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Foreword

Annual world production of concrete was about 700 million tons in 1920. It will exceed 10,000 million tons before the year 2000 due to the continuous growth of the population of the world, the demands on social development, and the absence of practical alternative materials. This brings up the question of the continued availability of the resources required to make concrete, and reveals the need for intensive research to improve the resource efficiency of concrete technology. The present Volume II of Materials Science of Concrete is, like Volume I, a valuable reservoir of updated scientific knowledge which is required for the planning and management of this essential enterprise.

The chapters of this book contain new information related to both the processing of concrete and its properties in the subsequent hardened state as a building material.

Crude, empirical methodology and testing methods for mix design, compaction, and curing still prevail in engineering practice. The chapter on particle packing brings forward a rational basis for optimum mix design, and the chapters dealing with hydration contain essential information for further development of modern techniques for control and monitoring of concrete curing.

The chapters on the properties and reactions of hardened concrete offer new insight in the far too long neglected field of concrete chemistry. In conjunction with the chapters on the physico-mechanical aspects of hardened concrete, this is a promising basis for further efforts to explore the interactive effects of chemical, physical, and mechanical processes of concrete in service.

The contents of this book, therefore, should also encourage strategic planning for further engagement of materials scientists in concrete research with the aim of making the production and utilization of concrete more resource efficient.

With Volumes I and II in hand, it is tempting to ask for a Volume III which will deal with innovation in the concrete industries and new engineering practices based on application of the scientific knowledge presented in these volumes.

G. M. Idorn January 1991

Introduction

I prefer the errors of enthusiasm to the indifference of wisdom.

Anatole France

The first volume of the Materials Science of Concrete was published in 1989. Now, two years later, we are happy to present Volume II. The chapters presented in this volume are meant to complement the critical reviews published in Volume I and to explore new issues relevant to the materials science of concrete.

A few colleagues have asked us why we decided to call this series Materials Science of Concrete rather than Materials Science of Cementitious Materials. There are several reasons for it, but the main reason is our belief that this book should serve primarily the engineering community, the people in the field, the construction specialists who do not have the opportunity to follow new scientific developments on a continuous basis. Cementitious materials implies the use of cement and other inorganic binders for non-construction applications, and that is not the purpose of this book. Technology progresses rapidly these days, even in the conservative construction materials area. New materials, new analytical and testing techniques, new environmental and energy conservation-related pressures...all these cause our community to adopt our construction practices. Thus, we see this series of books as an opportunity to learn about the state-of-the-art from a series of critical reviews focused on the real world of concrete technology. New, advanced materials are crucial if they serve in improving the quality of our life.

This January, a forum was held in Washington, D.C. to discuss national civil engineering research needs. It was sponsored by the Civil Engineering Research Foundation, National Science Foundation, and numerous governmental and trade institutions, with the goal of discussing the research and technology transfer needs caused by the deteriorating infrastructure, changes in world market, and the need to protect the environment. Thus, methods for revitalization of the public infrastructure, enhancement of the international competitiveness of the U.S. construction industry, enhancement of our environmental awareness, and development and application of innovating technologies and systems were discussed in detail. One of the sessions concentrated on identification and prioritization of materials-related technical needs and, not surprisingly, selected structural concrete as a material in need of further development, primarily with respect to its long-term durability at an acceptable cost. One of the barriers to further development was identified as lack of awareness of existing new materials and technologies, and inadequate mechanisms of transfer of such knowledge to engineering practice...both related to education.

It is our hope, that by disseminating the knowledge presented in individual chapters of Materials Science of Concrete, we can at least modestly help in solving the difficult challenges that we face.

We would like to acknowledge the first-class professional help received from the staff of The American Ceramic Society during the preparation of this second volume. Special thanks are due to our professional colleagues and secretaries for their critical comments and help in preparation of the manuscript. Finally, we would like to thank the authors of the chapters for their enthusiasm and humor during their writing.

> Jan Skalny Sidney Mindess February 1991

Particle Packing and Concrete Properties

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"Science is what you know, philosophy is what you don't know."

Bertrand Russel

The packing density of monosized spherical particles can be estimated by a number of models described in the literature. These models are summarized with emphasis on their application to multicomponent particle systems of relevance to concrete. These models can be applied to estimate the packing density of mixtures of concrete materials. Experiments show that the packing density of concrete mixtures and the flow properties of the corresponding fresh concrete are related. The optimal flow properties are obtained for mixture compositions close to the maximum packing density. In this way the packing density has an important effect on concrete properties such as porosity, permeability, and indirectly, through its effect on the workability and compactability of the fresh concrete, on compressive strength.

Particle Packing

The field of particle packing can be defined as investigations into the problem of selecting appropriate sizes and proportions of particulate materials to fill larger voids with smaller particles, containing smaller voids that again are filled with smaller particles, and so on. Control of particle packing is of major importance to many branches of industry and science. The attainment of a dense packing is of interest to a number of technological fields (e.g., packed beds, ceramics, concrete, asphalts, and powder metallurgy), whereas the reverse is the case in, for instance, the packing of shaft kilns.

Most of the literature on the subject was published in the 1930s describing the optimization of packing for optimal flow of fluids in packed towers, filtration of slurries containing fine solids, and sintering of pressed solids. The first experimental and theoretical attempts to study idealized packing of spheres of different sizes were performed by Furnas^{1,2} in 1929 and by Westman and Hugill³ in 1930.

The subject gained renewed interest in the 1950s and 1960s due to atomic energy and space research.⁴ Most of these studies concerned the packing of uranium oxide in metal tubes by determining the optimal particle-size distribution for efficient packing.⁴⁻⁶

The research on the subject of particle packing is rather complex. In the field of concrete technology, as stated by Mehta, concrete proportioning is to be considered more of an art than a science and, as a result, there are many different procedures, even within one country, to meet the needs and preferences of the concrete proportioning professional. According to Bache, the design of cement-based products becomes very limited when using the well-established terms and concepts; for example, the empiric rules of water demand and reference grading curves that are normally used in concrete technology. To develop high-technology tailored products, Bache suggests the use of classical physics for understanding the concepts of particle packing, form stability, workability, and water demand.

One of the first articles on the subject of particle packing for concrete production was published by R. Feret in 1892. The main issues of this publication were the possibilities of choosing the correct type of aggregate for the optimal concrete and relating the porosity of the hardened mortar to the compressive strength of the concrete.

According to Powers, ¹⁰ in choosing the correct type of aggregate to be used for a given concrete mixture, the aggregate with the lowest percentage of voids is not necessarily the best choice for the mix designer: "The production of satisfactory concrete nevertheless requires aggregates with low content of voids even if not the lowest possible, and this requires finding proper combinations of sizes within the allowable size range."

The work performed by Powers and coworkers at the Portland Cement Association¹⁰ resulted in empiric analytical relationships for the estimation of the void ratio of concrete aggregates. The work by Powers contains the roots of the most widely accepted American mix design practice known as "The American Concrete Institute Standard Recommended Practice for Selecting Proportions for Concrete" and the work by ACI Committee 211 which resulted in the standard¹¹: "Recommended Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete," ACI 211.1-81.

Joisel studied the work of Feret and Caquot⁹ extensively, searching for the optimal particle size and particle packing by experimental binary and ternary

packings using concrete materials. Bache¹² describes the use of the principles of particle packing in developing a high-strength mortar, patented under the trade name "Densit." This mortar is proportioned on the basis of cement, fine sand, and silica fume.

The following parameters may have an effect on the packing density:

- 1. The particle-size distribution.
- 2. The wall effect.
- 3. The method of compaction.

Most experimental packing studies reported in the literature are carried out using monosized and spherical particles of various materials (e.g., polyethylene, ¹³ metal shot, ^{4-6,13} coke, and smooth wooden spheres ¹⁴), while others study the packing of nonspherical monosized particles of quartz; feldspar; dolomite and sillimanite; ¹⁵ cement and silica fume; ¹⁶ and cement, sand, and coarse aggregate. ^{3,9}

The theory of particle packing by Furnas¹ describes the *ideal* packing of spherical particles. In reality, the packing density will, however, be influenced by the "wall effect" as discussed by several authors. 4,13,17-19 The wall effect is of major importance considering the packing of small particles on the surface of larger particles; as illustrated in Fig. 1, the porosity at the surface of the larger particles will be higher than in the bulk, extending out into the bulk at a range of up to five diameters of the smaller particle. From experiments on the packing of particles in a cylinder, it has been found that the diameter of the cylinder, in general, has to be more than ten times the diameter of the largest particle in order to avoid a significant "wall effect."

The packing densities of ternary particle systems can be represented on a triangular diagram such as is illustrated in Fig. 2. Studies of the packing density of ternary mixtures were reported by Joisel, Ridgway and Tarbuck, Standish and Borger, dand Fedor and Landel. McGeary found that the packing of the finest and the coarsest material will dominate the ternary packing.

Considering quaternary packings, McGeary⁴ found that, by adding a fourth component, it was possible to achieve a packing of 95.1% of the theoretical packing density. In other words, by the addition of more components it should be possible to obtain higher packing densities.

Considering the experimental packing techniques, most articles report the use of cylindrical steel or glass containers and the use of vibratory techniques as the method of compaction, 4.15 whereas some 13 report the use of a steel cylinder that is spun about its longitudinal axis in a suspension of water and ethylene glycol.

Theoretical models for the calculation of the packing density are described by Stovall et al., ¹⁷ Fedor and Landel, ¹⁸ Aim and Goff, ¹⁹ Toufar et al., ^{20,21} and Larrard and Buil. ²²

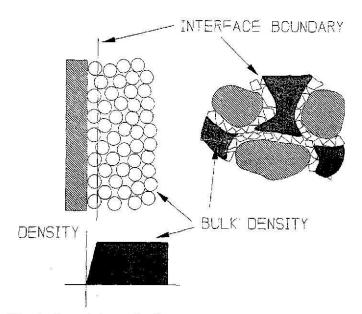


Fig. 1. Illustration of the wall effect.

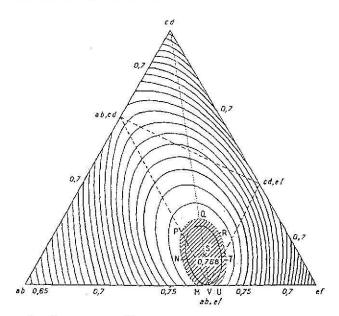


Fig. 2. Example of ternary packing diagram of the packing density of fine (ab), medium (cd), and coarse (ef) aggregate (From Ref. 9, used with permission.). Isodensity curves are shown within the triangle.

Petersen²³ discusses the use of packing models in relation to the mechanical and rheological properties of the material during the clinker burning process. Based on literature data, the general findings by Petersen were that the model by Aim and Goff¹⁹ gave the best fit of the theoretical to the experimental packing densities for particle diameter ratios below 0.22 and that the model described by Toufar et al.^{20,21} gave the best fit for diameter ratios above 0.22.

The following summarizes the concepts of particle packing, models for packing in binary systems, and their application in the estimation of the packing density of multicomponent systems with emphasis on ternary systems related to concrete technology.

Packing Models

The important parameter regarding packing of polydisperse particle systems is the packing density, which is defined as the volume fraction of the system occupied by the solids. By this definition, the packing density is equal to one minus the porosity of the system. In the description of the packing density the volume fractions of the components are used instead of the weight fractions. The fraction of the *i*th component is $r_i = m_i/\rho_i/\Sigma(m_i/\rho_i)$, where m_i and ρ_i are its mass and specific gravity, respectively, considering g grams of solid material with volume (calculated by means of the specific gravity) equal to one. Due to the void space between the particles, the total volume occupied, ν , is larger than one. The following parameters and relationships are defined:

v = specific volume of mixture = total volume/solid volume φ = packing density of mixture = 1/v $1 - \epsilon$ = porosity of mixture

The concept of the definitions is illustrated in Fig. 3.

The Furnas Model

The ideal packing of spherical particles, to obtain the maximum density of a packed bed in a binary system, was considered by Furnas.^{1,2} In his description the diameters of the particles differed and the smaller particles could be accommodated in the voids between the larger particles. The model may be summarized as follows^{20,21,23}:

Consider the packing of a mixture of two materials, 1 and 2, consisting of spherical particles with diameters $d_1 << d_2$, volume fractions r_1 and r_2 , and

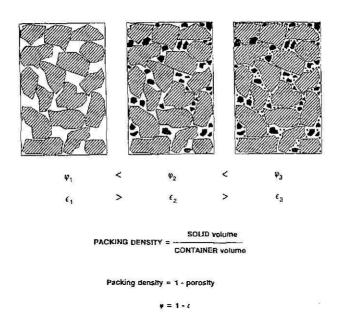


Fig. 3. Concept of packing density definitions.

packing densities of φ_1 and φ_2 . In this mixture two limiting cases may be considered:

- 1. The volume fraction of small particles is large $(r_1 >> r_2)$.
- 2. The volume fraction of coarse particles is large $(r_2 >> r_1)$.

In case 1, the mixture may be considered to consist of a matrix of smaller particles containing discrete larger particles. The matrix of smaller particles will have a packing density φ_1 and contribute to the specific volume of the mixture by r_1/φ_1 . The larger particles contribute to the volume by the solid volume fraction of coarse particles r_2 . Thus, the specific volume and the packing density of the mixture are:

$$v = \frac{r_1}{\varphi_1} + r_2$$

$$\varphi = \frac{1}{(r_1/\varphi_1) + r_2}$$

In case 2, the particle mixture may be considered to consist of a matrix of the smaller particles distributed in interstices between the larger particles. The smaller particles, as they are contained within the interstices, do not contribute to the overall specific volume of the mixture, whereas the larger particles contribute with the specific volume of a monodisperse packing of large particles. The specific volume and hence the packing density of the mixture are:

$$v = \frac{r_2}{\varphi_2}$$

$$\varphi = \frac{\varphi_2}{r_2}$$

From the equations, it can be seen that the packing density of the mixture in either case is larger than for the individual components. The maximum value of the packing density is found for the value of $r^* = r_1 = 1 - r_2$ for which both cases give the packing density:

$$r_1^* = \frac{\varphi_1 \cdot (1 - \varphi_2)}{\varphi_2 + (1 - \varphi_2) \cdot \varphi_1}$$

With the composition corresponding to $r_1 = r_1^*$ all interstices between larger particles are filled with packed smaller particles and the maximum packing density φ^* of the binary mixture is obtained:

$$\varphi^{\bullet} = \varphi_2 + (1 - \varphi_2) \cdot \varphi_1$$

The model by Furnas is valid only in the case of $d_1 << d_2$. If this condition is not fulfilled, the packing density of the binary mixture will also depend on the diameter ratio d_1/d_2 . The reasons for this are:

- 1. The smaller particles may be too large to be situated within the interstices of the larger particles.
- 2. The packing of smaller particles along the surface of a larger particle gives a lower packing density than in the bulk of the binary packing due to the wall effect.

The Model According to Aim and Goff

Aim and Goff¹⁹ proposed a simple geometrical model to account for the excess porosity observed experimentally in the first layer of spherical grains in contact with a plane and smooth wall. The model also considers the variations that occur in the porosity of binary mixtures of spherical grains as a function of the composition.

For a description of the model, first consider N spherical grains, each of a volume $w = \pi \cdot d^3/6$. If V is the apparent volume of the packing of N grains in a container with the characteristic dimension D, and V_0 is the ideal volume of packing without the perturbation of the container wall, then:

$$N \cdot w = V_0 \cdot (1 - \epsilon_0) = V \cdot (1 - \overline{\epsilon})$$

where ϵ_0 is the ideal porosity and $\overline{\epsilon}$ is the experimental porosity. The "wall perturbation coefficient" can therefore be defined by the equation:

$$p = \frac{V}{V_0} = \frac{1 - \epsilon_0}{1 - \overline{\epsilon}}$$

Variations in the local porosity have also been studied by other authors. $^{4.13}$ The general experimental observation is that the maximum porosity is found at the container wall and extends through a minimum at a distance of d/2 of the particle diameter. It then varies sinousoidally toward the constant bulk porosity at a distance of four to five diameters from the wall. Variations in the integrated porosity are, however, limited to a layer, approximately d/2 thick, close to the container wall, as is also illustrated in Fig. 1.

As a model of the observed variations in the porosity of spheres packed next to a wall, Aïm and Goff suggest the following equation:

$$\frac{V}{V_0} = 1 + a \cdot \frac{\epsilon' - \epsilon_0}{1 - \epsilon_0} \cdot \frac{Z}{D}$$

where $Z \approx d/2$, ϵ' is the porosity in the region next to the surface, D is the dimension of the container, and a is equal to 4 or 6 for a cylindrical and a spherical container, respectively.

To find the relationship between p and d/D it is necessary to evaluate the magnitude of ϵ' . By introducing a wall in a bed of packed monodisperse particles,

and considering the geometrical arrangements of the spheres, Aim and Goff derived the following equation to describe the required relationship:

$$\frac{1-\epsilon'}{1-\epsilon_0}=\frac{11}{16}$$

They assumed that the porosity of the matrix of small particles is $\epsilon_0 = 0.36$, which gives $\epsilon' = 0.56$. The variations found in the porosity, close to the wall of a spherical container, can therefore be described by the formula:

$$\frac{V}{V_0} = 1 + 0.9 \frac{d}{D}$$

Based on the analogy to molar and partial volumes of liquids, Aim and Goff estimated the apparent partial volume of a large isolated particle in a bed of small particles. Applying this partial volume, a model for the porosity of a binary mixture of coarse and fine particles is derived.

Similar to the considerations in the Furnas model, the porosity is described for the two cases:

- 1. The volume fraction of fine particles is small.
- 2. The volume fraction of fine particles is large.

Assuming that the particles are spherical, and that the fine and coarse particles pack with the same porosity, the volume fraction, y^* , of fine particles that represents the boundary between the two cases, gives the mixture with the maximum packing density:

$$y^* = \frac{1 - (1 + 0.9 \cdot d_1/d_2) \cdot (1 - \epsilon_0)}{2 - (1 + 0.9 \cdot d_1/d_2) \cdot (1 - \epsilon_0)}$$

where d_1 is the diameter of fine particles, d_2 the diameter of coarse particles, and ϵ_0 the porosity of the pure components.

In case the shapes of the fine and coarse particles deviate from the spherical form and have different porosities, the volume fraction of the fine particles for the maximum density mixture is given by:

$$y^* = \frac{[(\varphi_1/\varphi_2) - (1 + 0.9 \cdot d_1/d_2) \cdot \varphi_1]}{[(\varphi_1/\varphi_2) - (1 + 0.9 \cdot d_1/d_2) \cdot \varphi_1 + 1]}$$

where φ_1 is the experimental packing density of fine particles and φ_2 is the experimental packing density of coarse particles.

In case the volume fraction of the finer particles is small (i.e., $< y^*$) the porosity and the packing density can be determined by the formula:

$$\overline{\epsilon} = \frac{\epsilon_0 - y_1}{1 - y_1}$$

$$\varphi = 1 - \overline{\epsilon} = \frac{\varphi_2}{1 - y_1}$$

where φ is the packing density of the binary mixture. This is similar to the formulas derived by Furnas.

In case the volume fraction of finer particles is large (i.e., $> y^*$), the packing density can be determined by the formula:

$$\varphi = \frac{1}{\frac{y_1}{\varphi_1} + (1 - y_1) \cdot \left[1 + 0.9 \cdot \frac{d_1}{d_2}\right]}$$

The Toufar, Klose, and Born Model

Toufar et al.^{20,21} described a model to calculate the packing density of multicomponent mixtures as the weighted average of the total number of binary mixtures for diameter ratios $0.22 < d_1/d_2 < 1.0$, based on a model by the Russian author Cernych.²¹

The fundamental concept of the model is that the smaller particles, for diameter ratios >0.22, will actually be too large to be situated within the interstices between the larger particles. The result is a packing of the matrix that may be considered as a mixture of packed areas mainly consisting of larger particles, and packed areas that mainly consist of smaller particles with larger particles distributed discretely throughout the matrix of smaller particles.

Toufar et al. considered the three limiting cases for a binary system, each characterized by the diameter ratio and the relative amount of the components:

9	Case particle size	Volume fraction fine	Packing density
1.	$d_1 >> d_2$	$r_1 >> r_2$	$\varphi = r_1/\varphi_1 + r_2$
2.	$d_1 << d_2$	$r_1 << r_2$	$\varphi = r_2/\varphi_2$
3.	$d_1 \approx d_2$		$\varphi = r_1/\varphi_1 + r_2/\varphi_2$

To describe all three cases by one formula, the function z is defined by the following:

$$\varphi = \frac{1}{\frac{r_1}{\varphi_1} + r_2 + z \cdot \left(\frac{1}{\varphi_2} - 1\right)}$$

The third member of the denominator corrects for the void space created by the volume of larger particles which are not densely packed and distributed in a matrix of the smaller particles.

For the three limiting cases described, z has the value:

Case	Limit	z
1.	$d_1/d_2 \rightarrow 0$	0
2.	$d_1/d_2 \rightarrow 0$	$r_2 \cdot \left[1 + \frac{\varphi_2}{\varphi_1 - \varphi_1 \cdot \varphi_2}\right] - \frac{\varphi_2}{\varphi_1 - \varphi_1 \cdot \varphi_2}$
3.	$d_1/d_2 \rightarrow 1$	r_2

z is a function of r_2 and the diameter ratio d_1/d_2 . To establish the mathematical expression for z, Toufar et al. considered the statistical probability of the number of interstices between the coarser particles that are free from smaller particles and ended up with the following formula, which may be used to calculate the packing density of a binary mixture:

$$\varphi = \frac{1}{\frac{r_1}{\varphi_1} + \frac{r_2}{\varphi_2} - r_2 \cdot \left[\frac{1}{\varphi_2} - 1\right] \cdot \frac{d_2 - d_1}{d_1 + d_2} \cdot \left\{1 - \frac{1 + 4 \cdot \frac{r_1}{r_2} \cdot \frac{\varphi_2}{\varphi_1 \cdot (1 - \varphi_2)}}{\left[1 + \frac{r_1}{r_2} \cdot \frac{\varphi_2}{\varphi_1 \cdot (1 - \varphi_2)}\right]}\right\}$$

where r_1 is the volume fraction of small particles, r_2 is the volume fraction of large particles, d_1 is the diameter of small particles, d_2 is the diameter of large particles,

 φ_1 is the packing density of small particles, and φ_2 is the packing density of large particles.

For estimating the packing density of a multicomponent system, it is assumed that any two components form binary mixtures. The fraction of component i forming a binary mixture with component k is assumed to be:

$$r_{i-k} = r_i \cdot \frac{r_k}{1 - r_i}$$

and similarly for component k:

$$r_{k-i} = r_k \cdot \frac{r_i}{1 - r_k}$$

The total fraction of components i and k forming binary mixtures is²³:

$$r_{ij} = r_{i-j} + r_{j-i}$$

For this binary mixture, the volume fraction of the smaller particles is equal to $r_{i\rightarrow}/r_{ij}$ and, similarly, for the larger particles is equal to $r_{j\rightarrow}/r_{ij}$. Its packing density can then be calculated according to the models for the binary mixtures. The packing density for the total multicomponent mixture is calculated by summation of the contributions from all the binary mixtures:

$$\varphi = \frac{1}{\sum_{j=2}^{n} \sum_{i=1}^{j-1} \frac{r_{ij}}{\varphi_{ij}}}$$

The Linear Packing Density Model

Larrard,²⁴ Stoval et al.,¹⁷ and Larrard and Buil²² described their linear packing density model for multicomponent mixtures. They considered mixtures of n components with diameters d_i , where d_1 is the largest particle. The packing density of the *i*th component is φ_i , its partial volume in a unit volume of the mixture is f_i , and the volume fraction is r_i .

For a binary system they considered the two cases: $r_1 >> r_2$ and $r_2 >> r_1$. In the first case, the introduction of the smaller particles may perturbate the packing of the larger particles in such a way that the partial volume of these is

 $f_1 = \varphi_1 - \lambda(1,2) \cdot f_2$, where $\lambda(1,2)$ is a function describing the local expansion of the packing of the larger particles due to the introduction of the smaller ones. Similarly, for the second case, where the smaller particles pack differently on the surface of the larger particles than in the bulk (the wall effect), the partial volume of component 2 is $f_2 = \varphi_2 \cdot (1 - f_1 - \lambda(2,1) \cdot f_1)$.

The packing density of binary mixtures will then be:

For
$$r_1 >> r_2$$
:
$$\varphi = \varphi_1 + (1 - \lambda(1,2)) \cdot f_2$$

$$= \varphi_1 + f(1,2) \cdot f_2$$
where $f(1,2) = 1 - \lambda(1,2)$. Since $y_i = f_i/\Sigma_i f_i$, then
$$\varphi = \varphi_1/(1 - f(1,2) \cdot y_2)$$
For $r_2 >> r_1$:
$$\varphi = \varphi_2 + \{1 - \varphi_2 \cdot [1 + \lambda(2,1)]\} \cdot f_1$$

$$= \varphi_2 + (1 - \varphi_2) \cdot g(2,1) \cdot f_1$$

where $g(2,1) = 1 + \lambda(2,1)$.

For $d_2 << d_1$, the particles do not interact and f(1,2) and g(2,1) become equal to one, and the two expressions for the estimation of the binary density become identical to those of the Furnas model. In the general case, the packing density of the binary mixture will be the smallest of the two calculated above. For a multicomponent mixture, described by a cumulative distribution y(x) (y(d) = 0, y(D) = 1), the packing density is given by:

 $= \varphi_{1}/(1 - (1 - \varphi_{1}) \cdot g(2,1) \cdot y_{1})$

$$\varphi = \inf_{d < t \le D} \left[\frac{\varphi(t)}{1 - [1 - \varphi(t)] \cdot \int_{t}^{D} g(t, x) \cdot y(x) \cdot dx - \int_{d}^{t} f(t, x) \cdot y(x) \cdot dx} \right]$$

where $\varphi(t)$ is the packing density of the fraction of size t, and the functions f and g are:

$$f(d_j, d_i) = (1 - d_i/d_j)^{3.1} + 3.1 \cdot (d_i/d_j) \cdot (1 - d_i/d_j)^{2.9}$$

$$g(d_j, d_i) = g(d_i, d_j) = (1 - d_i/d_j)^{1.6}$$

Experimental Results and the Models

For binary mixtures Petersen²³ found, based on literature data, that the best description of the experimental data for systems with a diameter ratio smaller than 0.22 is provided by the Aïm and Goff model, and for systems with diameter ratios larger than 0.22, by the Toufar et al. model.

Figures 4 to 9 show the results of McGeary⁴ for binary mixtures of steel shot compared to results obtained by either the Aïm and Goff or the Toufar et al. model, depending on the diameter ratios of the particles. In Fig. 10, experimental results are shown from the literature compared to the results calculated by the two models. In constructing the graph in Fig. 10, data from Furnas, ¹⁸ Westman and Hugill, ¹⁸ Caqout, ⁹ Larrard, ²⁴ and Pantakar and Mandal ¹⁵ were used.

The graphs representing the experimental results of the packing density (or the porosity) were read for given compositions of the binary mixtures, and the corresponding theoretical values were calculated using the actual particle sizes and packing densities for the pure components. The data obtained by Furnas

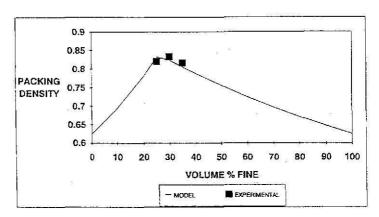


Fig. 4. Binary packing densities of steel shot of diameter ratio 0.052 (Ref. 4) compared to model estimations.

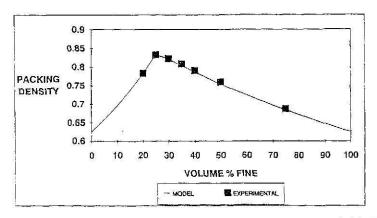


Fig. 5. Binary packing densities of steel shot of diameter ratio 0.06 (Ref. 4) compared to model estimations.

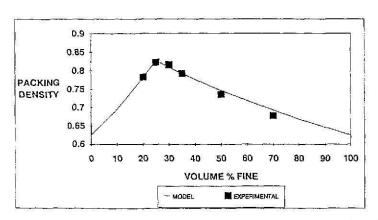


Fig. 6. Binary packing densities of steel shot of diameter ratio 0.089 (Ref. 4) compared to model estimations.

were from packings of steel shot with diameter ratios from 0.5 to 0. The data of Westman and Hugill were from packings of sand with diameter ratios between 0.053 and 0.291, and those of Caqout from packings with sized gravel from the river Seine in France. The data of Pantakar and Mandal were from packings of unisized fractions of quartz, feldspar, sillimanite, and dolomite.

The data were plotted with two different signatures depending on whether the data were calculated according to the Aim and Goff or the Toufar et al. models and, as can be seen, they seem to follow the same regression line. From

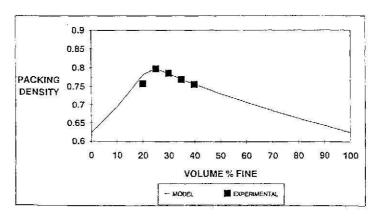


Fig. 7. Binary packing densities of steel shot of diameter ratio 0.153 (Ref. 4) compared to model estimations.

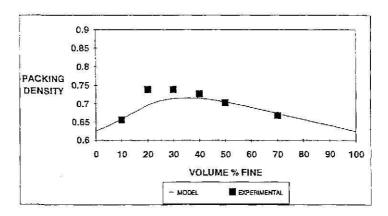


Fig. 8. Binary packing densities of steel shot of diameter ratio 0.21 (Ref. 4) compared to model estimations.

the figure it can also be seen that there is a tendency for the models to overestimate the higher packing densities.

The models dealt with above calculate the packing density of mixtures of monodisperse particles. In reality, however, particles are seldom monodisperse, but polydisperse, and described by a particle-size distribution, PSD. Several of the models cited have been developed to take continuous particle-size distributions into consideration. ^{17,20-22} In these expressions, the modeled packing densities of the mixtures involve integrations of functions of the PSDs for the components

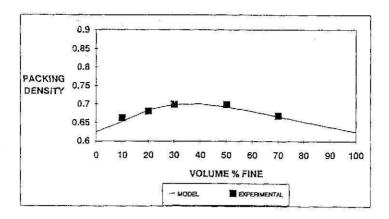


Fig. 9. Binary packing densities of steel shot of diameter ratio 0.29 (Ref. 4) compared to model estimations.

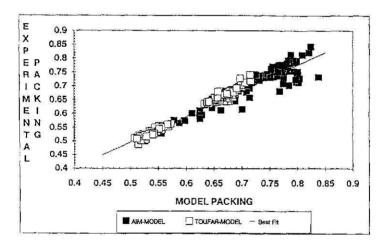


Fig. 10. Correlation of model estimations of binary packing densities to literature data (Refs. 3, 9, 15, 18).

used. To obtain mathematical expressions for the PSDs, the materials in question are sieved and from the experimental results it is then possible to describe the PSDs by fitting them to some mathematical function. The incorporation of mathematical functions will, however, not increase the accuracy of the information contained in the experimental results, and in practice the packing density is calculated using numerical integration. It is the writers' experience that the

position parameter of the Rosin-Rammler-Sperling-Bennett²⁵ representation of the PSD, together with the experimentally determined packing density of the component, gives results with accuracies comparable to the experimental reproducibility of packing the materials.

The Rosin-Rammler-Sperling-Bennett distribution is described by the equation:

$$R(D) = \exp \left\{ -\left(\frac{d}{d'}\right)^n \right\}$$

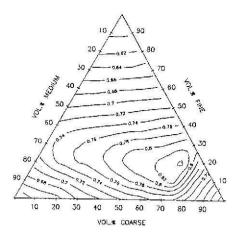
where d is the particle diameter, R(D) the cumulative probability that the diameter is less than d, and d' the position parameter for which R(d') = 0.368, corresponding to 36.8% residue on that sieve size.

As an approximation, each polydisperse material can then be represented by d' and the packing density of the material. The experimental packing density of each individual component reflects and incorporates the deviations from the monodisperse distribution and from the spherical particle form.

Toufar et al.^{20,21} suggested that the packing density for a multicomponent system can be estimated by calculating the weighted average of all binary mixtures in the system. For ternary mixtures of particle diameter ratios >0.22, the estimated packing densities are consistent with the experimental data. For ternary systems with very small diameter ratios, as in concrete, the binary mixture of sand and coarse aggregate without cement in the interstices is not realistic from a physical point of view and will contribute too low packing densities. One way to overcome this problem is to start by calculating the binary packing of the two coarsest materials. This calculated binary packing density, together with a calculated pseudodiameter representing the average particle size of the two coarsest materials, is then used to calculate the binary packing density with the finest component. This resulting packing density then represents the ternary packing density of the mixture.

Experimental data for ternary systems are available from Westman and Hugill,³ Joisel,⁹ Standish and Borger,¹⁴ and Larrard.^{22,24} These ternary literature data are compared with the calculated packing densities in Figs. 11 to 13. As can be seen from the figures, the topography of the model calculations corresponds well with the experimental results. However, the absolute values of the packing densities are generally overestimated by the models.

Figures 14 and 15 show the results^{26,27} of experimental packing densities for binary mixtures of cement and sands with different PSDs, and for ternary mixtures of the two sands and cement, respectively. Figure 15 shows the results from ternary mixtures of the cement and the coarse sand component with constant volume fraction, 0.2, of the fine sand component. In both cases the correlation



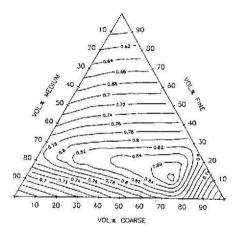


Fig. 11. Ternary diagram showing isodensity lines in mixtures of sized sands as estimated by the models (bottom) compared to the experimental results of Westman and Hugill (Ref. 3) (top).

between the experimental and the estimated values is fair. The highest density for the packings is seen at a volume composition of about 0.7 volume fraction of the coarse component.

Experimental results²⁷ and model estimations of the packing densities of ternary mixtures of cement, quartzite sand (0-2 mm) and crushed coarse granite aggregate (8-16 mm) are shown in Figs. 16 and 17. A good correlation is seen

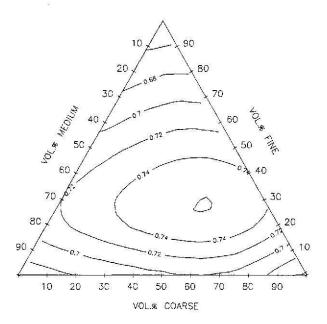


Fig. 12. Ternary diagram showing isodensity lines in mixtures of sand of diameters 0.5, 1.4, and 2.6 mm as estimated by the models. For comparison, please refer to the experimental data of Joisel (Ref. 9) shown in Fig. 2; note that the axes have been reversed as compared to Fig. 2.

between the topography obtained by the model and the experimental results; however, the absolute packing densities calculated by the model are overestimated in the range of about 5% for compositions of maximum packing.

The experimental data for the packing densities of the binary packings of cement and sands and the ternary packings of concrete materials are correlated with the values estimated by the model in Fig. 18 and, as can be seen, the correlation is good. This is used to correct the estimated packing densities throughout this chapter.

Packing Density and the Properties of Mortars and Concrete

In practice it has been found that the largest possible volume fraction of aggregate (and especially coarse aggregate) in concrete is advantageous with regard to strength and stiffness, creep, drying shrinkage, and permeability.

The cement paste may be considered the weakest part of the concrete. It is, however, necessary as a binder to hold the skeleton of sand and coarse aggregate

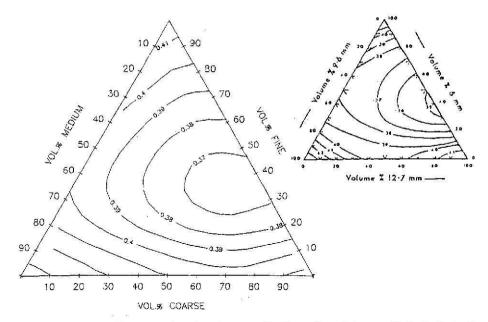


Fig. 13. Ternary diagram showing isoporosity lines in mixtures of steel shot of diameters 6, 9.6, and 12.7 mm as estimated by the models (bottom) compared to the experimental results of Standish and Borger (From Ref. 14, used with permission.).

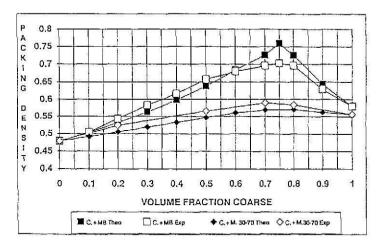


Fig. 14. Experimental binary packing densities of cement with sands of average diameters 0.038 (C.+ M.30-70) and 0.43 mm (C.+ MB) (Refs. 26,27) compared to model estimations.

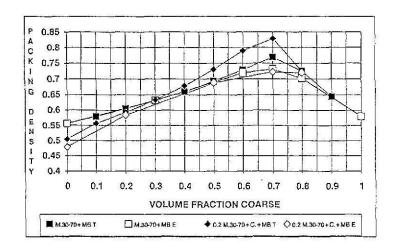


Fig. 15. Experimental binary packing densities of sands of average diameters 0.038 and 0.43 mm (M.30-70 + MB), and experimental ternary packing densities of cement and sand of diameter 0.43 mm with a constant 0.2 volume of sand of diameter 0.038 compared to model estimations (Ref. 27).

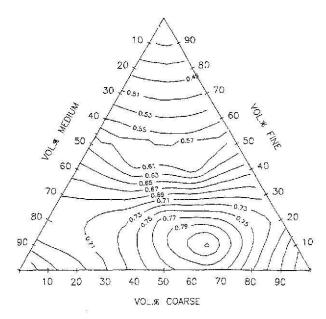


Fig. 16. Experimental determined packing density of ternary mixtures of cement, quartz sand (0-2 mm), and crushed granite (8-16 mm) (Ref. 27).

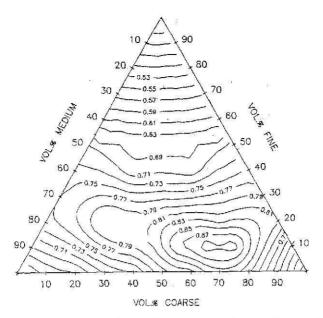


Fig. 17. Estimated packing densities of ternary mixtures of cement, quartz sand (0-2 mm), and crushed granite (8-16 mm).

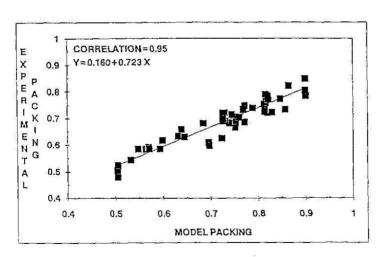


Fig. 18. Correlation between experimental and estimated packing densities for binary mixtures of cement and sand, and ternary mixtures of concrete materials (Ref. 27).

particles together. Assuming that the aggregate is sound and of high quality, it is advantageous to ensure that the aggregate skeleton is as closely packed as possible and to bind it with just the right amount of high-quality cement paste to fill the voids between the aggregate particles. This will give the best-quality concrete with regard to both mechanical and durability characteristics.

Concrete proportioning is usually undertaken by selecting water requirement, sand, aggregate, and cement contents as functions of required slump, maximum particle size and aggregate type, strength requirement, and so on, using empirically established tables. By taking the packing properties into consideration, additional information about the system is obtained as shown in the following examples.

Packing Density and Rheology

The area for normal concrete compositions, when represented in ternary diagrams, is small compared to the total area of the diagram. Small variations of the composition within this area often have, however, large effects on the rheological behavior of the fresh concrete. The rheological properties of fresh concrete or cement paste have been studied by many researchers. ²⁹⁻³¹ It has been found that the rheological properties of cement paste change with the chemical composition, specific surface area of the cement, mixing procedure, hydration time, and temperature. At fixed hydration time, temperature, and mixing procedure, the rheology of paste, mortar, and fresh concrete can be adequately described by the Bingham model:

$$\tau = \tau_0 + \eta \cdot \dot{\gamma}$$

where τ is the shear stress, τ_0 the yield stress (yield value), η the plastic viscosity, and $\dot{\gamma}$ the shear rate.

A model that specifically considers the effects of the particle-size distribution, temperature, the hydration process, and the composition has not yet been formulated. Neither do the models consider the effect of admixtures on rheology. Thus, it is difficult for a concrete designer to anticipate rheology and loss of flow based on known properties such as aggregate grading.

The results which will be discussed in the following paragraphs were obtained according to the Bingham model with mixer-type equipment for which the revolutions per minute and the corresponding power consumption were recorded simultaneously. In this way the revolutions per minute are proportional to the shear rate and the power consumption to the shear stress, and the plastic viscosity is represented by the slope of the graph in a plot of the power consumption in amperes versus the revolutions per minute. ^{26,27,29,32}

To investigate the possible relationship between the packing properties of ternary mixtures and their rheological behavior, a series of concrete mixtures using cement, sand (0-4 mm), and rounded coarse aggregate (8-16 mm) were studied²⁷ along horizontal lines in the ternary diagram of constant cement content (10 and 20 vol%), keeping the theoretical solid volume to the water volume constant. The packing density was altered by varying the volume fractions of sand and coarse aggregate. By keeping the total volume of water constant, the water-to-cement ratio became very high when choosing mixtures along the line of 10 vol% cement, but this was accepted in order to study the effects of variations in the packing of the solids.

For every concrete mixture, the Bingham flow curve was recorded, from which the yield value and the plastic viscosity were determined by linear regression. The results obtained, as well as the corresponding experimental packing densities, can be seen in Table I. The viscosity as a function of the yield value for all mixtures is plotted in Fig. 19. The figure shows that the minimum yield value is obtained at a sand content of about 30 to 40 vol% and the minimum viscosity is obtained at a sand content of about 50 vol%.

As can be seen from Table I, the packing along the horizontal ternary line of 20 vol% cement is nearly constant ($\varphi = 0.78$). As the packing density along this line is to be considered identical for *all mixtures*, the difference in rheology, as shown in Fig. 19, may be interpreted as being caused by the variations in the packing density of the sand and coarse aggregate. This is further substantiated by plotting the volume of the coarse aggregate in percent of the total volume of aggregate as a function of the yield value and the plastic viscosity (Figs. 20 and 21).

Table I. Mix Compositions of Cement, Quartz Sand (0-4 mm) and Coarse Aggregate (8-16 mm)

Mixture No.	Sand	Stone (Vol%)	Cement	w/c	φ	η • 10 ⁴ (amp • min)	τ ₀ (amp)
1	40	40	20	0.5	0.78	4.4	0.13
2	60	20	20	0.5	0.77	8.0	0.27
3	20	60	20	0.5	0.77	8.0	0.15
4	50	30	20	0.5	0.78	4.0	0.15
5	30	50	20	0.5	0.78	7.0	0.08
6	20	70	10	1.0		8.5	0.22
7	30	60	10	1.0	0.85	8.0	0.12
8	40	50	10	1.0		6.2	0.12
9	50	40	10	1.0	0.82	3.7	0.19
10	60	30	10	1.0		6.3	0.25

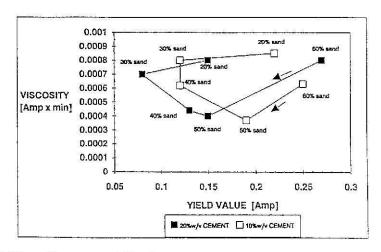


Fig. 19. Viscosity versus yield value for concrete mixtures using cement, sand (0-4 mm), and rounded aggregates (8-16 mm) (Ref. 27).

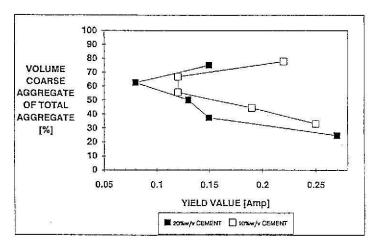


Fig. 20. Yield value versus the percentage of coarse aggregate of the total amount of aggregates (Ref. 27).

As can be seen in Fig. 20, the minimum yield value along both horizontal lines representing cement contents of 10 and 20 vol% is found at about 60 vol% of the coarse aggregate. This corresponds to the composition of maximum

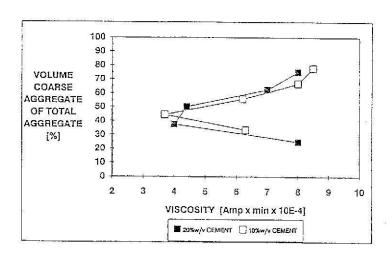


Fig. 21. Viscosity versus percentage of coarse aggregate of the total amount of aggregates (Ref. 27).

density in the binary system of fine and coarse aggregates. These results seem to indicate that the best workability of a concrete mixture is obtained with the densest packing of sand and coarse aggregate. This is in accordance with the findings of several researchers.^{33,34}

However, the observation that a concrete mixture has the best workability for mixtures with a composition corresponding to the maximum packing density of sand and coarse aggregate is only conditionally true. For low shear processing of concrete, it is the value of the yield stress, τ_0 , which is decisive for the workability. As can be seen from the Bingham model, at low shear rates $\eta \cdot \dot{\gamma} \simeq 0$ and, hence, $\tau \simeq \tau_0$. Under these conditions, a close correlation exists between the yield stress and the slump or flow value as measured by conventional workability test methods. ^{27,29}

For processes using higher shear rates, for example, intensive vibration or precasting involving the combination of vibration and static pressure, the size of $\eta \cdot \dot{\gamma}$ may exceed the size of τ_0 and the mixture with the best workability may therefore not be the mixture of the highest packing density and hence the lowest τ_0 , but the mixture of the lowest plastic viscosity.

These considerations are of major importance in designing mixture formulations for special applications, such as concrete to be pumped at high volume rates or zero slump concrete to be used for precast concrete.

Table II. Average Particle Size and Packing Density of the Cement, Sand, and Coarse Aggregates Used

Material	ď (mm)	$oldsymbol{arphi}_0$
Cement	0.017	0.5
Sand	1.37	0.659
Coarse agg. 1	13.6	0.485
Coarse agg. 2	14.3	0.743

Influence of Packing Properties of Components on the Packing Density of the Mixture

Evaluating the possible use of two different types of coarse crushed aggregates (8–16 mm) for concrete mixtures consisting of cement and sand (0–4 mm), the packing characteristics were studied by using the Aim and Goff and the Toufar et al. models.

The average particle sizes of the cement, sand, and coarse aggregates used, d', and the packing density, φ_0 , were determined experimentally, as shown in Table II. The coarse aggregates had similar average particle sizes, d', but significantly different packing densities.

Figures 22 and 23 show ternary diagrams of all possible combinations of the three components: cement, sand, and coarse aggregate based on volume percentage, by using coarse aggregates 1 and 2, respectively. There are two points of special interest in the packing triangle, namely:

- 1. The maximum packing density.
- 2. The volumetric composition at the point of maximum packing.

As seen from the figures, both packing triangles of Figs. 22 and 23 have a distinct packing maximum. In the triangles, the maximum packing slowly decreases toward the sand/cement side on the left, whereas there is a sharp decline toward the coarse aggregate corner to the right. This has certain practical consequences in that a concrete mixture with a composition to the right of the packing maximum will be more sensitive to component variations than a mixture with a composition to the left of the packing maximum. The position of the packing maximum varies greatly for the two mixtures, as shown in Table III. From the figures it is seen that the mixture with the coarse aggregate 1 has a packing maximum of 0.78, whereas the mixture with the coarse aggregate 2 has a packing maximum of 0.82.

A mixture based on coarse aggregate 2 will have a lower water requirement than a corresponding mixture with coarse aggregate 1 for the same workability

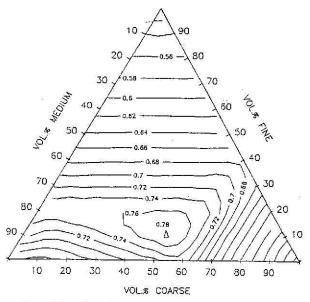


Fig. 22. Estimated packing densities of ternary mixtures of cement, sand (0-4 mm), and aggregate No. 1 (8-16 mm).

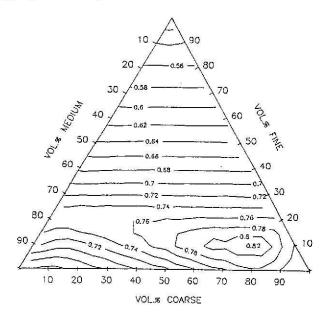


Fig. 23. Estimated packing densities of ternary mixtures of cement, sand (0-4 mm), and No. 2 (8-16 mm).

Table III. Mixture Compositions in Maximum Packing

Maximum	for coarse aggregate 1 mixtu	ıre	
	Cement	11 vol%	
	Sand	41 vol%	
	Coarse agg.	48 vol%	
Maximum	for coarse aggregate 2 mixtu	re	
	Cement	10 vol%	
	Sand	17 vol%	
	Coarse agg.	73 vol%	

and, as a result, will give a lower porosity and permeability in the hardened concrete.

Packing Density and Concrete Properties

The relationship between the packing density of concrete mixtures, their workability, and related properties²⁷ were studied on a number of mixtures using quartz sand and crushed granite in size fractions: 0 to 2 mm sand, 2 to 8 mm coarse aggregate, 8 to 16 mm coarse aggregate, and 16 to 25 mm coarse aggregate. Packing densities and average particle diameters were determined as shown in Table IV.

Figure 24 shows the estimated packing densities for all possible compositions of the three fractions of coarse aggregates. As shown in the figure, the maximum packing density, 0.62, can be achieved with the following composition: 35 vol% coarse aggregate (2–8 mm), 25 vol% coarse aggregate (8–16 mm), and 40 vol% (16–25 mm). Figure 25 shows the packing triangle of the ternary mixture consisting of cement, sand, and the combined coarse aggregate with maximum packing density. The maximum packing density of 0.8 can be achieved with the combination, as shown in Table V. As in the previous example, the mixtures with maximum packing constitute a flat area in the "coarse" section of the packing triangle.

The relationship between the workability of fresh concrete and the characteristics of hardened concrete was studied by casting concrete of 26 different mixture compositions with a fixed water-to-cement ratio of 0.5, as illustrated in Fig. 26.

The qualitative interpretation of the results of the workability of the fresh concrete is shown in Fig. 27. The various hatchings indicate the workability behavior of the mixtures investigated: whether they separated, showed signs of bleeding, were moldable, and so on.

Table IV. Packing Densities and Average Particle Diameters of Concrete Materials

Material	d' (mm)	$arphi_0$
Cement	0.022	0.480
0-2 mm sand	0.85	0.658
2-8 mm coarse agg.	6.8	0.561
8-16 mm coarse agg.	17.3	0.555
16-25 mm coarse agg.	24.1	0.552

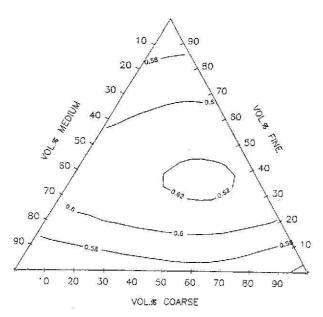


Fig. 24. Estimated packing densities of ternary mixtures of crushed granite aggregates: 2-8 mm, 8-16 mm, and 16-25 mm (Ref. 27).

From investigations of the mixtures' porosity, permeability, compressive strength, and the slump it was found that the minimum porosity, the minimum permeability, the maximum slump, and the maximum compressive strength were achieved for the mixtures with the maximum packing density (in Figs. 26 and 27 for mixtures on the line of 66 vol% aggregate of sand plus aggregate in the moldable area). The results of the tests of various concrete properties of samples positioned within the compositional area of concretes that were moldable are given in Table VI.

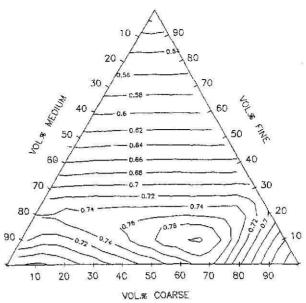


Fig. 25. Estimated packing densities of ternary mixtures of cement, sand (0-2 mm), and the combined coarse aggregate corresponding to the composition with maximum packing density in Fig. 24 (Ref. 27).

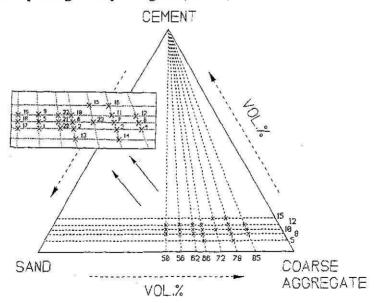


Fig. 26. Position in the ternary diagram of the concrete mixtures used for relating the properties of fresh and hardened concrete (Ref. 27).

Table V. Mixture Composition of Maximum Ternary Packing Density

Cement	10 vol%
Sand	28 vol%
Coarse agg.	62 vol%
	Sand

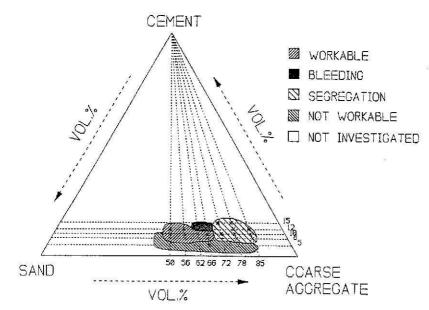


Fig. 27. Qualitative evaluation of the properties of the concrete mixtures in Fig. 26 (Ref. 27).

Consistent with experience, the binary packing densities of the two coarsest components, sand and aggregate, appear to be the most influential with regard to the concrete's flowability. The practical consequence of this is that the concrete with the best workability with a given cement content and water-to-cement ratio can be reached with a sand-to-aggregate ratio equal to the maximum binary packing of these elements. At higher cement paste contents, the concrete, of course, appears more workable. As can be seen, the packing of the concrete materials has an important effect on the properties of hardened concrete indirectly through its effect on the workability and compactability.

Summary and Conclusion

In this chapter we have summarized models describing the packing density of particles, with emphasis on binary and ternary mixtures of concrete raw

Table VI. Properties of Concrete Mixtures Investigated

	Cement	Ratio Sand/					Rapid Chloride
Mixture	Content	Coarse	Slump	Strength	Density (4,5,4,5)	Porosity	Perm.
TAO.	(0/10v)	Agg.	(mini)	(IMICA)	(mga)	(v017/0)	(contoure)
17	œ	20/20	0	14.4	2288	15.9	> 5000
	∞	44/56	0	17.9	2279	15.3	> 5000
20	∞	38/62	0	18.2	2362	13.4	> 5000
2	∞	34/66	0	17.5	2374	11.5	>2000
					81		
18	10	50/50	7	19.8	2352	13.5	4157
5	10	44/56	2	22.3	2361	11.5	3003
21	10	38/62	15	25.7	2388	13.3	3382
9	10	34/66	35	44.6	2435	11.0	1802
19	12	20/20	14	19.4	2372	13.8	4019
6	12	44/56	120	34.5	2403	12.2	2972
22,	12	38/62	58	25.2	2469	10.2	2940
10.	.12	34/66	į	25.7	2470	11.4	2929
				57.50			

'Bleeding and segregation observed.

materials. For monosized, spherical particles the correlation between the experiments and the models is usually good. Concrete materials are neither monosized nor spherical, but it is nevertheless possible to obtain a good correlation between the estimated values for the packing densities and the experimental results. With regard to practical applications of the packing models and a thorough understanding of the properties of the fresh and hardened concrete, it is important that information about variations in the packing density caused by variations in either the mix composition or the properties of the components can be obtained by means of the models from a minimum of experimental data.

The flow properties or the workability are important parameters for the mixing process and the placement of fresh concrete. These parameters may be difficult to quantify. For certain types of concrete, the Bingham model is an adequate description and, as indicated by the examples, there seems to be a close relationship between the rheological properties and the packing density of the concrete mixture. Taking into consideration that the concrete microstructure is controlled by the rheological properties of concrete during the mixing and placement processes, while the durability of concrete largely depends on the inherent microstructure, the packing density and its control suddenly take a central part in the proportioning of concrete.

The representation of the packing densities estimated by the models in a ternary diagram makes it possible to survey the variations of packing densities for all combinations of the materials in question. From the "packing triangle" it is then simple and quick to estimate the highest packing density and the corresponding composition with the given materials.

In concrete proportioning it is then possible to evaluate the effect of combinations of a large variety of mixture components for various manufacturing processes with regard to the optimization of porosity, workability, shrinkage and creep, special economical considerations, and so on.

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