REGIONE DEL VENETO

SUPERSTRADA A PEDAGGIO PEDEMONTANA VENETA

CONCESSIONARIO	CONTRAENTE GENERALE
Superstrada Pedemontana Veneta SpA Via Invorio 24/A 10146 Torino	**SIS Scpa** Via Invorio 24/A 10146 Torino

RESPONSABILE AMBIENTALE

ORDINE DEI DOTTORI AGRONOMI E DOTTORI FORESTALI DELLA PROV. DI VICENZA
Dott. For.
RENIERO
STEFANO
n. 277
- ALBO -

Note Provincia di Vicenza – servizio ambiente – prot. n. GE2021/0032193 del 27.07.2021 e prot. n. GE2021/0033316 del 03.08.2021 – relazione tecnica di riscontro al p.to 3 della nota ARPAV prot. n. 65984 del 21.07.2021

TITOLO ELABORATO: Valutazione della dispersione di prodotto durante l’applicazione del cemento

REV	DESCRIZIONE	REDATTO	DATA	VERIFICATO	DATA	APPROVATO	DATA
0	Prima emissione	NEXTECO	13/09/2021	NEXTECO	13/09/2021	SIS	14/09/2021

Sommario

1 Premessa

Con riferimento alle note Provincia di Vicenza – Servizio Ambiente Prot. n. GE2021/0032193 del 27/07/2021 e prot. n. GE2021/0033316 del 03/08/2021 ed alla nota ARPAV prot. n. 65984 del 21/07/2021, con la presente relazione, si fornisce riscontro al punto 3: *“**deve essere valutato se durante l’applicazione del cemento con l’accelerante di presa contenente PFBA possano esservi dispersioni di prodotto. Infatti, la dispersione del cemento fresco ed il contatto con l’acqua possono causare lo scioglimento del PFBA in acqua che potrebbe anche contaminare le acque sotterranee**”.*

Richiamando tutte le informazioni sul punto già fornite nei precedenti elaborati degli scriventi, al fine di fornire una descrizione dei meccanismi di legame tra gli acceleranti di presa e il cemento stesso durante le fasi di applicazione, si riporta una sintesi del par. 3.3.4 dell’articolo “*Liquid- Based set accelerating admixtures for sprayed concrete: a comparison between alkali-free and alkali-rich accelerators*”, riportato integralmente in Allegato 1, fornito dalla ditta MAPEI.

2 Valutazione della possibilità di dispersione di prodotto nell’applicazione del cemento

2.1 Meccanismi di legame tra gli acceleranti di presa alcali-free e il cemento

L’articolo “*Liquid- Based set accelerating admixtures for sprayed concrete: a comparison between alkali-free and alkali-rich accelerators*”, che si riporta in Allegato 1, fornito e redatto dalla ditta MAPEI, riporta una revisione della chimica, della microstruttura, delle prestazioni, degli aspetti ambientali e gli aspetti sanitari degli additivi acceleranti di presa a base liquida per calcestruzzo spruzzato.

L'applicazione di calcestruzzo proiettato nell’ambito dello scavo in roccia richiede l'aggiunta di additivi acceleranti di presa. Recentemente, il metodo di miscelazione a umido è diventata la tecnica più utilizzata nelle applicazioni nel campo del calcestruzzo proiettato.

L’articolo è focalizzato sul confronto tra acceleranti privi di alcali (alcali-free) e acceleranti ricchi di alcali, ma nel seguito si sintetizzerà l’argomento di interesse, ovvero l’influenza degli acceleranti alcali free sull’idratazione del cemento.

Il processo di idratazione del cemento consiste in una serie di reazioni chimiche dei componenti anidri costituenti il cemento stesso, il gesso e l'acqua d'impasto. Le conseguenze di tali reazioni sono la presa e l'indurimento della "pasta" (così viene chiamata la miscela tra cemento e acqua).

Durante le prime fasi di idratazione del cemento, a causa della presenza di ioni alluminato e solfato negli acceleranti alcali-free, il principale prodotto di reazione è un composto chimico denominato ettringite. La sua formazione comporta il consumo di una grande quantità di acqua, necessaria alla formazione dei tipici cristalli prismatici esagonali.

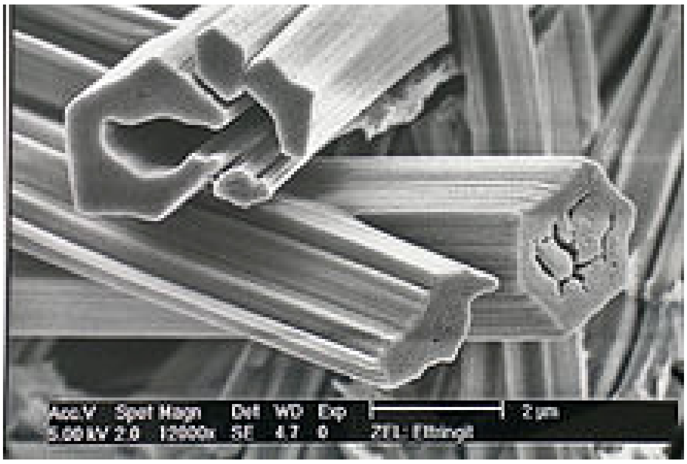


Figura 1
Ettringite al microscopio

Questo fenomeno comporta una presa istantanea (*flash setting*) del materiale. La dimensione, la forma e la quantità dei cristalli possono variare a seconda della soluzione chimica (disponibilità di calcio, zolfo, alluminio e pH).

Le figure seguenti mostrano l'evoluzione microstrutturale del cemento in presenza di un accelerante alcali-free.

Figura 1 -a
Formazione prevalente di ettringite nei primi 10 minuti

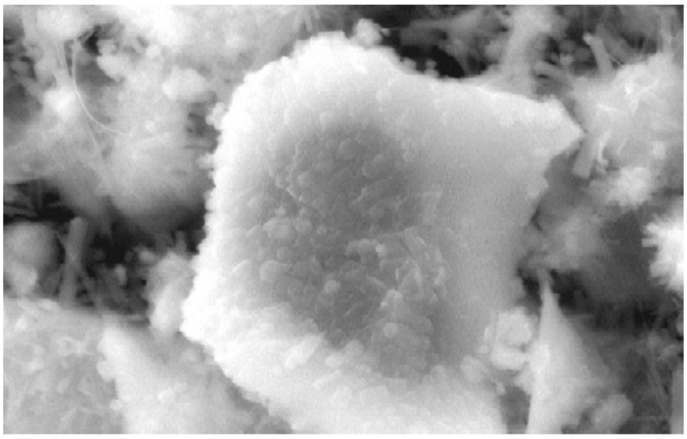


Figura 1 -b
Crescita dello strato di gel che circonda le particelle di cemento (durante le prime 2-3 ore di idratazione)

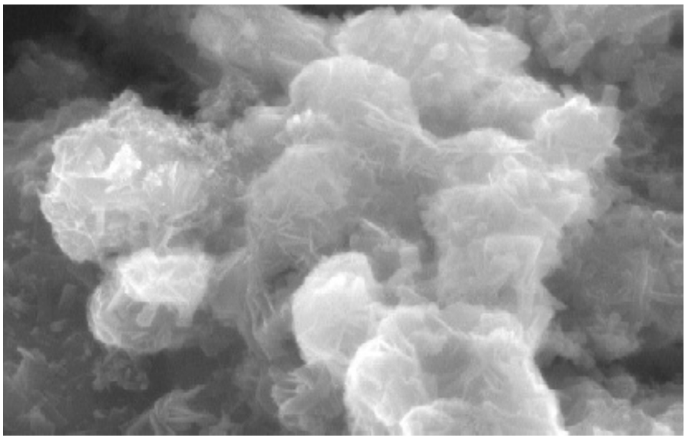


Figura 1 -c
Conversione di ettringite in monosolfato

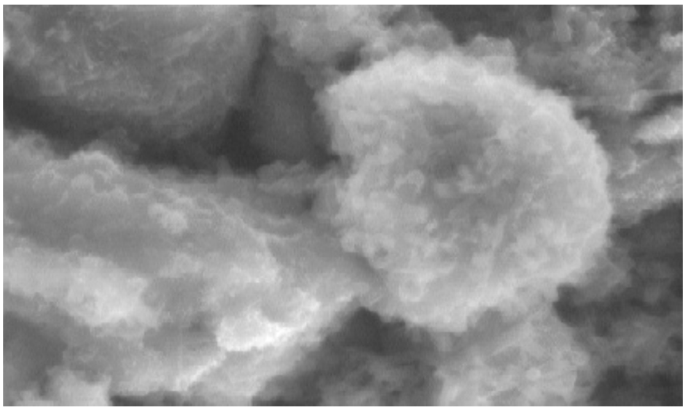


Figura 1 -d
Formazione iniziale di silicati di calcio idrati C-S-H (tipo II)

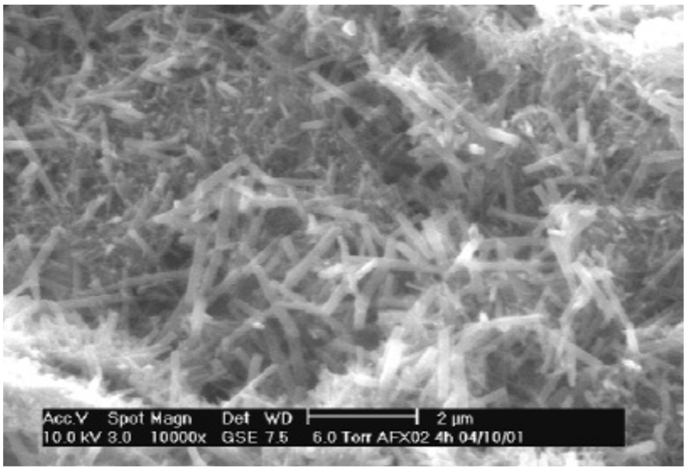


Figura 1 -e
Ulteriore formazione di ettringite e silicati di calcio idrati C-S-H (tipo I) dopo 4 ore

Nei primi 5-10 minuti successivi all'introduzione dell'acceleratore nella miscela, si osserva la formazione di ettringite incorporata all'interno di uno strato di gel che circonda le particelle di cemento (Figura 1-a).

La crescita dello strato di gel così come la formazione di ettringite continua nelle successive 2 o 3 ore di idratazione (Figura 1-b).

All'esaurimento degli ioni solfato, l'ettringite viene convertita in monosolfato (struttura a lastre) come illustrato nella Figura 1-c. Si noti che la microstruttura del monosolfato interrompe lo strato continuo di gel che ricopre le particelle di cemento, e quindi espone il cemento a ulteriore idratazione.

In figura 1-d si osserva la formazione di silicati di calcio idrati C-S-H, responsabili dell’indurimento del cemento, e di utleriore formazione di ettringite (Figura 1-e).

Per maggiori dettagli tecnico-scientifici si rimanda alla trattazione in Allegato 1.

2.2 Considerazioni sulla dispersione di prodotto

L'applicazione dello spritz beton avviene sfruttando la velocità dell'impatto della miscela contro le pareti del fronte di scavo. Al fine di evitare che il conglomerato venga dilavato dall'acqua potenzialmente presente sulle pareti dello scavo, lo spritz beton deve possedere una presa istantanea (*flash set*) che viene ottenuta ricorrendo appunto all'aggiunta di acceleranti di presa, che agiscono nel processo di idratazione come facilitatori del processo di indurimento del cemento, come meglio riportato nel paragrafo precedente.

Figura 2
Calcestruzzo proiettato in galleria

Come si evince dalla figura sopra, che mostra la fase di applicazione dello spritz, durante il getto/proiezione la miscela composta da boiacca e accelerante non rilascia acqua grazie alla velocità con cui avviene il processo di presa.

3 Conclusioni

Anche gli ulteriori approfondimenti eseguiti sull'accelerante di presa Mapequik AF 1000 confermano la conclusione che la contaminazione da PFBA riscontrata allo scarico non può essere imputabile all'utilizzo di questo prodotto in quanto nella fase di applicazione del prodotto (spritz beton), non sono possibili dispersioni dello stesso, in ragione della velocità del processo di presa.

Ciò premesso, anche alla luce dei risultati ottenuti a seguito dell'analisi delle acque di drenaggio della galleria, sintetizzati nell'elaborato "*Relazione sugli esiti delle indagini integrative condotte*" del 26/08/2021 (trasmesso con nota SIS-LO1-245-21-LCO-lco del 27.08.2021), è possibile considerare la presenza di PFBA riconducibile a fonti di contaminazione esterne al cantiere e presenti nell'area, potenzialmente veicolate dalla falda di subalveo del rio Poscola.

4 Allegati

ALLEGATO 1: D. Zampini, A. Walliser, M. Oppliger, T. Melbye (MBT – International Underground Construction Group), C. Maltese, C. Pistolesi, G. Tansini, E. Portigliatti, E. Dal Negro (MAPEI – Underground Technology Team) *"Liquid- Based set accelerating admixtures for sprayed concrete: a comparison between alkali-free and alkali-rich accelerators"*

ALLEGATO 1

“Liquid- Based set accelerating admixtures for sprayed concrete: a comparison between alkali-free and alkali-rich accelerators”

D. Zampini, A. Walliser, M. Oppliger, T. Melbye (MBT – International Underground Construction Group), C. Maltese, C. Pistolesi, G. Tansini, E. Portigliatti, E. Dal Negro (MAPEI – Underground Technology Team)

Liquid-Based Set Accelerating Admixtures for Sprayed Concrete: A Comparison between Alkali-Free and Alkali-Rich Accelerators

D. Zampini, A. Walliser, M. Oppliger, T. Melbye
MBT – International Underground Construction Group

C. Maltese, C. Pistolesi, G. Tansini, E. Portigliatti, E. Dal Negro
MAPEI – Underground Technology Team

Abstract

A review of the chemistry, microstructure, performance, environmental aspects, and health aspects of liquid-based set accelerating admixtures for sprayed concrete is presented. The application of sprayed concrete for rock support requires the addition of set accelerating admixtures, more commonly known as accelerators. Recently, the wet mix method has become the most frequently used technique in field applications of sprayed concrete. Therefore, the performance as well as the development of liquid-based set accelerating admixtures has gained increasing interest. The present paper provides a comparison between alkali-free and alkali-rich accelerators. Advantages and the proper selection criteria for sprayed concrete set accelerating admixtures are presented.

1 Background

The aim of the following publication is to provide a review of the chemistry, performance, environmental impact, and health aspects of liquid-based set accelerating admixtures used in sprayed concrete applications. One of the motivating factors for such an exercise is the ongoing contraversy surrounding the two major types of sprayed concrete accelerators – namely sodium silicates (water glass) and alkali-free. For instance, in a very recent publication in *Gallerie e Grandi Opere Sotteranee* [1], it was stated that *"the criticisms made on the use of sodium silicate cannot be justified from an experimental point of view, nor justify the development of alternative products such as the so-called alkali-free accelerants."* The latter statement is quite harsh and does not provide the necessary stimulus for innovation and further development of advanced as well as alternative technologies. Therefore, it is important to present, in an explicit manner, facts and figures that properly demonstrate advantages and disadvantages of the different types of set accelerating admixtures for sprayed concrete, and understand the driving force behind the technological developments undertaken in this business sector.

2 Introduction: The Evolution of Sprayed Concrete Technology

Before elaborating on the details, a general overview is provided on the evolution and standardization process in sprayed concrete technology. The evolution of the sprayed concrete technology and the associated improvements in quality is schematically summarized in Figure 1. Initially, sprayed concrete was applied adopting the dry-mix method where cement powder and dry sand are conveyed by compressed air through a hose, and the water needed for hydration was introduced at the spraying nozzle. As early as the 1950's, a wet-mix process was developed in which mortar or concrete are pumped to a nozzle and pneumatically projected onto a substrate. However, due to poor/inefficient equipment, lack of know-how, and lack of experience, the quality of the first "generation" of wet sprayed concrete was extremely decadent. Thus, the reputation of the wet method was quite negative, thereby hindering its diffusion. In many countries where sprayed concrete was applied, the dry-mix method was the preferred method of application. However, with the development of more sophisticated spraying machines (automated dosing and powerful pumps), advanced robotics, and experience, wet sprayed concrete became increasingly more attractive.

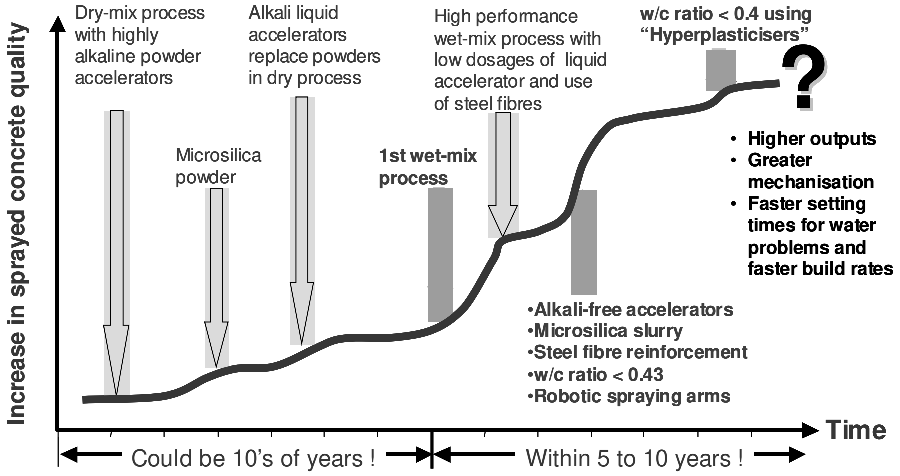


Figure 1. The evolution of sprayed concrete qualilty in the United Kingdom[2].

More importantly, more stringent requirements on the working environment and the performance of sprayed concrete were additional factors that made wet sprayed concrete more desirable as well as necessary. For instance, with wet sprayed concrete one can significantly reduce dust generation, rebound (i.e. chemically contaminated waste), and control the quality of the concrete (water-to-cement ratio/strength, workability, and homogeneity). Today, wet sprayed concrete has become a well-established and highly advanced technology in civil and mining applications in the construction industry. Recently, rigid guidelines for constituent materials, concrete composition requirements, durability requirements, mix composition, execution of spraying, final product requirements, test methods, quality control, health and safety have been established by EFNARC[3], CEN[4], and the Austrian Concrete Association[5] for wet sprayed concrete applications. More importantly, the guidelines specify how the different types of sprayed concrete accelerators should be employed in order to gaurantee good and durable performance.

Undoubtedly, the wet-mix method has become the standard technology in most sprayed concrete applications. Therefore, liquid-based sprayed concrete accelerators have assumed an extremely important role. New technologies in the area of set accelerating admixtures have to be developed that can provide increasing tunneling rates, economical structures, and improved safety (people and work environment). The following sections will be dedicated primarily, but not exclusively, to the comparison of the two most widely used *liquid-based accelerators* in sprayed concrete, namely alkali-based (alkali silicates and alkali aluminates) and alkali-free.

3 Chemistry and Microstructure

The following sections are intended to provide general information on the definitions that underlie the nomenclature and chemisty of the different types of sprayed concrete accelerators. Secondly, a brief description is given of the major liquid-based accelerators outlining their principal characteristics and chemical properties. The last part of this section is an attempt to provide a general overview of how the chemistry of the most widely used accelerators influence cement microstructure and hydration.

3.1 Definitions

There is often confusion on the terminology associated with the chemistry of sprayed concrete set accelerating admixtures. Thus, it is important to clearly delineate what is exactly meant when discussing different types of accelerator chemistry.
In the context of sprayed concrete accelerators, the actual meaning of the terms *non-caustic* and *alkali-free* is frequently misunderstood [6]. The reason for this confusion is the dual meaning of *alkaline* in the English professional language. The term *alkaline* can be understood as:

1) A basic solution (pH value in the range between 7 and 14). An example is the dissolution of calcium oxide in water, where a high concentration of hydroxyl (OH^-) ions is obtained and consequently the pH reaches a value of 14. This solution is a strong base (highly alkaline), but it contains no alkali cations.
2) A solution containing alkali cations such as Na^+, K^+, Li^+ or any other element found in the first column of the periodic table. An example is common salt dissolved in water (NaCl solution). This solution contains alkali cations, however its pH is approximately 7, and therefore it is a neutral solution (non-alkaline).

Alkalinity and alkali content are two independent properties. *For sprayed concrete accelerators the term alkali-free should have only one meaning: the accelerator contains no alkali cations (%Na_2O-equivalent < 1%)*. Their absence reduces the risk of alkali cations reacting with sensitive minerals (soluble silica, opals, flints, and some zeolites) [7], which are sometimes present in the aggregates used for the concrete production. The so-called “alkali-aggregate reaction” (AAR) or “alkali silica reaction” (ASR) causes fracture and swelling of cement-based materials due to an expansive formation of alkali-silica gel. This may have a detrimental effect on the durability of sprayed concrete, a topic that will be discussed in section 4.3.
As shown in pH scale in Figure 2, most alkali silicate and aluminate accelerators are strong bases (pH = 10-14), and therefore aggressive to the human skin (i.e. caustic).

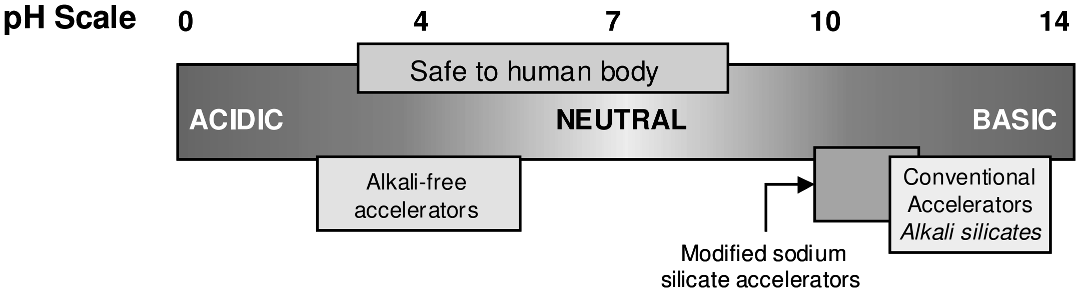


Figure 2. The pH scale. Alkali-free accelerators are in a pH range that is safe for the human skin.

There are also examples of accelerators that are strong acids: pH = 2-4. Alkali-free accelerators belong to the latter category. Chemicals in the later pH range are less harmful to the skin (pH=5; Figure 2).

3.2 Liquid-based sprayed concrete accelerators

3.2.1 Alkali Silicates and Alkali Aluminates

The accelerators in this category are based on alkali metals due to the simple fact that they are more soluble than their non-alkali counterpart, and this makes it possible to produce solutions that are necessary for wet spraying of concrete applications.
Sodium silicates (Na_2SiO_4), more popularly known as water glass, is the most classical accelerator for sprayed concrete. The pH of sodium silicates accelerators are typically in the range between 10 and 12, and therefore considered to be aggressive to the skin (Figure 2). Furthermore, the alkali content, espressed as $\%Na_2O$-equivalent ($\%Na_2O$ equivalent = %Na2O + 0.658*$\%K_2O$), is about 10%.
Alkali aluminates, on the other hand, consist of solutions of $NaAl(OH)_4$ and $KAl(OH)_4$. However, the stability of the aluminates is dependent on the pH. The $Al(OH)_4^-$ anion only is stable in a high pH environment – as more OH^- ions are introduced into solution the stronger the tendency for the equilibrium to drive the reaction to the left (see equation 1), thereby avoiding the precipitation of $Al(OH)_3$. Therefore, solution stability in the presence of alkali aluminates is often achieved by increasing the pH with extra alkali hydroxide (NaOH and KOH). The latter tends to increase the pH up to 14, and the alkali content can reach non-desirable Na_2O-equivalents in the range of 15 to 20%. Thus, alkali aluminates are extremely caustic and harmful to the human skin as well as health.

$$(1) \qquad Al(OH)_4^- <=> Al(OH)_{3(solid)} + \mathbf{OH^-}$$

3.2.2 Alkali-free

The driving force behind the development of the alkali-free/non-caustic accelerators was the demand from the construction industry for a product that could satisfy the following requirements:

a) Improved durability by reducing the risk of alkali-aggregate reaction, by reducing or even eliminating the alkalis present in the common alkali silicate and aluminate accelerators.
b) Improved safety conditions in the working environment by reducing accelerator aggressiveness in order to avoid skin burns, loss of eyesight and respiratory health problems.
c) Positive environmental impact by reducing the amounts of soluble components in sprayed concrete and its rebound that are harmful to ground water.

d) Reduction in the loss of concrete final (long-term) strength, which is typically in the range of 15 to 50% for concrete sprayed with alkali-rich accelerators (alkali silicates or alkali aluminates).
e) Continuous and consistent early age strength development of concrete during the critical intermediary construction phases.
f) Reduction of construction costs.

It is evident that the conventional types of sprayed concrete accelerators such as the alkali silicates and alkali aluminates could not fulfill the above mentioned requirements (discussed in more detail in section 4). Therefore, a new generation of sprayed concrete accelerators were developed to satisfy the aforementioned requirements. Thus, admixture suppliers set out to develop alkali-free and safer (enviromentally and health-wise) products.

Unlike the alkali silicates and alkali aluminates, the chemistry of alkali-free accelerators is rather complex, and there is a significant amount of proprietary know-how that is generated during their development. Nonetheless, there are chemical features that are common to the different types of alkali-free accelerators currently available on the market. One of the prevailing ingredients in alkali-free accelerators is water soluble aluminum salts and complexes thereof. The Al^{3+} ions that enter in solution induce the hydrolysis of water molecules [8] thorough a series of reactions, which generate H_3O^+ ions. Therefore alkali-free accelerators are typically acidic with a pH that can range between 2.0 and 4.0 (depending on the formulation). However, it is difficult to bring the pH of alkali-free accelerators above 4.0 because this will lead to the precipitation of $Al(OH)_3$.

An important characteristic of alkali-free accelerators for sprayed concrete is the low or zero alkali content - $\%Na_2O$-equivalents are typically < 1.0 (as required by Austrian norms [5]). This is an important property of alkali-free accelerators from an environmental and durability view point (see discussion in sections 4.3.3 and 5).

3.3 Cement-Sprayed Concrete Accelerator Interactions

It is useful to have some knowledge of basic cement chemistry in order to gain some insight on how the different types of liquid accelerators for sprayed concrete influence cement hydration and microstructure, which is ultimately responsible for material performance. Cement chemistry is an extremely complex science, and a lot of aspects (kinetics and thermodynamics) pertaining to hydration are far from being well understood. Therefore, what is presented in the following paragraphs is only a very general introduction intended to provide some background information. A more comprehensive review of cement chemistry can found in the following references: Taylor[9] and Jennings[10].

Nonetheless, there are some key properties that a set accelerating admixture should possess: ability to improve the reactivity/hydration rate of reaction of cement, proper evolution and development of microstructure, and maintain or improve material properties (durability and mechanical) with respect to reference concrete.

3.3.1 General Hydration Kinetics

Hydration kinetics of cements can be represented by the general rate of heat evolution curve given in Figure 3. When cement particles come into contact with water there is a very rapid release of heat that is due to the wetting and dissolution of particles having high surface area (stage I). After approximately 10 to 15 minutes, cement undergoes an induction (dormant) period (stage II) during which cement reactivity is low. Hence, the role of set accelerating admixtures is to reduce as much as possible, if not eliminate, the induction period. The mechanism responsible for the induction period is still not well understood. However several theories have been proposed and are discussed in Taylor[9]. Hydrated cement resumes activitiy after 2 to 5 hours (depending on the cement). This is commonly referred to as initial set, and the rate of reaction increases significantly (stage III). At some point, the rate of heat of evolution reaches a maximum, and this is defined as the time of final set. Following final set, the reaction slows down (stage IV), and the reactions are chemical and diffusion controlled. Eventually the reaction kinetics reach a steady state where diffusion becomes the rate determining process (stage V). The rate of heat evolution curve or related parameters (e.g. temperature evolution) is a means to assess how sprayed concrete accelerators influence the chemical reactions in cement. Therefore it is important to know which cement reactions are responsible for determining the heat evolution (i.e. rates of reaction), and how does this influence the properties and ultimately the performance of the material.

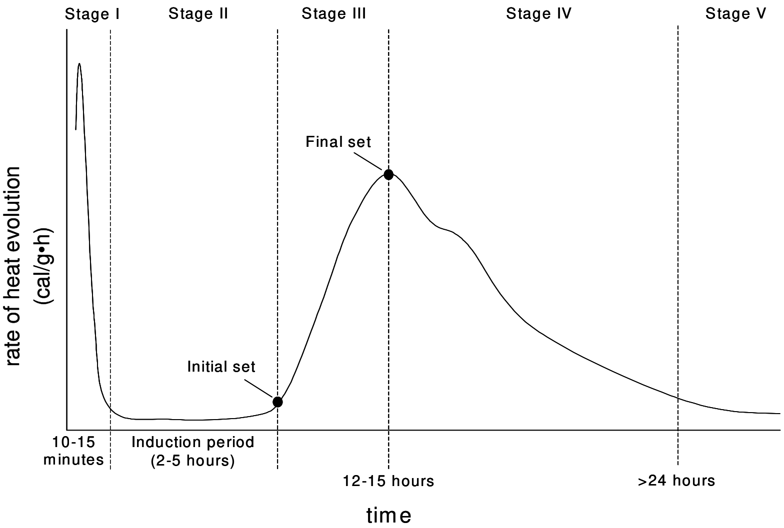


Figure 3. A typical heat evolution curve of cement obtained under isothermal curing conditions.

3.3.2 Cement Chemistry Basics– Solid and Liquid State

The following chemical equations outline the main hydration reactions that can occur during cement hydration. Standard ceramic notation is used to abbreviate the chemical equations: **C**=CaO, **S**=SiO_2, **H**=H_2O, **A**=Al_2O_3, **F**=Fe_2O_3, **$\underline{S}$**=SO_4.

a) Calcium silicate phases:

(2) $2C_3S + 6H \Leftrightarrow C\text{-}S\text{-}H + 3CH$
(3) $2C_2S + 4H \Leftrightarrow C\text{-}S\text{-}H + CH$

b) Calcium aluminate phase:

(4) $C_3A + C\underline{S}H_2 + 26H \Leftrightarrow C_6A\underline{S}_3H_{32}$ (ettringite)
(5) $C_3A + C_6A\underline{S}_3H_{32} + 4H \Leftrightarrow 3C_4A\underline{S}H_{12}$ (monosulfate)

(6) $2C_3A + 21H \Leftrightarrow C_4AH_{13} + C_2AH_8$

(7) $C_4AH_{13} + C_2AH_8 \Leftrightarrow 2C_3AH_6 + 9H$ (hydrogarnet)
(8) $C_3A + CH + 12H \Leftrightarrow C_4AH_{13}$

c) Calcium aluminoferrite phase:

$$\boxed{(9)\ C_4AF + 13H \Leftrightarrow C_4(A_2F)H_{13}}$$

The chemical equations that are boxed-in represent the major reactions in an ordinary portland cement (OPC), and the most relevant to the understanding of sprayed concrete accelerator chemistry.

For instance, the main heat evolution peak (Figure 2 – final set in Stage III) and strength development in the first 28 days of concrete is primarily due to the reaction in equation 2 (i.e. the formation of calcium silicate hydrates, C-S-H). The above chemical reactions also indicate that the calcium aluminate phases (C_3A and C_4AF) play an important role in cement hydration due to the multiple reaction paths that can be undertaken, and consequently this leads to the formation of different reaction products that influence the performance of concrete. In OPC, due to the presence of gypsum, the calcium aluminates typically follow the reaction path given in equation 4. Thus, the main hydration product of the aluminate phases is ettringite. In real cements, it is rare to find gypsum as the sole sulfate carrier. The two other types of sulfate carriers such hemihydrate ($CaSO_4 \cdot 1/2H_20$) and anhydrite ($CaSO_4$) are often also present. Solubility of the the different types of sulfate carriers is not the same: hemihydrate > gypsum > anhydrite. Therefore, the availability of sulfate ions to the calcium aluminate phase can vary, and this can lead to different hydration products (equations 5, 6, 7, 8). Eventhough calcium aluminates do not contribute significantly to the long term strength of concrete, they can play an important role on the setting behavior and early (< 24 hours) strength development. Sprayed concrete accelerators are known to have a significant influence on the reactions of the calcium aluminates, but more importantly on the solid-to-liquid phase equilibrium governing this cement phase.

In sprayed concrete applications, the accelerator is never added to the concrete immediately after batching, and often there is an elapse of time between the concrete production and actual application – at least the time to transport the concrete to the area of application. During this time, the cement in concrete has undergone the initial hydration reactions. Therefore, when accelerators are introduced in concrete, the latter is most likely to be in the induction period (stage II – Figure 3). Therefore, its not only important to know what are the initial hydration reactions, but it is also important to know what is the nature of the solution (acqueous phase) chemistry surrounding the hydrating particles, and how the different ions present in the aqueous phase interact with the chemicals subsequently introduced into the mix (i.e. set accelerating admixture). The introduction of the accelerator in sprayed concrete disrupts the solution "equilibrium," and thereby alters the hydration reactions. This leads to new "equilibrium" conditions that alter the evolution of the reactions in cement.

The kinetics and solution chemistry define the microstructure of the hydration products. Therefore, characterization and understanding of the microstructural development in materials is important, because often it is the microstructure that is responsible for properties and ultimately the overall performance of materials.

3.3.3 Influence of Alkali Silicates and Alkali Aluminates on Cement Chemistry and Microstructure

Hydration studies on the interactions between cement and alkali silicates, and more specifically sodium silicates (Na_2SiO_4), using Environmental Scanning Electron Microscopy (ESEM)[11], have suggested that a possible hydration product is a dense "C-S-H-like" gel covering the unhydrated cement grains (Figure 4a). The dense gel that forms around the cement particles has the negative effect of hindering and slowing down further hydration of cement particles.

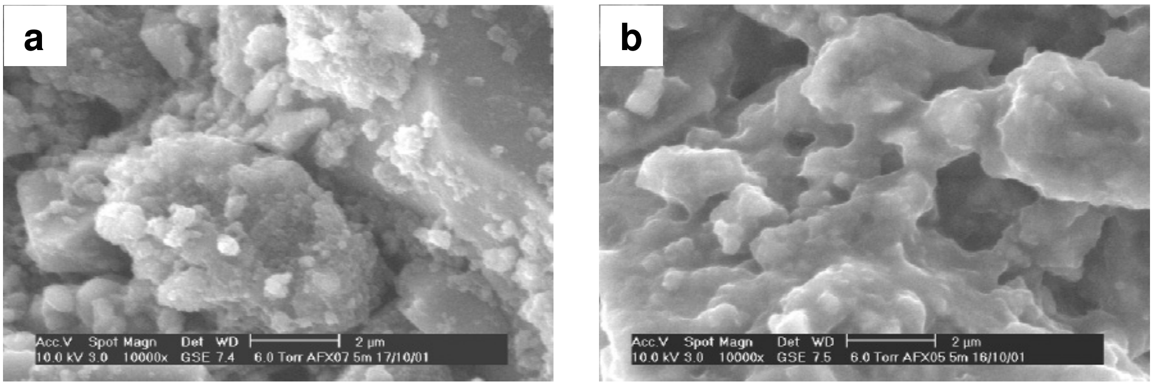


Figure 4. ESEM micrographs of: a) cement paste mixed with a waterglass (right) after 5 minutes of hydration and b) cement paste mixed sodium aluminate after 5 minutes of hydration.

Microstructure investigations carried out by SINTEF[12] on cement paste samples mixed with a sodium silicate accelerator (Figure 5b) indicated the formation of a dense and thick hydrated layer around the cement particles. As the cement hydrates, the water trapped in the pores is not efficiently used to further hydrate the unreacted cement particles and is lost during the drying process. Consequently, the water filled space does not get replaced by solid material, and there is a tendency for the pore structure to coarsen. This leads to a higher and more interconnected porosity. Secondly, the gel that forms around the cement particles is observed to be initially poor in calcium, and prevalently rich in sodium. This latter observation suggests that the calcium deprived alkali silicate hydrate gel is very similar to that formed in an akali silica reaction (ASR) (Urhan[13] and Kirkpatrick[14]).

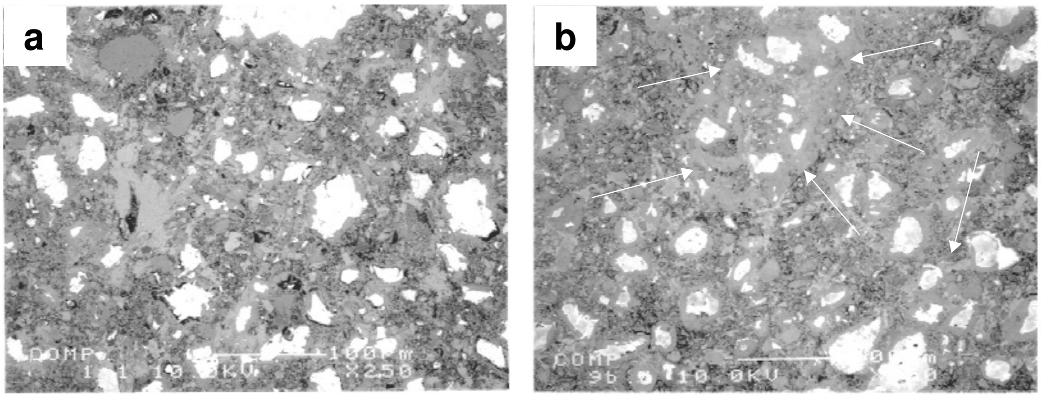
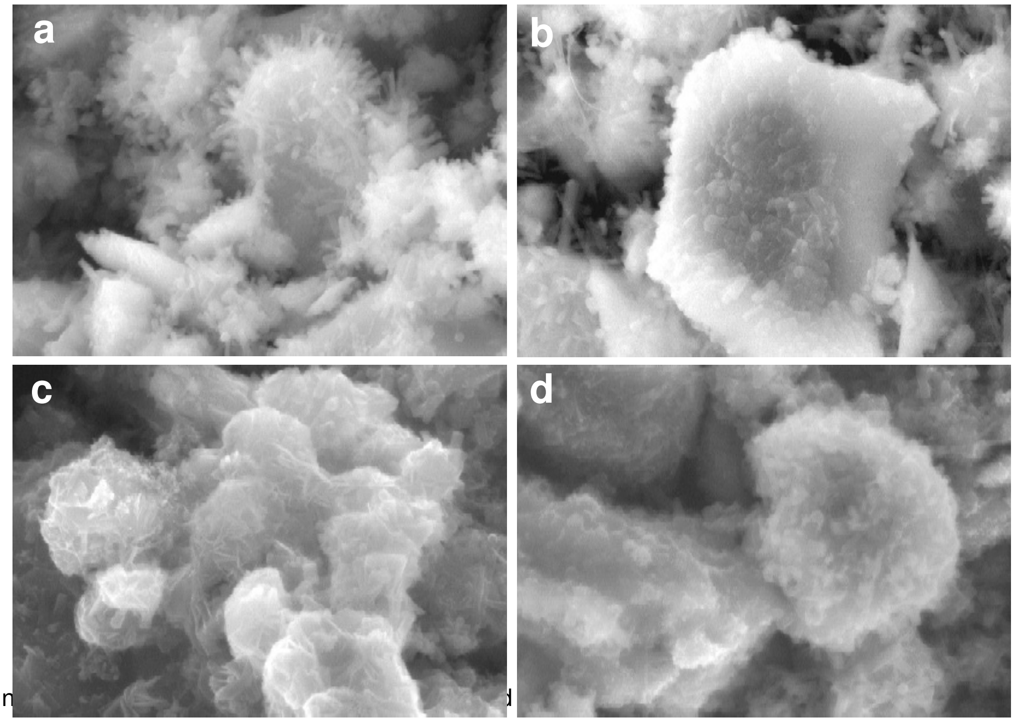


Figure 5. Polished sections of a reference cement paste (a) and a polished section from a cement paste containing sodium silicate accelerator (10% - low dosage). Note the presence of a dense and thick gel surrounding unhydrated cement particles in the cement paste with sodium silicate accelerator (b).

The other class of alkaline accelerators, namely the alkali aluminates, influence cement hydration in a different manner. The high content of aluminium ions, supplied by the alkali aluminates, react very rapidly with the available calcium and sulfate ions present in solution to give ettringite (equation 4, section 2.3.2) or hydrogarnet (equation 7, section 2.3.2) phases. Initially, the ettringite and calcium sulfoaluminate phases formed is observed to be present in a gel-like form (Figure 4b). Subsequently, all of the sulfate ions in solution are consumed, favoring the conversion of ettringite to monosulfate (equation 9, section 2.3.2). During the latter reaction water is liberated from the water-rich ettringite crystal, and made available for further hydration. The monosulfate phase is often incorporated into the predominant gel-like hydrate layer that surrounds the cement particles. The formation of a “C-S-H-like” phase is also observed, but the amounts are considerably less than those observed with the sodium silicate accelerators as well as the alkali-free accelerators[15]. A significant strength loss is typically observed with alkali aluminates, and this is very likely due to the gel-like microstructure that hinders proper hydration of the anhydrous particles.

3.3.4 Influence of Alkali-Free Accelerators on Cement Hydration and Microstructure

Due to the presence of aluminate and sulfate ions in alkali-free accelerators, the main reaction product during the early stages of cement hydration is ettringite [11,16]. The formation of ettringite consumes a large quantity of water (equation 8) to form hexagonal prismatic crystals. This leads to a rapid physical setting (flash setting) of the material. The size, shape, and amounts of the crystals can vary depending on the solution chemistry (availability of calcium, sulfur, aluminium, and pH). Figure 6 shows the microstructural evolution of cement in the presence of an alkali-free accelerator. In the first 5 to 10 minutes following the introduction of the accelerator to the mix, one observes the formation of ettringite intimately incorporated within a gel layer that surrounds the cement particles (Figure 6a). The growth of the gel layer (most likely a mixture of metastable C-S-H-like phase and calcium sulfoaluminate phase) as well as the formation of ettringite continues in the following 2 to 3 hours of hydration (Figure 6b). Upon depletion of the sulfate ions, the ettringite is converted to plate/sheet-like monosulfate phase as depicted in Figure 6c.



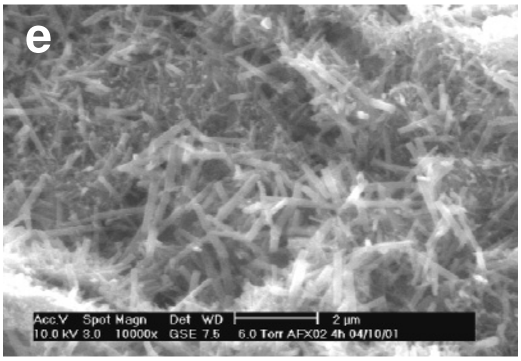


Figure 6. Microstructure evolution in cement with an alkali-free accelerator: a) prevalent ettringite formation in first 10 minutes, b) growth of gel layer (C-S-H-like phase) surrounding cement particles (during intial 2-3 hours of hydration), c) conversion of ettringite to monosulfate and d) initial formation of C-S-H (type II), e) additional formation of ettringite and type I C-S-H after 4 hours.

Note that the monosulfate microstructure disrupts the continuous gel layer covering the cement particles, and thereby exposes the cement to further hydration. In Figure 6d one observes the formation of C-S-H as well as the renewed formation of ettringite (Figure 6e). There is experimental evidence that a significant amount C-S-H is also formed in the early stages of hydration. In a study using NMR[15], it was observed that alkali-free accelerators promoted the formation of C-S-H, and the quantities formed were significantly greater that those measured in an alkali aluminate accelerator. This finding is important considering that C-S-H is the phase responsible for the material’s good strength development. One significant microstructural difference between alkali-free and sodium silicates or alkali aluminates is the formation of crystalline phases in the presence of alkali-free accelerators. The greater volume of crystalline hydration products formed on the surface of cement particles leads to a higher exposure of unhydrated areas that can undergo further hydration.

It is apparent that the chemistry of alkali-free accelerators can be quite complex. Nonetheless, the microstructre and chemistry of the cement-alkali-free accelerator interactions promote setting behavior that is favorable for sprayed concrete, and allows for proper gain in strength and long term properties necessary for durable concrete.

4 Performance

Often, high performance is associated with a material’s mechanical properties. In sprayed concrete this is usually true in the early stages of hydration. However, concrete technology is continuously evolving, and specifications for tunneling and mining applications are becoming more demanding from a technical, environmental, and technological standpoint. For this reason, more frequently, structures are evaluated on the basis of their ability to resist time-dependent degradation. Therefore, the definition of “high performance” needs to be carefully reviewed – high performance should not be evaluated solely on the basis of mechanical properties, but also encompass properties that are indicators of durability. As pointed out earlier, due to economics as well as savings on time, single shell permanent sprayed concrete structures are becoming a more attractive solution in tunneling and mining jobs. This implies that the sprayed concrete must not only demonstrate good strength development, but it must have characteristics that gaurantee a long service life. The following sections compare the performance of sprayed concrete containing either alkali-based or alkali-free set accelerating admixtures.

4.1 Setting and Hardening Behavior

4.1.1 Early Age Strength Development

As previously mentioned, one important and most frequent (due to the relative ease of performing the tests) material property used in the evaluation of early age performance of sprayed concrete is strength development during the first 24 hours of hydration. Here, strength development is viewed as an indirect and physical means of following the setting and hardening evolution in sprayed concrete. Currently, most of the evaluation of early age strength development is carried out according to the specifications outlined by the Austrian Concrete Association[5]. The method basically consists of correlating strength to the penetration of different size needles (depending on defined strength classes) in sprayed concrete specimens.

Strength development data has been collected for different types of sprayed concrete specimens from actual jobsites [17] and “laboratory” spraying trials. The results are plotted in Figure 7, and superimposed onto the J-curves specified by the Austrian Concrete Association[5]. Sprayed concrete falling in the J1 envelope are considered to be suited for placing in thin layers, on a dry rock substrate, and no load-bearing capacity is required. However, if concrete is to be sprayed in thick layers, overhead, at high delivery rates, and sustain immediate loading, then it must have a strength development that falls in the J2 envelope. J3 sprayed concrete typically exhibits rapid development of high early strength, and this typically leads to dust formation and high rebound, which can cause health and environmental risks (see section 5). In order to achieve J3 behavior, concrete sprayed with sodium silicates have to reach dosages of 18%. Therefore, it is strictly specifed by the EFNARC, CEN, and Austrian Concrete Association guidelines that only alkali-free accelerators should be used in spraying of concrete falling in the J3 category.

A portion of the results shown in Figure 7 indicate the early age strength development of concrete sprayed with alkali-free accelerators in their typical dosage range: 5% to 8%. On average, in the first hour of hydration the strength values fall inside the J2 envelope. Between 2 to 24 hours the average strength of concrete sprayed with alkali-free accelerator follows line C, thus indicative of strength fulfilling the J2 and J3 requirements.

Although concrete sprayed with sodium silicates at dosages between 12% and 18% can show a higher strength development (J3) during the first 2-4 hours of hydration compared to concrete sprayed with alkali-free accelerators, they tend to undergo a severe loss in strength (up to 50% at ages $\geq$ 28 days) when compared to the identical reference concrete without accelerator (see section 4.2). In order to minimize this negative consequence, the dosage of sodium silicates in spraying applications is reduced to a range between 5% and 10%. The early age strength development for sprayed concrete in the lower dosage range is also given in Figure 7. Note that in the first 4 hours, the strength development (on average) of concrete sprayed with a lower dosage of sodium silicates falls predominantly in the J1 range. Beyond 4 and 24 hours the strength development of sprayed concrete, with the lower dosage of sodium silicate accelerator, falls in upper bound of the J2 envelope. A problem with using sodium silicate accelerator in the low dosage range is that the build-up of the sprayed concrete layer is limited, and overhead spraying is practically not possible. Therefore, high dosages are required for sodium silicates if a thicker lining is to be achieved, but, as mentioned previously, this is at the cost of extremely poor long-term strength development as well as other health and environmental problems (see section 4).

Based on the large number of results collected on sprayed concrete specimens, the early age strength development data show that on average, concrete sprayed with the alkali-free accelerators, show good strength development that is comparable between 4 hours and 24 hours to concrete sprayed with high dosages of sodium silicates. However, compared to sprayed concrete within the lower dosage range of sodium silicates, concrete sprayed with alkali-free accelerator definitely show a superior early age strength development.

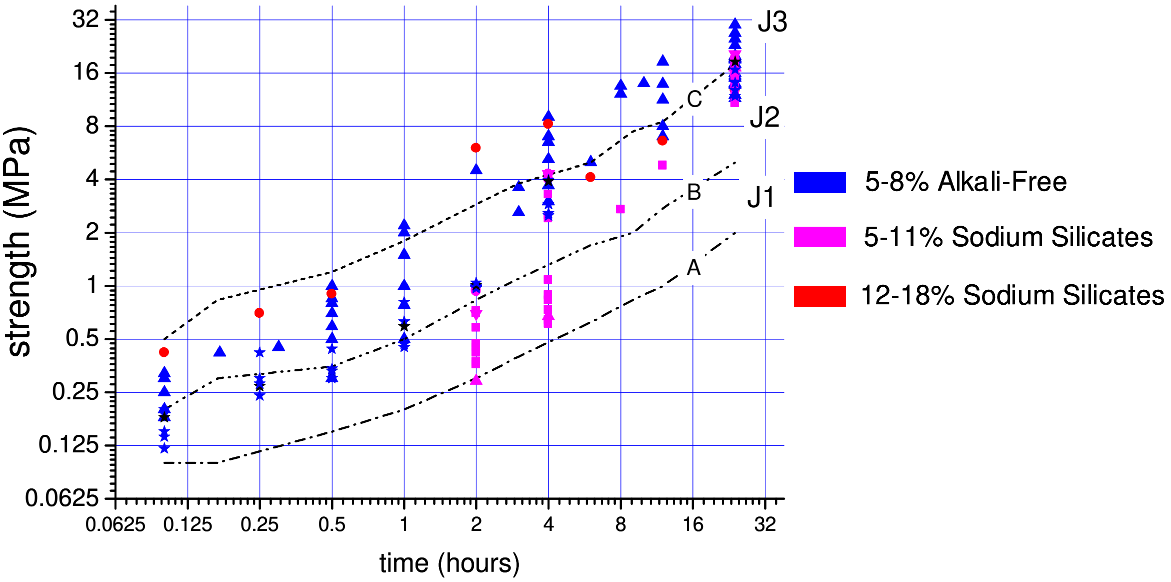


Figure 7. A comparision of the early strength development of sprayed concretes with different types of set accelerating admixtures.

4.1.2 Temperature Evolution Behavior

Besides the early age strength development discussed above, there are other means to evaluate the setting and hardening behavior in sprayed concrete. Although, not as common as the penetration tests, calorimetry can be carried out in order to evaluate the rate of hydration. One approach is to measure the temperature evolution in cement-based materials. Researchers have demonstrated that it is possible to correlate accelerator efficiency and temperature increase[11]. Figure 8 shows typical temperature evolution curves for a reference cement paste, paste with an alkali-free, and paste with sodium silicate accelerator. There noticeable differences in the hydration reactions between alkali-free and sodium silicate set accelerating admixtures. One typically observes a significant initial temperature rise when an alkali-free accelerator is used in sprayed concrete. Then the reaction slows down resulting in a slight drop in temperature. This initial heat evolution is attributed to the formation of ettringite (section 3.3.1 and 3.3.2). At a certain age, the rate of reaction increase as indicated by a sudden rise in temperature, which is primarily due to the hydration of C_3S, and to a minor extent to the additional formation of ettringite.

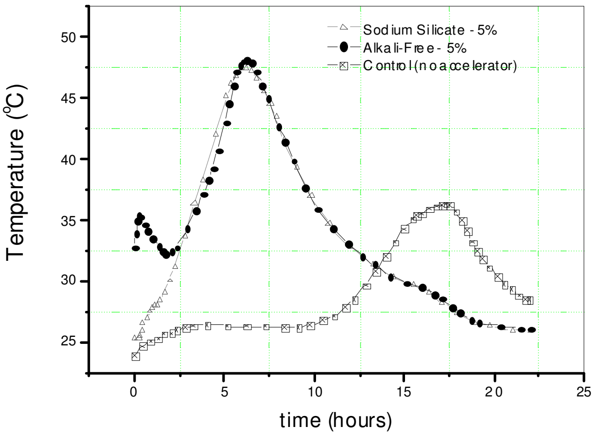


Figure 8. Temperature evolution curves showing the influence of sodium silicates and an alkali-free accelerators on the hydration kinetics.

On the other hand, in cement-based systems containing sodium silicates, one does not observe an initial heat evolution peak, but instead the temperature rises in a continuous fashion until a maximum is reached. As indicated by the chemical and microstructure data, the continuous rise in temperature indicates that sodium silicates react with cement to form a dense gel that covers the unreacted cement particles. Therefore, the heat evolution of cement-admixture reaction can give us an indication of the rates of reaction. It is important to be aware of the fact that, for a given type of set accelerating admixture, the temperature/rate of reaction curves can be quite different for different cements.

4.1.3 Chemical Shrinkage

Another means to get information on the extent of reaction is through measurements of chemical shrinkage[18]. Figure 9 shows that when 20% of sodium silicate is added to a 30 minute old cement paste the chemical shrinkage is higher than that measure in a cement paste with an alkali-free accelerator.

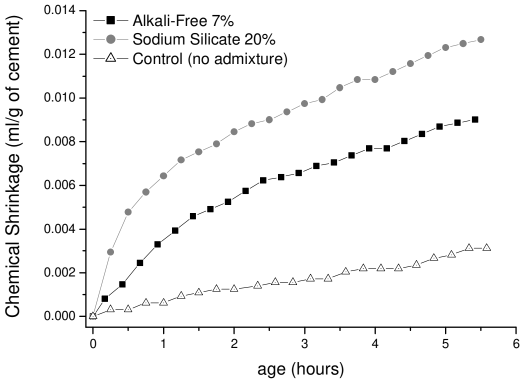


Figure 9. Influence of sodium silicate and alkali-free set accelerating admixtures on chemical shrinkage at dosage levels that enable the build-up of a thick layer (>10cm) of sprayed concrete (i.e. at least J2 strength classification).

The higher chemical shrinkage is indicative of greater reactivity, but the high stiffness (i.e. high modulus and low creep) gained through early age strength development coupled with high chemical shrinkage can lead to damage in the form of cracking. Consequently, this will lead to poor material performance.

4.1.4 Vicat Tests

Also Vicat tests can be used to evaluate the setting and hardening behavior of cement-based materials. Borralleras [15] compared the setting times of pastes containing alkali aluminates and alkali-free set accelerating admixture. The study considered additional variables such as cement type and water-to-cement ratio (W/C). As shown in Figure 10, the differences in setting behavior as measured by the Vicat method are not significantly different between the alkali-free and alkali aluminate accelerators.

Other Vicat measurements were also carried out on cement pastes mixed with alkaline and alkali-free accelerators (Table 1 - Maltese et al [11]). The results confirm Borralleras findings. The results of the latter investigation indicated a very high reactivity of sodium silicate (end setting time lower than 2 minutes). Such fast setting could be the main reason of high rebound normally observed for concrete sprayed with sodium silicates [15]. This implies a greater waste of concrete, and consequently higher construction costs.

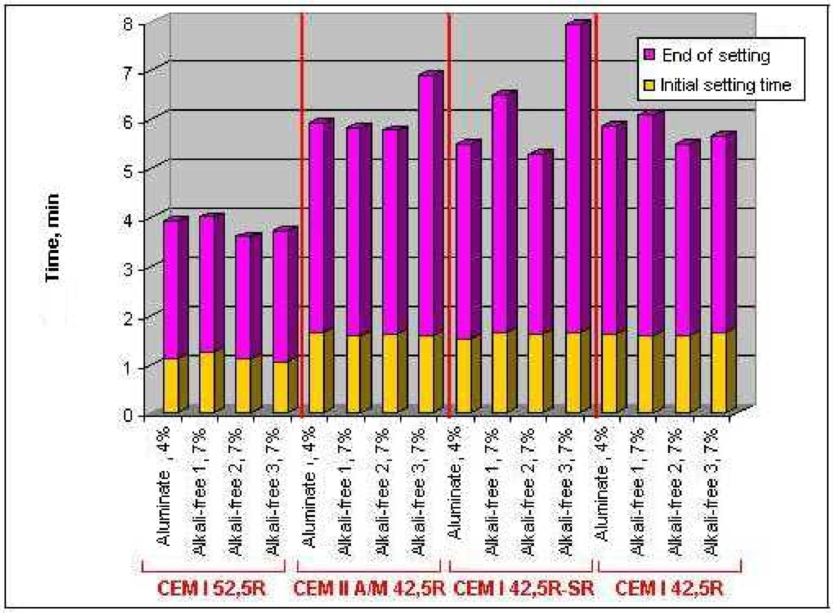


Figure 10. Comparison of the setting times measured with Vicat needle (W/C 0.32)

	8% Sodium Silicate	10% Sodium aluminate	10% Alkali free	Reference
END SETTING TIME	<<2’	2’	2’	5 hours

Table 1. End setting time of cement pastes (W/C=0,40) mixed with different accelerators.

4.2 Mechanical Behaviour

The discussion presented on setting and hardening behavior in section 4.1 and information on the chemical as well as microstructure given in sections 3.3.3 and 3.3.4 have, to some extent, anticipated the topic of this section - mechanical performance of concrete sprayed with sodium silicate and alkali-free set accelerating admixtures. It is well documented [19-24] that the alkali silicates and alkali aluminates are detrimental to the long term strength development of sprayed concrete. Figure 11 is compilation of data showing strength losses as high as 60% in concretes sprayed with alkali-based (sodium silicates primarily) set accelerating admixtures. Due to the self-evident data provided in Figure 11, there is no reason to elaborate further on the details. These strength losses obtained when using alkali-rich accelerators (specifically sodium silicates) are not acceptable. Furthermore, the EFNARC norms impose a maximum allowable strength loss of 25%.

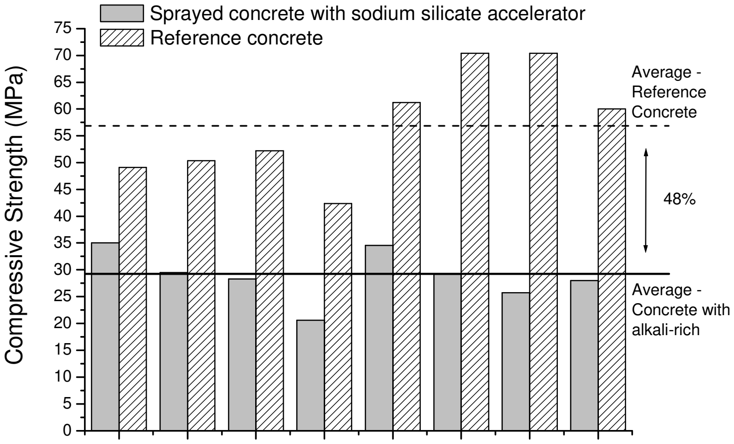


Figure 11. Compilation of compressive strength data showing the extent of strength loss for concrete sprayed with alkali-rich set accelerating admixtures.

A collection of data on strength development of numerous sprayed concrete mixes carried out in Switzerland with alkali-free set accelerating admixture is presented in Figure 12.

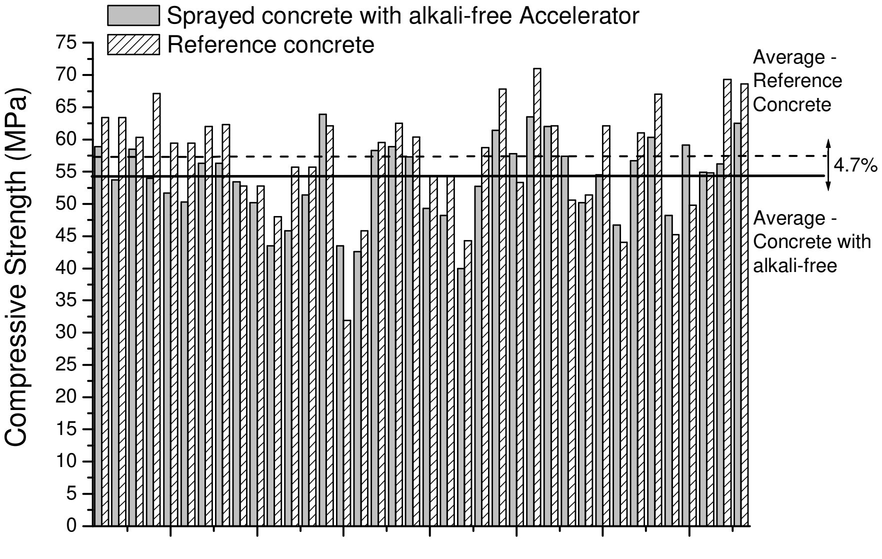


Figure 12. Compressive strength data on concrete sprayed with alkali-free set accelerating admixtures. Highlighted areas represent the average values.

Notice that the strength losses (average loss = 4%) are well below the aforementioned maximum allowable limit. More importantly, in many cases, optimally dosed alkali-free accelerators can even lead to strength developments greater than the reference concrete. As testified by the data presented in this section, the use of alkali-free accelerators in sprayed concrete unquestionably improves the development of long term strength in comparison to concrete sprayed with sodium silicates and alkali-rich set accelerating admixtures in general.

Figure 13 shows the strength development of sprayed concrete containing alkali-free accelerators over a 5-year period under different types of curing conditions. Notice that the concretes do not exhibit a loss in strength, but continue to gain strength beyond the age of 28 days.

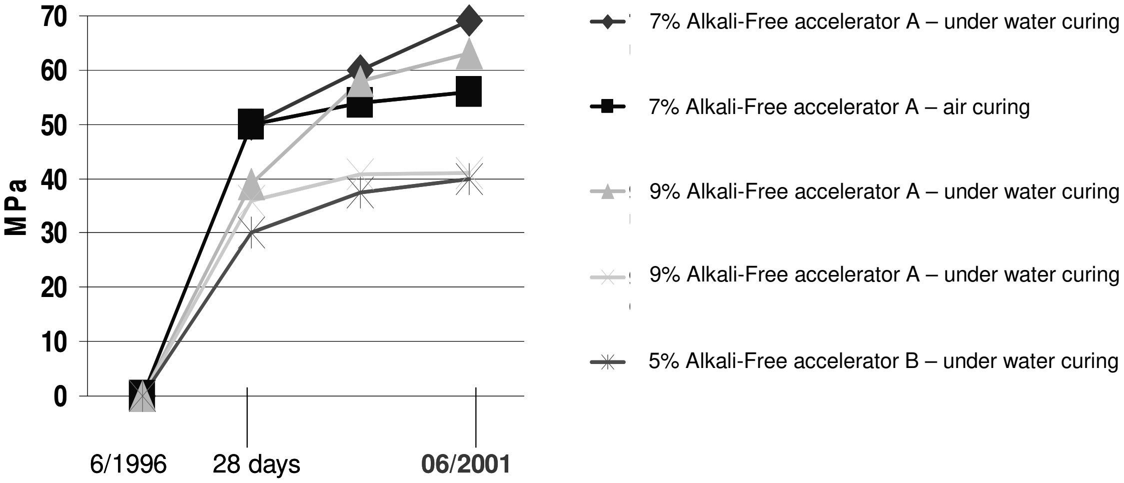


Figure 13. Strength development of concrete with akali-free accelerators under different curing conditions.

4.3 Durability

Sprayed concrete is often subjected to harsh conditions such as continuous and heavy ventilation, variable relative humidity, running water, and water leakage that are typical of tunnels. In addition, sprayed concrete has a high cement content (350-500 kg/m^3) compared to conventional concrete, undergoes rapid setting, and is sprayed in layers of variable thickness (5-50cm). These are all aspects of sprayed concrete that make it susceptible to poor hydration, rapid self-desiccation, increase shrinkage, cracking, and leaching – all material properties that reduce durability. Other durability issues of concern in sprayed concrete is alkali-silica reaction (ASR) and sulfate attack. For this reason guidelines highly recommend the use of alkali-free accelerators in sprayed concrete when a structure is required to withstand time-dependant degradation. The following sections will treat the subjects of leaching, ASR, sulfate attack, and steel corrosion.

4.3.1 Leaching of Sprayed Concrete

One of the material properties that is the most influential in determining the durability of concrete is permeability. The ingress of moisture and water in sprayed concrete is controlled by its permeability. It is through the movement of water that chemicals are transported either in or out of concrete, and the chemicals can be aggressive or lead to reactions that are detrimental to the material itself or surrounding structures as well as the environment. Permeability can be aggravated by the cracking of as a result of high shrinkage – a problem that is not uncommon to sprayed concrete.

A consequence of high concrete permeability is leaching, which leads to material deterioration and loss in strength through an increase in porosity. One major reaction product (20-25% by volume) resulting from the hydration of the calcium silicates is calcium hydroxide (CH – section 2.3.2), which is also the most water soluble phase (1.6g/l at 20°C and increases at lower temperatures). Thus, water permeating through concrete can quickly lead to the depletion of CH, resulting in a porosity increase. Upon contact with a source of CO_2, the CH saturated eluent readily precipitates calcium cabonate ($CaCO_3$). This can have severe consequences as demonstrated by the extensive clogging of pipes shown in Figure 14 [25].

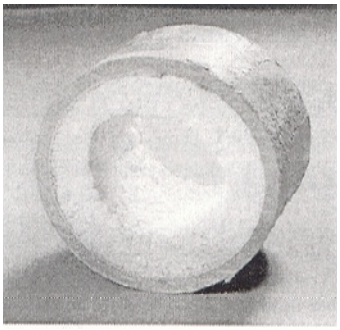


Figure 14. Clogged pipe from a tunnel site due to leaching of $Ca(OH)_2$.

However, CH is not the only chemical that can be leached, and the ions either in the acqueous phase or deposited in the pores can also be found in the eluent of sprayed concrete structures subjected to flowing water [22, 25, 26]. Some of these ions, for example the alkalis (Figure 15), can also promote the deposition of precipitates upon contact with CO_2.

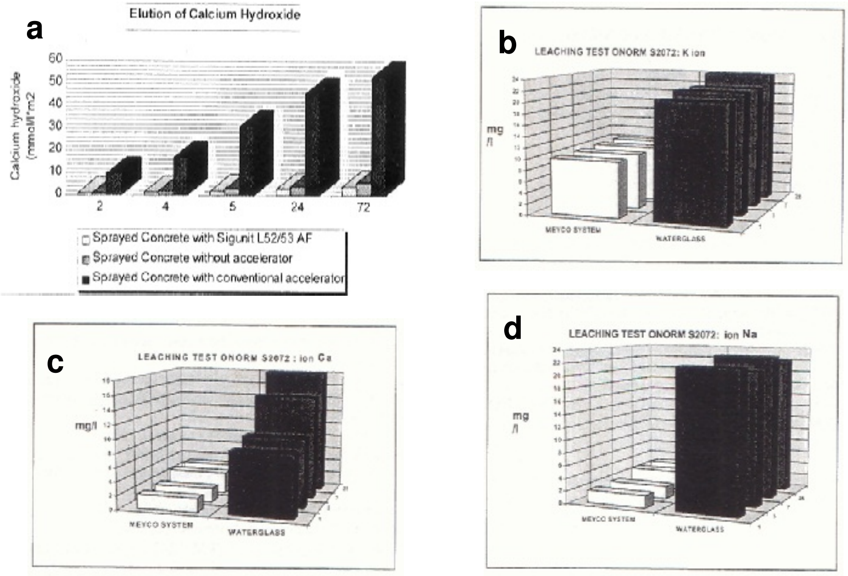


Figure 15. A comparison of the eluent chemistry of concrete samples prepared with conventional (waterglass/sodium silicate) accelerators and alkali-free accelerators (a-[26]; b,c,d-[25]).

Another consequence of highly permeable concrete is the contamination of ground water by the ions in the eluent, and this has a negative environmental impact (section 5).

Results of tests carried out to evaluate the permeability [42] of alkali-free based sprayed concrete with respect to water, oxygen, and chloride ions as shown in Figure 16. As one can observe, the permeability of concrete sprayed with alkali-free accelerators is on average low, and this implies good durability.

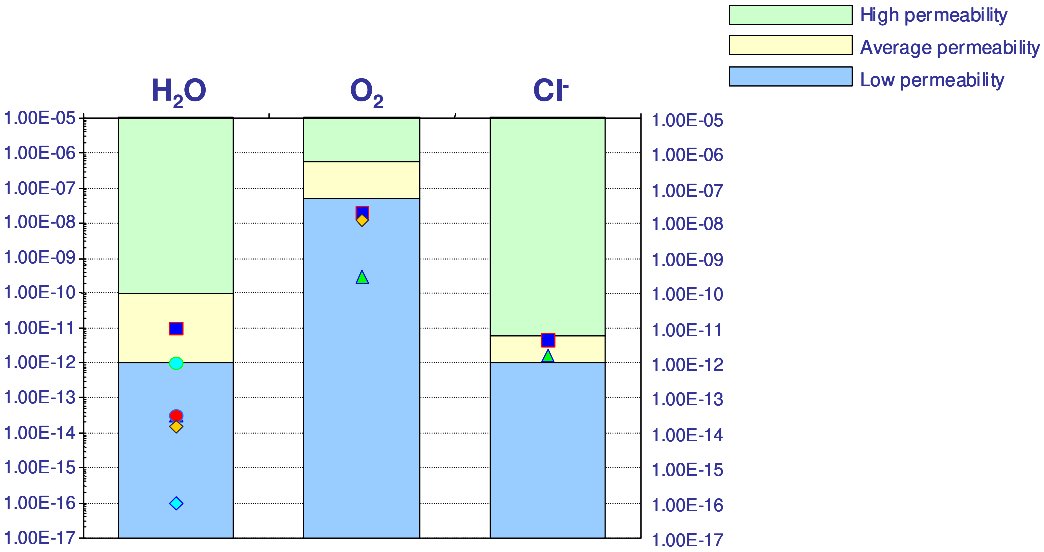


Figure 16. Permeability of concrete sprayed with alkali-free accelerators.

As indicated in the previous section, concrete sprayed with sodium silicates shows a substantial decrease in the long term strength. Usually this is a sign that the quality of the concrete is extremely poor, and its cement chemistry and microstructure make it susceptible to further degradation, and consequently the material exhibits low durability. It has been previously discussed that the microstructure of concrete sprayed with sodium silicates exhibits poor hydration beyond the age of 24 hours due to the thick gel formed around the unreacted cement particles. The poor hydration coupled with drying lead to a coarsening of the pore structure, not to mention cracking due to shrinkage. Therefore the pore structure of an alkali-rich sprayed concrete is more permeable. In addition, it has been pointed out by researchers as well as engineers [20,27] that sprayed concrete containing sodium silicates tends to have a higher porosity compared to sprayed concrete with alkali-free accelerators.

As previously shown by the early age strength development, calorimetry and chemical shrinkage data, at typical dosages required to build-up thickness, concrete sprayed with sodium silicate develops a high stiffness almost instantneously (section 4.1.4), and consequently material that is formed becomes difficult to compact as additional concrete is sprayed. This leads to a concrete with high porosity. On the contrary, due to the nature of the chemical reactions in alkali-free set accelerating admixtures, sprayed concrete does not stiffen so rapidly , and therefore it is possible to achieve a better compaction of the material. It is apparent that the sprayed concrete composed of sodium silicates is highly vulnerable to degradation resulting from leaching. The problem is aggravated by the fact that the sodium silicate-based sprayed concrete also possess a high concentration of alkalis that can be leached into the ground water. Another negative result from leaching is efflorescence which is often recognizable by non esthetically pleasing surface depositions on tunnel surfaces.

4.3.2 Sulphate Resistance

In terms of sulphate resistance, a number of tests have been carried out by SINTEF [28], Norway and the results are summarised as follows:

- Alkali-free accelerators can be used to produce sulphate resisting sprayed concrete up to dosages of 10%.
- Alkali-free accelerators perform better than modified sodium silicate accelerators with OPC cements.
- The use of 6% microsilica provides comparable sulphate resistance with OPC as with sulphate resisting cement (SR). This is important as it is preferential to use OPC rather than SR cement in sprayed concrete due to the faster setting and early strength development.
- The lower the water-cement ratio, the higher the sulphate resisting performance. It is recommended to have a w/c ratio below 0.45, and preferably with the aid of new hyperplasticisers, attain a w/c ratio of less than 0.4.

4.3.3 Alkali Silica Reaction (ASR)

Severe damage can occur in concrete if certain reactive forms of silica present in aggregates react with the alkalis present in the acqueous phase. Currently, the possible mechanisms of the alkali silica reaction are not well understood, and a more comprehensive review of the topic is provided in the following references: [7], [9], [29], and [30]. Nonetheless, the processes responsible for the damage of concrete resulting from ASR can be simplified in the following steps: a) dissolution of silica and formation of ASR gel, b) swelling of the ASR gel, and c) expansion and microcracking of concrete. A more detailed explaining is provided in the following paragraphs.

During the first phase some of the acidic silanol groups of amorphous silica (like opal), in alkaline environment react with alkalis (for example sodium) according to the following reaction:

$$H_2O_2(SiO_2)_n + 2\,Na^+ \xrightarrow{(OH^-)} Na_2O_2(SiO_2)_n + 2H^+ \qquad (10)$$

New formed sodium-oxygen bond is much more ionic than the ordinary oxygen-hydrogen one, resulting in a higher water molecules attraction that causes a slight swelling of rigid silica network.

During the second stage of reaction, when high amount of hydroxyl ions are present, a decomposition of silica-oxygen bond occurs according to the reaction:

$Na_2O_2(SiO_2)_n + 2OH^- \longrightarrow Na_2O_2(SiO_2)^{2-} + H_2O_2(SiO_2)_{n-1}$ (11)

Other reactive acidic silanol groups are created and the chemical reaction (10) can be repeated until alkali ions are available. The increase of gel like alkali silicates (N-S-H) causes a more intensive water absorption, which leads to swelling of the material.

When Na_2O content is lower than 0,6% (on cement weight) or 3kg/m^3, a so-called safe reaction can happen [31,32]. In fact, an insoluble high calcium alkali silicate is formed from the reaction of calcium hydroxide with gel like alkali silicate:

$Na_2O_2(SiO_2)_n + Ca^{2+} \longrightarrow [CaNaO_2(SiO_2)_n]^+ + Na^+$ (12)

This calcium rich derivative (which is usually defined C-N-S-H) has a reduced swelling capability. Although some alkalis are liberated, reaction (12) reduces alkali concentration, thereby promoting the increase of calcium ions in the pore solution. This effect favours C-N-S-H formation, and the material swelling does not occur. This is the case for safe alkali silica reaction.

If the alkali content is higher than 0,6% (on cement weight) or 3 kg/m^3, therefore calcium concentration in the pore solution is lowered and reaction (12) is hindered. More N-S-H is formed which causes swelling and cracks. This is the case for unsafe alkali silica reaction.

The effect, on the alkaline concentration of a concrete, resulting from the use of sodium silicate, can be evaluated. The following hypothesis could reasonably be made:

Alkali concentration in cement: 0,6% (as Na_2O)

Cement content: 450 kg/m^3

Alkali concentration in a typical sodium silicate: 8%(as Na_2O)

Dosage of sodium silicate: 12% (on the cement weight)

Thus,

(450x0,6)100= 2,7kg/m^3 (concrete dosage of Na_2O coming from cement)

(450x12)/100=54kg/mc (kg of sodium silicate added for each m^3 of concrete)

(54x8)/100=4,3kg/m^3 (kg of Na_2O coming from sodium silicate each m^3 of concrete)

4,3+2,7=7kg/m^3 (total amount of alkali contained in a concrete sprayed with sodium silicate)

Considering the limit of 3 kg/m^3, the above reported results emphasize that the use of sodium silicate favours unsafe alkali-aggregate reaction.

Obviously, ASR can be avoided with proper mix design practices and the use of non-reactive (silica-free) aggregates. However, it should be pointed out that when sodium silicate set accelerating admixtures are used in sprayed concrete the risk of ASR is very high due to the high alkali content of the product. In fact, a study carried out by SINTEF [33] has demonstrated that concrete composed of a normal OPC, reactive aggregates, and 10% (low dosage) sodium silicate accelerator exhibited severe damage due to ASR.

4.3.4 Steel corrosion

Due to the acidic nature of alkali-free accelerators, many demonstrations have been carried out showing how the immersion of steel in alkali-free accelerators leads to severe corrosion [1]. Of course this has a negative impact on durability. However, this is quite misleading because steel in concrete structures is typically surrounded by concrete and not the liquid accelerator. In fact, a well known fact is that concrete has a pH that is in the basic range (12-13), and therefore when the alkali-free accelerator comes into contact with the concrete it is immediately neutralized. Therefore, steel corrosion is not even an issue in concrete sprayed with alkali-free set accelerating admixtures. Furthermore, the alkaline concrete environment determines steel passivation and its corrosion cannot occur. Moreover a slight delayed hardening reaction, due to the use of alkali free accelerator, allows a uniform distribution of accelerator particles that can be completely consumed by the hardening cementitious matrix. Such suppositions are confirmed by Bravo et al. [34], which have demonstrated that soluble aluminium and sulphates, in a cement paste mixed with alkali free accelerators, disappear completely after 20 hours of hydration.

4.4 Application – Chemistry Compatibility

The production of sprayed concrete structures involves a very unique as well as complex methodology for processing the material – specialized equipment designed for the projection of concrete onto a substrate at high pressures. Furthermore, the material has to develop unique properties as soon as it makes contact with the substrate: adherance, good compaction, build-up of thickness without fall-off, minimum rebound, minimum dust generation, and rapid strength development. Therefore, the proper production of sprayed concrete has an important impact on material performance, and this requires equipment with a certain level of sophistication – proper dosing, pumping efficiency, nozzle design, etc. In order to make the application process meet the aforementioned requirements it is important to have a set accelerating admixture that is compatible with the application process (i.e. render most efficient the process).

Once again, data collected from different jobsites and experiments are presented in order to provide a comparison of alkali-free and alkali-rich set accelerating admixtures. Rebound data collected from different applications show that on average the rebound of conrete sprayed with alkali-free accelerator is, on average, less than 10% (7.7% ±2.3). This is lower than the typical rebound values (> 10%) measured for concrete sprayed with sodium silicates.

The chemistry of alkali-free accelerators is such that the rate of setting and hardening is not too fast allowing for better compaction (i.e lower porosity), build-up of layers greater that 10cm, and low dust generation when compared to the spraying of concrete with sodium silicates. As pointed out earlier, a study by Zaffaroni et al [20] clearly demonstrated that the average porosity of concrete sprayed with alkali-free accelerators is significantly lower than the porosity in concrete sprayed with sodium silicates.

4.4.1 Economics

Underground construction usually involves many technical issues, high risks and time pressures. The contractor needs a reliable partner that can offer the complete solution with high quality products and equipment together with competent service for efficient, safe and economic execution of the project.

Many of the costs of a final in-place price of sprayed concrete in a large underground infrastructure project are underestimated by contractors e.g. cost of maintenance, cost of collecting, loading, carting away and dumping of rebound from a project to a suitable approved site due to environmental legislation, cost of breaking out, removal and replacement of areas of defective sprayed concrete resulting from the application of low quality material.

A significant reduction in rebound is one of the key advantages of using alkali-free accelerators for sprayed concrete application:

Rebound data collected from different applications, different jobsites and experiments provide a comparison of alkali-free and alkali-rich set accelerating admixtures and show that the rebound of concrete sprayed with alkali-free accelerator is, on average, less than 10% (7.7% ±2.3). This is lower than the typical rebound values (> 10%) measured for concrete sprayed with sodium silicates.

The following parameters have a greater impact than the admixture cost on the project cost:

- Application speed
- Rebound
- Potential savings of having a durable permanent tunnel lining in one pass

Case study : North Downs Tunnel (UK)

Part of the rail link connecting mainline London stations and the Channel Tunnel, the 3.2 km long North Downs Tunnel is of twin-track configuration [36]. The £ 80 million tender was based on a double shell structure: a temporary sprayed concrete lining, followed by a reinforced permanent in-situ concrete lining. The alkali-free accelerators have allowed to increase the specification for primary sprayed concrete linings so that they would be of permanent quality. This approach has allowed to reduce the excavation profile, to decrease the total lining thickness, to eliminate the need for secondary lining reinforcement and to save £10 million.

Alkali-free accelerators account for less than 10% of the total cost of applied steel fiber reinforced wet mix sprayed concrete. Reduction of rebound and increased capacity reduce application time and standstill of the excavation process, which is one of the major saving in tunneling.

4.4.2 Environmental Impact and Work Safety

It is evident from the review provided in section 3 on the different characteristics of liquid accelerators that unquestionably the development of alkali-free accelerators addresses head-on one of the primary concerns of the construction industry and responsible entities for establish standards — environmentally safe products and safety at the jobsite (i.e. reduction in health risks). The alkali content in alkali-free liquid accelerators is extremely low (%Na_20-equivalents < 1.0) and this brings advantages from an environmental safety point of view.
Many guidelines for sprayed concrete like the Austrian [5] have required since the mid 90's that the maximum percentage by weight of alkali ions expressed as sodium oxide equivalent has to be lower than 1.0 in order to reduce the risk of carbonation and sintering in the drainage systems (see section 4.3.1).

The use of alkali-free accelerators in sprayed concrete does not only lead to a significant reduction of the contamination of ground water but furthermore, due to the nature of the chemical reactions between concrete and alkali-free accelerators the dust generation during spraying is significantly reduced.
The maximum allowable dust concentration is less than 15 mg/m^3 (total dust) but less than 6 mg/m^3 for fine dust and less than 4 mg/m^3 for quartz containing dust (according to the Austrian guidelines).
Testor and Kusterle [37] work demonstrates that the dust concentration varies between 6.6 and 18.9 mg/m^3 for the dry-mix process and reaches only 2.8 to 3.9 mg/m^3 for the wet-mix process.

In terms of the operator's health, concrete sprayed with alkali-free accelerators leads to a reduction of dust generation as demonstrated by the measurements carried out at the North Cape Tunnel in Norway. The total dust content of the air when concrete is sprayed with a liquid alkali-free accelerator was 3.7 mg/m^3 of air which is half the value of dust generation measured when concrete is sprayed with a modified silicate-based accelerator (Figure 17).

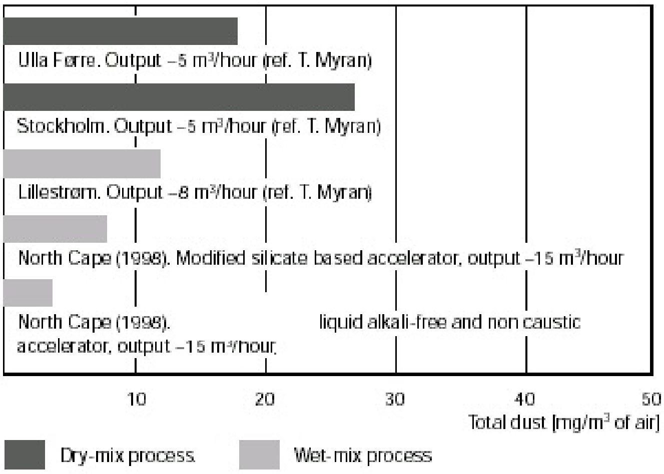


Figure 17. Evaluation of the dust generation in sprayed concrete.

As a product, alkali-free accelerators impart properties to concrete that make it more compatible with the process of application. This leads to additional performance advantages that go beyond the setting behavior, mechanical properties, and durability.

5 Conclusion

An extensive and comprehensive comparison of liquid-based *alkali-free* and *alkali-rich* (alkali silicates and alkali aluminates) sprayed concrete set accelerating admixtures (accelerators) is presented with the aim of clarifying the ongoing controversy regarding their advantages and disadvantages. The admixtures are compared on the basis of their chemistry, microstructure development, setting behavior, mechanical performance, durability, suitability for the spraying, economics, environmental impact, and work safety.

There are important features of the set accelerating admixtures discussed in this paper that should to be pointed out :

- The chemistry associated with alkali-free set accelerating admixtures present a new and alternative technology to the sodium silicates:
  a. Completely different type of chemistry. Alkali-free accelerators are admixtures without alkali metals.
  b. The chemical reactions lead to a different microstructural development that is beneficial to the early age as well as long-term strength development.

- It has been demostrated that there are significant economical advantages, positive environmental impact, and improved work safety through the use of alkali-free accelerators:
  a. Safer product for the skin (pH = 5): pH of alkali-free set accelerating admixtures is typically between 2 and 4. The pH of alkali silicates and more specifically sodium silicates have a pH that is typically greater that 11 which is caustic as well as corrosive [41].
  b. Lower dust generation during spraying.
  c. Significant reduction in reboud (i.e. less waste is produced for landfills and more cost-effective).
  d. Reduced alkali contamination of eluent.

- The material properties of concrete sprayed with alkali-free accelerators are significantly superior to those observed for concrete sprayed with alkali silicates or aluminates:
  a. Long term strength development shows strength reductions that are typically less than the limit imposed by the various European guidelines for sprayed concrete (EFNARC, CEN, and Austrian Concrete Association), and in some cases concrete sprayed with alkali-free accelerators can even exhibit long-term strengths that are equivalent or even higher than the reference concrete.
  b. Durability of concrete sprayed with alkali-free accelerators is significantly improved with respect to sodium silicates: reduced early age shrinkage, lower permability, lower risk of ASR, greater sulfate resistance.

- Good compatibility between the chemistry of alkali-free set accelerating admixture and the technology of sprayed concrete – it is a product that suits best the method of application:

a. Proper material compaction and good build-up of layers especially overhead.
b. Continous construction is possible due to adequate strength development.

- Alkali-rich accelerators (alkali silicates and alkali aluminates) are banned from use in several countries due to poor safety and performance.

Taking into consideration all of the above parameters, one can conclude that alkali-free accelerators out perform alkali-rich accelerators. More importantly, recent trends and requirements of the construction industry have become more demanding, and sprayed concrete for rock support and mining applications needs to have long term properties that prolong its service life. The development and advent of alkali-free set accelerating admixtures represents an important step forward in sprayed concrete technology. Chemical admixtures company have put forth great efforts and innovation to improve material behavior and bring benefits to the environment and safety of workers. Further developments and alternative technologies should be promoted with aim of improving the performance and quality of sprayed concrete.

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