MODIFYING CONCRETE MATRICES WITH BENEFICIATED DREDGED MATERIAL OR OTHER CLAYEY CONSTITUENTS

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ABSTRACT

Modifying Concrete Matrices with Beneficiated Dredged Material or Other Clayey Constituents

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Conventional wisdom suggests that for concrete production no clay minerals should be used, which aside from sands and silts are the main components of dredged material. It was the main goal of this research to investigate the feasibility of modifying concrete with clayey components in spite of the initial reservations found in the literature.

The disposal of dredged material is a challenge most of the harbors worldwide have to face. Traditionally, the excavated material was dumped in the ocean or other places next to the dredging site. Today, most of the material is placed in landfills or specially designed facilities. Diminishing capacities of existing facilities, increasing volume of contaminated material, new regulatory restrictions, and rising public awareness towards environmental issues are applying pressure on the port authorities to search for alternative disposal methods. Ideally such techniques reuse or recycle the material as a valuable resource. In this work, methods of beneficiating dredged material for concrete applications were investigated.

The large fraction of sands and silts in dredged material suggested replacing regular fine aggregate with dredged material. However, the results were not very promising. In a second approach, dredged material was added as a filler, which introduced "undesirable" clay minerals as the main active component to a given concrete. Kaolin served as a model for these minerals. Concrete mixes were thus modified with untreated or treated dredged material, with natural or thermally activated kaolin, or selected combinations thereof.

It was found that the loss of workability of fresh concrete required the addition of a superplasticizer when clayey constituents were used as filler in concrete applications. However, such components prevented segregation and bleeding. The properties of fresh concrete, such as coherence, flow, homogeneity, compactability, and air content depend on the type of filler and superplasticizer. They relate closely to all physico-chemical and mechanical properties of the hardened product. The amount of dredged material used as filler can be adjusted to meet given requirements. The findings are encouraging and indicate that it should be possible to beneficially use dredged material and other clayey constituents in concrete production.

ABSTRACT

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Thank you very much!

To Sunshine,

1. INTRODUCTION

Concrete is the most commonly used building material worldwide. Its versatility allows applications for a large number of purposes. Over the last decades, concrete compositions have been modified with various admixtures. Among these are several waste products, which were initially added to concrete to reduce a disposal problem, but over the years showed their ability to alter the concrete properties in a favorable manner. Common examples are lignosulfonate, silica fume and fly ash.

At Columbia University, research has been conducted on the beneficiation of dredged material from the Port of New York and New Jersey. This problem is of major concern to the Greater New York Metropolitan region, because shipping lanes need to be dredged to keep the Port operable and economically viable. Dredged material consists mainly of sand, silts, and clay minerals but may contain any of a large number of organic and inorganic pollutants. The most common disposal method for dredged material is to dump such material in landfills or specially designed confined disposal facilities. This approach requires vast storage areas and does not include any productive reuse. Moreover, with increasing public awareness and legal restrictions such environmentally questionable disposal methods are becoming less acceptable and alternative techniques are needed.

For stabilization and partial immobilization of contaminants, dredged material or contaminated soils are often mixed with cement [81]. Cement is also the binding material for concrete production. By combining these two separate applications of cement the idea of using dredged material in concrete applications was born. The largest fraction of dredged material is quartz, which also is the most common ingredient of regular concrete aggregate. This fact led to the suggestion to partially replace regular sand aggregate with dredged material. However, the physico-chemical nature of dredged material is dominated by its clay minerals. This chemical prevalence of clays as well as their particle size range suggest the use of dredged material as filler.

The adsorption capacity of clay minerals is generally much higher when compared with other concrete constituents. This causes a drastic decrease in workability when clay minerals are added to concrete mixes. Some clay minerals such as montmorillonite are capable of swelling, and therefore may initiate structural damage in the hardened concrete when they change their volume during drying or wetting. Thus, clay minerals are generally considered harmful for concrete production [18]. On the other hand, it was found that the thermal activation of kaolinite produces a highly reactive material with a high pozzolanic contribution that improves concrete properties and has been recently used in concrete applications [27, 60, 67].

The influence of kaolin after thermal treatment on concrete has been the subject of research in the past few years, but the emphasis of those studies always seemed to be on the activation rather than the beneficiation of natural clays [11, 29]. Yet, it should be possible to draw conclusions from the use of kaolin to other clay minerals in general and dredged material in particular, because of their similar properties, such as specific surface, surface charge, and activity.

In the past most concrete properties were typically related to its compressive strength. In recent years, other criteria have been added to define performance. For the purposes of the research described herein, the main performance criteria were the workability of fresh concrete and the compressive strength of hardened concrete.

It was the purpose of the present work to answer a number of different questions:

1. According to conventional wisdom, clay minerals should not be used in concrete compositions because of their detrimental effect on the workability of fresh concrete and the strength and durability of hardened concrete. What are the scientific explanations for these detrimental effects, and what are the specific factors governing this behavior? In other words, how are the properties of the concrete matrix affected by clayey components, such as dredged material or kaolin?
2. Under what circumstances is it possible to incorporate clayey materials into concrete mixes without experiencing negative effects?

3. Is it possible to beneficially use dredged material as a concrete constituent, either as a replacement of fine aggregate or as a filler?
4. Are there possible benefits of incorporating dredged material into the concrete mix, thereby beneficiating this material, which otherwise imposes a considerable environmental burden? What treatment methods are necessary to optimize the beneficial effects of dredged material or to improve certain concrete properties?

In Chapter 2, an overview will be given of the various types of materials of interest here, namely cement, aggregate, admixtures (fillers, pozzolans, and superplasticizers), clays and dredged material. Fundamental properties of these materials will be reviewed, followed by a general discussion of concrete and how its properties (chemical composition, workability, and strength) are affected by clays and dredged material.

Chapter 3 outlines the experimental test program, including a detailed description of the various test protocols. The test results are presented in Chapter 4, and Chapter 5 contains an in-depth analysis and discussion of these results. Chapter 6 summarizes the major conclusions and provides an outlook on its significance.

2 MATERIALS AND FUNDAMENTALS

2.1 CEMENT

Cement is one of the most important hydraulic binders, which are defined as non-metallic, inorganic substances. They chemically react with water to form a solid medium. This reaction should take place under different conditions: under water or above, in a sealed container or outside. The reaction product, an artificial stone, should remain durably hard at relatively constant volume in any environment, even under water. Cement meets these definitions while other binders commonly used for construction do not. Gypsum, for example, is unstable in water, and the hardening process of lime does not start under water.

Cement is a product generally manufactured from limestone, chalk, clay, sand, or iron ore. The raw materials are proportioned, ground, blended, and fed into a tilted rotating, cylindrical kiln reaching temperatures of 2600°F to 3000°F (1430°C to 1650°C). At these temperatures, the feed melts and fuses into polymineralic products. The chemical reactions create grayish-black pellets, so-called cement clinker. After cooling, the clinker is ground into a fine gray powder and about 3-5 % gypsum (by mass) is added. The result is portland cement [56]. Its reactivity is achieved by grinding the clinker fine enough to create large specific surfaces of about 400 m^2/kg Blaine fineness [26].

Because the raw material and the hydration products of portland cement are mostly oxides the following abbreviated notations are commonly used in cement chemistry [42]:

C	CaO	S	SiO_2	A	Al_2O_3
F	Fe_2O_3 / FeO	M	MgO	K	K_2O
N	N_2O	$\bar{S}$	SO_3	H	H_2O / $(OH)_X$

The main chemical components of cement are silicium oxide and calcium oxide (Table 1), both of which are essential for hydraulic binders since the hardening process is based on calcium-silicate hydrates (C-S-H) [42]. The main compound compositions or clinker phases and their hydration characteristics are summarized in Table 2. These main components determine all major properties of the hardened concrete such as microstructure, strength, and durability but also setting time and even workability.

Table 1 Chemical composition (in % by mass) and fineness of portland cement [38]

ASTM Type	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI [1)]	Blaine
I	20.9	64.4	5.2	2.3	2.8	2.9	1.0	370 m^2/kg
II	21.7	63.6	4.7	3.6	2.9	2.4	0.8	370 m^2/kg
III	21.3	64.9	5.1	2.3	3.0	3.1	0.8	540 m^2/kg
IV	24.3	62.3	4.3	4.1	1.8	1.9	0.9	380 m^2/kg
V	25.0	64.4	3.4	2.8	1.9	1.6	0.9	380 m^2/kg

[1)] Loss on ignition

Table 2 Compounds (clinker phases) of portland cement Type I [26, 50, 74]

Compound	Formula	Other name	% by mass	Hydration characteristics
C_3S	$3(CaO)\ SiO_2$	Alite	42-66	Rapid, moderate heat
C_2S	$2(CaO)\ SiO_2$	Belite	9-30	Slow but steady, low heat
C_3A	$3(CaO)\ Al_2O_3$		6-14	Very rapid, very high heat
C_4AF	$4(CaO)\ Al_2O_3 \cdot Fe_2O_3$		1-12	Moderate heat
	Na_2SO_4/K_2SO_4	Na_2O eq:	0.14-1.5	On surface of clinker
$C\bar{S}$	$CaSO_3 \cdot 2H_2O$ $CaSO_3 \cdot \frac{1}{2}H_2O$ $CaSO_3$	Gypsum Hemihydrate Anhydrate		Controls setting time, soluble SO_4^{2-} retards hardening of C_3A and C_4AF

Five major cement types are available in the U.S. as defined by ASTM C150 [4]. Type I is a general cement, suitable for most purposes. Type II is often used for concrete exposed to seawater because it offers moderate sulfate resistance (no more than 8% C_3A). Type III is chemically similar to Type I but ground finer to produce higher early strengths. Type IV generates a specifically low amount of heat from hydration and is thus suitable for mass concrete structures. The low heat generation is accompanied by slow strength development at early ages. Type V is highly sulfate resistant with no more than 5% C_3A [42]. In this study, only portland cement of Type I was used.

When cement is exposed to water a chemical reaction, the hydration, begins. During the first fifteen minutes of the hydration, a gelatinous, semi-permeable layer forms around cement particles as a product of reactions involving C_3A, calcium sulfate and partly C_3S. Eventually some ettringite will crystallize. An inactive phase follows due to supersaturation and hindering of diffusion into the cement grains. After about four hours, differences in concentration outside and inside the layers cause osmotic pressures high enough to rupture the membrane. This is the beginning of an acceleration period characterized by an intense growth of crystals such as portlandite ($Ca(OH)_2$), calcium-silicate-hydrate phases (C-S-H), calcium-alumino-hydrates (C-A-H), and ettringite. This period lasts until about eight hours after contact with water and is followed by slow chemical reactions (deceleration stage) [62]. The C-S-H phases can vary widely in their composition and can be generally expressed as $C_lS_mH_n$ (similar for C-A-H). Some of the governing reactions involved in cement hydration are given below [61, 62, 73]:

$$2\ C_3S + 6\ H \rightarrow C_3S_2H_3 + 3\ CH \qquad \{1\}$$

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH \qquad \{2\}$$

$$C_3A + CH + 12\ H \rightarrow C_4AH_{13} \qquad \{3\}$$

$$C_4AF + 4\ CH + 22\ H \rightarrow C_4AH_{13} + C_4FH_{13} \qquad \{4\}$$

$$C_3A + 3\ C\bar{S}H_2 + 26\ H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \quad \text{(ettringite)} \qquad \{5\}$$

$$C_3A + C\bar{S}H_2 + 10\ H \rightarrow C_3A \cdot C\bar{S} \cdot 12H \quad \text{(monosulfate)} \qquad \{6\}$$

2.2 AGGREGATE

Aggregate consists of inert granular materials such as sand, gravel, or crushed stone. ASTM standards require the aggregate to consist of clean, hard, strong particles and specify tests to ensure these properties, e.g. ASTM C40, C87, and C142 [5]. It has to be free of absorbed chemicals or coatings of clay and other fine materials that could have undesirable effects on certain concrete properties. Clay lumps or friable particles on the aggregate surface may affect the workability and durability and in some cases even cause pop-outs [18, 38]. Aggregate is divided into two fractions: fine and coarse aggregate, with the dividing point being a rather arbitrary selected particle size of 0.19 inch (4.75 mm). Gravels constitute the majority of coarse aggregate, with crushed stone making up most of the remainder. Fine aggregate is commonly referred to as sand.

Size and shape of the aggregate play an important role in concrete mix design. The void content between particles determines the amount of cement paste required. Angular aggregate introduces additional voids. Larger sizes of well-graded aggregate and improved grading decrease the void content. Absorption and surface moisture of aggregate need to be measured when selecting aggregate because the internal structure of aggregate may adsorb or free water. Therefore, the amount of water in the concrete mix design must be adjusted to include the moisture content of the aggregate [56].

Finer particles have larger specific surfaces and thus require more water. In general, clay minerals are not desirable concrete ingredients. Whereas activated kaolin or zeolites have been shown to have beneficial effects, natural clays are typically treated as contaminants to be avoided. This study will address this problem in great detail.

Under certain conditions, the physico-chemical interaction between products of the cement hydration and aggregate can have detrimental effects on concrete. A chemical reaction can occur that involves alkali ions (mostly from portland cement), hydroxyl ions (as product of the cement hydration), and certain hydrous or amorphous forms of silica (as part of the aggregate) and leads to the formation of alkali-silica gels. These gels are expansive when in contact with water, which can cause cracking and pop-outs. The governing mechanisms are the subject of ongoing research [42].

The most important factors that control the so-called *Alkali-Silica Reaction* (ASR) are the alkali-content and alkali-reactivity of the individual components, the moisture content of the structure, and the ambient temperature. The alkali content depends strongly on the cement composition but various salts may contribute significantly when concrete constituents originate from marine environments. The likelihood of ASR generally increases with increasing concentrations of hydroxyl ions in the pore solution of concrete [42]. While the reaction mechanisms of ASR are not the main subject of this work, tests on the reactivity of specific mixes were conducted (Section 3.1.4).

2.3 ADMIXTURES AND ADDITIVES

Admixtures and additives generally modify certain properties of fresh or hardened concrete and are administered to the fresh mix of sand, gravel, water, and cement before setting. There is no clear distinction between the two terms. Most common types are either named after their purpose (e.g., air entraining agents, accelerators, retarders, high-range water reducers or superplasticizers, foaming agents) or after their origin or nature (e.g., silica fume, fly ash, calcined clays, limestone, ground blast furnace slag). The following sections focus on fillers, pozzolans, and superplasticizers, which strongly interact with calcium-aluminates and calcium–alumino-silicates [62].

2.3.1 Fillers

Fillers are generally materials of such size that they can fill the voids between larger particles (Figure 1). For example, only 74% of a given volume can theoretically be filled with spheres of one size. If a second set of spheres of different size is added, where the ratio of the two diameters is 0.315, the mix can fill 86% of the volume [34, 72]. In theory, the volume can be filled completely, if a sufficiently large number of sets of successively smaller spheres is added.

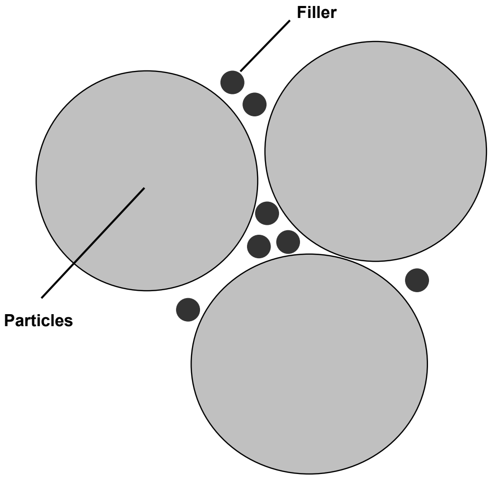


Figure 1 Fillers in a given particle arrangement

In concrete, voids between aggregates are filled with a slurry of water and cement, which hardens, glues the solid particles together, and creates an artificial rock with aggregate inclusions. If the aggregate grading is optimized such as in the above approach, a minimum amount of "glue" is required. This is of economic interest because cement is usually the most expensive concrete component. At the beginning of the 20th century, Fuller and Thompson conducted first comprehensive tests on the optimum particle grading [24]. Subsequently, researchers concentrated on the grading of the fine particles [e.g., 34, 58].

The term *filler* in concrete technology usually refers to materials smaller than cement particles, which have a diameter of 10-30 µm. In general, the porosity, permeability and durability of concrete depend mostly on the properties of the cement paste, i.e., the denser the cement matrix the better the concrete performance [33]. Hence, the primary goal of using fillers in concrete applications is to fill voids between cement particles. Inert fillers, such as finely ground limestone and quartz, serve only the purpose of filling voids, while active fillers with pozzolanic properties also contribute to the hydration process.

2.3.2 Pozzolans

Pozzolans were originally defined as natural volcanic ashes (found close to the Italian town Pozzuoli) and calcinated soils, which react with lime at ambient temperatures in the presence of water. Nowadays the term pozzolan refers to all siliceous/aluminous materials, which chemically react with calcium-hydroxide solutions to form compounds possessing cementitious properties [73].

ASTM C618 [5] requires a combined content of SiO_2, Al_2O_3, and Fe_2O_3 greater than 70% by mass for a mineral admixture to qualify as a pozzolan (Class N). In addition, the loss of ignition (LOI) has to be smaller than 10% by mass, and the moisture content is limited to 3% by mass. Popular examples of pozzolans are fly ash, metakaolin and silica fume. Such materials can be activated during the hydration process of cement, and their contribution is acknowledged to some degree in the design of concrete mixes [19, 72]. They often form similar reaction products as the ones associated with cement hydration:

$$\text{Fly ash:}\quad x\,CH + y\,S + z\,H \rightarrow C_{3x}S_{2y}H_{3(x\text{-}k)} + (z\text{-}k)\,H \qquad \{7\}$$

$$\text{Metakaolin:}\quad 5\,CH + AS_2 + 5\,H \rightarrow C_5AS_2H_5 \qquad \{8\}$$

With $C_5AS_2H_5$ consisting of C-S-H, C_4AH_{13}, C_3AH_6, and C_2AH_8

$$\text{Silica fume:}\quad x\,CH + y\,S + z\,H \rightarrow C_xS_yH_{(kx+z)} + (x\text{-}kx)\,H \qquad \{9\}$$

(compare with Equations 1-6) [61, 62, 73]. Kaolin and thermally activated kaolin, also known as metakaolin, are introduced in greater detail in Section 2.4. Their influence on concrete will be discussed in Chapter 2.7.

2.3.3 Superplasticizers

Superplasticizers are added to the concrete mix to either increase the workability of fresh concrete for a given water/cement ratio (w/c) or to decrease the w/c for a given workability. This is the reason why they are commonly referred to as "high-range water reducers".

Since the 1940s, lignosulfonate has been used as a water-reducer at relatively low cost because it is based on a waste product of paper mills. Like most other superplasticizers, lignosulfonate consists of repeatedly chained basic molecular units adding up to a high molecular weight. Its functional group is sulfonate-based like that of most other superplasticizers (Figure 2). The main disadvantage of lignosulfonate is the retardation of the setting process due to its uncontrolled sugar content [62].

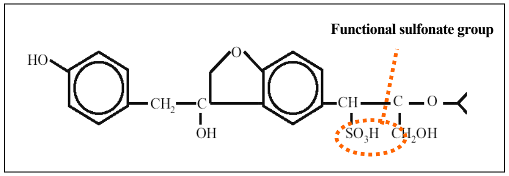


Figure 2 Basic molecular unit of lignosulfonate (after [62]*)*

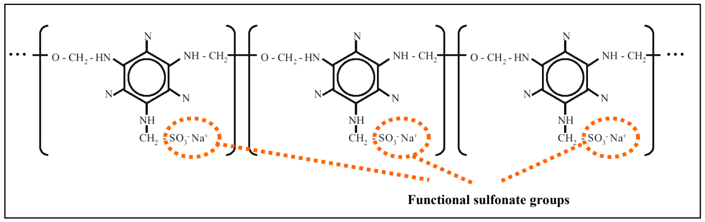


Figure 3 Basic molecular unit of sulfonated melamine-formaldehyde (after [62]*)*

Alternative superplasticizers are generally based on surfactants with hydrophilic and hydrophobic groups. Most of them are water-soluble polymers with a functional group of sulfonate (SO_3^-), e.g., sulfonated naphthalene-formaldehyde condensate or sulfonated melamine-formaldehyde condensate (Figure 3). These polymeric admixtures are usually added to the fresh concrete mix as salts or solutions thereof. Recent developments in concrete technology favor superplasticizers based on melamine and/or naphthalene utilizing sulfonate, phosphonate (PO_3^-), carboxyl ($COOH^-$), or hydroxyl (OH^-) as functional groups. Often, these admixtures are long-chained polymers with their hydrophilic and hydrophobic groups projected outwards (comb-polymer) [62].

One physical operating mechanism of superplasticizers is to prevent fine particles from flocculation. In suspensions, negatively charged plasticizing admixtures are able to compensate or even reverse particle charges and thus break down agglomerates. This becomes also visible in sedimentation tests, in which the "sinking" of cement paste in water or other carrier liquids is studied. After administration of superplasticizers the cement paste changes its behavior from settling ("all-at-once") to progressive sedimentation ("step-by-step") [71]. Due to electrostatic or Van-der-Waals interactions cement particles adsorb superplasticizer molecules on their surfaces. This generates repulsive forces, which are responsible for such deflocculation [62].

In sum, superplastizicers reduce the thickness of the water film around particles necessary to overcome adhesive forces and change surface charges and thus increase workability. Highly flowable mix designs were introduced some years ago and guided the development of self-compacting concrete. The introduction of superplasticizers was the main factor that made the development of high-strength and high-performance concrete possible [53].

2.4 CLAYS

Clays are multi-component systems, in which solid, liquid and gaseous phases can be present. The solid phase is mostly polycrystalline, commonly with a fraction of 90% inorganic minerals. Near the surface the solids generally make up about 50% of the volume and are mostly composed of inorganic components in crystalline formations. Secondary clay minerals are the most important mineralogical fraction. They are hydrous alumino-silicates, which have distinctive properties due to their structure, shape, and particle size. These minerals are responsible for the main characteristic properties of clays [25].

2.4.1 Types of Clay Minerals

Generally, clays can be divided into four major groups [31]:

- the kaolinite group,
- the illite (or clay-mica) group,
- the montmorillonite (or smectite) group,
- the chlorite group.

The following sections will introduce the first three groups but disregard the last one, which often is not listed as a separate mineral type. Chlorites exhibit a structure similar to illite and montmorillonite but have intergrown layers. Isomorphous replacement of aluminum and magnesium is very common. Detailed information on chlorites can be found in References [25] and [31].

Clays are often fine-grained, have cohesive properties, and exhibit some plasticity. The presence of water affects their behavior markedly. They have to be distinguished from silts, which are also fine-grained and water affects their behavior, yet they are non-cohesive and have little plasticity. Clay particles are colloidal-sized (mostly < 1 µm in diameter) and electrochemically active [31]. Clays belong to the group of phyllosilicates or sheet materials. Their basic components are silica tetrahedral or aluminum (magnesium) octahedral units, which can form sheets with quasi-infinite length (Figure 4).

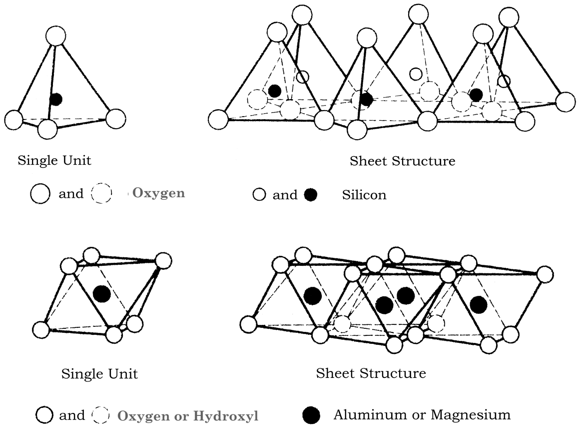
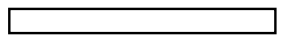


Figure 4 *Basic elements of clay minerals: silica tetrahedral and aluminum octahedral units (after* [31]*)*

The substitution of different cations into the octahedral sheets leads to different clay minerals. This process is usually isomorphous, i.e. the exchanged ions have approximately the same physical size. If the anions are hydroxyls, the octahedral sheets are called gibbsite for aluminum cations and brucite in case of magnesium cations [31]. The various compositions and combinations lead to minerals with different behavior, yet they all consist of the two basic sheets.

Table 3 summarizes the most important properties of kaolinite, illite and montmorillonite. The surface activity depends strongly on the specific surface area, which correlates with particle size. In comparison to clay minerals, quartz crystals as found in regular sand aggregate are almost inactive.

Table 3 *Dimensional properties of clay minerals (after* [31]*),*

	Edge view 1)	**Thickness**	**Diameter**	**Specific surface area 2)**
Unit		*nm*	*nm*	*m^2/g*
Kaolinite		50 - 2,000	300 - 4,000	15 (10-20)
Illite		30	10,000	80 (80-100)
Montmorillonite		3	100 – 1000	800 (400-800)

1) General qualitative particle shape

2) Values in parenthesis for specific surfaces after [68]

Clay minerals have usually negative surface charges due to isomorphous substitution of ions and imperfect crystals, such as “broken” edges. The smaller the particle size and the higher the specific surface the more likely is the occurrence of charge deficiencies. Thus, montmorillonite exhibits a much higher attraction to exchangeable cations than kaolinite. The valence of exchanged ions does not necessarily have to be the same and depends greatly on the environment. Also, the adsorption of dipolar water molecules favors small particles. As a result, hydrogen bonds tie water molecules to clay crystals. Thus, clay minerals are almost always found with high moisture contents [31].

2.4.2 Kaolinite

Kaolin or *kaolinite* is a clay mineral formed by a weathering and modification process over ages. Once these particles were rocks or mountains, but through ice and water treatment they were ground to small size. During this aging or weathering process certain components were washed out so that kaolin has usually a "clean" occurrence. It has a potential pozzolanic reactivity due to its relatively high content of aluminum-silicates, i.e., kaolin may participate in a hydration process that forms stable crystals.

Kaolin consists mainly of polymorph alumino-silicates ($Al_2Si_2O_5(OH)_4$). Its structure is governed by silicate sheets (Si_2O_5) tightly bonded to aluminum oxide or hydroxide sheets ($Al_2(OH)_4$ or gibbsite) [31]. These two sheets form one layer, which is 0.72 nm (i.e. $0.72 \cdot 10^{-9}$ m) thick but can reach indefinite dimensions in the two other directions. Successive layers are held together by strong hydrogen bonds between hydroxyls of the gibbsite and oxygens of the silicate sheet (Figure 5). The hydrogen bonds prevent hydration of single layers but cause formation of minerals with multiple layers. Kaolin crystals usually consist of 70-100 layers resulting in comparably large clay minerals (see Table 3).

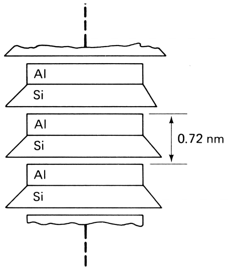


Figure 5

Schematic layer-structure of kaolinite: alternate sheets of gibbsite and silicates form a 1:1 mineral (after [31]*)*

Kaolin is widely used in various applications from tablets to rubber and ceramics. Its particle size suggests a use as filler material. It is odorless, pure and bacteria-free and not very active so that it can be used for pharmaceutical products. Kaolinite can easily be blended in rubber, latex, PVC, and other plastics. It smoothens the surface of cardboard and paper, creating glossy appearances, and is used in blackboard chalk. Kaolin can also function as the base material for ceramics with excellent properties, such as chemical and thermal resistance [64].

When activated at high temperatures (around 1300°C) and ground fine enough, kaolinite turns into a material with partially cementitious properties. For porcelain manufacturing pure white kaolin is preferred ("China Clay") while the raw mix for portland cement production is based on a clay composition called mergel, which often includes high amounts of kaolin clays. Metakaolin, an important derivative of kaolin, also consists mainly of alumino-silicates. It is processed from high-purity kaolin clay by calcination at temperatures of 600-900°C. This thermal activation leads to a partial or complete breakdown of the crystal lattice structure and forms a highly reactive transition phase [67].

2.4.3 Illite

Illite is a 2:1 mineral, i.e., it consists of layers formed by two silicate sheets and one gibbsite sheet (Figure 6). Isomorphous substitution in the silica sheet occurs frequently in illite minerals, and its main components are aluminum, calcium and silicium oxides combined with all sorts of minor compounds, mostly alkalis. Single layers are bonded together by potassium atoms. Illite has a crystal structure similar to that of mica minerals but is chemically more active. If any clay mineral can be called regular it is illite. It is not as active as montmorillonite nor can it easily be activated like kaolin. That is probably the reason for its relatively limited commercial use.

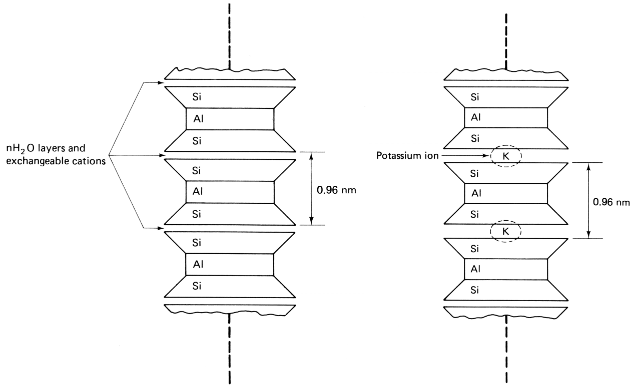


Figure 6 Schematic layer-structure of montmorillonite (left) and illite (right): a sandwich layer of one gibbsite sheet between two silicate sheets form 2:1 minerals (after [31]*)*

2.4.4 Montmorillonite

Montmorillonite, also known as *smectite*, is another 2:1 mineral similar to illite. However, the single layers of two silicate sheets embracing one gibbsite sheet form relatively weak van-der-Waal's bonds. In combination with the clay-typical surface charge deficiency, the interlayer bonds attract water and exchangeable ions [31]. Montmorillonite contains a relatively high amount of alkalis such as sodium, potassium and magnesium. The two facing silica sheets are separated by variable water content. Hence, montmorillonite is susceptible to swelling. Due to the weak bond the number of layers forming one stable crystal is limited. Therefore the particle size of the very thin flake-like crystals is very small with a typical thickness of only 3 nm (Table 3).

Montmorillonite is used in construction as the main component of bentonite, e.g. for in-ground concrete walls and columns (also known as slurry walls). Its plate-shaped particles create a stable suspension, which is capable to hold load (in general earth and water pressure) in one direction, and when vibrated or shaken it becomes liquid. These tixotropic properties make bentonite valuable for temporary installations. Montmorillonite can swell, holding water up to 1.6 times its own weight [25]. Because of its fineness montmorillonite can be found in industrial and pharmaceutical applications and even in chocolate products [31].

2.5 DREDGED MATERIAL

Dredged material is naturally accumulated sediment or, in the case of channel deepening and construction, rock or soil, which is excavated from the bottom of waterways. Dredging is necessary to maintain or create sufficient navigational depth and to keep harbors accessible. In addition, environmental remediation may require dredging operations. The ecological impact of dredging processes and disposal techniques has been studied thoroughly since the early 1970s. Facing strict environmental regulations, ports worldwide are currently changing their dredged material management plans to remain economically viable [44].

Dredged material consists mainly of clays, silts and sand mingled with rocks, debris of variable sizes, and to some extent organic matter. Dredged material properties change in time and vary from place to place. Geology, mineralogy, morphology, and composition strongly depend on the geographic location and as a result, physical and chemical behavior can vary greatly. Also the type, level of concentration, and chemical activity of contaminants cover a wide spectrum [45].

Almost any thinkable pollutant can be found in dredged material: from heavy metals, such as lead and mercury, to organics, such as pesticides and polychlorinated biphenyls (PCBs), and bacteria, such as E-Coli. Contaminated sediments are very difficult to dispose of in an environmentally acceptable way, either in designated disposal facilities or for beneficiation.

Especially the beneficial use of the fine-grained particle fraction, i.e. clays and silts, poses a challenge because this tends to attract the pollutants [81, 86].

Usually, the water content of the dredged material is very high and thus, one of the first steps in any processing train is the dewatering of the material for volume reduction. Often, stabilization with mineral binders is necessary for safe handling during transportation. Unless long-term storage is desired dredged material can be treated either partially or without any separation. Different beneficiation techniques are available. The choice of a particular treatment depends on the "cleanliness" of the material. In general, the approaches involve specific chemicals, micro- and macro-organisms (biological remediation), mechanical or thermal treatment. Their respective advantages and disadvantages can be found in the literature [e.g. 43, 81].

Sediments found in the Port of New York and New Jersey are generally fine silts and clays mixed with coarser particles, mainly sand. The fine-particle content changes with location and time. Typical values quoted in the literature are 80-95% fines [81], or 4-46% clays and 4-54% sands / silts [89]. The mean particle diameter is of the order of 10 µm (Figure 7). The main mineral components are quartz, mica, albite and feldspar [43].

Clays are generally capable of swelling and water absorption. Their specific surface areas can be 100 times greater than those of sand, which, in combination with their surface charge and ion-exchange ability, leads to the sorption of contaminants. Oil products and salts may cover the fine particles. As a result, fine particles attract each other and conglomerate. The microstructure consists of networks, which form layers of agglomerates with water intrusions.

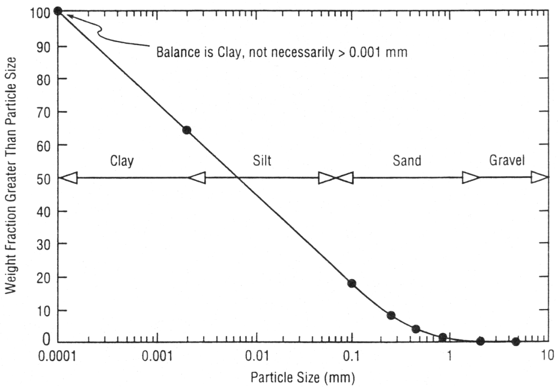


Figure 7 *Typical particle size distribution of dredged material from NY/NJ Harbor* [81]

The two dominating chemical compounds in dredged material are silicium (SiO_2) and aluminum (Al_2O_3) oxides with fractions of 65-80% and 8-15%, respectively. Since the NY/NJ Harbor consists of marine estuaries, 1-4% sodium chloride (NaCl) was detected in various sediments [81]. This saline environment alters the surface charge of clay particles, making agglomeration more likely to occur.

Due to their relatively large surface-area-to-volume ratio and electro-chemical character, clay layers are very likely to adsorb heavy metals and oil products. Obviously, this affects the mode of interaction between contaminants and any admixtures that may be added to

treat the material. The influence of various powder admixtures and other additives on dredged material was the subject of a research project at Columbia University, which led to the development of a material processing method, which reorganizes the (micro-) structure and immobilizes contaminants [43, 44, 45, 46]. This treatment will be briefly introduced in Section 3.3.

2.6 CONCRETE

In its simplest form, concrete is a mixture of cement, water and aggregates (Figure 8). Typically, a mix contains about 10-15 V% cement, 15-20 V% water, and 60-75 V% aggregate. In addition, 2-8 % air may be entrained. Cement and water form a slurry or paste, which covers the surface of aggregates and fills the voids between the particles. Through a chemical reaction of the cement with water, the hydration, the aggregate is permanently glued together, forming a rock-like structure, i.e., concrete. Historically, the ancient Egyptians used concrete-like materials, and the Romans called their synthetic stone *Opus Caementitium*, which is the origin of the name "cement" [42, 50, 90].

Because concrete is plastic and formable directly after mixing and strong, durable and hard after the hydration of the cement, it has become the most common construction material. Admixtures and additives administered to the fresh mix can modify the behavior of fresh concrete or properties of the hardened concrete. Progressive research has created recipes for concrete in countless shapes, for multiple purposes, in severe climates, under various loads in almost every engineering application thinkable.

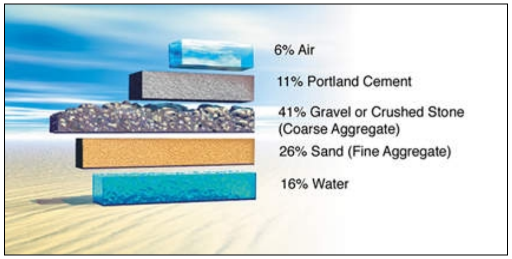


Figure 8 *Basic components of concrete (typical mix without admixtures or additives)* [56]

Note: Proportions are based on the *<u>volumes</u>* *of the individual components*

However, concrete has to be designed carefully in order to function reliably. Due to its heterogeneous structure, it can carry heavy loads when under compression, but its capacity to carry tensile forces is usually neglected for design purposes. Phenomena such as alkali-silica reaction, carbonatisation, or chemical attack have undesirable long-term effects on the concrete. Careful consideration and selection of the raw materials is necessary to avoid partial failure or even collapse of a concrete member during its service life. The components of concrete most relevant for this study were introduced briefly in the previous sections.

Fresh concrete and hardened concrete have completely different behavior, therefore both phases have to be studied separately. While the fresh mix can be characterized mainly by its workability (mainly flow and "compactability)", the performance criteria for hardened concrete can vary considerably (compressive strength, density, chemical resistance, surface hardness, fracture toughness etc.).

Generally, the water content plays the most dominant role in mix optimization. Aggregates or admixtures with large specific surface areas show high adsorption capacities so that more water has to be added to achieve sufficient workability. On the other hand, a higher water-cement ratio is associated with lower strength. The main mechanical properties and the parameters governing the concrete mix design to meet certain performance criteria are given in the following sections.

2.7 CLAYS AND CONCRETE

Clays are often considered to jeopardize the production of durable concrete. Specifications for concrete aggregate suggest that any conglomeratic, thin-layered, narrowly stratified material with high water absorption and/or capability of cation exchange is undesirable for concrete production. Clays and limonite are explicitly mentioned as being "potentially objectionable" [18]. One common way to determine deleterious aggregate components is to use tests based on specific dyes. The chemicals were originally chosen at a time when all clays were considered harmful. Modifications were recommended to allow for the use of kaolinite and smectite in mortar production [93].

Soft and highly absorptive particles may cause cracks in concrete members or, when close to the surface, even pop-outs. Such soft minerals can be clays, micas, or gypsum. Laminated clays containing sheet minerals may introduce large volume changes on wetting and drying, possibly causing disintegration of the structure. Damage may be severe if saturated particles freeze [18]. Due to the fineness of clay minerals, their specific surface area is exceptionally high, and so is their water adsorption capacity. This imposes a major problem in fresh concrete, because free water is removed from the mix and the material becomes sticky and less plastic. As a consequence, a drastic drop in workability is experienced, making the addition of a superplasticizer imperative [36, 67, 88].

It also was suggested that the initial adsorption might create a water reservoir in the concrete mix, which acts like a buffer by releasing stored water later during the hydration process [67]. Work has been conducted on phase changes that take place under alkaline conditions, under which bentonite and tuffs are converted into zeolites [52, 59, 75]. Zeolites were subjected to research on lightweight and regular concrete [8, 9, 52, 54, 75]. In the last decade, the thermal activation and calcination of kaolinite was studied, which established metakaolin as an admixture for concrete production [11, 16, 21, 41, 67, 88, 95].

Some clay minerals are capable of base-exchange reactions. Hence, calcium ions in the pore solution of concrete may substitute for alkaline bases of clay minerals. In exchange, these alkalis dissolve into the pore solution to create a more reactive and thus more aggressive environment, increasing the risk of alkali-aggregate reaction [18]. On the other hand, active clay minerals such as metakaolin tend to counteract this phenomenon [27, 60, 67]. The nature of the alkali-aggregate reaction is complex and will not be subject of this work. However, additional research is suggested.

The addition of metakaolin to concrete mixes increases the early strength due to filler effects and accelerated cement hydration [88]. Metakaolin was shown to increase ASR resistance [60] by reacting in the presence of water with the calcium hydroxide in the pore solution to form cementitious CSH phases (see Section 3.2). In addition, crystalline products containing aluminum are developed such as calcium-aluminate-hydrates and calcium-alumino-silicate-hydrates (C_2ASH, C_4AH_{13}, C_3AH_6) [2]. Due to its pozzolanic properties, metakaolin can be used as partial cement replacement [65, 66, 85].

Portland cement generally liberates calcium hydroxide (CH) after complete hydration, usually about 28% of its own weight. Calcium hydroxide does not significantly contribute to strength and is associated with poor durability. Excessive amounts are undesirable for this reason. However, the passivation of (steel) reinforcement strongly depends on the high pH level of concrete. Therefore, some standards give threshold values for the addition of silica fume to reinforced concrete to ensure sufficient amounts of calcium hydroxide in the pore solution. Similarly, there may be a threshold value for metakaolin.

The reaction between calcium hydroxide and pozzolans enhances the concrete's properties by removing excessive calcium hydroxide and generating additional cementitious phases. The relatively short experience with clay minerals does not suggest any quantitative limitation for their use in concrete mix designs due to consumption of calcium hydroxide but rather because of decreasing workability. However, because of its purity and color-consistence, metakaolin has been used for architectural concrete [27, 35]. For example, to achieve and maintain light-colored, high-quality concrete, metakaolin was added to mixes for the Cathedral of Our Lady of the Angels, Los Angeles, CA [69].

This study also employs natural and thermally activated kaolin as fillers in concrete applications to evaluate the performance of dredged material, and especially of the clay fraction thereof. Different superplasticizers are administered to the various mixes not only to improve the workability but also to gain additional understanding of the chemistry behind the governing reactions.

2.8 DREDGED MATERIAL AND CONCRETE

Typically, dredged material contains up to 90% clay, silt, and fine sand so that it is like a paste or thick suspension of fine particles when found in natural conditions (often referred to as "Black Mayonnaise"). It may be contaminated with oil products and contains, depending on local conditions, up to 80% salt water. In addition, heavy metals and other toxic substances can be present, which pose a health threat.

Chemical, biological, or thermal treatment methods to beneficiate dredged material have targeted mostly low performance applications like backfill or cover material. Attempts to utilize dredged material in bricks by firing them like natural clays were shown to be technically feasible but did not gain the necessary public acceptance [28, 82, 86]. Separation of the fines in combination with some soil washing techniques is the most promising and most established way of beneficiation, although several other areas of application have

been explored extensively such as production of cement, light-weight aggregate, glass products, just to name a few.

The components of dredged material offer several reasons why dredged material should not be used in concrete production. The salts, organic contaminants, and clay minerals impose great challenges, because they negatively alter the properties of fresh and hardened concrete. The pollution with heavy metals may not affect the physical characteristics directly but raise concern about leaching of contaminants into the surrounding environment.

The quantitatively dominant sand fraction suggests the use of the material as aggregate replacement. On the other hand, the chemically and physico-chemically prevailing clay minerals exhibit similarities to natural clays such as kaolin (Figure 9, a and c). The quartz minerals in dredged material are much smaller in size than regular sand particles and exhibit surface defects (Figure 9, b and d). Such imperfections may create a reactive potential. Therefore, a replacement of fine sand particles should lead to inconsistent results.

However, the use of clay and clayey dredged material was investigated here because the fine particle range of such material may fill the gap in particle size between cement and aggregate (filler effect). In addition, the crystalline similarity of clay minerals and the products of cement hydration (CSH phases) suggests chemical bonding even if no pozzolanic reaction is expected [88].

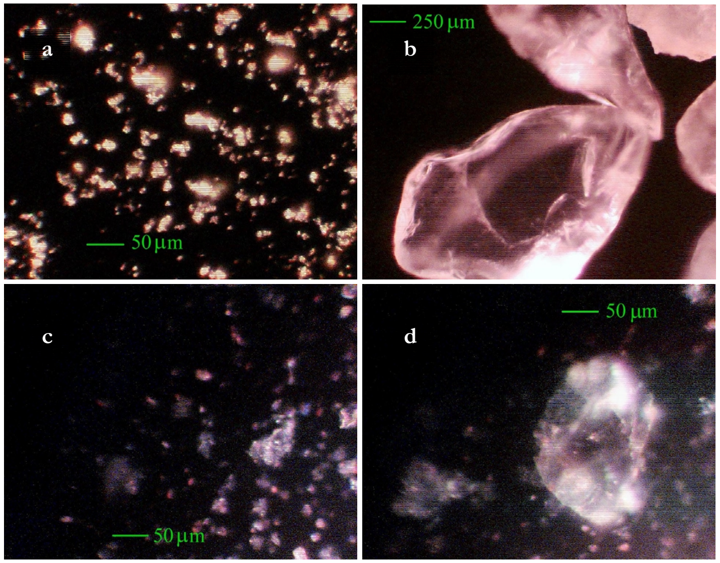


Figure 9 *Light microscope observation* [44]:
a) Kaolinite (500x) *b) Regular sand (100x)*
c) Dredged material (500x) *d) Quartz crystal in dredged material (500x)*

One of the tasks of this work is to find an optimum or limiting amount of dredged material in concrete composites. While the use of large amounts of dredged material is desirable to beneficiate a maximum of such waste material, satisfying concrete specifications such as sufficient workability and strength are other goals, which may be in conflict and thus require a compromise. Since dredged material is basically a mixture of sand (a regular concrete component) and clays (a potential filler), its use in concrete may offer one possibility to easing the disposal problem of contaminated dredged material.

It is highly recommended to reorganize the (micro-) structure of dredged material with a homogenization treatment developed at Columbia University [43, 44, 45, 46], if such material is used for commercial products (see Section 3.3). The positive effects of such prior treatment have been evaluated in those earlier studies. To identify the basic interactions between dredged material and the other constituents of concrete, such prior treatment does not seem prerequisite for the purposes of this study.

2.9 SELECTED CONCRETE PROPERTIES

2.9.1 Chemical Composition

It is possible to modify the chemistry of hydration products by proper choice of the various concrete components, especially clayey admixtures. Equations {1–9} establish possible reactions during the hardening of cement. The chemical compositions of selected mineral admixtures are given in Table 4. It will be a goal of this work to evaluate if and how these components interact and react with the regular concrete matrix. Their chemical composition not only determines the products of a reaction between the individual concrete components during the hardening process but it also influences the properties of fresh concrete by its physicochemical behavior, such as surface charges and capability of ion-exchange.

Table 4 Chemical compositions of selected mineral fillers

Type	Base	SiO_2	Al_2O_3	Fe_2O_3	CaO / MgO	Na_2O / K_20
Clay/Sand	Dredged material [44]	42-58%	8-13%	4-6%	3-23%	3-4.5%
Clay	Bentonite [3]	45-66%	16-22%	2.5-17%	0.8-2%	2-4%
Clay	Kaolin [88]	52%	41%	4.3%	0.3%	0.9%
Sand	Quartz (fines)	~95 %				

2.9.2 Workability

The workability, which is related to flowability and compactability, is probably the most important property of fresh concrete. It is affected simultaneously by the flow, coherence, homogeneity, rheology, and consolidation of a given mix. Common tests provide only a first indication of workability by measuring one of these properties.

A sufficient flow is required to give the concrete its desired form in a given mold. A high adsorption capacity of any one of the constituent concrete components requires more water to achieve a certain flow. Generally, coarse aggregate has a negligible adsorption capacity compared to fine sand particles and especially clays. The finer the particle the higher the specific surface, and the more water can be bound on the surface. Therefore, finer mixes, in particular clay minerals, require additional mixing water.

The workability of a mix is a function of a number of binder and aggregate parameters, such as particle size, size distribution, shape, specific surface, surface charges, adsorption capacity, and chemical composition. This set of variables defines the water content needed to achieve a certain flow or workability. In this work special emphasis is placed on the role of workability as a primary criterion in concrete mix design. Rational tools to establish the necessary relationships are available.

For example, Krell [39] found that a specific mix starts to flow when a sufficiently thick layer of water is established around each particle. Superplasticizers can decrease the required film thickness and interact physico-chemically with charged surfaces especially of cement particles and clay minerals, or homogenize a given slurry or suspension by deflocculation. Hence, the addition of a superplasticizer either reduces the amount of water required for a given workability ("high-range water reducers") or increases the flow of a mix with a given water content [73].

The role of superplasticizers on workability has already been addressed in Section 2.3.3. It may be added that superplasticizers increase the flow of a given mix due to increased zeta potential, increased solid-liquid affinity (dispersion) and steric hindrance (oriented adsorption). The adsorption of superplasticizers on hydrates and cement particles creates repulsive forces, which prevent flocculation [57, 62, 73]. It is suggested to wait for a few minutes during mixing before administering superplasticizers because they are more effective interacting with hydration products than with cement particles [62, 73].

The use of superplasticizers has been associated with secondary effects such as rapid and unrecoverable loss in slump, retardation, segregation or bleeding [57]. To avoid such problems, careful evaluation of the appropriate type and dosage is mandatory. Superplasticizers such as formaldehyde-condensate or melamine-formaldehyde are less retarding and air-entraining than the older lignosulfonate because they do not have hydrophobic regions, which are created by repeated polar groups [73]. All three types of superplasticizers will be evaluated in this work with regard to their effectiveness in reducing the required volume of water and any secondary effects. In addition, a mixture of various superplasticizers was evaluated, which had been developed at Columbia University as a by-product of the research on glass concrete.

The influences of particle size, specific surface, chemical activity, and ultimately, adsorption of different mineral clayey fillers were evaluated for mixes with or without superplasticizer. A correlation between type and particle size of mineral additives and workability of various concrete mixes was sought and it was attempted to predict the water requirement of a specific composition.

2.9.3 Compressive Strength

Generally, concrete performs exceptionally well in compression while its tensile and flexural strengths are comparably low. Therefore, concrete is usually classified by its compressive strength. Other performance criteria may be equally important and recently have gained more and more attention, but the compressive strength remains the most important property when evaluating certain compositions.

The compressive strength of concrete is governed by the transition phase between aggregate and cement matrix and the individual strengths of its components. High-performance concrete derives its properties from an increased formation of CSH phases, especially in the contact zone between aggregate (basically SiO_2) and cement matrix ($Ca(OH)_2$ and/or CSH) [33, 83].

High strength can be obtained using low water-cement ratios (<0.40), admixtures such as silica fume and superplasticizers, and following specific production protocols. Researchers were able to produce a 280 MPa concrete (35,000 psi) using a water/cement ratio of 0.15, a high dosage of silica fume and superplasticizer, and special laboratory techniques [1]. Reactive powder concrete can reach strengths up to 800 MPa (96,000 psi) if regular sand aggregate is replaced by metallic powder [2].

In this work, the workability of fresh concrete shall be the primary mix design criterion. However, for quantifying the performance of the hardened concrete, the compressive strength will remain the main measure.

3 TEST PROGRAM

The workability is one of the major concrete mix criteria to provide the basis for comparison of individual mixes. Prior flow tests are conducted to find the appropriate water/cement ratio and dosage of superplasticizers to ensure similar workability, i.e. comparable flow. The evaluation of the various concrete mixes follows the traditional common approach of determining the compressive strength. In addition, for selected mixes also the tensile strength, setting time, alkali-silica reactivity, or leaching performance are determined, supplemented in selected cases by optical or scanning electron microscopy (SEM) investigations. These tests are described in the following section.

3.1 TEST PROTOCOLS

3.1.1 Workability

The workability of fresh mortar is evaluated using the "Cone Test" according to ASTM C230 [4], which determines the flow of a specific mix as an indicator of workability. A conical ring (2" height, inner diameter of 2.75" at the top and 4" at the base) is filled with mortar in two steps and then lifted. The mortar is subjected to 25 drops of a standard flow table. Afterwards the diameter of the spread-out material is measured four times with a standard caliper. The sum of those four measurements provides an index of the flowability in % (with respect to an empirical reference value). Henceforth, this method will be referred to as "Cone Test" (Figure 10).

In a modified flow test, a metal ring (1.5" inner diameter and 2" height) replaces the standard cone. The procedure is similar to the cone test with the exception that the final flow is the average of four measurements of the radius of the spread-out material in mm. This method will be referred to as "Ring Test" (Figure 11).

Figure 10 Cone for the "Cone Test"

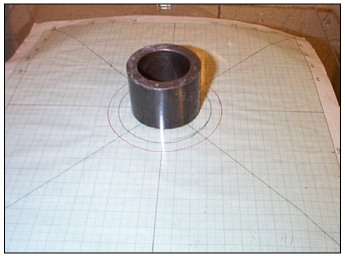


Figure 11 Ring for the "Ring Test"

3.1.2 Compressive Strength

The compressive strength of hardened concrete is determined by the "Cube Test" according to ASTM C109 [4]. For each test series, six two-inch cubes are prepared for testing at the age of 7 and 28 days. In a modified test, small cylinders of 1 inch diameter and

1 inch height are used instead of cubes. The procedure is similar to that of ASTM C109. This method will be referred to as "Cylinder Test" (Figure 12). The main advantage of using small cylinders is the comparably small amount of material required to prepare six cylinders. However, the accuracy of compressive strength tests with cylinders may be lower than that with cubes because of the size and shape factors. A correlation between the two tests might be established.

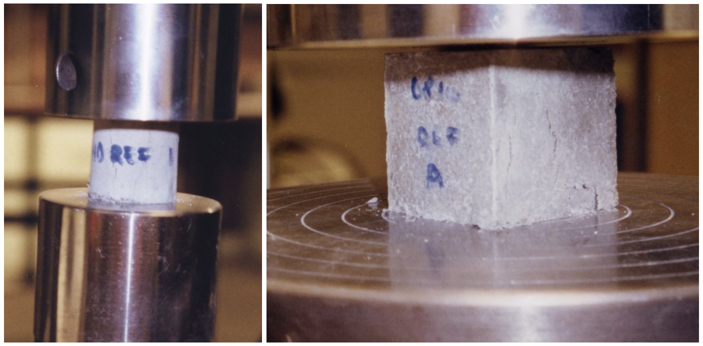


Figure 12 One-inch cylinder for the "Cylinder Test" and two-inch cube for the "Cube Test"

The use of one-inch cylinders was a compromise between test accuracy and the need for large amounts of dredged material. The end surfaces of the small cylinders are not perfectly plane, which affects the strength test results. However, they require far less material than larger test specimens. For example, one two-inch cube requires the same amount of material as ten small cylinders. It was assumed that the tests would still yield valid results for comparative purposes.

3.1.3 Setting Time

The setting time of fresh concrete is tested according to ASTM C191 [4]. A procedure after Vicat is used to measure the penetration depth of a needle at regular time intervals. The time when the penetration depth is less than 10mm is defined as the setting time, which is an indication of rate of hydration and strongly depends on the chemical composition of a mix. The Vicat test is especially helpful if organic components are present, which may act as retarding agents and delay significantly the setting of a given concrete mix.

3.1.4 Alkali-Silica Reactivity

Two different methods are used to evaluate the concrete reactivity, the ASTM C1260 test [5] and an autoclave test [36]. In the ASTM C1260 test, 1 by 1 by 10 inch^3 mortar bars are immersed in a bath of sodium-hydroxide solution of 80 ± 2°C, and the bar expansions are measured. In the autoclave test, the specimens are treated with steam at a temperature of 123°C ± 2°C and a steam pressure of 0.136 to 0.15 MPa. The elevated temperature and alkaline conditions of the ASTM C 1260 test provide useful results after a period of 16 days [5]. The autoclave conditions maintain sufficient moisture to accelerate a potential alkali-silica reaction and thus shorten the treatment process to only 24 hours [36].

For each different mix six identical specimens are tested. Three of these are subjected to the ASTM C1260 test, and the other three are tested in the autoclave, an AMSCO laboratory unit with a 1 by 0.48 by 0.48m^3 chamber that allows simultaneous testing of more than 20 specimens. In the autoclave test, the cooling process and method of length change measurement follow the procedure of ASTM C151 [4].

3.1.5 Tensile Strength

The tensile strength of hardened concrete is determined in accordance with ASTM C307 [6] by testing three briquet specimens for each case at the age of 28 days.

3.1.6 Leaching of Contaminants

To evaluate the potential health hazard of contaminated dredged material used in concrete applications it is essential to show that harmful pollutants cannot leach out. Critical in any leaching test procedure is the method of contaminant extraction, i.e. which carrier is used and under what conditions (time, temperature, pressure, solid or liquid samples). Herein, an extraction method described in Reference [30] is used. Three "rain chambers" are installed using plastic containers (polypropylene) with independent water circulation (Figure 13). For comparability, demineralised water is used to extract the pore solution over about 110 days. The flow rate is held constant over the test period. Sample-to-water ratio is 1:5 (by volume), as suggested in Reference [30]. For each rain chamber, three two-inch mortar cubes are prepared and placed on small pedestals in the containers.

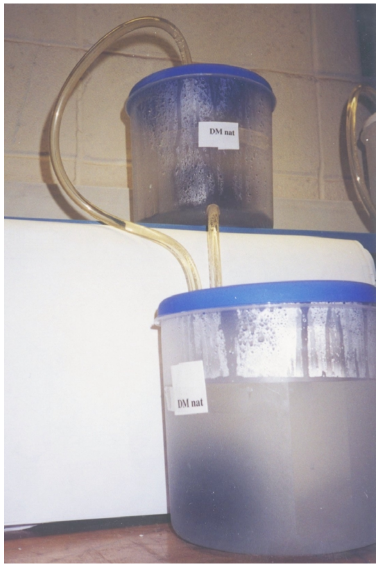


Figure 13 Test set-up for "Rain Chamber Test"

After extraction during the "raining" period, samples of the circulating water in each system are analyzed for any contaminants leached out of the pore solution of the specimens. The specimens themselves are crushed after the rain chamber test and chemically analyzed afterwards. Most of the analyses follow the *Toxicity Characteristic Leaching Procedure* (TCLP), which "is designed to determine the mobility of both organic and inorganic contaminants in liquid and solid, and multiphasic wastes" [77, page 40643]. The Baron Consulting Company, CT conducts the chemical analyses of all samples, using the methods described in [78, 79, 80].

3.1.7 Durability

Durability designates the ability of a material to maintain its properties over its service life. Depending on loading and environmental conditions, concrete can undergo undesirable changes with time. Especially if unknown detrimental substances are present or if the chemical composition of a concrete component changes with time and place of origin, as in the case of dredged material, long-term effects have to be taken into consideration.

Durability is a relatively general term and includes ASR related issues (see Section 2.2), which can be evaluated using the tests described in Chapter 3.1.4. In addition, the durability of a given composition is affected by performance during freeze-thaw cycles, resistance against chemical attack (typically by sulfuric acid or through chloride ingress), and carbonization. In this work, durability cannot be addressed completely. Further work is desirable for future research.

As a first approximation of durability performance, the compressive strength of one-inch cylinders is determined at much higher ages than the customary 7 and 28 days, to detect possible deterioration over time. During this work, additional durability evaluations are confined to ASR tests and leaching performance, a rather atypical durability issue, because of health concerns that may be raised by the contaminants in dredged material.

3.2 MATERIALS

Cement:	*Allentown Cement* Portland cement Type I, chemical composition as shown in Table 5.
Dredged material:	Material dredged in November 1999 at Newtown Creek, New Jersey, chemical composition as shown in Table 5; used either untreated, dried, or after *Columbia University Treatment* (CUT, see Chapter 3.3); contamination before and after CUT treatment as shown in Table 6.
Kaolin:	*Dry Branch Kaolin Company* untreated kaolinite.
Metakaolin:	*Engelhard MetaMax* thermally activated kaolinite, chemical composition as shown in Table 5.
Aggregate:	Non-reactive manufactured sand, with five different sieve curves as shown in Table 6.
Superplasticizers:	SP-Lig: based on lignosulfonate (*Darvan 2*), SP-FC: based on formaldehyde-condensate (*Tamal*), SP-Mel: based on melamine-formaldehyde (*Melment*), SP-Mix: proprietary admixture blended from multiple substances (37% water by mass).

Table 5 Chemical composition (in % by mass) of selected components

Component	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	LOI [1]
Cement	21.29	63.83	4.42	2.87	1.78	0.21	0.76	0.77
Dredged material	41.56	22.84	8.48	4.14	1.56	1.81	1.08	16.65
Metakaolin	51.2	0.05	45.3	0.6	NA	0.21	0.16	0.51

[1] Loss on ignition at 950°C

Table 6 Level of contamination in dredged material before and after treatment (determined by TCLP)

Dredged material	Cadmium [2]	Lead	Leachable cyanide [2]
Untreated	0.23 ppm	0.38 ppm	0.27 ppm
CUT treated (see Section 3.3)	ND < 0.02 ppm	0.17 ppm	ND < 0.1 ppm

[2] ND: not detected

Table 7 Aggregate grading for dredged material as sand replacement (% by mass retained)

Grading Curve	Sand					Dredged material (solids)
US Standard Sieve #	***8***	***16***	***30***	***50***	***100***	**<100**
R1	10	25	25	25	15	-
R2	10	25	25	25	10	5
R3	10	25	25	25	5	10
R4	10	25	25	25	-	15
R5	10	25	25	20	-	20

3.3 DREDGED MATERIAL PROCESSING

Dredged material is used in three different conditions:

1.) The "natural" state, i.e. as a thick slurry without prior separation, de-watering, or treatment;

2.) A solid, powdery state after drying;

3.) A solid, powdery state after treatment.

Dredged material sludge contains about 55% water (by mass) and has a thick consistency, which is the reason for its nickname, "black mayonnaise". The water content is determined by weighing the material periodically during drying on a small laboratory hot plate until consecutive measurements exhibit no change in weight. The water contained in dredged material is credited as gauging water since it is assumed that this water is more or less freely available for cement hydration.

In the drying process (Figure 14), the natural dredged material is stored at room temperature and pressure. These conditions are expected to leave the chemical composition and general physical properties of the material unaltered. Such natural drying decreases the water content to about 6% by mass, which is taken into account during the concrete mix design. In a second step, the material is ground in a customary coffee blender, which is the fastest and least expensive method of reducing the particle size.

Figure 14 Drying process of dredged material: 1) *sludge,* 2) *dried "cakes",* 3) *ground filler*

After the drying process, the dredged material is much easier to process, handle, and store than the slurry in its original condition. It appears to be slightly more homogeneous because large agglomerates with weak bonds may be partially destroyed. As a side effect small foreign particles, e.g. pieces of woods or metal screws, can be removed manually in the process.

An alternate treatment procedure was developed at Columbia University [43, 44, 45, 46], which is referred to as "CUT" and described in a U.S. patent application [37]. The treatment is based on the physico-chemical reorganization of the (micro-) structure of the dredged material. The addition of a mineral admixture causes a reaction, during which agglomerates are destroyed and the structure is spread out. Thereby, the dredged material properties can be adjusted and homogenized. With the subsequent administration of a chelating agent contaminants can be encapsulated or permanently immobilized by forming stable macromolecules. The CUT lowered the contaminant concentrations significantly, as can be seen in Table 6. After such treatment the material is ground to fine particle size. The residual water content can be considered to be negligible and need not to be counted for the gauging water of any concrete mix.

3.4 TEST PLAN

3.4.1 Natural Dredged Material as Aggregate Replacement

The first approach to beneficially use dredged material in concrete applications is based on the assumption that the quantitative dominance of sand-like particles would justify a replacement of regular aggregate. In Test Series RN (Table 8), the material is used in its natural untreated condition as sludge with about 55% water content (by mass). The dredged material amount refers to the dry weight and is given in percentage of the aggregate. Because dredged material replaces parts of the fine sand, the overall amount of aggregate remains constant. The aggregate-to-cement ratio (a/c) is 2.25 for all mixes.

In sub-series RN-A, the water-to-cement ratio (w/c) is held constant so that the flow is expected to decrease with the addition of dredged material. In the second sub-series RN-B, the w/c ratio is adjusted with increasing dredged material content to achieve comparable flow. To determine these w/c ratios, prior flow tests were necessary. The same mix proportions are used in sub-series RN-C as in RN-B, but without dredged material to permit an evaluation of the dredged material in comparison to fine sand. In sub-series RN-D, the amount of water required to obtain comparable flow is reduced because of the administration of a superplasticizer.

Table 8 Test series RN (Replacement of aggregate with Natural untreated dredged material)

Name	Composition					Test	
	w/c	a/c	Grading Curve	Dredged Material[1]	SP-Mix[2]	Flow	Compr.
RN-A1	0.70	2.25	0.70	-	0.70	Ring	Cylinder
RN-A2	0.70	2.25	0.70	5	0.70	Ring	Cylinder
RN-A3	0.70	2.25	0.70	10	0.70	Ring	Cylinder
RN-A4	0.70	2.25	0.70	15	0.70	Ring	Cylinder
RN-A5	0.70	2.25	0.70	20	0.70	Ring	Cylinder
RN-B1	0.45	2.25	R1	-	-	Ring	Cylinder
RN-B2	0.52	2.25	R2	5	-	Ring	Cylinder
RN-B3	0.64	2.25	R3	10	-	Ring	Cylinder
RN-B4	0.75	2.25	R4	15	-	Ring	Cylinder
RN-B5	0.88	2.25	R5	20	-	Ring	Cylinder
RN-C2	0.52	2.25	R1	-	-	Ring	Cylinder
RN-C3	0.64	2.25	R1	-	-	Ring	Cylinder
RN-C4	0.75	2.25	R1	-	-	Ring	Cylinder
RN-C5	0.88	2.25	R1	-	-	Ring	Cylinder
RN-D2	0.45	2.25	R2	5	0.6	Ring	Cylinder
RN-D3	0.50	2.25	R3	10	1.2	Ring	Cylinder
RN-D4	0.57	2.25	R4	15	1.8	Ring	Cylinder
RN-D5[3]	0.63	2.25	R5	20	2.3	Ring	Cylinder

[1] In % by mass of aggregate

[2] In % by mass of cement

[3] Additional determination of compressive strength test at increased age (durability)

3.4.2 Dredged Material as Filler

It is hypothesized that there might be a potential to use dredged material more profitably as filler rather than aggregate replacement. For that purpose, the material was administered to the various concrete mixes either without further treatment after drying (Test Series NF, Table 9) or after CUT treatment (Test Series TF, Table 10). In the following tables, the test series are grouped according to the additional filler that is used. The amount of filler is given in percentage of the cement by mass. Further details about these two test series will be presented in Chapter 4.

3.4.3 Dredged Material and Kaolin as Fillers

After a first analysis of selected test results of Test Series NF-A and TF-A, a dredged material content of 30% by mass was considered to be large enough to clearly determine the influence of this material as a filler. At the same time, this percentage is small enough to not negatively affect all concrete properties and in some cases to even improve its performance. Because of the similarity between natural clay minerals and the ones present in dredged material (see Chapter 2.8), the addition of varying amounts of dredged material and of kaolin is evaluated at a combined content of 30% by mass (Test Series KF, Table 11, and Test Series NK, NM, Table 12).

However, clay minerals in dredged material are subject to aging and weathering processes, which may alter their physicochemical properties. The crystal structures and especially the surfaces of the minerals contain (partial) defects and may exhibit increased reactivity. The performance of dredged material filler was therefore compared with that of metakaolin with well-known pozzolanic properties (Test Series NM, Table 12).

Table 9 Test series NF (N̲atural untreated dredged material as F̲iller)

Name	**Composition**				**Test**		
	w/c	**a/c**	**Dredged Material1)**	**SP1)**	**Flow**	**Compr.**	**Other2)**
NF-A1	0.70	3.0	20	-	Ring	Cylinder	-
NF-A2	0.42	3.0	-	Mix 1.0	Ring	Cylinder	D
NF-A3	0.42	3.0	5	Mix 2.0	Ring	Cylinder	D
NF-A4	0.42	3.0	10	Mix 3.0	Ring	Cylinder	D
NF-B1	0.41	3.0	-	Mix 2.5	Ring/Cone	Cube	L
NF-B2	0.48	3.0	30	Mix 2.5	Ring/Cone	Cube	L
NF-C1	0.52	3.0	-	-	Ring/Cone	-	S/A/1260
NF-C2	0.75	3.0	30	-	Ring/Cone	-	S/A/1260
NF-D1	0.54	3.0	-	-	Ring/Cone	Cube	T
NF-D2	0.42	3.0	-	Lig 0.5	Ring/Cone	Cube	T
NF-D3	0.81	3.0	30	-	Ring/Cone	Cube	T
NF-D4	0.69	3.0	30	Lig 1.0	Ring/Cone	Cube	T
NF-D5	0.66	3.0	30	FC 1.0	Ring/Cone	Cube	T

1) In % by mass of cement
2) S: setting time test
A: autoclave ASR test
1260: ASTM C1260 ASR test
T: tensile strength test

Table 10 Test series TF (T̲reated dredged material as F̲iller)

Name	**Composition**				**Test**		
	w/c	**a/c**	**Dredged Material1)**	**SP-Mix1)**	**Flow**	**Compr.**	**Other**
TF-A1	0.70	3.0	20	-	Ring	Cylinder	-
TF-A2	0.50	3.0	20	2.0	Ring	Cylinder	-
TF-A3	0.55	3.0	30	2.0	Ring	Cylinder	-
TF-A4	0.60	3.0	35	2.0	Ring	Cylinder	-
TF-A5	0.65	3.0	40	2.0	Ring	Cylinder	-
TF-A6	0.70	3.0	45	2.0	Ring	Cylinder	-
TF-B1	0.42	3.0	30	2.5	Cone	Cube	L
TF-C1	0.61	3.0	30	-	Ring/Cone	-	S/A/1260

1) In % by mass of cement
2) L: leaching test
A: autoclave ASR test
S: setting time test
1260: ASTM C1260 ASR test

Table 11 Test series KF (K̲aolin as F̲iller)

Name	**Composition**				**Test**		
	w/c	**a/c**	**Kaolin1)**	**SP1)**	**Flow**	**Compr.**	**Other2)**
KF-1	0.88	3.0	30	-	Ring/Cone	Cyl./Cube	S/A/ 1260/T
KF-2	0.58	3.0	30	Lig 1.0	Ring/Cone	Cyl./Cube	T
KF-3	0.56	3.0	30	FC 1.0	Ring/Cone	Cyl./Cube	T

1) In % by mass of cement
2) S: setting time test
A: autoclave ASR test
1260: ASTM C1260 ASR test
T: tensile strength test

Table 12 Test series NK / NM (Natural dredged material, Kaolin and Metakaolin as fillers)

Name	Composition					Test	
	w/c	a/c	Dredged Material$^{1)}$	Clay$^{2)}$	SP-Mix$^{1)}$	Flow	Compr.
NK-1	0.55	3.0	-	-	-	Ring	Cyl./Cube
NK-2	0.63	3.0	-	K 30	1.5	Ring	Cyl./Cube
NK-3	0.58	3.0	7.5	K 22.5	1.5	Ring	Cyl./Cube
NK-4	0.62	3.0	15	K 15	1.5	Ring	Cyl./Cube
NK-5	0.65	3.0	22.5	K 7.5	1.5	Ring	Cyl./Cube
NM-1	0.66	3.0	30	-	1.5	Ring	Cyl./Cube
NM-2	0.62	3.0	22.5	M 7.5	1.5	Ring	Cyl./Cube
NM-3	0.58	3.0	15	M 15	1.5	Ring	Cyl./Cube
NM-4	0.52	3.0	7.5	M 22.5	1.5	Ring	Cyl./Cube
NM-5	0.45	3.0	-	M 30	1.5	Ring	Cyl./Cube

1) In % by mass of cement

2) Clay mineral content as filler in % by mass of cement: K kaolin, M metakaolin

4 TEST RESULTS

As outlined in the overview of Section 3.4, the various test series were arranged with respect to the materials used, i.e. to determine the effect of a particular constituent in comparison to a given reference composition ("material oriented"). While the first Test Series RN with dredged material as aggregate was limited to one additional component and thus well defined, the other test series were more involved, incorporated various components in "inter-material" comparisons, were based on previous findings, and required additional tests. Hence it was necessary to re-group the test results corresponding to the test performed and also the chronological test sequence ("test oriented"). This chapter will utilize both ways to present or to group the test results.

The results of preliminary flow tests are not presented here because the data do not contain much valuable information in spite of the large number of tests that were involved. For each individual test series, w/c ratio and superplasticizer dosage had to be adjusted to obtain comparable flow. First, the w/c ratio was varied until the targeted flow was achieved. Secondly, the superplasticizer dosage was changed and the first step repeated. For example, to determine the influence of lignosulfonate, the dosage of SP-Lig was varied in increments of 0.5% from 0% up to 2% by mass of cement. For each of those five values, the w/c ratio was adjusted between two and five times. For three variations per value, the optimization of the three mixes containing SP-Lig required 45 prior flow tests.

4.1 NATURAL DREDGED MATERIAL AS AGGREGATE REPLACEMENT

Because of its sandy nature it was first attempted to use dredged material as aggregate replacement in concrete applications (see Section 2.8). This approach appeared to be promising, because both the liquid and solid phases of the dredged material could be utilized without prior separation. Test Series RN used natural dredged material, i.e. without any treatment, as replacement of sand aggregate using the grading curves of Table 7. The test results are summarized in Table 13 and Figures 15-20.

The samples were grouped into four sub-series. In Sub-Series RN-A, the w/c ratio was held constant at 0.70, while it was varied in Sub-Series RN-B to obtain comparable flow (45-50 mm). In Sub-Series RN-C, the same w/c ratios were used as in Sub-Series RN-B but without dredged material. In Sub-Series RN-D, superplasticizer SP-Mix was administered to the mixes to reduce the w/c ratio while keeping the flow approximately constant. The superplasticizer dosage was increased in proportion to the amount of dredged material, which affected the workability the most. In prior flow tests, the optimum amount of SP-Mix with respect to dredged material was found to be 5% by mass. The goal of Test Series RN-A, RN-B, and RN-D was to correlate dredged material content with mechanical properties. The purpose of Sub-Series RN-C was to determine the influence of salts and contaminants contained in the dredged material on the concrete strength if any such exists.

Table 13 Test results of series RN (Replacement of aggregate with Natural dredged material)

Series	w/c	Dredged Material	Flow (Ring)	Density	Compressive strength 1)			
Age				**28d**	**7d**		**28d**	
					Ave	**CV**	**Ave**	**CV**
Units	-	% 2)	*mm*	g/cm^3	*MPa*	*%*	*MPa*	*%*
RN-A1	0.70	-	72	2.10	21.1	4.0	33.0	3.8
RN-A2	0.70	5	63	1.98	24.2	3.1	32.0	3.2
RN-A3	0.70	10	49	1.99	21.0	-	29.4	4.6
RN-A4	0.70	15	39	1.97	21.7	-	34.3	-
RN-A5	0.70	20	32	1.94	19.7	-	30.6	3.1
RN-B1	0.45	-	48	2.21	53.6	-	60.1	-
RN-B2	0.52	5	47	2.14	38.8	4.6	46.8	4.2
RN-B3	0.64	10	46	2.02	24.1	-	30.8 *	-
RN-B4	0.75	15	46	1.94	21.8	13.0	35.0	7.9
RN-B5	0.88	20	46	1.82	17.9	10.8	29.8	1.5
RN-C2	0.52	-	59	2.21	48.0	4.8	51.6	-
RN-C3	0.64	-	70	2.15	30.8	5.1	41.3	4.1
RN-C4	0.75	-	74	2.12	21.2	-	30.2	-
RN-C5	0.88	-	75	1.99	15.2	4.7	19.6	2.8
RN-D2	0.45	5	48	2.22	49.2 *	-	43.7 *	2.5
RN-D3	0.50	10	47	2.14	33.2	4.3	37.1	0.7
RN-D4	0.57	15	46	2.06	27.4	-	30.1	5.0
RN-D5	0.63	20	46	2.03	25.9	-	36.9 *	-
				150d	**105d**		**150d**	
RN-D5	0.63	20	46	1.94	43.4	-	48.0	-

1) Ave: Average strength of 3 specimens
CV: Coefficient of variation (if no value is given, less than 3 specimens tested)

2) By mass of aggregate

* Test data of low confidence

The use of one-inch cylinders throughout Test Series RN was a compromise between test accuracy and amount of dredged material (see Section 3.1.2). Test data defying expected trends are marked in Table 13 with asterisks.

The results of Test Series RN permit the following observations:

- At a fixed w/c ratio, an increase in dredged material content from 0 to 20% by mass of aggregate caused the flow to decrease by more than factor two, i.e., the workability dropped drastically, whereas the compressive strength was barely affected (Figure 15). The poor quality of specimens with insufficient flow can be visualized in Figure 21.

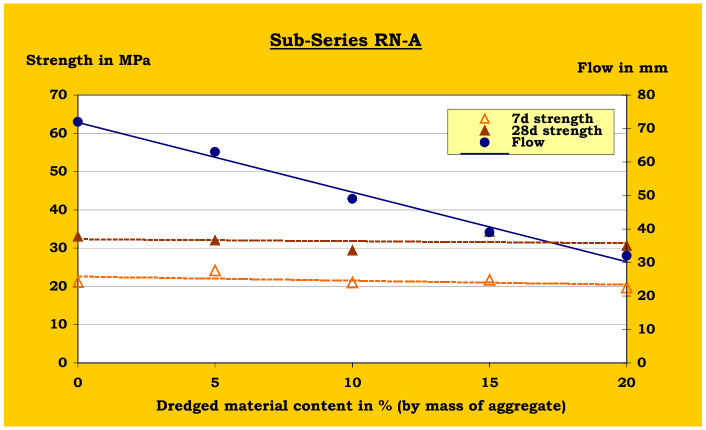


Figure 15 Sub-Series RN-A: Flow and compressive strength versus dredged material content at constant w/c ratio of 0.70

- To maintain a constant flow of about 45-50mm, the w/c-ratio had to be increased in near-linear proportion to the dredged material content. As a result, a considerable drop in compressive strength was experienced (Figure 16). For example, the 28-day strength of the reference mix without dredged material was cut in half when 20% of the aggregate (by mass) was replaced by dredged material (RN-B1 and RN-B5).

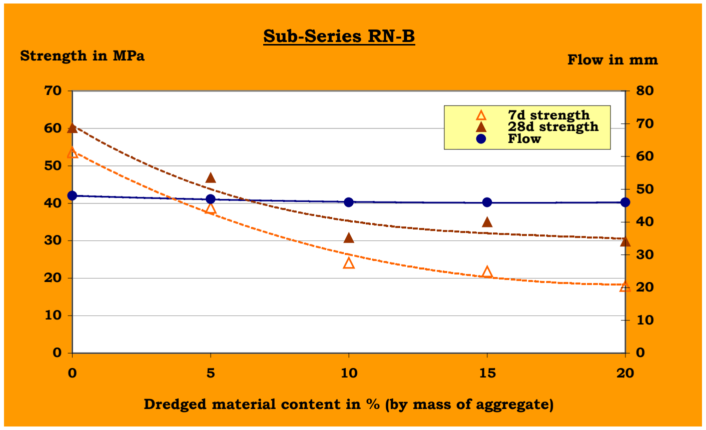


Figure 16 Sub-Series RN-B: Flow and compressive strength versus dredged material content at variable w/c ratios

- Increasing the w/c-ratio without adding dredged material caused an increase in flow and a loss in compressive strength after 28 days that was almost linearly proportional to the w/c ratio (Figure 17).

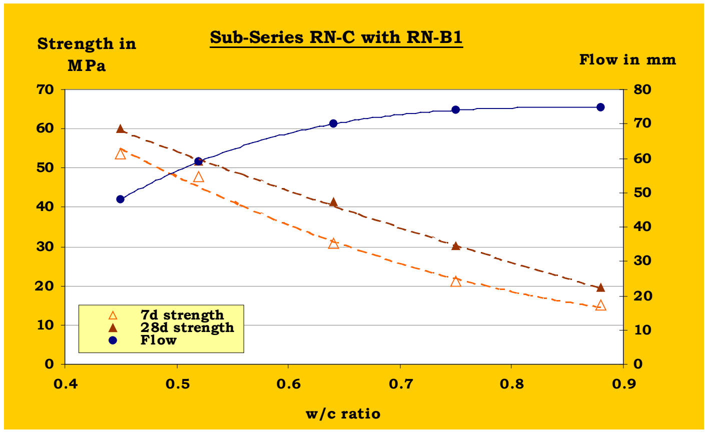


Figure 17 Sub-Series RN-C with RN-B1: Flow and compressive strength versus w/c ratio

- Comparing corresponding samples of Sub-Series RN-B and RN-C, it is noticeable that small percentages of dredged material lowered strength, but this was not the case for samples containing larger amounts of dredged material (Figure 18).

- Even if superplasticizer SP-Mix was administered, the w/c-ratio had to be adjusted with increasing dredged material content to achieve a comparable flow. The relative reduction of required gauging water was higher for increasing superplasticizer content. However, it was not possible to obtain both, comparable flow and similar w/c ratios for mixes with varying dredged material content. As a result, a considerable drop in strength was experienced (Figure 19).

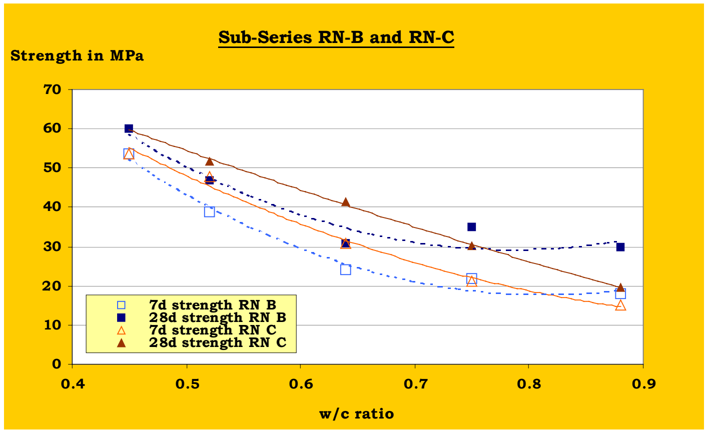


Figure 18 Sub-Series RN-B (with dredged material) and RN-C (without dredged material): Compressive strength versus w/c ratio

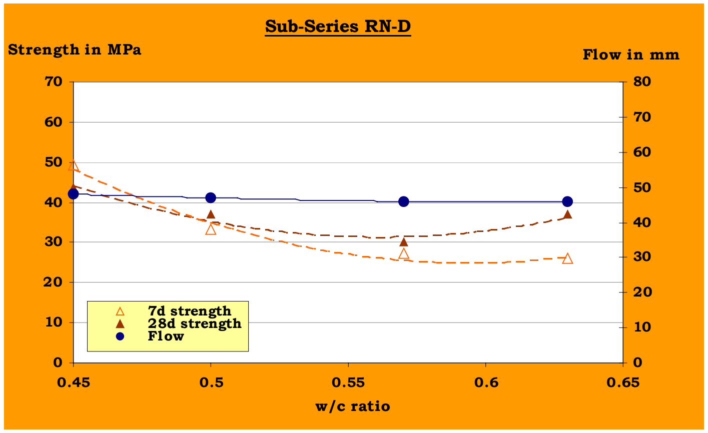


Figure 19 Sub-Series RN-D: Flow and compressive strength versus w/c ratio

- For Sub-Series RN-D, the compressive strengths after 7 and 28 days were surprisingly similar for dredged material contents of less than 15% by mass of aggregate, whereas the strength of sample RN-D5 with 20% dredged material increased considerably from 7 to 28 days (Figure 19).

- By adding a superplasticizer, the same flow of 45-50mm could be achieved with lower w/c-ratio at a given dredged material content; therefore the strength had been expected to be higher. However, the test results confirmed this expectation only for the 7-day strength while corresponding 28-days strengths were very close (Figure 20).

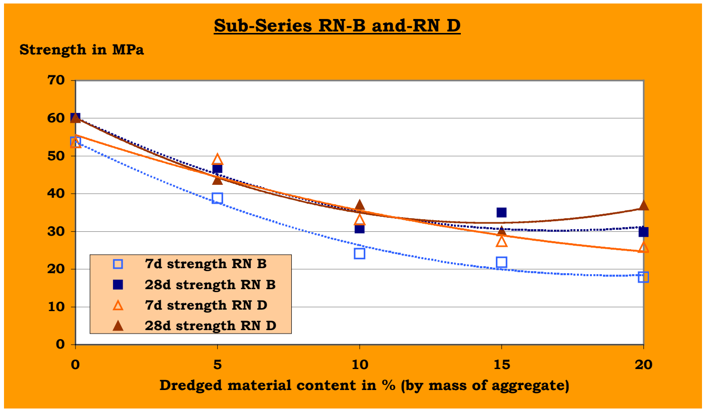


Figure 20 Sub-Series RN-B (without superplasticizer) and RN-D (with SP-Mix): Compressive strength versus dredged material content

- As a preliminary indicator of durability, the strength development over extended periods was expected to reveal possible deleterious effects, especially in combination with the small specimen size. However, the strength development of series RN-D5 exhibited no irregularities. The compressive strength increased steadily with time, i.e. after 28 days it was 40% higher than the 7-day strength and after 150 days it was 30% higher than the 28-day strength (Table 13).

- It was generally experienced that samples with comparably high density exhibited high compressive strength. Both properties are strongly related to the w/c ratio.

- A few strength test results deviated from the expected values because of the small specimen size. As an indication of the reliability of the results, the coefficient of variation (CV) was determined for all tests with at least three specimens per data point. For 7-day strength results, the CV was generally much larger than for 28-day data, and in many cases it was not computed because of the loss of one measurement.

In sum, the most prominent observation was the loss of workability, which can be visualized in Figure 21. Insufficient flow caused a porous, inhomogeneous structure and the samples could not be compacted properly. Poor performance was the consequence. Due to its sand-like properties, dredged material used as aggregate replacement did not greatly affect the strength. As in regular concrete, strength decreased much more rapidly with increasing w/c ratio.

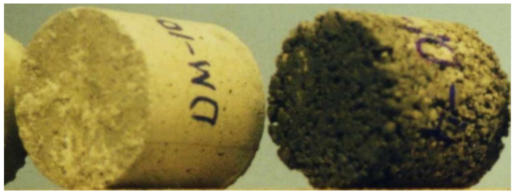


Figure 21 Insufficient workability caused severe defects on samples containing 10% dredged material as aggregate replacement (by mass of aggregate)

The addition of superplasticizer resulted in lower w/c ratios and in considerably higher compressive strength only after 7 days or when 20% dredged material (by mass of aggregate) was used. It is suspected that the interaction between dredged material and superplasticizer increases the reactivity of the mix and simultaneously frees water in the network structure of dredged material. If no superplasticizer is added this water may be released only with time, which would explain the different early strengths but similar long-term behavior of concrete mixes RN-B and RN-D with less than 15% dredged material.

The influence of irregular components such as contaminants in the dredged material could not clearly be identified. On the other hand, dredged material did affect the rate of hydration, i.e. the hardening of the concrete specimens. Samples containing 20% dredged material could be unmolded only two days after casting unlike the other specimens, which were usually unmolded after 24 hours.

In conclusion, the results indicate that replacing up to 20% of aggregate (by mass) with dredged material may be an acceptable option to beneficially use such material under the premise of its otherwise problematic disposal. The decrease in workability places this upper limit on the addition of dredged material. If the w/c ratio is held constant, the strength may be comparable for samples with and without dredged material, whereas fresh mixes without dredged material are too liquid to yield good results and samples containing dredged material exhibit poor workability (sub-series RN-A). In general, the substitution of dredged material for regular sand lowers the concrete performance but may still be feasible for applications with lesser requirements. Although present in larger quantities, the quartz minerals contained in dredged material do not seem to overcome the physico-chemical prevalence of the clay minerals, which are present in smaller quantities. This suggests the use of dredged material as filler.

4.2 DREDGED MATERIAL AS FILLER

While in Test Series RN the dredged material was used in its natural condition, i.e. without any separation, de-watering, or other treatment, in Test Series NF and TF the material was either dried and ground or underwent preliminary treatment when used as filler (see Section 3.3). The replacement of 10% regular aggregate (by mass) with dredged material caused the flow to fall within the target flow range at a w/c ratio of 0.70 and yielded reasonable results for the compressive strength (RN-A3, Table 13). This replacement value corresponds to 22.5% dredged material (by mass of cement), which was adjusted to 20% for samples NF-A1 and TF-A1 using the same w/c ratio. The a/c ratio was increased to 3.0 for all test series incorporating fillers to obtain more representative mix proportions for concrete production.

When natural dredged material was used as filler, i.e. as an additional component, the flow of mix NF-A1 dropped to 55% of that of mix RN-A3 (Table 14). In the case of dredged material after treatment the flow reduction was much less (TF-A1, Table 14). The decrease had been expected because the mix included additional, much finer material with a tendency to agglomerate and a comparably high adsorption capacity. However, the density of samples containing either untreated or treated material increased slightly although the workability was so poor that sufficient compaction of the fresh concrete was difficult.

Table 14 Mortar properties with natural and treated dredged material as filler

Sample	w/c	Dredged Material	Flow (Ring)	Density	Compressive strength [1]			
Age				**28d**	**7d**		**28d**	
					Ave	**CV**	**Ave**	**CV**
Units	-	*% by mass of cement*	*mm*	*g/cm^3*	*MPa*	*%*	*MPa*	*%*
RN-A3 [2]	0.70	22.5	49	1.993	21.0	-	29.4	4.6
NF-A1	0.70	20	27	1.995	23.3	17.7	29.1	-
TF-A1	0.70	20	41	2.002	26.5	3.3	38.7	10.5

[1] Ave: Average strength of 3 specimens
CV: Coefficient of variation (if no value is given, less than 3 specimens tested)

[2] Untreated dredged material as aggregate replacement and a/c ratio of 2.25

The compressive strength was comparable for samples with natural untreated dredged material whether used as replacement or as filler (RN-A3 and NF-A1, Table 14). This indicates that the drying and grinding did not substantially alter the physico-chemical properties of the dredged material. Sample TF-A1 with treated material had a 25% higher 28-day compressive strength than mix RN-N3, which contained natural dredged material. It can be concluded that the homogenization and re-structuring of the material treatment effectively improved the properties of the dredged material.

In Sub-Series NF-A2 through NF-A4, the w/c cement ratio was held constant at 0.42, while the amount of superplasticizer SP-Mix was added in proportion to the amount of filler. In spite of the superplasticizer, the workability decreased drastically with higher dredged material content. Also the 7-day strength decreased considerably, while differences were less significant at the age of 150 days (Table 15). The results indicate that there was no long-term deleterious effect of the dredged material.

The density was comparable for all three samples NF-A2 through NF-A4 because of two conflicting trends. On the one hand, sufficiently fine inert material fills the voids between particles and thus, increases the density. On the other hand, the density of dredged material is lower than those of the other solid components, which reduces the concrete density after addition of such material as filler.

Table 15 Mortar properties with natural untreated dredged material as filler

Sample	w/c	Dredged Material	SP-Mix	Flow (Ring)	Density	Compressive strength $^{1)}$			
Age					150d	7d		150d	
						Ave	CV	Ave	CV
Units	-	% $^{2)}$	% $^{2)}$	*mm*	*g/cm^3*	*MPa*	*%*	*MPa*	*%*
NF-A2	0.42	-	1.0	56	2.258	50.2	10.2	71.8	4.5
NF-A3	0.42	5	2.0	37	2.238	43.8	9.9	66.8	5.0
NF-A4	0.42	10	3.0	28	2.243	30.9	12.8	64.5	4.9

1) Ave: Average strength of 3 specimens
CV: Coefficient of variation (if no value is given, less than 3 specimens tested)

2) By mass of cement

Insufficient flow usually resulted in specimens with severe defects. Hence, for Sub-Series TF-A2 through TF-A6, the targeted flow was redefined at 55-60mm, which represents fairly flowable mixtures. This sub-series was tested to determine the optimum content of treated dredged material with comparable flow. The w/c ratio had to be increased for higher filler contents, which led to lower density and compressive strength (Table 16). If more than 30% treated dredged material (by mass of cement) were added, the density decreased drastically with higher filler content. Figure 22 visualizes the inverse relationship between compressive strength and dredged material content. One possible explanation for the loss of strength is the increase of the w/c ratio to achieve sufficient flowability. A pozzolanic contribution of the dredged material is doubtful. If such potential existed the compressive strength should not decrease as dramatically as it did.

Table 16 Mortar properties with treated dredged material as filler

Series	w/c	Dredged Material	Flow (Ring)	Density	Compressive strength$^{1)}$			
Age				28d	7d		28d	
					Ave	CV	Ave	CV
Units	-	*% by mass of cement*	*mm*	*g/cm^3*	*MPa*	*%*	*MPa*	*%*
NF-A2	0.70	-	56	-	50.2	10.2	60$^{2)}$	-
TF-A2	0.50	20	63	2.168	43.6	9.7	54.9	14.9
TF-A3	0.55	30	59	2.171	31.8	14.8	48.8	-
TF-A4	0.60	35	58	2.103	27.7	16.2	37.6	-
TF-A5	0.70	40	60	2.006	20.9	-	29.4	7.7
TF-A6	0.70	45	55	1.856	11.7	6.9	20.3	9.6

1) Ave: Average strength of 3 specimens
CV: Coefficient of variation (if no value is given, less than 3 specimens tested)

2) Projected value corresponding to compressive strength after 7 and 150 days (Table 13)

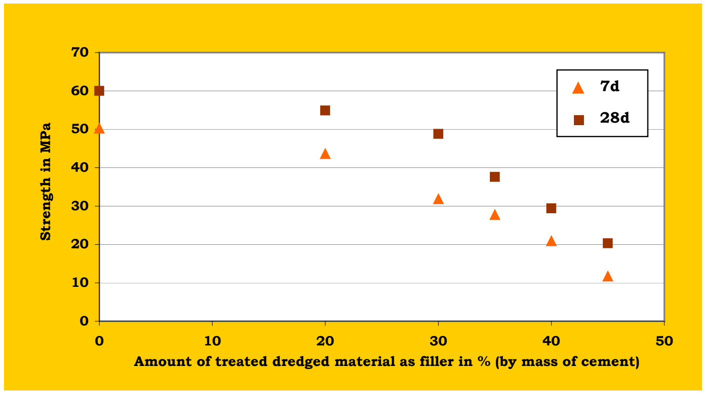


Figure 22 Compressive strength of mortar cylinders with different contents of treated dredged material as filler (NF-A2, TF-A2 through TF-A6)

In order to verify that no contaminants can leach out of concrete containing dredged material, leaching tests were performed. Each sub-series consisted of six two-inch cubes, of which three cubes were subjected to the rain chamber test (see Section 3.1.6). The other cubes were used to determine the standard 28-day compressive strength without exposure to the artificial rain and after the testing were stored at regular room conditions. After completion of the rain chamber test, all six cubes were crushed and sent for chemical analysis.

Mix NF-B1 contained no dredged material, NF-B2 contained 30% natural untreated material (by mass of cement), and TF-B1 contained 30% treated dredged material (Table 17). The dosage of SP-Mix was deliberately increased to 2.5% by mass of cement because of concerns that the superplasticizer might contain leachable contaminants, especially cyanide. Keeping the w/c ratio comparable for the three mixes, which led to inconsistent flow results. Mechanical properties are given in Table 17 and the results of the leaching test in Table 18.

Table 17 Mortar properties of rain chamber test specimens

Sample	**Dredged material**	**w/c**	**Flow (Cone)**	**28d density**	**28d compr. strength**	**148d compr. strength** [1]
	% by mass of cement	-	*%*	*g/cm³*	*MPa*	*MPa*
NF-B1	-	0.41	>150	2.29	64	67
NF-B2	30	0.48	56	2.19	52	54
TF-B1	30	0.42	85	2.23	50	65

[1] After rain chamber test

The reference sample, NF-B1, was extremely flowable, and bleeding and segregation were observed. The addition of natural dredged material led to poor workability, although the w/c ratio was increased (NF-B2). Although the flow was with only 85% relatively small, the mix containing treated dredged material, TF-B1, showed the best workability because the samples could easily be compacted and looked very homogeneous. The 28-day compressive strength dropped when either treated or untreated dredged material was added to the mix. However, the 148-day compressive strength of samples with treated dredged material was comparable to that of the reference mortar, while the strength of cubes containing untreated dredged material was 20% lower (Table 17).

Table 18 Leaching test results after rain chamber test (in ppm)

Series / **Contaminant**	**Raw untreated dredged material**	**NF-B1**		**NF-B2**		**TF-B1**	
		M [1]	**PS** [1]	**M** [1]	**PS** [1]	**M** [1]	**PS** [1]
Zinc (Zn)	7.50	0.02	0.01	ND	0.01	ND	0.02
Nickel (Ni)	0.20	ND	ND	ND	ND	ND	ND
Copper (Cu)	0.05	ND	0.05	ND	ND	ND	ND
Total Cyanide (CN)	1.12	0.10		0.12		0.07	
Leachable Cyanide	0.82		ND		ND		ND
Pesticides / PCBs	ND (below detection limit)						

[1] M Analysis of mortar specimen
PS Analysis of pore solution extracted from those same samples in rain chamber test

According to the results of Table 18, appreciable concentrations of contaminants were present in the raw untreated dredged material. In contrast, the same contaminants were mostly non-detectable in mortar samples. The three compositions did not differ much in the levels of detectable leachates such as heavy metals and cyanides. There was no difference in leaching test results, whether cubes were subjected to the rain chamber test or not. The results show that the cement matrix effectively prevents the leaching of contaminants.

Contaminant concentrations in mortar samples were far below the levels found in the natural untreated dredged material. It was shown elsewhere that heavy metals are detectable even in "clean" aggregate [49]. This may also be the case for cyanides because comparable levels of total cyanides were found in all mortars, with or without dredged material. However, the leachable cyanide concentrations in the pore solution were below the detection limit. Hence, it can be concluded that no cyanide leached out of mortar samples. Interestingly, the concentration of copper was the highest in the case of reference sample NF-B1 where it was least expected. The concern that contaminants inside dredged material might leach out during the service life of concrete members seems to be unfounded.

During the preparation of the samples for the leaching test, it became clear that there is a beneficial effect of dredged material as filler because it prevents bleeding. The top surface of the reference sample was covered with a continuous, dried white-yellow cement-salt-superplasticizer layer as a result of bleeding. The sides of the same specimens exhibited signs of segregation. The samples with untreated or treated dredged material did not show these phenomena. None of the specimens of the three mixes exhibited any irregularities, such as surface damage or severe weathering, after exposure to artificial rain for 16 weeks, which can be interpreted as satisfying a first durability criterion.

In conclusion, for mortars containing dredged material a target flow greater than 50mm in the ring test is needed to assure an adequate workability. However, the preliminary flow test results may not reflect the actual workability completely, depending on the amount of material of a given batch. The addition of superplasticizer SP-Mix in proportion to the untreated dredged material content compensates only partially for the decrease in workability. The use of 10% dredged material (by mass of cement) as filler reduced the flow of the fresh concrete to half of that of samples without any filler. The 7-day compressive strength also dropped to about 60%. However, after 150 days the difference in compressive strength was only about 20%.

Treated dredged material seems to have superior properties compared with natural material. The compressive strength after 7 and 28 days decreases with the amount of treated dredged material but not as drastically as in the case of natural untreated material. If up to 30% treated material (by mass of cement) is used the matrix looks very homogenous. If more than 30% are added the density decreases and the accompanying strength reduction is unacceptable. In the subsequent test series the filler content was set to 30% by mass of cement.

The leaching test showed that the cement matrix is capable of encapsulating contaminants. It was impossible to extract significant levels of contaminants from any of the specimens.

Both, treated and untreated dredged material prevented bleeding of mixes with high amounts of superplasticizer SP-Mix. None of the samples suffered severe damage while being exposed to artificial rain for over 100 days.

4.3 DREDGED MATERIAL AND KAOLIN AS FILLERS

Because of the similarity of natural clay minerals and those found in dredged material, the third part of the test program focussed on the comparison of concrete samples with kaolin and dredged material (compare Chapters 2.7 and 2.8). The comparably high adsorption capacity of clay minerals was considered helpful in evaluating the influence of such fillers on the workability of fresh concrete.

The clay minerals in dredged material are intermingled with various other components, interact with various contaminants, are exposed to changing conditions, and the crystal surfaces exhibit defects (see Chapter 2.8). Therefore, their behavior and reactivity may differ greatly from that of naturally occurring clays, such as kaolinite, which can be found in relatively pure form. Kaolin can be thermally treated and become metakaolin, which is highly reactive and pozzolanic. The beneficial effects of metakaolin have been subject to extensive research and its pozzolanic properties are well known. Based on the assumption that kaolin acts as an inert filler (lower bound) and metakaolin as a highly reactive filler (upper bound), an envelope was created to evaluate the pozzolanic contribution of dredged material if such exists.

In a first set of tests the setting time was determined with a Vicat needle in accordance with ASTM C191 [4]. The ASR reactivity was evaluated following ASTM C1260 [5] and a procedure for autoclave testing as described in Reference [36]. After the ASR tests, one-inch cubes were cut from the mortar bars, and the 28-day compressive strengths were determined with the newly won specimens.

Three different fillers, untreated and treated dredged material and kaolin (samples NF-C2, TF-C1, and KF-1, respectively) were evaluated and the results compared to those of reference sample without any filler (NF-C1). The flow was held constant at about 120% (Cone Test) while the w/c ratios were varied.

Table 19 summarizes the flows, setting times, ASR expansions, and compressive strengths. It can be seen that treated dredged material barely affected the setting time while the untreated material delayed it by 105 minutes, an increase of almost 60% (NF-C1, NF-C2 and TF-C1). Concrete with kaolin set after 255 minutes, 75 minutes later than the reference sample without filler (NF-C1 and KF-1). It was determined in prior tests that mortar containing metakaolin already set after 120 minutes, compared to sample NF-C1 a reduction of 33%. Metakaolin had been known to be highly reactive, hence this result was no surprise.

The studies of potential alkali-silica reactivity (ASR) showed that none of the expansions exceeded the 0.10% limit for innocuous behavior of the ASTM C1260 specification [5].

After autoclave testing mixes TF-C1 and KF-1 exhibited small negative length changes, which was found to be a sign of innocuous behavior [36]. For mixes NF-C1 and NF-C2 additional ASR testing would be necessary to compare their relative expansions to that of a reference mix with known reactivity. Figure 23 shows that samples containing treated dredged material or kaolin also exhibited shrinkage during the first two days of their exposure to the alkaline solution in the ASTM C1260 test. This early shrinkage may indicate a high reactivity of the filler [36].

Table 19 Test results of setting time determination and ASR testing

Sample	*Units*	NF-C1	NF-C2	TF-C1	KF-1
Filler (30 M% of cement)		-	Natural dredged mat.	Treated dredged mat.	Kaolin
w/c		0.52	0.75	0.61	0.88
Flow (Cone)	*%*	124	118	102	123
Flow (Ring)	*mm*	44	45	46	49
Ratio Flow (Cone)/Flow (Ring)		2.82	2.62	2.22	2.51
Setting time	*min*	180	285	175	255
Relative length change after ASTM C1260	*%*	0.06%	0.04%	0.05%	0.02%
Relative length change after autoclave test	*%*	0.02%	0.03%	-0.01%	-0.02%
28d compressive strength (after ASTM C1260)	*MPa*	45	27	29	20
28d compressive strength (after autoclave test)	*MPa*	27	15	20	19

In both cases, after the autoclave and the ASTM C1260, test sample NF-C1 (without filler) had the highest 28-day compressive strength. Samples NF-C2 and TF-C1 (with untreated and treated dredged material, respectively) exhibited about 30 and 40% lower strength. The strength of sample KF-1 with kaolin after autoclave treatment was almost as high as after the ASTM C1260 test, whereas in the other cases the samples after autoclaving were about 30-40% weaker than the specimens that underwent the ASTM C1260 test (Table 19).

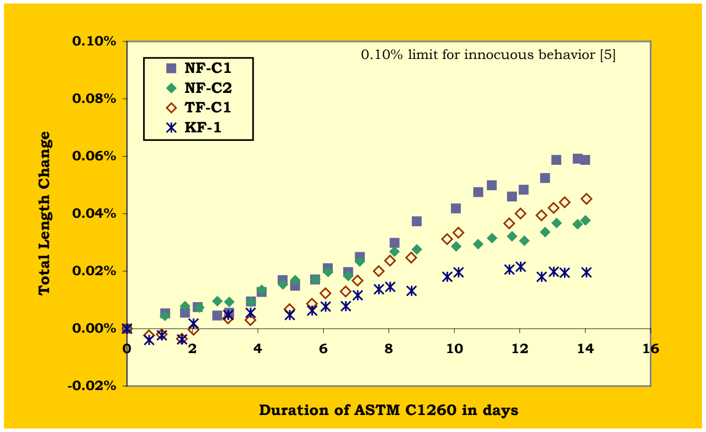


Figure 23 Relative length changes with time of mortar bars during the ASTM C1260 test

Tables 20 and 21 summarize the results of samples containing different amounts of metakaolin, kaolin, and dredged material, while the combined overall amount of filler was held constant at 30% by mass of cement (Test Series NK and NM). The incremental substitution of dredged material for either kaolin or metakaolin should reveal similarities between these materials if such exist and increase our understanding of pozzolanic properties of dredged material.

In both test series, NK and NM, it was the goal to achieve comparable flow, which required adjusting the amount of gauging water. The addition of superplasticizer SP-Mix allowed keeping the w/c ratios comparably low. For example, in the case of NM-4 it had been determined earlier that a w/c ratio of 0.75 was required to achieve the targeted flow when no superplasticizer was used. After addition of 1.5% SP-Mix (by mass of cement) the w/c ratio could be reduced to 0.45. This is a decrease of about 40% gauging water. A similar comparison was performed for the reference sample without filler (NK-1), where the addition of SP-Mix lowered the w/c ratio from 0.55 to 0.42, a 25% reduction. However, in this case the sample with superplasticizer exhibited bleeding and segregation, which resulted in poor homogeneity of the specimens. Therefore, mix NK-1 was prepared without any superplasticizer.

The addition of dredged material and kaolin caused a decrease in density with growing dredged material content. The mean value of the w/c ratios of concrete containing kaolin and/or dredged material was 0.63 and variations for this value stayed below 8% (Tables 20 and 21). The compressive strength of cylinders seemed to have a slight pessimum when 15% kaolin and15% dredged material (by mass of cement) were added, whereas the cube strength was lowest for a dredged material content of 22.5% and a kaolin content of 7.5% (Figure 24).

Table 20 Mortar properties with dredged material and kaolin as fillers

	Units	**NK-1**	**NK-2**	**NK-3**	**NK-4**	**NK-5**
Dredged material	*%* 1)	-	-	7.5	15	22.5
Kaolin	*%* 1)	-	30	22.5	15	7.5
SP-Mix	*%* 1)	-	1.5	1.5	1.5	1.5
w/c	-	0.55	0.63	0.58	0.62	0.65
Flow (Cone)	%	125 2)	102	101	108	112
7d compr. strength (Cylinder)	*MPa*	26	25	24	21	23
CV of 7d strength (Cylinder)	%	-	5.4	10.6	-	1.9
7d density of cylinders	*g/cm^3*	2.262	2.205	2.203	2.172	2.187
28d compr. strength (Cylinder)	*MPa*	42	40	35	29	36
CV of 28d strength (Cylinder)	%	-	-	1.6	4.4	1.8
28d density of cylinders	*g/cm^3*	2.210	2.133	2.144	2.078	2.078
Ratio of 7d strength (Cylinder) / 28d strength (Cylinder)	-	1.63	1.65	1.47	1.40	1.54
28d compr. strength (Cube)	*MPa*	57	46	42	39	32
CV of 28d strength (Cube)	%	5.7	0.9	7.6	2.4	4.9
28d density of cubes	*g/cm^3*	2.204	2.158	2.153	2.143	2.140
Ratio of 28d strength (Cube) / 28d strength (Cylinder)	-	1.37	1.13	1.18	1.34	0.93

1) By mass of cement

2) Projected flow corresponding to a flow of 53mm determined with the Ring Test

While samples with untreated dredged material and/or kaolin (NK-2 through NK-5, NM-1) exhibited lower compressive strength than those without any filler (NK-1), the strength of samples with metakaolin and/or dredged material exceeded those of the other samples. One reason is the reduction of the w/c ratio with increasing metakaolin content from 0.66 to 0.45 (NM-1 with only dredged material and NM-5 with only metakaolin, respectively).

Table 21 Mortar properties with dredged material and metakaolin as fillers

	Units	**NM-1**	**NM-2**	**NM-3**	**NM-4**	**NM-5**
Dredged material	% 1)	30	22.5	15	7.5	-
Metakaolin	% 1)	-	7.5	15	22.5	30
SP-Mix	% 1)	1.5	1.5	1.5	1.5	1.5
w/c	-	0.66	0.62	0.58	0.52	0.45
Flow (Cone)	%	106	109	114	108	120
7d compr. strength (Cylinder)	*MPa*	24	32	42	45	61
CV of 7d strength (Cylinder)	%	5.1	4.9	11.0	-	6.4
7d density of cylinders	*g/cm^3*	2.169	2.213	2.255	2.259	2.277
28d compr. strength (Cylinder)	*MPa*	34	49	54	62	65
CV of 28d strength (Cylinder)	%	10.7	5.7	6.6	4.1	-
28d density of cylinders	*g/cm^3*	2.057	2.156	2.193	2.242	2.264
Ratio of 7d strength (Cylinder) / 28d strength (Cylinder)	-	1.42	1.54	1.30	1.38	1.05
28d compr. strength (Cube)	*MPa*	37	51	65	78	101
CV of 28d strength (Cube)	%	1.9	6.3	2.8	0.9	3.1
28d density of cubes	*g/cm^3*	2.099	2.148	2.202	2.214	2.267
Ratio of 28d strength (Cube) / 28d strength (Cylinder)	-	1.09	1.02	1.19	1.25	1.57

1) By mass of cement

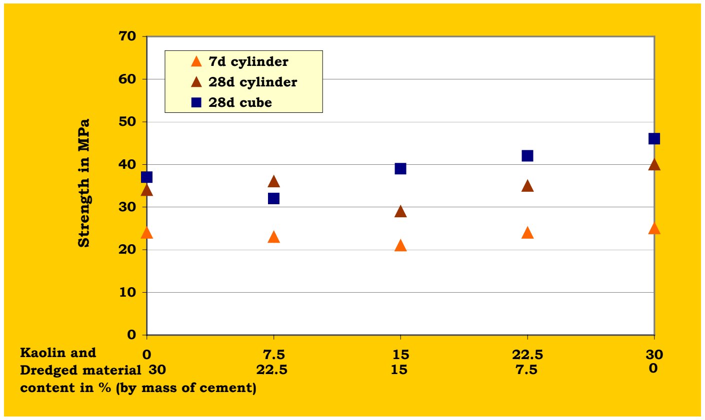


Figure 24 Compressive strength of mortars with different contents of natural dredged material and kaolin as fillers (Samples NM-1, NK-2 through NK-5)

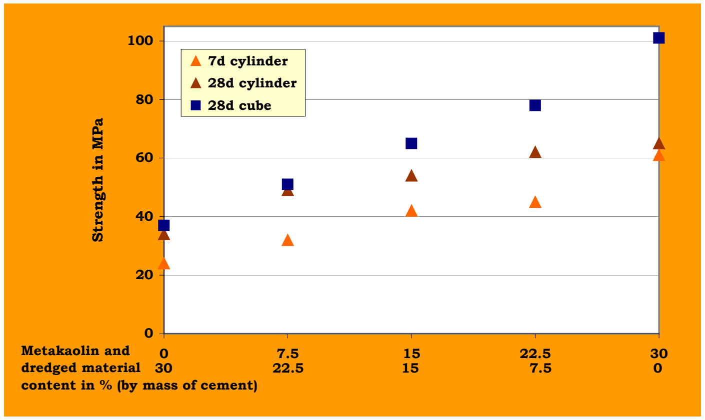


Figure 25 Compressive strength of mortars with different contents of natural dredged material and metakaolin as fillers (Sub-Series NM)

The test data exhibit an almost linear relationship between strength and metakaolin content (Figure 25). The density also increases with rising metakaolin amount and equals that of the reference samples (NK-1) after 28 days when about 15% dredged material and 15% metakaolin (by mass of cement) were added (NM-3). At the same time the w/c ratios were about the same for these two series. It has been known that there is a strong inverse correlation of strength and density with the w/c ratio but the improvement of homogeneity and isotropy by adding metakaolin may be equally important.

With the exception of sample NM-5, the 28-day compressive strengths were 30-65% higher than the corresponding 7-day strengths. The average increase was 43%, which represents a fairly regular value [73]. The ratio of cube strength to cylinder strength had been expected to be relatively constant but values range widely, from 0.93 to 1.57. Possible reasons are the scatter of results and difference in compactablity during the casting of the specimens.

4.4 INFLUENCE OF SUPERPLASTICIZERS

To investigate the (beneficial) influence of various superplasticizers it was decided to test samples containing four different superplasticizers: 1. SP-Lig, based on lignosulfonate, 2. SP-Mel, based on melamine-formaldehyde, 3. SP-FC, based on formaldehyde-condensate, and 4. SP-Mix, a blend of various superplasticizers. In preliminary tests, the optimum dosage for SP-Lig and SP-FC had been found to be 1.0-1.5% by mass of cement.

It was impossible to sufficiently liquefy the mixes with SP-Mel, which therefore was not considered in subsequent tests. In most tests reported herein so far, 1.5% SP-Mix was used, which equaled about 1.0% dry mass. To be consistent, the same dosage was adopted for SP-Lig and SP-FC in Sub-Series NF-D and KF.

The major design criterion was the workability, which necessitated slightly modified prior flow tests. Aside from the requirement of a high flow of >50mm (Ring Test), mixes were not allowed to exhibit excessive segregation or bleeding, as the reference samples without filler did. The amount of water was also optimized to address the adsorption of gauging water by clayey fillers. While the immediate workability decreased, the adsorbed water might be partially released during the hardening process. As a consequence, the range of targeted flow was broadened to 50-60mm in order to allow adjustments of the w/c ratios.

The addition of the lignosulfonate-based superplasticizer caused two phenomena. It introduced voids, which led to a foamy appearance, and it retarded the cement hydration. Excessive formation of pores caused poor workability at dosages higher than 1.5% by mass of cement, which was much more pronounced in the case of the reference mix without any filler than for mixes containing dredged material or kaolin. Hence, in case NF-D2 the superplasticizer dosage was limited to 0.5%. The retardation effect had been known previously [62, 73] and affected mainly the mixes with dredged material or kaolin. For this reason, cylinders were unmolded after 72 instead of the customary 24 hours, while the cubes had to be removed from their forms prematurely after 24 hours for logistical reasons. The test results are presented in Table 22 and Figures 26 and 27.

Table 22 Influence of superplasticizers SP-Lig and SP-FC on mortar properties

	Units	NF-D1	NF-D2	NF-D3	NF-D4	NF-D5	KF-1	KF-2	KF-3
Filler (30% by mass of cement)	-	-	-	DM	DM	DM	Kaolin	Kaolin	Kaolin
SP (by mass of cement)	%	-	Lig 0.5	-	Lig 1.0	FC 1.0	-	Lig 1.0	FC 1.0
w/c	-	0.54	0.42	0.81	0.69	0.56	0.88	0.58	0.54
Flow (Cone)	%	135	125	126	136	128	99	~140	~140
Flow (Ring)	mm	57	51	56	56	56	48	58	59
Ratio of Flow (Cone) / Flow (Ring)	-	2.37	2.48	2.28	2.44	2.31	2.05	2.41	2.37
7d compr. strength (Cyl.)	MPa	23.9	27.2	19.4	19.4	21.6	14.8	22.5	18.7
CV of 7d strength (cylinder)	%	2.4	-	-	-	3.5	-	-	6.3
7d density of cylinders	g/cm^3	2.229	2.150	2.133	2.153	2.095	2.134	2.195	2.076
7d compr. strength (Cube)	MPa	27.1	28.5	18.6	15.6	23.2	15.7	27.5	22.6
CV of 7d strength (Cube)	%	2.9	-	1.0	4.7	2.6	1.7	8.5	1.3
7d density of cubes	g/cm^3	2.168	2.020	2.137	2.052	2.025	2.116	2.202	2.073
28d compr. strength (Cyl.)	MPa	35.5	37.3	28.8	29.9	32.1	23.6	34.5	34.4
CV of 28d strength (Cyl.)	%	12.0	4.2	4.3	2.5	-	8.2	-	-
28d density of cylinders	g/cm^3	2.151	2.094	2.003	2.046	2.045	1.939	2.138	2.055
28d comp. strength (Cube)	MPa	41.6	39.1	31.1	25.1	35.3	27.0	42.9	35.0
CV of 28d strength (Cube)	%	2.9	6.4	0.7	6.0	2.9	1.7	2.3	3.5
28d density of cubes	g/cm^3	2.111	2.014	2.015	1.974	1.996	1.977	2.137	2.016
28d tensile strength	MPa	3.05	3.31	3.07	3.80	2.80	2.16	-	2.95
CV of 22	%	8.9	10.2	-	-	-	13.0	-	-

The following observations could be made:

- Because both flow and w/c ratio were kept approximately constant, it was possible to gauge the effect of just one variable, namely the addition of either 30% dredged material or kaolin as filler together with 1% superplasticizer (by mass of cement).

- The addition of superplasticizer SP-Lig lowered the density of reference samples (without filler) by causing a considerable degree of porosity (compare NF-D1 and NF-D2). This fact explains why in spite of the much lower w/c ratio strength results were not significantly higher, as one could expect.

- When the cubes containing untreated dredged material and SP-Lig (NF-D4) had to be unmolded after 24 hours, it was immediately obvious that they had not yet hardened sufficiently, because they underwent visible deformations during and after unmolding. These deformations possibly caused structural damage, which lowered both density and compressive strength when compared to the cubes that contained dredged material but no superplasticizer (NF-D3). In contrast, the cylinders were unmolded after 72 hours and thus had time to sufficiently harden. Therefore specimens with and without SP-Lig had comparable strength and density.

- In case of kaolin as filler, the addition of superplasticizer SP-Lig did not produce the porosity as it did in case of the reference mix without filler (compare KF-1 and KF-2). It is suspected that the superplasticizer was adsorbed on the surfaces of the clay minerals and thus spread homogeneously throughout the fresh concrete, thereby preventing the foaming effect. The result was a substantial increase in strength (and density), which is expected when lower w/c ratios are made possible (Figure 26).

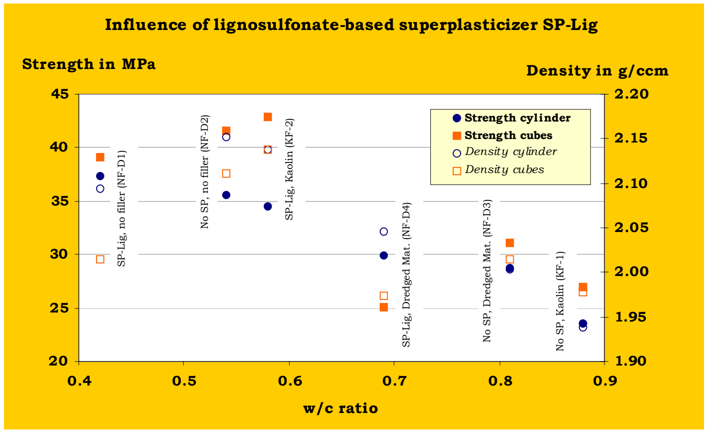


Figure 26 Evaluation of superplasticizer SP-Lig: Compressive strength and density versus w/c ratio (Samples NF-D1 through NF-D4, KF-1 and KF-2)

- The formaldehyde-condensate-based superplasticizer SP-FC did not cause the delayed setting and porosity as the lignosulfonate-based SP-Lig did. However, the addition of filler and superplasticizer SP-FC lowered the density of samples containing either dredged material or kaolin and led to a 20% decrease in 28-day compressive strength (Cube Test) when compared with the reference sample NF-D1 (Figure 28).

- SP-FC allowed to drastically lower the w/c ratios of samples containing dredged material and kaolin. Thus, the compressive strengths of the modified concrete increased with the addition of this superplasticizer (compare NF-D3 and NF-D5, KF-1 and KF-3).

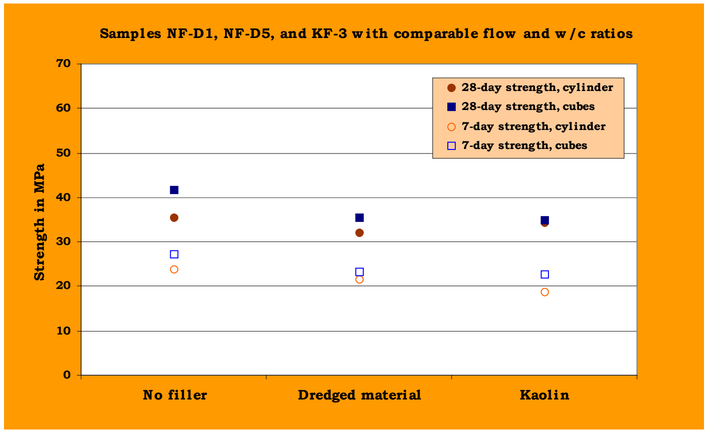


Figure 27 Evaluation of superplasticizer SP-FC: 7 and 28-day compressive strength in dependence of filler type (Samples NF-D1, NF-D5, and KF-3)

- The ratio of compressive strength to tensile strength was the lowest for samples containing dredged material and the highest for the reference cases without filler, which indicates that the degree of anisotropy decreases with the addition of clayey fillers, such as kaolin and dredged material.

In conclusion, the addition of formaldehyde-based SP-FC led to the highest reduction of the w/c ratio for mixes containing dredged material or kaolin as filler. However at the same time, the compressive strength hardly increased although a drastic change could have been expected. The lignosulfonate-based SP-Lig performed well only when kaolin was added as a filler, while it should not be used in combination with dredged material.

The addition of dredged material or kaolin as filler caused a decrease in compressive strength, but other properties such as homogeneity and coherence could be improved. The test results indicate that natural untreated dredged material possesses similar properties as kaolin while treated dredged material can be partially activated. However, a pozzolanic contribution such as is experienced with metakaolin cannot be expected from dredged material.

5 ANALYSIS AND DISCUSSION OF RESULTS

5.1 WORKABILITY

The term workability generally describes the ease of handling, coherence, and homogeneity of fresh concrete during mixing, placing, and compaction. Common tests measure only the slump or flow (e.g., ASTM C143 and ASTM C230 [4]). These tests do not suffice to completely address the static and dynamic behavior or time-dependent changes related to workability. The flow tests introduced in Section 3.1.1 provide a first indication of workability but do not capture the differences between flow and workability.

During the research presented herein, it has been suggested to use dredged material either as aggregate replacement or as filler in concrete applications. In case of aggregate replacement, high dredged material contents either drastically decrease the workability or require additional gauging water, which reduces strength at comparable flow. Figure 28 illustrates the interdependence of compressive strength and flow with the w/c ratio. Although of generic nature, the graph is based on the data of Test Series RN. If 10% fine sand (by mass of aggregate) is replaced with dredged material, the flow decreases drastically, which is visualized as a downward shift of the flow curve. The addition of a superplasticizer partially compensates for such loss in workability as it causes an upwards shift of the flow curve. These results are generically exemplified by the three flow curves of Figure 28. However, the strength is also affected by factors other than the w/c ratio so that strength values corresponding to a particular w/c ratio do not necessarily coincide with the strength curve of Figure 28.

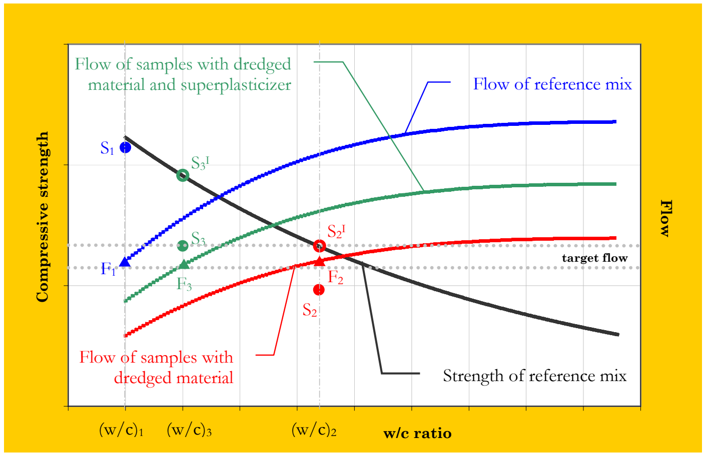


Figure 28 *Influence of w/c ratio on compressive strength and flow*

The primary design criterion in this study was to achieve comparable flow values, as signified by the "target flow range" of Figure 28. Starting out with a reference mix having the water/cement ratio $(w/c)_1$, strength S_1, and flow F_1, which falls within the target range, the addition of dredged material lowers the flow. To achieve sufficient flow (F_2) the larger ratio $(w/c)_2$ is needed. Although the corresponding strength should theoretically be S_2^I, as suggested by the strength curve, the actually recorded strength S_2 was lower than that. Likewise, by administering a superplasticizer, a reduced ratio $(w/c)_3$ brings the flow within the target range, F_3, but again, the strength S_3 was found to be less than the value S_3^I one would expect, if strength were only a function of the w/c ratio. It can be concluded that the replacement of fine aggregate with dredged material has a detrimental effect on the concrete properties. It was shown that it is far more promising to utilize dredged material as filler. Its performance can then be compared with that of kaolin, a natural clay.

In general, fillers decrease the flow because of their high adsorption capacities and large specific surfaces. They interact strongly with superplasticizers especially if their surfaces are charged. These properties are to some extent related to the particle size. Therefore it has been attempted to predict the volume of gauging water required to achieve a certain flow as a function the particle size d_P. Krell [39] found that a thin water layer covers the particles. Only if this film is sufficiently thick, the particles are able to move relative to each other and the fresh concrete becomes plastic and workable (see Section 2.9.1). Krell suggested the following formulation to determine that thickness:

$$t_W = \frac{V_W - \left(\frac{\varepsilon_F}{100 - \varepsilon_F} \cdot \frac{m_F}{\rho_F} \right)}{S_{SF} \cdot m_F} \cdot 10000 \qquad \{10\}$$

where	t_W	thickness of water film, in µm
	V_W	Volume of water, in cm^3
	ε_F	Volume of voids between fine particles, in V-%
	m_F	Mass of fine particles, in g
	ρ_F	Density of fine particles, in g/cm^3
	S_{SF}	Specific surface area of fine particles, in cm^2/g

Neglecting the unit conversion factor, Eq. {10} can be solved for the volume of water required to create that water film thickness:

$$V_W = t_W \cdot S_{SF} \cdot m_F + \frac{\varepsilon_F}{100 - \varepsilon_F} \cdot \frac{m_F}{\rho_F} \qquad \{11\}$$

Equation {11} suggests that the water content is directly proportional to the specific surface. However, the thickness of the water film has to be adjusted for the particle shape, which also affects the void content. For fine-grained soils, the smallest particle dimension controls the specific surface in an inverse relationship that has to be adjusted with a shape factor according to the particle geometry (1D: plate, 2D: prism or rod, 3D: cube or sphere) [68]. The binder and filler fraction of a given concrete mixture will dominate the required volume of water due to their fineness. Hence, the influence of regular sand aggregate will be neglected herein.

Typically, cement has a specific surface area (Blaine) of about 4 m^2/g, while that of metakaolin varies from 12 m^2/g [88] to 16.8 m^2/g [95]. Assuming t_W (comparable water film thickness) and the second term of Eq. {11} to be constant (neglecting volume of voids) Eq. 11 allows to compare water requirements for different mixes that contain additional 30% mineral filler (by mass of cement). The results are listed in Table 23.

Table 23 Relative volume of water required for different fillers (Eq. {11}*)*

Main component	**Filler**	**S_{SF} of the filler**	**Relative V_W**
	30% (by mass of cement)	*m^2/g* [31, 39, 60, 68, 74]	$V_{W,Mix}/V_{W,Cem}$
Cement	Cement	0.4	1.0
Cement	Kaolinite	15	9.4
Cement	Illite	80	47
Cement	Montmorillonite	600	347

The values of Table 23 are unrealistic because the size distribution and shape of the particles cannot be ignored. The correct determination of the specific surface becomes especially difficult for swelling minerals and particles coated with smaller particles. For the former, aqueous suspensions are preferred, but results can vary drastically when different measurement techniques are used [68]. Furthermore it was suggested that for particles with specific surfaces larger than 1 m^2/g, surface-related forces control the behavior. To establish a correlation between specific surface and water requirement of given concrete mixes is very complicated. A simplified approach is suggested below.

Depending on their shape, particles can be considered one-dimensional (thin plates), two-dimensional (prisms or rods), or three-dimensional (cubes or spheres), which leads to adjusting shape factors f_{sh} of 1, 2, or 3, respectively [68]. Since sand and cement particles can be considered spherical, while clay particles are plate-like, these factors can be applied to concrete constituents. The geometry and particularly the smallest dimension d_P of a particle determines the specific surface, S_{SF} in an inverse proportional relationship [68]:

$$S_{SF} = \frac{2 \cdot f_{sh}}{d_P \cdot \rho_W \cdot G_S} \qquad \{12\}$$

where	f_{sh}	Component shape factor: 1 for plates, 3 for spheres
	d_P	Particle size
	ρ_W	Mass density of water (1 g/cm^3)
	G_{SP}	Specific gravity of the particle mineral

Combining this relationship with Eq. {11}, the following expression for the required water volume V_W is obtained, if voids are ignored:

$$V_W \propto f_{sh} \frac{t_W \cdot m_F}{d_P \cdot G_{SP}} \qquad \{13\}$$

Equation {13} identifies only a relative trend rather than an absolute value for the required amount of water. Values for some materials are listed in Table 24, but assuming constant thickness of water layer, similar geometry, and negligible shape functions, as well as ignoring the voids between particles introduces errors that need to be determined.

A new index W_{ind} is introduced for the water requirement of a modified mix, relative to the volume of gauging water for a reference mix without any additional filler. Assuming that the water film thickness around each particle is comparable and using Eq. {13}, W_{ind} can be defined for any given mix as:

$$W_{ind} = \frac{V_{W,add}}{V_{W,ref}} = \frac{\sum_{N=1}^{i+j} \left(f_{sh,N} \frac{m_{F,N}}{d_{P,N} \cdot G_{SP,N}} \right)}{\sum_{N=1}^{i} \left(f_{sh,N} \frac{m_{F,N}}{d_{P,N} \cdot G_{SP,N}} \right)} \qquad \{14\}$$

where	$V_{W,add}$	Water volume for a mix with at least one additional component
	$V_{W,ref}$	Water volume for the reference mix
	i	Number of solid components of the reference mix
	j	Number of additional solid components
	$f_{sh,N}$	Component shape factor: 1 for plates, 3 for spheres
	$m_{F,N}$	Mass of components
	$d_{P,N}$	Particle size
	$G_{SP,N}$	Specific gravity of the particle mineral

Table 24 Relative volume of water required for different mix components (Eq. {13})

Component	**Particle Size** (smallest dimension)	**Relative V_W**
	μm [7, 25, 31, 40, 81]	$V_{W,Comp}/V_{W,Cem}$
Cement	30	1.00
Fine sand aggregate	125	0.28
Coarse sand aggregate	1250	0.03
Dredged material (spheres)	12	2.93
Dredged material (plates)	6	1.95
Kaolin	8	1.46
Illite	3	3.90
Montmorillonite	0.3	39

Similarly, a ratio of the respective water-cement ratios is defined as:

$$W_{ind} = \frac{\left({}^{w}/_{c} \right)_{add}}{\left({}^{w}/_{c} \right)_{ref}} \qquad \{15\}$$

where	$\left({}^{w}/_{c} \right)_{add}$	w/c ratio of a mix with at least one additional component
	$\left({}^{w}/_{c} \right)_{ref}$	(experimental) w/c ratio of the reference mix

To predict the w/c ratio of a mix containing an additional component (needed to obtain comparable flow), one may combine Eq. {14} and Eq. {15}:

$$\left(W/C\right)_{add} = \left(w/c\right)_{ref} \cdot \frac{\sum_{N=1}^{i+j}\left(f_{sh,N}\,\frac{m_{F,N}}{d_{P,N}\cdot G_{SP,N}}\right)}{\sum_{N=1}^{i}\left(f_{sh,N}\,\frac{m_{F,N}}{d_{P,N}\cdot G_{SP,N}}\right)} \qquad \{16\}$$

The w/c ratios of mixes with and without filler (dredged material or kaolin) and with and without superplasticizer (lignosulfonate-based) can be predicted using Eq. {16} and compared to the actual, measured values as presented (Table 25). The index $\frac{\text{Flow}_{mix}}{\text{Flow}_{ref}}$ listed in the last column of Table 25 is the ratio of the actual flow of a modified mix to that of a given reference mix. This "flow index" indicates how well the objective of comparable flow was achieved. Ideally it should always be equal to 1.0.

The results of Table 25 show that the predictions for mixes NF-C2 and NF-D3 with dredged material are very close to the experimentally determined w/c ratios. It seems that the assumption of dredged material as a mix of spherical and plate-like particles yields realistic results, which agrees with the quantitative dominance of sand and silt particles and the physicochemical prevalence of clay minerals in dredged material. The flow index exhibits great sensitivity towards changes in the w/c ratio as can clearly be seen in the reference case NF-C1 and mix NF-D1.

In case KF-1 with kaolin as additional component, Eq. {16} suggests a w/c ratio that is 22% below the one determined experimentally. This discrepancy might be caused by the adsorption of water to the charged surfaces of clay minerals and the capability of particle agglomerates to confine water in between them. These phenomena contradict the assumption of similar water film thickness around all particles.

Table 25 Evaluation of w/c-ratios of selected mixes

Mix	Filler added	Calculated w/c {Eq. 16}	Experimental w/c	$\frac{\text{Flow}_{mix}}{\text{Flow}_{ref}}$
Without superplasticizer (assuming similar thickness of water film around particles)				
NF-C1	None (reference)	-	0.52	1.00
NF-D1	None	0.52	0.54	1.09
NF-C2	30% [1] dredged material (spheres)	0.85	0.75	0.95
	30% [1] dredged material (plates)	0.74		
NF-D3	30% [1] dredged material (spheres)	0.85	0.81	1.02
	30% [1] dredged material (plates)	0.74		
KF-1	30% [1] kaolin	0.68	0.88	0.99
With SP-Lig (assuming similar thickness of water film around particles)				
NF-D2	None (reference)	-	0.42	1.00
NF-D4	30% [1] dredged material (spheres)	0.69	0.69	1.09
	30% [1] dredged material (plates)	0.60		
KF-2	30% [1] kaolin	0.55	0.58	1.12

[1] By mass of cement

With the addition of superplasticizer SP-Lig (cases NF-D4 and KF-2), the predicted w/c ratios are lower than the experimental values. However, if adjustments are made to allow for the deviation of the flow index from 1.0, Eq. {16} gives even better results. In case of kaolin as filler, the superplasticizer SP-Lig functions as a deflocculant and surfactant, which prevents agglomeration and lessens the adsorption of gauging water. These phenomena become especially obvious in the case of plate-shaped particles with high water adsorption capacity, such as kaolin. For example, with the addition of SP-Lig the w/c ratio was reduced by 34% (KF-1 and KF-2), whereas in the reference cases (NF-D1 and NF-D2) and for mixes with dredged material (NF-D3 and NF-D4) the differences were below 20%.

The ratio of flow according to the Cone Test to the flow determined with the Ring Test was on average 2.41, with a coefficient of variation of 8.2% (Sections 4.3 and 4.4). The amount of material in a test sample influences the flow because fine material tends to adsorb water and to stick to the walls and bottom of the mixing container. With an increase in batch size it is easier to spread out the fines and to homogenize the mix. This explains why the w/c ratios determined in prior flow tests (Ring) did not result in comparable flows for a specific test series.

In conclusion, the addition of clayey components such as dredged material and kaolin causes a decrease in workability of fresh concrete when compared to that of unmodified reference mixes. The use of a superplasticizer can improve the workability. Yet, replacing regular aggregate with untreated natural dredged material causes such drastic decrease in workability, that even the addition of superplasticizer SP-Mix cannot reduce the w/c ratio to an acceptable level at comparable flow. However, if dredged material or kaolin is added as a filler, the superplasticizers can reduce w/c ratios while maintaining comparable flow.

The type and dosage of superplasticizer do not only control the flow and workability as function of the water volume but also affect the homogeneity of the mix and the spreading of clayey components without agglomeration. The chemical nature of a given superplasticizer determines if and how strongly it functions as a surfactant or deflocculant and how it interacts with the individual concrete constituents. Generally, superplasticizers are much more active if the particle surfaces are charged as it is the case for cement, (activated) clays, and hydration products. For this reason, it has been suggested to administer superplasticizers to the fresh concrete about two minutes after the first contact of cement, clay minerals, and water to increase their effectiveness [73].

The predictions using Eq. 16 were close to the experimentally determined values for mortars containing dredged material as filler with or without superplasticizer. If kaolin was added without a superplasticizer, the calculated w/c ratio differed greatly from the actual value. It is suspected that the adsorption of water on clay surfaces and the agglomeration of kaolin particles defy the hypothesis of similarly thick water layers. However, if kaolin and superplasticizer SP-Lig were added to the same mix, Eq. 16 yielded good results.

5.2 SETTING AND HYDRATION

It was experienced that samples containing natural dredged material were slower to set and hydrate than reference samples without dredged material. When more than 15% fine sand (by mass of aggregate) were replaced with dredged material, samples did not sufficiently harden to be safely removed from their forms within the first 24 hours. Similarly, samples that contained natural dredged material as filler needed to remain in their forms for three days after the lignosulfonate-based superplasticizer was added to the mix (see Section 4.4).

There are several hypotheses on how various substances affect cement hydration. Organic contaminants as well as heavy metals, such as lead and zinc, may cause retardation or delayed setting [63]. Although such contaminants may be present in dredged material, it is believed that the high adsorption capacity of clay minerals is the main cause for the delayed setting, which was observed for samples with untreated dredged material or with natural kaolin during the Vicat test when compared to the reference mix without any clayey constituents (see Section 4.3, Table 19).

Due to the high adsorption capacity of clay minerals, a large fraction of the gauging water is bound to the surfaces of the fine clay particles and thus, is not freely available for hydration. With the hydration process continuing, the accessible water diminishes and the chemical system becomes unbalanced, because there is an insufficient water supply for the cement to hydrate further. The forces to restore chemical equilibrium increase and at some point exceed the adsorptive forces, that bind the water to the clay particles. As a result, water is partially released from the clay surfaces and thereby becoming available for cement hydration. This process slows down the cement hydration and therefore, the addition of fine particles with high adsorption capacities increases the setting time.

The fine particles of treated dredged material or metakaolin have much lower water adsorption capacities than their natural counterparts [29]. Therefore the setting time is barely affected if treated dredged material is added to a mix. However, metakaolin actively participates in the cement hydration. The activated alumino-silicates accelerate this process because of their surfaces charges, thereby reducing the setting time (see Section 4.3).

The similarities in their chemical compositions suggest that the hydration products of cement and those of (activated) clay minerals are comparable. Optical and scanning electron microscopy (SEM) studies were conducted to verify this assumption. After determining the 28-day compression strength, small samples were cut from cylindrical specimens, which contained various amounts of dredged material, kaolin, and/or metakaolin (Test Series NK and NM). The samples were then polished and coated with gold for SEM observations.

One of the reasons why clayey components are commonly considered harmful for concrete products is their tendency to agglomerate and capability of swelling. Figure 29 illustrates an inhomogeneous structure caused by kaolinite clusters, which do not participate in any hydration process. The picture was taken from Reference [40] as such agglomerates were not found during the present study.

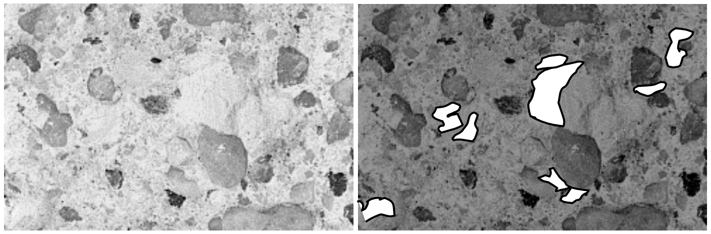


Figure 29 Optical microscope observation [40]*: Poor consolidation and spreading of kaolin*

Left) Original image

Right) Highlighted areas represent (some) agglomerates of kaolin particles

It is crucial to spread out the clay minerals during the mixing process without allowing the formation of any such particle agglomeration. The addition of a superplasticizer generally facilitates the homogenous distribution of fine particles. It can be seen in Figure 30 that the (micro-) structures of the various mixes look very similar, show no agglomeration, and in all cases the aggregate is closely embedded in the cement-clay matrix.

The SEM micrographs of Figure 31 suggest that it should be feasible to use clayey constituents in concrete applications. No irregularities in the inter-particle transition zone could be detected (Figure 31 a, b) and the structure and growth of hydration products in the reference and the clay modified concrete exhibited a great degree of similarity in the two cases (Figure 31 c, d).

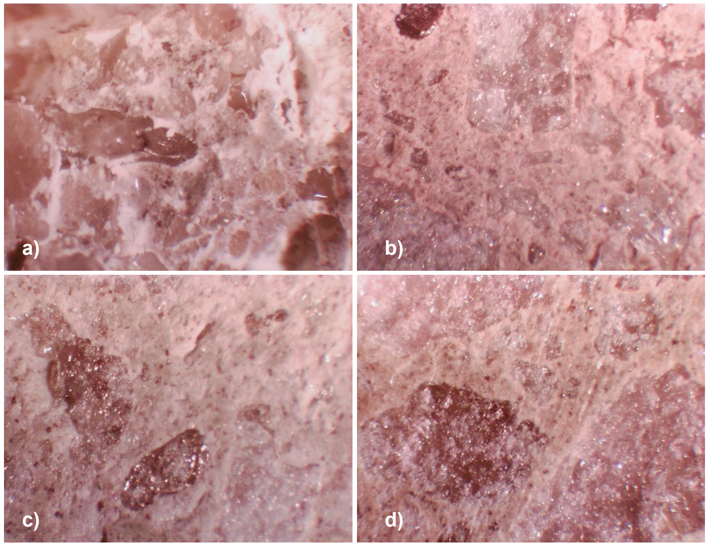


Figure 30 Optical microscope observation, magnification 4x

a) Reference sample without any filler (NK-1), unpolished and uncoated surface

b) Sample with 30% dredged material (by mass of cement) as filler (NM-1),

c) Sample with 30% kaolin (by mass of cement) as filler (NK-2), polished

d) Sample with 30% metakaolin (by mass of cement) as filler (NM-5),

b, c, d) polished and gold-coated surface

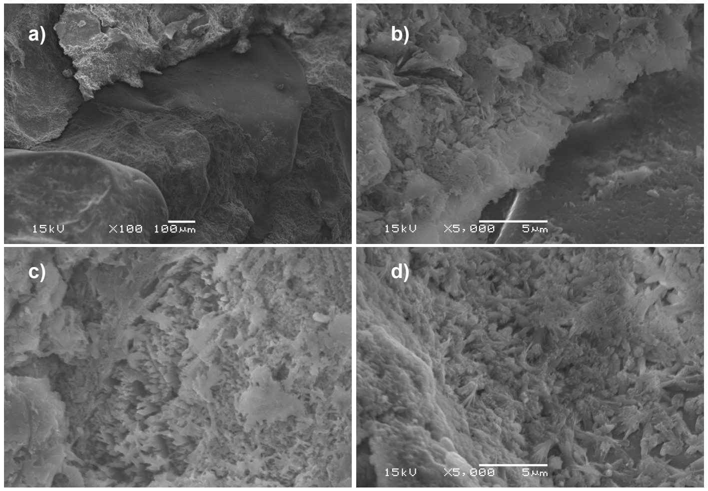


Figure 31 *Scanning electron microscope observation, polished and gold-coated surfaces*

- *a)* *Sample with 22.5% kaolin and 7.5% dredged material (by mass of cement) as fillers (NK-2), Magnification 100x*
- *b)* *Sample with 22.5% kaolin and 7.5% dredged material (by mass of cement) as fillers (NK-2), Magnification 1000x,*
- *c)* *Sample with 22.5% kaolin and 7.5% dredged material (by mass of cement) as fillers (NK-2), Magnification 5,000x*
- *d)* *Reference sample without any fillers (NK-1), Magnification 5,000x*

It can be concluded that the setting time was affected by clayey components, but the hydration process resulted in similar end products after 28 days. It is important to differentiate between setting and hydration when specific concrete applications are planned; i.e. the mix design has to be adjusted accordingly, such as meeting requirements

for earliest and latest time for unmolding. The (micro-) structures of all examined samples were homogeneous and similar to each other without any major inclusions of clay agglomerates, especially when superplasticizers were used.

5.3 STRENGTH

Figure 28 (in Section 5.1) illustrates the opposing effects of the w/c ratio on the flow of fresh mixes and the strength of hardened concrete. It appears to be impossible to optimize these two properties simultaneously. Therefore the mix design either requires a compromise or favors one of the two criteria. Traditionally, this would be the compressive strength, while in this work it is comparable flow. Thus, once the mix proportions have been determined according to workability requirements, the compressive strength and all other performance characteristics follow. In the first test series, natural untreated dredged material replaced fine sand aggregate. The compressive strength of samples containing dredged material as replacement decreases drastically with the amount of material added. Although this strength reduction suggests an alternative use of dredged material, i.e. as a filler, the results for aggregate replacement provide some interesting information.

For a given amount of natural dredged material, the administration of superplasticizer SP-Mix decreased the w/c ratios necessary to maintain comparable flow (Test Series RN-B and RN-C). The 7-day strengths increased for all samples with lower w/c ratio, but the 28-day strengths were barely effected. It is suspected that the superplasticizer functions as a surfactant and deflocculant and thereby increases the activity of the mix. This phenomenon is only effective in the early stage of the hardening process while the long-term behavior is influenced by the release of initially adsorbed water (see Section 5.2). Therefore it can be expected that the 28-day compressive strength is comparable for cases with or without superplasticizer.

After the first experience with dredged material as aggregate replacement, it was suggested to use it as a filler and compare its performance with that of samples modified with kaolinite. The compressive strength of concrete specimens seems to decrease when clayey fillers are added to the composition. This may be partially related to increased w/c ratios, dilution effects, or scatter of test results. Following Abram's rule, the compressive strength f_c can be expressed as a function of the w/c ratio [42]:

$$f_C = \frac{K_1}{(K_2)^{W/C}} \qquad \{17\}$$

where K_1 and K_2 are empirical constants.

Equation {17} does not take into account the influence of additional components such as clayey fillers. In case of the 28-day compressive strength, the constants were calibrated using average values of the cases without fillers (see Sections 4.3 and 4.4). $K_1 = 160$ and $K_2 = 16$ were calculated for cylindrical specimens and $K_1 = 180$ and $K_2 = 15$ for cubes. Using these values in Eq. {17} the strengths of selected mixes containing kaolin and dredged material as filler can be estimated (Table 26).

With the introduction of fillers the relative amount of cement per unit volume decreases. This dilution effect of additional components affects the compressive strength f_c and can be addressed with a modification of Feret's law as suggested in Reference [29]:

$$f_C = K_3\left(\frac{C+F}{C+F+W}\right)^2 \qquad \{18\}$$

where	K_3	(empirical) constant
	C, F, W	Volumes of cement, filler, and water, respectively

The constant in this formula was determined to be $K_3 = 250$ for cylinders and $K_3 = 280$ for cubes, using the average 28-day compressive strength of the cases where the reference concrete mixes were used without any modifications (see Sections 4.3 and 4.4). With these values, the strength conversions were calculated using to Eq. {18} and included in Table 26 for the same selected cases as for the evaluation of Abram's rule.

From the data of Table 26, the following observations can be made. Feret's rule generates higher values than the experimentally determined strengths. It converts the strength of a *diluted* system (with an additional component, e.g. a filler) to that of a reference mix without any filler so that it is expected to yield higher strengths. Abram's rule leads to values that are generally lower than the measured compressive strengths but the difference becomes smaller with decreasing w/c ratio. Mix NF-D4 defies this trend but it was most drastically affected by the retardation experienced when the lignosulfonate-based superplasticizer was used (see Section 4.4). It seems that Eq. {17} and Eq. {18} establish a strength envelope with Abram's rule formulating the lower bound and Feret's rule defining the upper limit (Figure 32).

Table 26 Conversion of 28-day compressive strength (using Eq. {17} and {18}*)*

				Cylinder strength			Cube strength		
Mix	**Filler 1)**	**SP 1)**	**w/c**	**Measured**	**Feret**	**Abram**	**Measured**	**Feret**	**Abram**
NF-D1	None (reference)	-	0.54	36	35	36	42	41	42
NF-D3	30% dredged material	-	0.81	29	35	17	31	41	20
NF-D4	30% dredged material	Lig 1.0%	0.69	30	43	24	25	50	28
NF-D5	30% dredged material	FC 1.0%	0.56	32	54	34	35	63	40
NM-1	30% dredged material	Mix 1.5%	0.66	34	45	26	37	53	30
KF-1	30% kaolin	-	0.88	24	32	14	27	37	17
KF-2	30% kaolin	Lig 1.0%	0.58	35	52	32	43	61	37
KF-3	30% kaolin	FC 1.0%	0.54	34	56	36	35	66	42
NK-2	30% kaolin	Mix 1.5%	0.63	40	48	28	46	55	33

1) By mass of cement

The influence of sample shape and size has been subject of extensive research, and it is known that the compressive strength decreases with smaller specimen size. This is commonly explained with the higher degree of statistical homogeneity for large specimens than for small ones [42, 50]. The strength also decreases with increasing specimen height-to-width ratio [42].

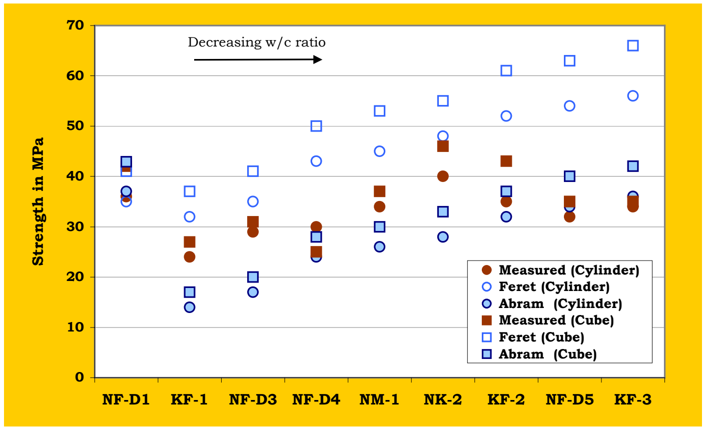


Figure 32 Conversion of the 28-day compressive strength of selected mixes using Feret's rule for dilution and Abram's rule for different w/c ratios

The results presented in this work indicate that there is no strong correlation between compressive strengths of one-inch cylinders and two-inch cubes of the same batch, as one would expect (compare Test Series NK and NM). On average, the ratio of cube strength to cylinder strength was 1.16 (see Sections 4.3 and 4.4), a value that agrees with previous findings [42, 50]. The coefficient of variation was 15.5%, while differences from the mean value were as high as 40%. For cube samples that had to be unmolded prematurely (see Section 4.4) or cylindrical specimens with major surface imperfections, such discrepancies are to be expected.

The addition of kaolin as filler led to a decrease in workability as anticipated. Previous findings reported a reduction in compressive strength of 40 to 45% when clayey components such as natural kaolin or illite were added to reference mixes [29, 47]. Possible reasons for such great strength decrease are the poor workability, caused by the adsorption of gauging water on the surfaces of clay minerals, and the agglomeration of clay particles, which decreases the degree of homogenization.

Moukwa [47] reported an increase in compressive toughness when clays are added to concrete, which he explained with a reduction in the volume of pores. Another possible reason is the homogenization of the (micro-) structure, which would reduce the degree of anisotropy and improve ductility.

Similarly, one could expect that the tensile strength increases with the addition of clay minerals as it was observed when dredged material had been added as filler. It was found herein that the density decreases with the addition of kaolin (Table 27). The combined addition of filler and superplasticizers SP-Lig and SP-Mix could prevent this reduction and as a result the compressive strength was much higher. Similarly, the compressive strength and density of samples containing dredged material could greatly be improved with the addition of superplasticizer SP-Mix and partially with SP-FC.

Table 27 Relative 28-day compressive strengths of mixes with dredged material or kaolin as filler

				Cylinder	**Cylinder strength**		**Cube strength**	
Mix	**Filler** 30% 1)	**SP** 1)	**w/c**	**Density** *in g/cm³*	**f_c** *in MPa*	**Ratio** $f_{c,add} / f_{c,ref}$	**f_c** *in MPa*	**Ratio** $f_{c,add} / f_{c,ref}$
NF-D1	None (reference)	-	0.54	2.151	35.5	1.00	41.6	1.00
NF-D3	Dredged material	-	0.81	2.003	28.8	0.81	31.1	0.75
NF-D4	Dredged material	SP-Lig 1.0%	0.69	2.045	29.9	0.84	25.1	0.60
NF-D5	Dredged material	SP-FC 1.0%	0.56	2.046	32.1	0.90	35.3	0.85
NM-1	Dredged material	Mix 1.5%	0.66	2.057	34.1	0.96	37.3	0.90
KF-1	Kaolin	-	0.88	1.939	23.6	0.66	27.0	0.65
KF-2	Kaolin	SP-Lig 1.0%	0.58	2.138	34.5	0.97	42.9	1.03
KF-3	Kaolin	SP-FC 1.0%	0.54	2.055	34.4	0.97	35	0.84
NK-2	Kaolin	SP-Mix 1.5%	0.63	2.133	40.3	1.14	45.7	1.10

1) By mass of cement

In sum, the use of dredged material as replacement for regular sand aggregate is only recommended for low-end applications, because of the associated concrete strength reduction. The use of dredged material as filler yielded more promising results, although the compressive strength generally decreased with the addition of untreated clayey constituents. Previous research focussed mainly on the replacement of cement by (pozzolanic) fillers and/or the optimum activation process for a specific mineral admixture. In this work the beneficial use of thermally activated kaolinite was confirmed.

It was shown that also the prior CUT treatment of dredged material led to better results than when natural untreated dredged material was used as filler. However, it was one of the objectives of this work to study the behavior of concrete modified with clayey components as inert filler. A pozzolanic contribution of untreated dredged material or kaolin was not expected, therefore none of these components were used as partial cement replacement.

The right combination of certain fillers and appropriate superplasticizers seems to give an optimum concrete composition with superior properties in comparison to those of a reference mix without any filler. For example, the homogeneity, coherence, and also the tensile strength could be improved with the addition of natural dredged material as filler. The compressive strengths of reference mixes without any filler and mixes modified with dredged material or kaolin were comparably high when the concrete was optimized with a superplasticizer. Since the amount of cement per unit volume decreases by about 7% when 30% (by mass of cement) filler is used, the beneficial role that dredged material and kaolin can play as filler becomes obvious. However, the relatively large statistical scatter of test results suggests further studies to substantiate these claims.

5.4 DURABILITY

The durability of concrete incorporating clayey materials such as kaolin or dredged material is a very complex matter. The clay minerals are associated with decrease in workability by adsorbing gauging water, with increased porosity if their network structure remains intact during the mixing and placing of concrete, and with poor durability because clay lumps may cause structural damage or even pop-outs by swelling [18, 42, 50]. In addition, (organic) contaminants in dredged material may affect the concrete performance. It is therefore crucial to take a closer look at the durability performance of modified concrete.

As shown in Section 5.2, the homogeneity of concrete and its structural integrity is barely affected, whether it contains various amounts of dredged material and/or kaolin as filler or not. The clayey constituents are very well spread throughout the matrix. Thorough mixing and the addition of an appropriate superplasticizer could prevent (harmful) agglomerations of fine particles. While it is common to reduce the role of one specific concrete admixture to only one property, the importance of the superplasticizer has to be highlighted with respect to durability. It was found that the addition of the appropriate superplasticizer:

- Reduces the amount of water required to maintain comparable flow,
- Prevents the agglomeration of fine particles,
- Accelerates the hardening process and enhance the hydration products by actively interacting with clayey components,
- Eases the homogenous spreading of clay minerals resulting in a lower degree of anisotropy and improved durability.

It was not within the scope of this work to perform a full-fledged evaluation of the durability properties of concrete containing clay minerals. However, as a preliminary indicator, the compressive strengths of one-inch cylinders of selected mixes with or without dredged material were determined at ages up to 150 days. None of the samples exhibited irregular behavior and the strength increased steadily with time. In none of the mixes tested in the rain chamber for more than 100 days any surface damage was observed nor was a decrease in 148-day compressive strength experienced. Thus, all samples passed these first criteria for durability.

The ASTM C1260 test results showed that all samples could be considered innocuous with respect to ASR. During the autoclave test the reference sample without any filler exhibited higher expansion than the samples containing natural or treated dredged material or kaolin. It can be concluded that none of the clayey constituents contribute to the alkali-silica reactivity but rather improve the performance of a given reference mix. It is recommended to test modified concrete compositions for additional durability aspects, such as freeze-thaw behavior and chemical resistance to sulfates, chlorides, etc.

6 CONCLUSIONS AND OUTLOOK

The main components of the concrete matrix are the products of the cement hydration. While water and cement alone suffice to form a stable matrix that glues together the aggregate particles, additional components can alter the matrix significantly. Admixtures such as retarders, superplasticizers, pozzolanic or inert fillers have been established as valuable tools to improve specific matrix properties and are widely used in concrete practice, whereas naturally occurring clays are considered harmful unless they are (thermally) activated.

Dredged material consists to a large extent of clays, can be contaminated with heavy metals and/or organic components, and has a high salt content due to the original marine environment. Typical clay minerals are illite, kaolin, and montmorillonite, with kaolin being a “perfect model” to study clay mineral behavior because it has a high adsorption capacity and is initially inert but can be thermally activated.

Conventional wisdom discourages the use of material containing clays, salts, and (organic) contaminants for concrete production. As all of these might be found in dredged material, it was one objective of this work to investigate the influence of clay minerals on the properties of fresh and hardened concrete. The similarities of clays in dredged material and naturally occurring clays make it useful to perform a comparative analysis of concrete modified with either dredged material or kaolin.

Four basic questions were raised in Chapter 1 to define the objectives of the research described herein. The following paragraphs summarize the major findings, such as to provide answers to those questions.

1. *Why are clay minerals considered harmful for concrete production? How are the properties of the concrete matrix affected by clayey components?*

The workability was expected to be one of the major problems caused by the addition of clay minerals to concrete mixes. Due to their high adsorption capacity clays decrease the plasticity of fresh concrete, which can only be compensated for by additional gauging water. As a result, the strength is expected to decrease. With the addition of superplasticizers comparable workability can be achieved with lower w/c ratios. It was attempted to formulate a relationship between particle size of the individual components and the water volume required to maintain sufficient flow (Equation {16}). After a first evaluation, the following conclusions can be drawn:

- Once the amount of gauging water has been determined experimentally for a reference mix, it is possible to calculate the amount of water needed if one or more additional components are added to the mix. Equation {16} permits relatively accurate predictions of the water required for compact-grained components such as sand, dredged material, and cement.

- The tendency of kaolin particles to agglomerate and their high adsorption capacity defy the basic assumption of similar water film thickness around each particle. The predicted w/c ratios are generally too low in this case.
- Equation {16} yields much better results when kaolin is used as a filler in combination with a lignosulfonate-based superplasticizer. It is suspected that the superplasticizer functions as a deflocculant preventing agglomeration of fine particles and as a surfactant resulting in similar water film thickness. This assumption is supported by optical and scanning electron microscopy observations, which identified homogenous (micro-) structures without any major inclusions of agglomerated clay minerals.
- If agglomeration of clayey particles can be avoided, for example by using a superplasticizer, it seems possible to predict the required w/c ratio for any given mix composition for preliminary purposes.

Another major concern associated with clay minerals is the concrete durability. The high water adsorption capacities, large specific surface areas, and surface charges cause strong interaction between individual particles, which therefore tend to agglomerate and bind gauging water to their surfaces. If such agglomerations include clay minerals capable of swelling, as in the case of montmorillonite, the volumetric changes upon wetting and drying can cause structural damage, such as pop-outs or disintegration of the concrete matrix.

In general, inclusions of particle clusters cause a drastic decrease in homogeneity, thereby introducing areas of lower material quality. The possibility of failure within these weak links affects primarily the durability of concrete modified with clay minerals but also influences the compressive strength and possibly other mechanical properties as well.

2. *Under what circumstances is it possible to incorporate clayey materials into concrete mixes without experiencing negative effects?*

As one could expect, the workability of concrete mixes with constant w/c ratio decreases with increasing contents of natural untreated dredged material as replacement for sand aggregate. If the flow (as a measure of workability) is held constant by adding supplementary gauging water and/or superplasticizer, the compressive strength of samples decreases in proportion to the replacement level. The workability decreases when either untreated or treated dredged material is used as filler. The addition of 30% treated dredged material as filler (by mass of cement), which is equivalent to 7% by mass of concrete seems to be the upper limit, beyond which the reduction of strength becomes unacceptable. This value was therefore chosen for most of the subsequent experiments in this study that involved clay minerals or dredged material as filler.

When concrete is modified with natural dredged material and kaolin at a combined content of 30% by mass of cement, strength and w/c ratio needed for constant flow show only little variation. The interaction between a blended superplasticizer and metakaolin allow a drastic reduction of the w/c ratio because of the charged particle surfaces. Combined with the known pozzolanic contribution of the thermally activated clay, this effect results in very high compressive strength of samples with increasing metakaolin/dredged material ratio.

The use of an appropriate superplasticizer is necessary to improve concrete properties if clayey constituents are used as fillers in a given composition. Without the addition of such superplasticizers either the workability decreases drastically, if no additional water is added, or the compressive is lowered, if the w/c ratio is increased to maintain comparable flow. A reasonable tradeoff between these two major concrete properties may still qualify concrete modified with untreated dredged material or natural kaolin for low-end applications. The addition of a superplasticizer will broaden the range of potential uses for such material.

Formaldehyde-based or blended superplasticizers seem to deflocculate clayey particles and thus, improve the homogenous spreading of such components throughout the cement matrix. They were found to be the key to a successful, i.e. beneficial modification of concrete with dredged material or natural clays because such superplasticizers can overcome the high adsorption capacities and tendencies to form agglomerates of the clayey components. A melamine-based superplasticizer failed to plasticize concrete containing dredged material or kaolin sufficiently. The addition of a lignosulfonate-based superplasticizer to concrete with natural dredged material as filler permitted a reduction of the w/c ratio but retarded the hydration. In addition, large quantities of lignosulfonate increased the porosity of mortar samples. The strength development was thereby impaired. This is the reason why other superplasticizers are preferred.

3. *Is it possible to use dredged material as a concrete constituent, either as a replacement of fine aggregate or as a filler?*

The replacement of regular sand aggregate with natural untreated dredged material causes either a drastic drop in compressive strength or in workability. Even the addition of a superplasticizer or high-range water reducer does not permit a reasonable compromise between required flow and adequate strength. The use of dredged material as filler seems to be more promising. The addition of up to 30M% (with respect to cement) of treated dredged material yields acceptable compressive strength at sufficiently high flow. In case of untreated dredged material, adding a superplasticizer can reduce the excessive loss of strength, but the performance of treated dredged material as filler was found to be better. Although crystal defects and surface charges of clay minerals in dredged material suggest a high reactivity, no evidence of a pozzolanic contribution of dredged material was found.

4. *Is it possible to improve certain concrete properties by incorporating dredged material into the mix, and what treatment methods are necessary to optimize such beneficial effects?*

The addition of dredged material or kaolin to fresh concrete prevents segregation and bleeding and increases the degree of homogeneity. The mixes appear to be more coherent. Similarly, a lower degree of anisotropy is experienced for mixes incorporating dredged material in comparison to the reference case without any filler.

The Columbia University Treatment (CUT) of dredged material improves the performance of such material as a filler in concrete applications. The workability and compressive strength of concrete containing such treated dredged material do not decrease as much as in the case of untreated dredged material. The treatment homogenizes the material and changes its physico-chemical properties, such as surface charge, thereby partially activating the dredged material. Its addition as a filler to concrete mixes without any superplasticizer does not increase the setting time, whereas untreated material causes a 60% delay. If the time until unmolding is a mix design criterion, a prior treatment of dredged material may be imperative. The variation of dredged material properties is expected to decrease with the CUT treatment. Therefore, it should be easier to accurately predict or adjust material characteristics of concrete modified with treated dredged material than in the case when untreated material is added to the mix.

The durability of concrete modified with clayey components has not yet been completely evaluated. Tested samples containing treated or untreated dredged material or kaolin passed the preliminary tests, i.e. determination of compressive strength at higher ages, exposure to artificial rain for over 100 days, leaching test, and alkali-silica reactivity tests according to the ASTM C1260 protocol and an autoclave procedure.

Cement is often used to stabilize and immobilize contaminated soils, and it was therefore no surprise that only traces of heavy metals leached out of mortar samples. It has to be stressed that proper homogenization is required to ensure that the contaminants remain encapsulated during the entire service-life through the demolition of a concrete member.

The beneficial reuse of dredged material, which is classified as hazardous waste, contributes to the environmentally friendliness of concrete. In this work, 30% filler by mass of cement was added to the mix, which reduced the amount of cement per unit volume of concrete by about 7%. Since cement is the component of concrete, which poses the greatest environmental challenges, such a reduction in demand for cement is significant.

The use of dredged material as aggregate replacement is problematic, even though its disposal by other means is costly. However, if added to concrete as a filler, dredged material may become a valuable resource. The amount of filler can be adjusted to meet any given requirement. Although it may be desirable to use as much dredged material as possible, the concrete performance needs to remain acceptable. This typically requires a compromise between sufficient workability and compressive strength, both linked through the w/c ratio. One solution might be to limit concrete containing relatively large amounts of dredged material to low-end applications, such as base material for road construction. A thorough economic and logistical study on a larger scale (demonstration or pilot project) is needed to show the feasibility of using dredged material and other clayey constituents for concrete production. Although the remaining durability issues, e.g., chemical resistance and freeze-thaw performance, need to be addressed, it is believed that both, dredged material and natural clays can be used beneficially in concrete production, provided the mix design is optimized with an appropriate superplasticizer.

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