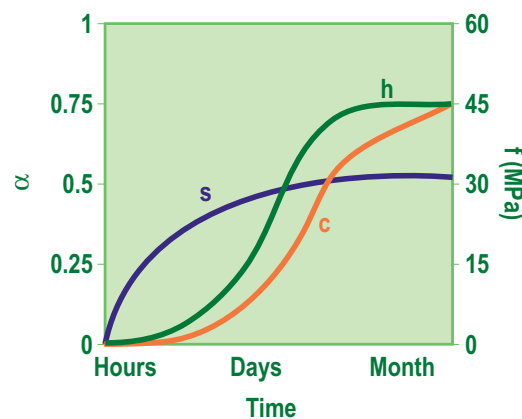


tion (α) of cement (§ 8.2). They can include setting or hardening accelerators if their action occurs in the plastic or hardened state, respectively. In other words, setting accelerators reduce the setting time (§ 2.5), whereas the hardening accelerators increase the strength at early ages (§ 3.1). Figure 13.1 schematically shows the effect of accelerators on the degree of hydration and compressive strength: setting accelerators act during the first minutes of the cement hydration, whereas the hardening accelerators act mainly during the first days.



ig. 13.1 – Influence of set accelerating (s) or hardening accelerating (h) admixture on the degree of hydration (α) and compressive strength (f) with respect to the control concrete (c)

13.2.1 SETTING ACCELERATORS

Setting accelerators are used in the application of sprayed concrete, also known as *shotcrete*, typically in tunnel works (Fig. 13.2) in order to increase the adhesion of the sprayed mixtures on the substratum (Chapter XXII). There are two types of setting accelerators: those based on sodium silicate (NS) and accelerators which are alkali-free (AF) and are based on aluminium sulphate water emulsion.

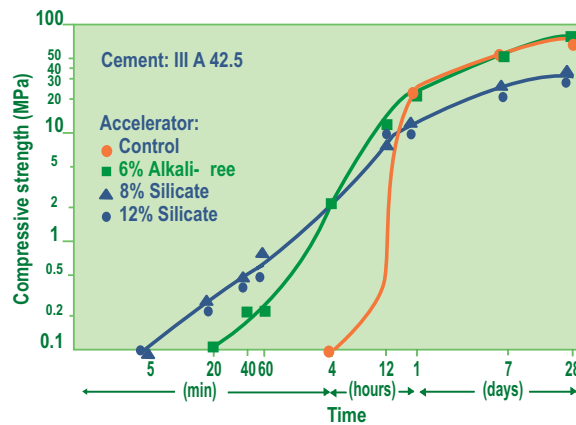
The setting accelerators based on NS reduce dramatically the setting time to 5-10 minutes but unfortunately they also reduce the strength at later ages (Fig. 13.3), particularly when blended cements are used instead of portland cements.

Moreover, alkali-based admixtures can promote the alkali-silica reaction if the aggregates contain some amounts of amorphous silica (§ 4.2.3 - 4.2.4 and § 10.4 - 10.4.2), and are dangerous to the health of workers for their caustic character which can attack the skin as well the lungs if they are inspired by the workers.

The new setting accelerators (AF) are slightly less effective in reducing the setting time, but they do not reduce the strength at later ages (Fig. 13.3) even when blended cements, such as slag cements CEM III, are used (Table 13.1), and more importantly they are not dangerous to the worker health.



ig. 13.2 – Application of a set-accelerated sprayed concrete in a tunnel



ig. 13.3 – Influence of sodium silicate (8% or 12%) and alkali-free (6%) accelerator on the strength development

Table 13.1 – Nominal compositions of concretes shown in ig. 13.3

Cement IIIA 42.5	450 kg/m ³
fine sand (0-4 mm)	1075 kg/m ³
Coarse sand (4-6 mm)	495 kg/m ³
Gravel (4-8 mm)	82 kg/m ³
Water	190 kg/m ³
Silica fume	20 kg/m ³
Superplasticizer*	5.4 kg/m ³
Accelerator without and with NS (8%-12%) or A (6%)	

* Polycarboxylate type

13.2.2 HARDENING ACCELERATORS

Hardening accelerators are used when, for some reasons, the early compressive strength (1-3 days) must be increased (Fig.13.1): this can occur in winter time when the low temperature reduces the early strength (§ 14.2 and Fig.14.1) and then retards the time of demoulding.

In the past time chloride salts used to be widely adopted as excellent accelerators since these salts strongly increase the hydration rate of the calcium silicates (§ 3.5) and in particular that of C_3S (M. Collepari and L. Massidda, "Hydration of Tricalcium Silicate", *Journal of the American Ceramic Society*, 54, pp. 419-422, 1971; available in www.encosrl.it → **Scientific Publications** → **Cement Chemistry**). Due to this chemical effect, chloride salts, and in particular calcium chloride ($CaCl_2$), have been used in concrete mixtures as hardening accelerators for their action on the early strength of the cement matrix (M. Collepari, A. Marcialis and V. Solinas, "The Influence of Calcium Chloride on the Properties of Cement Pastes", *Il Cemento*, pp 83-92, 1973; available on www.encosrl.it → **Scientific Publications** → **Chemical Admixtures for Mortars and Concretes**)

The use of chloride salts as hardening accelerators in concrete mixtures has been strongly discouraged at the beginning of 1980's for their action in promoting the corrosion of metallic bars, and presently chloride-free accelerators must be used in reinforced concrete structures (K. Rear and D.Chin "Non-chloride accelerating admixtures for early compressive strength", *Concrete International*, vol. 12, pp.55-58, 1990). The hardening accelerators used presently are based on calcium nitrate or $Ca(NO_3)_2$, calcium nitrite or $Ca(NO_2)_2$, calcium salts of thiocyanate or thiosulphate or formiate, and three-ethanol-amine also known as TEA (M.Pauri, S.Monosi, G.Moriconi and M.Collepari, "Effect of Three-ethanol-amine on the Tricalcium Silicate Hydration" *Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, Vol.III, pp.125-129, 1986; available on www.encosrl.it* → **Scientific Publications** → **Chemical Admixtures for Mortar and Concrete**).

The market of chloride-free hardening accelerators, in order to increase the early compressive strength in concrete mixtures, today is going down due to other chemical admixtures which can increase both early and later strength since they can reduce significantly the amount of mixing water and the water-cement ratio (§ 13.11.6.1).

Special types of accelerators are used as anti-freezing admixtures in concretes placed in winter times in countries (such as Russia or Finland, for instance) where the temperature can be as low as $-30^\circ C$. These admixtures in general contain two components: an usual hardening accelerator and a chemical product capable of depressing the freezing point of water in concrete such as carbamide, high-molecular-weight alcohols (H. Kukko and I. Koskinen, "RILEM recommendations for concreting in cold weather", *Technical research Center of Finland, Res. Notes*

827, pp.52, 1988)

13.3 RETARDERS

Retarders are chemical admixtures used to increase the setting time, particularly in warm weather when the high temperature accelerates the early cement hydration and then produces undesirable workability-loss particularly in ready mixed concretes. Retarding admixtures act in particular on the calcium aluminate hydration which plays a very important role in the cement hydration during the first minutes-hours (M.Colleparidi, S.Monosi, G.Moriconi and M. Pauri, "Influence of Gluconate, Lignosulphonate and Glucose on the C_3A Hydration in the Presence of Gypsum with or without Lime", *Cement Concrete Research*, vol.14. pp. 105-112, 1984; available on www.encosrl.it → **Scientific Publications** → **Chemical Admixtures for Mortars and Concretes**).

The raw materials used in retarding admixtures are in general organic products such as gluconate, carboxylic acids, glucose, lignosulphonate, etc. or inorganic products based on copper and zinc salts.

A special application of these admixtures in form of "super-retarders" is devoted to the re-use of returned concrete. There are now increasing environmental concerns and restrictions regulating the disposal of returned plastic concrete. In an effort to assist concrete producers, to comply with new environmental regulations, special admixtures have been developed with a cost effective alternative to disposal. These admixtures are based on two components added separately: a *stabilizer* and an *activator*.

The stabilizer is a strong retarder based on carboxylic acids and/or phosphorus-containing organic acid salts. By changing the dosage of this component within a large range of percentages (0.3-8% by weight of cement) the returned concrete can be stabilized in the plastic state for hours or days and then it can be re-used without any problem.

Depending on the dosage of the stabilizer, the activator, which is a chloride-free accelerating admixture (§ 13.2.2), is used at a dosage of 0.65-1%.

There is an other combined use of retarders and accelerators. In this case, the two components (such as lignosulphonate and *TEA*) are mixed together in order to produce a water-reducing admixture without any retarding effect on the concrete mixture due to the *TEA*'s action in compensating for the retarding effect of the lignosulphonate. This use will be examined later in the paragraph devoted to water-reducers (§ 13.10).

13.4 AIR-ENTRAINING AGENTS

Air-entraining agents (*AEA*) are used to counteract freezing and thawing attack on concrete (§ 11.5). Secondary useful effects of *AEA* are the reduction in the amount of mixing water (less 5%), reduction of segregation and bleeding of fresh

concrete, improved plasticity specially in lean fresh mixtures (Chapter VII).

Many factors such as variability in the raw material (*vinsol resin*), mixing, placing method, and temperature may make it difficult to adjust the required amount of air with required bubble size and spacing (§ 10.3.3.1; Fig. 10.28). In fly ash concretes to achieve a proper air volume becomes more difficult if the ash contains variable amounts of un-burnt carbon.

To overcome all these drawbacks, two alternative methods of manufacturing frost-resistant concrete have been developed. The former is based on chemical products other than vinsol resin which are capable of changing the surface tension of the water. The latter is based on the use porous particles such as fired clay bricks, diatomaceous earth, vermiculite, pumice and perlite (*G.G. Litvan and P. Sereda, "Particulate admixtures for enhanced freeze-thaw resistance of concrete", Cement and Concrete Research, Vol.8, pp 53-60, 1970*): results in terms of durability factor indicate that concretes with higher concentration of porous particulates are frost-resistant even after 350-400 cycles of freeze-thaw cycles, whereas the control concrete without air-entrainment failed after only 60 cycles.

13.5 CORROSION INHIBITORS

Corrosion inhibitors are added in concrete mixtures to delay the initiation and/or retard the propagation of corrosion of reinforcing bars, embedded in concrete structures exposed to carbonation (§ 10.2.1) or chloride penetration (§ 10.2.2).

The most popular corrosion inhibiting admixture is based on calcium nitrite, $\text{Ca}(\text{NO}_2)_2$, which at a dosage of about 2-3% by cement weight act as cathodic corrosion inhibitor:

- *C. Alonso, M. Acha and C. Andrade, "Inhibiting Effect of Nitrites on the Corrosion of Rebars Embedded in Carbonated Concrete", Proceedings of RILEM Symposium on Admixtures for Concrete, Barcelona, Chapman & Hall, London, pp 219-228, 1990;*
- *N.S. Berke and A. Resemberg, "Calcium Nitrite Corrosion Inhibitor in Concrete", ibidem, pp 251-268.*

Calcium nitrate $\text{Ca}(\text{NO}_3)_2$, which is much cheaper than calcium nitrite, act as anodic corrosion inhibitor (*H. Justnes, "Corrosion inhibitors for reinforced concrete", Proceedings of the Seventh CANMET-ACI International Conference on Durability of Concrete, Editor V. M. Malhotra, Montreal, Canada, pp. 53-70, 2006*).

Other chemical products which could act as corrosion inhibitors include organic products such as tetramethyl or tetraethyl or tetrabutyl or tetraphenyl phosphonium-nitrite (*D. Rosignoli, "Anticorrosion Repair and Prevention Systems*

for Reinforced Concrete Structures: Effectiveness and Durability”, Proceedings of the Sixth Canmet/ACI International Conference on Recent Advances in Concrete Technology, Bucharest , Rumania, Editor V.M Malhotra, pp. 421-430, 2003). These chemicals should be combined with other raw materials to counteract their intrinsic retarding or accelerating character.

The use of corrosion inhibitors, particularly in very aggressive environments for the corrosion of steel, cannot be disjoined by the use of impermeable concrete structures with low water-cement ratio and concrete cover relatively thick such as 40-50 mm (§ 11.2-11.4).

13.6 ASR-INHIBITORS

ASR (alkali-silica-reaction) is the expansive reaction between alkali, as sodium (*Na*) or potassium (*K*) salts, and certain forms of reactive silica of the aggregate (§ 4.2.3) producing cracking and/or localized expulsion of concrete (§ 10.4). Although there are chemical admixtures capable of reducing the ASR-expansion, there are other technical solutions - such as the use of pozzolans or ground slag - which are more cost effective than the use of chemical admixtures.

One of the most known ASR-inhibitors are based on lithium (*Li*) salts, in particular lithium nitrate. Paradoxically lithium too belongs to the alkalis elements as sodium and potassium. It seems that a lithium-based chemical admixture transforms the insoluble and expansive sodium or potassium silicate responsible of the ASR into a soluble and harmless lithium silicate (V.S. Ramachandran, "Concrete Admixtures Handbook", Noyes Publications, New Jersey, USA, pp.626, 1984).

A better application of lithium salts is to block the ASR which is just starting to occur in a concrete structure: in such a case, the application of lithium salts on the concrete surface by spraying or rolling techniques is the only available technique to block the occurring deterioration process. Afterwards, one can repair the damages without any risk of new activation of the ASR.

An alternative chemical admixture other than lithium salts is silane which acts through its hydrophobic character in repelling water (§ 13.7) needed for the ASR (M. Collepardi and V.S. Ramachandran ,1992 in § 13.1)

13.7 HYDROPHOBIC ADMIXTURES

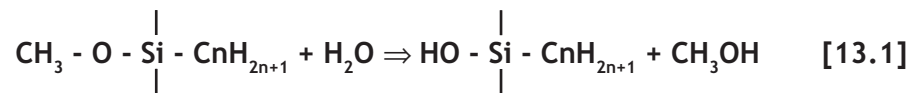
Hydrophobic products such as silane are in general applied on the surface of hydrophilic materials, including concrete, in order to transform them into water-repellent ones. However, they can also be used as chemical admixtures into concrete mixtures to make hydrophobic the concrete mass as shown in Fig.13.4 (R. Fratesi, G. Moriconi, F. Tittarelli and M. Collepardi "The Influence of Hydrophobic Concrete on the Corrosion of Rebars" Proceedings of the Fifth CANMET-ACI



ig. 13.4 – A drop of water on plain concrete specimen (left) or on concrete specimen after treatment with silane

International Conference on Superplasticizers and Other Chemical Admixtures, Rome (Italy) pp. 105-122, 1997; available on www.encosrl.it → Scientific Publications → Chemical Admixtures for Mortars and Concretes).

The hydrophobic effect of silane is due to the transformation of the group ($CH_3-O-Si-$) into a new one ($HO-Si-$) according to equation [13.1]:



The ($HO-Si-$) chemical group can be adsorbed on the hydrophilic hydrated cement particles through the hydroxilic OH group, so that the hydrophobic group C_nH_{2n+1} is fixed on the surface to repel the water molecules.

The most important applications of silane as chemical admixture into the concrete mixture or as sprayed film on the concrete surface are:

- to act as *ASR*-inhibitors by reducing the concrete humidity (§ 13.6);
- to act as bactericide and fungicide in order to avoid surface disfigurements (Fig. 13.5) related to the growth of moss (Figs.13.6-13.7) specially in north-oriented areas.

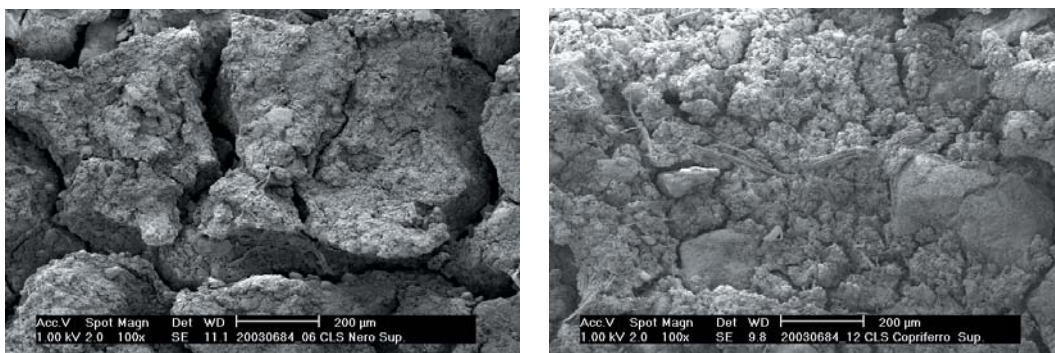
The latter action of silane-based products is based on the humidity reduction and can be enhanced by combination with other products endowed with a specific bactericide and fungicide actions such as sodium benzoate, phenol, copper salts, etc. Figure 13.8 shows the effect of silane-based admixtures in preventing surface darkness in north-oriented concrete structures permanently exposed to humid environment.



ig. 13.5 – Dark surface on the left site of the building and white surface on the right



ig. 13.6 – Microscopic view of mass on the dark surface of the building in ig. 13.5



ig. 13.7 – Scanning Electron Microscopy of the dark cement matrix of the building in ig. 13.5 (by courtesy of D. Salvioni, Mapei)



ig. 13.8 – The surfaces with (*) indicate white surface areas due to hydrophobic treatment

13.8 VISCOSITY MODIFYING AGENTS

Viscosity modifying agent (VMA) is used in general to reduce bleeding and segregation (Fig. 7.10). The most popular VMA is based on organic biopolymer (Fig. 18.9) particularly used to manufacture self-compacting concretes shown in § 18.3.1:

- V.A. Ghio, J.M. Monteiro, O.E. Giorv, “Effect of polysaccharide gums on fresh concrete properties”, *ACI Materials Journal*, Vol. 91. pp.602-606, 1994;
- K.H. Khayat and Z. Guizani, “Use of Viscosity Modifying Admixture to Enhance Stability of Fluid Concrete” *ACI Materials Journal*, Vol.94, pp.332-340, 1997).

Inorganic products acting as VMA are based on amorphous colloidal silica (Fig. 18.22) or silica fume (Fig. 2.4 in § 2.10) and they have been used to reduce or avoid bleeding and segregation in self-compacting concretes:

- M. Collepardi, S.Collepardi, U. Skaup, R.Troli, “Optimization of Silica Fume, fly ash and nano-silica in superplasticized concretes” *Proceedings of the 8th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Las Vegas (USA)*, Editor: V.M. Malhotra, pp.495-506,2004; available on www.encosrl.it → *Scientific Publications* → *Mineral Additions for Mortar and Concrete*;
- S. Collepardi, A. Borsoi, J.J. Ogomah Olagot, R. Troli, M. Collepardi and A. Quadrio Curzio, “Influence of nano-sized mineral additions on performance of SCC” *Proceedings of the 6th International Congress “Global Constructions : Ultimate Concrete Opportunities”*, Dundee, Scotland, Editor: K. Dhir, pp.56-66, 2005; available on www.encosrl.it → *Scientific publications* → *High Performance Concrete*.

13.9 SHRINKAGE-REDUCING ADMIXTURES

Inadequate wet curing of concrete is considered to be responsible for some drawbacks: the most serious one is the appearance of cracks on the concrete surface when the tensile stress (σ_t), induced by restrained drying shrinkage (ϵ_s) becomes higher than the tensile strength f_t (§ 15.4 and § 15.6):

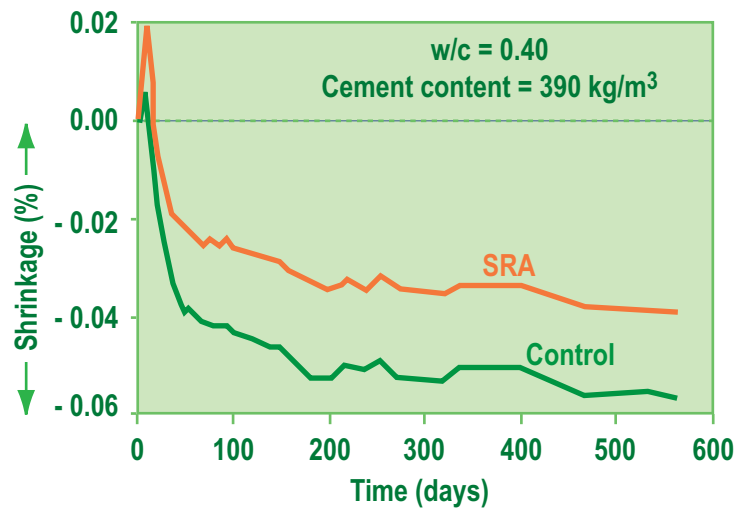
$$\sigma_t = E \cdot (\epsilon_s - \epsilon_c) > f_t \quad [13.2]$$

where E is the modulus of elasticity and ϵ_c the creep strain. Since the damage related to cracking is localized in the area of concrete cover, the risk of corrosion of metallic reinforcements increases significantly in concrete structures with inadequate curing for the quicker and easier penetration of CO_2 , O_2 , Cl^- and H_2O to the steel reinforcements (§ 15.3). This risk can paradoxically increase in High Performance Concrete (HPC) structures (Chapter XVII) due to the autogeneous shrinkage (§ 15.7) specially in concretes with w/c in the range of 0.30 - 0.40. In these concretes, the rapid development of a very fine pore network within the hydrated cement paste occurs and drains water from coarse capillaries. These dry out in the absence of water curing. This phenomenon, called self-desiccation, occurs when the cement hydration progresses because the coarse capillary pores became empty of water just as in a ordinary concrete exposed to drying. Autogeneous shrinkage does not occur in HPC provided that the formworks are removed as soon as possible and then immediately exposed to water curing for at least one week (P.C. Aitcin, "The art and science of durable high-performance concrete", *Industria Italiana del Cemento*, pp 798-814, Ottobre 2003, n° 791).

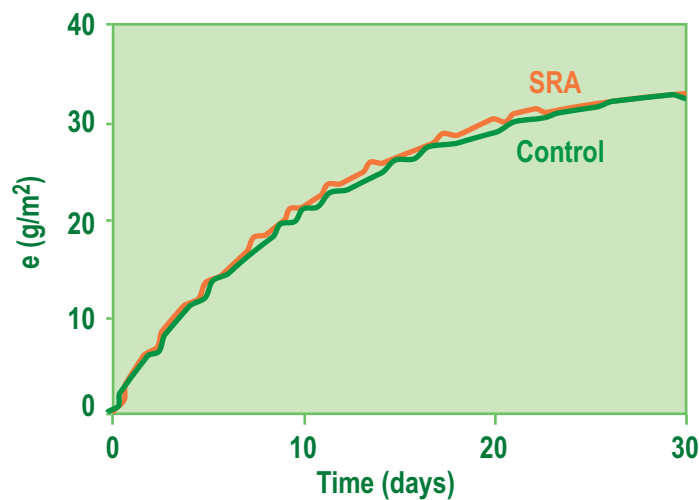
The use of Surface Reducing Admixtures (SRA) has been suggested to reduce both drying and autogeneous shrinkage. SRA is a chemical admixture (1-2% by mass of cement) based on neo-pentyl glycol or other similar products (propylene-glycols) which reduces the drying and/or autogeneous shrinkage (N.S. Berke, L. Li, M.C. Hicks and J. Bal, "Improving Concrete Performance with Shrinkage-Reducing Admixtures", *Proceedings of the Seventh CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Berlin, Germany, Ed. V.M. Malhotra*, pp 37-50, 2003). Figure 13.9 shows the shrinkage trend after 1 week of wet curing in concretes with a cement content of 390 kg/m³ and a w/c of 0.40, with and without SRA. In the presence of SRA there is a significant reduction with respect to the reference concrete in the drying shrinkage at 1 month from 0.04% to 0.02%.

Surprisingly SRA does not reduce the water evaporation from concrete when exposed to unsaturated air. Figure 13.10 shows a typical weight loss due to water evaporation from concretes with and without SRA, both exposed to the same air conditions (RH =6 0%, T = 25°C).

The effect of SRA on the shrinkage is ascribed (N.S. Berke *et al*, *ibidem* 2003) to the decrease in the surface tension of water (γ). This reduces the capillary



g. 13.9 – Influence of SRA on drying shrinkage (Berke et al. 2003)



g. 13.10 – Influence of SRA on water evaporation (e)

tension P caused by the formation of water menisci developed in capillary pores and responsible for the shrinkage of the cement paste (Fig. 13.11).

The capillary tension depends on the surface tension (γ) according to the equation [13.3]:

$$P = 2\gamma/r \cos\theta \quad [13.3]$$

where r is the pore radius and θ the wetting angle.