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SPECIAL REPORT

10th INTERNATIONAL CONGRESS ON THE CHEMISTRY OF CEMENT

(Monday, June 2 to Friday, June 6, 1997, Göteborg, Sweden)

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Chemistry of Cement congresses started with a one day meeting in London in 1918 when setting of cements and plasters were discussed. This was followed by International Symposia and Congresses in Stockholm, 1938; London, 1952; Washington, 1960; Tokyo, 1968; Moscow, 1974; Paris, 1980; Rio de Janeiro, 1986, and New Delhi, 1992. Sweden was honored to host the 10th anniversary of the International Congress on the Chemistry of Cement ICCC. The Jubilee congress was organized at the Swedish Congress Center (Svenska Mässan Congress) in Göteborg from June 2 to June 6, 1997, with Prof. F.P. Glasser as chairman of the Scientific Committee and Dr. H. Justnes as secretary.

There were 400 delegates from 45 countries. The major delegations were from Japan (36), Germany (36), France (33), Sweden (26), USA (21), U.K. (21), Italy (13), and India (13). A total of 330 papers from 40 countries were accepted for presentation and publication in the proceedings after careful scrutiny by the international leading scientists. The proceedings have been published in 4 volumes and are available through the editor and congress secretary H. Justnes, SINTEF, Trondheim, Norway.[1]

The congress was divided into five main themes, which included the introduction of two new topics focusing on "Utilization of Admixtures" and "Developments in Characterization Techniques." Three plenary lectures were delivered by invited speakers: Wieker et al., "Recent Results of Solid State NMR and its Possibilities of Use in Cement Chemistry;" Scrivener, "Microscopy Methods in Cement and Concrete Science;" and Mullick, "Why Concrete is not Always Durable." The other papers were presented in five parallel sessions.

The five themes of the congress are listed below.

Clinker Production

New process, low energy clinker formation, utilization of industrial by-products and wastes, application of mineralizers, modifiers and activators, correlating process parameters with clinker properties, clinker structure, and mineralogy.

In this section new processes for making clinker were highlighted. Development of special cements, use of kiln dust for clinker production, thermo-chemical activation of clinker formation, and melting process for clinkerization were reported. Influence of grinding on the quality of cements was also shown. Cement clinker formation from fly ash using microwave

[1]For North America, these are available from the Portland Cement Association.

processing attracted attention as it substantially cut short the sintering process. Low energy clinker formation, high-quality cement with low energy consumption, and the formation kinetics of C_2S by liquid state reaction were reported. Use of industrial waste as a fuel for production of cement was also highlighted.

Portland, Blended, and Special Cements

Rheology, hydration kinetics and microstructure development, structural models for hydrated cementitious pastes, chemical and physical shrinkage, influence of blends or additions of combustion ash, slag, silica fume, colloidal silica or rice husk ash, influence of mixing techniques, and curing conditions.

It was reported that flocculation of silica fume in cement paste can lead to alkali-silica reaction. There are no current methods for preventing the flocculation of silica fume. This flocculation creates uneven distribution of water, which subsequently leads to uneven hydration creating more heterogeneity in the concrete. Consequently, standard deviation increases. Besides this, there is an aesthetic problem in using silica fume. It is shown that the Silica Colloid, newly developed by Eka Chemicals, Sweden, reacts spontaneously with calcium hydroxide to produce C-S-H. This, being synthetically produced, is chemically pure and has a very high specific surface area. The addition of a small amount produces early high-strength mortars and concretes. It does not influence the color, and hence its use in white Portland cement, high-alumina cement, and lime-based mortars will be unique.

Utilization of admixtures, water reducers and polymers

Mechanisms, chemical admixtures and cement interactions, influence of admixtures in the microstructure development, combined admixture and their mixing techniques, influence of type, dose, addition time, and mixing time.

There was concern that the mechanisms of interaction involved with different binder systems and their influence on the microstructure development, instead of getting clearer, are becoming more complicated. Dose of admixture, their addition time, and mixing time play decisive roles in the properties of concrete in the fresh and hardened state. Pretrials before use are recommended.

Performance and Durability of Concrete and Cement Based Systems

Pore structure and its influence on the permeability and diffusivity of gasses (CO_2), liquid (water), and dissolved ions (chlorides), physico-chemical (sulphates), thermal, and synergistic effects, cement aggregates compatibility (e.g., alkali-aggregate reactions) and structure-performance relationships, influence of physico-chemical aspects during early material history on durability (e.g., high during temperature-secondary ettringite formation), modeling of degradation process, and life-cycle analysis.

Synergistic effects occur that affect the modeling of the degradation process; consequently, the life-cycle analysis is becoming difficult.

Development in Characterization Techniques

Nuclear magnetic resonance (NMR), X-ray diffraction (XRD), diffraction by synchrotron radiation or neutrons, scanning microscopy, and other techniques.

The use of NMR as a characterization technique has very much increased in the last 5 years. Many papers have been presented showing possibilities and limitations of this technique. The last day was devoted to the parallel open discussion groups on special topics like "Delayed Ettringite Formation;" "Chloride Binding and Ingress;" "Autogenous, and/or Chemical Shrinkage;" "Alkali Activation;" and "Active Belite." A summary of these group discussions as presented in the plenary session are briefly discussed below.

Alkali Activation

Alkali activation of slag is reported with the addition of sodium silicate, NaOH, Na_2CO_3, KOH, etc. It is shown that the setting time and early strength are improved. Early hydration and the microstructure development depend upon the nature of the activator used. The activation mechanism proposed is an attack on the SiO_2 or Al_2O_3-SiO_2 framework by OH ions, and the most possible hydration products are CSH gel and a hydrotalcite-type phase. It is also reported that sodium sulphate-rich waste can also be used as activator. It increases the early strength of blast furnace slag cements without affecting long-term compressive strength. Activation of metakaolin is also presented. It is shown that the activation depends upon the reactivity of metakaolinas, which consequently depends upon the specific surface area. High strengths are obtained using hydrothermal conditions (85° C, 2 h). It is a debatable subject and needs more research.

Active Belite

Active belite has been produced by rapid quenching of clinker. Activation increases with increase in the fineness. Its production by liquid-state (hydrothermal) reaction between lime and silicic acid via synthesis of intermediate C_2SH and by thermo-chemical stabilization of the more active high-temperature modification of C_2S were reported. Formation kinetics of active belite and their properties were discussed. Research has been done at various levels but there are many questions yet to be answered for industrial production of active belite.

Autogenous-Chemical Shrinkage

Autogenous shrinkage (AS) of concrete is a macroscopic volume reduction caused by hydration of cement and is significantly affected by the type of cement and the hydration process. Because AS strain of cement paste depends on the hydration of each mineral compound, it is equal to the sum of the strains due to these hydrations. The AS in the case of concrete is lower than that of the cement paste because of the presence of the aggregate particles. Models for calculating AS at a certain age by the mineral composition and the hydration ratio of each compound were proposed. It was shown that AS increases with increase in C_3A and C_4AF content. This enables calculation of AS of concrete with different types of cement at various water-to binder ratios. It was further shown that the external chemical shrinkage value of hydrating cement paste is highly dependent on the measuring

procedure. For example, the static method is unable to deal with the influence of bleeding at medium and high W/C ratio; whereas the rotation method does not take into consideration the bleeding of the cement pastes. It was emphasized that the rotation method is the best to obtain a "true" AS curve, especially to establish the knee where the shrinkage curve indicates that a skeleton is formed by the hydration allowing empty pores to form. Exothermic hydration of cement is accompanied by a chemical shrinkage leading to the internal volume change. A strength model based on chemical shrinkage volume was introduced for cement paste.

It was shown previously that the AS increases with a decrease in W/C and for the concrete containing silica fume. Further, it was shown that the AS is also dependent on the type of aggregate. For example, it is larger with limestone aggregate than with sandstone. It was shown that, in the case of high-performance concrete, the AS is dependent on the age, W/C, and type and content of silica fume. It is also related to the decline in the internal relative humidity. The use of some shrinkage-compensating admixtures was also reported.

It was concluded that there is a need for a more clear definition. We are still at a very early stage in research. It is a real issue especially when we deal with a low water-to-cement ratio. More data is required relating material properties, influence of chemical and mineralogical admixtures, and water-to-cement ratio on the Autogenous-Chemical Shrinkage.

Delayed Ettringite Formation (DEF)

Delayed ettringite formation is drawing attention and is a debatable subject. Many times the conclusions are drawn based upon, for example, microscopic pictures showing phases without support of complementary data. It is insufficient to postulate the distress of concrete due to the DEF. It was shown that the DEF formation is related to the cement composition and curing conditions, especially the temperature. Microanalysis has supported the hypothesis of DEF formation within CSH gel. In another paper it was reported that the DEF formation is not only temperature-dependent, it can occur when the hardened concrete is exposed to varying climatic conditions like frequent wetting and drying or freezing and thawing. It depends amongst other factors upon the moisture transport and other substances within the concrete structure. This enables the primary ettringite dissolution in the pore liquid and recrystallization in the larger pores and cracks. This process is, however, accelerated at higher temperature due to intensive drying. The artifical air voids produced by the use of air entraining admixtures can also be filled by DEF and consequently will not be available to fulfill their role in enhancing freeze-salt resistance of concrete. Thus, DEF can also be a party in freeze-salt damage of concrete. It was also shown that ASR can promote DEF formation. Based upon some research it is suggested that precuring at 65° C for 3 h avoids delayed ettringite formation.

It is inferred that nomenclature of DEF is to be developed. Causes of delayed ettringite formation like insufficient precuring time and temperature, role of alkali, influence of alkali-silica reaction, and carbonation are to be established. Measurement and identification methods are also to be explored.

Chloride Binding and Ingress

Chloride diffusion is tested by different methods that are very controversial. There is no good internationally accepted test method. The use of mineral admixtures, on the one hand,

improves the resistance to chloride ingress but it needs more water for making the concrete. This is optimized with the use of superplasticizers, which increases the shrinkage. Further, the chloride intrusion into concrete is a time-dependent phenomenon that involves both physical process and chemical interactions. Swamy has shown that the chloride diffusion measurements are based on the assumption that chloride penetration is a one-dimensional process and the diffusion coefficient derived from the tests does not represent what happens in practice. The process involves chloride transport both in the vertical and lateral directions. A two-dimensional diffusion model is proposed based upon the tests results obtained after long time exposure of reinforced concrete slabs comprised of cyclic ponding with 4% sodium chloride solution for 7 days and drying in ambient air for 3 days.

A criterion for assessing the quality of concrete is needed. More research is needed to develop a more realistic and reliable test method of international understanding.

This was followed by a special session, led by Mrs. H. Seniz Yalcindag of UNIDO, Vienna, Austria, emphasizing the environmental and ecological problems of vital global interest. In the Western world, people are more conscious about atmospheric pollution and take some measures to reduce it; whereas in the developing countries it is of more concern and needs the attention of the international organizations. The use of industrial and agro-waste was also elaborated, which do not only solve the ecological problem but also significantly increase the durability properties of the building materials. However, there are problems in their use as the technology is still not very well developed. Therefore, pretrials are to be done before use even if the technical aspects are known in some places.

Dr. A.K. Chatterjee has stated that, in India, special care is taken in controlling the environmental problems. One of the examples given was the use of CO_2 emitted from the cement kilns in making CHN. Similarly, Dr. Y. Kihara of Brasileria Cimento Portland discussed the use of 18,000 tons of waste in Brazilian kilns without hampering the cement quality.

The next ICCC will take place in South Africa in the year 2003.