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Chen, Wan; Ottosen, Lisbeth M.; Jensen, Pernille Erland; Kirkelund, Gunvor Marie; Schmidt, Jacob Wittrup

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A COMPARATIVE STUDY ON ELECTRODIALYTICALLY TREATED BIO-ASH AND MSWI APC-RESIDUE FOR USE IN BRICKS

W. CHEN*, L. M. OTTOSEN, P. E. JENSEN, G. M. KIRKELUND and J. W. SCHMIDT

Department of Civil Engineering, Technical University of Denmark, Denmark.

*Corresponding author: e-mail wach@byg.dtu.dk, telephone + 4545251816

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Abstract

Two main electrodialytically treated particulate residues: co-combusted straw and wood fly ash (TSWFA) and municipal solid waste incineration (MSWI) air pollution control residue (TMAPC), were considered for partly clay replacement (up to 25 %) in brick production. Another washed MSWI fly ash (WMFA) was also studied to compare with TMAPC. They had the main difference in calcite content.

Brick pellets containing maximum 25 % ash were shaped by pressing and fired at temperatures ≤ 1100 °C. The sintering properties of the materials were determined, including weight loss, shrinkage, vacuum water absorption, apparent porosity and bulk density. The heavy metal leaching from the pellets containing TMAPC and WMFA was also investigated.

The water absorption of the pellets increased as the addition of TSWFA and TMAPC increased, and it decreased as the sintering temperature increased. The total shrinkage decreased significantly due to the addition of the ashes. The results showed that brick pellets sintered at 1100 °C with 25 % TSWFA addition, or at 1000 °C with 5 % TMAPC met the water absorption requirement for Grade MW building bricks in ASTM C62 – 13a. Cr from TMAPC and WMFA, posed the major leaching problem among the heavy metals.

The results indicate that the treated fly ash from co-combusted straw and wood can be used in making clay bricks. The relatively high amount of calcite in TMAPC seemed to retard its use into yellow clay. This explains the different sintering behaviors of TMAPC and WMFA in this study.

1- INTRODUCTION

Clay, a non-renewable natural resource, is the major raw material for clay brick production. When mixed with water, clay minerals, e.g. hydrous aluminum silicates, show plasticity and formability. During firing at high temperatures, SiO_2 and Al_2O_3 in clay react to form brick network. Meanwhile, fusing occurs owing to the network modifiers (e.g. K_2O and Na_2O), and then bricks shrink and become dense and strong, possessing long durability. Such behaviors make clay born for ceramics. However, the ban of using solid clay bricks has been set in China [1, 2], for the main reasons to prevent farmland destruction, to reduce the energy consumption [3], and to reduce gas emission during firing clay bricks. New and sustainable building materials have been encouraged, and will be the inevitable trend of development. Commonly, additives are blended to modify clay compositions in order to produce different bricks for example in color and porosity, and to improve the properties, such as strength and chemical resistance [4]. The additives can be pure chemicals (e.g. BaCO_3), natural resources (e.g. sand to lower shrinkage) and even wastes.

Waste is generated continuously in high amounts, and requires proper management methods. Using particulate waste products as clay substitute has the following advantages: (1) to utilize the waste as secondary resources and landfill less; (2) to save clay. The waste recycling situation in fired clay bricks was reviewed in [5]. It reveals that replacing clay with waste (e.g. limestone dust, wood dust, fly ash and sludge) is promising and has positive effects on the materials' sintering behavior. In most cases in [5] covering the reuse of sludge, vegetal matters, grass, sawdust and combustion, porosity of the fired bricks increased, and density decreased, which could improve the insulation property of bricks [6], and reduce transport costs. Water absorption increased due to the increase in open pores, which could reduce the brick durability when too much water penetrates into brick. Fly ash is a by-product from waste incineration. The SiO_2 , Al_2O_3 and CaO contents in fly ash are attractive as a clay substitute [7]. However, the high heavy metal content retards its application to some extent. Municipal solid waste incineration fly ash is highly toxic [8], and straw and wood fly ash contains a relatively high amount of Cd [9]. To avoid health issues and ensure social acceptance, it would be preferential to remove these heavy metals before using the ash in construction materials.

There are techniques investigated to treat contaminated ash, such as washing treatment [10], thermal treatment [11], acid extraction and precipitation, and combination of water washing and electrokinetic stabilization [8, 9, 12, 13]. Washing removes easily soluble compounds in ash. It is a simple method that can be applied as an early-stage treatment, which could be followed by e.g. sintering to produce aggregates [14]. In comparison to the ash prior to washing, the washed ash shows significant reduction in soluble salts (e.g. alkaline chlorides), and could be enriched in some heavy metals [15]. Heavy metal dissolution is however also happening to some extent [16]. The ash application would benefit from the washing process, such as the most favorable aspects in reducing the heavy metal leaching [16], and improving the chemical and mechanical properties of the sintered products [15].

Electrodialytic remediation (EDR) is a method developed to reduce heavy metals in ash through electromigration in an applied electric field [8, 9, 12, 13, 17, 18]. The important functions of EDR are: (1) decreasing metal solubility, e.g. Ba, Cr and Pb [18]; (2) reducing heavy metal and salt leaching to some extent [12]; and (3) removing heavy metals, such as Cd, Cu, Pb and Zn [8, 9]. The combination of water washing and EDR can minimize the ash

dissolution and reduce the heavy metal leachability [8].

The aim of this study was to investigate the effect of partly replacing clay with electrodiallytically treated ash in clay brick production on the sintering behavior. Laboratory clay brick pellets were made to find out how the clay substitution affects the sintering behavior in terms of weight loss, shrinkage, vacuum water absorption, apparent porosity and bulk density. The heavy metal leaching was also investigated.

2- MATERIALS AND METHODS

Materials

Four raw materials (clay, two EDR treated ash, and washed MSWI fly ash) were used:

- (1) The clay was collected from a brickwork for the production of yellow bricks. Pure clay has plate-like structure, but the clay used in this study did not show this structure, so it suggests impurities in the clay. The yellow colour of the brick is caused from the mass of CaO being at least 3 times higher than the mass of Fe₂O₃ in the original clay.
- (2) EDR *Treated co-combusted Straw and Wood Fly Ash* (TSWFA): the ash originated from Enstedværket CHP plant (Dong Energy, Denmark). The raw ash was prewashed in distilled water prior to the treatment in a 3-compartment EDR cell.
- (3) *Water-Washed MSWI Fly Ash* (WMFA): the raw fly ash, which originated from a municipal waste incinerator in Denmark (REFA), was washed in the same way as prewashing the raw ash in (2).
- (4) *Treated MSWI Air Pollution Control* (TMAPC) residue: the raw residue was also collected from REFA. It included flue gas cleaning products formed upon injection of ammonia and slaked lime (Ca(OH)₂), while MSWI fly ash in (3) included only flue gas cleaning products formed upon injection of ammonia, taken out before lime injection. The residue was ED treated, and the process is reported in Kirkelund et al. [12]. During the treatment, the mobile fraction of heavy metals and the major part of soluble salts were removed in the electrodialytic stack.

Treatment experiment

Figure 1 shows the principle of electrodialytic remediation. The water-washed fly ash was suspended in water, and placed in the demineralization compartment (compartment II). Compartment I and III are electrode compartments, containing circulated electrolyte (0.01M NaNO₃ solution with pH 2 adjusted by HNO₃) during the experiment. Upon the electric field, mobile ions in the ash electromigrate to the concentration compartments through the ion exchange membranes, therefore achieving the extraction of ions from the ash suspension. The ash was treated for 66 days with liquid to solid ratio (L/S) of 7 at the current of 10 mA.

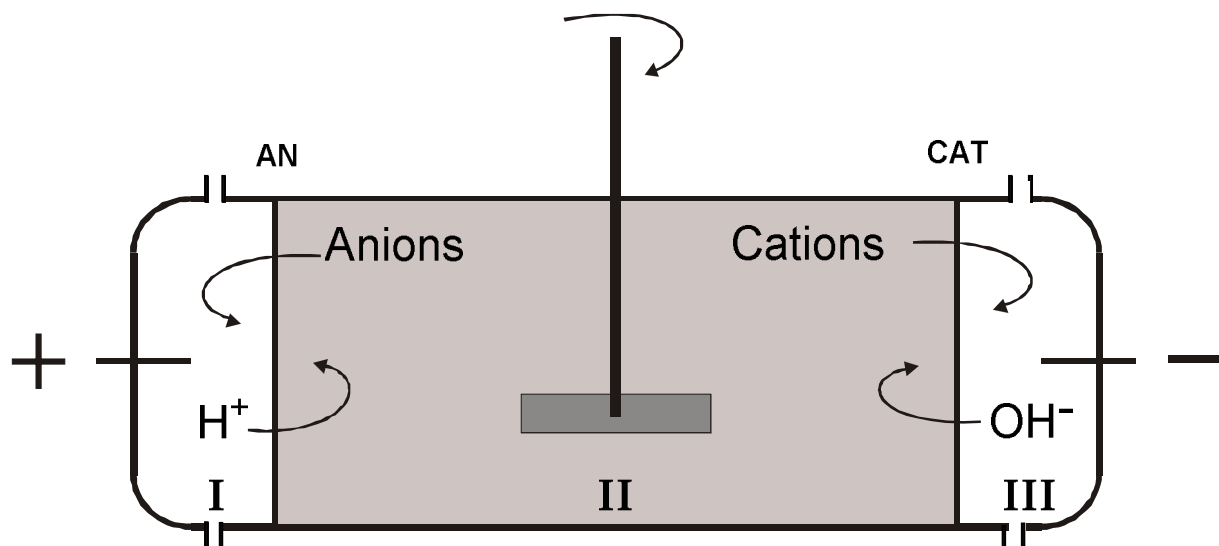


Figure 1: The principle of EDR treatment and the schematic drawing of a 3-compartment EDR cell. AN - Anion exchange membrane, and CAT - cation exchange membrane.

Analytical

The analytical methods are shown in Table 1.

Material	Elemental content	Atterberg test	CaCO ₃	XRD	pH
Ashes	√			√	√
Clay		√	√	√	

Table 1: Material characterization methods.

Elemental content determination by acid digestion according to Danish standard DS 259 [19]: 1 g of dry ash was digested by 20 ml (1:1) HNO₃ under the pressure of 200 kPa (120 °C) for 30 min. After digestion the sample was vacuum filtered through a 45 µm filter and diluted to 100 ml. Series of at least three replicates were made. The heavy metal concentration was measured by ICP-OES (Varian 720-ES, Software version: 1.1.0).

Atterberg test: Liquid limit (w_L ,%) and plastic limit (w_P ,%) were determined according to DS/CEN ISO/TS 17892 – (part 6 [20], 12 [21]). Using 76 g of fall-cone the liquid limit was measured. The difference between liquid and plastic limit is the plasticity index (I_P or PI).

CaCO₃ content: Using the Scheibler-method the CO₂ generated from clay reacting with 10 % HCl was measured volumetrically. Before this, a standard curve (V_{CO_2} vs m_{CaCO_3}) was plotted using pure CaCO₃. A corresponding CaCO₃ content therefore can be found in the standard curve based on the measured CO₂ volume from clay. The same measurement was not conducted on the ash samples due to the presence of reactive compounds that could release gas when encountering HCl.

X-ray diffraction (XRD, 2 θ Cu K α , 40 mA, 45 kV): The crystalline phases were studied using PANalytical X'pert Pro diffractometer.

Using a combined Radiometer pH electrode, pH_{H2O} was measured in the L/S of 5 after 1 h of agitation.

Preparation and testing of brick pellet specimens

All the materials (ash and clay) were manually grinded to fine particles before accurately mixed under different proportions (maximum 25 % ash), and distilled water was added into the mixture. The water contents in the wet clay and the wet clay-ash mixtures were 15 % and 20 - 22 %, respectively. The processes involved are shown in Figure 2.

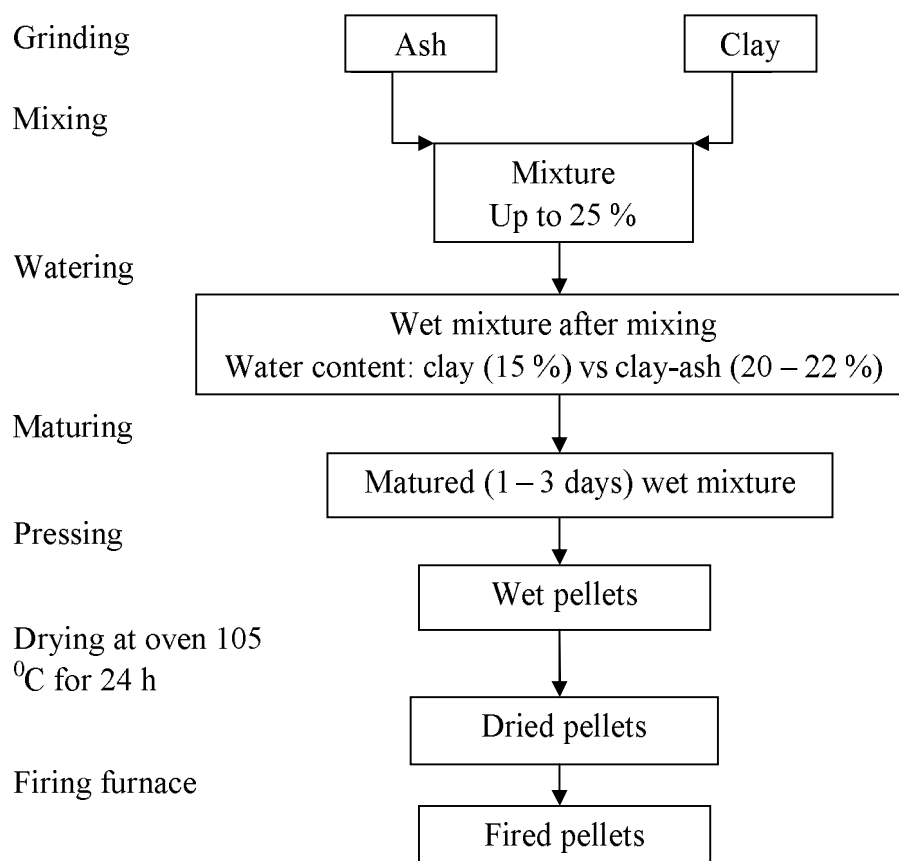


Figure 2: Brick pellet making processes.

The preliminary test method in [22] was adopted in the study. The wet pellets were made under the pressure around 47.0 ± 0.5 MPa by a man-made press die (Figure 3). The pellet press die was made from stainless steel. It consists of 5 main components, as detailed in Figure 3. The base of the press die and the piston (part 2) support frame is a whole unit. Part 3 and part 4 make a material holder. Part 3 is the base for the holder, and the wet pellet stands on it. In the pressing process, an external pressure is applied to the top of the piston. Part 5 was designed to aid the removal of wet pellets from the material holder. The wet pellets were dried at 105 °C for one day, and the diameter and weight were measured on the dried specimens. Every dry pellet had a total weight of around 2.0 ± 0.1 g with a diameter of 20.00 ± 0.09 mm. Then they were ready for sintering at a furnace.

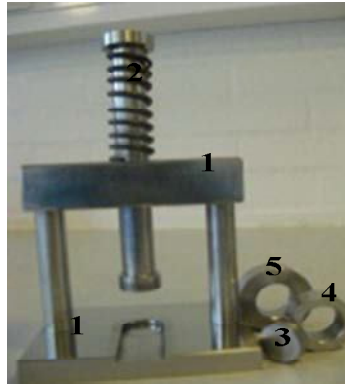


Figure 3: Press die.

The pellets were fired in a laboratory furnace. The heating and cooling profile for the furnace is presented in Figure 4. The heating rate was calculated with the assumption that the relation between temperature and time is linear in every 10 minutes time interval. It took about 2.5 h to reach 1000 °C, and the heating rate gradually reduced from 12.6 °C/min to 0. This heating rate was faster than in the typical Hoffman furnace [1]. The dwell time at sintering temperature (1000 °C) was 1 hour, and when the time was up, the furnace was turned off and the pellets cooled down naturally in the furnace, which took about 20 hour down to around 100 °C.

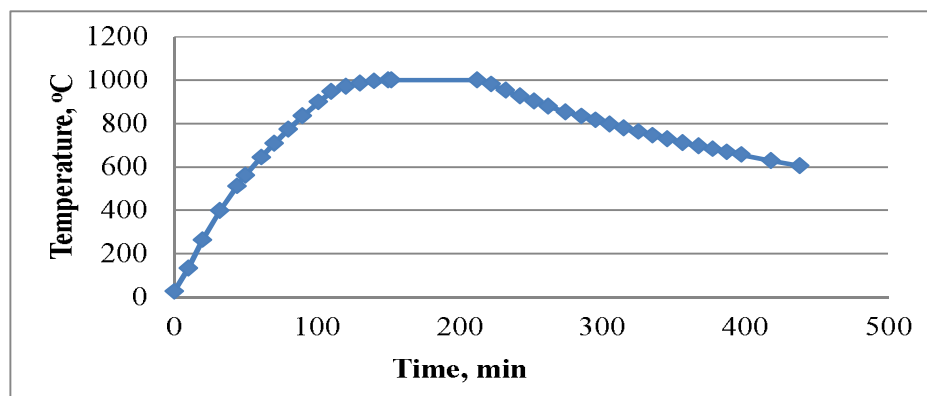


Figure 4: Corresponding heating and cooling profile versus time in the furnace.

The overall information about fired pellets and tests are summarized in Table 2.

Fired pellet	1000 °C	1050 °C	1075 °C	1100 °C	Leaching
Control (100% clay)	5				
95 % clay- 5 % TMAPC	5				x
85 % clay- 15 % TMAPC	5	2			x
75 % clay- 25 % TMAPC	4	2	2		x
75 % clay- 25 % TSWFA	5	3		3	
75 % clay- 25 % WMFA	5				x

Table 2: Test frame with pellet numbers.

Fired pellets were characterized by the following main properties, linear firing shrinkage in diameter, the weight loss, vacuum water absorption, apparent porosity, and bulk density. DS/EN ISO 10545-3:1997 [23] was referred to determine the vacuum water absorption, apparent porosity and bulk density at the same time. However, the vacuum process was modified and done according to LBM-Prøvemotode 2 (Fugtparametre, porosity and density) [24], as follows: (1) pump 3 hour to reach vacuum; (2) stop the pump and let pellets stay in water under pressure for 1 hour; (3) the pellets were in water for 24 hour at normal pressure, and then the pellets were ready for further measurement of saturated mass in air, and suspended mass in water.

The linear drying and firing shrinkage based on diameter were determined by the diameter difference between wet and dry pellet, and the difference between dry and fired pellet, respectively. Weight loss was determined by loss on ignition.

Leaching tests were done on the fired pellets made from MSWI ash, according to DS/EN 12457-3 [25], with slight modifications. The liquid (distilled water) to solid (crushed fired pellet ash) (L/S) ratio was 2. The suspension was agitated for 16 hour prior to vacuum filtration through a 45 μm filter. Concentrated HNO_3 was added to the leachate to preserve samples (0.1ml/10ml sample). The heavy metals, As, Ba, Cd, Cr_{tot} , Cu, Mn, Ni, Pb and Zn, in the leachate was measured on ICP-OES.

3- RESULTS AND DISCUSSION

Clay characterization

The Atterberg results are summarized in Table 3. The liquid limit and plastic limit for the clay were 27 % and 15% respectively. In comparison to the optimal values for good brick-making clays (Table 3), the clay is suitable for making good quality bricks.

Due to the insufficient TSWFA mass left after the EDR treatment, the washed SWFA (WSWFA) was used for Atterberg test as a reference for TSWFA. The liquid limit, plastic limit and plasticity index for the clay mixed with 25 % WSWFA are also presented in Table 3.

Properties	Clay	75 % Clay – 25 % WSWFA	Optimal value [26]
Natural water content (%)	17.4		
Liquid limit (%)	27	30	30-35
Plastic limit (%)	15	21	12-22
Plasticity index (%)	12	9	7-18

Table 3: Results from Atterberg test.

The amount of water used in the mixing and shaping process was determined based on the plastic limit of the clay and of the clay-WSWFA mixture. The amount of water for shaping clay-ash mixture was therefore larger than that in pure clay. After adding WSWFA, the plastic and liquid limit increased compared to that of clay, and the plasticity index decreased from 12 to 9 %. The same trend is seen in [27] by substituting clay with sludge. The plastic limit is a good indicator of optimum moisture content (OMC) for compaction to attain maximum density [28]. In [27], the difference between plastic limits and the determined OMCs was

within 3% in absolute terms when $PI \leq 18\%$, and the results may suggest that the OMC is much more close to W_p when PI is around 15 – 13 %. So 20 - 22 wt-% water was added to the clay-ash mixture in the shaping process, based on the observed relation between OMC and W_p . The shaping water content was kept the same in both TSWFA and T/WMSWI ash for comparison.

The clay minerals bring about the occurrence of plasticity in the clay-water system. The XRD measurement showed that the clay contained the following minerals: quartz (SiO_2), illite (potassium aluminium silicate hydroxide), dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$) and feldspar minerals (microcline intermediate and albite ordered). The alkaline oxides in e.g. feldspar act as fluxes to reduce the sintering temperature. The content of calcium carbonate in the clay was about 19% (equivalent to 10.64% of CaO). The carbonates decompose during sintering accompanied with pore formation in brick due to gas release.

Ash characterization

The elemental contents in the ash samples are presented in Table 4. The three ash was in category 3 according to the Danish limiting concentrations for heavy metals for application in construction industries [29]. Cd and Pb in TSWFA were beyond the range, but the Cd concentration had been changed from 31.8 ± 0.3 mg/kg TS in the washed ash to 1.6 ± 0.3 mg/kg TS after EDR treatment. Pb was also removed from the ash, but the mass of removed Pb was far lower than that of ash dissolved during the EDR treatment, so the Pb concentration was elevated and enriched in the final ash. The ash dissolution can also explain the high amount of heavy metals in TMAPC, although a significant amount of heavy metal had been removed during EDR treatment. The raw APC-residue contained high amount of easily soluble salts, and the solubility before ED-stack treatment reported in [8] was 35.2 ± 0.4 %. Thus the dominant mass loss was pronounced during treatment.

WMFA was hazardous, and had lower Ca concentration as expected. The water washing process resulted in lowering the soluble salts concentration (e.g. easily soluble chlorides, sulphates, potassium and sodium) [10, 30-32], and immobilizing some of the heavy metals therefore lowering leaching [8, 32], although some heavy metal concentrations were enriched in the washed ash. Given ash dissolution observed in both washing and EDR, WMFA could be used to compare with TMAPC, in order to study the different sintering behaviours of these two ash induced by adding $Ca(OH)_2$.

	Element	TSWFA	TMAPC	WMFA	Category-3 [29]
pH(H ₂ O)		< 6	12.50	11.17	
Bulk element (g/kgTS)	Al	2.8 ± 0.0	11.7 ± 0.3	31 ± 0	
	Ca	8.4 ± 0.1	406 ± 6	182 ± 1	
	Fe	6 ± 0	4.5 ± 0.0	15.5 ± 0.4	
	K	8.7 ± 0.2	4.2 ± 0.1	7.4 ± 0.3	
	P	6.3 ± 0.1	3.1 ± 0.1	8.5 ± 0.1	
	Si ¹	0.3 ± 0.0	0.3 ± 0.1	0.2 ± 0.0	
Trace element (mg/kgTS)	As	2.8 ± 1.0	188 ± 3	128 ± 7	> 20
	Cd	1.6 ± 0.3	197 ± 4	108 ± 1	> 0.5
	Cr	19.5 ± 1.1	108 ± 3	216 ± 3	> 500
	Cu	71.6 ± 1.5	876 ± 13	1427 ± 2	> 500
	Ni	3.8 ± 0.3	50 ± 0.1	94 ± 2	> 30
	Pb	210.4 ± 4.8	4516 ± 88	9239 ± 26	> 40
	Zn	260 ± 10	26131 ± 400	44060 ± 156	> 500

¹ Si is digestion-insufficient by HNO₃, so the concentration was expected to be lower than the total concentration determined by HF digestion. [33]

Table 4: Elemental compositions (mean of three measurements ± standard deviation) in the studied ash samples compared with the limiting concentrations in category 3 in Danish legislation for possible reuse of waste materials in the construction industry [29].

The mineral phases in the ashes are listed in Table 5. TSWFA differed from the MSWI ashes, and this has to do with the different constituents in the fuels, from which the ashes originated, and the different combustion techniques used. TSWFA mainly contained SiO₂ and plagioclase feldspar minerals, while MSWI ashes had high amount of carbonates and sulphates. They were primarily in form of calcite and anhydrite. Moreover, alkaline chlorides, such as sylvite and halite, existed in TMAPC. The occurrence of α-cristobalite and α-SiO₂ in TSWFA was because of the high calcination temperature [34] on the grate typically in the range 1000 – 1200 °C [35]. It is noteworthy that by introducing the ashes into the host material (e.g. clay), the mineralogy in the raw material would change, so would the mineralogy structure in the final sintered products [36]. Amorphous phases, which are ultrafine and highly reactive due to high specific surface area [34], were detected in all the three ash.

TSWFA	TMAPC	WMFA
α-Cristobalite	anhydrite	anhydrite
albite calcian	bassanite	bassanite
quartz	calcite	calcite
rutile	gehlenite	gehlenite
	halite	quartz
	quartz	rutile
	sylvite	
amorphous phases	amorphous phases	amorphous phases

Table 5: XRD determined mineral phases in the ashes.

Properties of sintered brick pellets

The overall results of weight loss on ignition, shrinkage, water absorption, bulk density and apparent porosity are shown in Table 6.

	Temp. °C	LOI %	Firing Shrinkage %	Water absorption %	Bulk density g/cm ³	Apparent porosity %	Drying shrinkage %
25% TSWFA	1000	12.7	0.5	27.6	1.53	42.1	<0.2
	1050	12.9	0.7	27.2	1.53	41.6	
	1100	13.0	5.4	15.4	1.82	28.0	
25% TMAPC	1000	14.7	0.4	29.3	1.52	44.6	0.1~0.2
	1050	14.7	0.4	29.3	1.53	44.8	
	1075	14.7	1.0	28.3	1.54	43.5	
15% TMAPC	1000	13.5	1.2	23.6	1.68	39.7	0.3
	1050	13.9	1.3	23.9	1.66	39.7	
5% TMAPC	1000	12.8	0.7	19.7	1.80	35.4	0.1
Control	1000	12.1	0.2	20.9	1.77	37.0	2.6
25% WMFA	1000	10.7	0.2	19.6	1.79	35.0	n.d.

Table 6: Overall results from pellets test. 'n.d.' - not determined.

The LOI increased slightly when introducing TSWFA and TMAPC into clay. The results may indicate that LOI increases slightly as the sintering temperature and the clay substitution level increase, exemplified by the pellets with 25 % TSWFA addition (12.7 - 13.0 % at temperatures 1000 - 1100 °C), and the substitution levels with TMAPC (0 - 25 % with corresponding LOI 12.1 - 14.7 %). This could be interpreted by the decomposition of the organic and inorganic materials from the clay and the ashes. The small LOI variation with temperature up to 1075 °C in the pellets containing 25 % TMAPC may indicate that the main decomposition process has been finished at 1000 °C. The compounds, e.g. sulfates, which decompose at higher temperature than 1000 °C, may be still in the brick, but not incorporated into brick network. Weng et al. [27] and Karaman et al. [37] reported the weight loss for a normal clay brick is 15%. With the ash addition, this criterion was not exceeded.

The drying and firing shrinkage degree in bricks can be considered as a factor for quality control. To avoid cracking, the drying shrinkage should not be too high, normally $\leq 7\%$ [26]. It is also important when it comes to determining the size of molds for making bricks with wanted dimensions. The linear drying shrinkage was 2.6 % in the control, and it decreased to less than 0.3 % through adding TSWFA and TMAPC up to 25 %. Compared to clay, ash is generally plastic limited [36] and coarser [36, 38], and thus the reduction in drying shrinkage was believed to be due to the reduction in the clay fine particle proportion in the pellets. Taking TSWFA, the burned bar-shaped straw fibers could retard the brick shrinkage when water was removed. The firing shrinkage determines the stability of the bricks in kiln, and should normally be below 8 % [26]. All the pellets exhibited small firing shrinkage, i.e. well below 8 %. The firing shrinkage increased in general as firing temperature increased, and the increase in vitrification degree was most probably responsible for this. The highest total shrinkage from wet to fired pellets was in the control.

Water absorption, which affects the brick durability, has close relation to porosity, which reveals the brick internal structure. The lower the open porosity, the lower the water penetration of brick, and therefore the higher the brick durability and resistance to environmental damage [39]. Substituting clay with 25 % TSWFA and TMAPC resulted in the increase in apparent porosity of sintered pellets at 1000 °C from 37 to higher than 42 %. The dominant pore-forming mechanisms in TSWFA and TMAPC seemed to be different: burn-off of carbon in the former, and decomposition of carbonates in the latter according to our mineralogy study. The apparent porosity increased as the substitution level increased, and it decreased as the sintering temperature increased. The substitution level of 5 % TMAPC was an exception, where the porosity decreased compared to that in the control. The variation of water absorption was in accordance with that of apparent porosity. The absorption ranged from 19.6 to 29.3 %. According to ASTM C62-13a [40] in terms of water absorption, bricks containing 25 % TSWFA sintered at 1100 °C may be used for building brick under severe weathering, and bricks containing 5 % TMAPC sintered at 1000 °C could be suitable for building brick under moderate weathering (Grade MW).

TSWFA and TMAPC had the same impact on the sintering properties in terms of shrinkage, mass loss, water absorption and apparent porosity, so did they in bulk density. Bulk density is generally inversely proportional to apparent porosity. Hence, the pellets containing 25 % TSWFA sintered at 1100 °C were the densest, followed by the ones containing 5 % TMAPC sintered at 1000 °C. WMFA from the same source of the raw APC had opposite effects on the pellets properties, such as decrease in mass loss, water absorption and porosity, and increase in density. This may indicate the lime injection made a big difference on the properties of WMFA and TMAPC, as exemplified by the different mineral phases.

CaO in the raw material could damage the brick products, e.g. 'lime blowing' in the most severe case. Commonly, CaO is in the form of calcite in materials, and the particle size should be fine enough (< 0.5 mm) to avoid 'lime blowing' [41]. CaO takes a significant share in MSWI ashes compared to that in clay. The CaO content was especially high in the studied raw APC-residue (64.4 %), and in the ED treated APC-residue (40.6 %) [42]. However, straw and wood fly ash contained mainly SiO₂. This could explain the lower substitution level (~ 5 %) of TMAPC, and the moderate level (~ 25 %) of TSWFA in the yellow clay brick pellets. Attentions also need to be paid on the role of SO₃ in TMAPC on the clay brick production. According to [42], the amount of SO₃ in ED treated APC-residue could be as high as 12.5 %. SO₃ content should be as low as possible. According to DS/EN 771-1 [43], active soluble salts content in bricks, which are intended for use with limited protection against water penetration, shall be declared in terms of K⁺, Na⁺ and Mg²⁺. Their sulfates in the fired bricks, which may originate from the ashes, may lead to efflorescence [44].

Lower clay substitution level with TMAPC, for example lower than 5 %, seemed to help the sintering process, considering the increase in density, the decrease in water absorption, and thus the improved durability of bricks. The reduction of density with higher ash content could however be beneficial to reduce the transport cost and improve thermal insulation. FA is probably better than APC in terms of slight influence on clay sintering properties even with 25 % addition, so it could be recovered not to mix with sorbent (e.g. slaked lime) at the waste incineration plants, or only use FA for construction materials, e.g. as in semidry flue gas cleaning systems.

Heavy metal leaching

The pellets with TMAPC and WMFA addition fired at 1000 °C were studied on the leaching behavior. Table 7 shows the results. For those pellets containing TMAPC, Pb and Cr were most problematic compared to category 3 in Table 7. Cr leaching from the fired pellets was far above the limit value in the three studied substitution levels, and the oxidation of Cr³⁺ to Cr⁶⁺ during firing, which is more soluble and toxic, is supposed to be the main reason. For the pellets with 5 % TMAPC and 25 % WMFA addition, which met Grade MW (moderate weathering) in water absorption i.e. 22 % in average, Pb content in the leachate was little, but Ni was slightly above 70 µg/L in the former and As was above 50 µg/L in the latter. Cr level in both cases was exceeded. Sintering at optimum conditions, i.e. optimum raw material proportions and sintering temperature, can reduce the heavy metal leaching [45], so finding the optimum conditions is necessary in further studies, and a further understanding of the Cr behavior would enhance the MSWI ash's application potential.

	Leaching (µg/L)	As	Ba	Cd	Cr _{tot}	Cu	Mn	Ni	Pb	Zn
Limit	Category-3 [29]	50	4000	40	500	2000	1000	70	100	1500
TMA PC	5 % - FB	35	128	0	1834	5	5	94	9	0
	15 % - FB	30	333	0	3029	18	1	42	419	240
	25 % - GB	34	386	0	229	389	2	14	195	572
	25 % - FB	28	242	0	4589	14	1	0	949	61
WMF	25 % - GB	39	159	0	1027	171	1	17	30	5
A	25 % - FB	92	145	0	3052	6	3	37	0	0

Table 7: Leaching properties of pellets made from TMAPC and WMFA. FB- fired brick pellet; GB- green brick pellet.

4- CONCLUSIONS

The treated biomass ashes, i.e. the fly ash from co-combustion of straw and wood chips and the MSWI APC-residue are pore-forming agents leading to increase in porosity. The dominating pore-forming mechanisms probably differ: the burn-off of carbon fibers in the former, and the decomposition of carbonates in the latter.

Treated straw and wood fly ash can be used in the production of clay bricks. Brick pellets sintered at 1100 °C with 25 % clay substitution have the average water absorption of 15.4 % that meets the requirement for Grade SW building bricks in ASTM C62 – 13a. Low clay replacement with APC-residue, e.g. 5 %, seems to be beneficial to form glassy phases during vitrification. The pellets containing 5 % TMAPC sintered at 1000 °C could be suitable for building brick under moderate weathering (Grade MW). Moreover, the leaching of Pb is low, while Cr leaching poses a main problem. Too much CaO and SO₃ content in the raw materials are deleterious to produce good quality clay bricks, so care must be exercised in finding the optimal clay and ash proportions. WMFA, whose raw ash was the source of the raw APC, has opposite effect on the pellets properties compared with TMAPC. This may indicate the lime injection made a big difference on the properties of WMFA and TMAPC. It could be advantageous to take FA out before APC as in semidry flue gas cleaning systems.

Using the bio ash in clay bricks is promising, with advantages of utilizing waste as secondary resources, reducing the burden on landfill, and less extracting natural resources. Further studies are needed to test the mechanical properties of the bricks in addition to screening the optimal conditions. Efforts are needed to remedy the Cr problem.

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