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Rheology Modifying Admixtures: The Key to Innovation in Concrete Technology – A General Overview and Implications for Africa

Wolfram Schmidt[1], Mohamed Sonebi[2], H. J. H. (Jos) Brouwers[3], Hans-Carsten Kühne[1], Birgit Meng[1]
[1]BAM Fed. Inst. for Materials Research and Testing, Division “Technology of Construction Materials” Berlin, Germany
[2]School of Planning, Architecture and Civil Engineering, Queen’s University Belfast, Belfast, BT7 1NN, UK
[3]Eindhoven Technical University, Eindhoven, Netherlands

Abstract. Innovative admixture technology has significantly widened up the range of possibilities of concrete engineers. For many decades the water to cement ratio (w/c) was the major influencing factor for the performance of concrete. Due to the need to adjust a consistency, which still allowed reasonable workability, the w/c was typically significantly higher than technologically reasonable. Rheology modifying admixtures support adjusting the concrete consistency largely independent of the w/c. It was only after the invention of the first superplasticizers that modern concrete technology significantly evolved in terms of flowability, strength, and durability, and only due to the steady evolution of the technology modern innovations, such as Self-Compacting Concrete, Ultra-High-Performance Concrete, or Engineered Cementitious Composites were made possible. Today’s superplasticizers are extremely versatile and can be adjusted to individual technological specifications. However, the other side of the coin of versatility is that cementitious systems incorporating superplasticizers have become more sensitive against environmental influences, such as the environmental temperature, which may cause unwanted effects or demand for supplementary admixture use such as stabilizing admixtures. Hence, concrete mixture composition with admixtures demands for a high level of expertise and often there is lack of awareness about the mode of operation of rheology modifying admixtures among concrete technologists. The paper gives a comprehensive overview about rheology modifying admixtures such as superplasticizers or stabilizing agents, and how they can be used depending upon the application in the most favourable way. Based on experiences with the sub-Saharan African concreting boundary conditions, which exhibit many challenges in terms of environmental boundary conditions and construction site logistics, conclusions are finally drawn, how admixtures can be used in the most beneficial way to improve the concrete casting situation.

1 Introduction

During the last three decades concrete has emerged from a rather simple mass construction material based on only the three components cement, water, and aggregates towards a high performance material, which can be adjusted according to high performance applications and ultimate user specifications. The reason for the rapid evolvement was the increasing awareness how to benefit from mineral additions and chemical admixtures. In particular the latter group can be considered as the most influential factor, which yielded a boost of technology as of approximately the 1980s.

Figure 1 shows the evolution of the history of concrete with the invention of superplasticizers, which played an important factor as accelerator. This figure presents also the bandwidth of consistencies and how the engineers can utilise it. At the same time, it can be observed that the widening range of consistencies correlates extremely well with the evolution of concrete compressive strengths. The incorporation of superplasticizers into concrete mixture composition eventually facilitated concrete engineers to improve the workability properties without need to increase the water-cement-ratio (w/c) and to significantly reduce the w/c, which finally resulted in concrete with higher performance and specified properties.

Therefore, without doubt, it can be concluded that the capability to control the rheology of concrete systems can be considered as the catalyst for the invention of the many recent mortar and concrete innovations such as polymer modified cementitious composites (PCC) self-compacting concrete (SCC), high-performance concrete (HPC), ultra-high performance concrete (UHPC) or engineered cementitious composites (ECC).

Therefore, understanding the rheology of cementitious systems and how to control the workability by the use of chemical admixtures is the key to innovations in concrete technology. On the other hand, the advantage of having possibilities to generate tailor-made properties comes with the disadvantage that mixture compositions are becoming more complex and variations in a single component have strong influence on the performance of the other components. Thus, a single component that reacts sensitively to unsteady process conditions can bring the whole concrete composition to fail. In order to improve the robustness of mixtures against such effects, the major processes at early stage have to be identified. An optimised adjustment of the key parameters allows the application of sophisticated concrete mixtures with high robustness.

This paper gives a comprehensive overview of the mode of operation of new admixtures and proposes how these can be used beneficially in order to improve concrete technology in challenging environments such as the sub-Saharan continent.

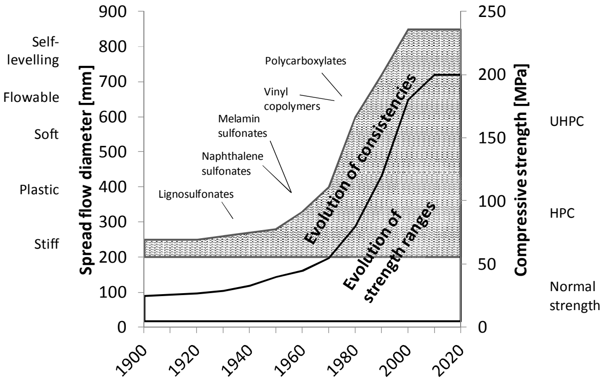

Fig. 1. Evolution of concrete consistencies and strengths.

3 Rheology background

Each material has a different resistance against an applied deformation. The material parameter that provides information about the fluid's resistance is the viscosity which is the gradient of the shear resistance versus the shear rate (deformation velocity). The minimum stress, which has to be applied before flow is initiated, is called the yield stress 0. In the easiest case, the viscosity is a constant value but systems can also exhibit more complicated behaviour with changing viscosities depending upon the shear velocity. Figure 2 provides an overview of the most common models that are used to describe the flow properties of flowable systems.

Cementitious systems are systems with two phases (solid, fluid) that both exhibit different influences on the rheology. Yield stress is typically a phenomenon, which occurs when particles in a fluid interact with each other in any kind. Although yield stress is a most ambiguous issue [1], since it cannot clearly cover time-dependent deformations, this concept has proven to be a useful concept for scientific and engineering applications. This is particular valid for systems that after relatively short period of time with respect to its lifespan change its material properties from fluid towards elastic behaviour, where different material laws (e.g. Hooke's law) are valid, and the resistance against deformations are described by the Young's modulus E, the Poisson's ratio ν and the shear modulus G.

Depending upon the range of shear rates, which need to be investigated, different flow models might apply. Typically fluids show different flow behaviour at different shear rate ranges. Often dispersions incorporating solid polymers show shear thinning behaviour at low shear rates due to the alignment of polymers and shear thickening behaviour at very high shear rates due to inertia effects. For most typical concrete applications, however, the Bingham model is sufficient to describe the flow properties sufficiently precise and to distinguish between different materials' properties. The yield stress can be considered as the relevant parameter that determines the flow, while viscosity is the relevant parameter that determines the flow velocity. For the stability of a concrete mixture both parameters play an important role. While a high yield stress is required to avoid segregation at rest, a high plastic viscosity is required to avoid segregation at flow.

Typical chemical admixtures can have a significant influence of the above mentioned rheological parameters, and in return, their effect on the rheology can be used in order to adjust specified workability properties.

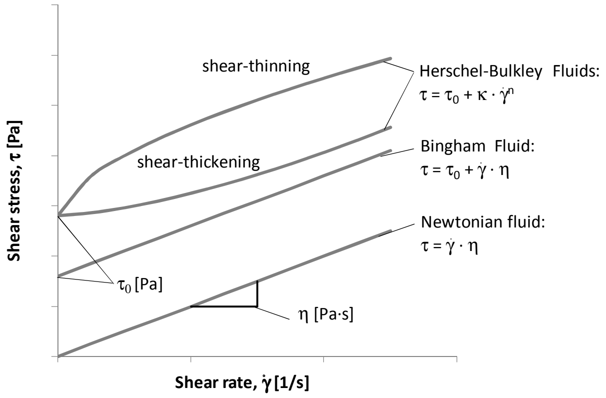

Fig. 2. Rheological laws applied in concrete and flow curves.

3 Rheology modifying admixtures

3.1 Superplasticizers

Modern concrete often contains plasticizer or superplasticizer. These admixtures typically contain an anionic backbone that can be adsorbed on positively charged surfaces of clinker and hydration products. The dispersion of particles takes place either by electrostatic or steric repulsion, or a combination of both effects.

The first group of superplasticizers (SP) used in concrete were lignosulphonates, which are a residue of the cellulose processing. Their effectiveness compared to synthetic polycondensates, which were invented in the early 1960s such as naphthalene or melamine sulfonates is limited [2, 3]. These groups were the major chemical admixtures used until approximately the millennium change [4, 5].

In the 1980s the first polycarboxylate SPs were introduced [6]. They were a significant breakthrough in technology and performance development with regard to self-compacting and high-performance concrete. Recently phosphonate based superplasticizers have become more popular, which differ from polycarboxylate ethers in the chemical composition of the backbone, which is phosphonate based instead of methacrylic. As a result, the

masses of these polymers are lower, which gives them a stronger tendency to adsorb.
Due to their important contribution to modern concrete technology and their significantly wider versatility polycarboxylate ether superplasticizers (PCEs) shall be discussed in more detail here.

3.1 Polycarboxylate superplasticizers (PCE)

PCEs consist of a methacrylic backbone and attached polyethylene oxide graft chains. Like in all common superplasticizers, the backbone contains anionic charges, which gives these polymers a strong tendency to be adsorbed on aluminate and ferrous clinker phases and on ettringite and monosulfate, which are formed by the reaction of sulphates and calcium aluminates [7]. Upon adsorption of the polymers, the graft chains support a steric repulsion of the particles.

The first generation of polycarboxylates exhibited an ester link between the backbone and the graft chains. Due to their better stability later the grafts were linked by ether bonds. Today the geometry parameters such as number of repeated units in the backbone, number of ethylene oxide units in the grafts, and grafting degree can be adjusted largely independently and within a wide range of modifications. Therefore differing from traditional superplasticizers, PCEs can have multiple polymeric architectures, which strongly affect their adsorption and figure and tendency to adsorb. Figure 3 shows samples of different possible polymeric architectures, depending on which steric or electrostatic repulsion effects dominate and depending on which the backbone contributes to steric repulsion.

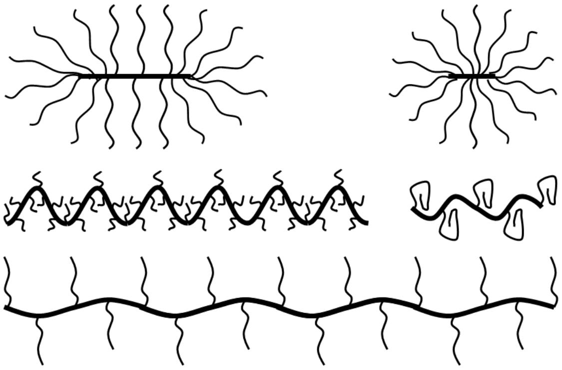

Fig. 3. Examples of PCE variations.

Despite the wide variety of polymeric architectures, its influence on how the rheology is affected, is largely limited to the degree, at which the charge of the polymer is affected by it [8]. This means that the tendency to adsorb increases with reduced graft length, reduced grafting degree, and reduced backbone length. The practitioner, therefore, should vary PCEs based on the charge density rather than on any other characteristic.

3.2 Time and temperature effects with PCE

PCEs have to be adsorbed on particle surfaces to be effective. The polymers compete with sulphate ions (e.g. from the set retarder) in the pore solution for adsorption sites [9, 10]. The charge density of PCEs determines how strongly they tend to be adsorbed on positively charged surfaces. Non-adsorbed polymers remain in solution and do not contribute to flowability. However, due to ongoing hydration, yielding further monosulfate and ettringite, polymers that do not adsorb initially can be adsorbed over the course of time [11, 12], thus contribution to the long term flowability. Therefore, the reduction of the yield stress as well as its time dependent performance is predominantly driven by the charge density of PCE (Figure 4). The higher the charge, the higher the tendency to adsorb, thus providing ultimate flowability. However, the more PCE is adsorbed at an early stage of time, the lower the potential for time shifted adsorption. Hence it can be concluded that increasing charge density also reduces the flow retention [8].

Due to its higher tendency to adsorb, high charge density PCEs are more efficient than low charge density PCEs and thus required in lower solid contents in order to adjust a specific yield stress reduction. In terms of setting of cementitious systems, the amount of PCEs is the dominating factor for the retardation of the hydration. Therefore, low charge density PCEs cause significantly stronger hydration retardation than high charge density PCEs. In return it was found that low charge density PCEs can be beneficial in order to reduce the risk of early cracks [13].

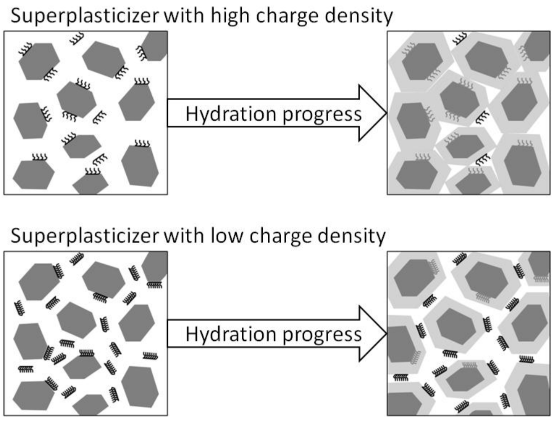

Fig. 4. Influence of the charge density of PCE on the flow retention [14]

When high amounts of PCE are used for a special type of concrete, the temperature dependent behaviour of this concrete can be more complicated than that of ordinary concrete. In general the environmental temperature has a strong influence on the hydration velocity. The higher the temperature, the more rapid the hydration takes place.

However, since the time-dependent adsorption of superplasticizer is determined by the hydration velocity, but the hydration velocity again is determined by the environmental temperature, two counteracting mechanisms emerge. High temperatures accelerate the growth of hydration products. This can cause stiffening due to more rapid hydration but also supplementary liquefaction due to the higher and more rapid availability of adsorption sites for polymers. In return, lower temperatures can maintain good workability over a longer period of time, but to the slower hydration, there might be too few adsorption sites for PCEs to become effective. Therefore, in presence of high PCE amounts, the risk of early uncontrolled segregation is high at high temperatures and at very low temperatures the system might completely lose its flow performance [11].

3.3 Stabilising agents (STA)

In order to improve the stability and to reduce the bleeding tendency, often polymeric stabilising agents STA) are used. These are typically polysaccharides [15]. Very common is the use of modified cellulose, which is a linear polysaccharide, based on linked glucose chains, which alter their direction (Figure 5). They can be amended by functional groups (e.g. carboxylate groups) through etherification. Other types of stabilizing admixtures are biopolymers such as Welan Gum or Diutan Gum. They are also linear polysaccharides like cellulose ethers but their side chains consist of one or two monosaccharides and their backbone contains carboxylate groups providing anionic charge (Figure 5).

For cellulose derivatives and welan gum, Khayat distinguished between different modes of operation, depending on the type and concentration: fixation of water molecules through adsorption, immobilization of water through association, and intertwining of polymers [15]. Due to the similarities to welan gum, these basic mechanisms of stabilisation should apply for diutan gum as well. However, the backbone of diutan gum is about three times longer than of welan gum so that it has a significantly higher molecular weight, resulting in different degrees of efficiency[16].

Another important STA type is modified starch. It can be retrieved from numerous plants such as potatoes, cassava, and maize. Like cellulose, starch consists of largely linear arranged glucose units, but differing from starch they are arranged in the same order (Figure 5). Furthermore, starches consist of two types of macromolecules, the linear amylose (0% - 30%) and the tree-like structured amylopectin (70% – 100%), where the chains are linked in the hydroxyl methyl group every 12 to 30 glucose units (Figure 5). Although the ratio of amylose to amylopectin is about 200, due to their high degree of polymerisation, the amylopectin molecules constitute about 80 % by mass of the total starch.

Due to the large size of the amylopectin, which exhibits radii of gyration between 50 nm and 500 nm, the stabilising mechanism of starches is more complex than that of cellulose and diutan gum. It is assumed that the large molecule spreads out between the particles to keep them in stable distance, particularly at rest [17]. Due to the strong interaction with particles, the stabilisation mechanism involves the whole system of finer particles and it strongly depends on the depends on the water to powder ratio [18].

Differing from cellulose, welan gum and diutan gum, starches do not significantly affect the yield stress in water-STA-systems or systems, where the water to solid ratio is high. It can be assumed that the effect of the amylopectin cannot be activated, if the space between the particles if large. Upon crossing a threshold volume of solid particles the spacing effect of amylopectin can be activated, thus contributing to a significant increase of the yield stress [18].

Hence, in a simplified way cellulose and bio gums mainly influence the rheology of the fluid phase with strong effect on the concrete rheology, while starches affect rather the particle-particle interactions.

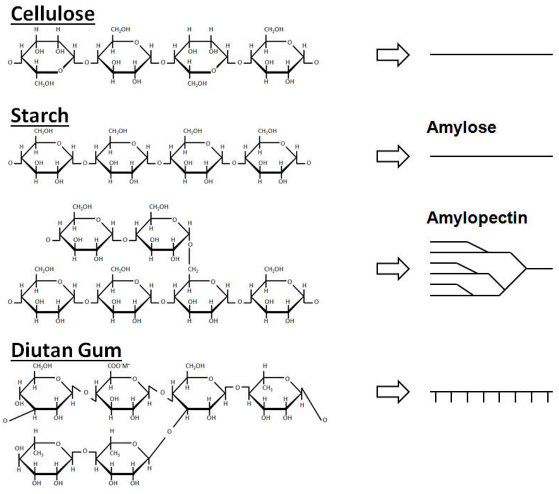

Fig. 5. Chemistry of cellulose, starch and diutan gum and respective macromolecular structure.

3.4 Stabilising agents and PCE

Often polymeric STA is added particularly in very flowable systems in order to control the stability. Therefore it is general practice to apply STA in combination with PCE. This can cause interactions, particularly when the STA shows a strong tendency to adsorb. Adsorptive STAs may reduce the amount of adsorbed superplasticizers, thus affecting both viscosity and yield stress, while non-adsorptive STAs mainly affect the plastic viscosity independently of the superplasticizer [19]. Due to the strong influence of PCE on the yield stress, STAs influences on the yield stress retreat into the background, so that their major effect is an increase of the viscosity.

Besides rheological effects, STA also affect the hydration to a certain extent. Compared to the strong effect of superplasticizers, their influence on the hydration is negligible. However, it was observed that the presence of STAs can reduce the retarding effect of PCE. The effect occurred the more pronounced, the higher the environmental temperature was. This effect was linked to interactions between STAs and superplasticizers and effects on their adsorption behaviour [18].

It was found that starch based STA may negatively affect the stability of flowable concrete types at very low temperatures, since the particle stabilising effect cannot be maintained over a very long period of time, which causes segregation problems, when the setting is significantly retarded [20]. Diutan gum stabilising agent was found to negatively affect the flow retention, which can be linked to competitive adsorption or interactions between STA and PCE [18].

3.5 Other admixtures with effect on the rheology

Besides the effects of SP and STA, which are typically added in order to directly affect the rheology, other chemical admixtures, which are added to the cementitious system in order to adjust specific properties may have effects on the rheology. Figure 6 provides an overview, how the addition of different admixtures typically affects the flow curves. Air entraining agents (AEA), which are typically added in order to improve the freeze-thaw resistance, reduce the fresh concrete density and increase the paste to aggregate ratio. Therefore AEAs significantly reduce the viscosity but they also reduce the yield stress slightly. Retarding agents also adsorb on clinker phases and hydration products. They may interact with PCE, thus affecting the rheology slightly. However, in particular, they extend the retention or workability.

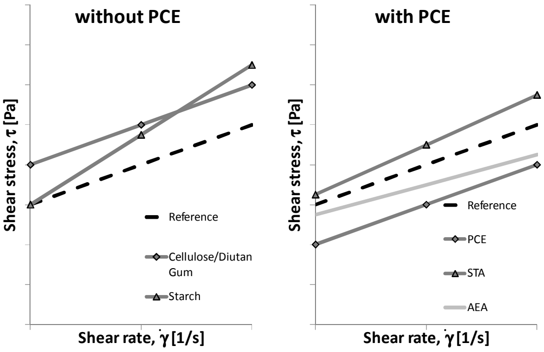

Fig. 6. Influence of the addition of different chemical agents on the flow curves of systems without and with PCE.

4 Selection criteria for admixtures

Understanding the rheology of cementitious systems, and particularly understanding the major influences on how the rheology can be controlled is of utmost importance to successfully apply new technologies. In this context awareness has to be raised about the enormous versatility of rheology modifying admixtures in order to benefit from the potentials. Hence, for the concrete engineer, it is not sufficient to use any PCE, it is important to know which PCE is best for the boundary parameters and the specified performance range. The same is valid with lesser impact for STAs.

In general, high charge density PCEs are therefore well suited for pre-cast applications, where ultimate flowability is required without necessity to cast over a longer period of time. Low charge density PCEs perform better in ready-mix applications, since they can maintain the flowability over long time. In order to individually adjust performances according to changing boundary conditions, blending of PCEs is possible, or a medium charge polymer can be chosen to increase the robustness against varying influences.

Due to the higher efficiency of high charge density PCEs should be used, when early setting is important, while low charge density PCEs may reduce the risk of early cracks. For high temperatures, low charge density PCEs should be used in order to provide sufficiently long flow retention. In return at low temperatures, when the hydration and thus the formation of hydrates are slowed down, high charge density PCEs are the better choice, due to their stronger tendency to adsorb on cement.

The influence of STA is less significant but increases when ambient temperatures during casting are of importance. At low temperatures, STA with particle stabilising effect may lose effectiveness over the course of time. At high temperatures, competitive adsorption of STA can reduce the adsorption of PCE, reducing the workability time.

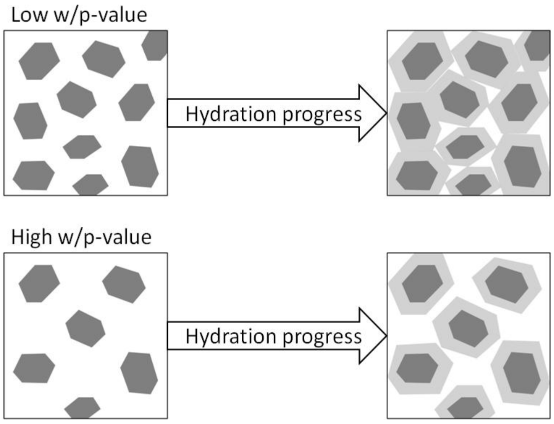

Fig. 7. Influence of the w/p on the flow retention [14].

5 Admixture concepts for Africa

Cement prices all over Africa are significantly higher, when expressed in purchasing power of the populace than in Europe or Northern America [14, 21]. This suggests the use of superplasticizers, since they allow reducing the w/c significantly even at improved workability, thus bearing high potentials to save cement as the major cost factor in Africa. Furthermore, many construction sites are not well equipped so that casting processes are unsteady.

The only method to control the workability and its retention is the addition of water, which finally yields to different concrete properties from mixing batch to mixing batch. Superplasticizers can significantly support the improvement of concrete towards steady consistencies and repeatable mechanical properties in a structure. Also the use of retarding agents would be reasonable.

The climate all over Africa is general characterised by high temperatures. Ready-mix concrete is scarce and limited to urban areas. Therefore, cement is typically stored and mixed together with the other constituents directly on the construction site. Most construction sites exhibit low levels of automation [14, 22].

Therefore, optimised concrete mixtures should be developed with low charge density PCE in order to cope with the high temperatures and in order to make sure that the consistency can be maintained despite eventually long lasting casting processes. Starch based stabilising agent might be a better choice, due to its lesser interactions with PCE. Since most of the constructions are designed for normal strength, it is reasonable to avoid extremely low w/c or water to powder ratios (w/p). A medium w/p supports a sufficiently long lasting flow performance, since the wider distance between the particles allows better mobility among the particles, even at high hydration rates caused by high temperatures (Figure 7)

Unfortunately, in most countries in Africa, the infrastructure for modern admixtures is not yet well established, which limits their application and increases the prices. Since the use of more sophisticated admixtures cannot be considered as a short term option. However, but since soft or flowable concrete consistencies can significantly enhance the concrete performance, it is reasonable to observe the local markets.

Even without availability of PCE, the raw materials for lignosulphonates are available, since this is a waste product from the cellulose industry [14]. Cassava is a widely spread plant on the African continent. Its starch is similar to that of potatoes, which is already used for the production of commercial STAs [14, 23].

4 Conclusions

Chemical admixtures for the enhancement of the rheological properties can be considered as the key factor for modern and innovative concrete. However, since their use significantly widens the range of possibilities to design concrete compositions, understanding of the effect of admixtures is of utmost importance. This is particularly valid for PCE superplasticizers due to their versatility.

The reasonable choice of admixtures can help developing individual concrete composition, which are tailored for individual boundary conditions. The focus of this paper was put on African boundary conditions, where flowable concrete with medium w/c and low charge density PCEs can be considered as the optimum choice to cope with the challenging boundary framework. The suggested higher w/c might require supplementary STA.

In order to design economically reasonable concrete types in Africa, local resources for admixtures, such as lignosulphonate and Cassava starch should be taken into account.

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