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Waste Materials in Construction: Putting Theory into Practice

Influence of the calcium content on the coal fly ash features in some innovative applications.

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Abstract

Despite a low chemical reactivity, recent trends in the innovative uses of coal fly ash based on the chemical properties have been successful. Lots of fly ash showing sharply alkaline reaction (water pH rising to 11-12 upon contact) usually are high-calcium (> 3-4%), most of which is present as CaO. These lots are suitable to be used as remotion agents of heavy metals in wastewater or retentive agents of them in polluted solids. Lots giving substantially neutral reaction are usually low-calcium (0-3%). They are suitable to be converted by hydrothermal treatments into zeolitic products, where higher calcium contents interfere. A reverse destination is destitute of good results. Causes are discussed.

1. INTRODUCTION.

The production of electric energy from coal combustion produces far more fly ash than is currently reused. Consequently, new uses have to be promoted in order to contain the need of disposal.

The conventional uses of coal fly ash (CFA) are mainly based on their physical properties. Despite a low chemical reactivity, recent trends addressed towards uses based on the chemical properties have been successful. These involve the conversion by hydrothermal treatments into partially zeolitised products, the use of CFA as an adsorber of heavy metal ions from wastewater, compost and soils or (less recently) as silicate supplier in lime and cement. In these uses of chemical type it is possible to observe different performances according to whether high calcium oxide or low calcium oxide CFA (i.e., basic or neutral CFA) are employed [1-5].

The presence of an excess of the free basic oxide differently influences the chemical behaviour of ashes: on one hand, it stops their conversion into zeolites [1,2]; on the other, it gives the ashes absorbtion properties which permit the removal of heavy metal from wastewater and a stronger retention of them when present in polluted soils and compost [3-5].

Calcium contents ranging from 1% to 10% have been found in coal fly ash produced in the Italian Electricity Board (ENEL) power stations [1,6,7]. In this communication we have tried to suggest, on the basis of previous work, the most convenient "chemical" utilization of coal fly ashes according to their calcium content.

2. BASIC OR NEUTRAL COAL FLY ASHES.

From the point of view that mainly concerns the present discussion, it is important to observe that there are lots of fly ash showing sharply alkaline reaction (water pH rising to 11-12 upon contact) and lots giving substantially neutral reaction. This different feature must depend on whether strong basic oxides (such as MgO, CaO, Na_2O, K_2O) exceed the acid ones (in particular SO_2 and SO_3) or not in the coal combustion products and therefore it is connected with the coal composition. Among strong basic oxides in fly ashes CaO, undergoes to the largest variation [6,7]. Thus, it is not surprising that the CaO content is the best indicator of the alkaline or neutral reaction of fly ash.

3. COAL FLY ASHES CONVERSION INTO ZEOLITIZED PRODUCTS.

It has been shown that, under hydrothermal conditions, it is possible to achieve the crystallization of zeolitic phases from the amorphous fraction of coal fly ash. For example, this fraction is capable of evolving into zeolite A after 4 hrs of hydrothermal treatment; this zeolite developes into zeolite P if the treatment time goes on for 6-8 hrs or if the Si/Al ratio grows up to 3.0 [8-10]. It has, however, been observed that materials with calcium content exceeding certain limits cannot be converted into zeolites [1,2]. The authors have investigated the effective interference of the concentration of calcium ions on the nucleation and /or crystallisation of zeolite A or P. It was found that in a broad range of concentrations (0.01-0.07 mol dm^{-3}) the calcium ion interferes with the crystallization without completely suppressing it, but rather causing it to decrease in proportion to its presence.

These results have been explained in terms of a specific interaction between calcium and silicate ions, which removes the latter from the formation of the aluminosilicate gel capable of evolving into zeolites with the exception of those hydroxysodalite-like [1,2].

According to the above reasoning, it is possible to discuss some results recently reported in the literature [11-14] just concerning coal fly ash hydrothermal treatments to obtain zeolitised products. In work reported by Singer and Berkgaut [11] the treatment has been applied to a fly ash sample containing 3,2% CaO (2,3 as Ca) and to one more containing 9,4% CaO (6,7 as Ca). The results significantly point out that zeolite P formation takes place with the first sample and hydroxysodalite with the second. An almost similar treatment reported by Lin and Hsi [12] has been applied to a single sample containing 5,2% CaO (3,7 as Ca). Again the zeolite P formed is consistent with our proposed rule. In this case HS has been obtained as well, but its formation was correctly explained by the authors with the higher NaOH concentration (4-10N) used in an alternative treatment of the same sample.

In the study performed by Amrhein et al. [13] the treatment has again been applied to a single sample containing 5,67% Ca (7,94 as CaO). In this case HS forms, that is recognizable from the reported diffraction patterns although the authors quote it as "unnamed sodium aluminum silicate hydrate". Again the kind of zeolite forming is in agreement with our proposed rule.

As regards less recent literature [14], the treatment was been applied to 17 coal ash samples. For all low- or lowest-calcium content, except one named DK. Well, the results show that, in the optimum range of alkali concentration, all samples give rise to zeolite P except the latter, where HS forms.

In none of the cited literature [11-14] were the authors able to explain the different feature, but we remark that those results should have been expected if our proposed rule had been employed by them.

Thus, if it is desired to change coal fly ash into true zeolite (HS has neither channels nor exchange properties), it is necessary to use Ca-poor samples.

The interference of calcium can be suppressed by complexation with EDTA, which has been shown to take place selectively in the conditions of zeolite synthesis [1-2]. By adding an amount of EDTA equivalent to that of calcium in the hydrothermal treatment, Ca-rich samples may zeolitise, as EDTA removes calcium combined with silicate, and this can then hydrolyse to hydrated silica. Nevertheless, in the conversion of coal fly ash into a partially zeolitised product the use of EDTA has a hardly bearable cost. Thus, it is reasonable to reserve to this use low-calcium grades.

4. COAL FLY ASHES AS "HEAVY METAL ABSORBERS".

On the contrary, Ca-rich samples are suitable as heavy metals absorbers. It has been noted that Ca-rich samples exhibit good absorbtion properties in removing from wastewater moderate amounts of metal ions as copper, zinc, cadmium and chromium [3-5,15]. Heavy metal absorbtion is maximized, pH rises from initial values of 5-6 to final values of 10-11. In the absence of them, a pH of 10-11 is quickly established. Ca-poor samples show constant pH values ($\equiv$ 6) and do not remove any amount of heavy metals from aqueous solutions. Consequently the use of coal fly ash for the removal of metals in wastewater streams, is strictly related to their chemical composition.

The absence of absorbtion properties seems evident in a material such as CFA, where unreactive phases are largely prevalent. Nevertheless, alkaline Ca-rich CFA containing reactive sub-micron sized CaO particles can explain the alkaline pH values (10-11) transmitted to the aqueous solutions and the heavy metal removal capacity, according to the slight solubility of the heavy metal hydroxides.

Heavy metals removal is therefore strictly connected with the initial chemical ash composition and particularly with the presence of calcium as oxide. Indeed, it must give an alkalinity to the solutions in order to precipitate heavy metals hydroxides (pH> 8-9).

5. CONCLUSIONS.

When fly ashes are destined to uses based on their chemical properties, in order to obtain good results it is useful to separate them into low-calcium, neutral, and high-calcium, basic, samples. The first are appropriate to be converted into zeolitic products by hydrothermal treatments, the latter are suitable as remotion agents of heavy metals in wastewater or retentive agents of them in polluted solids, but not vice versa.

Additional examination of this subject could however provide further insights.

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