



# Beneficiation of the huge waste quantities of barley and rice husks as well as coal fly ashes as additives for Portland cement



N.M. Khalil<sup>a,b,\*</sup>, E.M. Hassan<sup>c</sup>, M.M.E. Shakhdofa<sup>a,d</sup>, M. Farahat<sup>c</sup>

<sup>a</sup> Department of Chemistry, Faculty of Sciences and Arts, King Abdulaziz University, Khulais, Saudi Arabia

<sup>b</sup> Refractories, Ceramics and Building Materials Department, National Research Centre, P.O. 12622 Dokki, Cairo, Egypt

<sup>c</sup> Chemistry Department, Faculty of Sciences, Sebha University, Libya

<sup>d</sup> Inorganic Chemistry Department, National Research Centre, P.O. 12622 Dokki, Cairo, Egypt

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## ABSTRACT

This study aims at benefit from barely husk ash (BHA), rice husk ash (RHA), and coal fly ash (CFA) as a replacement of ordinary Portland cement (OPC) to eliminate the problems associated with cement industry involving energy consuming and air pollution. Three series of cement mixes were prepared from OPC with different contents (0–30 wt.%) of each additive. Different cementing and mechanical properties of the prepared mixes were tested according to the international standard specifications. It was concluded that OPC blended with 15–20 wt.% of BHA, RHA, or CFA show outstanding cementing properties.

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## 1. Introduction

The current cement production rate of the world, which is approximately 1.2 billion tons/year, is expected to grow exponentially to about 3.5 billion tons/year by 2015. Most of the increase in cement demand will be met by the use of supplementary cementing materials, as each ton of Portland cement clinker production is associated with a similar amount of CO<sub>2</sub> emission. Nowadays, pozzolanic materials are widely used as supplementary cementing material in Portland cements and may replace part of the clinker in order to enhance the performance of the hydrated cement. Such composite or blended cements are employed for their economic, ecological, and technological benefits i.e., reduction of energy consumption as well as CO<sub>2</sub> emission. Supplementary cementing materials reduce lime content in hydrated Portland cements and replace it with pore-filling cement hydrates, which are known to improve the ultimate strength, impermeability, and durability to chemical attack of cement. Different types of additions are used such as pozzolanic (natural pozzolan, low calcium fly ash, and silica fume), auto pozzolanic (high calcium fly ash and blast furnace slag), and crystalline (generally known as filler). Pozzolanic activity or hydraulicity of pozzolanic material is

mainly associated with their vitreous and/or amorphous structure [1,2]. Among of these additive is the ash resulted from the composition of agricultural byproducts such as rice and barley husks. Rice and Barely husks are recognized as two of the most economic and important cereals in the world. By area and production, rice and barley is the second and fourth of most important cultivated crop. On average 20% of the rice and barley paddy are husks, the majority of these husks are either burnt or dumped as waste [3–5]. Unlike other residues, rice and barley husks also contain large proportions of ash and silica, which to a large extent have been reported to affect the property and application of husks [6,7]. By burning husks under a controlled temperature and atmosphere, a highly reactive ash is obtained [8,9]. Ash containing little or no residual carbon has many potential uses ranging from soil amendment to abrasive component of tooth paste [10,11]. The most important property of husk ashes that determines pozzolanic activity is the amorphous phase content. RHA and BHA are highly reactive pozzolanic material suitable for use in lime-pozzolana mixes and for Portland cement replacement. RHA and BHA contain high amounts of silicon dioxide, and their reactivity related to lime depends on a combination of two factors, namely the non-crystalline silica content and their specific surface [12]. The ash being very light is easily carried by wind and water in its dry state [13]. Prior to 1970, husk ash was usually produced by uncontrolled combustion, [14] and the ash so produced was generally crystalline and had poor pozzolanic properties. In 1973, Mehta studies have shown that burning rice husks at 600 °C

\* Corresponding author. National Research Centre, Refractories, Ceramics and Building Materials Department, Dokki, Cairo 12622, Egypt. Tel.: +20 966548959278. E-mail address: [nagy2071@yahoo.com](mailto:nagy2071@yahoo.com) (N.M. Khalil).

produces an ash with an optimum composition for pozzolanic materials [15]. Several researchers have studied the durability variation of the concrete with pozzolanic materials (after complete combustion) [16–18]. Among the family of other agro-wastes, rice husk is a popular boiler fuel, and the ash generated usually creates disposal problems. The chemical process discussed not only provides a solution for waste disposal but also recovers a valuable silica product, together with certain useful associate recoveries [19]. In this century, the utilization of rice husk ash (RHA) as cement replacement is a new trend in concrete technology. Besides, as far as the sustainability is concerned, it will also help to solve problems otherwise encountered in disposing of the wastes. Disposal of the husks is a big problem, and open heap burning is not acceptable on environmental grounds, and so the majority of husk is currently going into landfill. The disposal of rice husks create environmental problem that leads to the idea of substituting RHA for silica in cement manufacturing [20]. Numerous investigations on the use of RHA in concrete production have been done and all produced positive results [21,22]. The main advantage of using RHA as a mineral admixture in concrete is the significant reduction in the permeability of the concrete [23–25]. The use of rice husk ash in concrete was patent in the year 1924 [26]. Up to 1972, all the researches were concentrated to utilize ash derived from uncontrolled combustion [27]. Controlled combustion influences the surface area of RHA, so that time, temperature and environment were to be considered to produce ash of maximum reactivity [28]. Fly ash material is composed primarily of complex alumino-silicate glass, mullite, hematite, magnetite spinel, and quartz. The proportion of quartz (crystalline silica) in the fly ash varies depending on the quartz content of the coal. Class C fly ash may have 1–7% free CaO and calcium sulfate as well as calcium alumino-silicate glass [29]. Fly ash is useful in many applications because it is a pozzolan, meaning it is a siliceous or alumino-siliceous material that, when in a finely divided form and in the presence of water, will combine with calcium hydroxide (from lime, Portland cement, or kiln dust) to form cementations compounds [30] and is found to have numerous advantages for use in the concrete industry. Some of the advantages include improved workability, reduced permeability, increased ultimate strength, reduced bleeding, better surface finishing, and reduced heat of hydration [31]. Mineral admixtures or pozzolans are used to improve strength, durability, and workability in concrete [32–35]. Freshly mixed concretes are generally more workable when a portion of the cementitious material is fly ash, in part because of the spherical shape of fly ash particles. Smoother mixtures are typically produced if the mineral admixture is substituted for sand rather than cement, but highly reactive or cementitious pozzolans can cause loss of workability through early hydration [36,37]. Very finely divided mineral admixtures, such as silica fume, can have a very strong negative effect on water demand and hence, workability, unless high-range water-reducing admixtures are used [38,39]. This work aims at benefit from the huge wasted quantities of barley, rice husks, and coal fly ashes as additives for Portland cement and study their effect on different physico-mechanical, chemical, and cementing properties of its hardened pastes.

## 2. Materials and experimental

### 2.1. Materials

The starting materials used in this investigation are:

1. Ordinary Portland cement (OPC) Type I.
2. Barley husk ash (BHA).
3. Rice husk ash (RHA)

### 4. Coal fly ash (CFA)

5. Some chemicals namely; methyl alcohol and diethylether were used for stopping the hydration of the cement pastes at different curing times of cement hydration 3, 7, 28, and 90 days.

## 2.2. Experimental

### 2.2.1. Processing of rice and barley husk ashes

Rice and barley husks were processed and washed separately by passing running water on them for a few times and then washed with distilled water, drying in a sunny place, burning at 600 °C for 8 h and screening through 0.125 mm standard sieve. Coal fly ash (CFA) was also screened through 0.125 mm standard sieve.

### 2.2.2. Preparation of cement pastes

Different cement mixes were prepared from OPC with different wt.% of BHA, RHA, or CFA ash as given in Table 1 using the optimum amount of water. After 2 min of well dry mixing for 10 min in an electrical cement mixer, the mixes were separately gauged with the suitable amount of water with a constant hand mixing using stainless steel spatula. During 4 min from the beginning of water addition, the pastes were molded into 1 × 1 × 1 inch cubic samples in steel mold. The molded pastes were left in a 100% relative humidity cupboard. After 1 day, the hardened samples were demolded obtaining cubic samples of the hardened cement pastes which were kept under water until time of investigation. Three representative samples from each cement mix were tested for their bulk density and apparent porosity at each curing time; 3, 7, 28, and 90 days. At each curing time, the hydration of the tested samples was stopped by grinding with 1:1 methanol:ether mixture. The chemically combined water was determined for the hydrated sample after stopping its hydration through ignition of 1 g of the hydrated cement sample at 800 °C using the following equation:

$$\begin{aligned} & \% \text{ of chemically combined water} \\ & = \frac{\text{Wt. before ignition} - \text{Wt. after ignition} \times 100}{\text{Wt. before ignition}} \end{aligned}$$

### 2.2.3. Instrumentation

Chemical compositions of OPC, BHA, RHA, and CFA were investigated using X-ray fluorescence (XRF) technique. The mineralogical compositions of the hydrated cement mixes were investigated through X-ray diffraction (XRD) technique, A Phillips PW 1710 diffractometer with Ni filtered Cu K $\alpha$  radiation operating at 30 mA and 40 kV was used. Thermal analysis, thermo gravimetry (TG) and differential thermo gravimetry (DTG) as well as differential scanning calorimetry (DSC), of some hydrated samples was also investigated using NETZSCH STA 409 analyzer, with Al<sub>2</sub>O<sub>3</sub> as a reference material over a range of temperature from room temperature up to  $\approx$ 1000 °C.

**Table 1**

The prepared mixes from OPC with either BHA, RHA, or CFA.

Mix no.	OPC (wt.%)	BHA, RHA, or CFA ash (wt.%)
1	100	–
2	95	5
3	90	10
4	85	15
5	80	20
6	75	25
7	70	30

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