utilized and the presence of fly ash, can affect how efficient  $\text{LiNO}_3$  is at Controlling ASR (Venkatanarayanan & Rangaraju, 2014; Zapała-Sławeta & Owsiak, 2017). Although it has been shown that  $\text{LiNO}_3$  decreases the expansion of ASR in traditional Portland cement systems, the high alkalinity and dense microstructure of AAS limit its usefulness in alkali-activated material (AAM) systems such as alkali-activated slag (AAS) mortars (Wang *et al.*, 2022). Inconclusive evidence of ASR mitigation and limited penetration of lithium

into the pavement have been observed in field studies applying  $\text{LiNO}_3$  to existing concrete pavements (Tuan, Kelly, Sun, & Buss, 2005). Factors such as aggregate reactivity and mineralogy determine the ideal  $\text{LiNO}_3$  dosage for inhibiting ASR (Ghafoori & Islam, 2010).

### 3. Conclusion

In summary, the global concrete infrastructure is facing serious challenges due to the alkali-silica reaction (ASR), which can cause gradual but possibly severe deterioration over time. The chemical reaction that occurs when alkalis in concrete react with reactive silica in aggregates causes gel to form, expand, and eventually crack, endangering the structural integrity and durability of the building. Aggregate reactivity, cementitious material's alkali content, moisture content, and environmental factors are some of the variables that affect the development and occurrence of ASR. Although it manifests slowly, ASR has been documented in many nations' structures, affecting airports, dams, bridges, and other vital infrastructure. Damage due to ASRs has significant financial consequences and requires expensive replacements and repairs. A variety of tactics, from the use of non-reactive aggregates to the addition of additional cementitious materials and chemical admixtures, are needed to mitigate ASR. Whether used alone or in conjunction with other methods,  $\text{LiNO}_3$  has shown promise as an ASR inhibitor. However, there are a number of variables that can affect how effective  $\text{LiNO}_3$  is, including the type of aggregate used, the composition of the concrete, and the surrounding environment. In conclusion, managing ASR is essential to ensure the durability and safety for concrete infrastructure. Maintaining

the durability and functionality of concrete structures in the face of this extensive chemical reaction requires ongoing study and development of mitigation techniques, such as the use of  $\text{LiNO}_3$ .

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