Characteristics of Aerated Concrete Composites Prepared with Biomass Carbonization Effluents

Luis E. Brossard Perez¹, Antonio L. Beraldo², Luis A. B. Cortez³

Abstract – An air entrainment agent for foamed concrete production was obtained by treating the dark insoluble bio-oil condensed from vegetable carbon making effluents with water NaOH solution. The resulting solution of alkaline bio-oil, SABO, was used to study the preparation of foamed concrete composites, at laboratory scale, following an experimental ternary mixture design. The mixtures had constant total mass and constant cement mass and variable mass proportions of SABO (from 0.03 to 0.09), water (from 0.65 to 0.71) and rice husk as vegetable aggregate (from 0 to 0.065). There were studied the hydration process of the fresh water-cement mixture as well as the water absorption of the hardened foamed specimens. It is concluded that the use of SABO could bring advantages over current commercial foaming agents due to its readily availability, low cost and performance characteristics equivalent to that found in usual commercial products. Copyright © 2011 Praise Worthy Prize S.r.l. - All rights reserved.

Keywords: Foamed Concrete, Carbonization, Bio-Oil

I. Introduction

Foamed or aerated concrete is a cement bonded material manufactured commercially by blending a very fluid cement paste (slurry) and adding an air entrainment agent into the slurry. Then air is introduced into the cement paste, with or without aggregates, producing a volume increase of the mixture due to the inclusion of tiny bubbles of air. The volume of this aerated slurry dictates the apparent density of the foamed (also known as cellular) concrete. As foaming agents there have been used many products. Among them, hydrolyzed protein (CAILLAU et al., 1989 [1]), pulping waste liquor solids (BOUCHARD and FARREL, 1983 [2]), long chain anionic and cationic organic compounds (CHAO and CHAO, 1997 [3]), alkyl sulfates (SAVOLY and ELKO, 1998 [4]) and hydrolyzed keratin (CHATTERJI et al., 2004 [5]). It can be appreciated that the list of air entrainment agents comprehends natural as well as synthetic products. An attractive raw material for this purpose is the dark, lignin composed bio-oil recovered from the condensed carbonization effluents (BROSSARD et al., 1997 [6]). The vegetable carbon making process is a pyrolysis thermo chemical transformation of lignocellulosic materials that produces besides vegetable carbon, a liquid fraction and incondensable gas. In the search for practical applications for pyrolysis products, solutions of alkaline bio-oil (SABO) were tested as an air entrainment agent for a variety of applications (BROSSARD et al., 1997 [6]). Bio-oil is composed of a mixture of many types of organic oxygenated compounds, mainly phenols and high molecular weight carboxylic acids (PAKDEL et al., 1994 [7]).

Depending on the type of pyrolysis process and the type of starting vegetable residue used, the yield and the properties of bio-oil are different (PAKDEL et al., 1994 [7]). Nevertheless according to author’s experiences, all types of bio-oil show air entrainment properties when added to cement mixtures.

Even though there is a number of commercial products for foamed concrete manufacture, the most used have basic components that also have high demand for alternative uses like in the case of animal blood for hydrolyzed protein or depend on the existence of a sound chemical industry to produce synthetic foaming products. Those shortcomings have their expression in higher production costs and therefore in a limited use, not to mention environmental problems associated to such productions.

On the other hand, the basic component of SABO can be collected, as almost costless byproducts, from common carbonization ovens or from any other type of pyrolytic installation provided the existence of an appropriate condensation system for the effluents. The conversion of bio-oil into SABO is a straightforward operation consisting in mixing it with an aqueous solution of NaOH.

The present paper intends to present evidences of the possibilities of SABO as an alternative low cost foaming agent for the manufacture of foamed concrete. The study includes the presence of rice husks as a filler to find out the possible effect of a vegetable aggregate on the water absorption of the hardened foamed specimens. For that purpose the study was divided in the following parts to determine:
a) The influence of blend’s composition on the mechanical properties of the hardened specimens;
b) The water absorption behavior of SABO foamed hardened specimens;
c) The effect of SABO doses on cement’s hydration process.

II. Material and Methods

II.1. Cement

It was used a high initial strength Portland cement – ARI. Specification. NBR 5733:1991. (BRAZILIAN STANDARDS, 1991 [8]).

II.2. Bio-Oil (SABO)

Bio-oil from lignocellulosic residues, obtained in the fast pyrolysis reactor located at University of Campinas, SP, Brazil, was dissolved in NaOH aqueous solution at room temperature under stirring. The resulting dark brown solution had 10.41% of dissolved solids and a density of 1.05 g cm\(^{-3}\) at 25°C.

II.3. Rice Husk

Previous to its use, rice husks were soaked 24 hrs at room temperature, in a 5% Ca(OH)\(_2\) water suspension. At the end of this time, rice husks were washed with water and finally air dried until constant moisture content.

II.3.1. Experimental Planning for Foamed Concrete Mixtures

It was followed a special cubic experimental factorial design for mixtures (MONTGOMERY, 2001 [9]) with the following characteristics:

- The mixture to be studied had 4 components: cement, water, SABO and rice husk as filler.
- The mass fractions for SABO used in this paper did not consider the mass percentage of dissolved solids, which means, that actual mass fraction of the active component in SABO has to be figured out multiplying SABO mass fractions by 0.1041.
- The experimental design was planned with constant cement (\(M\)) and mixture (\(M\) ) masses. So, only the difference between these two masses had a variable composition.
- \(\Delta = M-m\) (variable composition mass in the mixture)
- In this way the quaternary mixture was converted into a ternary one, conditioned to the fixed mass fraction of the fourth component.
- Constant mixture’s mass = \(M = 615\) g
- Constant cement’s mass = \(m = 353\) g
- Constant mixture’s mass with variable composition = \(\Delta = 615 – 353 = 262\) g
- Mass frictions in the ternary mixture were calculated as:

\[a = \text{water (g)/262 g};\]
\[e = \text{SABO (g)/262 g};\]
\[z = \text{rice husk (g)/262 g};\]

For every component’s mass fraction there were selected upper and lower limits according to usual industrial practice. Those limits were:

- \(0.874 \leq a \leq 0.962\) (actually between 64.8 and 71.4% of the constant cement mass)
- \(0.038 \leq e \leq 0.126\) (actually between 2.8 and 9.35% of cement’s mass)
- \(0 \leq z \leq 0.088\) (actually between 0 and 6.53% of cement’s mass)
- This is a case were there are mixture’s components that can’t have mass fraction equal to zero and therefore it is convenient to treat them as pseudo components
- The procedure is to code the mass fractions of each pseudo component in a way that the upper mass fraction will have a coded mass fraction equal to one (i.e., \(X_1 = 1\)), while the lower one will be coded as \(X_i = 0\).
- The equations for this conversion appears below:

Coded mass fraction for water

\[X1 = (a-0.874) / (0.088)\]  \hspace{1cm} (1)

Coded mass fraction for SABO

\[X2 = (e-0.038) / (0.088)\]  \hspace{1cm} (2)

Coded mass fraction for rice husks

\[X3 = (z-0) / (0.088)\]  \hspace{1cm} (3)

The expected regression model from a special cubic factorial design, in a coded form, is:

\[Y = b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 +
+ b_{23} X_2 X_3 + b_{123} X_1 X_2 X_3\]

where \(Y\) stands for the response and \(b_i\) and \(b_{ij}\) are experimentally determined coefficients. The final coded model can be expressed in terms of actual components using equations (1), (2) and (3).

According to the special cubic design, the experimental plan requires a total of 14 essays to include the evaluation of the experimental error (Table I).

The responses for this design were: apparent density of fresh foamed concrete (Dh); apparent density of specimens in dry condition at the age of 7 days (Ds); compressive strength (CS); module of rupture (MOR) and ultrasonic pulse velocity (USPV).
TABLE I
SPECIAL CUBIC EXPERIMENTAL DESIGN FOR AERATED CONCRETE MIXTURES WITH WATER (X1), SABO (X2) AND RICE HUSKS (X3) AS PSEUDO COMPONENTS

<table>
<thead>
<tr>
<th>Essay No</th>
<th>Coded mass fractions</th>
<th>Actual mass fractions*</th>
<th>% of cement’s mass **</th>
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<tr>
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<td>X1</td>
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<td>7</td>
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</tbody>
</table>

*All mass fractions are referred to 262 g of mixture
**The mixtures had a total mass of 615 g, which included 353 g of ARI cement. The percentages in this column are referred to this constant cement mass.

II.4. Preparation of Foamed Concrete

The preparation of foamed concrete for each essay of the special cubic experimental design had the following procedure:

- ARI cement (353 g) and the specified amounts of water and rice husk were mixed at the maximum speed of a mortar laboratory mixer during two minutes. At the end of that time the mixer was stopped and the specified amount of SABO was added, reaching a total mass of 615 g. Then, the mixer was turned on for additional 5 minutes at its maximum speed. From the just prepared aerated concrete, three samples were taken in containers of known volume and weight, for cast density determinations (Dh) and the fresh mixture was poured into 4x4x16 cm³ metallic moulds. The specimens were cured at room conditions for four days. At the age of 14 days, specimens had their dimensions and air dried masses registered for dry density (Ds). The hardened specimens showed a high shrinkage that was more pronounced with the very light ones.

- Flexural and compressive strength of the hardened specimens at the age of 7 days, were determined according to (BRASILIAN STANDARDS, 1991 [8]). Apparent density and water absorption were determined following the procedures described in the text.

- The hydration process was followed by means of a computer aided device provided of PT-100 thermocouples placed into plastic bags containing cement’s mixtures and located in an expanded polystyrene box. The temperature of each bag was registered every 10 minutes. The mixtures consisted in: ARI cement (100 g) with 25 % (w/w) of water and varying mass percentages of SABO (3, 6 and 9%) and with the same percentages of SABO but with de addition of 3% of calcium chloride.

- The ultrasonic pulse velocity (USPV) was measured in air dried specimens by means of a Steinkamp BP-7 ultrasonic device provided with transducers of 45 kHz.

III. Results and Discussion

III.1. Introductory Notes

The inclusion of rice husks as aggregate in the foaming mixtures was decided to detect any undesired interaction of this vegetable material with SABO especially in relation to the water absorption of the hardened foamed specimens and to the stability of the produced foam.

The methodology of experimental designs was applied to express in a quantitative way, the effect of the considered factors (i.e., mix proportions of SABO, water, and rice husks) on the studied foamed concrete properties (i.e., Dh, Ds, CS etc). The correspondent regression models were used to describe the relative influence of the significant factors on the studied property under the specific experimental conditions employed in this work. Therefore they were not intended to give general answers but to show general trends that could be used for comparison purposes.

The main objective of this study was to test if SABO could be used as an air entrainment agent for preparing foamed concrete. In this sense the experiments were planned to gather information about the performance of SABO in lowering the dry density of cement composites without interfering seriously with cement’s hydration and showing compatibility with eventual fillers and accelerators.

III.2. Regression Models

The regression models obtained from the special cubic design are shown in Table II.

It is good to remember that the coded variables in mixture’s designs are not independent variables and they must obey the following relation:

$$\Sigma X_i = 1$$  \hspace{1cm} (4)

The coded variables in a mixture’s model can assume values between zero and one. On the other hand coded models are easier to handle to obtain values of the response in a faster way.
The model for CS makes acceptable predictions especially at low values of CS as it can be observed from Figure 1(c).

High water and SABO proportion in the initial mixture contribute to a low cast density but also to a low Ds value. On the other hand, it can be figured out from the model that at the highest rice husk proportion (i.e., pseudo component \( X_3 = 1 \)), Ds drops from a cast density of 829 kgm\(^{-3} \) to a dry density of 683 kgm\(^{-3} \) indicating that the initial wet foamed structure could be preserved during the drying process. A plot of observed versus predicted values for this model is shown in Figure 1(b).

III.3. Regression Model for Cast Density (Dh)

The model predicts that if \( X_1 = 1 \), which is for water: cement mass ratio of 0.71 with \( X_2 \) and \( X_3 \) being equal to zero (mass ratio SABO; cement 0.028 with no rice husk added), the value of Dh should be 0.65 gL\(^{-1} \):

\[
Dh = 654X_1 + 349X_2 + 829X_3 - 340X_1X_2 - 197X_1X_3 - 300X_2X_3
\] (kg \( \text{m}^{-3} \))

This experimental condition belongs to essay No. 1 of the Table I, which gave for Dh the values 680 and a replicate with 630 kgm\(^{-3} \). It is important not to forget, that in these experiments, air was introduced in the simplest possible way and therefore more elaborated methods of foam making should lead not only to lower cast densities but also to a decrease in the dimensions of micro pores and consequently to a favorable change on the mechanical properties. The model predicts a cast density of 829 kgm\(^{-3} \) when pseudo component \( X_3 = 1 \), which means working with a mixture with the highest proportion of rice husks and the lowest proportions of water (i.e., pseudo component \( X_1 = 0 \)) and SABO (i.e., pseudo component \( X_2 = 0 \)). This result is to be expected because of the addition of a component that does not participate in the foam making process and also does not hinder it.

This model can be useful in predicting cast density from mixture’s composition within the experimental region defined by upper and lower limits of actual mass fractions for water, SABO and rice husk (Figure 1(a)).

III.4. Regression Model for Dry Density (Ds)

The role of individual effects (i.e. component’s mass fractions) is difficult to ascertain because of the existence of interaction terms.

Nevertheless, the individual coefficients for \( X_1 \) (coded mass fraction for water) and \( X_1 \) (coded mass fraction for rice husk) as well as for \( X_1X_2 \) interaction term, are the biggest in the model indicating that those components are the main responsible for Ds values:

\[
Ds = 588X_1 + 255X_2 + 683X_3 - 197X_1X_2 + 372X_1X_3 - 227X_2X_3
\] (kg \( \text{m}^{-3} \))

The model predicts that if \( X_2 = 1 \) means that water and SABO are present at their lowest levels leading to higher compressive strength. It can also be inferred that the presence of rice husks do not affect the mechanical properties of the hardened foamed specimens obtained with SABO. The model for CS makes acceptable predictions especially at low values of CS as it can be observed from Figure 1(c).
Figs. 1. Plot of observed vs predicted values for:
(a) Dh (Cast density of foamed concrete, kgm⁻³) regression model in special cubic experimental design; (b) Ds (Dry density of foamed concrete, kgm⁻³), regression model in special cubic experimental design; (c) CS (Compressive strength, MPa), regression model in special cubic experimental design; (d) USPV (Ultrasonic pulse velocity, kms⁻¹), regression model in special cubic experimental design; (e) MOR (Module of rupture, MPa), regression model in special cubic experimental design

III.6. Regression Model for Ultrasonic Pulse Velocity (USPV)

In this case, the model clearly explains that ultrasound speed depends on specimen’s porosity which in turn depends greatly on the proportions of the components in the mixture. The model has an interaction term (i.e., \(X_1 X_2\)) that predicts that a decrease of USPV is related to the proportions of water and SABO:

\[
\text{USPV} = 1.8 X_1 + 0.9 X_2 + 1.8 X_3 + -0.3 X_1 X_2 \text{ (kms}^{-1})
\]

As expected an increase in rice husk proportion, which acts only as a filler, brings with it an increase of USPV. This model shows a good fit along the measured USPV interval (Figure 1(d)).

III.7. Regression Model for Module of Rupture (MOR)

In the model, the proportion of SABO (i.e., \(X_2\)) has the lowest positive coefficient of the individual components and the largest negative one of the interaction terms:

\[
\text{MOR} = 0.7 X_1 + 0.05 X_2 + 1.4 X_3 - 1.4 X_1 X_3 + -1.5 X_2 X_3 \text{ (MPa)}
\]

The model predicts the lowest MOR value when SABO is used at its maximal proportion (i.e., \(X_2=1\)), while the highest MOR value appears at a maximum of the pseudo component rice husk (i.e., \(X_3=1\)). As in the case of the model for compressive strength, the model for MOR has good prediction behavior at low values of MOR (Figure 1(e)). It is also a model of relative low value of \(R^2\), which means that the found correlations for both responses do not quite describe the variations on these properties.

III.8. Water Absorption

The broken specimens from flexural strength determination, previously weighed, were immersed in water for 2, 24, 48 and 120 hours. At the end of those periods the specimens were weighed and the mass gain was registered.

It can be observed from Figure 2, that water absorption for SABO prepared foamed specimens is high at low dry densities (i.e., 180% for \(D_s = 300 \text{ kg} \cdot \text{m}^{-3}\)) and decreases rapidly with an increase in dry density (i.e., approximately 20% for \(D_s = 600-700 \text{ kg} \cdot \text{m}^{-3}\)).

The tested specimens were selected according to their dry density regardless of the presence of rice husk as filler. These results are similar to those reported in the specialized literature (KEARSLEY and WAINWRIGHT, 2001 [10]) without the presence of rice husk, showing that the vegetable aggregate does not interfere with the water absorption of the hardened SABO foamed specimens.
III.9. Effect of SABO on Cement’s Hydration Process

The retarding effect of SABO on cement’s hydration is shown in Figure 3.

When SABO doses were raised to 6 and 9% over cement (w/w), the temperature peak, which was not well defined at 3%, almost disappeared at the higher doses. On the other hand when the same doses were combined with 3% calcium chloride (mass percentage over cement) temperature maxima were significantly shifted towards lower time values (Figure 4) showing a good compatibility with this accelerator.

According to a report over the effect of lignin based admixtures on cement’s hydration (KUHLIL and WARD, 1973 [11]), the same kind of hydration products are formed at all stages in the presence of calcium lignosulfonate admixture and it appears to alter only the rate of cement hydration rather than effect fundamental changes on the products of hydration.

Since SABO is essentially a dissolved lignin salt, it is reasonable to apply the same conclusions to SABO.

III.10. Correlations between Responses of the Special Cubic Design

Besides finding the former regression models, it was made an attempt to find correlations between the responses of the experimental design.

III.10.1. Dry Density (Ds) as a Function of Cast Density (Dh)

Most of aerated or foamed concrete properties are usually referred to its dry density (Ds). The first and most used correlation is that of cast density Dh versus Ds.

This correlation is useful in designing a target dry density from the value of cast density, Dh. When the responses for Dh from the experimental design were plotted against the corresponding values for Ds, it was obtained a straight line with a positive slope and very well fitted to the following linear regression model:

\[ D_s = -1.42089 + 0.834802 \times D_h \quad (\text{kgm}^{-3}) \]

with \( R^2 = 97.9285\% \) and a p-value for the lack of fit equal to 0.2250.

This model was compared to the one reported by KEARSLEY, 1999 [12], which is very similar:

\[ D_s = 0.868 \times D_h - 55.07 \quad (\text{kgm}^{-3}) \]

with \( R^2 = 99.35\% \).

A plot of both equations is presented in Figure 5.

The difference in intercept values should be attributed to the different age of both types of specimens (i.e., 14 days age for SABO specimens and 28 days for KEARSLEY, 1999 [12]).
### III.10.2. Compressive Strength vs Dry Density

The following model relates compressive strength (CS) with dry density $D_s$:

$$CS = -1.73708 + 0.00672555 \ D_s \text{ (MPa)}$$

The model has $R^2 = 78.15\%$ and a p-value for the lack of fit equal to 0.1806.

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![Graph showing the relationship between compressive strength and dry density.](image1)

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From Figure 6(a), it is possible to appreciate that the model is a good predictor in the range of dry densities tested.

The values for CS from this model are similar to those reported for foamed concrete with low dry densities (KEARSLEY, 1999 [12]).

### III.10.3. Module of Rupture vs Dry Density

There were tested several types of models trying to fit the experimental data and it was found the best choice was a square root of MOR model:

$$MOR = (-0.00532162 + 0.00151801 \ D_s)^2 \text{ (MPa)}$$

with $R^2 = 82.73\%$ and p-value for the lack of fit equal to 0.2544.

Figure 6(b) shows observed versus predicted values.

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### III.10.4. Compressive strength vs Ultrasonic Pulse Velocity (USPV)

The compressive strength could be correlated with the USPV by means of a multiplicative model with an acceptable fit:

$$CS = 0.178976 \times USPV^{4.32997}$$

This model has $R^2 = 78.67\%$ and a p-value for lack of fit equal to 0.1712.

From Figure 6(c), it can be concluded that this equation could serve as a good approximation to CS values using non destructive test by ultrasound.

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### IV. Conclusion

The obtained regression models are considered as evidence that SABO use gives foamed concrete specimens with comparable properties to other known air entrainment products. The water absorption behavior of SABO foamed specimens is similar to that reported for foamed concrete specimens prepared with other foaming agents. The addition of SABO causes a retard on cement’s hydration which is offset by calcium chloride.

It is concluded that SABO is an alternative to the existing foaming agents and that its use could help to diversify the industrial applications of carbonization processes and to increase the availability of foaming agents for aerated concrete.
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References