



# Role of Fe compounds in light aggregate formation from a reservoir sediment

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## ABSTRACT

A one-step thermal process at 1050 °C and 1150 °C including bloating and sintering reactions produced lightweight aggregates (LWAs) with an apparent particle density of 2.08 and 1.18 g cm<sup>-3</sup>, respectively, from pellets made of the sediment of a local reservoir. The roles of Fe compounds occurred in the sediment in bloating mechanism were determined with X-ray absorption spectroscopy (XAS) technique. About 59 at% of the total Fe is in forms of Fe<sup>2+</sup> in the raw sediment; whereas most Fe was oxidized to Fe<sup>3+</sup> in all LWAs, except in core part of the LWA produced at 1150 °C. The bloating reactions occurred in the core of the 1150 °C LWA is suggested to be mainly associated with the decomposition of FeSO<sub>4</sub> into FeO with a concomitant release of SO<sub>2</sub>, SO<sub>3</sub>, and O<sub>2</sub>; the valence state of Fe was not changed. The generally accepted mechanism – the chemical reduction of Fe<sub>2</sub>O<sub>3</sub> component to FeO with a release of O<sub>2</sub> is responsible for the bloating phenomenon – is not observed in present study.

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## 1. Introduction

Deposited sediments in reservoirs in Taiwan are attributed to the scouring out of mudstone. The sediments have been severely shrinking the water-storage capacity of all Taiwan reservoirs; thus, dredging the sediments is an important issue for the governmental authority. Although the sediments used to be treated as wastes which needed proper disposal of, they are so rich in shale, slate, and clay that they can be recycled and serve as raw materials in the sector of construction engineering, as well as ceramics manufacture. Because the sediments can release gases when they are heated at high temperature, a previous study has used them to prepare lightweight aggregate (LWA) by the use of bloating and sintering processes in Taiwan [1]. Furthermore, given the adverse environmental impact and the potential depletion of natural mineral resource (e.g., clay, volcanic ash, pumice, siliceous rock, and others) suitable for preparing LWA, there is a trend to recycle wastes (e.g., reservoir sediment, sewage sediment and others) as a substitute for the natural mineral resource.

Two types of reactions are required for LWA formation from heating various suitable raw materials, as agreed by all previous LWA-related researches [1–3]. First, gases serving as bloating agents have to be released to create pores when the raw material is heated at a high temperature, the reaction being termed “bloating or vesicant reaction” [1–3]. Second, a glassy surface needs to be formed through sintering reaction when the raw material is heated at the

high temperature [1–3]. The glassy surface formed by the sintering reaction needs to encapsulate the gases released by the bloating reaction to produce LWA. Riley pointed out that the temperature range of 1000–1300 °C was most appropriate for the sintering and bloating reactions to take place to prepare LWA from clay mineral [4]. Being the fourth abundant element in the earth crust (i.e., seconded to O, Si, and Al), Fe compounds plays an important factor in the bloating reactions because they have been considered to release gases during the heating process [4,5]. Riley has considered the following chemical reactions for various Fe compounds in clay to bloat during LWA formation [4]; and thus far while considering Fe compounds as bloating components, most studies have generally agreed that these chemical reactions are responsible for the bloating mechanisms.



Note that rxns (1) and (2) involve the decomposition of Fe<sub>2</sub>O<sub>3</sub> with a concomitant release of O<sub>2</sub> that is responsible for the bloating mechanism. In order to let (3) occur, both sufficient oxygen source and good contact between the oxygen and FeS are required. The first decomposition reaction (i.e., (1)) chemically reduces trivalent Fe to divalent Fe, and (2) reduces the average oxidation state from 3+ to 2.67+. Note that the reaction product Fe<sub>3</sub>O<sub>4</sub> in (2) is a composite salt (i.e., Fe<sub>2</sub>O<sub>3</sub>·FeO); thus (2) can be conceptually regarded as partial decomposition of Fe<sub>2</sub>O<sub>3</sub> into FeO. This can be better understood by rewriting (2) as the following expression:



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Further, in contrast to rxs (1) and (2), (3) involves no change in the oxidation state of Fe.

Although the bloating mechanisms attributed to the chemical reactions involving Fe compounds for LWA formation have been accepted for more than half a century, to the best of our knowledge, so far rxs (1)–(3) have simply been proposed based on the information of general chemistry with very limited direct evidences. Recently, the change in valence state of Fe in a harbor sediment after the sintering/bloating process at elevated temperatures has been determined with synchrotron-based X-ray absorption spectroscopy (XAS) [6]. In contrast to the generally accepted mechanism that the average oxidation state of Fe would decrease or remain unchanged during the sintering/bloating process, they observed an increase in the Fe oxidation state after the sintering/bloating process based on the shift of the main edge peaks in their X-ray absorption near edge structure (XANES) spectra [6]. However, they failed to quantify the distribution of Fe species in their LWAs because the XANES simulation results from their samples were unsuccessful. The poor XANES simulation probably resulted from the influence of chlorides which have relatively low melting points and flow easily to react with other components present in the harbor sediment to form composite salt(s).

It might be reasonable to consider the aforementioned reactions (rxs (1)–(3)) as bloating reactions associated with Fe compounds from the aspects of chemistry. Nevertheless because Fe in raw material, such as harbor sediment, reservoir sediment and clay, may be present in various species, knowledge of quantitative distribution of various Fe species in the raw material and the produced LWAs would provide useful information for understanding the mechanisms of bloating when considering Fe compounds as bloating agents. Although it has been difficult to gain insight into the roles of various Fe compounds in bloating process, with the usage of XAS in present work to study LWA formation, this difficulty may be eased.

Synchrotron-based XAS technique has emerged to provide information needed for a long-term solution of waste management and environmental remediation [7–10]. Using Fe as an example, an Fe *K*-edge XAS spectrum, including XANES and extended X-ray absorption fine structure (EXAFS), is capable of revealing speciation, distribution, form transformations, and mobility of target metal Fe [7]. The objective of this study is to use XAS technique to investigate the change of Fe species distribution in samples due to the sintering/bloating process that was used to prepare LWAs from a reservoir sediment. This information will help us to better understand the real-world mechanisms of bloating reactions.

## 2. Experimental

The reservoir sediment was collected from Shihman Reservoir located in northern Taiwan that has been dredged yearly and was dried at 105 °C in an oven for 24 h. The dried sediment was ground to <50 meshes before a pressure of 5000 psi was applied to shape it into pellet form. Most elemental compositions of the dried and ground raw sediment were determined with an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 3000DV, PerkinElmer, USA) following a microwave (MDS-2000, CEM, USA)-assisted acidic digestion of the sediment. Si content in the sediment was determined based on the sample weight loss after its reaction with HF to form H<sub>2</sub>SiF<sub>6</sub> that is relatively volatile [11]. The water-extractable contents of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> were analyzed with an ion chromatographer (IC, DX-100, Dionex, USA). The “loss on ignition” was defined as the weight loss after heating at 900 °C for 3 h under atmospheric air condition. Particle size distribution of the raw sediment was determined by the use of sieve analysis for the sand fraction (<53 μm) and hydrometer method for the silt (2–53 μm) and clay (<2 μm) fractions [12].

To generate LWA by bloating and sintering the pellet at 1050 °C and 1150 °C without blasting it into small pieces, the pellet had to experience a de-volatile pretreatment process at a temperature much lower than 1050 °C [6]. For the de-volatile process, the pellet was heated from room temperature to 500 °C at a heating rate of 100 °C min<sup>-1</sup> in an electrically heated oven and stayed at the 500 °C plateau for 5 min. The temperature 500 °C was selected based on the results obtained with a thermogravimetric analyzer (TGA, SDT Q600, TA Instrument, USA). The de-volatilized pellets were cooled down to room temperature, and ready for the bloating/sintering reactions in atmospheric air at 1050 °C and 1150 °C for 20 min in the oven that has already reached the pre-set temperatures 1050 °C and 1150 °C.

After the LWA manufacturing process, both the green sediment and LWAs were examined with scanning electron microscopy (SEM, 3000-N, Hitachi, Japan), X-ray diffraction (XRD, D8 Advance, Bruker AXS, UK) technique, and XAS. Prior to the XAS-recording experiments, the materials of the glassy shells (termed “1050 °C-S” and “1150 °C-S”) and porous cores (termed “1050 °C-C” and “1150 °C-C”) of the LWAs were separated. The core and shell of the LWAs could be easily differentiated and they were separated with a glass rod after the LWAs were fractured with an agate stick because the core had porous chalky structure while the shell was a dense, hard continuous layer with approximately 1–2 mm thickness. Each of these cores, shells, and the dried green sediment (denoted as “105 °C raw”) was ground with an agate mortar and recorded for its XAS spectrum. Only a small amount of sample was required for the XAS experiment. Fe *K*-edge XAS spectra from all samples were recorded on the wiggler C (BL-17C) beamline at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. The facility had a ring storage energy of 1.5 GeV, an electric current of 120–200 mA, and an energy span of 4–15 keV for the monochromator during the data collection period. The energy resolution ( $\Delta E/E$ ) was  $1.9 \times 10^{-4}$ . The Fe *K*-edge jump locates at 7112 eV. All spectra were recorded in transmission mode at room temperature. The reference compounds used in this study were Fe metal, FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeS, FeS<sub>2</sub>, FeSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. WinXAS 3.0 software was employed for XAS data reduction [13]. With this software, we were able to simulate most sample XANES spectra to quantify Fe species fraction based on their fingerprints in the near edge region by linearly combining a set of the XANES spectra from reference compounds. The simulation is based on the least squares procedure, and it calculates two parameters (i.e., species fraction and energy correction) for each reference compound. Upon finishing the simulation refinement process, Fe references showing negative fraction or unreasonable energy shift are usually not present in the simulated sample [13].

## 3. Results and discussion

### 3.1. Characteristics of green reservoir sediment

Material containing SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and flux (Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, MgO and CaO) in appropriate proportion is suitable for vesicant/sintering process [4]. Table 1 shows the elemental compositions, expressed in oxide forms, of the reservoir sediment. Its primary composition is silica (64.55%) and the second one is Al<sub>2</sub>O<sub>3</sub> (16.06%). Flux, including the components Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, and CaO, represents 14.21% by weight of the total of the dried raw sediment. The data of the elemental compositions indicates that the reservoir sediment is suitable to serve as a raw material for producing LWA [4]. The particle size distribution of the reservoir sediment is shown in Fig. 1. The total fraction of silt and clay (<53 μm) is about 85%. The richness in the fraction of this small particle size makes the sintering process easy to occur to encapsulate the gases released by bloating reaction.

**Table 1**  
Elemental compositions expressed in oxide form in the reservoir sediment dried at 105 °C.

Constituent	Constituent percentage
Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	16.06
SiO <sub>2</sub> <sup>c</sup>	64.55
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	4.95
K <sub>2</sub> O <sup>a</sup>	1.99
Na <sub>2</sub> O <sup>a</sup>	6.85
CaO <sup>a</sup>	0.33
MgO <sup>a</sup>	0.086
PbO <sup>a</sup>	0.0095
ZnO <sup>a</sup>	0.019
Cr <sub>2</sub> O <sub>3</sub> <sup>a</sup>	0.0095
Cl <sup>-b</sup>	0.029
SO <sub>4</sub> <sup>2--b</sup>	1.15
LOI <sup>d</sup>	3.98

<sup>a</sup> Analyzed with ICP-AES.

<sup>b</sup> Water-soluble fraction, analyzed with ion chromatograph.

<sup>c</sup> Analyzed according to CNS 11393.

<sup>d</sup> Loss on ignition after heating at 900 °C for 3 h. The sum of the components is 104.8% and each component is normalized to a sum of 100%.

### 3.2. Properties of the LWA products

The apparent particle densities, defined as the ratio between weight and volume of a LWA particle, of the LWAs produced at 1050 °C and 1150 °C are 2.08 and 1.18 g cm<sup>-3</sup>, respectively. The individual LWA particle volume, excluding the pores available to water, was determined based on the Archimedes's principle. Note that the apparent particle density of the green pellet before the bloating/sintering process was 3.18 g cm<sup>-3</sup>. The apparent particle density decreases with increasing bloating/sintering temperature. Further, the bulk densities of the 1050 °C and 1150 °C samples are determined to be 1180 and 360 kg m<sup>-3</sup>, respectively. The bulk density is defined as the weight of the bulk LWA materials in a unit volume which includes the volume of the individual particles and that of the voids between the particles [14]. The water absorption for the LWAs produced at 1050 °C and 1150 °C are 10.6 and 7.3%, respectively. The lower water absorption for the 1150 °C LWA was due to the formation of a less-pore glassy surface because sintering a material at a higher temperature usually turns its surface into less porous surface. Both LWA samples meet the generally accepted requirement on the water absorption of LWAs (i.e., 2–20%).

The SEM micrographs (1000×) of fractured cores of the LWAs produced at 1050 °C and 1150 °C are shown in Fig. 2. The microstruc-

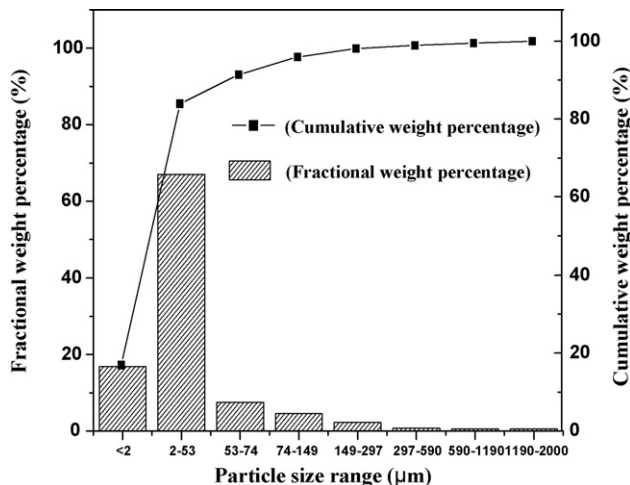
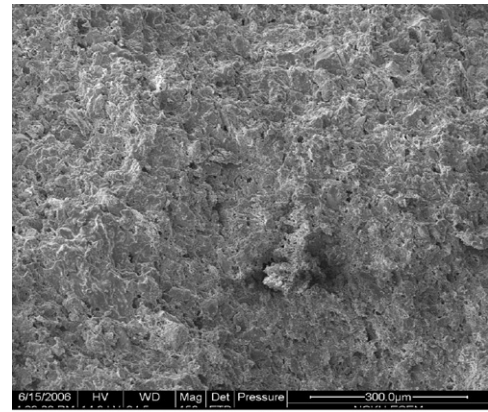
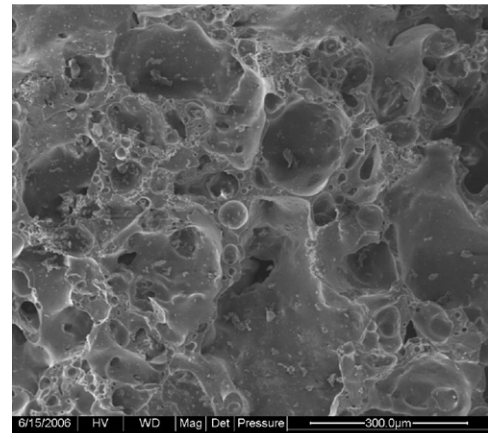


Fig. 1. Particle size distribution of reservoir sediment dried at 105 °C.



1050 °C



1150 °C

Fig. 2. SEM micrograph (1000×) from core of lightweight aggregates produced at 1050 °C and 1150 °C.

ture of core of the LWA produced at 1050 °C has many small spherical pores. In contrast, the core of the 1150 °C LWA is glassy with relatively large pores of various sizes, indicating that the gases released during the 1150 °C bloating/sintering process were effectively encapsulated by the glassy shell formed. The heating process at 1050 °C did not effectively trigger the bloating/sintering reactions. The results from the core micrographs (Fig. 2) are consistent with the results from the measurements of apparent particle density; the bloated product containing larger pore size has a lower apparent particle density.

Fig. 3 depicts the XRD patterns from the sediment dried at 105 °C and the LWA produced at 1150 °C. Major crystalline phases present in the “105 °C raw” sample were SiO<sub>2</sub> (quartz, syn), SiO<sub>2</sub> (hydrate), Al<sub>2</sub>O<sub>3</sub> (corundum, syn), and FeO (wustite, syn); diffraction patterns assigned to other components were not found. The 1150 °C LWA product contained a reduced level of both quartz and corundum with an absence of silicon oxide hydrate, wustite, and new crystalline phase. FeO crystalline phase is not observed in the XRD pattern from the 1150 °C sample; two possible reasons are suggested. First, after the high-temperature sintering/bloating process, FeO might exist in amorphous phase. Second, FeO chemically reacted with other matrix components to form composite salt(s) which is amorphous and/or too small in crystallite size to be detected with XRD technique. The second explanation will be shown to be consistent with the fact that the XANES simulation (Fig. 4) from the 1150 °C-C sample is a failure, due to the lack of incorporating appropriate Fe-containing composite reference compound(s) due to their commercial un-availability. The XRD patterns provide very limited information necessary for understanding

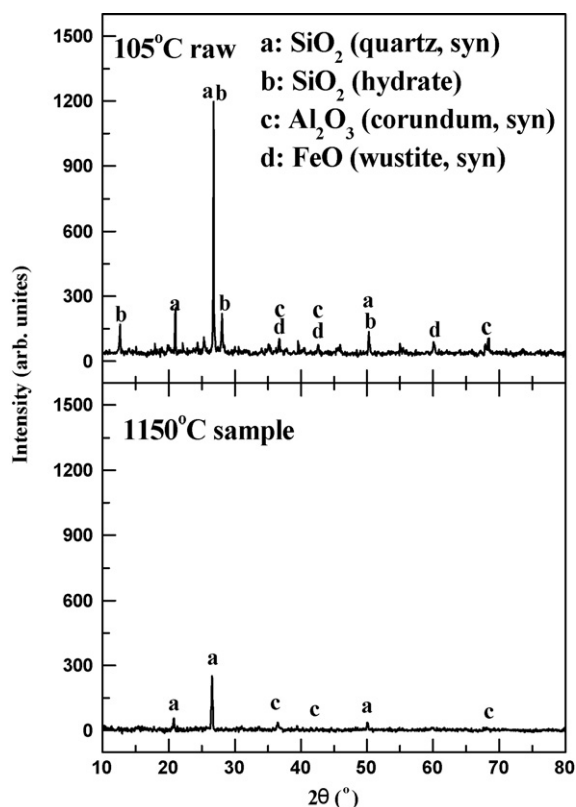


Fig. 3. XRD patterns from reservoir sediment dried at 105 °C and lightweight aggregate produced at 1150 °C.

the mechanisms of bloating/sintering process in the present study.

### 3.3. Bloating mechanism based on results from Fe K-edge XAS

Fig. 4 shows the simulation results of sample XANES spectra simulated with that of eight references: Fe(0), FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeSO<sub>4</sub>, FeS, FeS<sub>2</sub>, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The reasons for selecting these Fe compounds as references are described as follows. Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were chosen as reference compounds because previous studies considered them to be responsible for the bloating process; SO<sub>2</sub> + O<sub>2</sub> and O<sub>2</sub> were suggested to be released, respectively with a concomitant decrease in the valence state of the Fe to form FeSO<sub>4</sub>, FeO, and Fe<sub>3</sub>O<sub>4</sub> [4,6]. However no direct evidence regarding the decrease of iron valence state was previously shown. Further, the reasons for selecting FeSO<sub>4</sub>, FeS, and FeS<sub>2</sub> as reference compounds are because they may occur naturally in the reservoir sediment or formed in the LWAs.

The solid curve in each panel of Fig. 4 is the sample experimental XANES, and the open circle curve is the simulated one. The percents of the reference compounds listed in each panel are the results from the XANES simulation. The performance of the XANES is judged based on residual value of the XANES simulation. The mathematical expression of the residual value was given in a previous study [15]. It was defined as the ratio between the sum of the absolute values of the offsets of the simulated XANES from the normalized absorption of the experimental XANES and the normalized absorption of the experimental XANES. In this study all the residual values are <1.50, except for 1150 °C-C sample which has a residual value 2.73. Further, a visual examination of the “1150 °C-C” panel in Fig. 4 indicates that the simulation in the XANES edge region (around 7.12 keV) is poor; there is no clear match between the simulated XANES and the experimental one. Thus, only the results from

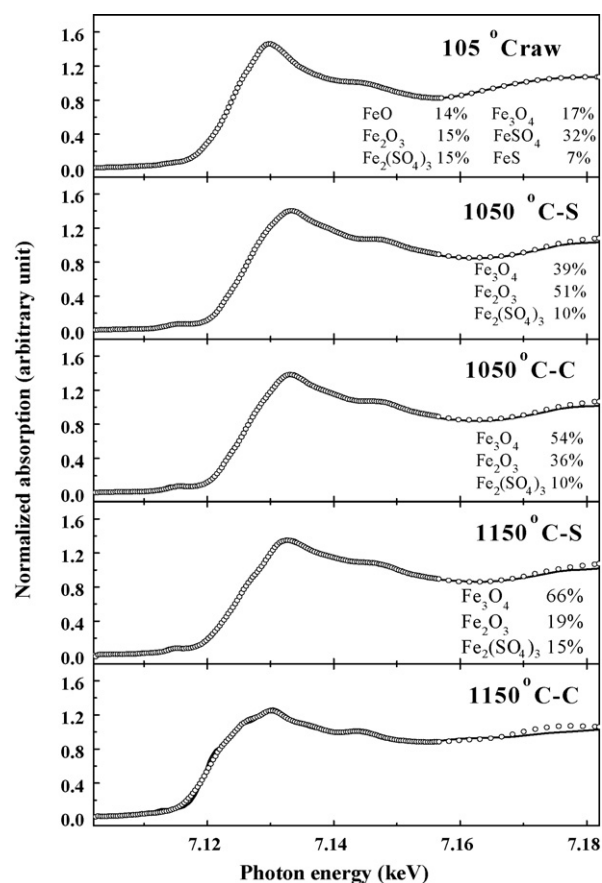
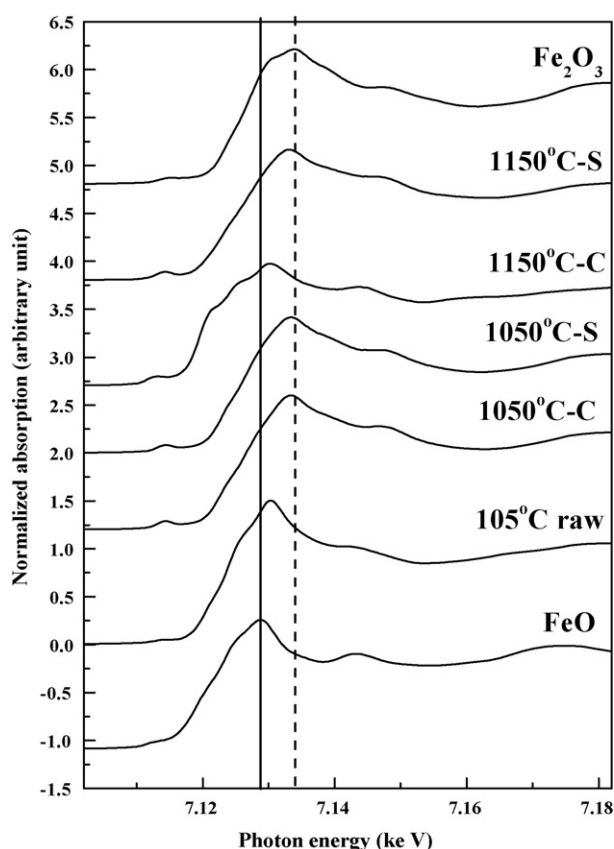


Fig. 4. Experimental and simulated XANES spectra from reservoir sediment dried at 105 °C and shells and cores of lightweight aggregates produced at 1050 °C and 1150 °C (— experimental; (ooo) simulated). The Fe species distribution in each panel results from XANES simulation.

successful XANES simulation, or the top four panels of Fig. 4, are presented in the respective panels. No Fe species distribution is presented in the “1150 °C-C” panel because the XANES simulation is poor with a significant level of residual value after the least square fitting. The poor simulation is suggested to result from the lack of incorporating Fe reference(s) other than the currently available references; it is thus inferred that fractional Fe might have chemically reacted with certain components present in the sediment to form composite salt(s). Poor simulation results similar to this study have also been observed and discussed in previous studies [7,8].

Since Fe<sub>3</sub>O<sub>4</sub> is a composite salt (Fe<sub>2</sub>O<sub>3</sub>·FeO), thus by conceptually decoupling Fe<sub>3</sub>O<sub>4</sub> into Fe<sub>2</sub>O<sub>3</sub> and FeO, the results in “105 °C raw” panel show that approximately 59% Fe in the raw sediment prior to bloating/sintering has divalent oxidation state (Fe<sup>2+</sup>) and the balance is trivalent (Fe<sup>3+</sup>). After the bloating/sintering process, the Fe<sup>2+</sup>/total Fe ratio significantly drops from 59% to 13% (in 1050 °C-S sample), 18% (in 1050 °C-C), and 22% (in 1150 °C-S). This study shows an increase in the average Fe oxidation state during the bloating/sintering process; this fact is contradictory to what suggested in previous studies [4,6]. Not taking the 1150 °C-C sample into consideration, our results do not support the conventionally accepted mechanism that bloating reactions are associated with an increase in the Fe<sup>2+</sup>/total Fe ratio. Based on the XANES simulation results, the decrease in the Fe<sup>2+</sup>/total Fe ratio in 1050 °C-S, 1050 °C-C, and 1150 °C-S samples is suggested to mainly result from three chemical reactions: decomposition of FeSO<sub>4</sub> into Fe<sub>2</sub>O<sub>3</sub> and oxidations of FeO and FeS into Fe<sub>2</sub>O<sub>3</sub> by oxygen. The latter two reactions would reduce FeO content in the 1050 °C-S, 1050 °C-C, and 1150 °C-



**Fig. 5.** Comparison among experimental XANES spectra from reservoir sediment dried at 105 °C, shells and cores of lightweight aggregates produced at 1050 °C and 1150 °C, and two oxide references: FeO and Fe<sub>2</sub>O<sub>3</sub>.

S samples. For the decomposition reaction of FeSO<sub>4</sub>, it is suggested as follows:

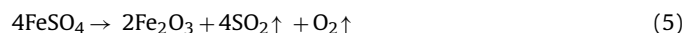


Fig. 5 presents a comparison among all XANES spectra from five samples and two Fe references: FeO and Fe<sub>2</sub>O<sub>3</sub>. The vertical lines running through all spectra are intended for an easier comparison among them. Bajt et al. have demonstrated that less Fe oxidation state in oxides is associated with lower photon energy for the pre-edge peak (located around 7115 eV), and the difference in the pre-edge photon energy between Fe-containing sample and FeO is linearly proportional to Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) [16]. Because Fe compounds other than oxides are present in our samples, it might not be appropriate for the present study to follow the quantitative method proposed by Bajt et al. But regarding the photon energies of the white band peak position of the XANES spectra, the 105 °C raw and 1150 °C-C XANES are quite close to each other (i.e., located at about 7130.5 eV); whereas the peaks of the other three samples (i.e., 1050 °C-S, 1050 °C-C, and 1150 °C-S) locate at about 7132.5 eV. Note that the white band peaks from FeO and Fe<sub>2</sub>O<sub>3</sub> references locate at about 7128 and 7134 eV, respectively. Thus it is suggested that both 105 °C raw and 1150 °C-C samples contain similar average Fe oxidation state. In summary, the present study suggests that the dominant bloating reaction for the “1150 °C-C” sample might be mainly associated with the decomposition of FeSO<sub>4</sub> into FeO with concomitant release of SO<sub>2</sub>, SO<sub>3</sub>, and O<sub>2</sub>. The resulting FeO might have reacted with other matrix components to form composite salt(s).

#### 4. Conclusions

With XAS technique the present study determined the roles of the Fe compounds during the bloating/sintering process at 1050 °C and 1150 °C to produce LWAs from reservoir sediment. The XANES simulation results indicated that about 59% of the total Fe in the raw sediment was in form of Fe<sup>2+</sup>; while most Fe was oxidized to Fe<sup>3+</sup> in the core and shell of LWA particle produced at 1050 °C, as well as in the shell of the LWA produced at 1150 °C.

The bloating phenomenon occurred in the core of the LWA produced at 1150 °C is suggested to be mainly associated with the decomposition of FeSO<sub>4</sub> into FeO with concomitant release of SO<sub>2</sub>, SO<sub>3</sub>, and O<sub>2</sub>. Iron oxidation state in this core sample is similar to that in the raw sediment dried at 105 °C. The generally accepted mechanism in literature – Fe<sub>2</sub>O<sub>3</sub> component is chemically reduced to FeO with a release of O<sub>2</sub> to generate the LWA – is not observed in present study.

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