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Optimization of copper slag waste content in blended cement production

Some industrial wastes such as blast furnace slag, fly ash, silica fume, by-product gypsum and nonferrous metal slag can be used as raw material and blending components in the cement industry.
The amount of any waste used in this way depends on many factors such as the chemical and mineralogical composition of the waste itself and of the Portland cement, the size and shape of their particles, the amount of glassy phase in them, etc. Commonly, the proportions of Portland cement and its partial substitutes are developed by trial and error.
Based on theoretical considerations proposed by the field researchers, this study deals with the determination of the proportions of copper slag and Portland cement in the blended cement, having the objective of adding just enough of copper slag to consume all the excess calcium hydroxide produced during the hydration of the Portland cement. In terms of the cement chemistry ternary phase diagram, this means finding the intersection between the line connecting the cement composition and the slag composition and the boundary line of calcium hydroxide stability field.
A copper slag (waste of Lac, Albania Copper Plant) and Portland cement (produced in Fushe-Kruja,Albania Cement Factory) are used as specific constituents in the binary mixes of blended cement experimented in this work. In addition to the pozzolanic tests of mixes, with various content of copper slag determined according to ternary phase diagram, the mechanical strength tests of mortars produced with these binary mixes are carried out, too.
***Key words**:copper slag, partial constituent, ternary phase diagram, calcium hydroxide stability field*

INTRODUCTION

Copper slag is a by-product obtained during the production of copper metal, which can be used as pozzolana in the production of cementing materials. Pozzolanas are materials which, although themselves are not cementitious, contain constituents which, when combined with lime, at ordinary temperatures and in the presence of water, form stable insoluble compound that posses cementing properties [1]. The properties of blended cements depend largely on the chemical and physical characteristics of copper slag as well as on the amount of the slag used as substitute of Portland cement.

Usually, the ratio of pozzolana-to-Portland cement is set by trial and error. Instead of this method, here is used a theoretical approach proposed by Livingston and Bumrongjaroen [2].

Cementitious hydration reactions that occur when blended cement is mixed with water are described as follows.

The main key reaction is the hydration of Portland cement, represented here by its main component, the tricalcium silicate [3]:

$$3CaO\ SiO_2 + zH_2O \rightarrow Ca_xSi(OH)_y \cdot nH_2O + (3-x)Ca(OH)_2$$

Thus, this reaction produces a calcium-silicate-hydrate gel (C-S-H), with the C/S ratio; the value of x usually is around 1.65. This reaction produces excess calcium hydroxide (CH), too.

The pozzolanic materials used in blended cement can react with the CH. According to the theoretical approach, the objective is to add just enough pozzolana in order to consume all the excess calcium hydroxide produced during the hydration of the Portland cement [2]. The practice of choosing an arbitrary value for the mixture proportions does not ensure the achievement of this optimum condition.

Pozzolanic materials can supply additional silicate ions (S) which react with CH to form more C-S-H gel.

$$SiO_4^{4-} + xCa(OH)_2 + (y-2x)OH^- + nH_2O \rightarrow Ca_xSi(OH)_y\ nH_2O$$

where SiO_4^{4-} stands for the entire collection of silicate species.

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The aluminium content (A) of certain pozzolanic materials can also react with CH to produce hydrogarnet phases:

$$2Al(OH)^{4-} + 3Ca^{2+} + SiO_4^{4-} \rightarrow Ca_3Al_2Si(OH)_8O_4$$

So, the C_3S hydration reaction produces excess CH while the pozzolanic reactions consume it. Theoretically, it is possible that these competing reactions end up with an equilibrium mineral assemblage mixture that contains C-S-H gel and calcium aluminate hydrates, but no CH. Assuming this; it is proposed the following equation for the boundary line of the calcium hydroxide stability field [2]:

$$A = (1- 2.65\ S) / 2.35$$

Which graphically is a straight line in the cement chemistry ternary phase diagram.

The mixtures that are plotted on the left of this line have excess CH, which is normal condition for Portland cement hydration. Whereas the mixtures plotted to the right of this line are pozzolanic materials.

In the phase diagram we can connect, with a straight line, any point representing the chemical composition of a certain Portland cement with any point representing the chemical composition of any pozzolana. The chemical composition of any mixture of these two phases is a point somewhere along this line. The ratio between the pozzolana and the Portland cement can be determined by the position of the point on the line according to the lever rule. The intersection point between to lines mentioned above indicates the optimal ratio of pozzolana-to-cement in order to achieve the condition of zero CH.

EXPERIMENTAL PART

The object of the experimental work was the determination of the optimal ratio of a certain pozzolanic material and a certain Portland cement to be used in production of blended cements.

As base material is used Portland cement CEM-I produced in Fushë Kruja Cement Factory, Albania and as partial substitute of Portland cement is used copper slag, waste of Laç Copper Plant, Albania.

For both materials (cement and copper slag) the chemical composition is determined according to the analytical standard analyses of EN-176 [4].

Several cementing materials are prepared with the optimal copper slag to Portland cement ratio, stipulated by theoretical considerations according to the lever rule and the boundary line of calcium hydroxide stability field, as well as with ratios around the optimal value. For each cementing material, the pozzolanic tests are made according to EN-196-5 [5]. These tests are carried out to check whether the slag in each cementing materials is present in sufficient quantity and if it is adequate to combine with the available lime liberated from the Portland cement.

The use of copper slag reduces the early age strength of mortar and concrete, but it improves its long – term strength. The disadvantage of the reduced strength at early age can be managed by adding an optimal amount of slag. For this reason, with each cementing material, mortar prisms 4x4x16 cm are moulded and tested in order to determine the limits of practical use of slag addition. Washed sand from Erzeni riverbed, (a river near Tirana, Albania) is used for producing of mortar prisms [6]. The mechanical strength of hardened mortars after 7 and 28 days are measured.

RESULTS AND DISCUSSION

The chemical compositions of two actual raw materials (Portland cement and copper slag) have been plotted in the cement chemistry ternary phase diagram $CaO-Al_2O_3-SiO_2$, (Figure 1).

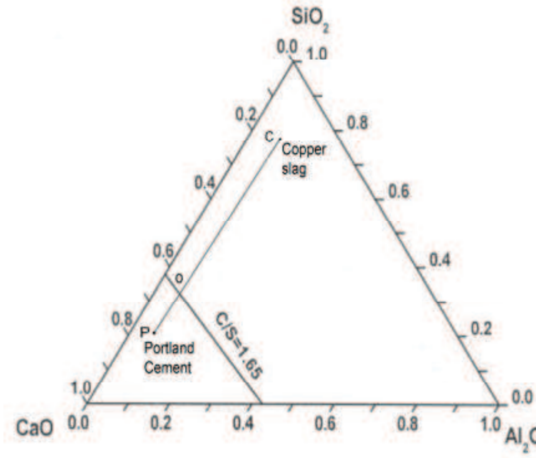

Figure 1 - The phase diagram for the ternary system CaO-Al2O3-SiO2, with plotted Portland cement and copper slag, the line (PC) representing their mixing ratios and point (O) where, based on zero CH, the optimum mixture ratio lies

The diagram shows that, the representative point for actual Portland cement is on the left of the boundary line of calcium hydroxide stability field. This is a normal condition for Portland cement hydration. Whereas the representative point for copper slag is on the right of the boundary line that is normal, too, taking into account that this slag is a pozzolanic material, with deficient calcium hydroxide content.

Points representing arbitrary mixture proportions can be found along the mixing line between the end points of the line defined by the chemical composition of the pure Portland cement (P) and the pure copper slag (C).

From the Figure 1, we find that the mixing line intersects the pozzolanic boundary line at point (O) where the ratio value is 20.1 %. This value is considered to be the theoretical optimum value of copper slag in the blended cement with zero content of calcium hydroxide. This optimum value is specific for the actual pair of copper slag and Portland cement composition.

It is clear that the position and the length of the mixing line depend on the composition of the Portland cement as well as the slag. Therefore, before the proportioning of mortar and concrete mixtures, both compositions are determined.

In the Figure 2 is shown the solubility curve of lime at 40°C in solution of varying total alkalinity and are plotted the results of pozzolanic tests carried out for the cementing materials with various content of copper slag (0, 10, 20, 30, 40%) substituting Portland cement.

These results are expressed in mmol/l. For the cementing material to be accepted as pozzolanic materials, the 15-day result must fall below the solubility curve, showing that the solution is not saturated with lime.

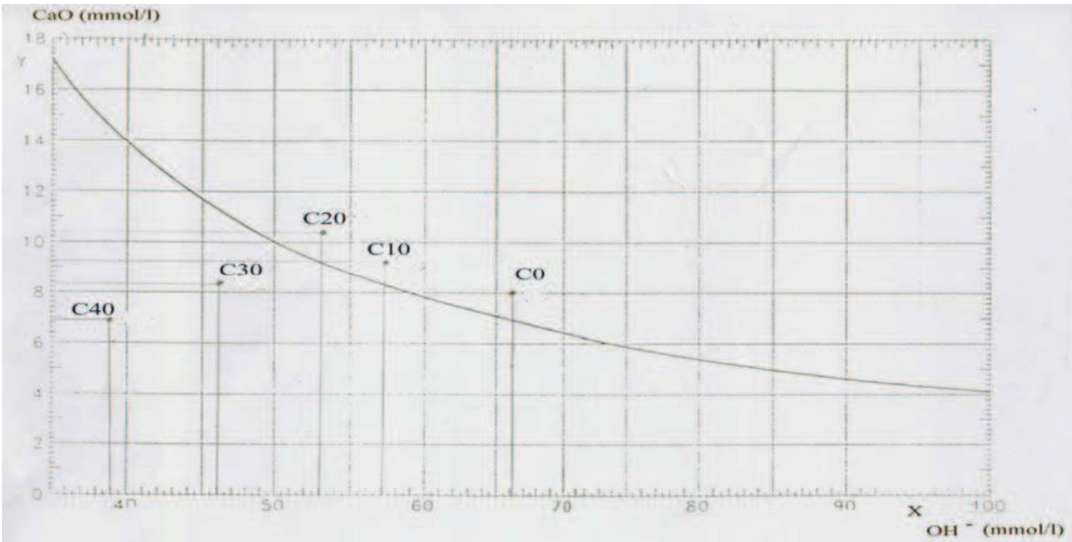

Figure 2 - Solubility of $Ca(OH)_2$ in solution of alkali hydroxides at 40°C

The Figure 2 shows that the representative points of cementing materials with 0, 10 and 20% of copper slag are above the solubility curve of lime at 40°C in solution of varying alkalinity. This shows that the content of pozzolana (copper slag) in cement is not in sufficient quantity. Whereas the representative points of cementing materials with 30 and 40% of slag, fall below the solubility curve, which means that the pozzolana in cement is present in sufficient quantity.

But, the theoretical method of optimizing the binary Portland cement/copper slag ratio is based simply on the stoichiometry of the equilibrium mineral assemblage [2]. However, other factors have to be taken into account. The most important one is the fact that the slag contains glassy and crystalline phases. Therefore, the bulk chemical composition of the slag does not adequately represent the amount of the reactive phase, because in fact only the glassy phase is the one that reacts with lime liberated during the hydration of cement Portland. The crystalline phases are essentially non reactive, and thus the percentage of their constituents should not be included in the calculation of the optimum mixture ratio. So, knowing that the copper slag, in addition to glassy phase, has even some crystalline phase; based on a detailed analysis of copper slag, adjustment is to be done in the optimum value by considering that above 20.1 %. This value resulted to be compatible with the results of pozzolanic tests.

In the Table 1, are shown the mechanical strengths of hardened mortars prepared with various content of copper slag as substitute of Portland cement.

Table 1 - The mechanical strengths of hardened mortars

The content of copper slag (%)	Water to cementing material ratio	Aggregate to cementing material ratio	Mechanical strength (in MPa)		
			Flexure strength (7-days)	Compressive strength (7-days)	Compressive strength (28-days)
0	0.47	2.25	6.65	29.24	44.20
10	0.47	2.25	6.00	25.00	40.00
20	0.47	2.25	5.62	22.95	36.99
30	0.47	2.25	4.50	15.50	30.00
40	0.47	2.25	3.64	12.95	26.39

The table above shows that the increase of the copper slag amount in cementing material decrease the mechanical strengths of hardened mortars, especially in the early ages. It is noted that, the strength reduction is a little bigger for the mortars with the content of slag 30 and 40% (that is above the theoretical optimum value according to Figures 1 and 2).

CONCLUSION

The copper slag, the by product of the melting plant of Lac, north Albania can be used successfully as Portland cement substitute in the cement industry. Its use is an example of industrial ecology since large quantities of this slag have occupied the plant sides creating a big environmental problem.

The use of this slag in blended cement production is conditioned by the selecting of the right proportions of Portland cement and slag in order to attain synergistic effects which give long term improved durability properties to mortar and concrete produced with such blended cement.

The optimum ratio value of copper slag determined according to the theoretical method can be used as guidance in the production practice.

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