Cementitious Materials-Nine Millennia and a New Century-Past, Present and Future

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http://www.cv.titech.ac.jp/~otsuki-l/o-cj-labo.html

Abstract

- In this century where sustainable construction is becoming an overriding considerations.
- To develop composite formulations of a high level performance.
- This paper reviews the past, present and future of cementitious materials and highlights the need for a comprehensive approach to maximize the advantages of the newly emerging cementitious materials and concrete.

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Introduction

- Construction has been an important element for society.
- Materials are at the top heart of the construction industry. 材料がないと始まらない。理論や計算も
- Innovation in construction is highly linked with development of advanced construction materials.
- Cementitious materials have been with us more than 9 millenia.

- Most of the cementitous materials can be considered calcareous. Their overall composition is defined within ternary diagram CaO-SiO2-Al2O3 in Fig.1.
- Do you know how to read the % of components? 今日の問題

In 1824

- A three-stage process for producing hydraulic cement was first developed by Joseph Aspdin. This process includes;
- 1. calcining limestone, calcine：か焼(焼いて揮発物質を除き灰状物質にする)
- 2. burning it with clay
- 3. recalcining the mixture to obtain the final products
- Aspdin called this product “portland cement”.

- In Japan, “portland cement” was firstly imported from France, to construct a dock in Yokohama. It was very expensive.
- In Fig.4, development over time of quality of Portland cement as characterized by strength of 1:3 (cement: sand) mortar cubes are shown.

Evolution of scientific foundations

- The foundations for the chemistry of cement were studied by Le Chaterie, a very famous chemist of France.
- The four composition were alite, belite, celite and felite.
- Ternary system CaO-SiO2-Al2O3
- In 1884, a reinforced system was patented.
- In 1927, Fressyinet developed the pre-stressing concept.

High temperature chemistry and cement production

The high temperature reactions of clinker formation can be divided into 5 steps.

1. 500-800C: Decomposition of clay minerals
2. 700-900C: Decomposition of calcite
3. 1000-1300C: Reactions calcite, quartz and decomposed clays to form C2S
4. 1300-1450C: Facilitate the formation of C3S through the reaction of C2S and lime.

- (So, from the point of energy saving, C_2S is better.)今、ビーライトセメントがブーム
- 5. During cooling, where liquid crystallizes forming the aluminate and ferrite phases.
- Notice: One particle may contain several phases.
- Much attention was given to the optimization of the clinkering process and the grinding thereafter with gypsum.

- 10月8日
- In 20th century, the aim is early strength, so it requires small particles and more C_3S. It means more energy.
- In recent years, much of change in the production processes has been driven by energy and environmental aspects.
- There is an increasing tendency to use wastes as partial replacement for the fuels and raw materials.

- The overall composition and burning process are affected by the ratio between the four major oxides in the raw materials, CaO, SiO2, Al2O3, Fe2O3.
- Silica ratio increases, then burnability reduces.
- Special attentions has been recent years to the influence of minor components.
- For example, the contents of alkali in cement can become higher.アルカリ成分
- Q: why?

Materials science of cement and concrete

- The hydrating behavior of hydrating cement and the concrete were studied on the chemistry of hydration reaction.
- These were followed by studies of microstructures and internal bonding using many techniques such as electron microscope, absorption isotherms, mercury porosimetry, etc.
- These serves as a basis for developing advanced systems and solving problems.

Chemistry of Cement

- In fig.5, the rates of reactions of the individual minerals and the hydration products formed.
- The process can be divided into several stages.
- 1. Pre-induction period: first few minutes (ion dissolves into water.)
- 2. Dormant stage: a few hours

- 3. Acceleration stage: 3-12 hours
- 4. Post-acceleration period: diffusion controlled process
-

- The K+,Na+ and SO42- ions are highly soluble.
- Then Ca2+ ions dissolve into the liquid slower rate.
- Therefore the pH of the pore solution is greater than 12.5 which is characteristics of a saturated Ca(OH)2, sometimes as high as 13.5, depending largely on the soluble alkalis contents.

Composition and microstructures of hydrated cement paste

- The major phases of the hydration products are; C-S-H, CH, sulfo-aluminate hydrates (ettringite- C3A-3CaSO4-31H2O, monosulfate- C3A-CaSO4-12H2O)
- The composition and structures are not so clear.
- In particular, the C-S-H are largely amorphous and show variety in their structures.

- They depend on many factors such as cement, w/c, and curing conditions.
- You should notice that cement paste is still a “live” system after many years.
- Even after many years, unhydrated grains always exists. Do you know the grain sizes?
- The hydrated phases are easy to change under environmental conditions, such as carbonation.
- 50μｍ以上のものは25年経ても残っている。

Three traditional models

- In Fig.6, three of the “traditional” models are presented.
- A. Powers’ model: the concept of types of pores- capillary and gel pores- is very important.
- In table1, characteristic size range of porosities in hydrated cement paste is shown.

- B. The microstructure of C-S-H is under discussion. This model can explain the role of waters – capillary water, interlayer water, and physically absorbed water.
- C. This model can explain the influence of spaces, namely, very low physical interactions for bigger spaces and stronger ones for smaller ones.

Variabilities (changes) in composition and hydrates

- Variabilities in composition in space that can be interpreted in terms of three main compositional regions:
- 1. Regions high in Ca and Si, low in Al and Fe – high in C-S-H.
- 2. Regions very high in Ca, low in Si, Al and Fe – high in CH.
- 3. Regions high in Ca, Al, and Fe and low in Si- high in monosulfate (AFm) and ettringite (AFt).

- In table2, average compositions of these phases, C-S-H, CH and Afm are shown.
- In a mature paste, polymerization (-Si-O-Si-) may be driven by conditions such as carbonation or drying. It may be one of the causes of irreversible shrinkage under carbonation and drying condition. (Also, cracks are causes.)

Composition and microstructure of concrete

- Concrete is not uniform.
- Several level of heterogeneity may be induced.
- First level is associated with the rheological characteristics, affecting the distribution of the cement and filler particles in the mass as well as effects such as bleeding.
- For the first level, of course, ideal dispersion is difficult to achieve.

- Second level may be due to aggregate- paste chemical interactions.

- There is an inherent "wall" effect.
- The coarser particles cannot pack near any surface.
- Since the cement particle distribution is in the range of 1-100um, a zone of about 10-50um is formed around surface, including aggregate surface, where w/c is higher.

- The hydrated structure of this zone is more porous. We call the interfacial transition zone.
- In fig.7, gradients of porosities at ITZ are shown.

Influence of ITZ

- Probably it's influence on strength and elasticity is moderate or small (-20%).
- The influence on transport properties may be larger. (We are doing research on this matter.)
- Bleeding creates a different micro-structure beneath aggregate and steel bars.

Modeling of concrete behavior

- There have been many models describing mechanical performance and transport characteristics. 力学的性質、物質移動、経時変化モデル
- Micro-structural modeling, modeling of transport properties, modeling of mechanical properties, modeling of time-dependent properties

Micro-structural modeling
微細構造モデル　10／16

- The computer models may be a good tool to predict many effects.

Modeling of transport

- The modeling frequency considers combined flow mechanisms of diffusion and convection, diffusion and permeation, and diffusion and electro-migration.
- Also, we should consider about mass balance including chemical and physical binding.
- In my lab., we developed an ion-transport model considering diffusion and electro-migration.
- 拡散、電気泳動、移流、マスバランス、電気バランス（キルヒホッフ）

Modeling of mechanical properties

- 1. As uniform porous materials, eqs.(3) and (4) are still can be used today (page 9).
- 2. Consider about the role of aggregates, fillers and fibers. For this purpose, concepts of composite materials and fracture mechanics can be applied.
- 3. Then the matrix-inclusion interaction is characterized.
- In fig.8., fracture process zone in front of advancing crack is shown.
- For these matters, Prof. Niwa can make better explanations.

Modeling of time-dependent deformation 11/13

- This pertains to shrinkage during drying and creep under load in combination with drying.
- There are numerous models, the earliest one may be with springs and dashpots. (which are adjusted by experimental results.)ﾀﾞｯｼｭﾎﾟｯﾄとバネモデル
- So complicated.

- 1. Taking into account a variety of interaction of water molecules with the hydrated material.水分子と水和物
- 2. including capillary stresses, disjoining pressures, surface tension and inter layer water movement.

毛細管圧力、表面張力、内部水層の移動

- 3. considering collapse of pore structure and chemical reactions.

空隙構造の破壊と化学反応（不可逆となりやすい）

Fresh concrete: rheology and admixtures レオロジー

- The properties of fresh concrete are important to determine mix proportions in which the concrete can be transported placed and consolidated.
- For usual concrete, the slump test may satisfy our requests. (directly related to yield stress.)
- However, for high performance including high flowable and self compacting concrete, we should study about rheology.

- Rheological properties are related to the various modes of suspension.
- In Fig.9: agglomerated, dispersed and dispersed with micro-fillers.粒径測定法も説明
- The stress and strain-rate behavior of cement paste and concrete can be approximately modeled as Bingham fluid with a yield stress and apparent viscosity. (very roughly Fig.10)
- 降伏応力と見かけの粘性
- At the yield stress, agglomerated particles will be dispersed and flow.

Water reducing chemical admixtures: also better fluidity

- Traditionally, the mix proportions of concrete are optimized to obtain a required slump with minimum segregation.最小の材料分離
- Then the situation is largely overcome by the use of various water reducing chemical admixtures.
- I can say Japan is the No.1 in this technology. Partly because of lack of good aggregates.

- Roughly:
- Air-entraining: 5%
- Water- reducing: 10%
- Super plasticizer: 15-20%
- High water reducing air-entraining admixture: 20%+ time
- In fig.12, the concept of steric hindrance is shown. For keep concrete fluidity longer time. Why?

Micro-filler effect
SF:シリカフユ-ム silica fume

- Another advanced concept of improving workability in low w/c (say less than 30%) is shown in fig.9(c).
- Here the microfiller particles, for example, SF particles serve to improve flowability.
- A rheological measurement of self-compacting concrete (SCC) is shown in fig.10. (low yield stress and plastic viscosity)

Sustainability and cementitious materials

- The ecological impact is becoming a factor of importance in the field of concrete.
- 1. Binders: less energy and less greenhouse gases, especially CO2.
- 2. Use by-products and recycled materials.
- 3. More durable over time.

Energy consumption- binders

- In these few decades, the energy consumption reduced from 5000KJ/kg to 3000KJ/kg.
- CO_2 emission $\propto$ energy consumption

- Several strategies
- Major reaction phase changes from alite (C3S) to belite (C2S). 20%saving (it is also good for reducing heat of hydration and less thermal cracks.)

- Activation of slag by alkalis (in eastern Europe – Poland)
- Blended cement or use of mineral admixtures, such as fly ash, blast furnace slag power and others. (this may be the best.)
- Also, developing binders with no cement. (steel making slag + blast furnace slag +fly ash + water)

Blended and composite cement11 ／20

- In table3, typical range of composition of GBFS (grounded blast furnace slag), Fly ash and SF (silica fume). Fly ash – low lime and high lime.
- In table4, blended and composite cements according to ASTM and EU.
- In Japan, BFS (5-30-70%)(cement 95-70-30%), FA(5-30%)(cement95-70%), SF(5-10%)(cement 95-90%)

Mineral admixtures can be classified (in terms of the nature of their reactivity)

- Latent hydraulic minerals（潜在水硬性）: one example is BFS powder (high lime FA) . They can react with the presence of activator (cement or alkalis ion). Thin film on the particle may be destroyed by the activator.（薄い皮膜がアルカリで破壊され反応が進む）

- Pozzolanic minerals: They have no-cementing properties. They require activation by $Ca(OH)2$. Examples are low lime FA and SF. metakaoline
- Non reactive powder: lime stone power etc. some reaction on the surface.

Recycling　日本は結構進んでいる

- We should use recycling materials, such as industrial by-products, concrete wastes.
- Japan is most advanced in this field. In fig.16, a schematic presentation of the wastes and their use in Japan is shown.
- It is difficult to make quality assurance of waste materials.
- 区分H, M, L

Long-term performance

- In these days, issues of long-term performance is very important.
- The reasons
- 1. Alkalis aggregate reaction: Now we are going to use unused or marginal aggregates.
- 2.Up to now, concrete structural design was made by consideration of optimization of the structural stability. Not so much consideration on long term performance.

- 3. Use of $CaCl_2$ for deicing, it is leading to corrosion.
- 4. Workmanship quality has declined.
- Those mean; If nothing is done – the durability will be decreased.
- Also; we need more durable concrete structures. From the viewpoint of sustainability. Esp., Japan, our economy and population will be smaller.

For better durability

- Quantifying or clarifying mechanism of diffusion of ions, permeation of fluids and capillary absorption.
- On this basis we can make an estimation of life-cycle.
- In fig.17, an example in the case of steel corrosion is shown.
- Incubation, progress, accelerated, and deterioration periods defined by JSCE and other organizations.

Many researches

- In Table5, recommended limiting values for concrete composition and properties against classified exposure conditions. This table is in EN206. (In my opinion, life time may be 50 years.)

Advanced means to provide extensive life 長寿命化

- From the viewpoint of materials.
- 1. Use of pozzolans
- 2. Use of low W/C.
- 3. Use of special chemical admixtures (for example: inhibitor)
- 4.Sealing of concrete with polymeric and inorganic materials
- 5. Stainless steel
- New rehabilitation methods (including electro-chemical methods)

Do not neglect the influence of curing

- We should take care of making a good concrete skins on the exposure surface of concrete. スキン
- In fig.18, concept of concrete cover and skin. In b shows its moisture state, and in c shows the influence of curing.
- (In my lab., this theme will be done.)

Advanced cementitious system11·27

- In the future as well as in these days, the cost of construction materials should be cheap.
- So the trend may be to use normal portland cement with mineral admixtures, it means including blended cement.
- Fillers, fibers, polymers

High-strength/high-performance system

- In fig.19, rough concept of the development of the strength is shown.
- Very low W/C ratio can be achieved by the development of high range water reducers and dense packing. The dense packing can be achieved by the use of SF.
- Now we can use over 100MPa strength concrete. It was used Petronus twin tower buildings (Kuala Lumpur). Over 200MPa in Musashi-Kosugi.

High strength concrete

- The weakest link is the aggregates (and ITZ). So we should use strong aggregates.
- Also the ultra high strength system known as DSP (densified cement/ ultra-fine particle based material) was proposed.
- Then the better grading for dense packing has been researched again.

however

- Low water-binder ratio increases the sensitivity to early age cracking and also the influences of cracks on corrosion is very large.
- This is related to combined effects of autogeneous shrinkage and heat of hydration induced by the high amount of binders.
- 現場では、それなりの人員、施工管理、（最初の２－３はOK）

Special workability characteristics

- These high-strength concrete have special workability characteristics, esp., very small segregation because of high viscosity with high amount of small particles.
- So, high-strength concrete can be self-compacting concrete.

Fiber-reinforced concrete

- In Japanese old houses, there are walls made by mixing straw and clay.
- In these days, fundamental studies have done and many kind of fibers can be used with cementitious materials. The fibers should be durable in alkaline conditions and should have a good bond with concrete.
- Low content (0.1% volume) of low modulus fibers are used for control of plastic shrinkage cracks.

- Higher contents of steel fibers (0.5-1.5% volume) are used for reinforcing concrete to replace steel mesh in shotcrete.
- Anyway, the current application of fibers is largely for purpose of crack control. However, the trend is the second purpose.（補強用も増加）

Cementitious materials of high tensile strength

- There have been many attempts.
- Simplest one: To reinforce the matrix with a relatively large content of steel fibers (10%).
- Materials with water soluble polymer with cement. In this case, compressive strength 300MPa and tensile strength 150MPa were achieved.

Cont.

- A modified concept was suggested based on strategy of using short and long fibers with densified matrix.
- In France, combining in the graded fine material, a fraction of graded quartz with particle size smaller than 600um, is termed RPC (reactive powder concrete). (Prof.Niwa’s lab.)高価、それなりの使用法必要
- As matrix, MDF (macro-defect free) can be used. あるものは水溶性ポリマーと

Future trend

- Only near future (20 years) trend
- Ecological constraints and environmental regulations will be stronger.
- For greater use of industrial by-products, special low-energy cements, locally available alumino silicate materials.

Cont.

- "Cement Industry" may be changed to "Hydraulic binder industry".
- Related to sustainability and LCC (life cycle cost)
- For BOT (build, operate, (own) and transfer), high tensile strength concrete may be reasonable in spite of high material cost.
- Innovative testing methods in site will be urgent need.

Summary and conclusions

- Cementitious materials have been used for thousand years and will remain the main construction material in this new century.
- (I would like check the long term performance of new materials. Also, I prefer normal concrete.特に、途上国、普通の材料・技術を間違いなく使う。のが重要、普通の材料がなくなるのをなんとか補うのが近未来)