CHAPTER 1

INTRODUCTION

1.1 FIELD OF STUDY

Concrete is the most commonly used construction material. Its component materials are widely available and cheap, and it is cost-effective compared to the other main structural materials. The flexible of fresh concrete makes it easy to cast different shapes, forms and sizes. Additionally, the concrete industry is faced many important challenges such as, technical, economical and environmental. On the technical side, although it may be relatively easy to attain the level of strength required by design criteria, development of criteria for a durability based design is still an open field. Numerous agents and mechanisms are known to be able to cause the degradation of the quality of concrete with time. Examples include aggregate-alkali reaction, carbonation, chloride ingress, delayed ettringite formation, pure water attack, microbial attack and internal or external sulfate attack. Many of these mechanisms of deterioration may be related to the microstructure of the material (Bijen 1996 and Tixier, 2000).

The economical side concerned with the relatively high cost of Portland cement. Because the manufacturing of Portland cement is highly energy-intensive complicated process, consists essentially of grinding the raw material, mixing them intimately in certain proportions and burning in a large rotary kiln at a temperature of up to 1450 ºC, where, the material sinters and partially fuses into balls known as clinker. The clinker is cooled and ground to a fine powder, with some gypsum added, the resulting product is the commercial Portland cement widely used throughout the world (Neville, 1998).

The process of manufacturing Portland cement causes many environmental air pollution problems by releasing significant quantities of carbon dioxide to the atmosphere. The carbon dioxide can be released from the combustion of the fuel and from the calcinations of the calcareous rocks which are part of the raw materials. Also, the world yearly cement production is about 1.6 billion ton, accounts for about 7% of the global loading of carbon dioxide into the atmosphere (Mehta, 2001).

Meanwhile, environmental pollution generated from the waste by-products in industrial sectors, is a serious problem allover the world. These include air-cooled slag, silica fume, fly ash and dealuminated kaolin. These waste materials being produced in large amounts occupy valuable space to be stockpiled or disposed in landfills, and present environmental hazards such as dust contamination or leaching of heavy metal in the groundwater (Puertas et al, 2000 and Mostafa et al, 2001a, Ahmed, 2009).

One of the proposed solutions for this problem is to recycle these waste by-products (air-cooled slag, silica fume and fly ash) to partially replace Portland cement in concrete industry. This could reduce the amount of waste disposal and conserve energy and natural resources during the production of cement. Furthermore, it appears that the introduction of these materials may improve the properties of concrete (Mehta, 1983 and Bakker**,** 1983).

To reach the maximum efficiency in using such materials in concrete industry, it is necessary firstly to study their intrinsic physical and chemical properties as a raw material. Secondly, when these materials were partially replaced cement, the microstructure of the resulted hardened blended cement paste has to be examined and compared to that of plain cement paste. The microstructural properties of the hardened cement paste and the interfacial zone between aggregate particle and cement paste determine most of microstructural characteristics, durability to different exposure conditions, mechanical behavior, porosity, diffusivity and permeability (Bentur and cohen , 1987, Bakker 1983, Bijen 1996 and Mitsui et al, 1994).

The problem of the durability of concrete usually involves the movements of aggressive gases such as oxygen and carbon dioxide, or/and liquids containing harmful dissolved salts such as chlorides and sulphates, from the surrounding environment into concrete through it's surface (covercrete) followed by physical and chemical reactions in it's internal structure, possibly leading to steel corrosion and/or concrete deterioration (Basheer, 1993). Therefore, microstructure and mass transport properties of concrete such as absorptivity, permeability and diffusivity can be considered as the most important factors affecting the service life of a concrete structure (Basheer, 1993).

Therefore, durability is very important for any construction material, because it directly affects the economics, serviceability, and maintenance of the structure. The durability of concrete depends on various factors such as external environment, internal properties of concrete (w/b ratio, moisture content, etc.), type and quantity of constituent materials. Because nearly all concrete deterioration processes are driven in some manner by the ingress of water and water-borne agents, such as chloride and sulphate ions. One way to minimize problems is to make the concrete less permeable by, for example, densifying the cementitious paste. This densification is achieved by using lower water cementitious materials ratio (w/b) and addition of supplementary cementitious materials (SCMs) (Mehta, 1983, Bakker 1983 and Bijen 1996).

Another industrial waste quite abundant in Egypt obtained from alum production factories is the dealuminated kaolin (DK). Daily production is about 200 tons of wet material, and a large amount has been stored at the factories causing great environmental problems (Mostafa et al, 2001a). DK is obtained after the extraction of aluminum from calcined kaolin by means of sulfuric acid, such treatment leaves behind silicate-rich acidic paste, which upon exposure to air dries intensively. Dealuminated kaolin (DK) appears as one of the local Egyptian calcined kaolin industrial waste by-product. The dealumination process of calcined kaolin increases the surface area of the resulted material. The amount of increase in the surface area is related to the type of dealuminated chemical reactants used (HCL, H_2SO_4 and $NaHSO_4$), reaction time and amount of aluminum extracted (Colina and Joan, 2007). Generally dealumination of calcined kaolin by acid leaching, produces amorphous silica with a high surface area this indicates the bases of high reactivity. It appears that the main effect of the acid attack on calcined kaolin is the dissolution of the aluminum from its octahedral and tetrahedral sites and the formation of free silica (Colina and Joan, 2007).

Mostafa et al, (2001a) characterized several Egyptian industrial waste by-products (air cooled slag, dealuminated kaolin and silica fume) chemically and mineralogically. They also, investigated the Pozzolanic activity of these materials towards lime using the accelerated chemical method (ASTM C114, 1999) and isothermal conduction calorimetry. They found that the main chemical composition of DK is SiO_2 and Al_2O_3. Moreover, they found that the mineralogical composition of DK using X-ray Diffraction contain quartz and a considerable amount of amorphous materials (SiO_2 and Al_2O_3). In addition they determined the surface area by BET analysis and found that DK has a much higher surface area than that of silica fume and exhibits much higher pozzolanic activity especially during early hydration. The presence of higher amount of amorphous SiO_2 and Al_2O_3 and the higher surface area means that DK can be considered as a highly reactive material and might be suitable for use as a cement replacement material in concrete industry.

As a result of the environmental concern related to the storage problems of the huge amount of DK, its low cost as a waste by-product material and its higher pozzolanic activity (Mostafa et al, 2001a), which may considered as an advantage in suitability of using it as a possible pozzolanic material, there is a currently great interest in exploiting this material as a cement replacement material in building industry. However, to the author's knowledge, there are a few published researches in the literature that have been dealt with the chemical, the physical, pozzolanic activity and mineral characterization of DK as a raw material for building industry. Generally, there is still a lack of information regarding the characterization of this material.

Most of studies carried out with DK were focused in DK/lime systems. However, there is a lack of investigations dealt with the reaction kinetics in DK-blended cement. So, an extensive study has to be conducted to improve the knowledge about the pozzolanic activity of DK with cement, and to identify the nature of the reaction products as well as to study the effect of DK on the microstructure of OPC matrix containing such waste by-product.

The microstructure of the cement paste-aggregate transition zone in concrete is significantly different from that of the bulk paste (Bentur and Cohen, 1987). They concluded that SCMs affect the microstructure of the transition zone and particularly decrease the thickness of this zone and the degree of orientation of calcium hydroxide crystals adjacent to aggregate particles. So, the notable improvements in concrete properties can be attributed to interfacial modification caused by the addition of highly reactive fine pozzolanic material. Therefore, to explain the role of DK as a cement replacement material in concrete industry, it is essential to investigate its effect on the microstructure of the bulk cement paste and the aggregate-paste interfacial transition zone.

The structure, nature of the grain surface and the very high specific surface area of any SCMs when partially replaced by cement in OPC matrix may lead to change in the amount of water demand during its fresh state. It has been also showed that incorporation of any SCMs in OPC concrete could change the initial and final setting times. Moreover its addition would affect the other fresh parameters, such as flowability and rate of flowability loss occurring during its fresh state (Mehta, 1983, and Malhotra, 1993). Therefore, it is important to have a good understanding to the effect of DK inclusion into OPC matrix on water demand, setting times and various fresh parameters such as flowability, flowability loss and rheology.

The extra fine pozzolanic materials improve the properties of concrete in two ways, one physical the other chemical. Physically these materials act as a filler in space between the cement particles (Detwiler and Mehta, 1989). The chemical effect is the pozzolanic reaction that is a result of the high surface area coupled with the material main component, amorphous silica oxide (SiO_2). This reaction is with the calcium hydroxide that released by the hydrating cement. The effect of the common SCMs (fly ash, ground granulated blast furnace slag, metakaolin, rice husk ash and silica fume) on concrete mechanical properties have been extensively studied (Mehta, 1983 and Malhotra, 1993), however, the effect of DK as a highly fine pozzolanic material on concrete mechanical properties has not been investigated yet.

It is essential to understand that every concrete structure should continue to perform its intended functions, which includes its required strength and serviceability throughout the expected service life. Therefore, concrete must be able to withstand the process of deterioration to which it can be exposed (Neville, 1998). So, the durability of DK concrete as well as the corrosion of its embedded steel is required to be clarified.

1.2 PURPOSE OF THE STUDY

In an effort to gain an improved understanding of the above-mentioned aspects, the present study was undertaken with the following objectives:

1. To characterize the chemical, physical and mineralogical properties of DK as well as evaluate its pozzolanic reactivity aiming to study the suitability of partially replacing Portland cement by such material.
2. To investigate the impacts of DK on the nature and the amount of hydration products and their effects on the pore structure of OPC/DK paste (total and capillary porosity).
3. To study the effect of DK on the microstructure of aggregate-paste interfacial transition zone as well as the bulk paste zone.
4. To clarify the impacts of incorporating DK on the setting time (initial and final) and fresh parameters of OPC mortar and concrete (flowability, rate of flowability loss, slump and rheology).

5. To elucidate the role of DK on the mechanical properties of OPC mortar (compressive and tensile strengths) and hardened properties of OPC concrete (compressive, splitting, flexural, modulus of elasticity, stress strain behavior and drying shrinkage) aiming to determine the optimum content of DK to be adopted in concrete mixes.
6. To investigate the effect of DK on the mass transport properties (sorptivity and water absorption) of OPC mortar and concrete.
7. To examine the impacts of DK on the various durability aspects, rate of compressive strength loss, weight and length change, of OPC mortar exposed to aggressive environments of sulfates.
8. To investigate the role of DK on the corrosion activity of OPC concrete exposed to chlorides aggressive environments.

1.3 OUTLINE OF THESIS

This thesis is divided into six chapters, following this chapter (chapter 1), chapter two, presents a general review in the field of durability of reinforced concrete and fresh properties of concrete. It also reviews the different cement replacement materials commonly used and their effects on various properties of concrete. Furthermore, the chemical, physical, mineralogical properties and pozzolanic activity of DK were presented as well as its partial replacement effect on heat of hydration evolved in OPC/DK paste.

Chapter 3 describes the experimental work, materials used, DK preparation and processing, mix proportion, mixing procedures, specimen's preparation, compaction, curing, exposure regimes and testing techniques adopted throughout the present investigation.

Chapter 4 analysis all obtained results concerned with DK characterization (chemically, physically and mineralogically) and evaluation of its pozzolanic activity. Moreover, the type and amount of hydration products of the cement paste containing either DK two forms with different contents were also examined. This chapter also, demonstrates the effect of DK content on the microstructure of both the aggregate-paste interfacial transition zone and bulk cement paste zone. The effect of DK inclusion on pore structure (total, capillary and gel porosity) of hydrated cement paste was also investigated. Moreover, it outlines the effect of DK content on setting times (initial and final) of OPC paste and on the fresh properties of OPC mortar (flowability, flowability loss and rheology). The effect of DK content on the mechanical properties (compressive and tensile strengths) of OPC mortar was also presented.

Additionally the effect of DK content on the mechanical properties (compressive, splitting, flexural, modulus of elasticity, stress strain behavior) and deformational properties (drying shrinkage) of OPC concrete was also discussed. The fluid transport properties (sorptivity, water permeability and initial surface absorption) of the hardened OPC mortar and concrete were also investigated. Finally it investigates the effect of DK on the compressive strength loss, weight and length change of DK mortar subjected to aggressive environments of sulfates ions. Moreover, the effect of DK on corrosion activity (corrosion potential and corrosion current density) of reinforced DK concrete subjected to chlorides was also evaluated.

Chapter 5 discusses all obtained results analyzed in the previous chapter.

Chapter 6 summarizes the general conclusions, arisen from the work reported herein, and the recommendations for further studies.